Physical Chemistry of Polymer Solutions

Theoretical Background

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To our families

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Preface

Numerous physical properties of polymer solutions are known to be significantly different from those of low molecular weight solutions. The most probable explanation of this obvious discrepancy is the large molar volume ratio of solute to solvent together with the large number of consecutive segments that constitute each single molecule of the polymer chains present as solute. Thorough understanding of the physical chemistry of polymer solutions requires some prior mathematical background in its students. In the original literature, detailed mathematical derivations of the equations are universally omitted for the sake of space-saving and simplicity, which physicists hold in high regard. However, students learning about the physical chemistry of polymer solutions are predominantly chemists, whose physical and mathematical skills are not necessarily high. In textbooks of polymer science only extremely rough schemes of the theories and then the final equations are shown. As a consequence, the student cannot unaided learn the details of the theory in which he or she is interested from the existing textbooks. Without a full understanding of the theory, one cannot analyze actual experimental data to obtain more basic and realistic physical quantities. In particular, if one intends to apply the theories in industry, accurate understanding and ability to modify the theory as one wishes are essential.

This book is mainly concerned with building a narrow but secure ladder which polymer chemists or engineers can climb from the primary level to an advanced level without great difficulty (but by no means easily, either). The need for a book of this kind has been widely recognized for many years among polymer scientists, including ourselves, but as far as we know, no such book has yet been published. We believe that this book is, in that sense, unique and unparalleled. The Japanese manuscript was originally written by Kamide and nearly completed in the 1970s and 1980s, but was not published. Based on these Japanese manuscripts, Kamide gave a series of intensive lecture courses to students at universities of Kanazawa, Hokkaido, Okayama, Osaka City, Essex, Bristol and Bradford. The manuscripts, thanks to this valuable experience, have been repeatedly revised and improved. The English edition was originally planned for the beginning of the 1990s and the Japanese manuscript was drastically reduced to fit the size requested by the publishers and transformed in part into an English version for this book. Although this attempt was interrupted by Kamide's illness, the book has now materialized through the enthusiastic cooperation of Professor Dobashi.

This book describes some fundamentally important topics, carefully chosen, covering subjects from thermodynamics to molecular weight and its distribution effects. For help in self-education the book adopts a "Questions and Answers" format. The mathematical derivation of each equation is shown in detail. For further reading, some original references are also given. The contents of the book frankly belong to the realm of classical physical chemistry, because it does not treat areas newly developed during the 1980s and 1990s, such as scaling theory and spectroscopic theory (e.g., NMR). To add chapters about these areas is beyond both our ability and the planned size of the book. The reader should not, however, consider that all the theories covered by the book have already been firmly established. Any topic, although apparently mature and fully grown, may start to develop quickly again due to the advent of a new motive force, hitherto unknown, and so may present important new unsolved problems. We experienced this in the study of phase separation and critical phenomena of multicomponent polymer solutions during the 1970s and 1980s (see, for example, K. Kamide, "Thermodynamics of Polymer Solutions : Phase Separation and Critical Phenomena", Elsevier, 1990). Throwing out "old" and jumping after "new" techniques seems an inevitable fashion intrinsic as inherent to polymer science as to other disciplines of applied science, but is not always unconditionally reasonable.

The authors will be very gratified if this book proves a help not only to students at universities and to industrial researchers, who may be studying the physical chemistry of polymer solutions and dissatisfied with existing books, but also, as a reference book, to technologists intending to apply the physical chemistry of polymer solutions to industrial practice (but not as a simple quality control method, like a fully automated analytical instrument!) and to educators teaching this or related subjects. We should like to thank Professor J. Eric McIntyre of University of Leeds, UK for his meticulous reading of the manuscript, and for important suggestions. The authors would like to offer thanks to Dr Masatoshi Saito, Dr Shigenobu Matsuda, Dr Hironobu Shirataki, Dr Kunio Hisatani, Professor Yukio Miyazaki, Mr Kazuishi Sato, Mr Yuji Ito and Mr Katsunari Yasuda of the Fundamental Research Laboratory of Fibers and Fiber-Forming Polymers, Asahi Chemical Industry Company, Ltd., Takatsuki, Osaka, Japan, who cooperated in the downsizing of the Japanese manuscript and in re-examination of the mathematical derivations in the text although the authors are, of course, responsible for any possible errors and mistakes in the book.

The authors have a pleasure of thanking Professor Motozo Kaneko of Hokkaido University for sending us complete solution of <<Problem 8-45>> and also wish to acknowledge the support of typing the manuscript to Mr Takashi Sato of Gunma University.

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Glossary

A: Area
A_i : *i* th virial coefficient
a_i : activity of *i* th component
B: enthalpy per contact area
b: bond length
b_m : *m* th cluster integral
C: weight concentration
c_p : specific heat under constant pressure
c_v : specific heat under constant volume
c: velocity of light in vacuum
D: diffusion coefficient
D: electric displacement
d: diameter
$d'Q$: differential heat
$d'W$: differential work
E: energy
E: electric field
E: unit tensor
e: strain
e: strain tensor
F: Helmholtz free energy
F_N: N -body partition function
F: force
f_D: friction coefficient for translational motion
f_s: friction coefficient for sedimentation
$f_n(n)dn$: number fraction of the polymer with the degree of polymerization n
$f_w(n)dn$: weight fraction of the polymer with the degree of polymerization n
G: Gibbs free energy
$\overline{G}$: mean molar Gibbs free energy
G_{ij} : differential of Gibbs free energy with respect to the mole fractions of *i* th component and *j* th component
g: velocity gradient
g: Huggins' free energy correction factor
$g_n(M)$: number distribution of molecular weight

$g_w(M)$: weight distribution of molecular weight
H: enthalpy
H_i : partial molar enthalpy of i th component
h: Planck constant
h: inhomogeneity parameter for molecular weight distribution
I_0: incident light intensity
I_s: scattered light intensity
I_t: transmitted light intensity
$\mathbf{I}$: inertia moment
J: extensive thermodynamic variable
$\mathbf{j}$: flow by diffusion
K: tension
K: Flory constant
K: optical constant
k: Boltzmann constant
k: degree of connectivity
k: reaction constant
k': Huggins' constant
L: camera length
L_0: molar heat of vaporization
l: segment length
$\mathbf{l}$: position vector of segment
M: molecular weight
M_n: number-average molecular weight
M_w: weight-average molecular weight
M_z: z-average molecular weight
M_v: viscosity-average molecular weight
M_{SD}: sedimentation-diffusion-average molecular weight
m_0: molecular weight of segment
N: number of moles of molecule
N: number of molecules
N_A: Avogadro's number
n: association number
n: segment number or chain length
n: number density
n_m: medium for the degree of polymerization

n_n: number-average degree of polymerization
n_w: weight-average degree of polymerization
n_z: z-average degree of polymerization
n_v: viscosity-average degree of polymerization
n_r: refractive index of solution
n_r^0: refractive index of solvent
P: pressure
$\mathbf{P}$: polarization
$\mathbf{P}$: stress tensor
P_i : vapor pressure of *i* th component
P_i^0 : vapor pressure of *i* th component before mixing
P(q): particle scattering factor
p: probability that condensation reaction occurs
p_i : coefficient for concentration dependence of χ
Q: heat
q_1: molecular partition function
$q_{w,z}$: correction factor for molecular weight distribution
$\mathbf{q}$: wave vector
R: gas constant
R: phase volume ratio
R: Reynolds number
R: end-to-end distance
$\mathbf{R}$: vector connecting one end to another end of polymer
R_e: radius of hydrodynamically identical sphere
R_θ: Rayleigh ratio
R_θ' : reduced scattered light intensity
$\langle R^2 \rangle$: mean square end-to-end distance
$\langle R^2 \rangle_0$: mean square end-to-end distance of unperturbed chain
r: radius
S: entropy
S: radius of gyration
S^0: entropy before mixing
S_i: partial molar entropy of *i* th component
$\langle S^2 \rangle$: mean square radius of gyration
s: scattering vector
s_0 : sedimentation coefficient at infinite dilution

T: absolute temperature
T: matrix for rotational mapping
T_c: critical solution temperature
t: time
U: internal energy
u: potential energy
V: volume
V': volume of dilute phase
V'': volume of concentrated phase
V_i : partial molar volume of *i* th component
V_0: molar volume
V_0^0: molar volume of solvent
V^0: molar volume before mixing
v_0 : volume of molecule
$\bar{v}$: partial specific volume
v: velocity
W: work
w: interchange energy
w: mean force potential between solute molecules
w_i : weight fraction of *i* th component
X: parameter for free draining
x: distance from rotational axis to surface
x_i : mole fraction of *i* th component
x_c : critical mole fraction
Y: increment of refractive index
Z: partition function for canonical ensemble
Z: excluded volume parameter
z: coordination number

α: expansion factor
α: polarizability
α: volumetric thermal expansion coefficient at constant pressure
α_R: end distance expansion factor
α_S : radius expansion factor
α_η : viscosity expansion factor

β : effective two-body excluded volume per segment pair or two-body cluster integral
γ : shear modulus
γ_i : activity coefficient of *i* th component
ΔG_{mix}: Gibbs free energy of mixing
ΔG_v: Gibbs free energy of mixing per unit volume
ΔH_{mix}: enthalpy of mixing
ΔQ_{mix}: heat of mixing
ΔS_{mix}: entropy of mixing
ΔV_{mix}: mixing volume
$\Delta\mu_i$: chemical potential of mixing of *i* th component
(superscripts id and E denote the quantities for ideal solution and excess quantities)
δC: fluctuation of concentration
ε : dielectric constant
ε : interaction energy
ζ : friction coefficient between fluid and small particle
η: viscosity coefficient
η_0:viscosity coefficient of solvent
η_r: relative viscosity
η_{sp}: specific viscosity
$[\eta]$: intrinsic viscosity or limiting viscosity number
η_v : volumetric viscosity
Ξ : partition function for grand canonical ensemble
ξ : partition function for semi-grand canonical ensemble
θ: Flory temperature
θ: bond angle
κ : isothermal compressibility
κ : enthalpy parameter
κ : elastic modulus
κ_0 : Flory enthalpy parameter at infinite dilution
λ: Lamè constant
λ : absolute activity
λ_0 : wave length of incident light
μ : permeability
μ : Lamè constant

μ : moment for molecular weight distribution
μ_i : chemical potential of *i* th component
μ'_i: chemical potential of *i* th component in vapor phase
μ^0 : chemical potential before mixing
$\mu_0{}^0$: chemical potential of solvent
μ_{ij} : differential of chemical potential with respect to mole fractions of *i* th component and *j* th component
Π: osmotic pressure
ρ: density
ρ_s: weight fraction of polymer partitioned in dilute phase
ρ_p : weight fraction of polymer partitioned in concentrated phase
σ : partition coefficient
σ: stress
σ: steric hindrance factor
σ: standard deviation
τ: turbidity
τ:delay time
Φ: Flory-Fox viscosity coefficient
ϕ_0:volume fraction of solvent
ϕ_1:volume fraction of solute
ϕ_n: volume fraction of polymer with the degree of polymerization n
χ: thermodynamic interaction parameter
Ψ : penetrating function
ψ: entropy parameter
ψ_0: Flory entropy parameter at infinite dilution
Ω: partition function for microcanonical ensemble
ω: vibration number
ω: angular velocity of molecular chain

Chapter 1 Fundamentals of Thermodynamics

<<Problem 1-1>> Internal energy, free energy and enthalpy

For an infinitesimal process of a system at constant temperature and constant pressure, infinitesimal changes in **internal energy** U, **Helmholtz free energy** F, **Gibbs free energy** G and **enthalpy** H are given by

$$dU = TdS - PdV + \sum_i \mu_i dN_i \tag{1.1.1}$$

$$dF = -SdT - PdV + \sum_i \mu_i dN_i \tag{1.1.2}$$

$$dG = -SdT + VdP + \sum_i \mu_i dN_i \tag{1.1.3}$$

$$dH = TdS + VdP + \sum_i \mu_i dN_i \tag{1.1.4}$$

Here, T is the temperature, S the **entropy**, P the pressure, V the volume, μ_i and N_i the **chemical potential** and the number of moles of *i* th component.

(1) Derive Eqs. (1.1.1)-(1.1.4).

(2) Define the chemical potential μ_i using Eqs. (1.1.1)-(1.1.4).

Answer

(1) Consider an open system which permits the transfer of mass into or out of it. Let's denote infinitesimal quantities of heat flow from the surroundings to the system as d'Q and work done on the system as d'W. From the first law, the following equation holds:

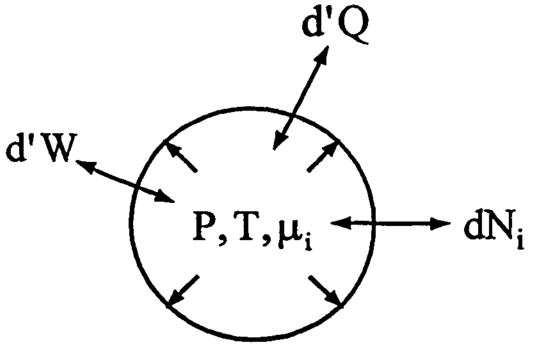

Fig. 1-1 Open system

$$dU = d'Q + d'W + \sum_i \mu_i dN_i \qquad (1.1.5)$$

If the work is only due to an infinitesimal volumetric change dV under constant pressure P, the work done by the system is

$$d'W = - PdV \qquad (1.1.6)$$

and if the change is quasi-static or reversible,

$$d'Q = TdS \qquad (1.1.7)$$

Then, substitution of Eqs.(1.1.6) and (1.1.7) into Eq. (1.1.5) gives

$$dU = TdS - PdV + \sum_i \mu_i dN_i \qquad (1.1.1)$$

F, G and H are defined by

$$F = U - TS \qquad (1.1.8)$$

$$G = F + PV = U - TS + PV \qquad (1.1.9)$$

$$H = U + PV \qquad (1.1.10)$$

The total differentiation of Eqs. (1.1.8)-(1.1.10) gives

$$dF = dU - TdS - SdT \qquad (1.1.11)$$

$$dG = dF + PdV + VdP \qquad (1.1.12)$$

$$dH = dU + PdV + VdP \qquad (1.1.13)$$

Combination of Eq. (1.1.1) with Eqs. (1.1.11)-(1.1.13) affords

$$dF = - SdT - PdV + \sum_i \mu_i dN_i \qquad (1.1.2)$$

$$dG = - SdT + VdP + \sum_i \mu_i dN_i \qquad (1.1.3)$$

$$dH = TdS + VdP + \sum_i \mu_i dN_i \qquad (1.1.4)$$

(2) Partial differentiation of Eqs. (1.1.1)-(1.1.4) with respect to N_i leads to

$$\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_j} \qquad (1.1.14)$$

$$\mu_i = \left(\frac{\partial F}{\partial N_i}\right)_{T,V,N_j} \qquad (1.1.15)$$

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_j} \qquad (1.1.16)$$

$$\mu_i = \left(\frac{\partial H}{\partial N_i}\right)_{S,P,N_j} \tag{1.1.17}$$

where the subscripts S, V, T, P and N_j mean that the partial differentiation is carried out under the condition of constant S, V, T, P and N_j (except for N_i), respectively.

<<Problem 1-2>> Partial molar quantities

Derive the following equations:

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N_i} = - S_i \tag{1.2.1}$$

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N_i} = V_i \tag{1.2.2}$$

$$\left\{\frac{\partial(\mu_i/T)}{\partial(1/T)}\right\}_{P,N_i} = H_i \tag{1.2.3}$$

Here, the partial molar quantities S_i, V_i and H_i are changes in entropy, volume and enthalpy accompanying the addition of one mole of component *i* to a mixture at constant temperature under constant pressure.

Answer

From the first law of thermodynamics,

$$dG = - SdT + VdP + \sum_i \mu_i dN_i \tag{1.1.3}$$

Partial differentiation of (1.1.3) with respect to T under constant pressure and constant number of moles of *i* th component N_i gives

$$\left(\frac{\partial G}{\partial T}\right)_{P,N_i} = - S \tag{1.2.4}$$

Further differentiation of Eq. (1.2.4) by N_i affords

$$\left\{\frac{\partial}{\partial N_i}\left(\frac{\partial G}{\partial T}\right)_{P,N_i}\right\}_{N_j} = \left\{\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial N_i}\right)_{N_j}\right\}_{P,N_i} \tag{1.2.5}$$

μ_i is defined by

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_j} \tag{1.1.16}$$

Similarly S_i is defined by

$$S_i = \left(\frac{\partial S}{\partial N_i}\right)_{T,P,N_j} = \left\{\frac{\partial}{\partial N_i}\left(-\frac{\partial G}{\partial T}\right)_{P,N_i}\right\}_{N_j} \tag{1.2.6}$$

Here, the partial differentiation is made at constant number (mole) of the components, except for component *i*. Then, we have

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N_i} = - S_i \tag{1.2.1}$$

After differentiation of Eq. (1.1.3) with respect to P, we obtain

$$\left(\frac{\partial G}{\partial P}\right)_{T,N_i} = V \tag{1.2.7}$$

Further differentiation of Eq. (1.2.7) by N_i and rearrangement of the resultant equation using Eq. (1.1.16) gives

$$\left(\frac{\partial V}{\partial N_i}\right)_{N_j} = \left\{\frac{\partial}{\partial N_i}\left(\frac{\partial G}{\partial P}\right)_{T,N_i}\right\}_{N_j} = \left\{\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial N_i}\right)_{N_j}\right\}_{T,N_i} = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,N_i} \tag{1.2.8}$$

Then, we have Eq.(1.2.2). G is expressed as

$$G = H - TS \tag{1.2.9}$$

Using Eq. (1.2.4), we have

$$H = G - T\left(\frac{\partial G}{\partial T}\right)_{P,N_i} = - T^2\left\{\frac{\partial (G/T)}{\partial T}\right\}_{P,N_i} = \left\{\frac{\partial (G/T)}{\partial (1/T)}\right\}_{P,N_i} \tag{1.2.10}$$

Eq. (1.2.10) is called the **Gibbs-Helmholtz equation.** Differentiating Eq. (1.2.10) by N_i , we obtain

$$\left(\frac{\partial H}{\partial N_i}\right)_{P,N_j} = \left\{\frac{\partial}{\partial N_i}\left\{\frac{\partial (G/T)}{\partial (1/T)}\right\}_{P,N_i}\right\}_{P,N_j} = \left\{\frac{\partial}{\partial (1/T)}\left(\frac{\partial G}{\partial N_i}\cdot\frac{1}{T}\right)_{P,N_j}\right\}_{P,N_i}$$

$$= \left\{ \frac{\partial(\mu_i/T)}{\partial(1/T)} \right\}_{P,N_i} \qquad (1.2.11)$$

From the definition

$$H_i = \left(\frac{\partial H}{\partial N_i} \right)_{P,N_j} \qquad (1.2.12)$$

we obtain

$$\left\{ \frac{\partial(\mu_i/T)}{\partial(1/T)} \right\}_{P,N_i} = H_i \qquad (1.2.3)$$

Using Eqs. (1.2.1) and (1.2.3), S_i and H_i can be evaluated from the temperature dependence of the chemical potential μ_i. In other words, if we can determine the chemical potentials as functions of T and P, the other thermodynamic quantities such as S_i, V_i and H_i are automatically determinable.

<<Problem 1-3>> Gibbs-Duhem relation

At constant temperature and constant pressure, the following relation (the Gibbs-Duhem relation) always holds:

$$\sum_i N_i d\mu_i = 0 \qquad (1.3.1)$$

Derive Eq. (1.3.1).

Answer

The extensive variables J are linear homogeneous functions of temperature T, pressure P and the number of moles of each component N_1, N_2... Thus, we may write

$$J(T,P,xN_1,xN_2,\cdots) = xJ(T,P,N_1,N_2,\cdots) \qquad (1.3.2)$$

Here, x is an arbitrary constant. Differentiating both sides of Eq. (1.3.2) with respect to x, we have

$$\frac{dJ\left(T,P,xN_1,xN_2,\cdots\right)}{dx}=\frac{\partial J\left(T,P,xN_1,xN_2,\ldots\right)}{\partial\left(xN_1\right)}\cdot\frac{\partial\left(xN_1\right)}{\partial x}$$

$$+\frac{\partial J\left(T,P,xN_1,xN_2,\cdots\right)}{\partial\left(xN_2\right)}\cdot\frac{\partial\left(xN_2\right)}{\partial x}+\cdots$$

$$=\sum_i\frac{\partial J\left(T,P,xN_1,xN_2,\cdots\right)}{\partial\left(xN_i\right)}\cdot N_i=J\left(T,P,N_1,N_2,\cdots\right) \tag{1.3.3}$$

Putting x=1 into Eq. (1.3.3), we have

$$J\left(T,P,N_1,N_2,\cdots\right)=\sum_i N_i\left(\frac{\partial J}{\partial N_i}\right)_{T,P,N_j} \tag{1.3.4}$$

Using the expression

$$J_i=\left(\frac{\partial J}{\partial N_i}\right)_{T,P,N_j} \tag{1.3.5}$$

Eq. (1.3.4) is written as

$$J\left(T,P,N_1,N_2,\cdots\right)=\sum_i N_iJ_i \tag{1.3.6}$$

* In case J=G, we have

$$G=\sum_i N_iG_i \tag{1.3.7}$$

Here, G_i is identical with μ_i, e.g.

$$G_i=\left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_j}=\mu_i \tag{1.3.8}$$

Thus, Eq. (1.3.7) is replaced by

$$G=\sum_i N_i\mu_i \tag{1.3.9}$$

Total differentiation of both sides of Eq. (1.3.6) gives

$$dJ(T,P,N_1,N_2,\cdots)=\sum_i\left(\frac{\partial J}{\partial N_i}\right)_{T,P,N_j}dN_i+\left(\frac{\partial J}{\partial T}\right)_{P,N_i}dT+\left(\frac{\partial J}{\partial P}\right)_{T,N_i}dP$$

$$=\sum N_i dJ_i+\sum J_i dN_i \qquad (1.3.10)$$

In case of constant temperature and constant pressure, we have

$$dJ=\sum_i\left(\frac{\partial J}{\partial N_i}\right)_{T,P,N_j}dN_i=\sum_i J_i dN_i=\sum N_i dJ_i+\Sigma J_i dN_i \qquad (1.3.11)$$

Thus,

$$\sum N_i dJ_i=0 \qquad (1.3.12)$$

Putting $J_i=\mu_i$, we have Eq. (1.3.1). If we put $J_i=V_i$, S_i or H_i into Eq.(1.3.12), we have corresponding equations.

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* J. Willard Gibbs deduced Eq. (1.3.1) in 1885 (*Gibbs Collected Works*, vol. 1, p88 and *The Scientific Papers of J. W. Gibbs, vol. 1, Thermodynamics*, Dover Pub., 1961) and later, P. Duhem independently derived the same equation (P. Duhem, *Le Potentiel Thermodynamique et ses Applications*, p33, 1886; P. Duhem, *Compt. rend.* **102**, 1449 (1886)).

<<Problem 1-4>> Mixing volume change and mixing entropy

When an arbitrary number of liquid and solid phases, each of which contains i components, are mixed with each other to conform a homogeneous solution, write the equations for differential changes in volume and entropy, i.e., mixing volumetric change $\Delta V_{mix}(=V-V^0)$ and mixing entropy $\Delta S_{mix}(=S-S^0)$, using partial molar quantities. Here, the superscript 0 denotes the state of the solution before mixing.

Answer

From the definition

$$V_i=(\partial V/\partial N_i) \text{ and } V_i^0=(\partial V^0/\partial N_i) \qquad (1.4.1)$$

we have

$$V=\Sigma V_i N_i \qquad (1.4.2)$$

and

$$V^0 = \Sigma V_i^0 N_i \tag{1.4.3}$$

Here, Σ denotes the summation over the components. From Eqs. (1.4.1)-(1.4.3), we have

$$\Delta V_{mix} = \Sigma V_i N_i - \Sigma V_i^0 N_i = \Sigma\left(V_i - V_i^0\right)N_i \tag{1.4.4}$$

Total differentiation of Eq. (1.4.4) gives

$$d\Delta V_{mix} = \Sigma V_i dN_i - \Sigma V_i^0 dN_i + \Sigma N_i dV_i - \Sigma N_i dV_i^0 \tag{1.4.5}$$

Using the **Gibbs-Duhem relation,**

$$\Sigma N_i dV_i = 0, \quad \Sigma N_i dV_i^0 = 0 \tag{1.4.6}$$

Combining Eqs. (1.4.5) and (1.4.6), we have

$$\left(\frac{\partial \Delta V_{mix}}{\partial N_i}\right)_{T,P,N_j} = V_i - V_i^0 \tag{1.4.7}$$

Similarly, we obtain

$$\Delta S_{mix} = S - S^{\circ} = \sum N_i\left(S_i - S_i^{\circ}\right) \tag{1.4.8}$$

and

$$\left(\frac{\partial \Delta S_{mix}}{\partial N_i}\right)_{T,P,N_j} = S_i - S_i^0 \tag{1.4.9}$$

<<Problem 1-5>> Gibbs condition for two-phase equilibrium

The condition that two phases, I and II, are in complete thermodynamic equilibrium at constant temperature under constant pressure is that the chemical potentials of any components in both phases should be the same. That is,

$$\mu_i^{I} = \mu_i^{II} \quad i = 1,2,3, \cdots \tag{1.5.1}$$

Derive Eq. (1.5.1).

Answer

Gibbs free energy G^{I+II} of a closed system which consists of phase I and phase II is the sum of the Gibbs free energy of each phase G^{I}, G^{II} as

$$G^{I+II} = G^{I} + G^{II} \tag{1.5.2}$$

Infinitesimal change in Gibbs free energy, keeping each phase at constant temperature and constant pressure, is

$$dG^{I+II}=0 \tag{1.5.3}$$

Thus,

$$dG^{I+II}=dG^{I}+dG^{II}=\sum\mu_i^{I}dN_i^{I}+\sum\mu_i^{II}dN_i^{II}=0 \tag{1.5.4}$$

Since the number of moles of the components in the closed system is constant, we have

$$dN^{I+II}=dN^{I}+dN^{II}=0 \tag{1.5.5}$$

Combining Eqs. (1.5.4) and (1.5.5), we obtain

$$\sum\left(\mu_i^{I}-\mu_i^{II}\right)dN_i^{I}=0 \tag{1.5.6}$$

Eq. (1.5.6) must hold for any values of dN_i^{I}. Thus, we have Eq. (1.5.1) (See The Scientific Papers of J. Willard Gibbs, vol. 1, Thermodynamics, p65, Dover, 1961; J. W. Gibbs, Trans. Connecticut Academy, III. pp. 108-248, Oct. 1875-May, 1876 and pp.343-524, May, 1877-July, 1878).

<<Problem 1-6>> Heat of mixing

Heat of mixing ΔQ_{mix} and differential heat of mixing for a system at constant temperature and constant pressure are expressed in terms of partial molar enthalpy of *i* th component in solution $H_i(=(\partial H/\partial N_i))$ and that in pure state H_i^0 as

$$\Delta Q_{mix}=\sum N_i\Delta H_i \tag{1.6.1}$$

and

$$\left(\frac{\partial\Delta Q_{mix}}{\partial N_i}\right)_{T,P,N_j}=H_i-H_i^0 \tag{1.6.2}$$

Derive Eqs. (1.6.1) and (1.6.2).

Answer

Heat of mixing ΔQ_{mix} is given by the difference in enthalpy of the solution H and that of pure state H^0:

$$\Delta Q_{mix} = H - H^0 \tag{1.6.3}$$

The enthalpies are expressed in terms of partial molar enthalpies H_i in the solution or H_i^0 in the pure state as

$$H = \Sigma H_i N_i \tag{1.6.4}$$

$$H^0 = \Sigma H_i^0 N_i \tag{1.6.5}$$

Substituting Eqs. (1.6.4) and (1.6.5) into Eq. (1.6.3), we have

$$\Delta Q_{mix} = \Sigma H_i N_i - \Sigma H_i^0 N_i = \Sigma \left(H_i - H_i^0 \right) N_i = \Sigma N_i \Delta H_i \tag{1.6.1}$$

Total differentiation of Eq. (1.6.1) yields

$$d\Delta Q_{mix} = \Sigma N_i dH_i - \Sigma N_i dH_i^0 + \Sigma H_i dN_i - \Sigma H_i^0 dN_i \tag{1.6.6}$$

Using the Gibbs-Duhem relation, we have

$$\Sigma N_i dH_i = 0$$

$$\Sigma N_i dH_i^0 = 0 \tag{1.6.7}$$

Thus, we obtain

$$d\Delta Q_{mix} = \Sigma H_i dN_i - \Sigma H_i^0 dN_i \tag{1.6.8}$$

and

$$\left(\frac{\partial \Delta Q_{mix}}{\partial N_i} \right)_{T,P,N_j} = H_i - H_i^0 \tag{1.6.2}$$

---

* Solutions of $\Delta Q_{mix}=0$ is called as **athermal solution**. Guggenheim wrote in his book that ' it was commonly believed that all athermal solution should be ideal'. This view was openly challenged in a discussion held by the Faraday Society in 1936, at which Fowler then suggested that this view could be proved or disproved by a statistical analysis of a mixture of two kinds of molecules arranged on a lattice, each molecule of the one kind occupying two neighbouring sites of the lattice and each molecule of the other kind occupying one site. This problem was attacked by Fowler and Rushbrooke (See R. Fowler and G. S. Rushbrooke, *Trans. Farad. Soc.* 33, 1272 (1937)) and by Guggenheim (See E. A. Guggenheim, *Mixture*, pp.183, Clarendon Press, 1952; E. A. Guggenheim, *Trans. Farad. Soc.* 33, 151 (1937))

Chapter 2 Ideal and Non-Athermal Solutions

<<Problem 2-1>> Ideal solution

When the chemical potential μ_i of a solution is expressed as

$$\mu_i(T,P) = \mu_i^0(T,P) + RT\ln x_i \tag{2.1.1}$$

the solution is defined as **ideal solution**. Here, $\mu_i^0(T,P)$ means the chemical potential of species i at pure state, which is a function of temperature T and pressure P, and x_i is the relative proportion of *i* th component in the solution (known as the mole fraction of species i),

$$x_i = \frac{N_i}{\sum_i N_i} \tag{2.1.2}$$

$R=kN_A$ is the gas constant, N_i the number of moles of species i, N the total number of moles, k the Boltzmann constant and N_A the Avogadro's number. Derive the equations of (1)H_i, (2)V_i and (3)S_i for ideal solution.

Answer

(1) From Eq. (1.2.3),

$$\left.\begin{aligned} H_i &= \frac{\partial(\mu_i/T)}{\partial(1/T)} \\ H_i^0 &= \frac{\partial(\mu_i^0/T)}{\partial(1/T)} \end{aligned}\right\} \tag{2.1.3}$$

Using Eq. (2.1.1), we have

$$\frac{\partial(\mu_i/T)}{\partial(1/T)} = \frac{\partial(\mu_i^0/T)}{\partial(1/T)} \tag{2.1.4}$$

Thus,

$$H_i = H_i^0 \tag{2.1.5}$$

(2) Similarly, from Eq. (1.2.2),

$$\left.\begin{aligned} V_i &= \left(\frac{\partial \mu_i}{\partial P}\right)_{T,N_j} \\ V_i^0 &= \left(\frac{\partial \mu_i^0}{\partial P}\right)_{T,N_j} \end{aligned}\right\} \tag{2.1.6}$$

Using Eq. (2.1.1), we have

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N_i} = \left(\frac{\partial \mu_i^0}{\partial P}\right)_{T,N_i} \tag{2.1.7}$$

Thus,

$$V_i = V_i^0 \tag{2.1.8}$$

(3) Similarly, from Eq.(1.2.1)

$$\left.\begin{aligned} S_i &= -\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N_j} \\ S_i^0 &= -\left(\frac{\partial \mu_i^0}{\partial T}\right)_{P,N_j} \end{aligned}\right\} \tag{2.1.9}$$

Using Eq.(2.1.1), we have

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N_j} = \left(\frac{\partial \mu_i^0}{\partial T}\right)_{P,N_j} + R\ln x_i \tag{2.1.10}$$

Thus,

$$-S_i = -S_i^0 + R\ln x_i \tag{2.1.11}$$

or

$$S_i = S_i^0 - R\ln x_i \tag{2.1.12}$$

or

$$\Delta S_i^{id} = -R\ln x_i \tag{2.1.13}$$

where the superscript id means the ideal solution.

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* Gilvert Newton Lewis named the solution which satisfies Eq. (2.1.1), as **ideal solution** (See G. N. Lewis, *J. Am. Chem. Soc.*, **30**, 668 (1908))

<<Problem 2-2>> Molar quantities in mixing

Derive the expressions for (1) **molar heat of mixing** $\Delta\tilde{Q}_{mix}$, (2)**molar volumetric change in mixing** $\Delta\tilde{V}_{mix}$ and (3) **molar entropy of mixing** $\Delta\tilde{S}_{mix}$ **for ideal solution.** For two-component ideal solution, (4) plot $\Delta\tilde{S}_{mix}$ vs. x_1(mole fraction of species 1) (5) show that $\Delta\tilde{S}_{mix}$ attains its maximum at $x_1=0.5$ and (6) for three-component ideal solution show that $\Delta\tilde{S}_{mix}$ attains its maximum at $x_1 = x_2 = x_3 = 1/3$.

Answer

(1)-(3) From Eqs. (1.6.1), (1.4.4) and (1.4.8),

$$\Delta\tilde{Q}_{mix} = \sum_i x_i\left(H_i - H_i^0\right) \tag{2.2.1}$$

$$\Delta\tilde{V}_{mix} = \sum_i x_i\left(V_i - V_i^0\right) \tag{2.2.2}$$

$$\Delta\tilde{S}_{mix} = \sum_i x_i\left(S_i - S_i^0\right) \tag{2.2.3}$$

(Note $\sum_i x_i = 1$)

Substituting Eqs. (2.1.5), (2.1.8) and (2.1.12) for ideal solution

$$H_i = H_i^0 \tag{2.1.5}$$

$$V_i = V_i^0 \tag{2.1.8}$$

$$S_i = S_i^0 - R\ln x_i \tag{2.1.12}$$

into the above equations, we have

$$\Delta\tilde{Q}_{mix} = 0 \tag{2.2.4}$$

$$\Delta\tilde{V}_{mix} = 0 \tag{2.2.5}$$

$$\Delta\tilde{S}_{mix} = -R\sum_i x_i \ln x_i \tag{2.2.6}$$

Thus, **ideal solution** is **athermal solution,** its volumetric change in mixing is zero and

$$\Delta\tilde{S}_{mix} \geq 0 \tag{2.2.7}$$

(4) For two-component ideal solution, Eq. (2.2.6) reduces to

$$\Delta\tilde{S}_{mix} = -R\left(x_1 \ln x_1 + x_2 \ln x_2\right) \tag{2.2.8}$$

Since $x_1 + x_2 = 1$, we have

$$\Delta\tilde{S}_{mix}/R = -\left\{x_1 \ln x_1 + \left(1-x_1\right)\ln\left(1-x_1\right)\right\} \tag{2.2.9}$$

Thus, $\Delta\tilde{S}_{mix}/R$ is plotted as a function of x_1, as shown in Fig.2-2.

(5) Differentiating Eq.(2.2.9) by x_1,

$$\frac{\partial\left(\Delta\tilde{S}_{mix}/R\right)}{\partial x_1} = \ln\left(\frac{1-x_1}{x_1}\right) \tag{2.2.10}$$

The condition for the extremum of $\Delta\tilde{S}_{mix}$

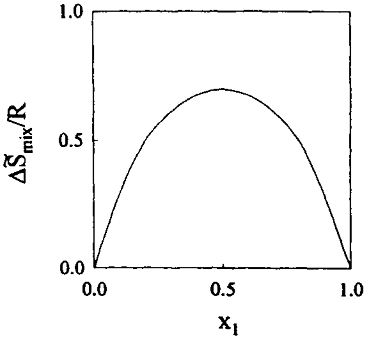

Fig. 2-2 Molar entropy of mixing as a function of mole fraction of solute for binary ideal solution

$$\frac{\partial\left(\Delta\tilde{S}_{mix}/R\right)}{\partial x_1} = 0 \tag{2.2.10a}$$

gives

$$x_1 = \frac{1}{2} \tag{2.2.11 }$$

Since $\partial^2 (\Delta\tilde{S}_{mix}/R)/\partial x_1^2 = -4 < 0$ at $x_1 = 1/2$, $\Delta\tilde{S}_{mix}$ has its maximum at $x_1 = 1/2$

(6) For three-component ideal solution, Eq. (2.2.6) reduces to

$$\begin{aligned}\Delta\tilde{S}_{mix} &= -R\left(x_1 \ln x_1 + x_2 \ln x_2 + x_3 \ln x_3\right)\\ &= -R\left\{x_1 \ln x_1 + x_2 \ln x_2 + \left(1 - x_1 - x_2\right)\ln\left(1 - x_1 - x_2\right)\right\}\end{aligned} \tag{2.2.12 }$$

The conditions for the extremum of $\Delta\tilde{S}_{mix}$

$$\frac{\partial\left(\Delta\tilde{S}_{mix}/R\right)}{\partial x_1} = \ln\frac{1 - x_1 - x_2}{x_1} = 0 \tag{2.2.13}$$

and

$$\frac{\partial\left(\Delta\tilde{S}_{mix}/R\right)}{\partial x_2} = \ln\frac{1 - x_1 - x_2}{x_2} = 0 \tag{2.2.14 }$$

give $x_1 = x_2 = x_3 = 1/3$. Since the second derivatives of $\Delta\tilde{S}_{mix}$

$$\frac{\partial^2\left(\Delta\tilde{S}_{mix}/R\right)}{\partial x_1^2} = -6 < 0 \tag{2.2.14a}$$

$$\frac{\partial^2\left(\Delta\tilde{S}_{mix}/R\right)}{\partial x_1 \partial x_2} = -3 < 0 \tag{2.2.14b}$$

$$\frac{\partial^2\left(\Delta\tilde{S}_{mix}/R\right)}{\partial x_2^2} = -6 < 0 \tag{2.2.14c}$$

are negative at

$$x_1 = x_2 = x_3 = \frac{1}{3} \tag{2.2.14d}$$

$\Delta\tilde{S}_{mix}$ has its maximum at this point.

<<Problem 2-3>> Entropy of mixing for ideal solution

Molar Gibbs free energy of mixing $\Delta\tilde{G}_{mix}$ of ideal solution, $\Delta\tilde{G}_{mix}{}^{id}$, is given by

$$\Delta\tilde{G}^{id}_{mix} = RT\sum_i x_i \ln x_i \tag{2.3.1}$$

Derive Eq. (2.3.1) and the equation which gives the entropy of mixing for ideal solution $\Delta\tilde{S}_{mix}{}^{id}$ using Eq. (2.3.1).

Answer

Molar Gibbs free energy of mixing is given by

$$\Delta\tilde{G}_{mix} = \sum_i \left(G_i - G_i^0\right) x_i = \sum_i \left(\mu_i - \mu_i^0\right) x_i \tag{2.3.2}$$

For ideal solution, from Eq. (2.1.1),

$$\mu_i - \mu_i^0 = RT\ln x_i \tag*{(2.1.1)'}$$

Substituting Eq. (2.1.1)' into Eq. (2.3.2), we obtain Eq. (2.3.1).
From Eq. (1.2.9) at constant temperature and constant pressure, we have

$$\Delta\tilde{G}_{mix} = \Delta\tilde{H}_{mix} - T\Delta\tilde{S}_{mix} \tag{2.3.3}$$

For ideal solution,

$$\Delta\tilde{H}_{mix} = \Delta\tilde{Q}_{mix} = 0 \tag{2.2.4}$$

Thus, we obtain

$$\Delta\tilde{S}^{id}_{mix} = -\frac{\Delta\tilde{G}^{id}_{mix}}{T} = -R\sum_i x_i \ln x_i \tag{2.3.4}$$

This result is consistent with <<Problem 2-2>>.

<<Problem 2-4>> Raoult's law

Consider an **equilibrium between solution and vapor phase** as shown in Fig. 2-4(a). Assuming the vapor to be a perfect gas, the chemical potential of species *i* in the vapor phase μ_i' is given by

$$\mu_i' = \mu_i^*(T) + RT\ln P_i \tag{2.4.1}$$

Here, $\mu_i^*(T)$ is the chemical potential of pure component *i*, which is in equilibrium with the solution at temperature T, and P_i is the vapor pressure of *i* th component, which is in equilibrium with the solution. By use of Eq.(2.4.1), verify that **Raoult's law**

$$P_i = P_i^0(T)x_i \tag{2.4.2}$$

is applicable to ideal solution. Here, P_i^0 is the vapor pressure of pure *i* th component liquid.

Answer

Chemical potential of ideal solution is given by

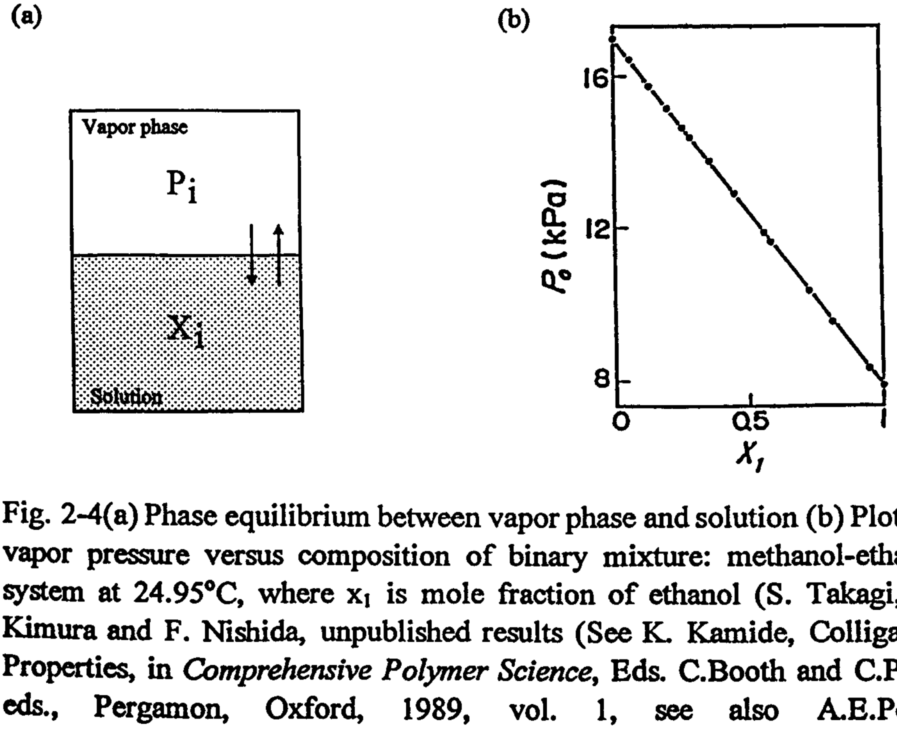

Fig. 2-4(a) Phase equilibrium between vapor phase and solution (b) Plots of vapor pressure versus composition of binary mixture: methanol-ethanol system at 24.95°C, where x_1 is mole fraction of ethanol (S. Takagi, T. Kimura and F. Nishida, unpublished results (See K. Kamide, Colligative Properties, in *Comprehensive Polymer Science*, Eds. C.Booth and C.Price eds., Pergamon, Oxford, 1989, vol. 1, see also A.E.Pope, H.D.Pflug,B.Dacre and G.C.Benson, *Can. J. Chem.* 45, 2665 (1967))

$$\mu_i = \mu_i^0(T,P) + RT\ln x_i \qquad (2.1.1)$$

The necessary and sufficient condition for the equilibrium between the vapor phase and the solution phase is given from Eq. (1.5.1) by

$$\mu_i' = \mu_i \qquad (2.4.3)$$

Substituting (2.4.1) and (2.1.1) in (2.4.3), we obtain

$$P_i = x_i \exp\left[\left\{\mu_i^0(T,P) - \mu_i^*(T)\right\} / RT\right] \qquad (2.4.4)$$

Since $P_i = P_i^0$ for $x_i = 1$, we have

$$P_i^0 = \exp\left[\left\{\mu_i^0(T,P) - \mu_i^*(T)\right\} / RT\right] \qquad (2.4.5)$$

Comparing Eq. (2.4.4) and (2.4.5), we have

$$P_i = P_i^0(T,P)x_i \qquad (2.4.2)$$

Here, P is the total pressure (See, François Marie Raoult (1830-1901), *Compt. rend.* **104**, 1430 (1887); *Z. physik. Chem.* **2**, 353 (1888)).

Figure 2-4.(b) is the vapor pressure as a function of mole fraction for the system methanol-ethanol.

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* A more exact treatment suggests that the molecules of solvent and solute should have the same size if Raoult's law holds (E. A. Guggenheim, *Trans. Farad. Soc.* **33**, 151 (1937)).

* Examples of solutions obeying Raoult's law are
(a) methylsalicylate in diethylether
(b) ethylene bromide-propylene bromide at 85°C (J. Z. von Zawidzki, *Z. phys. Chem.* **35**, 129 (1900)).
(c) benzene-bromobenzene at 80°C (M. L. McGlashan and R. J. Wingrove, *Trans. Farad. Soc.* **52**, 470 (1956)).
(d) benzene-chlorobenzene (R. S. Berry, S. A. Rice and J. Ross, *Physical Chemistry*, p912, John Wiley & Sons, 1980)
(e) benzene-toluene (methylbenzene) (P. W. Atkins, *Physical Chemistry*, p212, Oxford Univ. Press, Oxford, 1978)

* Gilbert Newton Lewis defined a 'perfect solution' as one which obeys Eq. (2.4.2) (Gilbert Newton Lewis, *J. Am. Chem. Soc.* **30**, 668 (1908)) and Washburn called a solution which obeys Raoult's law throughout the whole range of compositions as 'ideal' (Edward W. Washburn, *Z. phys. Chem.* **74**, 537 (1910)). Mixture of benzene and ethylene chloride obeys Raoult's law throughout the whole range of compositions (Gilbert Newton Lewis, *J. Am. Chem. Soc.* **30**, 668 (1908)).

<<Problem 2-5>> Boiling point elevation and freezing point depression (I)

Consider a solution which is in equilibrium with a vapor phase or a solid phase at T and P, and also consider the vapor phase or the solid phase to be in equilibrium with pure liquid solvent at T_0 and P. The temperature difference $T-T_0=\Delta T$ is directly related to the mole fraction of the solvent in the solution x_0 by

$$\frac{\Delta T}{T} = -\frac{RT}{L_0}\ln x_0 \tag{2.5.1}$$

Here, L_0 is the molar heat of vaporization. Derive Eq. (2.5.1).

Answer

The chemical potential of the solvent component in the vapor phase $\mu_0(T,P)$, and in the solution phase $\mu_0'(T,P)$, are the same at T and P (see Eq. (1.5.1)):

$$\mu_0(T,P) = \mu_0'(T,P) \tag{2.5.2}$$

The chemical potential of ideal solution $\mu_0'(T,P)$ is given from Eq. (2.1.1) by

$$\mu_0'(T,P) = \mu_0^0(T,P) + RT\ln x_0 \tag{2.5.3}$$

Combining Eq. (2.5.2) with Eq. (2.5.3), we obtain

$$\mu_0(T,P) = \mu_0^0(T,P) + RT\ln x_0 \tag{2.5.4}$$

from the condition of the equilibrium between the solution and the vapor phase. The chemical potentials of the solvent in the vapor phase and in the pure liquid phase are the same at T_0 and P:

$$\mu_0'(T_0,P) = \mu_0^0(T_0,P) \tag{2.5.5}$$

Subtracting Eq. (2.5.5) from Eq. (2.5.3), we have

$$\mu_0'(T,P) - \mu_0'(T_0,P) = \mu_0^0(T,P) - \mu_0^0(T_0,P) + RT\ln x_0 \tag{2.5.6}$$

Expanding this equation in a Taylor series under the condition of $\Delta T=(T-T_0) \ll T$, we have

$$\frac{\partial \mu_0}{\partial T}(T - T_0) = \frac{\partial \mu_0^0}{\partial T}(T - T_0) + RT\ln x_0 \tag{2.5.7}$$

Thus,

$$\left(\frac{\partial\mu_0'}{\partial T} - \frac{\partial\mu_0^0}{\partial T}\right)(T - T_0) = RT\ln x_0 \tag{2.5.8}$$

Using the relation

$$\left(\frac{\partial\mu_i}{\partial T}\right)_{P,N_i} = -S_i \tag{2.1.9}$$

we have

$$\frac{\partial\mu_0'}{\partial T} = -S_0' \tag{2.5.9}$$

and

$$\frac{\partial\mu_0^0}{\partial T} = -S_0^0 \tag{2.5.10}$$

Substituting Eqs. (2.5.9) and (2.5.10) into Eq. (2.5.8), we obtain

$$-\left(S_0' - S_0^0\right)\left(T - T_0\right) = -\frac{L_0}{T}\left(T - T_0\right) = RT\ln x_0 \tag{2.5.11}$$

Thus,

$$\frac{\Delta T}{T} = -\frac{RT}{L_0}\ln x_0 \tag{2.5.1}$$

<<Problem 2-6>> Boiling point elevation and freezing point depression (II)

Show that the molecular weight of solute evaluated using the relationship for (1) **boiling point elevation** and **freezing point depression**

$$\Delta T = -\frac{RT^2}{L_0}\ln x_0 \tag{2.5.1'}$$

and (2) **Raoult's law**

$$P_0 = P_0^0(T)x_0 \tag{2.4.2'}$$

is the number-average molecular weight

$$M_n = \Sigma' M_i N_i / \Sigma' N_i \tag{2.6.1}$$

where $P_0{}^0(T)$ is the vapor pressure of pure solvent phase and Σ' denotes the summation over all the components except i=0.

Answer

(1) **Boiling point elevation** and **freezing point depression:**

The weight concentration (g/cm^3) is given by

$$C = \Sigma' M_i N_i / V \tag{2.6.2}$$

From Eqs. (2.6.1) and (2.6.2), we have

$$\sum_i{}' N_i = \frac{1}{M_n}\sum_i{}' M_i N_i = \frac{1}{M_n} CV \cong \frac{1}{M_n} C N_0 V_0^0 \tag{2.6.3}$$

where $V_0{}^0$ is the molar volume of the pure solvent.

In dilute solution ($1 \gg \Sigma' x_i$, $N_0 \gg \Sigma' N_i$),

$$\ln x_0 = \ln\left(1 - \sum_i{}' x_i\right) \cong -\sum_i{}' x_i \cong -\sum_i{}' N_i/N_0 \tag{2.6.4}$$

Substituting Eq. (2.6.3) in Eq. (2.6.4), we have

$$\ln x_0 \cong \frac{-CV_0^0}{M_n} \tag{2.6.5}$$

Thus, Eq. (2.5.1)' reduces to

$$\Delta T = \frac{RT^2 V_0^0}{L_0}\frac{C}{M_n} \tag{2.6.6}$$

(2) **Raoult's law**:

In dilute solution,

$$x_0 = 1 - \sum_i{}' x_i \cong 1 - \frac{CV_0^0}{M_n} \tag{2.6.7}$$

Then Raoult's law is rewritten as

$$P_0 = P_0^0(T)\left(1 - \frac{CV_0^0}{M_n}\right) \qquad (2.6.8)$$

(See F. M. Raoult, *Compt. rend.*, **104**, 1430 (1887); *Z. physik. Chem.* **2**, 353 (1888))

<<Problem 2-7>>Membrane osmometry

When a solution is separated by a membrane permeable only to solvent but not to nonvolatile solutes (the membrane is referred to as a semipermeable membrane), the solute molecules are unable to pass through the membrane, resulting in a pressure difference, Π, between the liquid phases, which is defined as the **osmotic pressure**. Derive the relationship between Π and the difference $\Delta\mu_0$ in chemical potentials between the pure solvent $\mu_0^0(T,P)$ and the solvent component in the solution $\mu_0(T,P)$ at T and P:

$$\Pi = -\Delta\mu_0/V_0^0 \qquad (2.7.1)$$

where

$$\Delta\mu_0 = \mu_0(T,P) - \mu_0^0(T,P) \qquad (2.7.2)$$

and V_0^0 is the molar volume of the solvent.

Answer

From the equilibrium condition (see Eq. (1.5.1)), the following relationship

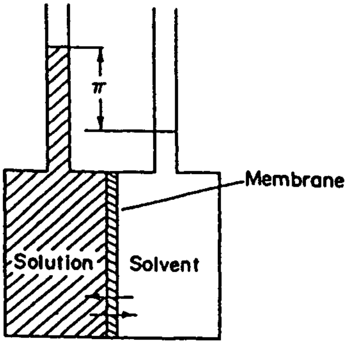

Fig. 2-7 Phase equilibrium between solution and pure solvent through semi-permeable membrane

holds:

$$\mu_0^0(T,P) = \mu_0(T,P+\Pi) \qquad (2.7.3)$$

This is called the condition of **osmotic equilibrium** or solution-membrane-solvent phase equilibrium. $\mu_0(T,P+\Pi)$ can readily be represented by

$$\mu_0(T,P+\Pi) = \mu_0^0(T,P+\Pi) + RT\ln a_0 \qquad (2.7.4)$$

Here, a_0 is called the **activity** of solvent, and in ideal solution, from Eq. (2.1.1), $a_0=x_0$ holds. If $\Pi \ll P$, we can use a Taylor series to expand $\Delta\mu_0{}^0(T,P)$ with respect to Π to obtain an approximate equation:

$$\mu_0^0(T,P+\Pi) = \mu_0^0(T,P) + \left(\frac{\partial \mu_0^0}{\partial P}\right)\Pi \qquad (2.7.5)$$

According to Eq. (1.2.2),

$$\left(\frac{\partial \mu_0^0}{\partial P}\right) = V_0^0 \qquad (2.7.6)$$

Combination of Eqs. (2.7.3)-(2.7.6) gives

$$\mu_0^0(T,P) = \mu_0^0(T,P) + V_0^0\Pi + RT\ln a_0 = \mu_0(T,P) + V_0^0\Pi \qquad (2.7.7)$$

Thus,

$$\Delta\mu_0 \equiv \mu_0(T,P) - \mu_0^0(T,P) = -\Pi V_0^0 \qquad (2.7.8)$$

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* A botanist Pfeffer discovered the phenomenon of osmosis (W. Pfeffer, *Osmotische Untersuchungen*, Leipzig, 1887).

<<Problem 2-8>> van't Hoff's equation

Show that the osmotic pressure Π of ideal solution is given by

$$\Pi = RTC/M_n \qquad (2.8.1)$$

Equation (2.8.1) is the well-known **van't Hoff's equation.**

Answer

$\mu_0(T,P)$ of ideal solution is expressed as:

$$\mu_0(T,P) = \mu_0^0(T,P) + RT\ln x_0 \tag{2.1.1}$$

According to Eq. (2.7.8),

$$\Pi = -\frac{\Delta\mu_0}{V_0^0} = -\frac{RT}{V_0^0}\ln x_0 \tag{2.8.2}$$

x_0 is expressed by using the mole fraction of solute x_i as

$$x_0 = 1 - \sum_i{}' x_i \tag{2.8.3}$$

For dilute solutions, $\Sigma' x_i$ and the total volume of solution V are approximated by

$$\sum_i{}' x_i = \frac{\sum_i{}' N_i}{N_0 + \sum_i{}' N_i} \cong \frac{\sum_i{}' N_i}{N_0} \tag{2.8.4}$$

$$V = V_0^0 N_0 + \sum_i{}' V_i^0 N_i \cong V_0^0 N_0 \tag{2.8.5}$$

Here, N_0 and N_i are the mole number of solvent and solute i, respectively, and V_0^0 and V_i^0 are the molar volume of solvent and solute i, respectively. By substituting Eqs. (2.8.3)-(2.8.5) into Eq. (2.8.2), we have an approximate relationship such as

$$\Pi = -RT\ln\left(1 - \frac{\sum_i{}' N_i}{N_0}\right)/V_0^0 = \frac{RT}{V_0^0 N_0}\sum_i{}' N_i \tag{2.8.6}$$

where $\Sigma N_i \ll N_0$. Total concentration of solute C is expressed as

$$C = \sum_i{}' C_i = \sum_i{}' N_i M_i / V = \left(\frac{\sum_i{}' N_i M_i}{\sum_i{}' N_i}\right)\left(\frac{\sum_i{}' N_i}{V}\right) = M_n \sum_i{}' N_i / V \tag{2.8.7}$$

If we substitute Eq. (2.8.7) in Eq.(2.8.6), the following relation is obtained:

$$\Pi=\frac{RT}{V_0^0N_0}CV\frac{\sum_i{}' N_i}{\sum_i{}' N_iM_i}=\frac{RTC}{M_n} \tag{2.8.8}$$

where the **number-average molecular weight** M_n is defined by

$$M_n=\frac{\sum_i{}' N_iM_i}{\sum_i{}' N_i}=\frac{\sum{}' x_iM}{\sum{}' x_i} \tag{2.6.1'}$$

---

* In case of non-ideal solution, Π is expressed using Eq. (2.10.1), in the form

$$\Pi=-\Delta\mu_0/V_0^0=-\frac{RT}{V_0^0}\ln a_0 \tag{2.8.9}$$

Here, a_0 is the **activity** of solvent. Expanding the term $\ln a_0$, Eq.(2.8.9) can be expressed as

$$\Pi/C=RT\left(\frac{1}{M_n}+A_2C+A_3C^2+\cdots\right) \tag{2.8.10}$$

with

$$A_2=V_0^0/(2M_n),\ A_3=(V_0^0)^2/(3M_n)\ \ \ldots\ \ A_n=(V_0^0)^{n-1}/(nM_n) \tag{2.8.11}$$

(See J. H. van't Hoff, Z. phys. Chem. **1**, 481 (1887) and confer <<Problem 5-2>>).

* In general van't Hoff's equation is valid only in extremely dilute solution (J. H. van't Hoff, *Vorlesungen über Theoretische und Physikalische Chemie*, Part 2, 1903).

* The ratio Π/C is called the reduced osmotic pressure.

* Osmotic pressure of solutions of polymers including dyestuff, gelatin, starch (1910-1916), rubber (1914), cellulose ester (1927-1934), and proteins (1919-1930) were measured as early as 1900-1930s, before the establishment of the concept of macromolecules.

* Wo Ostwald analyzed the literature data on rubber-benzene, guttapercha-benzene, cellulose nitrate-acetone, gelatine-water and hemoglobin-water systems, showing that van't Hoff's eqation did not hold for all the systems. He considered that the experimentally observed Π is the summation of osmotic pressure, defined by Eq. (2.8.1), Π_{os} and swelling pressure p_s, proposing the equation

$$\Pi/C=\Pi_{os}+p_s=RT/M+bC^{n-1} \tag{2.8.12}$$

where b and n are parameters. Experimentally, n~2 was confirmed (Compare with Eq. (2.8.10)). This means that the plot of Π/C against C is roughly linear and its slope depends on the degree of solvation (Wo Ostwald, *Kolloid Z.* **23**, 68 (1918), *ibid.* **69**, 60 (1929)).

* G. V. Schulz constructed a convenient osmometer (so-called Schulz-type osmometer) for polymer solutions (G. V. Schulz, *Z. physik. Chem.* **176**, 317 (1936)). He demonstrated that the plots of $(\Pi/C - RT/M)$ vs. C, for example, for polyvinylacetate-acetone system constructs roughly a single master curve, irrespective of M. lim $(\Pi/C)_{(C\to 0)}$ was confirmed to obey van't Hoff's law

$$\lim_{C\to 0}\left(\Pi / C\right) = RT/M_n \qquad (2.8.1)'$$

* Following polymer solutions were cofirmed to obey van't Hoff's law:
(a) glycogen ($M_n=2.80\times10^5$) in water, 0.1N $CaCl_2$ aqueous solution and formamide at 10°C (C=5-50g/l)
(b) egg albumin in water (C=52.8-238.5g/l)
(c) serum albumin in water (C=5.90-16.22g/l)
Note that these polymers are globular or highly branched molecules, and they do not swell in solvents (See I. Sakurada, *Kobunshi Kagaku Gairon (Polymer Chemistry)*, p49, Kobunshi Kagaku Kyokai (Polym. Pub. Assoc.), (1948)).

* Molecular theories of osmotic pressure (See, for example, (3.16.9), (5.2.7), (5.11.4), (5.14.4) and (5.19.2)) were proposed after large accumulation of experimental data.

<<Problem 2-9-a>> Empirical determination of osmotic pressure

Estimate the osmotic pressure in atm of a polymer solution consisting of polymer with the molecular weight 1×10^5 and solvent with the concentration of polymer,1g/100ml at 300K, using van't Hoff's equation.

Answer

Using the equation

$$\Pi = RTC/M \qquad (2.8.8)'$$

we have $\Pi=(0.082l/gK)(300K)(10g/l)/(1\times10^5)=2.46\times10^{-3}atm=2.54cmH_2O$.

<<Problem 2-9-b>> Empirical determination of number-average molecular weight

Estimate the number-average molecular weight M_n of polystyrene from the

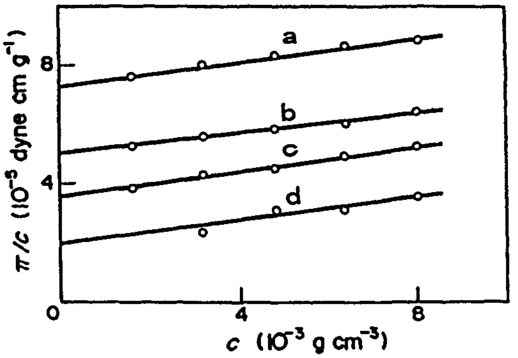

Fig. 2-9-b Plot of the ratio of osmotic pressure Π and concentration C against C for polystyrene in toluene at 25 °C (See K. Kamide, Colligative Properties, in *Comprehensive Polymer Science*, Eds. C.Booth and C.Price eds., Pergamon, Oxford, 1989, vol. 1)

osmotic pressure data for System a, b, c and d shown in Fig. 2-9-b.

Answer

From Eq. (2.8.10) and the intercepts in Fig. 2-9-b, we can estimate M_n for System a, b, c and d as 3.5, 6, 7.2 and 12.3x 10^4, respectively.

<<Problem 2-10>> Non-ideal solution (I)

Solutions whose components greatly differ in chemical structure and in polarity exhibit remarkable deviations from ideal solution. The chemical potential of the component *i* in nonideal solutions is generally given by

$$\mu_i = \mu_i^0(T,P) + RT\ln a_i \qquad (2.10.1)$$

with $a_i=\gamma_i x_i$. Here, a_i and γ_i are the activity and the activity coefficient of the component *i*, respectively. γ_i represents the extent of deviation from ideality and is a complicated function of x_j $(j \neq i)$ or the interaction between solutes and solvent. (1) Derive theoretical equations for (i) **vapor pressure depression**, (ii) **membrane osmotic pressure** and (iii) **boiling point elevation and/or freezing point depression.** (2)Derive the theoretical equation between the osmotic pressure Π and the vapor pressure P_0 given by

$$\Pi = -\frac{RT}{V_0^0}\ln\frac{P_0}{P_0^0} \qquad (2.10.2)$$

Answer

For nonideal solutions, the equations for ideal solution are modified by substituting a_i in place of x_i.

(1)(i)Vapor pressure depression; instead of Raoult's law (Eq. (2.4.2)),we have

$$P_0 = P_0^0(T)a_0 \tag{2.10.3}$$

(ii) Membrane osmotic pressure; instead of

$$\Pi = -\frac{RT}{V_0^0}\ln x_0 \tag{2.8.2}$$

we have

$$\Pi = -\frac{RT}{V_0^0}\ln a_0 \tag{2.10.4}$$

(iii)Boiling point elevation and/or freezing point depression: instead of Eq. (2.5.1), we have

$$\Delta T = -\frac{RT^2}{L_0}\ln a_0 \tag{2.10.5}$$

(2) Combination of Eqs. (2.10.3) and (2.10.4) gives Eq. (2.10.2). Note that this equation holds its validity irrespective of whether the solution is ideal or nonideal.

<<Problem 2-11>> Non-ideal solution (II)

Show that the following equations hold for nonideal solutions:

$$V_i \neq V_i^0 \tag{2.11.1}$$

$$S_i \neq S_i^0 \tag{2.11.2}$$

$$H_i \neq H_i^0 \tag{2.11.3}$$

The above equations mean, respectively, that partial molar quantities of volume, entropy and enthalpy of *i* th component of real solutions do not coincide with those of pure liquid.

Answer

Referring to Eq. (2.10.1), we have

$$\mu_i = \mu_i^0(T,P) + RT\ln a_i = \mu_i^0(T,P) + \Delta\mu_i(T,P,x_0,\cdots) \qquad (2.11.4)$$

On the other hand, the relations between chemical potential and partial molar volume for solution and pure solvent are:

$$\left.\begin{aligned} \left(\frac{\partial\mu_i}{\partial P}\right)_{T,N_j} &= V_i \\ \left(\frac{\partial\mu_i^0}{\partial P}\right)_{T,N_j} &= V_i^0 \end{aligned}\right\} \qquad (2.1.6)$$

Partially differentiating Eq. (2.11.4) with respect to pressure P at constant T and N_j and combining with Eq. (2.1.6) gives

$$\left(\frac{\partial\mu_i}{\partial P}\right)_{T,N_j} - \left(\frac{\partial\mu_i^0}{\partial P}\right)_{T,N_j} = V_i - V_i^0 = \left(\frac{\partial\Delta\mu_i}{\partial P}\right)_{T,N_j} \neq 0 \qquad (2.11.5)$$

In similar manners, the following equations are obtained:

$$\left(\frac{\partial\mu_i}{\partial T}\right)_{P,N_j} - \left(\frac{\partial\mu_i^0}{\partial T}\right)_{P,N_j} = -S_i + S_i^0 = \left(\frac{\partial\Delta\mu_i}{\partial T}\right)_{P,N_j} \neq 0 \qquad (2.11.6)$$

$$\left(\frac{\partial(\mu_i/T)}{\partial(1/T)}\right)_{P,N_j} - \left(\frac{\partial(\mu_i^0/T)}{\partial(1/T)}\right)_{P,N_j} = H_i - H_i^0 = \left(\frac{\partial(\Delta\mu_i/T)}{\partial(1/T)}\right)_{P,N_j} \neq 0 \qquad (2.11.7)$$

<<Problem 2-12>> Mixing in non-ideal solution

Derive the equations for (1) **heat of mixing,** (2) **volumetric change in mixing,** (3) **entropy of mixing,** (4) **Gibbs free energy of mixing** and (5) **excess Gibbs free energy of mixing** ΔG_{mix}^E defined by $\Delta G_{mix}^E = \Delta G_{mix} - \Delta G_{mix}^{id}$, for non-ideal solutions, where the subscript id means the ideal solution.

(1) **Heat of mixing:**

Combination of the equations for heat of mixing

$$\Delta Q_{mix} = \sum_i N_i\left(H_i - H_i^0\right) \tag{1.6.1}$$

and

$$H_i - H_i^0 = \left(\frac{\partial\left(\Delta\mu_i/T\right)}{\partial\left(1/T\right)}\right)_{P,N_j} \tag{2.11.7}$$

gives

$$\Delta Q_{mix} = \sum_i N_i\left(\frac{\partial\left(\Delta\mu_i/T\right)}{\partial\left(1/T\right)}\right)_{P,N_j} \neq 0 \tag{2.12.1}$$

(2) **Volumetric change in mixing**:
Following the same procedure as (1), we obtain

$$\Delta V_{mix} = \sum_i N_i\left(V_i - V_i^0\right) = \sum_i N_i\left(\frac{\partial\left(\Delta\mu_i\right)}{\partial P}\right)_{T,N_j} \neq 0 \tag{2.12.2}$$

(3) **Entropy of mixing**:
Following the same procedure as (1) and (2),

$$\Delta S_{mix} = \sum_i N_i\left(S_i - S_i^0\right) = -\sum_i N_i\left(\frac{\partial\left(\Delta\mu_i\right)}{\partial T}\right)_{P,N_j} \tag{2.12.3}$$

Using activity a_i and activity coefficient γ_i ($a_i = x_i\gamma_i$), $\Delta\mu_i$ is expressed as

$$\Delta\mu_i\left(T,P,x_0,x_1,\cdots\right) = RT\ln a_i = RT\ln x_i\gamma_i = RT\left(\ln x_i + \ln\gamma_i\right) \tag{2.12.4}$$

Differentiating $\Delta\mu_i$ by T, one obtains

$$\left(\frac{\partial\Delta\mu_i}{\partial T}\right)_{P,N_j} = R\ln x_i + R\ln\gamma_i + RT\frac{\partial\ln\gamma_i}{\partial T} \tag{2.12.5}$$

Combination of Eqs. (2.12.3) and (2.12.5) affords

$$\Delta S_{mix} = -\sum_i N_i\left(\frac{\partial \Delta\mu_i}{\partial T}\right)_{P,N_j}$$

$$= -R\sum_i N_i \ln x_i - R\sum_i N_i \ln \gamma_i - RT\sum_i N_i \frac{\partial \ln \gamma_i}{\partial T} \qquad (2.12.6)$$

(4) **Gibbs free energy of mixing**:
According to the definition (See Eq. (2.3.3)),

$$\Delta G_{mix} = \Delta Q_{mix} - T\Delta S_{mix} \qquad (2.12.7)$$

where

$$\Delta Q_{mix} = \sum_i N_i\left(\frac{\partial(\Delta\mu_i/T)}{\partial(1/T)}\right)_{P,N_j} \qquad (2.12.1)$$

Since $\Delta\mu_i$ is expressed as Eq. (2.12.4), we have

$$\frac{\partial(\Delta\mu_i/T)}{\partial(1/T)} = R\frac{\partial \ln \gamma_i}{\partial(1/T)} \qquad (2.12.8)$$

Combining Eqs.(2.12.1) and (2.12.8), we obtain

$$\Delta Q_{mix} = R\sum_i N_i\left(\frac{\partial \ln \gamma_i}{\partial(1/T)}\right)_{P,N_j} = -R\sum_i N_i T^2\left(\frac{\partial \ln \gamma_i}{\partial T}\right)_{P,N_j} \qquad (2.12.9)$$

Substituting Eqs.(2.12.9) and (2.12.6) into (2.12.7), we have

$$\Delta G_{mix} = RT\sum_i N_i \ln x_i + RT\sum_i N_i \ln \gamma_i = RT\sum_i N_i \ln a_i \qquad (2.12.10)$$

(5) **Excess Gibbs free energy of mixing**:
According to the definition, we obtain

$$\Delta G^E_{mix} = \Delta G_{mix} - \Delta G^{id}_{mix} = \Delta G_{mix} - RT\sum_i N_i \ln x_i \qquad (2.12.11)$$

Substituting Eq. (2.12.10) in Eq. (2.12.11), we have

$$\Delta G^{E}_{mix} = RT\sum_i N_i \ln\gamma_i \qquad (2.12.12)$$

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* Entropy of mixing for ideal solution is expressed as

$$\Delta S^{id}_{mix} = -R\sum_i N_i \ln x_i \qquad (2.1.13)'$$

According to the definition of excess entropy of mixing,

$$\Delta S^{E}_{mix} \equiv \Delta S_{mix} - \Delta S^{id}_{mix} \qquad (2.12.13)$$

Substituting Eqs. (2.12.6) and (2.1.13)' in Eq. (2.12.13), we have

$$\Delta S^{E}_{mix} = -R\left\{\sum_i N_i \ln\gamma_i + T\sum_i N_i \frac{\partial \ln\gamma_i}{\partial T}\right\} = -R\sum_i N_i\left(\ln\gamma_i + \frac{\partial \ln\gamma_i}{\partial \ln T}\right) \qquad (2.12.14)$$

From these equations, excess entropy of mixing and excess Gibbs free energy of mixing per mole are derived as

$$\Delta\tilde{S}^{E}_{mix} = \frac{\Delta S^{E}_{mix}}{\sum_i N_i} = -R\sum_i x_i\left(\ln\gamma_i + \frac{\partial \ln\gamma_i}{\partial \ln T}\right) \qquad (2.12.15)$$

$$\Delta\tilde{G}^{E}_{mix} = \Delta\mu^{E}_{mix} = \frac{\Delta G^{E}_{mix}}{\sum_i N_i} = RT\sum_i x_i \ln\gamma_i \qquad (2.12.16)$$

<<Problem 2-13>> Real solution

How can we learn that a real solution is not an ideal solution?

Answer

(1) Heat of mixing ΔQ_{mix} is not zero.

(2) Volumetric change in mixing ΔV_{mix} is not zero.

(3) Excess entropy of mixing $\Delta S_{mix}{}^{E}$ is not zero.

(4) Π/C, $\Delta T/C$ and $P_0/P_0{}^0$ depends on concentration,where ΔT is the boiling point elevation or freezing point depression.

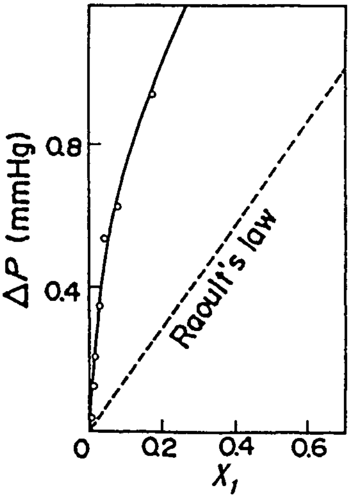

Fig. 2-13 Vapor pressure depression ΔP plotted as a function of mole fraction of atactic polystyrene with the number-average molecular weight $M_n = 2.59 \times 10^4$ in cyclohexane at 34 °C. Open circles are experimental results obtained by Krigbaum and Geymer. The broken line represents Raoult's law. (See K. Kamide, Colligative Properties, in *Comprehensive Polymer Science*, Eds. C.Booth and C.Price eds., Pergamon, Oxford, 1989, vol. 1)

Figure 2-13 shows the plot of $\Delta P(\equiv P_0 - P_0^0)$ against x_1 for atactic polystyrene-cyclohexane system at 34°C.

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* In ideal solution, cohesive energy is completely homogeneous. If any heat of mixing is neglected, the mixtures are called **athermal solutions**.

* We can characterize physico-chemical properties of real solutions from the deviation from well known standard solutions such as ideal solution, regular solution and athermal solution. The name regular solution was first introduced by Hildebrand (See J.H.Hildebrand, *J. Am. Chem. Soc.* **51**, 66 (1929)) to describe mixtures whose behavior was found experimentally to have certain regularities. So the definition was essentially an empirical one. Now we commonly use Guggenheim's definition of regular solution, i.e., any mixtures of molecules satisfying all the conditions for forming an ideal mixture except that interchange energy w defined in <<Problem 3-3>> is not zero (See E.A.Guggenheim, *Proc. Roy. Soc.* **A 148**, 304 (1935)). The molecules are thus assumed to be sufficiently alike in size and shape to be interchangeable on a lattice or quasi-lattice, but the configurational energy is no longer independent of the mutual disposition of the two or more kinds of molecules. When it is necessary to distinguish this use of the name from Hildebrand's original use of it, it is called

strictly regular solutions, or for brevity, s-regular solutions.

<<Problem 2-14>> Vapor pressure osmometry (I)

Consider the case where a drop of pure solvent at temperature T_0 and a drop of solution containing $N_0(t)$ moles of solvent and N_1 (=constant) moles of solute at temperature T(K), each located on a thermistor bead, are in contact with saturated vapor of the solvent at temperature T_0 and vapor pressure $P_0(T_0)$(gw/cm^2). Determine the **change in temperature of the drop with time dT/dt.**

Answer

Describe the surface area of the solution drop as A_1(cm^2) and the area of contact between the solution drop and the thermistor or the thermocouple including the lead wire as A_2 (=constant)(cm^2) as shown in Fig.2-14. By representing the condensation rate of the solvent vapor on to the solution drop with dN_0/dt(mole/s), the rate of heat transfer due to the condensation with dQ_1/dt (cal/s), the rate of heat exchange due to the solution drop/ ambient solvent vapor temperature difference (i.e., difference in temperature between the solution drop and the pure solvent drop)($T-T_0$) with dQ_2/dt(cal/s) and the rate of the heat conduction from the solution drop to the thermistor or the

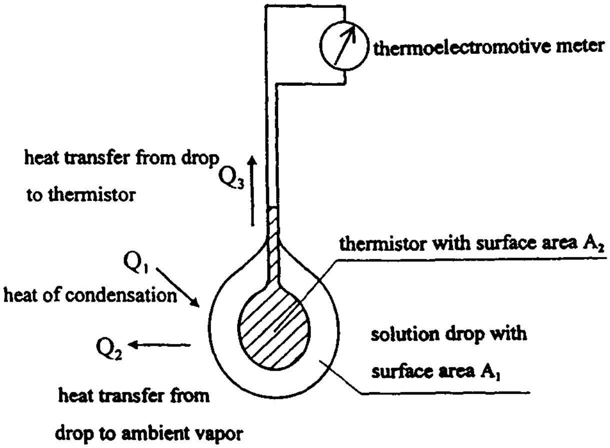

Fig. 2-14 Illustration of vapor pressure osmometer

thermocouple with dQ_3/dt(cal/s), these rates of heat transfer dQ_1/dt, dQ_2/dt, and dQ_3/dt are given by

$$\frac{dQ_1}{dt} = \Delta H \frac{dN_0(t)}{dt} \tag{2.14.1}$$

$$\frac{dQ_2}{dt} = k_1 A_1 (T - T_0) \tag{2.14.2}$$

$$\frac{dQ_3}{dt} = k_2 A_2 (T - T_0) \tag{2.14.3}$$

respectively, where ΔH is the heat of condensation (cal/mole), and k_1 and k_2 are the coefficients of the surface heat transfer (cal/cm^{2}sK). The following exothermic or endothermic changes in the solution drop/ambient vapor system could be disregarded: (1)heat loss required by solvent condensed at temperature T_0 for attaining to T, (2) heat production by the thermistor for self-heating, (3) heat dissipation due to radiation, and (4) heat of mixing of the condensed solvent and solution.

Taking into account the heat balance achieved by the solution drop in question, the change in temperature of the drop with time dT/dt can be written through use of Eqs.(2.14.1) to (2.14.3) in the form:

$$C_p \rho V \frac{dT}{dt} = \sum_{i=1}^{3} \frac{dQ_i}{dt} \tag{2.14.4}$$

where C_p(calg/K) represents the specific heat under a constant pressure, V (cm^3) the volume, and ρ (g/cm^3) the density of the solution drop. Substituting Eqs. (2.14.1)-(2.14.3) in Eq. (2.14.4), we have the relation for the temperature change of the solution droplet:

$$\frac{dT}{dt} = \frac{1}{C_p \rho V} \left\{ \left(\frac{dN_0(t)}{dt} \right) \Delta H - \left(k_1 A_1 + k_2 A_2 \right) \left(T - T_0 \right) \right\} \tag{2.14.5}$$

<<Problem 2-15>> Vapor pressure osmometry (II)

It seems plausible to assume that solvent molecules in the vapor phase transfer only through the diffusion mechanism when the solvent vapor condenses onto the solution drop. Therefore, the rate of condensation

$dN_0(t)/dt$ (here, $N_0(t)$ is the solvent molecules of the solution drop at time t) is shown to be related to the difference between the saturated vapor pressure $P_0(T_0)$ (g/cm^2) of the ambient pure solvent and the vapor pressure $P(T)$ (g/cm^2) of the solvent in the solution drop through the formula:

$$\frac{dN_0(t)}{dt} = k_3 A_1 \{P_0(T_0) - P(T)\} \tag{2.15.1}$$

where k_3 (mole/g sec) denotes the mass transfer coefficient which depends upon the detailed mechanism of diffusion. Modify Eq. (2.15.1) by expressing P(T) in terms of $P_0(T_0)$.

Answer

The vapor pressure of solvent in the solution drop P(T) at temperature T is related to the vapor pressure of pure solvent $P_0(T)$ through the relation:

$$P(T) = a_0 P_0(T) \tag{2.10.3 }$$

Here a_0 is the activity of solvent in the solution. Since the temperature of solution drop T is very close to that of ambient atmosphere T_0, then $P_0(T)$ can be expressed with sufficient accuracy in the form:

$$P_0(T) = P_0(T_0) + \left(\frac{dP_0(T)}{dT}\right)_{T=T_0}(T - T_0) + \frac{1}{2}\left(\frac{d^2P_0(T)}{dT^2}\right)_{T=T_0}(T - T_0)^2 + \cdots \tag{2.15.2 }$$

Assuming ideal gas for solvent vapor, $(dP_0(T)/dT)_{T=T_0}$ in Eq. (2.15.2) is related to $P_0(T_0)$ through the **Clausius-Clapeyron equation**:

$$\left(\frac{dP_0(T)}{dT}\right)_{T=T_0} = \left(\frac{\Delta H}{RT_0^{\,2}}\right)P_0(T_0) \tag{2.15.3}$$

(See Clapeyron, *J. L'ecole polytechnique* **14**, No. 23, 153 (1834))
Differentiation of both sides of Eq. (2.15.3) by T yields

$$\left(\frac{d^2P_0(T)}{dT^2}\right)_{T=T_0} = \left(\frac{\Delta H}{RT_0^{\,2}}\right)\left\{\left(\frac{\Delta H}{RT_0^{\,2}}\right) - \frac{2}{T_0}\right\}P_0(T_0) \tag{2.15.4}$$

Eq. (2.10.3) can be rewritten by using Eqs. (2.15.2)-(2.15.4) in the form:

$$P(T)$$
$$= a_0 P_0(T_0)\left[1 + \left(\frac{\Delta H}{RT_0^2}\right)(T - T_0) + \frac{1}{2}\left(\frac{\Delta H}{RT_0^2}\right)\left\{\left(\frac{\Delta H}{RT_0^2}\right) - \frac{2}{T_0}\right\}(T - T_0)^2 + \cdots\right] \tag{2.15.5}$$

Substituting Eq. (2.15.5) into Eq. (2.15.1) we obtain

$$\frac{dN_0(t)}{dt} = k_3 A_1 P_0(T_0)$$
$$\times\left[1 - a_0\left\{1 + \left(\frac{\Delta H}{RT_0^2}\right)(T - T_0) + \frac{1}{2}\left(\frac{\Delta H}{RT_0^2}\right)\left\{\left(\frac{\Delta H}{RT_0^2}\right) - \frac{2}{T_0}\right\}(T - T_0)^2 + \cdots\right\}\right] \tag{2.15.6}$$

<<Problem 2-16>> Vapor pressure osmometry (III)

Using Eq. (2.14.5) for dT/dt in <<Problem 2-14>> and Eq. (2.15.6) for $dN_0(t)/dt$ in <<Problem 2-15>>, derive the equation for the temperature difference $(T-T_0)$ at steady state, $(T-T_0)_s$.

Answer

Combination of Eqs. (2.14.5) and (2.15.6) gives

$$\frac{dT}{dt} = \frac{1}{C_p V \rho}\left[k_3 A_1\left\{1 - a_0\left(1 + \left(\frac{\Delta H}{RT_0^2}\right)(T - T_0)\right.\right.\right.$$
$$\left.\left. + \frac{1}{2}\left(\frac{\Delta H}{RT_0^2}\right)\left(\frac{\Delta H}{RT_0^2} - \frac{2}{T_0}\right)(T - T_0)^2\right)\right\}$$
$$\left. \times P_0(T_0)\Delta H - (k_1 A_1 + k_2 A_2)(T - T_0)\right] \tag{2.16.1}$$

In the steady state, dT/dt=0. Then we obtain

$$k_3 A_1\left\{1 - a_0\left(1 + \left(\frac{\Delta H}{RT_0^2}\right)(T - T_0)_s + \frac{1}{2}\left(\frac{\Delta H}{RT_0^2}\right)\left(\frac{\Delta H}{RT_0^2} - \frac{2}{T_0}\right)(T - T_0)_s^2\right)\right\}$$
$$\times P_0(T_0)\Delta H - (k_1 A_1 + k_2 A_2)(T - T_0)_s = 0 \tag{2.16.2}$$

(1) Approximate approach

If the term containing $(T\text{-}T_0)_s^2$ can be neglected, Eq. (2.16.2) is simplified into

$$\left(T-T_0\right)_s \cong \frac{1-a_0}{\dfrac{\Delta H}{RT_0^{\,2}}+\dfrac{k_1A_1+k_2A_2}{k_3A_1P_0\left(T_0\right)\Delta H}} \tag{2.16.3}$$

Eq. (2.16.3) was first derived in a different manner by Kamide and Sanada (See K. Kamide and M. Sanada, *Kobunshi Kagaku* **24**, 751 (1967)).

Note that the steady state can be applied not only to vapor pressure osmometry but also to **boiling point elevation method** and **cryoscopic method**. In other words, the classical equilibrium theory is not valid in these methods.

(2) Rigorous approach

Eq. (2.16.2) can be rearranged as

$$\frac{1}{2}a_0AB\left(\Delta T_s\right)^2+\left[a_0A+C'\right]\Delta T_s-\left(1-a_0\right)=0 \tag{2.16.4 }$$

where

$$\left.\begin{aligned}
&\Delta T_s=\left(T-T_0\right)_s\\
&A=\frac{\Delta H}{RT_0^{\,2}}\\
&B=\frac{\Delta H}{RT_0^{\,2}}-\frac{2}{T_0}\\
&C'=\frac{k_1A_1+k_2A_2}{k_3A_1P_0\left(T_0\right)\Delta H}\\
&D=\left(a_0A+C'\right)^2+2a_0\left(1-a_0\right)AB
\end{aligned}\right\} \tag{2.16.5 }$$

From Eq. (2.16.5), we obtain

$$\Delta T_s=\frac{-\left(a_0A+C'\right)\pm D^{1/2}}{a_0AB} \tag{2.16.6 }$$

$\Delta T_s \geqq 0$ is the necessary condition. So, Eq. (2.16.6) with plus sign ahead of $D^{1/2}$ has a physical meaning. On the other hand, ΔT_s can be expanded in a power series of (a_0-1) as

$$\Delta T = (\Delta T)_{a_0=1} + \left(\frac{d\Delta T}{da_0}\right)_{a_0=1}(a_0 - 1) + \frac{1}{2!}\left(\frac{d^2\Delta T}{da_0^{\,2}}\right)_{a_0=1}(a_0 - 1)^2 + \frac{1}{3!}\left(\frac{d^3\Delta T}{da_0^{\,3}}\right)_{a_0=1}(a_0 - 1)^3 + \cdots \tag{2.16.7}$$

From Eq. (2.16.6), we can calculate ($d\Delta T/da_0$), ($d^2\Delta T/da_0^2$) and ($d^3\Delta T/da_0^3$), and the results are:

$$\frac{d\Delta T}{da_0} = \frac{1}{ABa_0^{\,2}D^{1/2}}\left\{-a_0A\left(B+C'\right)-C'^2+C'D^{1/2}\right\} \tag{2.16.8}$$

$$\begin{aligned}\frac{d^2\Delta T}{da_0^{\,2}} = {} & \\ & \frac{1}{ABa_0^{\,4}D}\left[\left\{-A(B+C')+C'\frac{2A(a_0A+C')+2\{(1-a_0)-a_0\}AB}{2D^{1/2}}\right\}a_0^{\,2}D^{1/2}\right. \\ & -\left\{-a_0A(B+C')-C'^2+C'D^{1/2}\right\} \\ & \left.\times\left\{2a_0D^{1/2}+a_0^{\,2}\,\frac{2A(a_0A+C')+2\{(1-a_0)-a_0\}AB}{2D^{1/2}}\right\}\right] \\ = {} & \frac{1}{ABa_0^{\,3}D}\left[\left\{a_0A(B+C')-2C'^2\right\}D^{1/2}-2C'D+\frac{a_0\left\{a_0A(B+C')+C'^2\right\}}{D^{1/2}}\right. \\ & \left.\times\left\{A(a_0A+C')+(1-2a_0)AB\right\}\right]\end{aligned} \tag{2.16.9}$$

$$\begin{aligned}\frac{d^3\Delta T}{da_0^{\,3}} = {} & \frac{1}{ABa_0^{\,6}D^2} \\ & \times\Bigl(\Bigl[A(B+C')D^{1/2}+\left\{a_0A(B+C')+2C'^2\right\}\left\{A(a_0A+C')+(1-2a_0)AB\right\}D^{1/2} \\ & -4C'\left\{A(a_0A+C')+(1-2a_0)AB\right\}+D^{-1/2}\left\{a_0A(B+C')+C'^2\right\} \\ & \times\left\{A(a_0A+C')+(1-2a_0)AB\right\}+a_0A(B+C')\left\{A(a_0A+C')+(1-2a_0)AB\right\} \\ & +a_0\Bigl(\left\{a_0A(B+C')+C'^2\right\}\left(A^2-2AB\right)\Bigr)\end{aligned} \tag{2.16.10}$$

Using Eqs. (2.16.8)-(2.16.10), we obtain equations of ($d\Delta T/da_0$) at a_0=1 (designated as $(d\Delta T/da_0)_{a0=1}$), $(d^2\Delta T/da_0^2)$ at $a_0=1$, $(d^2\Delta T/da_0^2)_{a0=1}$ and $(d^3\Delta T/da_0^3)$ at $a_0=1$, $(d^3\Delta T/da_0^3)_{a0=1}$, respectively, as

$$\left(\frac{d\Delta T}{da_0}\right)_{a_0=1} = -\frac{1}{A+C'} \tag{2.16.11}$$

$$\left(\frac{d^2\Delta T}{da_0{}^2}\right)_{a_0=1} = \frac{A}{\left(A+C'\right)^3}\left\{2\left(A+C'\right)-B\right\} \tag{2.16.12}$$

$$\left(\frac{d^3\Delta T}{da_0{}^3}\right)_{a_0=1} = \frac{A}{\left(A+C'\right)^4}\left\{-6A\left(A+C'\right)+3B\left(A-C'\right)+3AB-\frac{3AB^2}{A+C'}\right\} \tag{2.16.13}$$

Substitution of the relationships between a_0 and C

$$1-a_0 = V_0\left[\frac{C}{M}+\left(A_2-\frac{1}{2}\frac{V_0}{M^2}\right)C^2+\left(A_3-A_2\frac{V_0}{M}+\frac{1}{6}\frac{V_0{}^2}{M^3}\right)C^3+\cdots\right] \tag{2.16.14}$$

$$\left(1-a_0\right)^2 = \left(\frac{V_0}{M}\right)^2 C^2+2\left(A_2-\frac{1}{2}\frac{V_0}{M}\right)\frac{V_0{}^3}{M}C^3+\cdots \tag{2.16.15}$$

$$\left(1-a_0\right)^3 = \left(\frac{V_0}{M}\right)^3 C^3+\cdots \tag{2.16.16}$$

(Note that Eqs. (2.16.15) and (2.16.16) are derived from Eq. (2.16.14), C in these equations means concentration (g/cm^3) and A_2, A_3 are the second- and third virial coefficients determined by membrane osmometry) into Eq. (2.16.7) gives

$$\begin{aligned}\Delta T_s = &-\left(\frac{d\Delta T_s}{da_0}\right)_{a_0=1}\frac{V_0}{M}C\\ &+\left[-\left(\frac{d\Delta T_s}{da_0}\right)_{a_0=1}\left(A_2-\frac{1}{2}\frac{V_0}{M^2}\right)V_0+\frac{1}{2}\left(\frac{d^2\Delta T_s}{da_0{}^2}\right)_{a_0=1}\left(\frac{V_0}{M}\right)^2\right]C^2\\ &+\left[-\left(\frac{d\Delta T_s}{da_0}\right)_{a_0=1}\left\{A_3-A_2\frac{V_0}{M}+\frac{1}{6}\left(\frac{V_0}{M}\right)^2\right\}V_0+\frac{1}{2}\left(\frac{d^2\Delta T_s}{da_0{}^2}\right)_{a_0=1}\right.\\ &\left.\times 2\left(A_2-\frac{1}{2}\frac{V_0}{M}\right)\frac{V_0{}^2}{M}-\frac{1}{6}\left(\frac{d^3\Delta T_s}{da_0{}^3}\right)_{a_0=1}\left(\frac{V_0}{M}\right)^3\right]C^3\end{aligned} \tag{2.16.17}$$

In deriving Eq. (2.16.17), $(\Delta T_s)_{a0=1}=1$ was considered.
Substitution of Eqs. (2.16.11)-(2.16.13) into Eq. (2.16.17) yields

Table 2-16 Limiting value for the ratio of steady-state temperature difference ΔT_s and concentration C, calibration parameter K_s, molecular weight M_n, and second virial coefficient $A_{2,v}$ determined by vapor pressure osmometry for solutions of atactic polystyrene in benzene at 40℃

Polystyrene Sample code	$\lim_{C=0}(\Delta T_s/C)$ / $K\,cm^3\,g^{-1}$	$K_s \cdot 10^{-3}$ / $K\,cm^3\,mol^{-1}$	$M_n \cdot 10^4$ as informed[a]	$M_n \cdot 10^4$ by VPO[b]	$M_n \cdot 10^4$ by VPO[c]	$A_{2,v} \cdot 10^3$ / $mol\,cm^3\,g^{-2}$
12a	0.576	1.169	0.2030	0.188	0.194	1.54
11a	0.310	1.448	0.480	0.348	0.361	0.48
8a	0.110	1.165	1.050	0.982	1.018	—
2b	0.059	1.200	2.04	1.83	1.90	0.58
7a	0.0192	0.979	5.10	5.63	5.83	1.12
4a	0.0124	1.21	9.72	8.71	9.03	0.72
1a	0.0052	0.83	16.00	20.77	21.50	1.17
3a	0.0030	1.23	41.10	36.00	37.30	0.92

[a] By supplier.

[b] M_n was determined by putting $K_s = 1.08 \cdot 10^3$, which was obtained for benzil.

[c] M_n was determined by putting $K_s = 0.5 \cdot 2.24 \cdot 10^3$

(See K.Kamide, T.Terakawa, H.Uchiki, *Macromol Chem* **177**,1447(1976))

$$\Delta T_s = K_s\left[\left(\frac{C}{M}\right) + A_{2,v}C^2 + A_{3,v}C^3 + \cdots\right] \qquad (2.16.18)$$

with

$$K_s = \frac{V_0}{A+C} = \frac{V_0}{\dfrac{\Delta H}{RT_0{}^2} + \dfrac{k_1A_1 + k_2A_2}{k_3A_1P_0(T_0)\Delta H}} \qquad (2.16.19)$$

where V_0(cm^3/mole) is the molar volume of solute, M the molecular weight of solute, $A_{2,v}$ (mole cm^3/g^2), $A_{3,v}$ (mole cm^6/g^3), the second- and third virial coefficients determined by vapor pressure osmometry, K_s the calibration parameter depending on the nature of solvent ($P_0(T_0)$, ΔH) as well as the dimensions of an apparatus (k_1, k_2, A_1 and A_2) in a very complicated manner. K_s is experimentally determined by using

$$K_s = \lim_{C\to 0}\left(\frac{\Delta T_s}{C}\right)M \qquad (2.16.20\ )$$

for the standard system of a solute with definite M in a solvent.
Combination of Eqs. (2.16.3) and (2.16.14) gives Eqs. (2.16.18) and (2.16.19). In this case both approaches yield the same results.

---

* Typical example for the application of the above method is shown for the system polystyrene in benzene in Table 2-16. (See K.Kamide K.Sagamiya & C.Nakayama, *Makromol. Chem.* **132,** 15(1970); K.Kamide, *Kobunshi Kagaku* **25,** 648 (1968))

<<Problem 2-17>> Vapor pressure osmometry (IV)

According to the classical equilibrium theory of vapor pressure osmometry, the temperature difference at equilibrium state $(T-T_0)_e$ is given by

$$(T - T_0)_e = K_e\left\{\left(\frac{C}{M}\right) + A_{2,v}C^2 + \cdots\right\} \qquad (2.17.1\ )$$

with

$$K_e = \frac{V_0}{A} = \frac{RT_0{}^2V_0}{\Delta H} \qquad (2.17.2\ )$$

Show that these relationships are a special solution of the general theory (steady state theory):

$$(T-T_0)_s = K_s\left\{\left(\frac{C}{M}\right)+A_{2,v}C^2+A_{3,v}C^3+\cdots\right\} \tag{2.16.18}$$

$$K_s = \frac{RT_0{}^2V_0}{\Delta H}\cdot\frac{1}{1+\left(\frac{k_1A_1+k_2A_2}{k_3A_1}\right)\left(\frac{RT_0{}^2}{P_0(T_0)\Delta H^2}\right)} = K_e/\left\{1+\left(\frac{k_1A_1+k_2A_2}{k_3A_1}\right)\left(\frac{RT_0{}^2}{P_0(T_0)\Delta H^2}\right)\right\} \tag{2.16.19}$$

Answer

In the equilibrium theory any heat transfer except heat of condensation (Q_1) is assumed to be neglected. In other words,

$$\left.\begin{aligned} dQ_2/dt &= 0 \\ dQ_3/dt &= 0 \end{aligned}\right\} \tag{2.17.3}$$

or

$$\left.\begin{aligned} k_1 &= 0 \\ k_2 &= 0 \end{aligned}\right\} \tag{2.17.4}$$

are assumed. Putting Eq. (2.17.4) into Eq. (2.16.19), we obtain

$$K_s(k_1=k_2=0)=\frac{RT_0{}^2V_0}{\Delta H}\equiv K_e \tag{2.17.5}$$

In any practical case $k_1 \neq 0$ and $k_2 \neq 0$, the equilibrium state can never be realized. The term $(k_1A_1+k_2A_2)RT_0{}^2/(k_3A_1P_0(T_0)\Delta H^2)$ in Eq. (2.16.19) is always positive. Then the inequality $K_s<K_e$ holds.

<<Problem 2-18>> Vapor pressure osmometry (V)

Derive the relationship between the second- and the third virial coefficient determined by vapor pressure osmometry (VPO) and those determined by membrane osmometry:

$$A_{2,v} = A_{2,o} + \left(\frac{V_0}{M^2}\right)\left\{\left(\frac{RT_0}{\Delta H} - \frac{1}{2}\right)\left(\frac{K_s}{K_e}\right)^2 + \frac{K_s}{K_e} - \frac{1}{2}\right\} \tag{2.18.1}$$

$$\begin{aligned}A_{3,v} &= A_{3,o} + 2A_{2,o}\left(\frac{V_0}{M}\right)\left\{\left(\frac{RT_0}{\Delta H} - \frac{1}{2}\right)\left(\frac{K_s}{K_e}\right)^2 + \frac{K_s}{K_e} - \frac{1}{2}\right\} \\ &+ \left(\frac{V_0{}^2}{M_1}\right)\left[\left(\frac{RT_0}{\Delta H} - \frac{1}{2}\right)\left\{\frac{1}{2}\left(\frac{RT_0}{\Delta H} - \frac{1}{2}\right)\left(\frac{K_s}{K_e}\right)^2 + \frac{K_s}{K_e} - 2\right\}\left(\frac{K_s}{K_e}\right)^2\right. \\ &\left. -2\left(\frac{K_s}{K_e}\right)^3 + \left(\frac{K_s}{K_e}\right)^2 - \frac{K_s}{K_e} + \frac{1}{6}\right]\end{aligned} \tag{2.18.2}$$

Here, $A_{2,o}$ and $A_{3,o}$ are the **second-** and the **third virial coefficients** in Eq. (2.8.10) determined by membrane osmometry

$$\frac{\Pi}{C} = RT\left\{\left(\frac{1}{M}\right) + A_{2,o}C + A_{3,o}C^2 + \cdots\right\} \tag{2.8.10)'$$

Answer

Eq. (2.16.17) is rearranged with Eqs. (2.16.11)-(2.16.13) in the form

$$\begin{aligned}\Delta T_s &= \frac{V_0}{A + C'} \cdot \frac{C}{M} \\ &+ \left[\frac{1}{A + C'}\left(A_{2,o} - \frac{1}{2}\frac{V_0}{M^2}\right)V_0 + \frac{1}{2}\frac{A}{(A + C')^3}\{2(A + C') - B\}\left(\frac{V_0}{M}\right)^2\right]C^2 \\ &+ \frac{1}{A + C'}\left\{A_{3,o} - A_{2,o}\frac{V_0}{M} + \frac{1}{6}\left(\frac{V_0}{M}\right)^2\right\}V_0 \\ &+ \frac{1}{2}\frac{A}{(A + C')^3}\{2(A + C') - B\}2\left(A_{2,o} - \frac{1}{2}\frac{V_0}{M^2}\right)\frac{V_0{}^2}{M} \\ &- \frac{1}{6}\frac{A}{(A + C')^4}\left\{-6A(A + C') + 3B(A - C') + 3AB - \frac{3AB^2}{A + C'}\right\}\left(\frac{V_0}{M}\right)^3\Big]C^3 + \cdots\end{aligned} \tag{2.18.3}$$

Comparison of Eq. (2.18.3) with

$$\Delta T_s = K_{s,0}\left[\left(\frac{C}{M}\right) + A_{2,v}C^2 + A_{3,v}C^3 + \cdots\right] \tag{2.16.18}$$

affords us the evaluation of $A_{2,v}$ and $A_{3,v}$. That is, we obtain

$$A_{2,v} = A_{2,o} - \frac{V_0}{M^2}\left\{\frac{1}{2} - \frac{K_s}{K_e} + \frac{1}{2}\left(\frac{K_{s,0}}{K_e}\right)^2 - \frac{K_{s,0}}{K_e}\cdot\frac{K_{s,0}}{V_0}\cdot\frac{1}{T}\right\} \tag{2.18.4}$$

Using the relationship

$$\frac{K_{s,0}}{K_e}\cdot\frac{K_{s,0}}{V_0}\cdot\frac{1}{T} = \left(\frac{K_{s,0}}{K_e}\right)^2\left(\frac{RT_0}{\Delta H}\right) \tag{2.18.5}$$

which is derived from Eqs. (2.16.19) and (2.17.5), Eq. (2.18.4) is directly converted into Eq. (2.18.1).

In a similar manner, we have

$$\begin{aligned} A_{3,v} = {} & \frac{A+C'}{V_0}\left[-\left(\frac{d\Delta T_s}{da_0}\right)_{a_0=1}\left(A_{3,o} - A_{2,o}\frac{V_0}{M} + \frac{1}{6}\frac{V_0^3}{M^3}\right)V_0\right. \\ & \left. + \left(\frac{d^2\Delta T_s}{da_0^2}\right)_{a_0=1}\left(A_{2,o} - \frac{1}{2}\cdot\frac{V_0}{M^2}\right)\frac{V_0^2}{M} - \frac{1}{6}\left(\frac{d^3\Delta T_s}{da_0^3}\right)_{a_0=1}\left(\frac{V_0}{M}\right)^3\right] \\ = {} & A_{3,o} - \frac{1}{3}\cdot\frac{V_0^2}{M^3} - \left(A_{2,o} - \frac{1}{2}\cdot\frac{V_0}{M^2}\right)\frac{V_0}{M}\cdot\frac{AB-(A+C')(A-C')}{(A+C')^2} \\ & + \frac{1}{2}\cdot\frac{A}{(A+C')^4}\left[(A+C')\left\{2A\left(C'-\frac{2}{T}\right)+C'\left(A-\frac{2}{T}\right)\right\} + A\left(A-\frac{2}{T}\right)^2\right]\frac{V_0^2}{M^3} \end{aligned} \tag{2.18.6 }$$

Here

$$\frac{(A+C')(C'-A)+AB}{(A+C')^2} = 1 - 2\left(\frac{K_s}{K_e}\right) + \left(\frac{K_s}{K_e}\right)^2 - \frac{K_s}{K_e}\cdot\frac{K_{s,0}}{K_e}\cdot\frac{2}{T} \tag{2.18.7 }$$

and

$$\frac{1}{2}\frac{A}{(A+C')^4}\left[(A+C')\left\{2A\left(C'-\frac{2}{T}\right)-C'\left(A-\frac{2}{T}\right)\right\}+A\left(A-\frac{2}{T}\right)^2\right]$$

$$= \frac{3}{2}\left(\frac{K_s}{K_e}\right)^2 - \frac{3}{2}\left(\frac{K_s}{K_e}\right)^3 + \frac{1}{2}\left(\frac{K_{s,0}}{K_e}\right)^4 - \frac{K_s}{K_e}\cdot\frac{K_s}{V_0}\cdot\frac{1}{T} - \left(\frac{K_s}{K_e}\right)^2\cdot\frac{K_s}{V_0}\cdot\frac{1}{T}$$

$$-\left(\frac{K_s}{K_e}\right)^3\cdot\frac{K_s}{V_0}\cdot\frac{1}{T} + \left(\frac{K_s}{K_e}\right)^2\cdot\left(\frac{K_s}{V_0}\right)^2\cdot\frac{2}{T^2} \qquad (2.18.8)$$

Substituting Eqs. (2.18.7) and (2.18.8) into Eq. (2.18.6), we obtain

$$A_{3,v} = A_{3,o} - \frac{V_0}{M}A_{2,o}\left[1 - 2\frac{K_s}{K_e} + \left(\frac{K_s}{K_e}\right)^2 - \left(\frac{K_s}{K_e}\right)\frac{K_s}{V_0}\cdot\frac{2}{T}\right]$$

$$+\frac{V_0{}^2}{M^3}\left[\frac{1}{6} - \frac{K_s}{K_e} + 2\left(\frac{K_s}{K_e}\right)^2 - \frac{3}{2}\left(\frac{K_s}{K_e}\right)^3 + \frac{1}{2}\left(\frac{K_{s,0}}{K_e}\right)^4 - 2\frac{K_s}{K_e}\cdot\frac{K_s}{V_0}\cdot\frac{1}{T}\right.$$

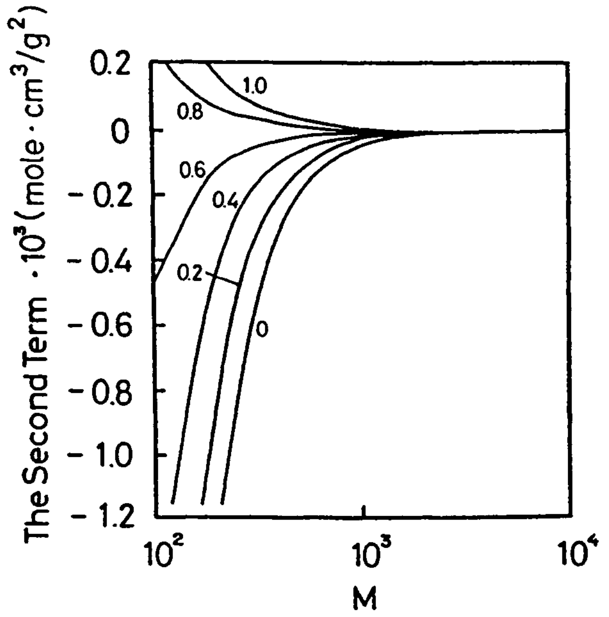

Fig. 2-18 Dependence of the second term in the right-hand side in Eq. (2.18.1) on molecular weight of solute M for benzene solution at 37 °C. Various values for K_s/K_e are indicated on curves. (See K. Kamide, K. Sugamiya and C. Nakayama, *Makromol. Chem.* **132**, 75 (1970))

$$-\left(\frac{K_s}{K_e}\right)^2 \cdot \frac{K_s}{V_0} \cdot \frac{1}{T} - 2\left(\frac{K_s}{K_e}\right)^3 \cdot \frac{K_s}{V_0} \cdot \frac{1}{T} + 2\left(\frac{K_s}{K_e}\right)^2 \cdot \left(\frac{K_s}{V_0}\right)^2 \cdot \frac{1}{T^2} \qquad (2.18.9)$$

It is worth noting that Eq. (2.18.9) was derived by neglecting the terms of the order higher than the third on the right-hand side in Eq. (2.18.3). Therefore, Eq. (2.18.9) is a closely approximate expression for $A_{3,v}$. Using Eq. (2.18.5), Eq. (2.18.9) is rearranged to Eq. (2.18.2). Eqs. (2.18.1) and (2.18.2) indicate that generally the second virial coefficient determined by VPO, $A_{2,v}$, does not coincide with that determined by membrane osmometry, $A_{2,o}$.

$$A_{2,v} \neq A_{2,o} \qquad (2.18.10)$$

<<Problem 2-19-a>> Vapor pressure osmometry (VI)

The efficiency of measurements in vapor pressure osmometry is defined by

$$\frac{(T-T_0)_s}{(T-T_0)_e} = \frac{K_s}{K_e} = \frac{1}{1+\frac{(k_1A_1+k_2A_2)}{k_3A_1}\cdot\frac{RT_0^{\,2}}{\Delta H^2P_0(T_0)}} \qquad (2.19.1)$$

Discuss the experimental conditions effective to improve the efficiency on the

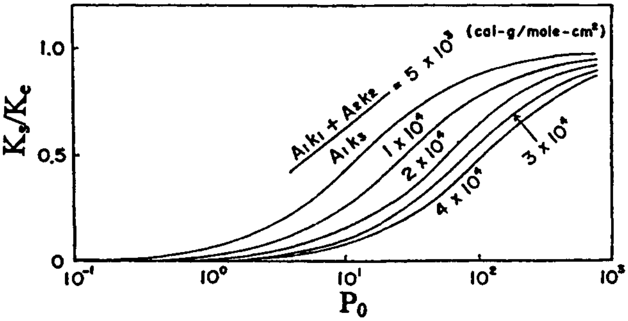

Fig. 2-19 Theoretical relationships between the efficiency K_s/K_e (ref. Eq. (2.19.1)) and vapor pressure of solvent $P_0(T_0)$ (mmHg), where $\Delta H = 7 \times 10^3$ (cal/mol) and T_0=300 K. (See K. Kamide, M. Sanada, *Kobunshi Kagaku* **29**, 751 (1967))

basis of Eq. (2.19.1).

Answer

In order to increase the ratio K_s/K_e, it is effective

(1) to increase drop size (through the increase in A_1)

(2) to measure at lower temperature (T_0)

(3) to utilize solvent with larger heat of condensation (ΔH)

(4) to utilize solvent with higher vapor pressure ($P_0(T_0)$)

(5) to measure at lower atmospheric pressure (diffusibility of gas is approximately inversely proportional to atmospheric pressure P_n. Then as P_n decreases diffusion coefficient increases and k_3 increases)

Note that the measuring efficiency does not mean the sensitivity.

<<Problem 2-19-b>> Vapor pressure osmometry (VII)

Discuss the effect of vapor pressure of solvent $P_0(T)$ on the sensitivity of vapor pressure osmometry on the basis of Eq. (2.16.19) or Eq. (2.19.1)

$$K_s=\frac{V_0}{A+C}=\frac{V_0}{\frac{\Delta H}{RT_0^2}+\frac{k_1A_1+k_2A_2}{k_3A_1P_0(T_0)\Delta H}} \qquad (2.16.19)$$

$$=\frac{K_e}{1+\frac{(k_1A_1+k_2A_2)}{k_3A_1}\cdot\frac{RT_0^2}{\Delta H^2P_0(T_0)}} \qquad (2.19.1)$$

and calculate K_s/K_e as a function of $P_0(T_0)$ in case of $(k_1A_1+k_2A_2)/k_3A_3$ (cal g/mol cm^3) = 5×10^3, 1×10^4, 2×10^4, 4×10^4; ΔH (cal/mol)=7×10^3, T(K)=300.

Answer

As $P_0(T_0)$ increases both K_s and K_s/K_e increase. Fig. 2-19 show $P_0(T_0)$ dependence of K_s/K_e .

<<Problem 2-20>> Vapor pressure osmometry (VIII)

Discuss the conditions under which

$$A_{2,v}=A_{2,o} \qquad (2.20.1)$$

is realized.

Answer

$A_{2,v}$ is related to $A_{2,o}$ through Eq. (2.18.1)

$$A_{2,v} = A_{2,o} + \left(\frac{V_0}{M^2}\right)\left\{\left(\frac{RT_0}{\Delta H} - \frac{1}{2}\right)\left(\frac{K_s}{K_e}\right)^2 + \frac{K_s}{K_e} - \frac{1}{2}\right\} \tag{2.18.1}$$

When Eq. (2.20.1) is satisfied, Eq. (2.18.1) is converted to

$$\left(\frac{RT_0}{\Delta H} - \frac{1}{2}\right)\cdot\left(\frac{K_s}{K_e}\right)^2 + \frac{K_s}{K_e} - \frac{1}{2} = 0 \tag{2.20.2}$$

From Eq. (2.20.2), we obtain

$$\frac{K_s}{K_e} = \frac{1}{1 + \left(\dfrac{2RT_0}{\Delta H}\right)^{\frac{1}{2}}} \tag{2.20.3}$$

When the ratio K_s/K_e is in agreement with Eq. (2.20.3), Eq. (2.20.1) is realized. In case where

$$K_s = K_e \tag{2.20.4}$$

is hypothetically valid, Eq. (2.18.1) is simplified into

$$A_{2,v} = A_{2,o} + \left(\frac{V_0}{M^2} \cdot \frac{RT_0}{\Delta H}\right) = A_{2,o} + \frac{K_e}{T_0} \cdot \frac{1}{M^2} \tag{2.20.5}$$

Generally, the relationship

$$K_e << T_0 M^2 \tag{2.20.6}$$

holds, then Eq. (2.20.5) is reduced to

$$A_{2,v} \cong A_{2,o} \qquad (2.20.1)'$$

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* Putting R(cal/(deg·mole))=1.987, T_0(K)=300, V_0(ml/mol)=100, ΔH(cal/mol)=1 x 10^4, M=300, we obtain $K_e = 1.8 \times 10^3 << T_0 M^2 = 2.7 \times 10^7$.

Chapter 3 Lattice Theory

<<Problem 3-1>> Lattice theory for low molecular weight solution

Suppose a binary mixture consisting of N_A molecules of A and N_B molecules of B on a lattice with a coordination number z (each molecule has z nearest neighbors). Here, the total number of sites N is the sum of N_A and N_B:

$$N = N_A + N_B \tag{3.1.1}$$

We consider only the interactions between the nearest neighbor molecules and denote the interaction (potential) energy for a pair of molecules A-A, B-B and A-B as ε_{AA}, ε_{BB} and ε_{AB} ($=\varepsilon_{BA}$), respectively, and the numbers of the three pairs by P_{AA}, P_{BB} and P_{AB}.

(1) Evaluate P_{AA} and P_{BB} when P_{AB} is given by

$$P_{AB} = zX \tag{3.1.2}$$

(2) Evaluate the total lattice energy E (with neglecting non-nearest neighbor interaction)

(3) Show that with a formation of single pair A-B, the increase in the lattice energy is given by

$$\varepsilon = \varepsilon_{AB} - \frac{\varepsilon_{AA} + \varepsilon_{BB}}{2} \tag{3.1.3}$$

(4) Discuss the sign of ε in relation to the solvent nature.

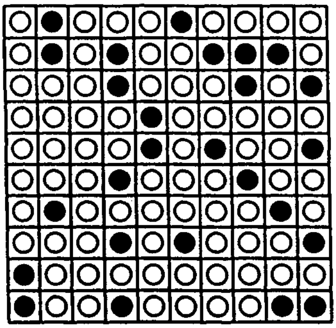

Fig. 3-1 Monomeric solute molecules distributed over a liquid lattice

Answer

(1) The total number of pairs being originated from A is zN_A, which is the summation of two times P_{AA} and P_{AB}, that is,

$$zN_A=2P_{AA}+P_{AB}=2P_{AA}+zX \tag{3.1.4}$$

Then we obtain

$$P_{AA}=z(N_A-X)/2 \tag{3.1.5}$$

Similarly,

$$P_{BB}=z(N_B-X)/2 \tag{3.1.6}$$

(2) Total lattice energy E is

$$E=P_{AA}\,\varepsilon_{AA}+P_{AB}\,\varepsilon_{AB}+P_{BB}\,\varepsilon_{BB} \tag{3.1.7}$$

From Eqs. (3.1.2), (3.1.5) and (3.1.6), we obtain

$$E=\frac{z}{2}N_A\varepsilon_{AA}+\frac{z}{2}N_B\varepsilon_{BB}+zX\left(\varepsilon_{AB}-\frac{\varepsilon_{AA}+\varepsilon_{BB}}{2}\right) \tag{3.1.8}$$

(3) In Eq. (3.1.8), the first two terms correspond to the interaction energy for pure components before mixing, and the third term to the interaction energy generated by mixing. Then, we have Eq. (3.1.3) for the interaction energy for forming a single pair A-B.

(4) The lattice energy E_0 for N_A molecules of pure A and N_B molecules of pure B before mixing is given by putting X=0 in Eq. (3.1.8) as

$$E_0=\frac{z}{2}N_A\varepsilon_{AA}+\frac{z}{2}N_B\varepsilon_{BB} \tag{3.1.9}$$

Then the energy of mixing ΔE is given by the difference $E-E_0$:

$$\Delta E=zX\left(\varepsilon_{AB}-\frac{\varepsilon_{AA}+\varepsilon_{BB}}{2}\right)=zX\varepsilon \tag{3.1.10}$$

The energy increases by mixing when $\varepsilon>0$. In this case, mixing is not favored. When $\varepsilon<0$, mixing is favored. Note that, in practice, the entropy contribution can never be ignored and we cannot judge the solubility simply from the sign of ε.

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* **Coordination number** z is defined as the number of the nearest-neighbor lattice points of an arbitrary lattice point. z of a simple cubic lattice, a body-centered cubic lattice and a face-centered cubic lattice are 6,8 and 12, respectively. A lattice with z=12 is called close-packed because no higher value of z is geometrically possible.

* Usefulness of the lattice theory in study of the mixing entropy of polymer solutions were suggested also by Meyer and Mark (K. H. Meyer and H. Mark, Hochpolymere Chemie, Bd. 2, p549 (1940)). (See also N. Saito, *Polymer Physics*, Shoka-Bo, p 108, 1960)

<<Problem 3-2>> Bragg-Williams approximation

Evaluate **P_{AB} in Eq. (3.1.7) in case of random mixing** [i.e., the case $\varepsilon_{AA}=\varepsilon_{BB}=\varepsilon_{AB}$].

Answer

Choose two neighboring sites ((i) and (ii)) on the lattice. Then the probability of molecule A on (i) is

$$\mathrm{A(i)}=\frac{N_A}{N_A+N_B} \tag{3.2.1}$$

and the probability of B on (ii) is

$$\mathrm{B(ii)}=\frac{N_B}{N_A+N_B} \tag{3.2.2}$$

Then the probability that a given (i)-(ii) pair is a pair A-B (A(i)B(ii) or A(ii)B(i)) is given by

$$2\times\frac{N_A}{N_A+N_B}\times\frac{N_B}{N_A+N_B}=2\frac{N_AN_B}{(N_A+N_B)^2} \tag{3.2.3}$$

In Eq. (3.2.3), the factor 2 is multiplied in order to take into consideration the two cases: Case 1; A is located on (i) and B is located on (ii) and Case 2; B is on (i) and A is on (ii). P_{AB} is given by the product of the factor of Eq. (3.2.3) with the total number of nearest neighbor pairs in the system $z(N_A+N_B)/2$ as

$$P_{AB} = z\frac{N_A N_B}{N_A + N_B} \tag{3.2.4}$$

Consequently, the parameter X is obtained as

$$X = \frac{N_A N_B}{N_A + N_B} \tag{3.2.5}$$

for random mixing. This assumption is called the **Bragg-Williams approximation**. This is also referred to as the zero-th approximation. Combination of Eqs.(3.1.10) and (3.2.5) leads to

$$\Delta H = \Delta E = \varepsilon\, z\, X = \varepsilon\, z\frac{N_A N_B}{N_A + N_B} \tag{3.2.6}$$

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* Bragg and Williams proposed the above assumption in their study of the arrangement of atoms in an alloy (See W. L. Bragg and E. J. Williams, *Proc. Roy. Soc.* **A145**, 699 (1934)).

<<Problem 3-3>> Free energy of mixing for random mixing

Consider two kinds of molecules A and B sufficiently similar in size and shape so that they are interchangeable on a lattice. Assume a crystal of the pure substance containing N molecules of A has an energy $-N\chi_A$ when all the molecules are at rest on their lattice points and the zero of energy is defined as that of the molecules at rest at infinite separation. If interactions between pairs of molecules are not nearest neighbors, we may regard $-2\chi_A/z$ as the mutual energy of neighbors both at rest on their lattice points. The mutual energy $-2\chi_B/z$ is similarly defined for the crystal B. If we mix the two substances, there will be contributions to the potential energy of the crystal from AB pairs of neighbors as well as from AA and BB pairs. The mutual energy of a pair of neighbors, one A and the other B, is denoted by $(-\chi_A-\chi_B+w)/z$ and w is called the **interchange energy**. Let's mix $N(1-x)$ molecules of A and Nx molecules of B on the lattice. Derive the expressions for (1) the **partition function** Z, (2) the **change in free energy** ΔF_{mix} **by mixing** (i.e., free energy of mixing), and (3) the **partial molar free energy of mixing for each component** $\Delta F_{mix}{}^{A}$ and $\Delta F_{mix}{}^{B}$, on the assumption of w=0 ($\varepsilon_{AA}=\varepsilon_{BB}=\varepsilon_{AB}$).

Answer

(1)The **partition function** Z is expressed as

$$Z = \omega\,(N,x)\,e^{-\Delta E/kT} \tag{3.3.1}$$

Here, $\omega(N,x)$ is the total number of distinguishable ways of arranging $N_A=N(1-x)$ identical molecules of A and $N_B=N\,x$ identical molecules of B on the lattice, and thus, the number of combinations of taking $N(1-x)$ lattice sites from total N lattice sites at a time,

$$\omega\,(N,x) = \frac{N!}{\{N(1-x)\}!\{Nx\}!} \tag{3.3.2}$$

ΔE, the energy of mixing is given by

$$\Delta E = -N(1-x)\chi_A - Nx\chi_B \tag{3.3.3}$$

Substituting Eqs. (3.3.2) and (3.3.3) in (3.3.1), we obtain

$$Z = \frac{N!}{\{N(1-x)\}!\{Nx\}!}\exp\left[\left\{N(1-x)\chi_A + Nx\chi_B\right\}/kT\right] \tag{3.3.4}$$

(2) Helmholtz free energy F is related to partition function Z through the relation

$$F = -kT\log Z \tag{3.3.5}$$

where k is the **Boltzmann constant**. Substituting Eq. (3.3.4) for Z in Eq. (3.3.5), we obtain the free energy for the binary mixtures of A and B,

$$F = -kT\log Z = -N(1-x)\chi_A - Nx\chi_B + NkT\left\{(1-x)\log(1-x) + x\log x\right\} \tag{3.3.6}$$

In derivation of Eq. (3.3.6) we utilize **Stirling's approximation**

$$\log N! = N\log N - N \tag{3.3.7}$$

The free energy of the system consisting of pure A and pure B, F_0, is given by

$$F_0 = -N(1-x)\chi_A - Nx\chi_B \tag{3.3.8}$$

Then the free energy of mixing ΔF_{mix} is obtained as

$$\Delta F_{mix} = F - F_0 = NkT\left\{(1-x)\log(1-x) + x\log x\right\} \tag{3.3.9}$$

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* Since at constant pressure the expression for Gibbs free energy of mixing ΔG_{mix} for the lattice is the same as that for Helmholtz free energy of mixing ΔF_{mix}, Eq. (3.3.9) is identical to Eq. (2.3.1) for ideal solution. Thus, the assumptions that two molecules in the solution are interchangeable and the interchange energy is zero (**random mixing**) are the conditions sufficient for a mixture to be ideal.

---

(3) Partial molar free energy of mixing of the component A is calculated as

$$\Delta F_{mix}^{A} = \frac{\partial \Delta F_{mix}}{\partial \mathcal{N}_A} = kT\log\left\{\frac{x}{1-x}\right\} \tag{3.3.10}$$

Similarly, ΔF_{mix}^{B} is obtained as

$$\Delta F_{mix}^{B} = kT\log\left\{\frac{1-x}{x}\right\} \tag{3.3.11}$$

<<Problem 3-4>> Free energy of mixing for athermal solution

The **partition function Z for athermal solution** is given by

$$Z = \frac{\left(\mathcal{N}_1 + \mathcal{N}_2\right)!}{\mathcal{N}_1!\mathcal{N}_2!} q_1^{\mathcal{N}_1} q_2^{\mathcal{N}_2} \exp\left\{-\frac{z}{2kT}\left(\mathcal{N}_1\varepsilon_{11} + \mathcal{N}_2\varepsilon_{22}\right)\right\} \tag{3.4.1}$$

where we consider the case that $\mathcal{N}_1$ molecules of A and $\mathcal{N}_2$ molecules of B are placed on $\mathcal{N}_1+\mathcal{N}_2$ lattice sites with lattice coordination number z (i.e., the number of the nearest neighbors of a site). q_1 and q_2 are the partition functions relating to the molecular motions of molecules A and B, respectively, around a lattice site, and ε_{11} and ε_{22}, the interaction energy of A-A pair and B-B pair, respectively. On the basis of Eq. (3.4.1), derive (1) **Gibbs free energy**, (2) **chemical potentials of A and B**, μ_1 and μ_2, and (3) **entropy of mixing** ΔS_{mix}. Here, assume that the total volume of the mixture V can be considered as the summation of the volumes of pure liquid A and pure liquid B, that is,

$$V = \mathcal{N}_1 V_1 + \mathcal{N}_2 V_2 \tag{3.4.2}$$

where V_1 and V_2 are the volume of a molecule in pure A and B liquids, respectively.

Answer

(1) **Partition function** Z is related to **Helmholtz free energy** F and **Gibbs free energy** G as

$$F = -kT\log Z \tag{3.3.5}$$

$$G = F + PV = -kT\log Z + PV \tag{3.4.3}$$

Substituting Eq. (3.4.1) for Z in Eqs. (3.3.5) and (3.4.3), we obtain

$$G = -kT\,[\,(N_1+N_2)\log(N_1+N_2) - N_1\log N_1 - N_2\log N_2 + N_1\log q_1 + N_2\log q_2 - \frac{z}{2kT}(N_1\varepsilon_{11} + N_2\varepsilon_{22})\,] + P(N_1V_1 + N_2V_2) \tag{3.4.4}$$

In derivation of Eq. (3.4.4), **Stirling's approximation** (Eq.(3.3.7)) is used.

(2) The chemical potential μ_i is obtained by partially differentiating Eq. (3.4.4) with respect to $N_1 N_A$ as

$$\mu_1 = \left(\frac{\partial G}{\partial N_1}\right)_{T,P,N_2} N_A$$

$$= \left(kT\log\frac{N_1}{N_1+N_2} - kT\log q_1 + \frac{z}{2}\varepsilon_{11} + PV_1\right)N_A \tag{3.4.5}$$

Here we denote the chemical potential of pure liquid A at T and P as $\mu_1{}^0$:

$$\mu_1{}^0 = \left(-kT\log q_1 + \frac{z}{2}\varepsilon_{11} + PV_1\right)N_A \tag{3.4.6}$$

Then Eq. (3.4.5) is reduced to

$$\mu_1 = \mu_1{}^0 + RT\log x_1 \tag{3.4.7}$$

where x_1 is the mole fraction

$$x_1 = \frac{N_1}{(N_1+N_2)} \tag{3.4.8}$$

Similarly, we obtain

$$\mu_2 = \mu_2{}^0 + RT\log x_2 \tag{3.4.9}$$

(3) The chemical potential μ_i is related to the partial molar entropy S_i by

$$\Delta S_i = S_i - S_i{}^0 = -\frac{\partial(\mu_i - \mu_i{}^0)}{\partial T} \tag{3.4.10}$$

Substituting Eqs. (3.4.7) and (3.4.9) in Eq. (3.4.10), we have

$$\Delta S_i = -R\log x_i \quad (i = 1,2) \tag{3.4.11}$$

The entropy of mixing is expressed as

$$\Delta S_{mix} = S - S^0 = \Sigma N_i (S_i - S_i^0) = \Sigma N_i \Delta S_i = -k(\mathcal{N}_1 \log x_1 + \mathcal{N}_2 \log x_2) \tag{3.4.12}$$

<<Problem 3-5>> Flory's theory (I): 0th approximation theory for polymer solution

Calculate the total number of ways w of arranging $\mathcal{N}_1$ identical polymer molecules, each of which is composed of n chain segments, and $\mathcal{N}_0$ identical solvent molecules on the lattice consisting of $\mathcal{N}$ $(=\mathcal{N}_0 + n\mathcal{N}_1)$ sites. Here, assume that a chain segment is equal in size to the solvent and neglect the possible variation of the energy for given ways of arranging the polymers and solvent molecules.

Answer

A segment or a solvent molecule can be located on a site of the lattice (Fig.

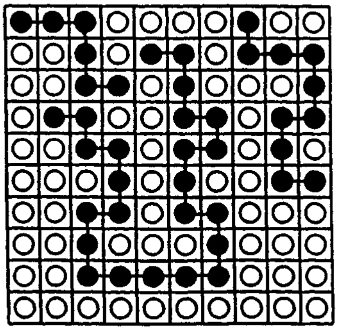

Fig. 3-5 Segments of chain polymer molecules located on a liquid lattice

3-5). Let's insert each segment of the first polymer molecule and the second, the third,... polymer molecules. After N' -1 polymer molecules have been inserted previously, polymer molecule N' is inserted. The total number of the arrangement of this case is denoted by $\nu_{N'}$. Then, w is given by the product of ν_i for each molecule added consecutively to the lattice divided by N_1 ! as

$$w = \frac{1}{N_1!} \nu_1 \nu_2 \nu_3 \cdots \nu_{N_1} \qquad (3.5.1)$$

Here, note that all N_1 polymer molecules are indistinguishable from each other. The way of arrangement of N_0 solvent molecules on the remaining lattice sites N-nN_1 $(=N_0)$ is evidently unity. Next let's evaluate $\nu_{N'}$ for polymer N'. Let's define the number of ways of arranging the first segment (in this case, the end segment) on the lattice as $\nu_{N',1}$, and that of the second segment neighbor to the first segment as $\nu_{N',2}$,..., then $\nu_{N'}$ is given by

$$\nu_{N'} = (1/\sigma)\, \nu_{N',1}\nu_{N',2}\cdots\nu_{N',n} \qquad (3.5.2)$$

Here, σ is two for the case when the head and the tail of a polymer molecule are indistinguishable and one for the case when the head and the tail are different. When we try to insert the first segment of molecule N' into the lattice, N'-1 polymer molecules, that is, n(N'-1) lattice sites have been arranged previously. Then the first segment can be inserted on the remaining sites N-(n(N'-1)). That is, $\nu_{N',1}$ coincides with the total number of vacant sites,

$$\nu_{N',1} = N - n\,(N' - 1) \qquad (3.5.3)$$

The second segment can only be inserted to any of the z neighbors of the site occupied by the first segment of polymer molecule N'. Note that the first and the second segments are directly connected. It can never be considered that all the z neighbors are vacant, because N' -1 polymer molecules have been arranged previously on the lattice. Let's assume that the probability of occupation of a given neighbor site by any segment of 1 ~ N' -1 polymer molecules equals the average probability of occupancy n(N'-1)/N, that is $\nu_{N',2}$ is given by

$$\nu_{N',2} = z\left\{1 - n\,(N' - 1)/N\right\} \qquad (3.5.4)$$

This assumption is equivalent to assuming that the average concentration of the polymer segments in the site adjacent to the sites unoccupied by the polymeric solute is taken to be equal to the overall average concentration. Similarly, the third segment is located at a site immediately adjacent to the site occupied by the second segment. In this case, one site occupied by the first segment eliminates one of the neighboring sites; one of the neighboring sites of the second segment has been occupied by the first segment, and the third segment can be located on a vacant site among (z-1) sites;

$$\nu_{N',3} = (z-1)\left\{1 - n(N'-1)/N\right\} \tag{3.5.5}$$

All expected numbers $\nu_{N',4}$, $\nu_{N',5}$,... for each successive segment are taken to be equal to (z-1){1-n(N'-1)/N}, that is,

$$\nu_{N',4} = \nu_{N',5} = \cdots \nu_{N',n} = (z-1)\left\{1 - n(N'-1)/N\right\} \tag{3.5.6}$$

Substituting Eqs.(3.5.3)-(3.5.6) in Eq. (3.5.2) yields

$$\nu_{N'} = \sigma^{-1} z(z-1)^{n-2}\left\{N - n(N'-1)\right\}^{n} N^{-(n-1)} \tag{3.5.7}$$

Substituting Eq. (3.5.7) for $\nu_{N'}$ in Eq. (3.5.1), we obtain

$$w = \frac{1}{N_1!\sigma^{N_1}} z^{N_1}(z-1)^{N_1(n-2)} N^{-(n-1)N_1}\left\{N(N-n)(N-2n)\cdots\left(N-n(N_1-1)\right)\right\}^{n} \tag{3.5.8}$$

The term { } in the right-hand side of this equation can be simplified as

$$\begin{aligned}
&\left\{N\left(N-n\right)\left(N-2n\right)\cdots\left(N-n\left(N_1-1\right)\right)\right\}\\
&=\left(\frac{N}{n}\right)\left(\frac{N}{n}-1\right)\left(\frac{N}{n}-2\right)\cdots\left(\frac{N}{n}-\left(N_1-1\right)\right)n^{N_1}\\
&=\frac{\left(N/n\right)!}{\left(\left(N-nN_1\right)/n\right)!}n^{N_1}=\frac{\left(N/n\right)!}{\left(N_0/n\right)!}n^{N_1}
\end{aligned} \tag{3.5.9}$$

Then, Eq.(3.5.8) reduces to

$$w = \frac{z^{N_1}(z-1)^{N_1(n-2)}}{N_1!\sigma^{N_1}} N^{-(n-1)N_1} n^{nN_1} \left\{ \frac{(N/n)!}{(N_0/n)!} \right\}^n \tag{3.5.10}$$

<<Problem 3-6>> Flory's theory (II): Entropy of polymer solution

The total number w of ways of arranging N_1 identical polymer molecules and N_0 identical solvent molecules on N $(=N_0+ nN_1)$ lattice sites with the coordination number z is given by Eq.(3.5.10). Derive the **entropy of the polymer solution** using **Boltzmann's principle**

$$S = k \log w \tag{3.6.1}$$

where k is the **Boltzmann constant.**

Answer

Substituting Eq. (3.5.10) for w in Eq. (3.6.1), we obtain

$$S = k \log w \ = k \log \frac{z^{N_1}(z-1)^{N_1(n-2)}}{\sigma^{N_1}}$$

$$- k \left[\log N_1! + (n-1) N_1 \log N - nN_1 \log n - n \log (N/n)! + n \log (N_0/n)! \right] \tag{3.6.2}$$

Using Stirling's approximation of Eq.(3.3.7), Eq. (3.6.2) reduces to

$$S = k \log \frac{z^{N_1}(z-1)^{N_1(n-2)}}{\sigma^{N_1}}$$

$$-k \left\{ N_1 \log N_1 + (n-1) N_1 \log N - nN_1 \log n - N \log \frac{N}{n} + N_0 \log \frac{N_0}{n} + N - (N_1+N_0) \right\} \tag{3.6.3}$$

Equation (3.6.3) can be rearranged in the form

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* Flory proposed 0th approximation theory in 1941-1942. (See P. J. Flory, *J. Chem. Phys.* **9**, 660 (1941); *ibid.* **10**, 51 (1942))

$$S = k\log\frac{z^{N_1}(z-1)^{N_1(n-2)}}{\sigma^{N_1}} - k\left\{N_0\log\frac{N_0}{N_0+nN_1} + N_1\log\frac{N_1}{N_0+nN_1} + (n-1)N_1\right\} \tag{3.6.4}$$

<<Problem 3-7>> Flory's theory (III): Entropy of mixing for polymer solution

Entropy of mixing ΔS for polymer solutions is defined by

$$\Delta S_{mix} = S - S^0 \tag{3.7.1}$$

Here, S is the entropy of the mixture and S^0 is the summation of the entropies of pure liquid solvent and the amorphous disorientated polymer solid. ΔS is closely correlated with the configurational entropy of the system. Using Eq.(3.6.4), determine ΔS_{mix}.

Answer

The entropy for pure liquid solvent is S at $N_1 = 0$ and the entropy for an absolutely amorphous solid is S at $N_0 = 0$ in Eq. (3.6.4). Then S^0 is given by

$$S^0 = S(N_1{=}0) + S(N_0{=}0) = k\log\frac{z^{N_1}(z-1)^{N_1(n-2)}}{\sigma^{N_1}} + kN_1\log n - k(n-1)N_1 \tag{3.7.2}$$

Then, ΔS_{mix} is obtained as

$$\Delta S_{mix} = S - S^0$$

$$= -k\left(N_0\log\frac{N_0}{N_0+nN_1} + N_1\log\frac{nN_1}{N_0+nN_1}\right) \tag{3.7.3}$$

If we define the volume fractions of solvent and polymer, ϕ_0 and ϕ_1, by

$$\phi_0 = \frac{N_0}{N_0+nN_1} \tag{3.7.4}$$

$$\phi_1 = \frac{nN_1}{N_0+nN_1} \tag{3.7.5}$$

Eq.(3.7.3) is rewritten as

$$\Delta S_{\text{mix}} = -\,k\,(\,\mathcal{N}_0\log\phi_0 + \mathcal{N}_1\log\phi_1\,) \tag{3.7.6}$$

---

* On the other hand, from Eq. (3.4.12) the entropy of mixing for ideal solution $\Delta S^{\text{id}}_{\text{mix}}$ is

$$\Delta S^{\text{id}}_{\text{mix}} = -\,k\left(\mathcal{N}_0\log\frac{\mathcal{N}_0}{\mathcal{N}_0+\mathcal{N}_1} + \mathcal{N}_1\log\frac{\mathcal{N}_1}{\mathcal{N}_0+\mathcal{N}_1}\right) = -\,k\left(\mathcal{N}_0\log x_0 + \mathcal{N}_1\log x_1\right) \tag{3.7.7}$$

where x_0 and x_1 are the mole fractions of solvent and solute, respectively. By comparing Eq.(3.7.6) with Eq.(3.7.7), it is clear that the entropy of mixing of polymer solutions can be expressed by the volume fraction in place of the mole fraction.

*Eq.(3.7.6) does not contain z. Therefore, Eq.(3.7.6) is expected to be valid, regardless of the lattice model. Figure 3-7 shows the plots of ΔS_{mix} vs. $\log x_1$ for polymer and ideal solutions.

* In deriving Eq.(3.7.2), we used the relationship

$$\lim_{x\to 0} x\log x = 0 \tag{3.7.8}$$

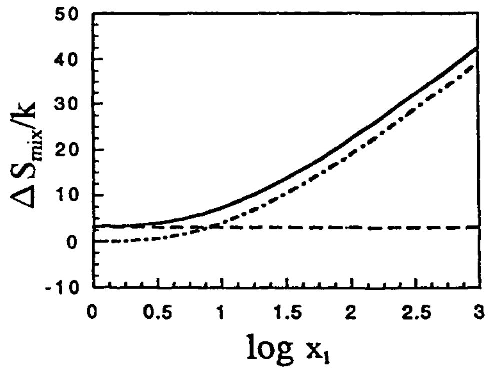

Fig. 3-7 Calculated entropy of mixing for $N_0=9$ and $N_1=1$. Solid, broken and chain lines denote the entropy of mixing for polymer solution (Eq. (3.7.6), ideal solution (Eq. (3.7.7)) and the difference of them (ΔS_{mix}-$\Delta S_{\text{mix}}^{\text{id}}$), respectively.

Proof: On putting x=1/t, the left-hand side of Eq. (3.7.8) can be rewritten as

$$\lim_{x\to 0} x \log x = \lim_{t\to\infty} -(\log t)/t = -\lim_{t\to\infty} 1/t = 0$$

<<Problem 3-8>> Flory's theory (IV): Partial molar entropy of mixing of solvent and polymer

Consider a system consisting of $\mathcal{N}_1$ polymer molecules, each occupying n sites, and $\mathcal{N}_0$ solvent molecules, each occupying one site, the total number of sites being $\mathcal{N}=n\mathcal{N}_1+\mathcal{N}_0$. The entropy of mixing of disorientated polymer and solvent is given by

$$\Delta S_{mix} = -k\left(\mathcal{N}_0 \log \phi_0 + \mathcal{N}_1 \log \phi_1\right) \tag{3.7.6}$$

Here, ϕ_0 and ϕ_1 are the volume fractions of solvent and polymer, respectively. Using Eq. (3.7.6), derive the **partial molar entropy of mixing of solvent and polymer**, ΔS_0 and ΔS_1.

Answer

The partial molar entropies of mixing of the solvent and the polymer are obtained by differentiating the entropy of mixing ΔS_{mix} with respect to the number of moles $\mathcal{N}_0/N_A$ of solvent molecules and to the number of moles $\mathcal{N}_1/N_A$ of polymer molecules, as given by

$$\Delta S_0 = \frac{\partial \Delta S_{mix}}{\partial \mathcal{N}_0} N_A \ , \ \Delta S_1 = \frac{\partial \Delta S_{mix}}{\partial \mathcal{N}_1} N_A \tag{1.2.6'}$$

respectively. From Eq. (3.7.6) we obtain

$$\frac{\partial \Delta S_{mix}}{\partial \mathcal{N}_0} N_A = -R\left\{\log \frac{\mathcal{N}_0}{\mathcal{N}_0 + n\mathcal{N}_1} + \frac{n\mathcal{N}_1}{\mathcal{N}_0 + n\mathcal{N}_1} - \frac{\mathcal{N}_1}{\mathcal{N}_0 + n\mathcal{N}_1}\right\}$$

$$= -R\left\{\log(1-\phi_1) + \left(1-\frac{1}{n}\right)\phi_1\right\} \tag{3.8.1}$$

$$\frac{\partial \Delta S_{\mathrm{mix}}}{\partial N_1} N_A = -R\left\{\frac{-nN_0}{N_0+nN_1} + \log\frac{nN_1}{N_0+nN_1} + \frac{N_0}{N_0+nN_1}\right\}$$

$$= -R\left\{(1-n)\,\phi_0 + \log(1-\phi_0)\right\} \tag{3.8.2}$$

Accordingly,

$$\Delta S_0 = -R\left\{\log(1-\phi_1) + \left(1-\frac{1}{n}\right)\phi_1\right\} \tag{3.8.3}$$

$$\Delta S_1 = -R\left\{(1-n)\,\phi_0 + \log(1-\phi_0)\right\} \tag{3.8.4}$$

Note that Eqs. (3.8.3) and (3.8.4) are valid for the solution of random mixing.

<<Problem 3-9>> Flory's theory (V): van Laar-Scatchard approximation

van Laar and Scatchard showed that the **heat of mixing for regular solution** which consists of N_0 solvent molecules and N_1 solute molecules is given by

$$\Delta H_{\mathrm{mix}} = \varepsilon z N_0 N_1 / \left(N_0 + N_1\right) \tag{3.2.6}$$

where ε is the change in energy for formation of an unlike contact pair (0-1 pair) and z is the lattice coordination number. Now consider N_1 polymer molecules, each consisting of n segments as solute, and derive expressions for the heat of mixing ΔH_{mix} and the partial molar heat of dilution of the solvent and of the polymer ΔH_0 and ΔH_1, respectively.

Answer

Suppose that ΔH_{mix} is proportional to the total contact number between polymer segments and solvent molecules. Eq. (3.2.6) can be rewritten by replacing N_1 with nN_1 in the form

$$\Delta H_{\mathrm{mix}} = \varepsilon z N_0 n N_1 / \left(N_0 + n N_1\right) \tag{3.9.1}$$

ΔH_0 and ΔH_1 are defined by (See Eq.(1.2.12))

$$\Delta H_0 = N_A \frac{\partial \Delta H}{\partial N_0} \tag{3.9.2}$$

$$\Delta H_1 = N_A \frac{\partial \Delta H}{\partial N_1} \tag{3.9.3}$$

respectively. Combination of Eq.(3.9.1) and Eq.(3.9.2) or Eq.(3.9.3) leads to

$$\Delta H_0 = BN_A \frac{n^2 N_1{}^2}{(N_0 + nN_1)^2} = BN_A \phi_1{}^2 \tag{3.9.4}$$

$$\Delta H_1 = B\,N_A \frac{nN_0{}^2}{(N_0 + nN_1)^2} = BN_A n\phi_0{}^2 \tag{3.9.5}$$

Here $B \equiv \varepsilon z$.

van Laar-Scatchard equation (Eq. (3.2.6)) is derived on the assumption of random mixing. (See J.J. van Laar, *Z. phys. Chem.* **A** **137**, 421 (1928); G.Scatchard, *Chem. Rev.* **8**, 321 (1931))

<<Problem 3-10>> Flory's theory (VI): Gibbs free energy of mixing of polymer solution

Suppose heat of mixing ΔH and entropy of mixing ΔS are given by the relations

$$\Delta H_{mix} = \varepsilon z N_0 n N_1 / (N_0 + nN_1) \tag{3.9.1}$$

$$\Delta S_{mix} = -k\,(N_0 \log \phi_0 + N_1 \log \phi_1) \tag{3.7.6}$$

respectively. Here the volumetric change of mixing ΔV_{mix} is implicitly assumed to be zero. Derive the expression for the free energy of mixing ΔG_{mix}.

Answer

Substituting Eq. (3.9.1) for ΔH_{mix} and Eq. (3.7.6) for ΔS_{mix} in the equation

$$\Delta G_{mix} = \Delta F_{mix} = \Delta H_{mix} - T\Delta S_{mix} \tag{2.3.3)'$$

at constant pressure and temperature, we obtain

$$\Delta G_{\mathrm{mix}} = \varepsilon z \mathcal{N}_0 n \mathcal{N}_1 / \left(\mathcal{N}_0 + n\mathcal{N}_1\right) + kT\left(\mathcal{N}_0 \log \phi_0 + \mathcal{N}_1 \log \phi_1\right)$$

$$= kT\left(\mathcal{N}_0 \log \phi_0 + \mathcal{N}_1 \log \phi_1\right) + \varepsilon z \mathcal{N}_0 \phi_1 \qquad (3.10.1)$$

<<Problem 3-11>> Flory's theory (VII): Chemical potential of solvent for non-athermal random mixing polymer solution

In <<Problem 3-8>> the partial molar entropy of mixing of solvent ΔS_0 was derived in the form

$$\Delta S_0 = -R\left\{\log\left(1 - \phi_1\right) + \left(1 - \frac{1}{n}\right)\phi_1\right\} \qquad (3.8.3)$$

In <<Problem 3-9>> the partial molar heat of mixing of solvent ΔH_0 was derived in the form

$$\Delta H_0 = BN_A \phi_1^{\,2} \qquad (3.9.4)$$

Derive the expression for the **chemical potential of solvent μ_0** for non-athermal random mixing polymer solutions using these equations.

Answer

At constant temperature and pressure, $\Delta\mu_0$ is related to ΔH_0 and ΔS_0 through the relation

$$\Delta\mu_0 = \Delta H_0 - T\Delta S_0 \qquad (3.11.1)$$

Substituting Eqs.(3.8.3) and (3.9.4) in Eq.(3.11.1), we have

$$\Delta\mu_0 = BN_A \phi_1^{\,2} + RT\left\{\log\left(1 - \phi_1\right) + \left(1 - \frac{1}{n}\right)\phi_1\right\}$$

$$= RT\left\{\log\left(1 - \phi_1\right) + \left(1 - \frac{1}{n}\right)\phi_1 + \frac{B}{kT}\phi_1^{\,2}\right\} \qquad (3.11.2)$$

Using the thermodynamic interaction parameter $\chi \equiv B/kT$, Eq. (3.11.2) is rewritten as

$$\Delta\mu_0 = RT\left\{\log\left(1 - \phi_1\right) + \left(1 - \frac{1}{n}\right)\phi_1 + \chi\phi_1^{\,2}\right\} \tag{3.11.3}$$

Equations (3.11.2) and (3.11.3) are the most popular equations for describing the chemical potential of polymer solutions.
If $\phi_1 \ll 1$, $\log(1-\phi_1)$ is expanded in a Taylor series as

$$\log\left(1 - \phi_1\right) = -\phi_1 - \frac{\phi_1^{\,2}}{2} - \frac{\phi_1^{\,3}}{3} + \cdots \tag{3.11.4}$$

Then Eq. (3.11.4) can be further rewritten into

$$\Delta\mu_0 = -RT\left\{\frac{1}{n}\phi_1 + \left(\frac{1}{2} - \frac{B}{kT}\right)\phi_1^{\,2} + \frac{1}{3}\phi_1^{\,3} + \cdots\right\} \tag{3.11.5}$$

---

* χ defined in Eq.(3.11.3) is the parameter for enthalpy of mixing and should be expressed as χ_h. ΔH_0 and χ are related to the Flory enthalpy parameter κ_0. (See << Problem 4-23>>)

<<Problem 3-12>> Flory's theory (VIII): Chemical potential of polymer for non-athermal random mixing polymer solution

The partial molar entropy of mixing of polymer ΔS_1 is expressed by

$$\Delta S_1 = -R\left\{\left(1 - n\right)\phi_0 + \log\left(1 - \phi_0\right)\right\} \tag{3.8.4}$$

The partial molar heat of mixing ΔH_1 is given by

$$\Delta H_1 = BN_A n\phi_0^{\,2} \tag{3.9.5}$$

Derive the **chemical potential of polymer** $\Delta\mu_1$ for non-athermal random mixing polymer solutions using these equations.

Answer

At constant temperature and pressure,

$$\Delta\mu_1 = \Delta H_1 - T\Delta S_1 \tag{3.12.1}$$

Then,

$$\Delta\mu_1 = BN_A n\phi_0^{\,2} + RT\left\{\left(1 - n\right)\phi_0 + \log\left(1 - \phi_0\right)\right\}$$

$$= RT\left\{\log\left(1-\phi_0\right)-\left(n-1\right)\phi_0+\frac{Bn}{kT}\phi_0{}^2\right\}$$

$$= RT\left\{-\phi_0-\frac{\phi_0{}^2}{2}-\frac{\phi_0{}^3}{3}-\cdots-\left(n-1\right)\phi_0+\frac{Bn}{kT}\phi_0{}^2\right\}$$

$$= -RT\left\{n\phi_0+\left(\frac{1}{2}-\frac{Bn}{kT}\right)\phi_0{}^2+\frac{\phi_0{}^3}{3}+\cdots\right\} \qquad (3.12.2)$$

<<Problem 3-13>> Flory's theory (IX): Gibbs-Duhem relation for polymer solution

Verify that $\Delta\mu_0$ in <<Problem 3-11>> and $\Delta\mu_1$ in <<Problem 3-12>> satisfy the **Gibbs-Duhem relation;**

$$\sum N_i d\mu_i = 0 \qquad (1.3.1)$$

Answer

The total differentiation of the equations

$$\Delta\mu_0 = RT\left\{\log\left(1-\phi_1\right)+\left(1-\frac{1}{n}\right)\phi_1+\chi\phi_1{}^2\right\} \qquad (3.11.3)$$

and

$$\Delta\mu_1 = RT\left\{\log\left(1-\phi_0\right)-\left(n-1\right)\phi_0+\chi n\phi_0{}^2\right\} \qquad (3.12.2)$$

is given by

$$d\Delta\mu_0 = RT\left\{\frac{-d\phi_1}{1-\phi_1}+\left(1-\frac{1}{n}\right)d\phi_1+2\chi\phi_1 d\phi_1\right\} \qquad (3.13.1)$$

$$d\Delta\mu_1 = RT\left\{\frac{-d\phi_0}{1-\phi_0}-\left(n-1\right)d\phi_0+2\chi n\phi_0 d\phi_0\right\} \qquad (3.13.2)$$

respectively. Considering

$$\phi_0 + \phi_1 = 1 \tag{3.13.3}$$

the relationship between the total differential $d\phi_0$ and $d\phi_1$

$$d\phi_0 = - d\phi_1 \tag{3.13.4}$$

holds. Then Eq. (3.13.2) can be modified into

$$d\Delta\mu_1 = RT\left\{\frac{d\phi_1}{\phi_1} + \left(n - 1 \right) d\phi_1 - 2\chi n\left(1 - \phi_1\right) d\phi_1\right\} \tag{3.13.5}$$

For binary systems, the Gibbs-Duhem relation (Eq. (1.3.1)) can be simplified into

$$N_0 d\Delta\mu_0 + N_1 d\Delta\mu_1 = 0 \tag{3.13.6}$$

Eq. (3.13.6) can be rewritten as

$$\frac{N_0}{N_0 + nN_1} d\Delta\mu_0 + \frac{N_1}{N_0 + nN_1} d\Delta\mu_1 = 0 \tag{3.13.7}$$

Then,

$$\left(1 - \phi_1\right) d\Delta\mu_0 + \left(\frac{\phi_1}{n}\right) d\Delta\mu_1 = 0 \tag{3.13.8}$$

Substitution of Eq.(3.13.1) for $d\Delta\mu_0$ and Eq. (3.13.5) for $d\Delta\mu_1$ in the left-hand side of Eq. (3.13.8) yields

$$\begin{aligned}
&\left(1 - \phi_1\right)\frac{- d\phi_1}{1 - \phi_1} + \left(1 - \frac{1}{n}\right)\left(1-\phi_1\right) d\phi_1 + 2\chi\phi_1\left(1 - \phi_1\right) d\phi_1 \\
&+ \left(\frac{\phi_1}{n}\right)\left(\frac{d\phi_1}{\phi_1}\right) + \left(\frac{\phi_1}{n}\right)\left(n - 1\right) d\phi_1 - 2\chi n\left(\frac{\phi_1}{n}\right)\left(1 - \phi_1\right) d\phi_1 \\
&= d\phi_1\left\{- 1 + \left(1 - \frac{1}{n}\right)\left(1 - \phi_1\right) + 2\chi\phi_1\left(1 - \phi_1\right) + \frac{1}{n} + \frac{n - 1}{n}\phi_1 - 2\chi\phi_1\left(1 - \phi_1\right)\right\}
\end{aligned}$$

$$= d\,\phi_1\left(-1+1-\frac{1}{n}-\phi_1+\frac{\phi_1}{n}+\frac{1}{n}+\phi_1-\frac{\phi_1}{n}\right)=0 \qquad (3.13.9)$$

<<Problem 3-14>> Flory's theory (X): Assumptions in Flory's 0th approximation theory

Discuss the approximations and assumptions employed in Flory's 0th approximation theory for polymer solutions in <<Problem 3-5>>.

Answer

Flory's theory of the zeroth approximation[1-5] assumes:

(1) There is no volume change on mixing.

(2) The lattice possesses a definite co-ordination number (i.e., the number of nearest neighbours of each segment per solvent molecule in the solution) z.

(3) The entropy of mixing ΔS_{mix} can be calculated without reference to the possible energy change caused by the pair formation (i.e., **Bragg-Williams approximation**[6]). In other words, the polymer segments mix with solvent randomly and ΔS_{mix} is the entropy of mixing of athermal solution.

(4) In the calculation of the total number of configurations w, from which the combinatory entropy of mixing is derived, the possibility that the nearest-neighbour lattice point to the lattice point in question has been already occupied by polymer segment equals the probability of the case where all the polymer segments are uniformly distributed over all the lattice points (i.e., the **average concentration approximation of the chain segment**). This means that the two segments belonging to the same polymer molecule are allowed to occupy the same lattice site. For rearrangement of the expression for w, Stirling's approximation is applicable.

(5) The potential energy of the mixture is the sum of contributions from each pair of the closest neighbouring segments (**van Laar-Scatchard approximation**[7,8]).

(6) The heat of mixing ΔH_{mix} can be calculated from the average contact numbers where all the segments comprising polymer chains are completely disconnected and randomly mixed with solvents (i.e., the **average concentration approximation**). In this case, the total number of polymer-solvent contact pairs n_c is given by

$$n_c = z\phi_0\phi_1 L \text{ (Average concentration approximation)} \qquad (3.14.1)$$

where L is the total number of lattice sites, ϕ_0 the volume fraction of solvent and ϕ_1 the volume fraction of polymer. The thermodynamic interaction parameter χ can be purely phenomenologically expressed by[9]

$$\chi=\chi_0(1+\Sigma p_i\phi_1{}^i)$$

$$\chi_0=\chi_{00}(1+k'/n)$$

$$k'=k_0(1-\theta/T)$$

for monodisperse polymer-single solvent system (Refer to Eqs. (3.16.4), (3.16.11) and (3.16.12)). Here χ_{00} is a parameter independent of ϕ_1 and n, k' and p_i ($i=1...n_t$), the molecular weight- and concentration-independent coefficients, k_0 the parameter independent of temperature T and the degree of polymerization n, and θ, the Flory temperature. χ_{00} coincides with 0.5 if the second virial coefficient A_2 vanishes at θ.

Generally speaking, the χ-parameter is not the parameter representing polymer-solvent interaction only (typical example is shown in Fig. 3-15), but can be divided semi-empirically into two parts:

$$\chi=\chi_h+\chi_s \tag{3.14.2}$$

Here χ_h is the enthalpy term and χ_s is the entropy term, and both terms may have concentration dependence as expressed by

$$\chi_h=(\Delta H_0-\Delta H_0{}^{q,id})/(RT\phi_1{}^2)=\Delta H_0/(RT\phi_1{}^2)=\chi_{h,0}\,(1+\Sigma p_{h,i}\phi_1{}^i) \tag{3.14.3}$$

$$\chi_s=-\,(\Delta S_0-\Delta S_0{}^{q,id})/(RT\phi_1{}^2)=\chi_{s,0}\,(1+\Sigma p_{s,i}\phi_1{}^i) \tag{3.14.4}$$

where ΔH_0 is the partial molar heat of dilution of solvent in real solution, $\Delta H_0{}^{q,id}$ is ΔH_0 in quasi-ideal (i.e., random mixing-zero heat of mixing ($n>>1$)) solution, ΔS_0 is the partial molar entropy of mixing of solvent in real solution, $\Delta S_0{}^{q,id}$ is ΔS_0 in quasi-ideal solution, and $p_{h,i}$ and $p_{s,i}$ are the concentration dependence parameter of χ_h and χ_s, respectively.

Hypothesis (6) means that in calculation of ΔH the consecutive characteristics of chain segments is neglected. In his theory ΔH is expected to be strictly proportional to $\phi_1(1-\phi_1)$ and χ-parameter consists of solely the enthalpy term χ_h (See Eq. (3.14.14)) as given by

$$\chi=\chi_0=\chi_{h,0} \tag{3.14.5}$$

and

$$p_i=p_{h,i}=p_{s,i}=0(i=1,...,n_t) \tag{3.14.6}$$

Only in the case where Eq. (3.14.5) holds the χ-parameter is strictly a polymer

-solvent interaction parameter, as first defined by Flory.[1]

1. P. J. Flory, *J. Chem. Phys.* **9**, 660 (1941).
2. P. J. Flory, *J. Chem. Phys.* **10**, 51 (1942).
3. P. J. Flory, *J. Chem. Phys.* **12**, 425 (1944).
4. P. J. Flory, *J. Chem. Phys.* **13**, 453 (1945).
5. P. J. Flory, *Principle of Polymer Chemistry*, Cornell Univ. Press, Ithaca, New York, 1953, Chapter XII.
6. W. L. Bragg and E. J. Williams, *Proc. Roy. Soc.* **A145**, 699 (1934)).
7. J. J. Van Laar, *Z. phys. Chem.* **A137**, 421 (1928).
8. G. Scatchard, *Chem. Rev.* **8**, 321 (1931).
9. See for example, K. Kamide, *Thermodynamics of Polymer Solutions, Phase Equilibria and Critical Phenomena* (Polymer Science Library 9), Elsevier, 1990.

Note 1* **Improved zeroth approximation theory (Athermal solution)

Within the scope of Bragg-Williams approximation and taking into account the succession of segments comprising a polymer molecule and rigorous pattern of arranging segments around a given lattice point Miller[10], Guggenheim[11], and Kurata et al.[12] calculated the partial molar entropy of mixing of solvent ΔS_0 as

$$\Delta S_0 / R = -\ln(1-\phi_1) + \frac{z}{2}\ln\left(1 - \frac{z}{2}\frac{n-1}{n}\phi_1\right) \qquad (3.14.7)$$

Eq. (3.14.7) is similar to that derived by Huggins[13-18], who took into consideration the effect of blocking of sites by other distant segments of the same polymer on the number of sites

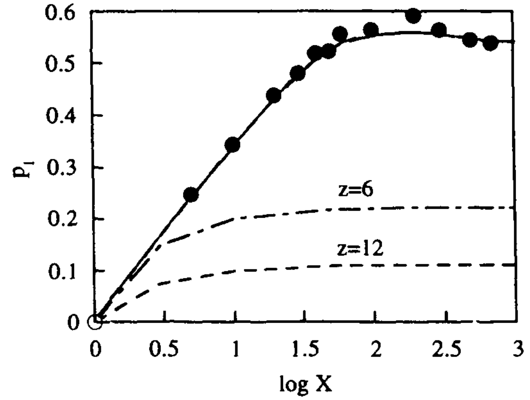

Fig. 3-14.1 Relationship between p_l and n (full line); broken line: improved zeroth approximation with z=12 chain line: improved zeroth approximation with z=6

available for the segments of each polymer molecule[10]. Eq. (3.14.7) indicates that χ_s is not zero and is given by[19]

$$\chi_s=(1-1/n)^2/z+4(1-1/n)^3\phi_1{}^3/(3z^2)+\ldots \tag{3.14.8}$$

$$\chi_{s,0}=(1-1/n)^2/z \tag{3.14.9}$$

$$p_{s,1}=4(1-1/n)/(3z) \tag{3.14.10}$$

Thus, Miller, Guggenheim, and Kurata et al.'s theories as well as Huggins classical theory predict that χ_s depends on concentration. This suggests that the consecutive properties of polymer chain segments might be one of causes, which lead to $p_i\neq0$. Note that $p_{s,1}$ value given by Eq. (3.14.10) is too small to explain the experimentally determined p_1 value for non-polar polymer- non-polar solvent systems (See Fig. 3-14.1). Table 3-14 summarizes ΔS and χ_s proposed by them, including Flory and Fig. 3-14.2 shows a typical example for careful determination of χ_h as a function of concentration.

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10. A. R. Miller, *Proc. Cambr. Phil. Soc.* **39**, 54 (1943).
11. E. A. Guggenheim, *Proc. Roy. Soc.* **A183**, 203 (1944).
12. M. Kurata, M. Tamura and T. Watari, *J. Chem. Phys.* **23**, 991 (1955).
13. M. L. Huggins, *J. Chem. Phys.* **9**, 440 (1941).

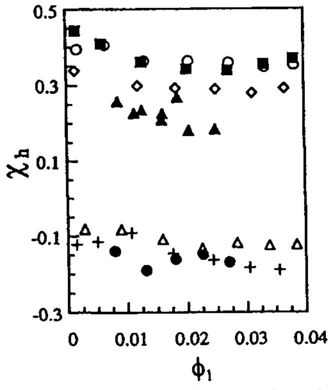

Fig. 3-14.2 χ_h determined from the heat of dilution as a function of volume fraction of polymer ϕ_1 for the systems polystyrene in cyclohexane and polystyrene in benzene. polystyrene/cyclohexane ■ M_w=6200, ○ M_w=10200, ◇ M_w=42800, ▲ M_w=107000; polystyrene/benzene △ M_w=6200, + M_w=10200, ● M_w=107000 (I. Fujihara and R. Fujishiro, unpublished results)

Table 3-14 Entropy of mixing and χ_s proposed theoretically

Reseacher	ΔS	χ_s
Flory[1)]	$-R\left[\log(1-\phi_1)+\phi_1\right]$	0
Huggins[2)]	$-R\left[\log(1-\phi_1)+\left(1-\frac{1}{n}\right)\left(\frac{z'}{2}\right)\log\left\{1-\left(\frac{2\phi_1}{z'}\right)\right\}\right]$	$\left(1-\frac{1}{n}\right)z'$
Miller[3)]	$-R\left[\log(1-\phi_1)-\left(\frac{z}{2}\right)\log\left\{1-\left(\frac{z}{2}\right)\phi_1\left(1-\frac{1}{n}\right)\right\}\right]$	$\left(1-\frac{1}{n}\right)^2/z$
Guggenhim[4)]	$-R\left[\log(1-\phi_1)-\left(\frac{zq_0}{2}\right)\log\left\{1-\left(\frac{2}{zq_1}\right)(n_1-n_0)\left(\frac{\phi_1}{n_1}\right)\right\}\right]$	
	$q_i=\{n_i(z-2)+2\}/z$	$\left(1-\frac{1}{n}\right)^2/z \quad (n_2>>n_1)$

1) P.J.Flory : *J.ChemPhys.* **9**, 660 (1941); *ibid.* **10**, 51 (1942)

2) M.L.Huggins : *JPhys.Chem.* **46** 151(1942);*Ann.N.Y.Acad.Sci* **41**,1(1942)

3) A.R.Miller : *Proc.CambPhil.Soc.* **35**, 109(1942); *ibid.* **39** 54, 131(1943)

4) E.A.Guggenheim : *Proc.Roy.Soc.* **A183**, 203(1944)

14. M. L. Huggins, *J. Phys. Chem.* **46**, 151 (1942).
15. M. L. Huggins, *Ann. N.Y. Acad. Sci.* **41**, 1 (1942).
16. M. L. Huggins, *J. Am. Chem. Soc.* **64**, 1712 (1942).
17. M. L. Huggins, *J. Phys. Colloid Chem.* **52**, 248 (1948).
18. M. L. Huggins, *Physical Chemistry of High Polymer*, John Wiley & Sons, Inc., New York, 1958, Chapter 6.
19. K Kamide and H. Shirataki, *Mem. Fac. Educ., Kumamoto Univ.* **47**, 137 (1998).

****Note 2* First approximation theory (Non-athermal solution)**

For non-athermal solutions ($\Delta H \neq 0$), Bragg-Williams and van Laar-Scatchard approximations (hypotheses (3) and (6), respectively) might seem more or less unrealistic and less appropriate. Then several attempts to improve Flory's zeroth approximation theory were made by calculating the total number of configurations w through the use of quasi-chemical equilibria method, which is equivalent to the mathematical technique originally developed by Bethe[20] for treating order-disorder transitions in alloys. This method was occasionally reffered to as the Flory-Huggins first approximation theory. The disparity of values of ΔH for polymethylmethacrylate/trichloroethylene[21] and ΔS for rubber/ ethylacetate[22], both calculated on the basis of the first approximation theory from their corresponding experimental data is significantly larger than those by the zeroth approximation theory, indicating that the first approximation is less reliable and cannot be recommended to use it for analysis[23,24]. This might appear to be somewhat surprising to note that allowance for hypotheses (3) and (6) does nothing to improve the agreement with experiments.

20. H. A. Bethe, *Proc. Roy. Soc.* **A150**, 552 (1935).
21. H. Tompa, *Polymer Solutions*, Butterworth Sci. Pub., 1956, §3.7.
22. C. Booth, G. Gee and G. R. Williams, *J. Polym. Sci.* **23**, 3 (1956).
23. See for example, N. Saito, *Polymer Physics* (revised ed.). Syoka-bo Pubs., Tokyo, 1967, Chapter 4.

****Note 3* Huggins' 'new' theory (1964)**

In his 'new' theory, Huggins[24] assumed as basic tenet that the interior segments of a convoluted molecule are partially shielded from contact with interior segments of other polymer molecules and the shielding factor depends on the concentration. He derived theoretical equations for χ_h and χ_s in closed form and as expansions in powers of the concentration, introducing a number of physical quantities, such as molecular surface area, effective surface area, multiple contact factor, shielding factor and empirical constant relating to shielding factor's concentration dependence. All of which cannot be determined by independent absolute method, although he described that these quantities are "observable". He considered that from experimental data of χ and its dependence on concentration and temperature one can evaluate all the parameters introduced. That is, the parameters introduced in his theory are only adjustable parameters to fit the experimental relations between χ, ϕ_1 and T. Note that in mid-1960s the methods based on phase separation and critical phenomena were not yet established and there was lack of extensive and reliable experimental data to judge theories. Huggins[24] described "Testing of the equations presented in the paper, using published experimental data, has been begun. The results will be reported in due course". Unfortunately as far as we know, there is no his succeeding paper.

24. M. L. Huggins, *J. Am. Chem. Soc.* **86**, 3535 (1964).

Note 4* **Validity of hypothesis 6

The most probable inadequate hypothesis in the Flory theory is that the total number of solvent-polymer contacts is strictly proportional to the product $\phi_0\phi_1$ (hypothesis 6). For example, κ defined by $\Delta H_0/(RT\phi_1^2)$ is expected, if the above hypothesis is accepted, to be constant over wide ranges of T and ϕ_1, but it was confirmed by numerous experiments that κ directly measured by accurate calorimetry, depends strongly on both T and ϕ_1.[25] Validity of the application of overall average concentration approximation of polymer segment to estimate the heat of mixing has never hitherto been tried to examine thoroughly due to mathematically extreme difficulty, although the first approximation, of course, did also treat this problem in rather rough and insufficient manner.

25. See for example, A. Kagemoto, S. Murakami and R. Fujishiro, *Bull. Chem. Soc. Jpn.* **39**, 15 (1966); I. Fujihara, PhD Dissertation in Osaka City Univ. (1979).

Note 5* **Strictness and adequacy of the model, and mathematical complexity and approximation

As Flory[26] pointed out at Fifteenth Spiers Memorial Lectures in 1970, sponcered by the Royal Society, that "to be ffective, any conceptual scheme, or theory of liquids and solutions must entail approximations, either in model or in mathematical technique, even for the simplest of real liquids". Mathematical approximations become more serious in the first approximation theory than in the zeroth approximation theory and this is the reason why introduction of more adequate concepts into the first approximation theory failed, on the contrary, to get rid of the disparity between the theory and actual experiments. This means that even if seemingly more adequate models are used, we cannot always derive accurate theoretical relations between the time-average observable physical quantities like ΔG, ΔS and ΔH, and the structural, molecular and thermodynamic parameters (for example, z, n and the enthalpy change of formation of an unlike contact pair $\Delta\varepsilon$) from the models by traditional method of statistical mechanics, because the system in question is too complicated. Since then, serious limit of further evolution of the lattice theory was widely recognized, although it was largely successful in semi-quantitatively accounting for unusual (from the stand point of low molecular weight solutions) behavior of ΔG, observed in polymer solutions, by differences in size and shape of the species that make up the solution, and there has been no generally accepted explanation of physical significance of the concentration- and molecular weight-dependences of χ-parameter, in spite of its experimentally unquestionable existence.

26. P. J. Flory, *Dis. Farad. Soc.* **49**, 7 (1970).

**Note 6* New strategy to give theoretically reasonable explanation to χ-parameter: Computer simulation of lattice model

Recently Kamide and Shirataki[27] examined the validity of average concentration approximation in hypotheses (4) and (6), employed in the Flory-Huggins lattice theory of polymer solution, and investigated the concentration- and molecular weight-dependences of χ (accordingly, the reliability of the expression of χ (Eqs. (3.16.4), (3.16.11) and (3.16.12))) for quasi-strictly regular solution (i.e., random mixing-nonathermal solution[28]). For this purpose, computer experiments by applying Monte Carlo simulation method to the lattice model, where hypotheses (1), (2) and (5) are strictly adopted, were carried out to calculate the total number of polymer segment-solvent pairs at equilibrium state $n_{c,e}$ as functions of the concentration ϕ_1 and the degree of polymerization n of the polymer solutes. Two types of chain motions (crankshaft motion and then reptation motion) were applied to all the polymer molecules in the lattice simultaneously and this operation (crankshaft-reptation motions) was repeated 1500 times. Any possible multiplicated arrangement of two or more segments belonging to the same or different chain was avoided.

By using Eq. (3.14.3), $n_{c,e}$ is given by

$$n_{c,e}/(\phi_0\phi_1 L)=C_x\,(1+\Sigma p_i\phi_1^{\,i}) \qquad (3.14.11)$$

with

$$C_x \equiv \lim_{\phi_1\to 0} n_{c,e}/(\phi_0\phi_1 L)=C_0(1+k'/n) \qquad (3.14.12)$$

$$C_0 = Rb/\Delta\varepsilon \qquad (3.14.13)$$

When the average concentration approximation (hypothesis (4) is applied, C_x and p_i are given by

$$C_x=z \qquad (3.14.14a)$$

$$p_i=0 \qquad (3.14.14b)$$

Then, from the plots of C_x vs. 1/n and the plots of $n_{c,e}/(\phi_0\phi_1 L)$ against ϕ_1 the validity of the expression of χ (Eqs. (3.16.4), (3.16.11) and (3.16.12)) could be confirmed by the computer experiments (Figs. 4a, 4b and 5 of reference 28). If Eqs. (3.16.4), (3.16.11) and (3.16.12) is applicable, k' and p_1 can be determined from the above plots, respectively. Figure 3-14.1 shows the plots of p_1 estimated thus against logn. p_1 first increases rapidly with an increase in n, then slowly approaching an asymptotic value (ca. 0.6) at $n\approx 200$. Inspection of the figure shows that successive connection of the polymer segments brings about the concentration dependence of χ-parameter. p_1 values of PS in non-polar solvents are close to 2/3 (See <<Problem 3-16-b>>), theoretically predicted at $T=\theta$ for random mixing-non zero heat of mixing solution[29] and are little higher than the value (ca. 0.6) obtained in this computer experiments, but no significantly so.

Computer experiments on random mixing-nonathermal polymer solutions indicated that the average concentration approximation hypothesis cannot be approved even if random mixing is assumed and Eqs. (3.16.4), (3.16.11) and (3.16.12) appears to be of correct form to represent χ-parameter. In other words, this hypothesis employed in Flory-Huggins theory can never be accepted even in the quasi-regular solutions and the concentration- and molecular weight-dependences of the χ-parameter, observed in actual experiments, can be explained reasonably, if the consecutive characteristics of linear chain molecules is strictly considered.

27. K. Kamide and H. Shirataki, *Mem. Fac. Educ., Kumamoto Univ.* **47**, 137 (1998).
28. K. Kamide, *Mem. Fac. Educ., Kumamoto Univ.*, **46**, 213 (1997).
29. K. Kamide, S. Matsuda and M. Saito, *Polym. J.* **17**, 1013 (1985).

<<Problem 3-15>> Thermodynamic interaction parameter χ

The thermodynamic interaction parameter χ in the Flory-Huggins theory [see Eq. (3.11.3)] can be experimentally evaluated by the following methods.

(1) Determination of the activity of solvent a_0 by vapor pressure depression,

$$P_0 = a_0 P_0^0 \tag{2.10.3}$$

or membrane osmometry,

$$\Pi = -\frac{RT}{V_0^0}\log a_0 \tag{2.10.4}$$

(2) Substitution of a_0, determined by the above methods into the equation:

$$\log a_0 = \log\left(1 - \phi_1\right) + \left(1 - \frac{1}{n}\right)\phi_1 + \chi\phi_1^2 \tag{3.15.1}$$

Originally, χ was assumed to be independent of polymer concentration ϕ_1. Figure 3-15 shows the plots of χ, experimentally determined, against ϕ_1 for polystyrene-cyclohexane. The figure shows a significant ϕ_1 dependence of χ. In this sense, χ should be considered to be an empirical parameter, defined by the equation:

$$\Delta\mu_0 = RT\left\{\log\left(1 - \phi_1\right) + \left(1 - \frac{1}{n}\right)\phi_1 + \chi\phi_1^2\right\} \tag{3.11.3}$$

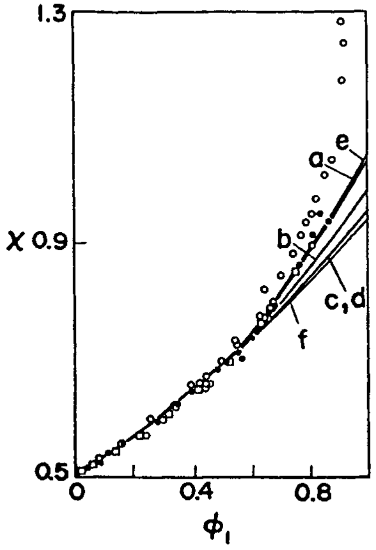

Fig. 3-15 Concentration dependence of χ parameter for polystyrene in cyclohexane. (○) osmotic pressure isothermal distillation by Krigbaum and Geymer[1], (●) vapor pressure by Krigbaum and Geymer[1], (□) ultracentrifuge by Scholte[2]. Lines a to f are calculated using p_1 and p_2, in the equation $\chi=\chi_0(1+p_1\phi_1+p_2\phi_1^2)$, obtained by experiment, (a) Krigbaum and Geymer[1]; (b) Scholte[2]; (c) Koningsveld et al.[3]; (d) Koningsveld et al.[4]; (e) Kuwahara et al.[5]; (f) Kamide et al[6]. This expression for χ yields a better fit compared with Eq. (3.16.1). (See K. Kamide, S. Matsuda, T. Dobashi and M. Kaneko, *Polym. J.* **16**, 839 (1984))

1. W.R.Krigbaum and D.O.Geymer, *J.Am.Chem.Soc.* **81**, 1859 (1959)
2. Th.G.Scholte, *Eur.Polym.J.* **6**,1063,(1970): *J.Polym.Sci.,Polym.Phys.Ed.* **9**, 1553 (1971)
3. R.Koningsveld, L.A.Kleintjens and A.R.Shultz, *J.Polym.Sci., Polym.Phys. Ed.* **8**, 1261 (1970)
4. R.Koningsveld and L.A.Kleintjens, *Macromolecules* **4**, 637 (1971)
5. N.Kuwahara, M.Nakata and M.Kaneko, *Polymer* **14**, 415 (1973)
6. K. Kamide, S.Matsuda, T.Dobashi and M.Kaneko, *Polym.J.* **16**, 839 (1984)

Derive the expression for $\Delta\mu_1$ in the case where χ depends on concentration using the Gibbs-Duhem relation of Eq.(1.3.1).

Answer

The number of molecules i, $\mathcal{N}_i$, is related to the mole fraction x_i through the equation

$$x_i = \frac{\mathcal{N}_i}{\sum_i \mathcal{N}_i} \tag{3.15.2}$$

Then, Eq. (1.3.1) can be rewritten as

$$\sum_i x_i \left(\frac{\partial \mu_i}{\partial x_j}\right)_{T,P,x_k} = 0 \tag{3.15.3}$$

The suffix denotes that the differentiation with respect to x_j is carried out at constant T, P and the composition except *j* th component.

For binary polymer solutions, the mole fraction of polymer x_1 is related to the volume fraction of polymer ϕ_1 as

$$x_1 = \frac{(\phi_1 / n)}{(1 - \phi_1) + (\phi_1 / n)} \tag{3.15.4}$$

where n is the number of segments constituting a polymer molecule.

From Eq. (3.15.4), $(1\text{-}1/x_1)$ is written as

$$(1\text{-}1/x_1)\text{=-}(1\text{-}\phi_1)/(\phi_1/n) \tag{3.15.5}$$

Equation (3.15.3) can be expressed in the form

$$\left\{\left(1 - x_1\right)\frac{\partial \mu_0}{\partial \phi_1} + x_1 \frac{\partial \mu_1}{\partial \phi_1}\right\}\frac{d\phi_1}{dx_1} = 0 \tag{3.15.6}$$

and then we have

$$\frac{\partial \mu_1}{\partial \phi_1} = \left(1 - \frac{1}{x_1}\right)\frac{\partial \mu_0}{\partial \phi_1} \tag{3.15.7}$$

Differentiation of Eq.(3.11.3) with respect to ϕ_1 leads to

$$\frac{\partial \mu_0}{\partial \phi_1} = \frac{\partial \Delta\mu_0}{\partial \phi_1} = RT\left\{-\frac{1}{1 - \phi_1} + \left(1 - \frac{1}{n}\right) + \frac{\partial}{\partial \phi_1}\left(\chi\phi_1^{\,2}\right)\right\} \tag{3.15.8}$$

Substitution of Eq.(3.15.5) for $(1-1/x_1)$ and Eq.(3.15.8) for $\partial\mu_0/\partial\phi_1$ both in Eq. (3.15.7) gives

$$\frac{\partial\mu_1}{\partial\phi_1} = RT\left\{\frac{1}{\phi_1} + (n-1) + n\left(1 - \frac{1}{\phi_1}\right)\frac{\partial}{\partial\phi_1}\left(\chi\phi_1{}^2\right)\right\}$$

$$= RT\left[\frac{1}{\phi_1} + (n-1) - n\frac{\partial}{\partial\phi_1}\left\{\chi\phi_1\left(1-\phi_1\right)\right\} - n\chi\right] \tag{3.15.9}$$

Then,

$$\Delta\mu_1 \equiv \mu_1 - \mu_1^0 = RT\int_{\phi_1}^{1}\left[\frac{1}{\phi_1} + (n-1) - n\frac{\partial}{\partial\phi_1}\left\{\chi\phi_1\left(1-\phi_1\right)\right\} - n\chi\right]d\phi_1$$

$$= RT\left\{\log\phi_1 - (n-1)\left(1-\phi_1\right) - \chi n\phi_1\left(1-\phi_1\right) + n\int_{\phi_1}^{1}\chi d\phi_1\right\} \tag{3.15.10}$$

If χ in Eq. (3.15.10) is constant, the last term in { } is reduced to

$$n\int_{\phi_1}^{1}\chi d\phi_1 = n\chi\left(1-\phi_1\right) \tag{3.15.11}$$

and we have

$$\Delta\mu_1 = RT\left\{\log\phi_1 - (n-1)\left(1-\phi_1\right) + \chi n\left(1-\phi_1\right)^2\right\} \tag{3.12.2}$$

Equation (3.12.2) was derived for the case where χ does not depend on polymer concentration.

<<Problem 3-16-a>> Concentration dependence of χ

When χ is linearly proportional to ϕ_1 in the form

$$\chi = \chi_0\left(1 + p_1\phi_1\right) \tag{3.16.1}$$

show that $\Delta\mu_1$ is given by the expression

$$\Delta\mu_1 = RT\left\{\log\phi_1 - (n-1)(1-\phi_1) + \chi_0 n(1-\phi_1)^2 + \chi_0 n p_1\left(\frac{1}{2} - \frac{3}{2}\phi_1{}^2 + \phi_1{}^3\right)\right\} \tag{3.16.2}$$

Answer

$\Delta\mu_1$ is generally expressed as

$$\Delta\mu_1 = RT\left\{\log\phi_1 - (n-1)(1-\phi_1) - \chi n\phi_1(1-\phi_1) + n\int_{\phi_1}^{1}\chi d\phi_1\right\} \tag{3.15.10}$$

Combination of Eq.(3.16.1) with Eq.(3.15.10) leads to

$$\begin{aligned}\Delta\mu_1 &= RT\left\{\log\phi_1 - (n-1)(1-\phi_1) - \chi_0(1+p_1\phi_1)n\phi_1(1-\phi_1) + n\int_{\phi_1}^{1}\chi_0(1+p_1\phi_1)d\phi_1\right\}\\ &= RT\left\{\log\phi_1 - (n-1)(1-\phi_1) - \chi_0 n\phi_1(1-\phi_1) - \chi_0 n\phi_1{}^2(1-\phi_1)\right.\\ &\quad\left. + \chi_0 n(1-\phi_1) + \chi_0 n p_1\left(\frac{1}{2} - \frac{\phi_1{}^2}{2}\right)\right\}\end{aligned} \tag{3.16.3}$$

Rearrangement of Eq. (3.16.3) gives Eq. (3.16.2).

<<Problem 3-16-b>> Virial coefficient at θ point

If higher order terms of the concentration dependence of χ is required, Eq.(3.16.1) is replaced by the equation

$$\chi = \chi_0(1 + p_1\phi_1 + p_2\phi_1{}^2 + \cdots + p_n\phi_1{}^n) \tag{3.16.4}$$

the condition that all the virial coefficients are concurrently zero at θ point is given by

$$\chi_0 = \frac{1}{2} \tag{3.16.5}$$

$$p_1 = \frac{2}{3},\quad p_2 = \frac{2}{4},\quad p_3 = \frac{2}{5},\quad \cdots,\quad p_n = \frac{2}{n+2} \tag{3.16.6}$$

Derive Eqs. (3.16.5) and (3.16.6).

Answer

If χ depends on volume fraction as Eq. (3.16.4), the chemical potential of the solvent $\Delta\mu_0$ can be given by

$$\Delta\mu_0 = RT\left\{ \ln\left(1-\phi_1\right) + \left(1-\frac{1}{n_n}\right)\phi_1 + \chi_0\left(1+\sum_{i=1}^{n} p_i\phi_1^i\right)\phi_1^2 \right\} \tag{3.16.7}$$

where n_n is the number-average chain length. $\Delta\mu_0$ in Eq. (3.16.7) can be rewritten by expanding the term $\ln(1-\phi_1)$ in a Taylor expansion form, and by expressing ϕ_1 by the weight concentration C, as

$$\Delta\mu_0 = -RTCV^0\left\{ \frac{1}{M_n} + \frac{v}{V^0}\left(\frac{1}{2}-\chi_0\right)C + \sum_{i=1}^{n}\frac{v^{i+2}}{V^0}\left(\frac{1}{i+2}-\chi_0 p_i\right)C^{i+1} \right\} \tag{3.16.8}$$

Here, v is the polymer specific volume, and M_n the **number-average molecular weight**. Osmotic pressure Π is given in a virial expansion form as

$$\Pi = -\frac{\Delta\mu_0}{V^0} = RTC\left(\frac{1}{M_n} + A_2C + A_3C^2 + \cdots\right) \tag{2.8.10}$$

For the case in question, the **virial coefficients** A_2, A_3,... are given with using Eq. (3.16.8) as

$$A_2 = \frac{v^2}{V^0}\left(\frac{1}{2}-\chi_0\right) \tag{3.16.9}$$

and

$$A_{i+2} = \frac{v^{i+2}}{V^0}\left(\frac{1}{i+2}-\chi_0 p_i\right) \qquad \left(i = 1,2,\cdots,n\right) \tag{3.16.10}$$

If we assume that $A_2=A_3=A_4=\cdots=0$, we obtain Eqs. (3.16.5) and (3.16.6).
Eq. (3.16.6) is only applicable to the systems of non-polar polymer in non-polar solvent.

---

* p_1 for atactic polystyrene (PS) in cyclohexane (CH) system was determined to be 0.630 by osmotic pressure (34°C)[1], 0.534 by ultracentrifuge (34°C)[2], 0.610 by solution critical point (SCP) (34°C)[3], 0.622 by SCP(34°C)[4], 0.607 by threshold cloud point[5], 0.642 by SCP[6], and 0.600 by cloud point curve combined with relationship between the relative amount of polymer partitioned in a polymer-rich phase and the phase separation temperature[7]. The results indicate that no significant difference in p_1 exists among various methods and p_1 values for atactic PS-CH system are averaged to 0.619 ± 0.023, except for the ultracentrifuge data[2]. The best and most widely used method for estimating p_1 and p_2 is SCP method. p_1 values for atactic PS in various non-polar or less polar solvents, whose upper or lower critical solution points (UCSP or LCSP) data in literature were analyzed systematically by Kamide et al.[6] according to Kamide-Matsuda method[8] (See <<Problem 4-23-b>>), are 0.618 (methylethylketone, LCSP), 0.615 (cyclopentane, UCSP), 0.631 (cyclopentane, LCSP), 0.642 (cyclohexane, UCSP), 0.638 (cyclohexane, LCSP), 0.602 (methylcyclohexane, UCSP), 0.649 (methylcyclohexane, LCSP), 0.673 (isopropylacetate, UCSP), 0.839 (isopropylacetate, LCSP), 0.643 (n-propylacetate, UCSP), 0.797 (n-propylacetate, LCSP), 0.650 (dimethoxymethane, LCSP), and 0.630 (trans-decalin, UCSP). p_1 values are averaged to 0.663 for all the above systems or 0.636 except two LCSP of PS in iso- and n-propylacetates. It can therefore be concluded that p_1 values of PS in non-polar solvents are close to 2/3, Eq. (3.16.6), and are slightly higher than the value (ca. 0.6) obtained in a computer experiment, but no significantly so. At the risk of oversimplifying, we could say p_1 will increase with decrease in z. Then, p_1 value estimated here for $z=12$ is not the maximum value theoretically attainable. The correct value of z should be, if possible, determined by other absolute method.

1. W. R. Krigbaum and D. O. Geymer, *J. Am. Chem. Soc.* **81**, 1859 (1959).
2. Th. G. Scholte, *J. Polym. Sci.* A-2, **8**, 841 (1970).
3. R. Koningsveld, L. A. Kleinjens and A. R. Shultz, *J. Polym. Sci.* A-2, **8**, 1261 (1970).
4. R. Koningsveld and L. A. Kleintjens, *Macromolecules* **5**, 637 (1971).
5. N. Kuwahara, M. Nakata and M. Kaneko, *Polym. J.* **20**, 231 (1988).
6. K. Kamide, S. Matsuda and M. Saito, *Polym. J.* **17**, 1013 (1985).
7. K. Kamide, *Mem. Fac. Educ. Kumamoto Univ.* **44**, 199 (1995).
8. K. Kamide and S. Matsuda, *Polym. J.* **16**, 825 (1984).

<<Problem 3-16-c>> Determination of χ from cloud-point curve

The parameter χ can be expressed in a power series of concentration as Eq. (3.16.4). The molecular weight dependence of χ is phenomenologically given by

$$\chi_0 = \chi_{00}(1 + k'/n_n) \tag{3.16.11}$$

The temperature dependence of k' and χ_{00} can be empirically expressed as

$$k' = k_0(1 - \theta/T) \tag{3.16.12}$$

and

$$\chi_{00} = a + b/T \tag{3.16.13}$$

where k_0, a and b are the constants independent of temperature and θ, the Flory temperature. Describe methods for determining the parameters a, b and p_j ($j=1,\ldots n$) from the cloud-point curve and an empirical relationship between temperature and relative amount of polymers partitioned in polymer-rich phase with the corresponding theoretical ones.

Answer

Parameters a, b, $p_j(j=1,\cdots,n)$ can be determined when the cloud point temperature $T_{cp,e}$, experimentally determined, coincides with that calculated by a computer simulation for phase equilibrium due to Eqs.(3.16.4) and (3.16.11)-(3.16.13), $T_{cp,c}$.

(1) Determine the relationships between ρ_p(ρ_p is the weight fraction of the polymer partitioned into the polymer-rich phase to the polymer dissolved in the initial solution) and the temperature T from the two-phase equilibrium experiments.

(2) Carry out a computer simulation assuming arbitrarily chosen values of p_j ($j=1,\ldots n$) to obtain the relationship between χ_{00} and ρ_p.

(3) Construct the relationship between χ_{00} and 1/T by using ρ_p vs. T relationship obtained in step (1) and χ_{00} vs. ρ_p relations obtained in step (2) and a and b determined as the intercept and slope of χ_{00} vs. T plot, respectively.

(4) Calculate CPC ($T_{cp,c}$ vs. ϕ_1 relationship) using a and b obtained in step (3)

(5) Compute $\delta \equiv \Sigma_N(T_{cp,c} - T_{cp,e})^2/N$ (N is the total number of the solutions, for which the cloud point was determined) and determine a set of p_j ($j=1,\ldots,n$) to minimize δ (where N>>n).

(6) Repeat steps 2-5 and evaluate a, b and p_j where δ is below the permissible limit. See <<Problem 4-21.d>> for the details of the simulation.

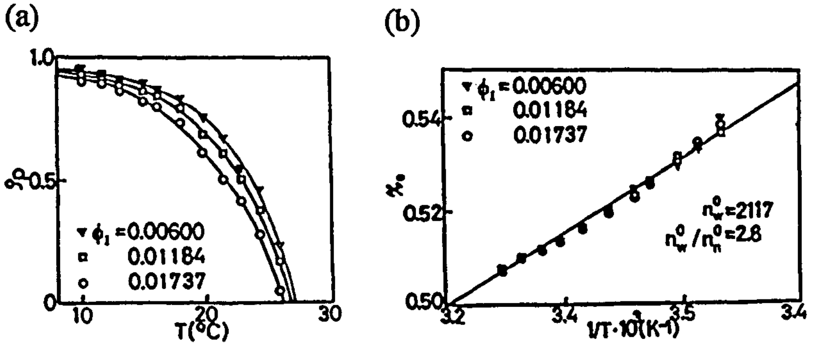

Fig. 3-16-c.1 (a) Experimental relationship between ρ_p and T and (b) temperature dependence of χ_0 in Eq. (3.16.4) for polystyrene (n_w^o=2117, n_w^o/n_n^o=2.8) in cyclohexane. The polymer volume fractions of the starting solution ϕ_1^o are 0.6x10^{-2} (▽), 1.184x10^{-2}(□) and 1.737x10^{-2}(○), respectively. Full line in (b) is the theoretical curve calculated by assuming p_1=0.62, p_2=0.20 and k_0=0. (See K. Kamide, S. Matsuda, T. Dobashi and M. Kaneko, *Polym. J.* **16**, 839 (1984))

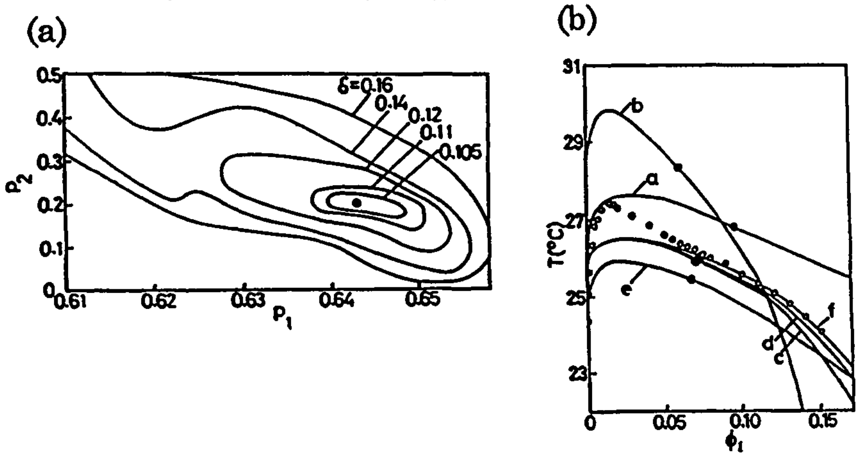

Fig. 3-16-c.2 (a) Relationship among p_1, p_2 and δ for polystyrene/ cyclohexane system: numbers denote δ and the full line is the contour line of the same δ. (b) Cloud point curves for polystyrene/cyclohexane system; full line shows the theoretical curve calculated using the values of a′,b′, p_1 and p_2 summarized in Table 3-16-c. Lines a-f have the same meaning as those in Fig. 3-15. Unfilled circles are experimental data points. (See K. Kamide, S. Matsuda, T. Dobashi and M. Kaneko, *Polym. J.* **16**, 839 (1984))

Table3-16-c.1 Parameters a', b', p_1 and p_2 in Eq.(3.16.14) for polystyrene-cyclohexane system (T=299K)

Author(s)	a'	b'	p_1	p_2
Krigbaum, Geymer(1959)	0.2496	76.67	0.630_4	0.480_8
Scholte(1970)	0.2631	74.31	0.534_4	0.430_4
Koningsveld et al. (1970)	0.2035	90.50	0.610_6	0.920_7
Koningsveld et al. (1971)	0.2211	85.313	0.622_2	0.289_1
Kuwahara et al. (1973)	0.2798	67.50	0.607_3	0.512_1
Kamide et al.(1984)	-0.0242_4	158.79	0.643	0.200
Kamide et al.(1995)	0.23	82.89	0.600	0.460

1)W.R.Krigbaum and D.O.Geymer, *J.Am.Chem.Soc.* **81**, 1859 (1959).
2)G.Scholte,*J. Polym.Sci.* **A-2**, **8**, 841 (1970).
3)R.Koningsveld, L.A.Kleintjens and A.R.Shultz, *J. Polym.Sci.* **A-2**, **8**, 1261 (1970).
4)R.Koningsveld and L.A.Kleintjens, *Macromolecules* **4**, 637 (1971).
5)N.Kuwahara,M.Nakata and M.Kaneko, *Polymer* **14**, 415 (1973).
6)K.Kamide,S.Matsuda, T.Dobashi and M.Kaneko, *Polym. J.* **16**, 839 (1984).
7)K.Kamide,S.Matsuda and H.Shirataki, *Mem. Fac. Education, Kumamoto Univ.* **44**, 199, (1995); They recalculated based on the data of ref. 6). (See K.Kamide, *Thermodynamics of Polymer Solutions: Phase Equilibria and Critical Phenomena*, Elsevier, 1990)

Table 3-16-c.2 Some characteristics of three typical solutions

Solutions	Characteristics		Equation
ideal	random mixing (solute=solvent in size) zero heat of mixing	↑	(3.2.6)
quasi-ideal	'random' mixing (solute>solvent in size) zero heat of mixing	↑ χ │ excess function	(3.8.3-4) (3.2.6)
real	non-'random' mixing (solute>>solvent in size) non- zero heat of mixing	↓ ↓ pseudo-excess function	(3.16.1-2)

---

*Fig. 3-16-c.1 (a) shows the relationship between ρ_p and T, obtained by an actual phase separation experiment for the system polystyrene(PS) in cyclohexane(CH). The relationship can be roughly approximated by a part of a circular arc with ρ_p approaching zero most appropriate set of p_1 and p_2, giving the minimum $\delta(\sim 0.1)$, could be determined as $p_1=0.643$ and $p_2=0.200$. These values are very close to the corresponding values evaluated from the critical point data (See K. Kamide and S. Matsuda, *Polym. J.* **16**, 807 (1984)). The cloud point curve, calculated with using these values of a', b', p_1 and p_2 can express accurately the experimental data except for the threshold point region ($\phi_1 \sim 0.07$). The concentration dependence of the parameter χ, evaluated for PS/CH system by many investigators, is plotted in Fig. 3-15. In the figure, the curves have been calculated from the p_1 and p_2 values evaluated from the critical points. The experimental data points can be reasonably represented by Eqs. (3.16.11), (3.16.12) and (3.16.4) for n=2, in which terms higher than ϕ_1^2 are neglected. That is, in the ϕ_1 range of 0-0.15, both p_2 and p_1 are necessary to represent the concentration dependence of χ and in a comparatively dilute range, there is no sharp distinction in χ between the investigators.

Table 3-16-c.1 shows the parameters determined for the system polystyrene in cyclohexane and Table 3-16-c.2 summarizes some characteristics of three typical solutions.

<<Problem 3-17>> Chemical potential of polymer in multicomponent polymer solution

Generalize Eq.(3.16.2) to the case where the polymer solute has a molecular weight distribution.

Answer

The chemical potential of *n* th polymer component $\Delta\mu_n$ in multicomponent polymer solutions with constant χ can be expressed as

$$\Delta\mu_n = RT\left\{\log\phi_n - (n-1) + \phi_1 n\left(1 - \frac{1}{n_n}\right) + \chi n\left(1-\phi_1\right)^2\right\} \qquad (3.17.1)$$

Here, n_n is the **number-average chain length** (average number of segments in a

polymer). Then, Eq.(3.16.2) can be generalized to this case as

$$\Delta\mu_n = RT\left\{\log\phi_n - (n-1) + \phi_1 n\left(1 - \frac{1}{n_n}\right) + \chi_0 n\left(1-\phi_1\right)^2\right.$$
$$\left. + \chi_0 p_1 n\left(\frac{1}{2} - \frac{3}{2}\phi_1{}^2 + \phi_1{}^3\right)\right\} \qquad (3.17.2)$$

Eqs. (3.16.2) and (3.17.2) are practical equations to describe the thermodynamic properties of multicomponent polymer solutions. Eq. (3.17.2) was derived by Huggins-Okamoto (See M. L. Huggins and H. Okamoto, *Polymer Fractionation* (Ed. by M. J. R. Cantow), Chapter 4, Academic Press, 1967) and Kamide-Sugamiya (See K. Kamide and K. Sugamiya, *Makromol.Chem.* **139**, 197 (1970))

<<Problem 3-18>> Huggins' free energy correction parameter g

An **alternative expression for free energy of mixing** is

$$\frac{\Delta G_{mix}}{NRT} = \left(1-\phi_1\right)\log\left(1-\phi_1\right) + \sum\phi_1 x_i{}^{-1}\log\phi_i + g\left(1-\phi_1\right)\phi_1 \qquad (3.18.1)$$

Here, g is the Huggins free energy correction parameter and $\Sigma\phi_i=\phi_1$ is the total polymer volume fraction. Verify the relationship between g and χ, given by

$$\chi = g - (1-\phi_1)\frac{\partial g}{\partial\phi_1} \qquad (3.18.2)$$

Answer

Differentiation of Eq.(3.18.1) with respect to solvent mole (N_0) and solute mole (N_1) yields

$$\Delta\mu_0 / RT = \log\left(1-\phi_1\right) + \left(1 - \frac{1}{n_n}\right)\phi_1 + \left\{g - \left(1-\phi_1\right)\frac{\partial g}{\partial\phi_1}\right\}\phi_1{}^2 \qquad (3.18.3)$$

$$\Delta\mu_i / RT = \log\phi_i + 1 - n_i\phi_1/n_n - n_i\left(1-\phi_1\right) + \left(g + \phi_1\frac{\partial g}{\partial\phi_1}\right)n_i\left(1-\phi_1\right)^2 \qquad (3.18.4)$$

On the other hand, referring to Eq.(3.11.2), $\Delta\mu_0$ is expressed as

$$\Delta\mu_0 / RT = \log\left(1 - \phi_1\right) + \left(1 - \frac{1}{n_n}\right)\phi_1 + \chi\phi_1^{\,2} \tag{3.18.5}$$

Comparison of Eq.(3.18.3) and Eq.(3.18.5) leads to Eq.(3.18.2).

<<Problem 3-19>> Gibbs free energy of mixing for ternary system

Consider a **solution of single-component polymer dissolved in a binary solvent mixture.** Derive expressions for ΔG_{mix}, μ_0, μ_1 and μ_2, by generalizing the Flory-Huggins theory for binary solutions.

Answer

The entropy change by mixing three amorphous solute ΔS^* is given by

$$\Delta S^*_{mix} = - k\left(\mathcal{N}_0 \log \phi_0 + \mathcal{N}_1 \log \phi_1 + \mathcal{N}_2 \log \phi_2\right) \tag{3.19.1}$$

Here, N_0, N_1 and N_2 are the numbers of molecules of components 0, 1 and 2, respectively, and ϕ_0, ϕ_1 and ϕ_2 are their volume fractions. The heat of dilution can be written, with reference to Eq. (3.9.1), as

$$\left.\begin{aligned} \Delta H_{mix} &= z\sum_{i<j} n_i \mathcal{N}_i \phi_j \varepsilon_{ij} \\ &= kT\sum_{i<j} \mathcal{N}_i \phi_j \chi_{ij} \\ &= kT\left(\mathcal{N}_0 \phi_1 \chi_{01} + \mathcal{N}_0 \phi_2 \chi_{02} + \mathcal{N}_1 \phi_2 \chi_{12}\right) \end{aligned}\right\} \tag{3.19.2}$$

with

$$\chi_{ij} = \frac{z n_i \varepsilon_{ij}}{kT}$$

ΔG_{mix} is given by the combination of Eqs. (3.19.1) and (3.19.2) as

$$\begin{aligned} \Delta G_{mix} &= \Delta H_{mix} - T\Delta S^*_{mix} \\ &= kT\left(\mathcal{N}_0 \log \phi_0 + \mathcal{N}_1 \log \phi_1 + \mathcal{N}_2 \log \phi_2 + \chi_{01}\mathcal{N}_0\phi_1 + \chi_{02}\mathcal{N}_0\phi_2 + \chi_{12}\mathcal{N}_1\phi_2\right) \end{aligned} \tag{3.19.3}$$

The chemical potentials are defined by

$$\left.\begin{aligned}\mu_0\text{-}\mu_0{}^0 = \Delta\mu_0 &= \left(\frac{\partial\Delta G}{\partial N_0}\right)_{N_j,T,P} N_A \\ \mu_1\text{-}\mu_1{}^0 = \Delta\mu_1 &= \left(\frac{\partial\Delta G}{\partial N_1}\right)_{N_j,T,P} N_A \\ \mu_2\text{-}\mu_2{}^0 = \Delta\mu_2 &= \left(\frac{\partial\Delta G}{\partial N_2}\right)_{N_j,T,P} N_A\end{aligned}\right. \qquad (3.19.4)$$

The subscript N_j means that the amounts N_j of all the components other than component j (0 or 1 or 2) are held fixed. The volume fractions of solvent 1, solvent 2 and solute 3 are expressed as

$$\left.\begin{aligned}\phi_0 &= \frac{n_0N_0}{n_0N_0 + n_1N_1 + n_2N_2} \\ \phi_1 &= \frac{n_1N_1}{n_0N_0 + n_1N_1 + n_2N_2} \\ \phi_2 &= \frac{n_2N_2}{n_0N_0 + n_1N_1 + n_2N_2}\end{aligned}\right\} \qquad (3.19.5)$$

Here, n_0, n_1 and n_2 are the degree of polymerization. Differentiation of Eq. (3.19.5) with respect to N_0 yields

$$\left.\begin{aligned}\frac{\partial\phi_0}{\partial N_0} &= \frac{n_0\left(n_0N_0 + n_1N_1 + n_2N_2\right) - \left(n_0N_0\right)n_0}{\left(n_0N_0 + n_1N_1 + n_2N_2\right)^2} \\ &= \frac{n_0}{\left(n_0N_0 + n_1N_1 + n_2N_2\right)}\left(1 - \phi_0\right) \\ \frac{\partial\phi_1}{\partial N_0} &= \frac{-n_1N_1n_0}{\left(n_0N_0 + n_1N_1 + n_2N_2\right)^2} = -\phi_1\frac{n_0}{n_0N_0 + n_1N_1 + n_2N_2} \\ \frac{\partial\phi_2}{\partial N_0} &= -\phi_2\frac{n_0}{n_0N_0 + n_1N_1 + n_2N_2}\end{aligned}\right\} \qquad (3.19.6)$$

From Eqs. (3.19.3) and (3.19.4), we obtain

$$\Delta\mu_0 = \left(\frac{\partial \Delta G}{\partial N_0}\right)_{N_j,T,P} N_A$$

$$= RT\left(\log\phi_0 + N_0\frac{1}{\phi_0}\,\frac{\partial\phi_0}{\partial N_0} + N_1\frac{1}{\phi_1}\,\frac{\partial\phi_1}{\partial N_0} + N_2\frac{1}{\phi_2}\,\frac{\partial\phi_2}{\partial N_0}\right.$$

$$\left. + \chi_{01}\phi_1 + \chi_{01}N_0\frac{\partial\phi_1}{\partial N_0} + \chi_{02}\phi_2 + \chi_{02}N_0\frac{\partial\phi_2}{\partial N_0} + \chi_{12}N_1\frac{\partial\phi_2}{\partial N_0}\right)$$

$$= RT\left\{\log\phi_0 + \frac{n_0N_0\left(n_0N_0 + n_1N_1 + n_2N_2\right)}{n_0N_0\left(n_0N_0 + n_1N_1 + n_2N_2\right)}\left(1 - \phi_0\right)\right.$$

$$+\frac{N_1\left(n_0N_0 + n_1N_1 + n_2N_2\right)}{n_1N_1}\left(-\phi_1\right)\frac{n_0}{n_0N_0 + n_1N_1 + n_2N_2}$$

$$+\frac{N_2\left(n_0N_0 + n_1N_1 + n_2N_2\right)}{n_2N_2}\left(-\phi_2\right)\frac{n_0}{\left(n_0N_0 + n_1N_1 + n_2N_2\right)} + \chi_{01}\phi_1 + \chi_{01}\left(-\phi_1\right)\phi_0$$

$$\left. + \chi_{02}\phi_2 + \chi_{02}\left(-\phi_2\right)\phi_0 + \chi_{12}\left(-\phi_2\right)\frac{n_0N_1}{n_0N_0 + n_1N_1 + n_2N_2}\right\}$$

$$= RT\left\{\log\phi_0 + \left(1 - \phi_0\right) - \left(\frac{n_0}{n_1}\right)\phi_1 - \left(\frac{n_0}{n_2}\right)\phi_2\right.$$

$$\left. + \chi_{01}\left(\phi_1 - \phi_0\phi_1\right) + \chi_{02}\left(\phi_2 - \phi_0\phi_2\right) - \chi_{12}\phi_2\left(\frac{n_0}{n_1}\right)\phi_1\right\}$$

$$= RT\left\{\log\phi_0 + \left(1-\phi_0\right) - \left(\frac{n_0}{n_1}\right)\phi_1 - \left(\frac{n_0}{n_2}\right)\phi_2 + \left(\chi_{01}\phi_1 + \chi_{02}\phi_2\right)\left(\phi_1+\phi_2\right) - \chi_{12}\left(\frac{n_0}{n_1}\right)\phi_1\phi_2\right\} \tag{3.19.7}$$

Similarly, we have

$$\Delta\mu_1 = RT\left\{\log\phi_1 + \left(1-\phi_1\right) - \left(\frac{n_1}{n_0}\right)\phi_0 - \left(\frac{n_1}{n_2}\right)\phi_2 + \left(\chi_{10}\phi_0 + \chi_{12}\phi_2\right)\left(\phi_0+\phi_2\right) - \chi_{02}\left(\frac{n_1}{n_2}\right)\phi_0\phi_2\right\} \tag{3.19.8}$$

$$\Delta\mu_2 = RT\left\{\log\phi_2 + \left(1-\phi_2\right) - \left(\frac{n_2}{n_0}\right)\phi_0 - \left(\frac{n_2}{n_1}\right)\phi_1 + \left(\chi_{21}\phi_1 + \chi_{20}\phi_0\right)\left(\phi_1+\phi_0\right) - \chi_{01}\left(\frac{n_2}{n_0}\right)\phi_0\phi_1\right\} \tag{3.19.9}$$

The following relationship holds between χ_{ji} and χ_{ij}:

$$\chi_{ji} = \chi_{ij}\left(\frac{n_j}{n_i}\right) \tag{3.19.10}$$

For ternary systems, Eq. (3.19.10) reads

$$\chi_{12} = \chi_{21}\left(\frac{n_1}{n_2}\right)$$

$$\chi_{13} = \chi_{31}\left(\frac{n_1}{n_3}\right)$$

$$\chi_{23} = \chi_{32}\left(\frac{n_2}{n_3}\right) \tag{3.19.11}$$

Therefore, three among six χ_{ij} are independent variables.

Chapter 4 Phase Equilibria

<<Problem 4-1>> Stability of thermodynamic system (I)

If a system is in contact with temperature and pressure reservoirs, the condition of equilibrium is that Gibbs free energy of the system has a minimum; i.e., virtual change in Gibbs free energy δG from a certain initial state to neighboring states must be positive,

$$(\delta G)_{P,T} \geq 0 \tag{4.1.1}$$

Prove this inequality.

Answer

From the **first law of thermodynamics**, the infinitesimal change in internal energy of the system dU is the sum of the work done by the surroundings to the system and the heat flow from the surroundings to the system

$$dU = d'Q + d'W \tag{4.1.2}$$

If the work is performed as a volumetric change by pressure, we have

$$d'W = -PdV \tag{4.1.3}$$

Thus,

$$dU = d'Q - PdV \tag{4.1.4}$$

From the **second law of thermodynamics**, the following equation must be satisfied for closed systems:

$$dS \geq \frac{d'Q}{T} \tag{4.1.5}$$

If the inequality condition

$$\delta S < \frac{\delta' Q}{T} \tag{4.1.6}$$

holds for any possible change from a certain initial state to neighboring states, such a process does not happen naturally. Thus, the initial state should be the equilibrium state. From Eqs. (4.1.4) and (4.1.6) we have

$$\delta U - T\delta S + P\delta V \geq 0 \qquad (4.1.7)$$

Equation (4.1.7) can be also expressed as

$$\delta(U - TS + PV)_{T,P} \geq 0 \qquad (4.1.8)$$

at constant temperature and pressure ($\delta T = \delta P = 0$). Using the relationship

$$G = U - TS + PV \qquad (1.1.9)$$

we finally obtain

$$(\delta G)_{T,P} \geq 0 \qquad (4.1.1)$$

In other words, the **equilibrium condition** is that G has the minimum.

<<Problem 4-2>> Stability of thermodynamic system(II)

Consider a closed system which consists of two phases,(1) and (2), each open to the other. The virtual variation in Gibbs free energy by a continuous process from a certain initial equilibrium state to a neighboring state can be expressed in a Taylor series as

$$\Delta G = \delta G + \delta^2 G + \delta^3 G + \cdots \qquad (4.2.1)$$

(1) Prove that the equality

$$(\delta G)_{T,P} = 0 \qquad (4.2.2)$$

holds at equilibrium state.

(2) Derive the criteria for **stable, metastable and unstable equilibrium states.**

Answer

(1)At constant temperature and pressure, ΔG can be expressed as

$$(\Delta G)_{T,P} = (\delta G)_{T,P} = \sum_i \mu_{i(1)} \delta N_{i(1)} + \sum_i \mu_{i(2)} \delta N_{i(2)} \qquad (4.2.3)$$

by neglecting the higher order terms in Eq.(4.2.1). Using the phase equilibrium condition

$$\mu_{i(1)} = \mu_{i(2)} \qquad (i = 1,2,3,\cdots) \qquad (1.5.1)$$

$$\delta N_{i(1)} = -\delta N_{i(2)} \qquad (i = 1,2,3,\cdots) \qquad (1.5.5)$$

we obtain

$$(\Delta G)_{T,P} = \sum_i (\mu_{i(1)} - \mu_{i(2)})\delta N_{i(1)} = 0 \qquad (4.2.4)$$

(2)If

$$(\delta^2 G)_{T,P} > 0 \qquad (4.2.5)$$

the Gibbs free energy has a minimum at the equilibrium state and then the state is stable. If

$$(\delta^2 G)_{T,P} < 0 \qquad (4.2.6)$$

the Gibbs free energy has a maximum and the equilibrium state is unstable. If

$$(\delta^2 G)_{T,P} = 0 \qquad (4.2.7)$$

it is called the **neutral state**. In this case, the sign of even higher order terms must be examined. The sign of the first non-zero term must be positive for stable state. If

$$\delta G = \delta^2 G = \cdots = \delta^{2n} G = 0 \qquad (4.2.8)$$

then

$$\delta^{2n+1} G > 0 \qquad (4.2.9)$$

must be satisfied for stable equilibrium. The variation $\delta^{2n+1}G$ cannot always be positive for bidirectional variations, thus it must be zero. Therefore,

$$(\delta^3 G)_{T,P} = 0 \qquad (n = 1) \qquad (4.2.10)$$

In this case, the criteria for stable equilibrium is

$$(\delta^4 G)_{T,P} > 0 \qquad (4.2.11)$$

In summary, the criteria for stable equilibrium is

$$(\delta G)_{T,P} = 0 \qquad (4.2.2)$$
$$(\delta^2 G)_{T,P} > 0 \qquad (4.2.5)$$

or

$$(\delta G)_{T,P} = 0 \qquad (4.2.2)$$
$$(\delta^2 G)_{T,P} = 0 \qquad (4.2.7)$$
$$(\delta^3 G)_{T,P} = 0 \qquad (4.2.10)$$
$$(\delta^4 G)_{T,P} > 0 \qquad (4.2.11)$$

If $\delta^4 G$ is zero, $\delta^5 G$ must be zero and $\delta^6 G$ must be positive.

<<Problem 4-3>> Stability of thermodynamic system(III)

The criterion for **stable equilibrium** in binary systems is given by

$$(\delta^2 G)_{T,P} = \frac{1}{2}\mu_{11}\delta N_1{}^2 > 0 \tag{4.3.1}$$

where μ_{ij} is a derivative,

$$\mu_{ij} = \frac{\partial^2 G}{\partial N_i \partial N_j} \tag{4.3.2}$$

Derive Eq. (4.3.1) using the result of <<Problem 4-2>>

Answer

Consider a solution which consists of N_0 solvent and N_1 solute molecules. A conceptual small region inside the solution (Region I) is defined such that at any instant it contains $N_{0(1)}$ moles of solvent and $N_{1(1)}$ moles of solute, and the complementary region (Region II) external to Region I contains $N_{0(2)}$ moles of solvent and $N_{1(2)}$ moles of solute. Using mole fractions x_0 and x_1 (=$1-x_0$), we have

$$N_{0(1)} = (1 - x_1)(N_{0(1)} + N_{1(1)}) \tag{4.3.3a}$$
$$N_{0(2)} = (1 - x_1)(N_{0(2)} + N_{1(2)}) \tag{4.3.3b}$$
$$N_{1(1)} = x_1(N_{0(1)} + N_{1(1)}) \tag{4.3.3c}$$
$$N_{1(2)} = x_1(N_{0(2)} + N_{1(2)}) \tag{4.3.3d}$$

Here we assumed $x_1=x_{1(1)}=x_{1(2)}$. By virtue of the assumption that Region II is very small in comparison with Region I,

$$N_{0(1)} + N_{1(1)} << N_{0(2)} + N_{1(2)} \tag{4.3.4}$$

If we transfer a small amount of solute $\delta N_{1(2)}$ from Region II to Region I while keeping $N_{0(1)}$ constant, we have

$$\delta N_{1(2)} = - \delta N_{1(1)} \tag{4.3.5}$$

from the mass balance. The variation of Gibbs free energy in Region (I), $\delta G_{(1)}$, and that in Region (II), $\delta G_{(2)}$, can be expressed as

$$(\delta G_{(1)})_{T,P} = \left(\frac{\partial G}{\partial N_{1(1)}}\right)_{T,P,N_0} \delta N_{1(1)} = \mu_{1(1)}\delta N_{1(1)} \tag{4.3.6}$$

and

$$(\delta G_{(2)})_{T,P} = \left(\frac{\partial G}{\partial N_{1(2)}}\right)_{T,P,N_0} \delta N_{1(2)} = \mu_{1(2)}\delta N_{1(2)} \tag{4.3.7}$$

Equations (4.3.6) and (4.3.7) can be expressed simply as

$$(\delta G_{(\alpha)})_{T,P} = \mu_{1(\alpha)}\delta N_{1(\alpha)} \qquad (\alpha = 1,2) \qquad (4.3.8)$$

The second-order variation of Gibbs free energy is written as

$$(\delta^2 G_{(\alpha)})_{T,P} = \frac{1}{2}\frac{\partial^2 G_{(\alpha)}}{\partial N_{1(\alpha)}{}^2}\delta N_{1(\alpha)}{}^2 = \frac{1}{2}\mu_{11(\alpha)}\delta N_{1(\alpha)}{}^2 \qquad (\alpha = 1,2) \qquad (4.3.9)$$

Here,

$$\mu_{11(\alpha)} = \left(\frac{\partial^2 G_{(\alpha)}}{\partial N_{1(\alpha)}\partial N_{1(\alpha)}}\right)_{T,P} = \left(\frac{\partial \mu_1}{\partial N_{1(\alpha)}}\right)_{N_{0(\alpha)}} \qquad (\alpha = 1,2) \qquad (4.3.10)$$

The total Gibbs free energy is the sum of those of Region I and Region II;

$$G = G_{(1)} + G_{(2)} \qquad (4.3.11)$$

Then, using Eq. (4.3.5), we have

$$\begin{aligned}(\delta G)_{T,P} &= (\delta G_{(1)})_{T,P} + (\delta G_{(2)})_{T,P} = \mu_{1(1)}\delta N_{1(1)} - \mu_{1(2)}\delta N_{1(1)} \\ &= (\mu_{0(1)} - \mu_{0(2)})\delta N_{1(1)} = 0 \end{aligned} \qquad (4.3.12)$$

From Eq. (4.3.12), we can directly obtain $\mu_{0(1)}=\mu_{0(2)}$ as the phase equilibrium condition. Using Eq. (4.3.9), we have

$$(\delta^2 G)_{T,P} = (\delta^2 G_{(1)})_{T,P} + (\delta^2 G_{(2)})_{T,P} = \frac{1}{2}(\mu_{11(1)} + \mu_{11(2)})\delta N_{1(1)}{}^2 \qquad (4.3.13)$$

The differential of μ with respect to mole number can be replaced by that with respect to mole fraction as

$$\begin{aligned}\mu_{11(\alpha)} &= \left(\frac{\partial \mu_{1(\alpha)}}{\partial N_{1(\alpha)}}\right)_{N_{0(\alpha)}} = \left(\frac{\partial \mu_{1(\alpha)}}{\partial x_{1(\alpha)}}\right)\left\{\frac{\partial}{\partial N_{1(\alpha)}}\left(\frac{N_{1(\alpha)}}{N_{0(\alpha)} + N_{1(\alpha)}}\right)\right\} \\ &= \frac{1 - x_{1(\alpha)}}{\left(N_{0(\alpha)} + N_{1(\alpha)}\right)}\left(\frac{\partial \mu_{1(\alpha)}}{\partial x_{1(\alpha)}}\right) \qquad (\alpha = 1,2) \end{aligned} \qquad (4.3.14)$$

From Eq. (4.3.4), we have

$$\mu_{11(1)} >> \mu_{11(2)} \qquad (4.3.15)$$

Thus, $\mu_{11(2)}$ in Eq. (4.3.13) can be neglected, resulting in

$$(\delta^2 G)_{T,P} = \frac{1}{2}\mu_{11}\delta N_1{}^2 \qquad (4.3.16)$$

Here, we abbreviate the superscript (1), since the two regions belong to the same phase. Combination of Eqs.(4.3.16) and (4.2.5) yields

$$\mu_{11} > 0 \qquad (4.3.17)$$

that is,

$$\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P} > 0 \qquad (4.3.18)$$

(See for example, R. Haase, *Thermodynamics of Irreversible Processes*, Addison-Wesley Pub. Co., Massachusetts, 1969 (translated from Germany); H. B. Callen, Thermodynamics, John Wiley & Sons, New York, 1960)

<<Problem 4-4>> Stability of thermodynamic system(IV)

(1) The criterion for stable equilibrium of binary mixtures is given by

$$(\delta^2 G)_{T,P} = \frac{1}{2}\sum_{i=0}^{1}\sum_{j=0}^{1}\mu_{ij}\delta N_i \delta N_j > 0 \qquad (4.4.1)$$

Derive Eq. (4.4.1).

(2) Prove that the necessary and sufficient condition for Eq.(4.4.1) is given by

$$\mu_{00} > 0 \qquad (4.4.2)$$

$$\mu_{11} > 0 \qquad (4.4.3)$$

$$\begin{vmatrix} \mu_{00} & \mu_{01} \\ \mu_{10} & \mu_{11} \end{vmatrix} \geq 0 \qquad (4.4.4)$$

(3) Prove that Eqs. (4.4.2)-(4.4.4) reduce to the equation

$$\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P} > 0 \qquad (4.4.5)$$

Answer

(1) The first order and the second order variations of Gibbs free energy are expressed as

$$(\delta G_{(\alpha)})_{T,P} = \mu_{0(\alpha)}\delta N_{0(\alpha)} + \mu_{1(\alpha)}\delta N_{1(\alpha)} \qquad (\alpha = 1,2) \qquad (4.4.6)$$

$$(\delta^2 G_{(\alpha)})_{T,P} = \frac{1}{2}\sum_{i=0}^{1}\sum_{j=0}^{1}\mu_{ij(\alpha)}\delta N_{i(\alpha)}\delta N_{j(\alpha)} \qquad (\alpha = 1,2) \tag{4.4.7}$$

where

$$\mu_{ij(\alpha)} = \left(\frac{\partial^2 G_{(\alpha)}}{\partial N_{i(\alpha)}\partial N_{j(\alpha)}}\right)_{T,P} = \left(\frac{\partial \mu_i}{\partial N_{j(\alpha)}}\right)_{N_{i(\alpha)}} \qquad (\alpha = 1,2) \tag{4.4.8}$$

Similarly to <<Problem 4-3>>, the following inequality is assumed.

$$N_{0(1)}+N_{1(1)} << N_{0(2)}+N_{1(2)} \tag{4.3.4}$$

Total G is the sum of G in Region I and Region II:

$$G = G_{(1)} + G_{(2)} \tag{4.3.11}$$

According to <<Problem 4-3>>, we have

$$(\delta G)_{T,P} = (\mu_{0(1)} - \mu_{0(2)})\delta N_{0(1)} + (\mu_{0(1)} - \mu_{0(2)})\delta N_{1(1)} = 0 \tag{4.4.9}$$

Similarly,

$$(\delta^2 G)_{T,P} = \frac{1}{2}\sum_{i=0}^{1}\sum_{j=0}^{1}(\mu_{ij(1)} + \mu_{ij(2)})\delta N_{i(1)}\delta N_{j(1)} \tag{4.4.10}$$

Differentials of the chemical potentials with respect to mole numbers can be replaced by those with respect to mole fractions as

$$\begin{aligned}\mu_{i0(\alpha)} &= \left(\frac{\partial \mu_{i(\alpha)}}{\partial N_{0(\alpha)}}\right)_{N_{1(\alpha)}} = \left(\frac{\partial \mu_{i(\alpha)}}{\partial x_{1(\alpha)}}\right)\left\{\frac{\partial}{\partial N_{0(\alpha)}}\left(\frac{N_{1(\alpha)}}{N_{0(\alpha)} + N_{1(\alpha)}}\right)\right\} \\ &= -\frac{x_{1(\alpha)}}{\left(N_{0(\alpha)}+N_{1(\alpha)}\right)}\left(\frac{\partial \mu_{i(\alpha)}}{\partial x_{1(\alpha)}}\right) \qquad \left(i = 0,1;\ \alpha = 1,2\right)\end{aligned} \tag{4.4.11}$$

$$\begin{aligned}\mu_{i1(\alpha)} &= \left(\frac{\partial \mu_{i(\alpha)}}{\partial N_{1(\alpha)}}\right)_{N_{0(\alpha)}} = \left(\frac{\partial \mu_{i(\alpha)}}{\partial x_{1(\alpha)}}\right)\left\{\frac{\partial}{\partial N_{1(\alpha)}}\left(\frac{N_{1(\alpha)}}{N_{0(\alpha)} + N_{1(\alpha)}}\right)\right\} \\ &= \frac{1 - x_{1(\alpha)}}{\left(N_{0(\alpha)} + N_{1(\alpha)}\right)}\left(\frac{\partial \mu_{i(\alpha)}}{\partial x_{1(\alpha)}}\right) \qquad \left(i = 0,1;\ \alpha = 1,2\right)\end{aligned} \tag{4.4.12}$$

From the condition (4.3.4),

$$\mu_{ij(1)} >> \mu_{ij(2)} \qquad (4.4.13)$$

Thus, Eq. (4.4.10) is reduced to

$$(\delta^2 G)_{T,P} = \frac{1}{2}\sum_{i=0}^{1}\sum_{j=0}^{1}\mu_{ij(1)}\delta N_{i(1)}\delta N_{j(1)} = \frac{1}{2}\sum_{i=0}^{1}\sum_{j=0}^{1}\mu_{ij}\delta N_i \delta N_j > 0 \qquad (4.4.1)$$

Here we abbreviate the subscript (1) because both regions belong to the same phase.

(2) Equation (4.4.1) is a quadratic form in δN_i with coefficients $\mu_{ij}/2$. The necessary and sufficient condition for $(\delta^2 G)_{T,P}$ to be positive definite is that all the minor determinants constructed on the principal diagonal line must be positive or zero. This condition is expressed as Eqs. (4.4.2)-(4.4.4) mathematically. In other words, $(\delta^2 G)_{T,P}$ is positive only when all the solutions of the determinant

$$\begin{vmatrix} \mu_{00} - \lambda & \mu_{01} \\ \mu_{10} & \mu_{11} - \lambda \end{vmatrix} = 0 \qquad (4.4.14)$$

are positive or

$$\lambda = \frac{(\mu_{00} + \mu_{11}) \pm \sqrt{(\mu_{00} + \mu_{11})^2 - 4(\mu_{00}\mu_{11} - \mu_{01}{}^2)}}{2} > 0 \qquad (4.4.15)$$

The conditions of Eqs. (4.4.2)-(4.4.4) are identical to the condition that Eq. (4.4.15) always holds.

(3) From the **Gibbs-Duhem relation**, we have

$$\sum_i N_i d\mu_i = 0 \qquad (1.3.1)$$

$$\sum_i N_i \frac{\partial \mu_i}{\partial N_j} = 0 \qquad (4.4.16)$$

For binary mixtures, Eq. (4.4.16) reads

$$\begin{aligned} N_0 \frac{\partial \mu_0}{\partial N_0} + N_1 \frac{\partial \mu_1}{\partial N_0} &= 0 \\ N_0 \frac{\partial \mu_0}{\partial N_1} + N_1 \frac{\partial \mu_1}{\partial N_1} &= 0 \end{aligned} \qquad (4.4.17)$$

Eq. (4.4.17) can be rewritten as

$$N_0\mu_{00} + N_1\mu_{10} = 0$$

$$N_0\mu_{01} + N_1\mu_{11} = 0 \qquad (4.4.18)$$

Then μ_{00} and μ_{01} can be expressed as $-(N_1/N_0)\mu_{10}$ and $-(N_1/N_0)\mu_{11}$, respectively. Substituting these expressions in the determinant of Eq.(4.4.4), we find it always zero. From Eqs. (4.4.11) and (4.4.12),

$$\mu_{00} = -\frac{x_1}{(N_0 + N_1)}\left(\frac{\partial\mu_0}{\partial x_1}\right)_{T,P} \qquad (4.4.19)$$

$$\mu_{11} = \frac{1 - x_1}{(N_0 + N_1)}\left(\frac{\partial\mu_1}{\partial x_1}\right)_{T,P} \qquad (4.4.20)$$

Hence, Eqs. (4.4.2) and (4.4.3) can be expressed as

$$\left(\frac{\partial\mu_0}{\partial x_1}\right)_{T,P} < 0 \qquad (4.4.21)$$

$$\left(\frac{\partial\mu_1}{\partial x_1}\right)_{T,P} > 0 \qquad (4.4.5)$$

respectively. The **Gibbs-Duhem relation** is expressed as

$$(1 - x_1)\left(\frac{\partial\mu_0}{\partial x_1}\right)_{T,P} + x_1\left(\frac{\partial\mu_1}{\partial x_1}\right)_{T,P} = 0 \qquad (4.4.22)$$

for binary mixtures. Thus, considering the constraint $0<x_1<1$, Eq.(4.4.21) is identical to Eq.(4.4.5) and either the condition Eq.(4.4.21) or Eq.(4.4.4) is required for stable equilibrium.

<<Problem 4-5>> Criteria for stable equilibrium for binary mixture

Gibbs free energy of mixing ΔG_{mix} is expressed as a function of mole fraction of solute x_1 in binary mixtures at constant temperature and pressure. If ΔG_{mix} has an upward curvature, the system is unstable, and if ΔG_{mix} has a downward curvature, the system is stable.

(1) Prove

$$\delta\Delta G_{mix} \geq 0 \qquad (4.5.1)$$

for the former case and

$$\delta\Delta G_{mix} \leq 0 \qquad (4.5.2)$$

for the latter case. For convenience, assume that the system contains one mole of solution. The Gibbs free energy variation ΔG_{mix} per one mole is also called the **mean molar Gibbs free energy** $\overline{G}$.

(2) $\Delta\mu_0$ and $\Delta\mu_1$ are related to ΔG_{mix} as

$$\Delta\mu_0 = \Delta G_{mix} - x_1\left(\frac{\partial \Delta G_{mix}}{\partial x_1}\right)_{P,T} \tag{4.5.3}$$

$$\Delta\mu_1 = \Delta G_{mix} + x_0\left(\frac{\partial \Delta G_{mix}}{\partial x_1}\right)_{P,T} \tag{4.5.4}$$

Derive these equations.

(3) Express the criteria for stable equilibrium in binary mixtures using Eq. (4.5.4) for ΔG_{mix}. If ΔG_{mix} has an upward curvature in a certain concentration range, the solution is unstable in this range. How stable is the system when ΔG_{mix} is at an inflection point?

Answer

(1) Figures 4-5(a) and 4-5(b) are schematic plots for ΔG_{mix} as a function of x_1. Molar Gibbs free energies of pure solvent and pure solute are expressed as A_0 and A_1, respectively. ΔG_{mix} for a certain concentration A ($AA_0 = x_1$) is AB. Now imagine a solution with concentration A separates into two phases with the concentrations A' and A". The weight ratio of these phases is AA":AA', according to the law of mass conservation. Thus, we have

$$A_0A = A_0A'\frac{AA''}{AA'+AA''} + A_0A''\frac{AA'}{AA'+AA''} \tag{4.5.5}$$

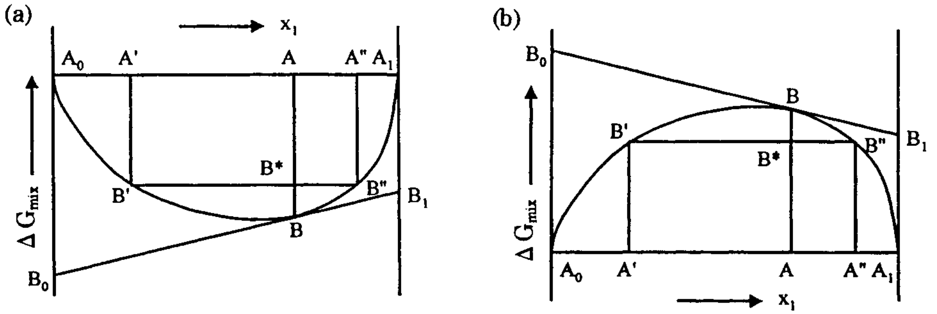

Fig. 4-5 Gibbs free energy of mixing as a function of mole fraction

If ΔG_{mix} has a downward curvature, the Gibbs free energy of mixing increases from B to B* by phase separation (See Fig. 4-5(a)).

$$\delta\, \Delta G_{mix} = \Delta G_{mix}(B^*) - \Delta G_{mix}(B) \geq 0 \qquad (4.5.6)$$

This fact implies that if ΔG_{mix} has a downward curvature, phase separation does not take place. On the other hand, if ΔG_{mix} has an upward curvature, ΔG_{mix} decreases from B to B* (See Fig.4-5(b)).

$$\delta \Delta G_{mix} = \Delta G_{mix}(B^*) - \Delta G_{mix}(B) \leq 0 \qquad (4.5.7)$$

Thus, if ΔG_{mix} has an upward curvature, phase separation occurs throughout the concentration range.

(2) ΔG_{mix} is expressed as

$$\Delta G_{mix} = x_0 \Delta\mu_0 + x_1 \Delta\mu_1 \qquad (4.5.8)$$

Differentiation of Eq. (4.5.8) with respect to mole fraction yields

$$\left(\frac{\partial \Delta G_{mix}}{\partial x_1}\right)_{T,P} = \Delta\mu_1 - \Delta\mu_0 \qquad (4.5.9)$$

Using Eqs. (4.5.8) and (4.5.9), we have

$$\Delta\mu_0 = \Delta G_{mix} - x_1 \left(\frac{\partial \Delta G_{mix}}{\partial x_1}\right)_{T,P} \qquad (4.5.3)$$

$$\Delta\mu_1 = \Delta G_{mix} - x_0 \left(\frac{\partial \Delta G_{mix}}{\partial x_1}\right)_{T,P} \qquad (4.5.4)$$

From Eqs. (4.5.3) and (4.5.4), we have

$$\left(\Delta G_{mix}\right)_{x_1=0} = A_0 B_0 = \Delta\mu_0 \qquad (4.5.10)$$

$$\left(\Delta G_{mix}\right)_{x_0=0} = A_1 B_1 = \Delta\mu_1 \qquad (4.5.11)$$

(3) Substituting Eq.(4.5.4) in the equation for the criterion of stable equilibrium for binary mixtures

$$\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P} > 0 \qquad (4.4.5)$$

we have

$$\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P} = (1 - x_1)\left(\frac{\partial^2 \Delta G_{mix}}{\partial x_1{}^2}\right)_{T,P} > 0 \tag{4.5.12}$$

Since $x_1<1$, we have

$$\left(\frac{\partial^2 \Delta G_{mix}}{\partial x_1{}^2}\right)_{T,P} > 0 \tag{4.5.13}$$

for the stable state. At the inflection point the sign of $(\partial^2\Delta G_{mix}/\partial x_1{}^2)$ varies from positive to negative. Then we have

$$\left(\frac{\partial^2 \Delta G_{mix}}{\partial x_1{}^2}\right)_{T,P} = 0 \tag{4.5.14}$$

or

$$\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P} = 0 \tag{4.5.15}$$

Thus, the system is at neutral equilibrium state at the inflection point of ΔG_{mix}.

<<Problem 4-6>> Gibbs free energy surface and phase diagram for binary mixture

Figure 4-6.1(a) is a plot of **mean molar Gibbs free energy** $\bar{G}$ defined by $\sum x_i \Delta\mu_i$ against mole fraction x_1 at various temperatures. At high temperatures, $\bar{G}$ has a downward curvature over the entire range of composition of the mixture. On the other hand, at low temperatures $\bar{G}$ has an upward curvature between C' and C" (inflection points). The points B' and B" are double tangential points.

(1) Where are the **stable region**, the **metastable region**, the **unstable region** and the critical point ?

(2) Fig. 4-6.1(b) is a plot of the phase diagram in mole fraction-temperature space. The solid curve is the binodal curve which is the locus of the double tangential points in Fig. 4-6.1(a), and the dashed curve is the spinodal curve which is the locus of the inflection point in Fig. 4-6.1(a). The line connecting

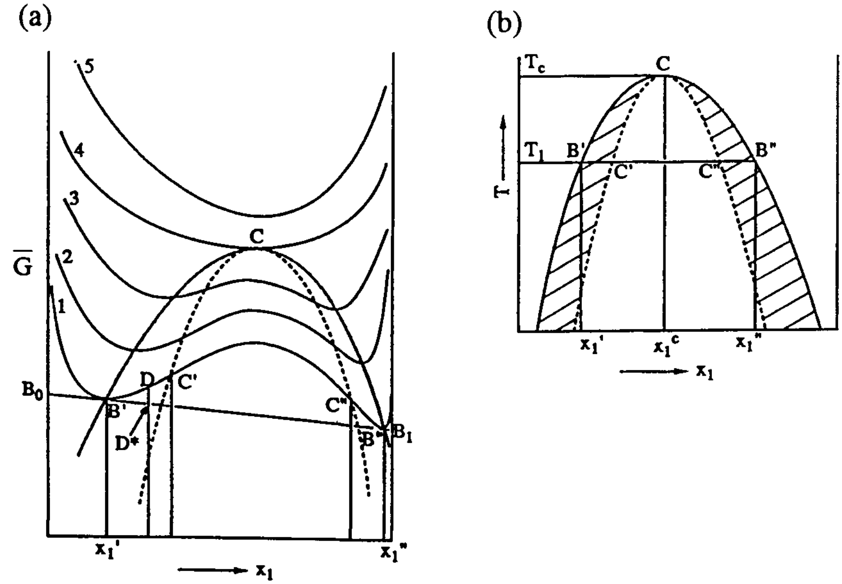

Fig. 4-6.1 (a) Mean molar Gibbs free energy as a function of mole fraction for various temperatures ($T_5>T_4>T_3>T_2>T_1$) and (b) phase diagram of binary solution

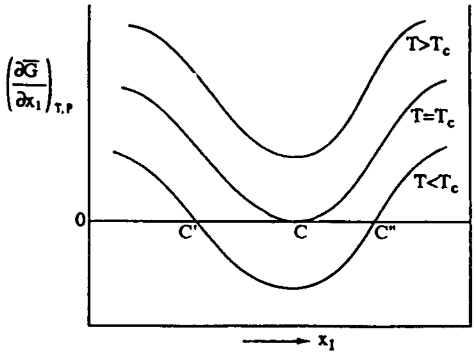

Fig. 4-6.2 Partial derivative of mean molar Gibbs free energy as a function of mole fraction

B' and B" is called the tie line. Where are the metastable region and the unstable region ?

Answer

(1) The extrapolation of the double tangential line B'-B" to the perpendicular axes at $x_1=0$ and $x_1=1$ gives μ_0 and μ_1, respectively (See Eqs. (4.5.10) and (4.5.11)). The compositions at B' and B" are denoted as x_1' and x_1'', respectively. Then we have phase equilibrium conditions

$$\mu_0(x_1') = \mu_0(x_1'') \tag{4.6.1}$$

$$\mu_1(x_1') = \mu_1(x_1'') \tag{4.6.2}$$

Now, we take a certain point D between B' and C' or between B" and C". Since $\overline{G}$ has a downward curvature in this region, the system is stable for continuous variations of the concentration of the components. However, the total $\overline{G}$ for the system which consists of two phases denoted by B' and B" is lower than $\overline{G}$ for D by DD*. That is,

$$\left(\delta\overline{G}\right)_{T,P} < 0$$

Thus the system is not stable. This region is called the **metastable region**. Between C' and C", $\overline{G}$ has an upward curvature and the system is unstable. The system corresponding to this region separates into two phases with the compositions x_1' and x_1''. Thus, all the systems corresponding to the region

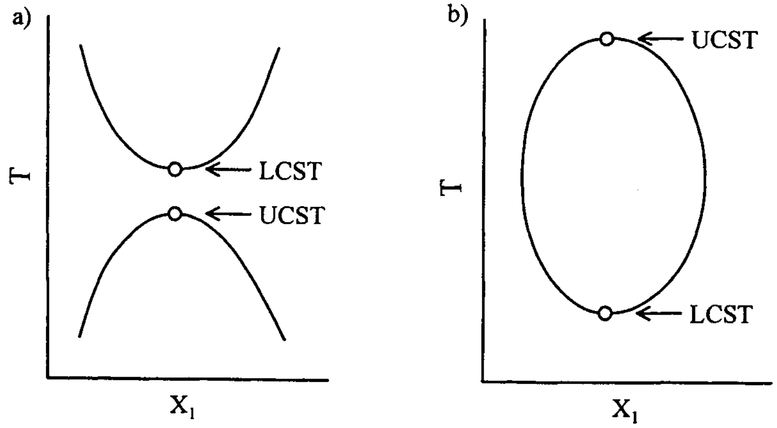

Fig. 4-6.3 Phase diagram of binary solutions with UCST and LCST

between B' and B" separate into two phases with concentrations x_1' and x_1''. **Stable regions** are in the range $0<x_1<x_1'$ and $x_1''<x_1<1$. At the temperature for Curve 4 in Fig. 4-6.1(a), both B' and B", and C' and C" coincide with each other. Since C is the inflection point of $\overline{G}$, we have

$$\left(\frac{\partial^2 \overline{G}}{\partial x_1^2}\right)_{T,P} = 0 \qquad (4.6.3)$$

at C. In Fig.4-6.2, $(\partial^2 \overline{G}/\partial x_1^2)_{T,P}$ has a downward curvature against x_1. Then we have

$$\left(\frac{\partial^3 \overline{G}}{\partial x_1^3}\right)_{T,P} = 0 \qquad (4.6.4)$$

and

$$\left(\frac{\partial^4 \overline{G}}{\partial x_1^4}\right)_{T,P} > 0 \qquad (4.6.5)$$

Here, C is the **critical point**. The concentration and the temperature at C are called the **critical solution concentration** and the **critical solution temperature**, respectively. Eqs. (4.6.4) and (4.6.5) correspond to the equations

$$(\delta^3 G)_{T,P} = 0$$

and

$$(\delta^4 G)_{T,P} > 0$$

Table 4-6 Polymer solutions having both UCST and LCST. ψ and κ are the entropty and enthalpy terms of χ (See <<Problem 4-25>>)

Polymer/solvent	UCST(°C)	LCST(°C)
polystyrene/cyclohexane	34(M→∞)	180 (M→∞)
polystyrene/cyclopentane	20(M→∞)	154 (M→∞)
polyisobutylene/benzene	25(M→∞)	160 (M=1.5x10^8)
thermodynamic properties	$\Psi>0$	$\Psi<0$
	$\kappa>0$	$\kappa<0$
	$\partial^2 S/\partial \phi^2<0$	$\partial^2 S/\partial \phi^2>0$

respectively. Eqs. (4.6.3), (4.6.4) and (4.6.5) are also expressed as

$$\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P} = 0 \qquad (4.6.6)$$

$$\left(\frac{\partial^2 \mu_1}{\partial x_1^2}\right)_{T,P} = 0 \qquad (4.6.7)$$

$$\left(\frac{\partial^3 \mu_1}{\partial x_1^3}\right)_{T,P} > 0 \qquad (4.6.8)$$

The degree of freedom at the critical point of binary mixtures is, obviously, 1.

(2) The solution which corresponds to the region between B' and B" separates into two phases with concentrations x' and x". The hatched region in Fig. 4-6.1(a) is the metastable region and the region enclosed by the curve CC'C" (called **spinodal** or **limit of stability**) is the unstable region.

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* The critical temperature is called the **upper critical solution temperature** (UCST) when the phase separation occurs at temperatures below the critical temperature, and it is called the **lower critical solution temperature** (LCST) when the **phase separation** occurs at temperatures above the critical temperature, as shown in Fig. 4-6.3. The mechanism of LCST could not be explained by the **lattice theory** alone but was further elucidated with the **free volume theory** proposed by Patterson and Flory et al. (See D. Patterson, *Macromolecules* **2**, 672 (1969); P. J. Flory, R. A. Orwoll, and A. Vrij, *J. Am. Chem. Soc.* **86**, 3507, 3515 (1964)). According to their theories, LCST is caused by a considerable difference in thermal expansion coefficients between polymer and solvent. For polymer solutions, UCST is commonly lower than LCST, as shown in Fig.4-6.3(a). Table 4-6 shows typical polymer solutions which exhibit both UCST and LCST.

* The term "limit of stability" was first utilized by Gibbs (J. W. Gibbs, *Collected works*, Vol. I, Yale University Press, 1948).

<<Problem 4-7>> Criteria for stable equilibrium for ternary mixture

(1) Prove that the criteria for stable equilibrium of ternary solutions are given by the following seven inequalities.

$$\mu_{00} > 0,\ \mu_{11} > 0,\ \mu_{22} > 0 \qquad (4.7.1)$$

$$\begin{vmatrix} \mu_{00} & \mu_{01} \\ \mu_{10} & \mu_{11} \end{vmatrix} \geq 0, \quad \begin{vmatrix} \mu_{00} & \mu_{02} \\ \mu_{20} & \mu_{22} \end{vmatrix} \geq 0, \quad \begin{vmatrix} \mu_{11} & \mu_{12} \\ \mu_{21} & \mu_{22} \end{vmatrix} \geq 0 \qquad (4.7.2)$$

$$\begin{vmatrix} \mu_{00} & \mu_{01} & \mu_{02} \\ \mu_{10} & \mu_{11} & \mu_{12} \\ \mu_{20} & \mu_{21} & \mu_{22} \end{vmatrix} \geq 0 \tag{4.7.3}$$

Here, the partially differential coefficients are defined by

$$\mu_{ij} = \left(\frac{\partial^2 \overline{G}}{\partial N_i \partial N_j} \right)_{T,P,N_k} \qquad (i,j = 0,1,2)$$

(2)Prove that the seven inequalities can be reduced to the following three inequalities.

$$\mu_{11} > 0, \ \mu_{22} > 0 \tag{4.7.4}$$

$$\begin{vmatrix} \mu_{11} & \mu_{12} \\ \mu_{21} & \mu_{22} \end{vmatrix} = \mu_{11}\mu_{22} - \mu_{12}^2 \geq 0 \tag{4.7.5}$$

(3) Prove that Eqs. (4.7.4) and (4.7.5) can be rewritten as

$$\overline{G}_{11} > 0, \ \overline{G}_{22} > 0 \tag{4.7.6}$$

$$\left|\overline{G}\right| = \begin{vmatrix} \overline{G}_{11} & \overline{G}_{12} \\ \overline{G}_{21} & \overline{G}_{22} \end{vmatrix} = \overline{G}_{11}\overline{G}_{22} - \overline{G}_{12}^{\,2} \geq 0 \tag{4.7.7}$$

using partially differential coefficients of mean molar Gibbs free energy with respect to mole fraction of *i* th component x_i , $\overline{G}_{ij}$, defined by $(\partial^2 \overline{G} / \partial x_i \partial x_j)_{T,P}$.

Answer

(1) The **criterion for stable equilibrium of ternary solutions** is given by

$$\left(\delta^2 G\right)_{T,P} = \frac{1}{2} \sum_{i=0}^{2} \sum_{j=0}^{2} \mu_{ij} \delta N_i \delta N_j > 0 \tag{4.7.8}$$

The condition for $\delta^2 G$ to be positive-definite is that all the minor determinants which can be constructed on the principal diagonal line of the matrix

$$\begin{pmatrix} \mu_{00} & \mu_{01} & \mu_{02} \\ \mu_{10} & \mu_{11} & \mu_{12} \\ \mu_{20} & \mu_{21} & \mu_{22} \end{pmatrix}$$

are positive or zero. Thus, we obtain Eqs. (4.7.1)-(4.7.3).

(2) From the **Gibbs-Duhem relation** $\Sigma N_i d\mu_i=0$ (Eq. (1.3.1)), we have

$$\left.\begin{array}{l} N_0\mu_{00}+N_1\mu_{10}+N_2\mu_{20}=0 \\ N_0\mu_{01}+N_1\mu_{11}+N_2\mu_{21}=0 \\ N_0\mu_{02}+N_1\mu_{12}+N_2\mu_{22}=0 \end{array}\right\} \tag{4.7.9}$$

Since N_0,N_1 and N_2 are not zero, we have

$$\begin{vmatrix} \mu_{00} & \mu_{01} & \mu_{02} \\ \mu_{10} & \mu_{11} & \mu_{12} \\ \mu_{20} & \mu_{21} & \mu_{22} \end{vmatrix} > 0 \tag{4.7.10}$$

Therefore, Eq. (4.7.3) is automatically satisfied.
Eqs. (4.7.9) can be rewritten in the form

$$\left.\begin{array}{l} \mu_{01}=-\left(1/N_0\right)\left(N_1\mu_{11}+N_2\mu_{21}\right) \\ \mu_{02}=-\left(1/N_0\right)\left(N_1\mu_{12}+N_2\mu_{22}\right) \\ \mu_{00}=-\left(1/N_0\right)\left(N_1\mu_{10}+N_2\mu_{20}\right) \end{array}\right\} \tag{4.7.11}$$

Substituting the first and the second equations in the third equation of Eq. (4.7.11), we have μ_{00} as an explicit function;

$$\begin{aligned} \mu_{00}&= -\left(1/N_0\right)\left[N_1\left(-1/N_0\right)\left(N_1\mu_{11}+N_2\mu_{21}\right)+N_2\left(-1/N_0\right)\left(N_1\mu_{12}+N_2\mu_{22}\right)\right] \\ &=\left(1/N_0^2\right)\left[N_1^2\mu_{11}+2N_1N_2\mu_{12}+N_2^2\mu_{22}\right] \end{aligned} \tag{4.7.12}$$

Combination of Eqs. (4.7.11) and (4.7.12) yields

$$\begin{vmatrix} \mu_{00} & \mu_{01} \\ \mu_{10} & \mu_{11} \end{vmatrix} = \left(\frac{N_2^2}{N_0^2}\right) \begin{vmatrix} \mu_{11} & \mu_{12} \\ \mu_{21} & \mu_{22} \end{vmatrix} \tag{4.7.13}$$

Similarly, we have

$$\begin{vmatrix} \mu_{00} & \mu_{02} \\ \mu_{20} & \mu_{22} \end{vmatrix} = \left(\frac{N_2^2}{N_1^2}\right) \begin{vmatrix} \mu_{11} & \mu_{12} \\ \mu_{21} & \mu_{22} \end{vmatrix} \tag{4.7.14}$$

Eqs. (4.7.13) and (4.7.14) imply that three inequalities of Eq. (4.7.2) are identical with each other. Now let's assume arbitrarily two of three inequalities of Eq. (4.7.1) hold. For example, assume $\mu_{11}>0$ and $\mu_{22}>0$.

The case (i) $\mu_{12}>0$

Then we have $\mu_{00}>0$, from Eq. (4.7.12).

The case (ii) $\mu_{12}<0$

From the third inequality of Eq. (4.7.2),

$\mu_{11}\mu_{22} - \mu_{12}^2 > 0$

Then,

$$|\mu_{12}| < \sqrt{\mu_{11}\mu_{22}} \tag{4.7.15}$$

Substitution of Eq. (4.7.15) in Eq. (4.7.12) gives

$$\begin{aligned}\mu_{00} &= \left(1/N_0^2\right)\left(N_1^2\mu_{11} + N_2^2\mu_{22} + 2N_1N_2|\mu_{12}|\right)\\ &\geq \left(1/N_0^2\right)\left(N_1\sqrt{\mu_{11}} - N_2\sqrt{\mu_{22}}\right)^2 \geq 0\end{aligned} \tag{4.7.16}$$

Thus, if $\mu_{11}>0$ and $\mu_{22}>0$, then $\mu_{00}>0$. This result means that two inequalities arbitrarily chosen among three inequalities in Eq. (4.7.1) are independent. Therefore, Eqs. (4.7.1)-(4.7.3) reduce to Eqs. (4.7.4) and (4.7.5).

(3) Let's choose x_1 and x_2 as independent variables and x_0 $(=1-x_1-x_2)$ as a dependent variable. Referring to Eqs. (4.4.11) and (4.4.12), we have

$$\begin{aligned}\mu_{ij} &= \left(\frac{\partial\mu_i}{\partial N_j}\right)_{N_{k\neq j}} = \left(\frac{\partial\mu_i}{\partial x_1}\right)\left(\frac{\partial x_1}{\partial N_j}\right) + \left(\frac{\partial\mu_i}{\partial x_2}\right)\left(\frac{\partial x_2}{\partial N_j}\right) = \sum_{k=1}^{2}\left(\frac{\partial\mu_i}{\partial x_k}\right)\left(\frac{\partial x_k}{\partial N_j}\right)\\ &= \frac{1}{\left(N_0+N_1+N_2\right)}\left\{\left(\frac{\partial\mu_i}{\partial x_j}\right) - \sum_{k=1}^{2} x_k\left(\frac{\partial\mu_i}{\partial x_k}\right)\right\}\end{aligned} \tag{4.7.17}$$

With partial differentiation of both sides of the equation

$$\mu_i = \bar{G} + \left(\frac{\partial\bar{G}}{\partial x_i}\right) - \sum_{k=1}^{2} x_k\left(\frac{\partial\bar{G}}{\partial x_k}\right) \tag{4.7.18}$$

we have

$$\frac{\partial\mu_i}{\partial x_j} = \bar{G}_{ij} - \sum_{k=1}^{2} x_k\left(\frac{\partial^2\bar{G}}{\partial x_k\partial x_j}\right) = \bar{G}_{ij} - \sum_{k=1}^{2} x_k\bar{G}_{kj} \tag{4.7.19}$$

where

$$\overline{G}_{ij} = \left(\frac{\partial^2 \overline{G}}{\partial x_i \partial x_j} \right)_{T,P} \tag{4.7.20}$$

Substitution of Eq. (4.7.19) in Eq. (4.7.17) yields

$$\left(N_0 + N_1 + N_2\right) \mu_{ij} = \overline{G}_{ij} - \sum_{l=1}^{2} x_l \overline{G}_{lj} - \sum_{k=1}^{2} x_k \overline{G}_{ik} + \sum_{l=1}^{2} \sum_{k=1}^{2} x_l x_k \overline{G}_{lk} \tag{4.7.21}$$

Now we define the matrices

$$|\mu| = \begin{pmatrix} \mu_{11} & \mu_{12} \\ \mu_{21} & \mu_{22} \end{pmatrix} \tag{4.7.22}$$

$$|\overline{G}| = \begin{pmatrix} \overline{G}_{11} & \overline{G}_{12} \\ \overline{G}_{21} & \overline{G}_{22} \end{pmatrix} \tag{4.7.23}$$

$$|x| = \begin{pmatrix} x_1 & x_2 \\ x_1 & x_2 \end{pmatrix} \tag{4.7.24}$$

$$|E| = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{4.7.25}$$

Using these matrices, Eq. (4.7.21) can be rewritten as

$$\begin{aligned}(N_0+N_1+N_2)\,|\mu| &= |\overline{G}| - |x|\,|\overline{G}|\,|E| - |E|\,|\overline{G}|\,|x|^T + |x|\,|\overline{G}|\,|x|^T \\ &= (|E| - |x|)\,|\overline{G}|\,(|E| - |x|)^T\end{aligned} \tag{4.7.26}$$

If we denote the determinants which correspond to the matrices in Eqs. (4.7.22)-(4.7.25) as $|\mu|$, $|\overline{G}|$, $|x|$ and $|E|$, we can rewrite Eq. (4.7.26) as

$$\begin{aligned}(N_0+N_1+N_2)\,|\mu| &= |E - x|\,|\overline{G}|\,|(E - x)^T| = |E - x|^2\,|\overline{G}|\,|(E - x)^T|\,|E - x| \\ &= |E - x|^2\,|\overline{G}| = (1 - x_1 - x_2)^2\,|\overline{G}|\end{aligned} \tag{4.7.27}$$

Eq. (4.7.5) is rewritten as

$$|\mu| \geq 0 \tag{4.7.28}$$

The signs of $|\mu|$ and $|G|$ are the same from Eq. (4.7.27). Hence, Eq. (4.7.28) can be rewritten as

$$|\bar{G}| = \begin{vmatrix} \bar{G}_{11} & \bar{G}_{12} \\ \bar{G}_{21} & \bar{G}_{22} \end{vmatrix} = \bar{G}_{11}\bar{G}_{22} - (\bar{G}_{12})^2 \geq 0 \qquad (4.7.29)$$

Eq. (4.7.21) for 11 component is expressed as

$$(N_0+N_1+N_2)\,\mu_{11} = (1 - x_1)^2\,\bar{G}_{11} - 2x_2\,(1 - x_1)\,\bar{G}_{12} + x_2{}^2\bar{G}_{22} \qquad (4.7.30)$$

From the first inequality of Eq. (4.7.4), we have

$$\left(1 - x_1\right)^2 \bar{G}_{11} - 2x_2\left(1 - x_1\right)\bar{G}_{12} + x_2{}^2\bar{G}_{22} > 0 \qquad (4.7.31)$$

If

$$\bar{G}_{11} < 0 \qquad (4.7.32)$$

then

$$\bar{G}_{22} < 0 \qquad (4.7.33)$$

must be satisfied from the condition of Eq. (4.7.29). Then,
(i) The case $\bar{G}_{12}>0$:
All the terms in Eq. (4.7.31) are negative. Thus, Eq. (4.7.31) cannot hold.
(ii) The case $\bar{G}_{12}<0$:
Eq. (4.7.29) can be rewritten as

$$|\bar{G}_{12}| \leq \sqrt{|\bar{G}_{11}|\,|\bar{G}_{22}|} \qquad (4.7.34)$$

where | | means the absolute value. Substitution of Eq. (4.7.34) in Eq. (4.7.31) with refererence to Eq. (4.7.16) yields

$$\begin{aligned}(N_0+N_1+N_2)\,\mu_{11} &= -\,(1 - x_1)^2\,|\bar{G}_{11}| + 2x_2\,(1 - x_1)\,|\bar{G}_{12}| - x_2{}^2\,|\bar{G}_{22}| \\ &\leq -\,(1 - x_1)^2\,|\bar{G}_{11}| + 2x_2\,(1 - x_1)\,\sqrt{|\bar{G}_{11}|\,|\bar{G}_{22}|} - x_2{}^2\,|\bar{G}_{22}| \\ &= -\left\{(1 - x_1)\sqrt{|\bar{G}_{11}|} - x_2\sqrt{|\bar{G}_{22}|}\right\}^2 \leq 0\end{aligned} \qquad (4.7.35)$$

Thus, Eq. (4.7.31) does not hold either. These results imply that the assumption (4.7.32) must be wrong and we finally obtain

$$\bar{G}_{11} > 0 \qquad (4.7.36)$$

and then, from Eq.(4.7.29),

$$\bar{G}_{22} > 0 \qquad (4.7.37)$$

<<Problem 4-8>> Gibbs free energy on composition triangle

Consider the case in which $\overline{G}$ has a downward curvature in the entire range of concentration for a ternary system. Figure 4-8 shows the Gibbs free energy on the **composition triangle** (the magnitude of each side is unity and the apexes correspond to the pure components). $\overline{G}$ of the solution with concentration A is B and the intercepts of the tangential surface at B on the axes $x_0=0$, $x_1=0$ and $x_2=0$ are B_0, B_1 and B_2, respectively. The curve B'BB" is the intersection of the $\overline{G}$ surface with the plane which is parallel to the 0-1 axis and passes through the point B. Describe the physical meaning of (1) the length AB, (2) the line A'A" which is parallel to the 0-1 axis, (3) the curvature of B'BB" and (4) the heights A_0B_0, A_1B_1 and A_2B_2.

Answer

(1) Mean molar Gibbs free energy of the solution with concentration A. Here, the length of the perpendicular line drawn from A to the three axes gives the composition of each component.

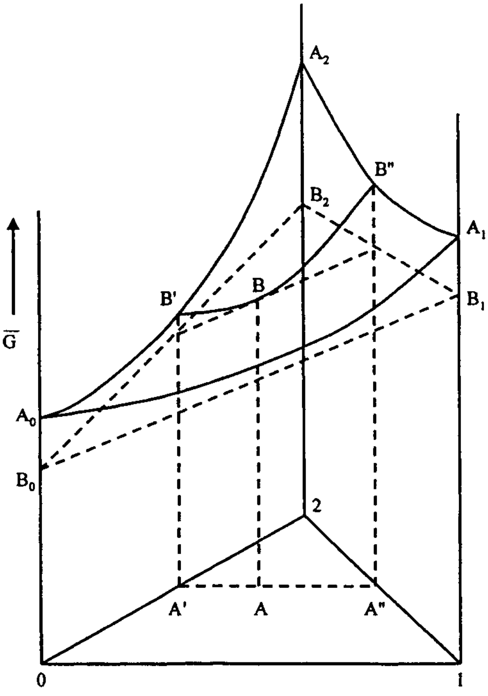

Fig. 4-8 Mean molar Gibbs free energy on the Gibbs composition triangle

(2)The line A'A" shows constant x_2.
(3) The curve B'BB" denotes G as a function of x_1 at constant x_2. The curvature is defined by $(\partial^2 \bar{G}/\partial x_1^2)_{x2}=\bar{G}_{11}$.
(4) $A_0B_0=\mu_0$, $A_1B_1=\mu_1$ and $A_2B_2=\mu_2$.

<Problem 4-9>> Critical condition for ternary mixture

The critical point of ternary mixtures can be calculated from the simultaneous equations: the **spinodal condition**

$$|\bar{G}| = \bar{G}_{11}\bar{G}_{22} - (\bar{G}_{12})^2 = 0 \qquad (4.9.1)$$

and the equation

$$\begin{vmatrix} \left(\dfrac{\partial|\bar{G}|}{\partial x_1}\right)_{x_2} & \left(\dfrac{\partial|\bar{G}|}{\partial x_2}\right)_{x_1} \\ \bar{G}_{21} & \bar{G}_{22} \end{vmatrix} = 0 \qquad (4.9.2)$$

where

$$\bar{G}_1 = \left(\frac{\partial \bar{G}}{\partial x_1}\right)_{x_2} \qquad (4.9.3)$$

$$\bar{G}_2 = \left(\frac{\partial \bar{G}}{\partial x_2}\right)_{x_1} \qquad (4.9.4)$$

Derive Eq. (4.9.2).

Answer

The total differentials of $\bar{G}_1$ and $\bar{G}_2$ are

$$d\bar{G}_1 = \bar{G}_{11}dx_1 + \bar{G}_{12}dx_2 \qquad (4.9.5)$$

$$d\bar{G}_2 = \bar{G}_{21}dx_1 + \bar{G}_{22}dx_2 \qquad (4.9.6)$$

where

$$\bar{G}_{ij} = \left(\frac{\partial^2 \bar{G}}{\partial x_i \partial x_j}\right) \qquad (i,j = 1,2) \qquad (4.9.7)$$

Using (4.9.6), the differential of x_2 at constant $\bar{G}_2$ is related to the differential of x_1 as

$$\left(dx_2\right)_{\bar{G}_2} = -\frac{\bar{G}_{21}}{\bar{G}_{22}}\left(dx_1\right)_{\bar{G}_2} \tag{4.9.8}$$

Substitution of Eq. (4.9.8) in Eq. (4.9.5) yields

$$\left(d\bar{G}_1\right)_{\bar{G}_2} = \left(\bar{G}_{11} - \frac{\left(\bar{G}_{21}\right)^2}{\bar{G}_{22}}\right)\left(dx_1\right)_{\bar{G}_2} \tag{4.9.9}$$

Then we obtain

$$\left(\frac{\partial \bar{G}_1}{\partial x_1}\right)_{\bar{G}_2} = \frac{\bar{G}_{11}\bar{G}_{22} - \left(\bar{G}_{21}\right)^2}{\bar{G}_{22}} = \frac{\left|\bar{G}\right|}{\Delta_{11}} \tag{4.9.10}$$

where Δ_{11} denotes the cofactor of ij component of the matrix;

$$\begin{pmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{pmatrix}$$

Thus Eq. (4.9.1) can be also written as

$$\left(\frac{\partial \bar{G}_1}{\partial x_1}\right)_{\bar{G}_2} = 0 \tag{4.9.11}$$

As shown in Fig. 4-6.2, $(\partial \bar{G}_1 / \partial x_1)_{\bar{G}_2}$ has the minimum with respect to x_1 at the critical point C. Then we have

$$\left(\frac{\partial^2 \bar{G}_1}{\partial x_1^2}\right)_{\bar{G}_2} = 0 \tag{4.9.12}$$

Substitution of Eq. (4.9.10) in Eq. (4.9.12) gives

$$\left\{\frac{\partial}{\partial x_1}\left(\frac{\partial \bar{G}_1}{\partial x_1}\right)\right\}_{\bar{G}_2} = \frac{1}{\Delta_{11}^2}\left\{\left(\frac{\partial |\bar{G}|}{\partial x_1}\right)_{x_2}\bar{G}_{22} - \left(\frac{\partial |\bar{G}|}{\partial x_2}\right)_{x_1}\bar{G}_{21}\right\} = 0 \tag{4.9.13}$$

Eq. (4.9.13) can be expressed in the form of determinant as

$$\begin{vmatrix} \left(\frac{\partial |\bar{G}|}{\partial x_1}\right)_{x_2} & \left(\frac{\partial |\bar{G}|}{\partial x_2}\right)_{x_1} \\ \bar{G}_{21} & \bar{G}_{22} \end{vmatrix} = 0 \tag{4.9.14}$$

<<Problem 4-10>> Critical condition for (r+1)-component system

Prove that the limit of stability (spinodal) for (r+1)-component systems is given by

$$|\overline{G}| = \begin{vmatrix} \overline{G}_{11} & \overline{G}_{12} & \overline{G}_{13} & \cdots & \overline{G}_{1r} \\ \overline{G}_{21} & \overline{G}_{22} & \overline{G}_{23} & \cdots & \overline{G}_{2r} \\ \vdots & \vdots & \vdots & & \vdots \\ \overline{G}_{r1} & \overline{G}_{r2} & \overline{G}_{r3} & \cdots & \overline{G}_{rr} \end{vmatrix} = 0 \qquad (4.10.1)$$

Then, prove that the critical condition for (r+1)-component systems is given by the combination of Eq. (4.10.1) and the equation

$$\begin{vmatrix} \dfrac{\partial|\overline{G}|}{\partial x_1} & \dfrac{\partial|\overline{G}|}{\partial x_2} & \dfrac{\partial|\overline{G}|}{\partial x_3} & \cdots & \dfrac{\partial|\overline{G}|}{\partial x_r} \\ \overline{G}_{21} & \overline{G}_{22} & \overline{G}_{23} & \cdots & \overline{G}_{2r} \\ \vdots & \vdots & \vdots & & \vdots \\ \overline{G}_{r1} & \overline{G}_{r2} & \overline{G}_{r3} & \cdots & \overline{G}_{rr} \end{vmatrix} = 0 \qquad (4.10.2)$$

Answer

The condition for stable equilibrium of (r+1)-component systems is given by

$$\left(\delta^2 G\right)_{T,P} = \frac{1}{2}\sum_{i=0}^{r}\sum_{j=0}^{r} \mu_{ij}\delta N_i \delta N_j > 0 \qquad (4.10.3)$$

where

$$\mu_{ij} = \sum_{k=1}^{r}\left(\frac{\partial \mu_i}{\partial x_k}\right)\left(\frac{\partial x_k}{\partial N_j}\right) = \frac{1}{\sum_{i=0}^{r} N_i}\left\{\left(\frac{\partial \mu_i}{\partial x_j}\right) - \sum_{k=1}^{r} x_k\left(\frac{\partial \mu_i}{\partial x_k}\right)\right\} \qquad (4.10.4)$$

and

$$\mu_i = \overline{G} + \left(\frac{\partial \overline{G}}{\partial x_i}\right) - \sum_{l=1}^{r} x_l\left(\frac{\partial \overline{G}}{\partial x_l}\right) \qquad (4.10.5)$$

$$\frac{\partial \mu_i}{\partial x_j} = \bar{G}_{ij} - \sum_{l=1}^{r} x_l \bar{G}_{lj} \tag{4.10.6}$$

Substitution of Eq. (4.10.6) into Eq. (4.10.4) gives

$$\left(\sum_{i=0}^{r} N_i\right) \|\mu\| = \left(\|E\| - \|x\|\right) \|\bar{G}\| \left(\|E\| - \|x\|\right)^T \tag{4.10.7}$$

where

$$\|\mu\| = \begin{pmatrix} \mu_{11} & \mu_{12} & \cdots & \mu_{1r} \\ \mu_{21} & \mu_{22} & \cdots & \mu_{2r} \\ \vdots & \vdots & & \vdots \\ \mu_{r1} & \mu_{r2} & \cdots & \mu_{rr} \end{pmatrix} \tag{4.10.8}$$

From Eq. (4.10.7), we have

$$\left(\sum_{i=0}^{r} N_i\right) |\mu| = |E - x| |\bar{G}| \left|(E - x)^T\right| = |E - x|^2 |\bar{G}| \tag{4.10.9}$$

Thus, the condition for the limit of stability

$$|\mu| = 0 \tag{4.10.10}$$

can be replaced by Eq. (4.10.1).
The total differentials of G_1, G_2,... G_r are expressed as

$$d\bar{G}_1 = \bar{G}_{11} dx_1 + \bar{G}_{12} dx_2 + \cdots + \bar{G}_{1r} dx_r \tag{4.10.11}$$

$$d\bar{G}_2 = \bar{G}_{21} dx_1 + \bar{G}_{22} dx_2 + \cdots + \bar{G}_{2r} dx_r \tag{4.10.12}$$

$$\cdots\cdots\cdots\cdots\cdots\cdots$$

$$d\bar{G}_r = \bar{G}_{r1} dx_1 + \bar{G}_{r2} dx_2 + \cdots + \bar{G}_{rr} dx_r \tag{4.10.13}$$

The relation between the differentials dx_1 and $dx_2,\ldots,dx_r$ at fixed $\bar{G}_i$ with i=2 to r ($dG_2 = dG_3 = \ldots = dG_r = 0$) is expressed as

$$-\bar{G}_{21} = \bar{G}_{22} \frac{dx_2}{dx_1} + \bar{G}_{23} \frac{dx_3}{dx_1} + \cdots + \bar{G}_{2r} \frac{dx_r}{dx_1}$$

$$-\bar{G}_{31} = \bar{G}_{32}\frac{dx_2}{dx_1} + \bar{G}_{33}\frac{dx_3}{dx_1} + \cdots + \bar{G}_{3r}\frac{dx_r}{dx_1}$$

$$\cdots$$

$$-\bar{G}_{r1} = \bar{G}_{r2}\frac{dx_2}{dx_1} + \bar{G}_{r3}\frac{dx_3}{dx_1} + \cdots + \bar{G}_{rr}\frac{dx_r}{dx_1} \qquad (4.10.14)$$

Eqs. (4.10.14) are simultaneous linear equations which have r unknown variables, dx_2/dx_1, dx_3/dx_1,..., dx_r/dx_1. According to the **Cramer's rule** (See e.g., V.I.Smirnov, *Linear Algebra and Group theory*, Dover, New York, 1961), we have

$$\left(\frac{dx_j}{dx_1}\right)_{\bar{G}_2,\bar{G}_3,\cdots,\bar{G}_r} = \frac{D_j}{D} \qquad (j = 2,3,\cdots,r) \qquad (4.10.15)$$

Here, D is the determinant, the elements of which are the coefficients for the unknown variables:

$$D = \begin{vmatrix} \bar{G}_{22} & \bar{G}_{23} & \cdots & \bar{G}_{2r} \\ \bar{G}_{32} & \bar{G}_{33} & \cdots & \bar{G}_{3r} \\ \vdots & \vdots & & \vdots \\ \bar{G}_{r2} & \bar{G}_{r3} & \cdots & \bar{G}_{rr} \end{vmatrix} = \Delta_{11} \qquad (4.10.16)$$

Here, Δ_{11} is the cofactor of 11 elements of the matrix $\|\bar{G}\|$. If $D=\Delta_{11}$ is non-zero, Eq. (4.10.14) has a set of solutions (Eq. 4.10.15). D_j is the determinant derived from D by replacing j1 row by $-G_{i1}$ (j=2 to r).

$$D_j = \begin{vmatrix} \bar{G}_{22} & \cdots & -\bar{G}_{21} & \cdots & \bar{G}_{2r} \\ \bar{G}_{32} & \cdots & -\bar{G}_{31} & \cdots & \bar{G}_{3r} \\ \vdots & & \vdots & & \vdots \\ \bar{G}_{r2} & \cdots & -\bar{G}_{r1} & \cdots & \bar{G}_{rr} \end{vmatrix} = \Delta_{1j}\left(-1\right)^{j-1} \qquad (4.10.17)$$

Here, Δ_{1j} is the cofactor of 1j element of the determinant $\|\bar{G}\|$. Substitution of Eq. (4.10.17) in Eq. (4.10.15) yields

$$\left(\frac{dx_j}{dx_1}\right)_{\bar{G}_2,\bar{G}_3,\cdots,\bar{G}_r} = \frac{\Delta_{1j}}{\Delta_{11}}(-1)^{j-1} \qquad (j = 2,3,\cdots,r) \tag{4.10.18}$$

Substitution of Eq. (4.10.18) in Eq. (4.10.11) yields

$$\begin{aligned}\left(d\bar{G}_1\right)_{\bar{G}_2,\cdots,\bar{G}_r} &= \left\{\bar{G}_{11} + \sum_{j=2}^{r} G_{1j}\left(\frac{dx_j}{dx_1}\right)\right\}\left(dx_1\right)_{\bar{G}_2,\cdots,\bar{G}_r} \\ &= \left\{\bar{G}_{11} + \sum_{j=2}^{r} \frac{G_{1j}\Delta_{1j}(-1)^{j-1}}{\Delta_{11}}\right\}\left(dx_1\right)_{\bar{G}_2,\cdots,\bar{G}_r}\end{aligned} \tag{4.10.19}$$

Partial derivative of $\bar{G}$ with respect to x_1 at constant $\bar{G}_i$ (i=2-r) is derived as

$$\left(\frac{\partial\bar{G}_1}{\partial x_1}\right)_{\bar{G}_2,\cdots,\bar{G}_r} = \frac{\sum_{j=1}^{r}(-1)^{j-1}G_{1j}\Delta_{1j}}{\Delta_{11}} = \frac{\left|\bar{G}\right|}{\Delta_{11}} \tag{4.10.20}$$

Thus, Eq. (4.10.1) can be rewritten as

$$\left(\frac{\partial\bar{G}_1}{\partial x_1}\right)_{\bar{G}_2,\cdots,\bar{G}_r} = 0 \tag{4.10.21}$$

Partial differentiation of Eq. (4.10.20) with respect to x_1 yields

$$\begin{aligned}\left(\frac{\partial^2\bar{G}_1}{\partial x_1^{\,2}}\right)_{\bar{G}_2,\cdots,\bar{G}_r} &= \frac{1}{\Delta_{11}}\left(\frac{\partial\left|\bar{G}\right|}{\partial x_1}\right)_{\bar{G}_2,\cdots,\bar{G}_r} = \frac{1}{\Delta_{11}}\sum_{j=1}^{r}\frac{\partial\left|\bar{G}\right|}{\partial x_j}\left(\frac{\partial x_j}{\partial x_1}\right)_{\bar{G}_2,\cdots,\bar{G}_r} \\ &= \frac{1}{\Delta_{11}^{\,2}}\sum_{j=1}^{r}\frac{\partial\left|\bar{G}\right|}{\partial x_j}\Delta_{1j}\end{aligned} \tag{4.10.22}$$

Using the second critical condition

$$\left(\frac{\partial^2\bar{G}_1}{\partial x_1^{2}}\right)_{\bar{G}_2,\cdots,\bar{G}_r} = 0 \tag{4.10.23}$$

we have

$$\sum_{j=1}^{r} \frac{\partial |\bar{G}|}{\partial x_j} \Delta_{1j} = 0 \tag{4.10.24}$$

Eq. (4.10.24) is expressed in the form of determinant as

$$|G| = \begin{vmatrix} \frac{\partial |G|}{\partial x_1} & \frac{\partial |G|}{\partial x_2} & \frac{\partial |G|}{\partial x_3} & \cdots & \frac{\partial |G|}{\partial x_r} \\ \bar{G}_{21} & \bar{G}_{22} & \bar{G}_{23} & \cdots & \bar{G}_{2r} \\ \vdots & \vdots & \vdots & & \vdots \\ \bar{G}_{r1} & \bar{G}_{r2} & \bar{G}_{r3} & \cdots & \bar{G}_{rr} \end{vmatrix} = 0 \tag{4.10.2}$$

<<Problem 4-11>> Critical condition for ideal solution and regular solution

Derive the conditions for the limit of stability and the critical point for homogeneous binary ideal solutions (1) and homogeneous binary regular solutions (2).

Answer

(1) Chemical potentials of solvent and solute μ_0 and μ_1 for ideal solution are given from Eq.(2.1.1) by

$$\mu_0 = \mu_0{}^0 + RT \ln x_0 \tag{4.11.1}$$

$$\mu_1 = \mu_1{}^0 + RT \ln x_1 \tag{4.11.2}$$

where $x_0 + x_1 = 1$

Mean molar Gibbs free energy for ideal solution is given by

$$\bar{G} = x_0 \left(\mu_0 - \mu_0{}^0\right) + x_1 \left(\mu_1 - \mu_1{}^0\right) = \left(1 - x_1\right) \Delta\mu_0 + x_1 \Delta\mu_1 \tag{4.11.3}$$

Substitution of Eqs. (4.11.1) and (4.11.2) in Eq. (4.11.3) yields

$$\bar{G} = RT \left\{ \left(1 - x_1\right) \ln\left(1 - x_1\right) + x_1 \ln x_1 \right\} \tag{4.11.4}$$

Substitution of Eq. (4.11.4) in the condition for the limit of stability

$$\bar{G}_{11} = 0 \tag{4.11.5}$$

gives

$$\bar{G}_{11} = RT\left(\frac{1}{x_1} + \frac{1}{1 - x_1}\right) = 0 \tag{4.11.6}$$

Thus,

$$\frac{1}{x_1} + \frac{1}{1 - x_1} = 0 \tag{4.11.7}$$

Here, Eq. (4.11.7) has no solution in the concentration range of physical meaning $0<x_1<1$. This result means that there is no limit of stability in binary ideal solution. Accordingly, ideal solution has no critical point. In ideal solution, only entropy of mixing contributes to $\bar{G}$, resulting in no phase separation.

(2) Chemical potentials of solvent and solute μ_0 and μ_1 for regular solutions are given by

$$\Delta\mu_0 = RT \ln x_0 + N_A z\varepsilon \left(1 - x_0\right)^2 \tag{4.11.8}$$

$$\Delta\mu_1 = RT \ln x_1 + N_A z\varepsilon \left(1 - x_1\right)^2 \tag{4.11.9}$$

where z and ε are the coordination number and the increase in the lattice energy for formation of a solute/solvent pair, respectively (See Note of <<Problem 2-13>>) Using Eqs. (4.11.8) and (4.11.9) for $\Delta\mu_0$ and $\Delta\mu_1$, mean molar Gibbs free energy of regular solutions is given by

$$\bar{G} = x_0\Delta\mu_0 + x_1\Delta\mu_1$$

$$= RT\left[\left(1 - x_1\right)\ln\left(1 - x_1\right) + x_1 \ln x_1\right] + N_A z\varepsilon x_1 \left(1 - x_1\right) \tag{4.11.10}$$

Substituting Eq. (4.11.10) in the condition for the **limit of stability**

$$\bar{G}_{11} = 0 \tag{4.11.5}$$

we have

$$\frac{\bar{G}_{11}}{RT} = \frac{1}{x_1} + \frac{1}{1 - x_1} - \frac{2z\varepsilon}{kT} = 0 \tag{4.11.11}$$

Substituting Eq. (4.11.10) in the second critical condition

$$\frac{\partial \overline{G}_{11}}{\partial x_1} = \frac{\partial^3 \overline{G}}{\partial x_1{}^3} = 0 \tag{4.11.12}$$

we have

$$\frac{1}{RT}\frac{\partial \overline{G}_{11}}{\partial x_1} = -\frac{1}{x_1{}^2} + \frac{1}{\left(1 - x_1\right)^2} = 0 \tag{4.11.13}$$

Simultaneous equations of (4.11.11) and (4.11.13) yield the **critical concentration** and the **critical temperature** as $x_1{}^c = 0.5$ and

$$T_c = \frac{2z\varepsilon}{k} \tag{4.11.14}$$

respectively.

<<Problem 4-12>> Critical condition for Flory-Huggins solution

The Gibbs free energy of mixing for polymer solutions ΔG_{mix} and chemical potentials can be expressed as a function of volume fractions of solvent and solute, ϕ_0 and ϕ_1. For example, according to the Flory-Huggins theory, the following equations hold their validity:

$$\Delta\mu_0 = RT\left[\ln\left(1 - \phi_1\right) + \left(1 - \frac{1}{n}\right)\phi_1 + \chi\phi_1{}^2\right] \tag{3.11.3}$$

$$\Delta\mu_1 = RT\left[\ln\left(1 - \phi_0\right) - \left(n - 1\right)\phi_0 + \chi n\phi_0{}^2\right] \tag{3.12.2}$$

where $\phi_0 = 1 - \phi_1$. In polymer solutions it is more convenient to define the **mean volume Gibbs free energy** G_V (or ΔG_V) in place of mean molar Gibbs free energy $\overline{G}$ (or $\Delta\overline{G}$). G_V is Gibbs free energy per unit volume of solution and ΔG_V is the Gibbs free energy change needed to make a unit volume of solution from pure solvent and pure solute. (1) Derive the equation for ΔG_V from Eqs. (3.11.3) and (3.12.2). (2) When $\overline{G}$ is expressed in terms of mole fraction x_1, the condition of stability limit (i.e., spinodal) is given by the relationship

$$\left(\frac{\partial^2 \overline{G}}{\partial x_1{}^2}\right)_{T,P} = 0 \tag{4.12.1}$$

Correspondingly, using G_V it is replaced by

$$\left(\frac{\partial^2 G_v}{\partial \phi_1{}^2}\right)_{T,P} = 0 \tag{4.12.2}$$

Derive the equation for the spinodal condition using Flory-Huggins theory.

(3) At the critical point both Eq. (4.12.2) and the relationship

$$\left(\frac{\partial^3 G_v}{\partial \phi_1{}^3}\right)_{T,P} = 0 \tag{4.12.3}$$

hold their validity. From Eqs. (4.12.2) and (4.12.3), derive the equation for the critical solution point of polymer solutions which obeys Flory-Huggins theory.

Answer

(1) Assume that one mole of solvent occupies volume of V_0 and one mole of solute occupies volume of nV_0. Then, ΔG_V is defined by

$$\Delta G_v = \left(1 - \phi_1\right)\left(\frac{\Delta\mu_0}{V_0}\right) + \phi_1\left(\frac{\Delta\mu_1}{nV_0}\right) \tag{4.12.4}$$

Substituting Eqs. (3.11.3) and (3.12.2) into Eq. (4.12.4), we obtain

$$\Delta G_v = \frac{RT}{V_0}\left\{\left(1 - \phi_1\right)\ln\left(1 - \phi_1\right) + \frac{\phi_1}{n}\ln\phi_1 + \chi\phi_1\left(1 - \phi_1\right)\right\} \tag{4.12.5}$$

(2) Differentiating Eq. (4.12.5) with respect to ϕ_1, we obtain

$$\left(\frac{\partial\Delta G_v}{\partial\phi_1}\right)_{T,P} = \frac{RT}{V_0}\left\{-\ln\left(1 - \phi_1\right) - \left(1 - \frac{1}{n}\right) + \frac{1}{n}\ln\phi_1 + \chi\left(1 - 2\phi_1\right)\right\} \tag{4.12.6}$$

Further partial differentiation of Eq. (4.12.6) with ϕ_1 gives

$$\left(\frac{\partial^2\Delta G_v}{\partial\phi_1{}^2}\right)_{T,P} = \frac{RT}{V_0}\left(\frac{1}{1 - \phi_1} + \frac{1}{n\phi_1} - 2\chi\right) \tag{4.12.7}$$

Thus, the condition for spinodal, Eq.(4.12.2), is expressed as

$$\frac{1}{1-\phi_1}+\frac{1}{n\phi_1}-2\chi=0 \tag{4.12.8}$$

Eq. (4.12.8) enables us to calculate the relationship between χ and ϕ_1 (spinodal curve) for given n.

(3) Differentiation of Eq. (4.12.7) with respect to ϕ_1 yields

$$\left(\frac{\partial^3\Delta G_v}{\partial\phi_1{}^3}\right)_{T,P}=\frac{RT}{V_0}\left\{\frac{1}{\left(1-\phi_1\right)^2}-\frac{1}{n\phi_1{}^2}\right\} \tag{4.12.9}$$

Accordingly, the condition for the critical solution point is given by

$$\frac{1}{\left(1-\phi_1\right)^2}-\frac{1}{n\phi_1{}^2}=0 \tag{4.12.10}$$

Among the solutions of simultaneous equations (4.12.8) and (4.12.10), the solution which satisfies the condition $0<\phi_1<1$ gives the critical solution point. That is,

$$\phi_1{}^c=\frac{1}{1+\sqrt{n}} \tag{4.12.11}$$

$$\phi_0{}^c=\frac{\sqrt{n}}{1+\sqrt{n}} \tag{4.12.12}$$

$$\chi_c=\frac{1}{2}\left(1+\frac{1}{\sqrt{n}}\right)^2 \tag{4.12.13}$$

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* On the other hand, χ can be assumed to be divided into an entropy term and an enthalpy term as

$$\chi=\chi_S+\chi_H \tag{4.12.14}$$

where

$$\chi_S=\frac{1}{2}-\psi \tag{4.12.15}$$

$$\chi_H\equiv\kappa=\frac{\psi\theta}{T} \tag{4.12.16}$$

Substituting Eqs. (4.12.15) and (4.12.16) in Eq. (4.12.14), we obtain

$$\chi = \frac{1}{2} - \psi + \frac{\psi\theta}{T} \tag{4.12.17}$$

Eq. (4.12.17) can be rewritten as

$$\frac{1}{T} = \frac{1}{\theta} + \frac{1}{\theta\psi}\left(\chi - \frac{1}{2}\right) \tag{4.12.18}$$

Using Eq. (4.12.18), χ_c can be converted to the **critical solution temperature** T_c. Substitution of Eq. (4.12.13) in Eq. (4.12.18) yields

$$\frac{1}{T_c} = \frac{1}{\theta} + \frac{1}{\theta\psi}\left(\frac{1}{\sqrt{n}} + \frac{1}{2n}\right) \tag{4.12.19}$$

Eq.(4.12.19) was first derived by Shultz-Flory and applied to the systems polystyrene in cyclohexane and polyisobutylene/diisobutyl ketone (See A.R.Shultz & P.J.Flory, *J.Am. Chem. Soc.* 74, 4760 (1952))

* The polymer concentration at the critical solution point of polymer solutions is shifted to extremely low concentration side. For example, ϕ_1^c=0.091 for n=100, ϕ_1^c=0.031 for n=1000 and ϕ_1^c=0.01 (i.e., 1%) for n=10^4 for Flory-Huggins solution. Therefore ϕ_1^c is at most in the range of ϕ_1^c <10%.

* If the overall volume fraction of the polymer ϕ_1^0 is larger than ϕ_1^c, the volume ratio R of polymer-lean phase to polymer-rich phase in the vicinity of the cloud point is rather smaller than 1, but if $\phi_1^0<\phi_1^c$, R>>1 is realized. Then, by measuring R in the vicinity of the cloud point as a function of ϕ_1^0 we can determine ϕ_1^c on the basis of this criterion, experimentally. See <<Probrem 4-41>>

<<Problem 4-13>> Range of critical temperature and critical composition

Discuss the **range of ϕ_1^c and χ_c**, which can be varied over a wide range of n, for Flory-Huggins solution.

Answer

In <<Problem 4-12>> we derived

$$\phi_1^c = \frac{1}{1+\sqrt{n}} \tag{4.12.11}$$

$$\chi_c = \frac{1}{2}\left(1 + \frac{1}{\sqrt{n}}\right)^2 \tag{4.12.13}$$

for Flory-Huggins solution. For n=1, we have

$$\phi_1{}^c = \frac{1}{2}, \ \chi_c = 2 \tag{4.13.1}$$

For n=∞, we have

$$\phi_1{}^c = 0, \ \chi_c = \frac{1}{2} \tag{4.13.2}$$

Therefore, with increase in molecular weight, $\phi_1{}^c$ decreases from 1/2 to zero and χ_c from 2 to 1/2. Accordingly, $\phi_1{}^c$ ranges from 1/2 to 0 and χ_c from 2 to 1/2.

<<Problem 4-14>> Determination of θ and ψ (I): Shultz-Flory plot

The following relationship holds between the critical solution temperature T_c and the Flory temperature θ.

$$\frac{1}{T_c} = \frac{1}{\theta} + \frac{1}{\theta\psi}\left(\frac{1}{\sqrt{n}} + \frac{1}{2n}\right) \tag{4.12.19}$$

Discuss **experimental methods for determining θ and** ψ based on Eq. (4.12.19).

Answer

If $\psi > 0$, T_c is always smaller than or equal to θ; $T_c \le \theta$. Eq. (4.12.19) shows that T_c approaches θ when $n \to \infty$. That is,

$$T_c(n \to \infty) = \theta \tag{4.14.1}$$

Eq. (4.14.1) means that T_c for the polymer with infinite molecular weight (or degree of polymerization) coincides with the Flory temperature. Thus, θ can be determined experimentally by measuring T_c for solutions of a series of polymers with different n and making a plot of $1/T_c$ versus $(1/n^{1/2}+1/(2n))$. The slope of the plot yields $1/(\theta\psi)$ and the intercept at n=∞ gives $1/\theta$. Then, we can determine θ and ψ concurrently. This plot is often called the Shultz-Flory plot (See A.R.Shultz and P.J.Flory, *J. Am. Chem. Soc.* 74, 4760 (1952)). Note that in this plot the concentration dependence of χ is not taken into account, so that the plot has a tendency to overestimate ψ.

<<Problem 4-15>> Determination of θ and ψ (II). Application to experimental data

Figure 4-15 shows the relationship between observed critical temperature T_c and the molecular weight of solute M for polyisobutylene in mixtures of ethylbenzene and diphenylether (See T.G Fox and P.J.Flory, *J.Am.Chem.Soc.*73, 1909 (1951)) Determine θ **and** ψ for this system.

Answer

For Flory-Huggins solution, we have

$$\frac{1}{T_c}=\frac{1}{\theta}+\frac{1}{\theta\psi}\left(\frac{1}{\sqrt{n}}+\frac{1}{2n}\right) \tag{4.12.19}$$

If n>>1, the equation reduces to

$$\frac{1}{T_c}=\frac{1}{\theta}\left(1+\frac{b}{\sqrt{M}}\right) \tag{4.15.1}$$

where

$$n=\frac{Mv_1}{V_0} \tag{4.15.2}$$

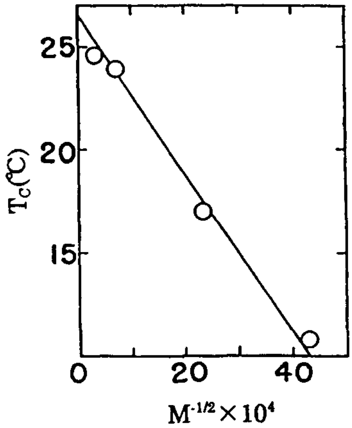

Fig. 4-15 Critical temperature as a function of molecular weight of polyisobutylene in mixtures of ethylbenzene and diphenylether (See T.G Fox and P.J.Flory, *J. Am. Chem. Soc.* 73, 1909 (1951))

$$b = \frac{\left(\frac{V_0}{v_1}\right)^{1/2}}{\psi} \qquad (4.15.3)$$

Here, M,v_1 and v_0 are the molecular weight of the polymer, the specific volume and the molar volume of the polymer. Eq. (4.15.1) is rewritten as

$$T_c = \theta \frac{1}{1 + \frac{b}{\sqrt{M}}} \cong \theta \left(1 - \frac{b}{\sqrt{M}}\right) \qquad (4.15.4)$$

The intercept of the plot of T_c vs. $M^{-1/2}$ at $M^{-1/2}=0$ gives θ and the negative sign of the slope gives b. Then, from the figure we obtain $\theta = 26.8^\circ C$ (=300K), and $M^{-1/2} = 43\times10^{-4}$ at $T_c=273K$. From Eq. (4.15.4), $273/300=1-b(43\times10^{-4})$ and $b= (1-273/300)(1/43\times10^{-4})=20.9$. In the original paper, b=13, which was erroneously determined.

<<Problem 4-16>> Determination of θ and ψ (III): Application to experimental data

Table 4-16 lists the viscosity-average degree of polymerization n_v for polyvinylbenzoate-xylene solutions. Determine the **Flory temperature** θ and the **entropy parameter** ψ for this system.

Answer

Chain length P, defined as the ratio of molar volume of polymer V_p to that

Table 4-16 Viscosity-average degree of polymerization and critical temperature of polyvinylbenzoate fractions in xylene

sample	n_v	T_c(K)
F1	1620	289.2
F2	1300	287.8
F3	990	285.0
F4	820	283.4

(See I. Sakurada, Y.Sakaguchi and S.Kokuryo, *Kobunshi Kagaku* **17**, 227 (1960)) of solvent V_s can be calculated from the degree of polymerization n using the relationship

$$P=\frac{V_p}{V_s}=\frac{\left(\frac{M}{\rho_p}\right)}{\left(\frac{M_s}{\rho_s}\right)}=\frac{\rho_s}{\rho_p}\frac{2M_0}{M_s}n \tag{4.16.1}$$

where ρ_s and ρ_p are the densities of solvent and polymer, $2M_0$ the molecular weight of repeating unit, M_s the solvent molecular weight. For the above system, we obtain ρ_s=0.881 (for o-xylene), ρ_p=1.23, $2M_0$=148, M_s=106. Therefore, if we use n_v in place of n, $P=0.998n_v \cong n_v$. From the intercept and the slope of the plot of $1/T_c$ against $(1/n^{1/2}+1/(2n))$, we obtain θ =305.8K and ψ =0.47.

---

* The experimental method for determining θ and χ in various concentrations is summarized in <<Probrem 4-23-b>>.

<<Problem 4-17>> Chemical potential in Flory-Huggins solution

Based on the Flory-Huggins theory, plot $\Delta\mu_0/RT$ **against** ϕ_1 for the cases of n=10, 100 and 1000.

Answer

The chemical potential of solvent $\Delta\mu_0$ is given by

$$\Delta\mu_0=RT\left\{\ln\left(1-\phi_1\right)+\left(1-\frac{1}{n}\right)\phi_1+\chi\phi_1^{\ 2}\right\} \tag{3.11.3}$$

Figures 4-17.(a)-(c) show the plots of $\Delta\mu_0/RT$ against ϕ_1 for various n and χ.

<<Problem 4-18>> Mean molar Gibbs free energy of regular solution

Mean molar Gibbs free energy ΔG_{mix} of the regular solution, in which low molecular weight solute is dissolved, is given by

$$\Delta G_{mix}=RT\left(x_0\ln x_0+x_1\ln x_1+z\varepsilon x_0x_1\ /kT\right) \tag{4.11.10'}$$

Plot ΔG_{mix} **against** x_1.

Answer

Figure 4-18(a) shows the plot ΔG_{mix} vs. x_1 for zε=1250, 1500 and 1750 cal/mol at 273K and (b) shows the plot for zε=1500 cal/mol at temperatures ranging from 248 to 373K. Two-phase separation occurs by increasing zε or decreasing temperature. The coexistence curve is symmetrical if the molar volumes of solvent and solute are the same.

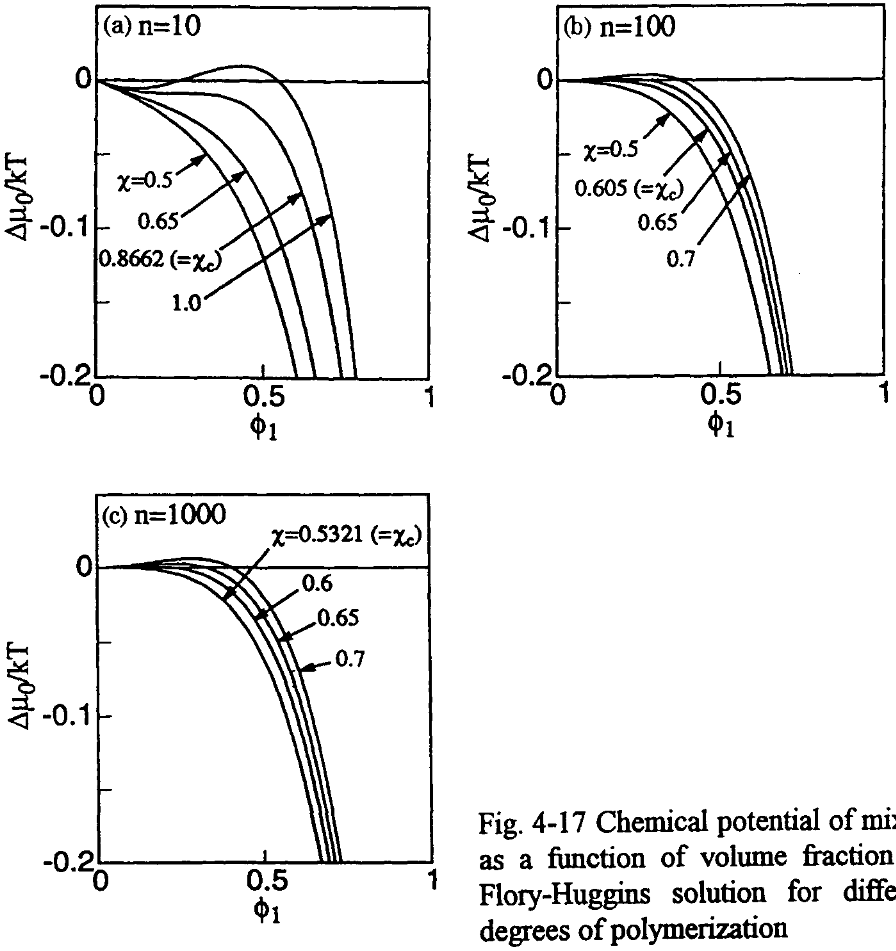

Fig. 4-17 Chemical potential of mixing as a function of volume fraction for Flory-Huggins solution for different degrees of polymerization

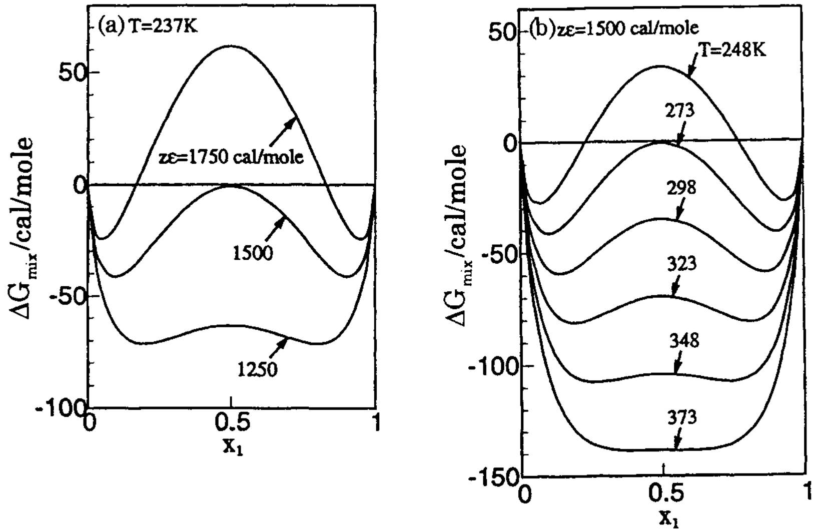

Fig. 4-18 Gibbs free energy of mixing as a function of mole fraction for regular solution for different interaction energies

<<Problem 4-19>> Mean volume Gibbs free energy and critical condition for Flory-Huggins solution

When the polymer-solvent interaction parameter χ in the Flory-Huggins theory depends on the solute concentration, the chemical potentials of solvent and polymer solute $\Delta\mu_0$ and $\Delta\mu_1$ are given by

$$\Delta\mu_0 = RT\left\{\ln\left(1-\phi_1\right)+\left(1-\frac{1}{n}\right)\phi_1+\chi\phi_1^{2}\right\} \qquad (3.11.3)$$

and

$$\Delta\mu_1 = RT\left\{\ln\phi_1-\left(n-1\right)\left(1-\phi_1\right)-\chi n\phi_1\left(1-\phi_1\right)+n\int_{\phi_1}^{1}\chi d\phi_1\right\} \qquad (3.15.10)$$

respectively. Based on Eqs. (3.11.3) and (3.15.10), derive (1) the **mean volume free energy of mixing**, and (2) the **expression for the condition of the spinodal (stability limit) and the critical point.**

Answer

(1) ΔG_v is defined by

$$\Delta G_v = (1 - \phi_1)\left(\frac{\Delta\mu_0}{V_0}\right) + \phi_1\left(\frac{\Delta\mu_1}{nV_0}\right) \tag{4.12.4}$$

Substituting Eq. (3.11.3) for $\Delta\mu_0$ and Eq. (3.15.10) for $\Delta\mu_1$ into Eq. (4.12.4), we obtain

$$\Delta G_v = \frac{RT}{V_0}\left\{(1 - \phi_1)\ln(1 - \phi_1) + \frac{\phi_1}{n}\ln\phi_1 + \phi_1\int_{\phi_1}^{1}\chi d\phi_1\right\} \tag{4.19.1}$$

(2) The spinodal condition is expressed by

$$\left(\frac{\partial^2 \Delta G_v}{\partial \phi_1{}^2}\right)_{T,P} = 0 \tag*{(4.12.2)'}$$

At the critical point, Eq. (4.12.2)' and the equation

$$\left(\frac{\partial^3 \Delta G_v}{\partial \phi_1{}^3}\right)_{T,P} = 0 \tag*{(4.12.3)'}$$

hold their validity.

Differentiation of Eq. (4.19.1) with respect to ϕ_1 yields

$$\left(\frac{\partial \Delta G_v}{\partial \phi_1}\right)_{T,P} = \frac{RT}{V_0}\left\{-\ln(1 - \phi_1) - \left(1 - \frac{1}{n}\right) + \frac{1}{n}\ln\phi_1 + \int_{\phi_1}^{1}\chi d\phi_1 - \chi\phi_1\right\} \tag{4.19.2}$$

and further differentiation of Eq. (4.19.2) with respect to ϕ_1 leads to

$$\left(\frac{\partial^2 \Delta G_v}{\partial \phi_1{}^2}\right)_{T,P} = \frac{RT}{V_0}\left\{\frac{1}{1 - \phi_1} + \frac{1}{n\phi_1} - 2\chi - \left(\frac{\partial\chi}{\partial\phi_1}\right)\phi_1\right\} \tag{4.19.3}$$

At **spinodal**, Eq. (4.19.3) is zero:

$$\frac{1}{1 - \phi_1} + \frac{1}{n\phi_1} - 2\chi - \left(\frac{\partial\chi}{\partial\phi_1}\right)\phi_1 = 0 \tag{4.19.4}$$

From Eq. (4.19.3),

$$\left(\frac{\partial^3 \Delta G_v}{\partial \phi_1{}^3}\right)_{T,P} = \frac{RT}{V_0}\left\{\frac{1}{\left(1-\phi_1\right)^2} - \frac{1}{n\phi_1{}^2} - 3\left(\frac{\partial \chi}{\partial \phi_1}\right) - \left(\frac{\partial^2 \chi}{\partial \phi_1{}^2}\right)\phi_1\right\} \tag{4.19.5}$$

Accordingly, at the critical point, the equation

$$\frac{1}{(1-\phi_1)^2} - \frac{1}{n\phi_1{}^2} - 3\left(\frac{\partial \chi}{\partial \phi_1}\right) - \left(\frac{\partial^2 \chi}{\partial \phi_1{}^2}\right)\phi_1 = 0 \tag{4.19.6}$$

should hold in addition to Eq. (4.19.4).

---

* When χ does not depend on ϕ_1, the following relations hold.

$$\int_{\phi_1}^{1} \chi d\phi_1 = \chi\left(1-\phi_1\right) \tag{4.19.7}$$

and

$$\frac{\partial \chi}{\partial \phi_1} = \frac{\partial^2 \chi}{\partial \phi_1{}^2} = 0 \tag{4.19.8}$$

Then Eqs. (4.19.4) and (4.19.6) coincide with Eqs. (4.12.8) and (4.12.10) in <<Problem 4-12>>, respectively. When χ depends linearly on ϕ_1, as given by the equation

$$\chi = \chi_0\left(1 + p_1\phi_1\right) \tag{3.16.1}$$

we have

$$\int_{\phi_1}^{1} \chi d\phi_1 = \chi_0\left[\left(1-\phi_1\right) + \frac{p_1}{2}\left(1-\phi_1{}^2\right)\right] \tag{4.19.9}$$

$$\frac{\partial \chi}{\partial \phi_1} = \chi_0 p_1 \tag{4.19.10}$$

$$\frac{\partial^2 \chi}{\partial \phi_1{}^2} = 0 \tag{4.19.11}$$

Then Eqs.(4.19.1), (4.19.4) and (4.19.6) are simplified as

$$\Delta G_v = \frac{kT}{V_0}\left[\left(1-\phi_1\right)\ln\left(1-\phi_1\right) + \frac{\phi_1}{n}\ln\phi_1 + \chi_0\phi_1\left\{\left(1-\phi_1\right) + \frac{p_1}{2}\left(1-\phi_1{}^2\right)\right\}\right] \tag{4.19.12}$$

$$\frac{1}{1-\phi_1}+\frac{1}{n\phi_1}-\chi_0\left(2+3p_1\phi_1\right)=0 \tag{4.19.13}$$

$$\frac{1}{\left(1-\phi_1\right)^2}-\frac{1}{n\phi_1{}^2}-3\chi_0p_1=0 \tag{4.19.14}$$

respectively. If we put $p_1=0$, Eqs. (4.19.12)-(4.19.14) is reduced straightforwardly to those for the simple case when χ does not depend on concentration (Eqs.(4.12.8) and (4.12.10)). Two methods have been proposed for calculating cloud-point curves of polydisperse polymer solutions, one by Kamide et al. and the other by Solc, the comparison of those is given in (K. Kamide, S. Matsuda and H. Shirataki, *Eur. Polym. J.* **26**, 379 (1990)).

<<Problem 4-20>> Critical condition for homologous polymer solution

The chemical potential of solvent $\Delta\mu_0$ and that of solute $\Delta\mu_i$ in multicomponent polymer solutions are given by

$$\Delta\mu_0=RT\left\{\ln\left(1-\phi_1\right)+\left(1-\frac{1}{n_n}\right)\phi_1+\chi\phi_1{}^2\right\} \tag{3.18.5}$$

$$\Delta\mu_i=RT\left\{\ln\phi_1-\left(n_i-1\right)\left(1-\phi_1\right)-\chi n_i\phi_1\left(1-\phi_1\right)+n_i\int_{\phi_1}^{1}\chi d\phi_1\right\} \tag{3.18.4'}$$

where

$$\phi_1=\sum_{i=1}^{r}\phi_i$$

By employing mean volume free energy of mixing ΔG_v in place of mean molar free energy of mixing, the conditions for spinodal and neutral equilibrium (See Eqs. (4.9.1) and (4.9.2)) are written in the form

$$\left|\Delta G_v\right|=\begin{vmatrix}\Delta G_{v_{11}} & \Delta G_{v_{12}} & \Delta G_{v_{13}} & \cdots & \Delta G_{v_{1r}}\\ \Delta G_{v_{21}} & \Delta G_{v_{22}} & \Delta G_{v_{23}} & \cdots & \Delta G_{v_{2r}}\\ \vdots & \vdots & \vdots & & \vdots\\ \Delta G_{v_{r1}} & \Delta G_{v_{r2}} & \Delta G_{v_{r3}} & \cdots & \Delta G_{v_{rr}}\end{vmatrix}=0 \tag{4.20.1}$$

$$\left|\Delta G_v'\right| \equiv \begin{vmatrix} \dfrac{\partial\left|\Delta G_v\right|}{\partial\phi_1} & \dfrac{\partial\left|\Delta G_v\right|}{\partial\phi_2} & \dfrac{\partial\left|\Delta G_v\right|}{\partial\phi_3} & \cdots & \dfrac{\partial\left|\Delta G_v\right|}{\partial\phi_r} \\ \Delta G_{v_{21}} & \Delta G_{v_{22}} & \Delta G_{v_{23}} & \cdots & \Delta G_{v_{2r}} \\ \vdots & \vdots & \vdots & & \vdots \\ \Delta G_{v_{r1}} & \Delta G_{v_{r2}} & \Delta G_{v_{r3}} & \cdots & \Delta G_{v_{rr}} \end{vmatrix} = 0 \qquad (4.20.2)$$

where

$$\Delta G_{vij} = \left(\frac{\partial^2 \Delta G_v}{\partial\phi_i \partial\phi_j}\right)_{T,P}.$$

Combination of Eqs. (4.20.1) and (4.20.2) leads to

$$\frac{1}{1-\phi_1} + \frac{1}{n_w\phi_1} - 2\chi - \left(\frac{\partial\chi}{\partial\phi_1}\right)\phi_1 = 0 \qquad (4.20.3)$$

and

$$\frac{1}{\left(1-\phi_1\right)^2} - \frac{n_z}{{n_w}^2{\phi_1}^2} - 3\left(\frac{\partial\chi}{\partial\phi_1}\right) - \left(\frac{\partial^2\chi}{\partial{\phi_1}^2}\right)\phi_1 = 0 \qquad (4.20.4)$$

Here, n_n, n_w and n_z are the number-, weight- and z-average degree of polymerizations, respectively. (1) Calculate ΔG_v using Eqs. (3.18.5) and (3.18.4)'. (2) Derive the **spinodal condition,** Eq. (4.20.3). (3) Derive the **condition for the neutral equilibrium,** Eq. (4.20.4).

Answer

(1) ΔG_v is defined by (See Eq.(4.12.4))

$$\Delta G_v = \left(1-\phi_1\right)\left(\frac{\Delta\mu_0}{V_0}\right) + \sum_{i=1}^{r}\phi_i\left(\frac{\Delta\mu_i}{n_i V_0}\right) \qquad (4.20.5)$$

Substitution of Eqs. (3.18.5) and (3.18.4)' in Eq. (4.20.5) gives

$$\Delta G_v = \frac{RT}{V_0}\left\{\left(1-\phi_1\right)\ln\left(1-\phi_1\right)+\sum_{i=1}^{r}\frac{\phi_i}{n_i}\ln\phi_i+\phi_1\int_{\phi_1}^{1}\chi d\phi_1\right\} \tag{4.20.6}$$

(2) Differentiation of Eq. (4.20.6) by ϕ_1 leads to

$$\frac{V_0}{RT}\left(\frac{\partial\Delta G_v}{\partial\phi_i}\right)_{T,P} = -\ln\left(1-\phi_1\right)-\left(1-\frac{1}{n_i}\right)+\frac{1}{n_i}\ln\phi_i+\int_{\phi_1}^{1}\chi d\phi_1-\chi\phi_1 \tag{4.20.7}$$

Further differentiation of Eq. (4.20.6) by ϕ_i and ϕ_j leads to

$$\frac{V_0}{RT}\left(\frac{\partial^2\Delta G_v}{\partial\phi_i\partial\phi_j}\right)_{T,P} = \frac{V_0}{RT}\Delta G_{v_{ij}} = \frac{1}{1-\phi_1}-2\chi-\left(\frac{\partial\chi}{\partial\phi_1}\right)\phi_1 \equiv L \tag{4.20.8}$$

$$\frac{V_0}{RT}\left(\frac{\partial^2\Delta G_v}{\partial\phi_i^{\,2}}\right)_{T,P} = \frac{V_0}{RT}\Delta G_{v_{ii}} = L+\frac{1}{n_i\phi_i} \equiv L+L_i \tag{4.20.9}$$

Substituting Eqs. (4.20.8) and (4.20,9) in Eqs. (4.20.1), we obtain

$$U \equiv \left(\frac{V_0}{RT}\right)^r \left|\Delta G_v\right| = \begin{vmatrix} L+L_1 & L & L & \cdots & \cdots & L \\ L & L+L_2 & L & \cdots & \cdots & L \\ L & L & L+L_3 & \cdots & \cdots & L \\ \vdots & \vdots & \vdots & \ddots & & \vdots \\ \vdots & \vdots & \vdots & & \ddots & \vdots \\ L & L & L & \cdots & \cdots & L+L_r \end{vmatrix} = 0 \tag{4.20.10}$$

$$U = \begin{vmatrix} L_1 & L & L & \cdots & \cdots & L \\ -L_2 & L+L_2 & L & \cdots & \cdots & L \\ 0 & L & L+L_3 & \cdots & \cdots & L \\ 0 & L & \vdots & \ddots & & \vdots \\ \vdots & \vdots & \vdots & & \ddots & \vdots \\ 0 & L & L & \cdots & \cdots & L+L_r \end{vmatrix}$$

$$= \begin{vmatrix} L_1 & 0 & 0 & \cdots & 0 & L \\ -L_2 & L_2 & 0 & \cdots & 0 & L \\ 0 & -L_3 & L_3 & \cdots & 0 & L \\ 0 & 0 & -L_4 & \ddots & & \vdots \\ \vdots & \vdots & \vdots & & L_{r-1} & L \\ 0 & 0 & 0 & \cdots & -L_r & L+L_r \end{vmatrix} \qquad (4.20.11)$$

U can be divided into two determinants as

$$U = L_1 \begin{vmatrix} L_2 & 0 & 0 & \cdots & 0 & L \\ -L_3 & L_3 & 0 & \cdots & 0 & L \\ 0 & -L_4 & L_4 & \cdots & 0 & L \\ 0 & 0 & -L_5 & \ddots & & \vdots \\ \vdots & \vdots & \vdots & & L_{r-1} & L \\ 0 & 0 & 0 & \cdots & -L_r & L+L_r \end{vmatrix}$$

$$+ L_2 \begin{vmatrix} 0 & 0 & 0 & \cdots & 0 & L \\ -L_3 & L_3 & 0 & \cdots & 0 & L \\ 0 & -L_4 & L_4 & \cdots & 0 & L \\ 0 & 0 & -L_5 & \ddots & & \vdots \\ \vdots & \vdots & \vdots & & L_{r-1} & L \\ 0 & 0 & 0 & \cdots & -L_r & L+L_r \end{vmatrix}$$

$$= L_1 V_1 + L_2 W_2 \qquad (4.20.12)$$

Note that the determinant of the right-hand side in Eq. (4.20.11) has the same form as the determinant V_1 in Eq. (4.20.12). The determinant W_2 can be further calculated as

$$W_2 = L_3 \begin{vmatrix} 0 & 0 & 0 & \cdots & 0 & L \\ -L_4 & L_4 & 0 & \cdots & 0 & L \\ 0 & -L_5 & L_5 & \cdots & 0 & L \\ 0 & 0 & -L_6 & \ddots & & \vdots \\ \vdots & \vdots & \vdots & & L_{r-1} & L \\ 0 & 0 & 0 & \cdots & -L_r & L+L_r \end{vmatrix}$$

$$= L_3 L_4 L_5 \cdots L_{r-1} \begin{vmatrix} 0 & L \\ -L_r & L+L_r \end{vmatrix}$$

$$= L_3 L_4 L_5 \cdots L_{T-1} L_r L \qquad (4.20.13)$$

V_1 is also divided into two parts as

$$V_1 = L_2 \begin{vmatrix} L_3 & 0 & 0 & \cdots & 0 & L \\ -L_4 & L_4 & 0 & \cdots & 0 & L \\ 0 & -L_5 & L_5 & \cdots & 0 & L \\ 0 & 0 & -L_6 & \ddots & & \vdots \\ \vdots & \vdots & \vdots & & L_{r-1} & L \\ 0 & 0 & 0 & \cdots & -L_r & L+L_r \end{vmatrix}$$

$$+ L_3 \begin{vmatrix} 0 & 0 & 0 & \cdots & 0 & L \\ -L_4 & L_4 & 0 & \cdots & 0 & L \\ 0 & -L_5 & L_5 & \cdots & 0 & L \\ 0 & 0 & -L_6 & \ddots & & \vdots \\ \vdots & \vdots & \vdots & & L_{r-1} & L \\ 0 & 0 & 0 & \cdots & -L_r & L+L_r \end{vmatrix}$$

$$= L_2 V_2 + L_3 W_3 \qquad (4.20.14)$$

U, V_1 and V_2 are of the same form, and W_2 and W_3 are of the same form. From Eqs. (4.20.13) and (4.20.14), we have

$$W_i = L \prod_{j=i+1}^{r} L_j \qquad (4.20.15)$$

$$V_i = L_{i+1}V_{i+1} + L_{i+2}W_{i+2} \qquad (4.20.16)$$

With aid of Eq. (4.20.16), Eq. (4.20.11) can be rearranged. As we can put $U=V_0$, then referring to Eq.(4.20.13), we have

$$\begin{aligned}
V_0 &= L_1V_1 + L_2W_2 \\
V_1 &= L_2V_2 + L_3W_3 \\
V_2 &= L_3V_3 + L_4W_4 \\
&\cdots \\
&\cdots \\
V_i &= L_{i+1}V_{i+1} + L_{i+2}W_{i+2} \\
&\cdots \\
&\cdots \\
V_{r-3} &= L_{r-2}V_{r-2} + L_{r-1}W_{r-1} && (4.20.17) \\
V_{r-2} &= \begin{vmatrix} L_{r-1} & L \\ -L_r & L+L_r \end{vmatrix} = L_{r-1}L_r + L\left(L_{r-1} + L_r\right) && (4.20.18)
\end{aligned}$$

and

$$W_{r-1} = \begin{vmatrix} 0 & L \\ -L_r & L+L_r \end{vmatrix} = L_rL \qquad (4.20.19)$$

From Eqs. (4.20.15) and (4.20.17), we obtain

$$\begin{aligned}
V_0 &= L_1\left(L_2V_2 + L_3W_3\right) + L_2W_2 \\
&= L_1L_2\left(L_3V_3 + L_4W_4\right) + L_1L_2W_2 + L_2W_2 \\
&= L_1L_2L_3V_3 + L_1L_2L_4W_4 + L_1L_3W_2 + L_2W_2 \\
&= L_1L_2L_3 \cdots L_{r-3}V_{r-3} + \sum_{i=2}^{r-2} \frac{\prod_{j=1}^{i} L_j}{L_{i-1}} W_i \\
&= L_1L_2L_3 \cdots L_{r-3}V_{r-3} + L\sum_{i=2}^{r-2} \frac{\prod_{j=1}^{i} L_j}{L_{i-1}} \prod_{k=i+1}^{r} L_k \\
&= L_1L_2L_3 \cdots L_{r-3}V_{r-3} + L\left(\prod_{i=1}^{r} L_i\right)\sum_{i=1}^{r-3} \frac{1}{L_i} && (4.20.20)
\end{aligned}$$

Substitution of Eqs. (4.20.18) and (4.20.19) for V_{r-3} and W_{r-1} in Eq.(4.20.17) yields

$$V_{r-3} = L_{r-2}L_{r-1}L_r + L_{r-2}L\left(L_{r-1}+L_r\right) + L_{r-1}L_rL \tag{4.20.21}$$

From Eqs. (4.20.20) and (4.20.21), we have

$$\begin{aligned} U &= \left(\prod_{i=1}^{r} L_i\right) + L\left(\prod_{i=1}^{r} L_i\right)\left(\frac{1}{L_{r-2}} + \frac{1}{L_{r-1}} + \frac{1}{L_r}\right) + L\left(\prod_{i=1}^{r} L_i\right)\left(\sum_{i=1}^{r-3} \frac{1}{L_i}\right) \\ &= \left(\prod_{i=1}^{r} L_i\right)\left[1 + L\left(\sum_{i=1}^{r} \frac{1}{L_i}\right)\right] \end{aligned} \tag{4.20.22}$$

Finally, Eq. (4.20.10) is reduced to

$$1 + L\left(\sum_{i=1}^{r} \frac{1}{L_i}\right) = 0 \tag{4.20.23}$$

From Eq. (4.20.23), (4.20.8) and (4.20.9), we have

$$1 + \left\{\frac{1}{1 - \phi_1} - 2\chi - \left(\frac{\partial \chi}{\partial \phi_1}\right)\phi_1\right\}\left(\sum_{i=1}^{r} n_i\phi_i\right) = 0 \tag{4.20.24}$$

Using n_w defined by

$$n_w = \frac{\sum_{i=1}^{r} n_i\phi_i}{\phi_1} \tag{4.20.25}$$

Eq. (4.20.24) can be rewritten as

$$1 + \left\{\frac{1}{1 - \phi_1} - 2\chi - \left(\frac{\partial \chi}{\partial \phi_1}\right)\phi_1\right\} n_w\phi_1 = 0 \tag{4.20.26}$$

or

$$\frac{1}{n_w\phi_1} + \frac{1}{1 - \phi_1} - 2\chi - \left(\frac{\partial \chi}{\partial \phi_1}\right)\phi_1 = 0 \tag{4.20.27}$$

Eq. (4.20.27) enables us to calculate the spinodal curve by using experimental data of n_w and χ. This equation has been first derived by Koningsveld and Staverman in a different way. (See R. Koningsveld and A.J.Staverman, *J. Polym, Sci* **A-2**, **6**, 325(1968)) For monodisperse polymer solutions the condition of stability limit (i.e., spinodal) is expressed as

$$\frac{1}{n\phi_1} + \frac{1}{1 - \phi_1} - 2\chi - \left(\frac{\partial\chi}{\partial\phi_1}\right)\phi_1 = 0 \tag{4.19.4}$$

(3) First, let's calculate $(\partial\,|\Delta G_v|\,/\partial\phi_i)$ using Eq. (4.20.22). Here, U_i is defined by

$$U_i \equiv \frac{\partial U}{\partial\phi_i} = \left(\frac{V_0}{R_B T}\right)^r \frac{\partial|\Delta G_V|}{\partial\phi_i} = \left(\prod_{i=1}^{r} L_i\right)\left(\frac{\partial L}{\partial\phi_i} n_w\phi_1 - \frac{n_i}{n_w\phi_1}\right) \tag{4.20.28}$$

Substitution of L, L_i and U_i defined by Eqs.(4.20.8), (4.20.9) and (4.20.28) in Eq.(4.20.2) leads to

$$V = \begin{vmatrix} U_1 & U_2 & U_3 & \cdots & U_{r-1} & U_r \\ L & L+L_2 & L & \cdots & L & L \\ L & L & L+L_3 & \cdots & L & L \\ L & L & L & \ddots & & \vdots \\ \vdots & \vdots & \vdots & & & L \\ L & L & L & \cdots & L & L+L_r \end{vmatrix} = 0 \tag{4.20.29}$$

Cofactor expansion of the determinant V results in

$$V = (-1)^2 U_1 A_1 + \sum_{j=2}^{r} (-1)^{j+1} (-1)^j A_j \tag{4.20.30}$$

where

$$A_1 = \begin{vmatrix} L+L_2 & L & L & \cdots & L & L \\ L & L+L_3 & L & \cdots & L & L \\ L & L & L+L_4 & \cdots & L & L \\ L & L & L & \ddots & & \vdots \\ \vdots & \vdots & \vdots & & & L \\ L & L & L & \cdots & L & L+L_r \end{vmatrix} = 0 \tag{4.20.31}$$

and

$$A_j = \begin{vmatrix} L & L & \cdots & L & L & \cdots & L & L \\ L & L+L_2 & \cdots & L & L & \cdots & L & L \\ \vdots & \vdots & \ddots & \vdots & \vdots & & \vdots & \vdots \\ L & L & \cdots & L+L_{i-1} & L & \cdots & L & L \\ L & L & \cdots & L & L+L_{i+1} & \cdots & L & L \\ \vdots & \vdots & & \vdots & \vdots & \ddots & \vdots & \vdots \\ L & L & \cdots & L & L & \cdots & L+L_{r-1} & L \\ L & L & \cdots & L & L & \cdots & L & L+L_r \end{vmatrix}$$

$$(j = 2,3,4, \cdots, r) \tag{4.20.32}$$

Equation (4.20.31) can be rewritten with the aid of Eq. (4.20.22) in the form

$$A_1 = \left(\prod_{i\neq 1}^{r} L_i\right)\left(1 + L\sum_{i\neq 1}^{r}\frac{1}{L_i}\right) = \frac{1}{L_1}\left(\prod_{i=1}^{r} L_i\right)\left\{1 + L\left(\sum_{i=1}^{r}\frac{1}{L_i} - \frac{1}{L_1}\right)\right\} \tag{4.20.33}$$

Subtraction of the first column from each second to *r* th column of the determinant of Eq. (4.20.32) yields

$$A_j = \begin{vmatrix} L & 0 & \cdots & 0 & 0 & \cdots & 0 & 0 \\ 0 & L_2 & \cdots & 0 & 0 & \cdots & 0 & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots & & \vdots & \vdots \\ 0 & 0 & \cdots & L_{j-1} & 0 & \cdots & 0 & 0 \\ 0 & 0 & \cdots & 0 & L_{j+1} & \cdots & 0 & 0 \\ \vdots & \vdots & & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & \cdots & 0 & 0 & \cdots & L_{r-1} & 0 \\ 0 & 0 & \cdots & 0 & 0 & \cdots & 0 & L_r \end{vmatrix} = \frac{L}{L_1 L_j}\left(\prod_{i=1}^{r} L_i\right) \tag{4.20.34}$$

Substituting Eqs.(4.20.33) and (4.20.34) in Eq. (4.20.30), we have

$$V = \frac{U_1}{L_1}\left(\prod_{i=1}^{r} L_i\right)\left\{1 + L\left(\sum_{i=1}^{r} \frac{1}{L_i}\right)\right\} - \left(\prod_{i=1}^{r} L_i\right)\left(\frac{L}{L_1}\right)\left(\sum_{i=1}^{r} \frac{U_i}{L_i}\right) \tag{4.20.35}$$

From the spinodal condition of Eq. (4.20.23), it is clear that { } in the first term of the right-hand side of Eq. (4.20.35) is zero. Then, we have

$$V = -\left(\prod_{i=1}^{r} L_i\right)\left(\frac{L}{L_1}\right)\left(\sum_{i=1}^{r} \frac{U_i}{L_i}\right) = 0 \tag{4.20.36}$$

$$\sum_{i=1}^{r} \frac{U_i}{L_i} = 0 \tag{4.20.37}$$

Substituting Eq. (4.20.28) and

$$L_i = \frac{1}{n_i \phi_i} \tag{4.20.9)'}$$

in Eq. (4.20.37), we have

$$\left(\prod_{i=1}^{r} L_i\right)\left\{\left(\frac{\partial L}{\partial \phi_1}\right)\left(n_w \phi_1\right)^2 - n_z\right\} = 0 \tag{4.20.38}$$

and then

$$\left(\frac{\partial L}{\partial \phi_1}\right)\left(n_w \phi_1\right)^2 - n_z = 0 \qquad (4.20.39)$$

Partial differentiation of Eq. (4.20.8) with respect to ϕ_1 yields

$$\frac{\partial L}{\partial \phi_1} = \frac{1}{(1 - \phi_1)^2} - \left(\frac{\partial^2 \chi}{\partial {\phi_1}^2}\right)\phi_1 - 3\,\frac{\partial \chi}{\partial \phi_1} \qquad (4.20.40)$$

Combining Eq. (4.20.40) with Eq. (4.20.39), we have

$$\frac{\left(n_w \phi_1\right)^2}{\left(1 - \phi_1\right)^2} - \left(\frac{\partial^2 \chi}{\partial {\phi_1}^2}\right) {n_w}^2 {\phi_1}^3 - 3\left(\frac{\partial \chi}{\partial \phi_1}\right)\left(n_w \phi_1\right)^2 - n_z = 0 \qquad (4.20.41)$$

Eq. (4.20.41) is finally rearranged by dividing each term by $n_w {\phi_1}^2$ to

$$\frac{1}{\left(1 - \phi_1\right)^2} - \frac{n_z}{\left(n_w \phi_1\right)^2} - 3\left(\frac{\partial \chi}{\partial \phi_1}\right) - \left(\frac{\partial^2 \chi}{\partial {\phi_1}^2}\right)\phi_1 = 0 \qquad (4.20.42)$$

---

* In deriving Eq.(4.20.33), it is recommended to employ the following relationship:

$$|D| = \begin{vmatrix} x_1 & a & \cdots & a \\ a & x_2 & \cdots & a \\ \vdots & \vdots & \ddots & \vdots \\ a & a & \cdots & x_m \end{vmatrix} = f(a) - a\left(\frac{df(x)}{dx}\right)_{x=a} \qquad (4.20.43)$$

where

$$f(x) = \prod_{i=1}^{m}\left(x_i - x\right) \qquad (4.20.44)$$

and

$$|D| = \prod_{i=1}^{m}\left(x_i - a\right)\left[1 + a\sum_{k=1}^{m}\frac{1}{x_k - a}\right] \qquad (4.20.45)$$

(See K.Kamide, S. Matsuda, T.Dobashi and M. Kaneko, *Polym. J.* 16, 839 (1984))

<<Problem 4-21-a>> Critical parameters for homologous polymer solutions with concentration-independent χ

Derive expressions for **the critical concentration ϕ_1^c and the critical value**

of χ (χ_c) for multicomponent (i.e., molecularly heterogeneous) polymer solutions with concentration-independent χ, based on Eqs.(4.20.27) and (4.20.42).

Answer

The condition for the critical solution point (CSP) is given for polymer solutions by

$$\frac{1}{n_w\phi_1}+\frac{1}{1-\phi_1}-2\chi-\left(\frac{\partial\chi}{\partial\phi_1}\right)\phi_1=0 \tag{4.20.27}$$

$$\frac{1}{(1-\phi_1)^2}-\frac{n_z}{(n_w\phi_1)^2}-3\left(\frac{\partial\chi}{\partial\phi_1}\right)-\left(\frac{\partial^2\chi}{\partial{\phi_1}^2}\right)\phi_1=0 \tag{4.20.42}$$

If the concentration dependence of χ can be neglected, these equations are reduced straightforwardly to

$$\frac{1}{n_w\phi_1}+\frac{1}{1-\phi_1}-2\chi=0 \tag{4.21.1}$$

$$\frac{1}{(1-\phi_1)^2}-\frac{n_z}{(n_w\phi_1)^2}=0 \tag{4.21.2}$$

By solving these simultaneous equations, we have

$$\phi_1^c=\frac{1}{1+\dfrac{n_w}{\sqrt{n_z}}} \tag{4.21.3}$$

$$\chi_c=\frac{1}{2}\left(1+\frac{1}{\sqrt{n_w}}\right)^2+\frac{\left(\sqrt{n_z}-\sqrt{n_w}\right)^2}{n_w\sqrt{n_z}} \tag{4.21.4}$$

<<Problem 4-21-b>> Chemical potential for polydisperse polymer in single solvent (P/S) with concentration-dependent χ

When the thermodynamic interaction parameter χ_i of *i* th polymer component is expressed by Eqs. (3.16.4) and (3.16.11), the heat of dilution ΔH

of the solution and the chemical potential of the solvent $\Delta\mu_0$ can be written by

$$\Delta H = RT\left\{\chi_{00}\left(1+\frac{k'}{n_n}\right)\left(1+\sum_{j=1}^{n} p_j\phi_1^j\right)\right\}\phi_0\phi_1 \tag{4.21.5}$$

$$\Delta\mu_0 = RT\left\{\ln(1-\phi_1)+\left(1+\frac{1}{n_n}\right)\phi_1+\chi_{00}\left(1+\frac{k'}{n_n}\right)\left(1+\sum_{j=1}^{n} p_j\phi_1^j\right)\phi_1^2\right\} \tag{4.21.6}$$

Using the Gibbs-Duhem relation (See Eq.(1.3.1)), the chemical potential of n_i-mer, $\Delta\mu_i$, is expressed as

$$\begin{aligned}\Delta\mu_i = RT\Bigg[\ln\phi_i-(n_i-1)+n_i\left(1+\frac{1}{n_n}\right)\phi_1 \\ +n_i(1-\phi_1)^2\chi_{00}\Bigg[\left(1+\frac{k'}{n_n}\right)\left\{1+\sum_{j=1}^{n}\frac{p_j}{j+1}\left(\sum_{q=0}^{j}(q+1)\phi_1^q\right)\right\} \\ +k'\left(\frac{1}{n_i}+\frac{1}{n_n}\right)\left\{\frac{1}{1-\phi_1}+\sum_{j=1}^{n}\frac{p_j}{j+1}\left(\sum_{q=0}^{j}\frac{\phi_1^q}{1-\phi_1}\right)\right\}\Bigg]\Bigg]\end{aligned} \tag{4.21.7}$$

Derive Eqs. (4.21.6) and (4.21.7). Note that the applicability of Eq. (4.21.7) is not restricted only to the lattice model used originally in the Flory-Huggins theory.

Answer

The chemical potentials of the solvent and n-mer, $\Delta\mu_0$ and $\Delta\mu_i$ (i=1,...m) for a multicomponent polymer-single solvent system are given by

$$\Delta\mu_0 = RT\left\{\ln(1-\phi_1)+\left(1+\frac{1}{n_n}\right)\phi_1+\chi\phi_1^2\right\} \tag{4.21.8}$$

and

$$\Delta\mu_i = RT\left\{\ln\phi_i+(n_i-1)+n_i\left(1+\frac{1}{n_n}\right)\phi_1\right\}+\frac{\partial\Delta H}{\partial N_i} \tag{4.21.9}$$

where N_i is the number of moles of n_i-mer. Substituting Eqs. (3.16.4) and (3.16.11) into Eq. (4.21.8), we obtain Eq. (4.21.6). In Eq. (4.21.8), $\chi\phi_1^2$

must be of the form

$$RT\chi\phi_1^2=\frac{\partial \Delta H}{\partial N_0} \tag{4.21.10}$$

where N_0 is the number of moles of solvent. The necessary and sufficient condition under which $\Delta\mu_0$ and $\Delta\mu_i$ satisfy the Gibbs-Duhem relation Eq.(1.3.1) is

$$\frac{\partial \Delta H}{\partial N_i}=\frac{\partial}{\partial N_i}\left\{\int_0^{N_0}\left(\frac{\partial \Delta H}{\partial N_0}\right)dN_0\right\} \tag{4.21.11}$$

On substituting Eq. (4.21.5) in Eq. (4.21.11), we obtain

$$\begin{aligned}\frac{1}{RT}\cdot\frac{\partial \Delta H}{\partial N_i}=&\chi_{00}n_i\left(1+\frac{k'}{n_n}\right)\left\{(1-\phi_1)^2+\sum_{j=1}^{m}p_j\left(\frac{1}{j+1}-\frac{j+2}{j+1}\phi_1^{j+1}+\phi_1^{j+2}\right)\right\}\\&+\chi_{00}k'n_i\left(\frac{1}{n_i}-\frac{1}{n_n}\right)\left\{(1-\phi_1)+\sum_{j=1}^{m}\frac{p_j}{j+1}\left(1-\phi_i^{j+1}\right)\right\}\end{aligned} \tag{4.21.12}$$

Combination of Eq. (4.21.12) with Eq. (4.21.9) leads to Eq. (4.21.7).

<<Problem 4-21-c>> Critical condition for polydisperse polymer in single solvent (P/S) with concentration-dependent χ

Substituting Eqs. (4.21.6) and (4.21.7) into Eq.(4.20.5), we obtain

$$\begin{aligned}\Delta G_v=\frac{RT}{V_0}\Bigg[&(1-\phi_1)\ln(1-\phi_1)+\sum_{i=1}^{m}\frac{\phi_i\ln\phi_i}{n_i}+\chi_{00}\left\{1+\frac{k'}{n_n}(1+n_n-n_w)\right\}\\&\times\left\{1+\sum_{j=1}^{n}\frac{p_j}{j+1}\left(\sum_{q=0}^{j}\phi_1^q\right)\right\}\phi_1(1-\phi_1)\Bigg]\end{aligned} \tag{4.21.13}$$

The critical solution point for the Gibbs free energy expressed as Eq. (4.21.13) is given by the following equations

$$\frac{1}{n_w\phi_1}+\frac{1}{1-\phi_1}-\chi_{00}\left\{1+k'\left(1+\frac{1}{n_n}-\frac{n_w}{n_n}\right)\right\}\left\{2+\sum_{j=1}^{n}p_j(j+2)\phi_1^j\right\}=0 \tag{4.21.14}$$

$$\frac{1}{(1-\phi_1)^2}-\frac{n_z}{(n_w\phi_1)^2}-\chi_{00}\left\{1+k'\left(1+\frac{1}{n_n}-\frac{n_w}{n_n}\right)\right\}\left\{\sum_{j=1}^{n}p_j j(j+2)\phi_1^{j-1}\right\}=0 \quad (4.21.15)$$

Derive Eqs. (4.21.14) and (4.21.15) using the condition for the critical point, Eqs. (4.20.1) and (4.20.2).

Answer

The derivative of Gibbs free energy is given by

$$\frac{V_0}{RT}\Delta G_{vij}=\frac{1}{1-\phi_1}-\chi_{00}\left\{1+k'\left(1+\frac{1}{n_n}-\frac{n_w}{n_n}\right)\right\}\left\{2+\sum_{q=1}^{n}p_q(q+2)\phi_1^q\right\}\equiv M$$

$$(\text{for } i\neq j) \qquad (4.21.16)$$

or

$$\frac{V_0}{RT}\Delta G_{vii}=M+\frac{1}{n_i\phi_i}\equiv M+M_i \qquad (\text{for } i=j) \qquad (4.21.17)$$

From Eqs. (4.21.16), (4.21.17) and (4.20.1) , we obtain

$$|\Delta G_v|=\left(\frac{RT}{V_0}\right)^m\begin{vmatrix} M+M_1 & M & \cdots & M \\ M & M+M_2 & \cdots & M \\ \vdots & \vdots & \ddots & \vdots \\ M & M & \cdots & M+M_m \end{vmatrix}$$

$$=\left(\frac{RT}{V_0}\right)^m\left(\prod_{i=1}^{m}M_i\right)\left(1+M\sum_{i=1}^{m}\frac{1}{M_i}\right)=0 \qquad (4.21.18)$$

Then we have

$$1+M\sum_{i=1}^{m}\frac{1}{M_i}=0 \qquad (4.21.19)$$

for the spinodal. Rearrangement of Eq. (4.21.19) with the aid of Eqs. (4.21.16) and (4.21.17) gives Eq. (4.21.14). In deriving Eq. (4.21.18), we employed Eq. (4.20.43).

Differentiating Eq. (4.21.18) by ϕ_i, we obtain

$$\frac{\partial|\Delta G_v|}{\partial\phi_i}=\left(\frac{RT}{V_0}\right)^m\left(\prod_{i=1}^m M_i\right)\left(\frac{\partial M}{\partial\phi_1}\phi_1 n_w-\frac{n_i}{n_w\phi_1}\right)\equiv W_i \tag{4.21.20}$$

Then, from Eqs. (4.21.16), (4.21.17) and (4.21.20) and using Eq. (4.21.19), we obtain

$$|\Delta G'_v|=(-1)^2W_1\begin{vmatrix} M+M_2 & M & \cdots & M \\ M & M+M_3 & \cdots & M \\ \vdots & \vdots & \ddots & \vdots \\ M & M & \cdots & M+M_m \end{vmatrix}+\sum_{j+2}^{m}W_j(-1)^{j+1}(-1)^j$$

$$\times\begin{vmatrix} M & M & & & \cdots & & M \\ M & M+M_2 & & & & & \\ \vdots & \vdots & \ddots & & & & \\ M & M & & M+M_{j-1} & M & & \\ M & M & & M & M+M_{j+1} & & \\ \vdots & \vdots & & & & \ddots & \\ M & M & & \cdots & & & M+M_m \end{vmatrix}$$

$$-\left(\prod_{i=1}^m M_i\right)\left(\frac{M}{M_i}\right)\left(\sum_{i=1}^m\frac{W_i}{M_i}\right)=0 \tag{4.21.21}$$

Eq. (4.21.21) can be rewritten, using Eqs. (4.21.16) and (4.21.17), as Eq. (4.21.15).

<<Problem 4-21-d>> Determination of cloud point curve for polydisperse polymer in single solvent (P/S) with concentration-dependent χ

Describe methods for determining the cloud point curve (CPC) of multicomponent polymer-single solvent systems from the chemical potentials.

Answer

The Gibbs condition for the phase equilibrium of quasi-binary solutions at constant temperature and constant pressure is given by (See <<Probrem 1-5>>)

$$\Delta\mu_{0(1)} = \Delta\mu_{0(2)} \tag{4.21.22}$$

$$\Delta\mu_{i(1)} = \Delta\mu_{i(2)} \quad (i=1,\cdots,m) \tag{4.21.23}$$

Here, the suffixes (1) and (2) denote the polymer-lean and the polymer-rich phases, respectively. Combining Eqs. (4.21.6), (4.21.7), (4.21.22) and (4.21.23), we have

$$\chi_{00} = \frac{\left\{\ln\frac{1-\phi_{1(1)}}{1-\phi_{1(2)}} + \left(\phi_{1(1)} - \phi_{1(2)}\right) - \left(\frac{\phi_{1(1)}}{n_{n(1)}} - \frac{\phi_{1(2)}}{n_{n(2)}}\right)\right\}}{\left\{\left(\phi_{1(1)}^{2} - \phi_{1(2)}^{2}\right) + k'\left(\frac{\phi_{1(2)}^{2}}{n_{n(2)}} - \frac{\phi_{1(1)}^{2}}{n_{n(2)}}\right) + \sum_{j=1}^{n} p_j \left(\phi_{1(2)}^{j+2} - \phi_{1(1)}^{j+2}\right) + k'\left(\frac{\phi_{1(2)}^{j+2}}{n_{n(2)}} - \frac{\phi_{1(1)}^{j+2}}{n_{n(1)}}\right)\right\}} \tag{4.21.24}$$

and

$$\sigma_i \equiv \frac{1}{n_i}\ln\frac{\phi_{i(2)}}{\phi_{i(1)}} = \sigma_0 + \frac{\sigma_{01}}{n_i} \tag{4.21.25}$$

with

$$\begin{aligned}\sigma_0 = {} & \left(\phi_{1(1)} - \phi_{1(2)}\right) - \left(\frac{\phi_{1(1)}}{n_{n(1)}} - \frac{\phi_{1(2)}}{n_{n(2)}}\right) \\ & + \chi_{00}\left[2\left(\phi_{1(1)} - \phi_{1(2)}\right) - \left(\phi_{1(1)}^{2} - \phi_{1(2)}^{2}\right) + \sum_{j=1}^{n} p_j \left\{\frac{j+2}{j+1}\left(\phi_{1(1)}^{j+1} - \phi_{1(2)}^{j+1}\right) - \left(\phi_{1(1)}^{j+2} - \phi_{1(2)}^{j+2}\right)\right\}\right] \\ & - \chi_{00}k'\left[\left(\frac{\phi_{1(1)}}{n_{n(1)}} - \frac{\phi_{1(2)}}{n_{n(2)}}\right) - \left(\frac{\phi_{1(1)}^{2}}{n_{n(1)}} - \frac{\phi_{1(2)}^{2}}{n_{n(2)}}\right) - \sum_{j=1}^{n} p_j \left\{\left(\frac{\phi_{1(1)}^{j+1}}{n_{n(1)}} - \frac{\phi_{1(2)}^{j+1}}{n_{n(2)}}\right) - \left(\frac{\phi_{1(1)}^{j+2}}{n_{n(1)}} - \frac{\phi_{1(2)}^{j+2}}{n_{n(2)}}\right)\right\}\right]\end{aligned} \tag{4.21.26}$$

and

$$\sigma_{01} = k'\left\{\left(\phi_{1(1)} - \phi_{1(2)}\right) + \sum_{j=1}^{n} \frac{p_j}{j+1}\left(\phi_{1(1)}^{j+2} - \phi_{1(2)}^{j+2}\right)\right\} \tag{4.21.27}$$

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* An example of the flow chart of the computer simulation of cloud point curves is given as follows.The volume fraction of n_i-mer in two coexisting phases, $\phi_{(1)}(n_i)$ and $\phi_{(2)}(n_i)$, are given by

$$\phi_{(1)}(n_i) = \frac{R+1}{R+\exp(\sigma_i n_i)}\phi_0(n_i) \tag{4.21.28}$$

$$\phi_{(2)}(n_i) = \frac{(R+1)\exp(\sigma_i n_i)}{R+\exp(\sigma_i n_i)}\phi_0(n_i) \tag{4.21.29}$$

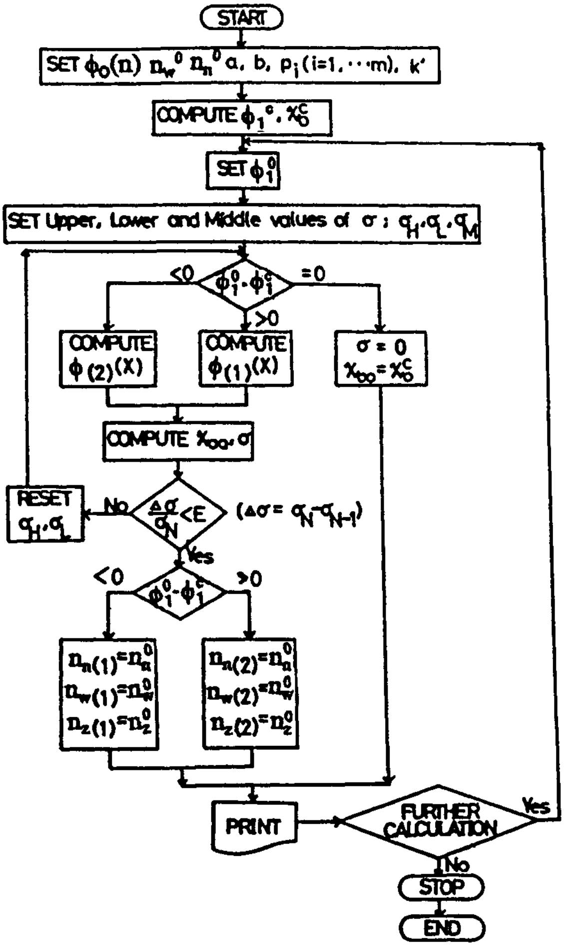

Fig. 4-21-d.1 Flow chart for calculating the cloud point of a multicomponent polymer/single solvent system (See K. Kamide, S. Matsuda, T. Dobashi and M. Kaneko, *Polym. J.* **16**, 839 (1984)) where R is the ratio of the volume of the polymer-lean phase $V_{(1)}$ to that of the polymer-rich phase $V_{(2)}$ and $\phi_0(n_i)$ is the volume fraction of n_i-mer in the starting solution. The $\phi_{(1)}(n_i)$ and $\phi_{(2)}(n_i)$ at the cloud point, (referred to as $\phi_{(1)}^{cp}(n_i)$, $\phi_{(2)}^{cp}(n_i)$), are given from Eq. (4.21.28) and (4.21.29) as limiting cases of $R \to \infty$ when the polymer volume fraction of the starting solution ϕ_1^0 is lower than ϕ_1^c and $R \to 0$ for $\phi_1^0 > \phi_1^c$ in the form

(1)

$$\phi_{(1)}^{cp}(n_i) = \phi_0(n_i)$$

$$\phi_{(2)}^{cp}(n_i) = \phi_0(n_i)\exp(-\sigma_i n_i) \tag{4.21.30}$$

for $\phi_1^0 < \phi_1^c$ $(i=1,\cdots,m)$

(2)

$$\phi_{(1)}^{cp}(n_i) = \phi_0(n_i)\exp(-\sigma_i n_i)$$

$$\phi_{(2)}^{cp}(n_i) = \phi_0(n_i) \tag{4.21.31}$$

for $\phi_1^0 > \phi_1^c$ $(i=1,\cdots,m)$

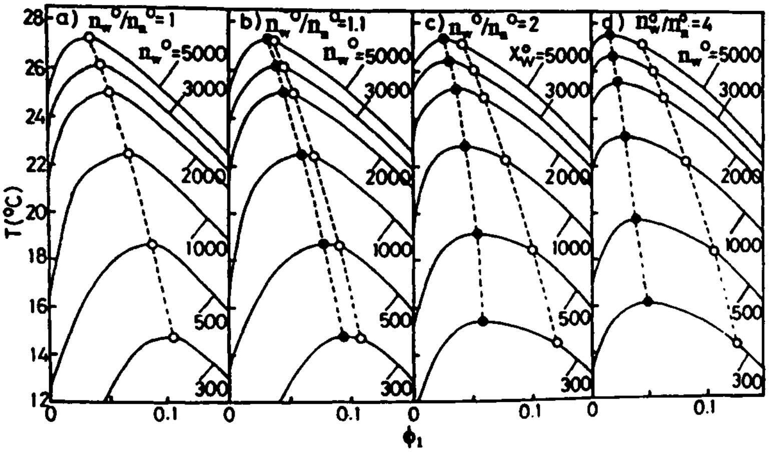

Fig. 4-21-d.2 Effect of weight-average molar volume ratio n_w^0 of the polymer in a single solvent on cloud point curve (Eqs. (4.21.24)-(4.21.27)) for χ in Eq. (3.16.14) for $p_1=0.5$, $p_2=0$ and $k_0=0$: $n_w^0/n_n^0=1$ (a), 1.1 (b), 2 (c), and 4 (d); (○), critical point (Eqs. (4.21.14) and (4.21.15)); (●), precipitation threshold point; number on the curve denotes n_w^0 (See K. Kamide, S. Matsuda, T. Dobashi and M. Kaneko, *Polym. J.* **16**, 839 (1984))

Thus, on the basis of Eqs. (4.21.24)-(4.21.27), (4.21.30) and (4.21.31) χ_{00} at the cloud point ($\chi_{00}{}^{cp}$), σ, $\phi_{(1)}(n_i)$ and $\phi_{(2)}(n_i)$, $\phi_{l(1)}$ and $\phi_{l(2)}$ can be directly calculated for a solution with given $\phi_l{}^0$. A brief flow chart for computer simulation is shown in Fig. 4-21-d.1. The prerequisites for this simulation are

(a) molecular weight distribution and accordingly the weight- and number-average degree of polymerization n of the original polymer ($n_w{}^0$ and $n_w{}^0/n_n{}^0$)

(b) polymer volume fraction of the starting solution $\phi_l{}^0$

(c) parameters k_0 and θ in the expression of χ

(d) concentration dependence parameters $p_j(j=1,2,...,n)$ in the expression of χ

* Figure 4-21-d.2 shows the effect of $n_w{}^0$ on CPC, calculated for the solutions of four polymers (Schulz-Zimm molecular weight distribution, $n_w{}^0/n_n{}^0=1$, 1.1, 2 and 4) in a single solvent ($p_1=0.6$, $p_2=0$ and $k_0=0$ in Eq. (3.16.14)). The unfilled circle in the figure is the critical point and the filled circle, the threshold cloud point. (See K. Kamide, S. Matsuda, T. Dobashi and M. Kaneko, *Polym. J.* **16**, 839 (1984))

<<Problem 4-22>> Effect of molecular weight distribution on critical concentration

When the molecular weight distribution (MWD) of a polymer is expressed by Schulz-Zimm type distribution or Wesslau type distribution, estimate the **dependence of the breadth of MWD, n_w/n_n, on $\phi_1{}^c$** for the cases of n_w=10 and 1000. Here, the weight distribution of the degree of polymerization $f_w(n)$ of Schulz-Zimm-type distribution is expressed by

$$f_w(n)=\frac{y^{h+1}}{\Gamma(h+1)}n^h\exp\left(-yn\right) \tag{4.22.1}$$

$$y=\frac{h}{n_n}=\frac{h+1}{n_w}=\frac{h+2}{n_z} \tag{4.22.2}$$

and $f_w(n)$ of Wesslau-type distribution is expressed by

$$f_w(n)=\frac{1}{\beta\pi^{1/2}n^0}\exp\left[-\frac{1}{\beta^2}\left(\ln\frac{n}{n^0}\right)^2\right] \tag{4.22.3}$$

$$\beta^2=2\ln\left(\frac{n_w}{n_n}\right),\qquad n^0=\left(n_wn_n\right)^{\frac{1}{2}} \tag{4.22.4}$$

where the weight fraction of polymer molecules with molecular weight between n and n+dn is denoted by $f_w(n)dn$ (See <<Problem 9-8>>).

Answer

If χ is independent of ϕ_1 and n, ϕ_1^c is given by

$$\phi_1^c = \frac{1}{1 + \dfrac{n_w}{\sqrt{n_z}}} \qquad (4.21.3)$$

Table 4-22 shows the critical concentration of solutions of the polymer with Schulz-Zimm-type and Wesslau-type molecular weight distribution for typical values of n_w and n_w/n_n. The critical concentration ϕ_1^c decreases with increasing the average molecular weight of the sample n_w and increases with the

Table 4-22 Critical volume fraction of polymers with different molecular weight distribution

(a) n_w=10				
n_w/n_n	1	2	3	10
Schulz-Zimm				
n_z	10	15	17	19
ϕ_1^c	0.240	0.279	0.290	0.304
Wesslau				
n_z	10	20	30	100
ϕ_1^c	0.240	0.309	0.354	0.500

(b) n_w=1000				
n_w/n_n	1	2	3	10
Schulz-Zimm				
n_z	1000	1500	1666	1900
ϕ_1^c	0.0307	0.0373	0.0392	0.0418
Wesslau				
n_z	1000	2000	3000	10000
ϕ_1^c	0.0307	0.0428	0.0519	0.0909

breadth of the molecular weight distribution. ϕ_1^c for the polymer with Schulz-Zimm distribution is larger than that for the polymer with Wesslau-type distribution.

<<Problem 4-23-a>> Experimental method for determining Flory's θ condition

Describe experimental methods for determining Flory's θ condition of polymer solutions and compare the methods.

Answer

(1) Critical point method

θ is T_c of the solution of a polymer with infinite molecular weight. Plot $1/T_c$ versus $1/n^{1/2}+1/2n$ for a series of combinations of T_c and n, both experimentally determined. θ is determined by extrapolating $1/T_c$ to $n \to \infty$, according to the relationship

$$\frac{1}{T_c}=\frac{1}{\theta}+\frac{1}{\theta\psi}\left(\frac{1}{\sqrt{n}}+\frac{1}{2n}\right) \tag{4.14.1}$$

The plot is usually curved when χ depends on concentration or when the polymer has a molecular weight distribution. Solutions of crystallizing polymers do not yield two phase separation, frequently, for which the above method cannot be used. (See K. Kamide, S. Matsuda, *Polym. J.* **16**, 825 (1984))

(2) Second virial coefficient method

Second virial coefficient A_2 is given by the relationship

$$A_2=\left(\frac{v^2}{N_A V_0}\right)\Psi\left(1-\frac{\theta}{T}\right)F(x) \tag{4.23.1}$$

(See <<Problem 5-21>>) Then, the temperature at which A_2 equals zero, is θ. The method is based on experiments by means of membrane osmometry, light scattering, etc. as a function of temperature or solvent composition for determining the temperature at $A_2=0$ or the composition at $A_2=0$.

(3) Limiting viscosity number-molecular weight method

The exponent *a* in the **Mark-Houwink-Sakurada equation**

$$[\eta] = K_m M^a \tag{4.23.2}$$

becomes 0.5 in θ solvent. Here, [η] is the limiting viscosity number, M the molecular weight and K_m a constant (See <<Problem 8-30>>). Then, we can determine θ or solvent composition at θ condition by measuring [η] at various temperatures or solvent compositions for a series of polymers with different molecular weights, dissolved in solvents.

<<Problem 4-23-b>> Experimental method for determining θ and ψ

Describe methods for determining the Flory theta temperature θ and entropy parameter ψ, and the concentration dependence of the parameter χ of single- or multicomponent polymer-single solvent system from the critical solution point (CSP) data.

Answer

(1) Koningsveld et al. method

The interaction parameter g defined in Eq.(3.18.1) is expanded as

$$g = \sum_{i=0}^{n} g_i \phi_1^{\ i} \tag{4.23.3}$$

Here g_0 could be devided into temperature-independent and -dependent components given by

$$g_0 = g_{00} + g_{01}/T \tag{4.23.4}$$

Ψ and θ can be calculated from

$$\psi = \frac{1}{2} - g_{00} - g_1 \tag{4.22.5}$$

$$\theta = g_{01}/\psi \tag{4.22.6}$$

Note that the concentration- and temperature-dependence of the parameter g, in the other words, the parameters g_{00}, g_{01}, g_1 and g_2 are evaluated so that the deviation of the experimental critical volume fraction $\phi_1^{\ c}$ and critical temperature T_c data for all the samples from the theory would be the minimum.

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* This method was applied to PS-CH and PS-methylcyclohexane (MCH) and ψ values were

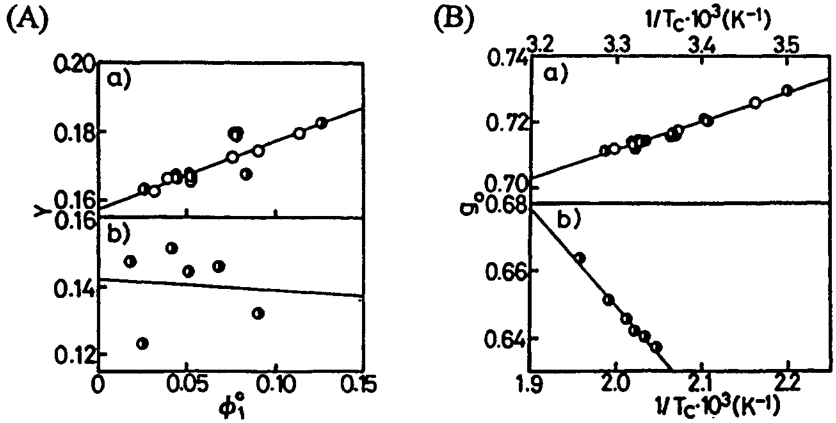

Fig. 4-23-b.1 (A) Plot of Y in Eq. (4.23.7) against ϕ_1^c and (B) plot of g_0 in Eq. (4.23.8) vs. $1/T_c$ for UCSP (a) and LCSP (b) of the system polystyrene/cyclohexane. (○) Koningsveld et al. (1970); (●) Kuwahara et al. (1973); (○) Saeki et al. (1973) (See K. Kamide and S. Matsuda, *Polym. J.* **16**, 825 (1984))

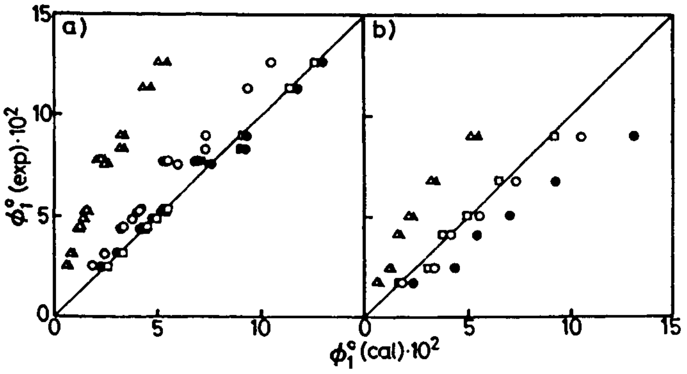

Fig. 4-23-b.2 The critical concentration experimentally determined, ϕ_1^c (exp), plotted against the critical concentration theoretically calculated, ϕ_1^c(theo) for UCSP (a) and LCSP (b) of the polystyrene/cyclohexane system. (△) Shultz-Flory [Eq. (4.23.14)']; (▲) Stockmayer [Eq. (4.23.14)]; (○) Kamide-Matsuda [Eq. (4.23.9-10), $p_1=0.6$, $p_2=0$]; (●) Kamide-Matsuda [$p_1=0.623$, $p_2=0.290$]; (□) Kamide-Matsuda [$p_1=0.642$, $p_2=0.190$ for UCSP and $p_1=0.602$, $p_2=-0.347$ for LCSP]. (See K. Kamide and S. Matsuda, *Polym. J.* **16**, 825 (1984))

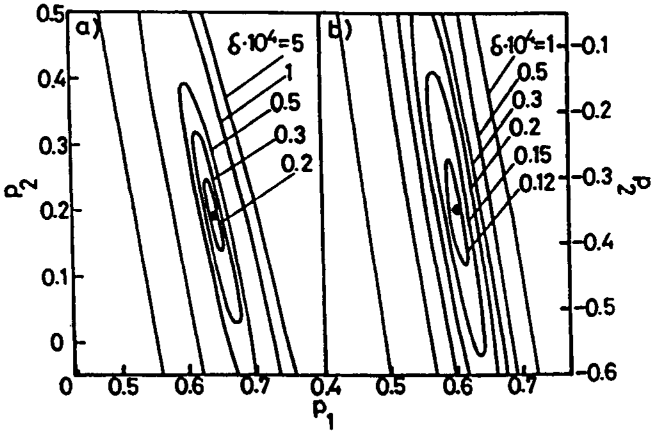

Fig. 4-23-b.3 Relationship among p_1, p_2 and δ for UCSP (a) and LCSP (b) of the polystyrene/cyclohexane system. Numbers on the curve denotes $\delta x10^4$. Filled circle corresponds to the most ideal combination of p_1 and p_2 to describe the critical solution point. (See K. Kamide and S. Matsuda, *Polym. J.* **16**, 825 (1984))

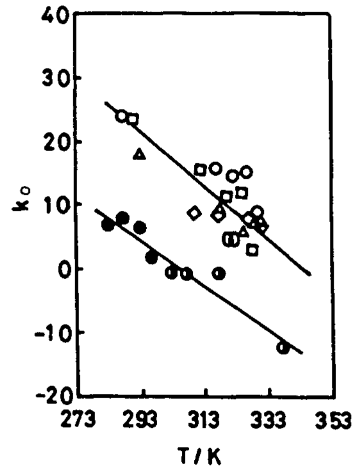

Fig. 4-23-b.4 Changes in k_0-parameter in Eq. (3.16.14) with temperature T; closed and half-closed marks, PS/CH system (●) Kamide-Miyazaki; (○) Scholte by light scattering: open marks, PS/MCH system ;(□) $\phi_1^o=0.50x10^{-2}$; (◇) $\phi_1^o=0.47x\ 10^{-2}$; (○) $\phi_1^o=0.86x10^{-2}$; (△) $\phi_1^o=2.0x10^{-2}$; (▽) $\phi_1^o=1.86x10^{-2}$. (See K. Kamide, T. Abe and Y. Miyazaki, *Polym. J.* **14**, 355 (1982)) calculated. In their method, the curve fitting was repeatedly used to determine g_i (for example, see Fig. 4-23-b.1). The concentration dependence of the parameter g (accordingly that of the parameter χ) can be determined not only from the critical point, but by various other methods such as osmotic pressure, light scattering, ultracentrifuge, vapor pressure, and phase separation. In the present method, g_1 and g_2 in Eq. (4.23.3) are calculated from ϕ_1^c, weight- and z- average degree of polymerization, n_w and n_z by applying the curve fitting method to the equation

$$Y \equiv g_1 - g_2 + 4g_2\phi_1^c = \frac{1}{6}\left(\frac{1}{\left(1-\phi_1^c\right)^2} - \frac{n_z}{\left(n_w - \phi_1^c\right)^2}\right) \tag{4.23.7}$$

for neutral equilibrium condition. g_0 is evaluated from g_1 and g_2 thus determined and ϕ_1^c and n_w, by using the spinodal equation

$$2g_0 = \frac{1}{1-\phi_1^c} + \frac{1}{\phi_1^c n_w} + 2g_1(1-3\phi_1^c) + 6g_2(1-2\phi_1^c)\phi_1^c \tag{4.23.8}$$

g_{00} and g_{01} can be estimated from the plot of g_0 vs. $1/T_c$, according to Eq. (4.23.4).
(See R. Koningsveld, L. A. Kleintjens and A. R. Shultz, *J. Polym. Sci.* **A-2**, **8**, 1261 (1970))

(2) Kamide-Matsuda method

The parameter χ can be phenomenologically expressed as Eq. (3.16.4). At the critical point, the following equations can be derived:

$$\frac{1}{n_w\phi_1^c} + \frac{1}{1-\phi_1^c} - \chi_0^c\left(2 + \sum_{j=1}^{n} p_j(j+2)\phi_1^{cj}\right) = 0 \tag{4.23.9}$$

and

$$\frac{1}{(1-\phi_1^c)^2} - \frac{n_z}{(n_w\phi_1^c)^2} - \chi_0^c\sum_{j=1}^{n} p_j j(j+2)\phi_1^{cj-1} = 0 \tag{4.23.10}$$

where n_w and n_z are the weight- and z-average degree of polymerization. Both χ_0^c and ϕ_1^c can be obtained concurrently through the application of Eqs. (4.23.9) and (4.23.10), using a numerical method, to the data of n_w, n_z and p_j (j=1,2). χ_0^c is related to T_c, ψ and θ through the relation

$$\frac{1}{T_C}=\frac{\chi_0^C}{\theta\psi}+\frac{1}{\theta}(1-\frac{1}{2\psi}) \qquad (4.23.11)$$

with

$$\psi\equiv 1/2-\chi_{0,s},\quad \theta\equiv\chi_{0,h}/(1/2-\chi_{0,s}) \qquad (4.23.12)$$

where $\chi_{0,s}$ and $\chi_{0,h}$ are the entropy and enthalpy components of χ_0, respectively (i.e., $\chi_0=\chi_{0,s}+\chi_{0,h}$). Using χ_0^c, calculated from Eqs. (4.23.9) and (4.23.10) and experimental T_c, we can determine θ and ψ from the plot of $1/T_c$ against χ_0^c. (See K.Kamide and S.Matsuda, *Polym.J.* **16**, 825 (1984))

(3) Stockmayer method

Putting $p_j=0$ (for $j=1,\ldots, n$) in Eq. (4.23.9), we obtain

$$\chi_0^C=\frac{1}{2}(\frac{1}{n_w\phi_1^C}+\frac{1}{1-\phi_1^C}) \qquad (4.23.13)$$

Substitution of the Stockmayer equation which was derived for multicomponent polymer-single solvent system

$$\phi_1^C=\frac{1}{1+n_w/n_z^{1/2}} \qquad \text{(Stockmayer equation)} \qquad (4.23.14)$$

into Eq. (4.23.13) yields

$$\chi_0^C=\frac{1}{2}(\frac{n_z^{1/2}}{n_w}+\frac{1}{n_w})(\frac{n_w}{n_z^{1/2}}+1) \qquad (4.23.15)$$

Combining Eq. (4.23.11) with Eq. (4.23.15), we obtain

$$\frac{1}{T_C}=\frac{1}{\theta\psi}\{\frac{1}{2}(\frac{1}{n_w^{1/2}}+(\frac{n_z}{n_w})^{1/2})\times(\frac{1}{n_w^{1/2}}+(\frac{n_w}{n_z})^{1/2})\}+\frac{1}{\theta}(1-\frac{1}{2\psi}) \qquad (4.23.16)$$

(See W. H. Stockmayer, *J. Chem. Phys.* **17**, 588 (1949))

(4) Shultz-Flory method

When $n_w=n_z$ is assumed, Eqs. (4.23.14) and (4.23.16) are reduced to the well

Table 4-23-b.1 Various methods for estimating θ and ψ from critical point data

Method	Parameter prerequisite for applying method			Parameters deduced from the method
	Molecular characteristics	Critical point data	Concentration dependence of χ	
Schulz-Flory [Eq.(4.23.14)']	n_w	T_c	_	θ, ψ, ϕ_1^c
Stockmayer [Eq.(4.23.14)]	n_w, n_z	T_c	_	θ, ψ, ϕ_1^c
Koningsveld et al. [Eq.(4.23.7,8)]	n_w, n_z	T_c, ϕ_1^c	g_1, g_2	$\theta, \psi, g_{00}, g_{01}, g_1, g_2$
Kamide-Matsuda [Eq.(4.23.9,10)]	n_w, n_z	T_c	p_1, p_2	$\theta, \psi, \phi_1^c, \chi_{00}$

(See K.Kamide and S.Matsuda, *Polym.J.* **16**, 825 (1984))

Table 4-23-b.2 Flory θ temperature and entropy parameter ψ for the upper solution critical point of the polystyrene-cyclohexane system

	Method	Equation	Concentration dependence of χ		θ/K	ψ
			p_1	p_2		
	Shultz-Flory	(4.23.14)'	0	0	306.2	0.75
Critical point	Stockmayer	(4.23.14)	0	0	306.5	0.80
	Koningsveld el al.	(4.23.7,8)	0.623	0.308	305.2	0.29
			0.623	0.290	305.6	0.30
	Kamide-Matsuda:					
	Phase separation		0.6	0	306.4	0.35
	Cloud point	(4.23.9,10)	0.643	0.200	306.6	0.27
	Critical point		0.623	0.290	305.6	0.27
	Critical point		0.642	0.190	305.1	0.27
	Membrane osmometry		_	_	307.6	0.36
			_	_	307.6	0.23
Second virial coefficient	Light scattering		_	_	308.4	0.19
			_	_	307.0	0.36
			_	_	307.4	0.18

(See K.Kamide and S. Matsuda, *Polym, J.* **16** 825 (1984))

Table 4-23-b.3 Concentration dependence of χ-parameter p_1, p_2, Flory temperature θ, and entropy parameter ψ at the critical point for polystyrene-solvent systems

Polymer:Polystyrene	UCSP or LCSP	Method									
Solvent		Kamide-Matsuda				Koningsveld et al.				Shultz-Flory	
		p_1	p_2	θ	ψ	p_1	p_2	θ	ψ	θ (θ ref)	ψ (ψ ref)
Methyl ethyl ketone	LCSP	0.618	-0.208	423.6	-0.44	0.550	-0.262	423.8	-0.31	423.1 (422)	-0.63 (-0529)
Cyclopentane	UCSP	0.615	0.404	292.1	0.16	0.606	0.497	292.1	0.18	292.7(293)	0.53 (0.548)
	LCSP	0.631	0.331	428.5	-0.25	0.611	0.468	428	-0.27	427.4 (427)	-0.81 (-0.858)
Cyclohexane	UCSP	(0.642	0.190	305.1	0.27)	(0.623	0.308	305.2	0.29)	306.5 (306.2)	0.75 (0.78)
		-	-	-	-	(0.623	0.290	306.4	0.30)	-	- (0.79)
	LCSP	0.638	-0.498	488.6	-0.58	0.621	-0.305	488.3	-0.60	486.8 (486.0)	-1.21 (-1.19)
		(0.602	0.347	487.2	-0.42)	(0.571	-0.047	487.8	-0.61)	-	- (-1.20)
Methyl cyclohexane	UCSP	(0.602	0.234	340.2	0.25)	(0.602	0.363	339.6	0.27	342.3 (344)	0.61 (0.56)
	LCSP	(0.649	-1.183	487.9	-0.54)	(0.643	-1.008	487.8	-0.56	485.1 (484)	-0.96 (-0.94)
Toluene	LCSP	0.494	-0.922	550.4	-1.36	0.501	-0.475	550.3	-1.20	549.8 (550)	-2.02 (-1.92)
Benzene	LCSP	0.388	-1.781	524.3	-1.81	0.382	-1.655	524.2	-1.82	523.7 (523)	-2.19 (-1.79)
Isopropyl acetate	UCSP	0.673	-0.034	240.8	0.11	0.673	-0.082	240.6	0.13	245.3 (246)	0.29 (0.32)
	LCSP	0.839	-2.000	398.1	-0.46	0.773	-1.594	394.6	-0.46	389.5 (380)	-0.71 (-0.46)
n-Propyl acetate	UCSP	0.643	-0.018	192.3	0.21	0.623	0.168	192.7	0.22	193.2 (193)	0.60 (0.63)
	LCSP	0.797	-1.440	456.3	-0.47	0.769	-1.204	455.6	-0.49	451.1 (451)	-0.96 (-0.85)
Dimethoxy methane	LCSP	0.650	-0.202	389.1	-0.25	0.642	-0.083	388.0	-0.24	386.0 (-)	-0.61 (-)
trans-Decalin	UCSP	0.630	0.240	292.7	0.33	0.623	0.338	292.5	0.36	293.7 (-)	0.95 (-)

(See K. Kamide, S. Matsuda and M. Saito, *Polym. J.* 17, 1013 (1985))

Table 4-23-b.4 Temperature-dependence (a and b in the equation χ =a+b/T or a=0.5-ψ_0, b=$\psi_0\theta$) and concentration-dependence (p_1 and p_2 in Eq.(3.16.4)) parameters of themodynamic interaction parameter χ, Flory entropy parameter ψ_0 and Flory theta temperature θ for atactic polystyrene/cyclohexane system (T=299K).

Author(s)	Method	a	b	p_1	p_2	ψ_0	θ /K
Krigbaum and Geymer(1959)	Osmotic Pressure	0.2469	76.67	0.630_4	0.480_8	0.25	302.9
Scholte(1970)	Ultracentrifuge	0.2631	74.31	0.534_4	0.430_4	0.24	313.7
Koningsveld et al.(1970)	Critical point	0.2035	90.50	0.610_6	0.920_7	0.30	305.2
Koningsveld et al.(1970)	Critical point	0.2211	85.31_3	0.622_2	0.289_1	0.28	305.9
Kuwahara et al.(1973)	Threshold cloud point	0.2798	67.50	0.607_3	0.512_1	0.22	306.5
Kamide et al.(1984)	Cloud point curve and ρ_p vs. T relationship	- 0.0242_4	158.79	0.643	0.200	0.52	305.2
Kamide and Matsuda(1984)	Critical point	0.23	82.37_7	0.642	0.190	0.27	305.1
Kamide et al.(1995)	Cloud point curve and ρ_p vs. T relationship	0.23	82.89	0.600	0.460	0.27	307.0

* ρ_p, the relative amount of polymer partitioned in polymer-rich phase

*T, temperature

(See K.Kamide, S.Matsuda and H.Shirataki, *MemFac.Educ.Kumamoto Univ.* No.44, Natural Science,199 (1995)) known equations derived by Shultz and Flory

$$\phi_1^c = \frac{1}{1+n_w^{1/2}} \tag{4.23.14)'}$$

and

$$\frac{1}{T_c} = \frac{1}{\theta\psi}\{\frac{1}{2}(\frac{1}{n_w^{1/2}}+1)^2\} + \frac{1}{\theta}(1-\frac{1}{2\psi}) = \frac{1}{\theta\psi}(\frac{1}{n_w^{1/2}}+\frac{1}{2n_w}) + \frac{1}{\theta} \tag{4.23.16)'}$$

(See A. R. Shultz and P. J. Flory, *J. Am. Chem. Soc.* **74**, 4760 (1952))

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* Eq. (4.23.16)' is strictly valid only for a monodisperse polymer-single solvent system, in which the parameter χ is assumed to be independent of the molecular weight and the concentration of the polymer. Whether the concentration dependence of the parameter χ and the polymolecularity of the polymer should be taken into account to explain the critical point and, in the former case what would be the most reasonable values of p_1, p_2,...,p_n , can be decided by comparing the experimental critical volume fraction of the total polymer (ϕ_1^c(exp)) and the theoretical one (ϕ_1^c(theo)) calculated using Eqs. (4.23.9) and (4.23.10) (Kamide-Matsuda), Eq. (4.23.14) (Stockmayer), and Eq. (4.23.14)' (Shultz-Flory). An analysis of the data on ϕ_1^c(exp), n_z and n_w would provide the most ideal values of p_1, p_2, ...and p_n as a combination yielding the minimum δ, defined by

$$\delta = \sum_{i=1}^{N_0}(\phi_1^c(\exp) - \phi_1^c(\text{theo}))_i^2 \,/\, N \tag{4.23.17}$$

where N_0 is the total number of samples. That is, using an appropriate choice of p_1, p_2, ..., p_n, ϕ_1^c(theo) will fit ϕ_1^c(exp) for the entire set of data. If ϕ_1^c(exp) and experimental T_c (T_c(exp)) data are available for a polymer-solvent system, we can determine p_1, ...,p_n from the plot of ϕ_1^c(exp) vs. ϕ_1^c(theo) and θ and ψ from the plot $1/T_c$ vs. χ_0^c concurrently, as shown in Fig.4-23-b.2,3, and 4.

Table 4-23-b.1 presents the features of the various methods proposed for estimating θ and ψ from the critical point data. When Eq. (3.16.12) is applicable, Eqs. (4.23.9) and (4.23.10) can be modified as,

$$\frac{1}{n_w\phi_1^c} + \frac{1}{1-\phi_1^c} - \chi_{00}^c\left(1 + k_0\left(1 - \frac{\theta}{T_c}\right) \times \left(1 + \frac{1}{n_n} - \frac{n_w}{n_n}\right)\right) \times \left(2 + \sum_{j=1}^{n} p_j(j+2)\phi_1^{cj}\right) = 0 \tag{4.23.9)'}$$

$$\frac{1}{\left(1-\phi_1^c\right)^2}-\frac{n_z}{\left(n_w\phi_1^c\right)^2}-\chi_{00}^c\left(1+k_0\left(1-\frac{\theta}{T_c}\right)\right)\left(1+\frac{1}{n_n}-\frac{n_z}{n_n}\right)\left(\sum_{j=1}^{n}p_j(j+2)\phi_1^{c^j}\right)=0 \tag{4.23.10)'$$

Parameters in χ determined for polystyrene solutions by various methods are summarized in Tables 4-23-b.2,3, and 4.

*In contrast to the systems of non-polar polymer in non-polar solvent, for PS-aromatic solvent systems p_1 value at CSP deviates significantly from 2/3. (See Note in <<Probrem 3-16-b>>). For examples, p_1=0.494 (toluene) and 0.388 (benzene) were obtained. Kamide et al. pointed out, from an analysis of ^{1}HNMR spectra with the aid of infra-red spectra and adiabatic compressibility, that the PS phenyl ring is stacked in parallel to the solvent phenyl ring for PS/aromatic solvent system. This strongly suggests that marked difference in thermodynamic parameters, including the concentration dependence coefficients p_1 and p_2 of the parameter χ, and **Flory entropy parameter at infinite dilution** ψ_0, observed for atactic PS in aromatic and aliphatic solvents, are accounted for, at least in part, by the formation of some supramolecular structure in the former solutions, which may affect the entropy term in the parameter χ and the entropy of mixing. (See K. Kamide, S. Matsuda and K. Kowsaka, *Polym. J.* **20**, 231 (1988))

<<Problem 4-23-c>> Experimental method for determining κ_0

Describe the methods for determining the **Flory enthalpy parameter at infinite dilution** κ_0, defined by

$$\kappa_0=\lim_{\phi_1\to 0}\{\Delta H_0/(RT\phi_1^2)\} \tag{4.23.18}$$

Answer

(1) The **temperature dependence of vapor pressure and osmotic pressure** through the use of the relationship

$$\kappa_0=\lim_{\phi_1\to 0}\{1/(RT\phi_1^2)\}\{\partial(\Delta\mu_0/T)/\partial(1/T)\}_{P,\phi_1} \tag{4.23.19}$$

(See Eq.(1.2.3) and the relationship between chemical potential and osmotic pressure, Eq. (2.7.8)). The partial differentiation of $\Delta\mu_0/T$ with respect to $1/T$ is carried out under constant pressure and constant composition except the polymer.

(2) The **critical parameters** (critical solution temperature T_c and the critical polymer volume fraction ϕ_1^c). κ_0 is related to the Flory theta temperature θ and the Flory entropy parameter ψ_0 through the definition of θ as

$$\kappa_0 = \theta\psi_0 / T \tag{4.23.20}$$

with

$$\psi_0 = \lim_{\phi_1^0 \to 0}(\Delta S_0 - \Delta S_0^{\mathrm{comb}})/(R\phi_1^2) = \lim_{\phi_1^0 \to 0}(\Delta\mu_0 - \Delta H_0 - T\Delta S_0^{\mathrm{comb}})/(RT\phi_1^2) \tag{4.23.21}$$

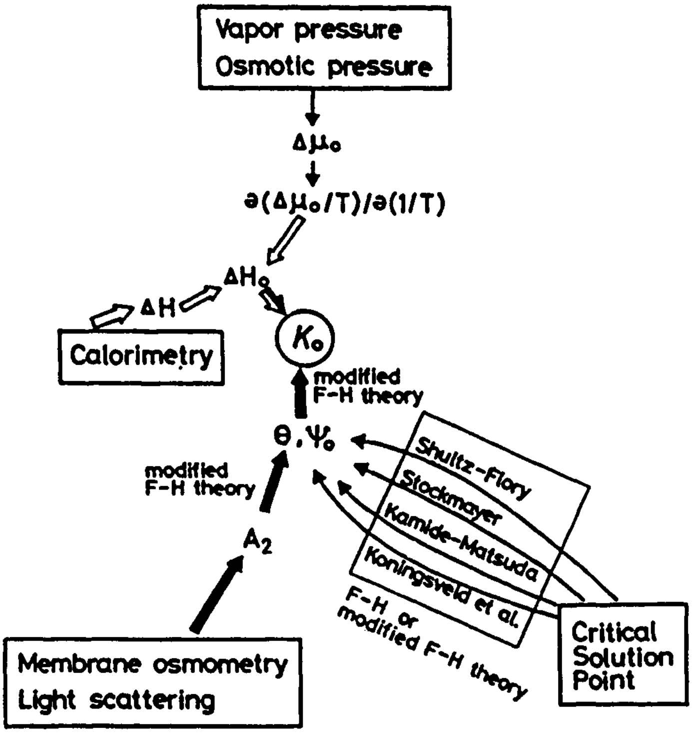

Fig. 4-23-c.1 Routes of calculation of the Flory enthalpy parameter from experimental data of vapor pressure, osmotic pressure, light scattering, and critical solution points (see K. Kamide, S. Matsuda and M. Saito, *Polym. J.* **20**, 31 (1988))

Here, ΔS_0 is the partial molar entropy of dilution and ΔS_0^{comb} the combinatorial entropy. θ and ψ_0 can be evaluated from T_c and ϕ_1^c for a series of solutions of polymers having different molecular weights by the following methods.

(a) Shultz and Flory (SF) method (*J.Am.Chem.Soc.*74, 4760 (1952))
(b) Stockmayer method (*J.Chem.Phys.* **17**,588 (1949))
(c) Koningsveld et al. (KKS) method (*J.Polym.Sci.* **A-2**, **8**, 1261 (1970))
(d) Kamide-Matsuda (KM) method (*Polym.J.* **16**, 825 (1984))
(See <<Problem 4-23-b>> for detailed description)

(3) **Temperature dependence of A_2 by membrane osmometry or light scattering** measured in the vicinity of θ temperature via θ and ψ_0 as

$$\psi_0 = (V_0^0 / v^2)\theta(\partial A_2 / \partial T)_\theta \qquad (4.23.22)$$

Here v is the specific volume of polymer (See also <<Problem 5-17>>) and note that ψ_0 estimated by Eq. (4.23.22) corresponds to a finite molecular weight. θ is determined as the temperature at which A_2 becomes zero. κ_0 can be evaluated by substituting θ and ψ_0 thus obtained into Eq. (4.23.20).

(4) **Calorimetry**

The heat of dilution ΔH and accordingly $\Delta H_0(\equiv(\partial \Delta H/\partial N_0)_{T,P}$, N_0 is the mole number of solvent) can be directly measured with calorimetry. Figure 4-23-c.1 demonstrates schematic routes for determining κ_0.

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* In order to obtain a better understanding of the molecular weight dependence of κ_0, a log-log plot of κ_0 against M_w^{-1} or M_n^{-1} for atactic polystyrene (PS)- cyclohexane (CH) system at 307.2K is shown in Fig. 4-23-c.2 All available data points yielded a straight line given by

$$\kappa_0(\equiv \psi_0) = 0.924 M_w (\text{or } M_n)^{-0.089} \qquad (4.23.23)$$

Eq. (4.23.23) is valid over the entire experimentally accessible molecular weight range from 6.2 x 10^3 to 5.68 x 10^7. It should be concluded that the most probable κ_0 value is, in a strict sense, dependent on M_w (or M_n), irrespective of the method employed and that if Eq. (4.23.23) can be expanded its applicability to $M_w=\infty$, κ_0 at infinite molecular weight may be zero. This is an experimental indication that both the randomness in the mixing of a polymer

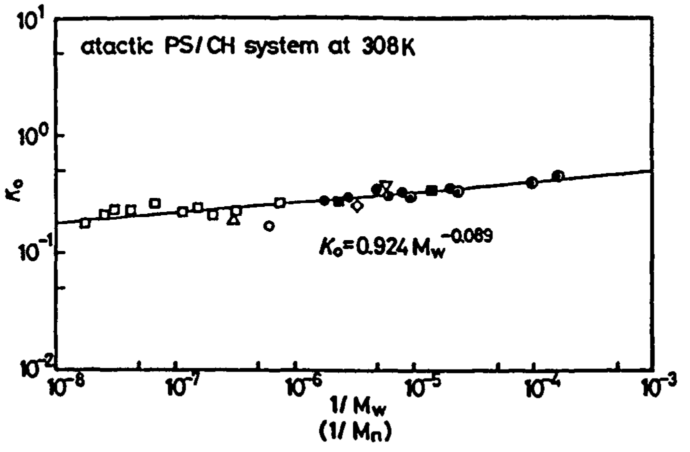

Fig. 4-23-c.2 Log-log plot of Flory enthalpy parameter at infinite dilution κ_0, evaluated by the temperature dependence of the chemical potential and the second virial coefficient A_2 in the vicinity of the theta temperature and by calorimetry versus the reciprocal weight- (or number-) average molecular weight M_w (M_n) for atactic polystyrene/cyclohexane system: (●) Krigbaum[1] by membrane osmometry (MO);(■) Krigbaum-Geymer[2] (MO); (○) Scholte[3] by ultracentrifuge; (△) Krigbaum-Carpenter[4] by light scattering (LS); (▽) Schulz-Baumann[5] (LS); (◇) Kotera et al.[6] (LS); (○) Outer et al.[7] (LS); (□) Miyaki[8] (LS); (◉) Fujihara[9] by calorimetry. Solid line, the equation $\kappa_0=0.92M_w^{-0.089}$. (See K. Kamide, S. Matsuda and M. Saito, *Polym. J.* **20**, 31 (1988))

[1] W.R.Krigbaum, *J.Am.Chem.Soc.* **76**, 3785 (1954). [2] W.R.Krigbaum and D.O.Geymer, *J.Am.Chem.Soc.* **81**, 1859 (1959). [3] Th.G.Scholte, *J.Polym.Sci.* **A-2, 8**, 841 (1970). [4] W.R.Krigbaum and D.K.Carpenter, *J.Phys.Chem.* **59**, 1166 (1955). [5] G.V.Schulz and H. Baumann, *Macromol. Chem.*, **60**,120 (1963). [6] A.Kotera, T.Saito, and N.Fujisaki, *Repts.Progr.Polym.Phys.Jpn.* **6**, 9 (1963). [7] P.Outer, C.I.Carr, and B.H.Zimm, *J.Chem. Phys.* **18**, 830 (1950). [8] Y.Miyaki, PhD. Dissertation, Osaka Univ (1981). [9] I.Fujihara, PhD. Dissertation, Osaka Univ (1979).

Table 4-23-c Flory θ temperature and enthalpy parameter κ_0 at infinite dilution for the upper critical solution point of atactic polystylene-cyclohexane system

Method		$\frac{\theta}{K}$	κ_0(M_n or $M_w \times 10^{-4}$) at 308℃		(Data)
(1) Chemical potential	Membrane osmometry	—	0.21(44)		(Krigbaum-Geymer)[1]
	Sedimentation equilibrium	—	0.32(15.4)		(Scholte)[2]
(2) Critical point	Shultz-Flory	306.2	0.75(−)		
	Stockmayer	306.5	0.80(−)		(Koningsveld et al.,
	Koningsveld et al.	305.2	0.29(−)	[0.28][a]	Kuwahara et al.,
	Kamide-Matsuda	305.1	0.27(−)	0.26(∞)	Saeki et al.)[3-5]
(3) Second virial coefficient	Membrane osmometry	307.6	0.28(∞)	[0.28][a]	(Krigbaum)[6]
		307.6	0.27(∞)		(Krigbaum-Geymer)[1]
	Light scattering	308.0	0.19(163)		(Outer et al.)[7]
		308.4	0.19(320)		(Krigbaum-Carpenter)[8]
		307	0.39(17)		(Schulz-Baumann)[9]
		307.4	0.26(30)	[0.26][a]	(Kotera et al.)[10]
		308	0.22(∞)		(Miyaki-Fujita)[11,12]
		307.7	0.30(∞)		(Tong et al.)[13]
(4) Heat of dilution	Calorimetry	—	0.28(∞)		(Fujihara)[14]

[a] Averaged value (See K.Kamide, S.Matsuda and M.Saito, *Polym. J.* **20**, 31 (1988))

[1] W.R.Krigbaum and D.O.Geymer, *J.Am.Chem.Soc.* **81**, 1859 (1959). [2] Th.G.Scholte, *J.Polym.Sci.* **A-2, 8**, 841 (1970). [3] R.Koningsveld, L.A.Kleintjens and A.R.Shultz, *J.Polym.Sci.* **A-2, 8** 1261 (1970). [4] N.Kuwahara, N.Nakata and M.Kaneko, *Polymer* **14**, 415 (1973). [5] S.Saeki, N.Kuwahara, S.Konno and M.Kaneko, *Macromolecules* **6**, 246 (1973). [6] W.R.Krigbaum, *J.Am.Chem.Soc.* **76**, 3785 (1954) [7] P.Outer, C.I.Carr and B.H.Zimm, *J.Chem.Phys.* **18**, 830 (1950). [8] W.R.Krigbaum and D.K.Carpenter, *J.Phys.Chem.* **59**, 1166 (1955). [9] G.V.Schulz and H.Baumann, *Makromol.Chem.* **60**, 120 (1963). [10] A.Kotera, T.Saito and N.Fujisaki, *Repts.Progr.Polym.Phys.Jpn.* **6**, 9 (1963). [11] Y.Miyaki and H.Fujita, *Macromolecules* **14**, 742 (1981). [12] Y.Miyaki, PhD. Dissertation, 1981 Osaka Univ. [13] Z.Tong, S.Ohashi, Y.Einaga and H.Fujita, *Polym. J.* **15**, 835 (1983). [14] I.Fujihara, PhD. Dissertation, 1979, Osaka City Univ.

and solvent and the spacial homogeneity of the polymer segment density in solution are expected to be realized in dilute solutions of polymer with infinitely large molecular weight (i.e., $\Delta S_0 = \Delta S_0^{comb}$). The fact that the above methods give essentially identical κ_0 value within ±0.02 for a given PS sample in CH, strongly supports the validity of the modified Flory-Huggins theory. Flory θ tempereture and enthalpy parameter κ_0 determined for PS/CH with various methods are summarized in Table 4-23-c.

<<Problem 4-24>> Critical condition in terms of g

The spinodal condition for multicomponent Flory-Huggins solution is given by

$$\frac{1}{n_w\phi_1} + \frac{1}{1-\phi_1} - 2\chi - \left(\frac{\partial\chi}{\partial\phi_1}\right)\phi_1 = 0 \tag{4.20.27}$$

The critical point is determined by solving simultaneous equations of Eq. (4.20.27) and the following equation:

$$\frac{1}{\left(1-\phi_1\right)^2} - \frac{n_z}{\left(n_w\phi_1\right)^2} - 3\left(\frac{\partial\chi}{\partial\phi_1}\right) - \left(\frac{\partial^2\chi}{\partial{\phi_1}^2}\right)\phi_1 = 0 \tag{4.20.42}$$

According to <<Problem 3-18>>,

$$\chi = g - \left(1-\phi_1\right)\frac{\partial g}{\partial\phi_1} \tag{3.18.2}$$

holds between χ and g.

Derive equations corresponding to Eqs. (4.20.27) and (4.20.42) for spinodal and neutral equilibrium conditions in terms of g and $\partial g/\partial\phi_1$ and rewrite the equations for the case when ϕ_1 dependence of g obeys the equation

$$g = \sum_{k=0}^{3} g_k{\phi_1}^k \tag{4.24.1}$$

Answer

Substituting Eq. (3.18.2) for χ in Eq. (4.20.27), we obtain

$$\frac{1}{1-\phi_1} - 2g + 2\left(1-2\phi_1\right)\left(\frac{\partial g}{\partial\phi_1}\right) + \phi_1\left(1-\phi_1\right)\left(\frac{\partial^2 g}{\partial{\phi_1}^2}\right) = -\frac{1}{n_w\phi_1} \tag{4.24.2}$$

and similarly, using Eq. (4.20.42), we obtain

$$\frac{1}{\left(1-\phi_1\right)^2}-6\left(\frac{\partial g}{\partial \phi_1}\right)+3\left(1-2\phi_1\right)\left(\frac{\partial^2 g}{\partial \phi_1{}^2}\right)+\phi_1\left(1-\phi_1\right)\left(\frac{\partial^3 g}{\partial \phi_1{}^3}\right)=\frac{n_z}{\left(n_w\phi_1\right)^2} \tag{4.24.3}$$

If g is expressed as Eq. (4.24.1), we have

$$\frac{\partial g}{\partial \phi_1}=g_1+2g_2\phi_1+3g_3\phi_1{}^2$$

$$\frac{\partial^2 g}{\partial \phi_1{}^2}=2g_2+6g_3\phi_1$$

$$\frac{\partial^3 g}{\partial \phi_1{}^3}=6g_3 \tag{4.24.4}$$

Substitution of Eq. (4.24.4) in Eq. (4.24.2) yields

$$2\left(g_0+g_1\phi_1+g_2\phi_1{}^2+g_3\phi_1{}^3\right)=\frac{1}{1-\phi_1}+\frac{1}{n_w\phi_1}$$
$$+2\left(1-2\phi_1\right)\left(g_1+2g_2\phi_1+3g_3\phi_1{}^2\right)+\phi_1\left(1-\phi_1\right)\left(2g_2+6g_3\phi_1\right) \tag{4.24.5}$$

Equation (4.24.5) is rearranged as

$$2g_0=\frac{1}{1-\phi_1}+\frac{1}{n_w\phi_1}+2g_1\left(1-3\phi_1\right)+6g_2\phi_1\left(1-2\phi_1\right)+4g_3\phi_1{}^2\left(3-4\phi_1\right) \tag{4.24.6}$$

In a similar manner, from Eqs. (4.24.3) and (4.24.4), we obtain

$$\frac{1}{\left(1-\phi_1\right)^2}-\frac{n_z}{\left(n_w\phi_1\right)^2}=6g_1-6g_2+24g_2\phi_1+60g_3\phi_1-3g_3\phi_1{}^2 \tag{4.24.7}$$

In case of $g_3=0$, Eqs. (4.24.6) and (4.24.7) are reduced to:

$$2g_0=\frac{1}{1-\phi_1}+\frac{1}{n_w\phi_1}+2g_1\left(1-3\phi_1\right)+6g_2\phi_1\left(1-2\phi_1\right) \tag{4.24.8}$$

$$g_1-g_2+4g_2\phi_1=\frac{1}{6}\left\{\frac{1}{\left(1-\phi_1\right)^2}-\frac{n_z}{\left(n_w\phi_1\right)^2}\right\} \tag{4.24.9}$$

respectively. These equations were derived by Koningsveld et al. (See R. Koningsveld, L.A.Kleintjens and A.R.Shultz, *J. Polym. Sci.* **A-2, 8**, 1261 (1970)).

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* When ϕ_1 dependence of g are completely negligible, Eqs. (4.24.8) and (4.24.9) are simplified as

$$2g_0 = \frac{1}{1-\phi_1} + \frac{1}{n_w\phi_1} \qquad (4.24.10)$$

$$\phi_1{}^c = \frac{1}{1 + \dfrac{n_w}{\sqrt{n_z}}} \qquad (4.21.3)$$

Then, if g does not depend on ϕ_1, $\phi_1{}^c$ can be calculated from n_w and n_z. But ample experiments demonstrate significant ϕ_1 dependence of g. If we consider temperature dependence of g_0 as

$$g_0 = g_{00} + \frac{g_{01}}{T} \qquad (4.24.11)$$

Eq.(4.24.8) can be rewritten in the form

$$\frac{1}{T_c} = \frac{0.5 - g_{00}}{g_{01}} + \frac{1}{g_{01}}\left(\frac{1}{\sqrt{n}} + \frac{1}{2n}\right) \qquad (4.24.12)$$

where g_{00} and g_{01} are the phenomenological coefficients. This is no more than Shultz-Flory equation (4.12.19). In θ solvent (χ_0=1/2), g_0-g_1=1/2. θ can be determined from T_c at g_0-g_1=1/2 in the plot of g_0 vs. $1/T_c$.

* Comparing Eq. (3.16.4) with the general form of Eq. (4.24.1) or

$$g = \sum_{i=0}^{n} g_i \phi_1^i \qquad (4.24.13)$$

and using Eq. (3.18.2), we can derive the relationship between the coefficients of χ and g as

$$\chi_0 = g_0 - g_1 \qquad (4.24.14)$$

$$P_i = (i+1)(g_i - g_{i+1})/(g_0 - g_1) \quad (i = 1, \cdots, n-1) \qquad (4.24.15)$$

$$P_n = (n+1)g_n/(g_0 - g_1) \qquad (4.24.16)$$

Koningsveld and Kleintjens expressed g in a closed form of ϕ_1 as

$$g = \alpha + \beta/(1 - \gamma\phi_1) \tag{4.24.17}$$

where α, β and γ are phenomenological parameters. In the range of $0<\gamma<1$, the relation $0<\gamma\phi_1<1$ is valid and the second term of the right-hand side of Eq. (4.24.17) can be expanded in infinite series so that Eq. (4.24.17) may be rewritten as

$$g = \alpha + \beta + \sum_{i=1}^{\infty} \beta(\gamma\phi_1)^i \cong \alpha + \beta + \sum_{i=1}^{n} \beta(\gamma\phi_1)^i \tag{4.24.18}$$

By putting $\alpha + \beta = \gamma_0$ and $\beta\gamma^i = g_i$ $(i=1,\dots,n)$, Eq. (4.24.18) is reduced to Eq. (4.24.13). Parameters χ_0, p_i, and p_n can be expressed in terms of α, β and γ as follows:

$$\chi_0 = \alpha + \beta(1 - \gamma) \tag{4.24.19}$$

$$p_i = (i+1)\beta\gamma^i(1-\gamma)/\{\alpha + \beta(1-\gamma)\} \qquad (i = 1, \cdots, n-1) \tag{4.24.20}$$

$$p_n = (n+1)\beta\gamma^n/\{\alpha + \beta(1-\gamma)\} \tag{4.24.21}$$

<<Problem 4-25>> Relationship between g, θ and ψ

Show that the equation

$$g_0 - g_1 = \frac{1}{2} - \psi + \frac{\psi\theta}{T} \tag{4.25.1}$$

holds between g_0, g_1, **ψ and θ.**

Answer

In the Flory-Huggins theory, χ_0 can be divided into two parts: entropy term ψ and enthalpy term κ, that is,

$$\frac{1}{2} - \chi_0 = \psi - \kappa = \psi\left(1 - \frac{\theta}{T}\right) \tag{4.25.2}$$

where $\kappa = \psi\theta/T$.

χ_0 is related to g_0 and g_1 through Eqs. (3.18.2), (4.24.1) and (4.24.4) as

$$\chi_0 = g_0 - g_1 \tag{4.24.14}$$

Then Eq. (4.25.1) is directly derived.

---

* If temperature dependence of g_0 is given by Eq. (4.24.11), Eq. (4.25.1) can be rewritten as

$$\psi = \frac{1}{2} - g_{00} + g_1 \tag{4.25.3}$$

Thus we can determine ψ from g_{00} and g_1. This method is more reasonable than the method of Flory-Shultz plot because in the former method ϕ_1 dependence of χ is taken into account.

<<Problem 4-26>> Slope of spinodal curve

Determine the **slope of the spinodal curve** as defined by $(dT/d\phi_1)_{sp}$.

Answer

From Eqs. (4.24.8) and (4.24.11), we have

$$2g_{00}+\frac{2g_{01}}{T}=\frac{1}{1-\phi_1}+\frac{1}{n_w\phi_1}+2g_1\left(1-3\phi_1\right)+6g_2\phi_1\left(1-2\phi_1\right) \tag{4.26.1}$$

Differentiation of Eq. (4.26.1) with respect to ϕ_1 yields

$$\left(\frac{dT}{d\phi_1}\right)_{SP}=\frac{T^2}{2g_{01}}\left\{\frac{1}{n_w{\phi_1}^2}+6\left(g_1-g_2\right)\frac{1}{\left(1-\phi_1\right)^2}+24g_2\phi_1\right\} \tag{4.26.2}$$

At the critical solution point, Eq. (4.26.2) is expressed as

$$\left\{\left(\frac{dT}{d\phi_1}\right)_{SP}\right\}_{\phi=\phi_1^c}=\frac{T_c^2}{2g_{01}}\left\{\frac{1}{n_w{\phi_1^c}^2}+6\left(g_1-g_2\right)\frac{1}{\left(1-\phi_1^c\right)^2}+24g_2\phi_1^c\right\} \tag{4.26.3}$$

Provided that g_1 and g_2 are known in advance, we can determine g_{01} from the slope of the spinodal curve at the critical point by using Eq. (4.26.3).

<<Problem 4-27>> Phase equilibria of polymer blend (P_1/P_2) (I): Gibbs free energy of mixing per unit volume for monodisperse polymer / monodisperse polymer

Derive the **chemical potentials of mixing and Gibbs free energy of mixing per unit volume of polymer blends** which consist of polymer (0) with the degree of polymerization $n=n_0$ and polymer (1) with $n=n_1$.

Answer

Referring to Eqs. (3.11.3) and (3.12.2), we have

$$\Delta\mu_0 = RT\left\{\ln\left(1 - \phi_1\right) + \left(1 - \frac{n_0}{n_1}\right)\phi_1 + n_0\chi\phi_1{}^2\right\} \tag{4.27.1}$$

$$\Delta\mu_1 = RT\left\{\ln\phi_1 + \left(1 - \frac{n_1}{n_0}\right)\left(1 - \phi_1\right) + n_1\chi\left(1 - \phi_1\right)^2\right\} \tag{4.27.2}$$

with a generalization of the Flory-Huggins theory. Gibbs free energy of mixing per unit volume ΔG_v is given by

$$\Delta G_v = \phi_0\left(\frac{\Delta\mu_0}{n_0 V_0}\right) + \phi_1\left(\frac{\Delta\mu_1}{n_1 V_0}\right)$$

$$= \frac{RT}{V_0}\left\{\frac{\phi_0}{n_0}\ln\phi_0 + \frac{\phi_1}{n_1}\ln\phi_1 + \chi\phi_0\phi_1\right\} \tag{4.27.3}$$

<<Problem 4-28-a>> Flory-Huggins free energy for multicomponent solution

Gibbs free energy of mixing ΔG_{mix} for binary Flory-Huggins mixtures is given by

$$\Delta G_{mix} = RT\left\{\left(N_0\ln\phi_0 + N_1\ln\phi_1\right) + \varepsilon z N\phi_0\phi_1 / kT\right\} \tag{4.28.1}$$

where

$$N = N_0 + nN_1 \tag{4.28.2}$$

Note here the number of molecule (not number of moles of molecule) is used. (Compare with Eq.(3.10.2)). Gibbs free energy of mixing per unit volume (mean volume Gibbs free energy) ΔG_v is given by

$$\Delta G_v = \frac{RT}{V_0}\left\{\left(1 - \phi_1\right)\ln\left(1 - \phi_1\right) + \frac{\phi_1}{n}\ln\phi_1 + \chi\phi_1\left(1 - \phi_1\right)\right\} \tag{4.12.5}$$

(1) Generalize these equations to **multicomponent solutions** which consist of N_i molecules of *i* th component with the degree of polymerization n_i with the

volume fraction ϕ_i (i=1 to r).
(2) Using Eq.(4.12.5), derive the expressions for the differential coefficients

$$L_{ij} = \frac{V_0}{kT}\left(\frac{\partial^2 \Delta G_v}{\partial \phi_i \partial \phi_j}\right) \tag{4.28.3}$$

$$L_{ii} = \frac{V_0}{kT}\left(\frac{\partial^2 \Delta G_v}{\partial \phi_i^2}\right) \tag{4.28.4}$$

Answer

(1) A generalized equation of Eq. (4.28.1) is given by

$$\Delta G_{mix} = RT\sum_{i=0}^{r} N_i \ln\phi_i + zNN_A \sum_{i<j} \phi_i\phi_j\varepsilon_{ij} \tag{4.28.5}$$

where

$$N = \sum_{i=0}^{r} N_i$$

and ε_{ij} is the energy for forming a pair of *i* th segment and *j* th segment. Referring to χ for binary solutions, we can define

$$\chi_{ij} = \frac{z\varepsilon_{ij}}{kT} \tag{4.28.6}$$

Equation (4.28.5) reduces to

$$\Delta G_{mix} = RT\sum_{i=0}^{r} N_i \ln\phi_i + NRT\sum_{i<j} \phi_i\phi_j\chi_{ij} \tag{4.28.7}$$

Similarly, Eq.(4.28.2) can be generalized as

$$\Delta G_v = \frac{RT}{V_0}\left(\sum_{i=0}^{r}\frac{\phi_i \ln\phi_i}{n_i} + \sum_{i<j}\phi_i\phi_j\chi_{ij}\right) \tag{4.28.8}$$

(2) Considering the constraint

$$\sum_{i=0}^{r}\phi_i = 1 \tag{4.28.9}$$

Eq. (4.28.8) can be expressed as

$$\Delta G_v = \frac{RT}{V_0}\left\{ \frac{1 - \sum_{k=1}^{r} \phi_k}{n_0} \ln\left(1 - \sum_{k=1}^{r} \phi_k\right) + \sum_{i=1}^{r} \frac{\phi_i \ln \phi_i}{n_i} + \sum_{\substack{i<j \\ (i=1, \cdots, r)}} \phi_i \phi_j \chi_{ij} \right\} \tag{4.28.10}$$

Differentiation of ΔG_v by ϕ_i and ϕ_j yields

$$\begin{aligned} \frac{V_0}{RT}\left(\frac{\partial \Delta G_v}{\partial \phi_i}\right) = & -\frac{1}{n_0}\ln\left(1 - \sum_{k=1}^{r} \phi_k\right) - \frac{1}{n_0} + \frac{\ln \phi_i}{n_i} + \frac{1}{n_i} \\ & - \sum_{l=1}^{r} \phi_l \chi_{0l} + \left(1 - \sum_{k=1}^{r} \phi_k\right)\chi_{0i} + \sum_{j=i+1}^{r} \phi_j \chi_{ij} \end{aligned} \tag{4.28.11}$$

$$\frac{V_0}{RT}\left(\frac{\partial^2 \Delta G_v}{\partial \phi_i \partial \phi_j}\right) = \frac{1}{n_0 \phi_0} - \chi_{0i} - \chi_{0j} + \chi_{ij} = L_{ij} \qquad (i,j = 1, \cdots, r) \tag{4.28.12}$$

$$\frac{V_0}{RT}\left(\frac{\partial^2 \Delta G_v}{\partial {\phi_i}^2}\right) = \frac{1}{n_0 \phi_0} + \frac{1}{n_i \phi_i} - 2\chi_{0i} = L_{ii} \qquad (i = 1, \cdots, r) \tag{4.28.13}$$

For homologous polymer solutions (polymers of the same species with different molecular weights in a solvent), we may put

$$\begin{aligned} & L_{ij} = L \\ & \chi_{ij} = 0 \\ & \chi_{0i} = \chi_{i0} = \chi \\ & n_0 = 1 \end{aligned} \tag{4.28.14}$$

Then we have

$$\frac{V_0}{RT}\left(\frac{\partial^2 \Delta G_v}{\partial \phi_i \partial \phi_j}\right) = \frac{1}{\phi_0} - 2\chi = L \qquad (i,j = 1, \cdots, r) \tag{4.28.12'}$$

$$\frac{V_0}{RT}\left(\frac{\partial^2 \Delta G_v}{\partial {\phi_i}^2}\right) = \frac{1}{\phi_0} + \frac{1}{n_i \phi_i} - 2\chi = L_i \qquad (i = 1, \cdots, r) \tag{4.28.13'}$$

<<Problem 4-28-b>> Phase equilibria of polymer blend (P_1/P_2) (II): Critical parameters for monodisperse polymer/ monodisperse polymer

Scott is probably the first who carried out a theoretical study on phase equilibria of polymer solutions consisting of two kinds of polymer with different chemical compositions (polymer 1 and polymer 2), without solvent (i.e., quasibinary polymer mixture). He derived, based on Flory-Huggins solution theory, relationships giving the chemical potentials of monodisperse polymer 1 and monodisperse polymer 2, $\Delta\mu_X$ and $\Delta\mu_Y$:

$$\Delta\mu_X = RT[\ln\phi_1 + (1-X/Y)\phi_2 + X\chi_{12}\phi_2^2] \tag{4.28.15a}$$

$$\Delta\mu_Y = RT[\ln\phi_2 + (1-Y/X)\phi_1 + Y\chi_{12}\phi_1^2] \tag{4.28.15b}$$

where χ_{12} is the thermodynamic interaction parameter between polymers 1 and 2, X and Y are the degree of polymerization, DP (in a strict sense, the molecular volume ratio of the polymer and the lattice unit (the polymer segment)), and ϕ_1 and ϕ_2 are the volume fractions of polymers 1 and 2 ($\phi_1 + \phi_2 = 1$). Derive the equation for spinodal curve (SC) and the neutral equilibrium condition for the above system and derive the equations for χ_{12}, ϕ_1 and ϕ_2 at the critical solution point (CSP).

Answer

The spinodal curve and the neutral equilibrium condition are given by $\partial\Delta\mu_X/\partial\phi_1=0$ and $\partial^2\Delta\mu_X/\partial\phi_1^2=0$ (or $\partial\Delta\mu_Y/\partial\phi_2=0$ and $\partial^2\Delta\mu_Y/\partial\phi_2^2=0$) and finally we obtain

$$X\phi_1 + Y\phi_2 - 2XY\chi_{12}\phi_1\phi_2 = 0 \tag{4.28.16}$$

for SC and

$$X - Y + 2XY\chi_{12}(\phi_1 - \phi_2) = 0 \tag{4.28.17}$$

for the neutral equilibrium condition. At the critical solution point (CSP), both Eqs. (4.28.16) and (4.28.17) should be satisfied concurrently and χ_{12}, ϕ_1 and ϕ_2 at CSP are given by

$$\chi_{12}^C = 1/2(X^{-1/2} + Y^{-1/2})^2 \tag{4.28.18}$$

$$\phi_1^C = Y^{1/2}/(X^{1/2} + Y^{1/2}) \tag{4.28.19}$$

$$\phi_2^c = X^{1/2}/(X^{1/2} + Y^{1/2}) \tag{4.28.20}$$

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* Scott predicted that values of χ_{12} for these systems are several digits smaller than those for a mixture of two low molecular weight liquids (χ_{12}~2.0) and those for polymer-solvent systems (χ_{12}~0.5) (See R. L. Scott, *J. Chem. Phys.* **17**, 268 (1949)). An attempt to generalize CSP equations (Eqs. (4.28.18)-(4.28.20)) for two monodisperse polymer mixture to the case of multicomponent polymer 1/ multicomponent polymer 2 systems was made by Koningsveld et al. (See R. Koningsveld, H. A. G. Chermin and M. Gordon, *Proc. Roy. Soc. London* **A 319**, 331 (1970)). They derived the equations of spinodal and neutral equilibrium conditions (Eqs. (12) and (13) in their paper) for systems of multicomponent polymer 1/ multicomponent polymer 2/ single solvent. As Kamide et al. pointed out, they did not show the detailed mathematical derivation of the equations. Koningsveld et al. described that the spinodal condition for the multicomponent polymer 1/ multicomponent polymer 2 system was derived as Eq. (23) of their paper after multiplying Eq. (12) of their paper by ϕ_0 and reducing ϕ_0 to zero. But we should first define the Gibbs free energy of mixing ΔG (See Eq. (4.28.21)) and derive the equation straightforwardly from the determinant (Eq. (4.28.26)) constructed using ΔG. They described that the equation of the neutral equilibrium condition (Eq. (24) in their paper) for two different multicomponent polymers was derived using a method analogous to the spinodal condition. The equation should be rigorously derived from the determinant (Eq. (4.28.29)) of the neutral equilibrium condition. (See H. Shirataki, S. Matsuda and K. Kamide, *Brit. Polym. J.* **23**, 285 (1990))

* Compare Eq. (4.28.18) with χ_{12}^c for polymer solutions Eq.(4.12.13) or

$$\chi_{12}^c = \frac{\left(1+\sqrt{n}\right)^2}{2n}$$

χ_{12}^c of polymer blends is much smaller than that of polymer solutions (polymer in low molecular weight solvent). For example, if we put n_0=100 and n_1=100, Eq. (4.28.18) yields

$$\chi_{12}^c = \frac{\left(10+10\right)^2}{2\times 10^4} = 0.02$$

whereas, if we put n=100 in Eq. (4.12.13), we have

$$\chi_{12}^{c}=\frac{(1+10)^2}{2\times 10^2}=0.605$$

The former is one thirtieth of the latter.

<<Problem 4-28-c>> Phase equilibria of polymer blend (P_1/P_2) (III): Chemical potential for polydisperse polymer/ polydisperse polymer

The mean molar Gibbs free energy of mixing ΔG_{mix} for a multicomponent polymer 1/multicomponent polymer 2 system is given by

$$\Delta G_{mix}=RTL\left[\sum_{i=1}^{m_1}\frac{\phi_{X_i}}{X_i}\ln\phi_{X_i}+\sum_{j=1}^{m_2}\frac{\phi_{Y_j}}{Y_j}\ln\phi_{Y_j}+\chi_{12}\phi_1\phi_2\right] \qquad (4.28.21)$$

where L is the total number of lattice site ($\equiv\Sigma_i X_i N_{Xi}+\Sigma_j Y_j N_{Yj}$; N_{Xi} and N_{Yj} are the numbers of X_i-mer of polymer 1 and that of Y_j-mer of polymer 2, respectively), m_1 and m_2 are the total numbers of the components consisting polymer 1 and polymer 2, ϕ_{Xi} is the volume fraction of X_i-mer of multicomponent polymer 1, ϕ_{Yj} is the volume fraction of Y_j-mer of multicomponent polymer 2, and ϕ_1 and ϕ_2 are the total volume fractions of polymer 1 and polymer 2 as defined by the relations $\phi_1=\Sigma_i\phi_{Xi}$ and $\phi_2=\Sigma_j\phi_{Yj}$. The first and the second terms in the right-hand side of Eq. (4.28.21) are the combinatory terms and the third term is the term relating to the mutual thermodynamic interaction. Derive the **equation for the chemical potentials of X_i-mer and Y_j-mer, $\Delta\mu_{Xi}$** and $\Delta\mu_{Yj}$.

Answer

Differentiation of Eq. (4.28.21) with respect to N_{Xi} and N_{Yj} gives rise to

$$\Delta\mu_{X_i}=RT[\ln\phi_{X_i}-(X_i-1)+X_i\left(1-\frac{1}{X_n}\right)\phi_1+X_i\left(1-\frac{1}{Y_n}\right)\phi_2+X_i\chi_{12}\phi_2^2] \qquad (4.28.22)$$

$$\Delta\mu_{Y_j}=RT[\ln\phi_{Yj}-(Y_j-1)+Y_j\left(1-\frac{1}{X_n}\right)\phi_1+Y_j\left(1-\frac{1}{Y_n}\right)\phi_2+Y_j\chi_{12}\phi_1^2] \qquad (4.28.23)$$

where X_n and Y_n are the number-average X and Y (i.e., the number-average DP of the original polymers). In deriving Eqs. (4.28.22) and (4.28.23), we assumed that, first the molar volume of the segment of polymer 1 is the same as that of polymer 2; secondly, polymer 1 and polymer 2 are volumetrically additive; and thirdly, the densities of polymer 1 and polymer 2 are the same (i.e., unity). Note that Eqs. (4.28.22) and (4.28.23) are symmetrical with respect to the exchange of polymer 1 and polymer 2. When both polymer 1 and polymer 2 are monodisperse (i.e., single component), Eqs. (4.28.22) and (4.28.23) straightforwardly reduce to Eqs (4.28.15a) and (4.28.15b), respectively.

<<Problem 4-28-d>> Phase equilibria of polymer blend (P_1/P_2) (IV): Critical condition for polydisperse polymer/ polydisperse polymer

The equations of spinodal and neutral equilibrium conditions for a multicomponent polymer 1 and multicomponent polymer 2 system are expressed in the form:

$$\sum_{i=1}^{m_1}\frac{1}{M_i}+\sum_{j=1}^{m_2}\frac{1}{N_j}+(N-M)\left(\sum_{i=1}^{m_1}\frac{1}{M_i}\right)\left(\sum_{j=1}^{m_2}\frac{1}{N_j}\right)=0 \qquad (4.28.24)$$

$$\left(\sum_{i=1}^{m_1}\frac{W_{X_i}}{M_i}\right)\left(\sum_{i=1}^{m_1}\frac{1}{M_i}\right)^{-1}-\left(\sum_{j=1}^{m_2}\frac{W_{Y_j}}{N_j}\right)\left(\sum_{j=1}^{m_2}\frac{1}{N_j}\right)^{-1}=0 \qquad (4.28.25)$$

Derive Eqs. (4.28.24) and (4.28.25).

Answer

The thermodynamic requirement for spinodal is that the second variation of Gibbs free energy of mixing is always zero and this requirement can be described for multicomponent polymer 1/multicomponent polymer 2 systems as the spinodal condition of $(m_1-1+m_2)\mathrm{x}(m_1-1+m_2)$ determinant:

$$|\Delta G_V| = \begin{vmatrix} \Delta G_{VX_2X_2} & \Delta G_{VX_2X_3} & \cdots & \Delta G_{VX_2X_{m1}} & \Delta G_{VX_2Y_1} & \Delta G_{VX_2Y_2} & \cdots & \Delta G_{VX_2Y_{m2}} \\ \Delta G_{VX_3X_2} & \Delta G_{VX_3X_3} & \cdots & \Delta G_{VX_3X_{m1}} & \Delta G_{VX_3Y_1} & \Delta G_{VX_3Y_2} & \cdots & \Delta G_{VX_3Y_{m2}} \\ \vdots & \vdots & \cdots & \vdots & \vdots & \vdots & \cdots & \vdots \\ \Delta G_{VX_{m1}X_2} & \Delta G_{VX_{m1}X_3} & \cdots & \Delta G_{VX_{m1}X_{m1}} & \Delta G_{VX_{m1}Y_1} & \Delta G_{VX_{m1}Y_2} & \cdots & \Delta G_{VX_{m1}Y_{m2}} \\ \Delta G_{VY_1X_2} & \Delta G_{VY_1X_3} & \cdots & \Delta G_{VY_1X_{m1}} & \Delta G_{VY_1Y_1} & \Delta G_{VY_1Y_2} & \cdots & \Delta G_{VY_1Y_{m2}} \\ \Delta G_{VY_2X_2} & \Delta G_{VY_2X_3} & \cdots & \Delta G_{VY_2X_{m1}} & \Delta G_{VY_2Y_1} & \Delta G_{VY_2Y_2} & \cdots & \Delta G_{VY_2Y_{m2}} \\ \vdots & \vdots & \cdots & \vdots & \vdots & \vdots & \cdots & \vdots \\ \Delta G_{VY_{m2}X_2} & \Delta G_{VY_{m2}X_3} & \cdots & \Delta G_{VY_{m2}X_{m1}} & \Delta G_{VY_{m2}Y_1} & \Delta G_{VY_{m2}Y_2} & \cdots & \Delta G_{VY_{m2}Y_{m2}} \end{vmatrix} = 0 \tag{4.28.26}$$

Here, we employed the Gibbs free energy change of mixing per unit volume of the solution, ΔG_v, defined by

$$\Delta G_V = \sum_{i=1}^{m_1} \phi_{X_i} \left(\frac{\Delta\mu_{X_i}}{X_i V_0} \right) + \sum_{j=1}^{m_2} \phi_{Y_j} \left(\frac{\Delta\mu_{Y_j}}{Y_j V_0} \right) \tag{4.28.27}$$

The second-order partial derivative of ΔG_V is defined by

$$\Delta G_{VXiYj} = \left(\frac{\partial^2 \Delta G_V}{\partial \phi_{X_i} \partial \phi_{Y_j}} \right)_{T,P,\phi_k} \tag{4.28.28}$$

$$(i = 2,3,\ldots,m_1 ; j = 1,2,\ldots,m_2 ; k \neq X_i , Y_j)$$

where the subscripts T, P and ϕ_k indicate that the differentiation is carried out at constant temperature, pressure and volume fraction (except for X_i-mer and Y_j-mer), respectively. As compared with the determinant giving spinodal condition for multicomponent polymer 1/ multicomponent polymer 2/ single solvent systems, the term $\Delta G_{\mathrm{v}X_1X_1}$ is dropped and the matrix starts with X_2 in Eq. (4.28.26), making the calculation somewhat complicated (See Eq. (10) in K. Kamide, S. Matsuda and H. Shirataki, *Polym. J.* **20**, 949 (1988)). At the critical solution point (CSP), in addition to Eq. (4.28.26), it is simultaneously needed that the third variation of Gibbs free energy change is also zero; in other words, the neutral equilibrium condition Eq. (4.28.29) should be satisfied.

$$|\Delta G'| = \begin{vmatrix} \frac{\partial|\Delta G_{\mathrm{v}}|}{\partial\phi_{X_2}} & \frac{\partial|\Delta G_{\mathrm{v}}|}{\partial\phi_{X_3}} & \cdots & \frac{\partial|\Delta G_{\mathrm{v}}|}{\partial\phi_{X_{m1}}} & \frac{\partial|\Delta G_{\mathrm{v}}|}{\partial\phi_{Y_1}} & \frac{\partial|\Delta G_{\mathrm{v}}|}{\partial\phi_{Y_2}} & \cdots & \frac{\partial|\Delta G_{\mathrm{v}}|}{\partial\phi_{Y_{m2}}} \\ \Delta G_{\mathrm{v}X_3X_2} & \Delta G_{\mathrm{v}X_3X_3} & \cdots & \Delta G_{\mathrm{v}X_3X_{m1}} & \Delta G_{\mathrm{v}X_3Y_1} & \Delta G_{\mathrm{v}X_3Y_2} & \cdots & \Delta G_{\mathrm{v}X_3Y_{m2}} \\ \vdots & \vdots & \cdots & \vdots & \vdots & \vdots & \cdots & \vdots \\ \Delta G_{\mathrm{v}X_{m1}X_2} & \Delta G_{\mathrm{v}X_{m1}X_3} & \cdots & \Delta G_{\mathrm{v}X_{m1}X_{m1}} & \Delta G_{\mathrm{v}X_{m1}Y_1} & \Delta G_{\mathrm{v}X_{m1}Y_2} & \cdots & \Delta G_{\mathrm{v}X_{m1}Y_{m2}} \\ \Delta G_{\mathrm{v}Y_1X_2} & \Delta G_{\mathrm{v}Y_1X_3} & \cdots & \Delta G_{\mathrm{v}Y_1X_{m1}} & \Delta G_{\mathrm{v}Y_1Y_1} & \Delta G_{\mathrm{v}Y_1Y_2} & \cdots & \Delta G_{\mathrm{v}Y_1Y_{m2}} \\ \Delta G_{\mathrm{v}Y_2X_2} & \Delta G_{\mathrm{v}Y_2X_3} & \cdots & \Delta G_{\mathrm{v}Y_2X_{m1}} & \Delta G_{\mathrm{v}Y_2Y_1} & \Delta G_{\mathrm{v}Y_2Y_2} & \cdots & \Delta G_{\mathrm{v}Y_2Y_{m2}} \\ \vdots & \vdots & \cdots & \vdots & \vdots & \vdots & \cdots & \vdots \\ \Delta G_{\mathrm{v}Y_{m2}X_2} & \Delta G_{\mathrm{v}Y_{m2}X_3} & \cdots & \Delta G_{\mathrm{v}Y_{m2}X_{m1}} & \Delta G_{\mathrm{v}Y_{m2}Y_1} & \Delta G_{\mathrm{v}Y_{m2}Y_2} & \cdots & \Delta G_{\mathrm{v}Y_{m2}Y_{m2}} \end{vmatrix} = 0 \qquad (4.28.29)$$

In Eq. (4.28.29), the term of partial derivative of ΔG_{v} with respect to ϕ_{X_1} is dropped and this also makes the calculation tedious. Substitution of Eqs. (4.28.22) and (4.28.23) into Eq. (4.28.27) leads to

$$\Delta G_v = \left(\frac{RT}{V_0}\right)\left[\sum_{i=1}^{m_1}\frac{\phi_{X_i}\ln\phi_{X_i}}{X_i} + \sum_{j=1}^{m_2}\frac{\phi_{Y_j}\ln\phi_{Y_j}}{Y_j} + \chi_{12}\phi_1\phi_2\right] \tag{4.28.30}$$

From Eqs. (4.28.28) and (4.28.30), we obtain

$$\left(\frac{V_0}{RT}\right)\Delta G_{vkl} = \frac{1}{X_1\phi_{X_1}} \equiv M \qquad (\text{for } k \neq l \quad (k,l) = (X_i, X_j)) \tag{4.28.31a}$$

$$\left(\frac{V_0}{RT}\right)\Delta G_{vkl} = \frac{1}{X_1\phi_{X_1}} - 2\chi_{12} \equiv N \qquad (\text{for } k \neq l \quad (k,l) = (Y_i, Y_j)) \tag{4.28.31b}$$

$$\left(\frac{V_0}{RT}\right)\Delta G_{vkl} = \frac{1}{X_1\phi_{X_1}} \equiv M \qquad (\text{for } k \neq l \quad (k,l) = (X_i, Y_j) \text{ or } (Y_i, Y_j)) \tag{4.28.31c}$$

$$\left(\frac{V_0}{RT}\right)\Delta G_{vkl} = \frac{1}{X_1\phi_{X_1}} + \frac{1}{X_i\phi_{X_i}} \equiv M + M_i \qquad (\text{for } k = l = X_i) \tag{4.28.31d}$$

$$\left(\frac{V_0}{RT}\right)\Delta G_{vkl} = \frac{1}{X_1\phi_{X_1}} - 2\chi_{12} + \frac{1}{Y_j\phi_{Y_j}} \equiv N + N_j \qquad (\text{for } k = l = Y_j) \tag{4.28.31e}$$

Combining Eqs. (4.28.31a)-(4.28.31e) with Eq. (4.28.26), we finally obtain

$$|\Delta G_V| = \left(\frac{RT}{V_0}\right)^{m1+m2-1}$$

$$\times\left|\begin{array}{cccc|cccc} M+M_2 & M & \cdots & M & M & M & \cdots & M \\ M & M+M_3 & \cdots & M & M & M & \cdots & M \\ \vdots & \vdots & & \vdots & \vdots & \vdots & & \vdots \\ M & M & \cdots & M+M_{m1} & M & M & \cdots & M \\ \hline M & M & \cdots & M & N+N_1 & N & \cdots & N \\ M & M & \cdots & M & N & N+N_2 & \cdots & N \\ \vdots & \vdots & & \vdots & \vdots & \vdots & & \vdots \\ M & M & \cdots & M & N & N & \cdots & N+N_{m2} \end{array}\right|$$

$$\begin{aligned} &=\left(\frac{RT}{V_0}\right)^{m1+m2-1}\left(\prod_{i=1}^{m1}M_i\right)\left(\prod_{j=1}^{m2}N_j\right) \\ &\times\left[\sum_{i=1}^{m1}\frac{1}{M_i}+\sum_{j=1}^{m2}\frac{1}{N_j}+(N-M)\left(\sum_{i=1}^{m1}\frac{1}{M_i}\right)\left(\sum_{j=1}^{m2}\frac{1}{N_j}\right)\right]=0 \end{aligned} \tag{4.28.32}$$

Similarly, combination of Eqs. (4.28.31a)-(4.28.31e) with Eq. (4.28.29) yields

$$\left|\Delta G_v{}'\right|=\left(\frac{RT}{V_0}\right)^{m1+m2-1}$$

$$\left|\begin{array}{cccc|cccc} W_{X_2} & W_{X_3} & \cdots & W_{X_{m1}} & W_{Y_1} & W_{Y_2} & \cdots & W_{Y_{m2}} \\ \hline M & M+M_3 & \cdots & M & M & M & \cdots & M \\ \vdots & \vdots & & \vdots & \vdots & \vdots & & \vdots \\ M & M & \cdots & M+M_{m1} & M & M & \cdots & M \\ \hline M & M & \cdots & M & N+N_1 & N & \cdots & N \\ M & M & \cdots & M & N & N+N_2 & \cdots & N \\ \vdots & \vdots & & \vdots & \vdots & \vdots & & \vdots \\ M & M & \cdots & M & N & N & \cdots & N+N_{m2} \end{array}\right|$$

$$\begin{aligned} &=\left(\frac{RT}{V_0}\right)^{m1+m2-2}\frac{1}{M_2}\left(\prod_{i=1}^{m1}M_i\right)\left(\prod_{j=1}^{m2}N_j\right)\times\left(\sum_{j=1}^{m2}\frac{1}{N_j}\right)\left[\left(\sum_{i=1}^{m1}\frac{W_{Xi}}{M_i}\right)\left(\sum_{i=1}^{m1}\frac{1}{M_i}\right)^{-1}\right. \\ &\qquad\left.-\left(\sum_{j=1}^{m2}\frac{W_{Yj}}{N_j}\right)\left(\sum_{j=1}^{m2}\frac{1}{N_j}\right)^{-1}\right]=0 \end{aligned} \tag{4.28.33}$$

Here, W_{Xi} and W_{Yj} are given by

$$W_{X_i} \equiv \left(\frac{\partial|\Delta G_v|}{\partial\phi_{X_i}}\right)_{T,P,\phi k} \qquad (k \neq X_i, k = X_1, \cdots, X_{m1}, Y_1, \cdots, Y_{m2}) \tag{4.28.34a}$$

$$W_{Y_j} \equiv \left(\frac{\partial|\Delta G_v|}{\partial\phi_{Y_j}}\right)_{T,P,\phi k} \qquad (k \neq Y_j, k = X_1, \cdots, X_{m1}, Y_1, \cdots, Y_{m2}) \tag{4.28.34b}$$

From Eqs. (4.28.32) and (4.28.33), Eqs. (4.28.24) and (4.28.25) are derived.

<<Problem 4-28-e>> Phase equilibria of polymer blend (P_1/P_2) (V): Critical condition for polydisperse polymer/ polydisperse polymer

Express all the parameters in Eqs. (4.28.24) and (4.28.25) by using Eqs. (4.28.31.a)-(4.28.31e), (4.28.34a) and (4.28.34b) in terms of experimentally determinable physical quantities such as volume fraction, average DP and χ_{12}.

Answer

We finally obtain

$$\frac{1}{\phi_1 X_w^0} + \frac{1}{\phi_2 Y_w^0} - 2\chi_{12} = 0 \tag{4.28.35}$$

$$\frac{X_z^0}{(\phi_1 X_w^0)^2} - \frac{Y_z^0}{(\phi_2 Y_w^0)^2} = 0 \tag{4.28.36}$$

<<Problem 4-28-f>> Phase equilibria of polymer blend (P_1/P_2) (VI): Critical parameters for polydisperse polymer/ polydisperse polymer

By solving simultaneous equations, Eqs. (4.28.35) and (4.28.36), and using the relationship $\phi_1+\phi_2=1$ with given values of X_w^0, Y_w^0, X_z^0 and Y_z^0 of the original polymers, derive the expression for the **critical values for χ_{12} and ϕ_1^0 and ϕ_2^0.**

Answer

We obtain

$$\chi_{12}^{C}=\frac{1}{2X_{w}^{0}Y_{w}^{0}}\left(\frac{X_{w}^{0}}{\left(X_{z}^{0}\right)^{1/2}}+\frac{Y_{w}^{0}}{\left(Y_{z}^{0}\right)^{1/2}}\right)\left[\left(X_{z}^{0}\right)^{1/2}+\left(Y_{z}^{0}\right)^{1/2}\right] \qquad (4.28.37)$$

$$\phi_{1}^{C}=\left[\frac{Y_{w}^{0}}{\left(Y_{z}^{0}\right)^{1/2}}\right]\Bigg/\left[\frac{X_{w}^{0}}{\left(X_{z}^{0}\right)^{1/2}}+\frac{Y_{w}^{0}}{\left(Y_{z}^{0}\right)^{1/2}}\right] \qquad (4.28.38)$$

$$\phi_{2}^{C}=\left[\frac{X_{w}^{0}}{\left(X_{z}^{0}\right)^{1/2}}\right]\Bigg/\left[\frac{X_{w}^{0}}{\left(X_{z}^{0}\right)^{1/2}}+\frac{Y_{w}^{0}}{\left(Y_{z}^{0}\right)^{1/2}}\right] \qquad (4.28.39)$$

Thus, we can calculate these values analytically. In the case when both polymer 1 and polymer 2 are single-component polymers, Eqs. (4.28.35)-(4.28.39) reduce to the well known equations (4.28.16)-(4.28.20), originally derived by Scott.

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* We can take into consideration the concentration (in this case compositional) dependence of χ_{12}, given in the form

$$\chi_{12}=\chi_{12}^{0}\left[1+\sum_{t=1}^{n_t}\left(p_{1,t}\phi_1^{t}+p_{2,t}\phi_2^{t}\right)\right] \qquad (4.28.40)$$

where t=1,2,...n_t, and n_t is the highest order number of concentration dependence parameter taken into account in the calculation. Eq. (4.28.40) is symmetrical with respect to the exchange of polymer 1 and polymer 2. The coefficient $\chi_{12}{}^{0}$ in Eq. (4.28.40) is a parameter, independent of ϕ_1 and ϕ_2 and inversely proportional to T. The coefficients $p_{1,t}$ and $p_{2,t}$ are the parameters of concentration dependence. After combining Eq. (4.28.21) with Eq. (4.28.40), we can obtain $\Delta\mu_{Xi}$ and $\Delta\mu_{Yj}$ in the case when χ_{12} is concentration-dependent in a similar manner as the derivation of Eqs. (4.28.22) and (4.28.23).

$$\Delta\mu_{Xi}=\left(\frac{\partial\Delta G}{\partial N_{Xi}}\right)_{T,P,N_{Xk}} \qquad (k=1,\cdots,m_1\,;k\neq i)$$

$$=RT\Big[\ln\phi_{Xi}-(X_i-1)+X_i\left(1-\frac{1}{X_n}\right)\phi_1+X_i\left(1-\frac{1}{Y_n}\right)\phi_2+\chi_{12}^{0}X_i\phi_2^{2}$$

$$\times\left\{1+\sum_{t=1}^{n_t}\left(p_{1,t}\phi_1^{t}+p_{2,t}\phi_2^{t}\right)+\sum_{t=1}^{n_t}t\left(p_{1,t}\phi_1^{t-1}-p_{2,t}\phi_2^{t-1}\right)\phi_1\right\}$$

$$(i=1,\cdots,m_1) \tag{4.28.41}$$

$$\Delta\mu_{Xj} = \left(\frac{\partial \Delta G}{\partial N_{Yj}}\right)_{T,P,N_{Yk}} \qquad (k = 1,\cdots,m_2\,;k \neq j)$$

$$= RT\Big[\ln\phi_{Yj} - (Y_j - 1) + Y_j\left(1 - \frac{1}{X_n}\right)\phi_1 + Y_j\left(1 - \frac{1}{Y_n}\right)\phi_2 + \chi_{12}^0 Y_j \phi_2^2$$

$$\times\left\{1 + \sum_{t=1}^{n_t}\left(p_{1,t}\phi_1^t + p_{2,t}\phi_2^t\right) + \sum_{t=1}^{n_t} t\left(p_{2,t}\phi_2^{t-1} - p_{1,t}\phi_1^{t-1}\right)\phi_2\right\}$$

$$(i=1,\cdots,m_1) \tag{4.28.42}$$

Substitution of Eqs. (4.28.41) and (4.28.42) into Eq. (4.28.27) yields ΔG_v in the form

$$\Delta G_v = \left(\frac{RT}{V_0}\right)\Bigg[\sum_{i=1}^{m_1}\frac{\phi_{Xi}}{X_i}\ln\phi_{Xi} + \sum_{j=1}^{m_2}\frac{\phi_{Yj}}{Y_j}\ln\phi_{Yj} + \chi_{12}^0$$

$$\times\left\{1 + \sum_{t=1}^{n_t}\left(p_{1,t}\phi_1^t + p_{2,t}\phi_2^t\right)\right\}\phi_1\phi_2\Bigg]$$

$$= \left(\frac{RT}{V_0}\right)\left[\sum_{i=1}^{m_1}\frac{\phi_{Xi}}{X_i}\ln\phi_{Xi} + \sum_{j=1}^{m_2}\frac{\phi_{Yj}}{Y_j}\ln\phi_{Yj} + \chi_{12}\phi_1\phi_2\right] \tag{4.28.43}$$

From Eqs. (4.28.43) and (4.28.28), we obtain

$$\left(\frac{V_0}{RT}\right)\Delta G_{vkl} = \frac{1}{X_l\phi_{Xl}} \equiv M \tag{4.28.44a}$$

$$(\text{for } k \neq l \quad (k,l) = (X_i, X_j))$$

$$\left(\frac{V_0}{RT}\right)\Delta G_{vkl} = \frac{1}{X_l\phi_{Xl}} - 2\chi_{12} + 2(1 - 2\phi_2)\frac{\partial \chi_{12}}{\partial \phi_2}$$

$$+ \phi_2(1 - \phi_2)\frac{\partial^2 \chi_{12}}{\partial \phi_2^2} \equiv N \tag{4.28.44b}$$

$$(\text{for } k \neq l \quad (k,l) = (Y_i, Y_j))$$

$$\left(\frac{V_0}{RT}\right)\Delta G_{vkl} = \frac{1}{X_l\phi_{Xl}} \equiv M \tag{4.28.44c}$$

$$(\text{for } k \neq l \quad (k,l) = (X_i, Y_j) \text{ or } (Y_i, X_j))$$

$$\left(\frac{V_0}{RT}\right)\Delta G_{vkl} = \frac{1}{X_l\phi_{Xl}} + \frac{1}{X_i\phi_{Xi}} \equiv M + M_i \qquad (\text{for } k = l = X_i) \tag{4.28.44d}$$

$$\left(\frac{V_0}{RT}\right)\Delta G_{vkl} = \frac{1}{X_l\phi_{Xl}} - 2\chi_{12} + \frac{1}{Y_j\phi_{Yj}} + 2(1-2\phi_2)\frac{\partial\chi_{12}}{\partial\phi_2} + \phi_2(1-\phi_2)\frac{\partial^2\chi_{12}}{\partial\phi_2^2} \equiv N + N_j \qquad (\text{for } k = l = Y_j) \tag{4.28.44e}$$

Substitution of Eq. (4.28.30) into Eqs. (4.28.34a) and (4.28.34b) gives W_{Xi} and W_{Yj}, respectively:

$$W_{Xi} \equiv \left(\frac{\partial|\Delta G_v|}{\partial\phi_{X_i}}\right)_{T,P,\phi_k} = \left(\frac{RT}{V_0}\right)^{m1+m2-1}\left(\prod_{i=1}^{m1}M_i\right) \times \left(\prod_{j=1}^{m2}N_j\right)\left(-X_l + X_i\right)\left[1 + (N-M)\sum_{j=1}^{m2}\frac{1}{N_j}\right]$$
$$(k \neq X_i, k = X_1,\cdots,X_{m1}, Y_1,\cdots,Y_{m2}) \tag{4.28.45a}$$

$$W_{Yj} \equiv \left(\frac{\partial|\Delta G_v|}{\partial\phi_{Yj}}\right)_{T,P,\phi_k} = \left(\frac{RT}{V_0}\right)^{m1+m2-1}\left(\prod_{i=1}^{m1}M_i\right)\times\left(\prod_{j=1}^{m2}N_j\right) \times\left[-X_l\left\{1 + (N-M)\sum_{j=1}^{m2}\frac{1}{N_j}\right\} + Y_j\left\{1 + (N-M)\sum_{i=1}^{m1}\frac{1}{M_i}\right\} + \frac{\partial(N-M)}{\partial\phi_{Yj}}\left(\sum_{i=1}^{m1}\frac{1}{M_i}\right)\left(\sum_{j=1}^{m2}\frac{1}{N_j}\right)\right]$$
$$(k \neq Y_j, k = X_1,\cdots,X_{m1}, Y_1,\cdots,Y_{m2}) \tag{4.28.45b}$$

By substituting Eqs. (4.28.44a)-(4.28.44e) into Eq. (4.28.24) and substituting Eqs. (4.28.44a)-(4.28.44e) and (4.28.45a)-(4.28.45b) into Eq. (4.28.25), we obtain the equations for spinodal and neutral equilibrium conditions:

$$\frac{1}{\phi_1 X_w^0} + \frac{1}{\phi_2 Y_w^0} - 2\chi_{12} + 2(\phi_1 - \phi_2)\frac{\partial \chi_{12}}{\partial \phi_2} + \phi_1 \phi_2 \frac{\partial^2 \chi_{12}}{\partial \phi_2^2} = 0 \tag{4.28.46}$$

$$\frac{X_z^0}{(\phi_1 X_w^0)^2} - \frac{Y_z^0}{(\phi_2 Y_w^0)^2} - 6\frac{\partial \chi_{12}}{\partial \phi_2} + 3(\phi_1 - \phi_2)\frac{\partial^2 \chi_{12}}{\partial \phi_2^2} + \phi_1 \phi_2 \frac{\partial^3 \chi_{12}}{\partial \phi_2^3} = 0 \tag{4.28.47}$$

We can calculate the differential term of χ_{12} in Eqs. (4.28.46) and (4.28.47) with using Eq. (4.28.40) to obtain the following equations:

$$\begin{aligned} &\frac{1}{\phi_1 X_w^0} + \frac{1}{\phi_2 Y_w^0} - 2\chi_{12}^0\left[1 + \sum_{t=1}^{n_t}\left(p_{1,t}\phi_1^t + p_{2,t}\phi_2^t\right)\right] \\ &-2(\phi_1 - \phi_2)\chi_{12}^0 \sum_{t=1}^{n_t} t\left(p_{1,t}\phi_1^{t-1} + p_{2,t}\phi_2^{t-1}\right) \\ &+\phi_1\phi_2\chi_{12}^0 \sum_{t=1}^{n_t} t(t-1)\left(p_{1,t}\phi_1^{t-2} + p_{2,t}\phi_2^{t-2}\right) = 0 \end{aligned} \tag{4.28.48}$$

$$\begin{aligned} &\frac{X_z^0}{\left(\phi_1 X_w^0\right)^2} - \frac{Y_z^0}{\left(\phi_2 Y_w^0\right)^2} + 6\chi_{12}^0 \sum_{t=1}^{n_t} t\left(p_{1,t}\phi_1^{t-1} - p_{2,t}\phi_2^{t-1}\right) \\ &+3(\phi_1 - \phi_2)\chi_{12}^0 \sum_{t=1}^{n_t} t(t-1)\left(p_{1,t}\phi_1^{t-2} - p_{2,t}\phi_2^{t-2}\right) \\ &-\phi_1\phi_2\chi_{12}^0 \sum_{t=1}^{n_t} t(t-1)(t-2)\left(p_{1,t}\phi_1^{t-3} + p_{2,t}\phi_2^{t-3}\right) = 0 \end{aligned} \tag{4.28.49}$$

Note that Eqs. (4.28.48) and (4.28.49)(and (4.28.46) and (4.28.47)) are symmetrical with respect to the exchange of polymer 1 and polymer 2. In the case when all the concentration-dependence parameters are zero (i.e., $p_{1,t}=p_{2,t}=0$; $t=1,\ldots,n_t$), Eq. (4.28.48) reduces to Eq. (4.28.35), and Eq. (4.28.49) to Eq. (4.28.36). We can calculate SC from Eq. (4.28.48) and CSP by solving simultaneous equations (4.28.48) and (4.28.49). Then, SC (i.e., χ_{12}^0 versus ϕ_1 (or ϕ_2) relation) can be calculated, using Eq. (4.28.48), from X_w^0, Y_w^0 and the concentration-dependence parameters. CSP (i.e., ϕ_1^c (or ϕ_2^c) and χ_{12}^c) can also be determined, using Eqs. (4.28.48) and (4.28.49), from X_w^0, X_z^0, Y_w^0, Y_z^0 and the concentration-dependence parameters.

*Koningsveld and Kleintjens expressed the Gibbs free energy of mixing in terms of g as follows:

$$\Delta G_{mix} = RTL\left[\sum_{i=1}^{m1}\frac{\phi_{Xi}}{X_i}\ln\phi_{Xi} + \sum_{j=1}^{m2}\frac{\phi_{Yj}}{Y_j}\ln\phi_{Yj} + g\phi_1\phi_2\right] \tag{4.28.21}$$

with

$$g = \sum_{t=0}^{n_t} g_t\phi_2^t = g_0 + g_1\phi_2 + g_2\phi_2^2 + \cdots + g_{nt}\phi_2^{nt} \tag{4.28.50}$$

Here, g_0 is a parameter depending on T alone and g_1, g_2,... g_{nt} are concentration-dependent but T- and ϕ_2-independent. Substituting Eq. (4.28.50) into χ_{12} in Eqs. (4.28.46) and (4.28.47), we obtain the spinodal and neutral equilibrium conditions, given in the framework of Koningsveld and Kleintjens expression in the forms

$$\begin{aligned}\frac{1}{\phi_1 X_w^0} + \frac{1}{\phi_2 Y_w^0} - 2\sum_{t=0}^{n_t} g_t\phi_2^t + 2(\phi_1 - \phi_2)\sum_{t=1}^{n_t} tg_t\phi_2^{t-1}\\ + \phi_1\phi_2\sum_{t=1}^{n_t} t(t-1)g_t\phi_2^{t-2} = 0\end{aligned} \tag{4.28.51}$$

$$\begin{aligned}\frac{1}{(\phi_1 X_w^0)^2} + \frac{1}{(\phi_2 Y_w^0)^2} - 6\sum_{t=1}^{n_t} tg_t\phi_2^{t-1} + 3(\phi_1 - \phi_2)\\ \times\sum_{t=1}^{n_t} t(t-1)g_t\phi_2^{t-2} + \phi_1\phi_2\sum_{t=1}^{n_t} t(t-1)(t-2)g_t\phi_2^{t-3} = 0\end{aligned} \tag{4.28.52}$$

Using these equations, we can also determine SC and CSP in the same manner as in the case of using Eqs. (4.28.48) and (4.28.49). Differing from χ_{12}, given by Eq. (4.28.40), g is expanded into a series of ϕ_2 alone and then is not symmetrical with respect to the exchange of polymer 1 and polymer 2. In addition, it is assumed that the expanded terms in Eq. (4.28.50) are independent of temperature. This is equivalent to an assumption that the third, fourth and higher order virial coefficients are absolutely temperature-independent. Therefore, in Koningsveld et al's theory it can be said that the concentration dependence of g was simplified under the sacrifice of the physical strictness. It follows that χ_{12}=g.

*To confirm the reliability of the theory of phase equilibria of multicomponent polymer 1/multicomponent polymer 2 systems (i.e., quasi-binary systems) and the method of computer experiment based on this theory (See H. Shirataki, S. Matsuda and K. Kamide, *Brit. Polym. J.* **23**, 285 (1990); *ibid.* **23**, 299 (1990); *Polym. Int.* **29**, 219 (1992)), CSP has been determined experimentally for the quasi-binary mixtures of poly(ethylene oxide) (M_w=647, M_w/M_n=1.15) and poly(propylene oxide) (M_w=2028, M_w/M_n=1.08 and M_w=2987, M_w/M_n=1.13). χ_{12} and the concentration dependence parameters for the above quasi-binary systems were determined and cloud point curve (CPC), phase volume ratio R and CSP values

Table 4-28 Comparison of experimental and calculated CSPs

System	polymers	ϕ_1^c(exp.)	ϕ_1^c(calc.)	T^{CSP}(exp.)/℃	T^{CSP}(calc.)/℃
A	E-600/P-2000	0.5875	0.5841	46.3	47.0
B	E-600/P-3000	0.613	0.6264	59.8	61.2

(See H.Shirataki and K.Kamide, *Polym.Int.* **34**,73(1994))

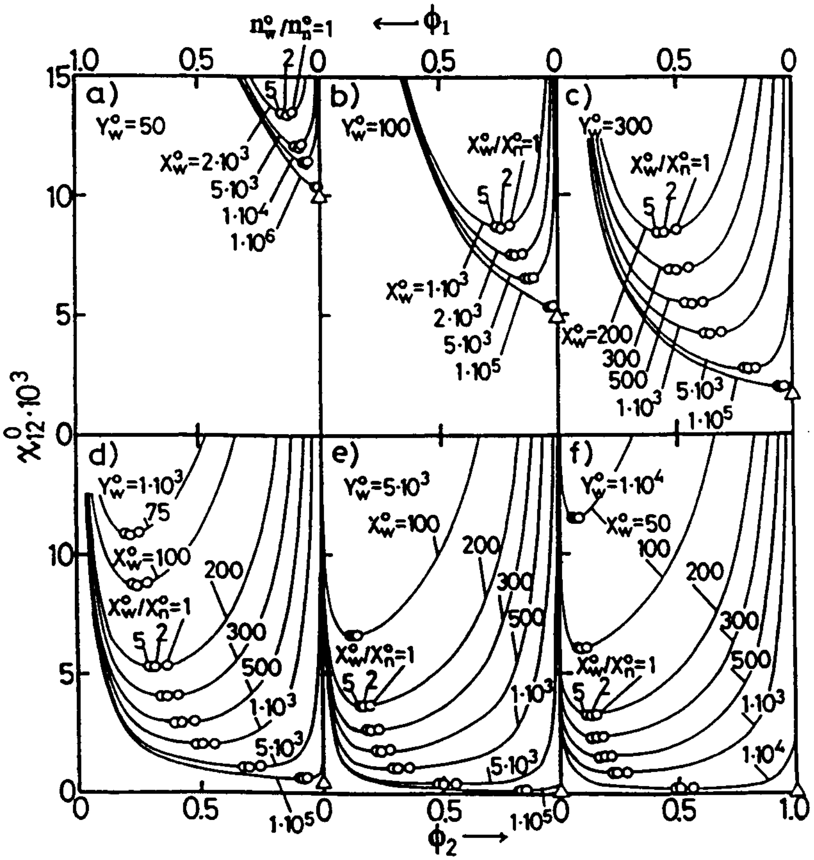

Fig. 4-28.1 Effects of molecular weight distribution and weight-average degree of polymerization of the original polymer 1 on SC and CSP: Original polymers 1 and 2,Schulz-Zimm type distribution; $Y_w^0/Y_n^0=2$, and (a) $Y_w^0=50$, (b) $Y_w^0=100$, (c) $Y_w^0=300$, (d) $Y_w^0=1x10^3$, (e) $Y_w^0=5x10^3$ and (f) $Y_w^0=1x10^4$; $p_{1,t}=p_{2,t}=0$; (○), CSP;(△), Flory θ point. (See H. Shirataki, S. Matsuda and K. Kamide, *Brit. Polym. J.* **23**, 285 (1990))

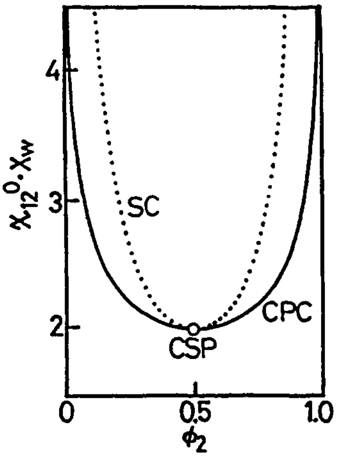

Fig. 4-28.2 Phase diagram of monodisperse polymer 1/monodisperse polymer 2 (X=Y) system with χ in Eq. (4.28.40) for $p_{1,u}=p_{2,u}=0$. Solid line and dotted line denote CPC and SC, respectively. The open circle denotes CSP. Coexistence curve (CC) coincides with CPC. (See H. Shirataki, S. Matsuda and K. Kamide, *Polym. Int.* **29**, 219 (1992))

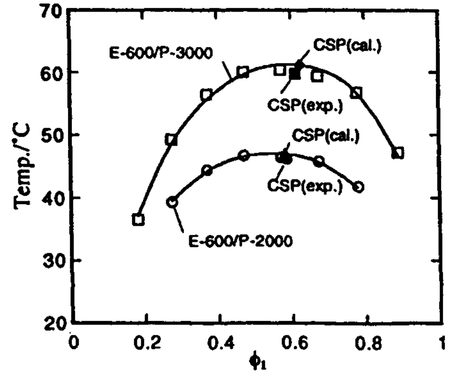

Fig. 4-28.3 Theoretical CPC and CSP for PEO/PPO systems. Solid lines, theoretical CPC with $p_{1,1}=-0.0917$ and $p_{1,2}=0.0022$ for E-600/P-2000, and with $p_{1,1}=-0.1120$ and $p_{1,2}=0.0027$ for E-600/P-3000; (□) and (○) experimental CPC for E-600/P-3000 and E-600/P-2000. (■) and (●) experimental CSP for E-600/P-3000 and E-600/P-2000. (◆) and (▲) theoretical CSP for E-600/P-3000 and E-600/P-2000. (See H. Shirataki and K. Kamide, *Polym. Int.* **34**, 73 (1994))

calculated on the basis of the theory are in good agreement with the values determined experimentally (See H. Shirataki, S. Matsuda and K. Kamide, *Brit. Polym. J.* **23**, 299 (1990)). Fig. 4-28.1 shows the calculated effects of average molecular weight and molecular weight distribution of the polymer on SC and CSP, and Fig. 4-28.2 shows the calculated phase diagram for monodisperse polymer blends. Figure 4-28.3 shows the experimental and theoretical CPCs and CSPs for the system A and B in Table 4-28. The full lines are the theoretical CPCs calculated taking into consideration the concentration dependence of χ_{12}. The theoretical CPCs are in excellent agreement with the actual experiments for both systems. The parameters in Eq. (4.28.40) were found to be $p_{1,1}=-0.0917$, $p_{1,2}=0.0022$, $a=-0.3125$ and $b=131.59$ for System A and $p_{1,1}=-0.1120$, $p_{1,2}=0.0027$, $a=-0.2045$ and $b=98.09$ for System B.

<<Problem 4-28-g>> Second-order derivatives of Gibbs free energy for ternary mixtures $P_2/S_1/S_0$, $P_2/P_1/S_0$ and $P_2/P_1/P_0$

Derive the **expression for L_{11}, L_{12} and L_{22}** in Eqs. (4.28.12) and (4.28.13)
(1) for the system solvent(0)/solvent(1)/polymer(2),
(2) for the system solvent(0)/polymer(1)/polymer(2),
(3) for the system polymer(0)/polymer(1)/polymer(2).
These are the cases for i,j=1,2 in the equations.

Answer

(1) Putting $n_0=1$ and $n_1=1$ in Eqs.(4.28.12) and (4.28.13), we have

$$L_{12} = L_{21} = \frac{1}{\phi_0} - \chi_{02} - \chi_{01} + \chi_{12} \tag{4.28.53}$$

$$L_{11} = \frac{1}{\phi_0} + \frac{1}{\phi_1} - 2\chi_{01} \tag{4.28.54}$$

$$L_{22} = \frac{1}{\phi_0} + \frac{1}{n_2\phi_2} - 2\chi_{02} \tag{4.28.55}$$

(2) Putting $n_0=1$ in Eqs.(4.28.12) and (4.28.13), we have

$$L_{12} = L_{21} = \frac{1}{\phi_0} - \chi_{02} - \chi_{01} + \chi_{12} \tag{4.28.56}$$

$$L_{11} = \frac{1}{\phi_0} + \frac{1}{n_1\phi_1} - 2\chi_{01} \tag{4.28.57}$$

$$L_{22} = \frac{1}{\phi_0} + \frac{1}{n_2\phi_2} - 2\chi_{02} \tag{4.28.58}$$

(3) From Eqs.(4.28.12) and (4.28.13), we have

$$L_{12} = L_{21} = \frac{1}{n_0\phi_0} - \chi_{02} - \chi_{01} + \chi_{12} \qquad (4.28.59)$$

$$L_{11} = \frac{1}{n_0\phi_0} + \frac{1}{n_1\phi_1} - 2\chi_{01} \qquad (4.28.60)$$

$$L_{22} = \frac{1}{n_0\phi_0} + \frac{1}{n_2\phi_2} - 2\chi_{02} \qquad (4.28.61)$$

* Spinodal condition is given by

$$|\Delta G_v| = \begin{vmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{vmatrix} = 0 \qquad (4.28.62)$$

Critical conditions are given by solving simultaneous equations of Eq. (4.28.62) and

$$\begin{vmatrix} \left(\dfrac{\partial|\Delta G_v|}{\partial\phi_1}\right)_{\phi_2} & \left(\dfrac{\partial|\Delta G_v|}{\partial\phi_2}\right)_{\phi_1} \\ L_{21} & L_{22} \end{vmatrix} = 0 \qquad (4.28.63)$$

<<Problem 4-29-a>> Spinodal condition for quasi-ternary system polydisperse polymer/ polydisperse polymer/ solvent ($P_2/P_1/S_0$)

Gibbs free energy of mixing ΔG_{mix} for quasi-ternary systems consisting of multicomponent polymers 1 and 2 in a single solvent is given, based on the Flory-Huggins lattice theory of dilute polymer solutions, by

$$\Delta G_{mix} = RTL\left[\phi_0 \ln\phi_0 + \sum_{i=1}^{m_1}\frac{\phi_{X_i}}{X_i}\ln\phi_{X_i} + \sum_{j=1}^{m_2}\frac{\phi_{Y_j}}{Y_j}\ln\phi_{Y_j} + \chi_{01}\phi_0\phi_1 + \chi_{02}\phi_0\phi_2 + \chi_{12}\phi_1\phi_2\right] \qquad (4.29.1)$$

where L is the total number of lattice points $\equiv N_0 + \Sigma_i X_i N_{Xi} + \Sigma_j Y_j N_{Yj}$, N_0, N_{Xi} and N_{Yj} the number of solvents, X_i-mer and Y_j-mer, respectively. The chemical potentials of solvent, polymer 1 (X_i-mer), and polymer 2 (Y_j-mer), $\Delta\mu_0$, $\Delta\mu_{Xi}$, and $\Delta\mu_{Yj}$, are directly derived from Eq. (4.29.1) as

$$\Delta\mu_0 = RT\left[\ln\phi_0 + \left(1-\frac{1}{X_n}\right)\phi_1 + \left(1-\frac{1}{Y_n}\right)\phi_2 + \chi_{01}\phi_1(1-\phi_0) + \chi_{02}\phi_2(1-\phi_0) - \chi_{12}\phi_1\phi_2\right] \tag{4.29.2}$$

$$\Delta\mu_{X_i} = RT\left[\ln\phi_{X_i} - (X_i - 1) + X_i\left(1-\frac{1}{X_n}\right)\phi_1 + X_i\left(1-\frac{1}{Y_n}\right)\phi_2 + X_i\{\chi_{12}\phi_2(1-\phi_1) + \chi_{01}\phi_0(1-\phi_1) - \chi_{02}\phi_0\phi_2\}\right]$$
$$(i = 1, \cdots, m_1) \tag{4.29.3}$$

$$\Delta\mu_{Y_j} = RT\left[\ln\phi_{Y_j} - (Y_j - 1) + Y_j\left(1-\frac{1}{X_n}\right)\phi_1 + Y_j\left(1-\frac{1}{Y_n}\right)\phi_2 + Y_j\{\chi_{12}\phi_1(1-\phi_2) + \chi_{02}\phi_0(1-\phi_2) - \chi_{01}\phi_0\phi_1\}\right]$$
$$(j = 1, \cdots, m_2) \tag{4.29.4}$$

Assume that (a) χ_{01}, χ_{02} and χ_{12} are independent of concentration and molecular weight of polymers, (b) the molar volume of solvent and the segment of polymers 1 and 2 are the same, (c) solvent, polymers 1 and 2 are volumetrically additive, and (d) the density of solvent is the same as that of polymers 1 and 2. Note that Eqs. (4.29.3) and (4.29.4) are strictly symmetrical with regards to the exchange of polymer 1 and polymer 2. Derive the **expression for the spinodal condition** for the Gibbs free energy of Eq. (4.29.1).

Answer

Thermodynamic requirement for the spinodal curve is that the second-order derivative of Gibbs free energy should always be zero on the curve and then the conditions of spinodal are given by the (m_1+m_2)x(m_1+m_2) determinant in the form:

$$|\Delta G_{V}|=$$

$$\begin{vmatrix} \Delta G_{VX_1X_1} & \Delta G_{VX_1X_2} & \cdots & \Delta G_{VX_1Xm_1} & \Delta G_{VX_1Y_1} & \Delta G_{VX_1Y_2} & \cdots & \Delta G_{VX_1Y_{m2}} \\ \Delta G_{VX_2X_1} & \Delta G_{VX_2X_2} & \cdots & \Delta G_{VX_2X_{m1}} & \Delta G_{VX_2Y_1} & \Delta G_{VX_2Y_2} & \cdots & \Delta G_{VX_2Y_{m2}} \\ \vdots & \vdots & & \vdots & \vdots & \vdots & & \vdots \\ \Delta G_{VX_{m1}X_1} & \Delta G_{VX_{m1}X_2} & \cdots & \Delta G_{VX_{m1}X_{m1}} & \Delta G_{VX_{m1}Y_1} & \Delta G_{VX_{m1}Y_2} & \cdots & \Delta G_{VX_{m1}Y_m} \\ \Delta G_{VY_1X_1} & \Delta G_{VY_1X_2} & \cdots & \Delta G_{VY_1Xm_1} & \Delta G_{VY_1Y_1} & \Delta G_{VY_1Y_2} & \cdots & \Delta G_{VY_1Ym_2} \\ \Delta G_{VY_2X_1} & \Delta G_{VY_2X_2} & \cdots & \Delta G_{VY_2Xm_1} & \Delta G_{VY_2Y_1} & \Delta G_{VY_2Y_2} & \cdots & \Delta G_{VY_2Ym_2} \\ \vdots & \vdots & & \vdots & \vdots & \vdots & & \vdots \\ \Delta G_{VY_{m2}X_1} & \Delta G_{VY_{m2}X_2} & \cdots & \Delta G_{VY_{m2}X_{m1}} & \Delta G_{VY_{m2}Y_1} & \Delta G_{VY_{m2}Y_2} & \cdots & \Delta G_{VYm_2Ym_2} \end{vmatrix} = 0 \tag{4.29.5}$$

Here ΔG_v is the Gibbs free energy of mixing per unit volume defined by

$$\Delta G_{V} = \phi_0\left(\frac{\Delta\mu_0}{V_0}\right) + \sum_{i=1}^{m_1}\phi_{X_i}\left(\frac{\Delta\mu_{X_i}}{X_iV_0}\right) + \sum_{j=1}^{m_2}\phi_{Y_j}\left(\frac{\Delta\mu_{Y_j}}{Y_jV_0}\right) \tag{4.29.6}$$

$$\Delta G_{Vkl} = \left(\frac{\partial^2\Delta G_V}{\partial\phi_k\partial\phi_l}\right)_{T,P,\phi_n} \qquad \left(k,l = X_1,X_2,\cdots,X_{m_1},Y_1,Y_2,\cdots,Y_{m_2};n \neq k,l\right) \tag{4.29.7}$$

ΔG_v can be rewritten by combination of Eqs. (4.29.2)-(4.29.4) and (4.29.6) as

$$\Delta G_V = \left(\frac{RT}{V_0}\right)\left[\phi_0 \ln\phi_0 + \sum_{i=1}^{m_1}\frac{\phi_{X_i}\ln\phi_{X_i}}{X_i} + \sum_{j=1}^{m_2}\frac{\phi_{Y_j}\ln\phi_{Y_j}}{Y_j} + \chi_{01}\phi_0\phi_1 + \chi_{02}\phi_0\phi_2 + \chi_{12}\phi_1\phi_2\right] \tag{4.29.8}$$

Substitution of Eq. (4.29.8) into Eq. (4.29.7) yields five types of derivatives of ΔG_{Vkl}:

$$\left(\frac{V_0}{RT}\right)\Delta G_{Vkl} = \frac{1}{\phi_0} - 2\chi_{01} \equiv M \quad \left(\text{for } k \neq l, (k,l) = (X_i, X_j)\right) \tag{4.29.9a}$$

$$\left(\frac{V_0}{RT}\right)\Delta G_{Vkl} = \frac{1}{\phi_0} - 2\chi_{02} \equiv N \quad \left(\text{for } k \neq l, (k,l) = \left(Y_i, Y_j\right)\right) \tag{4.29.9b}$$

$$\left(\frac{V_0}{RT}\right)\Delta G_{Vkl} = \frac{1}{\phi_0} + \chi_{12} - \chi_{01} - \chi_{02} \equiv K \quad \left(\text{for } k \neq l, (k,l) = \left(X_i, Y_j\right) \text{ or } \left(Y_j, X_i\right)\right) \tag{4.29.9c}$$

$$\left(\frac{V_0}{RT}\right)\Delta G_{Vkl} = \frac{1}{\phi_0} - 2\chi_{01} + \frac{1}{X_i\phi_{X_i}} \equiv M + M_i \quad \left(\text{for } k = l = X_i\right) \tag{4.29.9d}$$

$$\left(\frac{V_0}{RT}\right)\Delta G_{Vkl} = \frac{1}{\phi_0} - 2\chi_{02} + \frac{1}{Y_j\phi_{Y_j}} \equiv N + N_j \quad \left(\text{for } k = l = Y_j\right) \tag{4.29.9e}$$

Spinodal condition can be rewritten by substituting Eqs. (4.29.9a)-(4.29.9e) into Eq. (4.29.5) as

$$\left|\Delta G_V\right| = \left(\frac{RT}{V_0}\right)^{m_1+m_2} \times \left|\begin{array}{cccc|cccc} M+M_1 & M & \cdots & M & K & K & \cdots & K \\ M & M+M_2 & \cdots & M & K & K & \cdots & K \\ \vdots & \vdots & & \vdots & \vdots & \vdots & & \vdots \\ M & M & \cdots & M+M_{m_1} & K & K & \cdots & K \\ \hline K & K & \cdots & K & N+N_1 & N & \cdots & N \\ K & K & \cdots & K & N & N+N_2 & \cdots & N \\ \vdots & \vdots & & \vdots & \vdots & \vdots & & \vdots \\ K & K & \cdots & K & N & N & \cdots & N+N_{m_2} \end{array}\right| \tag{4.29.10}$$

Using the addition rule, Laplace expansion, and cofactor expansion of the determinant, $|\Delta G_V|$ is reduced to

$$\left(\frac{RT}{V_0}\right)^{m_1+m_2} \left|\Delta G_V\right| = \begin{vmatrix} M-K+M_1 & \cdots & M-K \\ \vdots & \ddots & \vdots \\ N-K & \cdots & M-K+M_{m_1} \end{vmatrix} \times \begin{vmatrix} N+N_1 & \cdots & N \\ \vdots & \ddots & \vdots \\ N & \cdots & N+N_{m_2} \end{vmatrix}$$

$$
+\sum_{i=1}^{m_1}\left[K\begin{vmatrix} M-K+N_1 & \cdots & M-K \\ & \ddots & \\ \vdots & [i] & \vdots \\ & & \ddots \\ M-K & \cdots & M-K-M_{m_1} \end{vmatrix}\right.
$$

$$
\left.-\sum_{j\neq i}^{m_1}K(M-K)\frac{1}{M_iM_j}\prod_{k=1}^{m_i}M_k\right]\times\begin{vmatrix} N-K+N_1 & \cdots & N-K \\ \vdots & \ddots & \vdots \\ N-K & \cdots & N-K+N_{m_1} \end{vmatrix}
$$

$$
=\left(\prod_{k=1}^{m_1}M_k\right)\cdot\left[1+(M-K)\sum_{k=1}^{m_1}\frac{1}{M_k}\right]\cdot\left(\prod_{k=1}^{m_2}N_k\right)\cdot\left[1+N\sum_{k=1}^{m_2}\frac{1}{N_k}\right]
$$

$$
+\sum_{i=1}^{m_1}\left[K\cdot\frac{1}{M_i}\left(\prod_{k=1}^{m_1}M_k\right)\left[1+(M-K)\left\{\sum_{k=1}^{m_1}\frac{1}{M_k}-\frac{1}{M_i}\right\}\right]\right.
$$

$$
\left.-K(M-K)\sum_{j\neq i}^{m_1}\frac{1}{M_iM_j}\left(\prod_{k=1}^{m_1}M_k\right)\right]\cdot\left(\prod_{k=1}^{m_2}N_k\right)\left[1+(N-K)\sum_{k=1}^{m_2}\frac{1}{N_k}\right] \qquad (4.29.11)
$$

In the derivation of Eq. (4.29.11), we used the relationship (4.20.43). Now we can readily rewrite Eq. (4.29.11) as

$$
|\Delta G_v|=\left(\frac{RT}{V_0}\right)^{m_1+m_2}=\left(\frac{RT}{V_0}\right)^{m_1+m_2}\left(\prod_{i=1}^{m_1}M_i\right)\left(\prod_{j=1}^{m_2}N_j\right)
$$

$$
\times\left[\left(1+M\sum_{i=1}^{m_1}\frac{1}{M_i}\right)\left(1+N\sum_{j=1}^{m_2}\frac{1}{N_j}\right)-K^2\left(\sum_{i=1}^{m_1}\frac{1}{M_i}\right)\left(\sum_{j=1}^{m_2}\frac{1}{N_j}\right)\right]=0
$$

$$(4.29.12)$$

Spinodal condition is then given by

$$
\left(1+M\sum_{i=1}^{m_1}\frac{1}{M_i}\right)\left(1+N\sum_{j=1}^{m_2}\frac{1}{N_j}\right)-K^2\left(\sum_{i=1}^{m_1}\frac{1}{M_i}\right)\left(\sum_{j=1}^{m_2}\frac{1}{N_j}\right)=0 \qquad (4.29.13)
$$

<<Problem 4-29-b>> Neutral equilibrium condition for quasi-ternary system polydisperse polymer/ polydisperse polymer/ solvent ($P_2/P_1/S_0$)

For quasi-binary systems consisting of multicomponent polymers 1 and 2 in a single solvent, the neutral equilibrium condition is given by

$$\left(\sum_{i=1}^{m_1}\frac{W_{X_i}}{M_i}\right)\left(1+N\sum_{j=1}^{m_2}\frac{1}{N_j}\right)-K\left(\sum_{i=1}^{m_1}\frac{1}{M_i}\right)\left(\sum_{j=1}^{m_2}\frac{W_{Y_j}}{N_j}\right)=0 \qquad (4.29.14)$$

Derive Eq.(4.29.14).

Answer

At CSP, in addition to Eq. (4.29.5), the following neutral equilibrium condition should be satisfied concurrently:

$$|\Delta G'_V| =$$

$$\begin{vmatrix} \dfrac{\partial|\Delta G_V|}{\partial\phi_{X_1}} & \dfrac{\partial|\Delta G_V|}{\partial\phi_{X_2}} & \cdots & \dfrac{\partial|\Delta G_V|}{\partial\phi_{X_{m1}}} & \dfrac{\partial|\Delta G_V|}{\partial\phi_{Y_1}} & \dfrac{\partial|\Delta G_V|}{\partial\phi_{Y_2}} & \cdots & \dfrac{\partial|\Delta G_V|}{\partial\phi_{Y_{m2}}} \\ \Delta G_{VX_2X_1} & \Delta G_{VX_2X_2} & \cdots & \Delta G_{VX_2X_{m1}} & \Delta G_{VX_2Y_1} & \Delta G_{VX_2Y_2} & \cdots & \Delta G_{VX_2Y_{m2}} \\ \vdots & \vdots & & \vdots & \vdots & \vdots & & \vdots \\ \Delta G_{VX_{m1}X_1} & \Delta G_{VX_{m1}X_2} & \cdots & \Delta G_{VX_{m1}X_{m1}} & \Delta G_{VX_{m1}Y_1} & \Delta G_{VX_{m1}Y_2} & \cdots & \Delta G_{VX_{m1}Y_m} \\ \Delta G_{VY_1X_1} & \Delta G_{VY_1X_2} & \cdots & \Delta G_{VY_1Xm_1} & \Delta G_{VY_1Y_1} & \Delta G_{VY_1Y_2} & \cdots & \Delta G_{VY_1Ym_2} \\ \Delta G_{VY_2X_1} & \Delta G_{VY_2X_2} & \cdots & \Delta G_{VY_2Xm_1} & \Delta G_{VY_2Y_1} & \Delta G_{VY_2Y_2} & \cdots & \Delta G_{VY_2Ym_2} \\ \vdots & \vdots & & \vdots & \vdots & \vdots & & \vdots \\ \Delta G_{VY_{m2}X_1} & \Delta G_{VY_{m2}X_2} & \cdots & \Delta G_{VY_{m2}X_{m1}} & \Delta G_{VY_{m2}Y_1} & \Delta G_{VY_{m2}Y_2} & \cdots & \Delta G_{VYm_2Ym_2} \end{vmatrix} = 0$$

$$(4.29.15)$$

Eq. (4.29.15) can be rewritten through the use of Eq. (4.29.9a)-(4.29.9e) as

$$|\Delta G'_V| = \left(\frac{RT}{V_0}\right)^{m_1+m_2-1}$$

$$\times\begin{vmatrix} W_{X_1} & W_{X_2} & \cdots & W_{X_{m1}} & W_{Y_1} & W_{Y_2} & \cdots & W_{Y_{m2}} \\ M & M+M_2 & \cdots & M & K & K & \cdots & K \\ \vdots & \vdots & & \vdots & \vdots & \vdots & & \vdots \\ M & M & \cdots & M+M_{m1} & K & K & \cdots & K \\ K & K & \cdots & K & N+N_1 & N & \cdots & N \\ K & K & \cdots & K & N & N+N_2 & \cdots & N \\ \vdots & \vdots & & \vdots & \vdots & \vdots & & \vdots \\ K & K & \cdots & K & N & N & \cdots & N+N_{m2} \end{vmatrix} \qquad (4.29.16)$$

Eq. (4.29.16) can be rewritten with the help of a cofactor expansion, Laplace expansion, and Eq. (4.29.12) as

$$
\begin{aligned}
\left(\frac{V_0}{RT}\right)^{m_1+m_2-1}\left|\Delta G'_v\right| = {} & W_{X_i}\left(\frac{1}{M}\prod_{k=1}^{m_1} M_k\right)\left(\prod_{k=1}^{m_2} N_k\right) \\
& \times\left[\left\{1+M\left(\sum_{k=1}^{m_1}\frac{1}{M_k}-\frac{1}{M_1}\right)\right\}\left(1+N\sum_{k=1}^{m_2}\frac{1}{N_k}\right)-K^2\left(\sum_{k=1}^{m_1}\frac{1}{M_k}-\frac{1}{M_1}\right)\left(\sum_{k=1}^{m_2}\frac{1}{N_k}\right)\right] \\
& -\sum_{i=2}^{m_1} W_{X_i}\left[\frac{M}{M_1 M_i}\left(\prod_{k=1}^{m_1} M_k\right)\left(\prod_{k=1}^{m_2} N_k\right)\left(1+N\sum_{k=1}^{m_2}\frac{1}{N_k}\right)\right. \\
& \left.-\sum_{j=1}^{m_2}\frac{K^2}{M_1 M_i}\left(\prod_{k=1}^{m_1} M_k\right)\frac{1}{N_j}\left(\prod_{k=1}^{m_2} N_k\right)\right]-\sum_{i=1}^{m_2} W_{Yj}\,\frac{K}{M_1}\left(\prod_{k=1}^{m_1} M_k\right)\frac{1}{N_i}\left(\prod_{k=1}^{m_2} N_k\right) \\
= {} & \frac{1}{M_1}\left(\prod_{k=1}^{m_1} M_k\right)\left(\prod_{k=1}^{m_2} N_k\right)\left[\left(\sum_{i=1}^{m_1}\frac{W_{Xi}}{M_i}\right)\left\{K^2\sum_{j=1}^{m_2}\frac{1}{N_j}-M\left(1+M\sum_{j=1}^{m_2}\frac{1}{N_j}\right)\right\}\right. \\
& \left.-K\left(\sum_{j=1}^{m_2}\frac{W_{Yj}}{N_j}\right)\right]
\end{aligned}
\tag{4.29.16)'}
$$

Combination of Eqs. (4.29.12) and (4.29.16)' yields

$$
\begin{aligned}
\left|\Delta G'_v\right| = {} & \left(\frac{RT}{V_0}\right)^{m_1+m_2-1}\left(\prod_{i=1}^{m_1} M_i\right)\left(\prod_{j=1}^{m_2} N_j\right)\left(M_1\sum_{i=1}^{m_1}\frac{1}{M_i}\right)^{-1} \\
& \times\left[\left(\sum_{i=1}^{m_1}\frac{W_{X_i}}{M_i}\right)\left(1+N\sum_{j=1}^{m_2}\frac{1}{N_j}\right)-K\left(\sum_{i=1}^{m_1}\frac{1}{M_i}\right)\left(\sum_{j=1}^{m_2}\frac{W_{Yj}}{N_j}\right)\right]=0
\end{aligned}
\tag{4.29.17}
$$

where W_{xi} and W_{Yj} are

$$
W_{X_i}\equiv\left(\frac{\partial\left|\Delta G'\right|}{\partial\phi_{X_i}}\right)_{T,P,\phi_k}\qquad\left(k\neq X_i, k=X_1,\cdots,X_{m_1},Y_1,\cdots,Y_{m_2}\right)\tag{4.29.18a}
$$

$$
W_{Y_j}\equiv\left(\frac{\partial\left|\Delta G'\right|}{\partial\phi_{Y_j}}\right)_{T,P,\phi_k}\qquad\left(k\neq Y_j, k=X_1,\cdots,X_{m_1},Y_1,\cdots,Y_{m_2}\right)\tag{4.29.18b}
$$

---

* Equations (4.29.13) and (4.29.14) agree completely with Koningsveld-Chermin-Gordon equations (Eqs. (12) and (13) in their paper), respectively (See R. Koningsveld, H. A. G.

Chermin and M. Gordon, *Proc. R. Soc. London Ser. A* **319**, 331 (1970)). The parameters in Eqs. (4.29.13) and (4.29.14) can be replaced with experimentally determinable parameters such as ϕ_0, ϕ_1, ϕ_2, χ_{01}, χ_{02}, χ_{12}, the weight- and z-average X_i (and Y_j), $X_w{}^0$ and $X_z{}^0$ ($Y_w{}^0$ and $Y_z{}^0$) and

the theoretical expressions finally rewritten as

$$\left(\frac{1}{\phi_0}+\frac{1}{\phi_1 X_w^0}-2\chi_{01}\right)\left(\frac{1}{\phi_0}+\frac{1}{\phi_2 Y_w^0}-2\chi_{02}\right)$$
$$-\left(\frac{1}{\phi_0}+\chi_{12}-\chi_{01}-\chi_{02}\right)^2=0 \qquad (4.29.19)$$

and

$$\left[\left(\frac{1}{\phi_0^2}-\frac{X_Z^0}{\left(\phi_1 X_W^0\right)^2}\right)\left(\frac{1}{\phi_0}+\frac{1}{\phi_2 X_W^0}-2\chi_{02}\right)+\frac{1}{\phi_0^2}\left(\frac{1}{\phi_0}+\frac{1}{\phi_1 X_W^0}\right)-2\chi_{01}\right.$$
$$\left.-\frac{2}{\phi_0^2}\left(\frac{1}{\phi_0}+\chi_{12}-\chi_{01}-\chi_{02}\right)\right]\left(\frac{1}{\phi_0}+\frac{1}{\phi_2 Y_W^0}-2\chi_{02}\right)$$
$$\left[\left(\frac{1}{\phi_0^2}-\frac{Y_Z^0}{\left(\phi_2 Y_W^0\right)^2}\right)\left(\frac{1}{\phi_0}+\frac{1}{\phi_1 X_W^0}-2\chi_{01}\right)+\frac{1}{\phi_0^2}\left(\frac{1}{\phi_0}+\frac{1}{\phi_2 Y_W^0}\right)-2\chi_{02}\right.$$
$$\left.-\frac{2}{\phi_0^2}\left(\frac{1}{\phi_0}+\chi_{12}-\chi_{01}-\chi_{02}\right)\right]\left(\frac{1}{\phi_0}+\chi_{12}-\chi_{01}-\chi_{02}\right)=0 \qquad (4.29.20)$$

with

$$\phi_0+\phi_1+\phi_2=1 \qquad (4.29.21)$$

*Symmetry of (4.29.19) and (4.29.20)

By introducing parameters Q_X and Q_Y defined by the following equations

$$\frac{1}{Q_X}\equiv\sum_{i=1}^{m_1}\frac{1}{M_i}=\phi_1 X_w^0 \qquad (4.29.22)$$

$$\frac{1}{Q_Y}\equiv\sum_{j=1}^{m_2}\frac{1}{N_j}=\phi_2 Y_w^0 \qquad (4.29.23)$$

into Eq. (4.29.10), we obtain

$$\begin{vmatrix} M+Q_X & K \\ K & M+Q_Y \end{vmatrix} = 0 \tag{4.29.24}$$

Eq. (4.29.24) can be rewritten as

$$(M+Q_X-K)(N+Q_Y-K)+K(M+Q_X-K)+K(N+Q_Y-K)=0 \tag{4.29.25}$$

Substitution of Eqs. (4.29.9a)-(4.29.9e), (4.29.22) and (4.29.23) into Eq. (4.29.25) yields

$$\begin{aligned} &\left(\frac{1}{X_w^0\phi_1}+\chi_{02}-\chi_{01}-\chi_{02}\right)\left(\frac{1}{Y_w^0\phi_2}+\chi_{01}-\chi_{02}-\chi_{12}\right) \\ &\quad+\left(\frac{1}{\phi_0}+\chi_{12}-\chi_{01}-\chi_{02}\right)\left(\frac{1}{X_w^0\phi_1}+\chi_{02}-\chi_{01}-\chi_{02}\right) \\ &\quad+\left(\frac{1}{\phi_0}+\chi_{12}-\chi_{01}-\chi_{02}\right)\left(\frac{1}{Y_w^0\phi_2}+\chi_{01}-\chi_{02}-\chi_{12}\right)=0 \end{aligned} \tag{4.29.26}$$

The neutral equilibrium condition (Eq. (4.29.14)) can also be represented as

$$\begin{vmatrix} Q_X R_X & Q_X R_Y \\ K & N+Q_Y \end{vmatrix} = 0 \tag{4.29.27}$$

where R_X and R_Y are defined by

$$R_X \equiv \sum_{i=1}^{m_1} \frac{W_{X_i}}{M_i} \tag{4.29.28}$$

$$R_Y \equiv \sum_{j=1}^{m_2} \frac{W_{Y_j}}{M_j} \tag{4.29.29}$$

Eq. (4.29.27) is rewritten with the help of Eq. (4.29.25) as

$$\begin{aligned} &\frac{1}{\phi_0^2}(M+Q_X-K)^3(N+Q_Y-K)^3 \\ &\qquad+X_Z^0 Q_X^2 K^3(N+Q_Y-K)^3+Y_Z^0 Q_Y^2 K^3(M+Q_X-K)^3=0 \end{aligned} \tag{4.29.30}$$

Substituting Eqs. (4.29.9a)-(4.29.9e), (4.29.22) and (4.29.23) into Eq. (4.29.30), the following equation is obtained:

$$\frac{1}{\phi_0^2}\left(\frac{1}{X_w^0\phi_1}+\chi_{02}-\chi_{01}-\chi_{12}\right)^3\left(\frac{1}{Y_w^0\phi_2}+\chi_{01}-\chi_{02}-\chi_{12}\right)^3$$
$$+\frac{X_z^0}{\left(X_w^0\phi_1\right)^2}\left(\frac{1}{Y_w^0\phi_2}+\chi_{01}-\chi_{02}-\chi_{12}\right)^3\left(\frac{1}{\phi_0}+\chi_{12}-\chi_{01}-\chi_{02}\right)^3$$
$$+\frac{Y_z^0}{\left(Y_w^0\phi_2\right)^2}\left(\frac{1}{X_w^0\phi_1}+\chi_{02}-\chi_{01}-\chi_{12}\right)^3\left(\frac{1}{\phi_0}+\chi_{12}-\chi_{01}-\chi_{02}\right)^3=0 \qquad (4.29.31)$$

Eqs. (4.29.26) and (4.29.31) are obviously symmetrical with respect to the exchange of polymers 1 and 2, respectively.

*Multiplying both sides of Eq. (4.29.26) by $\phi_0\phi_1\phi_2$ gives

$$\phi_0\left\{\frac{1}{X_w^0}+\left(\chi_{02}-\chi_{01}-\chi_{12}\right)\right\}\left\{\frac{1}{Y_w^0}+\left(\chi_{01}-\chi_{02}-\chi_{12}\right)\phi_2\right\}$$
$$+\phi_1\left\{1+\left(\chi_{12}-\chi_{01}-\chi_{02}\right)\phi_0\right\}\left\{\frac{1}{Y_w^0}+\left(\chi_{01}-\chi_{02}-\chi_{12}\right)\phi_2\right\}$$
$$+\phi_2\left\{1+\left(\chi_{12}-\chi_{01}-\chi_{02}\right)\phi_0\right\}\left\{\frac{1}{X_w^0}+\left(\chi_{02}-\chi_{01}-\chi_{12}\right)\phi_1\right\}=0 \qquad (4.29.32)$$

By putting $\phi_0=0$ (and of course utilizing the relationship $\phi_1+\phi_2=1$) in Eq. (4.29.32), we can obtain the condition for the crossing point of SC and the three axes (ϕ_0 axis) of the Gibbs composition triangle as

$$\frac{\phi_0}{Y_w^0}+\phi_2-2\chi_{02}\phi_0\phi_2=0 \qquad (4.29.33)$$

The following equations are similarly derived:

$$\frac{\phi_0}{X_w^0}+\phi_1-2\chi_{01}\phi_0\phi_1=0 \qquad (4.29.34)$$

$$\frac{\phi_1}{X_w^0}+\frac{\phi_2}{Y_w^0}-2\chi_{12}\phi_1\phi_2=0 \qquad (4.29.35)$$

<<Problem 4-30-a>> Chemical potential of mixing for (r+1)-component Flory-Huggins solution

Gibbs free energy of mixing for (r+1)-component Flory-Huggins

solutions is given by

$$\Delta G_{\mathrm{mix}} = RT\sum_{i=0}^{r} N_i \ln\phi_i + LRT\sum_{i<j}^{r}\phi_i\phi_j\chi_{ij} \tag{4.30.1}$$

where $N=\Sigma N_i$, $L=\Sigma n_i N_i$ and $\Sigma\phi_i=1$.

(1) Derive the expression for the chemical potential of mixing

$$\Delta\mu_k = \left(\partial\Delta G_{\mathrm{mix}}/\partial N_k\right)_{P,T,N_i}$$

(2) Derive the expression for the chemical potential of mixing $\Delta\mu_k (k=0,1,2)$ and the Gibbs free energy of mixing per unit volume for the system

(i) solvent(0)/solvent(1)/polymer(2),

(ii) solvent(0)/polymer(1)/polymer(2),

(iii) polymer(0)/polymer(1)/polymer(2).

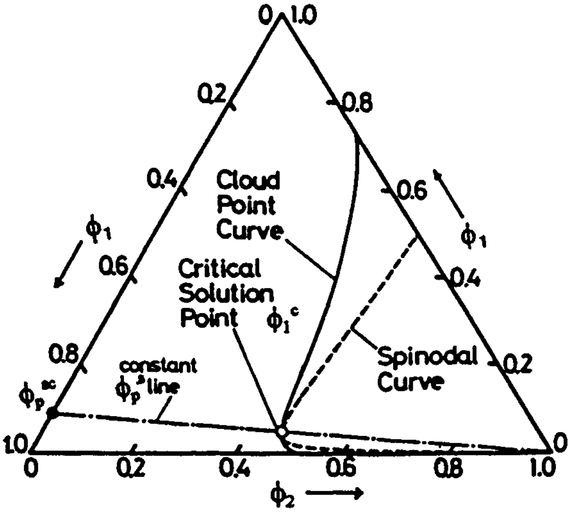

Fig. 4-30 Cloud point curve (full line), spinodal curve (broken line) and critical solution point (unfilled circle) of a quasi-ternary system. Original polymer, Schulz-Zimm type distribution ($n_w^0=300$, $n_w^0/n_n^0=2$); $\chi_{12}=0.5$, $\chi_{13}=0.2$ and $\chi_{23}=1.0$. (See K. Kamide and S. Matsuda, *Polym. J.* **18**, 347 (1986))

Answer

(1) Differentiating ΔG_{mix} with respect to N_i, we have

$$\Delta\mu_i = RT\left[\ln\phi_i + \sum_{j\neq i}^{r}\left(1 - \frac{n_i}{n_j}\right)\phi_j + n_i\left\{\left(1 - \phi_i\right)\sum_{j\neq i}^{r}\phi_j\chi_{ij} - \frac{1}{2}\sum_{j,k\neq i}^{r}\phi_j\phi_k\chi_{jk}\right\}\right]$$

$$= RT\left[\ln\phi_i + \sum_{j\neq i}^{r}\left(1 - \frac{n_i}{n_j}\right)\phi_j + n_i\left\{\left(1 - \phi_i\right)\sum_{j\neq i}^{r}\phi_j\chi_{ij} - \sum_{\substack{j<k\\ j,k\neq i}}^{r}\phi_j\phi_k\chi_{jk}\right\}\right] \tag{4.30.2}$$

(2) For r=3, we have

$$\Delta\mu_0 = RT\left[\ln\phi_0 + \left(1 - \frac{n_0}{n_1}\right)\phi_1 + \left(1 - \frac{n_0}{n_2}\right)\phi_2 \right.$$
$$\left. + n_0\left\{\chi_{01}\left(1 - \phi_0\right)\phi_1 + \chi_{02}\left(1 - \phi_0\right)\phi_2 - \chi_{12}\phi_1\phi_2\right\}\right] \tag{4.30.3}$$

$$\Delta\mu_1 = RT\left[\ln\phi_1 + \left(1 - \frac{n_1}{n_0}\right)\phi_0 + \left(1 - \frac{n_1}{n_2}\right)\phi_2 \right.$$
$$\left. + n_1\left\{\chi_{01}\left(1 - \phi_1\right)\phi_0 + \chi_{12}\left(1 - \phi_1\right)\phi_2 - \chi_{02}\phi_0\phi_2\right\}\right] \tag{4.30.4}$$

$$\Delta\mu_2 = RT\left[\ln\phi_2 + \left(1 - \frac{n_2}{n_0}\right)\phi_0 + \left(1 - \frac{n_2}{n_1}\right)\phi_1 \right.$$

$$+ n_2 \left\{ \chi_{02} \left(1 - \phi_2\right) \phi_0 + \chi_{12} \left(1 - \phi_2\right) \phi_1 - \chi_{01}\phi_0\phi_1 \right\} \Bigg] \tag{4.30.5}$$

Gibbs free energy of mixing per unit volume ΔG_v is given by

$$\Delta G_v = \phi_0 \frac{\Delta\mu_0}{n_0 V_0} + \phi_1 \frac{\Delta\mu_1}{n_1 V_0} + \phi_2 \frac{\Delta\mu_2}{n_2 V_0} \tag{4.30.6}$$

Substituting Eqs. (4.30.3)-(4.30.5) in Eq. (4.30.6), we have

$$\Delta G_v = \left(\frac{RT}{V_0}\right)\left[\frac{\phi_0 \ln\phi_0}{n_0} + \frac{\phi_1 \ln\phi_1}{n_1} + \frac{\phi_2 \ln\phi_2}{n_2} + \chi_{01}\phi_0\phi_1 + \chi_{02}\phi_0\phi_2 + \chi_{12}\phi_1\phi_2\right] \tag{4.30.7}$$

(i) For the system solvent(0)/solvent(1)/polymer(2), putting $n_0 = n_1 = 1$ in Eq.(4.30.3)-(4.30.6), we have

$$\Delta\mu_0 = RT\left[\ln\phi_0 + \left(1 - \frac{1}{n_2}\right)\phi_2 + \chi_{01}\left(1 - \phi_0\right)\phi_1 + \chi_{02}\left(1 - \phi_0\right)\phi_2 - \chi_{12}\phi_1\phi_2\right] \tag{4.30.8}$$

$$\Delta\mu_1 = RT\left[\ln\phi_1 + \left(1 - \frac{1}{n_2}\right)\phi_2 + \chi_{01}\left(1 - \phi_1\right)\phi_0 + \chi_{12}\left(1 - \phi_1\right)\phi_2 - \chi_{02}\phi_0\phi_2\right] \tag{4.30.9}$$

$$\Delta\mu_2 = RT\left[\ln\phi_2 + \left(1 - n_2\right)\left(1 - \phi_2\right) + n_2\left\{\chi_{02}\left(1 - \phi_2\right)\phi_0 + \chi_{12}\left(1 - \phi_2\right)\phi_1 - \chi_{01}\phi_0\phi_1\right\}\right] \tag{4.30.10}$$

$$\Delta G_v = \left(\frac{RT}{V_0}\right)\left(\phi_0 \ln\phi_0 + \phi_1 \ln\phi_1 + \frac{\phi_2 \ln\phi_2}{n_2} + \chi_{01}\phi_0\phi_1 + \chi_{02}\phi_0\phi_2 + \chi_{12}\phi_1\phi_2\right) \tag{4.30.11}$$

(ii) For the system solvent(0)/polymer(1)/polymer(2), putting $n_0 = 1$ in

Eqs.(4.30.3)-(4.30.6), we have

$$\Delta\mu_0 = RT \left[\ln\phi_0 + \left(1 - \frac{1}{n_1}\right)\phi_1 + \left(1 - \frac{1}{n_2}\right)\phi_2 + \chi_{01}\left(1 - \phi_0\right)\phi_1 + \chi_{02}\left(1 - \phi_0\right)\phi_2 - \chi_{12}\phi_1\phi_2 \right] \tag{4.30.12}$$

$$\Delta\mu_1 = RT \left[\ln\phi_1 + \left(1 - n_1\right)\phi_0 + \left(1 - n_1\right)\phi_2 + n_1\left\{\chi_{01}\left(1 - \phi_1\right)\phi_0 + \chi_{12}\left(1 - \phi_1\right)\phi_2 - \chi_{02}\phi_0\phi_2\right\} \right] \tag{4.30.13}$$

$$\Delta\mu_2 = RT \left[\ln\phi_2 + \left(1 - n_2\right)\phi_0 + \left(1 - n_2\right)\phi_1 + n_2\left\{\chi_{02}\left(1 - \phi_2\right)\phi_0 + \chi_{12}\left(1 - \phi_2\right)\phi_1 - \chi_{12}\phi_1\phi_2\right\} \right] \tag{4.30.14}$$

$$\Delta G_v = \left(\frac{RT}{V_0}\right)\left(\phi_0\ln\phi_0 + \frac{\phi_1\ln\phi_1}{n_1} + \frac{\phi_2\ln\phi_2}{n_2} + \chi_{01}\phi_0\phi_1 + \chi_{02}\phi_0\phi_2 + \chi_{12}\phi_1\phi_2\right) \tag{4.30.15}$$

(iii) For the system polymer(0)/polymer(1)/polymer(2), we have just Eqs. (4.30.3)-(4.30.6).

<<Problem 4-30-b>> Critical condition for quasi-ternary system polydisperse polymer in mixed solvent ($P_3/S_2/S_1$)

The chemical potentials of solvent 1, solvent 2 and X_i-mer $\Delta\mu_1$, $\Delta\mu_2$, and $\Delta\mu_{xi}$ are given by (See Eq. (3.19.2))

$$\Delta\mu_1 = RT\left[\ln\phi_1 + \left(1 - \frac{1}{X_n}\right) + \chi_{12}\phi_2(1 - \phi_1) + \chi_{13}\phi_p(1 - \phi_1) - \chi_{23}\phi_2\phi_p\right] \tag{4.30.16}$$

$$\Delta\mu_2 = RT\left[\ln\phi_2 + \left(1 - \frac{1}{X_n}\right)\phi_p + \chi_{12}\phi_1(1-\phi_2) + \chi_{23}\phi_p(1-\phi_2) - \chi_{13}\phi_1\phi_p\right] \tag{4.30.17}$$

$$\Delta\mu_{x_i} = RT\Big[\ln\phi_{x_i} - (X_i - 1) + X_i\left(1 - \frac{1}{X_n}\right)\phi_p$$

$$+ X_i\left\{\chi_{13}\phi_1(1-\phi_p) + \chi_{23}\phi_2(1-\phi_p) - \chi_{12}\phi_1\phi_2\right\}\Big] \tag{4.30.18}$$

where ϕ_1, ϕ_2 and ϕ_p are the volume fractions of solvent 1, solvent 2 and polymer, and χ_{12}, χ_{13} and χ_{23} are the interaction parameters for the pairs solvent 1/solvent 2, solvent 1/polymer and solvent 2/polymer.

For this system the condition of CSP is given by

$$\left(\frac{1}{\phi_1} + \frac{1}{\phi_2} - 2\chi_{12}\right)\left(\frac{1}{\phi_p X_w^0} + \frac{1}{\phi_1} - 2\chi_{13}\right) - \left(\frac{1}{\phi_1} + \chi_{23} - \chi_{13} - \chi_{12}\right)^2 = 0 \tag{4.30.19}$$

$$\left[\frac{1}{\phi_p X_w^0}\left(\frac{1}{\phi_1^2} - \frac{1}{\phi_2^2}\right) + \frac{1}{\phi_1^2}\left(\frac{1}{\phi_2} - 2\chi_{23}\right) - \frac{1}{\phi_2^2}\left(\frac{1}{\phi_1} - 2\chi_{13}\right)\right]\left(\frac{1}{\phi_p X_w^0} + \frac{1}{\phi_1} - 2\chi_{13}\right)$$

$$-\left(\frac{1}{\phi_1} + \chi_{23} - \chi_{13} - \chi_{12}\right)\Bigg[\frac{1}{\phi_1^2}\left(\frac{1}{\phi_2} - 2\chi_{23}\right) + \frac{1}{\phi_1^2\phi_p X_w^0} +$$

$$\frac{X_z^0}{\phi_p X_w^0}\left\{\frac{1}{\phi_1\phi_2} - \frac{2\chi_{13}}{\phi_2} - \frac{2\chi_{23}}{\phi_1} + 2(\chi_{12}\chi_{13} + \chi_{13}\chi_{23} + \chi_{23}\chi_{12}) - (\chi_{12}^2 + \chi_{13}^2 + \chi_{23}^2)\right\}\Bigg] \tag{4.30.20}$$

Derive Eqs. (4.30.19) and (4.30.20).

Answer

Substitution of Eqs. (4.30.16)-(4.30.18) into the equation

$\Delta G_v = \phi_1(\Delta\mu_1/V_0) + \phi_2(\Delta\mu_2/V_0) + \Sigma_i\, \phi_{xi}(\Delta\mu_{xi}/X_jV_0)$
yields

$$\Delta G_v = \left(\frac{RT}{V_0}\right)\left[\phi_1\ln\phi_1 + \phi_2\ln\phi_2 + \sum_{i=1}^{m}\frac{\phi_{x_i}}{V_0}\ln\phi_{x_i} + \chi_{12}\phi_1\phi_2 + \chi_{13}\phi_1\phi_p + \chi_{23}\phi_2\phi_p\right] \tag{4.30.21}$$

The second-order derivatives of ΔG_v

$$\Delta G_{vij} = \left(\frac{\partial^2 \Delta G_v}{\partial \phi_{x_i} \partial \phi_{x_j}} \right)_{T,P,v_{x_k}} \qquad (i,j = N,1,2,\cdots,m; k \neq i,j) \tag{4.30.22}$$

are given by

$$\left(\frac{V_0}{RT} \right) \Delta G_{vij} = \frac{1}{\phi_1} - 2\chi_{13} \equiv M \quad (\text{for } i \neq j, i \text{ and } j \neq N) \tag{4.30.23a}$$

$$\left(\frac{V_0}{RT} \right) \Delta G_{vij} = M + \chi_{13} + \chi_{23} - \chi_{12} \equiv M + K \quad (\text{for } i \neq j, i \text{ or } j = N) \tag{4.30.23b}$$

$$\left(\frac{V_0}{RT} \right) \Delta G_{vij} = M + \frac{1}{\phi_2} + 2(\chi_{13} - \chi_{12}) \equiv M + U \quad (\text{for } i = j = N) \tag{4.30.23c}$$

$$\left(\frac{V_0}{RT} \right) \Delta G_{vij} = M + \frac{1}{X_i \phi_{x_i}} \equiv M + M_i \quad (\text{for } i = j \neq N) \tag{4.30.23d}$$

Substituting Eqs. (4.30.23a)-(4.30.23d) into the spinodal condition, we obtain

$$|\Delta G_v| = \left(\frac{RT}{V_0} \right)^{m+1} \begin{vmatrix} M+U & M+K & M+K & \cdots & M+K \\ M+K & M+M_1 & M & \cdots & M \\ M+K & M & M+M_2 & \cdots & M \\ \vdots & \vdots & \vdots & & \vdots \\ M+K & M & M & \cdots & M+M_m \end{vmatrix}$$

$$= \left(\frac{RT}{V_0} \right)^{m+1} \left[(-1)^2 (M+U) \begin{vmatrix} M+M_1 & M & \cdots & M \\ M & M+M_2 & \cdots & M \\ \vdots & \vdots & & \vdots \\ M & M & \cdots & M+M_m \end{vmatrix} \right.$$

$$+ \sum_{j=1}^{m} (-1)^{2j+3} (M+K) \{ (-1)^2 (M+K)$$

$$
\times\begin{vmatrix}
M+M_1 & M & \cdots & M & M & \cdots & M \\
M & M+M_2 & \cdots & M & M & \cdots & M \\
\vdots & \vdots & & \vdots & \vdots & & \vdots \\
M & M & \cdots & M+M_{j-1} & M & \cdots & M \\
M & M & \cdots & M & M+M_{j+1} & \cdots & M \\
\vdots & \vdots & & \vdots & \vdots & & \vdots \\
M & M & \cdots & M & M & \cdots & M+M_m
\end{vmatrix}
$$

$$
+\sum_{i\neq j}^{m}(-1)^{2i+3}(M+K)
$$

$$
\left.\left.\times\begin{vmatrix}
M & & & & & & & & & \\
M & M_1 & & & & & & 0 & & \\
\vdots & & \ddots & & & & & & & \\
M & & & M_{i-1} & & & & & & \\
M & & & & M_{i+1} & & & & & \\
\vdots & & & & & \ddots & & & & \\
M & & & & & & M_{j-1} & & & \\
M & & & & & & & M_{j+1} & & \\
\vdots & & 0 & & & & & & \ddots & \\
M & & & & & & & & & M_m
\end{vmatrix}\right\}\right]
$$

$$
=\left(\frac{RT}{V_0}\right)^{m+1}\left[(M+U)\left(\prod_{j=1}^{m}M_j\right)\left(1+M\prod_{j=1}^{m}\frac{1}{M_j}\right)-\sum_{j=1}^{m}(M+K)\left[(M+K)\right.\right.
$$

$$
\left.\left.\times\left(\frac{1}{M_j}\prod_{i=1}^{m}M_i\right)\left\{1+M\left(\sum_{i=1}^{m}\frac{1}{M_i}-\frac{1}{M_j}\right)\right\}-\sum_{i\neq j}^{m}(M+K)\frac{M}{M_iM_j}\left(\prod_{k=1}^{m}M_k\right)\right]\right]
$$

$$
=\left(\frac{RT}{V_0}\right)^{m+1}\left(\prod_{j=1}^{m}M_j\right)\left[(M+U)\left\{1+M\sum_{j=1}^{m}\frac{1}{M_j}\right\}-(M+K)^2\sum_{j=1}^{m}\frac{1}{M_j}\right]=0
\tag{4.30.24}
$$

Eq. (4.30.24) can be rewritten as

$$
(M+U)\left\{1+M\sum_{j=1}^{m}\frac{1}{M_j}\right\}-(M+K)^2\sum_{j=1}^{m}\frac{1}{M_j}=0
\tag{4.30.25}
$$

Combining Eq. (4.30.25) with Eqs. (4.30.23a)-(4.30.23d), we obtain Eq. (4.30.19). Here, in deriving Eq. (4.30.19), we employ Eq. (4.20.43).
Partial differentiation of Eq. (4.30.24) with $\phi_{xi}(i=N,1,2,...m;\phi_{XN}=\phi_2)$ yields

$$
\begin{aligned}
\left(\frac{\partial|\Delta G_v|}{\partial\phi_{x_i}}\right)_{T,P,\phi_{x_k}} &= \left(\frac{RT}{V_0}\right)^{m+1}\left(\prod_{j=1}^{m} M_j\right) \\
&\quad \times\frac{\partial}{\partial\phi_{Xi}}\left\{(M+U)\left(1+M\phi_p X_w^0\right)-(M+K)^2\phi_p X_w^0\right\}_{T,P,\phi_{x_k}} \\
&\equiv W_i \qquad (k\neq i, k=N,1,2,\cdots,m;\phi_{xN}=\phi_2)
\end{aligned}
\qquad (4.30.26)
$$

Substituting Eqs. (4.30.23a)-(4.30.23d) and Eq. (4.30.26) into the neutral equilibrium condition, we obtain

$$
\begin{aligned}
\left(\frac{V_0}{RT}\right)^{m+1}|\Delta G_v'| &= \begin{vmatrix} W_N & W_1 & W_2 & \cdots & W_m \\ M+K & M+M_1 & M & \cdots & M \\ M+K & M & M+M_2 & \cdots & M \\ \vdots & \vdots & \vdots & & \vdots \\ M+K & M & M & \cdots & M+M_m \end{vmatrix} \\
&= (-1)^2 W_N \begin{vmatrix} M+M_1 & M & \cdots & M \\ M & M+M_2 & \cdots & M \\ \vdots & \vdots & & \vdots \\ M & M & \cdots & M+M_m \end{vmatrix} \\
&\quad +\sum_{j=1}^{m}(-1)^{2j+3}W_j\Big[(-1)^2(M+K) \\
&\quad \times\begin{vmatrix} M+M_1 & M & \cdots & M & M & \cdots & M \\ M & M+M_2 & \cdots & M & M & \cdots & M \\ \vdots & \vdots & & \vdots & \vdots & & \vdots \\ M & M & \cdots & M+M_{j-1} & M & \cdots & M \\ M & M & \cdots & M & M+M_{j+1} & \cdots & M \\ \vdots & \vdots & & \vdots & \vdots & & \vdots \\ M & M & \cdots & M & M & \cdots & M+M_m \end{vmatrix}
\end{aligned}
$$

$$+\sum_{i\neq j}^{m}(-1)^{2i+3}(M+K)$$

$$\times\begin{vmatrix} M & & & & & & & & & & & \\ M & M_1 & & & & & & & & & 0 & \\ M & & M_2 & & & & & & & & & \\ \vdots & & & \ddots & & & & & & & & \\ M & & & & M_{i-1} & & & & & & & \\ M & & & & & M_{i+1} & & & & & & \\ \vdots & & & & & & \ddots & & & & & \\ M & & & & & & & M_{j-1} & & & & \\ M & & & & & & & & M_{j+1} & & & \\ \vdots & & 0 & & & & & & & \ddots & & \\ M & & & & & & & & & & & M_m \end{vmatrix}\Bigg]$$

$$=W_N\left(\prod_{j=1}^{m}M_j\right)\left(1+M\sum_{j=1}^{m}\frac{1}{M_j}\right)$$

$$-\sum_{j=1}^{m}W_j\left\{(M+K)\left(\frac{1}{M_j}\prod_{i=1}^{m}M_i\right)\left(1+M\sum_{i\neq j}^{m}M_i\right)-\sum_{i\neq j}^{m}(M+K)\left(\frac{M}{M_iM_j}\right)\prod_{i=1}^{m}M_i\right\}$$

$$=\left(\prod_{j=1}^{m}M_j\right)\left[W_N\left(1+M\sum_{j=1}^{m}\frac{1}{M_j}\right)-(M+K)\sum_{j=1}^{m}\frac{W_j}{M_j}\right]=0 \tag{4.30.27}$$

In deriving Eq. (4.30.27), we utilized Eqs. (4.20.43) and (4.30.26). Eq. (4.30.27) can be rewritten in the form:

$$W_N\left(1+M\sum_{j=1}^{m}\frac{1}{M_j}\right)-(M+K)\sum_{j=1}^{m}\frac{W_j}{M_j}=0 \tag{4.30.28}$$

Eq. (4.30.20) can be derived from Eq. (4.30.28), considering Eqs. (4.30.23a)-(4.30.23d) and Eq. (4.30.26). Figure 4-30 exemplifies CPC, the spinodal curve and CSP for quasi-ternary solutions. As the theory requires, the cloud point and spinodal curves intercept beautifully on CSP. This strongly implies that both the present theory and the simulation technique used here are reasonable and unconditionally acceptable. (See K. Kamide, S. Matsuda and Y.Miyazaki, *Polym. J.* **16**, 479 (1984); K. Kamide and S. Matsuda, *Polym. J.*

18, 347 (1986))

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* The conditions for spinodal and neutral equilibrium for monodisperse polymer with the degree of polymerization X in binary solvent mixtures are given by applying Eqs. (4.9.1) and (4.9.2) to this case ($P_3/S_2/S_1$) as

$$\left(\frac{1}{\phi_1}+\frac{1}{\phi_2}-2\chi_{12}\right)\left(\frac{1}{\phi_X X}+\frac{1}{\phi_1}-2\chi_{13}\right)-\left(\frac{1}{\phi_1}+\chi_{23}-\chi_{13}-\chi_{12}\right)^2=0 \qquad (4.30.29)$$

$$\begin{aligned}&\Bigg[\frac{1}{\phi_x X}\left(\frac{1}{\phi_1^2}-\frac{1}{\phi_2^2}\right)+\frac{1}{\phi_1^2}\left(\frac{1}{\phi_2}-2\chi_{23}\right)-\frac{1}{\phi_2^2}\left(\frac{1}{\phi_1}-2\chi_{13}\right)\Bigg]\left(\frac{1}{\phi_x X}+\frac{1}{\phi_1}-2\chi_{13}\right)\\&-\left(\frac{1}{\phi_1}+\chi_{23}-\chi_{13}-\chi_{12}\right)\Bigg[\frac{1}{\phi_1^2}\left(\frac{1}{\phi_2}-2\chi_{23}\right)+\frac{1}{\phi_1^2\phi_x X}+\\&\frac{1}{\phi_x}\left\{\frac{1}{\phi_1\phi_2}-\frac{2\chi_{13}}{\phi_2}-\frac{2\chi_{23}}{\phi_1}+2(\chi_{12}\chi_{13}+\chi_{13}\chi_{23}+\chi_{23}\chi_{12})-(\chi_{12}^2+\chi_{13}^2+\chi_{23}^2)\right\}\Bigg]=0\end{aligned}$$

(4.30.30)

In deriving Eqs. (4.30.29) and (4.30.30), the equation (4.30.22) with m=1 (monodisperse polymer) was employed. Eqs. (4.30.19) and (4.30.20) reduce to Eqs. (4.30.29) and (4.30.30) by putting $X_w=X_z=X$ and $\phi_1=\phi_x$ and are equivalent to Kurata's equations (2.3.30) and (2.3.31) in his book (See M.Kurata, *Thermodynamics of Polymer Solutions*, Harwood Acad. Publ., New York, Chap.2, p.127 (1982)). In addition, Eq. (4.30.29) coincides completely with Eq. 26 in Scott's equation (See R.L.Scott, *J. Chem. Phys.* 17, 268 (1949)).

<<Problem4-30-c>> Symmetry of critical condition

Prove that Eqs. (4.30.19) and (4.30.20) are symmetrical with respect to the exchange of solvents 1 and 2.

Answer

Eq. (4.30.25) can be rewritten as follows:

$$\{(M+K)(U-K)+(U-K)(Q_w-K)+(Q_w-K)(M+K)\}=0 \qquad (4.30.31)$$

where

$$\frac{1}{Q_w}=\sum_{j=1}^{m}\frac{1}{M_j}=\phi_p X_w^0 \qquad (4.30.32)$$

Substitution of Eqs. (4.30.23a)-(4.30.23c) and (4.30.31) yields

$$\left(\frac{1}{\phi_1}+\chi_{23}-\chi_{13}-\chi_{12}\right)\left(\frac{1}{\phi_2}+\chi_{13}-\chi_{23}-\chi_{12}\right)$$
$$+\left(\frac{1}{\phi_2}+\chi_{13}-\chi_{23}-\chi_{12}\right)\left(\frac{1}{\phi_p X_w^0}+\chi_{12}-\chi_{13}-\chi_{23}\right)$$
$$+\left(\frac{1}{\phi_p X_w^0}+\chi_{12}-\chi_{13}-\chi_{23}\right)\left(\frac{1}{\phi_1}+\chi_{23}-\chi_{13}-\chi_{12}\right)=0 \tag{4.30.33}$$

We can rearrange Eq. (4.30.28) into the form:

$$W_N\{(M+K)+(Q_W-K)\}-(M+K)\left(\frac{1}{\phi_p X_w^0}\sum_{i=1}^{m}\frac{W_i}{M_i}\right)$$
$$=\frac{W_N}{U-K}\{(M+K)(U-K)+(U-K)(Q_W-K)+(Q_W-K)(M+K)\}$$
$$-\frac{M+K}{U-K}\left\{\left(\frac{1}{\phi_p X_w^0}\sum_{j=1}^{m}\frac{W_j}{M_j}\right)(U-K)+W_N(Q_W-K)\right\}=0 \tag{4.30.34}$$

Eq. (4.30.34) can be simplified using Eq. (4.30.31) as

$$\frac{1}{Q_W-K}\left(\frac{1}{\phi_p X_w^0}\sum_{i=1}^{m}\frac{W_i}{M_i}\right)+\frac{W_N}{U-K}=0 \tag{4.30.35}$$

Combination of Eq. (4.30.31) and (4.30.27) gives

$$W_i=\left(\frac{RT}{V_0}\right)^{m+1}\left(\prod_{j=1}^{m}M_j\right)\left[\frac{(Q_W-K)+(U-K)}{\phi_1^2}-\frac{X_i\{(M+K)+(U-K)\}}{\left(\phi_p X_w^0\right)^2}\right] \tag{4.30.36}$$

$$W_N=\left(\frac{RT}{V_0}\right)^{m+1}\left(\prod_{j=1}^{m}M_j\right)\left[\frac{(Q_W-K)+(U-K)}{\phi_1^2}-\frac{(M+K)+(Q_W-K)}{\phi_2^2}\right] \tag{4.30.37}$$

From Eqs. (4.30.35)-(4.30.37), we obtain

$$\frac{\{(Q_W-K)+(U-K)\}^2}{\phi_1^2(Q_W-K)(U-K)}-\frac{(M+K)+(U-K)}{\left(\phi_p X_w^0\right)^2(Q_W-K)}-\frac{(M+K)+(Q_W-K)}{\phi_2^2(U-K)}=0 \tag{4.30.38}$$

By combining Eq. (4.30.31) with Eq. (4.30.38), we can derive

$$\frac{1}{M+K}\left(1-\frac{\chi_{12}+\chi_{13}-\chi_{23}}{M+K}\right)^2+\frac{1}{U-K}\left(1+\frac{\chi_{12}+\chi_{23}-\chi_{13}}{U-K}\right)^2$$
$$+\frac{X_z}{Q_w-K}\left(1-\frac{\chi_{13}+\chi_{23}+\chi_{12}}{Q_w-K}\right)^2=0 \tag{4.30.39}$$

Eq. (4.30.39) can be rewritten using Eqs. (4.30.23a)-(4.30.23c) and Eq. (4.30.32) as

$$\frac{1}{\phi_1^2}\left(\frac{1}{\phi_2}-\chi_{12}-\chi_{23}+\chi_{13}\right)^3\left(\frac{1}{X_w^0\phi_p}-\chi_{13}-\chi_{23}+\chi_{12}\right)^3$$
$$+\frac{1}{\phi_2^2}\left(\frac{1}{\phi_1}-\chi_{12}-\chi_{13}+\chi_{23}\right)^3\left(\frac{1}{X_w^0\phi_p}-\chi_{13}-\chi_{23}+\chi_{12}\right)^3$$
$$+\frac{X_z}{\left(X_w^0\phi_p\right)^2}\left(\frac{1}{\phi_1}-\chi_{12}-\chi_{13}+\chi_{23}\right)^3\left(\frac{1}{\phi_2}-\chi_{12}-\chi_{23}+\chi_{13}\right)^3=0 \tag{4.30.40}$$

Eqs. (4.30.33) and (4.30.40) are obviously symmetrical with respect to the exchange of the solvents 1 and 2 and are consistent with Eqs. (4.30.19) and (4.30.20).

<<Problem 4-31>> Fractionation (I): Coexistence curve of polymer solution

Describe how to determine the **coexistence curve of polymer solutions** consisting of monodisperse polymer with the degree of polymerization n and a single solvent using chemical potentials of polymer and solvent.

Answer

Phase equilibrium condition for binary solutions is that chemical potentials of two phases are the same for each component (See Eq. (1.5.1)). That is,

$$\Delta\mu_{0(1)} = \Delta\mu_{0(2)} \tag{4.21.22}$$

$$\Delta\mu_{1(1)} = \Delta\mu_{1(2)} \tag{4.21.23}$$

Of course, the following equations hold at equilibrium state.

$$\begin{aligned} T_{(1)} &= T_{(2)} \\ P_{(1)} &= P_{(2)} \end{aligned} \tag{4.31.1}$$

Here, the subscripts (1) and (2) denote different phases. According to the Flory-Huggins theory, the chemical potentials of solvent and polymer are given by

$$\mu_0 = \mu_0^0 + RT\left\{\ln\left(1 - \phi_1\right) + \left(1 - \frac{1}{n}\right)\phi_1 + \chi\phi_1{}^2\right\} \tag{3.11.3}$$

$$\mu_1 = \mu_1^0 + RT\left\{\ln\phi_1 - \left(n - 1\right)\left(1 - \phi_1\right) + \chi n\phi_0{}^2\right\} \tag{3.12.2}$$

respectively. Substituting Eqs. (3.11.3) and (3.12.2) in Eqs. (4.21.22) and (4.21.23), we have

$$\chi = \frac{1}{\phi_{1(2)}{}^2 - \phi_{1(1)}{}^2}\left\{\ln\frac{1 - \phi_{1(1)}}{1 - \phi_{1(2)}} + \left(\phi_{1(1)} - \phi_{1(2)}\right) - \left(\frac{\phi_{1(1)}}{n} - \frac{\phi_{1(2)}}{n}\right)\right\} \tag{4.31.2}$$

$$\sigma \equiv \frac{1}{n}\ln\frac{\phi_{1(2)}}{\phi_{1(1)}} = \left(\phi_{1(1)} - \phi_{1(2)}\right) - \left(\frac{\phi_{1(1)}}{n} - \frac{\phi_{1(2)}}{n}\right) - \chi\left\{2\left(\phi_{1(1)} - \phi_{1(2)}\right) - \left(\phi_{1(2)}{}^2 - \phi_{1(1)}{}^2\right)\right\} \tag{4.31.3}$$

A pair of volume fractions $\phi_1(1)$ and $\phi_1(2)$ or $\phi_0(1)(=1-\phi_1(1))$ and $\phi_0(2)$ $(=1-\phi_0(2))$ which satisfy the conditions Eq. (4.31.2) and (4.31.3) are the volume fractions in conjugate phases for arbitrary χ (or temperature T). Here, σ is called the partition coefficient. Substituting Eq.(4.31.2) in Eq. (4.31.3), we have

$$\begin{aligned} \frac{1}{n}\ln\frac{\phi_{1(2)}}{\phi_{1(1)}} = \left(\phi_{1(1)} - \phi_{1(2)}\right) - \left(\frac{\phi_{1(1)}}{n} - \frac{\phi_{1(2)}}{n}\right)&\frac{2\left(\phi_{1(1)} - \phi_{1(2)}\right) - \left(\phi_{1(2)}{}^2 - \phi_{1(1)}{}^2\right)}{\phi_{1(2)}{}^2 - \phi_{1(1)}{}^2} \\ \times\left\{\ln\frac{1 - \phi_{1(1)}}{1 - \phi_{1(2)}} + \left(\phi_{1(1)} - \phi_{1(2)}\right) - \left(\frac{\phi_{1(1)}}{n} - \frac{\phi_{1(2)}}{n}\right)\right\}& \end{aligned} \tag{4.31.4}$$

Imagine that polymer with weight g_0 is divided into phase(1) and phase(2) which contain polymers with weights $g_{(1)}$ and $g_{(2)}$, respectively,

$$g_0 = g_{(1)} + g_{(2)} \tag{4.31.5}$$

and the total volume V is divided into the two phases with volumes $V_{(1)}$ and $V_{(2)}$, i.e.,

$$V = V_{(1)} + V_{(2)} = V_0 + V_P \tag{4.31.6}$$

Here, V_0 and V_P are the volume of solvent and polymer, respectively. Now we define phase-volume ratio as

$$R = \frac{V_{(1)}}{V_{(2)}} \tag{4.31.7}$$

From Eqs. (4.31.6) and (4.31.7), we have

$$V_{(1)} = \frac{R}{R+1} V \tag{4.31.8}$$

$$V_{(2)} = \frac{1}{R+1} V \tag{4.31.9}$$

The volume fractions of the polymer in phase (1) and phase (2) are given by $\phi_{1(1)}=V_P g_{(1)}/g_0 V_{(1)}=v_p^0\ \rho_s\ (R+1)/R$ and $\phi_{1(2)}= V_P g_{(2)}/g_0 V_{(2)}=v_p^0(R+1)$.

Here, v_p^0 is the overall polymer volume fraction

$$v_p^0 = \frac{V_P}{V} \tag{4.31.10}$$

ρ_s and ρ_p are the relative amount of polymer partitioned in polymer-lean phase (1) and polymer-rich phase (2) or the fraction size, defined by

$$\rho_s = \frac{g_{(1)}}{g_0} \tag{4.31.11a}$$

$$\rho_p = \frac{g_{(2)}}{g_0} \tag{4.31.11b}$$

If the overall concentration v_p^0 and the fraction size $\rho_p(=1-\rho_s)$ are known, $\phi_{1(1)}$ and $\phi_{1(2)}$ are functions of R. Thus, the coexistence curve is calculated by solving Eq. (4.31.4) for R.

<<Problem 4-32>> Fractionation (II)

Chemical potentials of solvent and solute for polydisperse Flory-Huggins solutions are given by

$$\Delta\mu_0 = RT\left\{ \ln\left(1 - \phi_1\right) + \left(1 - \frac{1}{n_n}\right)\phi_1 + \chi\phi_1^2 \right\} \tag{3.18.5}$$

$$\Delta\mu_i = RT\left\{ \ln\phi_i - \left(n_i - 1\right) + \phi_1 n_i\left(1 - \frac{1}{n_n}\right) + \chi n_i\left(1 - \phi_1\right)^2 \right\} \tag{3.18.4'}$$

where

$$\phi_1 = \sum_{i=1}^{r} \phi_i$$

Phase equilibrium condition for this system is

$$\Delta\mu_{0(1)} = \Delta\mu_{0(2)} \tag{4.21.22}$$

$$\Delta\mu_{i(1)} = \Delta\mu_{i(2)} \qquad \left(i=1,2,3,\cdots\right) \tag{4.21.23}$$

The ratio $\phi_{1(2)}/\phi_{1(1)}$ is given by the equation $\phi_{1(2)}/\phi_{1(1)}=\exp(\sigma n)$. σ is the partition coefficient which determines how polymers are divided into two phases. Derive the **relationship between σ ,$\phi_{1(1)}$ and** $\phi_{1(2)}$ and clarify the factors which control σ.

Answer

Substituting Eqs. (3.18.5) and (3.18.4)' in the phase equilibrium conditions of Eqs. (4.21.22) and (4.21.23), we have

$$\chi = \frac{1}{{\phi_{1(2)}}^2 - {\phi_{1(1)}}^2}\left[\ln\frac{1 - \phi_{1(1)}}{1 - \phi_{1(2)}} + \left(\phi_{1(1)} - \phi_{1(2)}\right) - \left(\frac{\phi_{1(1)}}{n_{n(1)}} - \frac{\phi_{1(2)}}{n_{n(2)}}\right) \right] \tag{4.32.1}$$

and

$$\ln\frac{\phi_{i(2)}}{\phi_{i(1)}} = n_i\left[\chi\left\{ \left(1 - \phi_{1(1)}\right)^2 - \left(1 - \phi_{1(2)}\right)^2 \right\} + \left(1 - \frac{1}{n_n}\right)\phi_{1(1)} - \left(1 - \frac{1}{n_n}\right)\phi_{1(2)} \right] = n_i\sigma$$

(4.32.2)

Here,

$$\sigma = \frac{2}{\phi_{1(1)} + \phi_{1(2)}} \left[\ln \frac{1 - \phi_{1(1)}}{1 - \phi_{1(2)}} + \left(1 - \frac{1}{n_n}\right) \phi_{1(1)} - \left(1 - \frac{1}{n_n}\right) \phi_{1(2)} \right] - \ln \frac{1 - \phi_{1(1)}}{1 - \phi_{1(2)}} \tag{4.32.3}$$

Eq.(4.32.3) shows that σ depends only on $\phi_{1(1)}$, $\phi_{1(2)}$ and n_n. If σ does not depend on n, the volume fraction ratio $\phi_{1(2)}/\phi_{1(1)}$ increases with n exponentially. Eqs. (4.32.2) and (4.32.3) are the **fundamental equations for molecular weight fractionation based on the solubility difference** of polymers with different molecular weights.

<<Problem 4-33>> Fractionation (III): Partition coefficient

Chemical potentials for polydisperse polymer solutions with χ having a linear concentration dependence

$$\chi = \chi_0 \left(1 + p_1 \phi_1\right) \tag{3.16.1}$$

are given by

$$\Delta\mu_0 = RT \left[\ln\left(1 - \phi_1\right) + \left(1 - \frac{1}{n_n}\right) \phi_1 + \chi_0 \left(1 + p_1 \phi_1\right) \phi_1^{\,2} \right] \tag{4.33.1}$$

$$\Delta\mu_i = RT \left[\ln\phi_i - \left(n_i - 1\right) + n_i \left(1 - \frac{1}{n_n}\right) \phi_1 \right.$$
$$\left. + \chi_0 n_i \left(1 - \phi_1\right)^2 + \chi_0 n_i p_1 \left(\frac{1}{2} + \frac{3}{2}\phi_1^{\,2} + \phi_1^{\,3}\right) \right] \tag{4.33.2}$$

Eq. (4.33.1) is derived straightforwardly from Eq. (3.11.3). Derive the **expression for σ** defined by

$$\ln \frac{\phi_{i(2)}}{\phi_{i(1)}} = \sigma n_i \tag{4.32.2'}$$

Answer

Substituting Eq. (4.33.1) in the phase equilibrium conditions of Eq. (4.32.1), we have

$$\chi_0=\frac{1}{\left(\phi_{1(2)}{}^2-\phi_{1(1)}{}^2\right)+p_1\left(\phi_{1(2)}{}^3-\phi_{1(1)}{}^3\right)}$$

$$\left\{\ln\frac{1-\phi_{1(1)}}{1-\phi_{1(2)}}+\left(\phi_{1(1)}-\phi_{1(2)}\right)-\left(\frac{\phi_{1(1)}}{\langle n\rangle_{n(1)}}-\frac{\phi_{1(2)}}{\langle n\rangle_{n(2)}}\right)\right\} \qquad (4.33.3)$$

Substituting Eq. (3.16.1) in Eq. (4.32.2) and rearranging the equation, we have

$$\sigma=\left(1-\frac{1}{n_n}\right)\phi_{1(1)}-\left(1-\frac{1}{n_n}\right)\phi_{1(2)}+\chi_0\left\{2\left(\phi_{1(2)}-\phi_{1(1)}\right)-\left(\phi_{1(2)}{}^2-\phi_{1(1)}{}^2\right)\right\}$$

$$+p_1\chi_0\left\{\frac{3}{2}\left(\phi_{1(2)}{}^2-\phi_{1(1)}{}^2\right)-\left(\phi_{1(2)}{}^3-\phi_{1(1)}{}^3\right)\right\} \qquad (4.33.4)$$

Substituting Eq. (4.33.3) in Eq. (4.33.4), we obtain

$$\sigma=\frac{\left\{2+\frac{3}{2}p_1\left(\phi_{1(1)}+\phi_{1(2)}\right)\right\}\left\{\ln\frac{1-\phi_{1(1)}}{1-\phi_{1(2)}}+\left(1-\frac{1}{\langle n\rangle_n}\right)\phi_{1(1)}-\left(1-\frac{1}{\langle n\rangle_n}\right)\phi_{1(2)}\right\}}{\left(\phi_{1(1)}+\phi_{1(2)}\right)+p_1\left(\phi_{1(1)}{}^2+\phi_{1(1)}\phi_{1(2)}+\phi_{1(2)}{}^2\right)}$$

$$-\ln\frac{1-\phi_{1(1)}}{1-\phi_{1(2)}} \qquad (4.33.5)$$

If we put $p_1=0$, Eq.(4.33.5) is reduced to Eq.(4.32.3).

<<Problem 4-34>> Fractionation (IV): Mass of polymer partitioned in each phase

Let's denote the volumes of the dilute phase and the concentrated phase are $V_{(1)}$ and $V_{(2)}$, respectively and the weight (equal to the volume, if the specific gravity is regarded as 1) of polymers with the degree of polymerization n in the dilute phase, in the concentrated phase and in the overall system are $g_{(1)}(n)$, $g_{(2)}(n)$ and $g_0(n)$, respectively. Derive the **expressions for $g_{(1)}(n)$ and $g_{(2)}(n)$**

as a function of partition coefficient σ and phase volume ratio $R=V_{(1)}/V_{(2)}$.

Answer

From the definition, we have

$$g_{(1)}(n_i) = V_{(1)}\phi_{(1)}(n_i) \qquad (4.34.1)$$

$$g_{(2)}(n_i) = V_{(2)}\phi_{(2)}(n_i) \qquad (4.34.2)$$

$$g_0(n_i) = g_{(1)}(n_i) + g_{(2)}(n_i) \qquad (4.34.3)$$

Substituting Eqs.(4.34.1) and (4.34.2) in the definition of the partition coefficient

$$\ln \frac{\phi_{(2)}(n_i)}{\phi_{(1)}(n_i)} = \sigma n_i \qquad (4.32.2)''$$

we have

$$\frac{\left\{\dfrac{g_{(2)}(n_i)}{V_{(2)}}\right\}}{\left\{\dfrac{g_{(1)}(n_i)}{V_{(1)}}\right\}} = \exp(\sigma n_i) \qquad (4.34.4)$$

Eq. (4.34.4) can be rewritten as

$$\frac{g_{(2)}(n_i)}{g_{(1)}(n_i)} = \frac{V_{(2)}}{V_{(1)}} \exp(\sigma n_i) = \frac{1}{R} \exp(\sigma n_i) \qquad (4.34.5)$$

From Eqs. (4.34.3) and (4.34.5), we have

$$g_{(1)}(n_i) = g_0(n_i) \frac{R}{R + \exp(\sigma n_i)} \qquad (4.34.6)$$

Substituting Eq. (4.34.6) in Eq. (4.34.3), we have

$$g_{(2)}(n_i) = g_0(n_i) \frac{\exp(\sigma n_i)}{R + \exp(\sigma n_i)} \qquad (4.34.7)$$

<<Problem 4-35>> Fractionation (V): Characteristic specific value for the degree of polymerization n_a

There exists a characteristic specific value for the degree of polymerization $n=n_a$ such that the polymer with $n>n_a$ is found more in the concentrated phase and the polymer with $n<n_a$ is found more in the dilute phase. Discuss this phenomenon with the aid of the results in <<Problem 4-34>>.

Answer

Imagine equal amounts of polymers with $n=n_a$ separate into two phases. In this case, we have

$$1 = \frac{g_{(2)}(n_i)}{g_{(1)}(n_i)} = \frac{1}{R}\exp(\sigma n_a) \tag{4.35.1}$$

That is, using the relationship

$$\frac{\ln R}{\sigma} = n_a \tag{4.35.2}$$

we can calculate n_a. For $n \neq n_a$, the combination of Eqs.(4.32.2)'' and (4.35.2) yields

$$\frac{g_{(2)}(n_i)}{g_{(1)}(n_i)} = \frac{1}{R}\exp(\sigma n) = \exp\{\sigma(n - n_a)\} \tag{4.35.3}$$

Since σ is defined as positive, $g_{(2)(n)} \lessgtr g_{(1)(n)}$ for $n \lessgtr n_a$.
According to Eq. (4.35.2), the characteristic degree of polymerization n_a increases with increasing R and decreasing σ. The volume fraction of polymers in the concentrated phase is larger than that in the dilute phase for polymers for arbitrary degree of polymerization, while the amount of polymers is not always larger in the concentrated phase.

<<Problem 4-36>> Fractionation (VI): Fractionation efficiency

The probability $f_{n(2)}$ for finding n-mer in the concentrated phase can be calculated by using Eq. (4.34.7). Calculate the **fractionation efficiencies** defined by

$$\varepsilon = \left(\frac{\partial f_{n(2)}}{\partial \ln n}\right)_{n_a} \tag{4.36.1}$$

and

$$\varepsilon' = \left(\frac{\partial f_{n(2)}}{\partial n}\right)_{n_a} \tag{4.36.2}$$

and discuss which coefficient should be used as a measure of fractionation efficiency.

Answer

According to the definition,

$$f_{n(2)} = \frac{g_{(2)}(n)}{g_0(n)} \tag{4.36.3}$$

Substituting Eq. (4.34.7) in Eq. (4.36.3), we have

$$f_{n(2)} = \frac{1}{1 + R\exp(-\sigma n_i)} \tag{4.36.4}$$

Differentiating $f_{n(2)}$ by ln n and rearranging it with Eq. (4.35.2), we have

$$\varepsilon = \frac{\sigma n_a}{4} = \frac{\ln R}{4} \tag{4.36.5}$$

Differentiating $f_{n(2)}$ by n, we have

$$\varepsilon' = \frac{\sigma}{4} \tag{4.36.6}$$

From the mass balance, R is related to the difference in the overall concentration $\phi_1{}^0$ and the concentration in each phase $\phi_{1(1)}$ or $\phi_{1(2)}$ as

$$R = \frac{\phi_{1(2)} - \phi_1^0}{\phi_1^0 - \phi_{1(1)}} \tag{4.36.7}$$

Since $\phi_{1(2)} >> \phi_1{}^0$, the value of R depends essentially on the denominator in the right-hand side of Eq. (4.36.7). Thus, R increases with decreasing $\phi_1{}^0$ or decreasing $\phi_1{}^0 - \phi_{1(1)}$. The latter condition is realized by decreasing the fraction size $\rho(=\Sigma g_{(2)(n)}/\Sigma g_{0(n)})$. According to Eq.(4.36.5), we need to increase R for increasing ε. ε' could be enhanced by increasing σ. According to systematic simulations by Kamide et al., ε' reflects the width of the molecular weight distribution more sensitively than ε does. (See K. Kamide and C. Nakayama, *Makromol. Chem.* **129**, 289 (1969)). The parameters ε and ε' were first defined by Flory (See P.J. Flory, *J. Chem. Phys.* **12**, 425 (1944)).

<<Problem 4-37>> Fractionation (VII): Molecular weight distribution of polymers remaining in concentrated phase

Derive the **expression for $f_{n(2)}$ in case of the degree of polymerization $n \to \infty$ and $n \to 0$** using the equation

$$f_{n(2)} = \frac{1}{1 + R\exp(-\sigma n_i)} \tag{4.36.4}$$

and discuss the molecular weight distribution of the polydisperse polymer in the concentrated phase.

Answer

Eq. (4.36.4) is the equation for the probability of finding n-mer in the concentrated phase. For $n \to \infty$, then $f_{\infty(2)}=1$, that is, if the degree of polymerization is infinite, all the polymer components move to the concentrated phase. For $n \to 0$, $f_{0(2)}=1/(1+R) \neq 0$, that is, a finite amount of molecules moves to the concentrated phase. It's inevitable to find a certain amount of extremely low molecular weight components in the dilute phase. This phenomenon is called the tail effect. It is desired to increase R for reducing this effect. It should be also noted that R depends on σ.

<<Problem 4-38>> Fractionation (VIII): Effect of fraction size

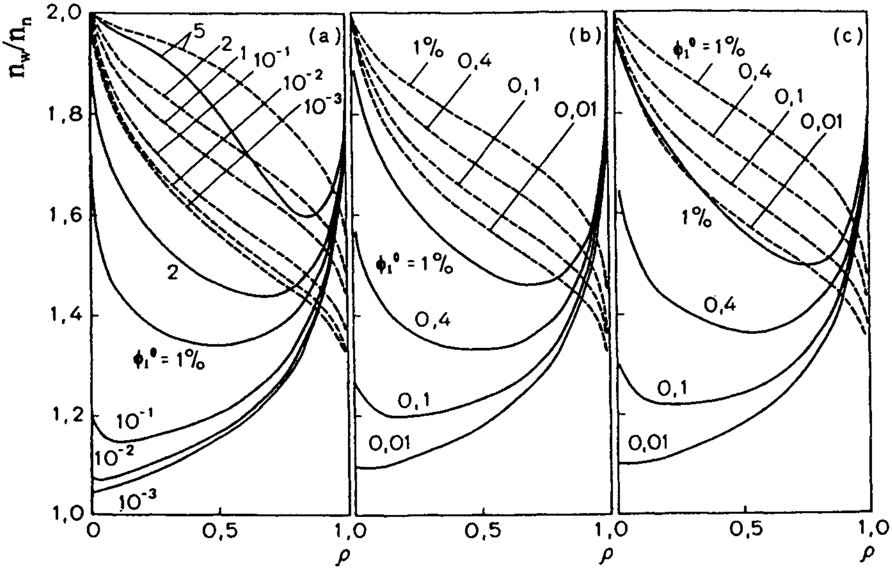

Fig. 4-38.1 Effect of ρ on n_w/n_n of the first fractionation at constant $p_1(=0)$ (in Eq. (3.16.1)). Solid line; polymer-rich phase, dashed line; polymer-lean phase (Original polymer, Schulz-Zimm distribution $n_w/n_n=2.0$; ϕ_1^0 is indicated on the curves) (a) $n_n=150$, (b) $n_n=900$, (c) $n_n=1500$ (See K. Kamide, Y. Miyazaki and K. Yamaguchi, *Makromol. Chem.* **173**, 157 (1973))

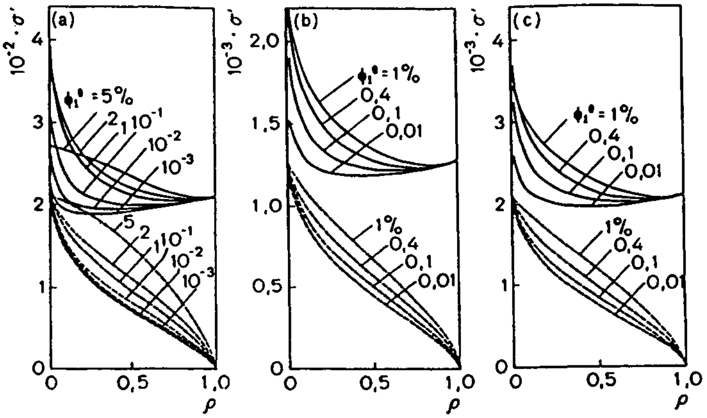

Fig. 4-38.2 Standard deviation σ' for polymer in polymer-rich phase (solid line) and polymer-lean phase (dashed line), plotted vs. ρ (Original polymer, Schulz-Zimm distribution, $n_w/n_n=2.0$, $p=0$; ϕ_1^0 is indicated on the curves). (a) $n_n=150$, (b) $n_n=900$, (c) $n_n=1500$ (See K. Kamide, Y. Miyazaki and K. Yamaguchi, *Makromol. Chem.* 173, 157 (1973))

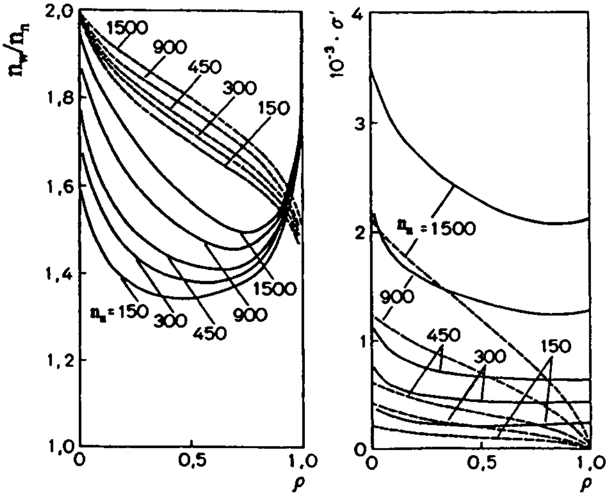

Fig. 4-38.3 Effect of the average molecular weight of the original polymer on the relations n_w/n_n, of the polymers in both phases (solid line; polymer-rich phase, dashed line; polymer-lean phase), and ρ (Original polymer, Schulz-Zimm distribution, $n_w/n_n=2.0$ and different n_n; $p=0$;$\phi_1^0=1\%$) (See K. Kamide, Y. Miyazaki and K. Yamaguchi, *Makromol. Chem.* 173, 157 (1973))

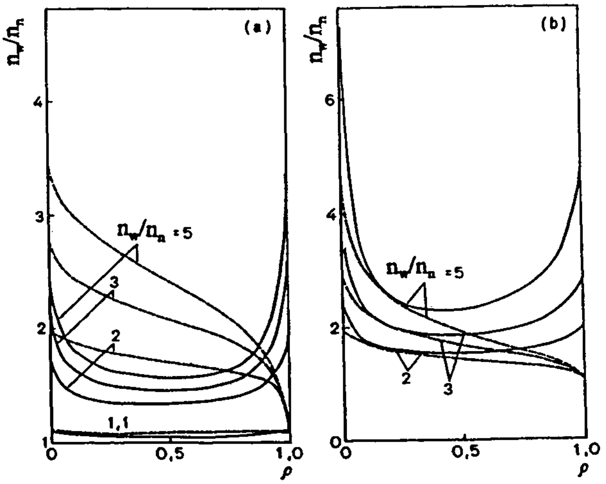

Fig. 4-38.4 Effect of the molecular weight distribution of the original polymer on n_w/n_n relationships for polymer in polymer-rich phase (solid line) and polymer-lean phase (dashed line) (Original polymer, n_w=300; p=0; ϕ_1^0=1%) (a) Schulz-Zimm distribution (b) Wesslau distribution (See K. Kamide, Y. Miyazaki and K. Yamaguchi, *Makromol. Chem.* **173**, 157 (1973))

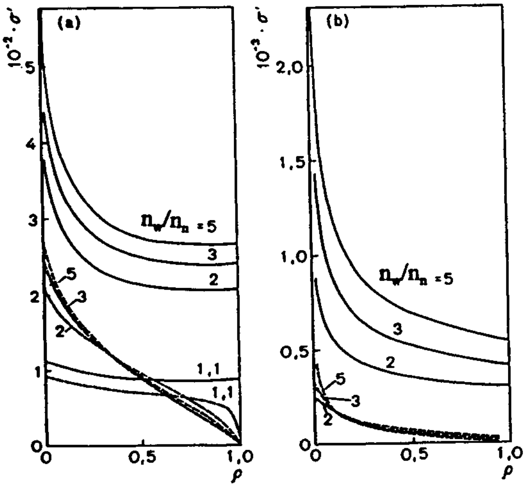

Fig. 4-38.5 Effect of the molecular weight distribution of the original polymer on σ' vs. ρ relationships for polymers in polymer-rich phase (solid line) and polymer-lean phase (dashed line) (Original polymer, n_w=300; p=0; ϕ_1^0=1%) (a) Schulz-Zimm distribution (b) Wesslau distribution (See K. Kamide, Y. Miyazaki and K. Yamaguchi, *Makromol. Chem.* **173**, 157 (1973))

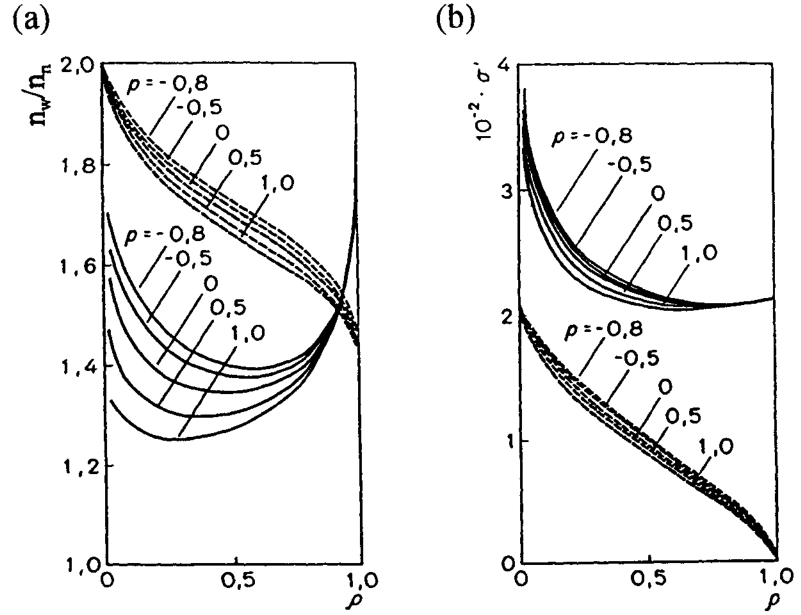

Fig. 4-38.6 (a) Effect of p (in Eq. (3.16.1)) on n_w/n_n vs. ρ relationships for polymers in polymer-rich phase (solid line) and polymer-lean phase (dashed line) (Original polymer, Schulz-Zimm distribution, n_w/n_n=2.0; n_w=300; ϕ_1^0=1%) (b) Effect of p on σ' vs. ρ relationships for polymers in polymer-rich phase (solid line) and polymer-lean phase (dashed line) (Original polymer, Schulz-Zimm distribution, n_w/n_n=2.0; n_w=300;ϕ_1^0=1%) (See K. Kamide, Y. Miyazaki and K. Yamaguchi, *Makromol. Chem.* **173**, 157 (1973))

"R should be increased by reducing the fraction size, then it results in narrowing the molecular weight distribution of each fraction". Is this discussion reasonable?

Answer

We can take n_w/n_n and the standard deviation σ' as measures of the width of the molecular weight distribution. Figures 4-38.1-6 are the examples for the relationship between the width of the molecular weight distribution and the fraction size. As demonstrated in these figures, in most cases, by coarsening the fraction size (increasing ρ), the molecular weight distribution initially narrows and then passes through a minimum (ρ_{min}). Take n_w/n_n as a measure of the width of the distribution. ρ_{min} increases with increasing ϕ_1^0 or increasing the average molecular weight of the original polymer or decreasing the concentration dependence of χ. Thus, it is not meaningful to decrease ρ in precipitation fractionation.

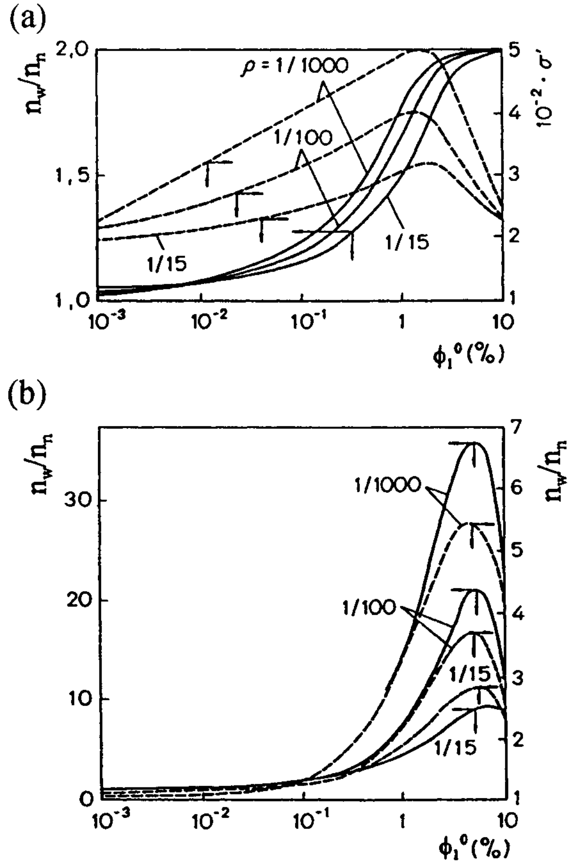

Fig. 4-39 (a) Dependence of n_w/n_n (solid line) and standard deviation σ' (dashed line) on the first fraction of ϕ_1^0 (Original polymer, Schulz-Zimm distribution, n_w/n_n=2.0;n_w=300;p=0;ρ is indicated on the curves) (b) Dependence of n_w/n_n of the first fraction on ϕ_1^0 (Original polymer, Wesslau distribution, n_w=300; n_w/n_n=2.0 (dashed line) and 5.0 (solid line); ρ is indicated on the curves) (See K. Kamide, Y. Miyazaki and K. Yamaguchi, *Makromol. Chem.* **173**, 157 (1973))

<<Problem 4-39>> Fractionation (IX): Effect of overall concentration on efficiency

"In order to improve the efficiency of the fractionation, the overall concentration $\phi_1{}^0$ must be decreased (<<Problem 4-36>>), in other words, we need to decrease the temperature of a dilute solution at the fractionation". Is this conclusion always correct?

Answer

We restrict our discussion to the precipitation fractionation. Figures 4-39(a) and (b) are the examples of the plot for width of the distribution (n_w/n_n or σ') vs. overall concentration $\phi_1{}^0$. There happens to be a maximum in these plots. Such maximum is always found in the plot of σ' vs. $\phi_1{}^0$. It should be noted that n_w/n_n and σ' at this maximum are far above those of the original polymer. For example, in Fig.4-39(b), n_w/n_n is 5 in the original polymer, while it is more than 30 in the fractionated polymer. Thus, fractionation does not always yield a polymer with narrower molecular weight distribution than the original polymer.

<<Problem 4-40>> Fractionation (X): Shape of molecular weight distribution

Can we always obtain polymers with a unimodal molecular weight distribution from the original polymer with a unimodal molecular weight distribution by successive precipitation fractionation?

Answer

From unimodal polymers with a wide molecular weight distribution, bimodal fractionated polymers can be obtained. The examples are shown in Fig. 4-40.1 and 4-40.2. When the original polymer contains a large amount of low molecular weight component (for example, Wesslau-type distribution), a new peak appears on the low molecular weight side by increasing the overall concentration or reducing the fraction size.

<<Problem 4-41>> Fractionation (XI): Successive precipitation fractionation and successive solution fractionation

Compare the successive precipitation fractionation (SPF) method in which the concentrated phase is extracted and the successive solution fractionation (SSF) method in which the dilute phase is extracted as the fractionated fraction.

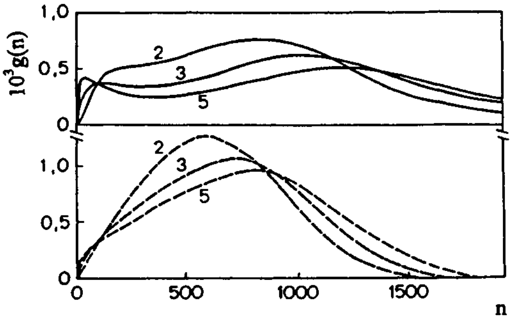

Fig. 4-40.1 Molecular weight distribution of the first fraction precipitated from 1.0% solutions of polymers (Wesslau distribution (solid line) and Schulz-Zimm distribution (dashed line); n_w/n_n=2,3, and 5; n_w=300; p=0, ρ=1/15)(See K. Kamide, K. Yamaguchi and Y. Miyazaki, *Makromol. Chem.* **173**, 133 (1973))

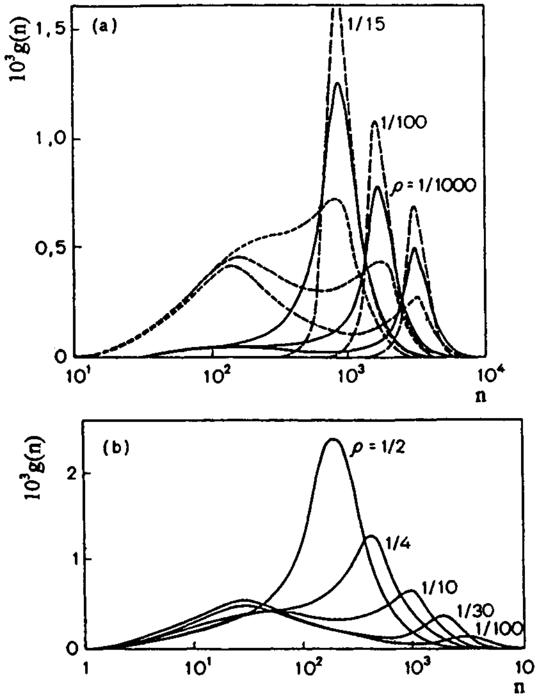

Fig. 4-40.2 Effect of the fraction size ρ on the molecular weight distribution curve of the first fractions (Original distribution, Wesslau distribution, n_w=300; p=0). (a) n_w/n_n=2.0; $\phi_1^0=10^{-3}$% (dashed line), 0.1% (solid line), and 1% (dotted line) (b) n_w/n_n=5.0; ϕ_1^0=1%

Table 4-41 Comparison of successive solution fractionation (SSF) with successive precipitation fractionation (SPF)

	Parameter	Comparison	Advantage of SSF
1.	Partition coefficient σ	SSF> SPF	yes
2.	Volume ratio R	SSF$\ll$SPF	yes
3.	Breadth in MWD of te fractions	SSF<SPF (except for extremely low n_w range)	yes
4.	Operation conditions for controlling factionation	SSF: ρ SPF:ϕ_1^0	-
5.	Effect of n_w^0/n_n^0	SSF<SPF	yes
6.	Effect of n_w^0	SSF<SPF	yes
7.	Reverse-order fractionation	only for SPF	yes
8.	Double-peaked MWD in fraction	only for SPF	yes
9.	Upper limit of initial polymer conc. ϕ_1^0	SSF>SPF	yes
10.	Easiness of phase separation	SSF$\gg$SPF	yes
11.	Accuracy of controlling faction size ρ	SSF$\gg$SPF	yes
12.	Total amount of solvent in a given run	SSF$\gg$SPF	no
13.	Ratio of n_w^0/n_n^0 of the first fraction to n_w^0/n_n^0 of the original polymer	SSF: always less than 1 SPF: always larger than 1	yes
14.	Effect of p_1 [a)]	SSF<SPF	-

a) For definition of p_1 see Eq.(3.16.4), $p_2=\cdots=p_n=0$.

(See K.Kamide, *Thermodynamics of Polymer Solutions: Phase Equilibria and Critical Phenomena*, Elsevier, 1990)

Answer

The difference between SPF and SSF is summarized in Table 4-41.

(See K. Kamide, *Fractionation of Synthetic Polymers* (Ed. by L. H. Tung), Chapter 2 Batch Fractionation, Marcel Dekker (1977) and K. Kamide, *IUPAC Macromolecular Chemistry* -8, p144, Butterworth (1973))

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* There was an extremely large gap between oversimplified theories of phase equilibria of polymer solutions and operational conditions of the fractionation in practice. In particular, the study of operational conditions of the fractionation from the standpoint of solution theory, even though qualitative, was limited to very special cases. The main reason for this limitation is that the theory of the phase equilibrium on rigorous monodisperse polymer/single solvent system cannot be generalized by simple mathematical analysis to polydisperse polymer/single solvent system, corresponding to the fractionation. It was only after many years, that by the use of electronic computers, the principal mechanism underlying the fractionation was well understood. In 1968 Kamide et al. (See K. Kamide, T. Ogawa, M. Sanada and M. Matsumoto, *Kobunshi Kagaku* **25**, 440 (1968) and K. Kamide, T. Ogawa and M. Matsumoto, *ibid.* **25**, 788 (1968)) and Koningsveld et al. (See R. Koningsveld and A. J. Staverman, *J. Polym. Sci.* **A-2**, **6**, 367, 383 (1968)) bridged this gap by using large (at that time) electronic digital computers.

Chapter 5 Colligative Properties and Virial Coefficients of Polymer Solutions

<<Problem 5-1>> Osmotic pressure (I): Vapor pressure and osmotic pressure of polymer solution

As shown in <<Problem 3-11>>, the chemical potential of solvent in monodisperse polymer solutions is given by the equation

$$\Delta\mu_0 = RT\left\{\ln\left(1 - \phi_1\right) + \left(1 - \frac{1}{n}\right)\phi_1 + \frac{B}{kT}\phi_1{}^2\right\} \tag{3.11.2}$$

Derive the **vapor pressure and osmotic pressure of the solution** as functions of volume fraction of solute ϕ_1 by using Eq.(3.11.2).

Answer

Activity of solutions a_0 is defined in Eq.(2.10.1) as

$$\Delta\mu_0 = \mu_0 - \mu_0^0 = RT\ln a_0 \tag{2.10.1'}$$

Vapor pressure and osmotic pressure of solutions are related to the activity of the solution as

$$\frac{P_0}{P_0^0} = a_0 \tag{2.10.3}$$

and

$$\Pi = -\frac{RT}{V_0^0}\ln a_0 \tag{2.10.4}$$

respectively. Thus, we have

$$\ln\frac{P_0}{P_0^0} = \frac{\Delta\mu_0}{RT} \tag{5.1.1}$$

and

$$\Pi = -\frac{\Delta\mu_0}{V_0^0} \tag{2.7.1}$$

Substitution of Eq.(3.11.2) for chemical potential in Eqs.(5.1.1) and (2.7.2) gives

$$\ln\frac{P_0}{P_0^0} = \ln\left(1 - \phi_1\right) + \left(1 - \frac{1}{n}\right)\phi_1 + \frac{B}{kT}\phi_1{}^2 \tag{5.1.2}$$

$$\Pi = -\frac{RT}{V_0^0}\left\{\ln\left(1 - \phi_1\right) + \left(1 - \frac{1}{n}\right)\phi_1 + \frac{B}{kT}\phi_1{}^2\right\}$$

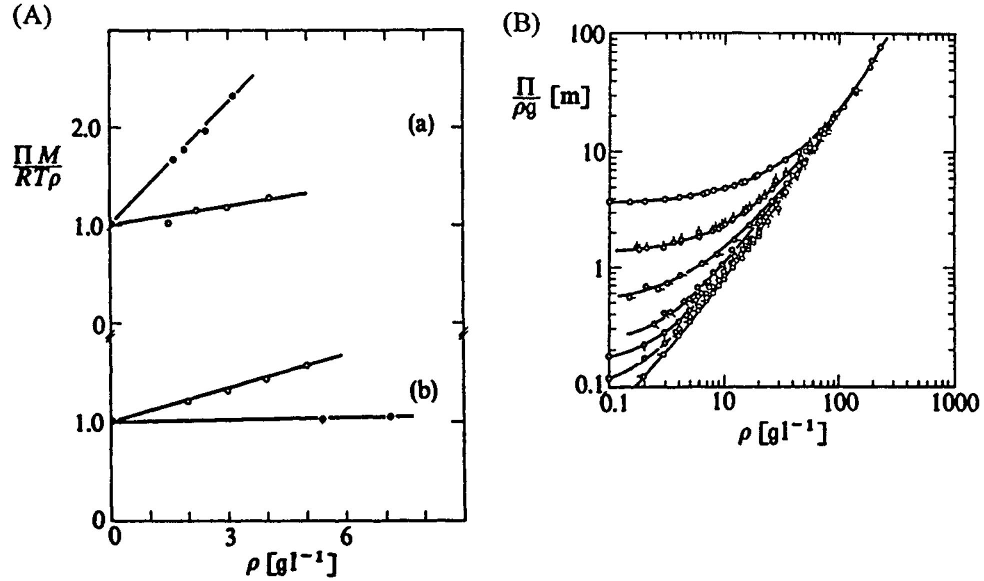

Fig. 5-1 (A) Reduced osmotic pressure for the system poly-α-methylstyrene in toluene at 25 °C against density ρ for various molecular weights. $10^{-4}M_n$= ○7,○20,○ 50.6,○ 119,○182, ○330, ○747. (B)(a) Osmotic pressure for the system polyisobutylene in cyclohexane (●) and in benzene (○) at 37 °C as a function of ρ. (b) Osmotic pressure of polystyrene in cyclohexane (●) and in benzene (○) at 37 °C as a function of ρ. (See I. Noda, N. Kato, T. Kitano and M. Nagasawa, *Macromolecules* **14**, 668 (1981); J. des Cloizeaux and G. Jannink, *Polymers in Solution: Their modelling and structure*, Oxford Sci. Publ., Oxford (1990))

$$= \frac{RT}{N_A v_0^0} \left\{ \frac{1}{n} \phi_l + \left(\frac{1}{2} - \frac{B}{kT} \right) \phi_l^{\,2} + \frac{1}{3} \phi_l^{\,3} \right\} \tag{5.1.3}$$

Here, v_0^0 is the volume of a solvent molecule and N_A is Avogadro's number. Figue 5.1 shows osmotic pressure plotted against density for various molecular weights of polymer.

<<Problem 5-2>> Osmotic pressure (II): Virial expansion

Virial expansion of osmotic pressure Π with respect to solute concentration C is given by

$$\Pi = RT\left(A_1 C + A_2 C^2 + A_3 C^3 + \cdots\right) \tag{5.2.1}$$

Derive the expression for the coefficients A_1, A_2 and A_3, referring to the relationship between C and ϕ_l.

Answer

Combination of the equations

$$\phi_l = \frac{\text{Volume of solute}}{\text{Total volume}} = \frac{n N_1 v_0^0}{\left(N_0 + n N_1\right) v_0^0} \tag{5.2.2}$$

and

$$C = \frac{\text{Weight of solute}}{\text{Total volume}} = \frac{\dfrac{M}{N_A} \cdot N_1}{\left(N_0 + n N_1\right) v_0^0} \tag{5.2.3}$$

leads to the relationship between C and ϕ_l as

$$\phi_l = \frac{N_A v_0^0 n}{M} C \tag{5.2.4}$$

Substitution of Eq.(5.2.4) for ϕ_l in Eq.(5.1.3) yields

$$\Pi = \frac{RT}{N_A v_0^0} \left\{ \frac{N_A v_0^0}{M} C + \left(\frac{1}{2} - \frac{B}{kT} \right) \frac{N_A^{\,2} v_0^{0\,2} n^2}{M^2} C^2 + \frac{N_A^{\,3} v_0^{0\,3} n^3}{3M^2} C^3 + \cdots \right\}$$

$$= RT\left\{\frac{C}{M} + \left(\frac{1}{2} - \frac{B}{kT}\right)\frac{N_A v_0^0}{m_0^{\,2}}C^2 + \frac{1}{3}\frac{\left(N_A v_0^0\right)^2}{m_0^{\,3}}C^3 + \cdots\right\} \tag{5.2.5}$$

Here, m_0=M/n is the molecular weight of a segment. Comparison of Eqs.(5.2.5) and (5.2.1) gives

$$A_1 = \frac{1}{M} \tag{5.2.6}$$

$$A_2 = \left(\frac{1}{2} - \frac{B}{kT}\right)\frac{N_A v_0^0}{m_0^2} \tag{5.2.7}$$

$$A_3 = \frac{1}{3}\frac{\left(N_A v_0^0\right)^2}{m_0^3} \tag{5.2.8}$$

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* Eq. (5.1.3) can also be expressed as

$$\frac{\Pi V_0}{RT} = \frac{\phi_1}{n} + \left(\frac{1}{2} - \chi\right)\phi_1^{\,2} + \frac{1}{3}\phi_1^{\,3} + \cdots \tag{5.2.9}$$

Here, χ=B/kT is a thermodynamic interaction parameter and $V_0=N_A\ v_0^0$ is the molar volume of solvent. If $\phi_1 << 1/n$, the higher order terms in Eq.(5.2.9) can be neglected. The first term is called van't Hoff's term.

<<Problem 5-3>> Osmotic pressure (III)

Derive the **equation for osmotic pressure**:

Table 5-3 Second virial coefficient of polystyrene solutions for various solvents at 20 °C

solvent	molecular weight (10^3g/mol)	A_2 (10^{-4}mol cm^3/g^2)
benzene	1330 to 7100	3.6 to 3.3
bromobenzene	35.5 to 1750	6.38 to 2.15
decalin	390	-0.06
toluene	12.3 to 40.2	2.18 to 1.37
trans-decalin	179.3	-0.036

$$\frac{\Pi}{C} = \frac{RT}{M} + RT\frac{\bar{v}^2}{V_0}\left(\frac{1}{2} - \chi\right)C + \cdots \tag{5.3.1}$$

Here, $\bar{v}$ is the partial specific volume of solute polymer.

Answer

Referring to Eq. (5.2.4), we can readily derive the relationship

$$\frac{\phi_1}{V_0 n} = \frac{C}{M} = \frac{Cv}{V_0 n} \tag{5.3.2}$$

Here,

$$\left.\begin{aligned} N_A v_0^0 &= V_0 \\ \phi_1 &= C\bar{v} = \frac{V_0}{m_0}C \end{aligned}\right\} \tag{5.3.3}$$

Substitution of Eq. (5.3.2) in (5.1.3) using the definition of χ yields

$$A_2 = \frac{\bar{v}^2}{V_0}\left(\frac{1}{2} - \chi\right) \tag{5.3.4}$$

and Eq. (5.3.1).

<<Problem 5-4>> Second virial coefficient (I): Internal energy and entropy terms

According to Flory's theory, the **second virial coefficient A_2 of polymer solutions** is given by

$$A_2 = \frac{\bar{v}^2}{V_0}\varphi\left(1 - \frac{\theta}{T}\right) \tag{5.4.1}$$

Express φ and θ in terms of the internal energy Δu_{12} and entropy ΔS_{12} for forming a 1-2 pair. Here the subscripts 1 and 2 denote solvent and polymer segment, respectively.

Answer

The variation in Gibbs free energy ε for forming a 1-2 pair is expressed as

$$\varepsilon = \Delta w_{12} = \Delta u_{12} - T\Delta S_{12} \tag{5.4.2}$$

Thus,

$$\chi = \frac{z\varepsilon}{kT} = \frac{z\Delta u_{12}}{kT} - \frac{z\Delta S_{12}}{k} \tag{5.4.3}$$

Substitution of Eq. (5.4.3) in Eq. (5.3.4) yields

$$A_2 = \frac{\bar{v}^2}{V_0}\left(\frac{1}{2} + \frac{z\Delta S_{12}}{k} - \frac{z\Delta u_{12}}{kT}\right)$$

$$= \frac{\bar{v}^2}{V_0}\left(\frac{1}{2} + \frac{z\Delta S_{12}}{k}\right)\left(1 - \frac{z\Delta u_{12}}{k\left(\frac{1}{2} + \frac{z\Delta S_{12}}{k}\right)}\cdot\frac{1}{T}\right) \tag{5.4.4}$$

Comparing Eqs.(5.4.1) with (5.4.4), we have

$$\varphi = \frac{1}{2} + \frac{z\Delta S_{12}}{k} \tag{5.4.5}$$

$$\theta = \frac{z\Delta u_{12}}{k\left(\frac{1}{2} + \frac{z\Delta S_{12}}{k}\right)} \tag{5.4.6}$$

<<Problem 5-5>> Second virial coefficient (II): van der Waals equation

Derive the expression for the **second virial coefficient for van der Waals equation**

$$\left(\Pi + \frac{N^2 a}{V^2}\right)\left(V - Nb\right) = NRT \tag{5.5.1}$$

(a and b are the van der Waals parameters representing intermolecular attraction and repulsion, respectively, (V-Nb) is the free volume, aN^2/V^2 is the reduction of pressure and n is the number of moles in volume V) for the osmotic pressure

$$\frac{\Pi}{C} = RT\left(A_1 + A_2C + A_3C^2 + \cdots\right) \tag{5.2.1}$$

Answer

Eq. (5.5.1) is expanded as a series of the inverse of volume as

$$\Pi+\frac{N^2a}{V^2}=\frac{NRT}{V}\left(1-\frac{Nb}{V}\right)^{-1}=\frac{NRT}{V}\left(1+\frac{Nb}{V}+\frac{(Nb)^2}{V^2}+\cdots\right) \tag{5.5.2}$$

Rearrangement of Eq. (5.5.2) yields

$$\frac{\Pi V}{RT}=N+\frac{1}{V}\left(N^2b-\frac{N^2a}{RT}\right)+\frac{N^3b^2}{V^2}+\cdots \tag{5.5.3}$$

Putting C=NM/V in Eq. (5.2.1), we have

$$\Pi=CRT(A_1+A_2C+A_3C^2+\cdots) \tag{5.5.4}$$

$$\frac{\Pi V}{RT}=A_1NM+\frac{A_2N^2M^2}{V}+\frac{A_3N^3M^3}{V^2}+\cdots \tag{5.5.5}$$

Comparison of Eq.(5.5.3) with Eq. (5.5.5) yields

$$N=A_1NM \quad \text{or} \quad A_1=\frac{1}{M} \tag{5.5.6}$$

$$N^2b-\frac{N^2a}{RT}=A_2N^2M^2 \quad \text{or} \quad A_2=\left(b-\frac{a}{RT}\right)\frac{1}{M^2} \tag{5.5.7}$$

<<Problem 5-6>> Flory temperature for van der Waals equation

Derive the expression for the **Flory temperature (θ temperature)** defined as the temperature at $A_2=0$ for van der Waals equation.

Answer

Using Eq. (5.5.7), the temperature θ for $A_2=0$ is obtained as

$$\theta=\frac{a}{Rb} \tag{5.6.1}$$

This temperature is called the **Boyle temperature** for van der Waals gas.

<<Problem 5-7>> Partition function for semi-grand canonical ensemble (I)

Consider a solution with volume V which contains N_1 solute molecules, enclosed by a wall, which is permeable only to solvent molecules from pure solvent outside. After a certain time much longer than the time required for molecular motion, the temperature inside and outside of the volume V becomes the same (thermal equilibrium) and the chemical potentials of solvent inside and outside of V agree with each other. At this stage, the osmotic pressure of the solution Π is given by

$$\Pi = kT\left(\frac{\partial \ln \xi^*\left(T,V,\mu_0,N_1\right)}{\partial V}\right)_{T,\mu_0,N_1} \tag{5.7.1}$$

where

$$\xi^*\left(T,V,\mu_0,N_1\right) = \frac{\xi\left(T,V,\mu_0,N_1\right)}{\xi\left(T,V,\mu_0,0\right)} \tag{5.7.2}$$

Here, ξ is the partition function of the system in question which is called **constant μ_0 ensemble or semi-grand canonical ensemble**. Derive Eq. (5.7.1).

Answer

For the case both mass and heat flow through the wall of the system are not possible (microcanonical ensemble), the partition function $\Omega(E)$ is the volume for the energy between E and E+dE in the phase space. For the case heat flow

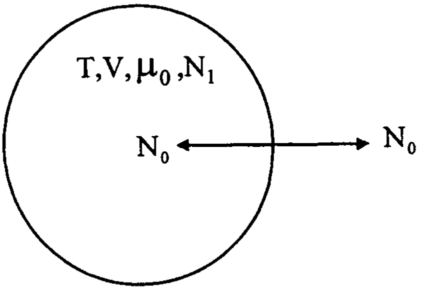

Fig. 5-7 Constant μ_0 ensemble

is permitted while mass flow is not permitted (canonical ensemble), the partition function $Z(T,V,N_0,N_1)$ is the integral of the product of $\Omega(E)$ and Boltzmann's factor exp(-E/kT):

$$Z\left(T,V,N_0,N_1\right) = \int \Omega(E)e^{-E/kT}dE \tag{5.7.3}$$

In the case when all molecular species can pass through the wall, taking account of the change in the number of molecules, the **grand partition function** Ξ is given by

$$\Xi\left(T,V,\mu_0,\mu_1\right) = \sum_{N_0}\sum_{N_1} Z\left(T,V,N_0,N_1\right)\lambda_0^{N_0}\lambda_1^{N_1} \tag{5.7.4}$$

where

$$\left.\begin{aligned}\lambda_0 &= e^{\mu_0/kT}\\ \lambda_1 &= e^{\mu_1/kT}\end{aligned}\right\} \tag{5.7.5}$$

N_0 is the number of solvent molecules and μ_0 and μ_1 are the chemical potentials of solvent and solute, respectively.

The wall of the system in question is only permeable to the solvent. Thus, this system is an ensemble which has an intermediate character between the canonical ensemble and the grand canonical ensemble. Referring to Eq. (5.7.4), the partition function ξ is given by

$$\xi\left(T,V,\mu_0,N_1\right) = \sum_{N_0} Z\left(T,V,N_0,N_1\right)\lambda_0^{N_0} \tag{5.7.6}$$

A new thermodynamic function F' is defined by

$$F' = -kT\ln\xi \tag{5.7.7}$$

F' is related to the **Helmholtz free energy** as

$$F' = F - \mu_0 N_0 \tag{5.7.8}$$

Total differentiation of Eq. (5.7.8) gives

$$dF' = dF - N_0 d\mu_0 - \mu_0 dN_0 \tag{5.7.9}$$

Substitution of the total differential

$$dF = -SdT - PdV + \sum_{i=1} \mu_i dN_i \tag{5.7.10}$$

in Eq. (5.7.9) yields

$$dF' = - SdT - PdV - N_0 d\mu_0 + \mu_1 dN_1 \qquad (5.7.11)$$

From Eq. (5.7.11), we have

$$P = - \left(\frac{\partial F'}{\partial V}\right)_{T,\mu_0,N_1} \qquad (5.7.12)$$

Substitution of (5.7.7) in Eq. (5.7.12) gives

$$P = kT\left(\frac{\partial \ln \xi\left(T,V,\mu_0,N_1\right)}{\partial V}\right)_{T,\mu_0,N_1} \qquad (5.7.13)$$

Osmotic pressure is defined by the difference of the pressure of the solution P and that of pure solvent P_0. Thus, we have the expression for osmotic pressure as

$$\Pi = P - P_0$$

$$= kT\left\{\left(\frac{\partial \ln \xi\left(T,V,\mu_0,N_1\right)}{\partial V}\right)_{T,\mu_0,N_1} - \left(\frac{\partial \ln \xi\left(T,V,\mu_0,0\right)}{\partial V}\right)_{T,\mu_0,N_1}\right\}$$

$$= kT\left\{\frac{\partial}{\partial V}\left(\ln \xi\left(T,V,\mu_0,N_1\right) - \ln \xi\left(T,V,\mu_0,0\right)\right)\right\}_{T,\mu_0,N_1}$$

$$= kT\left(\frac{\partial}{\partial V}\ln \xi^*\left(T,V,\mu_0,N_1\right)\right)_{T,\mu_0,N_1} \qquad (5.7.1)$$

<<Problem 5-8>> Partition function for semi-grand canonical ensemble (II)

When the wall of the system in <<Problem 5-7>> is impermeable to both solvent and solute (**canonical ensemble**), the partition function is given by

$$Z\left(T,V,N_0,N_1\right)=\frac{1}{N_0!N_1!}\cdot\frac{1}{h^{f_0N_0}h^{f_1N_1}}\int\cdots\int\exp\left(-\frac{E\left(N_0,N_1\right)}{kT}\right)d\tau_{N_0}d\tau_{N_1}$$

$$d\tau_{N_i}=\prod_{k=1}^{N_i}\prod_{j=1}^{f_i}dp_{k_j}^{(i)}dq_{k_j}^{(i)} \tag{5.8.1}$$

Here, the factors $N_0!$ and $N_1!$ in the right-hand side indicate that the problem handles indistinguishable N_0 solvent molecules and N_1 solute molecules. h is Planck's constant. For one molecule with the degree of freedom f, the inside of the volume of h^f in the phase space is indistinguishable. Thus, for N-molecule system, the inside of the volume $(h^f)^N=h^{fN}$ is indistinguishable. $h^{f_0N_0}$ and $h^{f_1N_1}$ are inserted for this reason. $E(N_0,N_1)$ is the total energy (the sum of potential energy and kinetic energy) of the system consisting of N_0 solvent molecules and N_1 solute molecules. $p_{k_j}^{(i)}$ and $q_{k_j}^{(i)}$ are the conjugate momentum and coordinate for the j th degree of freedom of k th molecule (for solvent, k th molecule in total N_0 molecules) of i th species (solvent or solute). Let's define W' by the equation

$$\frac{\displaystyle\sum_{N_0}\frac{1}{N_0!N_1!}\cdot\frac{1}{h^{f_0N_0}h^{f_1N_1}}\lambda_0^{N_0}\int\cdots\int\exp\left(-\frac{E\left(N_0,N_1\right)}{kT}\right)d\tau_{N_0}}{\displaystyle\sum_{N_0}\frac{1}{N_0!}\cdot\frac{1}{h^{f_0N_0}}\lambda_0^{N_0}\int\cdots\int\exp\left(-\frac{E\left(N_0\right)}{kT}\right)d\tau_{N_0}}=\frac{1}{N_1!}\cdot\frac{1}{h^{f_1N_1}}\exp\left(-\frac{W'}{kT}\right) \tag{5.8.2}$$

Derive the expression for ξ^* using Eq. (5.8.2).

Answer

ξ^* defined by Eq. (5.7.2) is obtained from Eq. (5.8.1) and (5.8.2) as

$$\xi^*\left(T,V,\mu_0,N_1\right)=\frac{\xi\left(T,V,\mu_0,N_1\right)}{\xi\left(T,V,\mu_0,0\right)}=\frac{\displaystyle\sum_{N_0}Z\left(T,V,\mu_0,N_1\right)\lambda_0{}^{N_0}}{\displaystyle\sum_{N_0}Z\left(T,V,\mu_0,0\right)\lambda_0{}^{N_0}}$$

$$= \frac{\sum_{N_0} \frac{1}{N_0!N_1!}\cdot\frac{1}{h^{f_0N_0+f_1N_1}}\lambda_0^{N_0}\int\cdots\int \exp\left(-\frac{E(N_0,N_1)}{kT}\right)d\tau_{N_0}d\tau_{N_1}}{\sum_{N_0}\frac{1}{N_0!}\cdot\frac{1}{h^{f_0N_0}}\lambda_0^{N_0}\int\cdots\int\exp\left(-\frac{E(N_0)}{kT}\right)d\tau_{N_0}}$$

$$= \frac{1}{N_1!}\cdot\frac{1}{h^{f_1N_1}}\int\cdots\int\exp\left(-\frac{W'}{kT}\right)d\tau_{N_1} \qquad (5.8.3)$$

Eq.(5.8.3) has the same form as the partition function $Z(T,V,N_1)$ in case of no solvent. (Compare with Eq. (5.8.1))

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* W′ is a function of momentum and coordinate of solvent molecules. When $N_1=0$ (pure solvent), the left-hand side of Eq. (5.8.2) is $1/N_1!h^{f_1N_1}$, then $W'=0$. Suppose the internal energy can be divided into kinetic energy E_1 and potential energy u as

$$E = E_1 + u \qquad (5.8.4)$$

Correspondingly, W′ is divided as

$$W' = E_1' + W'' \qquad (5.8.5)$$

Here, W″ is a function of coordinate of solute molecules. In order to clarify the physical meaning of W′ and W″, we differentiate W′ with respect to the coordinate of solute molecules and denote it as $\mathrm{grad}_S W'$:

$$-\frac{\partial W'}{\partial S} = -\mathrm{grad}_s W' = -\mathrm{grad}_s W''$$

$$= -kT\frac{\partial}{\partial S}\left(\ln\sum_{N_0}\frac{1}{N_0!N_1!}\cdot\frac{1}{h^{f_0N_0+f_1N_1}}\lambda_0^{N_0}\int\cdots\int\exp\left(-\frac{E(N_0,N_1)}{kT}\right)d\tau_{N_0}\right)$$

$$= \frac{-kT\sum_{N_0}\frac{1}{N_0!N_1!}\cdot\frac{1}{h^{f_0N_0+f_1N_1}}\lambda_0^{N_0}\frac{\partial}{\partial S}\int\cdots\int\exp\left(-\frac{E(N_0,N_1)}{kT}\right)d\tau_{N_0}}{\sum_{N_0}\frac{1}{N_0!N_1!}\cdot\frac{1}{h^{f_0N_0+f_1N_1}}\lambda_0^{N_0}\int\cdots\int\exp\left(-\frac{E(N_0,N_1)}{kT}\right)d\tau_{N_0}}$$

$$= \frac{\displaystyle\sum_{N_0} \frac{1}{N_0!N_1!} \cdot \frac{1}{\mathrm{h}^{f_0N_0+f_1N_1}} \lambda_0^{N_0} \int \cdots \int \left(- \mathrm{grad}_s \mathrm{E} \right) \exp\left(- \frac{\mathrm{E}(N_0,N_1)}{\mathrm{kT}} \right) d\tau_{N_0}}{\displaystyle\sum_{N_0} \frac{1}{N_0!N_1!} \cdot \frac{1}{\mathrm{h}^{f_0N_0+f_1N_1}} \lambda_0^{N_0} \int \cdots \int \exp\left(- \frac{\mathrm{E}(N_0,N_1)}{\mathrm{kT}} \right) d\tau_{N_0}} \tag{5.8.6}$$

Eq.(5.8.6) means that the statistical average of $-\mathrm{grad}_s\mathrm{E}$ is $-\mathrm{grad}_s \mathrm{W}''$. Thus, W'' is the mean-force potential between solute molecules.

<<Problem 5-9>> N-body distribution function

As shown in <<Problem 5-8>>, W' is divided into two factors corresponding to the kinetic energy E_1' and the potential energy W''as $\mathrm{W}' = \mathrm{E}_1' + \mathrm{W}''$. Substituting this expression in Eq. (5.8.6), we have

$$\begin{aligned} &\xi^* \left(\mathrm{T},\mathrm{V},\mu_0,N_1\right) \\ &= \frac{1}{N_1!} \cdot \frac{1}{\mathrm{h}^{f_1N_1}} \int \cdots \int \exp\left(- \frac{\mathrm{E}_1'}{\mathrm{kT}} \right) \prod_{k=1}^{N_i} \prod_{j=1}^{f_i} dp_{k_j}^{(1)} \int \cdots \int \exp\left(- \frac{\mathrm{W}''}{\mathrm{kT}} \right) \prod_{k=1}^{N_i} \prod_{j=1}^{f_i} dq_{k_j}^{(1)} \\ &= \frac{1}{N_1!} \cdot \frac{1}{\mathrm{h}^{f_1N_1}} c(\mathrm{T}) \int \cdots \int \exp\left(- \frac{\mathrm{W}''}{\mathrm{kT}} \right) d\{N_i\} \end{aligned} \tag{5.9.1}$$

where

$$d\{N_i\} \equiv \prod_{k=1}^{N_i} \prod_{j=1}^{f_i} dq_{k_j}{}^{(1)}$$

Now we define $\mathrm{W_N}$ as W'' plus a certain constant and assign numbers $1,2,\cdots,N$ to the solvent molecules. Then the function $\mathrm{F_N}$ defined by

$$\mathrm{F_N}(1,2,\cdots,N) = \exp\left(- \frac{\mathrm{W_N}}{\mathrm{kT}} \right) \tag{5.9.2}$$

is a function of coordinates of N solvent molecules. We denote the coordinate of i th molecule as $\{\mathrm{i}\}$ and similarly the coordinate of m th molecule as $\{\mathrm{m}\}$. The constant used for defining $\mathrm{W_N}$ is determined so that $\mathrm{F_N}$ satisfies the normalization condition

$$\lim_{V\to\infty}\frac{1}{V^N}\int\cdots\int F_N(1,2,\cdots,N)d\{N\}=1 \tag{5.9.3}$$

where F_N is the **N-body distribution function**. Then we define $g_1(i), g_2(i,j)$, …

by

$$\begin{aligned}
F_1(1)&=g_1(1)\\
F_2(1,2)&=g_1(1)g_1(2)+g_2(1,2)\\
F_3(1,2,3)&=g_1(1)g_1(2)g_1(3)+g_1(1)g_2(2,3)+g_1(2)g_2(3,1)\\
&\quad+g_1(3)g_2(1,2)+g_3(1,2,3)
\end{aligned} \tag{5.9.4}$$

For example, $g_2(1,2)$ is defined by

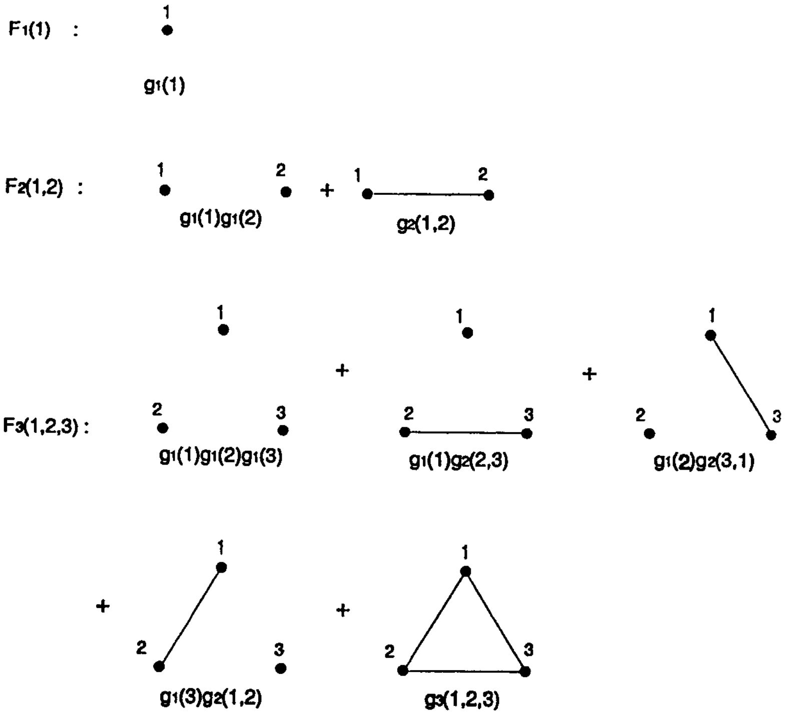

Fig. 5-9 N-body distribution function

$$g_2(1,2)=F_2(1,2)-F_1(1)F_1(2) \tag{5.9.5}$$

Here, 1 and 2 denote the coordinates of 1st and 2nd molecule, respectively. Then, we divide N solute molecules into k set of n_i (i=1,2,3...k) molecules. F_N can be expressed as

$$F_N(1,2,\cdots,N)=\sum_{\{k\{n_i\}\}}\prod_{i=1}^{k} g_{n_i}(\{n_i\}) \tag{5.9.6}$$

$$n_1+n_2+\cdots+n_k=N \tag{5.9.7}$$

Here, $\Sigma\,\{k\{n_i\}\}$ denotes the sum over all ways of division and number of sets (integer partition). On the other hand, **cluster integrals** are defined by

$$\left.\begin{aligned} b_1&=\frac{1}{V}\int_V g_1(1)d(1)\\ b_2&=\frac{1}{V2!}\int\cdot\int_V g_2\{2\}d\{2\}\\ &\vdots\\ b_m&=\frac{1}{Vm!}\int\cdots\int_V g_m(\{m\})d\{m\}\end{aligned}\right\} \tag{5.9.8}$$

Prove that Eq. (5.9.1) reduces to

$$\xi^*(T,V,\mu_0,N)=\frac{1}{N!}\cdot\frac{1}{h^{fN}}c(T)\sum_{\{k\{n_i\}\}}\prod_{i=1}^{k}\left(Vn_i!b_{n_i}\right) \tag{5.9.9}$$

Answer

Eq. (5.9.3) for N=1 is written as

$$\lim_{V\to 0}\frac{1}{V}\int_V F_1(1)d(1)=\lim_{V\to 0}\frac{1}{V}\int_V g_1(1)d(1)=1=b_1 \tag{5.9.10}$$

Referring to Eq. (5.9.8), b_{n_i} is expressed as

$$b_{n_i}=\frac{1}{Vn_i!}\int\cdots\int g_{n_i}(\{n_1\})d\{n_i\} \tag{5.9.11}$$

From Eq. (5.9.6), we have

$$\int\cdots\int F_N(\{N\})d\{N\} = \int\cdots\int \sum_{\{k\{n_i\}\}} \prod_{i=1}^{k} g_{n_i}(\{n_i\})d\{n_i\} \tag{5.9.12}$$

Substituting Eq. (5.9.11) in Eq. (5.9.12), we have

$$\int\cdots\int F_N(\{N\})d\{N\} = \sum_{\{k\{n_i\}\}} \prod_{i=1}^{k} \int\cdots\int g_{n_i}(\{n_i\})d\{n_i\} = \sum_{\{k\{n_i\}\}} \prod_{i=1}^{k} \left(b_{n_i} V n_i!\right) \tag{5.9.13}$$

Eq. (5.9.1) can be reduced to

$$\xi^*(T,V,\mu_0,N) = \frac{1}{N!}\cdot\frac{1}{h^{fN}}c(T)\int\cdots\int F_N(1,2,\cdots,N)d\{N\} \tag{5.9.14}$$

Substitution of Eq. (5.9.13) in Eq. (5.9.14) yields Eq. (5.9.9).

---

* $F_1(1)d(1)$ is the probability that the first molecule is found at the coordinate between (1) and (1) +d(1). $F_2(1,2)d(1)d(2)$ is the probability that the first molecule is located at the coordinate between (1) and (1)+d(1) and the second molecule is located at the coordinate between (2) and (2)+d(2) simultaneously. $F_1(1)$ and $F_2(1,2)$ are called the **molecular distribution function**.

* Eq. (5.9.3) means that the probability for N molecules being found somewhere in the volume V is unity, in other words, there are N molecules in the volume V.

<<Problem 5-10>> Osmotic pressure (IV): Cluster integrals

Osmotic pressure is given by

$$\Pi = kT\left(\frac{\partial \ln \xi^*(T,V,\mu_0,N)}{\partial V}\right)_{T,\mu_0,N} \tag{5.7.1}$$

where ξ^* is expressed as

$$\xi^*(T,V,\mu_0,N) = \frac{1}{N!}\cdot\frac{1}{h^{fN}}c(T) \sum_{\{k\{n_i\}\}} \prod_{i=1}^{k} \left(V n_i! b_{n_i}\right) \tag{5.9.9}$$

Using Eqs. (5.7.1) and (5.9.9), derive the equation

$$\Pi = \mathrm{kT}\left(\frac{N}{\mathrm{V}}-\frac{N^2}{\mathrm{V}^2}\mathrm{b}_2+4\frac{N^3}{\mathrm{V}^3}\mathrm{b}_2{}^2-2\frac{N^3}{\mathrm{V}^3}\mathrm{b}_3+\cdots\right) \tag{5.10.1}$$

Answer

Substituting Eq. (5.9.9) in Eq. (5.7.1), we have

$$\Pi = \mathrm{kT}\left(\frac{\partial \ln \xi^*(\mathrm{T},\mathrm{V},\mu_0,N)}{\partial \mathrm{V}}\right)_{\mathrm{T},\mu_0,N} = \mathrm{kT}\frac{\partial \ln}{\partial \mathrm{V}}\left\{\frac{1}{N!}\cdot\frac{1}{\mathrm{h}^{fN}}\mathrm{c}(\mathrm{T})\sum_{\{\mathrm{k}\{\mathrm{n}_i\}\}}\prod_{\mathrm{i}=1}^{\mathrm{k}}\left(\mathrm{Vn}_i!\mathrm{b}_{\mathrm{n}_i}\right)\right\}$$

$$= \mathrm{kT}\frac{\partial \ln}{\partial \mathrm{V}}\sum_{\{\mathrm{k}\{\mathrm{n}_i\}\}}\prod_{\mathrm{i}=1}^{\mathrm{k}}\left(\mathrm{Vn}_i!\mathrm{b}_{\mathrm{n}_i}\right) \tag{5.10.2}$$

$\mathrm{P}(\mathrm{Vn}_i!\mathrm{b}_{\mathrm{n}i})$ can be calculated as follows:

(1) Divide N solute molecules into each individual molecule giving N groups ($\mathrm{n}_1=\mathrm{n}_2=\ldots\mathrm{n}_N=1$). The number of ways to divide in such a way is unity. Then $\mathrm{n}_i=1$ and
$\mathrm{b}_1=1$. That is,

$$\sum_{\mathrm{k}=N}\prod_{\mathrm{i}=1}^{N}\left(\mathrm{Vn}_i!\mathrm{b}_{\mathrm{n}_i}\right)=\prod_{\mathrm{i}=1}^{N}(\mathrm{V}\cdot 1)=\mathrm{V}^N \tag{5.10.3}$$

(2) Divide N solute molecules into one group consisting of two molecules ($\mathrm{n}_1=2$) and all other groups consisting of one molecule ($\mathrm{n}_2=\mathrm{n}_3=\ldots\mathrm{n}_{N-1}=1$) to make N-1 groups. The number of ways to take one group consisting of two molecules from N solute molecules is $N(N-1)/2$. That is,

$$\sum_{\mathrm{k}=N-1}\prod_{\mathrm{i}=1}^{\mathrm{k}}\left(\mathrm{Vn}_i!\mathrm{b}_{\mathrm{n}_i}\right)=\frac{N(N-1)}{2}(\mathrm{V})^{N-2}\left(\mathrm{V}2!\mathrm{b}_2\right)=\frac{N(N-1)}{2}\mathrm{V}^{N-1}\left(2!\mathrm{b}_2\right) \tag{5.10.4}$$

(3) Divide N solute molecules into two groups consisting of two molecules ($\mathrm{n}_1=\mathrm{n}_2=2$) and all other groups consisting of one molecule ($\mathrm{n}_3=\mathrm{n}_4=\ldots\mathrm{n}_{N-2}=1$) to make N-2 groups. The number of ways to take two groups consisting of two molecules from N solute molecules is $N!/((N-4)!2!2!2!)$. Here, 2!s are inserted for eliminating indistinguishable configurations.

$$\sum_{k=N\text{-}2}\prod_{i=1}^{k}\left(\mathrm{V}n_i!b_{n_i}\right)=\frac{N!}{(N-4)!2!2!2!}(\mathrm{V})^{N\text{-}4}\left(\mathrm{V}2!b_2\right)^2=\frac{N!}{(N-4)!2!2!2!}(\mathrm{V})^{N\text{-}2}\left(2!b_2\right)^2 \tag{5.10.5}$$

(4) Divide N solute molecules into one group consisting of three molecules (n_1=3) and all other groups consisting of one molecule (n_2=n_3=...$n_{N\text{-}2}$=1) to make N-2 groups. The number of ways to take one group consisting of two molecules from N solute molecules is $N!/((N\text{-}3)!3!)$. That is,

$$\sum_{k=N\text{-}2}\prod_{i=1}^{k}\left(\mathrm{V}n_i!b_{n_i}\right)=\frac{N!}{(N-3)!3!}\mathrm{V}^{N\text{-}3}\left(\mathrm{V}3!b_3\right)=\frac{N!}{(N-3)!3!}\mathrm{V}^{N\text{-}2}\left(\mathrm{V}3!b_3\right) \tag{5.10.6}$$

Substituting Eqs. (5.10.3)-(5.10.6) in Eq. (5.10.2), we obtain

$$\Pi=\mathrm{kT}\frac{\partial\ln}{\partial\mathrm{V}}\left\{\mathrm{V}^N+\frac{N(N-1)}{2}\mathrm{V}^{N\text{-}1}\left(2!b_2\right)+\frac{N!}{(N-4)!2!2!2!}\mathrm{V}^{N\text{-}2}\left(2!b_2\right)^2\right.$$
$$\left.+\frac{N!}{(N-3)!3!}\mathrm{V}^{N\text{-}2}\left(3!b_3\right)+\cdots\right\}$$
$$=\mathrm{kT}\frac{\partial}{\partial\mathrm{V}}\left[\ln\mathrm{V}^N+\ln\left\{1+\frac{N(N-1)}{2}\cdot\frac{2!b_2}{\mathrm{V}}+\frac{N!}{(N\text{-}4)!2!2!2!}\cdot\frac{\left(2!b_2\right)^2}{\mathrm{V}^2}\right.\right.$$
$$\left.\left.+\frac{N!}{(N-3)!3!}\cdot\frac{3!b_3}{\mathrm{V}^2}+\cdots\right\}\right] \tag{5.10.7}$$

The partial differentiation of the second logarithmic term in Eq. (5.10.7) yields

$$\frac{\partial}{\partial\mathrm{V}}\ln\left\{1+\frac{N(N-1)}{\mathrm{V}}b_2+\frac{N!}{(N-4)!2!}\cdot\frac{{b_2}^2}{\mathrm{V}^2}+\frac{N!}{(N-3)!}\cdot\frac{b_3}{\mathrm{V}^2}+\cdots\right\}$$

$$=\frac{\partial}{\partial V}\ln\left\{1+\frac{\mathcal{N}(\mathcal{N}-1)}{V}b_2+\frac{\mathcal{N}(\mathcal{N}-1)(\mathcal{N}-2)(\mathcal{N}-3)}{2}\cdot\frac{b_2^{\,2}}{V^2}+\frac{\mathcal{N}(\mathcal{N}-1)(\mathcal{N}-2)}{V^2}b_3+\cdots\right\}$$

$$=\frac{-\mathcal{N}(\mathcal{N}-1)\frac{b_2}{V^2}-\mathcal{N}(\mathcal{N}-1)(\mathcal{N}-2)(\mathcal{N}-3)\frac{b_2^{\,2}}{V^3}-2\mathcal{N}(\mathcal{N}-1)(\mathcal{N}-2)\frac{b_3}{V^3}-\cdots}{1+\frac{\mathcal{N}(\mathcal{N}-1)}{V}b_2+\frac{\mathcal{N}(\mathcal{N}-1)(\mathcal{N}-2)(\mathcal{N}-3)}{2}\cdot\frac{b_2^{\,2}}{V^2}+\frac{\mathcal{N}(\mathcal{N}-1)(\mathcal{N}-2)}{V^2}b_3+\cdots}$$

$$\simeq\left\{-\mathcal{N}(\mathcal{N}-1)\frac{b_2}{V^2}-\mathcal{N}(\mathcal{N}-1)(\mathcal{N}-2)(\mathcal{N}-3)\frac{b_2^{\,2}}{V^3}-2\mathcal{N}(\mathcal{N}-1)(\mathcal{N}-2)\frac{b_3}{V^3}-\cdots\right\}\left\{1-\frac{\mathcal{N}(\mathcal{N}-1)}{V}b_2\right.$$

$$\left.-\frac{\mathcal{N}(\mathcal{N}-1)(\mathcal{N}-2)(\mathcal{N}-3)}{2}\cdot\frac{b_2^{\,2}}{V^2}-\frac{\mathcal{N}(\mathcal{N}-1)(\mathcal{N}-2)}{V^2}b_3-\frac{\mathcal{N}^2(\mathcal{N}-1)^2}{2}\cdot\frac{b_2^{\,2}}{V^2}+\cdots\right\}$$

$$=-\mathcal{N}(\mathcal{N}-1)\frac{b_2}{V^2}-\mathcal{N}(\mathcal{N}-1)(\mathcal{N}-2)(\mathcal{N}-3)\frac{b_2^{\,2}}{V^3}+\mathcal{N}^2(\mathcal{N}-1)^2\frac{b_2^{\,2}}{V^3}$$

$$+\frac{\mathcal{N}^2(\mathcal{N}-1)^2(\mathcal{N}-2)(\mathcal{N}-3)}{2}\cdot\frac{b_2^{\,3}}{V^4}-2\mathcal{N}(\mathcal{N}-1)(\mathcal{N}-2)\frac{b_3}{V^3}+\cdots \qquad (5.10.8)$$

Substituting Eq.(5.10.8) in Eq.(5.10.7), we have

$$\Pi=kT\left[\frac{N}{V}-\mathcal{N}(N-1)\frac{b_2}{V^2}-\mathcal{N}(N-1)\left\{(N-2)(N-3)-\mathcal{N}(N-1)\right\}\frac{b_2^{\,2}}{V^3}\right.$$

$$\left.-2\mathcal{N}(N-1)(N-2)\frac{b_3}{V^3}+\cdots\right]$$

$$= kT\left[\frac{N}{V} - N(N-1)\frac{b_2}{V^2} - N(N-1)(-4N+6)\frac{b_2^{\,2}}{V^3} - 2N(N-1)(N-2)\frac{b_3}{V^3} + \cdots\right] \tag{5.10.9}$$

If $N >> 1$, then we obtain Eq.(5.10.1).

<<Problem 5-11>> Osmotic pressure (V): Relationship for second and third virial coefficients with cluster integrals

The results of <<Problem 5-10>> can be rewritten as

$$\Pi = RT\left(A_1C + A_2C^2 + A_3C^3 + \cdots\right) \tag{5.2.1}$$

Prove that A_2 and A_3 in Eq. (5.2.1) can be expressed as

$$A_2 = -\frac{N_A}{M^2}b_2 = -\frac{N_A}{2M^2V}\iint g_2(1,2)d(1)d(2) \tag{5.11.1}$$

$$A_3 = -\frac{2N_A^{\,2}}{M^3}\left(b_3 - 2b_2^{\,2}\right) = -\frac{N_A^{\,3}}{2M^3V}\iint g_3(\{3\})d\{3\} + 4MA_2^{\,2} \tag{5.11.2}$$

Answer

Concentration of polymer C(g/cm^3) is expressed as

$$C = \frac{MN}{VN_A} \quad \text{or} \quad \frac{RC}{M} = \frac{NR}{VN_A} = \frac{Nk}{V} \tag{5.11.3}$$

Substituting Eq. (5.11.3) in Eq. (5.10.1) yields

$$\Pi = RT\frac{C}{M} - kTN_A^{\,2}\frac{C^2}{M^2}b_2 + kTN_A^{\,3}\frac{C^3}{M^3}\left(4b_2^{\,2} - 2b_3\right) + \cdots$$

$$= RT\left[\frac{C}{M} - \frac{N_Ab_2}{M^2}C^2 + \frac{2N_A^{\,2}}{M^3}\left(2b_2^{\,2} - b_3\right)C^3 + \cdots\right] \tag{5.11.4}$$

Comparing Eq.(5.11.4) with Eq.(5.2.1), we obtain Eqs.(5.11.1) and (5.11.2).

<<Problem 5-12>> Second virial coefficient (III): Relationship with pair segment potential

The second virial coefficient A_2 is given by

$$A_2 = -\frac{N_A}{2M^2V}\iint g_2(1,2)d(1)d(2) \tag{5.11.1}$$

Here, $g_2(1,2)$ is expressed using $F_2(1,2)$, $F_1(1)$ and $F_1(2)$ as

$$g_2(1,2) = F_2(1,2) - F_1(1)F_1(2) \tag{5.9.5}$$

Then A_2 is expressed as

$$A_2 = -\frac{N_A}{2M^2V}\iint [F_2(1,2) - F_1(1)F_1(2)]d(1)d(2) \tag{5.12.1}$$

Now let's assume that the mean force potential corresponding to $F_2(1,2)$, $W_2(1,2)$, can be expressed as the sum of the mean force potential for the system consisting of the first molecule in pure solvent, $w_1(1)$, that for the system consisting of the second molecule in pure solvent, $w_1(2)$, and the remaining part $W_2(1,2)$ as

$$W_2(1,2) = w_1(1) + w_1(2) + w_2(1,2) \tag{5.12.2}$$

Then if we apply two-body approximation, i.e., $w_2(1,2)$ is expressed as the sum of the interactions between arbitrary λ_1 th segment of the first molecule and ν_2 th segment of the second molecule $u(\lambda_1,\nu_2)$ as

$$w_2(1,2) = \sum_{\lambda_1}\sum_{\nu_2} u(\lambda_1,\nu_2) \tag{5.12.3}$$

$w_1(1)$ and $w_1(2)$ agree with $W_1(1)$ and $W_1(2)$, respectively.
Express the second virial coefficient A_2 of Eq. (5.12.1) in terms of $u(\lambda_1,\nu_2)$.

Answer

Referring to Eq. (5.9.2),

$$F_2(1,2) = \exp\left[-\frac{W_2(1,2)}{kT}\right] \tag{5.12.4}$$

Substituting Eq. (5.12.2) in Eq. (5.12.4), we have

$$F_2(1,2) = \exp\left[-\frac{w_1(1)}{kT}\right]\exp\left[-\frac{w_1(2)}{kT}\right]\exp\left[-\frac{w_2(1,2)}{kT}\right]$$

$$= \exp\left[-\frac{W_1(1)}{kT}\right]\exp\left[-\frac{W_1(2)}{kT}\right]\exp\left[-\frac{w_2(1,2)}{kT}\right]$$

$$= F_1(1)F_1(2)\exp\left[-\frac{w_2(1,2)}{kT}\right] \qquad (5.12.5)$$

Using the expression Eq. (5.12.3), Eq. (5.12.5) is rewritten as

$$F_2(1,2) = F_1(1)F_1(2)\exp\left[-\sum_{\lambda_1}\sum_{\nu_2}\frac{u(\lambda_1,\nu_2)}{kT}\right] \qquad (5.12.6)$$

Substituting Eq. (5.12.6) in Eq. (5.12.1), we have

$$A_2 = -\frac{N_A}{2M^2V}\iint F_1(1)F_1(2)\left\{\exp\left(-\sum_{\lambda_1}\sum_{\nu_2}\frac{u(\lambda_1,\nu_2)}{kT}\right)-1\right\}d(1)d(2) \qquad (5.12.7)$$

(See W. G. McMillan and J. E. Mayer, *J. Chem. Phys.* **13**, 276 (1945); B. H. Zimm, *J. Chem. Phys.* **14**, 164 (1946))

<<Problem 5-13>> Second virial coefficient (IV)

The pair segment potential $u(\lambda_1,\nu_2)$ (See Eq. (5.12.3)) rapidly approaches zero with increasing separation of the segments, so we can use the approximation

$$\exp\left(-\frac{u(\lambda_1,\nu_2)}{kT}\right) = 1 + f(\lambda_1,\nu_2) \qquad (5.13.1)$$

Substituting Eq. (5.13.1) in Eq. (5.12.7), we have

$$A_2 = -\frac{N_A n^2}{2M^2}\int f(r)4\pi r^2 dr \qquad (5.13.2)$$

where r is the separation of the two segments. Derive Eq. (5.13.2).

Answer

Eq. (5.13.1) can be rewritten as

$$\exp\left(-\sum_{\lambda_1}\sum_{\nu_2}\frac{u(\lambda_1,\nu_2)}{kT}\right)=\prod_{\lambda_1}\prod_{\nu_2}\exp-\frac{u(\lambda_1,\nu_2)}{kT}=\prod_{\lambda_1}\prod_{\nu_2}\left(1+f(\lambda_1,\nu_2)\right)$$
$$=1+\sum_{\lambda_1}\sum_{\nu_2}f(\lambda_1,\nu_2)+\sum_{\lambda_1}\sum_{\nu_2}\sum_{\kappa_1}\sum_{\mu_2}f(\lambda_1,\nu_2)f(\kappa_1,\mu_2)+\cdots \tag{5.13.3}$$

Substituting Eq. (5.13.3) in Eq. (5.12.7), we have

$$A_2=-\frac{N_A}{2M^2v}\times$$
$$\iint F_1(1)F_1(2)\left[\sum_{\lambda_1}\sum_{\nu_2}f(\lambda_1,\nu_2)+\sum_{\lambda_1}\sum_{\nu_2}\sum_{\kappa_1}\sum_{\mu_2}f(\lambda_1,\nu_2)f(\kappa_1,\mu_2)+\cdots\right]d(1)d(2)$$
$$\cong-\frac{N_A}{2M^2V}\iint F_1(1)F_1(2)\left[\sum_{\lambda_1}\sum_{\nu_2}f(\lambda_1,\nu_2)\right]d(1)d(2) \tag{5.13.4}$$

Here, we neglect higher order terms. The integration is carried out as follows. Let's fix the location of the λ_1 th segment of the first molecule and the ν_2 th segment of the second molecule and integrate $F_1(1)F_1(2)$ over the coordinates of all other segments. Then we obtain unity. Next, fix the location of the λ_1 th segment and integrate over the coordinate of ν_2, then we obtain the integral which only depends on the relative coordinate as

$$\beta=-\int f(r)4\pi r^2dr \tag{5.13.5}$$

Finally, by integrating over λ_1, we have the volume V. Thus,

$$A_2=-\frac{N_A}{2M^2}\sum_{\lambda_1}\sum_{\nu_2}\int_0^\infty f(r)4\pi r^2dr \tag{5.13.6}$$

Since the integral in Eq. (5.13.6) does not depend on λ_1 and ν_2, the sum over λ_1 and ν_2 reduces to n^2. Thus we obtain

$$A_2 = -\frac{N_A n^2}{2M^2}\int_0^\infty f(r)4\pi r^2 dr = -\frac{N_A n^2}{2M^2}\beta \qquad (5.13.2)$$

β in Eq. (5.13.5) means the **effective excluded volume per segment pair.**

<<Problem 5-14>> Second virial coefficient (V): Polymer segment with rigid sphere potential

Derive the expression for A_2 **for the polymer segments with rigid sphere potential** using Eq.(5.13.2).

Answer

The rigid sphere potential for the segment with radius a_0 is expressed as a function of r as

$$\left.\begin{aligned} u(r) &= \infty \quad r < a_0 \\ u(r) &= 0 \quad r \geq a_0 \end{aligned}\right\} \qquad (5.14.1)$$

Using the approximation

$$\exp\left(-\frac{u(\lambda_1, v_2)}{kT}\right) = 1 + f(\lambda_1, v_2) \qquad (5.13.1)$$

or

$$f(r) = \exp\left(-\frac{u(\lambda_1, v_2)}{kT}\right) - 1 \qquad (5.14.2)$$

we have

$$\left.\begin{aligned} f(r) &= \exp\left(-\frac{\infty}{kT}\right) - 1 = -1 \quad r < a_0 \\ f(r) &= \exp\left(-\frac{0}{kT}\right) - 1 = 0 \quad r \geq a_0 \end{aligned}\right\} \qquad (5.14.3)$$

Thus, we obtain

$$A_2 = -\frac{N_A n^2}{2M^2}\int_0^\infty f(r)4\pi r^2 dr$$

$$= \frac{N_A n^2}{2M^2} 4\pi \int_0^{a_0} r^2 dr = \frac{N_A n^2}{2M^2}\left(\frac{4}{3}\pi a_0^3\right) = \frac{N_A n^2}{2M^2} v_0 \qquad (5.14.4)$$

Here, v_0 is the volume of a single rigid sphere and $\beta = v_0$.

<<Problem 5-15>> Second virial coefficient (VI): Comparison of Flory lattice theory with imperfect gas theory

The second virial coefficient is expressed as

$$A_2 = \left(\frac{1}{2} - \frac{B}{kT}\right)\frac{N_A v_0^0}{m_0^2} \qquad (5.2.7)$$

in the Flory lattice theory and

$$A_2 = \frac{N_A n^2}{2M^2} v_0 = \frac{N_A v_0}{2m_0^2} \qquad (5.14.4)$$

for the rigid sphere model in **imperfect gas theory** (Refer to <<Problem 5-12>>-<<5-14>>). Compare and discuss these two theoretical equations.

Answer

In the lattice theory, the segment is defined so that the volume of the segment is equal to that of solvent. Thus, if we apply the rigid sphere model to the lattice theory, i.e., B=0, we have

$$A_2 = \frac{N_A v_0}{2m_0^2} \qquad (5.15.1)$$

This is equivalent to A_2 for the imperfect gas theory.

<<Problem 5-16>> Second virial coefficient (VII): Mean force potential

Suppose **mean force potential u(r)** is given by

$$\left.\begin{array}{ll} u(r) = \infty & r < a_0 \\ u(r) = -\varepsilon_0 h(r) & r \geq a_0 \end{array}\right\} \qquad (5.16.1)$$

where ε_0 is a constant and h(r) is a function which decreases rapidly with increasing r. Calculate

$$A_2 = -\frac{N_A n^2}{2M^2}\int_0^\infty f(r)4\pi r^2 dr \tag{5.13.2}$$

and compare the result with A_2 for the Flory lattice theory.

Answer

f(r) is expressed as

$$f(r) = \exp\left(-\frac{u(\lambda_1, v_2)}{kT}\right) - 1 \tag{5.14.2}$$

Thus, in this problem,

$$\left.\begin{aligned} f(r) &= \exp\left(-\frac{\infty}{kT}\right) - 1 = -1 & r < a_0 \\ f(r) &= \exp\left(\frac{\varepsilon_0 h(r)}{kT}\right) - 1 = \frac{\varepsilon_0 h(r)}{kT} & r \geq a_0 \end{aligned}\right\} \tag{5.16.2}$$

The integral in Eq. (5.13.7), β, is calculated as

$$\begin{aligned} \beta &= -4\pi\int_0^\infty f(r)r^2 dr = -4\pi\int_0^{a_0} f(r)r^2 dr - 4\pi\int_{a_0}^\infty f(r)r^2 dr \\ &= \frac{4\pi}{3}a_0^3 - \frac{4\pi\varepsilon_0}{kT}\int_{a_0}^\infty h(r)r^2 dr = v_0\left[1 - \frac{1}{kT}\left\{\frac{3\varepsilon_0}{a_0^3}\int_{a_0}^\infty h(r)r^2 dr\right\}\right] \end{aligned} \tag{5.16.3}$$

Substituting Eq. (5.16.3) in Eq. (5.13.2), we have

$$A_2 = \frac{N_A v_0}{m_0^2}\left[\frac{1}{2} - \frac{1}{kT}\left\{\frac{3}{2}\frac{\varepsilon_0}{a_0^3}\int_{a_0}^\infty h(r)r^2 dr\right\}\right] \tag{5.16.4}$$

Comparing this expression with A_2 for Flory's theory (See Eq. (5.2.7) and (5.3.4))

$$A_2 = \frac{N_A v_0}{m_0^2}\left(\frac{1}{2} - \frac{B}{kT}\right) = \frac{N_A v_0}{m_0^2}\left(\frac{1}{2} - \chi\right) \tag{5.16.5}$$

we have

$$B = \left\{\frac{3\varepsilon_0}{2a_0^3}\int_{a_0}^{\infty} h(r) r^2 dr\right\} \tag{5.16.6}$$

---

* Since β is not very sensitive to u(r), or the magnitude of ε_0 and the shape of h(r), we need not know the details of u(r) (See W. Stockmayer, *Makromol. Chem.* **35**, 54 (1960)). At θ temperature, u(r) =0 and then β=0 and A_2=0.

<<Problem 5-17>> Second virial coefficient (VIII): Temperature dependence

Prove **the relationship between the heat of dilution ΔH and the temperature dependence of the second virial coefficient $(\partial A_2/\partial T)_P$** as

$$\Delta H = V_0^0 R C^2 T^{-2}\left(\frac{\partial A_2}{\partial T}\right)_P \tag{5.17.1}$$

This equation indicates that the sign of $(\partial A_2/\partial T)_P$ determines the sign of ΔH (poor solvent or good solvent).

Answer

According to the Gibbs-Helmholtz relationship, we have

$$H_i = \left(\frac{\partial(\mu_i/T)}{\partial(1/T)}\right)_P \tag{1.2.3}$$

and then

$$\Delta H = \left(\frac{\partial(\Delta\mu_0/T)}{\partial(1/T)}\right)_P \tag{5.17.2}$$

From the relationship between osmotic pressure and chemical potential

$$\Delta\mu_0 = - V_0^0 \Pi \tag{2.7.1}$$

and the virial expansion of osmotic pressure

$$\Pi = RT\left(\frac{C}{M} + A_2C^2 + A_3C^3 + \cdots\right) \tag{5.2.1}$$

we have

$$\frac{\Delta\mu_0}{T} = -\frac{V_0^0\Pi}{T} = -V_0^0R\left(\frac{C}{M} + A_2C^2 + A_3C^3 + \cdots\right) \tag{5.17.3}$$

Heat of dilution is then obtained as

$$\Delta H = -V_0^0R\frac{\partial}{\partial(1/T)}\left(\frac{C}{M} + A_2C^2 + A_3C^3 + \cdots\right) \tag{5.17.4}$$

Because of the inequality $A_2C^2 >> A_3C^3 > A_4C^4$, higher order terms of $O(C^3)$ are negligible and then we have

$$\Delta H = -V_0^0R\left(\frac{\partial A_2}{\partial(1/T)}\right)_P C^2 = V_0^0RC^2T^{-2}\left(\frac{\partial A_2}{\partial T}\right)_P \tag{5.17.5}$$

Thus, with increasing temperature, A_2 decreases in good solvent and increases in poor solvent.

<<Problem 5-18>> Second virial coefficient (IX): Ideal solution

The **second virial coefficient of ideal solution A_2^{id}** is given by

$$A_2^{id} = \frac{N_AV_0^0}{2M^2} \tag{5.18.1}$$

Derive Eq. (5.18.1).

Answer

Chemical potential of solvent in ideal solution μ_0 is expressed as

$$\mu_0 - \mu_0^0 = RT\ln x_0 \tag{2.1.1}$$

where x_0 is the mole fraction of solvent. For dilute binary solutions, $x_0 >> x_1$. Then,

$$\ln x_0 = \ln(1 - x_1) = -x_1 - \frac{1}{2}x_1^2 \cdots \tag{5.18.2}$$

Substituting Eq. (5.18.2) in Eq. (2.1.1), we have

$$\mu_0 - \mu_0^0 = -RT\left(x_1 + \frac{1}{2}x_1{}^2 + \cdots\right) \tag{5.18.3}$$

Using the relationship between x_1 and weight concentration C(g/cm^3)

$$x_1 = \frac{CV_0^0 N_A}{M} \tag{5.18.4}$$

Eq. (5.18.3) can be rewritten as

$$\mu_0 - \mu_0^0 = -RTV_0\left\{\frac{C}{M} + \left(\frac{V_0^0 N_A}{2M^2}\right)C^2 + \cdots\right\} \tag{5.18.5}$$

where we use the relation $N_A v_0{}^0 = V_0$.
Using the relationship

$$\Delta\mu_0 = \mu_0 - \mu_0^0 = -V_0\Pi \tag{2.7.1}$$

osmotic pressure is expressed as

$$\Pi = RT\left\{\frac{C}{M} + \left(\frac{V_0^0 N_A}{2M^2}\right)C^2 + \cdots\right\} \tag{5.18.6}$$

Comparing this expression with Eq. (5.2.1) we have Eq. (5.18.1).

<<Problem 5-19>> Second virial coefficient (X): Rigid sphere solution

Derive **the expression for the second virial coefficient for the solution of rigid spheres with radius r.**

Answer

The radius of the excluded volume of a rigid sphere with radius r is 2r, Thus, the result of <<Problem 5-14>> can be applied directly to this problem with replacing a_0 by 2r :

$$a_0 = 2r \tag{5.19.1}$$

If we put n=1 in Eq. (5.14.4), we have

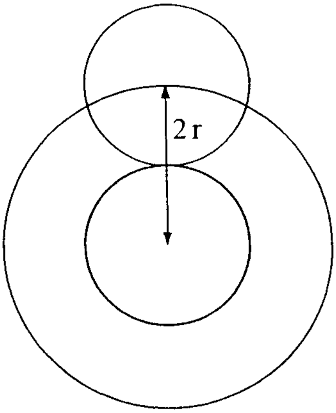

Fig. 5-19 Excluded volume of rigid spheres

$$A_2 = \frac{N_A}{2M^2} v_0 = \frac{N_A}{2M^2}\left(\frac{4}{3}\pi a_0{}^3\right) \tag{5.19.2}$$

Substituting Eq. (5.19.1) in Eq. (5.19.2), we have

$$A_2 = \frac{N_A}{2M^2}\left(\frac{4}{3}\pi (2r)^3\right) = \frac{16\pi N_A}{3M^2} r^3 \tag{5.19.3}$$

If we denote the volume of one mole of rigid spheres as V, then we have

$$A_2 = \frac{4V}{M^2} \simeq \frac{4v}{M} \tag{5.19.4}$$

where v is the specific volume of the rigid sphere.

<<Problem 5-20>> Second virial coefficient (XI): Molecular weight dependence

Eq.(5.13.2) is rewritten with the molecular weight of a segment $(M/n)=m_0$ as

$$A_2 = -\frac{N_A}{2m_0{}^2}\int_0^\infty f(r) 4\pi r^2 dr \tag{5.20.1}$$

Thus, the second virial coefficient is independent of the molecular weight M. However, observed A_2 increases with increasing M. Discuss this inconsistency between the theory and experiment.

Answer

In <<Problem 5-13>> we calculated only the first term in the bracket of Eq.(5.13.4) (**single contact approximation**). In order to obtain the strict result, we need to calculate higher order terms or higher order contacts. If we take these interactions into account, A_2 is generally expressed as

$$A_2 = \frac{N_A}{2{m_0}^2}\beta F(Z) \tag{5.20.2}$$

with a factor F(Z) for correction due to the higher order terms in Eq. (5.13.4). Here, Z is defined by

$$Z = \beta n^{1/2}\left(\frac{3}{2\pi b^2}\right)^{3/2} \tag{5.20.3}$$

where b is the bond length and β is defined by Eq. (5.13.5).(See B.H.Zimm, *J. Chem. Phys.* **14**, 164 (1946).) If we put F(Z)=1, Eq. (5.20.2) is reduced to Eq. (5.20.1). The explicit form of F(Z) depends on how to estimate the higher order terms. For example, according to Flory-Krigbaum-Orofino (P. J. Flory, W. R. Krigbaum and T. A. Orofino, *J. Chem. Phys.* **18**, 1086 (1950): *ibid.*, **26**, 1067(1957)),

$$F_{FKO}(Z) = \frac{\ln\left(1 + \frac{3\sqrt{3\pi}}{4} z\alpha^{-3}\right)}{\frac{3\sqrt{3\pi}}{4} z\alpha^{-3}} \tag{5.20.4}$$

According to Ishihara-Koyama (See A. Ishihara and R. Koyama, *J. Chem. Phys.* **25**, 712 (1956)),

$$F_{IK}(Z) = \frac{0.158}{Z}\left(\ln 8.75Z\right)^{3/2} \tag{5.20.5}$$

According to Casassa-Markovitz (See E. F. Casassa and H. Markovitz, *J. Chem. Phys.* **29**, 493 (1958)),

$$F_{CM}(Z) = \frac{1 - \exp\left(-5.68Z\alpha^{-3}\right)}{5.68Z\alpha^{-3}} \tag{5.20.6}$$

According to Kurata-Yamakawa (See M. Kurata and H. Yamakawa, *J. Chem. Phys.* **29**, 311 (1958)),

$$F_{KY}(Z) = 1 - 2.865Z + 18.51Z^2 - \cdots \qquad (5.20.7)$$

---

* The molecular weight dependance of A_2 is experimentally expressed in the form

$$A_2 \propto M^{-\lambda} \qquad (5.20.8)$$

The exponent λ in Eq. (5.20.8) can be assessed from the slope of the plot of $\ln A_2$ vs. ln M:

$$\lambda = -\frac{d\ln A_2}{d\ln M} \qquad (5.20.9)$$

Substituting Eq. (5.20.2) in Eq. (5.20.9), we have

$$\lambda = -\frac{d\ln F(Z)}{d\ln M} = -\frac{n}{F(Z)}\cdot\frac{dF(Z)}{dn} = -\frac{n}{F(Z)}\cdot\frac{d(Z)}{dZ}\cdot\frac{dZ}{dn} \qquad (5.20.10)$$

Using the expression for Z and the first derivative of Z

$$\frac{dZ}{dn} = \beta\left(\frac{3}{2\pi b^2}\right)^{3/2}\frac{1}{2}n^{-1/2} \qquad (5.20.11)$$

Eq. (5.20.10) is rewritten as

$$\lambda = \frac{n}{F(Z)}\cdot\frac{dF(Z)}{dZ}\beta\left(\frac{3}{2\pi b^2}\right)^{3/2}\frac{1}{2}n^{-1/2} = -\frac{1}{F(Z)}\cdot\frac{dF(Z)}{dZ}\cdot\left(\frac{1}{2}\right)\beta\left(\frac{3}{2\pi b^2}\right)^{3/2}n^{1/2}$$
$$= -\left(\frac{1}{2}\right)\frac{Z}{F(Z)}\cdot\frac{dF(Z)}{dZ} \qquad (5.20.12)$$

<<Problem 5-21>> Two-body cluster integral

Prove that the **effective excluded volume per segment** or **two-body cluster integral** β is expressed as

$$\beta = 2V_0^0\psi_1\left(1 - \frac{\theta}{T}\right) \qquad (5.21.1)$$

with

$$A_2 = \frac{N_A}{2m_0{}^2}\beta F(Z) \qquad \text{(Zimm)} \qquad (5.21.2)$$

and

$$A_2 = \frac{v^2}{N_A V_0^0}\psi_1\left(1 - \frac{\theta}{T}\right)F\left(J\xi^3\right) \qquad \text{(Flory-Krigbaum)} \qquad (5.21.3)$$

where $v = N_A V_0{}^0/m_0$ being the specific volume of polymer.

Answer

Near the θ temperature,

$$F(Z) = F\left(J\xi^3\right) \approx 1 \qquad (5.21.4)$$

Comparing Eqs. (5.21.2) and (5.21.3) we have

$$\frac{N_A}{2m_0{}^2}\beta = \frac{v^2}{N_A V_0^0}\psi_1\left(1 - \frac{\theta}{T}\right) = \frac{N_A\left(V_0^0/m_0\right)^2}{V_0^0}\psi_1\left(1 - \frac{\theta}{T}\right) \qquad (5.21.5)$$

and then we have Eq. (5.21.1)

(See W.H.Stockmayer, *J.Polym. Sci.* **15**, 595 (1955);W.R.Krigbaum, P.J. Flory, *J. Am. Chem. Soc.* **75**, 1775 (1953)).

<<Problem 5-22>> Second virial coefficient (XII): Various polymer solutions

Calculate the second virial coefficient for the solution of polymers with the molecular weight being 1x 10^5 in the case
(1) ideal solution (assume $N_A V_0{}^0$ =100cc/mole)
(2) rigid sphere solution (assume v=1cc/g)
(3) flexible polymers in good solvent (assume ψ_1=0.30, θ=270K,T=350K, F(Z)=1, m=100 and $N_A V_0{}^0$=100)
(4) flexible polymers in θ-solvent

Answer

(1) Using Eq. (5.18.1)

$$A_2 = \frac{N_A V_0^0}{2M^2} = \frac{100}{2\left(10^5\right)^2} = 5 \times 10^{-9} \quad \text{mole·cc/gram}^2 \tag{5.22.1}$$

(2) Using Eq. (5.19.4)

$$A_2 = \frac{4v}{M} = \frac{4}{10^5} = 4 \times 10^{-5} \quad \text{mole·cc/gram}^2 \tag{5.22.2}$$

(3) Using Eqs. (5.21.1) and (5.21.2)

$$A_2 = \frac{N_A}{2m_0^2} 2\psi_1 V_0^0 \left(1 - \frac{\theta}{T}\right) F(Z) = \frac{N_A V_0^0}{m_0^2} \psi_1 \left(1 - \frac{\theta}{T}\right) F(Z)$$

$$= \frac{100}{\left(100\right)^2} 0.3 \left(1 - \frac{270}{350}\right) = 6.86 \times 10^{-4} \quad \text{mole·cc/gram}^2 \tag{5.22.3}$$

(4) At T=θ,

$$A_2 = 0 \tag{5.22.4}$$

A_2 of flexible polymers in good solvent is extremely large, as clearly shown from these typical examples.

<<Problem 5-23>> Second virial coefficient (XIII): Rod-like molecule

Prove that the **second virial coefficient for the solution of rod-like molecules** with length l and radius r is expressed as

$$A_2 = \frac{\pi N_A r l^2}{4M^2} \tag{5.23.1}$$

Answer

The second and third virial coefficients are calculated from

$$A_2 = -\frac{N_A}{M^2} b_2 = -\frac{N_A}{2M^2 V} \iint g_2(1,2) d(1) d(2) \tag{5.11.1}$$

$$A_3 = -\frac{2N_A{}^2}{M^3}\left(b_3 - 2b_2{}^2\right) = -\frac{N_A{}^3}{2M^3V}\iint g_3(\{3\})d\{3\} + 4MA_2{}^2 \qquad (5.11.2)$$

Suppose one end of the rod-like molecule locates at (x_1,y_1,z_1) on Cartesian coordinate and the direction of the rod is expressed as (θ_1, ϕ_1) on the polar coordinate, as shown in Fig. 5-23 (a). When two molecules completely overlap with each other,

$$F_2(1,2) = 0 \qquad (5.23.2)$$

From the normalization condition

$$\lim_{V\to\infty}\frac{1}{V^N}\int\cdots\int F_N(1,2,\cdots,N)d\{N\} = 1 \qquad (5.9.3)$$

we have

$$\frac{1}{V}\int F_1(1)d(1) = 1 \qquad (5.23.3)$$

Similarly,

$$F_1(1)\int_0^{2\pi}\int_0^{\pi}\sin\theta_1 d\theta_1 d\varphi_1 = 4\pi F_1(1) = 1 \qquad (5.23.4)$$

or

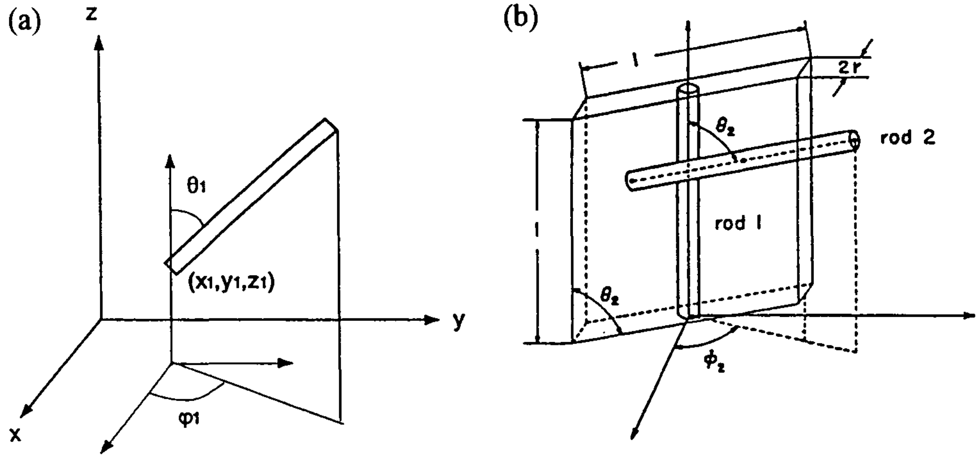

Fig. 5-23 (a) A rod-like molecule on rectangular and polar coordinates and (b) overlapping of two rods with diameter d=2r and length l (l being much larger than d).

$$F_1(1) = \frac{1}{4\pi} = F_1(2) \tag{5.23.5}$$

Thus, if two molecules overlap each other, we have

$$g_2(1,2) = 0 - \left(\frac{1}{4\pi}\right)^2 = -\frac{1}{16\pi^2} \tag{5.23.6}$$

If there is no overlap, $F_2(1,2)=1/16\pi^2$ and

$$g_2(1,2) = \frac{1}{16\pi^2} - \frac{1}{16\pi^2} = 0 \tag{5.23.7}$$

The volume for the overlap of two molecules is $2rl^2\sin\theta_2$, as illustrated as the rectangle enclosed by dotted lines in Fig. 5-23(b) Here, θ_2 and ϕ_2 are the coordinates on the polar coordinate which is constructed such that one of the principal coordinates is the direction of the first molecule. The integral in Eq. (5.11.1) for the overlap volume is carried out as

$$A_2 = \left(-\frac{N_A}{2M^2V}\right)\left(-\frac{1}{16\pi^2}\right)\iiint_0^{\infty} dxdydz\int_0^{2\pi}\int_0^{\pi} \sin\theta_1 d\theta_1 d\varphi_1$$

$$\times\int_0^{2\pi}\int_0^{\pi}\left(2rl^2\sin\theta_2\right)\sin\theta_2 d\theta_2 d\varphi_2$$

$$= \left(-\frac{N_A}{2M^2V}\right)\left(-\frac{1}{16\pi^2}\right)V\cdot 4\pi\cdot\left(2\pi^2 rl^2\right) = \frac{\pi N_A rl^2}{4M^2} \tag{5.23.1}$$

The volume of the rod molecule is

$$V_l = \pi r^2 l \tag{5.23.8}$$

Then, A_2 is rewritten as

$$A_2 = \frac{N_A V_l}{4M^2}\left(\frac{l}{r}\right) = \frac{N_A}{4}\cdot\frac{1}{\pi r^3}\cdot\left(\frac{V_l}{M}\right)^2 \tag{5.23.9}$$

Thus, A_2 does not depend on M in this case, too.

<<Problem 5-24>> Second virial coefficient (XIV): Chain molecule with n sequential rigid rod segments

Derive the **expression for the second virial coefficient for the solution of chain molecules with n sequential rigid rod segments** with length λ and diameter d=2r as shown in Fig. 5-24. Assume that the joints of the segments are freely rotated and nd>>1.

Answer

A_2 of rod-like molecules is given by Eq. (5.23.1) with replacing λ by l as

$$A_2 = \frac{\pi N_A r\lambda^2}{4M^2} \tag{5.23.1}$$

The integral over d(2) in the equation

$$A_2 = -\frac{N_A}{2M^2V}\iint g_2(\lambda_1,\mu_2)d(1)d(2) \tag{5.11.1}$$

gives the volume of a segment V= π r^2 λ. Comparing Eqs.(5.23.1) with (5.11.1), we have

$$\int g_2(\lambda_1,\mu_2)r(1) = -\frac{\pi}{2}r\lambda^2 \tag{5.24.1}$$

Eq. (5.13.2) is written for the present case with replacing f(r) by $g_2(\lambda_1,\mu_2)$ as

$$A_2 = -\frac{N_A n^2}{2M^2}\int g_2(\lambda_1,\mu_2)4\pi r^2 dr \tag{5.24.2}$$

Substituting Eq.(5.24.1) in Eq.(5.24.2), we have

$$A_2 = \frac{N_A n^2 \pi}{2M^2 \, 2} r\lambda^2 = \frac{\pi N_A}{4M^2} rn^2\lambda^2 \tag{5.24.3}$$

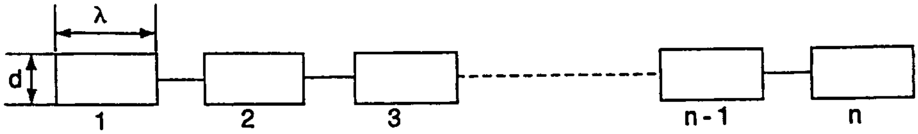

Fig. 5-24 Chain molecules with n sequential rigid rod segments with length λ and diameter d

If we put $n\lambda=l$, Eq. (5.24.3) gives the expression for A_2 for chain molecules with n sequential rigid rod segments with length λ and radius $r=d/2$. Thus, A_2 does not directly depend on flexibility of the molecular chain.

<<Problem 5-25>> Relationship between second virial coefficient and excess chemical potential

The second virial coefficient A_2 relates with excess chemical potential $\Delta\mu_0{}^E$ as

$$A_2 = -\frac{\Delta\mu_0^E}{RTC^2V_0^0} \tag{5.25.1}$$

A_2 can be divided into enthalpy term $A_{2,h}$ and entropy term $A_{2,s}$ as

$$A_2 = A_{2,h} + A_{2,s} \tag{5.25.2}$$

Then $A_{2,h}$ is given by

$$A_{2,h} = -T\left[\left(\frac{\partial A_2}{\partial T}\right)_P + \alpha_0 A_2\right] \tag{5.25.3}$$

where α_0 is the volumetric thermal expansion coefficient. Derive Eqs. (5.25.1) and (5.25.3).

Answer

From the relationships

$$\Delta\mu_0 = \Delta\mu_0^{id} + \Delta\mu_0^E \tag{5.25.4}$$

$$\Delta\mu_0 = -\Pi V_0^0 \tag{2.7.1}$$

$$\Pi = RT\left(\frac{C}{M} + A_2C^2 + A_3C^3 + \cdots\right) \tag{5.2.1}$$

and the expression for the osmotic pressure and the chemical potential for ideal solution

$$\Pi = \frac{RTC}{M} = -\frac{\Delta\mu_0^{id}}{V_0^0} \quad \text{or} \quad \Delta\mu_0^{id} = -\frac{RTCV_0^0}{M}$$

we have

$$\Delta\mu_0 = \Delta\mu_0^{id} - RTV_0^0A_2C^2 - \cdots \tag{5.25.5}$$

Here, we can neglect higher order terms in dilute solution. Then excess chemical potential is derived as

$$\Delta\mu_0^E = -RTV_0^0A_2C^2 \tag{5.25.6}$$

From the thermodynamic relationship

$$\Delta\mu_0^E = \Delta H_0 - T\Delta S_0^E \tag{5.25.7}$$

we have

$$A_2 = -\frac{\Delta\mu_0^E}{RTV_0^0C^2} = -\frac{\Delta H_0}{RTV_0^0C^2} + T\frac{\Delta S_0^E}{RTV_0^0C^2} \tag{5.25.8}$$

Comparing Eq. (5.25.2) with Eq. (5.25.8), we have

$$A_{2,h} = -\frac{\Delta H_0}{RTV_0^0C^2} \tag{5.25.9}$$

$$A_{2,s} = \frac{\Delta S_0^E}{RV_0^0C^2} \tag{5.25.10}$$

Eq. (5.25.1) is rewritten as

$$A_2V_0^0 = -\frac{\Delta\mu_0^E}{RTC^2} \tag{5.25.1'}$$

Differentiating both sides of this equation with respect to temperature, we have

$$\left(\frac{\partial A_2}{\partial T}\right)_P V_0^0 + A_2\left(\frac{\partial V_0^0}{\partial T}\right)_P = -\frac{\left(\frac{\partial \Delta\mu_0^E}{\partial T}\right)_P}{RTC^2} + \frac{\Delta\mu_0^E}{RT^2C^2} \tag{5.25.11}$$

Using the thermal expansion coefficient

$$\alpha_0 = \frac{1}{V_0^0}\left(\frac{\partial V_0^0}{\partial T}\right)_P \tag{5.25.12}$$

and excess entropy

$$\Delta S_0^E = -\left(\frac{\partial \Delta\mu_0^E}{\partial T}\right)_P \tag{5.25.13}$$

Eq. (5.25.11) is rewritten as

$$T\left\{\left(\frac{\partial A_2}{\partial T}\right)_P + A_2\alpha_0\right\} = \frac{\Delta S_0^E}{RV_0^0C^2} - A_2 = A_{2,s} - A_2 = - A_{2,h} \tag{5.25.14}$$

Then, we have Eq. (5.25.3)
Here, $A_{2,h}$ and $A_{2,s}$ are not independent variables. In general, there is a negative correlation in these variables. At θ-temperature, $A_{2,h}=A_{2,s}=0$.

<<Problem 5-26>> Third virial coefficient of rigid sphere solution

Derive the expression for the third virial coefficient A_3 and the following equation:

$$A_3/ A_2^2 M=5/8 \tag{5.26.1}$$

Answer

A_3 is defined by

$$A_3 = - \frac{2N_A^2}{M^3}\left(b_3 - 2b_2^2\right) = - \frac{N_A^3}{2M^3V}\iint g_3(\{3\})d\{3\} + 4MA_2^2 \tag{5.11.2}$$

From Eq. (5.9.4),

$$g_3(1,2,3)= F_3(1,2,3)- F_1(1)\, F_2(2,3)- F_1(2)\, F_2(3,1)- F_1(3)\, F_2(1,2)+2\, F_1(1)\, F_1(2)\, F_1(3) \tag{5.26.2}$$

If mean force potential can be approximated by the sum of intermolecular potentials of each pair of two molecules, we have

$$F_3(1,2,3)=\frac{F_2(1,2)\, F_2(2,3)\, F_3(3,1)}{F_1(1)\, F_1(2)\, F_1(3)} \tag{5.26.3}$$

where

$$F_2(i, j)= \exp\left[\frac{-w(i, j)}{kT}\right]F_1(i)\, F_1(j) \tag{5.26.4}$$

Using a function f(i,j) defined by

$$f(i, j)= \exp\left[\frac{-w(i, j)}{kT}\right]-1 \tag{5.26.5}$$

Eq. (5.11.2) is reduced to

$$A_3=\frac{N_A{}^2}{3\,M^3\,V}\int f(1,2)\,f(2,3)\,f(3,4)\,d(1)\,d(2)\,d(3) \qquad (5.26.6)$$

Now we consider three molecules and denote the three vectors connecting each pair of centers of mass of the molecules as $\mathbf{r}_{12}$, $\mathbf{r}_{23}$ and $\mathbf{r}_{31}$, respectively as shown in Fig 5.26(a). Then there is a relationship between the vectors as

$$\mathbf{r}_{12}+\mathbf{r}_{23}+\mathbf{r}_{31}=0 \qquad (5.26.7)$$

Let's denote the coordinate of the center of mass of the first molecule as (x_1,y_1,z_1). Then Eq. (5.26.6) is rewritten as

$$A_3=-\frac{N_A^2}{3\,M^3\,V}\int f(1,2)\,f(2,3)\,f(3,1)\,dr_{12}\,dr_{23}\,dr_{31}\iiint_V dx_1\,dy_1\,dz_1$$

$$=-\frac{N_A^2}{3\,M^3}\int f(1,2)\,f(2,3)\,f(3,1)\,dr_{12}\,dr_{23}\,dr_{31} \qquad (5.26.8)$$

If the distance between the center of mass of the two molecules with radius 2r is fixed, the excluded volume of a molecule is the volume of the sphere with radius 2D. The volume of overlap one another of the two molecules is

$$V(r_{12})=\frac{2}{3}\pi(2\,r)^3\left(1-\frac{r_{12}}{4\,r}\right)^2\left(2+\frac{r_{12}}{4\,r}\right) \qquad (5.26.9)$$

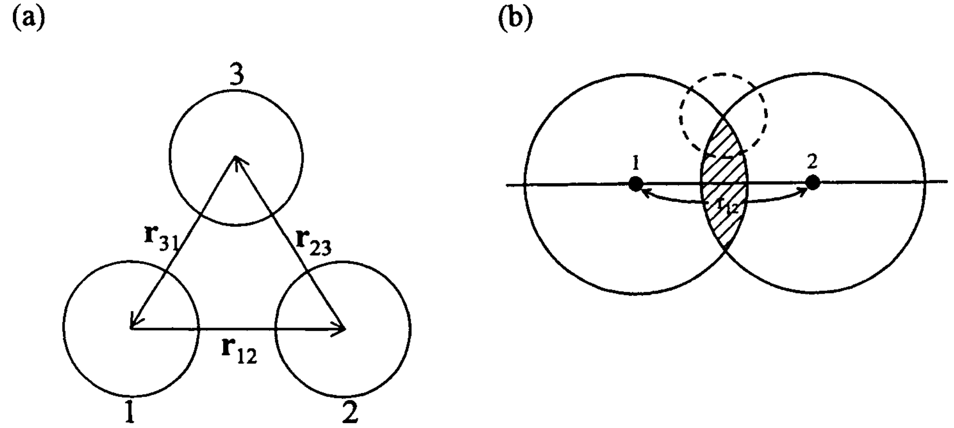

Fig. 5-26 Relative location of three molecules (a) and overlapping of two spheres (b)

When the center of mass of the third molecule enters into this volume,

$$w(1,2)=w(2,3)=w(3,1)=\infty \tag{5.26.10}$$

Thus,

$$f(1,2)=f(2,3)=f(3,1)=-1 \tag{5.26.11}$$

or

$$f(1,2)\,f(2,3)\,f(3,1)=-1 \tag{5.26.12}$$

Otherwise (in the volume of $V-V(r_{12})$),

$$f(1,2)\,f(2,3)\,f(3,1)=0 \tag{5.26.13}$$

Substitution of Eqs. (5.26.9), (5.26.12) and (5.26.13) in Eq. (5.26.8) yields

$$
\begin{aligned}
A_3&=\frac{N_A^2}{3\,M^3}\int_0^{2r}(-1)\,V(r_{12})4\pi\,r_{12}^2\,dr_{12}\\
&=\frac{N_A^2}{3\,M^3}\int_0^{2r}\frac{2}{3}\pi(2\,r)^3\left(1-\frac{r_{12}}{4\,r}\right)^2\left(2+\frac{r_{12}}{4\,r}\right)4\pi\,r_{12}^2\,dr_{12}\\
&=\frac{N_A^2}{3\,M^3}\left(\frac{2}{3}\pi\right)8\,r^3\int_0^{2r}4\pi\,r_{12}^2\left(1-\frac{r_{12}}{4\,r}\right)^2\left(2+\frac{r_{12}}{4\,r}\right)dr_{12}\\
&=\frac{N_A^2}{3\,M^3}\left(\frac{2}{3}\pi\right)8\,r^3\cdot4\pi\left|\frac{2}{3}\,r_{12}^3-\frac{3\,r_{12}^4}{16\,r}+\frac{r_{12}^6}{(6)(64\,r^3)}\right|_0^{2r}\\
&=\frac{N_A^2}{3\,M^3}\left(\frac{2}{3}\pi\right)8\,r^3\cdot4\pi\left(\frac{16}{3}\,r^3-3\,r^3+\frac{1}{6}\,r^3\right)\\
&=\frac{N_A^2}{3\,M^3}\left(\frac{2}{3}\pi\right)8\,r^3\cdot4\pi\left(\frac{5}{2}\,r^3\right)=\frac{160\pi^2N_A{}^2r^6}{9M^3}
\end{aligned}
\tag{5.26.14}
$$

The second virial coefficient for rigid sphere solutions is given by

$$A_2=\frac{16\pi\,N_A r^3}{3\,M^2} \tag{5.19.3}$$

Comparing Eq. (5.26.14) with Eq. (5.19.3), we have

$$A_3/\,A_2^2\,M=\frac{160\pi^2\,N_A{}^2\,r^6 9\,M^4}{9\,M^3(16)^2\pi^2\,N_A{}^2\,r^6\,M}=\frac{160}{(16)^2}=\frac{5}{8} \tag{5.26.15}$$

---

* If we expand the osmotic pressure as

$$\frac{\Pi}{C}=\left(\frac{\Pi}{C}\right)_0\left[1+\Gamma_2 C+\Gamma_3 C^2+\cdots\right] \tag{5.26.16}$$

Γ_2 and Γ_3 are related to A_2 and A_3 as

$$\left.\begin{array}{l}\Gamma_2=A_2 M\\ \Gamma_3=A_3 M\end{array}\right\} \tag{5.26.17}$$

by comparing Eq. (5.26.16) and

$$\frac{\Pi}{C}=RT\left[\frac{1}{M}+A_2 C+A_3 C^2+\cdots\right] \tag{5.2.1}$$

Thus Eq. (5.26.15) is rewritten as

$$\frac{\Gamma_3}{\Gamma_2^2}=\frac{A_3}{A_2^2 M}=\frac{5}{8} \tag{5.26.18}$$

Γ_3/Γ_2^2 of random coil solutions is zero for the expansion factor α being 1 and increases with increasing α. (See W.H.Stockmayer and E.F.Casassa, *J. Chem. Phys.* **20**, 1560 (1952)).

* Derivation of Eq. (5.26.9)

Let's take the center of mass of one molecule at the origin. The volume of overlap of two molecules with the distance of the centers of mass being r_{12} is calculated as

$$V=2\pi\int_{r_{12}/2}^{2r} y^2 dx \tag{5.26.19}$$

where

$$y^2+x^2=(2r)^2 \tag{5.26.20}$$

The integration is carried out to yield

$$V=2\pi\int_{r_{12}/2}^{2r}\left\{(2r)^2-x^2\right\}dx=2\pi\left[(2r)^2 x-\frac{1}{3}x^3\right]_{\frac{r_{12}}{2}}^{2r}$$

$$=\frac{2}{3}\pi(2r)^3\left\{2-\left(\frac{r_{12}}{2}\right)\frac{3}{2r}+\left(\frac{r_{12}}{2}\right)^3\frac{1}{(2r)^3}\right\}=\frac{2}{3}\pi(2r)^3\left\{1-\frac{r_{12}}{4r}\right\}^2\left\{2+\frac{r_{12}}{4r}\right\} \tag{5.26.21}$$

<<Problem 5-27>> Relationship between second and third virial coefficients

Assume the relationship

$$\Gamma_3 = g\Gamma_2^2 \tag{5.27.1}$$

with g=1/4 in the equation for osmotic pressure

$$\frac{\Pi}{C} = \left(\frac{\Pi}{C}\right)_0 \left[1 + \Gamma_2 C + \Gamma_3 C^2 + \cdots\right] \tag{5.26.16}$$

Here, g=1/4 is a typical empirical value for polymer solutions. Show the linearity in the plot $(\Pi/C)^{1/2}$ vs. C.

Answer

From Eqs. (5.27.1) and (5.26.16),

$$\frac{\Pi}{C} = \left(\frac{\Pi}{C}\right)_0 \left[1 + \Gamma_2 C + \frac{1}{4}\Gamma_2^2 C^2\right] = \left(\frac{\Pi}{C}\right)_0 \left(1 + \frac{1}{2}\Gamma_2 C\right)^2 \tag{5.27.2}$$

Here, the higher order terms are neglected. Eq. (5.27.2) is rewritten as

$$\left(\frac{\Pi}{C}\right)^{\frac{1}{2}} = \left(\frac{\Pi}{C}\right)_0^{\frac{1}{2}} \left(1 + \frac{1}{2}\Gamma_2 C\right) \tag{5.27.3}$$

Thus $(\Pi/C)^{1/2}$ is linearly proportional to C and the slope is $\Gamma_2/2$.

Chapter 6 Statistical Mechanics and Excluded Volume of Polymer Chains

<<Problem 6-1>> Probability density distribution for Gaussian chain

The **probability density distribution** that the end-to-end distance of one-dimensional random chain assumes R is given by

$$W(R,n) = \frac{1}{(2\pi n l^2)^{1/2}} \exp\left(- \frac{R^2}{2nl^2} \right) \tag{6.1.1}$$

Here, n is the number of segments in the chain and l is the length of the segment. This chain is called the **Gaussian chain**. Derive Eq. (6.1.1), by using Stirling's approximation

$$\ln x = (x + \frac{1}{2}) \ln x - x + \frac{1}{2} \ln (2\pi) \tag{6.1.2}$$

and Taylor expansion

$$\ln (1 \pm x) = \pm x - \frac{x^2}{2} \cdots \cong \pm x \tag{6.1.3}$$

Answer

[Solution 1] **Method of one-dimensional random walk proposed by Chandrasekhar**

Suppose a particle takes n successive steps of the same length on a line. The probabilities that the step is to the right and to the left are the same, i.e., 1/2, irrespective of past history. Then the probability of an arbitrary sequence of n steps is $(1/2)^n$. The number of different ways that the particle performs n steps and its net displacement is m is

$$\frac{n!}{\left\{\frac{1}{2}(n + m)\right\}! \times \left\{\frac{1}{2}(n - m)\right\}!} \tag{6.1.4}$$

and the probability W(m,n) is expressed as

$$W(m,n) = \frac{n!}{\left[\frac{1}{2}(n+m)\right]! \times \left[\frac{1}{2}(n-m)\right]!}\left(\frac{1}{2}\right)^n = {}_nC_{\frac{(n+m)}{2}}\left(\frac{1}{2}\right)^n \tag{6.1.5}$$

The actual displacement from the origin R is ml. Since m assumes integral values separated by an amount 2 for fixed n, the range ΔR contains ΔR/2l possible values of m, which occur with nearly the same probability.
For m<<n and n→∞,

$$\ln W(m,n) \cong -\frac{1}{2}\ln n + \ln 2 - \frac{1}{2}\ln 2\pi - \frac{m^2}{2n}$$

$$W(m,n) \cong \left(\frac{2}{\pi n}\right)^{1/2} \exp\left(-\frac{m^2}{2n}\right) \tag{6.1.6}$$

Here, we use the approximation

$$\ln(n \pm m) \cong \pm\frac{m}{n} + \ln n$$

$$n + 1 \cong n \tag{6.1.7}$$

Then the probability W(R,n)ΔR is obtained as

$$W(R,n)\Delta R = W(m,n)\left(\frac{\Delta R}{2l}\right) \tag{6.1.8}$$

where

$$W(R,n) = \frac{1}{\left(2\pi n l^2\right)^{1/2}} \exp\left(-\frac{R^2}{2nl^2}\right) \tag{6.1.1}$$

(See S. Chandrasekahr, *Rev. Mod. Phys.* **15**, 1 (1943))

---

* **Bernoulli distribution** is defined by

$$w(x) = \frac{n!}{x!(n-x)!}p^x(1-p)^{n-x}$$

or

$$w = {}_nC_x p^x p^{n-x} \tag{6.1.9}$$

Here, the commutation ${}_nC_X$ is a binomial coefficient and q=1-p. The average <x> and the standard deviation σ^2 are given by np and npq, respectively.

[Solution 2] Strict solution for diffusion phenomena

Suppose a molecular chain consists of z+1 segments. Let's denote the probability distribution function that the end-to-end distance of a one-dimensional chain assumes R as w(z+1,R). This is identical to the probability distribution function that the projection of the position vector **r** of a molecular chain with z+1 segments on the x axis is R. The distribution function $\varphi(\Delta)$ of the projection of the molecular chain with z segments on x axis, Δ, should satisfy the conditions

$$\int_{-\infty}^{\infty} \varphi(\Delta)d\Delta = 1, \quad \int_{-\infty}^{\infty} \Delta\varphi(\Delta)d\Delta = 0 \tag{6.1.10}$$

From the definition of $\varphi(\Delta)$, we have

$$w(z+1,R) = \int_{-\infty}^{\infty} w(z,R-\Delta)\varphi(\Delta)d\Delta \tag{6.1.11}$$

If z is large enough, we can expand both sides of Eq. (6.1.11) as a Taylor series :

$$\begin{aligned} w(z,R) + \frac{\partial w(z,R)}{\partial z} + \cdots &= w(z,R)\int_{-\infty}^{\infty} \varphi(\Delta)d\Delta \\ &- \frac{\partial w(z,R)}{\partial R}\int_{-\infty}^{\infty} \Delta\varphi(\Delta)d\Delta + \frac{1}{2}\frac{\partial^2 w(z,R)}{\partial R^2}\int_{-\infty}^{\infty} \Delta^2\varphi(\Delta)d\Delta \end{aligned} \tag{6.1.12}$$

Here, we put dz=1. From Eqs. (6.1.10) and (6.1.12), we have

$$\frac{\partial w(z,R)}{\partial z} = D\frac{\partial^2 w(z,R)}{\partial R^2} \tag{6.1.13}$$

where

$$D = \frac{1}{2}\int_{\infty}^{\infty} \Delta^2\varphi(\Delta)d\Delta \tag{6.1.14}$$

Eq.(6.1.13) is called the **diffusion equation**. The boundary condition of Eq.(6.1.13) is w(z,R)=w(R) for z=0 and w=∂w/∂R=0 for R=±∞. It is convenient to use the **Fourier transform**

$$<w(p)> = \int_{-\infty}^{\infty} e^{-ipR} W(z,R)dR \tag{6.1.15}$$

Then, Eq. (6.1.13) is reduced to

$$\frac{\partial}{\partial z}<w(p)> = - Dp^2<w(p)> \tag{6.1.16}$$

The solution of Eq. (6.1.16) is

$$<w(z,p)> = \exp\left(- Dp^2 z\right)\int_{-\infty}^{\infty} W(y)e^{-jpy}dy \tag{6.1.17}$$

w(z,R) is obtained by an **inverse Fourier transformation** as

$$w(z,R) = \frac{1}{2\pi}\int_{-\infty}^{\infty} W(y)dy\int_{-\infty}^{\infty} \exp\left(- Dp^2 z - jpt + jpR\right)dp \tag{6.1.18}$$

Putting

$$u = p\sqrt{Dz} - j\frac{(R - y)}{2} \tag{6.1.19}$$

and then integrating Eq. (6.1.18) over p, we have

$$<w(z,R)> = \frac{1}{2\sqrt{\pi z D}}\int_{-\infty}^{\infty} W(R)\exp\left\{ - \frac{(R - y)^2}{4zD}\right\}dy \tag{6.1.20}$$

The distribution function W(R) is symmetrical with respect to R=0. Then the integral over the whole range of R is unity. Thus, we finally obtain

$$<w(z,R)> = \frac{1}{2\sqrt{\pi z D}} \exp\left(- \frac{R^2}{4zD}\right) \tag{6.1.21}$$

The problem of random walk was proposed by K. Pearson (1905) and developed for the problem of Brownian motion by Einstein and Langevin (See A. Einstein, *Ann. Physik.* **17**, 549 (1905); P. Langevin, *Compt. Rend. Acad. Sc. (Paris)* **146**, 530 (1908))

<<Problem 6-2>> Distribution function of end-to-end distance of random chain (I)

Generalize the distribution function of end-to-end distance of a one-dimensional random chain

$$W(R) = \frac{3}{\sqrt{2\pi\langle R^2\rangle}} \exp\left(-\frac{3R^2}{2\langle R^2\rangle}\right) \tag{6.2.1}$$

to a three-dimensional chain (See also <<Problem 6-5>>).

Answer

Let's locate one end of the three-dimensional chain at the origin of a rectangular coordinate as shown in Fig. 6-2.1. The probability that another end of the chain be in a small volume at x~x+dx, y~y+dy, z~z+dz, W(x,y,z)dxdydz, is the product of the probability that the x coordinate of the end be in the range between x and x+dx, W(x)dx, the probability that the y coordinate of the end be in the range between y and y+dy, W(y)dy, and the probability that the z coordinate of the end be in the range between z and

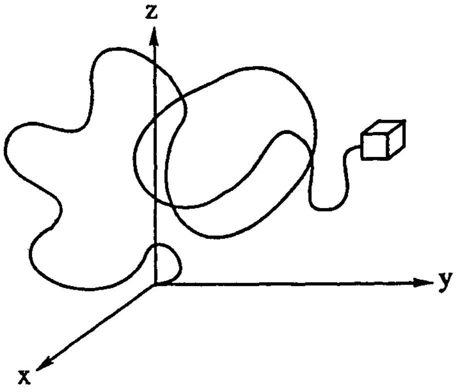

Fig. 6-2.1 Three dimensional random chain

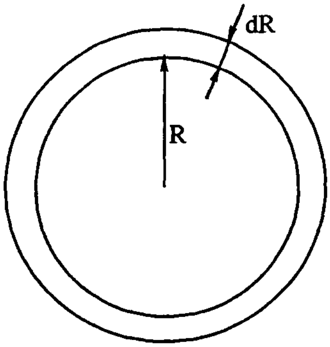

Fig. 6-2.2 Concentric spheres with the center at one end of the chain

z+dz, W(z)dz, since these probabilities are regarded as independent. W(x)dx, W(y)dy, and W(z)dz can also be defined as the probabilities that the projections of a position vector on the x axis, y axis and z axis be W(x), W(y) and W(z), respectively. Therefore,

$$W(x,y,z)dxdydz = W(x)dxW(y)dyW(z)dz = W(x)W(y)W(z)dxdydz \qquad (6.2.2)$$

Then we obtain

$$W(x,y,z) = W(\mathbf{R}) = \left(\frac{3}{2\pi<\mathbf{R}^2>}\right)^{3/2} \exp\left(-\frac{3\mathbf{R}^2}{2<\mathbf{R}^2>}\right) \qquad (6.2.3)$$

Here,W(**R**) means the probability that the end of the chain is located at a point **R** in the three-dimensional space as shown in Fig. 6-2.2. The differential coefficient of W(**R**) with respect to **R** is obtained as

$$\frac{\partial W(\mathbf{R})}{\partial \mathbf{R}} = \left(\frac{3}{2\pi<\mathbf{R}^2>}\right)^{3/2} \left(\frac{-3\cdot 2\mathbf{R}}{2<\mathbf{R}^2>}\right) \exp\left(-\frac{3\mathbf{R}^2}{2<\mathbf{R}^2>}\right) \qquad (6.2.4)$$

The value of **R** which satisfies the equation dW(**R**)/d**R**=0, $\mathbf{R}_m$, is zero. On the other hand, the probability distribution function that the end of the molecular chain is in the range between R and R+dR, W(R), is expressed as

$$W(R) = \left(\frac{3}{2\pi<\mathbf{R}^2>}\right)^{3/2} \exp\left(-\frac{3\mathbf{R}^2}{2<\mathbf{R}^2>}\right)\cdot 4\pi R^2 \qquad (6.2.5)$$

The differential coefficient of W(R) with respect to R is obtained as

$$\frac{\partial W(R)}{\partial R} = \left(\frac{3}{2\pi<\mathbf{R}^2>}\right)^{3/2} \left\{\frac{-6R}{2<\mathbf{R}^2>}\cdot(4\pi R^2) + 4\pi\cdot 2R\right\} \exp\left(-\frac{3\mathbf{R}^2}{2<\mathbf{R}^2>}\right) \qquad (6.2.6)$$

The value of R at the maximum of W(R) is given by the equation

$$\frac{-12\pi R^3}{\langle \mathbf{R}^2 \rangle} + 8\pi R = 0 \qquad (6.2.7)$$

Then, we have

$$\mathbf{R}_{\max}{}^{2} = \frac{8\pi\langle \mathbf{R}^2\rangle}{12\pi} = \frac{2}{3}\langle \mathbf{R}^2\rangle,\ \mathbf{R}_{\max} = \left(\frac{2}{3}\langle \mathbf{R}^2\rangle\right)^{1/2} \qquad (6.2.8)$$

W(R) has a maximum at the origin, while W(R) has a maximum at R=(2<R^2>/3)$^{1/2}$. Thus, the probability point density W(R) has a maximum at the origin. On the other hand, the probability that R is located in a spherical shell, W(**R**), is (point density) x (volume of spherical shell) ∝ (point density) x (radius)^2. The point density W(R) is a decreasing function of R, but the volume of the spherical shell with a fixed thickness is an increasing function of R. Then W(R) has a maximum at a certain value of R as given by Eq. (6.2.8).

<<Problem 6-3>> Distribution function of end-to-end distance of random chain (II)

Plot W(R) and W(**R**) as a function of R by using the equation

$$W(\mathbf{R})d\mathbf{R} = \left(\frac{3}{2\pi<\mathbf{R}^2>}\right)^{3/2} \exp\left(-\frac{3\mathbf{R}^2}{2<\mathbf{R}^2>}\right)d\mathbf{R} \qquad (6.2.5)'$$

Answer

Eq. (6.2.5)' is rewritten as

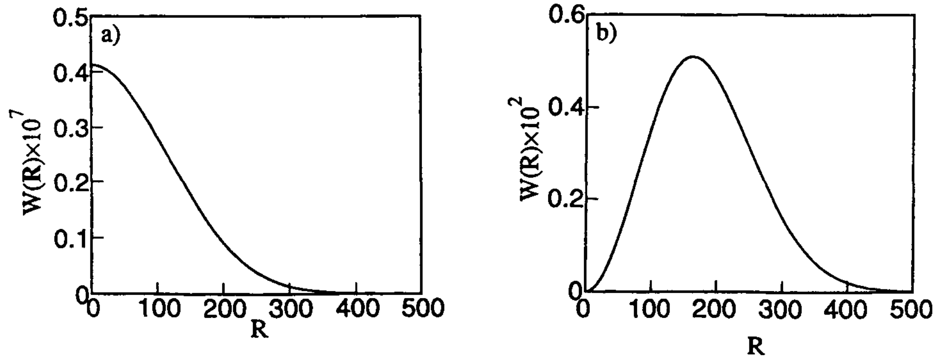

Fig. 6-3 Distribution function W(**R**) (a) and W(R) (b) for <R^2>$^{1/2}$=200

$$\mathrm{W}(\mathbf{R})\,4\pi\mathrm{R}^2\mathrm{dR} = \left(\frac{3}{2\pi\langle\mathbf{R}^2\rangle}\right)^{3/2} \exp\left(-\frac{3\mathbf{R}^2}{2\langle\mathbf{R}^2\rangle}\right) 4\pi\mathrm{R}^2\mathrm{dR} \tag{6.3.1}$$

Figure 6-3 shows W(**R**) and W(R) as a function of $|\mathbf{R}|$=R for $\langle R^2\rangle^{1/2}$=200.

<<Problem 6-4-a>> Elastic force of Gaussian chain (I)

Prove that the elastic force of Gaussian chain obeys Hooke's law.

Answer

The probability distribution function that the vector connecting the two ends of a Gaussian chain is in the range between **R** and **R**+d**R** is

$$\mathrm{W}(\mathbf{R}) = \left(\frac{3}{2\pi n l^2}\right)^{3/2} \exp\left(-\frac{3\mathbf{R}^2}{2nl^2}\right) \tag{6.4.1}$$

where n is the number of segments and l is the length of a segment. The change in internal energy of the Gaussian chain is written as

$$\mathrm{dU} = \mathrm{TdS} + \mathbf{K}\mathrm{d}\mathbf{R} \tag{6.4.2}$$

Thus, K is obtained as the differential coefficient

$$\mathbf{K} = -\mathrm{T}\left(\frac{\partial \mathrm{S}}{\partial \mathbf{R}}\right)_{\mathrm{U}} \tag{6.4.3}$$

According to Boltzmann's principle

$$\mathrm{S} = \mathrm{k}\ln \mathrm{W}(\mathbf{R}) + \mathrm{const.} \tag{6.4.4}$$

Then we have

$$\mathbf{K} = -\mathrm{kT}\frac{\partial \ln \mathrm{W}(\mathbf{R})}{\partial \mathbf{R}} \tag{6.4.5}$$

Using Eq. (6.4.1), we have

$$\frac{\partial \ln \mathrm{W}(\mathbf{R})}{\partial \mathbf{R}} = -\frac{3\mathrm{R}}{nl^2} \tag{6.4.6}$$

From Eqs. (6.4.5) and (6.4.6), we have

$$\mathbf{K} = (-kT)\left(-\frac{3\mathbf{R}}{nl^2}\right) = \left(\frac{3kT}{nl^2}\right)\cdot\mathbf{R} \tag{6.4.7}$$

The coefficient $3kT/nl^2$ is a constant when the temperature is constant. Thus, **K** is proportional to **R**, that is, **Hooke's law** holds.

<<Problem 6-4-b>> Elastic force of Gaussian chain (II)

Prove that the distribution function of the end-to-end distance of a three-dimensional random chain obeys the equation

$$W(R) \propto \exp\left\{-n\int_0^{\frac{R}{nl}} L^{-1}(y)dy\right\} \tag{6.4.8}$$

where L(x)=cothx-1/x is called **Langevin's function.**

Answer

Consider the Brownian motion of a particle which is observed at a certain time interval. Let's denote the displacement of the particle during the time interval from t_i to t_{i+1} as $\mathbf{l}_{i+1}$, and the probability density as $w(\mathbf{l}_{i+1})$. The probability density for such a successive value is $w(\mathbf{l}_1)w(\mathbf{l}_2)...w(\mathbf{l}_n)$. The probability distribution function that the particle which was at the origin at time t_0, is at R at time t_n is

$$W(\mathbf{R}) = \int\cdots\int w(\mathbf{l}_1)w(\mathbf{l}_2)\cdots w(\mathbf{l}_n)d\mathbf{l}_1d\mathbf{l}_2\cdots d\mathbf{l}_n$$

where the integral must be carried out with the restriction:

$$\sum \mathbf{l}_i = \mathbf{R} \tag{6.4.9}$$

Using **Laplace transformation** of W(**R**), we can remove this restriction as follows. The generating function is expressed as

$$Q(s) = \int W(\mathbf{R})\exp(\mathbf{R}s)d\mathbf{R}$$

$$= \int\cdots\int w(\mathbf{l}_1)w(\mathbf{l}_2)\cdots w(\mathbf{l}_n)\exp(\mathbf{l}_1 + \mathbf{l}_2 + \cdots + \mathbf{l}_n)s\, d\mathbf{l}_1d\mathbf{l}_2\cdots d\mathbf{l}_n$$

$$\left\{\int w(\mathbf{l}_1)\exp(\mathbf{l}_1\mathbf{s})\,d\mathbf{l}_1\right\}\left\{\int w(\mathbf{l}_2)\exp(\mathbf{l}_2\mathbf{s})\,d\mathbf{l}_2\right\}\cdots\left\{\int w(\mathbf{l}_n)\exp(\mathbf{l}_n\mathbf{s})\,d\mathbf{l}_n\right\} \tag{6.4.10}$$

Now, there is no restriction for each integral in Eq. (6.4.10). Then Eq. (6.4.10) can be rewritten as

$$Q(\mathbf{s}) = \left\{\int w(\mathbf{l})\exp(\mathbf{l}\mathbf{s})\,d\mathbf{l}\right\}^{n} \tag{6.4.11}$$

When the length of the step is constant, i.e.,

$$l\ \left(=|\mathbf{l}_1| = |\mathbf{l}_2| = \cdots = |\mathbf{l}_n|\right) \tag{6.4.12}$$

and the direction is arbitrary, then

$$\int_0^{\infty} w(\mathbf{l})d\mathbf{l} = 1 \tag{6.4.13}$$

must be satisfied. Hence, we have

$$w(\mathbf{l}) = \left(\frac{1}{4\pi l^2}\right)\delta\left(|\mathbf{l}| - l\right) \tag{6.4.14}$$

Here $\delta(|\mathbf{l}|-l)$ is **Dirac's δ-function.**
From Eqs. (6.4.11) and (6.4.14), we have

$$Q(\mathbf{s}) = \left\{\int \left(\frac{1}{4\pi l^2}\right)\delta\left(|\mathbf{l}| - l\right)\exp(\mathbf{l}\mathbf{s})d\mathbf{l}\right\}^{n} \tag{6.4.15}$$

Here,

$$\mathbf{l}\mathbf{s} = l\, s\cos\varphi \tag{6.4.16}$$

and $\int\ldots d\mathbf{l}$ can be rewritten as

$$\int_0^{\infty}\int_0^{\pi}\int_0^{2\pi}\left(\frac{1}{4\pi l^2}\right)\exp(l\, s\cos\varphi)\,\delta\left(|\mathbf{l}| - l\right) l^{2}\sin\varphi\, dl\, d\varphi\, d\theta$$

$$=\frac{1}{2l^{2}}\int_{0}^{\infty}\int_{0}^{\pi}\exp(l\,\mathrm{s}\cos\varphi)\,\delta\big(|\mathbf{l}|-l\big)\,l^{2}\sin\varphi\,dl\,d\varphi \qquad (6.4.17)$$

Putting cosφ=X (dcosφ=-sinφdφ=dX), Eq. (6.4.17) can be calculated as

$$\int_{0}^{\infty}\left(\frac{1}{4\pi l^{2}}\right)\exp(\mathbf{ls})\;\delta\big(|\mathbf{l}|-l\big)\,d\mathbf{l}$$

$$=\frac{1}{2l^{2}}\int_{0}^{\infty}\left\{\int_{1}^{-1}\exp(l\,\mathrm{s}\,\mathrm{X})l^{2}\,\delta\big(|\mathbf{l}|-l\big)\,(-d\mathrm{X})\right\}dl$$

$$=-\frac{1}{2l^{2}}\int_{0}^{\infty}\left|\frac{\exp(l\,\mathrm{s}\,\mathrm{X})}{l\,\mathrm{s}}\right|_{1}^{-1}l^{2}\,\delta\big(|\mathbf{l}|-l\big)\,dl$$

$$=\frac{1}{l^{2}}\int_{0}^{\infty}\frac{\exp(l\,\mathrm{s}\,\mathrm{X})-\exp(-l\,\mathrm{s}\,\mathrm{X})}{2l\,\mathrm{s}}\,l^{2}\,\delta\big(|\mathbf{l}|-l\big)\,dl$$

$$=\frac{e^{l\,\mathrm{s}}-e^{-l\,\mathrm{s}}}{2l\,\mathrm{s}}=\frac{\sinh(l\,\mathrm{s})}{l\,\mathrm{s}} \qquad (6.4.18)$$

where s=|**s**|. Substituting Eq. (6.4.18) in Eq. (6.4.15), we have

$$Q(\mathbf{s})=\left\{\frac{\sinh(l\,\mathrm{s})}{l\,\mathrm{s}}\right\}^{n} \qquad (6.4.19)$$

On the other hand, when the end-to-end distance of the molecular chain is fixed at R,we have

$$e^{-\frac{F}{kT}}=Z(T,\mathbf{R})=\int\cdots\int_{\mathbf{R}\ \text{fixed}}e^{-\frac{E}{kT}}\,d\Gamma \qquad (6.4.20)$$

Here, E is the sum of kinetic energy and potential energy. The total differential of **Helmholtz free energy** of this system is written as

$$dF=-SdT+\mathbf{K}d\mathbf{R} \qquad (6.4.21)$$

Using Gibbs free energy derived by **Legendre transformation**

$$G=F-\mathbf{KR} \qquad (6.4.22)$$

we have

$$dG = - SdT - \mathbf{R}d\mathbf{K} \tag{6.4.23}$$

Then,

$$e^{-\frac{G}{kT}} = Q(T,\mathbf{K}) = \int Z(T,\mathbf{R}) \exp\left(- \frac{\mathbf{KR}}{kT} \right) d\mathbf{R} \tag{6.4.24}$$

Comparing equations

$$Q(s) = \int W(\mathbf{R}) \exp(\mathbf{Rs})\, d\mathbf{R} \tag{6.4.10}$$

and

$$Q(T,\mathbf{K}) = \int Z(T,\mathbf{R}) \exp\left(- \frac{\mathbf{KR}}{kT} \right) d\mathbf{R} \tag{6.4.25}$$

we understand Q(**s**) is the partition function in case the force **K**=kTs exerts on the chain. From Eq. (6.4.23), **R** is obtained as

$$\mathbf{R} = - \left(\frac{\partial G}{\partial K} \right)_T \tag{6.4.26}$$

From Eq. (6.4.24),

$$- \frac{G}{kT} = \ln Q(T,\mathbf{K}) = \ln Q(T,s) \tag{6.4.27}$$

By combination of the equation ds=dK/kT and Eqs. (6.4.26) and (6.4.27), we have

$$\mathbf{R} = \frac{\partial}{\partial s} \ln Q(s) \tag{6.4.28}$$

Substituting Eq. (6.4.19) for Q(s) in Eq. (6.4.28), we have

$$\mathbf{R} = \frac{\partial}{\partial s} \ln Q(s) = \frac{\partial}{\partial s} \left\{ n \ln \frac{\sinh(l\, s)}{l\, s} \right\} = n \frac{\partial}{\partial s} \left[\left\{ \ln \sinh(l\, s) \right\} - \ln(l\, s) \right] \tag{6.4.29}$$

Substituting equations

$$\frac{\partial}{\partial s}\ln\left\{\sinh\left(l\,s\right)\right\}=\frac{1}{\sinh\left(l\,s\right)}\cdot\frac{\partial}{\partial s}\left(\frac{e^{l s}-e^{-l s}}{2}\right)=l\coth\left(l\,s\right) \tag{6.4.30}$$

and

$$\frac{\partial}{\partial s}\ln\left(l\,s\right)=\frac{1}{s} \tag{6.4.31}$$

in Eq. (6.4.29), we have

$$R=nl\left\{\coth\left(l\,s\right)-\frac{1}{l\,s}\right\}=nl\left(\coth x-\frac{1}{x}\right),\quad \left(x=l\,s=\frac{l\,K}{kT}\right) \tag{6.4.32}$$

or using the **Langevin function L(x)**, we have

$$R=nl\,\mathbf{L}(x)\ ,\ x=\frac{l\,K}{kT} \tag{6.4.33}$$

x is expressed with the **inverse Langevin function** as

$$x=\mathbf{L}^{-1}\left(\frac{R}{nl}\right) \tag{6.4.34}$$

or

$$K=\frac{kT}{l}\mathbf{L}^{-1}\left(\frac{R}{nl}\right) \tag{6.4.35}$$

From Eqs. (6.4.23) and (6.4.27)

$$S=-\left(\frac{\partial G}{\partial T}\right)_K=\frac{\partial kT\ln Q(s)}{\partial T}=k\ln Q(s)+kT\left(\frac{d\ln Q(s)}{ds}\right)\left(\frac{\partial s}{\partial T}\right)_K \tag{6.4.36}$$

From the equation s=K/kT,

$$\left(\frac{\partial s}{\partial T}\right)_K=-\frac{K}{kT^2} \tag{6.4.37}$$

Accordingly,

$$S=k\left[\ln Q(s)-s\frac{d}{ds}\ln Q(s)\right]=-k\int_0^s s\frac{d^2}{ds^2}\ln Q(s)ds \tag{6.4.38}$$

Using the equation

$$\mathbf{R} = \frac{\partial}{\partial s} \ln Q(s) \tag{6.4.28}$$

Eq. (6.4.38) can be reduced to

$$S = -k\int_0^s s\frac{dR}{ds}\,ds = -k\int_0^R s dR \tag{6.4.39}$$

Using **Boltzmann's principle**, we have

$$W(\mathbf{R}) \propto \exp\left[-\frac{1}{l}\int_0^R \mathbf{L}^{-1}\left(\frac{R}{n\,l}\right) dR\right] = \exp\left[-n\int_0^{\frac{R}{n\,l}} \mathbf{L}^{-1}(y)\,dy\right] \tag{6.4.40}$$

where we put y=R/n*l* (dR=n*l*dy). Expanding the **inverse Langevin function** as

$$\mathbf{L}^{-1}(y) = 3y + \frac{9}{5}y^3 + \frac{297}{175}y^5 + \cdots \tag{6.4.41}$$

the integral in Eq. (6.4.40) is reduced to

$$-n\int_0^{\frac{R}{n\,l}}\left(3y + \frac{9}{5}y^3 + \frac{297}{175}y^5 + \cdots\right)dy$$

$$= -n\left[\frac{3}{2}y^2 + \frac{9}{5\times4}y^4 + \frac{297}{175\times6}y^6 + \cdots\right]_0^{R/nl}$$

$$= -\frac{3R^2}{2n\,l^2}\left\{1 + \frac{3}{10}\left(\frac{R}{n\,l}\right)^2 + \frac{33}{175}\left(\frac{R}{n\,l}\right)^4 + \cdots\right\} \tag{6.4.42}$$

Substituting Eq. (6.4.42) in Eq. (6.4.40) and rearranging the equation, we have

$$W(\mathbf{R}) = \text{const. exp}\left[-\frac{3R^2}{2nl^2}\left\{ 1 + \frac{3}{10}\left(\frac{R}{nl}\right)^2 + \frac{33}{175}\left(\frac{R}{nl}\right)^4 + \cdots \right\}\right] \qquad (6.4.43)$$

When $R/nl \ll 1$, the inside of the braces in Eq. (6.4.43) is approximated to unity and we have

$$W(\mathbf{R}) = \text{const. exp}\left(-\frac{3R^2}{2nl^2}\right) \qquad (6.4.44)$$

Here the constant is determined from the normalization condition:

$$\int_0^R W(\mathbf{R})dR = 1 \qquad (6.4.45)$$

Then we have

$$W(\mathbf{R}) = \left(\frac{3}{2\pi nl^2}\right)^{3/2} \exp\left(-\frac{3\mathbf{R}^2}{2nl^2}\right) \qquad (6.4.1)$$

This is the equation for the **three-dimensional Gaussian distribution.**Thus, a random chain obeys the following equation strictly:

$$K = \frac{kT}{l}\mathbf{L}^{-1}\left(\frac{R}{nl}\right) \qquad (6.4.35)$$

This equation is nonlinear with respect to (R/nl) and **Hooke's law** holds only in case of $R/nl \ll 1$.

<<Problem 6-5>> Mean square end-to-end distance of Gaussian chain

Suppose that the probability density of the end-to-end distance of one-dimensional chain or the distribution of the length of radial vector is in the Gaussian form:

$$W(x) = \frac{1}{\left(2\pi nl^2\right)^{1/2}} \exp\left(-\frac{x^2}{2nl^2}\right) \qquad (6.1.1)$$

Here, n is the number of segments in a chain and l is the bond length of the segments.

(1) Calculate <x> and $<x^2>$.

(2) Derive the expression for $<r^2>$ for three-dimensional Gaussian chain.

Answer

(1) Since W(x) is an even function (W(x)=W(-x)), we have

$$\langle x\rangle = \int_{-\infty}^{\infty} \frac{x}{\left(2\pi n l^2\right)^{1/2}} \exp\left(-\frac{x^2}{2nl^2}\right) dx = 0 \tag{6.5.1}$$

Using the well known relation, we have

$$\langle x^2\rangle = \int_{-\infty}^{\infty} \frac{x^2}{\left(2\pi n l^2\right)^{\frac{1}{2}}} \exp\left(-\frac{x^2}{2nl^2}\right) dx = n l^2 \tag{6.5.2}$$

---

*

$$\int_{-\infty}^{\infty} x^2 e^{-Ax^2} dx = \frac{1}{2A}\sqrt{\frac{\pi}{A}} \tag{6.5.3}$$

$$\int_{-\infty}^{\infty} x^4 e^{-Ax^2} dx = \frac{3}{4A^2}\sqrt{\frac{\pi}{A}} \tag{6.5.4}$$

---

(2) Using Eq. (6.5.2), Eq. (6.1.1) can be rewritten as

$$W(x) = \frac{1}{\left(2\pi\langle x^2\rangle\right)^{1/2}} \exp\left(-\frac{x^2}{2\langle x^2\rangle}\right) \tag{6.5.5}$$

Eq. (6.5.5) can be generalized for a three-dimensional Gaussian chain as

$$W(\mathbf{R}) = \left(\frac{3}{2\pi\langle \mathbf{R}^2\rangle}\right)^{3/2} \exp\left(-\frac{3\mathbf{R}^2}{2\langle \mathbf{R}^2\rangle}\right) \tag{6.2.3}$$

where

$$\langle \mathbf{R}^2\rangle = \int R^2 W(\mathbf{R})d\mathbf{R} = \int_0^\infty 4\pi R^4 W(\mathbf{R})dR$$

$$= \frac{1}{2}\left[4\pi\left(\frac{3}{2\pi\langle \mathbf{R}^2\rangle}\right)^{3/2} \times \frac{6}{4}\left(\frac{2\langle \mathbf{R}^2\rangle}{3}\right)^2 \times \left(\frac{2\pi\langle \mathbf{R}^2\rangle}{3}\right)^{1/2}\right] = \langle \mathbf{R}^2\rangle = n\,l^2 \tag{6.5.6}$$

---

* The equation derived for three-dimensional Gaussian chains

$$\langle \mathbf{R}^2\rangle = n\,l^2$$

also holds for more general three-dimensional random chains. On putting the bond vector of *i* th segment as $\mathbf{l}_i$, we have

$$\langle \mathbf{R}^2\rangle = \left\langle \sum_i^n (\mathbf{l}_i)^2 \right\rangle = \sum_{i,k=1}^n \langle \mathbf{l}_i \cdot \mathbf{l}_k\rangle \tag{6.5.7}$$

If $i \neq k$,

$$\mathbf{l}_i \cdot \mathbf{l}_k = 0 \tag{6.5.8}$$

since $\mathbf{l}_i$ and $\mathbf{l}_k$ are independent.
If i=k,

$$\mathbf{l}_i \cdot \mathbf{l}_k = l^2 \tag{6.5.9}$$

Thus, we have

$$\langle \mathbf{R}^2\rangle = n\left\langle \sum_{i=1}^n \mathbf{l}_i \cdot \mathbf{l}_i \right\rangle + \sum_{i\neq k} \langle \mathbf{l}_i \cdot \mathbf{l}_k\rangle = n\,l^2 \tag{6.5.10}$$

<<Problem 6-6-a>> End-to-end distance for chain molecule with internal rotation (I)

Consider a set of unit vectors for bonds lying along a molecular chain. Let $\pi-\theta$ be the angle which two consecutive vectors i-1 and i make with each other. Choose sets of rectangular coordinate frames in such a way that each unit vector i coincides in the position and direction with the z_i axis of *i* th frame. x_i axis lies on the place determined by z_i axis and z_{i-1} axis and at the trans position of the vector i-2. ϕ is measured from the trans position. y_i lies in the direction to make a right-handed coordinate. Figure 6-6-a is an illustration of the coordinate systems for *i* th bond (x_i,y_i,z_i) and *(i+1)* th bond $(x_{i+1},y_{i+1},z_{i+1})$. The relationship between a vector $\mathbf{l}_i$ (x_i,y_i,z_i) described on the $x_iy_iz_i$ frame and the same vector $\mathbf{l}'_{i+1}$ $(x_{i+1},y_{i+1},z_{i+1})$ described on the $x_{i+1}y_{i+1}z_{i+1}$ frame is expressed as

$$\mathbf{l}'_{i+1} = \mathbf{T}_i\,\mathbf{l}_i \qquad (6.6.1)$$

where

$$\mathbf{T} = \begin{pmatrix} \cos\theta\cos\phi & \cos\theta\sin\phi & \sin\theta \\ \sin\theta & -\cos\phi & 0 \\ \sin\theta\cos\phi & \sin\theta\sin\phi & -\cos\theta \end{pmatrix} \qquad (6.6.2)$$

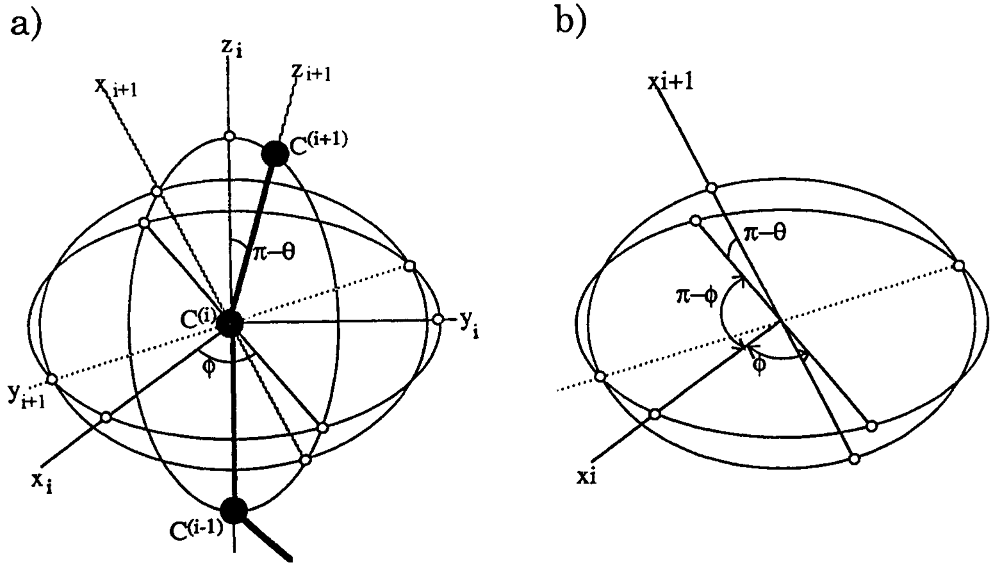

Fig. 6-6-a Two coordinates and the angles between them

Derive Eq. (6.6.2).

Answer

The angle between z_{i+1} and z_i is $\pi-\theta$. Then, the angle determined by x_{i+1} axis and x_iy_i plane is $\pi-\theta$. The angle determined by x_i axis and the intersection of $x_{i+1}z_{i+1}$ plane and x_iy_i plane is ϕ. y_{i+1} axis is on x_iy_i plane. The angle determined by y_{i+1} axis and x_i axis is $\pi/2-\phi$. Now, let's consider $\mathbf{l}'_{i+1}=(x_{i+1}, y_{i+1}, z_{i+1})$ and $\mathbf{l}_i=(x_i, y_i, z_i)$. The component of the unit vector x_{i+1} in the direction of x_iy_i plane is $\cos(\pi-\theta)=-\cos\theta$ and that on z_i axis is $\sin(\pi-\theta)=\sin\theta$. x_i and y_i component of the former component are $-\cos\theta\cos(\pi-\theta)=\cos\theta\cos\phi$ and $\cos\theta\sin\phi$, respectively. Then we have

$$x_{i+1} = \cos\theta\cos\phi\, x_i + \cos\theta\sin\phi\, y_i + \sin\theta\, z_i \tag{6.6.3}$$

y_{i+1} has no z_i component. Referring to Fig. 6-6-a, we have

$$y_{i+1} = \sin\phi\, x_i - \cos\phi\, y_i \tag{6.6.4}$$

Note that y_i component of y_{i+1} and y_i is in the opposite direction. Similarly, z_i component of z_{i+1} is $\cos(\pi-\phi)=-\cos\theta$. The component of the unit vector in the direction of z_{i+1} on x_iy_i plane is $\sin(\pi-\theta)=\sin\theta$, x_i and y_i components of which are $\sin\theta\cos\phi$ and $\sin\theta\sin\phi$, respectively. Accordingly, we have

$$z_{i+1} = \sin\theta\cos\phi\, x_i - \sin\theta\sin\phi\, y_i - \cos\theta\, z_i \tag{6.6.5}$$

In summary, we have

$$x_{i+1} = \cos\theta\cos\phi\, x_i + \cos\theta\sin\phi\, y_i + \sin\theta\, z_i$$

$$y_{i+1} = \sin\phi\, x_i - \cos\phi\, y_i$$

$$z_{i+1} = \sin\theta\cos\phi\, x_i - \sin\theta\sin\phi\, y_i - \cos\theta\, z_i \tag{6.6.6}$$

Rewriting Eq. (6.6.6) in a form of matrix, we have

$$\begin{pmatrix} x_{i+1} \\ y_{i+1} \\ z_{i+1} \end{pmatrix} = \begin{pmatrix} \cos\theta\cos\phi & \cos\theta\sin\phi & \sin\theta \\ \sin\phi & -\cos\phi & 0 \\ \sin\theta\cos\phi & \sin\theta\sin\phi & -\cos\theta \end{pmatrix} \begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix} \tag{6.6.7}$$

<<Problem 6-6-b>> End-to-end distance for chain molecule with internal rotation (II)

Mean square end-to-end distance <R^2> is given by the average of the scalar product of **R** with itself. That is,

$$\mathbf{R} = \sum_{i=1}^{n} \mathbf{l}_i \tag{6.6.8}$$

$$\left\langle \mathbf{R}^2 \right\rangle = nl^2 + 2\sum_{j>i}^{n} \left\langle \mathbf{l}_j \cdot \mathbf{l}_i \right\rangle \tag{6.6.9}$$

The second term of the right-hand side in Eq.(6.6.9) can be written as

$$\mathbf{l}_j^T \cdot \mathbf{l}_i = \mathbf{l}^T \mathbf{T}_{j-1} \mathbf{T}_{j-2} \cdots \mathbf{T}_{i+1} \mathbf{T}_i \, \mathbf{l} \tag{6.6.10}$$

Combining Eqs. (6.6.9) and (6.6.10), derive the following equation for the case where the internal rotations of consecutive bonds are independent:

$$\left\langle \mathbf{R}^2 \right\rangle = nl^2 + 2\mathbf{l}^T \frac{\langle \mathbf{T} \rangle}{1 - \langle \mathbf{T} \rangle} \left(n - \frac{1 - \langle \mathbf{T} \rangle^n}{1 - \langle \mathbf{T} \rangle} \right) \mathbf{l} \tag{6.6.11}$$

Answer

Substituting Eq. (6.6.10) in Eq. (6.6.9), we have

$$\left\langle \mathbf{R}^2 \right\rangle = nl^2 + 2\mathbf{l}^T \sum_{j>i} \left\langle \mathbf{T}_{j-1} \mathbf{T}_{j-2} \cdots \mathbf{T}_{i+1} \mathbf{T}_i \right\rangle \mathbf{l} \tag{6.6.12}$$

Since the internal rotations of consecutive bonds are independent,

$$\left\langle \mathbf{T}_{j-1} \mathbf{T}_{j-2} \cdots \mathbf{T}_{i+1} \mathbf{T}_i \right\rangle = \left\langle \mathbf{T}_{j-1} \right\rangle \left\langle \mathbf{T}_{j-2} \right\rangle \cdots \left\langle \mathbf{T}_{i+1} \right\rangle \left\langle \mathbf{T}_i \right\rangle \tag{6.6.13}$$

Here, the average of **T** for an arbitrarily chosen *m* th bond <$\mathbf{T}_m$> is obtained from

$$\left\langle \mathbf{T}_m \right\rangle = \frac{\int_0^{2\pi} \mathbf{T}_m \exp\left\{ - U_m(\phi) / kT \right\} d\phi}{\int_0^{2\pi} \exp\left\{ - U_m(\phi) / kT \right\} d\phi} \tag{6.6.14}$$

where $U_m(\phi)$ is the rotational potential of *m* th bond. When $<T_m>$ is identical for all the bonds (in case that the chain comprises an identical kind of bond, for example, polymethylene), we can take $<T>\equiv<T_m>$. Then, from Eqs. (6.6.12) and (6.6.13), we obtain

$$\langle \mathbf{R}^2\rangle = nl^2 + 2\mathbf{l}^T\sum_{j>i}\langle \mathbf{T}\rangle^{j-i}\mathbf{l} \tag{6.6.15}$$

The summation in the second term in Eq.(6.6.15) can be simplified as

$$\sum_{j>i}\langle \mathbf{T}\rangle^{j-i} = (n-1)\langle \mathbf{T}\rangle + (n-2)\langle \mathbf{T}\rangle^2 + (n-3)\langle \mathbf{T}\rangle^3 + \cdots + 2\langle \mathbf{T}\rangle^{n-2} + \langle \mathbf{T}\rangle^{(n-1)}$$

$$= n\langle \mathbf{T}\rangle\left(1 + \langle \mathbf{T}\rangle + \langle \mathbf{T}\rangle^2 + \cdots + \langle \mathbf{T}\rangle^{n-2}\right) - \langle \mathbf{T}\rangle\left(1 + \langle \mathbf{T}\rangle + \langle \mathbf{T}\rangle^2 + \cdots + \langle \mathbf{T}\rangle^{n-2}\right)$$

$$-\langle \mathbf{T}\rangle^2\left(1 + \langle \mathbf{T}\rangle + \langle \mathbf{T}\rangle^2 + \cdots + \langle \mathbf{T}\rangle^{n-3}\right) - \cdots - \langle \mathbf{T}\rangle^{n-1}$$

$$= \frac{n\left(1 - \langle \mathbf{T}\rangle^{n-1}\right)\langle \mathbf{T}\rangle}{1 - \langle \mathbf{T}\rangle} - \sum_{i=2}^{n}\frac{\langle \mathbf{T}\rangle^{i-1}\left(1 - \langle \mathbf{T}\rangle^{n-i+1}\right)}{1 - \langle \mathbf{T}\rangle}$$

$$= \frac{\langle \mathbf{T}\rangle}{1 - \langle \mathbf{T}\rangle}\left(n - n\langle \mathbf{T}\rangle^{n-1} - \sum_{i=2}^{n}\langle \mathbf{T}\rangle^{i-2} - \sum_{i=2}^{n}\langle \mathbf{T}\rangle^{n-1}\right)$$

$$= \frac{\langle \mathbf{T}\rangle}{1 - \langle \mathbf{T}\rangle}\left(n - \frac{1 - \langle \mathbf{T}\rangle^{n}}{1 - \langle \mathbf{T}\rangle} - (n-1)\langle \mathbf{T}\rangle^{n-1} + (n-1)\langle \mathbf{T}\rangle^{n-1}\right)$$

$$= \frac{\langle \mathbf{T}\rangle}{1 - \langle \mathbf{T}\rangle}\left(n - \frac{1 - \langle \mathbf{T}\rangle^{n}}{1 - \langle \mathbf{T}\rangle}\right) \tag{6.6.16}$$

Thus, Eq. (6.6.11) is directly obtained from Eqs. (6.6.15) and (6.6.16).

<<Problem 6-6-c>> End-to-end distance for chain molecule with internal rotation (III): Oka's equation

When n>>1, Eq. (6.6.11) can be approximated as

$$\left\langle \mathbf{R}^2 \right\rangle = \mathrm{n}\left(l^{\,2} + 2\mathbf{l}^{\mathrm{T}} \frac{\langle \mathbf{T} \rangle}{1 - \langle \mathbf{T} \rangle} \mathbf{l} \right) \tag{6.6.17}$$

Using this equation, derive the equation [**Oka's equation**]

$$\left\langle \mathbf{R}^2 \right\rangle = \mathrm{n} l^{\,2} \frac{1 - \cos\theta}{1 + \cos\theta} \cdot \frac{1 + \left\langle \cos\phi \right\rangle}{1 - \left\langle \cos\phi \right\rangle} \tag{6.6.18}$$

Answer

From the definition of inverse matrix, the equation

$$\frac{1}{1 - \langle \mathbf{T} \rangle} = \left(1 - \langle \mathbf{T} \rangle\right)^{-1} \tag{6.6.19}$$

is rewritten as

$$\left(1 - \langle \mathbf{T} \rangle\right)\left(1 - \langle \mathbf{T} \rangle\right)^{-1} = 1 \tag{6.6.20}$$

$$\langle \mathbf{T} \rangle \left(1 - \langle \mathbf{T} \rangle\right)^{-1} = \left(1 - \langle \mathbf{T} \rangle\right)^{-1} - 1 \tag{6.6.21}$$

Substituting Eq. (6.6.21) in Eq. (6.6.17), we have

$$\left\langle \mathbf{R}^2 \right\rangle = \mathrm{n}\left\{ l^{\,2} + 2\mathbf{l}^{\mathrm{T}}(-1)\,\mathbf{l} + 2\mathbf{l}^{\mathrm{T}}\left(1 - \langle \mathbf{T} \rangle\right)^{-1}\mathbf{l} \right\} \tag{6.6.22}$$

where **I** is the unit matrix

$$\mathbf{I} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{6.6.23}$$

$\mathbf{l}^{\mathrm{T}}$ and $\mathbf{l}$ are expressed as

$$\mathbf{l}^{\mathrm{T}} = \begin{pmatrix} 0 & 0 & l \end{pmatrix} \tag{6.6.24}$$

and

$$\mathbf{l} = \begin{pmatrix} 0 \\ 0 \\ l \end{pmatrix} \tag{6.6.25}$$

respectively. From Eqs. (6.6.23)-(6.6.25), we have

$$\mathbf{l}^{\mathrm{T}}(-1)\,\mathbf{l} = -\begin{pmatrix} 0 & 0 & l \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ l \end{pmatrix} = -l^2 \tag{6.6.26}$$

Substituting Eq. (6.6.26) in Eq. (6.6.22), we have

$$\left\langle \mathbf{R}^2 \right\rangle = \mathrm{n}\left\{ l^2 - 2l^2 + 2\mathbf{l}^{\mathrm{T}}\left(1 - \left\langle \mathbf{T} \right\rangle\right)^{-1}\mathbf{l} \right\} = \mathrm{n}\left\{ -l^2 + 2\mathbf{l}^{\mathrm{T}}\left(1 - \left\langle \mathbf{T} \right\rangle\right)^{-1}\mathbf{l} \right\} \tag{6.6.27}$$

Here,

$$\mathbf{l}^{\mathrm{T}}\left(1 - \left\langle \mathbf{T} \right\rangle\right)^{-1}\mathbf{l} = \sum_{\substack{i,j=1 \\ k,m=1}}^{3} l^{\mathrm{T}}_{ij}\left(1 - \left\langle \mathbf{T} \right\rangle\right)^{-1}_{jk} l_{km} \tag{6.6.28}$$

l_{ij} and l_{km} are zero except for j=3 and k=3, from Eqs. (6.6.24) and (6.6.25). Thus, we need to calculate only 33 component of the matrix in Eq. (6.6.28). Then we can calculate the average of **T**:

$$\mathbf{T} = \begin{pmatrix} \cos\theta\cos\phi & \cos\theta\sin\phi & \sin\theta \\ \sin\theta & -\cos\phi & 0 \\ \sin\theta\cos\phi & \sin\theta\sin\phi & -\cos\theta \end{pmatrix} \tag{6.6.2}$$

in the following way. Since the chains comprise identical bonds subject to independent rotational potentials $U(\phi)$, $<\sin\phi>=0$. Then, <T> and 1-<T> can be simplified as

$$\langle \mathbf{T} \rangle = \begin{pmatrix} \cos\theta\langle\cos\phi\rangle & 0 & \sin\theta \\ 0 & -\langle\cos\phi\rangle & 0 \\ \sin\theta\langle\cos\phi\rangle & 0 & -\cos\theta \end{pmatrix} \tag{6.6.29}$$

and

$$1 - \langle \mathbf{T} \rangle = \begin{pmatrix} 1 - \cos\theta\langle\cos\phi\rangle & 0 & -\sin\theta \\ 0 & 1 + \langle\cos\phi\rangle & 0 \\ -\sin\theta\langle\cos\phi\rangle & 0 & 1 + \cos\theta \end{pmatrix} \tag{6.6.30}$$

From the definition of inverse matrix, we have

$$\left(1 - \langle \mathbf{T} \rangle\right)_{33}^{-1} = \frac{\Delta_{33}}{D} \tag{6.6.31}$$

Here, D is the determinant of the matrix $(1\text{-}\langle T \rangle)^{-1}$ and expressed as

$$D = (1 - \cos\theta\langle\cos\phi\rangle)\begin{vmatrix} 1 + \langle\cos\phi\rangle & 0 \\ 0 & 1 + \cos\theta \end{vmatrix} + \sin\theta \begin{vmatrix} 0 & 1 + \langle\cos\phi\rangle \\ \sin\theta\langle\cos\phi\rangle & 0 \end{vmatrix}$$

$$= (1 + \cos\theta)\left(1 + \langle\cos\phi\rangle\right)\left(1 - \langle\cos\phi\rangle\right) \tag{6.6.32}$$

and Δ_{33} is the determinant of the cofactor of 33 component of the matrix (1-<T>) and is expressed as

$$\Delta_{33} = \begin{vmatrix} 1 - \cos\theta\langle\cos\phi\rangle & 0 \\ 0 & 1 + \langle\cos\phi\rangle \end{vmatrix} = (1 - \cos\theta\langle\cos\phi\rangle)(1 + \langle\cos\phi\rangle) \tag{6.6.33}$$

From Eqs. (6.6.32) and (6.6.33), we have

$$\left(1 - \langle \mathbf{T} \rangle\right)_{33}^{-1} = \frac{(1 - \cos\theta\langle\cos\phi\rangle)(1 + \langle\cos\phi\rangle)}{(1 + \cos\theta)(1 + \langle\cos\phi\rangle)(1 - \langle\cos\phi\rangle)} = \frac{1 - \cos\theta\langle\cos\phi\rangle}{(1 + \cos\theta)(1 - \langle\cos\phi\rangle)} \tag{6.6.34}$$

Substituting Eq. (6.6.34) in Eq. (6.6.27), we have

$$\langle \mathbf{R}^2\rangle = n\left(-l^2 + 2l^2\left(1 - \langle \mathbf{T}\rangle\right)_{33}^{-1}\right) = nl^2\left(-1 + 2\left(1 - \langle \mathbf{T}\rangle\right)_{33}^{-1}\right)$$

$$= nl^2\left(\frac{2 - 2\cos\theta\langle\cos\phi\rangle}{(1+\cos\theta)(1-\langle\cos\phi\rangle)} - 1\right) = nl^2\frac{(1-\cos\theta)(1+\langle\cos\phi\rangle)}{(1+\cos\theta)(1-\langle\cos\phi\rangle)} \qquad (6.6.18)$$

(See S.Oka, *Proc. Phys.-Math. Soc. Japan* **24**, 657 (1942), W. Taylor, *J. Chem. Phys.* **15**, 412 (1947)) For **freely rotating chain,** $<\cos\phi>=0$. Then we have

$$\langle \mathbf{R}^2\rangle = nl^2\frac{1-\cos\theta}{1+\cos\theta} \qquad (6.6.35)$$

(See W. Kuhn, *Kolloid-Z* **68**, 2 (1934), R. Kubo, *J. Phys. Soc. Japan* **3**, 119 (1948), H. Eyring, *Phys. Rev.* **39**, 746 (1932), F. T. Wall, *J. Chem. Phys.* **11**, 67 (1943), and H. Benoit, *J. Polym. Sci.* **3**, 376 (1948))

<<Problem 6-7>> Distribution function of end-to-end distance of a polymer chain

Derive the **distribution function of end-to-end distance of a polymer chain** W(**R**) in the case when the valence angle of the consecutive segments is constant and the rotation about single bond is not completely free but is restricted by energy barriers. Then derive the probability W(R)dR for finding the end-to-end distance between R and R+dR.

Answer

W(**R**) for random chain is given by

$$W(\mathbf{R}) = \left(\frac{3}{2\pi\langle\mathbf{R}^2\rangle}\right)^{3/2}\exp\left(-\frac{3\mathbf{R}^2}{2\langle\mathbf{R}^2\rangle}\right) \qquad (6.2.3)$$

For restricted rotation, $<\mathbf{R}^2>$ is given by

$$\langle \mathbf{R}^2\rangle = nl^2\frac{(1-\cos\theta)(1+\langle\cos\phi\rangle)}{(1+\cos\theta)(1-\langle\cos\phi\rangle)} \qquad (6.6.35)$$

Eq. (6.6.35) is also expressed as

$$l'^2 = l^2 \frac{(1 - \cos\theta)(1 + \langle\cos\phi\rangle)}{(1 + \cos\theta)(1 - \langle\cos\phi\rangle)} \tag{6.7.1}$$

$$\langle R^2 \rangle = nl'^2 \tag{6.7.2}$$

Thus, this chain can be considered as the random coil chain with the effective bond length l'. For this chain, Eq. (6.2.3) is replaced by

$$W(\mathbf{R}) = \left(\frac{3}{2\pi n l'^2}\right)^{3/2} \exp\left(-\frac{3\mathbf{R}^2}{2nl'^2}\right) \tag{6.7.3}$$

Similarly, we have

$$W(R)dR = \left(\frac{3}{2\pi n l'^2}\right)^{3/2} \exp\left(-\frac{3R^2}{2nl'^2}\right) 4\pi R^2 dR \tag{6.7.4}$$

<<Problem 6-8>> Bresler-Frenkel's equation

Suppose the potential for the molecular rotation is expressed as

$$U(\phi) = \frac{1}{2}u_0(1 - \cos\phi) \tag{6.8.1}$$

as illustrated in Fig.6-8. When the rotation of the consecutive segments is

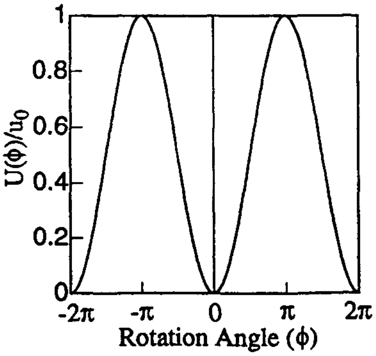

Fig. 6-8 Potential energy for molecular rotation

not possible near the room temperature and only small torsional vibrations around the equilibrium position $\phi=0$ are permitted, calculate $<\cos\phi>$. Then, prove that the **mean square end-to-end distance** is given by

$$\left\langle \mathbf{R}^2 \right\rangle = n l^2 \frac{1-\cos\theta}{1+\cos\theta} \cdot \frac{2u_0}{kT} \tag{6.8.2}$$

where u_0 is the peak potential on the potential curve. Assume $u_0 \ll kT$.

Answer

Expanding $\cos\phi$ in a form of Maclaurin series as

$$\cos\phi = 1 - \frac{\phi^2}{2!} + \frac{\phi^4}{4!} - \cdots \cong 1 - \frac{\phi^2}{2} \tag{6.8.3}$$

Then, Eq. (6.8.1) can be approximated by

$$U(\phi) \cong u_0 \frac{\phi^2}{4} \tag{6.8.4}$$

and the average of $\cos\phi$ is calculated as

$$\left\langle \cos\phi \right\rangle \cong \frac{\displaystyle\int_0^{2\pi} \left(1 - \frac{\phi^2}{2}\right) \exp\left(-\frac{-u_0\phi^2}{4kT}\right) d\phi}{\displaystyle\int_0^{2\pi} \exp\left(-\frac{-u_0\phi^2}{4kT}\right) d\phi} \cong 1 - \frac{1}{2} \frac{\displaystyle\int_0^{\infty} \phi^2 \exp\left(-\frac{-u_0\phi^2}{4kT}\right) d\phi}{\displaystyle\int_0^{\infty} \exp\left(-\frac{-u_0\phi^2}{4kT}\right) d\phi} = 1 - \frac{kT}{u_0} \tag{6.8.5}$$

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$$\int_0^{2\pi} \phi^2 \exp\left(-\frac{-u_0\phi^2}{4kT}\right) d\phi \cong \int_0^{\infty} \phi^2 \exp\left(-\frac{-u_0\phi^2}{4kT}\right) d\phi \tag{6.8.6}$$

$$\int_0^\infty \phi^2 \exp\left(-\frac{-u_0\phi^2}{4kT}\right)d\phi = \frac{1}{4}\left(\frac{4kT}{u_0}\right)\sqrt{\frac{4kT}{u_0}\pi} = \frac{1}{4}\left(\frac{4kT}{u_0}\right)^{3/2}\pi^{1/2} \qquad (6.8.7)$$

$$\int_0^\infty \exp\left(-\frac{-u_0\phi^2}{4kT}\right)d\phi = \frac{1}{2}\sqrt{\frac{4kT}{u_0}\pi} = \left(\frac{kT}{u_0}\right)^{1/2}\pi^{1/2} \qquad (6.8.8)$$

From Eqs. (6.8.7) and (6.8.8), we have

$$\frac{\displaystyle\int_0^\infty \phi^2 \exp\left(-\frac{-u_0\phi^2}{4kT}\right)d\phi}{\displaystyle\int_0^\infty \exp\left(-\frac{-u_0\phi^2}{4kT}\right)d\phi} = \frac{2\left(\frac{kT}{u_0}\right)^{3/2}\pi^{1/2}}{\left(\frac{kT}{u_0}\right)^{1/2}\pi^{1/2}} = 2\left(\frac{kT}{u_0}\right) \qquad (6.8.9)$$

$<\mathbf{R}^2>$ is expressed as

$$\left\langle \mathbf{R}^2 \right\rangle = nl^2\frac{(1-\cos\theta)(1+\langle\cos\phi\rangle)}{(1+\cos\theta)(1-\langle\cos\phi\rangle)} \qquad (6.6.35)$$

Using the approximation

$$\langle\cos\phi\rangle \cong 1 - \frac{kT}{u_0} \qquad (6.8.5)$$

Eq. (6.6.35) is reduced to

$$\left\langle \mathbf{R}^2 \right\rangle = n\,l^2\frac{1-\cos\theta}{1+\cos\theta}\cdot\frac{2u_0}{kT} \qquad (6.8.2)$$

Eq. (6.8.2) holds for long and stiff polymer chains. This equation is called **Bresler-Frenkel's equation**. (See S. E. Bresler and Ya. I. Frenkel, *Zhur. Eksp. i Teoret. Fiz.* **9**, 1094 (1939); M. V. Volkenstein, *Configurational Statistics of Polymeric Chains*, (*High Polymers*, vol XVII), translated by

S.N.Timasheff and M.J.Timasheff, Interscience, 1963, Chap. 4)) If we determine $\langle \mathbf{R}^2 \rangle / nl$ and θ empirically, we can calculate rotational potential u_0 by using Eq. (6.8.2).

<<Problem 6-9>> Mean square radius of gyration

The **mean square radius of gyration** defined as the mean square distance of the collection of atoms from their center of gravity is one sixth of the mean square end-to-end distance for a freely jointed molecular chain, that is,

$$\langle S^2 \rangle = \frac{1}{6} \langle \mathbf{R}^2 \rangle \tag{6.9.1}$$

Derive Eq. (6.9.1) using **pearl necklace model** in which small particles are assumed to be located at the junctions of the bonds and all the mass of each structure unit is concentrated on each particle.

Answer

Let's number the small particles serially from an end of the necklace as 1,2...n and denote the position vector from an arbitrary chosen origin as $\mathbf{r}_1$, $\mathbf{r}_2,\ldots\mathbf{r}_{n-1}$, $\mathbf{r}_n$. Then the position vector of the center of gravity $\mathbf{r}_G$ is expressed as

$$\mathbf{r}_G = \frac{1}{n} \sum_{i=1}^{n} \mathbf{r}_i \tag{6.9.2}$$

The vector connecting a small particle i and the origin is expressed as

$$\mathbf{r}_{Gi} = \mathbf{r}_i - \mathbf{r}_G \tag{6.9.3}$$

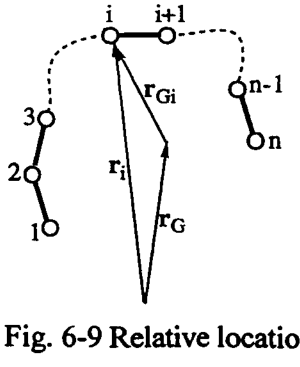

Fig. 6-9 Relative location of each sphere in pearl necklace model

Taking a summation of both sides over i=1 to n, we have

$$\sum_{i=1}^{n} \mathbf{r}_{Gi}^{2} = \sum_{i=1}^{n} \left(\mathbf{r}_i - \mathbf{r}_G\right)^2 = \sum_{i=1}^{n} \left(\mathbf{r}_i^{2} - 2\mathbf{r}_i\mathbf{r}_G + \mathbf{r}_G^{2}\right)$$

$$= \sum_{i=1}^{n} \mathbf{r}_i^{2} - 2\sum_{i=1}^{n} \mathbf{r}_i\mathbf{r}_G + \sum_{i=1}^{n} \mathbf{r}_G^{2} = \sum_{i=1}^{n} \mathbf{r}_i^{2} - n\mathbf{r}_G^{2} \qquad (6.9.4)$$

From Eq. (6.9.2),

$$\mathbf{r}_G^{2} = \mathbf{r}_G \cdot \mathbf{r}_G = \frac{1}{n^2}\sum_{i}^{n}\sum_{j}^{n} \mathbf{r}_i \cdot \mathbf{r}_j = \frac{1}{n^2}\sum_{i}^{n}\sum_{j}^{n} \frac{\left(\mathbf{r}_i^{2} + \mathbf{r}_j^{2} - \mathbf{r}_{ij}^{2}\right)}{2} \qquad (6.9.5)$$

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$$\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i \qquad (6.9.6)$$

The scalar product of $\mathbf{r}_{ij}$ with itself is

$$\mathbf{r}_{ij}^{2} = \mathbf{r}_{ij} \cdot \mathbf{r}_{ij} = \left(\mathbf{r}_j - \mathbf{r}_i\right)\left(\mathbf{r}_j - \mathbf{r}_i\right) = \mathbf{r}_i^{2} + \mathbf{r}_j^{2} - 2\mathbf{r}_{ij}^{2} \qquad (6.9.7)$$

Then we have

$$2\mathbf{r}_{ij} \cdot \mathbf{r}_{ij} = \mathbf{r}_i^{2} + \mathbf{r}_j^{2} - \mathbf{r}_{ij}^{2} \qquad (6.9.8)$$

Eq. (6.9.5) is rewritten as

$$\mathbf{r}_G^{2} = \frac{1}{n}\sum_{i=1}^{n} \mathbf{r}_i^{2} - \frac{1}{2n^2}\sum_{i=1}^{n}\sum_{j=1}^{n} \mathbf{r}_{ij}^{2} \qquad (6.9.9)$$

Substituting Eq. (6.9.9) for $\mathbf{r}_G^2$ in Eq. (6.9.4), we have

$$\sum_{i=1}^{n} \mathbf{r}_{Gi}^{2} = \frac{1}{2n}\sum_{i=1}^{n}\sum_{j=1}^{n} \mathbf{r}_{ij}^{2} = \frac{1}{n}\sum_{i>j} \mathbf{r}_{ij}^{2} \qquad (6.9.10)$$

From the definition,

$$\left\langle S^2 \right\rangle = \frac{1}{n} \sum \mathbf{r}_{Gi}{}^2 \tag{6.9.11}$$

Here, < > means the average over all molecular conformations. Using Eq. (6.9.10), Eq. (6.9.11) is rewritten as

$$\left\langle S^2 \right\rangle = \frac{1}{n^2} \sum_{i>j} \mathbf{r}_{ij}{}^2 \tag{6.9.12}$$

When the molecule is a Gaussian chain, the mean square length between *i* th particle and *j* th particle is expressed as

$$\left\langle \mathbf{r}_{ij}{}^2 \right\rangle = \left| i - j \right| l'^2 \tag{6.9.13}$$

for $|i-j| \gg 1$. The number of ways for choosing two particles with the difference $|i-j|$ being t, i.e., the length of a partial chain cut from the original chain consisting of n particles being $|i-j|=t$, is n-t. Then we have

$$\left\langle S^2 \right\rangle \cong \frac{1}{n^2} \sum_{i=1}^{n} t\,(n-t)\, l'^2 = \frac{l'^2}{n^2} \left\{ \frac{n^2(n+1)}{2} - \frac{n(n+1)(2n+1)}{6} \right\} \tag{6.9.14}$$

Since $n \gg 1$, $\langle S^2 \rangle$ is approximated by

$$\left\langle S^2 \right\rangle \cong \frac{l'^2}{n^2} \left(\frac{n^3}{2} - \frac{n^3}{3} \right) = \frac{n l'^2}{6} \tag{6.9.15}$$

Using the equation

$$\left\langle \mathbf{R}^2 \right\rangle = n l'^2 \tag{6.7.2}$$

we have

$$\left\langle S^2 \right\rangle \cong \frac{1}{6} \left\langle \mathbf{R}^2 \right\rangle \tag{6.9.1}$$

<<Problem 6-10>> End-to-end distance of partial chain

Using the Gaussian distribution of the end-to-end distance for random coil chain consisting of n bonds

$$W(\mathbf{R}) = \left(\frac{3}{2\pi n l^2}\right)^{3/2} \exp\left(-\frac{3\mathbf{R}^2}{2nl^2}\right) \tag{6.4.1}$$

derive the expression for (1)$<1/|\mathrm{R}|>$, (2)$<\mathbf{R}_{\mathrm{Gk}}{}^2>$ and (3)$<\mathbf{R}_{\mathrm{Gk}}\mathbf{R}_{\mathrm{Gk'}}>$. Here, $\mathbf{R}_{\mathrm{Gk}}$ denotes the vector connecting the center of gravity and *k* th segment and $<\mathbf{R}_{\mathrm{gk}}{}^2>$ is the same as $<\mathbf{S}^2>$.

Answer

(1) From the definition,

$$\left\langle\frac{1}{|\mathbf{R}|}\right\rangle = \int \frac{1}{|\mathbf{R}|} W(\mathbf{R}) d\mathbf{R} \tag{6.10.1}$$

Substituting Eq. (6.4.1) in Eq. (6.10.1), we have

$$\left\langle\frac{1}{|\mathbf{R}|}\right\rangle = 4\pi\left(\frac{3}{2\pi n l^2}\right)^{3/2}\int_0^\infty \frac{1}{\mathrm{R}}\exp\left(-\frac{3\mathrm{R}^2}{2nl^2}\right)\mathrm{R}^2 d\mathrm{R}$$

$$= 4\pi\left(\frac{3}{2\pi n l^2}\right)^{3/2}\int_0^\infty \mathrm{R}\exp\left(-\frac{3\mathrm{R}^2}{2nl^2}\right) d\mathrm{R}$$

$$= 4\pi\left(\frac{3}{2\pi n l^2}\right)^{3/2}\left[-\frac{\mathrm{n}l^2}{3}\exp\left(-\frac{3\mathrm{R}^2}{2nl^2}\right)\right]_0^\infty$$

$$= \frac{4\pi}{l}\left(\frac{3}{2\pi n l^2}\right)^{3/2}\frac{nl^2}{3} = \left(\frac{6}{n\pi}\right)^{1/2}\cdot\frac{1}{l^2} \tag{6.10.2}$$

(2) For convenience, we place one end of the molecular chain at the origin.

$\mathbf{R}_k$ denotes the vector connecting the end of the chain and *k* th segment. Then,

$$\mathbf{R}_{Gk} = \mathbf{R}_k - \mathbf{R}_G \tag{6.10.3}$$

and

$$\mathbf{R}_{Gk}{}^2 = \mathbf{R}_k{}^2 - 2\mathbf{R}_k\mathbf{R}_G + \mathbf{R}_G{}^2 \tag{6.10.4}$$

From the definition,

$$\mathbf{R}_G = \frac{1}{n}\sum_i \mathbf{R}_i \tag{6.10.5}$$

and

$$\mathbf{R}_G{}^2 = \frac{1}{n}\sum_i \mathbf{R}_i{}^2 - \frac{1}{2n^2}\sum_i\sum_j \mathbf{R}_{ij}{}^2 \tag{6.10.6}$$

Substituting Eq. (6.10.6) in Eq. (6.10.4), we have

$$\mathbf{R}_{Gk}{}^2 = \mathbf{R}_k{}^2 - \frac{2}{n}\sum_i \mathbf{R}_i\mathbf{R}_j + \frac{1}{n}\sum_i \mathbf{R}_i{}^2 - \frac{1}{2n^2}\sum_i\sum_j \mathbf{R}_{ij}{}^2 \tag{6.10.7}$$

With the aid of the relationship

$$\mathbf{R}_k \cdot \mathbf{R}_i = \frac{\mathbf{R}_k{}^2 + \mathbf{R}_i{}^2 - \mathbf{R}_{ki}{}^2}{2} \tag{6.10.8}$$

Eq. (6.10.7) can be simplified as

$$\begin{aligned}\mathbf{R}_{Gk}{}^2 &= \mathbf{R}_k{}^2 - \frac{1}{n}\sum_i \left(\mathbf{R}_k{}^2 + \mathbf{R}_i{}^2 - \mathbf{R}_{ki}{}^2\right) + \frac{1}{n}\sum_i \mathbf{R}_i{}^2 - \frac{1}{2n^2}\sum_i\sum_j \mathbf{R}_{ij}{}^2 \\ &= \frac{1}{n}\sum_i \mathbf{R}_{ki}{}^2 - \frac{1}{2n^2}\sum_i\sum_j \mathbf{R}_{ij}{}^2\end{aligned} \tag{6.10.9}$$

Averaging both sides of Eq. (6.10.9), we have

$$\left\langle \mathbf{R}_{GK}{}^2 \right\rangle = \frac{1}{n}\sum_i \left\langle \mathbf{R}_{ki}{}^2 \right\rangle - \frac{1}{2n^2}\sum_i\sum_j \left\langle \mathbf{R}_{ij}{}^2 \right\rangle \tag{6.10.10}$$

The first and the second term in the right-hand side of Eq.(6.10.10) are calculated as

$$\sum_i \left\langle \mathbf{R}_{ki}{}^2 \right\rangle = \sum_i \left| k - i \right| l^2 = \left(\sum_{t=1}^{n-k} t + \sum_{t=1}^{k} t \right) l^2$$

$$= \frac{1}{2}\left\{ (n-k)(n-k+1) + k(k+1) \right\} l^2 \tag{6.10.11}$$

and

$$\sum_i\sum_j \left\langle \mathbf{R}_{ij}{}^2 \right\rangle = 2\sum_{t=1}^{n} t(n-t) l^2$$

$$= \left\{ n^2(n+1) - \frac{n}{3}(n+1)(2n+1) \right\} l^2 \tag{6.10.12}$$

respectively. Substituting Eqs. (6.10.11) and (6.10.12) in Eq. (6.10.10), we obtain

$$\left\langle \mathbf{R}_{Gk}{}^2 \right\rangle = \frac{l^2}{2n}\left\{ (n-k)(n-k+1) + k(k+1) \right\} - \frac{l^2}{2n}\left\{ n^2(n+1) - \frac{n}{3}(n+1)(2n+1) \right\}$$

$$= \frac{l^2}{2n}\left(\frac{2}{3}n^2 - 2nk + 2k^2 + n + \frac{1}{3} \right) \cong \frac{l^2}{3n}\left(n^2 - 3nk + 3k^2 \right) \tag{6.10.13}$$

(3) As clearly shown from Fig.6-10,

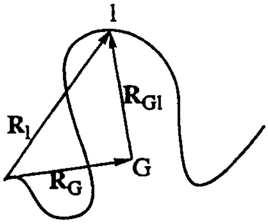

Fig. 6-10 Relative location of a chain from the center of gravity

$$\begin{aligned}\mathbf{R}_{Gk}\cdot\mathbf{R}_{Gk'} &= \left(\mathbf{R}_k - \mathbf{R}_G\right)\cdot\left(\mathbf{R}_{k'} - \mathbf{R}_G\right)\\ &= \mathbf{R}_k\cdot\mathbf{R}_{k'} - \left(\mathbf{R}_k + \mathbf{R}_{k'}\right)\cdot\mathbf{R}_G + \mathbf{R}_G^{\,2}\end{aligned} \tag{6.10.14}$$

Substituting Eqs. (6.10.5), (6.10.6) and (6.10.8) into Eq. (6.10.14), we have

$$\begin{aligned}\mathbf{R}_{Gk}\cdot\mathbf{R}_{Gk'} &= \frac{\mathbf{R}_k^{\,2} + \mathbf{R}_{k'}^{\,2} - \mathbf{R}_{kk'}^{\,2}}{2}\\ &\quad - \frac{1}{n}\sum_i \mathbf{R}_k\cdot\mathbf{R}_i - \frac{1}{n}\sum_i \mathbf{R}_{k'}\cdot\mathbf{R}_i + \frac{1}{n}\sum_i \mathbf{R}_i^{\,2} - \frac{1}{2n^2}\sum_i\sum_j \mathbf{R}_{ij}^{\,2}\\ &= \frac{\mathbf{R}_k^{\,2} + \mathbf{R}_{k'}^{\,2} - \mathbf{R}_{kk}^{\,2}}{2} - \frac{1}{2n}\sum_i\left(\mathbf{R}_k^{\,2} + \mathbf{R}_i^{\,2} - \mathbf{R}_{ki}^{\,2}\right)\\ &\quad - \frac{1}{2n}\sum_i\left(\mathbf{R}_{k'}^{\,2} + \mathbf{R}_i^{\,2} - \mathbf{R}_{k'i}^{\,2}\right) + \frac{1}{n}\sum_i \mathbf{R}_i^{\,2} - \frac{1}{2n^2}\sum_i\sum_j \mathbf{R}_{ij}^{\,2}\\ &= -\frac{\mathbf{R}_{kk'}^{\,2}}{2} + \frac{1}{2n}\left(\sum_i \mathbf{R}_{ki}^{\,2} + \sum_i \mathbf{R}_{k'i}^{\,2}\right) - \frac{1}{2n^2}\sum_i\sum_j \mathbf{R}_{ij}^{\,2}\end{aligned} \tag{6.10.15}$$

Averaging both sides of Eq. (6.10.15), we have

$$\begin{aligned}&\left\langle \mathbf{R}_{Gk}\cdot\mathbf{R}_{Gk'}\right\rangle\\ &= -\frac{\left\langle \mathbf{R}_{kk'}^{\,2}\right\rangle}{2} + \frac{1}{2n}\left(\sum_i\left\langle \mathbf{R}_{ki}^{\,2}\right\rangle + \sum_i\left\langle \mathbf{R}_{k'i}^{\,2}\right\rangle\right) - \frac{1}{2n^2}\sum_i\sum_j\left\langle \mathbf{R}_{ij}^{\,2}\right\rangle\\ &= -\frac{1}{2}\left|k - k'\right| l^2\\ &\quad + \frac{1}{2n}\left[\frac{1}{2}(n-k)(n-k+1) + \frac{1}{2}k(k+1) + \frac{1}{2}(n-k')(n-k'+1) + \frac{1}{2}k'(k'+1)\right] l^2\end{aligned}$$

$$-\frac{1}{2n}\left[n(n+1)-\frac{1}{3}(n+1)(2n+1)\right]l^2$$

$$=\frac{l^2}{6n}\left[2n^2+3\left(k^2+k'^2\right)-3n\left(k+k'+\left|k-k'\right|\right)\right] \tag{6.10.16}$$

<<Problem 6-11>> Distribution function of separation between segments and the center of gravity

The distribution function of the separation between the segments and the center of gravity of a Gaussian polymer chain is approximated by

$$\rho(r)dr = n\left(\frac{3}{2\pi\langle S^2\rangle}\right)^{\frac{3}{2}}\exp\left(-\frac{3r^2}{2\langle S^2\rangle}\right)4\pi r^2dr \tag{6.11.1}$$

Here, n is the number of segments of the polymer chain and $<S^2>$ is the mean square radius of gyration (Fig. 6-11). Derive Eq. (6.11.1).

Answer

The Gaussian distribution function is expressed as

$$W(R)dR = 4\pi\left(\frac{3}{2\pi n l^2}\right)^{\frac{3}{2}}\exp\left(-\frac{3R^2}{2nl^2}\right)R^2dR \tag{6.7.5}$$

If we replace j-i for n in Eq. (6.7.5), the equation expresses the probability that

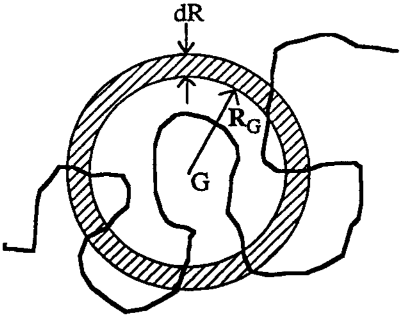

Fig. 6-11 Relative location of a chain from the center of gravity

the distance between *j* th segment and *i* th segment be R. If we place *i* th segment near the center of gravity, then Eq. (6.7.5) approximately stands for the segment distribution about the center of gravity. Then we can reasonably assume the probability for finding segments anywhere in the range of the distance from the center of gravity between r and r+dr to be proportional to $\exp(-B^2r^2)4\pi r^2dr$:

$$\rho(r)dr = A\exp\left(-B^2r^2\right)4\pi r^2dr \tag{6.11.2}$$

Here, A is a proportional constant. Normalization condition is written as

$$n = \int_0^\infty \rho(r)dr = 4\pi A\int_0^\infty r^2\exp\left(-B^2r^2\right)dr = \pi^{3/2}\frac{A}{B^3} \tag{6.11.3}$$

or

$$A = \frac{nB^3}{\pi^{3/2}} \tag{6.11.4}$$

From the definition, we have

$$\left\langle S^2\right\rangle = \frac{\int_0^\infty r^2\rho(r)\,dr}{\int_0^\infty \rho(r)\,dr} = \frac{3\pi^{3/2}}{2}\frac{A}{B^5} \tag{6.11.5}$$

Substituting Eq. (6.11.4) in Eq. (6.11.5), we have

$$\left\langle S^2\right\rangle = \frac{3}{2}B^{-2} \tag{6.11.6}$$

or

$$B^2 = \frac{3}{2}\left\langle S^2\right\rangle^{-1} \tag{6.11.7}$$

Then we have

$$A = n\left(\frac{3}{2\pi}\left\langle S^2\right\rangle^{-1}\right)^{3/2} \tag{6.11.1}$$

Substituting Eqs. (6.11.7) and (6.11.1) in Eq. (6.11.2), we finally obtain Eq. (6.7.5).

<<Problem 6-12-a>> Excluded volume effect (I)

Consider the **pearl necklace model** and suppose the particles interact with each other and cannot approach each other within a certain distance (Fig. 6-12.1 and 6-12.2). In other words, the particles have a finite excluded volume. The probability $W(\mathbf{R})d\mathbf{R}$ that the end-to-end distance of the chain be in the range between $\mathbf{R}$ and $\mathbf{R}+d\mathbf{R}$ is proportional to

$$Q(\mathbf{R})d\mathbf{R}=\int\cdots\int \exp\left(-\frac{U}{kT}\right)d\mathbf{r}_1 d\mathbf{r}_2\cdots d\mathbf{r}_n \tag{6.12.1}$$

Here, $\mathbf{r}_i$ denotes the position vector connecting *i* th segment and one end of the chain and $U=U(\mathbf{r}_1,\mathbf{r}_2,\ldots\mathbf{r}_n)$ is the interaction potential for a set of the position vector $\mathbf{r}_1$, $\mathbf{r}_2,\ldots\mathbf{r}_n$. Let's assume the molecule be the Gaussian chain and the potential U be the sum of the potential between *i* th particle and *j* th particle as

$$U=\sum_{i>j} u(\mathbf{r}_{ij})$$

Referring to the virial expansion, $Q(\mathbf{R})d\mathbf{R}$ can be approximated as

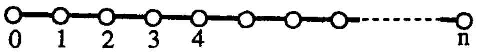

Fig. 6-12.1 Pearl necklace model

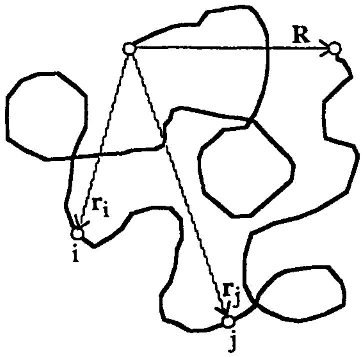

Fig. 6-12.2 Three partial chains in a random coil

$$Q(\mathbf{R})d\mathbf{R}=\left(4\pi l^{2}\right)^{n}\left[\left(\frac{3}{2\pi n l^{2}}\right)^{3/2}\exp\left(-\frac{3\mathbf{R}^{2}}{2nl^{2}}\right)\right.$$

$$+\sum_{i>j}\int\int\left(\frac{3}{2\pi i l^{2}}\right)^{3/2}\exp\left(-\frac{3\mathbf{r}_{i}^{2}}{2il^{2}}\right)\chi\left(\mathbf{r}_{ij}\right)\left(\frac{3}{2\pi(j-i)l^{2}}\right)^{3/2}\exp\left(-\frac{3\left(\mathbf{r}_{j}-\mathbf{r}_{i}\right)^{2}}{2(j-i)l^{2}}\right)$$

$$\left.\times\left(\frac{3}{2\pi(n-j)l^{2}}\right)^{3/2}\exp\left(-\frac{3\left(\mathbf{R}-\mathbf{r}_{j}\right)^{2}}{2(n-j)l^{2}}\right)d\mathbf{r}_{i}d\mathbf{r}_{j}\right]d\mathbf{R} \tag{6.12.2}$$

with

$$\exp\left(-\frac{u\left(\mathbf{r}_{ij}\right)}{kT}\right)=1+\chi\left(\mathbf{r}_{ij}\right) \tag{6.12.3}$$

Derive Eq. (6.12.2).

Answer

The integrant in Eq. (6.12.1) is expressed as

$$\exp\left(-\frac{U}{kT}\right)=\exp\left\{-\frac{\sum_{i>j}u\left(\mathbf{r}_{ij}\right)}{kT}\right\}=\prod\exp\left\{-\frac{u\left(\mathbf{r}_{ij}\right)}{kT}\right\}=\prod\left\{1+\chi\left(\mathbf{r}_{ij}\right)\right\}$$

$$\cong 1+\sum_{i>j}\chi\left(\mathbf{r}_{ij}\right)+\sum_{j>i}\sum_{m>k}\chi\left(\mathbf{r}_{ij}\right)\chi\left(\mathbf{r}_{km}\right)\cong 1+\sum_{i>j}\chi\left(\mathbf{r}_{ij}\right) \tag{6.12.4}$$

and then

$$Q(\mathbf{R})d\mathbf{R}=\int\cdots\int\left\{1+\sum_{i>j}\chi\left(\mathbf{r}_{ij}\right)\right\}d\mathbf{r}_{1}d\mathbf{r}_{2}\cdots d\mathbf{r}_{n}$$

$$=\int\cdots\int d\mathbf{r}_{1}d\mathbf{r}_{2}\cdots d\mathbf{r}_{n}+\int\cdots\int\left\{\sum_{i>j}\chi\left(\mathbf{r}_{ij}\right)\right\}d\mathbf{r}_{1}d\mathbf{r}_{2}\cdots d\mathbf{r}_{n} \tag{6.12.5}$$

The integration over $\mathbf{r}_i$, $\mathbf{r}_j$ and $\mathbf{R}$

$$\underset{d\mathbf{r}_i\, d\mathbf{r}_j\, d\mathbf{R}}{\int \cdots \int} d\mathbf{r}_1 \cdots d\mathbf{r}_n \tag{6.12.6}$$

is given by the product of Gaussian distribution functions for the end-to-end distance of three partial chains 0~*i* th particles, *i*~*j* th particles and *j*~*n* th particles being $\mathbf{r}_i$, $\mathbf{r}_j$-$\mathbf{r}_i$ and $\mathbf{R}$-$\mathbf{r}_j$, respectively. That is,

$$\Bigg[\left(4\pi l^{2}\right)^{n}\left(\frac{3}{2\pi i l^{2}}\right)^{3/2} \exp\left(-\frac{3\mathbf{r}_i^{2}}{2il^{2}}\right) \times \left(\frac{3}{2\pi(j-i)l^{2}}\right)^{3/2} \exp\left(-\frac{3\left(\mathbf{r}_j-\mathbf{r}_i\right)^{2}}{2(j-i)l^{2}}\right)$$

$$\times\left(\frac{3}{2\pi(n-j)l^{2}}\right)^{3/2} \exp\left(-\frac{3\left(\mathbf{R}-\mathbf{r}_j\right)^{2}}{2(n-j)l^{2}}\right) d\mathbf{r}_i d\mathbf{r}_j d\mathbf{R}\Bigg] \tag{6.12.7}$$

Substituting both Eq. (6.12.7) and the equation

$$\underset{\sum \mathbf{r}_i = \mathbf{R}}{\int \cdots \int} d\mathbf{r}_1 d\mathbf{r}_1 \cdots d\mathbf{r}_n = \left(4\pi l^{2}\right)^{n}\left(\frac{3}{2\pi n l^{2}}\right)^{3/2} \exp\left(-\frac{3\mathbf{R}^{2}}{2nl^{2}}\right) \tag{6.12.8}$$

in Eq. (6.12.5), we have Eq. (6.12.2).

<<Problem 6-12-b>> Excluded volume effect (II)

Perform the integration of Eq. (6.12.2) with the aid of Laplace transformation under the assumption that the interaction potential is expressed as

$$u(\mathbf{r}_{ij}) = \infty \qquad |\mathbf{r}_j-\mathbf{r}_i| < a$$

$$\frac{u(\mathbf{r}_{ij})}{kT} << 1 \qquad |\mathbf{r}_j-\mathbf{r}_i| \geq a \tag{6.12.9}$$

Then show that the **effective excluded volume** defined by

$$\beta = -\int_0^{\infty} \chi\left(\mathbf{r}_{ij}\right) d\mathbf{r}_{ij} = -\int_0^{\infty} 4\pi r_{ij}{}^{2} \chi\left(\mathbf{r}_{ij}\right) dr_{ij}{}^{2} \qquad \left(\chi\left(\mathbf{r}_{ij}\right) = e^{u(r_{ij})} - 1\right) \tag{6.12.10}$$

is expressed as

$$\beta = \frac{4\pi a^3}{3}\left[1 - \frac{\theta}{T}\right] \tag{6.12.11}$$

with

$$\theta = \frac{3}{4\pi a^3 k}\int_0^{\infty} u(\mathbf{r}_{ij})4\pi r_{ij}^2 dr_{ij}$$

$$r_{ij} = |\mathbf{r}_j - \mathbf{r}_i| \tag{6.12.12}$$

Answer

The **Laplace transformation** of Q(**R**) is defined by

$$L(s) = \int Q(\mathbf{R})\exp\left(- \mathbf{Rs}\right)d\mathbf{R} \tag{6.12.13}$$

The Laplace transformation of the first term in the right hand side of Eq. (6.12.2) is calculated as

$$\left(4\pi l^{\,2}\right)^n \int \left(\frac{3}{2\pi n l^2}\right)^{3/2} \exp\left(-\frac{3\mathbf{R}^2}{2nl^2}\right)\exp\left(-\mathbf{Rs}\right)d\mathbf{R}$$

$$= \left(4\pi l^{\,2}\right)^n \prod_{i=1}^{3}\left\{\int \left(\frac{1}{2\pi n l^2}\right)^{\frac{1}{2}} \exp\left(-\frac{3R_i^2}{2nl^2} - R_i s_i\right)dR_i\right\} \tag{6.12.14}$$

Here, i=1,2 and 3 denote x, y and z components, respectively, in the rectangular coordinate. The magnitudes of $\mathbf{R}^2$ and s^2 are expressed as

$$\begin{cases} R^2 = R_1^{\,2} + R_2^{\,2} + R_3^{\,2} \\ s^2 = s_1^{\,2} + s_2^{\,2} + s_3^{\,2} \end{cases} \tag{6.12.15}$$

Eq. (6.12.14) is reduced to

$$= \left(4\pi l^2\right)^n \prod_{i=1}^{3} \left[\int_{-\infty}^{\infty} \left(\frac{1}{2\pi n l^2} \right)^{1/2} \exp\left\{ -\frac{3}{2nl^2} \left(R_i - \frac{nl^2}{3} s_i \right)^2 \right\} \exp\left(\frac{nl^2 s_i^2}{6} \right) dR_i \right]$$

$$= \left(4\pi l^2\right)^n \exp\left\{ \frac{nl^2\left(s_1^2 + s_2^2 + s_3^2\right)}{6} \right\}$$

$$\times \prod_{i=1}^{3} \left[\int_{-\infty}^{\infty} \left(\frac{1}{2\pi n l^2} \right)^{1/2} \exp\left\{ -\frac{3}{2nl^2} \left(R_i - \frac{nl^2}{3} s_i \right)^2 \right\} dR_i \right]$$

$$= \left(4\pi l^2\right)^n \exp\left\{ \frac{nl^2 s^2}{6} \right\} \tag{6.12.16}$$

Here we use

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}} \tag{6.12.17}$$

The Laplace transformation of the second term in the right-hand side of Eq. (6.12.2) yields

$$\sum_{i<j} \exp\left(\frac{n - j + i}{6} l^2 s^2 \right) f(s, j - i) + \cdots \tag{6.12.18}$$

where

$$f(s,i) = \int \chi(\mathbf{r}_{ij}) \left(\frac{3}{2\pi i l^2} \right)^{3/2} \exp\left(-\frac{3\mathbf{r}_{ij}^2}{2il^2} \right) \exp(-\mathbf{r}_{ij}\mathbf{s}) d\mathbf{r}_{ij} \tag{6.12.19}$$

For the interaction potential Eq. (6.12.9), $\chi(\mathbf{r})$ has a finite value only in the limited range $\mathbf{r}\cong 0$, and then

$$\left(-\frac{3\mathbf{r}_{ij}^{2}}{2il^{2}}\right)\exp(-\mathbf{r}_{ij}\mathrm{s})\cong 1 \tag{6.12.20}$$

Eq. (6.12.19) is reduced to

$$f(s,i)=\int \chi(\mathbf{r}_{ij})\left(\frac{3}{2\pi il^{2}}\right)^{3/2}d\mathbf{r}_{ij}\cong\left(\frac{3}{2\pi il^{2}}\right)^{3/2}\int \chi(\mathbf{r}_{ij})\,d\mathbf{r}_{ij} \tag{6.12.21}$$

or

$$f(s,i)\simeq-\left(\frac{3}{2\pi il^{2}}\right)^{3/2}\beta \tag{6.12.22}$$

with

$$\beta=-\int_{0}^{\infty}\chi\left(\mathbf{r}_{ij}\right)\;d\mathbf{r}_{ij}=-\int_{0}^{\infty}4\pi r^{2}\chi\left(\mathbf{r}_{ij}\right)dr \tag{6.12.23}$$

For the interaction potential, Eq. (6.12.9),

$$\chi\left(\mathbf{r}_{ij}\right)=\exp\left\{-\frac{u\left(\mathbf{r}_{ij}\right)}{kT}\right\}-1\cong-\frac{u\left(\mathbf{r}_{ij}\right)}{kT}\qquad (r_{ij}\geq a) \tag{6.12.24}$$

and

$$\chi\left(\mathbf{r}_{ij}\right)=-1\qquad (r_{ij}<a) \tag{6.12.25}$$

Then Eq. (6.12.23) is reduced to

$$\beta=-\int_{0}^{a}4\pi r_{ij}^{2}\chi\left(\mathbf{r}_{ij}\right)dr_{ij}-\int_{a}^{\infty}4\pi r_{ij}^{2}\chi\left(\mathbf{r}_{ij}\right)dr_{ij}$$

$$=\frac{4\pi a^{3}}{3}+\frac{1}{kT}\int_{a}^{\infty}u\left(\mathbf{r}_{ij}\right)4\pi r_{ij}^{2}\,dr_{ij}$$

$$= \frac{4\pi a^3}{3}\left(1 + \frac{3}{4\pi a^3 kT}\right)\int_a^\infty u\left(\mathbf{r}_{ij}\right)4\pi r_{ij}^{\ 2}\,dr_{ij} \tag{6.12.26}$$

Substituting θ defined by Eq. (6.12.12) in Eq. (6.12.26), we have Eq. (6.12.11) for β.

<<Problem 6-12-c>> Excluded volume effect (III)

In <<Problem 6-12-b>>, the **Laplace transformation** of Q(R) was obtained as

$$L(s) = \int Q(\mathbf{R})\exp\left(-\mathbf{Rs}\right)d\mathbf{R}$$

$$= \left(4\pi l^{\,2}\right)^n\left\{\exp\left(\frac{n}{6}\,l^{\,2}s^2\right) + \sum_{i<j}\exp\left(\frac{n-j+i}{6}\,l^{\,2}s^2\right)f(s,j-i) + \cdots\right\} \tag{6.12.27}$$

Expanding the exponential terms in braces as a Taylor series, derive the equation

$$L(s) = L(0)\left\{1 + \frac{1}{3!}\left\langle \mathbf{R}^2\right\rangle\, s^2 + \frac{1}{5!}\left\langle \mathbf{R}^4\right\rangle\, s^4 + \cdots + \frac{1}{(2p+1)\,!}\left\langle R^{2p}\right\rangle s^{2p} + \cdots\right\} \tag{6.12.28}$$

with

$$\left\langle \mathbf{R}^2\right\rangle = n\,l^{\,2}\left(1 + \frac{4}{3}Z\right) \tag{6.12.29}$$

and

$$Z = \beta n^{1/2}\left(\frac{3}{2\pi l^{\,2}}\right)^{3/2} \tag{5.20.3}$$

Answer

Using the polar coordinate system, L(s) is written as

$$L(s) = \int_0^{\infty} \int_0^{\pi} Q(R)\exp\left(- Rs\cos\theta\right) 2\pi R \sin\theta \, R d\theta dR \tag{6.12.30}$$

On putting X=-cosθ (dX=sinθdθ), the integration over X is performed as

$$L(s) = \int_0^{\infty} Q(\mathbf{R})2\pi R^2 \int_{-1}^{1} \exp\left(Rs\, X\right) \, dXdR$$

$$= \int_0^{\infty} Q(\mathbf{R})2\pi R^2 \left| \frac{e^{Rs}}{Rs} \right|_{-1}^{1} dR = \int_0^{\infty} Q(\mathbf{R})4\pi R^2 \frac{\sinh Rs}{Rs} dR \tag{6.12.31}$$

sinh(Rs) is expanded as a Taylor series:

$$\frac{\sinh Rs}{Rs} = 1 + \frac{1}{3!}R^2s^2 + \frac{1}{5!}R^4s^4 + \cdots \tag{6.12.32}$$

Then we have

$$L(s) = \int_0^{\infty} Q(\mathbf{R}) \left(1 + \frac{1}{3!}R^2s^2 + \frac{1}{5!}R^4s^4 + \cdots \right) 4\pi R^2 d\,R$$

$$= \int_0^{\infty} Q(\mathbf{R})4\pi R^2 d\,R + \frac{s^2}{3!}\int_0^{\infty} R^2 Q(\mathbf{R})4\pi R^2 d\,R + \frac{s^4}{5!}\int_0^{\infty} R^4 Q(\mathbf{R})4\pi R^2 d\,R + \cdots \tag{6.12.33}$$

L(0) is obtained by putting s=0 in Eq. (6.12.27) as

$$L(0) = \int_0^{\infty} Q(\mathbf{R}) \, d\,\mathbf{R} = \int_0^{\infty} Q(R) \; 4\pi R^2 d\,R \tag{6.12.34}$$

From the definition,

$$\frac{\int_0^{\infty} R^2 Q(R) \; 4\pi R^2 d\,R}{\int_0^{\infty} Q(R) \; 4\pi R^2 d\,R} = \left\langle R^2 \right\rangle \tag{6.12.35}$$

and

$$\frac{\int_0^\infty R^4 Q(R)\ 4\pi R^2 dR}{L(0)} = \left\langle R^4 \right\rangle \tag{6.12.36}$$

Then, Eq. (6.12.33) reduces to

$$L(s) = L(0)\left(1 + \frac{1}{3!}\left\langle R^2 \right\rangle s^2 + \frac{1}{5!}\left\langle R^4 \right\rangle s^4 + \cdots \right) \tag{6.12.37}$$

Substitution of the equation

$$f(s,i) = -\left(\frac{3}{2\pi i l^2}\right)^{3/2} \beta \tag{6.12.22}$$

for f in Eq. (6.12.27) and series expansion of the right-hand side of the equation yields

$$\left(4\pi l^2\right)^n \left[1 + \frac{n}{6} l^2 s^2 + \frac{n^2}{2!\cdot 6^2} l^4 s^4 + \cdots + \sum_{i<j} \exp\left(\frac{n-j+i}{6} l^2 s^2\right) \left\{ -\left(\frac{3}{2\pi(j-i) l^2}\right)^{3/2} \beta \right\} \right]$$

$$= \left(4\pi l^2\right)^n \left[1 + \frac{n}{6} l^2 s^2 + \frac{n^2}{2!\cdot 6^2} l^4 s^4 + \cdots \right.$$

$$\left. - \sum_{i<j} \left(\frac{3}{2\pi(j-i) l^2}\right)^{3/2} \beta \left\{ 1 + \frac{n-j+i}{6} l^2 s^2 + \frac{(n-j+i)^2}{2!\cdot 6^2} l^4 s^4 + \cdots \right\} \right]$$

$$= \left(4\pi l^2\right)^n \left[1 + \frac{n}{6} + l^2 s^2 + \frac{n^2}{2!\cdot 6^2} l^4 s^4 + \cdots - \left(\frac{3}{2\pi l^2}\right)^{3/2} \right.$$

$$\left\{ \beta \sum_{j>i} \frac{1}{(j-i)^{3/2}} + \sum_{j>i} \frac{n-j+i}{6\cdot(j-i)^{3/2}} l^2 s^2 + \dots \right\}\Bigg| \tag{6.12.38}$$

The coefficient of s^2 in the right-hand side of Eq. (6.12.38) is

$$\left(4\pi l^2\right)^n \left\{ \frac{n}{6} l^2 - \left(\frac{3}{2\pi l^2}\right)^{3/2} \beta \sum_{j>i} \frac{n-j+i}{6\cdot(j-i)^{3/2}} l^2 \right\} \tag{6.12.39}$$

The summation in the brace is calculated as

$$\begin{aligned} \sum_{j>i} \frac{n-(j-i)}{(j-i)^{3/2}} &= \sum_{k=1}^{n} \frac{k(n-k)}{k^{3/2}} = n\sum_{k=1}^{n} k^{-1/2} - \sum_{k=1}^{n} k^{1/2} \\ &= n\cdot n^{1/2}\left(2 + \frac{1}{2n}\right) - n\cdot n^{1/2}\left(\frac{1}{\frac{1}{2}+1} + \frac{1}{2n}\right) = n\cdot n^{1/2}\frac{4}{3} \end{aligned} \tag{6.12.40}$$

Then Eq. (6.12.39) is further reduced to

$$\left(4\pi l^2\right)^n \frac{n}{6} l^2 \left\{ 1 + \left(\frac{3}{2\pi l^2}\right)^{3/2} \beta \frac{4}{3} n^{1/2} \right\} \tag{6.12.41}$$

This coefficient has to be identical to the coefficient of s^2 in Eq. (6.12.29):

$$L(0)\frac{1}{3!}\left\langle R^2 \right\rangle \tag{6.12.42}$$

Substitution of the definition of Z (Eq. (5.20.3)) in Eq. (6.12.41) yields

$$L(0)\frac{1}{3!}\left\langle R^2 \right\rangle = \frac{nl^2}{6}\left\{1 + \frac{4}{3} Z\right\}\left(4\pi l^2\right)^n \tag{6.12.43}$$

Using the relationship

$$L(0) = \left(4\pi l^{2}\right)^{n}\left\{1+\left(\frac{3}{2\pi l^{2}}\right)^{3/2}\beta\sum_{j>i}\frac{1}{(j-i)^{3/2}}\right\} \tag{6.12.44}$$

we finally obtain

$$\left\langle R^{2}\right\rangle = n\,l^{2}\left(1+\frac{4}{3}Z\right) \tag{6.12.29}$$

Thus, when the excluded volume effect is not negligible, Gaussian approximation cannot be applicable.

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* For Z =0, we have

$$\left\langle R^{2}\right\rangle_{0} = nl^{2} \tag{6.12.45}$$

The **swelling coefficient** (or **expansion factor**) **based on the end-to-end distance** α_R is defined by

$$\alpha_R^2 = \frac{\left\langle R^{2}\right\rangle}{\left\langle R^{2}\right\rangle_{0}} \tag{6.12.46}$$

Using Eq. (6.12.29),

$$\alpha_R^2 = 1+\frac{4}{3}Z \tag{6.12.47}$$

Similarly to Eq. (6.12.29), we have

$$\left\langle r_{ij}\right\rangle = (j-i)\,l^{2}\left(1+\frac{4}{3}Z\right) \tag{6.12.48}$$

for the partial chain consisting of *i* to *j* th particles. In this context, the interactions only between l and m segments in the range i<l<m<j are taken into account and the interactions between k, l and k' segments with 0≤k<l<j<k'≤n are not included. Taking the latter interactions into account, Yamakawa and Kurata derived the equation

$$\left\langle r_{ij}^{2}\right\rangle = (j-i)\,l^{2}\left\{1+\frac{4}{3}\beta\left(\frac{3}{2\pi l^{2}}\right)^{3/2}D+\cdots\right\}$$

$$D = \frac{8}{3}(j-i)^{1/2} - 4(n-i)^{1/2} - 4j^{1/2} + \frac{(j-i)}{\sqrt{n}} - \frac{8}{3(j-i)} \times \left\{ (n-j)^{3/2} - (n-i)^{3/2} - j^{3/2} + i^{3/2} \right\} \qquad (6.12.49)$$

Substitution of Eq. (6.12.49) for $<r_{ij}^2>$ in the equation

$$\left\langle S^2 \right\rangle = \frac{1}{n^2} \sum_{i>j} \left\langle r_{ij}^2 \right\rangle \qquad (6.12.50)$$

yields

$$\left\langle S^2 \right\rangle = \frac{nl^2}{6}\left(1 + \frac{134}{105} Z + \cdots \right) \qquad (6.12.51)$$

(See H. Yamakawa and M. Kurata, *J. Phys. Soc. Japan* **13**, 78 (1958)).
The swelling coefficient based on the radius of gyration is defined by

$$\alpha_s^2 = \frac{\left\langle S^2 \right\rangle}{\left\langle S_0^2 \right\rangle} \qquad (6.12.52)$$

If we take higher order terms into account,

$$\alpha_R^2 \neq \alpha_s^2 \qquad (6.12.53)$$

***Excluded volume parameter** Z is defined by

$$Z = \left(\frac{3}{2\pi l^2} \right)^{3/2} \beta n^{1/2} \qquad (5.20.3)$$

where l is the length of a segment, β the excluded volume of an arbitrary chosen segment pair. The number of different segment pairs in a polymer chain with n segments is

$${}_nC_2 = \frac{n!}{2!(n-2)!} = \frac{n(n-1)}{2} \cong \frac{n^2}{2}$$

The excluded volume of a polymer chain is calculated as the sum of the excluded volume of segment pairs and is proportional to

$b_nC_2 \cong bn^2/2$.

For Gaussian chain, the root of the mean square end-to-end distance is

$$\left\langle R^2\right\rangle^{1/2}=\left(nl^2\right)^{1/2} \tag{6.12.54}$$

The volume of a molecular chain is proportional to the third power of $<R^2>^{1/2}$ (or $(nl^2)^{3/2}$). Hence, the ratio of the excluded volume to the volume of a molecular chain is

$$\frac{\beta n^2}{2}\cdot\frac{1}{\left(nl^2\right)^{3/2}}=\frac{\beta n^{1/2}}{2\left(l^2\right)^{3/2}}\propto Z \tag{6.12.55}$$

Thus, Z is proportional to the volume fraction of the excluded volume in the molecular volume (See Reference below Eq. (5.20.3)). The parameter Z was first introduced by Zimm-Stockwayer-Fixman (See B. H. Zimm, W. H. Stockmayer and M. Fixman, *J. Chem. Phys.* **21**, 1716 (1953)).

<<Problem 6-13-a>> Increase in free energy by swelling

Derive the expression for the **increase in free energy by swelling** ΔF_{el} with expansion factor α for Gaussian polymer chains:

$$N_j=N\left(\frac{\beta}{\sqrt{\pi}}\right)^3\exp\left(-\beta^2R_j^{\,2}\right)\cdot 4\pi R_j^{\,2}dR_j \tag{6.13.1}$$

where N is the number of total polymer chains, N_j the number of polymer chains with the end-to-end distance being R_j, $\beta^2=3/(2<S^2>)=9/<R^2>$, $<S^2>$ the mean square radius of gyration and $<R^2>$ the mean square end-to-end distance. Assume the entropy change associated with the conformational change of the polymer chains is negligible.

Answer

Consider polymer chains at swollen state. The probability for finding polymer chains with the end-to-end distance in the range between R_j and R_j+dR_j is

$$W_j=\frac{N_j}{N}=\left(\frac{\beta}{\sqrt{\pi}}\right)^3\exp\left(-\beta^2R_j^{\,2}\right)\cdot 4\pi R_j^{\,2}dR_j \tag{6.13.2}$$

The end-to-end distance of the polymer chains before swelling is R_j/α. If we assume the number of polymer chains does not change by swelling, the corresponding probability x_j and the number of polymer chains N_j before swelling are expressed as

$$\begin{cases} x_j = \left(\dfrac{\beta}{\sqrt{\pi}}\right)^3 \exp\left\{-\beta^2\left(\dfrac{R_j}{\alpha}\right)^2\right\} \cdot 4\pi\left(\dfrac{R_j}{\alpha}\right)^2 d\left(\dfrac{R_j}{\alpha}\right) \\ N_j = N x_j \end{cases} \tag{6.13.3}$$

respectively. The number of ways for dividing N polymer chains into N_1, $N_2, \ldots N_j \ldots$ polymers is

$$\frac{N!}{N_1! N_2! N_3! \cdots N_j! \cdots} = \frac{N!}{\prod_j N_j!} \tag{6.13.4}$$

Hence, the number of states is obtained as

$$\Omega = N! \prod_j \left(\frac{W_j^{N_j}}{N_j!}\right) \tag{6.13.5}$$

Using **Stirling's law**, the logarithm of W is calculated as

$$\begin{aligned} \ln \Omega &= N \ln N - N + \sum_j \left(\ln W_j^{N_j} - N_j \ln N_j + N_j\right) \\ &= \sum_j \left(N_j \ln N - N_j + \ln W_j^{N_j} - N_j \ln N_j + N_j\right) \\ &= \sum_j \ln \left\{\frac{N W_j}{N_j}\right\}^{N_j} = N \sum_j \ln \left\{\frac{W_j}{x_j}\right\}^{x_j} \end{aligned} \tag{6.13.6}$$

From Eqs. (6.13.2) and (6.13.3),

$$\frac{W_j}{x_j} = \alpha^3 \exp\left\{\left(-\beta^2 R_j^2\right)\left(1 - \frac{1}{\alpha^2}\right)\right\} \tag{6.13.7}$$

Then, we have

$$\ln\left(\frac{W_j}{x_j}\right) = \beta^2 R_j^2 \left(\frac{1}{\alpha^2} - 1\right) + 3 \ln \alpha$$

$$\ln\Omega = N\sum_j x_j\left\{\beta^2 R_j^2\left(\frac{1}{\alpha^2}-1\right)+3\ln\alpha\right\}$$

$$= N\beta^2\left(\frac{1}{\alpha^2}-1\right)\sum_j\left\{x_jR_j^2\right\}+3N\ln\alpha \qquad (6.13.8)$$

Approximation of sum by integral yields

$$\sum_j x_jR_j^2 \rightarrow \int_0^\infty r^2x(r)dr$$

$$= \int_0^\infty \left(\frac{\beta}{\sqrt{\pi}}\right)^3\left(\frac{4\pi}{\alpha^3}\right)r^4\exp\left(-\frac{\beta^2r^2}{\alpha^2}\right)dr = \frac{3}{2}\left(\frac{\alpha}{\beta}\right)^2 \qquad (6.13.9)$$

We finally obtain

$$\ln\Omega = \frac{3}{2}N\left(1-\alpha^2\right)+3N\ln\alpha \qquad (6.13.10)$$

Since we can assume that the swelling process occurs without significant change in internal energy, we have $\Delta F_{el} = -T\Delta S_{el}$ and

$$\Delta F_{el}(\alpha) = F_{el}(\alpha) - F_{el}(1) = F_{el}(\alpha)$$

$$= -kT\ln\Omega = -\frac{3}{2}NkT\left\{\left(1-\alpha^2\right)+\frac{\ln\alpha}{2}\right\} \qquad (6.13.11)$$

(See P. J. Flory, *J. Chem. Phys.* **17**, 303 (1949))

<<Problem 6-13-b>> α^5-law

Suppose the center of gravity of a Gaussian polymer chain be at the origin. The volume of the shell with the center at the origin and with inner radius s_j and thickness ds_j is $4\pi s_j^2 ds_j$. The number of segments at a distance from the center of gravity in the range between s_j and s_j+ds_j is

$$n_j = n\left(\frac{\beta}{\sqrt{\pi}}\right)^3 \exp\left(-\beta^2 s_j^2\right)\cdot 4\pi s_j^2 ds_j \qquad (6.13.12)$$

Here, n is the total number of segments. If the polymer chain expands isotropically with an expansion factor α, the resultant volume of the shell is $4\pi\alpha^3 s_j^2 ds_j$. The number of solvent molecules in the shell is

$$N_j = \frac{4\pi\alpha^3 s_j^2 ds_j\left(1 - \phi_{1j}\right)}{V_0} \qquad (6.13.13)$$

where ϕ_{1j} is the volume fraction of the polymer in the shell $(=n_j/(n_j+N_j))$, V_0 the molecular volume of the solvent. Referring to the expression for the chemical potential of solvent in **Flory-Huggins theory**

$$\Delta\mu_0 = RT\left\{\ln\left(1 - \phi_1\right) + \left(1 - \frac{1}{n}\right)\phi_1 + \chi\phi_1^2 + \cdots\right\} \qquad (3.11.3)$$

the chemical potential of solvent in the shell is

$$\Delta\mu_{0j} = RT\left\{\ln\left(1 - \phi_{1j}\right) + \left(1 - \frac{1}{n}\right)\phi_{1j} + \chi\phi_{1j}^2 + \cdots\right\} \qquad (6.13.14)$$

If n_j is much smaller than N_j, we can expand the logarithmic term in Eq. (6.13.14) as a series of ϕ_{1j}. Neglecting the higher order terms, we have

$$\Delta\mu_{0j} \cong -RT\left\{\frac{1}{2} - \chi\right\}\phi_{1j}^2 = -RT\psi_1\left(1 - \frac{\theta}{T}\right)\phi_{1j}^2 \qquad (6.13.15)$$

The change in free energy by swelling is the sum of the change in free energy of mixing ΔF_M and the change in elastic free energy as

$$\Delta F = \Delta F_M + \Delta F_{el} = \sum_j \Delta F_{Mj} + \Delta F_{el} \qquad (6.13.16)$$

Fig. 6-13-b shows an illustration of ΔF_M and ΔF_{el} against α. The value of α at the equilibrium state is determined as α at the minimum of the free energy. Derive the **relationship between α and Z.**

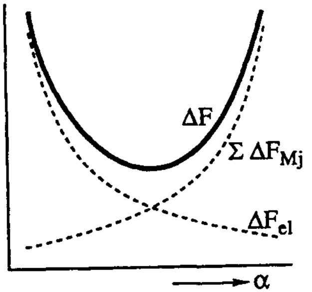

Fig. 6-13-b Illustration of change in free energy of mixing $\Sigma\Delta F_{Mj}$, elastic free energy ΔF_{el} and total free energy ΔF as a function of swelling coefficient

Answer

From Eq. (6.13.16), we have

$$\frac{\partial \Delta F}{\partial \alpha} = \sum_j \frac{\partial \Delta F_{Mj}}{\partial \alpha} + \frac{\partial \Delta F_{el}}{\partial \alpha} \tag{6.13.17}$$

The first term in the right-hand side is rewritten as

$$\sum_j \frac{\partial \Delta F_{Mj}}{\partial \alpha} = \sum_j \frac{\partial \Delta F_{Mj}}{\partial N_j} \cdot \frac{\partial N_j}{\partial \alpha} = \sum_j \Delta\mu_{0j} \cdot \frac{\partial N_j}{\partial \alpha}$$

$$= - kT\Psi_1\left(1 - \frac{\theta}{T}\right)\sum_j \phi_{1j}{}^2 \cdot \frac{\partial N_j}{\partial \alpha} \tag{6.13.18}$$

In case $N_j >> n_j$,

$$\begin{cases} \phi_{1j} = \dfrac{n_j}{n_j + N_j} \cong \dfrac{n_j}{N_j} \\ 1-\phi_{1j} \cong 1 \end{cases} \tag{6.13.19}$$

From Eqs. (6.13.12) and (6.13.13), we have

$$\frac{\partial N_j}{\partial \alpha} = \frac{12\,\pi\alpha^2 s_j{}^2}{V_0}\, ds_j \tag{6.13.20}$$

$$\phi_{1j} = \frac{n_j}{N_j} = \frac{V_0}{4\,\pi\alpha^3 s_j{}^2\, ds_j} \cdot n\left(\frac{\beta}{\sqrt{\pi}}\right)^3 \exp\left(- \beta^2 s_j{}^2\right) 4\,\pi s_j{}^2\, ds_j$$

$$= \frac{n\,V_0}{\alpha^3}\left(\frac{\beta}{\sqrt{\pi}}\right)^3 \exp\left(-\beta^2 s_j{}^2\right) \tag{6.13.21}$$

and then

$$\sum_j \phi_{1j}{}^2 \cdot \frac{\partial N_j}{\partial \alpha} = \frac{12n^2V_0\beta^6}{\pi^2\alpha^4} \cdot \sum_j s_j{}^2 \exp\left(-2\beta^2 s_j{}^2\right) ds_j \tag{6.13.22}$$

$$\cong \frac{12n^2V_0\beta^6}{\pi^2\alpha^4} \cdot \int_0^\infty s^2 \exp\left(-2\beta^2 s^2\right)\, ds = \frac{3n^2V_0\beta^3}{\left(2\pi\right)^{3/2}\alpha^4} \tag{6.13.23}$$

Here we approximate sum by integral. Using the relationship

$$\beta^2 = \frac{3}{\langle R^2\rangle},\ \beta^3 = \left\{\frac{3}{\langle R^2\rangle}\right\}^{3/2} \tag{6.13.24}$$

and

$$nv_0 = \frac{M\bar{v}}{N_A} \cong nV_0\ , v_0\ \cong V_0 \tag{6.13.25}$$

we have

$$\left\{\begin{aligned} &\sum_j \phi_{1j}{}^2 \cdot \frac{\partial N_j}{\partial \alpha} = \frac{6\,C_M M^{1/2}}{\alpha^4} \\ &C_M = \frac{27}{2^{5/2}\pi^{3/2}}\left(\frac{\bar{v}^2}{N_A{}^2 v_0^2}\right)\left(\frac{\langle R^2\rangle}{M}\right)^{-3/2} \end{aligned}\right. \tag{6.13.26}$$

Here, $\bar{v}$ is the partial specific volume of polymer and v_0 the segment volume. The coefficient C_M does not depend on the kind of solvent and molecular weight of polymer but only depends on the kind of polymer. Substitution of Eq. (6.13.26) for the summation in the right-hand side of Eq. (6.13.18) yields

$$\frac{\partial \Delta F_M}{\partial \alpha} = -kT\psi_1\left(1 - \frac{\theta}{T}\right)\frac{6\,C_M M^{1/2}}{\alpha^4} \tag{6.13.27}$$

From Eq. (6.13.11), we have

$$\frac{\partial \Delta F_{el}}{\partial \alpha} = -3kT\left(\frac{1}{\alpha} - \alpha\right) \tag{6.13.28}$$

for N=1. We finally obtain

$$\frac{\partial \Delta F}{\partial \alpha} = \sum_j \frac{\partial \Delta F_{Mj}}{\partial \alpha} + \frac{\partial \Delta F_{el}}{\partial \alpha}$$

$$= -kT\psi_1\left(1 - \frac{\theta}{T}\right)\frac{6\,C_M M^{1/2}}{\alpha^4} - 3kT\left(\frac{1}{\alpha} - \alpha\right) \tag{6.13.29}$$

At the equilibrium state, $\partial\Delta F/\partial\alpha=0$. Thus, we derive the **Flory-Fox equation**

$$\alpha^5 - \alpha^3 = 2\,C_M\psi_1\left(1 - \frac{\theta}{T}\right) M^{1/2} \tag{6.13.30}$$

(See P. J. Flory and T. G Fox, Jr., *J. Polym. Sci.* **5**, 745 (1950))
Using the relationships

$$l^2 = \frac{\langle R_0^2\rangle}{n}, \quad n = \frac{M\bar{v}}{N_A V_0} \tag{6.13.31}$$

the excluded volume parameter Z can be expressed from Eqs. (5.20.3) and (5.21.1) as

$$Z = 2\,\psi_1\left(1 - \frac{\theta}{T}\right)\frac{n^{1/2}}{\left(\frac{2\pi l^2}{3}\right)^{3/2}} \tag{6.13.32}$$

Z is further rewritten as

$$Z = \frac{3^{3/2}}{2^{1/2}\pi^{3/2}}\psi_1\left(1 - \frac{\theta}{T}\right)\left(\frac{M}{\langle R_0^2\rangle}\right)^{3/2}\left(\frac{\bar{v}}{N_A V_0}\right)^2 M^{1/2} \tag{6.13.33}$$

Then, Eq. (6.13.30) can be rewritten as

$$\alpha^5 - \alpha^3 = \frac{3^{3/2}}{2} Z$$

or

$$\alpha^5 - \alpha^3 = 2.60\,Z \tag{6.13.34}$$

Eq. (6.13.34) is called α^5**-law** (See P. J. Flory and T. G Fox, Jr., *J. Polym. Sci.* **5**, 745 (1950)).

<<Problem 6-13-c>> Segment density at the origin

Show that the **segment density at the origin** $\rho(0)$ is proportional to $M^{-0.5}$~ $M^{-0.8}$ by using the Flory-Fox equation:

$$\alpha^5 - \alpha^3 = 2\,C_M \psi_1 \left(1 - \frac{\theta}{T}\right) M^{1/2}$$

$$\propto M^{1/2} \tag{6.13.30}$$

Answer

For a Gaussian chain, we have

$$\rho(\mathbf{r})dr = n\left(\frac{3}{2\pi\langle S^2\rangle}\right)^{3/2} \exp\left(\frac{-3\mathbf{r}^2}{2\langle S^2\rangle}\right) 4\pi r^2 dr \tag{6.11.1}$$

At the origin (**r**=0),

$$\rho(0) = n\left(\frac{3}{2\pi\langle S^2\rangle}\right)^{3/2} \tag{6.13.35}$$

From <<Problem 6-9>>, we have

$$\langle S^2\rangle = \frac{1}{6} n l''^2 \tag{6.13.36}$$

Here l'' is related to the parameter α as

$$l''^2 = \alpha^2 l'^2 \tag{6.13.37}$$

According to the Flory-Fox theory (See Eq. (6.13.34)),

$$\alpha^5 - \alpha^3 \propto M^{0.5} \tag{6.13.38}$$

If $\alpha >> 1$, we have

$$\alpha^3 \propto M^{0.3} \propto n^{0.3} \tag{6.13.39}$$

Substitution of Eqs. (6.13.36) and (6.13.37) for $<S^2>$ in Eq. (6.13.35), we have

$$\rho(0) \propto \frac{1}{\alpha^3 n^{1/2}} \tag{6.13.40}$$

In case $\alpha \cong 1$, we have

$$\rho(0) \propto M^{-0.5} \tag{6.13.41}$$

In case $\alpha >> 1$, we have

$$\rho(0) \propto M^{-0.8} \tag{6.13.42}$$

Thus,

$$\rho(0) \propto M^{-0.8} \sim M^{-0.5} \tag{6.13.43}$$

This result indicates that the segment density near the center of gravity is small when the solvent is good.

<<Problem 6-14-a>> Mean internal energy

Consider a Gaussian polymer chain having n segments with the radius of gyration being S^2. The probability density for finding segments at the distance from the center of gravity in the range between r and r+dr is

$$\rho(r) = \left(\frac{3}{2\pi\langle S\rangle^2}\right)^{3/2} \exp\left(-\frac{3}{2}\frac{r^2}{\langle S\rangle^2}\right) \tag{6.11.1}$$

Assume the potential energy of the polymer is approximated by the sum of the potential energy for arbitrarily chosen segment pairs i and j as

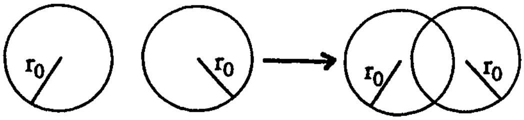

Fig. 6-14 Interaction of two spheres

$$U\left(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_i,\cdots,\mathbf{r}_j,\cdots,\mathbf{r}_n\right)=\sum_{i,j}u\left(\mathbf{r}_{ij}\right) \tag{6.14.1}$$

and the force between segment pairs is a short range interaction as

$$\begin{cases} u\left(\mathbf{r}_{ij}\right)=\infty\ ,\ \mathbf{r}<a & (6.14.2)\\ \dfrac{u\left(\mathbf{r}_{ij}\right)}{kT}<<1\ ,\mathbf{r}\geq a & (6.14.3)\end{cases}$$

β is defined by

$$\beta=\frac{1}{kT}\int_0^\infty u(r)4\pi r^2 dr \tag{6.14.4}$$

(See Eq.(5.13.5)). The total number of segment pairs in a molecule is $n^2/2$. Calculate the **mean internal energy for a fixed value of S**:

$$\langle U(S)\rangle=\frac{n^2}{2}\int\int u\left(\mathbf{r}_{ij}\right)\rho\left(\mathbf{r}_i\right)\rho\left(\mathbf{r}_j\right)d\mathbf{r}_i d\mathbf{r}_j \tag{6.14.5}$$

Answer

Let's change the integration variables from the set $\mathbf{r}_i$ and $\mathbf{r}_j$ to the set $\mathbf{r}_i$ and $\mathbf{r}_{ij}$.

$$\mathbf{r}_j=\mathbf{r}_i+\mathbf{r}_{ij} \tag{6.14.6}$$

Since **Jacobian**

$$d\mathbf{r}_j\cdot d\mathbf{r}_i=J\left(\frac{x_i,y_i,z_i,\ x_{ij},y_{ij},z_{ij}}{x_i,y_i,z_i,\ x_j,y_j,z_j}\right)d\mathbf{r}_j\cdot d\mathbf{r}_{ij} \tag{6.14.7}$$

is 1, then

$$d\mathbf{r}_j\cdot d\mathbf{r}_i=d\mathbf{r}_j\cdot d\mathbf{r}_{ij} \tag{6.14.8}$$

Using the relationship

$$\mathbf{r}_i^2+\mathbf{r}_j^2=\mathbf{r}_i^2+\left(\mathbf{r}_i+\mathbf{r}_{ij}\right)^2=2\left(\mathbf{r}_i+\frac{\mathbf{r}_{ij}}{2}\right)^2+\frac{\mathbf{r}_{ij}^2}{2} \tag{6.14.9}$$

and Eq. (6.14.1), we have

$$u(\mathbf{r}_{ij})\,\rho(\mathbf{r}_i)\,\rho(\mathbf{r}_j) = u(\mathbf{r}_{ij})\,\rho(\mathbf{r}_i)\,\rho(\mathbf{r}_i + \mathbf{r}_{ij})$$

$$= \left(\frac{3}{2\pi S^2}\right)^3 u(\mathbf{r}_{ij})\,\exp\left[-\frac{3}{2S^2}\left\{2\left(\mathbf{r}_i + \frac{\mathbf{r}_{ij}}{2}\right)^2 + \frac{\mathbf{r}_{ij}{}^2}{2}\right\}\right] \qquad (6.14.10)$$

The integration of U(S) over $\mathbf{r}_i$ in Eq. (6.14.5) yields

$$\langle U(S)\rangle = \frac{n^2}{2}\left(\frac{3}{2\pi S^2}\right)^3 \int u(\mathbf{r}_{ij})\exp\left(-\frac{3}{4S^2}\mathbf{r}_{ij}{}^2\right)d\mathbf{r}_{ij} \int \exp\left(-\frac{3}{S^2}\left(\mathbf{r}_i + \frac{\mathbf{r}_{ij}}{2}\right)^2\right)d\mathbf{r}_i$$

$$= \frac{n^2}{2}\left(\frac{3}{2\pi S^2}\right)^3 \int u(\mathbf{r}_{ij})\exp\left(-\frac{3}{4S^2}\mathbf{r}_{ij}{}^2\right)d\mathbf{r}_{ij}\left(\sqrt{\frac{\pi}{\left(\frac{3}{S^2}\right)}}\right)^3$$

$$= \frac{n^2}{16}\left(\frac{3}{\pi S^2}\right)^{\frac{3}{2}} \int u(\mathbf{r}_{ij})\exp\left(-\frac{3}{4S^2}\mathbf{r}_{ij}{}^2\right)d\mathbf{r}_{ij} \qquad (6.14.11)$$

Since the interaction potential is finite only in the range $\mathbf{r}\cong 0$, $\exp\{-3\mathbf{r}_{ij}{}^2/(4S^2)\}$ in the integrant can be approximated by 1. Then, using Eq. (6.14.4), we have

$$\langle U(S)\rangle = \frac{n^2}{16}\left(\frac{3}{\pi S^2}\right)^{3/2} \int u(\mathbf{r}_{ij})\,d\mathbf{r}_{ij} = \frac{\beta kT}{16}\left(\frac{3}{\pi}\right)^{3/2}\frac{n^2}{S^3} \qquad (6.14.12)$$

<<Problem 6-14-b>> Relationship between α and Z (I)

Eq. (6.14.12) can be rewritten as

$$\langle U(S)\rangle = \frac{\beta kT}{16}\left(\frac{3}{\pi}\right)^{3/2}\frac{n^2}{S^3} = \frac{n^2\beta ckT}{2S^3}$$

$$c = \frac{1}{16}\left(\frac{3}{\pi}\right)^{3/2} \tag{6.14.13}$$

The radius of gyration of **ideal chain** obeys Gaussian distribution, i.e., $<S^2>_0$. The radius of gyration of the excluded volume chain is calculated as the statistical mean:

$$\langle S^2 \rangle = \frac{\displaystyle\int_0^{\infty} S^2 \rho_1(s)\exp\left(-\frac{\langle U(S)\rangle}{kT}\right) dS}{\displaystyle\int_0^{\infty} \rho_1(S)\exp\left(-\frac{\langle U(S)\rangle}{kT}\right) dS} \tag{6.14.14}$$

with

$$\rho(S) = \left(\frac{3}{2\pi\langle S^2\rangle_0}\right)^{3/2} \exp\left(\frac{-3S^2}{2\langle S^2\rangle_0}\right) \tag{6.14.15}$$

and

$$\langle S^2\rangle_0 = \frac{nl^2}{6} \tag{6.14.16}$$

Derive the **relationship between α_s and Z** by substituting Eqs. (6.14.13) and (6.14.15) in Eq. (6.14.14). Here, Z is defined by

$$Z = \beta n^{1/2}\left(\frac{3}{2\pi l^2}\right)^{3/2} \tag{5.20.3}$$

If we define S* as the value of S when the function

$$S^3 \exp\left(-\frac{3}{2}\frac{S^2}{\langle S^2\rangle_0} - \frac{n^2}{2}\frac{\beta c}{S^3}\right) \tag{6.14.17}$$

has a maximum, the integral of this function is calculated as

$$\int_0^{\infty} S^3 \exp\left(-\frac{3}{2}\frac{S^2}{\langle S^2\rangle_0}-\frac{n^2}{2}\frac{\beta c}{S^3}\right) dS$$

$$= \lim_{\delta S\to 0}\int_{S^*-\delta S}^{S^*+\delta S} S^3 \exp\left(-\frac{3}{2}\frac{S^2}{\langle S^2\rangle_0}-\frac{n^2}{2}\frac{\beta c}{S^3}\right) dS = 1 \qquad (6.14.18)$$

That is, Eq. (6.14.17) can be replaced by Dirac's δ function δ(S-S*). Use this relationship.

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* In a strict sense, we must use exp(-F/kT)=<exp(-U(S)/kT)> in place of exp(-<U(S)>/kT).

Answer

Eq. (6.14.14) can be rewritten as

$$\langle S^2\rangle = \frac{\displaystyle\int_0^{\infty} \frac{\delta\left(S-S^*\right)}{S} 4\pi S^2\, dS}{\displaystyle\int_0^{\infty} \frac{\delta\left(S-S^*\right)}{S^3} 4\pi S^2\, dS} = \frac{\displaystyle\int_0^{\infty} \delta\left(S-S^*\right) 4\pi S\, dS}{\displaystyle\int_0^{\infty} \frac{\delta\left(S-S^*\right)}{S} 4\pi\, dS} \qquad (6.14.19)$$

Using the relationship

$$\int_0^{\infty} f(S)\,\delta\left(S-S^*\right)\, dS = f(S^*) \qquad (6.14.20)$$

Eq. (6.14.19) is further reduced to

$$\left\langle S^2 \right\rangle = \frac{4\pi S^*}{4\pi \frac{1}{S^*}} = S^{*2} \tag{6.14.21}$$

Thus, we need to calculate S*^{2} instead of <S^2>. Differentiation of the function Eq. (6.14.18) with respect to S yields

$$\frac{\partial}{\partial S}\left[S^3 \exp\left(-\frac{3}{2}\frac{S^2}{\left\langle S^2 \right\rangle_0} - \frac{n^2}{2}\frac{\beta c}{S^3} \right) \right]$$

$$= \left(3S^2 - \frac{3S^4}{\left\langle S^2 \right\rangle_0} + \frac{3n^2}{2}\frac{\beta c}{S} \right) \exp\left(-\frac{3}{2}\frac{S^2}{\left\langle S^2 \right\rangle_0} - \frac{n^2}{2}\frac{\beta c}{S^3} \right) \tag{6.14.22}$$

The maximum of Eq. (6.14.17) is obtained from the equation

$$3S^{*2} - \frac{3S^{*4}}{\left\langle S^2 \right\rangle_0} + \frac{3n^2}{2}\frac{\beta c}{S^*} = 0 \tag{6.14.23}$$

or

$$\frac{S^{*5}}{\left\langle S^2 \right\rangle_0} - S^{*3} = \frac{n^2}{2}\beta c \tag{6.14.24}$$

Dividing both sides of Eq. (6.14.24) by

$$\left\langle S^2 \right\rangle_0^{3/2} = \frac{n^{3/2}}{6^{3/2}} l^3 \tag{6.14.25}$$

we have

$$\frac{S^{*5}}{\left\langle S^2 \right\rangle_0^{5/2}} - \frac{S^{*3}}{\left\langle S^2 \right\rangle_0^{3/2}} = \frac{6^{3/2}}{n^{3/2} l^3}\frac{n^2}{2}\beta c = \frac{6^{3/2}}{n^{3/2} l^3}\frac{n^2 \beta}{2} \times \frac{1}{16}\frac{3^{3/2}}{\pi^{3/2}} = \frac{3^{3/2}}{2} Z \tag{6.14.26}$$

From Eqs. (6.14.21) and (6.12.52), we have

$$\frac{S^{*2}}{\langle S^2\rangle_0}=\frac{\langle S^2\rangle}{\langle S^2\rangle_0}=\alpha_S{}^2 \tag{6.14.27}$$

Combining Eqs. (6.14.26) and (6.14.27), we have

$$\alpha_s^5-\alpha_s^3=\frac{3^{3/2}}{2}Z \tag{6.14.28}$$

This result agrees with the Flory-Fox equation (6.13.34).
(See M. Fixman, *J. Chem. Phys.* **23**, 1656 (1955) and T. B. Grimley, *Trans. Faraday Soc.* **55**, 681 (1959))

<<Problem 6-15-a>> α^3-law

Fixman derived the equation

$$\alpha_R{}^3-1=2Z \tag{6.15.1}$$

by assuming that the variance of Gaussian distribution function be enhanced by α^2 times by the excluded volume effect. Derive Eq.(6.15.1).

Answer

The end-to-end distance of a polymer chain is expressed as a series expansion of the excluded volume parameter Z as

$$\langle R^2\rangle=nl^2\left(1+\frac{4}{3}Z+\cdots\right) \tag*{(6.12.29)'}$$

with

$$Z=\beta n^{1/2}\left(\frac{3}{2\pi l^2}\right)^{3/2} \tag{5.20.3}$$

When the excluded volume effect is large, the higher order terms are not negligible. Thus, it is more convenient if a closed form of $<R^2>$ is available. We start from the equation

$$\langle R^2\rangle=nl^2\alpha_R{}^2=n\left(l\,\alpha_R\right)^2 \tag{6.15.2}$$

This equation gives the mean square end-to-end distance of a Gaussian polymer chain with the segment length $l\,\alpha_R$. If the interaction between segment pairs changes, resulting in a change in Z, Eqs. (6.12.29)' and (5.20.3) are replaced by

$$\langle R^2 \rangle = n l^2 \alpha_R^2 \left[1 + \frac{4}{3} Z' + \cdots \right] \tag{6.15.3}$$

and

$$Z' = \beta n^{1/2} \left(\frac{3}{2\pi l^2 \alpha_R^2} \right)^{3/2} \tag{6.15.4}$$

Let's denote the infinitesimal change in $<R^2>$ caused by an infinitesimal change in Z', dZ', as $d<R^2>$. Then we have

$$d\langle R^2 \rangle = \frac{4}{3} n l^2 \alpha_R^2 dZ' = \frac{4}{3\alpha_R} \left(\frac{3}{2\pi l^2} \right)^{3/2} n^{3/2} l^2 d\beta \tag{6.15.5}$$

Here we assume that α_R be constant. Similarly, from Eq. (6.15.2), we have

$$d\langle R^2 \rangle = 2 n l^2 \alpha_R d\alpha_R \tag{6.15.6}$$

Since the change in α_R is associated with the change in β, Eqs. (6.15.5) and (6.15.6) should be identical. Thus,

$$2 n l^2 \alpha_R d\alpha_R = \frac{4}{3\alpha_R} \left(\frac{3}{2\pi l^2} \right)^{3/2} n^{3/2} l^2 d\beta \tag{6.15.7}$$

Rearrangement of Eq. (6.15.7) yields

$$2 \alpha_R^2 d\alpha_R = \frac{4}{3} \left(\frac{3}{2\pi l^2} \right)^{3/2} n^{1/2} d\beta = \frac{4}{3} dZ \tag{6.15.8}$$

Integration of Eq. (6.15.8) gives

$$\int_1^{\alpha_R} 2 \alpha_R^2 d\alpha_R = \left| \frac{2}{3} \alpha_R^3 \right|_1^{\alpha_R} = \frac{2}{3} \alpha_R^3 - \frac{2}{3} = \frac{4}{3} Z = \int_0^Z \frac{4}{3} dZ \tag{6.15.9}$$

Here we use the boundary condition $\alpha_R=1$ for $Z=0$, i.e., $\beta=0$. Thus we obtain

$$\frac{2}{3}\alpha_R{}^3 - \frac{2}{3} = \frac{4}{3}Z$$

$$\alpha_R{}^3 - 1 = \left(\frac{3}{2}\right)\left(\frac{4}{3}\right) Z \tag{6.15.1}$$

Eq. (6.15.1) shows $\alpha_R{}^3 \propto M^{1/2}$ or $\alpha_R{}^3 \propto Z$ for $M \rightarrow \infty$ or $Z \rightarrow \infty$. This is called **α^3-law**. The method used in this problem is a perturbation theory. (See M. Fixman, *J. Chem. Phys.* **36**, 306, 3123 (1962))

<<Problem 6-15-b>> Relationship between α and Z (II)

According to Kurata-Yamakawa theory, the radius of gyration of a polymer chain is given by

$$\langle S^2 \rangle = \frac{nl^2}{6}\left(1 + \frac{134}{105} Z + \cdots\right) \tag{6.12.51}$$

with

$$Z = \beta n^{1/2}\left(\frac{3}{2\pi l^2}\right)^{3/2} \tag{5.20.3}$$

Derive the equation

$$\alpha_s^3 - 1 = 1.91\, Z \tag{6.15.10}$$

by means of Fixman's method used in <<Problem 6-15-a>>.

Answer

Suppose the radius of gyration of a random coil chain

$$\langle S^2 \rangle_0 = \frac{nl^2}{6} \tag{6.14.16}$$

is modified by intermolecular interaction to

$$\langle S^2 \rangle = \frac{nl^2 \alpha_s{}^2}{6} \tag{6.15.11}$$

For a change in α_s, $\Delta\alpha_s$, associated with the change in the interaction, say $\Delta\beta$, we have

$$\langle S^2\rangle = \frac{nl^2}{6}\left(\alpha_s + \Delta\alpha_s\right)^2 = \frac{nl^2\alpha_s^2}{6}\left(1 + \frac{\Delta\alpha_s}{\alpha_s^2}\right)^2$$

$$\cong \frac{n\left(l\,\alpha_s\right)^2}{6}\left(1 + \frac{2\Delta\alpha_s}{\alpha_s} + \cdots\right) \tag{6.15.12}$$

Eq. (6.15.11) gives the radius of gyration of a random coil chain with segment length $l\,\alpha_s$. Eq. (6.15.12) gives that of the excluded volume chain affected by the interaction $\Delta\beta$. Thus, from Eq. (6.12.51),

$$\langle S^2\rangle = \frac{n\left(l\,\alpha_s\right)^2}{6}\left[1 + \frac{134}{105}\Delta\beta n^{1/2}\left\{\frac{3}{2\pi\left(l\,\alpha_s\right)^2}\right\}^{3/2}\right] \tag{6.15.13}$$

Combining Eqs. (6.15.12) and (6.15.13), we have

$$\frac{2\Delta\alpha_s}{\alpha_s} = \frac{134}{105}\Delta\beta n^{1/2}\left\{\frac{3}{2\pi\left(l\,\alpha_s\right)^2}\right\}^{3/2} \tag{6.15.14}$$

For an infinitesimal change, Eq. (6.15.14) is reduced to

$$2\alpha_s^2 d\alpha_s = \frac{134}{105}dZ \tag{6.15.15}$$

Integration of Eq. (6.15.15) under the boundary condition (α_s=1 for Z=0) yields

$$\alpha_s^3 - 1 = \frac{134\times 3}{105\times 2}Z = 1.91\,Z \tag{6.15.10}$$

The coefficient of Z is slightly different from that obtained in <<Problem 6-15-a>> based on the end-to-end distance:

$$\alpha_R^3 - 1 = 2Z \tag{6.15.1}$$

<<Problem 6-15-c>> Relationship between α and z (III)

The equation for three-dimensional polymer chains

$$\alpha_R{}^3 - 1 = 2Z \tag{6.15.1}$$

is replaced by

$$\alpha_R{}^2 - 1 = \frac{1}{2}Z^* \tag{6.15.16}$$

with

$$Z^* = \frac{\beta^*}{\pi l^2} n \tag{6.15.17}$$

for two-dimensional polymer chains. Derive Eq. (6.15.16).

Answer

For two-dimensional chains, Eq. (6.4.1) reads

$$W(\mathbf{R}) = \frac{1}{\pi n l^2} \exp\left(- \frac{\mathbf{R}}{n l^2} \right) \tag{6.15.18}$$

where

$$\left\langle \mathbf{R}^2 \right\rangle = \left\langle \mathrm{R}^2 \right\rangle = n l^2 \tag{6.5.7)'}$$

Here **R** is a two-dimensional vector. Referring to Eq. (6.12.7) and replacing $4\pi l^2$ by $2\pi l$ and 3/2 by 1, we have

$$\begin{aligned}
&\underset{d\mathbf{r}_i d\mathbf{r}_j d\mathbf{R}}{\int\cdots\int} d\mathbf{r}_1 \cdots d\mathbf{r}_n \\
&= \left(2\pi l^2\right)^n \left(\frac{1}{\pi i l^2}\right) \exp\left(-\frac{\mathbf{r}_i{}^2}{i l^2}\right) \left(\frac{1}{\pi (j - i) l^2}\right) \exp\left\{-\frac{\left(\mathbf{r}_j - \mathbf{r}_i\right)^2}{(j - i) l^2}\right\} \\
&\quad \times \left(\frac{1}{\pi (n - j) l^2}\right) \exp\left\{-\frac{\left(\mathbf{R} - \mathbf{r}_j\right)^2}{(n - j) l^2}\right\} d\mathbf{r}_i d\mathbf{r}_j d\mathbf{R}
\end{aligned} \tag{6.15.19}$$

Using the approximation

$$\exp\left(-\frac{U}{kT}\right) = \prod_{(i,j)} \exp\left\{-\frac{u(\mathbf{r}_{ij})}{kT}\right\} \cong 1 + \sum_{j>i} \chi(\mathbf{r}_{ij}) + \cdots \qquad (6.12.4)$$

with

$$\chi(\mathbf{r}_{ij}) = \exp\left\{-\frac{u(\mathbf{r}_{ij})}{kT}\right\} - 1 \qquad (6.12.3)$$

the equation

$$Q(\mathbf{R})d\mathbf{R} = \int \cdots \int \exp\left(-\frac{U}{kT}\right) d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_n \qquad (6.12.1)$$

is reduced to

$$Q(\mathbf{R})d\mathbf{R} = \left[\left(2\pi l^2\right)^n \left(\frac{1}{\pi n l^2}\right) \exp\left(-\frac{\mathbf{R}^2}{n l^2}\right) \right.$$
$$+ \left\{ \sum_{j>i} \int \int \left(\frac{1}{\pi i l^2}\right) \exp\left(-\frac{\mathbf{r}_i{}^2}{i l^2}\right) \chi(\mathbf{r}_{ij}) \right.$$
$$\left.\left. \times \left(\frac{1}{\pi (j-i) l^2}\right) \exp\left(-\frac{(\mathbf{r}_j - \mathbf{r}_i)^2}{(j-i) l^2}\right) \times \left(\frac{1}{\pi (n-j) l^2}\right) \exp\left(-\frac{(\mathbf{R} - \mathbf{r}_j)^2}{(n-j) l^2}\right) d\mathbf{r}_i d\mathbf{r}_j \right\} \right] d\mathbf{R}$$

(6.15.20)

The Laplace transformation of Q(**R**) is defined by

$$L(s) = \int Q(\mathbf{R}) \exp(-\mathbf{R}s) d\mathbf{R} \qquad (6.12.13)$$

The Laplace transformation of $\exp(-\mathbf{R}^2/n l^2)$ in the bracket of the right-hand side in Eq. (6.15.20) is given by

$$\int \exp\left(-\frac{\mathbf{R}^2}{nl^2}\right)\exp(-\mathbf{R}\mathbf{s})d\mathbf{R}$$

$$=\int \exp\left(-\frac{X^2}{nl^2}-Xs_x\right)dX\times\int \exp\left(-\frac{Y^2}{nl^2}-Ys_y\right)dY$$

$$=\sqrt{\pi l^2}\exp\left(\frac{nl^2s_x^2}{4}\right)\times\sqrt{\pi l^2}\exp\left(\frac{nl^2s_y^2}{4}\right)$$

$$=\pi l^2\exp\left(\frac{nl^2s^2}{4}\right) \qquad (6.15.21)$$

Thus, we have

$$L(s)=\left(2\pi l\right)^n\left[\exp\left(\frac{nl^2s^2}{4}\right)+\sum_{j>i}\left\{\exp\left(\frac{n-j+i}{4}l^2s^2\right)f(s,j-i)\right\}\right] \qquad (6.15.22)$$

where

$$f(s,i)=\int\left(\frac{\chi(\mathbf{r})}{\pi il^2}\right)\exp\left[-\left(\frac{\mathbf{r}^2}{il^2}\right)\right]\exp(-\mathbf{r}\mathbf{s})d\mathbf{r} \qquad (6.15.23)$$

The numerical values $4\pi l^2$, 6 and 3/2 in Eq. (6.12.16) are replaced by $2\pi l$, 4 and 1 in Eqs. (6.15.22) and (6.15.23). Since the integrant has a finite value only in a limited range of small r, we have

$$f(s;i)=\frac{1}{\pi il^2}\int\chi(\mathbf{r})\,d\mathbf{r}=\frac{1}{\pi il^2}\int\chi(r)\;2\pi r dr$$

$$=-\frac{1}{\pi il^2}\int_0^\infty\left\{1-\exp\left(-\frac{u(\mathbf{r}_{ij})}{kT}\right)\right\}2\pi r dr=-\frac{1}{\pi il^2}\beta^* \qquad (6.15.24)$$

with

$$\beta^* = \int_0^\infty \left\{ 1 - \exp\left(- \frac{u(\mathbf{r}_{ij})}{kT} \right) \right\} 2\pi r dr \tag{6.15.25}$$

The exponential term in Eq. (6.12.13) is expanded in a Taylor series as

$$\exp(-\mathbf{Rs}) = \sum_k \frac{1}{k!}(-\mathbf{Rs})^k = \sum_k \frac{1}{k!}(-Rs\cos\theta)^k \tag{6.15.26}$$

Then Eq. (6.12.13) is rewritten as

$$L(s) = \int Q(\mathbf{R}) \sum_k \frac{1}{k!}(-Rs\cos\theta)^k d\mathbf{R} \tag{6.15.27}$$

The probability distribution function that the end-to-end distance of a chain be R, Q(**R**), depends only upon R and does not depend on θ. Thus, the integration over θ can be performed as

$$L(\mathbf{s}) = \sum_k \frac{1}{k!} s^k \int Q(\mathbf{R})(-R)^k R dR \int (\cos\theta)^k d\theta$$

$$= \sum_k \frac{(-1)^k}{k!} s^k \int Q(\mathbf{R}) R^k R dR \begin{cases} \times \dfrac{4\sqrt{\pi}}{2} \dfrac{\Gamma\left(\frac{k+1}{2}\right)}{\Gamma\left(\frac{k+2}{2}\right)}, & k: \text{even} \\ \times 0 & , k: \text{odd} \end{cases}$$

$$= \sum_k \frac{1}{k!} 2\sqrt{\pi} \frac{\Gamma\left(\frac{k+1}{2}\right)}{\Gamma\left(\frac{k+2}{2}\right)} s^k \int Q(\mathbf{R}) R^k R dR, \quad k = 0, 2, 4, \cdots \tag{6.15.28}$$

For s=0, Eq. (6.12.13) is reduced to

$$L(0)=\int Q(\mathbf{R})d\mathbf{R}=\int Q(\mathbf{R})\,RdR\int d\theta=2\pi\int Q(\mathbf{R})\,RdR \qquad (6.15.29)$$

Then the integration over R in Eq. (6.15.28) yields

$$L(s)=\sum_k \frac{1}{k!}2\sqrt{\pi}\,\frac{\Gamma\left(\frac{k+1}{2}\right)}{\Gamma\left(\frac{k+2}{2}\right)}s^k\frac{1}{2\pi}\int Q(\mathbf{R})R^k 2\pi RdR$$

$$=\sum_k \frac{1}{k!}2\sqrt{\pi}\,\frac{\Gamma\left(\frac{k+1}{2}\right)}{\Gamma\left(\frac{k+2}{2}\right)}s^k\frac{1}{2\pi}\int Q(\mathbf{R})R^k d\mathbf{R}$$

$$=\sum_k \frac{1}{k!}2\sqrt{\pi}\,\frac{\Gamma\left(\frac{k+1}{2}\right)}{\Gamma\left(\frac{k+2}{2}\right)}s^k\frac{1}{2\pi}L(0)\left\langle R^k\right\rangle$$

$$=L(0)\sum_k \frac{1}{k!}\frac{1}{\sqrt{\pi}}\frac{\Gamma\left(\frac{k+1}{2}\right)}{\Gamma\left(\frac{k+2}{2}\right)}s^k\left\langle R^k\right\rangle,\ (k\text{=even})$$

$$=L(0)\left\{1+\frac{1}{2!}\frac{1}{2}\left\langle R^2\right\rangle s^2+\frac{1}{4!}\frac{6!}{8}\left\langle R^4\right\rangle s^4+\cdots\right\} \qquad (6.15.30)$$

Expanding the exponential terms of Eq. (6.15.22) in a Taylor series and neglecting higher order terms, we have

$$L(s)=\left(2\pi l\right)^n\left[\sum_k\frac{1}{k!}\left(\frac{nl^2s^2}{4}\right)^k+\sum_{j>i}\sum_k\frac{1}{k!}\left\{\left(\frac{n\text{-}j\text{+}i}{4}l^2s^2\right)^k f(s,j\text{-}i)\right\}\right]$$

$$= \left(2\pi l\right)^{n} \sum_{k} \frac{1}{k!} \left[\left(\frac{nl^{2}}{4} \right)^{k} + \sum_{j>i} \left\{ \left(\frac{n\text{-}j\text{+}i}{4} l^{2} \right)^{k} f(s,j\text{-}i) \right\} \right] s^{2k} \qquad (6.15.31)$$

Comparison of the terms for s=0 (k=0) in Eqs. (6.15.30) and (6.15.31) yields

$$L(0) = \left(2\pi l\right)^{n} \left[1 - \sum_{j>i} \frac{\beta^{*}}{\pi(j\text{-}i)l^{2}} \right] \qquad (6.15.32)$$

Then Eq. (6.15.31) is rewritten as

$$L(s) = \frac{L(0) \sum_{k} \frac{1}{k!} \left[\left(\frac{nl^{2}}{4} \right)^{k} + \sum_{j>i} \left\{ \left(\frac{n - j + i}{4} l^{2} \right)^{k} \frac{\beta^{*}}{\pi(j - i)l^{2}} \right\} \right] s^{2k}}{1 - \sum_{j>i} \frac{\beta^{*}}{\pi(j - i)l^{2}}} \qquad (6.15.33)$$

Comparing the coefficients of s^{2k} in Eqs. (6.15.30) and (6.15.33), we have

$$\frac{1}{(2k)!} \frac{1}{\sqrt{\pi}} \frac{\Gamma\left(\frac{2k+1}{2}\right)}{\Gamma\left(\frac{2k+2}{2}\right)} \left\langle R^{2k} \right\rangle = \frac{\frac{1}{k\,!} \left[1 - \sum_{j>i} \left(\frac{n - j + ,i}{n} \right)^{k} \frac{\beta^{*}}{\pi(j - i)l^{2}} \right] \left(\frac{nl^{2}}{4} \right)^{k}}{1 - \sum_{j>i} \frac{\beta^{*}}{\pi(j - i)l^{2}}}$$

(6.15.34)

Approximating sum by integral and putting k=1, we have

$$\frac{1}{2!} \frac{1}{\sqrt{\pi}} \frac{\Gamma\left({}^{3}\!/_{2}\right)}{\Gamma(2)} \left\langle R^{2} \right\rangle = \frac{nl^{2}}{4} \left\{ \frac{1 - {}^{\beta^{*}}\!/_{\pi l^{2}} \int_{1}^{n} {}^{(n - t)^{2}}\!/_{nt}\, dt}{1 - {}^{\beta^{*}}\!/_{\pi l^{2}} \int_{1}^{n} n - {}^{t}\!/_{t}\, dt} \right\} \qquad (6.15.35)$$

With the numerical values $\Gamma(3/2)= \sqrt{\pi}/2$ and $\Gamma(2)=1$, the coefficient of $\langle R^2 \rangle$ is calculated as 1/4. Using the parameter Z* defined by

$$Z^* = \left(\frac{\beta^*}{\pi l^2} \right) n \tag{6.15.17}$$

Eq. (6.15.34) is reduced to

$$\left\langle R^2 \right\rangle = nl^2 \left\{ \frac{1 - Z^* \displaystyle\int_1^n \frac{(n-t)^2}{n^2 t} \, dt}{1 - Z^* \displaystyle\int_1^n \frac{n-t}{nt} \, dt} \right\} = nl^2 \left\{ \frac{1 - Z^* \displaystyle\int_1^n \left(\frac{1}{t} - \frac{2}{n} - \frac{t}{n^2} \right) dt}{1 - Z^* \displaystyle\int_1^n \left(\frac{1}{t} - \frac{1}{n} \right) dt} \right\}$$

$$= nl^2 \left\{ \frac{1 - Z^* \left(\ln n - \frac{3}{2} + \frac{2}{n} - \frac{1}{2n^2} \right)}{1 - Z^* \left(\ln n - 1 + \frac{1}{n} \right)} \right\}$$

$$= nl^2 \left\{ 1 - Z^* \left(\ln n - \frac{3}{2} + \frac{2}{n} - \frac{1}{2n^2} \right) \right\} \left\{ 1 + Z^* \left(\ln n - 1 + \frac{1}{n} \right) \right\}$$

$$= nl^2 \left(1 + \frac{Z^*}{2} + \frac{Z^*}{n} + \cdots \right) \tag{6.15.36}$$

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* Compare with $\langle R^2 \rangle$ for the three-dimensional chain given by

$$\left\langle R^2 \right\rangle = nl^2 \left\{ 1 + \frac{4}{3} Z + \cdots \right\} \tag*{(6.12.29)'}$$

The relationship between α and Z^* is obtained referring to Fixman's method as follows. $\langle R^2 \rangle$ of the polymer swollen by the interaction β^* is given by

$$\langle R^2 \rangle = nl^2 \alpha_R^2 \qquad (6.15.2)$$

If α_R changes by $\Delta\alpha_R$ associated with a change in β^*, $\Delta\beta^*$, Eq. (6.15.2) is replaced by

$$\langle R^2 \rangle = nl^2 (\alpha_R + \Delta\alpha_R)^2 \cong nl^2 \alpha_R^2 \left(1 + 2\frac{\Delta\alpha_R}{\alpha_R} + \cdots \right) \qquad (6.15.37)$$

Combining Eqs. (6.15.17) and (6.15.36), we have

$$\langle R^2 \rangle = nl^2 \alpha_R^2 \left(1 + \frac{1}{2} \frac{\Delta\beta^*}{\pi l^2 \alpha_R^2} n + \cdots \right) \qquad (6.15.38)$$

Comparing Eqs. (6.15.37) and (6.15.38), we have

$$\frac{2\Delta\alpha_R}{\alpha_R} = \frac{1}{2} \frac{\Delta\beta^*}{\pi l^2 \alpha_R^2} n = \frac{1}{2} \frac{\Delta Z^*}{\alpha_R^2} \qquad (6.15.39)$$

For an infinitesimal change, we have

$$2\alpha_R \, d\alpha_R = \frac{1}{2} dZ^* \qquad (6.15.40)$$

Integration of Eq. (6.15.40) under the boundary condition $\alpha_R = 1$ for $Z^* = 0$ yields Eq. (6.15.1).

<<Problem 6-16-a>> Relationship between α and Z (IV)

In Fixman's theory, it was assumed that the segment length of the excluded volume chain increased by α times the segment length of the original random coil chain and the value of α was coincident with that of α_R. However, when the excluded volume effect is not negligible, the random coil approximation is no longer applied. Thus, α should not be always identical to α_R. If we denote the former value of α as α^*, Eq. (6.15.8) should be replaced by

$$d\alpha_R{}^2 = C_1 \frac{dZ}{\alpha^*} \tag{6.16.1}$$

with

$$C_1 = \frac{4}{3} = 1.33 \cdots \tag{6.16.2}$$

Here, $\alpha_R{}^2$ and $\alpha_s{}^2$ were calculated as

$$\alpha_R{}^2 = \frac{\langle R^2 \rangle}{\langle R_0{}^2 \rangle} = 1 + \sum_{i=1}^{\infty} C_i Z^i \tag{6.16.3}$$

$$\begin{cases} C_1 = \dfrac{4}{3} \cong 1.333 \\ C_2 = -\dfrac{16}{3} + \dfrac{28}{27}\pi \cong -2.075385396 \\ C_3 = \dfrac{64}{3} - \left(\dfrac{73679}{8100} - \dfrac{13202}{2025} \ln 2 + \dfrac{1616}{405} \ln \dfrac{3}{2} \right) \pi \\ \quad + \dfrac{512}{45} \displaystyle\int \dfrac{\theta d\theta}{\left(1 + 3 \sin^2\theta\right)^{1/2}} \cong 6.296879676 \\ C_4 = -25.05725072 \\ C_5 = 116.134785 \\ C_6 = -594.71663 \end{cases} \tag{6.16.4}$$

(See M.Muthukumar and B.G.Nickel, *J.Chem.Phys*.**80**,5839 (1984) ; H.Suzuki, *Macromolecules* **18**,2082 (1985))

$$\alpha_s{}^2 = \frac{\langle S^2 \rangle}{\langle S^2 \rangle_0} = 1 + C'_1 Z - C'_2 Z^2 + C'_3 Z^3 + \cdots \tag{6.16.5}$$

$$\begin{cases} C'_1 = \dfrac{134}{105} \cong 1.276 \\ C'_2 = \dfrac{536}{105} - \dfrac{1247}{1296}\pi \cong 2.082 \end{cases} \tag{6.16.6}$$

(See H. Yamakawa and G. Tanaka, *J. Chem. Phys.* **45**, 1938 (1966), *ibid.* **47**, 3991 (1967) and M. Fixman, *ibid.* **23**, 1656 (1955))
Express α^* in a power series of Z using Eqs. (6.16.1) and (6.16.2). Next, on assuming that $d\alpha^{*2}/dZ$ can be expressed in a similar form as Eq. (6.16.1), derive α^* in a closed form of Z. Then derive the equation

$$4.67\,\alpha_R{}^2 = 3.67 + \left(1+9.34Z\right)^{2/3} \tag{6.16.7}$$

Answer

Differentiating Eq.(6.16.3) with respect to Z, we have

$$\frac{d\alpha_R{}^2}{dZ} = C_1 - 2C_2Z + 3C_3Z^2 - \cdots \tag{6.16.8}$$

Substitution of Eq. (6.16.8) for $d\alpha_R{}^2/dZ$ in Eq. (6.16.1) yields

$$C_1 - 2C_2Z + 3C_3Z^2 - \cdots = \frac{C_1}{\alpha^*} \tag{6.16.9}$$

and then we have

$$\alpha^{*2} = \frac{1}{\left(1 - 2\dfrac{C_2}{C_1}Z + 3\dfrac{C_3}{C_1}Z^2 - \cdots\right)^2}$$

$$= 1 + 4\frac{C_2}{C_1}Z + \left\{12\left(\frac{C_2}{C_1}\right)^2 - 6\left(\frac{C_3}{C_1}\right)\right\}Z^2 + \cdots \tag{6.16.10}$$

The differential of α^{*2} with respect to Z at Z=0 is

$$\left(\frac{d\alpha^{*2}}{dZ}\right)_{Z=0} = 4\frac{C_2}{C_1} \tag{6.16.11}$$

On the other hand, the differential of $\alpha_R{}^2$ with respect to Z at Z=0, $(d\alpha_R{}^2/dZ)_{Z=0}$, is C_1. Combining Eqs. (6.16.8) and (6.16.9), we have

$$\left(\frac{d\alpha_R{}^2}{dZ}\right)=\frac{C_1}{\alpha^*} \tag{6.16.12}$$

for Z>0. We assume a similar relationship between the values at Z=0 and Z>0 for $d\alpha^{*2}/dZ$:

$$\left(\frac{d\alpha^{*2}}{dZ}\right)=\frac{4C_2}{C_1\alpha^*} \tag{6.16.13}$$

The solution of Eq. (6.16.13) is

$$\frac{\alpha^{*3}}{3}=2\left(\frac{C_2}{C_1}\right)Z+k_1 \tag{6.16.14}$$

Under the boundary condition ($\alpha^*=1$ for Z=0), we have $k_1=1/3$. Thus, we have α^* in a closed form of Z as

$$\alpha^{*3}=1+6\left(\frac{C_2}{C_1}\right)Z \tag{6.16.15}$$

Substitution of Eq. (6.16.15) for α^* in Eq. (6.16.1) yields

$$\frac{d\alpha_R{}^2}{dZ}=\frac{C_1}{\left(1+6\left(\frac{C_2}{C_1}\right)Z\right)^{1/3}} \tag{6.16.16}$$

The solution of Eq. (6.16.16) is

$$\alpha_R^2=\int\frac{C_1\,dZ}{\left\{1+6\left(\frac{C_2}{C_1}\right)Z\right\}^{1/3}}=\frac{3C_1}{6\left(\frac{C_2}{C_1}\right)}\left[\frac{\left\{1+6\left(\frac{C_2}{C_1}\right)Z\right\}^{2/3}}{2}\right]+k_2$$

$$= \frac{1}{4}\frac{C_1^{\;2}}{C_2}\left\{1 + 6\left(\frac{C_2}{C_1}\right)Z\right\}^{2/3} + k_2 \tag{6.16.17}$$

Under the boundary condition of $\alpha_R=1$ for $Z=0$, we have

$$k_2 = -\frac{C_1^{\;2}}{4C_2} \tag{6.16.18}$$

Thus we obtain

$$\alpha_R^2 = \frac{C_1^{\;2}}{4C_2}\left\{1 + 6\left(\frac{C_2}{C_1}\right)Z\right\}^{2/3} + 1 - \frac{C_1^{\;2}}{4C_2}$$

$$= \frac{C_1^{\;2}}{4C_2}\left[\frac{4C_2}{C_1^{\;2}} - 1 + \left\{1 + 6\left(\frac{C_2}{C_1}\right)Z\right\}^{\frac{2}{3}}\right] \tag{6.16.19}$$

Substituting Eq. (6.16.4) for C_1 and C_2 in Eq. (6.16.19), we have Eq. (6.16.7) which is called **Ptitsyn's equation**. (See O. B. Ptitsyn, *Vyskomol. Soedin.* **3**, 1673 (1961))

<<Problem 6-16-b>> Relationship between α and Z (V)

Ptitsyn's theory is more strict than Fixman's theory since the former takes account of non-Gaussian expantion factor for the excluded volume chain. However, in this derivation, an adjustable parameter k was introduced as

$$\alpha^{*3} = 1 - kZ \tag{6.16.20}$$

In the equation of α^{*2} in a power series of Z

$$\alpha^{*2} = 1 + 4\left(\frac{C_2}{C_1}\right)Z + \left\{12\left(\frac{C_2}{C_1}\right)^2 - 6\left(\frac{C_3}{C_1}\right)\right\}Z^2 + \cdots \tag{6.16.21}$$

the numerical value of the coefficient for Z^2 is

$$12\left(\frac{2.075}{1.333}\right)^2 - 6\left(\frac{6.459}{1.333}\right) = 29.078\text{-}29.073 = 5\times10^{-3}$$

which is only 1/1245 of the coefficient for Z. Thus, we can rewrite Eq. (6.16.21) as

$$\alpha^{*2} = 1+4\left(\frac{C_2}{C_1}\right)Z+O\left(Z^3\right) \tag{6.16.22}$$

With the aid of Eq. (6.16.22), solve the equation

$$\frac{d\alpha_R{}^2}{dZ} = \frac{C_1}{\alpha^*} \tag{6.16.23}$$

Answer

Substitution of Eq. (6.16.20) for α^* in Eq. (6.16.23) yields

$$\frac{d\alpha_R{}^2}{dZ} = \frac{C_1}{\left\{1+4\left(\frac{C_2}{C_1}\right)Z\right\}^{1/2}} \tag{6.16.24}$$

The solution of the differential equation (6.16.24) is

$$\alpha_R{}^2 = \frac{C_1{}^2}{2C_2}\left\{1+4\left(\frac{C_2}{C_1}\right)Z\right\}^{1/2} + k_1 \tag{6.16.25}$$

Under the boundary condition ($\alpha_R=1$ for $Z=0$), we have

$$k_1 = 1 - \frac{C_1{}^2}{2C_2} \tag{6.16.26}$$

then

$$\alpha_R{}^2 = \frac{C_1{}^2}{2C_2}\left[\frac{2C_2}{C_1{}^2} - 1 + \left\{1+4\left(\frac{C_2}{C_1}\right)Z\right\}^{1/2}\right] \tag{6.16.27}$$

Substitution of the numerical values $C_1=1.333$ and $C_2=2.075$ (Eq. (6.16.4)) in

Eq. (6.16.27) yields

$$\alpha_R^2 = 0.572 + 0.428\left(1 + 6.23\,Z\right)^{1/2} \tag{6.16.28}$$

(See H. Suzuki, *Macromolecules* **3**, 373 (1970) and H. Yamakawa and G. Tanaka, *J. Chem. Phys.* **47**, 3991 (1967))

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* The equation for α_s^2 which corresponds to Eq. (6.16.28) is given as follows: α_s^2 is expanded in a power series of Z as

$$\alpha_s^2 = 1 + C_1 Z - C_2 Z^2 + \cdots \tag{6.16.29}$$

where

$$C_1 = 1.276\,,\ C_2 = 2.082 \tag{6.16.30}$$

If we use Eq. (6.16.29) in place of Eq. (6.16.4) and perform similar calculations as <<Problem 6-16-a>> and <<6-16-b>>, we have

$$\alpha_s^2 = \frac{C_1^2}{4C_2}\left[\frac{4C_2}{C_1^2} - 1 + \left\{1 + 6\left(\frac{C_2}{C_1}\right)Z\right\}^{2/3}\right] \tag{6.16.31}$$

(Ptitsyn's equation)

which corresponds to Eq. (6.16.19), and

$$\alpha_s^2 = \frac{C_1^2}{2C_2}\left[\frac{2C_2}{C_1^2} - 1 + \left\{1 + 4\left(\frac{C_2}{C_1}\right)Z\right\}^{1/2}\right] \tag{6.16.32}$$

(Suzuki's equation)

which corresponds to Eq. (6.16.28). Substitution of numerical values C_1 and C_2 in Eqs. (6.16.31) and (6.16.32) yields

$$\alpha_s^2 = 0.805 + 0.195\left\{1 + 9.79\,Z\right\}^{1/2} \tag{6.16.33}$$

and

$$\alpha_s^2 = 0.609 + 0.391\left\{1 + 6.53\,Z\right\}^{1/2} \tag{6.16.34}$$

respectively. Since α_s is readily determined empirically, Eqs. (6.16.33) and (6.16.34) can be assessed by experiments.

<<Problem 6-17-a>> Relationship between α and Z (VI): Kurata-Stockmayer-Roig's equation

For a Gaussian chain, the segment density at the point where the distance from the center of gravity is **r** is expressed as

$$\rho(\mathbf{r})d\mathbf{r} = \left(\frac{3}{2\pi\langle S^2\rangle}\right)^{3/2} \exp\left(-\frac{3r^2}{2\langle S^2\rangle}\right) 4\pi\mathbf{r}^2 d\mathbf{r} \qquad (6.11.1)'$$

Now let's assume that $\langle R^2 \rangle$ is given by (See Eq. (6.14.14))

$$\langle R^2\rangle = \frac{\int R^2\rho(\mathbf{R})\exp\left(-\frac{\langle U_R\rangle}{kT}\right)d\mathbf{R}}{\int \rho(\mathbf{R})\exp\left(-\frac{\langle U_R\rangle}{kT}\right)d\mathbf{R}} \qquad (6.17.1)$$

where $\rho(\mathbf{R})$ is the probability distribution function that the end-to-end distance of the chain is **R** and U_R is the interaction energy for **R**, as expressed by

$$\rho(\mathbf{R}) = \text{const.}\exp\left(-\frac{3R^2}{2nl^2}\right) \qquad (6.17.2)$$

$$\langle U_R\rangle = \frac{\text{const.}}{2}\beta kT\int \rho_R(\mathbf{R})\rho_R(\mathbf{R})\,4\pi s^2\,ds \qquad (6.17.3)$$

Here, $\rho_R(\mathbf{R})$ is the segment density at the point where the distance from the center of gravity is **R** for the chain with the end-to-end distance being **R**. For a fixed value of the end-to-end distance **R**, the shape of the molecular chain is assumed to be an ellipsoid of revolution with the direction of the major axis being the direction of **R**. The radius of gyration for a fixed **R** in the three principal directions is given by

$$\langle s_x{}^2\rangle = \frac{nl^2}{36}\left[1+\left(\frac{3R^2}{nl^2}\right)\right] \qquad (6.17.4)$$

and

$$\langle s_y^2\rangle = \langle s_z^2\rangle = \frac{nl^2}{36} \qquad (6.17.5)$$

The volume of the ellipsoid of revolution constructed by revolving the ellipsoid

$$\frac{x^2}{\langle s_x^2\rangle} + \frac{y^2}{\langle s_y^2\rangle} = 1 \qquad (6.17.6)$$

along the major axis x is given by

$$V_R = \pi \int_{-\langle s_x^2\rangle^{1/2}}^{\langle s_x^2\rangle^{1/2}} y^2\, dx = \pi \int_{-\langle s_x^2\rangle^{1/2}}^{\langle s_x^2\rangle^{1/2}} \langle s_y^2\rangle \left(1 - \frac{x^2}{\langle s_x^2\rangle}\right) dx$$

$$= \frac{4}{3}\langle s_x^2\rangle^{1/2}\langle s_y^2\rangle \pi \qquad (6.17.7)$$

Substitution of Eqs. (6.17.4) and (6.17.5) for $<s_x^2>$ and $<s_y^2>$ in Eq. (6.17.7) yields

$$V_R = \frac{4}{3}\pi\left(\frac{nl^2}{36}\right)^{1/2}\left(\frac{nl^2}{36}\right)\left(1 + \frac{3R^2}{nl^2}\right)^{1/2}$$

$$= \frac{4}{3}\left(\frac{1}{36}\right)^{3/2} 3^{1/2}\pi\, nl^2 R\left(1 + \frac{nl^2}{3R^2}\right)^{1/2}$$

$$= \text{const. } nl^2 R\left(1 + \frac{nl^2}{3R^2}\right)^{1/2} \qquad (6.17.8)$$

If we assume n segments are distributed homogeneously inside the ellipsoid of revolution, the segment density is obtained as

$$\rho_R(s) = \frac{n}{V_R} = \frac{\text{const.}}{nl^2 R\left\{\left(1 + {nl^2}/{3R^2}\right)\right\}^{1/2}} \qquad (6.17.9)$$

According to the method used in <<Problem 6-14>>, derive the relationship between α_R and Z as

$$\alpha_R{}^3 - \alpha_R = \frac{C'Z}{1 + \left(\dfrac{1}{3\alpha_R{}^2}\right)^{3/2}} \tag{6.17.10}$$

for the present model. Here C' is a constant.

Answer

Substitution of Eq. (6.17.9) for $\rho_R(\mathbf{R})$ in Eq. (6.17.3) yields

$$\frac{\langle U_R \rangle}{kT} = \frac{\text{const.}\beta}{2} \int_0^\infty \rho_R{}^2(s)\, 4\pi s^2\, ds = \frac{\text{const.}\beta}{2} \rho_R{}^2(s) \int_0^\infty 4\pi s^2\, ds$$

$$= \frac{\text{const.}\beta}{2} \frac{n^2}{V_R} = \text{const.} \frac{\beta n^{1/2}}{l^3} \left(\frac{\dfrac{nl^2}{R^2}}{1 + \dfrac{nl^2}{3R^2}} \right)^{1/2} \tag{6.17.11}$$

Then substitution of this expression for $<U_R>/kT$ in Eq. (6.17.1) yields

$$\langle R^2 \rangle = \frac{\int_0^\infty R^2 \exp\left(-\dfrac{3R^2}{2nl^2}\right) \exp\left[-C\dfrac{\beta n^{1/2}}{l^3}\left\{\dfrac{nl^2}{R^2\left(1 + nl^2/3R^2\right)}\right\}^{1/2}\right] 4\pi R^2 dR}{\int_0^\infty \exp\left(-\dfrac{3R^2}{2nl^2}\right) \exp\left[-C\dfrac{\beta n^{1/2}}{l^3}\left\{\dfrac{nl^2}{R^2\left(1 + nl^2/3R^2\right)}\right\}^{1/2}\right] 4\pi R^2 dR}$$

$$= \frac{\int_0^\infty R^4 \exp\left[-\dfrac{3R^2}{2nl^2} - C\dfrac{\beta n^{1/2}}{l^3}\left\{\dfrac{nl^2}{R^2\left(1 + nl^2/3R^2\right)}\right\}^{1/2}\right] dR}{\int_0^\infty R^2 \exp\left[-\dfrac{3R^2}{2nl^2} - C\dfrac{\beta n^{1/2}}{l^3}\left\{\dfrac{nl^2}{R^2\left(1 + nl^2/3R^2\right)}\right\}^{1/2}\right] dR} \tag{6.17.12}$$

Using the relationships

$$\alpha_R{}^2 = \frac{R^2}{nl^2} = \frac{R^2}{\langle R^2 \rangle} \tag{6.15.2}$$

and

$$Z = \frac{\beta n^{1/2}}{l^3}\left(\frac{3}{2\pi}\right)^{3/2} \tag{5.20.3}$$

Eq. (6.17.12) is further rewritten as

$$\langle \alpha_R^2 \rangle = \frac{\int_0^\infty \alpha_R^4 \exp\left[-\frac{3}{2}\alpha_R^2 - C\left(\frac{2\pi}{3}\right)^{2/3} Z \left\{\frac{1}{\alpha_R^2\left(1+1/3\alpha_R^2\right)}\right\}^{1/2}\right] d\alpha_R}{\int_0^\infty \alpha_R^2 \exp\left[-\frac{3}{2}\alpha_R^2 - C\left(\frac{2\pi}{3}\right)^{2/3} Z \left\{\frac{1}{\alpha_R^2\left(1+1/3\alpha_R^2\right)}\right\}^{1/2}\right] d\alpha_R}$$

$$= \frac{\int_0^\infty \alpha_R^4 \exp\left\{-\frac{3}{2}\alpha_R^2 - \frac{3C'Z}{\alpha_R}\left(1+\frac{1}{3\alpha_R^2}\right)^{-1/2}\right\} d\alpha_R}{\int_0^\infty \alpha_R^2 \exp\left\{-\frac{3}{2}\alpha_R^2 - \frac{3C'Z}{\alpha_R}\left(1+\frac{1}{3\alpha_R^2}\right)^{-1/2}\right\} d\alpha_R} \tag{6.17.13}$$

where

$$C' = \frac{(2\pi)^{3/2}}{3^{5/2}} C = \text{const.} \tag{6.17.14}$$

Let's denote the value of α_R when the function

$$\alpha_R{}^3 \exp\left\{-\frac{3}{2}\alpha_R{}^2 - \frac{3C'Z}{\alpha_R}\left(1+\frac{1}{3\alpha_R{}^2}\right)^{-1/2}\right\} \tag{6.17.15}$$

has its maximum as $\alpha_R{}^*$. Then Eq. (6.17.13) can be rewritten as

$$\left\langle \alpha_R^2 \right\rangle = \frac{\int_0^\infty \alpha_R \, \delta\left(\alpha_R - \alpha_R^*\right) \, d\alpha_R}{\int_0^\infty \delta\left(\alpha_R - \alpha_R^*\right) \big/ \alpha_R \, d\alpha_R} = \alpha_R^{*2} \tag{6.17.16}$$

Thus, we need to calculate $\alpha_R{}^{*2}$ in order to obtain $<\alpha_R{}^2>$. $\alpha_R{}^*$ is given by solving the equation

$$\frac{\partial}{\partial \alpha_R}\left[\alpha_R{}^3 \exp\left\{-\frac{3}{2}\alpha_R{}^2 - \frac{3C'Z}{\alpha_R}\left(1+\frac{1}{3\alpha_R{}^2}\right)^{-1/2}\right\}\right]$$

$$= \left[3\alpha_R{}^2 + \alpha_R{}^3\left\{-3\alpha_R + \frac{3C'Z}{\alpha_R{}^2}\left(1+\frac{1}{3\alpha_R{}^2}\right)^{-1/2} - \frac{3C'Z}{\alpha_R}\left(-\frac{1}{2}\right)\left(1+\frac{1}{3\alpha_R{}^2}\right)^{-2/3}\left(-\frac{2}{3\alpha_R{}^3}\right)\right\}\right]$$

$$\times \exp\left\{-\frac{3}{2}\alpha_R{}^2 - \frac{3C'Z}{\alpha_R}\left(1+\frac{1}{3\alpha_R{}^2}\right)^{-1/2}\right\} = 0 \tag{6.17.17}$$

or

$$3\alpha_R^{*2} - 3\alpha_R^{*4} + 3C'Z\alpha_R^*\left(1+\frac{1}{3\alpha_R^{*2}}\right)^{-1/2} - \frac{3C'Z}{3\alpha_R^*}\left(1+\frac{1}{3\alpha_R^{*2}}\right)^{-3/2} = 0 \tag{6.17.18}$$

$$\alpha_R^{*3} - \alpha_R^* = C'Z\left(1+\frac{1}{3\alpha_R^{*2}}\right)^{-3/2} = 0 \tag{6.17.19}$$

If we denote $<\alpha_R>$ simply as α_R, by using Eq. (6.17.17), we have Eq. (6.17.10). Eq. (6.17.10) is called **Kurata-Stockmayer-Roig's equation** which gives a closed form of α_R as a function of Z. When $\alpha_R \rightarrow \infty$, then

$Z \propto \alpha_R{}^3$. (See M. Kurata, W. H. Stockmayer and A. Roig, *J. Chem. Phys.* **33**, 151 (1960))

<<Problem 6-17-b>> Relationship between α and Z (VII)

The coefficient C' in the equation for the ellipsoid of revolution model

$$\alpha_R^3 - \alpha_R = C'Z\left(1 + \frac{1}{3\alpha_R^2}\right)^{-3/2} \tag{6.17.11}$$

is determined as

$$C' = \left(\frac{4}{3}\right)^{5/2} \tag{6.17.20}$$

by comparison with the coefficient of the equation

$$\alpha_R{}^2 - 1 = \frac{4}{3}Z + \cdots \tag{6.16.3}$$

Derive Eq. (6.17.20).

Answer

Eq. (6.16.3) can be approximated by

$$\alpha_R \cong \left(1 + \frac{4}{3}Z\right)^{1/2} \tag{6.17.21}$$

and then

$$\alpha_R{}^3 - \alpha_R \cong \left(1 + \frac{4}{3}Z\right)^{3/2} - \left(1 + \frac{4}{3}Z\right)^{1/2} \cong \frac{4}{3}Z \tag{6.17.22}$$

By comparing the right-hand sides of Eqs. (6.17.11) and (6.17.22), we have

$$C' = \frac{4}{3}\left(1 + \frac{1}{3\alpha_R{}^2}\right)^{3/2} = \frac{4}{3}\left(\frac{1 + 3\alpha_R{}^2}{3\alpha_R{}^2}\right)^{3/2}$$

$$= \frac{4}{3}\left(\frac{4 + 4Z}{3 + 4Z}\right)^{3/2} = \frac{4}{3}\left(\frac{4}{3}\right)^{3/2} = \left(\frac{4}{3}\right)^{5/2} \tag{6.17.23}$$

Thus, Eq. (6.16.3) can be rewritten as

$$\alpha_R{}^3 - \alpha_R = \left(1 + \frac{1}{3\alpha_R{}^2}\right)^{-3/2} \left(\frac{4}{3}\right)^{5/2} \left(\frac{3}{2\pi}\right)^{3/2} \left(\frac{\beta n^{1/2}}{l^3}\right) \qquad (6.17.24)$$

<<Problem 6-18>> Determination of Flory constant K

Assume the ratio of the root of the mean square end-to-end distance for nonideal conformation $<R^2>$ and ideal conformation $<R^2>_0$ (or perturbed state and unperturbed state), $\alpha \equiv <R^2>^{1/2}/<R^2>_0{}^{1/2}$, be related to the excluded volume parameter

$$Z = \beta n^{1/2} \left(\frac{3}{2\pi l^2}\right)^{3/2} \qquad (5.20.3)$$

as

$$\alpha_R{}^3 - 1 = 2Z \qquad \text{(Fixman's relation)} \qquad (6.15.1)$$

Combine this relationship with the Flory-Fox equation for the intrinsic viscosity

$$[\eta] = KM^{1/2}\alpha_\eta{}^3 \qquad (6.18.1)$$

and discuss how to determine the Flory constant K in Eq. (6.18.1) from $[\eta]$ and M. Here,

$$K = \Phi_0 \left(\frac{\langle R^2 \rangle_0}{M}\right)^{3/2} = \Phi_0 A^3 \qquad (6.18.2)$$

$$A^2 = \frac{\langle R^2 \rangle_0}{M} = \frac{nl^2}{M} = \frac{l^2}{m_0} \qquad (6.18.3)$$

$$Z = \beta \left(\frac{n}{M}\right)^{1/2} \left(\frac{3}{2\pi}\right)^{3/2} \frac{M^{1/2}}{l^3} = \frac{\beta}{m_0{}^2} \left(\frac{3}{2\pi}\right)^{3/2} A^{-3} M^{1/2} \qquad (6.18.4)$$

where m_0 is the molecular weight of a segment. Eq. (6.18.4) is identical with Eq. (8.33.1) (See also <<Problem 8-32>> and <<8-33>>).

Answer

Using the parameter

$$B = \frac{\beta}{m_0^2} \tag{6.18.5}$$

Eq. (6.18.4) can be rewritten as

$$Z = \left(\frac{3}{2\pi}\right)^{3/2} B\, A^{-3} M^{1/2} = 0.330B\, A^{-3} M^{1/2} \tag{6.18.6}$$

According to Fox and Flory (See *J. Phys. Colloid Chem.* **53**, 197 (1949)), we have

$$\alpha_\eta^{\ 3} = \alpha^{2.43} \tag{6.18.7}$$

Let's assume a functional form similar to Eq. (6.15.1) for the relationship between α_η and Z;

$$\alpha_\eta^{\ 3} - 1 = CZ + O\left(Z^2\right) + \cdots \tag{6.18.8}$$

Combining Eqs. (6.18.7) and (6.18.8), C is estimated as

$$C = \frac{2.43 \times 2}{3} = 1.62$$

If higher order terms in Eq. (6.18.8) are negligible, we have the equation

$$\alpha_\eta^{\ 3} - 1 \cong 1.62Z \tag{6.18.9}$$

Substitution of Eqs. (6.18.1), (6.18.2) and (6.18.6) in this equation yields

$$\frac{[\eta]}{M^{1/2}} = K + \Phi_0 A^3 \times 1.62 \times 0.330B\, A^{-3} M^{1/2} = K + 0.535B\, \Phi_0\, M^{1/2} \tag{6.18.10}$$

Thus, we can determine K from the intercept of the plot for $[\eta]/M^{1/2}$ against $M^{1/2}$ $(M \to \infty)$. This plot was first proposed by Burchard and then a similar plot was carried out by Stockmayer-Fixman based on Kurata-Yamakawa theory:

$$\alpha_\eta^3 - 1 = 1.55Z \tag{6.18.11}$$

in place of Eq. (6.18.9). In this case, Eq. (6.18.10) is replaced by

$$\frac{[\eta]}{M^{1/2}} = K + 0.5\Phi_0 B\, M^{1/2} \tag{6.18.12}$$

The coefficients of $M^{1/2}$ in the right-hand sides of Eqs. (6.18.10) and (6.18.12) are slightly different.

---

* α_η is defined by

$$\alpha_\eta{}^3 = \frac{[\eta]}{[\eta]_\theta} = \frac{F(x)}{F_0(x)} \tag{6.18.13}$$

where $[\eta]_\theta$ is the intrinsic viscosity at θ state. For x→∞ (complete non-free draining), we have

$$\alpha_\eta{}^3 = \frac{F(x)}{F_0(x)} = 1 + 1.55Z + O(Z^2) + \cdots \tag{6.18.14}$$

from Kurata-Yamakawa theory (See <<Problem 8-34>>). If higher order terms are negligible, we can derive Eq. (6.18.11). The parameters A and B in Eq. (6.18.6) stand for short range interaction and long range interaction, respectively. The former is the interaction between close segments along the main chain. It depends on the valence angle and the restriction of molecular rotation and also slightly depends on temperature, but does not depend on molecular weight and kinds of solvent very much. The latter is the van der Waals type interaction between segments distant on the main chain but temporarily close. It depends strongly upon molecular weight, kinds of solvent and temperature. The theory developed with use of only these two parameters for describing solution properties of polymer is called the **two-parameter theory**. (See W. Burchard, *Makromol. Chem.* **50**, 20 (1961), W. H. Stockmayer and M. Fixman, *J. Polym. Sci.* **C1**, 137 (1963))

<<Problem 6-19>> Determination of Z

Discuss how to determine the excluded volume parameter Z

Answer

Z is expressed as

$$Z = \left(\frac{3}{2\pi}\right)^{3/2} BA^{-3} M^{1/2} = 0.330BA^{-3} M^{1/2} \tag{6.18.6}$$

with the parameters

$$A^2 = \frac{\langle R^2 \rangle_0}{M} \tag{6.18.3}$$

and

$$B = \frac{\beta}{m_0^{\ 2}} \tag{6.18.5}$$

Here, A can be determined with the aid of the relationship $A^2 = \langle R^2 \rangle_0 / M = 6 \langle S^2 \rangle_0 / M$

or

$$A = \left(\frac{[\eta]_\theta}{\Phi_0 M^{1/2}} \right)^{1/3} \tag{6.19.1}$$

empirically from the ratio of $\langle S_0^{\ 2} \rangle$ and M or the ratio of $[\eta]$ and M in θ solvent.

---

* The parameter B is determined by the following methods.

(1) A_2 is related to B as

$$A_2 \cong \frac{N_A B}{2} = \frac{N_A B_0}{2} \left(1 - \frac{\theta}{T} \right) \tag{6.19.2}$$

near the θ temperature (See Eq.(5.21.2)). Differentiation of A_2 with respect to T at $T=\theta$ yields

$$B_0 \cong \theta \left(\frac{\partial A_2}{\partial T} \right)_\theta \frac{2}{N_A} \tag{6.19.3}$$

Thus, from the temperature dependence of A_2, we can determine

$$B = B_0 \left(1 - \frac{\theta}{T} \right) \tag{6.19.4}$$

(2) With the aid of the relationship

$$A_2 = \frac{\bar{v}^2}{N_A V_0} \psi_1 \left(1 - \frac{\theta}{T} \right) F(Z)$$

$$= \frac{N_A B_0}{2}\left(1 - \frac{\theta}{T}\right) F(Z) \tag{5.21.2}$$

we can determine B from the slope of the plot for $A_2/F(Z)$ vs. $(1-\theta/T)$.

(3) With the aid of Stockmayer-Fixman equation (See Eqs. (6.18.12) and (6.19.2))

$$\frac{[\eta]}{[\eta]_\theta} = 1 + 1.55 \times 0.330 B A^{-3} M^{1/2} \tag{6.19.5}$$

we can determine B from the slope of the plot for $[\eta]/[\eta]_\theta$ vs. $M^{1/2}$. Here, the approximation

$$\alpha_s^3 = 1 + 2Z \tag{6.19.6}$$

is used for the derivation of Eq. (6.19.5). Thus, Eq. (6.19.5) cannot hold for large Z.

(4) According to the Flory-Huggins theory, apparent second virial coefficient S for concentrated solutions is given by

$$RTS = RT\left\{\frac{v^2}{V}\left(\frac{1}{2} - \chi_1\right) + \frac{v^3}{V}\left(\frac{1}{3} - \chi_2\right)C + \sum_{i=4}\left(\frac{v^i}{iV}\right)C^{i-2}\right\} \tag{6.19.7}$$

where

$$\chi = \chi_1 + \chi_2 \phi_1 \tag{6.19.8}$$

The intercept of the plot for RTS vs. C at C=0 is given by

$$RT\frac{\bar{v}^2}{V}\left(\frac{1}{2} - \chi_1\right) = RT\frac{N_A B}{2} \tag{6.19.9}$$

We can determine B from the intercept based on Eq. (6.19.9). (See N. Kuwahara, T. Okazawa and M. Kaneko, *J. Chem. Phys.* **47**, 3357 (1967))

* Thus, no direct method for determining B or β is available. If the excluded volume theory is exact, we have an explicit function

$$Z = f(\alpha_s) \tag{6.19.10}$$

Then, we can determine Z from Eq. (6.19.10). The theory can be checked by confirming the proportionality between Z thus obtained and $M^{1/2}$. However, if we determine Z based on Fixman's α_s^3-law for solutions of polystyrene, poly α-methylstyrene, polychloroprene and polyisobutyrene, the resultant Z is a nonlinear function of $M^{1/2}$.

<<Problem 6-20>> α_s and ψ; comparison between experiment and theory

According to McMillan-Mayer theory, A_2 is given by

$$A_2 = -\frac{N_A}{M^2}/^2 = -\frac{N_A}{2M^2V}\int_V g_2(1,2)d(1)d(2) \tag{5.11.1}$$

and

$$\frac{\Pi^*}{RT} = \frac{C}{M} + A_2C^2 + A_3C^3 + \cdots \tag{5.2.1'}$$

On the other hand, A_2 for gas is given by

$$A'_2 = -N_A/^2 = -2\pi N_A\int_0^\infty r^2\left[1 - \exp\left\{\frac{u(r)}{kT}\right\}\right]dr \tag{6.20.1}$$

$$\frac{\Pi}{RT} = \frac{1}{V} + \frac{A'_2}{V^2} + \frac{A'_3}{V^3} + \cdots \tag{6.20.2}$$

where u(r) is the two-body potential. Similarly to Eq. (6.20.1), A_2 for polymer solutions is expressed as

$$A_2 = \frac{N_A}{2M^2V}\int_V F_1(1)F_2(2)\left[1 - \exp\left\{-\sum_{i_1,i_2}\frac{w(i_1,i_2)}{kT}\right\}\right]d(1)d(2) \tag{5.12.7'}$$

where $w(i_1, i_2)$ is the interaction potential between i_1 th segment and i_2 th segment and F_N is the N-body distribution function. (See <<Problem 5-12>>)

In case of

$$u(r)=\begin{Bmatrix}\infty\ ,\ r<r_0\\ u(r)\ ,\ r\geq r_0\end{Bmatrix}\quad,\quad \exp\left\{-\sum_{i_1,i_2}\frac{w(i_1,i_2)}{kT}\right\}\cong 1-\frac{u(r)}{kT} \tag{6.20.3}$$

we have

$$A_2\cong N_A\left\{2\pi\int_0^{r_0}r^2\,dr+2\pi\int_{r_0}^{\infty}\frac{r^2u(r)}{kT}\,dr\right\} \tag{6.20.4}$$

Thus, A_2 stands for the excluded volume of a polymer chain (first term) when the attraction force (second term) is negligible. Eq. (5.12.7)' can be expressed in a series of Z, $\psi(Z)$, as

$$A_2=4\pi^{3/2}N_A\frac{\left\langle S^2\right\rangle^{3/2}}{M^2}\psi(Z) \tag{6.20.5}$$

Generally, $\psi(Z)\cong 0$ for $Z\cong 0$ and converges to a finite value for large Z. This result indicates that the excluded volume is proportional to $\langle S^2\rangle^{3/2}$ for large Z and decreases with decreasing Z, i.e., polymer chains do not penetrate each other for large Z but penetrate with decreasing Z. $\psi(Z)$ is called the **penetrating function**. Summarize the theoretically explicit functional form of $\psi(Z)$ and describe how experiments can be compared with the theories.

Answer

Theoretical functional forms for $\psi(Z)$ are summarized as follows:

(1) **Flory theory**

$$\alpha_s^5-\alpha_s^3=2.60Z$$

$$\psi=\left(\frac{1}{2.30}\right)\left\{\ln\left(1+\frac{2.30Z}{\alpha_s^3}\right)\right\} \tag{6.20.6}$$

(2) **modified Flory theory**

$$\alpha_s^5 - \alpha_s^3 = \frac{134}{105}Z$$

$$\psi = \left(\frac{1}{5.73}\right)\left\{\ln\left(1+\frac{5.73Z}{\alpha_s^3}\right)\right\} \qquad (6.20.7)$$

(3) **Yamakawa theory**

$$\alpha_s^2 = 0.541 + 0.459\left(1+6.04Z\right)^{0.46}$$

$$\psi = \left(\frac{1}{1.276}\right)\left\{1-\left(1+\frac{4.45Z}{\alpha_s^3}\right)^{-0.2865}\right\} \qquad (6.20.8)$$

(4) **Fixman-Kurata theory**

$$\alpha_s^3 = 1 + 1.91\,Z$$

$$\psi = \left(\frac{1}{5.047}\right)\left\{1-\left(1+\frac{0.683Z}{\alpha_s^3}\right)^{-7.389}\right\} \qquad (6.20.9)$$

These theories are compared with experiments. Modified Flory equation and Fixman equation can be rewritten with the parameter

$$Z = 0.330BA^{-3}M^{1/2} \qquad (6.20.10)$$

as

$$\frac{\alpha_s^5 - \alpha_s^3}{M^{1/2}} = 1.27\times 0.330BA^{-3} \qquad (6.20.11)$$

and

$$\frac{\alpha_s^3 - 1}{M^{1/2}} = 1.91\times 0.330BA^{-3} \qquad (6.20.12)$$

respectively. Therefore, we can discuss the validity of these theories by plotting $(\alpha_s^5-\alpha_s^3)/M^{1/2}$ and $(\alpha_s^3-1)/M^{1/2}$ against $M^{1/2}$, using light scattering data. Typical example is shown in Fig. 6-20. It should be noted that the observed

<S^2> includes effects of the interaction between segments and solvent, since different kinds of solvent are used in the experiments. Generally, the solvent-polymer interaction parameter exhibits anomalous behavior, then <S^2> or α depends on molecular weight in low molecular weight range, resulting in inconsistency with theories. In Flory's theory, molecular weight dependence

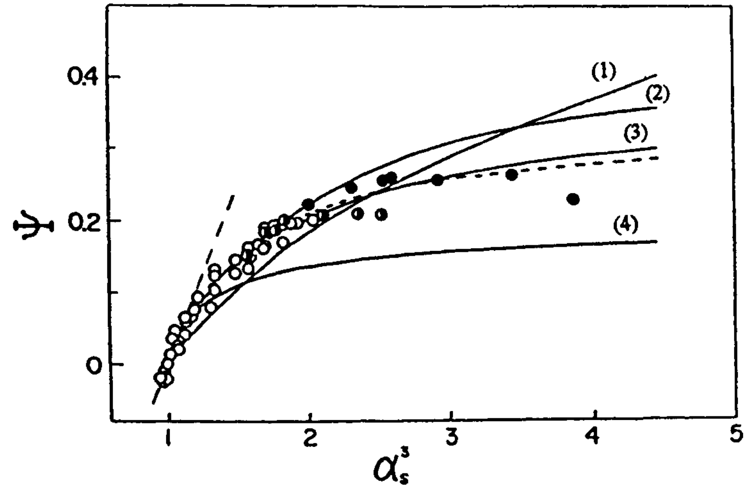

Fig. 6-20 Ψ as a function of α_s^3 observed and calculated using different theories. Polychloroprene fractions in trans-decalin at different temperatures(○), in n-butyl acetate at 25°C (◑), in carbon tetrachloride at 25°C (●). Solid lines, calculated from various theories cited in the text; (1)Flory (2) modified Flory (3)Yamakawa (4)Fixman-Kurata. Dashed line is the best fit to the plotted points. (See T.Norisuye, K.Kawahara, A.Teramoto, and H.Fujita, *J.Chem.Phys.* **49**, 4330 (1968))

[1] P.J.Flory, *J.Chem. Phys.* **17**, 303 (1949); P.J.Flory and W.R.Krigbaum, *J. Chem. Phys.* **18**, 1086 (1950); T.A.Orofino and P.J.Flory, *J.Chem.Phys.* **26**, 1067 (1957) [2] B.H.Zimm, W.H.Stockmayer and M.Fixman, *J. Chem. Phys.* **21**, 1716 (1953); M.Fixman, *J. Chem. Phys.* **23**, 1656 (1955); H. Yamakawa, *J. Phys. Soc. Japan* **13**, 87 (1958); A.C.Albrecht, *J.Chem.Phys.* **27**, 1002 (1957) [3] H.Yamakawa and G.Tanaka, *J. Chem. Phys.* **47**, 3991 (1967); H.Yamakawa, *J.Chem. Phys.* **48**, 2103 (1968) [4] M.Kurata, M.Fukatsu,H.Sotobayashi and H.Yamakawa, *J.Chem.Phys.* **41**, 139 (1964); M.Fixman, *J.Chem. Phys.* **36**, 3123 (1962).

of ΔF_{el} is not taken into account and an approximation of $M \rightarrow \infty$ is used for the estimation of concentration inside the coil. In Fixman's theory, molecular weight effects are included only in a many-body effect of cluster expansion, i.e., in higher order coefficients of Z.

Chapter 7 Light Scattering

<<Problem 7-1>> Rayleigh's equation for scattered light intensity

Suppose *N* optically isotropic scattering particles of the same shape in a scattering volume V. Perpendicularly polarized incident monochromatic light with vibration number ω_0 travels along positive x-axis with the electric vector polarized along xz plane. Calculate the **scattered light intensity $\mathbf{I_s(r)}$** observed at a point P where r is the distance from the standard particle at the origin O to the point P and prove that $I_s(r)$ is inversely proportional to the fourth power of the wave length λ (**Rayleigh's λ^{-4} law**). The optical geometry is shown in Fig. 7-1.

Answer

Light is electromagnetic field which propagates in time and space. The electric field of light in the direction **r** is expressed as

$$\mathbf{E}=\mathbf{E}_0\cos\left(2\pi\nu\,t-\frac{2\pi}{\lambda}\,\mathbf{r}\right) \tag{7.1.1}$$

where ν is the frequency, λ the wave length of light, t the time and **r** denotes

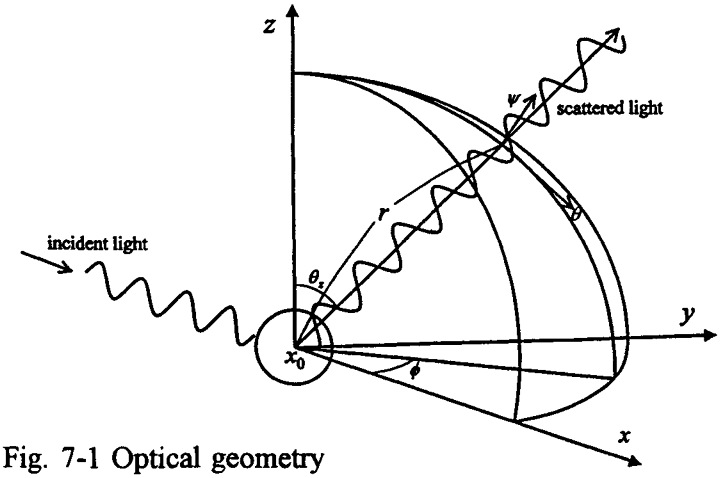

Fig. 7-1 Optical geometry

an arbitrary point. When an isolated particle is illuminated by a parallel beam of linearly polarized radiation, the particle becomes polarized in the electromagnetic field due to the displacement of the electrons with respect to the nuclei. For the harmonically oscillating electric field **E** of Eq. (7.1.1), a synchronously vibrating electric dipole **P** is induced (Lord Rayleigh, 1871). Then a scattered light is emitted from the dipole (secondary wave). The relation between **E** and **P** for the particle at a point $\mathbf{r}_0$ is given by

$$\mathbf{P} = \alpha\mathbf{E} = \alpha\mathbf{E}_0 \cos\left(2\pi\nu t - \frac{2\pi}{\lambda}\mathbf{r}_0\right) = \mathbf{P}_0 \cos\left(2\pi\nu t - \frac{2\pi}{\lambda}\mathbf{r}_0\right) \qquad (7.1.2)$$

where the proportional coefficient α is the polarizability. Since Eq. (7.1.2) should be independent of the position of the particle, it is sufficient to consider the equation

$$\mathbf{P} = \alpha\mathbf{E} = \alpha\mathbf{E}_0 \cos(2\pi\nu t) = \mathbf{P}_0 \cos(2\pi\nu t) \qquad (7.1.3)$$

instead of Eq. (7.1.2). Here, we assume that the solution of the scattering particles be sufficiently dilute so that the scattered light from the particles are regarded as independent and the multiple scattering is negligible. The scattered light at a point P which is distant from the particle by r has an electric field polarized along θ, E_θ, and a magnetic field polarized along ψ, H_ψ. According to the electromagnetic theory,

$$E_\theta = \frac{(2\pi)^2 P_0 \sin\theta_z}{\lambda^2 r}\cos\left(2\pi\nu t - \frac{2\pi}{\lambda} r\right) \qquad (7.1.4)$$

$$H_\psi = \frac{(2\pi)^2 P_0 \sin\theta_z}{\lambda^2 r}\sin\left(2\pi\nu t - \frac{2\pi}{\lambda} r\right) \qquad (7.1.5)$$

The time average of the electric energy per unit volume $\overline{E^2}/(8\pi)$ is given by the integration of Eq. (7.1.4) as

$$\begin{aligned}
\frac{1}{8\pi}\overline{E^2} &= \frac{1}{T}\cdot\frac{1}{8\pi}\int_0^T E^2 dt \\
&= \frac{1}{T}\cdot\frac{1}{8\pi}\int_0^{1/\nu}\frac{(2\pi)^4 P_0{}^2 \sin^2\theta_z}{\lambda^4 r^2}\cos^2\left(2\pi\nu t - \frac{2\pi}{\lambda} r\right)dt \\
&= \frac{1}{T}\cdot\frac{1}{8\pi}\cdot\frac{(2\pi)^4 P_0{}^2 \sin^2\theta_z}{\lambda^4 r^2}\cdot\int_0^{1/\nu}\cos^2\left(2\pi\nu t - \frac{2\pi}{\lambda} r\right)dt \\
&= \frac{1}{T}\cdot\frac{1}{8\pi}\cdot\frac{(2\pi)^4 P_0{}^2 \sin^2\theta_z}{\lambda^4 r^2}\cdot\frac{T}{2} \qquad (7.1.6)
\end{aligned}$$

Here, the integration is performed by putting x=2πνt-2πr/λ (dt=dx/2πν) as

$$\begin{aligned}\int_0^{1/\nu}\cos^2\left(2\pi\nu t-\frac{2\pi}{\lambda}r\right)dt&=\int_0^{x_0}\frac{\cos^2 x}{2\pi\nu}dx=\frac{1}{2\pi\nu}\left[\frac{1}{4}\sin 2x+\frac{x}{2}\right]_0^{x_0}\\&=\frac{1}{2\pi\nu}\left[\frac{1}{4}\sin\left(4\pi\nu t-\frac{4\pi}{\lambda}r\right)+\frac{1}{2}\left(2\pi\nu t-\frac{2\pi}{\lambda}r\right)\right]_0^{1/\nu}\\&=\frac{1}{2\pi\nu}\left\{\frac{1}{4}\left[\sin 4\pi\nu t\cos\frac{4\pi}{\lambda}r-\cos 4\pi\nu t\sin\frac{4\pi}{\lambda}r\right]_0^{1/\nu}+\frac{1}{2}\left[2\pi\nu t-\frac{2\pi}{\lambda}r\right]_0^{1/\nu}\right\}\\&=\frac{\pi}{2\pi\nu}=\frac{1}{2\nu}=\frac{T}{2}\end{aligned}\tag{7.1.7}$$

Similarly, we can calculate the time average of magnetic field and obtain

$$\frac{1}{8\pi}\overline{E^2}=\frac{1}{8\pi}\overline{H^2}=\frac{(2\pi)^4 P_0{}^2\sin^2\theta_z}{8\pi\lambda^4 r^2}\cdot\frac{1}{2}\tag{7.1.8}$$

The electromagnetic energy per unit volume is given by Eq. (7.1.8), and is transferred with velocity of light c. The intensity of light is defined by the energy transferred per unit cross sectional area and unit time. Thus we have the scattered light intensity I as

$$I_z=\frac{\left(\overline{E^2}+\overline{H^2}\right)c}{8\pi}=\frac{c}{4\pi}\cdot\frac{(2\pi)^4\sin^2\theta_z}{\lambda^4 r^2}\cdot\frac{P_0^2}{2}=\frac{c}{4\pi}\cdot\frac{(2\pi)^4\sin^2\theta_z}{\lambda^4 r^2}\cdot\frac{\alpha^2 E_0^2}{2}\tag{7.1.9}$$

From Eq. (7.1.1), incident light intensity I_0 is obtained as

$$\overline{E^2}=\frac{E_0{}^2}{T}\int_0^{1/\nu}\cos^2\left(2\pi\nu t-\frac{2\pi}{\lambda}r\right)dt=\frac{E_0{}^2}{T}\cdot\frac{T}{2}=\frac{E_0{}^2}{2}\tag{7.1.10}$$

$$I_0=\frac{c}{8\pi}\left(\overline{E^2}+\overline{H^2}\right)=\frac{c}{4\pi}\cdot\frac{E_0^2}{2}\tag{7.1.11}$$

From Eqs. (7.1.9) and (7.1.11), we have

$$I_z=\frac{(2\pi)^4\sin^2\theta_z\alpha^2}{\lambda^4 r^2}I_0\tag{7.1.12}$$

Thus, the scattered light intensity is inversely proportional to fourth power of wave length λ.

---

* Lord Rayleigh (J. W. Strutt) in 1871 gave the first theoretical explanation (the dipole radiator theory) to the phenomena of light scattering by molecules in a gas in terms of the electromagnetic theory. Rayleigh considered that the oscillating electric field of light incident upon a transparent optically isotropic particle when radiation is small compared with the wave length of the light induce an oscillating electric moment in the particle (See Lord Rayleigh, *Phil. Mag. Ser. 4*, **41**, 447 (1871) and G. Oster, *Chem. Rev.* **43**, 319 (1948)).

* Electric field can also be expressed using an exponential form as

$$\mathbf{E}=\mathbf{E}_0\exp(-i(\omega_0 t+\mathbf{q}_0\cdot\mathbf{r})) \qquad (7.1.13)$$

where ω_0 is the vibration number and $\mathbf{q}_0$ is the wave vector of the incident beam.
If there are N particles in a volume V, the relation between **E** and **P** for *j* th particle is given by

$$\mathbf{P}_j=\alpha\mathbf{E}_j \qquad (7.1.14)$$

If we denote the vector from the standard particle at the origin to the *j* th particle as $\mathbf{r}_j$, then the total electric field is expressed as

$$\mathbf{E}_s(t)=\sum_{j=1}^{N}\mathbf{E}_j=\sum_{j=1}^{N}\mathbf{E}_{0j}(t)\exp\left[i\mathbf{q}\cdot\mathbf{r}_j(t)\right]\exp(-i\omega_0 t)\exp(-i\mathbf{q}_s\cdot\mathbf{r}) \qquad (7.1.15)$$

where $\mathbf{q}_s$ and $\mathbf{q}$ are the wave vector of the scattered light and the scattering wave vector ($=\mathbf{q}_s-\mathbf{q}_0$), respectively, the magnitude of $\mathbf{q}$ is $q=4\pi/\lambda\sin(\theta/2)=4\pi n/\lambda_0\sin(\theta/2)$ where n is the refractive index of the solvent and λ_0 is the wavelength in vacuo.
The scattered light intensity I_z observed at P is calculated as the time average $<\mathbf{E}_s{}^*\mathbf{E}_s>$ as

$$I_z=\text{\AE}_0^2\frac{\omega_0^4\alpha^2\sin^2\theta_z}{c^4r^2}\frac{1}{T}\int_0^T\cos^2(\omega_0 t-q_s r)dt$$

$$=\text{\AE}_0^2\frac{\omega_0^4\alpha^2\sin^2\theta_z}{c^4r^2}\frac{1}{T}\left\{\frac{1}{\omega_0}\left[\frac{1}{4}\sin^2\omega_0 t\cos 2q_s r-\cos 2\omega_0 t\sin 2q_s r\right]+\frac{1}{2}\left[\omega_0 t-q_s r\right]\right\}_0^T$$

$$=\text{\AE}_0^2\frac{\omega_0^4\alpha^2\sin^2\theta_z}{c^4r^2}=\text{\AE}_0^2\frac{16\pi^4\alpha^2\sin^2\theta_z}{\lambda^4r^2} \qquad (7.1.16)$$

Eq. (7.1.16) is, of course, consistent with Eq. (7.1.12).
Similarly, when the incident light is polarized along xy plane, the scattered light intensity I_y is calculated as

$$I_y = \mathcal{N}E_0^2 \frac{16\pi^4\alpha^2\sin^2\theta_y}{\lambda^4 r^2} \tag{7.1.17}$$

If the incident light is natural light or non-polarized light, the scattered light intensity I_s is the sum of Eqs. (7.1.16) and (7.1.17) as

$$\begin{aligned} I_s &= I_y + I_z \\ &= \mathcal{N}E_0^2 \frac{8\pi^4\alpha^2(\sin^2\theta_y + \sin^2\theta_z)}{\lambda^4 r^2} = \mathcal{N}E_0^2 \frac{8\pi^4\alpha^2}{\lambda^4 r^2}(1+\cos^2\theta) \end{aligned} \tag{7.1.18}$$

Here we use the relatioship $\sin^2\theta_y + \sin^2\theta_z = (1-\cos^2\theta_y) + (1 - \cos^2\theta_z) = 2 - (1 -\cos^2\theta) = 1 + \cos^2\theta$.

<<Problem 7-2-a>> Total scattered light intensity

Using Eq. (7.1.17), derive the equation for the total scattered light intensity for a particle in unit volume

$$I_{total} = \frac{128\pi^5}{3\lambda^4}\alpha^2 I_0 \tag{7.2.1}$$

Answer

The total scattered light intensity is calculated by integrating Eq. (7.1.18) over all directions as

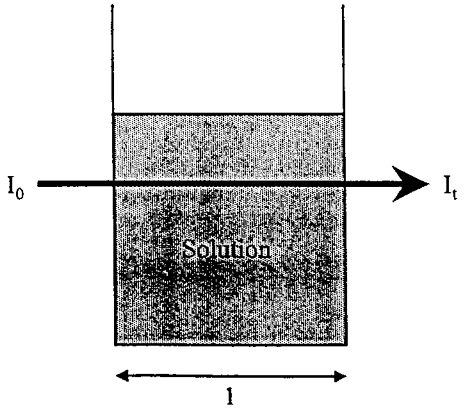

Fig. 7-2 Attenuation of light intensity in solution.

$$\begin{aligned} I_{\text{total}} &= \int_0^{2\pi}\int_0^{\pi} I r^2 \sin\theta d\theta d\varphi = \int_0^{2\pi}\int_0^{\pi}\frac{8\pi^4}{\lambda^4 r^2} r^2 \sin\theta(1+\cos^2\theta)\alpha^2 I_0 d\theta d\varphi \\ &= \frac{8\pi^4}{\lambda^4}\alpha^2 I_0 \int_0^{2\pi}\int_0^{\pi}(\sin\theta + \sin\theta\cos^2\theta)d\theta d\varphi \\ &= \frac{8\pi^4}{\lambda^4}\alpha^2 I_0 2\pi\int_0^{\pi}(\sin\theta + \sin\theta\cos^2\theta)d\theta = \frac{128\pi^5}{3\lambda^4}\alpha^2 I_0 \end{aligned} \tag{7.2.2}$$

Note that the area element at the radius r is given by $(rd\theta)(r\sin\theta d\psi)=r^2\sin\theta d\theta d\psi$.

<<Problem 7-2-b>> Turbidity (I)

When incident light with intensity I_0 passes through a polymer solution, the intensity decreases due to the light scattered by the polymer molecules. The transmitted light intensity of the beam emerging at a distance l is given by

$$I_t = I_0 \exp(-\tau l) \tag{7.2.3}$$

The attenuation coefficient τ is called the **turbidity**. Suppose there are N_1 molecules in unit volume. Show turbidity is proportional to N_1.

Answer

Equation (7.2.3) is rewritten as

$$\tau = -(\frac{1}{l})\ln(\frac{I_t}{I_0}) = -(\frac{1}{l})\ln(1-\frac{I_0-I_t}{I_0}) \tag{7.2.4}$$

In dilute solutions, $(I_0-I_t)/I_0<<1$. Then, we can neglect the higher order terms of the Taylor series of the logarithmic term as

$$\tau = -\left(\frac{1}{l}\right)\ln\left(1-\frac{I_0-I_t}{I_0}\right) \cong (\frac{1}{l})\frac{I_0-I_t}{I_0} \tag{7.2.5}$$

The intensity decrease in the solution is identical to the total intensity scattered by the molecules in the solution. The intensity scattered by a particle in unit volume is calculated as

$$I_{\text{total}} = \frac{128\pi^5}{3\lambda^4}\alpha^2 I_0 \tag{7.2.1}$$

Then the turbidity per unit length is obtained as

$$\tau = \frac{I_0 - I_t}{I_0} = \frac{\mathcal{N}_1 I_{\text{total}}}{I_0} = \frac{128\pi^5}{3\lambda^4}\alpha^2 \mathcal{N}_1 \tag{7.2.6}$$

Thus, the turbidity is proportional to the number of molecules in unit volume.

<<Problem 7-3>> Rayleigh ratio

Derive the relationship between the **Rayleigh ratio** defined by

$$R_\theta = \frac{I_s r^2}{I_0} \tag{7.3.1}$$

and the number of molecules per unit volume of a polymer solution, $\mathcal{N}_1$, where r is the distance from the solution to the detector and I_s and I_0 are the scattered and incident light intensity, respectively.

Answer

According to Eq. (7.1.18), the intensity I_s in the direction of θ scattered by $\mathcal{N}_1$ particles in unit volume of the polymer solution is given by

$$I_s = \frac{8\pi^4}{\lambda^4 r^2}(1+\cos^2\theta)\alpha^2 I_0 \mathcal{N}_1 \tag{7.3.2}$$

Thus, R_θ is rewritten as

$$R_\theta = \frac{8\pi^4}{\lambda^4}(1+\cos^2\theta)\alpha^2 \mathcal{N}_1 \tag{7.3.3}$$

---

* **Rayleigh ratio** R_θ is independent of the distance from the observed particle to the detector and the intensity of the incident beam. It only depends on the shape and the size of the scattering particle, the scattering angle and the concentration. The factor $(1+\cos^2\theta)$ is the correction for natural light. Reduced scattered light intensity R'_θ is defined by R_θ divided by $(1+\cos^2\theta)$.

* The **turbidity per unit length** τ is related to R'_θ as

$$I_0 - I_t = 2\pi R'_\theta I_0 \int_0^\pi (1+\cos^2\theta)\sin\theta d\theta$$

$$= 2\pi R'_\theta I_0 \left[\int_0^\pi \sin\theta d\theta + \int_0^\pi \cos^2\theta \sin\theta d\theta\right] = \frac{16}{3}\pi R'_\theta I_0$$

$$\tau = \frac{I_0 - I_t}{I_0} = \frac{16}{3}\pi R'_\theta \tag{7.3.4}$$

According to <<Problem 7-10>>, KC/R_θ can be expanded as a power series of C as

$$\frac{KC}{R'_\theta} = \frac{1}{M} + 2A_2C + 3A_3C^2 + \cdots \tag{7.3.5}$$

with

$$K = \frac{2\pi^2}{\lambda^4 N_A} n^2 \left(\frac{dn}{dC}\right)^2 \tag{7.3.6}$$

In the limit of C →0, we have

$$\lim_{C\to 0} \tau = MHC = \frac{32}{3}\frac{\pi^3 n^2}{\lambda^4 N_A}\left(\frac{dn}{dC}\right)^2 MC \tag{7.3.7}$$

where

$$H \equiv \frac{16}{3}\pi K = \frac{32}{3}\frac{\pi^3 n^2}{\lambda^4 N_A}\left(\frac{dn}{dC}\right)^2$$

Thus, we can determine the molecular weight of the polymer M by measuring the turbidity of the dilute polymer solution and the difference in refractive index of solution and solvent, and extrapolating it to C→0, without introducing any kind of empirical constants.

$$H \lim_{c\to 0}(C/\tau) = 1/M \tag{7.3.7'}$$

<<Problem 7-4>> Scattering from large particles

If scattering particles (such as polymers) are large compared with the wave length of the incident light, we must take account of the interference of the light scattered by different parts in the single particle. Derive the intensity of the scattered light from particles of arbitrary size.

Answer

We consider an optical geometry as shown in Fig.7-4. The induced dipoles at B and B', each scattered by *i* th or *j* th particle (or segment) are expressed from Eq. (7.1.2) as

$$P_i = P_0 \cos\left(2\pi\nu t - \frac{2\pi}{\lambda}\overline{Ai}\right) \tag{7.4.1}$$

$$P_j = P_0 \cos\left(2\pi\nu t - \frac{2\pi}{\lambda}\overline{A'j}\right) \tag{7.4.2}$$

The electric fields of the scattered light are expressed from Eq. (7.1.4) as

$$E_i = \frac{(2\pi)^2 P_0 \sin\theta_z}{\lambda^2 \overline{iB}} \cos\left\{\left(2\pi\nu t - \frac{2\pi}{\lambda}\overline{Ai}\right) - \frac{2\pi}{\lambda}\overline{iB}\right\} \tag{7.4.3}$$

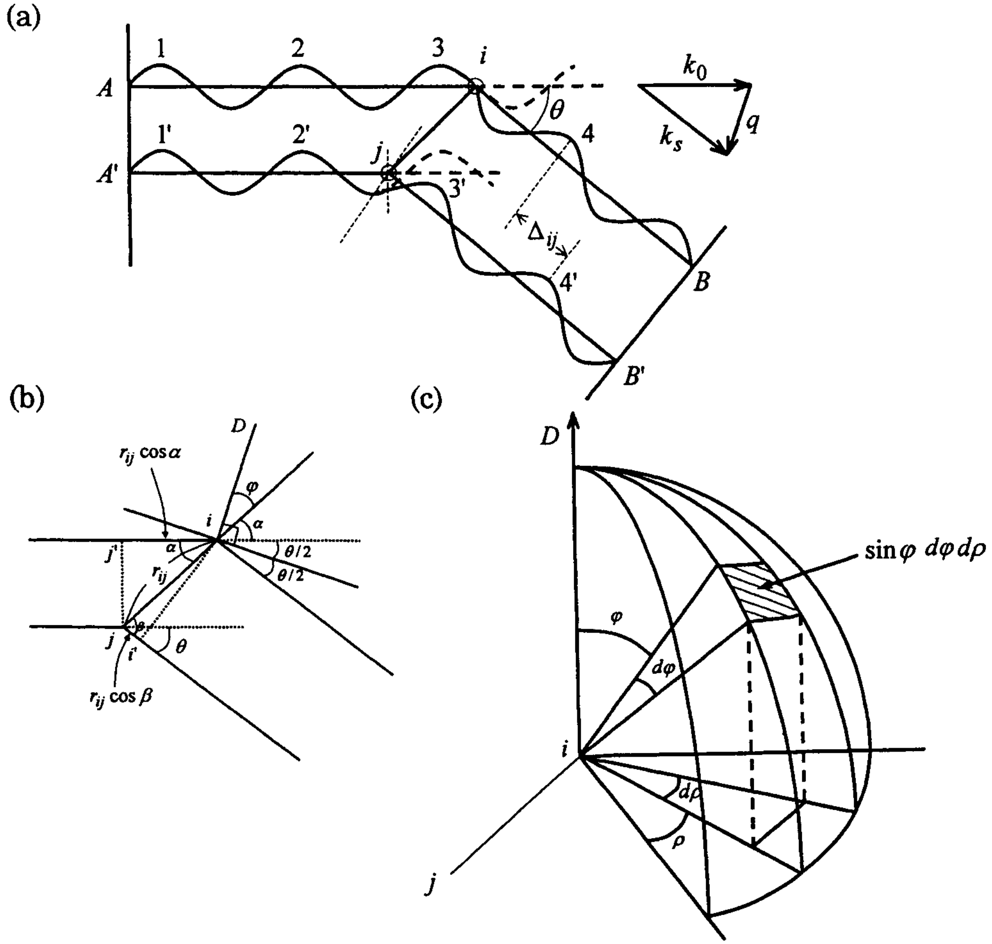

Fig. 7-4 Difference in phase of scattered light from points *i* and *j*

$$E_j = \frac{(2\pi)^2 P_0 \sin\theta_z}{\lambda^2 \overline{jB'}} \cos\left\{\left(2\pi\nu t - \frac{2\pi}{\lambda}\overline{A'j}\right) - \frac{2\pi}{\lambda}\overline{jB'}\right\} \tag{7.4.4}$$

respectively. The difference in phase of the scattered light is

$$\begin{aligned}\Delta_{ij} &= \frac{2\pi}{\lambda}\left(\overline{Ai} + \overline{iB}\right) - \frac{2\pi}{\lambda}\left(\overline{A'j} + \overline{jB'}\right) = \frac{2\pi}{\lambda}\left\{\left(\overline{Ai} - \overline{A'j}\right) - \left(\overline{jB'} - \overline{iB}\right)\right\} \\ &= \frac{2\pi}{\lambda}\left(\overline{j'i} - \overline{ij'}\right)\end{aligned} \tag{7.4.5}$$

Using the relationship

$$\left.\begin{aligned}\overline{j'i} &= r_{ij}\cos\alpha \\ \overline{ji'} &= r_{ij}\cos\beta\end{aligned}\right\} \tag{7.4.6}$$

Eq. (7.4.5) is rewritten as

$$\begin{aligned}\Delta_{ij} &= \frac{2\pi}{\lambda}\left(\overline{j'i} - \overline{ij'}\right) = \frac{2\pi}{\lambda} r_{ij}(\cos\alpha - \cos\beta) \\ &= \frac{4\pi}{\lambda} r_{ij} \sin\frac{\beta-\alpha}{2}\sin\frac{\beta+\alpha}{2}\end{aligned} \tag{7.4.7}$$

Putting the relationship $\beta-\alpha=\theta$ in Eq. (7.4.7), we have

$$\Delta_{ij} = \frac{4\pi}{\lambda} r_{ij}\sin\frac{\theta}{2}\sin\left(\frac{\theta}{2}+\alpha\right) = \frac{4\pi}{\lambda} r_{ij}\sin\frac{\theta}{2}\cos\left(\frac{\pi}{2}-\frac{\theta}{2}-\alpha\right) \tag{7.4.8}$$

Introducing parameters (See Note of Eq. (7.1.15))

$$\left.\begin{aligned}q &= \frac{4\pi}{\lambda}\sin\frac{\theta}{2} \\ \varphi &= \frac{\pi}{2} - \frac{\theta}{2} - \alpha\end{aligned}\right\} \tag{7.4.9}$$

Eq. (7.4.8) is reduced to

$$\Delta_{ij} = r_{ij} q \cos\varphi \tag{7.4.10}$$

If we approximate $iB \cong jB' = r$, Eqs. (7.4.3) and (7.4.4) are reduced to

$$E_i = \frac{(2\pi)^2 P_0 \sin\theta_z}{\lambda^2 r}\cos(2\pi\nu t') \tag{7.4.11}$$

$$E_j = \frac{(2\pi)^2 P_0 \sin\theta_z}{\lambda^2 r}\cos\left(2\pi\nu t' + \Delta_{ij}\right) \tag{7.4.12}$$

If a polymer consists of n segments, the electric field of the scattered light from the polymer is

$$E = E_0 + E_1 + \cdots + E_n = \sum_{i=0}^{n} E_i \tag{7.4.13}$$

The intensity of the scattered light is expressed as

$$I = \frac{c}{8\pi}\left(\overline{E^2} + \overline{H^2}\right) = \frac{c}{4\pi}\overline{E^2} = \frac{c}{4\pi}\overline{\left(\sum_{i=0}^{n} E_i\right)^2} = \frac{c}{4\pi}\sum_{i=0}^{n}\sum_{j=0}^{n}\overline{E_i E_j} \tag{7.4.14}$$

The average in Eq. (7.4.14) is calculated using Eqs. (7.4.11) and (7.4.12) as

$$\begin{aligned}
\overline{E_i E_j} &= \frac{1}{T}\int_0^T \left(\frac{(2\pi)^2 P_0 \sin\theta_z}{\lambda^2 r}\right)^2 \cos(2\pi\nu t')\cos\left(2\pi\nu t' + \Delta_{ij}\right)dt' \\
&= \frac{1}{2}\frac{(2\pi)^4 {P_0}^2 \sin{\theta_z}^2}{\lambda^4 r^2}\left[\frac{1}{T}\int_0^T \cos\left(4\pi\nu t' + \Delta_{ij}\right)dt' + \frac{1}{T}\int_0^T \cos\Delta_{ij}dt'\right] \\
&= \frac{1}{2}\frac{(2\pi)^4 {P_0}^2 \sin{\theta_z}^2}{\lambda^4 r^2}\cos\Delta_{ij}
\end{aligned} \tag{7.4.15}$$

The integration of the first term in the bracket of Eq. (7.4.15) is carried out using a parameter $X = 4\pi\nu t' + \Delta_{ij}$ ($dX = 4\pi\nu dt'$) as

$$\begin{aligned}
\int_0^T \frac{\cos X}{4\pi\nu}dX &= \left|\frac{\sin\left(4\pi\nu t' + \Delta_{ij}\right)}{4\pi\nu}\right|_0^{1/\nu} = \frac{1}{4\pi\nu}\left|\sin 4\pi\nu t' \cos\Delta_{ij} - \cos 4\pi\nu t' \sin\Delta_{ij}\right|_0^{1/\nu} \\
&= \left(\frac{1}{4\pi\nu}\right)\left\{\left(\sin 4\pi \cos\Delta_{ij} + \cos 4\pi \sin\Delta_{ij}\right) - \left(0\cdot\cos\Delta_{ij} + 1\cdot\sin\Delta_{ij}\right)\right\} \\
&= \frac{\left(\sin\Delta_{ij} - \sin\Delta_{ij}\right)}{4\pi\nu} = 0
\end{aligned} \tag{7.4.16}$$

Substitution of Eq. (7.4.15) in Eq. (7.4.14) yields

$$I = \frac{c}{4\pi}\cdot\frac{1}{2}\cdot\frac{(2\pi)^4 {P_0}^2 \sin{\theta_z}^2}{\lambda^4 r^2}\sum_{i=0}^{n}\sum_{j=0}^{n}\cos\Delta_{ij} \tag{7.4.17}$$

From Eq. (7.4.10), Eq. (7.4.17) is rewritten as

$$I=\frac{c}{4\pi}\cdot\frac{1}{2}\cdot\frac{(2\pi)^4 P_0{}^2 \sin\theta_z{}^2}{\lambda^4 r^2}\sum_{i=0}^{n}\sum_{j=0}^{n}\cos\left(qr_{ij}\cos\varphi\right) \tag{7.4.18}$$

The average in Eq. (7.4.18) is calculated as

$$\left\langle\cos\left(qr_{ij}\cos\varphi\right)\right\rangle=\frac{\int_0^{2\pi}\int_0^{\pi}\cos\left(qr_{ij}\cos\varphi\right)\sin\varphi d\varphi d\rho}{\int_0^{2\pi}\int_0^{\pi}\sin\varphi d\varphi d\rho}=\frac{\sin\left(qr_{ij}\right)}{qr_{ij}} \tag{7.4.19}$$

The integration is carried out by using a parameter X=cosφ (dX=-sinφdφ),

$$\int_0^{-1}-\cos\left(qr_{ij}x\right)dx=-\left|\frac{\sin\left(qr_{ij}x\right)}{qr_{ij}}\right|_0^{-1}=-\left|\frac{\sin\left(qr_{ij}\cos\varphi\right)}{qr_{ij}}\right|_0^{\pi}$$

$$=\frac{-1}{qr_{ij}}\left(\sin\left(-qr_{ij}\right)-\sin\left(qr_{ij}\right)\right)=\frac{2\sin\left(qr_{ij}\right)}{qr_{ij}} \tag{7.4.20}$$

$$\int_0^{2\pi}\int_0^{\pi}\cos\left(qr_{ij}\cos\varphi\right)\sin\varphi d\varphi d\rho=\int_0^{2\pi}\frac{2\sin\left(qr_{ij}\right)}{qr_{ij}}d\rho=4\pi\frac{\sin\left(qr_{ij}\right)}{qr_{ij}} \tag{7.4.21}$$

$$\int_0^{2\pi}\int_0^{\pi}\sin\varphi d\varphi d\rho=\int_0^{2\pi}\left|-\cos\varphi\right|_0^{\pi}d\rho=2\pi(2)=4\pi \tag{7.4.22}$$

Thus we finally obtain

$$I(\theta)=\frac{c}{4\pi}\cdot\frac{8\pi^4 P_0^2\sin^2\theta_z}{\lambda^4 r^2}\sum_{i=0}^{n}\sum_{j=0}^{n}\frac{\sin qr_{ij}}{qr_{ij}}=I_0\frac{16\pi^4\sin^2\theta_z}{\lambda^4 r^2}\sum_{i=0}^{n}\sum_{j=0}^{n}\frac{\sin qr_{ij}}{qr_{ij}} \tag{7.4.23}$$

(See M. Kaneko and K. Ogino, *Polymer Science (Kobunshi Kagaku)*, Kyouritsu Pub. Co., 1965, p130)

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* If we use exponential form of electric field (Eq. (7.1.13)), the problem is solved as follows. We consider the scattered light from the positions $\mathbf{r}_j$ and $\mathbf{r}_l$ at time t=0. The scattered light intensity is calculated as

$$\underset{t=0}{I_s(\theta)}=\left\langle\mathbf{E}_s^*\cdot\mathbf{E}_s\right\rangle$$

$$=\frac{\omega^4\alpha^2E_0^2(1+\cos^2\theta)}{c^4r^2}\left\langle\sum_{j=1}^{N}\exp\left[i\mathbf{q}\cdot\mathbf{r}_j(0)\right]\sum_{l=1}^{N}\exp\left[-i\mathbf{q}\cdot\mathbf{r}_l(0)\right]\right\rangle$$

$$= A^2\left\langle \sum_{j=1}^{N}\sum_{l=1}^{N} \exp\left\{-i\mathbf{q}\cdot\left[\mathbf{r}_l(0)-\mathbf{r}_j(0)\right]\right\}\right\rangle = A^2\sum_{j=1}^{N}\sum_{l=1}^{N}\left\langle \cos \mathbf{q}\cdot\mathbf{r}_{jl}\right\rangle \tag{7.4.24}$$

with

$$\mathbf{q} = \mathbf{q}_s - \mathbf{q}_0,\ \mathbf{r}_{jl} = \mathbf{r}_j - \mathbf{r}_l \tag{7.4.25}$$

and

$$A = \frac{\omega^2 \alpha E_0 (1 + \cos^2\theta)^{1/2}}{c^2 r} \tag{7.4.26}$$

Let's denote the angle between $\mathbf{r}_j$ and $\mathbf{r}_l$ as β, that is,

$$\mathbf{q}\cdot\mathbf{r}_{jl} = qr_{jl}\cos\beta \tag{7.4.27}$$

The average of $\cos(\mathbf{q}\mathbf{r}_{jl})$ is calculated as

$$\left\langle \cos(\mathbf{q}\cdot\mathbf{r}_{jl})\right\rangle = \frac{\int_0^{\pi} \cos\left(qr_{jl}\cos\beta\right)\sin\beta\, d\beta}{\int_0^{\pi}\sin\beta\, d\beta} = \frac{\sin qr_{jl}}{qr_{jl}} \tag{7.4.28}$$

and then

$$I_s(\theta) = \frac{\omega^4\alpha^2 E_0^2\left(1+\cos^2\theta\right)}{c^4 r^2}\sum_{j=1}^{N}\sum_{l=1}^{N}\frac{\sin qr_{jl}}{qr_{jl}} \tag{7.4.29}$$

which agrees with Eq. (7.4.23).

<<Problem 7-5>> Particle scattering factor P(θ)

Particle scattering factor P(θ) is defined by

$$P(\theta) = \frac{I_S(\theta)}{I_S(0)} \tag{7.5.1}$$

Calculate P(θ) for $I_s(\theta)$ of a large particle

$$I_s(\theta)=\frac{\omega^4\alpha^2E_0^2\left(1+\cos^2\theta\right)}{c^4r^2}\sum_{j=1}^{N}\sum_{l=1}^{N}\frac{\sin qr_{jl}}{qr_{jl}} \tag{7.4.29}$$

in case of $\mathbf{q}\mathbf{r}_{jl} \ll 1$.

Answer

$\sin(\mathbf{q}\mathbf{r}_{jl})$ is expanded in a Taylor series as

$$\sin q\,r_{jl}=q\,r_{jl}-\frac{1}{6}(q\,r_{jl})^3+ \tag{7.5.2}$$

Then Eq. (7.4.29) is expressed as

$$I_s(\theta)=\frac{\omega^4\alpha^2E_0^2\left(1+\cos^2\theta\right)}{c^4r^2}\sum_{j=1}^{N}\sum_{l=1}^{N}\left\{1-\frac{1}{6}\left(qr_{jl}\right)^2+\cdots\right\} \tag{7.5.3}$$

I(0) is obtained by putting

$\mathbf{q}\cdot(\mathbf{r}_i-\mathbf{r}_j)\cong 0$

in Eq. (7.5.3) as

$$I(0)=\frac{\omega^4\alpha^2E_0^2\left(1+\cos^2\theta\right)}{c^4r^2}\sum_{j=1}^{N}\sum_{l=1}^{N}1=\frac{N^2\omega^4\alpha^2E_0^2\left(1+\cos^2\theta\right)}{c^4r^2} \tag{7.5.4}$$

The ratio of Eqs. (7.5.3) and (7.5.4) is

$$\begin{aligned}P(\theta)&=\frac{1}{N^2}\sum_{j=1}^{N}\sum_{l=1}^{N}\left\{1-\frac{1}{6}\left(qr_{jl}\right)^2+\cdots\right\}=1-\frac{q^2}{6N^2}\sum_{j}\sum_{l}r_{jl}^{\,2}+\cdots\\&=1-\frac{1}{3}q^2\left\langle S^2\right\rangle+\cdots\end{aligned} \tag{7.5.5}$$

Here $\langle S^2\rangle$ is the mean square radius of gyration defined by

$$\left\langle S^2\right\rangle=\frac{1}{2N^2}\sum_{j}\sum_{l}r_{jl}^{\,2}$$

(See Eq. (6.9.12))

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* Debye noticed that 'dissymmetry in angular distribution of scattered light intensity (See P(θ)) can be used to obtain information about particle size' and 'it is much easier to relate

particle form and particle size to the observed scattering and 'the molecular weight of the substance in solution can be evaluated without introducing any kind of empirical parameters'. (See P. Debye, *J. Appl. Phys.* **15**, 338 (1944))

<<Problem 7-6>> Guinier plot

Show how to determine the radius of gyration of molecular chains by means of light scattering.

Answer

According to <<Problem 7-5>>

$$P(\theta) = 1 - \frac{1}{3}q^2 \left\langle S^2 \right\rangle + \cdots \qquad (7.5.5)$$

When θ is sufficiently small, P(θ) is approximated as

$$P(\theta) \cong 1 - \frac{1}{3}q^2 \left\langle S^2 \right\rangle \qquad (7.6.1)$$

Thus, we can determine $<S^2>$ from the slope of the plot P(θ) vs. q^2 (See A. Guinier, *Ann. Phys. (Paris)* **12**, 161 (1939); *J. chim.Phys.* **40**, 133 (1943)).

<<Problem 7-7-a>> Determination of the shape of particles from P(θ) (I)

Derive the expression for **P(θ) for**

(a) **spherical particle with radius a**

(b) **rod-like particle with length L**

(c) **Gaussian chain.**

Answer

(a) **Spherical particle**:

Let's denote the scattering vector as **q**, the vector connecting the center of the spherical particle and an arbitrary point P in the particle as $\mathbf{r}_p$ and the angle between **q** and $\mathbf{r}_p$ as α. The phase of the light scattered from the points where $\mathbf{q}\mathbf{r}_p$ is a constant is the same. The volume of the element in the range of α between α and α+dα and $\mathbf{r}_p$ between $\mathbf{r}_p$ and $\mathbf{r}_p$+dr is $2\pi r_p^2 \sin\alpha d\alpha dr$

The scattered light intensity is given by

$$I_s = \left|E_s\right|^2 = \left|\sum_p \exp\left[i\mathbf{q}\cdot\mathbf{r}_p\right]\right|^2 \tag{7.7.1}$$

with

$$\left|\quad\right| = 2\pi\int_0^a \int_0^\pi \exp\left[i\mathbf{q}\cdot\mathbf{r}_p\right] r_p{}^2 \sin\alpha\, d\alpha\, dr_p \tag{7.7.2}$$

Putting $\cos\alpha=\xi$, $d\xi=-\sin\alpha d\alpha$, Eq. (7.7.2) is calculated as

$$\left|\quad\right| = -2\pi\int_0^a \int_1^{-1} \exp\left[i\mathbf{q}\cdot\mathbf{r}_p\right] r_p{}^2 d\xi\, dr_p = 2\pi\int_0^a \frac{1}{iqr}\left[\exp(iqr)\right]_1^{-1} r^2 dr$$

$$= 4\pi\int_0^a \frac{1}{q}\sin(qr) r dr = \frac{4\pi}{q}\left(-\frac{a}{q}\cos(aq) + \frac{1}{q^2}\sin(aq)\right)$$

Thus,

$$I_s = \left|E_s\right|^2 = \left(\frac{4\pi}{q}\right)^2 \left(-\frac{a}{q}\cos(aq) + \frac{1}{q^2}\sin(aq)\right)^2 = \frac{(4\pi)^2}{q^6}(-aq\cos(aq)+\sin(aq))^2$$

$$= \frac{a^6(4\pi)^2}{x^6}(\sin x - x\cos x)^2 \tag{7.7.3}$$

with $x \equiv aq$ and

$$q=(4\pi n/\lambda_0)(\sin\theta/2) \tag{7.7.4}$$

in the medium with the refractive index n.

I_0 is obtained by expanding sinx and cosx as a Taylor series and extrapolating to $q \to 0$ as

$$I_0 = \lim_{q\to 0} I_s = \lim_{x\to 0} \frac{a^6(4\pi)^2}{x^6}\left(x - \frac{x^3}{3!} + \frac{x^5}{5!} - \cdots - x\left(1 - \frac{x^2}{2!} + \cdots\right)\right)^2$$

$$= \lim_{x\to 0} a^6(4\pi)^2\left(\left(\frac{1}{2!} - \frac{1}{3!}\right) + \left(\frac{1}{5!} - \frac{1}{4!}\right)x^2 + \cdots\right)^2 = \frac{a^6(4\pi)^2}{9} \tag{7.7.5}$$

Then we find the **particle scattering factor for spherical particles** as

$$P(\theta) = \frac{I_s}{I_0} = \frac{9}{a^6(4\pi)^2}\frac{a^6(4\pi)^2}{x^6}\left(\sin x - x\cos x\right)^2$$

$$= \left[\frac{3}{x^3}\left(\sin x - x\cos x\right)\right]^2 \qquad (7.7.6)$$

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* Eq. (7.7.6) was first derived by Rayleigh (Lord Rayleigh, *Proc. Roy. Soc.* **A90**, 219 (1914).

(b) **Rod-like particle**:
The difference in phase of the light scattered at the points P and P′ along the rod depends on the distance between the two points. The total scattered light intensity I_s is calculated by summing up the intensity of the scattered light over the distance.

$$I_s \propto \sum_{P}\sum_{P'}\frac{\sin qr}{qr} \qquad (7.7.7)$$

The integral over P for $\mathbf{r}_{pp'}$=const. is

$$2(L - r_{pp'}) \qquad (7.7.8)$$

Approximating sum by integral, we have

$$I_s \propto 2\int_0^L \left(L - r\right)\frac{\sin qr}{qr}dr = 2L\int_0^L \frac{\sin qr}{qr}dr - 2\int_0^L \frac{\sin qr}{q}dr$$

$$= 2L\int_0^L \frac{\sin qr}{qr}dr - 2\frac{1}{q^2}\left(1 - \cos Lq\right) \qquad (7.7.9)$$

I_0 is obtained by expanding sin(qr) and cos(Lq) as a Taylor series and extrapolating to q→ 0 as

$$I_0 \cong \lim_{q\to 0} I_s = \lim_{q\to 0}\left[2L\int_0^L \left(\frac{qr - \frac{(qr)^3}{3!} + \cdots}{qr}\right)dr - \frac{2}{q^2}\left(1 - \frac{(qL)^2}{2!} + \cdots - 1\right)\right]$$

$$\cong 2L\int_0^L dr - L^2 = L^2 \tag{7.7.10}$$

Then we have the **particle scattering factor for rod-like molecules** as

$$P(\theta) = \frac{I_s}{I_0} = \frac{2}{L}\int_0^L \frac{\sin qr}{qr}dr - \frac{2}{(qL)^2}(1 - \cos Lq)$$

$$= \frac{q}{x}\int_0^L \frac{\sin qr}{qr}dr - \frac{2}{(2x)^2}(1 - \cos 2x) = \frac{1}{x}\int_0^{2x} \frac{\sin z}{z}dz - \left(\frac{\sin x}{x}\right)^2 \tag{7.7.11}$$

where

$$x \equiv \frac{1}{2}Lq \ , \ z \equiv qr$$

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* Eq. (7.7.11) was derived by Neugebauer (See T. Neugebauer, *Ann. Physik* **42**, 509 (1943)).

(c) **Gaussian chain**:

Let's take the pearl-necklace model. We denote the vector connecting the *k* th segment and *j* th segment as $\mathbf{r}_{jk}$. The number of combinations for a constant value of k-j is n-k-j. Since the number of ways of numbering to j and k is 2 (from left end or right end), the total number should be doubled. The scattered light intensity

$$I_s \propto \sum_j \sum_k \exp i\mathbf{q}\cdot\mathbf{r}_{pp'} \tag{7.7.12}$$

is calculated by approximating sum by integral as

$$I_s(\theta) \propto 2\int \sum_{j<k} \left(n - |k - j|\right) \exp\left(i\mathbf{q}\cdot\mathbf{r}_{jk}\right) W(\mathbf{r}_{jk})\, d\mathbf{r}_{jk} \tag{7.7.13}$$

with the distribution function of $\mathbf{r}_{jk}$;

$$W(\mathbf{r}_{jk}) = \left(\frac{3}{2\pi|k\text{-}j|b'^2}\right)^{\frac{3}{2}} \exp\left(-\frac{3\mathbf{r}_{jk}{}^2}{2|k\text{-}j|b'^2}\right)$$

where b' is the bond length. Using a rectangular coordinate $x_{jk}y_{jk}z_{jk}$, we have

$d\mathbf{r}_{jk} = dx_{jk}dy_{jk}dz_{jk}$, $\mathbf{r}_{jk} = x_{jk}{}^2 + y_{jk}{}^2 + z_{jk}{}^2$

Approximating sum by integral and using a parameter $p \equiv |k\text{-}j|$, we have

$$I_s(\theta) \propto 2\int_0^n (n\text{-}p)\,dp \int_{-\infty}^{\infty} dx_p \int_{-\infty}^{\infty} dy_p \int_{-\infty}^{\infty} dz_p \exp i(q_x x_p + q_y y_p + q_z z_p)$$

$$\times \left(\frac{3}{2\pi p b'^2}\right)^{\frac{3}{2}} \exp\left(-\frac{3\left(x_p{}^2 + y_p{}^2 + z_p{}^2\right)}{2pb'^2}\right) \tag{7.7.14}$$

Integration over x_p is carried out as

$$\int_{-\infty}^{\infty} \exp\left(iq_x x_p\right)\left(\frac{3}{2\pi p b'^2}\right)^{\frac{3}{2}} \exp\left(-\frac{3x_p{}^2}{2pb'^2}\right)dx_p$$

$$= \left(\frac{3}{2\pi p b'^2}\right)^{\frac{3}{2}} \int \exp\left(iq_x x_p - \frac{3x_p{}^2}{2pb'^2}\right)dx_p$$

$$= \left(\frac{3}{2\pi p b'^2}\right)^{\frac{3}{2}} \int \exp - \left(\left(\frac{3}{2pb'^2}\right)^{\frac{1}{2}} x_p - \frac{iq_x}{2}\left(\frac{3}{2pb'^2}\right)^{\frac{1}{2}}\right)^2 \exp\left(\frac{q_x{}^2}{4}\frac{2pb'^2}{3}\right)dx_p$$

$$= \exp\left(-\frac{2}{3}pb'^2 q_x{}^2\right) \tag{7.7.15}$$

Thus, $I_s(\theta)$ is calculated as

$$I_s(\theta) \propto 2\int_0^n (n\text{-}p)\, dp\, \exp\left(-\frac{2}{3}pb'^2q^2\right)$$

$$= 2\int_0^n n\exp\left(-\frac{2}{3}pb'^2q^2\right)dp \ - \ 2\int_0^n \exp\left(-\frac{2}{3}pb'^2q^2\right)p\, dp$$

$$= 2\int_0^n n\exp\left(-Ap\right)dp \ - \ 2\int_0^n p\exp\left(-Ap\right)dp$$

$$= \frac{2}{A^2}\exp\left(-An\right) - \frac{2}{A^2} + \frac{2n}{A} \tag{7.7.16}$$

with

$$A \equiv \frac{2}{3}b'^2q^2$$

Putting x=An, we have

$$I_s(\theta) \propto \frac{2n^2}{x^2}\left\{ \exp\left(-x\right) + x - 1\right\} \tag{7.7.17}$$

I_0 is calculated by extrapolating x to 0 as

$$I_0 \propto \lim_{x\to 0}\frac{2n^2}{x^2}\left\{ \exp\left(-x\right) + x - 1\right\} = \lim_{x\to 0}\frac{2n^2}{x^2}\left\{ 1 - x + \frac{x^2}{2!} \cdots + x - 1\right\} = n^2 \tag{7.7.18}$$

Thus the **particle scattering factor for a Gaussian chain** is obtained as

$$P(\theta) = \frac{I_s}{I_0} = \frac{2}{x^2}\left(\exp\left(-x\right) + x - 1\right) \tag{7.7.19}$$

with $x \equiv \frac{2}{3}nb'^2q^2$

---

* Eq. (7.7.19) was obtained by Debye (Lecture given at Polytechnic Institute of Brooklyn, New York, November 25, 1944, according to Oster's review (See G. Oster, *Chem. Rev.* **43**, 319 (1948), ref. 32)) and derived in detail by Zimm, Stein and Doty (See B. H. Zimm, R. S. Stein and P. Doty, *Polym. Bull.* **1**, 90 (1945) and see also Debye (P. Debye, *J. Phys. Colloid Chem.* **51**, 18 (1847))).

<<Problem 7-7-b>> Determination of the shape of particles from $P(\theta)$ (II)

Calculate the relative scattering intensity at $\theta=90^\circ$ with respect to $\theta=0^\circ$ for a spherical particle with diameter $2a=2000$Å in a solvent with refractive index $n=1.333$ for the incident light wavelength 628nm.

Answer

The parameter in Eq. (7.7.4), $x=aq$, is $(4\pi n/\lambda_0)a\sin(90^\circ/2)=2.17$. Thus, from Eq. (7.7.6), $P(90^\circ)=[(3/2.17^3)(0.826-2.17x\{-0.564\})]^2=0.361$.

<<Problem 7-8>> Determination of the shape of particles from $P(\theta)$ (III)

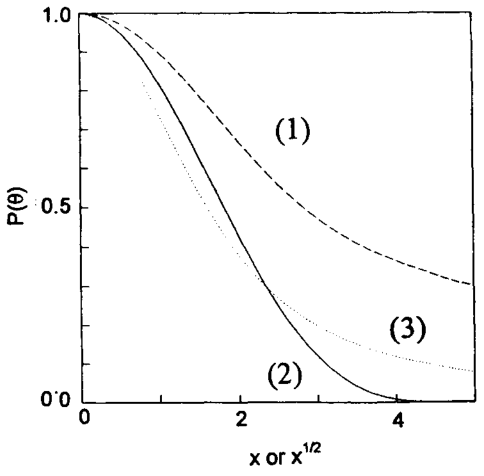

Fig. 7-8 Particle scattering factor $P(\theta)$ for basic particle shapes; abscissa is x for rods (1) and spheres (2), and $x^{1/2}$ for coils (3), where $x=(2\pi/\lambda)L\sin(\theta/2)$ for rods, $x=(4\pi/\lambda)a\sin(\theta/2)$ for spheres, and $x=(8\pi^2/3\lambda^2)nb'^2\sin^2(\theta/2)$ for coils.

---

* The scientist who first suggested the importance of light scattering approach to polymer solutions is P.Debye. He submitted a paper entitled "Light Scattering in Solutions" in *J. Appl. Phys* **15**, 338 (1944), where he said," In a general way the theoretical work involved is rather complicated. However, in the special field of polymers advantage can be taken from the fact that it is possible in many cases to adjust the solvent in such a way that the difference in refractivity between the solvent and the solute can be considered as small."

The **particle scattering factor P(θ) for rod-like particles, spherical particles and random coils** is given by

$$P(\theta) = \frac{I_s}{I_0} = \frac{1}{x}\int_0^{2x} \frac{\sin z}{z}dz - \left(\frac{\sin x}{x}\right)^2 \qquad (7.7.11)$$

$$x \equiv \frac{1}{2}Lq \ , \ z \equiv qr$$

$$P(\theta) = \left[\frac{3}{x^3}(\sin x - x\cos x)\right]^2 \qquad (7.7.6)$$

$$x \equiv aq$$

$$P(\theta) = \frac{2}{x^2}(\exp(-x) + x - 1) \qquad (7.7.19)$$

$$x \equiv \frac{2}{3}b'^2q^2n$$

respectively. Calculate P(θ) as a function of x or $x^{1/2}$.

Answer

Figure 7-8 shows P(θ) as a function of x for particles with various shapes.

<<Problem 7-9>> Determination of polarizability α

Show that the polarizability α can be determined by measuring the differential coefficient of the refractive index n with respect to the concentration C, dn/dC, as a function of C, and extrapolating it to C→ 0.

Answer

The polarization **P** induced in a homogeneous solvent in an electric field **E** is given by

$$\mathbf{P} = \varepsilon_0\mathbf{E} \qquad (7.9.1)$$

where ε_0 is the dielectric constant of the solvent. Suppose solutes are dissolved to make a sufficiently dilute solution. Then a new polarization $\mathbf{P}_i$ is induced on each solute particle. The total polarization of the solution containing N_1 particles in unit volume, observed at a far point from the solution, is given by

$$\mathbf{D}_{\text{total}} = \varepsilon_0\mathbf{E} + 4\pi N_1\mathbf{P}_i \tag{7.9.2}$$

The observed polarization $\mathbf{P}_{ob}$ is related to the electric field using the dielectric constant of the solution, ε, as

$$\mathbf{P}_{ob} = \varepsilon\mathbf{E} \ , \quad \varepsilon\mathbf{E} = \varepsilon_0\mathbf{E} + 4\pi N_1\mathbf{P}_i$$

$$\varepsilon = \varepsilon_0 + 4\pi N_1\frac{P_i}{E} \ , \quad \varepsilon - \varepsilon_0 = 4\pi N_1\alpha \ , \quad \alpha \equiv \frac{P_i}{E} \tag{7.9.3}$$

where α is the polarizability of the solute. Here, the direction of **P** is assumed to be the same as **E**. The velocity v of electromagnetic wave in homogeneous substanes is given by

$$v = \sqrt{\frac{1}{\varepsilon\mu}} = \frac{c}{n} = \frac{1}{n\sqrt{\varepsilon_0\mu_0}} \tag{7.9.4}$$

where μ and μ_0 are the magnetic permeabilities of the solution and the solvent, respectively, c the velocity of light in vacuo and n the refractive index of the solution. Thus,

$$n = \sqrt{\frac{\varepsilon\mu}{\varepsilon_0\mu_0}} = \sqrt{\varepsilon^*\mu^*} \tag{7.9.5}$$

with $\varepsilon^* = \varepsilon/\varepsilon_0$ and $\mu^* = \mu/\mu_0$. Since $\mu^* \cong 1$ in most substances, we have

$$n \cong \sqrt{\varepsilon^*}$$

$$n^2 \cong \varepsilon^* \tag{7.9.6}$$

Thus, Eq. (7.9.3) is rewritten as

$$n^2 - n_0^2 = 4\pi N_1\alpha \tag{7.9.7}$$

where n and n_0 are the refractive indices of the solution and the solvent, respectively. The term $n^2 - n_0^2$ depends only on the concentration C and can be expanded as a series of C as

$$n^2 - n_0^2 \cong \left(\frac{dn^2}{dC}\right)_{C=0} C + \frac{1}{2}\left(\frac{d^2n^2}{dC^2}\right)C^2 \tag{7.9.8}$$

In dilute solutions, α is approximated by

$$\alpha = \frac{n^2 - n_0^2}{4\pi \mathcal{N}_1} \cong \frac{1}{4\pi \mathcal{N}_1}\left(\frac{dn^2}{dC}\right)_{C=0} C = \frac{n_0}{2\pi \mathcal{N}_1}\left(\frac{dn}{dC}\right)_{C=0} C \tag{7.9.9}$$

Thus, α can be determined by measuring $(dn/dC)_{C=0}$. Here, note that $(dn/dC)_{C=0}$ depends on wave length of incident light.

<<Problem 7-10-a>> Scattering from small particles

The **scattered light intensity of natural light from a solution of small particles** (smaller than 1/20 of wave length) is given by

$$\frac{I_s}{I_0} = \frac{2\pi^2 n^2}{\lambda_0{}^4}\left(\frac{\partial n}{\partial C}\right)^2 \frac{1}{r^2}\left(1 + \cos^2\theta\right) CkT \Big/ \left(\frac{\partial \Pi}{\partial C}\right)_{C\to 0} \tag{7.10.1}$$

(See <<Problem 7-13>> and <<7-14>>). Derive the equation for determining the molecular weight of the particles M and the second virial coefficient A_2 in the virial expansion of osmotic pressure

$$\frac{\Pi}{C} = RT\left(\frac{1}{M} + A_2 C + A_3 C^2 + \cdots\right) \tag{2.8.10}$$

from the **Rayleigh ratio** $\mathbf{R_\theta}$.

Answer

Optical constant K and reduced scattered light intensity R'_θ for natural light are defined by

$$K \equiv \frac{2\pi^2 n^2}{N_A \lambda_0{}^4}\left(\frac{\partial n}{\partial C}\right)^2 \tag{7.3.6}$$

$$R'_\theta \equiv \frac{I_s r^2}{I_0\left(1 + \cos^2\theta\right)} \tag{7.10.2}$$

respectively (See <<Problem 7-3>>). Eq. (7.10.1) is rewritten as

$$\frac{KC}{R'_\theta} = \frac{1}{RT}\left(\frac{\partial \Pi}{\partial C}\right)_{C\to 0} = \frac{1}{M} + A_2 C + A_3 C^2 + \cdots \tag{7.10.3}$$

Thus, we have

$$\left(\frac{KC}{R'_\theta}\right)_{c\to 0}=\frac{1}{M}$$

A_2 can be determined from the initial slope in the plot of KC/R'_θ vs. C. Using the relationship

$$\Pi=-\frac{\Delta\mu_0}{V_0^0} \qquad (2.7.8)$$

Eq. (7.10.3) is rewritten as

$$\frac{KC}{R'_\theta}=\frac{1}{RTV_0^0}\left(-\frac{\partial\Delta\mu_0}{\partial C}\right)_{T,P} \qquad (7.10.4)$$

<<Problem 7-10-b>> Scattering from polymer solution

Consider a polymer solution which contains N polymer molecules with the degree of polymerization n in volume V. Derive the equation for the scattering from the polymer solution and compare the equation with Eq. (7.10.3).

Answer

The scattered light from polymer solutions comes from the interference of the scattered light of two segments in the same molecule I_i and in different molecules I_d:

$$I=I_i+I_d \qquad (7.10.5)$$

Referring to Eq. (7.4.24), the former is proportional to $I_i \propto N\sum\sum \exp(i\mathbf{q}\mathbf{r}_{ij})$ for the segment pairs in the same molecule and the latter is proportional to $I_d \propto N^2\sum\sum\exp(i\mathbf{q}\mathbf{r}_{ij})$ for the segment pairs in different molecules.

Using P(θ) defined by Eq. (7.5.1),

$$I_i = Nn^2\,P(\theta) \qquad (7.10.6)$$

Using the segment distribution function $F_2(1,2)$ defined by Eq. (5.12.4),

$$I_d \propto N^2\sum_{P}\sum_{P'}\exp i(kr_{PP'})=\frac{N^2}{V^2}\sum_{\mu_1}\sum_{\nu_2}\int\cdots\int F_2(1,2)\exp i(kr_{\mu_1\nu_2})d(1)d(2)$$

$$(7.10.7)$$

Here, the subscripts 1 and 2 denote arbitrarily chosen molecules, μ_1 and ν_2 denote the μ_1 th segment of the molecule 1 and ν_2 th segment of the molecule 2, respectively, and $\mathbf{r}_{\mu_1\nu_2}$ is the distance between the two segments. Eq. (7.10.7) can be rewritten as

$$\mathcal{N}^2\sum_{P}\sum_{P'}\exp i(kr_{PP'})=\frac{\mathcal{N}^2}{V}\int_0^\infty \rho_2(r)\exp i\left(kr\right)dr \tag{7.10.8}$$

with

$$\rho_2(r)=\frac{1}{V}\sum_{\mu_1}\sum_{\nu_2}\int\underset{r_{\mu_1\nu_2}=r}{\cdots}\int F_2(1,2)\,d(1)\,d(2) \tag{7.10.9}$$

where the integration in Eq. (7.10.9) is carried out under the restriction $\mathbf{r}_{\mu_1\nu_2}=\mathbf{r}$ (const.). If we rewrite $F_2(1,2)$ as $\{F_2(1,2)-F(1)F(2)\}+F(1)F(2)$, then Eq. (7.10.9) is devided into two terms as

$$\rho_2(r)=\frac{1}{V}\sum_{\mu_1}\sum_{\nu_2}\int\underset{r_{\mu_1\nu_2}=r}{\cdots}\int\left\{F_2(1,2)-F(1)\,F(2)\right\}d(1)\,d(2)+n^2 \tag{7.10.10}$$

Substitution of Eq. (7.10.10) for $\rho_2(\mathbf{r})$ in Eq. (7.10.8) yields

$$\mathcal{N}^2\sum_{P}\sum_{P'}\exp i(kr_{PP'})=\frac{\mathcal{N}^2}{V^2}\sum_{\mu_1}\sum_{\nu_2}\int\cdots\int\ \{F_2(1,2)-F(1)F(2)\}\exp i(kr_{\mu_1\nu_2})d(1)d(2) \tag{7.10.11}$$

Here, the contribution of the term n^2 is neglected. Now we define $P_2(\theta)$ by

$$P_2(\theta)=\frac{\sum_{\mu_1}\sum_{\nu_2}\int\cdots\int\ \{F_2(1,2)-F(1)F(2)\}\exp i(kr_{\mu_1\nu_2})d(1)d(2)}{n^2\int\cdots\int\{F_2(1,2)-F(1)F(2)\}d(1)d(2)} \tag{7.10.12}$$

From Eq. (5.12.1), we have

$$\int\cdots\int\ \{F_2(1,2)-F(1)F(2)\}d(1)d(2)=-\frac{2A_2M^2V}{N_A} \tag{7.10.13}$$

Eq. (7.10.11) is rewritten as

$$\mathcal{N}^2\sum_{P}\sum_{P'}\exp i(kr_{PP'})=-2A_2\frac{\mathcal{N}^2}{V}\frac{M^2}{N_A}n^2P_2(\theta) \tag{7.10.14}$$

If we denote the proportional coefficient in Eq.(7.10.7) as k'/V, Eq.(7.10.5) is rewritten as

$$I(\theta) = \frac{k'\mathcal{N}n^2}{V}\{P(\theta) - 2A_2MP_2(\theta)C + \cdots\} \tag{7.10.15}$$

with $C=\mathcal{N}M/N_AV$ or

$$I(\theta) = KC\{MP(\theta) - 2A_2M^2P_2(\theta)C + \cdots\} \tag{7.10.16}$$

or

$$\frac{KC}{I(\theta)} = \frac{1}{MP(\theta)} + 2A_2\frac{P_2(\theta)}{P(\theta)^2}C + \cdots \tag{7.10.17}$$

with $K=k'N_An^2/M^2$

<<Problem 7-11-a>> Effect of molecular weight distribution of polymer chains on P(θ)

From <<Problem 7-7-a (c)>>, the particle scattering factor for dilute random coil solutions is given by

$$P(\theta) = \frac{I_s}{I_0} = \frac{2}{x^2}\left(\exp(-x) + x - 1\right) \tag{7.7.19}$$

$$x \equiv \frac{2}{3}nb'^2q^2$$

where n and b' are the degree of polymerization and the bond length, respectively. Derive the expression for P(θ) for a polydisperse polymer with the number distribution function $f_n(n)$ and the weight distribution function $f_w(n)$.

Answer

$I_s(\theta)$ is given by the integration of the intensity of the scattered light from the polymer with the degree of polymerization, $I_n(\theta)$, over n as

$$I_S(\theta) = \int_0^\infty I_n(\theta)\, f_n(n)dn \propto \int_0^\infty P_n(\theta)n^2f_n(n)dn = \int_0^\infty P_n(\theta)nf_w(n)dn \tag{7.11.1}$$

Here, $f_n(n)dn$ is the fraction of the polymer with the degree of polymerization being in the range n and n+dn. From the normalization condition, we have

$$\int_0^\infty f_n(n)dn = \int_0^\infty f_w(n)dn = 1 \tag{7.11.2}$$

The particle scattering factor for the polydisperse polymer is calculated as

$$P(\theta) = \frac{I_s}{I_0} = \frac{\int_0^\infty P_n(\theta) n f_w(n) dn}{\int_0^\infty n f_w(n) dn} \tag{7.11.3}$$

Eq. (7.11.3) is rewritten as

$$P(\theta) = \frac{1}{n_w}\int_0^\infty P_n(\theta) n f_w(n) dn \tag{7.11.4}$$

with

$$n_w = \int_0^\infty n f_w(n) dn \tag{7.11.5}$$

With reference to <<Problem 7-5>>, $P_n(\theta)$ is expressed as

$$P_n(\theta) = 1 - \frac{1}{3n} q^2 \left\langle \sum R_{GP}{}^2 \right\rangle + \cdots \tag{7.11.6}$$

For Gaussian chains, we have

$$\frac{1}{n}\left\langle \sum R_{GP}{}^2 \right\rangle = \frac{1}{6}\left\langle n b'^2 \right\rangle = \frac{1}{6}\left\langle R^2 \right\rangle = \left\langle S^2 \right\rangle \tag{6.9.1}$$

Putting

$$\mu \equiv \frac{2}{3} b'^2 q^2 \tag{7.11.7}$$

Eq. (7.11.6) is rewritten as

$$P_n(\theta) = 1 - \frac{1}{3}\mu n + \cdots \tag{7.11.8}$$

Substitution of Eq. (7.11.8) for $P_n(\theta)$ in Eq. (7.11.4) yields

$$P(\theta) = \frac{1}{n_w}\int_0^\infty \left(1 - \frac{1}{3}\mu n + \cdots\right) n f_w(n) dn$$

$$= \frac{1}{n_w}\left\{\int_0^\infty nf_w(n)dn - \int_0^\infty \frac{1}{3}\mu n^2 f_w(n)dn + \int_0^\infty O\left(q^4\right)nf_w(n)dn + \cdots\right\}$$

$$= 1 - \frac{1}{3}\mu n_z + \cdots \tag{7.11.9}$$

with

$$n_z \equiv \frac{\int_0^\infty n^2 f_w(n)dn}{\int_0^\infty nf_w(n)dn} \tag{7.11.10}$$

Using Eq. (6.9.1), Eq. (7.11.6) is rewritten as

$$P_n(\theta) = 1 - \frac{1}{3}\langle S^2\rangle q^2 + \cdots \tag{7.11.11}$$

Substitution of Eq. (7.11.11) for $P_n(\theta)$ in Eq. (7.11.4) yields

$$P(\theta) = \frac{1}{n_w}\int_0^\infty \left(1 - \frac{1}{3}q^2\langle S^2\rangle + \cdots\right)nf_w(n)dn$$

$$= \frac{1}{n_w}\int_0^\infty nf_w(n)dn - \frac{1}{n_w}\frac{1}{3}q^2\int_0^\infty \langle S^2\rangle nf_w(n)dn + \cdots$$

$$= 1 - \frac{1}{3}q^2\left\langle\langle S^2\rangle\right\rangle_z + \cdots \tag{7.11.12}$$

with

$$\left\langle\langle S^2\rangle\right\rangle_z = \frac{1}{n_w}\int_0^\infty \langle S^2\rangle nf_w(n)dn = \frac{1}{M_w}\int_0^\infty \langle S^2\rangle Mf_w(M)dM \tag{7.11.13}$$

---

* Thus, $<S^2>$ determined by the light scattering method is z-average one. If θ is small,

$$\lim_{\theta\to 0}\frac{1}{P(\theta)} = 1 + \frac{1}{3}q^2\left\langle\langle S^2\rangle\right\rangle_z = 1 + \frac{16\pi^2 n^2}{3\lambda^2}\left\langle\langle S^2\rangle\right\rangle_z \tag{7.11.14}$$

where n is the refractive index of the medium and λ the wave length of the incident light in vacuo. Then, referring to Eq. (7.10.16), Eq. (7.10.3) is replaced by

$$\frac{KC}{R'_\theta}=\left(\frac{1}{M}+2A_2C\right)\left(1+\frac{16\pi^2 n^2\left\langle\left\langle S^2\right\rangle\right\rangle_z}{3\lambda^2}\sin^2\frac{\theta}{2}\right) \tag{7.11.15}$$

For solutions of large particles, K/R_θ' of unknown solutions is determined using R_θ' for standard substances such as benzene as

$$\frac{K}{R'_\theta}=\frac{2\pi^2 n^2\left(\frac{dn}{dC}\right)^2}{\frac{(I-I_0)}{I_{BZ,90}}N_A\lambda_0^4}\cdot\frac{1}{R'_{BZ,90}} \tag{7.11.16}$$

where $I_{BZ,90}$ is the intensity for pure benzene and $R_{BZ,90}$ in benzeneat 25°C is 29.1, 23.1 and 7.81 $\times 10^{-6}$cm^{-1} for λ= 488, 514.5 and 647.1nm, respectively.

<<Problem 7-11-b>> Zimm plot

From Eq.(7.11.15), we can determine the radius of gyration, the second virial coefficient and the molecular weight from the initial slope at $C \to 0$ and $\theta \to 0$ and the intercept in the plot of KC/R_θ vs. $\sin^2\theta+kC$, where k is a constant, respectively, as shown in Fig. 7-11-b. This plot called the **Zimm plot** (See B.H.Zimm, *J.Chem.Phys.* **16**. 1099 (1948)) is widely used for the analysis of polymer solutions by means of light scattering.

Suppose that from the angular dependence of the scattered light from a monodisperse flexible polymer solution extrapolated to zero concentration, the initial slope k_s and the intercept with the y axis, k_i, in the plot of $(KC/R'_\theta)_{C=0}$ vs. $\sin^2(\theta/2)$ was obtained as 2.0×10^{-6} and 4.0×10^{-7}, respectively. Helium-Neon laser with wavelength in vacuo λ_0=628nm and a solvent with refractive index n_0=1.39 were used. Calculate the molecular weight and the end-to-end distance of the polymer.

Answer

From Eq. (7.10.17), the molecular weight of the polymer is $M=1/k_i=2.5\times10^6$ and the radius of gyration $<S^2>=3\lambda^2k_sM/(16\pi^2n_0^2)=1.32\times10^6$ Å. Hence $<S^2>^{1/2}=1.15\times10^3$Å. For the linear coil (Eq. (6.9.1)), the end-to-end distance is $<R^2>^{1/2}=6^{1/2}<S^2>^{1/2}=2.8\times10^3$Å.

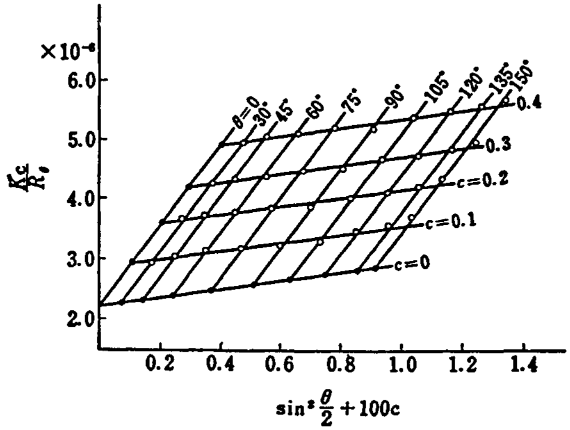

Fig. 7-11-b Zimm plot for the system polystyrene in toluene at 34.5°C which gives M_w=4.5x10^5 and 6<S^2>/M=0.70x10^{-16} (by courtesy of Prof. Nakata in Hokkaido University)

<<Problem 7-12-a>> Particle scattering factor of polymers with Schulz-Zimm molecular weight distribution (I)

Calculate P(θ) for the polymers with Schulz-Zimm type distribution of the degree of polymerization as

$$f_w(n) = \frac{y^{z+1}}{z!} n^z \exp(-yn) \tag{7.12.1}$$

where the two parameters, z and y, specify the width and the position of the peak of the distribution, respectively (See Eq. (9.8.13)).

Answer

According to <<Problem 7-11>>,

$$P(\theta) = \frac{1}{n_w}\int_0^{\infty} P_n(\theta) n f_w(n) dn \tag{7.11.4}$$

Substitution of Eq. (7.12.1) for $f_w(n)$ in Eq. (7.11.4) yields

---

* It is easily shown that the ratio of the weight and number-average degrees of polymerization is given by the relationship $n_w/n_n=(z+1)/z$. For a monodisperse sample, z=∞. With decreasing z the distribution broadens. The important case of the normal distribution of molecular weight, which results from polycondensation reactions, is characterized by z=1.

$$P(\theta) = \frac{1}{n_w}\int_0^\infty P_n(\theta) n \frac{y^{z+1}}{z!} n^z \exp(-yn) dn$$

$$= \frac{1}{n_w}\int_0^\infty \left\{1 - \frac{1}{3}\langle S^2\rangle q^2 + \cdots\right\}\frac{y^{z+1}}{z!} n^{z+1}\exp(-yn)dn \qquad (7.12.2)$$

The first term and the second term in the right-hand side of Eq. (7.12.2) are calculated as

$$\frac{1}{n_w}\int_0^\infty \frac{y^{z+1}}{z!} n^{z+1} \exp(-yn)\, dn = \frac{n_w}{n_w} = 1 \qquad (7.12.3)$$

and

$$\frac{1}{n_w}\int_0^\infty \frac{1}{3}\langle S^2\rangle q^2 \frac{y^{z+1}}{z!} n^{z+1}\exp(-yn)dn = \frac{1}{n_w}\int_0^\infty \frac{1}{18} q^2 \frac{y^{z+1}}{z!} n^{z+2}\exp(-yn)dn$$

$$= \frac{q^2}{18 n_w}\int_0^\infty \frac{y^{z+1}}{z!} n^{z+2}\exp(-yn)dn = \frac{q^2}{18} n_z \qquad (7.12.4)$$

respectively. The particle scattering factor for monodisperse Gaussian chains

$$P_n(\theta) = \frac{2}{x^2}\left(\exp(-x) + x - 1\right), \; x \equiv n\mu, \; \mu \equiv \frac{2}{3} b'^2 q^2 \qquad (7.7.19)$$

is rewritten as

$$P_n(\theta) = \frac{2}{n^2\mu^2}\left(\exp(-n^2\mu^2) + n\mu - 1\right) \qquad (7.12.5)$$

Then $P(\theta)$ for the polydisperse chains is obtained as

$$P(\theta) = \frac{1}{n_w}\int_0^\infty \frac{2}{n^2\mu^2}\left(\exp\left(-n^2\mu^2\right) + n\mu - 1\right)\frac{y^{z+1}}{z!} n^{z+1}\exp(-yn)dn$$

$$= \frac{1}{n_w}\int_0^\infty \frac{2}{\mu^2}\left(\exp\left(-n^2\mu^2 - yn\right) + n\mu - 1\right)\frac{y^{z+1}}{z!} n^{z-1}\, dn$$

$$-\frac{1}{n_w}\int_0^\infty \frac{2}{\mu^2}\frac{y^{z+1}}{z!}\exp(\text{-}yn)n^{z\text{-}1}dn+\frac{1}{n_w}\int_0^\infty \frac{2}{\mu}\frac{y^{z+1}}{z!}\exp(\text{-}yn)n^{z}dn \qquad (7.12.6)$$

Integration over n yields

$$P(\theta)=2/n_w\mu-2\left[(z+1)/z(n_w\mu)^2\right]\cdot\left[1-(z+1)^2/(z+1+n_w\mu)^2\right] \qquad (7.12.7)$$

For $z=\infty$, Eq. (7.12.7) is reduced to Eq. (7.7.19). For $z=1$, we have

$$\left.\begin{aligned}
&\int_0^\infty \frac{2}{\mu^2}\exp\left(\text{-}n^2\mu^2\text{-}yn\right)\frac{y^{z+1}}{z!}n^{z\text{-}1}\,dn=\frac{2y^2}{\mu^2}\int_0^\infty \exp\left(\text{-}n^2\mu^2\text{-}yn\right)dn\\
&\int_0^\infty \frac{2}{\mu^2}\frac{y^{z+1}}{z!}\exp(\text{-}yn)n^{z\text{-}1}dn=\frac{2y^2}{\mu^2}\int_0^\infty \exp(\text{-}yn)dn\\
&\int_0^\infty \frac{2}{\mu}\frac{y^{z+1}}{z!}\exp(\text{-}yn)n^{z}dn=\frac{2y^2}{\mu}\int_0^\infty n\exp(\text{-}yn)dn
\end{aligned}\right\} \qquad (7.12.8)$$

and

$$P(\theta)^{-1}=1+n_w\mu/2 \qquad (7.12.9)$$

For large values of x, Eq. (7.7.19) is reduced to

$$P(\theta)=\frac{2}{x}-\frac{2}{x^2}=\frac{2}{n\mu}-\frac{2}{n^2\mu^2} \qquad (7.12.10)$$

and

$$P^{-1}(\theta)=\frac{1}{2}+\frac{x}{2}+\frac{1}{2}+\frac{n\mu}{2} \qquad (7.12.11)$$

Eq. (7.12.11) indicates that $P^{-1}(\theta)$ should be proportional to $\sin^2(\theta/2)$ for sufficiently large x. For polydisperse systems, $P(\theta)$ defined by Eq. (7.11.4), in combination with the asymptotic form of $P(\theta)$, Eq. (7.12.10), yields

$$P(\theta)=n_w^{-1}\left(\frac{2}{\mu}\right)\int_0^\infty f_w(n)dn-n_w^{-1}\left(\frac{2}{\mu^2}\right)\int_0^\infty n^{-1}f_w(n)dn \qquad (7.12.12)$$

where

$$n_n = \frac{1}{\int_0^\infty n^{-1} f_w(n) dn} \tag{7.12.13}$$

The reciprocal of the asymptotic form of P(θ) is given by

$$P^{-1}(\theta) = \frac{n_w \mu}{2} + \frac{n_w}{2n_n} \tag{7.12.14}$$

<Problem 7-12-b>> Particle scattering factor of polymers with Schulz-Zimm molecular weight distribution (II)

Consider a linear polymer having weight-average degree of polymerization $n_w = 3 \times 10^4$ and the effective length of the monomer unit in the chain $b' = 8$Å. The polydispersity of n of the polymer is described by the Schulz-Zimm distribution Eq. (7.12.1) with z=0.5. The light scattering measurement has been performed for the polymer in an ideal solution with refractive index n=1.400, with incident light wavelength in vacuo $\lambda_0 = 628$nm. Compare the range of the asymptotic behavior of Eq. (7.12.14) at the highest angle of the measurement being 150°.

Answer

The value of $n_w\mu$ is $(8\pi^2/3\lambda^2)n_w b'^2 \sin^2(\theta/2) = 3.10$. From Eq. (7.12.7), P(150°)=0.377 or $P^{-1}(150°) = 2.65$. For z=0.5, $n_w/n_n = (z+1)/z = 3$. The asymptote Eq. (7.12.14) assumes, for $n_w\mu = 3.10$, $P^{-1}(\theta) = 3.10/2 + 3/2 = 3.05$. Thus, the asymptotic form cannot be applicable experimentally in the present case (See *Light Scattering from Polymer Solutions*, Ed. M. B. Huglin, Academic Press, London, 1972, Chap. 7).

<<Problem 7-13> Light scattering arising from concentration fluctuation

The scattered light intensity from a solution which contains *N* small particles per unit volume is given by

$$I_s = N I_0 \frac{8\pi^4 \alpha^2}{\lambda^4 r^2} (1 + \cos^2\theta) \tag{7.1.18}$$

for natural light. Rewrite Eq. (7.1.18) by using the **solute concentration fluctuation** $\overline{\delta C^2}$ defined by the mean square deviation of concentration from the mean concentration.

Answer

The thermal motion of molecules generates concentration fluctuations, i.e., local concentration does not agree with the mean concentartion, resulting in the fluctuation of polarizability. Let's denote the local polarizability and the mean polarizability as α and α', respectively;

$$\alpha = \alpha' + \delta\alpha \tag{7.13.1}$$

where $\delta\alpha$ is the deviation in polarizability from the mean value. Eq. (7.1.18) is rewritten as

$$I_s = N\frac{8\pi^4}{\lambda^4 r^2}(1+\cos^2\theta)\overline{(\alpha' + \delta\alpha)^2}\, I_0 \tag{7.13.2}$$

The time average of α denoted by the bar is expressed as the sum of averages as

$$\overline{(\alpha' + \delta\alpha)^2} = \overline{\alpha'^2} + \overline{2\alpha'\delta\alpha} + \overline{\delta\alpha^2} \tag{7.13.3}$$

The contribution of the first term in the right-hand side (corresponding to no fluctuation) to I_s is much smaller than that of the third term. The second term is zero since $\delta\alpha$ takes plus and minus equally. Thus,

$$\overline{(\alpha' + \delta\alpha)^2} \cong \overline{\delta\alpha^2} \tag{7.13.4}$$

The fluctuation of α comes from that of pressure, temperature and concentration, that is,

$$\delta\alpha = \left(\frac{\partial\alpha}{\partial P}\right)_{T,C}\delta P + \left(\frac{\partial\alpha}{\partial T}\right)_{P,C}\delta T + \left(\frac{\partial\alpha}{\partial C}\right)_{T,P}\delta C \tag{7.13.5}$$

In dilute solutions the first and the second terms are negligible compared to the third term. From <<Problem 7-9>>, the refractive indices of solution n_r and solvent n_r^0 are related to the polarizability as

$$n_r^{\,2} - n_r^{0\,2} = 4\pi N\alpha \tag{7.13.6}$$

In dilute solutions, n_r can be expanded as a Taylor series and the higher order terms are negligible. Then we have

$$4\pi N\alpha = 2n_r^0\left(\frac{\partial n_r}{\partial C}\right)C \tag{7.13.7}$$

Differentiation of both sides of Eq. (7.13.7) with respect to C yields

$$\frac{\partial \alpha}{\partial C}=\frac{2}{4\pi \mathcal{N}}n_r^0\left(\frac{\partial n_r}{\partial C}\right) \tag{7.13.8}$$

Substituting Eq. (7.13.8) in Eq. (7.13.5) and taking the time average, we find

$$\overline{(\delta\alpha)^2}=\left(\frac{n_r^0}{2\pi \mathcal{N}}\right)^2\left(\frac{\partial n_r}{\partial C}\right)^2\overline{\delta C^2} \tag{7.13.9}$$

Substitution of Eq. (7.13.9) for $(\overline{\delta\alpha})^2$ in Eq. (7.13.2) yields

$$\begin{aligned}\frac{I_s}{I_0}&=\mathcal{N}\frac{8\pi^4}{\lambda^4 r^2}(1+\cos^2\theta)\left(\frac{n_r^0}{2\pi \mathcal{N}}\right)^2\left(\frac{\partial n_r}{\partial C}\right)^2\overline{\delta C^2}\\&=\frac{2\pi^2}{\lambda^4 r^2 \mathcal{N}}n_r^{02}(1+\cos^2\theta)\left(\frac{\partial n_r}{\partial C}\right)^2\overline{\delta C^2}\end{aligned} \tag{7.13.10}$$

<<Problem 7-14>> Relationship between concentration fluctuation and chemical potential

Derive the equation for the concentration fluctuation of solute

$$\overline{\delta C^2}=-\frac{kT}{\dfrac{V}{CV_0^0}\left(\dfrac{\partial \mu_0}{\partial C}\right)_{T,P}} \tag{7.14.1}$$

where V_0^0 is the partial molar volume of the solvent, V the volume of the solution, C the concentration of solute and μ_0 the chemical potential of solvent.

Answer

The fluctuation of free energy is expressed as a series expansion of concentration fluctuation as

$$\delta F = \left(\frac{\partial F}{\partial C}\right)_{T,P} \delta C + \frac{1}{2}\left(\frac{\partial^2 F}{\partial C^2}\right)_{T,P} (\delta C)^2 + \cdots \qquad (7.14.2)$$

If the system is at the equilibrium state, the free energy is at its minimum with respect to concentration. Thus, $(\partial F/\partial C)_{T,P}=0$, as shown in Fig. 7-14. Then neglecting higher order terms in Eq. (7.14.2), we have

$$\delta F = \frac{1}{2}\left(\frac{\partial^2 F}{\partial C^2}\right)_{T,P} (\delta C)^2 \qquad (7.14.3)$$

The mean square fluctuation of concentration is evaluated as follows. Probability distribution function $\psi(\delta C)$ obeys Boltzmann's law as

$$\psi(\delta C) = \exp\left(-\frac{\delta F}{kT}\right) \qquad (7.14.4)$$

Using Eq. (7.14.3), Eq. (7.14.4) is rewritten as

$$\psi(\delta C) = \exp\left(-\left(\frac{\partial^2 F}{\partial C^2}\right)_{T,P} \frac{(\delta C)^2}{2kT}\right) \qquad (7.14.5)$$

From the definition,

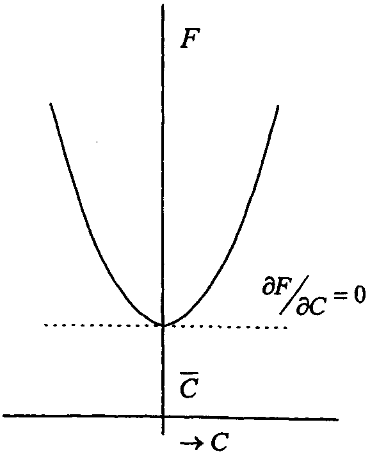

Fig. 7-14 Free energy near the equilibrium state

$$\overline{\delta C^2} = \frac{\int_0^\infty (\delta C)^2 \psi(\delta C)\, d(\delta C)}{\int_0^\infty \psi(\delta C)\, d(\delta C)} \tag{7.14.6}$$

Substitution of Eq. (7.14.5) for $\psi(\delta C)$ in Eq. (7.14.6) yields

$$\overline{\delta C^2} = \frac{\int_0^\infty (\delta C)^2 \exp\left(- \left(\frac{\partial^2 F}{\partial C^2} \right)_{T,P} \frac{(\delta C)^2}{2kT} \right) d(\delta C)}{\int_0^\infty \exp\left(- \left(\frac{\partial^2 F}{\partial C^2} \right)_{T,P} \frac{(\delta C)^2}{2kT} \right) d(\delta C)} \tag{7.14.7}$$

Putting $A = \frac{1}{2kT}\frac{\partial^2 F}{\partial C^2}$, $X = (\delta C)$

the numerator and the denominator in Eq. (7.14.7) are calculated as

$$\int_0^\infty X^2 \exp(- AX^2)\, dX = \frac{1}{4}\sqrt{\frac{\pi}{A^3}} \tag{7.14.8}$$

and

$$\int_0^\infty \exp(- AX^2)\, dX = \frac{1}{2}\sqrt{\frac{\pi}{A}} \tag{7.14.9}$$

respectively. Then, we have

$$\overline{\delta C^2} = \frac{kT}{\left(\frac{\partial^2 F}{\partial C^2} \right)_{T,P}} \tag{7.14.10}$$

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* Einstein derived a similar equation as Eq. (7.14.10) (See A. Einstein, *Ann. Physik* **33**, 1275 (1910)).

If a volume element consists of N_0 moles of solvent and N_1 moles of solute and the partial molar volume of solvent and solute are V_0 and V_1 respectively, the volume of the element is given by

$$V = N_0V_0 + N_1V_1 \tag{7.14.11}$$

The differential change in moles of solvent is related to that in solute as

$$dN_0 = -\frac{V_1}{V_0}dN_1 \tag{7.14.12}$$

Using gram concentration C and molecular weight of polymer M, we have

$$\frac{N_1}{V} = \frac{C}{M} \tag{7.14.13}$$

Then we have

$$dN_1 = \frac{V}{M}dC \tag{7.14.14}$$

and

$$dN_0 = -\frac{V_1}{V_0}\frac{V}{M}dC \tag{7.14.15}$$

According to the thermodynamic relationship,

$$dF = \mu_0 dN_0 + \mu_1 dN_1 \tag{7.14.16}$$

Substitution of Eqs. (7.14.14) and (7.14.15) for dN_0 and dN_1 in Eq. (7.14.16) yields

$$dF = -\mu_0\frac{V_1V}{V_0M}dC + \mu_1\frac{V}{M}dC \tag{7.14.17}$$

then

$$\frac{\partial F}{\partial C} = \left(\mu_1 - \frac{V_1}{V_0}\mu_0\right)\frac{V}{M} \tag{7.14.18}$$

Further differentiation gives

$$\frac{\partial^2 F}{\partial C^2} = \left(\frac{\partial\mu_1}{\partial C} - \frac{V_1}{V_0}\frac{\partial\mu_0}{\partial C}\right)\frac{V}{M} \tag{7.14.19}$$

The Gibbs-Duhem relation for binary solutions reads

$$N_0 d\mu_0 + N_1 d\mu_1 = 0 \tag{7.14.20}$$

(See Eq. (1.5.6))
The change in μ_1 relates to the change in μ_0 as

$$d\mu_1 = -\frac{N_0}{N_1} d\mu_0 \tag{7.14.21}$$

Substitution of Eq. (7.14.21) in Eq. (7.14.19) yields

$$\left(\frac{\partial^2 F}{\partial C^2}\right)_{T,P} = -\frac{V}{M}\left(\frac{n_0 V_0 + n_1 V_1}{n_1 V_0}\right)\left(\frac{\partial \mu_0}{\partial C}\right)_{T,P} \tag{7.14.22}$$

Using the relationship

$$\frac{n_1 M}{n_0 V_0 + n_1 V_1} = C \tag{7.14.23}$$

we have

$$\left(\frac{\partial^2 F}{\partial C^2}\right)_{T,P} = -\frac{V}{CV_0}\left(\frac{\partial \mu_0}{\partial C}\right)_{T,P} \tag{7.14.24}$$

Combining Eqs. (7.14.10) and (7.14.24), we have

$$\overline{\delta C^2} = -\frac{kT}{\dfrac{V}{CV_0}\left(\dfrac{\partial \mu_0}{\partial C}\right)_{T,P}} \tag{7.14.25}$$

Eq. (7.14.25) coincides with Eq. (7.14.1) when $V_0 \cong V_0^0$. Combination of Eq. (7.14.25) and Eq. (7.13.10) gives Eq. (7.10.1).

<<Problem 7-15-a>>Light scattering from copolymer (I)

The increment of refractive index Y of copolymer solutions which contains A and B components is assumed to be

$$Y = Y_A w_A + Y_B w_B \tag{7.15.1}$$

where w_A and w_B are the weight fractions of A and B component, respectively and Y_A and Y_B are the increments of refractive index of homopolymers A and B, respectively. Derive the **expression for P(θ) of the copolymer**.

Answer

The weight average molecular weight of the copolymer is given by

$$M_w = w_A M_w^A + w_B M_w^B \tag{7.15.2}$$

where M_w^A and M_w^B are the weight-average molecular weights of A and B component, respectively. $P(\theta)$ is given by

$$P(\theta) = \frac{1}{n_s^2 Y^2} \sum_i \sum_j Y_i Y_j \left\langle \frac{\sin qr_{ij}}{qr_{ij}} \right\rangle \tag{7.15.3}$$

where n_s denotes the degree of polymerization. Let's divide the particle scattering factor into three parts; $P_A(\theta)$ for the combination where both Y_i and Y_j elements are A components, $P_B(\theta)$ for the one where both elements are B components and $Q_{AB}(\theta)$ for the one where either element is A component and the other is B component. Then we have

$$P_A(\theta) = \frac{1}{\left(n_s^A\right)^2} \sum_i^{n_s^A} \sum_j^{n_s^A} \left\langle \frac{\sin qr_{ij}}{qr_{ij}} \right\rangle \tag{7.15.4}$$

$$P_B(\theta) = \frac{1}{\left(n_s^B\right)^2} \sum_i^{n_s^B} \sum_j^{n_s^B} \left\langle \frac{\sin qr_{ij}}{qr_{ij}} \right\rangle \tag{7.15.5}$$

$$Q_{AB}(\theta) = \frac{1}{n_s^A n_s^B} \sum_i^{n_s^A} \sum_j^{n_s^B} \left\langle \frac{\sin qr_{ij}}{qr_{ij}} \right\rangle \tag{7.15.6}$$

The particle scattering factor of the copolymer is given by

$$P(\theta) = \frac{1}{Y^2}\left[w_A^2 Y_A^2 P_A(\theta) + w_B^2 Y_B^2 P_B(\theta) + 2 w_A w_B Y_A Y_B Q_{AB}(\theta)\right] \tag{7.15.7}$$

Similarly apparent mean square radius of gyration $\langle S^2\rangle_z^{app}$ is given by

$$\langle S^2\rangle_z^{app} = \frac{1}{Y^2}\left[w_A^2 Y_A^2 \langle S_A^2\rangle + w_B^2 Y_B^2 \langle S_B^2\rangle + 2 w_A w_B Y_A Y_B \langle S_{AB}^2\rangle\right] \tag{7.15.8}$$

where $\langle S_A^2\rangle$ and $\langle S_B^2\rangle$ are the mean square radii of gyration about the center of inertia of A and B, G_A and G_B, respectively, $\langle S_{AB}^2\rangle = (\langle S_A^2\rangle + \langle S_B^2\rangle + l^2)/2$ and l is the distance between G_A and G_B.

<<Problem 7-15-b>>Light scattering from copolymer (II)

Consider solutions of copolymer which is polydisperse in chain composition as well as in molecular weight. Denote the overall weight fraction of monomer A and B as w_A and w_B, respectively, the overall weight-average molecular weight and weight fractions of A and B of *i*th copolymer as M_i, w_{Ai} and w_{Bi}, respectively, and the volume concentration of total copolymers and *i*th copolymer as c_P and c_i, respectively. Derive the expression for the **apparent molecular weight** M_{app} of the copolymer.

Answer

The molar mass of monomer A in *i*th copolymer is $w_{Ai}M_i$ and the weight-average molar mass of monomer A included in a copolymer is $M_A=\Sigma(w_{Ai}M_i)(w_{Ai}c_i)/w_Ac_P$. Similarly, we have $M_B=\Sigma(w_{Bi}M_i)(w_{Bi}c_i)/w_Bc_P$. From the definition, $w_Ac_P=\Sigma w_{Ai}c_i$ and $w_Bc_P=\Sigma w_{Bi}c_i$. Let's denote the deviations of w_{Ai} and w_{Bi} from their average values w_A and w_B as $\delta w_i=w_{Ai}-w_A=w_B-w_{Bi}$ and define parameters for the degree of width of distribution for molecular weight and composition as

$$P = \Sigma c_iM_i\delta w_i/c_P \tag{7.15.9}$$

and

$$Q = \Sigma c_iM_i(\delta w_i)^2/c_P \tag{7.15.10}$$

Using the relationship $M_w=\Sigma M_ic_i/c_P$, Eqs. (7.15.9) and (7.15.10) are rewritten as

$$P = [-w_A(M_w - M_A) + w_B(M_w - M_B)]/2 \tag{7.15.11}$$

$$Q = w_Aw_B(M_A + M_B - M_w) \tag{7.15.12}$$

The increment of refractive index for *i*th copolymer $Y_i=dn/dn_{ci}$ is expressed as

$$Y_i = w_{Ai}Y_A + w_{Bi}Y_B \tag*{(7.15.1)'}$$

where Y_A and Y_B are the increments of refractive index for monomer A, dn/dc_A, and monomer B, dn/dc_B, respectively. The increment for total copolymer $Y_P=dn/dc_P$ is given by

$$Y_B = w_AY_A + w_BY_B \tag*{(7.15.1)''}$$

Then we have apparent molecular weight

$$M_{app} = [\Sigma(w_{Ai}Y_A + w_{Bi}Y_B)^2M_ic_i]/[(w_AY_A + w_BY_B)^2c_P]$$

$$= [Y_AY_BM_w + Y_A(Y_A - Y_B)M_A + Y_B(Y_B - Y_A)M_B]\ /Y_P$$

$$= M_w + 2P(Y_A - Y_B)/Y_P + Q(Y_A - Y_B)^2/Y_P^2 \qquad (7.15.13)$$

(See W. Bushuk and H. Benoit, *Can. J. Chem.* **36**, 1616 (1958); M. Kurata, in "*Experimental Method for Light Scattering*", Eds. M. Nakagaki and H. Itagaki, Nankodo, Tokyo, 1965)

<<Problem 7-16>> Light scattering arising from optically anisotropic particles (1)

Suppose scattering particles are optically anisotropic so that the polarizability α is expressed by a tensor $(\alpha_1, \alpha_2, \alpha_3)$. When the incident light is polarized along x-y plane and the scattered light is observed in y direction, the scattered light is not completely polarized along x-y plane, since the polarization has x component as well as z component. Let's define the **polarization extinction coefficient** (or **the degree of depolarization**) ρ by the intensity of the light vibrating in z direction divided by that in x direction. Derive the equation

$$\rho = \frac{\langle \overline{P_z^2} \rangle}{\langle \overline{P_x^2} \rangle} = \frac{6B^2}{(6A^2 + 7B^2)} \qquad (7.16.1)$$

where $\langle \overline{P_z} \rangle$and $\langle \overline{P_x} \rangle$ are the average polarization in z direction and x direction, respectively,

$$A = \frac{\alpha_1 + \alpha_2 + \alpha_3}{3} \qquad (7.16.2)$$

and

$$B^2 = -\frac{1}{15}\left\{(\alpha_1 - \alpha_2)^2 + (\alpha_2 - \alpha_3)^2 + (\alpha_3 - \alpha_1)^2\right\} \qquad (7.16.3)$$

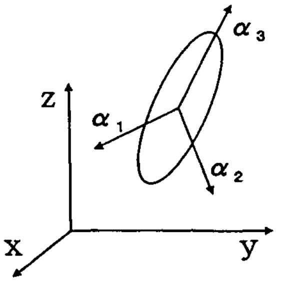

Fig. 7-16 Principal axis of polarizability tensor

Answer

Let's denote the cosine of the three principal axes α_1, α_2, α_3 of the polarizability tensor against the three axes of x-y-z coordinate as (l_1,m_1,n_1), (l_2,m_2,n_2) and (l_3,m_3,n_3). That is, $l_1=\cos(\alpha_1{}^\wedge x)$, $m_1=\cos(\alpha_1{}^\wedge y)$ and $n_1=\cos(\alpha_1{}^\wedge z)$. Suppose the incident electric field **E** has x and y components, E_x and E_y, respectively.

$$\mathbf{E}=\begin{pmatrix} E_x \\ E_y \\ 0 \end{pmatrix} \qquad (7.16.4)$$

If we denote the rectangular coordinate which consists of the principal axes of polarizability of the particles as 1,2 and 3 in place of x, y and z, we have

$$\mathbf{E}'=\begin{pmatrix} E_1 \\ E_2 \\ E_3 \end{pmatrix} \qquad (7.16.5)$$

The components of **E** and **E′** are related to each other as

$$\begin{aligned} E_1 &= E_x l_1 + E_y m_1 + E_z n_1 = E_x l_1 + E_y m_1 \\ E_2 &= E_x l_2 + E_y m_2 + E_z n_2 = E_x l_2 + E_y m_2 \\ E_3 &= E_x l_3 + E_y m_3 + E_z n_3 = E_x l_3 + E_y m_3 \end{aligned} \qquad (7.16.6)$$

These series of equations are rewritten as

$$\mathbf{E}'=\begin{pmatrix} l_1 & m_1 & n_1 \\ l_2 & m_2 & n_2 \\ l_3 & m_3 & n_3 \end{pmatrix}\mathbf{E}=\mathbf{LE} \qquad (7.16.7)$$

If we denote the polarization induced in the direction of the three principal axes as P_1, P_2 and P_3, then

$$\begin{aligned} P_1 &= \alpha_1 E_1 \\ P_2 &= \alpha_2 E_2 \\ P_3 &= \alpha_3 E_3 \end{aligned} \qquad (7.16.8)$$

Combining Eqs. (7.16.6) and (7.16.8), we have

$$P_1=\alpha_1\left(E_x l_1+E_y m_1\right)$$

$$P_2 = \alpha_2\left(E_x l_2 + E_y m_2\right)$$

$$P_3 = \alpha_3\left(E_x l_3 + E_y m_3\right) \qquad (7.16.9)$$

Thus the polarization **P**(P_x, P_y, P_z) is related to **P′** (P_1,P_2,P_3) as

$$\mathbf{P} = L^{-1}\mathbf{P}' \qquad (7.16.10)$$

with

$$L^{-1} = \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \\ n_1 & n_2 & n_3 \end{pmatrix} \qquad (7.16.11)$$

Here L^{-1} is the inverse matrix of L, i.e., $LL^{-1}=1$. Here, note that for rectangular matrices, the transposed matrix L^T is identical to the inverse matrix L^{-1}; $L^T=L^{-1}$. P_x, P_y and P_z are calculated by using Eqs. (7.16.8)-(7.16.11) as

$$\begin{pmatrix} P_x \\ P_y \\ P_z \end{pmatrix} = \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \\ n_1 & n_2 & n_3 \end{pmatrix} \begin{pmatrix} \alpha_1(E_x l_1 + E_y m_1) \\ \alpha_2(E_x l_2 + E_y m_2) \\ \alpha_3(E_x l_3 + E_y m_3) \end{pmatrix} \qquad (7.16.12)$$

or

$$\begin{aligned} P_x &= \left(\alpha_1 l_1^2 + \alpha_2 l_2^2 + \alpha_3 l_3^2\right)E_x + (\alpha_1 l_1 m_1 + \alpha_2 l_2 m_2 + \alpha_3 l_3 m_3)E_y \\ P_y &= (\alpha_1 l_1 m_1 + \alpha_2 l_2 m_2 + \alpha_3 l_3 m_3)E_x + \left(\alpha_1 m_1^2 + \alpha_2 m_2^2 + \alpha_3 m_3^2\right)E_y \\ P_z &= (\alpha_1 l_1 m_1 + \alpha_2 l_2 m_2 + \alpha_3 l_3 m_3)E_x + (\alpha_1 m_1 n_1 + \alpha_2 m_2 n_2 + \alpha_3 m_3 n_3)E_y \end{aligned} \qquad (7.16.13)$$

These expressions are for a specified particle in a specified direction. Thus it is necessary to average them all over the directions. We assume the distribution of the direction of the particles be homogeneous. Let's express l_1, m_1,...as

$$\begin{aligned} l_1 &= \cos \alpha_1{}^\wedge x = \cos\theta_{1x} \\ m_1 &= \cos \alpha_1{}^\wedge y = \cos\theta_{1y} \\ &\vdots \end{aligned} \qquad (7.16.14)$$

The average of l_i^{2m},m_i^{2m} and n_i^{2m} is given by

$$\langle l_i{}^{2m}\rangle = \frac{\int_0^\pi \cos^{2m}\theta_{ix}\sin\theta_{ix}\,d\theta_{ix}}{\int_0^\pi \sin\theta_{ix}\,d\theta_{ix}} \tag{7.16.15}$$

$$\langle m_i{}^{2m}\rangle = \frac{\int_0^\pi \cos^{2m}\theta_{iy}\sin\theta_{iy}\,d\theta_{iy}}{\int_0^\pi \sin\theta_{iy}\,d\theta_{iy}} \tag{7.16.16}$$

$$\langle n_i{}^{2m}\rangle = \frac{\int_0^\pi \cos^{2m}\theta_{iz}\sin\theta_{iz}\,d\theta_{iz}}{\int_0^\pi \sin\theta_{iz}\,d\theta_{iz}} \tag{7.16.17}$$

respectively. The integration is carried out as follows:

$$\begin{aligned}\int \cos^{2m}\theta_{ix}\sin\theta_{ix}d\theta_{ix} &= \frac{\sin^2\theta_{ix}\cos^{2m-1}\theta_{ix}}{2m+1} + \frac{2m-1}{2m+1}\int \sin\theta_{ix}\cos^{2m-2}\theta_{ix}d\theta_{ix} \\ &= -\frac{\sin^0\theta_{ix}\cos^{2m+1}\theta_{ix}}{2m+1} + \frac{1-1}{2m+1}\int \sin^{-1}\theta_{ix}\cos^{2m}\theta_{ix}d\theta_{ix} \\ &= -\frac{\cos^{2m+1}\theta_{ix}}{2m+1}\end{aligned}$$

$$\left|-\frac{\cos^{2m+1}\theta_{ix}}{2m+1}\right|_0^\pi = -\frac{(-1)^{2m+1}}{2m+1} - \frac{(-1)(1)^{2m+1}}{2m+1} = \frac{1}{2m+1}\left(1-(-1)^{2m+1}\right)$$

Using the relationships

$(-1)^{2m+1} = -1$

$$\int_0^\pi \cos^{2m}\theta_{ix}\sin\theta_{ix}d\theta_{ix} = \frac{1}{2m+1}\times 2$$

$$\int_0^{\pi} \sin\theta_{ix} d\theta_{ix} = \left| -\cos\theta_{ix} \right|_0^{\pi} = -(-1) - (-1) = 2$$

we have

$$\left\langle l_i^{2m} \right\rangle = \left\langle m_i^{2m} \right\rangle = \left\langle n_i^{2m} \right\rangle = \frac{1}{2m+1} \tag{7.16.18}$$

Using the relationships

$$\begin{aligned} l_1^2 + m_1^2 + n_1^2 &= 1 \\ l_2^2 + m_2^2 + n_2^2 &= 1 \\ l_3^2 + m_3^2 + n_3^2 &= 1 \end{aligned} \tag{7.16.19}$$

we have

$$\begin{aligned} \left\langle \left(l_i^2 + m_i^2 + n_i^2 \right)^2 \right\rangle &= \left\langle l_i^4 + m_i^4 + n_i^4 + 2l_i^2 m_i^2 + 2l_i^2 n_i^2 + 2m_i^2 n_i^2 \right\rangle \\ &= 3\left\langle l_i^4 \right\rangle + 6\left\langle l_i^2 m_i^2 \right\rangle = 1 \end{aligned} \tag{7.16.20}$$

Eq. (7.16.18) for m=2 gives

$$\left\langle l_i^4 \right\rangle = \frac{1}{5} \tag{7.16.21}$$

Combining Eqs. (7.16.20) and (7.16.21), we have

$$\left\langle l_i^2 m_i^2 \right\rangle = \frac{1 - 3\left\langle l_i^4 \right\rangle}{6} = \frac{1}{6}\left(1 - \frac{3}{5} \right) = \frac{1}{15} \tag{7.16.22}$$

Similarly we have

$$\left\langle l_i l_j m_i m_j \right\rangle = -\frac{1}{30} \tag{7.16.23}$$

Using the relationships Eq. (7.16.21)-(7.16.23) and with reference to Eq. (7.16.13), we can calculate $<\overline{P_x^2}>$, $<\overline{P_y^2}>$ and $<\overline{P_z^2}>$. For example,

$$\begin{aligned} \left\langle P_x^2 \right\rangle = {} & \left\langle \overline{\left(\alpha_1 l_1^2 + \alpha_2 l_2^2 + \alpha_3 l_3^2 \right)^2 E_x^2} \right\rangle + \left\langle \overline{\left(\alpha_1 l_1 m_1 + \alpha_2 l_2 m_2 + \alpha_3 l_3 m_3 \right)^2 E_y^2} \right\rangle \\ & + 2\left\langle \overline{\left(\alpha_1 l_1^2 + \alpha_2 l_2^2 + \alpha_3 l_3^2 \right) E_x \left(\alpha_1 l_1 m_1 + \alpha_2 l_2 m_2 + \alpha_3 l_3 m_3 \right) E_y} \right\rangle \end{aligned} \tag{7.16.24}$$

Here < > and - denote the average all over the directions and the time average, respectively. Since $E=E_x=E_y$,

$$\begin{aligned}
\left\langle\overline{P_x{}^2}\right\rangle =& \left\{\left\langle\overline{l_1{}^4}\right\rangle + 2\left\langle\overline{l_1{}^2m_1{}^2}\right\rangle + 2\left\langle\overline{l_1{}^3m_1}\right\rangle\right\}\alpha_1{}^2\overline{E^2} \\
&+ \left\{\left\langle\overline{l_2{}^4}\right\rangle + 2\left\langle\overline{l_2{}^2m_2{}^2}\right\rangle + 2\left\langle\overline{l_2{}^3m_2}\right\rangle\right\}\alpha_2{}^2\overline{E^2} \\
&+ \left\{\left\langle\overline{l_3{}^4}\right\rangle + 2\left\langle\overline{l_3{}^2m_3{}^2}\right\rangle + 2\left\langle\overline{l_3{}^3m_3}\right\rangle\right\}\alpha_3{}^2\overline{E^2} \\
&+ \left\{2\left\langle\overline{l_1{}^2l_2{}^2}\right\rangle + 2\left\langle\overline{l_1l_2lm_1m_2}\right\rangle + 2\left\langle\overline{l_1{}^2l_2m_2}\right\rangle + 2\left\langle\overline{l_1l_2{}^2m_1}\right\rangle\right\}\alpha_1\alpha_2\overline{E^2} \\
&+ \left\{2\left\langle\overline{l_2{}^2l_3{}^2}\right\rangle + 2\left\langle\overline{l_2l_3lm_2m_3}\right\rangle + 2\left\langle\overline{l_2{}^2l_3m_3}\right\rangle + 2\left\langle\overline{l_2l_3{}^2m_2}\right\rangle\right\}\alpha_2\alpha_3\overline{E^2} \\
&+ \left\{2\left\langle\overline{l_3{}^2l_1{}^2}\right\rangle + 2\left\langle\overline{l_3l_1lm_3m_1}\right\rangle + 2\left\langle\overline{l_3{}^2l_1m_1}\right\rangle + 2\left\langle\overline{l_3l_1{}^2m_3}\right\rangle\right\}\alpha_3\alpha_1\overline{E^2} \\
=& \left\{\left\langle\overline{l_1{}^4}\right\rangle + 2\left\langle\overline{l_1{}^2m_1{}^2}\right\rangle + 2\left\langle\overline{l_1{}^3m_1}\right\rangle\right\}\left\{\alpha_1{}^2 + \alpha_2{}^2 + \alpha_3{}^2\right\}\overline{E^2} \\
&+ 2\left\{\left\langle\overline{l_1{}^2l_2{}^2}\right\rangle + \left\langle\overline{l_1l_2lm_1m_2}\right\rangle + \left\langle\overline{l_1{}^2l_2m_2}\right\rangle + \left\langle\overline{l_1l_2{}^2m_1}\right\rangle\right\} \\
&\times\left(\alpha_1\alpha_2 + \alpha_2\alpha_3 + \alpha_3\alpha_1\right)\overline{E^2}
\end{aligned} \tag{7.16.25}$$

From Eqs. (7.16.21) and (7.16.22),

$$\left\langle\overline{l_1{}^4}\right\rangle = \frac{1}{5},\quad \left\langle\overline{l_1{}^2m_1{}^2}\right\rangle = \frac{1}{15},\quad \left\langle\overline{l_1{}^3m_1}\right\rangle = 0$$

Then we obtain

$$\left\langle\overline{P_x{}^2}\right\rangle = \frac{4}{15}\left\{\alpha_1{}^2 + \alpha_2{}^2 + \alpha_3{}^2\right\}\overline{E^2} + \frac{1}{15}\left(\alpha_1\alpha_2 + \alpha_2\alpha_3 + \alpha_3\alpha_1\right)\overline{E^2} \tag{7.16.26}$$

Comparing the expressions for P_y and P_x in Eq. (7.16.13),

$$\left\langle\overline{P_y{}^2}\right\rangle = \left\langle\overline{P_x{}^2}\right\rangle \tag{7.16.27}$$

Following the same procedure, the average of P_z in Eq. (7.16.13) is given by

$$\left\langle \overline{P_z^2} \right\rangle = \frac{2}{15}(\alpha_1^2 + \alpha_2^2 + \alpha_3^2 - \alpha_1\alpha_2 - \alpha_2\alpha_3 - \alpha_3\alpha_1)\overline{E^2} \tag{7.16.28}$$

From <<Problem 7-1>>, the scattered light intensity I_s relates with the polarization P as

$$I_s = \frac{1}{4\pi}\frac{\omega_0^4}{c^4}\frac{\sin^2\theta_z}{r}\overline{P^2} \tag{7.16.29}$$

If the incident light travels along z direction and the scattered light is observed in y direction, θ_z should be 90° both for $\left\langle \overline{P_x^2} \right\rangle$ and $\left\langle \overline{P_y^2} \right\rangle$ and then

$$\rho = \frac{I\left(\left\langle \overline{P_z^2} \right\rangle\right)}{I\left(\left\langle \overline{P_x^2} \right\rangle\right)} = \frac{\left\langle \overline{P_z^2} \right\rangle}{\left\langle \overline{P_x^2} \right\rangle} \tag{7.16.30}$$

Substitution of Eqs. (7.16.26) and (7.16.28) in Eq. (7.16.30) yields

$$\rho = \frac{\frac{2}{15}(\alpha_1^2 + \alpha_2^2 + \alpha_3^2 - \alpha_1\alpha_2 - \alpha_2\alpha_3 - \alpha_3\alpha_1)}{\frac{4}{15}\{\alpha_1^2 + \alpha_2^2 + \alpha_3^2\} + \frac{1}{15}(\alpha_1\alpha_2 + \alpha_2\alpha_3 + \alpha_3\alpha_1)}$$

$$= \frac{6B^2}{6A^2 + 7B^2} \tag{7.16.31}$$

<<Problem 7-17>> Light scattering arising from optically anisotropic particles (II)

When the scattering particles are small compared with the wavelength and optically isotropic, the total scattered light intensity from a particle in unit volume is given by

$$I_{total} = \frac{128\pi^5}{3\lambda^4}\alpha^2 I_0 \tag{7.2.1}$$

On the other hand, when the scattering particles are optically anisotropic small ones, it is given by

$$I_{total} = f\,\frac{128\pi^5}{3\lambda^4}\left(\frac{\alpha_1 + \alpha_2 + \alpha_3}{3}\right)^2 I_0 \tag{7.17.1}$$

with the **Cabaness factor**

$$f = \frac{(6 + 3\rho)}{(6 - 7\rho)} \tag{7.17.2}$$

Derive Eq. (7.17.2).

Answer

Using the relationship

$$I_0 = \frac{E_0^2}{4\pi} \tag{7.17.3}$$

we have

$$\langle \overline{P^2} \rangle = \alpha^2 E_0{}^2 = 4\pi\alpha^2 I_0 \tag{7.17.4}$$

Eq. (7.2.1) is rewritten as

$$I_{total} = \frac{32\pi^4 \langle \overline{P^2} \rangle}{3\lambda^4} \tag{7.17.5}$$

where

$$\langle \overline{P^2} \rangle = \langle \overline{P_x{}^2} \rangle + \langle \overline{P_y{}^2} \rangle + \langle \overline{P_z{}^2} \rangle \tag{7.17.6}$$

Substitution of Eqs. (7.16.26)-(7.16.28) in Eq. (7.17.6) yields

$$\langle \overline{P^2} \rangle = \langle \overline{P_x{}^2} \rangle + \langle \overline{P_y{}^2} \rangle + \langle \overline{P_z{}^2} \rangle = \frac{2}{3}\left(\alpha_1{}^2 + \alpha_2{}^2 + \alpha_3{}^2\right)\overline{E^2} \tag{7.17.7}$$

Substitution of Eq. (7.17.7) for $<\overline{P^2}>$ in Eq. (7.17.5) yields

$$I_{total} = \frac{64\pi^4}{9\lambda^4}(\alpha_1{}^2 + \alpha_2{}^2 + \alpha_3{}^2)\overline{E^2} \tag{7.17.8}$$

Using the parameters

$$A = \frac{\alpha_1 + \alpha_2 + \alpha_3}{3} \tag{7.17.9a}$$

and

$$B^2 = \frac{1}{15}\left\{(\alpha_1 - \alpha_2)^2 + (\alpha_2 - \alpha_3)^2 + (\alpha_3 - \alpha_1)^2\right\} \tag{7.17.9b}$$

we have

$$\alpha_1^2+\alpha_2^2+\alpha_3^2=3A^2+5B^2 \tag{7.17.10}$$

Substitution of this expression in Eq. (7.17.8) yields

$$I_{total} = \frac{64\pi^4}{9\lambda^4}\left(3A^2+5B^2\right)\overline{E^2} \tag{7.17.11}$$

If the incident light is natural light,

$$I_0 = \frac{\overline{E^2}}{2\pi} \tag{7.17.12}$$

Then Eq. (7.17.11) is rewritten as

$$I_{total} = \frac{64\pi^4}{9\lambda^4}\left(3A^2+5B^2\right)2\pi I_0 \tag{7.17.13}$$

From <<Problem 7-16>>,

$$\rho = \frac{6B^2}{\left(6A^2+7B^2\right)} \tag{7.17.14}$$

Eq. (7.17.14) is rewritten as

$$3A^2+5B^2 = 3A^2\frac{6+3\rho}{6-7\rho} \tag{7.17.15}$$

Then substitution of Eq. (7.17.15) in Eq. (7.17.11) yields

$$I_{total} = \frac{128\pi^5}{3\lambda^4}\left(\frac{6+3\rho}{6-7\rho}\right)\left(\frac{\alpha_1+\alpha_2+\alpha_3}{3}\right)^2 I_0 \tag{7.17.16}$$

(Compare with Eq. (7.2.1)). Thus the total scattered light intensity of optically anisotropic scattering particles is larger than that of optically isotropic ones (See P. Cabannes, *La Diffusion Moleculaire de la Lumier*, Presses Universitaires de France, Paris (1929)).

<<Problem 7-18>> Fluctuation theory of light scattering

Light scattering can be calculated both from fluctuations of molecular distribution and local distribution of refractive index in the order of wave length. Imagine a small volume V in a solution where there is a thermal motion of solute particles. Let's denote the components of the solution as i=0,1,2,..., s, the corresponding number of molecules and chemical potentials of the components as N_i and μ_i, respectively, the temperature as T and the pressure as P. Derive the expression for the **correlations of fluctuations** $<\Delta P^2>$, $<\Delta P \Delta N_i>$ and $<\Delta N_i \Delta N_j>$. Here $\Delta P = P - <P>$, $\Delta N_i = N_i - <N_i>$ $(i \geq 1)$ and the symbol < > denotes the equilibrium value.

Answer

We consider an ensemble described by thermodynamic variables P, N_0, $\mu_1, \mu_2, \ldots, \mu_s$ for treating the fluctuations of V, N_1, $N_2, \ldots,$ N_s in a region of the solution at constant N_0. The probability that a state of the solution with V, E and N_i $(i \geq 1)$ is realized is proportional to

$$\exp\{-(E + PV - \sum_{i=1}^{s} \mu_i N_i)/kT\} \tag{7.18.1}$$

where E is the energy and k is Boltzmann's factor. Since the total number of the states with E and N_i $(i \geq 1)$, $W(E, N_i)$, is $\exp(S/k)$, the probability that the states with E and N_i $(i \geq 1)$ are realized is proportional to

$$\exp\{-(F + PV - \sum_{i=1}^{s} \mu_i N_i)/kT\} \tag{7.18.2}$$

where F(=E-TS) is Helmholz free energy. Expanding the function in the parenthesis in Eq. (7.18.2) in a Taylor series of $\Delta V (= V - <V>)$ and ΔN_i and neglecting the higher order terms, we have

$$\begin{aligned}\Delta(F + PV - \sum_{i=1}^{s} \mu_i N_i) = & \left(\frac{\partial F}{\partial V}\right)\Delta V + \sum_{i=1}^{s}\left(\frac{\partial F}{\partial N_i}\right)\Delta N_i + \left(\frac{1}{2}\right)\left(\frac{\partial^2 F}{\partial V^2}\right)\Delta V^2 \\ & + \left(\frac{1}{2}\right)\sum_{i=1}^{s}\left(\frac{\partial^2 F}{\partial V \partial N_i}\right)\Delta V \Delta N_i + P\Delta V - \sum_{i=1}^{s} \mu_i \Delta N_i \\ & + \left(\frac{1}{2}\right)\sum_{j=1}^{s}\sum_{i=1}^{s}\left(\frac{\partial^2 F}{\partial N_j \partial N_i}\right)\Delta N_i \Delta N_j \end{aligned} \tag{7.18.3}$$

Using the relationships

$$-\Delta P = \Delta\left(\frac{\partial F}{\partial V}\right) = \left(\frac{\partial^2 F}{\partial V^2}\right)\Delta V + \sum_{i=1}^{s}\left(\frac{\partial^2 F}{\partial V \partial N_i}\right)\Delta N_i$$

$$\Delta \mu_i = \Delta\left(\frac{\partial F}{\partial N_i}\right) = \left(\frac{\partial^2 F}{\partial V \partial N_i}\right)\Delta V + \sum_{j=1}^{s}\left(\frac{\partial^2 F}{\partial N_i \partial N_j}\right)\Delta N_j$$

Eq. (7.18.3) is reduced to

$$\Delta\left(F+PV-\sum_{i=1}^{s}\mu_i\mathcal{N}_i\right)=-\left(\frac{1}{2}\right)\Delta P\Delta V+\left(\frac{1}{2}\right)\Delta\mu_i\Delta\mathcal{N}_i \tag{7.18.4}$$

Now we change the independent variables from V to P using the relationships

$$\Delta V=\Delta\left(\frac{\partial G}{\partial P}\right)_{T,\mathcal{N}_j}=\left(\frac{\partial^2 G}{\partial P^2}\right)\Delta P+\sum_{i=1}^{s}\left(\frac{\partial^2 G}{\partial\mathcal{N}_i\partial P}\right)\Delta\mathcal{N}_i \tag{7.18.5}$$

$$\Delta\mu_i=\Delta\left(\frac{\partial G}{\partial\mathcal{N}_i}\right)_{P,T,\mathcal{N}_j}=\left(\frac{\partial^2 G}{\partial P\partial\mathcal{N}_i}\right)\Delta P+\left(\frac{\partial^2 G}{\partial\mathcal{N}_i\partial\mathcal{N}_j}\right)\Delta\mathcal{N}_j \tag{7.18.6}$$

Then Eq. (7.18.4) is rewritten as

$$\begin{aligned}\Delta\left(F+PV-\sum_{i=1}^{s}\mu_i\mathcal{N}_i\right)&=\left(-\frac{1}{2}\right)\Delta P\left\{\left(\frac{\partial^2 G}{\partial P^2}\right)\Delta P+\sum_{j=1}^{s}\left(\frac{\partial^2 G}{\partial\mathcal{N}_i\partial P}\right)\Delta\mathcal{N}_i\right\}\\&+\left(\frac{1}{2}\right)\sum_{j=1}^{s}\left\{\left(\frac{\partial^2 G}{\partial P\partial\mathcal{N}_i}\right)\Delta P+\sum_{j=1}^{s}\left(\frac{\partial^2 G}{\partial\mathcal{N}_i\partial\mathcal{N}_j}\right)\Delta\mathcal{N}_j\right\}\Delta\mathcal{N}_i\\&=\left(-\frac{1}{2}\right)G_{pp}\Delta P^2+\left(\frac{1}{2}\right)\sum_{i=1}^{s}\sum_{j=1}^{s}G_{ij}\Delta\mathcal{N}_i\Delta\mathcal{N}_j\end{aligned}$$

Thus, the probability p for the fluctuation ΔP and $\Delta\mathcal{N}_i$ ($i\geq 1$) is expressed as

$$p=A\exp\left\{-\left(-G_{pp}\Delta P^2+\sum_{i=1}^{s}\sum_{j=1}^{s}G_{ij}\Delta\mathcal{N}_i\Delta\mathcal{N}_j\right)/2kT\right\} \tag{7.18.7}$$

where

$$G_{pp}=\left(\frac{\partial^2 G}{\partial P^2}\right)_{T,\mathcal{N}_i} \tag{7.18.8}$$

$$G_{ij}=\left(\frac{\partial^2 G}{\partial\mathcal{N}_i\partial\mathcal{N}_j}\right)_{T,P} \tag{7.18.9}$$

and A is the constant determined by the normalization condition

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}p\,d(\Delta P)\,d(\Delta\mathcal{N}_1)\,d(\Delta\mathcal{N}_2)\cdots d(\Delta\mathcal{N}_s)=1 \tag{7.18.10}$$

The integration over ΔP is calculated as

$$\int_{-\infty}^{\infty} \exp\left[-\left\{-G_{pp}(\Delta P)^2\right\}/2\,kT\right] d(\Delta P)=\left(\frac{2\pi kT}{-G_{pp}}\right)^{1/2} \tag{7.18.11}$$

For the integration over ΔN_i, we introduce a matrix X with s column and 1 row, the components of which are $x_i \equiv \Delta N_i$ (i=1 to s). Then the quadratic form

$$\sum_{i=1}^{s}\sum_{j=1}^{s} G_{ij}\Delta N_i \Delta N_j$$

is rewritten as ${}^tXGX$, where ${}^tX$ is the transposed matrix of X and G is (s,s) square matrix having G_{ij} as (i,j) components. Using the diagonalization transformation of X as X=TY, the quadratic form is further rewritten as

$${}^tXGX={}^tY({}^tTGT)Y \tag{7.18.12}$$

where T is the diagonalization matrix. If we denote the eigen value of G as $\lambda_1,\lambda_2,\ldots,\lambda_s$,

$${}^tTGT=\begin{bmatrix}\lambda_1 & & 0\\ & \lambda_2 & \\ & & \ddots \\ 0 & & \lambda_s\end{bmatrix}$$

Then we have

$${}^tXGX={}^tY\begin{bmatrix}\lambda_1 & & 0\\ & \lambda_2 & \\ & & \ddots \\ 0 & & \lambda_s\end{bmatrix}Y=\sum_{i=1}^{s}\lambda_i y_i{}^2 \tag{7.18.13}$$

The volume of the integration element does not change by orthogonal transformation as

$$d(\Delta N_1)\, d(\Delta N_1)\cdots d(\Delta N_s)= dx_1\, dx_2\cdots dx_s= dy_1\, dy_2\cdots dy_s \tag{7.18.14}$$

Then the integration over ΔN_i in Eq. (7.18.10) is carried out as

$$\int_{-\infty}^{\infty}\exp\left(-\sum_{i=1}^{s}\sum_{j=1}^{s}G_{ij}\Delta\mathcal{N}_i\Delta\mathcal{N}_j/2\,kT\right)d(\Delta\mathcal{N}_1)\,d(\Delta\mathcal{N}_2)\cdots d(\Delta\mathcal{N}_s)$$

$$=\int_{-\infty}^{\infty}\exp\left(-\sum_{i=1}^{s}\lambda_i y_i^2/2\,kT\right)dy_1\,dy_2\cdots dy_s$$

$$=\prod_{i=1}^{s}\int_{-\infty}^{\infty}\exp\left(-\lambda_i y_i^2/2\,kT\right)dy_i=\left\{(2\pi kT)^s/\prod_{i=1}^{s}\lambda_i\right\}^{1/2}=\left\{(2\pi kT)^s/\|G\|\right\}^{1/2} \tag{7.18.15}$$

Here we use the equivalency of the product of the eigen values $\Pi\lambda_i$ of the matrix G and the determinant of G, $\|G\|$. $\|G\|$ is obtained by substituting $\lambda=0$ in the characteristic equation

$$\psi(\lambda)=\|G-\lambda E\|=(\lambda-\lambda_1)(\lambda-\lambda_2)\cdots(\lambda-\lambda_s)=0 \tag{7.18.16}$$

Then we have

$$A=\left(\frac{-G_{pp}}{2\pi kT}\right)^{1/2}\left\{\frac{\|G\|}{(2\pi kT)^s}\right\}^{1/2} \tag{7.18.17}$$

Now we can calculate $<(\Delta P)^2>$ as

$$\left\langle(\Delta P)^2\right\rangle=\int_{-\infty}^{\infty}\cdots\int(\Delta P)^2\,P\,d(\Delta P)\,d(\Delta\mathcal{N}_1)\,d(\Delta\mathcal{N}_2)\cdots d(\Delta\mathcal{N}_s)$$

$$=A\int_{-\infty}^{\infty}(\Delta P)^2\exp\left[\frac{-G_{pp}(\Delta P)^2}{2\,kT}\right]d(\Delta P)$$

$$\int_{-\infty}^{\infty}\cdots\int\exp\left(-\sum_{i=1}^{s}\sum_{j=1}^{s}G_{ij}\Delta\mathcal{N}_i\Delta\mathcal{N}_j/2\,kT\right)\times d(\Delta\mathcal{N}_1)\,d(\Delta\mathcal{N}_2)\cdots d(\Delta\mathcal{N}_s)$$

$$=\left(\frac{-G_{pp}}{2\,kT}\right)^{1/2}\cdot\left(\frac{1}{2}\right)\cdot\left(\frac{-G_{pp}}{2\,kT}\right)\cdot\left(\frac{2\,kT}{-G_{pp}}\right)^{1/2}=\frac{kT}{G_{pp}} \tag{7.18.18}$$

Here we use the well-known relationship

$$\int_{-\infty}^{\infty} x^2 \exp(-\beta x^2) dx = 1/(2\beta)\left(\frac{\pi}{\beta}\right)^{1/2} \tag{7.18.19}$$

$<\Delta P \Delta N_i>$ is calculated as

$$\begin{aligned}\left\langle \Delta P \Delta N_i \right\rangle &= \int_{-\infty}^{\infty} \cdots \int \Delta P \Delta N_i P d(\Delta P) d(\Delta N_1)\, d(\Delta N_2) \cdots d(\Delta N_s) \\ &= A \int_{-\infty}^{\infty} \Delta P \exp\left[-\left\{-G_{pp}(\Delta P)^2\right\}/2\,kT\right] d(\Delta P) \times \\ &\quad \int_{-\infty}^{\infty} \cdots \int \Delta N_i \exp\left(-\sum_{i=1}^{s} \sum_{j=1}^{s} G_{ij} \Delta N_i \Delta N_j / 2\,kT\right) d(\Delta N_1)\, d(\Delta N_2) \cdots d(\Delta N_s)\end{aligned} \tag{7.18.20}$$

As the integral of the product of an odd function and an even function over minus infinity to plus infinity is zero,

$$\int_{-\infty}^{\infty} x \exp(-\beta\, x^2)\, dx = 0 \tag{7.18.21}$$

Then we have

$$\left\langle \Delta P \Delta N_i \right\rangle = 0 \tag{7.18.22}$$

Using the relationship

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} p d(\Delta P)\, d(\Delta N_1)\, d(\Delta N_2) \cdots d(\Delta N_s) = 1 \tag{7.18.10}$$

$<\Delta N_i \Delta N_j>$ is calculated as

$$\begin{aligned}&\int_{-\infty}^{\infty} \int \exp\left(-\sum_{i=1}^{s} \sum_{j=1}^{s} G_{ij} \Delta N_i \Delta N_j / 2\,kT\right) d(\Delta N_1)\, d(\Delta N_2) \cdots d(\Delta N_s) \\ &= \left\{\frac{(2\pi\, kT)^s}{|G|}\right\}^{1/2}\end{aligned} \tag{7.18.23}$$

Partially differentiating both sides of Eq. (7.18.23) by G_{ij} and using the determinant of the cofactor $\|G\|_{ij} = \partial \|G\| / \partial G_{ij}$, we have

$$\int_{-\infty}^{\infty}\cdots\int \Delta\mathcal{N}_i\Delta\mathcal{N}_j\exp\left(-\sum_{i=1}^{s}\sum_{j=1}^{s}G_{ij}\Delta\mathcal{N}_i\Delta\mathcal{N}_j/2kT\right)d(\Delta\mathcal{N}_1)d(\Delta\mathcal{N}_2)\cdots d(\Delta\mathcal{N}_s)=\frac{kT\|G_{ij}\|}{\|G\|}$$

(7.18.24)

Then we have

$$\langle\Delta\mathcal{N}_i\Delta\mathcal{N}_j\rangle=\frac{kT\|G\|_{ij}}{\|G\|} \tag{7.18.25}$$

Thus, the fluctuations of pressure and concentration are independent, whereas the fluctuations of each component correlate with each other.

<<Problem 7-19>> Turbidity (II)

Imagine a sphere with the volume V and the dielectric constant $\varepsilon+\Delta\varepsilon$ in a medium with the dielectric constant ε. Then the polarizability of the sphere α is equal to $(V/4\pi)(\Delta\varepsilon/\varepsilon)$. The scattered light intensity of natural light is expressed as

$$\frac{I}{I_0}=\left(\frac{2\pi^2}{\lambda^4}\right)\cdot\left(\frac{V^2}{r^2}\right)\cdot\left(\frac{\Delta n}{n}\right)^2\cdot\left(1+\cos^2\theta\right)$$

$$=\left(\frac{2\pi^2V^2}{\lambda_0{}^4r^2}\right)\cdot(n\Delta n)^2\cdot\left(1+\cos^2\theta\right) \tag{7.19.1}$$

where $n=(\varepsilon)^{1/2}$ is the refractive index and $\lambda_0=\lambda n$ is the wave length of light in vacuo. Derive the expression for turbidity using Eqs. (7.18.18), (7.18.22) and (7.18.25).

Answer

Let's consider the refractive index as a function of P and $\mathcal{N}_i$ ($i\geq1$). Then

$$\Delta n=\left(\frac{\partial n}{\partial P}\right)\Delta P+\sum_{i=1}^{s}\left(\frac{\partial n}{\partial\mathcal{N}_i}\right)\Delta\mathcal{N}_i \tag{7.19.2}$$

$$\Delta n^2=\left(\frac{\partial n}{\partial P}\right)^2\Delta P^2+2\sum_{i=1}^{s}\left(\frac{\partial n}{\partial P}\right)\left(\frac{\partial n}{\partial\mathcal{N}_i}\right)\Delta P\Delta\mathcal{N}_i+\sum_{i=1}^{s}\sum_{j=1}^{s}\left(\frac{\partial n}{\partial\mathcal{N}_i}\right)\left(\frac{\partial n}{\partial\mathcal{N}_{ji}}\right)\Delta\mathcal{N}_i\Delta\mathcal{N}_j$$

(7.19.3)

Using Eqs. (7.18.18), (7.18.22) and (7.18.25), we have

$$\langle \Delta n^2 \rangle = -\left(\frac{\partial n}{\partial p}\right)^2 kT/G_{pp} + \sum_{i=1}^{s}\sum_{j=1}^{s}\left(\frac{\partial n}{\partial \mathcal{N}_i}\right)\left(\frac{\partial n}{\partial \mathcal{N}_j}\right) kT|G|_{ij}/|G| \qquad (7.19.4)$$

If we denote the isothermal compressibility as κ and the density as ρ, G_{pp} and $(\partial n/\partial P)$ are expressed as

$$-G_{pp} = -\frac{\partial^2 G}{\partial P^2} = -\frac{\partial V}{\partial P} = -\frac{1}{V}\cdot\left(\frac{\partial V}{\partial P}\right)V = \kappa V \qquad (7.19.5)$$

and

$$\frac{\partial n}{\partial P} = \left(\frac{\partial n}{\partial \rho}\right)\cdot\left(\frac{\partial \rho}{\partial P}\right) = \left(\frac{\partial n}{\partial \rho}\right)\cdot\left\{\frac{\partial (1/V)}{\partial P}\right\} = \left(\frac{\partial n}{\partial \rho}\right)\cdot\left(-\frac{1}{V^2}\right)\cdot\left(\frac{\partial V}{\partial P}\right)$$

$$= \left(\frac{\partial n}{\partial \rho}\right)\cdot\left(\frac{1}{V}\right)\cdot\left(-\frac{1}{V}\cdot\frac{\partial V}{\partial P}\right) = \left(\frac{\partial n}{\partial \rho}\right)\rho\kappa \qquad (7.19.6)$$

respectively. The scattered light intensity induced by the first term of the right-hand side in Eq. (7.19.4) is obtained by substituting it in Eq. (7.19.1) as

$$\frac{I_\rho}{I_0} = \left(\frac{2\pi^2 V^2}{\lambda_0^4 r^2}\right) n^2 \langle \Delta n^2 \rangle \left(1+\cos^2\theta\right) = \left(\frac{2\pi^2 V^2}{\lambda_0^4 r^2}\right) n^2 \left\{\left(\frac{\partial n}{\partial \rho}\right)^2 \rho^2 \kappa^2 kT/\kappa V\right\}\left(1+\cos^2\theta\right)$$

$$= \left(\frac{2\pi^2 kT\kappa V}{\lambda_0^4}\right)\left\{n\rho\left(\frac{\partial n}{\partial \rho}\right)\right\}^2 \left(1+\cos^2\theta\right)/r^2$$

$$(7.19.7)$$

The total scattered light intensity is calculated by integrating Eq. (7.19.7) over all the directions. The integration yields

$$\int_0^\pi (1+\cos^2\theta) 2\pi r^2 \sin\theta \, d\theta = \frac{16}{3}\pi \qquad (7.19.8)$$

then we have

$$\tau_\rho = \left(\frac{32}{3}\pi\right)\cdot\left(\frac{kT\kappa}{\lambda_0^4}\right)\cdot\left\{n\rho\left(\frac{\partial n}{\partial \rho}\right)\right\}^2 \qquad (7.19.9)$$

The scattered light intensity induced by the second term of the right-hand side in Eq. (7.19.4) is obtained by substituting it in Eq. (7.19.1) as

$$\tau_0=\left(\frac{32}{3}\pi^3\right)\cdot\left(\frac{kTV}{\lambda_0^4}\right)\cdot\left(\frac{n^2}{\|G\|}\right)\sum_{i=1}^{s}\sum_{j=1}^{s}\partial n/\partial \mathcal{N}_i\cdot\partial n/\partial \mathcal{N}_j\|G\|_{ij} \tag{7.19.10}$$

If s=1 (binary system), using the relationship $\|G\|_{ij}=\partial\|G\|/\partial G_{ij}=1$, we have

$$\tau_0=\left(\frac{32}{3}\pi^3\right)\cdot\left(\frac{kTV}{\lambda_0^4}\right)\cdot\left(\frac{n^2}{G_{11}}\right)\cdot\left(\frac{\partial n}{\partial \mathcal{N}_1}\right)^2 \tag{7.19.11}$$

From the Gibbs-Duhem relationship $\mathcal{N}_0 d\mu_0+\mathcal{N}_1 d\mu_1=0$, we have $d\mu_1=-(\mathcal{N}_0/\mathcal{N}_1)d\mu_0$. Then

$$G_{11}=\frac{\partial}{\partial \mathcal{N}_1}\left(\frac{\partial G}{\partial \mathcal{N}_1}\right)=\frac{\partial\mu_1}{\partial \mathcal{N}_1}=-\left(\frac{\mathcal{N}_0}{\mathcal{N}_1}\right)\frac{\partial\mu_0}{\partial \mathcal{N}_1} \tag{7.19.12}$$

Using the relationship $w=M_1\mathcal{N}_1/(M_0\mathcal{N}_0+M_1\mathcal{N}_1)$ and $\rho=(M_0\mathcal{N}_0+M_1\mathcal{N}_1)/VN_A$, we have $dw=M_1M_0\mathcal{N}_0/(M_0\mathcal{N}_0+M_1\mathcal{N}_1)^2\,d\mathcal{N}_1$. Then

$$\tau_c=\left(\frac{32\pi^3kT}{3\lambda_0^4}\right)\cdot\left(\frac{M_{0w}}{N_A\rho}\right)\cdot\left(\frac{n\partial n}{\partial w}\right)^2/\left(-\frac{\partial\mu_0}{\partial w}\right) \tag{7.19.13}$$

Weight concentration is related to w as $C=\rho w$. Since ρ is approximated by solvent density in dilute solution, w can be replaced by C in Eq. (7.19.13). Using the relationships $d\mu_0=kTd\log a_0$ and $\log a_0=-\Pi V_0^0/RT$, we have

$$\left(\frac{32\pi^3\,kT}{3\lambda_0^4}\right)\cdot\left(\frac{M_{0w}}{N_A\rho}\right)\cdot\left(\frac{n\partial n}{\partial w}\right)^2/\tau_c=-\frac{\partial\mu_0}{\partial C}=-kT\partial\log a_0/\partial C=kT\partial/\partial C\left(\Pi V_0^0/RT\right) \tag{7.19.14}$$

where V_0^0 is the volume per one mole of solvent. In dilute solution, we can approximate $V_0^0\rho=M_0$. Then we obtain

$$\frac{HC}{\tau_c}=\left(\frac{1}{RT}\right)\cdot\frac{\partial\Pi}{\partial C}=1/M+2A_2C+3A_3C^2+\cdots \tag{7.19.15}$$

where

$$H=\left(\frac{32\pi^3n^2}{3N_A\lambda_0^4}\right)\cdot\left(\frac{\partial n}{\partial C}\right)^2 \tag{7.19.16}$$

<<Problem 7-20>> Light scattering arising from polymer solution with molecular weight distribution

Generalize Eq. (7.19.15) to the solution of polymers with molecular weight distribution.

Answer

Chemical potential of *i* th component of the system with molecular weight distribution is expressed as

$$\mu_i=\mu_i^0+kT\log\gamma_i C_i\ ,\quad C_i=\frac{\mathcal{N}_i M_i}{N_A V} \tag{7.20.1}$$

In dilute solutions, $\gamma_i \to 1$ and $\gamma_0 C_0 \to 1$. Expansion of $\log\gamma_i$ in a Taylor series of C yields

$$\log\gamma_i=\sum_{k}^{s} A_{ik}C_k+\sum_{j,k}^{s} B_{ijk}C_jC_k+\cdots \tag{7.20.2}$$

Then we have

$$G_{ij}=\frac{\partial\mu_i}{\partial N_j}=\left(\frac{M_j}{N_A V}\right)\cdot\frac{\partial\mu_i}{\partial C_j}=\left(\frac{M_j kT}{N_A V C_i}\right)\cdot\left(\delta_{ij}+C_i A_{ij}+C_i\sum_{k}^{s} B_{ijk}C_k+\cdots\right) \tag{7.20.3}$$

and

$$|G|=\left(\frac{M_1 M_2\cdots M_s}{C_1 C_2\cdots C_s}\right)\cdot\left(\frac{kT}{N_A V}\right)^s\times$$
$$\left\{1+\sum_{i}^{s} C_iA_{ii}+\sum_{i>j}^{s}\sum^{s} C_iC_jA_{ii}A_{jj}-\sum_{i>j}^{s}\sum^{s} C_iC_jA_{ij}A_{ji}+\sum_{i,j}^{s,s} B_{iij}C_iC_j+O(C^3)\right\} \tag{7.20.4}$$

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* τ_c is the scattering due to fluctuations in concentration and τ_p is that due to density fluctuations. $\tau_c>\tau_p$ is expected for high enough molecular weights (See P. Debye, *J. Appl. Phys.* **15**, 338 (1944); H. C. Brinkman and J. J. Hermans, *J. Chem. Phys.* **17**, 574 (1949); J. G. Kirkwood and R. J. Goldberg, *J. Chem. Phys.* **18**, 54 (1950); W. H. Stockmayer, *J. Chem. Phys.* **18**, 58 (1950); N. Saito, *Polymer Physics*, Chapter 5, § 34, Shokabo Pub., (1958))

Neglecting higher order terms in the equation $dG_{ij}=(M_jkT/N_AV)$x $(dA_{ij}+C_i\Sigma C_k dB_{ijk}+\ldots)$, we have $dG_{ij}=(M_jkT/N_AV)dA_{ij}$. Using this relationship, we have

$$\|G\|_{ij}=\frac{\partial\|G\|}{\partial G_{ij}}=\left(\frac{N_AV}{M_jkT}\right)\cdot\frac{\partial\|G\|}{\partial A_{ij}} \tag{7.20.5}$$

and then

$$\frac{\partial\|G\|_{ij}}{\partial\|G\|}=\left(\frac{N_AV}{M_jkT}\right)\cdot\left\{C_i\delta_i-C_iC_jA_{ji}+O(C^3)\right\}\Big/\left(1+\sum C_iA_{ii}+\cdots\right) \tag{7.20.6}$$

If we approximate $\partial n/\partial C_i=\partial n/\partial C$ (independent of molecular weight) in Eq. (7.19.10), using Eq. (7.20.6) and the relationship $\mathcal{N}_i=(N_AV/M_i)C_i$, we have

$$\begin{aligned}\tau_c&=\left(\frac{32\pi^3kTV}{3\lambda_0^4}\right)\cdot\left(\frac{n^2}{|G|}\right)\sum_i^s\sum_j^s\left(\frac{\partial n}{\partial\mathcal{N}_i}\right)\cdot\left(\frac{\partial n}{\partial\mathcal{N}_j|G|_{ij}}\right)\\&=\left(\frac{32\pi^3}{3\lambda_0^4N_A}\right)\cdot\left(\frac{n\partial n}{\partial C}\right)^2\sum_i^s\sum_j^s M_i\left\{C_i\delta_i-C_iC_jA_{ji}+O(C^3)\right\}\\&=\left(\frac{32\pi^3}{3\lambda_0^4N_A}\right)\cdot\left(\frac{n\partial n}{\partial C}\right)^2\sum_i^s\left\{M_iC_i-\sum_i^s\sum_j^s M_iC_iC_jA_{ji}+O(C^3)\right\}\end{aligned} \tag{7.20.7}$$

Using the definitions

$$M_w=\frac{\sum_i^s\mathcal{N}_iM_i^2}{\sum_i^s\mathcal{N}_iM_i}\ ,\quad w_i=\frac{\sum_i^s\mathcal{N}_iM_i}{\sum_i^s\mathcal{N}_iM_i}\ ,\ C=\sum_i^s C_i$$

we have

$$\begin{aligned}\sum_i^s C_iM_i&=\frac{\sum_i^s\mathcal{N}_iM_i^2}{N_AV}=\left(\frac{\sum_i^s\mathcal{N}_iM_i^2}{\sum_i^s\mathcal{N}_iM_i}\right)\cdot\left(\frac{\sum_i^s\mathcal{N}_iM_i^2}{N_AV}\right)\\&=M_w\sum_i^s C_i=M_w\sum_i^s C\end{aligned} \tag{7.20.8}$$

and

$$M_iC_iC_j=\frac{M_i^{\,2}\,\mathcal{N}_i\mathcal{N}_jM_j}{\left(N_AV\right)^2}=\left\{\frac{M_i^{\,2}\,\mathcal{N}_i\mathcal{N}_jM_j}{\left(\sum_i^s \mathcal{N}_iM_i\right)^2}\right\}\cdot\left(\frac{\sum_i^s \mathcal{N}_iM_i}{\left(N_AV\right)^2}\right)$$

$$=M_iw_iw_jC^2 \tag{7.20.9}$$

Then we finally obtain

$$\frac{HC}{\tau_c}=C/\left\{M_iC_i-\sum_i^s\sum_j^s M_iC_iC_jA_{ij}+O\left(C^3\right)\right\}$$

$$=1/\left\{\sum_i^s M_iC_i/C-\sum_i^s\sum_j^s M_i\left(C_i/C\right)\left(C_j/C\right)A_{ij}+O\left(C^2\right)\right\}$$

$$=1/\left\{\sum_i^s \mathcal{N}_iM_i^{\,2}/\sum_i^s \mathcal{N}_iM_i-\sum_i^s\sum_j^s M_i\left(\mathcal{N}_iM_i/\sum_i^s \mathcal{N}_iM_i\right)\right.$$

$$\left.\times\left(\mathcal{N}_jM_j/\sum_j^s \mathcal{N}_jM_j\right)CA_{ij}+O\left(C^2\right)\right\}$$

$$=1/\left\{M_w-C\sum_i^s\sum_j^s M_iw_iw_jA_{ij}+O\left(C^2\right)\right\}$$

$$=1/M_w+\left(C/M_w^{\,2}\right)\sum_i^s\sum_j^s M_iw_iw_jA_{ij}+O\left(C^2\right) \tag{7.20.10}$$

Thus the scattered light intensity of the system with molecular weight distribution gives the weight average molecular weight.

<<Problem 7-21>> Osmotic pressure of polymer solution with molecular weight distribution

Derive the expression for osmotic pressure of the solution of polymers with molecular weight distribution

Answer

From the Gibbs-Duhem relationship

$$\mathcal{N}_0\,\mathrm{d}\log\gamma_0 C_0+\sum_{i=1}^{s}\mathcal{N}_i\mathrm{d}\log\gamma_i C_i=0 \tag{7.21.1}$$

Using the relationship $C_i=\mathcal{N}_iM_i/N_AV$,

$$\left(\frac{N_AV}{M_0}\right)\mathrm{d}\log\gamma_0C_0=-\sum_{i=1}^{s}\left(\frac{N_AVC_i}{M_i}\right)\mathrm{d}\log\gamma_iC_i \tag{7.21.2}$$

Using Eq. (7.20.2),

$$\begin{aligned}-\left(\frac{C_0}{M_0}\right)\mathrm{d}\log\gamma_0C_0&=\sum_{i=1}^{s}\left(\frac{C_i}{M_i}\right)\cdot\left(\mathrm{d}\log C_i+\mathrm{d}\log\gamma_i\right)\\&=\sum_{i=1}^{s}\left(\frac{C_i}{M_i}\right)\cdot\left\{(1/C_i)\mathrm{d}C_i+\sum_{k=1}^{s}A_{ik}C_k+\cdots\right\}\\&=\sum_{i=1}^{s}\left(\frac{\mathrm{d}C_i}{M_i}\right)+\sum_{i=1}^{s}\sum_{k=1}^{s}\left(\frac{1}{M_i}\right)A_{ik}C_i\,\mathrm{d}C_k+\cdots\end{aligned} \tag{7.21.3}$$

Integrating Eq. (7.21.3) at constant C_0, we have

$$\begin{aligned}\mathrm{d}\sum_{i=1}^{s}\sum_{j=1}^{s}\left(\frac{A_{ij}}{M_i}\right)C_iC_j&=\sum_{i=1}^{s}\sum_{j=1}^{s}\sum_{k=1}^{s}\left(\frac{A_{ij}}{M_i}\right)\left\{C_j\left(\frac{\partial C_i}{\partial C_k}\right)\mathrm{d}C_k+C_i\left(\frac{\partial C_j}{\partial C_k}\right)\mathrm{d}C_k\right\}\\&=\sum_{i=1}^{s}\sum_{\substack{j=1\\(k=i)}}^{s}\left(\frac{A_{ij}}{M_i}\right)C_j\mathrm{d}C_i+\sum_{\substack{i=1\\(k=j)}}^{s}\sum_{j=1}^{s}\left(\frac{A_{ij}}{M_i}\right)C_i\mathrm{d}C_j\\&=\sum_{j=1}^{s}\sum_{i=1}^{s}\left(\frac{A_{ji}}{M_j}\right)C_i\mathrm{d}C_j+\sum_{i=1}^{s}\sum_{j=1}^{s}\left(\frac{A_{ij}}{M_i}\right)C_i\mathrm{d}C_j\\&=\sum_{i=1}^{s}\sum_{j=1}^{s}\left(\frac{A_{ij}}{M_i}\right)C_i\mathrm{d}C_j+\sum_{i=1}^{s}\sum_{j=1}^{s}\left(\frac{A_{ij}}{M_i}\right)C_i\mathrm{d}C_j\\&=2\sum_{i=1}^{s}\sum_{j=1}^{s}\left(\frac{A_{ij}}{M_i}\right)C_i\mathrm{d}C_j\end{aligned} \tag{7.21.4}$$

and then

$$-\left(\frac{C_0}{M_0}\right)\mathrm{d}\log\gamma_0C_0=\sum_{i=1}^{s}\frac{C_i}{M_i}+\frac{1}{2}\sum_{i=1}^{s}\sum_{j=1}^{s}\left(\frac{1}{M_i}\right)C_iC_jA_{ij}+\cdots \tag{7.21.5}$$

Here we use the relationship $A_{ji}M_j=A_{ij}M_i$. Using the definitions

$$M_n=\frac{\sum_{i=1}^{s}\mathcal{N}_iM_i}{\sum_{i=1}^{s}\mathcal{N}_i}\ ,\ n_i=\frac{\mathcal{N}_i}{\sum_{i=1}^{s}\mathcal{N}_i}$$

similarly to Eqs. (7.20.8)-(7.20.10), we have

$$\frac{\sum_{i=1}^{s}C_i}{M_i}=\frac{\sum_{i=1}^{s}\mathcal{N}_i}{N_AV}=\left(\frac{\sum_{i=1}^{s}\mathcal{N}_iM_i}{N_AV}\right)\frac{\sum_{i=1}^{s}\mathcal{N}_i}{\sum_{i=1}^{s}\mathcal{N}_iM_i}=\frac{\sum_{i=1}^{s}C_i}{M_n}=\frac{C}{M_n} \qquad (7.21.6)$$

$$\begin{aligned}\sum_{i=1}^{s}\sum_{j=1}^{s}\left(\frac{A_{ij}}{M_i}\right)C_iC_j&=\sum_{i=1}^{s}\sum_{j=1}^{s}\left(\frac{A_{ij}}{M_i}\right)\cdot\left(\frac{\mathcal{N}_iM_i}{N_AV}\right)\cdot\left(\frac{\mathcal{N}_jM_j}{N_AV}\right)\\&=\left(\frac{1}{N_AV}\right)^2\sum_{i=1}^{s}\sum_{j=1}^{s}A_{ij}\left(n_i\sum_{k=1}^{s}\mathcal{N}_k\right)\cdot\left(n_j\sum_{k=1}^{s}\mathcal{N}_k\right)M_j\\&=\sum_{i=1}^{s}\sum_{j=1}^{s}A_{ij}n_in_j\left(\frac{\sum_{k=1}^{s}\mathcal{N}_k}{\sum_{k=1}^{s}\mathcal{N}_kM_k}\right)^2\left(\frac{\sum_{k=1}^{s}\mathcal{N}_kM_k}{\sum N_AV}\right)^2M_j\\&=\left(\frac{C^2}{M_n^{\,2}}\right)\sum_{i=1}^{s}\sum_{j=1}^{s}A_{ij}n_in_jM_j\end{aligned} \qquad (7.21.7)$$

Therefore, we obtain

$$\begin{aligned}\Pi&=-\left(\frac{RT}{V_0^{\,0}}\right)\log\gamma_0C_0\\&=\left(\frac{RT}{V_0^{\,0}}\right)\cdot\left(\frac{N_AV}{N_0}\right)\cdot\left\{\frac{C}{M_n}+\frac{1}{2}\left(\frac{C^2}{\langle M\rangle_n^{\,2}}\right)\sum_{i=1}^{s}\sum_{j=1}^{s}M_jn_in_jA_{ij}+\cdots\right\}\end{aligned} \qquad (7.21.8)$$

<<Problem 7-22>> Light scattering arising from the system polymer in mixed solvent ($P_2/S_1/S_0$)

Derive the expression for the turbidity of the system polymer in mixed solvent, using Eq. (7.19.10).

Answer

Let's denote two solvents as 0 and 1 and polymer as 2. Then Eq. (7.19.10) is rewritten as

$$\begin{aligned}\tau_c &= \left(\frac{32\pi^3 kTV}{3\lambda_0{}^4}\right)\cdot\left(\frac{n^2}{\|G\|}\right)\sum_{i=1}^{s}\sum_{j=1}^{s}\partial n/\partial \mathcal{N}_i\cdot\partial n/\partial \mathcal{N}_j\|G\|_{ij} \\ &= \left(\frac{32\pi^3 kTV}{3\lambda_0{}^4}\right)n^2\sum_{i=1}^{s}\sum_{j=1}^{s}\partial n/\partial C_i\cdot\partial n/\partial C_j\left(\frac{N_A V}{M_j kT}\right)\times \\ &\quad \left\{C_i\delta_i - C_iC_jA_{ji} + O(C^3)\right\}\left\{\frac{M_iM_j}{(N_AV)^2}\right\} \\ &= \left(\frac{32\pi^3}{3\lambda_0{}^4 N_A}\right)\sum_{i=1}^{s}\sum_{j=1}^{s}\left(n\partial n/\partial C_i\right)\cdot\left(n\partial n/\partial C_j\right)M_i\left\{C_i\delta_i - C_iC_jA_{ji} + O(C^3)\right\}\end{aligned} \tag{7.22.1}$$

Using the relationship $M_2A_{12}=M_1A_{21}$, we have

$$\begin{aligned}\tau_c = \left(\frac{32\pi^3}{3\lambda_0{}^4 N_A}\right)\cdot&\left\{\left(\frac{n\partial n}{\partial C_1}\right)^2 M_1\left(C_1 - C_1{}^2A_{11}\right)\right. \\ &\left. -2\left(\frac{n\partial n}{\partial C_1}\right)\cdot\left(\frac{n\partial n}{\partial C_2}\right)M_2C_1C_2A_{12} + \left(\frac{n\partial n}{\partial C_2}\right)^2 M_2\left(C_2 - C_2{}^2A_{22}\right)\right\}\end{aligned} \tag{7.22.2}$$

The first term in { } of Eq. (7.22.2) comes from the concentration fluctuation of mixed solvent only and we denote this contribution as τ_1:

$$\tau_1 = H_2\left\{\left(\frac{\partial n}{\partial C_1}\right)/\left(\frac{\partial n}{\partial C_2}\right)\right\}^2\cdot M_i\left(C_1 - C_1{}^2A_{11}\right) \tag{7.22.3}$$

Then we have

$$\tau_c - \tau_1 = H_2M_2C_2\left(1 - C_2A_{22}\right) - 2H_2\left(\frac{\partial n}{\partial C_1}\right)/\left(\frac{\partial n}{\partial C_2}\right)\cdot M_2C_1C_2A_{12} \tag{7.22.4}$$

where

$$H_2 = \left(\frac{32\pi^3}{3\lambda_0{}^4 N_A}\right)\cdot\left(\frac{n\partial n}{\partial C_2}\right)^2 \qquad (7.22.5)$$

or

$$\frac{H_2C_2}{(\tau_c - \tau_1)} = \left(\frac{1}{M_2}\right)\cdot 1/\left\{1 - C_2A_{22} - 2\left(\frac{\partial n}{\partial C_1}\right)/\left(\frac{\partial n}{\partial C_2}\right)\cdot C_1A_{12}\right\}$$

$$= \left(\frac{1}{M_2}\right)\left\{1 + C_2A_{22} + 2\left(\frac{\partial n}{\partial C_1}\right)/\left(\frac{\partial n}{\partial C_2}\right)\cdot C_1A_{12} + \cdots\right\} \qquad (7.22.6)$$

(See N. Saito, *Polymer Physics*, Shoka-bo, Tokyo, 1959, Chap. 5, Section 34)

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* For further reading on practical and experimental problems, see M. B. Huglin, *Light scattering from Polymer Solutions*, Academic Press, 1972; B. Chu, *Laser Light Scattering,:Basic Principles and Practice*, 2d. ed., Academic Press, Boston, 1991.

Chapter 8 Hydrodynamic properties

<<Problem 8-1>> Equation of motion for viscoelastic fluids (I)

There are two kinds of force. One is proportional to area (**surface force**, for example, friction force) and the other is proportional to weight or volume (**body force**, for example, gravitational force). Now consider a small cube with volume V flowing with velocity **v** in a fluid. Let's denote the surface force per unit area acting on the surface perpendicular to x, y and z-axis as $\mathbf{P}_x$, $\mathbf{P}_y$ and $\mathbf{P}_z$. $\mathbf{P}_x$ is expressed as

$$\mathbf{P}_x = P_{xx}\mathbf{i}+P_{xy}\mathbf{j}+P_{xz}\mathbf{k} \tag{8.1.1}$$

where $\mathbf{P}_{xx}$, $\mathbf{P}_{xy}$ and $\mathbf{P}_{xz}$ are the x,y and z component of $\mathbf{P}_x$ and **i**, **j** and **k** are unit vectors in the direction of x, y and z-axis, respectively. $\mathbf{P}_y$ and $\mathbf{P}_z$ are expressed similarly. **P** has nine components and is expressed as a tensor:

$$\mathbf{P} = \begin{pmatrix} P_{xx} & P_{yx} & P_{zx} \\ P_{xy} & P_{yy} & P_{zy} \\ P_{xz} & P_{yz} & P_{zz} \end{pmatrix} \tag{8.1.2}$$

Here P_{xx}, P_{yy} and P_{zz} are normal stresses and other components are tangential stresses. The body force $\mathbf{F}'$ is expressed as

$$\mathbf{F}' = m\mathbf{B} = \rho dxdydz\mathbf{B} = \rho dxdydz(B_x\mathbf{i} + B_y\mathbf{j} + B_y\mathbf{k}) \tag{8.1.3}$$

where ρ is the density, $\mathbf{B}(B_x, B_y, B_z)$ the body force per weight $m=\rho dxdydz$. The force acting on a fluid **F** is related to the acceleration $\dot{\mathbf{v}}$ by Newton's second law as

$$\mathbf{F} = m\mathbf{v} \tag{8.1.4}$$

Express the **equation of motion of viscoelastic fluids** exerted by both surface force and body force in an explicit form.

Answer

x component of the surface force acting on the surface perpendicular to x-axis (ABCD and EFGH in Fig.8-1) is the difference of x component of the force acting on EFGH and ABCD and expressed as

$\{(P_{xx}+ (\partial P_{xx}/\partial x)dx)-P_{xx}\}dydz= (\partial P_{xx}/\partial x)dxdydz$

x component of the surface force acting on the surface perpendicular to y-axis and z-axis is similarly obtained as $(\partial P_{yx} /\partial y)$ dxdydz and $(\partial P_{zx}/\partial z)$ dxdydz, respectively. Thus the sum of these three components is expressed as

$((\partial P_{xx}/\partial x)+ (\partial P_{yx} /\partial y)+ (\partial P_{zx}/\partial z))$ dxdydz

x component of the force **F**, F_x, is expressed as

$$F_x = \left(\frac{\partial P_{xx}}{\partial x} + \frac{\partial P_{yx}}{\partial y} + \frac{\partial P_{zx}}{\partial z}\right)dxdydz + \rho B_x dxdydz \qquad (8.1.5)$$

Substitution of Eq. (8.1.5) for F_x in Eq. (8.1.4) yields

$$F_x = \left(\frac{\partial P_{xx}}{\partial x} + \frac{\partial P_{yx}}{\partial y} + \frac{\partial P_{zx}}{\partial z}\right)dxdydz + \rho B_x dxdydz = \rho dxdydz\, \dot{v}_x \qquad (8.1.6)$$

For unit volume of the fluid, we have Newton's law as

$$\frac{\partial P_{xx}}{\partial x} + \frac{\partial P_{yx}}{\partial y} + \frac{\partial P_{zx}}{\partial z} + \rho B_x = \rho\, \dot{v}_x \qquad (8.1.7)$$

in the direction of x,

$$\frac{\partial P_{xy}}{\partial x} + \frac{\partial P_{yy}}{\partial y} + \frac{\partial P_{zy}}{\partial z} + \rho B_y = \rho\, \dot{v}_y \qquad (8.1.8)$$

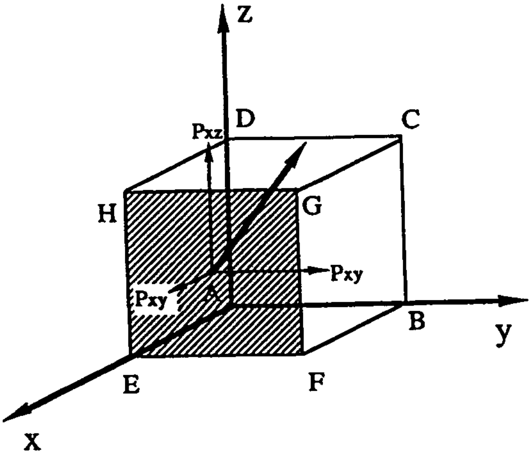

Fig. 8-1 Volume element in fluid

in the direction of y and

$$\frac{\partial P_{xz}}{\partial x} + \frac{\partial P_{yz}}{\partial y} + \frac{\partial P_{zz}}{\partial z} + \rho B_z = \rho\,\dot{v}_z \tag{8.1.9}$$

in the direction of z.

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* In fluid mechanics, it is more convenient to use **Eulerian description** than to use **Lagrangian description**, i.e., one describes physical quantities at every fixed point in space as a function of time rather than follows individual particles or expresses the time course of physical quantities along the stream line. Time derivative along the stream line is called the Lagrange differential or the material derivative and expressed as D/Dt. Suppose a physical variable F to be a function of x, y, z and t. The fluid element located at **r**(x,y,z) at time t moves to **r**+**v**Dt ($x+v_x$Dt, $y+v_y$Dt, $z+v_z$Dt) at t+Dt. Here v_x,v_y and v_z are the x, y and z component of the fluid velocity. The change in F, DF, during Dt is expressed as

$$\begin{aligned}\frac{DF}{Dt} &= \lim_{\Delta t\to 0}\frac{F\left(x+v_x\Delta t,\ y+v_y\Delta t,\ z+v_z\Delta t,\ t+\Delta t\right) - F\left(x,y,z,t\right)}{\Delta t}\\ &= \frac{\partial F}{\partial t} + v_x\frac{\partial F}{\partial x} + v_y\frac{\partial F}{\partial y} + v_z\frac{\partial F}{\partial z}\end{aligned} \tag{8.1.10}$$

Similarly for arbitrary physical variables, we can derive

$$\begin{aligned}\frac{D}{Dt} &= \frac{\partial}{\partial t} + \mathbf{v}\cdot\left(\frac{\partial}{\partial x}\mathbf{i} + \frac{\partial}{\partial y}\mathbf{j} + \frac{\partial}{\partial z}\mathbf{k}\right)\\ &= \frac{\partial}{\partial t} + \mathbf{v}\cdot\mathrm{grad}\end{aligned} \tag{8.1.11}$$

Lagrange derivative of **v** is expressed as

$$\frac{D\mathbf{v}}{Dt} = \frac{\partial \mathbf{v}}{\partial t} + \mathbf{v}\cdot\mathrm{grad}\mathbf{v} \tag{8.1.12}$$

where the first term of the right-hand side associated with unsteady time variation at a fixed position is called the **local derivative** and the second term is called the **convective derivative**. The differentials in v_x, v_y and v_z in Eqs. (8.1.7)-(8.1.9) are the Lagrange derivatives and expressed similarly to the right-hand side of Eq. (8.1.12).

<<Problem 8-2>> Stress-strain relationship

Derive the **stress-strain relationship for elastic bodies** with a small volume element dxdydz and the **corresponding relationship for viscous fluids.**

Answer

Let's denote the volume element of the elastic body after a transformation as $dx'dy'dz'$. If the displacement is sufficiently small, we have

$$dx' = dx(1 + e_{xx}) \tag{8.2.1}$$

$$dy' = dy(1 + e_{yy}) \tag{8.2.2}$$

$$dz' = dz(1 + e_{zz}) \tag{8.2.3}$$

where e_{xx} is the x component of the strain on the surface perpendicular to x-axis (e_{yy} and e_{zz} denote the corresponding y and z components). The volume of the element after the transformation is expressed as

$$\begin{aligned} dx'dy'dz' &= dx(1 + e_{xx})dy(1 + e_{yy})dz(1 + e_{zz}) \\ &= dxdydz(1 + e_{xx})(1 + e_{yy})(1 + e_{zz}) \end{aligned} \tag{8.2.4}$$

If the volume of the element before the transformation is unit volume, the increment of volume of the element by the transformation ε_v, is given by

$$\varepsilon_v = \frac{dx'dy'dz'}{dxdydz} - 1 = (1 + e_{xx})(1 + e_{yy})(1 + e_{zz}) - 1 \approx e_{xx} + e_{yy} + e_{zz} \tag{8.2.5}$$

The last expression is identical to the trace of the tensor

$$e = \begin{pmatrix} e_{xx} & e_{xy} & e_{xz} \\ e_{yx} & e_{yy} & e_{yz} \\ e_{zx} & e_{zy} & e_{zz} \end{pmatrix} \quad \text{(strain tensor)} \tag{8.2.6}$$

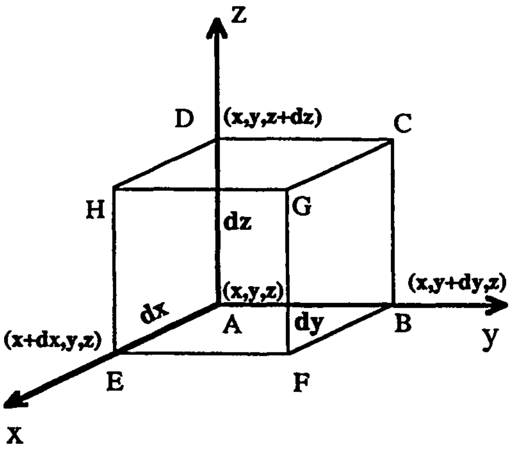

Fig. 8-2 Volume element in fluid

In general, the **strain tensor** e is expressed as the sum of the isotropic component corresponding to the volume change without shape change, ε_v , and the anisotropic component corresponding to the shape change without volume change, e_0, i.e.,

$$e = \varepsilon_v + e_0 \tag{8.2.7}$$

When the transformation is isotropic (e_0=0), the rate of the volume increment is independent of the direction. Then Eq. (8.2.5) is reduced to

$$\varepsilon_0 = \varepsilon + \varepsilon + \varepsilon = 3\varepsilon \tag{8.2.8}$$

where ε=e_{xx}=e_{yy}=e_{zz}. From Eqs. (8.2.7) and (8.2.8), we have

$$e_0 = e\text{-}\varepsilon_v = \begin{pmatrix} e_{xx}\text{-}\varepsilon & e_{xy} & e_{xz} \\ \cdot & e_{yy}\text{-}\varepsilon & e_{yz} \\ \cdot & \cdot & e_{zz}\text{-}\varepsilon \end{pmatrix} \tag{8.2.9}$$

where the dots denote the symmetrical components. Similarly, the mean pressure P_m is proportional to the trace of the **stress tensor**

$$P = \begin{pmatrix} P_{xx} & P_{xy} & P_{xz} \\ P_{yx} & P_{yy} & P_{yz} \\ P_{zx} & P_{zy} & P_{zz} \end{pmatrix} \quad \text{(stress tensor)} \tag{8.2.10}$$

and expressed as

$$P_m = \frac{P_{xx} + P_{yy} + P_{zz}}{3} = \frac{\text{-}P\ \text{-}P\ \text{-}P}{3} = \text{-}P \tag{8.2.11}$$

where P is the **hydrostatic pressure** having the opposite sign to P_{xx}, P_{yy} and P_{zz}. When the transformation is infinitesimally small, P_m is related to ε_v as

$$P_m = \kappa\varepsilon_v \tag{8.2.12}$$

where κ is the **elastic modulus**. The anisotropic component of P is the component P_{ij} with i≠j. If we denote this component as P_0, we have

$$P_0 = P\text{-}P_m = \begin{vmatrix} P_{xx}\text{-}P & P_{xy} & P_{xz} \\ \cdot & P_{yy}\text{-}P & P_{yz} \\ \cdot & \cdot & P_{zz}\text{-}P \end{vmatrix} \tag{8.2.13}$$

P_0 is related to e_0 as

$$P_0 = 2\gamma e_0 \tag{8.2.14}$$

where γ is the **shear modulus**. For viscous fluids (with no elasticity), the stress for arbitrary strain is zero and the pressure is proportional to the **strain rate**. If we denote the strain rate for the volume change as $\dot{\varepsilon}_v$ and that for the shape change as $\dot{e}_0$, the stress is proportional to the strain rate as

$$P_m = \eta_v \dot{\varepsilon}_v \tag{8.2.15}$$

and

$$P_0 = 2\eta \dot{e}_0 \tag{8.2.16}$$

where η_v and η are the **volumetric viscosity** and the **shear viscosity**, respectively. The viscosity of polymer solutions usually means η.

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* Strain is defined by $\varepsilon = \Delta l / l$ where l and Δl denote the original length and the displacement, respectively.

* Hooke's law holds for the stress and strain relationship in infinitesimal transformations of elastic bodies.

<<Problem 8-3>> Lamè constant

For isotropic elastic bodies, the stress P_{rs} is related to the strain e_{rs} as

$$P_{rs} = 2\mu e_{rs} + \lambda \delta_{rs}(e_{xx} + e_{yy} + e_{zz}) \tag{8.3.1}$$

where the subscript rs means the component in the direction of s on the surface perpendicular to r axis, λ and μ are the materials constants called the **Lamè constants** and δ_{rs} is **Kronecker delta** ($\delta_{rs}=0$ when $r \neq s$ and $\delta_{rs}=1$ when $r=s$). λ and μ are related to κ and γ defined by Eqs. (8.2.12) and (8.2.14), respectively, as

$$\lambda = \kappa - \frac{2}{3}\gamma, \ \mu = \gamma \tag{8.3.2}$$

Derive Eq. (8.3.2).

Answer

In the three dimensional space, stress P and strain e are described with nine components as shown by Eqs. (8.2.6) and (8.2.10), respectively. If the system is at an equilibrium state, the moment of rotation on an arbitrary infinitesimal rectangular prism about the coordinate axis must be zero. For example, the moment about z axis is

$$\left(P_{xy} + \frac{\partial P_{xy}}{\partial x}dx\right)dydz \times dx - \left(P_{yx} + \frac{\partial P_{yx}}{\partial y}dy\right)dxdz \times dx = 0 \qquad (8.3.3)$$

For the infinitesimal volume elements,

$$\left.\begin{array}{l} P_{xy} \gg \dfrac{\partial P_{xy}}{\partial x}dx \\ P_{yx} \gg \dfrac{\partial P_{yx}}{\partial y}dy \end{array}\right\} \qquad (8.3.4)$$

Then from Eq. (8.3.3), we have

$$P_{xy} = P_{yx} \qquad (8.3.5)$$

Similarly,

$$P_{zx} = P_{xz} \qquad (8.3.6)$$

$$P_{zy} = P_{yz} \qquad (8.3.7)$$

Thus the **stress tensor** P is the symmetrical tensor

$$P = \begin{pmatrix} P_{xx} & P_{xy} & P_{xz} \\ \cdot & P_{yy} & P_{yz} \\ \cdot & \cdot & P_{zz} \end{pmatrix} \qquad (8.3.8)$$

For the **strain tensor**, we have

$$\left.\begin{array}{l} e_{xy} = e_{yx} \\ e_{zx} = e_{xz} \\ e_{zy} = e_{yz} \end{array}\right\} \qquad (8.3.9)$$

Thus the strain tensor is also the symmetrical tensor. Each six among nine components of P and e are independent. For brevity, let's denote the independent components as

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* The moment of inertia about arbitrary axis, **I**, is defined by **I**=**r**x**F**. The vector **I** is in the direction perpendicular to the surface constructed by the vectors **r** and **F**.

$$\left.\begin{array}{l} P_1 = P_{xx} \\ P_2 = P_{yy} \\ P_3 = P_{zz} \\ P_4 = P_{yz} \\ P_5 = P_{zx} \\ P_6 = P_{xy} \end{array}\right\} \qquad (8.3.10)$$

and

$$\left.\begin{array}{l} e_1 = e_{xx} \\ e_2 = e_{yy} \\ e_3 = e_{zz} \\ e_4 = e_{yz} \\ e_5 = e_{zx} \\ e_6 = e_{xy} \end{array}\right\} \qquad (8.3.11)$$

P is a function of e. For example, r component of P is expressed as

$$P_r = f_r(e_1, e_2, e_3, e_4, e_5, e_6) \qquad (8.3.12)$$

Expanding f_r in a Taylor series and neglecting higher order terms, we have

$$P_r = k_{r1}e_1 + k_{r2}e_2 + k_{r3}e_3 + k_{r4}e_4 + k_{r5}e_5 + k_{r6}e_6 = \sum_{i=1}^{6} k_{ri}e_i \qquad (8.3.13)$$

where k_{ri} are the **elastic modulus**. The number of the elastic moduli is 6x6=36. For isotropic bodies, independent elastic moduli are only two:

$$k_{44} = \frac{1}{2}(k_{11} - k_{12}) = \mu \qquad (8.3.14)$$

and

$$k_{12} = \lambda \qquad (8.3.15)$$

Then Eq. (8.3.13) is expressed as $P_{rs}=2\mu e_{rs}+\lambda\delta_{rs}(e_{xx}+e_{yy}+e_{zz})$. For P_{xx}, we have

$$P_{xx} = 2\mu e_{xx} + \lambda e_{xx} + \lambda e_{yy} + \lambda e_{zz} \qquad (8.3.16a)$$

or

$$P_{xx} = (2\mu + \lambda)e_{xx} + \lambda e_{yy} + \lambda e_{zz} \qquad (8.3.16b)$$

Similarly we have

$$P_{yy} = \lambda e_{xx} + (2\mu + \lambda)e_{yy} + \lambda e_{zz} \qquad (8.3.17)$$

$$P_{zz} = \lambda e_{xx} + \lambda e_{yy} + (2\mu + \lambda)e_{zz} \qquad (8.3.18)$$

The sum of both sides of Eq. (8.3.16b), (8.3.17) and (8.3.18) yields

$$P_{xx} + P_{yy} + P_{zz} = \left(2\mu + 3\lambda\right)\left(e_{xx} + e_{yy} + e_{zz}\right) \qquad (8.3.19)$$

Substituting equations

$$3P_m = P_{xx} + P_{yy} + P_{zz} \qquad (8.2.11)$$

$$\varepsilon_v = e_{xx} + e_{yy} + e_{zz} \qquad (8.2.5)$$

in Eq. (8.3.19), we have

$$3P_m = \left(2\mu + 3\lambda\right)\varepsilon_v \qquad (8.3.20)$$

Comparing Eqs. (8.2.12) and (8.3.20), we find

$$\kappa = \frac{2\mu + 3\lambda}{3} \qquad (8.3.21)$$

For **pure shear**, Eq. (8.2.6) is reduced to

$$e = \begin{pmatrix} 0 & e_{xy} & 0 \\ \cdot & 0 & 0 \\ \cdot & \cdot & 0 \end{pmatrix} \qquad (8.3.22)$$

and Eq. (8.3.8) is reduced to

$$P = \begin{pmatrix} 0 & P_{xy} & 0 \\ \cdot & 0 & 0 \\ \cdot & \cdot & 0 \end{pmatrix} \qquad (8.3.23)$$

For infinitesimal transformations, from Eq. (8.2.14), we have

$$P_{xy} = 2\gamma e_{xy} \qquad (8.3.24)$$

From Eq. (8.3.1),

$$P_{xy} = 2\mu e_{xy} \qquad (8.3.25)$$

Then

$\mu=\lambda$

The substitution of this equation in Eq. (8.3.21) yields the relationship

$\lambda=\kappa-2/3\ \gamma$

Thus the mechanical properties of isotropic elastic bodies are expressed only by the **elastic modulus** and the **shear modulus**.

<<Problem 8-4>> Stress equation

Derive the **relationship between stress P_{rs} and shear rate $\dot{e}_{rs}(= \partial e_{rs}/\partial t)$ for viscous fluids**:

$$P_{rs} = 2\eta\dot{e}_{rs} + \left\{-P + \left(\eta_v - \frac{2}{3}\eta\right)\dot{\varepsilon}_v\right\}\delta_{rs} \tag{8.4.1}$$

Answer

Substitution of Eq. (8.3.2) in Eq. (8.3.1) yields

$$P_{rs} = 2\gamma e_{rs} + \left(\kappa - \frac{2}{3}\gamma\right)\delta_{rs}\varepsilon_v \tag{8.4.2}$$

for isotropic elastic bodies, where $\varepsilon_v = e_{xx} + e_{yy} + e_{zz}$ represents the unit expansion. A similar relationship holds for fluids if we replace γ by η, κ by η_v and e_{rs} by $\dot{e}_{rs}$, according to the **viscosity-elasticity analogy** as

$$P_{rs} = 2\eta\dot{e}_{rs} + \left(\eta_v - \frac{2}{3}\eta\right)\delta_{rs}\dot{\varepsilon}_v \tag{8.4.3}$$

If the fluid has viscosity as well as elasticity (viscoelastic body), by summing up the right-hand sides of Eqs. (8.4.2) and (8.4.3), we have

$$P_{rs} = 2\gamma e_{rs} + 2\eta\dot{e}_{rs} + \left(\kappa - \frac{2}{3}\gamma\right)\delta_{rs}\varepsilon_v + \left(\eta_v - \frac{2}{3}\eta\right)\delta_{rs}\dot{\varepsilon}_v \tag{8.4.4}$$

In general, shear modulus γ is zero and $\kappa\varepsilon_v = P_m = -P$ for fluids. Then Eq. (8.4.4) is reduced to Eq. (8.4.1).

<<Problem 8-5>> Equation of motion for viscoelastic fluids (II)

Derive the **equation of motion for fluids**

$$\eta\nabla^2 v_r - \frac{\partial P}{\partial r} + \left(\eta_v + \frac{1}{3}\eta\right)\frac{\partial\dot{\varepsilon}_v}{\partial r} + \rho B_r = \rho\dot{v}_r \quad (r = x, y, z) \tag{8.5.1}$$

by substituting Eq. (8.4.1) for P_{rs} in the equation of motion Eqs. (8.1.7)-(8.1.9).

Answer

Substitution of Eq. (8.4.1) in Eq. (8.1.7) yields

$$2\eta\left(\frac{\partial \dot{e}_{xx}}{\partial x}+\frac{\partial \dot{e}_{yx}}{\partial y}+\frac{\partial \dot{e}_{zx}}{\partial z}\right)-\frac{\partial P}{\partial x}+\left(\eta_v-\frac{2}{3}\eta\right)\frac{\partial \dot{\varepsilon}_v}{\partial x}+\rho B_x=\rho\dot{v}_x \tag{8.5.2}$$

Similarly, from Eqs. (8.1.8) and (8.1.9) and (8.4.1), we have

$$2\eta\left(\frac{\partial \dot{e}_{xy}}{\partial x}+\frac{\partial \dot{e}_{yy}}{\partial y}+\frac{\partial \dot{e}_{zy}}{\partial z}\right)-\frac{\partial P}{\partial y}+\left(\eta_v-\frac{2}{3}\eta\right)\frac{\partial \dot{\varepsilon}_v}{\partial y}+\rho B_y=\rho\dot{v}_y \tag{8.5.3}$$

$$2\eta\left(\frac{\partial \dot{e}_{xz}}{\partial x}+\frac{\partial \dot{e}_{yz}}{\partial y}+\frac{\partial \dot{e}_{zz}}{\partial z}\right)-\frac{\partial P}{\partial z}+\left(\eta_v-\frac{2}{3}\eta\right)\frac{\partial \dot{\varepsilon}_v}{\partial z}+\rho B_z=\rho\dot{v}_z \tag{8.5.4}$$

In general, the tensor which expresses an infinitesimal displacement D_{rs} is divided into the component corresponding to the strain e_{rs} and that corresponding to the rotation (rigid body displacement) o_{rs} as

$$D_{rs}=\frac{1}{2}\left(D_{rs}+D_{sr}\right)+\frac{1}{2}\left(D_{rs}-D_{sr}\right)=\frac{1}{2}\left(\frac{\partial u_r}{\partial s}+\frac{\partial u_s}{\partial r}\right)+\frac{1}{2}\left(\frac{\partial u_r}{\partial s}-\frac{\partial u_s}{\partial r}\right)=e_{rs}-o_{rs} \tag{8.5.5}$$

Here u_r and u_s denote the displacement along the surface perpendicular to r direction and s direction, respectively. The **strain rate tensor** $\dot{e}$ is expressed as

$$\dot{e}=\frac{de}{dt}=\begin{pmatrix}\frac{de_{xx}}{dt} & \frac{de_{xy}}{dt} & \frac{de_{xz}}{dt}\\ \cdot & \frac{de_{yy}}{dt} & \frac{de_{yz}}{dt}\\ \cdot & \cdot & \frac{de_{zz}}{dt}\end{pmatrix}=\begin{pmatrix}\dot{e}_{xx} & \dot{e}_{xy} & \dot{e}_{xz}\\ \cdot & \dot{e}_{yy} & \dot{e}_{yz}\\ \cdot & \cdot & \dot{e}_{zz}\end{pmatrix} \tag{8.5.6}$$

The partial differentiation of the components with respect to x yields

$$\frac{\partial \dot{e}_{xx}}{\partial x}=\frac{\partial}{\partial x}\left\{\frac{1}{2}\left(\frac{\partial v_x}{\partial x}+\frac{\partial v_x}{\partial x}\right)\right\}=\frac{1}{2}\left(2\frac{\partial^2 v_x}{\partial x^2}\right) \tag{8.5.7}$$

$$\frac{\partial \dot{e}_{xy}}{\partial x}=\frac{\partial}{\partial x}\left\{\frac{1}{2}\left(\frac{\partial v_x}{\partial x}+\frac{\partial v_y}{\partial y}\right)\right\}=\frac{1}{2}\left(\frac{\partial^2 v_x}{\partial x^2}+\frac{\partial^2 v_y}{\partial x\partial y}\right) \tag{8.5.8}$$

$$\vdots$$

From the definitions,

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} = \frac{d}{dt}\left(\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z}\right) = \dot{e}_{xx} + \dot{e}_{yy} + \dot{e}_{zz} = \dot{\varepsilon}_v \tag{8.5.9}$$

and

$$\frac{\partial^2 v_x}{\partial x^2} + \frac{\partial^2 v_x}{\partial y^2} + \frac{\partial^2 v_x}{\partial z^2} = \nabla^2 v_x \tag{8.5.10}$$

Substitution of Eqs. (8.5.7)-(8.5.10) in Eqs. (8.5.2)-(8.5.4) yields

$$\eta\left(\frac{\partial \dot{\varepsilon}_v}{\partial x} + \nabla^2 v_x\right) - \frac{\partial P}{\partial x} + \left(\eta_v - \frac{2}{3}\eta\right)\frac{\partial \dot{\varepsilon}_v}{\partial x} + \rho B_x = \rho \dot{v}_x \tag{8.5.11}$$

$$\eta\left(\frac{\partial \dot{\varepsilon}_v}{\partial y} + \nabla^2 v_y\right) - \frac{\partial P}{\partial y} + \left(\eta_v - \frac{2}{3}\eta\right)\frac{\partial \dot{\varepsilon}_v}{\partial y} + \rho B_y = \rho \dot{v}_y \tag{8.5.12}$$

$$\eta\left(\frac{\partial \dot{\varepsilon}_v}{\partial z} + \nabla^2 v_z\right) - \frac{\partial P}{\partial z} + \left(\eta_v - \frac{2}{3}\eta\right)\frac{\partial \dot{\varepsilon}_v}{\partial z} + \rho B_z = \rho \dot{v}_z \tag{8.5.13}$$

Eqs. (8.5.11)-(8.5.13) are summarized as Eq. (8.5.1).

<<Problem 8-6> Equation of continuity

Derive the equation of continuity for fluids

$$-\frac{d\rho}{dt} = \rho \cdot \mathrm{div}\ \mathbf{v} \tag{8.6.1}$$

where ρ is the density, t the time, **v** the fluid velocity, and $d\rho/dt$ the time derivative of density at the same position in the fluid.

Answer

Consider an infinitesimal rectangular prism with volume dV=dxdydz. Let's denote the fluid velocity in the direction of x, y and z direction as v_x, v_y and v_z, respectively. The volume flowing into the element through the surface ABCD (area dydz) per unit time is

$$\frac{dV_x}{dt} = v_x dydz \tag{8.6.2}$$

(See Fig.8-1) The volume flowing out from the element through the surface

EFGH (area dydz) per unit time is

$$\frac{dV_{x+dx}}{dt} = \left(v_x + \frac{\partial v_x}{\partial x}dx\right)dydz \tag{8.6.3}$$

Then the rate of the volume increment of the infinitesimal rectangular prism through the surfaces perpendicular to x direction is

$$\frac{dV_x}{dt} - \frac{dV_{x+dx}}{dt} = -\frac{\partial v_x}{\partial x}dxdydz = -\frac{\partial v_x}{\partial y}dv \tag{8.6.4a}$$

Similarly, those through the surfaces perpendicular to y and z directions are

$$-\frac{\partial v_y}{\partial y}dv \tag{8.6.4b}$$

and

$$-\frac{\partial v_z}{\partial z}dv \tag{8.6.4c}$$

respectively. The rate of the total volume decrease is given by

$$\frac{dV}{dt} = -\left(\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z}\right)dv \tag{8.6.5}$$

Flow flux density, the total amount of fluid flowing through unit area per unit time, is ρ**v** for the fluid with density ρ and velocity **v**. Then div(ρv)dV is the rate of the weight decrease per unit time. If there are no source and sink singularities in the volume element, the weight decrease is equal to -(∂ρ/ ∂t)dV. Here, ∂ρ/ ∂t means the time derivative of the density of the fluid element. Then

$$-\frac{\partial \rho}{\partial t}dv = \mathrm{div}(\rho \mathbf{v})dv \tag{8.6.6}$$

or

$$-\frac{\partial \rho}{\partial t} = \mathrm{div}(\rho \mathbf{v}) \tag{8.6.7}$$

Using the vector relationship

$$\mathrm{div}(\rho \mathbf{v}) = \mathrm{grad}\,\rho \cdot \mathbf{v} + \rho \cdot \mathrm{div}\,\mathbf{v} \tag{8.6.8}$$

Eq. (8.6.7) is rewritten as

$$-\frac{\partial \rho}{\partial t} = \text{grad}\ \rho \cdot \mathbf{v} + \rho \cdot \text{div}\ \mathbf{v} \qquad (8.6.9)$$

The rate of the increase in density of the infinitesimal fluid element locating at (x,y,z) at t is expressed as

$$\begin{aligned}\frac{d\rho}{dt} &= \frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial x}\frac{dx}{dt} + \frac{\partial \rho}{\partial y}\frac{dy}{dt} + \frac{\partial \rho}{\partial z}\frac{dz}{dt} \\ &= \frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial x} v_x + \frac{\partial \rho}{\partial y} v_y + \frac{\partial \rho}{\partial z} v_z = \frac{\partial \rho}{\partial t} + \text{grad}\rho \cdot \mathbf{v} \qquad (8.6.10)\end{aligned}$$

Combining Eqs. (8.6.9) and (8.6.10), we have

$$\frac{d\rho}{dt} + \rho \text{div}\ \mathbf{v} = 0 \qquad (8.6.1)$$

<<Problem 8-7> Navier-Stokes equation and Euler's equation

Derive the **equation of motion for incompressible fluids with or without viscosity**.

Answer

Equation of motion for fluids is given by Eq. (8.5.1). From Eq. (8.6.1) $\varepsilon_v=0$ for incompressible fluids. Then Eq. (8.5.1) is reduced to the equation

$$\eta \nabla^2 v_r - \frac{\partial P}{\partial t} + \rho B_r = \rho \dot{v}_r = \rho\left(\frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r}\right) \qquad \left(r = x, y, z\right) \qquad (8.7.1)$$

Eq. (8.7.1) is called the **Navier-Stokes equation**. If the fluid is perfect fluid ($\eta=0$), Eq. (8.7.1) further reduces to

$$-\frac{\partial P}{\partial t} + \rho B_r = \rho \dot{v}_r \qquad (8.7.2)$$

Eq. (8.7.2) is called **Euler's equation**. For a slow steady flow $\partial v_r/\partial t=0$, the inertia term $v_r\ \partial v_r/\ \partial r$ can be neglected, that is,

$$\dot{\mathbf{v}} = 0 \qquad (8.7.3)$$

If there is no external volumetric force ($B_r=0$), we have

$$\eta \nabla^2 v_r = \frac{\partial P}{\partial r} \qquad (8.7.4)$$

or

$$\eta\nabla^2\mathbf{v} = \text{grad } P \tag{8.7.5}$$

Eq. (8.7.5) is called the **Stokes equation** (or **Stokes formula**) which is one of the basic equations in the theory for viscosity of polymer solutions.

<<Problem 8-8> Reynolds number

Discuss the balance of the force of inertia and the force of viscosity in Eq. (8.7.1).

Answer

Let's denote typical length and velocity which characterize the flow as L and U,respectively. From a dimensional analysis, the force of inertia ~ $\rho U^2/L$ and the force of viscosity ~$\eta U/L^2$ and the ratio of the force of inertia and the force of viscosity = $(\rho U^2/L)/(\eta U/L^2)$ =$(\rho UL)/\eta$=R. Here, R is called the **Reynolds number**. When R is small the force of inertia is negligible, and when R is large the force of viscosity is negligible.

<Problem 8-9> Couette flow

Imagine the viscous fluid held between two plates with the upper plate moving with relative velocity u against the lower plate along x-axis on xz plane, as shown in Fig. 8-9 (a). Derive the equation

$$v_x = gy \tag{8.9.1}$$

by solving Stokes equation and then derive the relationship between P_{xy} and e_{xy} by substituting Eq. (8.9.1) in the stress equation (8.4.1).

Answer

In this problem all the physical quantities depend only on y coordinate. The fluid held on between two plates has velocity only in x direction, that is,

$$\left.\begin{array}{l} v_x \neq 0 \\ v_y = 0 \\ v_z = 0 \end{array}\right\} \tag{8.9.2}$$

According to <<Problem 8-7>>, Navier-Stokes equation for a slow steady flow of incompressible fluids is given by

$$\eta\nabla^2 \mathbf{v} = \text{grad } P \tag{8.7.6}$$

For the present condition,

$$\eta\frac{\partial^2 v_x}{\partial y^2} = \frac{\partial P}{\partial y} \tag{8.9.3}$$

Since pressure is constant,

$$\frac{\partial P}{\partial y} = 0 \tag{8.9.4}$$

Then Eq. (8.9.3) is reduced to

$$\eta\frac{\partial^2 v_x}{\partial y^2} = 0 \qquad (h \neq 0) \tag{8.9.5}$$

The solution of Eq. (8.9.5) is

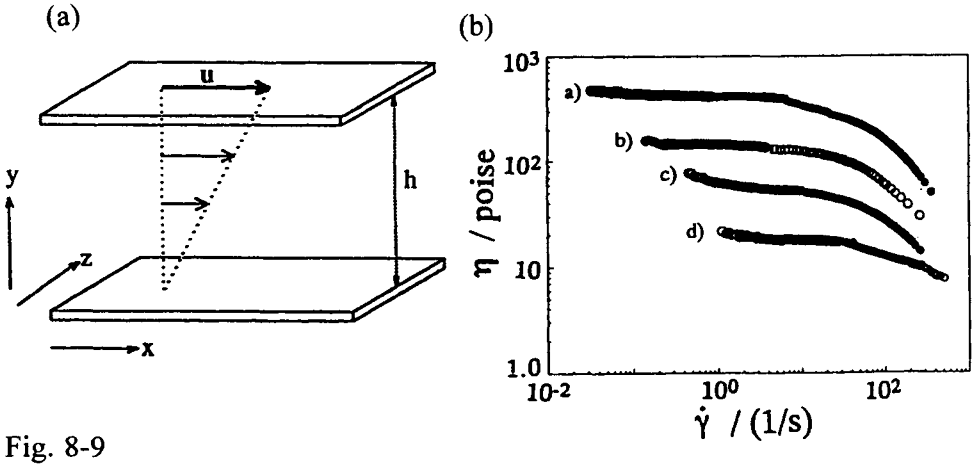

Fig. 8-9

(a) Couette flow

(b) The effect of the degree of polymerization DP of cellulose on the solution viscosity η as a function of shear rate $\dot{\gamma}$ for the system cellulose-cuprammonium : a) DP-1400, b) DP=1050, c) DP=800, and d) DP=550 under the condition of Cp(concentration of cellulose)=5wt%, NH_3/Cellulose=0.94(w/w), and Cu/Cellulose=0.36(w/w) (See I. Miyamoto, T. Matsui, M. Saito and K. Okajima, *J. Text. Mech. Soc. Jpn.* **50**, 73 (1996))

$$v_x = ay + b \tag{8.9.6}$$

with a and b being integration constants. Let's denote the distance between the two plates as h. Using the boundary condition (v_x=0 when y=0 and v_x=u when y=h (no slip condition)), we have v_x=uy/h=gy, where

$$g = \frac{u}{h} = \frac{\partial v_x}{\partial y} \tag{8.9.7}$$

is the velocity gradient. We finally obtain

$$\left.\begin{aligned} v_x &= gy \\ v_y &= 0 \\ v_z &= 0 \end{aligned}\right\} \tag{8.9.8}$$

From Eq. (8.5.8),

$$\dot{e}_{xy} = \frac{de_{xy}}{dt} = \frac{1}{2}\left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x}\right) \tag{8.9.9}$$

Combining Eqs. (8.9.8) and (8.9.9), we have

$$\dot{e}_{xy} = \frac{g}{2} \tag{8.9.10}$$

All the components of $\dot{e}$ except for $\dot{e}_{xy}$ are zero. Substitution of Eq. (8.9.10) and the incompressibility condition $\dot{e}_v$=0 in the relationship of P_{rs} and e_{rs} , Eq. (8.4.1), yields

$$P_{xx} = P_{yy} = P_{zz} = -P \tag{8.9.11}$$

$$P_{xy} = \eta g \tag{8.9.12}$$

$$P_{yz} = P_{zx} = 0 \tag{8.9.13}$$

---

* The notation σ_{xy} is used in place of P_{xy} frequently as

$$\sigma_{xy} = \eta g \tag{8.9.12'}$$

where σ_{xy} is the stress acting on the surface perpendicular to y axis along x direction. When η is constant, the fluid is called **Newtonian**. Polymer solutions are usually **non-Newtonian**, as shown for a typical case in Fig. 8-9 (b).

* The dimension of η is evaluated from Eq. (8.9.12) or

$$\eta = \frac{P_{xy}}{g} \qquad (8.9.12)''$$

Let's denote weight, length and time as M, L and T, respectively. Then we have the dimension of η as

$$(\eta) = \left(\frac{MLT^{-2}}{L^2}\right)\left(\frac{L}{LT^{-1}}\right) = L^{-1}MT^{-1} \qquad (8.9.14)$$

η is expressed by g/cm sec or dyn sec/cm^2 (poise) in cgs unit. Poise is named after Poiseuille.

<<Problem 8-10>> Equation of motion and equation of continuity for slow steady flow (I)

The solution for the equation of motion and the equation of continuity for slow steady flow

$$\eta\Delta\mathbf{u} = \text{grad } P \qquad (8.7.6)$$

$$\text{div } \mathbf{u} = 0 \qquad (8.10.1)$$

is given by

$$\mathbf{u} = \text{grad}(\mathbf{r}\cdot\phi) - 2\phi \qquad (8.10.2)$$

$$P = 2\eta \text{ div } \phi \qquad (8.10.3)$$

Here ϕ is the vector which satisfies the equation $\Delta\phi=0$. Prove Eqs. (8.10.2) and (8.10.3).

Answer

Divergence of both sides of Eq. (8.7.6) is given by

$$\eta \text{ div } \Delta\mathbf{u} = \eta\Delta\text{div } \mathbf{u} = \text{div grad } P = \Delta P \qquad (8.10.4)$$

Substitution of Eq. (8.10.1) in Eq. (8.10.4) yields

$$\Delta P = 0 \qquad (8.10.5)$$

This equation is called the **Laplace equation** and the function which satisfies the Laplace equation is a harmonic function. Let's denote an arbitrary harmonic function as $\phi(\phi_x,\phi_y,\phi_z)$; $\Delta\phi=0$. Then

$$\Delta(\mathbf{r}\cdot\phi) = \mathbf{r}\cdot\Delta\phi + 2\text{div } \phi = 2\text{div } \phi \qquad (8.10.6)$$

Thus $\mathbf{u}$ in Eq. (8.10.2) satisfies Eq. (8.10.1), since

$$\mathrm{div}\,\mathbf{u} = \Delta(\mathbf{r}\cdot\boldsymbol{\phi}) - 2\mathrm{div}\,\boldsymbol{\phi} = 0 \tag{8.10.7}$$

Substitution of Eq. (8.10.2) in the left-hand side of Eq. (8.7.6) yields

$$\eta\Delta\left(\mathrm{grad}(\mathbf{r}\cdot\boldsymbol{\phi}) - 2\boldsymbol{\phi}\right) = \eta\,\mathrm{grad}\Delta(\mathbf{r}\cdot\boldsymbol{\phi}) = 2\eta\,\mathrm{grad}(\mathrm{div}\,\boldsymbol{\phi}) \tag{8.10.8}$$

Then we have Eq. (8.10.3).

<<Problem 8-11>> Equation of motion and equation of continuity for slow steady flow (II)

Derive the equation

$$\Delta\phi = 0 \tag{8.11.1}$$

for

$$|\boldsymbol{\phi}| = \frac{1}{r} \tag{8.11.2}$$

Then derive the expressions for **u** and P for one-dimensional case in <<Problem 8-10>> by substituting $\boldsymbol{\phi}=\mathbf{i}/r$ in Eqs. (8.10.2) and (8.10.3).

Answer

Using the relationship $r^2=\Sigma x_i^2$,

$$\Delta\phi = \Delta\left(\frac{1}{r}\right) = \sum_i \frac{\partial^2}{\partial x_i^2}\left(\frac{1}{r}\right) = \sum_i \frac{\partial}{\partial x_i}\left(-\frac{1}{r^2}\frac{\partial r}{\partial x_i}\right) = \sum_i \left(\frac{2}{r^3}\left(\frac{\partial r}{\partial x_i}\right)^2 - \frac{1}{r^2}\frac{\partial^2 r}{\partial x_i^2}\right) \tag{8.11.3}$$

Here, $\partial r/\partial x_i = x_i/r$ and $\partial^2 r/\partial x_i^2 = 1/r - x_i/r^2\,(\partial r/\partial x_i) = 1/r - x_i^2/r^3$. Then we have

$$\Delta\left(\frac{1}{r}\right) = \sum_i \left(\frac{2}{r^3}\left(\frac{x_i}{r}\right)^2 - \frac{1}{r^2}\left(\frac{1}{r} - \frac{x_i^2}{r^3}\right)\right) = \frac{2}{r^3} - \frac{1}{r^3} - \frac{1}{r^3} = 0 \tag{8.11.4}$$

Substitution of $\boldsymbol{\phi}=\mathbf{i}/r$ in Eqs. (8.10.2) and (8.10.3) yields

$$\mathbf{u} = \mathrm{grad}(\mathbf{r}\cdot\boldsymbol{\phi}) - 2\boldsymbol{\phi} = r\,\mathrm{grad}\boldsymbol{\phi} - \boldsymbol{\phi} = -x\left(\frac{\partial}{\partial x}\frac{1}{r}\right)\mathbf{i} + \frac{\mathbf{i}}{r} = \left(\frac{x^2}{r^3} + \frac{1}{r}\right)\mathbf{i} \tag{8.11.5}$$

and

$$P = 2\eta\frac{\partial}{\partial x}\left(\frac{-1}{r}\right) = \frac{2\eta x}{r^2} \tag{8.11.6}$$

<<Problem 8-12>> Equation of motion and equation of continuity for slow steady flow (III)

Derive the expressions for **u** and P for the potential $\phi=-\lambda/r$ with $\lambda=(1,1,1)$

Answer

Substitution of $\phi=-\lambda/r$ in Eqs. (8.10.2) and (8.10.3) yields

$$\begin{cases} \mathbf{u} = (\mathbf{r}\cdot\boldsymbol{\lambda})\operatorname{grad}\left(-\frac{1}{r}\right) + \frac{\boldsymbol{\lambda}}{r} \\ P = -2\eta\boldsymbol{\lambda}\operatorname{grad}\left(\frac{1}{r}\right) \end{cases} \tag{8.12.1}$$

Eq. (8.12.1) is rewritten as

$$u = (x_1 + x_2 + x_3)\left[\frac{1}{r^3}(x_1\mathbf{i} + x_2\mathbf{j} + x_3\mathbf{k})\right] + \frac{\boldsymbol{\lambda}}{r} = \frac{\lambda}{r} + \frac{1}{r^3}(x_1 + x_2 + x_3)\,\mathbf{r} \tag{8.12.2}$$

or

$$u_i = \sum_k \left\{\frac{\delta_{ik}}{r} + \frac{x_i x_k}{r^3}\right\} \tag{8.12.3}$$

and

$$P = -2\eta\operatorname{grad}\left(\frac{1}{r}\right) = \left(\frac{2\eta}{r^2}\right)\sum_i x_i \tag{8.12.4}$$

<<Problem 8-13> Oseen tensor

When a body moves with the velocity **u** in a viscous fluid, it exerts a force on the fluid, resulting in disturbing the flow field. For a force **F** acting on the fluid at an arbitrary point, the velocity change **v′** of the fluid where the distance from the point is **R** is given by

$$\mathbf{v}' = \frac{\mathbf{F}}{8\pi\eta_0}\left[\frac{\mathbf{I}}{R} + \frac{\mathbf{RR}}{R^3}\right] \qquad R = |\mathbf{R}| \tag{8.13.1}$$

where **I** is the unit tensor, $\mathbf{R}=(x_1,x_2,x_3)$ and

$$\mathbf{RR} = \begin{pmatrix} x_1{}^2 & x_1x_2 & x_1x_3 \\ x_2x_1 & x_2{}^2 & x_2x_3 \\ x_3x_1 & x_3x_2 & x_3{}^2 \end{pmatrix} \tag{8.13.2}$$

Derive Eq. (8.13.1) on the assumption that the fluid be incompressible and the flow be a steady flow.

Answer

Stokes equation for a steady flow under external force **F** is expressed as

$$\text{grad } P = \eta\Delta\mathbf{u} + \mathbf{F} \tag{8.13.3}$$

(Refer to Eq. (8.7.6))
The equation of continuity is given by

$$\text{div } \mathbf{u} = 0 \tag{8.10.1}$$

Let's denote the solution of Eq. (8.13.3) as $\mathbf{u}(u_1,u_2,u_3)$ and P, and the solution of Eq. (8.7.6) (for **F**=0) as $\mathbf{v}(v_1,v_2,v_3)$ and P' at a certain region B in the fluid. If we assume all of these solutions be single-valued and twice successively differentiable, we have

$$\int_B \left\{ \mathbf{v}\left(\eta\Delta\mathbf{u} - \text{grad } P\right) - \mathbf{u}\left(\eta\Delta\mathbf{v} - \text{grad } P'\right) + \mathbf{F}\mathbf{v} \right\} d\tau = 0 \tag{8.13.4}$$

If we denote the boundary surface of B as S and the normal vector of the surface as **n**, we have

$$\eta\int_S \left(\mathbf{v}\frac{\partial\mathbf{u}}{\partial\mathbf{n}} - \mathbf{u}\frac{\partial\mathbf{v}}{\partial\mathbf{n}}\right) dS - \int_B \left(\mathbf{v}\text{grad } P - \mathbf{u}\text{grad } P - \mathbf{F}\mathbf{v}\right) d\tau$$

$$= \int_S \left\{ \mathbf{v}\left(\eta\frac{\partial\mathbf{u}}{\partial\mathbf{n}} - \frac{\partial P}{\partial n}\right) - \mathbf{u}\left(\eta\frac{\partial\mathbf{v}}{\partial\mathbf{n}} - \frac{\partial P'}{\partial n}\right) \right\} dS + \int_B \mathbf{F}\mathbf{v}\, d\tau$$

$$= \int_S \sum_i \left\{ v_i\left(\eta\frac{\partial u_i}{\partial n} - \frac{\partial P}{\partial n}\right) - u_i\left(\eta\frac{\partial v_i}{\partial n} - \frac{\partial P'}{\partial n}\right) \right\} dS + \int_B \sum_i F_i v_i\, d\tau = 0 \tag{8.13.5}$$

From the result of <<Problem 8-12>>, we have

$$v_i = \sum_k \left(\frac{\delta_{ik}}{r} + \frac{x_i x_k}{r^3} \right) \tag{8.12.3}$$

$$P_k = -2\eta \frac{\partial}{\partial x_k}\left(\frac{1}{r} \right) \tag{8.12.4}$$

Then we take the point P^0 at the origin and denote the position vector as $\mathbf{r}(x_1,x_2,x_3)$ and its magnitude as $|\mathbf{r}|=r$. We take B between a sphere with radius ε including P^0, σ_0, and a concentric larger sphere σ_1. If ϕ and φ are arbitrary twice differentiable continuous functions, we have

$$\int_B (\phi\Delta\varphi - \varphi\Delta\phi) d\tau = \int_S \left(\phi\frac{\partial\varphi}{\partial n} - \varphi\frac{\partial\phi}{\partial n} \right) dS \tag{8.13.6}$$

Here $\partial / \partial n$ is the partial derivative along $\mathbf{n}$ direction at the boundary surface S. Let's perform an integration on the surface σ_0

$$\lim_{\varepsilon\to 0} \int_{\sigma_0} \sum_i v_i \left(\eta\frac{\partial u_i}{\partial n} - \frac{\partial P_k}{\partial n} \right) dS \tag{8.13.7}$$

Since the inside of the parenthesis is finite, $v_i \propto 1/r$ and $dS \propto r^2$, the integral is proportional to r. Thus the integral is zero when $r \to 0$. Since the directions of $\mathbf{n}$ and $\mathbf{r}$ are opposite, we have

$$\lim_{\varepsilon\to 0} \int_{\sigma_0} \sum_i u_i \left(\eta\frac{\partial v_i}{\partial n} - \frac{\partial P'_k}{\partial n} \right) dS = \lim_{\varepsilon\to 0} \eta \int_{\sigma_0} \left[u_k + 3\sum_i u_i \left(\frac{x_i x_k}{r^3} + \frac{2x_k}{r} \right) \right] \frac{dS}{r^2} \tag{8.13.8}$$

Taking account of symmetry of spherical surfaces, we have

$\int_{\sigma_0} dS/r^2 = 4\pi$, $\int_{\sigma_0} x_i x_k/r^2 \, dS/r^2 = \int_{\sigma_0} x_k^2/r^4 \, dS$ and $\int_{\sigma_0} x_k/r \, dS/r^2 = 0$

Then, Eq. (8.13.8) is expressed only with the minus components of $\mathbf{r}$. Using the polar coordinate, $x_k = r\cos\theta$, $dS = 2\pi r^2 \sin\theta d\theta$ and

$$\int_{\sigma_0} \frac{x_k^2}{r^4} dS = 2\pi \int_0^{\pi} \cos^2\theta \left(\sin\theta \, d\theta \right) = \frac{4}{3}\pi$$

Thus, the integral of Eq. (8.13.5) over σ_0 surface is $-8\pi\eta u_k(P^0)$. Then we have

$$u_k(P^0) = \frac{1}{8\pi\eta}\int_{\sigma_1} \sum_i \left\{ v_i\left(\eta\frac{\partial u_i}{\partial n} - \frac{\partial P}{\partial n}\right) - u_i\left(\eta\frac{\partial v_i}{\partial n} - \frac{\partial P'}{\partial n}\right)\right\} dS + \int_B \sum_i F_i v_i d\tau \qquad (8.13.9)$$

From Eqs. (8.12.3) and (8.13.8), $v_i \to 0$ and $(\eta\,(\partial v_i/\partial n) - (\partial p'_k/\partial n)) \to 0$ on the surface when $r \to \infty$. The second term in the right hand side of Eq. (8.13.9) can be neglected. Thus we have

$$u_k(P^0) = \frac{1}{8\pi\eta}\int \left(\frac{F_k}{r} + \sum_i F_i \frac{x_i x_k}{r^3}\right) d\tau \qquad (8.13.10)$$

If $\mathbf{F}(F_x, F_y, F_z)$ acts at the origin, we have

$$\mathbf{u} = \frac{1}{8\pi\eta}\left[\frac{1}{r}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \frac{1}{r^3}\begin{pmatrix} x_1^2 & x_1x_2 & x_1x_3 \\ x_2x_1 & x_2^2 & x_2x_3 \\ x_3x_1 & x_3x_2 & x_3^2 \end{pmatrix}\right]\mathbf{F} \qquad (8.13.11)$$

Here if we denote

$$\mathrm{I} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \mathbf{RR} = \begin{pmatrix} x_1^2 & x_1x_2 & x_1x_3 \\ x_2x_1 & x_2^2 & x_2x_3 \\ x_3x_1 & x_3x_2 & x_3^2 \end{pmatrix}, \quad r = R, \quad \eta = \eta_0 \qquad (8.13.12)$$

Eq. (8.13.2) is rewritten as

u=TF

where

$$\mathbf{T} = \frac{1}{8\pi\eta}\left[\frac{\mathrm{I}}{r} + \frac{\mathbf{RR}}{r^3}\right]\mathbf{F} \qquad (8.13.13)$$

where the tensor **T** is called the **Oseen tensor**. If we replace **RR** by the average $(R^2/3)\mathrm{I}$ ($\langle x_i x_k\rangle = \delta_{ik} x_k^2$), then we have

$$\mathbf{u} = \frac{1}{6\pi\eta_0 R}\mathrm{I}\mathbf{F} \qquad (8.13.14)$$

Eq. (8.13.14) is rewritten, if Stokes formula is applicable (Eq. (8.7.6)) as

$$\mathbf{F} = 6\pi\eta R\mathbf{u} \equiv \zeta\mathbf{u}, \quad \zeta = 6\pi\eta R \tag{8.13.15}$$

where ζ is the friction coefficient (See, for example, J. N. Hunt, In Compressible Fluid Dynamics, p15-16, Longmans, 1964). Thus the force **F** acting on a small sphere with radius R flowing with velocity **u** is proportional to the radius of the sphere and the viscosity of the fluid.

<<Problem 8-14> Capillary flow

Consider a **steady flow of incompressible fluid in a capillary** (i.e., steady axially-symmetrical flow in a straight pipe of circular section). Let's denote the difference in pressure of both ends of the capillary, the radius and the length of the capillary and the fluid viscosity as ΔP, R, l and η, respectively. Show the volume V_t flowing through a cross section of the capillary in time t is given by

$$V_t = \frac{\pi R^4 \Delta P t}{8\eta l} \tag{8.14.1}$$

Answer

Let's take x axis in the direction of the center line of the capillary tube. Then the fluid velocity v is a function of only y and z. The Stokes equation (See Eq. (8.13.3)) is solved under the boundary condition

$$v_x \neq 0, \quad v_y = v_z = 0 \tag{8.14.2}$$

or

$$\Delta v_y = 0, \ \Delta v_z = 0 \tag{8.14.3}$$

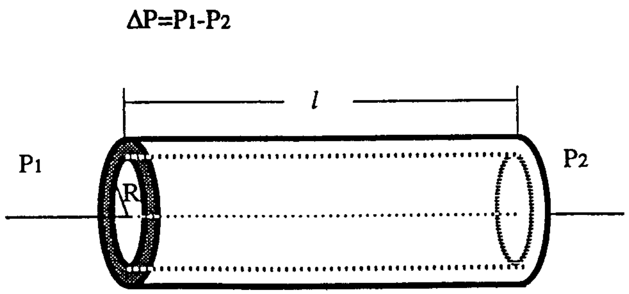

Fig. 8-14 Poiseuille flow

Then we have

$$\eta \Delta v_y = 0 = \frac{\partial p}{\partial y} \tag{8.14.4}$$

$$\eta \Delta v_z = 0 = \frac{\partial p}{\partial z} \tag{8.14.5}$$

$$\eta \Delta v_x = \eta\left(\frac{\partial^2 v_x}{\partial x^2} + \frac{\partial^2 v_x}{\partial y^2} + \frac{\partial^2 v_x}{\partial z^2}\right) = \left(\frac{\partial^2 v_x}{\partial y^2} + \frac{\partial^2 v_x}{\partial z^2}\right) = \frac{\partial P}{\partial x} \tag{8.14.6}$$

Here we use the relationship in the present situation:

$$\frac{\partial v_x}{\partial x} = \frac{\partial^2 v_x}{\partial x^2} = 0 \tag{8.14.7}$$

The right-hand side of Eq. (8.14.6) is a function of only x whereas the left-hand side is a function of only y and z. Thus, both sides should be a constant, that is,

$$\frac{\partial P}{\partial x} = \text{const.} \tag{8.14.8}$$

Since the difference in pressure for the tube length *l* is ΔP,

$$\frac{\partial P}{\partial x} = \frac{-\Delta P}{l} \tag{8.14.9}$$

Substitution of Eq. (8.14.9) for ∂P/∂x in Eq. (8.14.6) yields

$$\frac{\partial^2 v_x}{\partial y^2} + \frac{\partial^2 v_x}{\partial z^2} = \Delta v_x = \frac{-\Delta P}{\eta l} \tag{8.14.10}$$

Using the cylindrical coordinate, v_x is a function of only r and Eq. (8.14.10) is reduced to

$$\Delta v_x = \frac{1}{r}\frac{d}{dr}\left(r\frac{dv_x}{dr}\right) = -\frac{\Delta P}{\eta l} \tag{8.14.11}$$

Integration of Eq. (8.14.11) yields

$$v_x = -\frac{\Delta P}{4\eta l}r^2 + a\log r + b \tag{8.14.12}$$

with a and b being integration constants. Since v_x should be finite along the center line of the tube (r=0), the constant a must be zero. If we assume no-slip condition (v_x=0 at the capillary wall at r=R), we have

$$b = \frac{\Delta P}{4\eta l}R^2 \tag{8.14.13}$$

Substitution of Eq. (8.14.13) for b in Eq. (8.14.12) yields

$$v_x = \frac{\Delta P}{4\eta l}\left(R^2 - r^2\right) \tag{8.14.14}$$

Fluid of the volume $2\pi r v_x dr$ flows per unit time through the shell between circles with radius r and r+dr. Then the volume of fluid which flows through a cross section of the capillary tube in time t is given by

$$V_t = t\int_0^R 2\pi r v_x\, dr \tag{8.14.15}$$

Substituting Eq. (8.14.14) for v_x in Eq. (8.14.15) and integrating over r yields Eq. (8.14.1), which can be rewritten as

$$\eta = \frac{\pi R^4 \Delta P t}{8V_t l} \tag{8.14.16}$$

Thus the fluid viscosity η can be determined by measuring the time t required for a given volume of fluid flowing through a cross section of the capillary tube. Eq. (8.14.1) or (8.14.16) is called the **Hagen-Poiseuille law** which is a basis for the capillary viscometry. Poiseuille found in 1846 that the resistance of fluid flowing in a capillary tube is proportional to the fourth power of the inner diameter of the tube. Afterwards Hagen gave a theoretical explanation for this phenomenon. (See E. Hagenbach, *Pogg. Ann.* **109**, 385 (1960); J.L.M.Poiseuille, *Mem. Savants Etrangers* **9**, 433 (1846))

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* Since R,l and V_t (the volume of the fluid reservoir of the capillary viscometer) depend only on the dimension of the viscometer and ΔP is proportional to the density of the fluid ρ, Eq. (8.14.16) is reduced to

$$\eta \propto \rho t \tag{8.14.17}$$

Using a standard liquid, i.e., a liquid whose viscosity and density are known (usually pure solvent), we have

$$\frac{\eta}{\eta_0} = \left(\frac{\rho}{\rho_0}\right)\frac{t}{t_0} \tag{8.14.18}$$

where the subscript 0 denotes the standard liquid. Thus η can be determined by measuring the time t required for all the solution flowing out. For dilute solutions, the density of the solution ρ is nearly equal to that of the pure solvent ρ_0 , Then we can approximate

$$\frac{\eta}{\eta_0} = \frac{t}{t_0} \tag{8.14.19}$$

The prerequisite conditions for Hagen-Poiseuille law are
(1) fluid is incompressible
(2)steady flow (fluid viscosity is so slow that the force of inertia is negligible)
(3)Newtonian viscosity
(4)laminar flow
(5)correction for kinetic energy is not necessary

<<Problem 8-15-a>> Frictional heat and viscosity

Consider a **steady laminar flow in a horizontal cylindrical tube**. Take x and y axis in the direction of the length and in the radial direction of the tube, respectively. The change in fluid velocity in the direction of x axis, v_x, with respect to the radial direction y yields a velocity gradient g, that is,

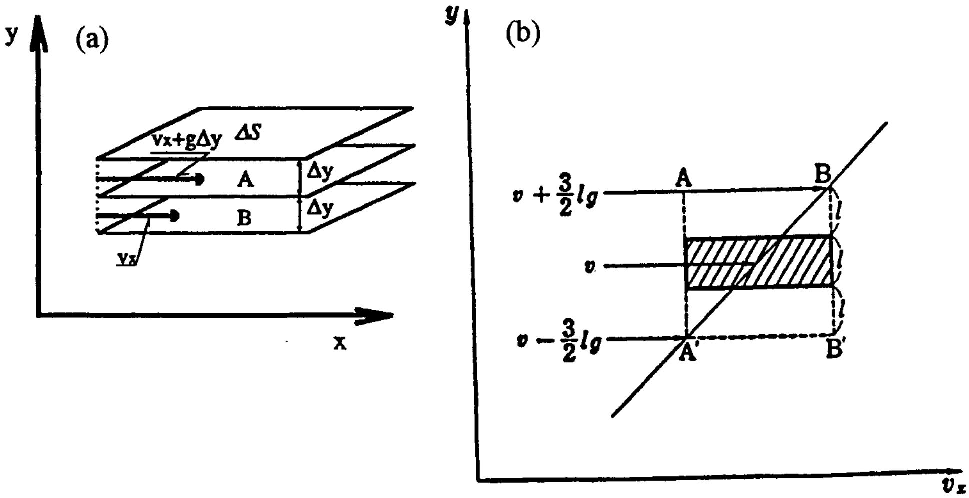

Fig. 8-15 Two layers in a shear flow (a) and shear flow near the planar particle (b)

$$g = \frac{\partial v_x}{\partial y} \tag{8.15.1}$$

Viscosity η is defined as the ratio of the frictional force (stress) on the surface along the flow X_y to the velocity gradient as

$$X_y = \eta g \tag{8.15.2}$$

η is also defined using the frictional heat ω produced in unit volume in unit time as

$$\omega = \eta g^2 \tag{8.15.3}$$

Derive Eq. (8.15.3).

Answer

Imagine two layers A and B, each having surface area ΔS and the thickness along y axis Δy, in the tube, as shown in Fig. 8-15(a). The layer A moves faster than the layer B by $g\Delta y$. The force which acts on the boundary of the two layers is $X_y\Delta S$. Then the work done by the layer A against the frictional force is ΔW=(velocity difference)x(frictional force) in unit time;

$$\Delta W = \left(\text{velocity difference}\right) \times \left(\text{frictional force}\right) = g\Delta y X_y \Delta S \tag{8.15.4}$$

The volume of the layer A is $\Delta S\Delta y$. Thus the work produced in unit volume and unit time is

$$\omega = \frac{\Delta W}{\Delta S\Delta y} = X_y g \tag{8.15.5}$$

Using Eq. (8.15.2), we have

$$\omega = \eta g \cdot g = \eta g^2 \tag{8.15.3}$$

<<Problem 8-15-b>> Estimation of volume fraction dependence of viscosity coefficient

Consider a planar rigid particle with the surface area S and thickness l in a steady laminar flow with a velocity gradient, as shown in Fig.8-15(b). We neglect the edge effect and the rotation of the plane. The fluid velocities on the plane and under the plane are different. Now we assume that the velocity of the plane is equal to that of the fluid on the center line, v. If we assume no-slip condition, the velocity of the fluid on the plane changes from v+(l/2)g to v and that under the plane changes from v-(l/2)g to v by the existence of the planar particle. Then we assume that such modification of flow caused by the existence of the plane appears at most over the length l from the plane. Then the velocity gradient from the center line of the planar particle to the surface which is l above the plane is $[\{v+(3l/2)g\}-v]/l=(3/2)g$. Similarly, the velocity gradient from the center line of the planar particle to the surface which is l below the plane is (3/2)g. Calculate the dissipation heat caused by the plane and derive the expression for the viscosity coefficient by comparing the heat ω in Eq. (8.15.3).

Answer

Using Eq. (8.15.3), the dissipation heat in the volume ABB′A′ in Fig. 8-15(b) caused by the plane is $\eta_0(3g/2)^2(2Sl)$. If there are N_1 planar particles per unit volume, total volume fraction of the particle ϕ_1 is SlN_1. The volume fraction, the flow field in which is not disturbed by the planar particles is $(1-3SlN_1)$. Thus, the dissipation heat in this volume is $\eta_0 g^2(1-3SlN_1)$. The total dissipation heat is the sum of these dissipation heats as

$$\omega=\eta_0\, g^2(1-3\ SlN_1)+\eta_0\left(\frac{3}{2}\ g\right)^2(2\ Sl)N_1=\eta_0(1+1.5\ SlN_1)\ g^2 \tag{8.15.6}$$

We can also say that this heat is the decrease in kinetic energy of the fluid, resulting in the fluid being more viscous due to the decrease in velocity of the fluid molecules. Comparing Eq. (8.15.6) with Eq. (8.15.3), we have

$$\eta=\eta_0(1+1.5\phi_1) \tag{8.15.7}$$

The coefficient of ϕ_1, 1.5, in Eq. (8.15.7) derived by the above rough estimation is slightly different from that of the exact Einstein's equation, 2.5, derived in Eq. (8.27.1). An instructive conclusion of this problem is that the viscosity coefficient only depends on the volume fraction of the suspended particles and the solution viscosity is proportional to the solvent viscosity. (See M. Kaneko and K. Ogino, *Polymer Science (Kobunshi Kagaku)*, Kyouritsu Pub. Co., 1965, p130)

<<Problem 8-16> Two-dimensional steady shear flow of solution of dumbbell-like molecule (I): Diffusion equation

Consider a **dumbbell-like molecule** which consists of a rod with spheres at the both ends. When this molecule is put in a shear flow of fluid with viscosity η_0, the center of gravity moves and rotates along the flow. If we take the origin at the center of gravity of the molecule, the probability density $f(\theta,\psi,t)$ of finding this molecule at a position (θ,ψ in the polar coordinate) at time t is described by the diffusion equation. Imagine a solvent flowing with the velocity $\mathbf{v}'$ by an external force $\mathbf{F}$. If we put the dumbbell-like molecule in the solvent, the equation of motion is expressed as

$$m\frac{d\mathbf{v}'}{dt} = \mathbf{F} - \zeta \mathbf{v}' \tag{8.16.1}$$

where ζ is the friction constant. If there is no external force, the first term in the right-hand side in Eq. (8.16.1) is removed. For a shear flow, the velocity of the solvent is given by

$$\mathbf{v}^0 = \begin{pmatrix} 0\,0\,0 \\ g\,0\,0 \\ 0\,0\,0 \end{pmatrix} \mathbf{r} = \begin{pmatrix} 0\,0\,0 \\ g\,0\,0 \\ 0\,0\,0 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = (0, gx, 0) \tag{8.16.2}$$

Then we have the **diffusion equation** expressed as

$$\frac{\partial f(\mathbf{r},t)}{\partial t} = -\mathrm{div}\, \mathbf{j}\, f \tag{8.16.3}$$

where $\mathbf{j}$ is the flow defined by

$$\mathbf{j} = \mathbf{v}' - D(\mathrm{grad}\ f)/f \tag{8.16.4}$$

with D being the diffusion coefficient. Eqs. (8.16.3) and (8.16.4) give the probability density when there are two forces; shear stress and diffusion force due to the thermal motion. Derive the **angular velocity for the molecular rotation, $\dot\theta$ and $\dot\phi$, in the steady state** when the thermal diffusion is negligible.

Answer

For convenience, we put $\mathbf{r}$=unit vector. Then grad f and div $\mathbf{j}$f can be rewritten in the polar coordinate as

$$\mathrm{grad}\ f = \mathbf{u}_\theta \frac{\partial f}{\partial \theta} + \mathbf{u}_\phi \frac{\partial f}{\sin\theta\, \partial\phi} \tag{8.16.5}$$

$$\mathrm{div}\, \mathbf{j} f = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(j_\theta f \sin\theta\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\phi}\left(j_\phi f\right) \tag{8.16.6}$$

where $\mathbf{u}_\theta$ and $\mathbf{u}_\phi$ are the unit vector and j_θ and j_ϕ are the components of j in the direction of θ and ϕ, respectively. Now, we redefine j_θ and j_ϕ as angular velocities, that is, $j_\theta \rightarrow j_\theta$ and $j_\phi \rightarrow j_\phi \sin\theta$, as shown in Fig. 8-16. Then Eq. (8.16.3) is rewritten as

$$\frac{\partial f}{\partial t} = -\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(j_\theta f \sin\theta) - \frac{1}{\sin\theta}\frac{\partial}{\partial\phi}(j_\phi f \sin\theta) \tag{8.16.7}$$

θ and ϕ components of Eq. (8.16.4) are rewritten as

$$j_\theta \cdot f = \dot{\theta} f - D\frac{\partial f}{\partial\theta} \tag{8.16.8}$$

$$j_\phi f \sin\theta = \dot{\phi}(\sin\theta) f - \frac{D}{\sin\theta}\frac{\partial f}{\partial\phi} \tag{8.16.9}$$

respectively. Next we calculate each component of the relative velocity $\mathbf{v}'(v'_r, v'_\theta, v'_\phi)$. Let's denote the velocity of the small sphere of the dumbbell-like molecule as V. Then we have

$$\mathbf{v}' = \mathbf{V} - \mathrm{v}^0$$

with

$$\mathbf{V} = \begin{pmatrix} 0 \\ \left(\frac{b}{2}\right)\dot{\theta} \\ \left(\frac{b}{2}\right)\sin\theta\sin\dot{\phi} \end{pmatrix} \tag{8.16.10}$$

The projection of the half length of the rod of the dumbell-like molecule b/2 on the x-y plane is b(sinθ)/2. The x component of the projection is (bsinθcosφ)/2. From Eq. (8.16.2), we have

$$v^0{}_y = gx \tag{8.16.11}$$

The θ component of $v_y{}^0$ is (b/2)gsinθcosθsinφcosφ. Similarly, we can derive the ϕ component of v^0, $v_\phi{}^0$, as $(bg\sin\theta\cos^2\phi)/2$. Thus

$$v^0 = \begin{pmatrix} 0 \\ \left(\frac{b}{2}\right) g \sin\theta \cos\theta \sin\phi \cos\phi \\ \left(\frac{b}{2}\right) g \sin\theta \cos^2\phi \end{pmatrix} \qquad (8.16.12)$$

Then θ and ϕ components of $\mathbf{v}'$ are obtained from Eqs. (8.16.10) and (8.16.12) as

$$v'_\theta = \left(\frac{b}{2}\right)\left(\dot{\theta} - \left(\frac{g}{4}\right)\sin 2\theta \sin 2\phi\right) \qquad (8.16.13)$$

$$v'_\phi = \left(\frac{b}{2}\right)\sin\theta\left(\dot{\phi} - g\cos^2\phi\right) \qquad (8.16.14)$$

respectively. In the steady state,

$$m\frac{dv'}{dt} = 0 \qquad (8.16.15)$$

Then Eq. (8.16.1) is reduced to

$$F_\theta = \zeta v'_\theta \qquad (8.16.16)$$

$$F_\phi = \zeta v'_\phi \qquad (8.16.17)$$

θ and ϕ components of the moment **M** to rotate the dumbell-like molecule induced by the force **F** are expressed as

$$M_\theta = F_{\theta,1}\frac{b}{2} + F_{\theta,2}\frac{b}{2} = b\zeta v'_\theta = b\zeta\left(\frac{b}{2}\right)\left(\dot{\theta} - \left(\frac{g}{4}\right)\sin 2\theta \sin 2\phi\right) \qquad (8.16.18)$$

$$M_\phi = F_{\phi,1}\left(\frac{b}{2}\right)\sin\theta + F_{\phi,2}\left(\frac{b}{2}\right)\sin\theta = b\sin\theta\,\zeta v'_\phi = b\zeta\left(\frac{b}{2}\right)\sin^2\theta\left(\dot{\phi} - g\cos^2\phi\right) \qquad (8.16.19)$$

respectively, where the subscripts 1 and 2 correspond to the small spheres 1 and 2. In the steady state,

$$\left.\begin{aligned} M_\theta &= 0 \\ M_\phi &= 0 \end{aligned}\right\} \qquad (8.16.20)$$

Then we have

$$\dot{\theta} = \left(\frac{g}{4}\right)\sin 2\theta \sin 2\phi \tag{8.16.21}$$

$$\dot{\phi} = g\cos^2\phi \tag{8.16.22}$$

Thus the dumbbell-like molecule performs a rotational motion with a constant angular velocity $\dot{\theta}$ and $\dot{\phi}$.

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* A dumbbell-like molecule is an element of a pearl-necklace molecule (or bead-and-bond molecule), which is used to represent a linear polymer molecule.

* Statistical approach to an equilibrium state is described by the forward equation of Fokker-Planck equations (See for example, C. Kittel, *Elementary Statistical Physics*, John Wiley & Sons, Inc., New York, 1977):

$$\frac{\partial f}{\partial t} = \frac{\partial}{\partial x^2}\left(a(t, x)f\right) - \frac{\partial}{\partial x}\left(b(t, x)f\right) + c(t, x)f \tag{8.16.23}$$

for one-dimensional case, where f is a probability density function and a, b and c are functions of time t and coordinate x. In case a=const.($\equiv$diffusion coefficient D) and b=c=0, i.e., the stochastic process is homogeneous in time and space), we have Brownian motion: $\partial f/\partial t = a\partial^2 f/\partial x^2$. In case $b = v'$ and c=0, we have Eqs. (8.16.3) and (8.16.4) in three-dimensional case.

* Eq. (8.16.5) is derived as follows.
Let's express the relationship between a rectangular coordinate (x,y,z) and a curvilinear coordinate (q_1,q_2,q_3) as

$$\left.\begin{aligned} x &= x(q_1, q_2, q_3) \\ y &= y(q_1, q_2, q_3) \\ z &= z(q_1, q_2, q_3) \end{aligned}\right\} \tag{8.16.24}$$

The operator grad is expressed using the coordinates as

$$\text{grad}(\equiv\nabla) = \mathbf{e}_x\frac{\partial}{\partial x} + \mathbf{e}_y\frac{\partial}{\partial y} + \mathbf{e}_z\frac{\partial}{\partial z} = \frac{\mathbf{u}_1}{Q_1}\frac{\partial}{\partial q_1} + \frac{\mathbf{u}_2}{Q_2}\frac{\partial}{\partial q_2} + \frac{\mathbf{u}_3}{Q_3}\frac{\partial}{\partial q_3} \tag{8.16.25}$$

where (e_x, e_y, e_z) and (u_1, u_2, u_3) are unit vectors in the rectangular coordinate and the curvilinear coordinate, respectively, and

$$Q_i^2 = \left(\frac{\partial x}{\partial q_1}\right)^2 + \left(\frac{\partial y}{\partial q_2}\right)^2 + \left(\frac{\partial z}{\partial q_3}\right)^2 \tag{8.16.26}$$

The divergence of an arbitrary vector **j** is expressed as

$$\mathrm{div}\,\mathbf{j}=\nabla\cdot\left(j_1u_1+j_2u_2+j_3u_3\right) \tag{8.16.27}$$

or

$$\nabla\cdot j_iu_i=j_i\nabla u_i+u_i\nabla j_i \tag{8.16.28}$$

The first term of the right-hand side in eq. (8.16.27) is expressed as

$$j_i\nabla u_i=\frac{1}{Q_1Q_2Q_3}\left(\frac{\partial Q_jQ_k}{\partial q_i}\right)\quad(i\neq j,k) \tag{8.16.29}$$

and the second term is expressed using Eq. (8.16.25) as

$$\mathrm{div}\,\mathbf{j}=\frac{1}{Q_1Q_2Q_3}\left\{\frac{\partial}{\partial q_1}\left(j_1Q_2Q_3\right)+\frac{\partial}{\partial q_2}\left(j_2Q_3Q_1\right)+\frac{\partial}{\partial q_3}\left(j_3Q_1Q_2\right)\right\} \tag{8.16.30}$$

Now we consider a dumbbell-like molecule represented by a vector **r** in a polar coordinate as shown in Fig. 8-16:

$$\left.\begin{array}{l}x=r\sin\theta\cos\phi\\ y=r\sin\theta\sin\phi\\ z=r\cos\theta\end{array}\right\} \tag{8.16.31}$$

then

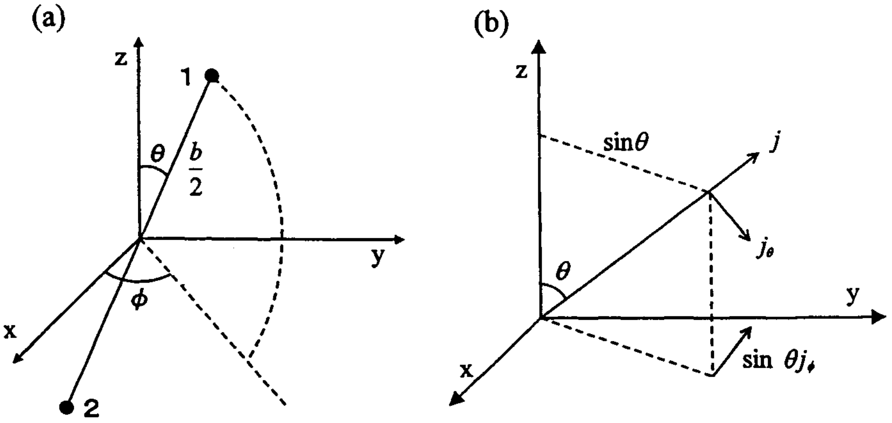

Fig. 8-16 A dumbbell-like molecule in a shear flow (a) and the components of j_θ and j_ϕ (b)

$$Q_r^2=1,\ Q_\theta^2=r^2,\ Q_\phi^2=r^2\sin^2\theta \tag{8.16.32}$$

As we put r=unit vector,

$$\frac{\partial f}{\partial r}=\frac{\partial j_r}{\partial r}=0 \tag{8.16.33}$$

From Eqs. (8.16.25) and (8.16.30), we have Eqs. (8.16.5) and (8.16.6), respectively.

<<Problem 8-17> Two-dimensional steady shear flow of solution of dumbbell-like molecule (II): Force and its corresponding moment acting on the molecule

Derive the force $\mathbf{F}(F_x, F_y, F_z)$ which acts on the small spheres of the dumbbell-like molecule in <<Problem 8-16>> and the corresponding moment $\mathbf{M}(M_x, M_y, M_z)$ both in the three-dimensional and two-dimensional spaces.

Answer

From Fig. 8-17(a), the relationship between the components of the rectangular coordinate and the polar coordinate is given by

$$\left.\begin{aligned}(j_\theta)_x&=(\cos\theta\cos\phi)j_\theta\\(j_\theta)_y&=(\cos\theta\sin\phi)j_\theta\\(j_\theta)_z&=(-\sin\phi)j_\phi\end{aligned}\right\} \tag{8.17.1}$$

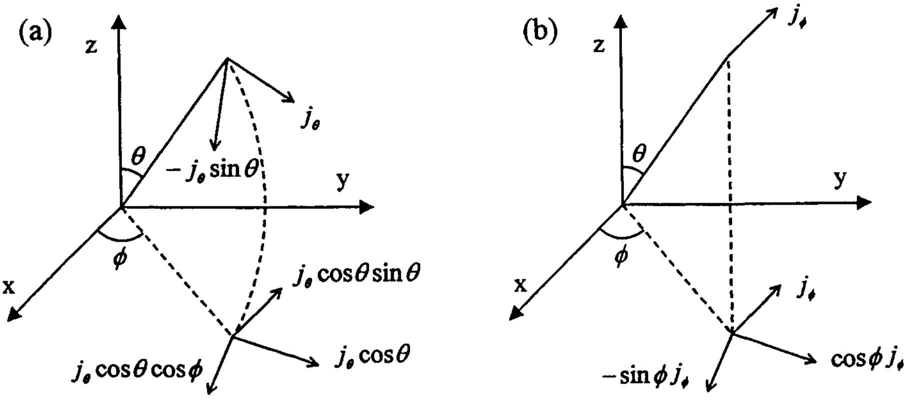

Fig. 8-17 Components of j_θ (a) and j_ϕ (b)

Similarly, from Fig. 8-17(b), we have

$$\left.\begin{aligned}(j_\phi)_x &= (-\sin\phi)j_\phi \\ (j_\phi)_y &= (\cos\phi)j_\phi \\ (j_\phi)_z &= 0\end{aligned}\right\} \tag{8.17.2}$$

Thus

$$j_x = (j_\theta)_x + \sin\theta(j_\phi)_x = (\cos\theta\cos\phi)j_\theta - (\sin\theta\sin\phi)j_\phi \tag{8.17.3}$$

$$j_y = (j_\theta)_y + \sin\theta(j_\phi)_y = (\cos\theta\sin\phi)j_\theta + (\sin\theta\cos\phi)j_\phi \tag{8.17.4}$$

$$j_z = (-\sin\theta)j_\theta \tag{8.17.5}$$

The velocity of the small sphere is given by (distance)x(angular velocity), that is,

$$\mathbf{V} = \mathbf{j}r \tag{8.17.6}$$

The relative velocity is given by

$$\mathbf{v}' = \mathbf{V} - \mathbf{v}^0 \tag{8.17.7}$$

The force acting on the sphere is

$$\mathbf{F} = \zeta(\mathbf{V} - \mathbf{v}^0) = \zeta(\mathbf{j}r - \mathbf{v}^0) \tag{8.17.8}$$

Substitution of Eqs. (8.17.3)-(8.17.5) in Eq. (8.17.8) yields

$$F_x = \zeta\left(\frac{b}{2}\right)\left[(\cos\theta\cos\phi)j_\theta - (\sin\theta\sin\phi)j_\phi\right] \tag{8.17.9}$$

$$F_y = \zeta\left(\frac{b}{2}\right)\left[(\cos\theta\sin\phi)j_\theta + (\sin\theta\cos\phi)j_\phi - g\sin\theta\cos\phi\right] \tag{8.17.10}$$

$$F_z = \zeta\left(\frac{b}{2}\right)\left[-(\sin\theta)j_\theta\right] \tag{8.17.11}$$

The moment **M** is defined by

$$\mathbf{M} = \sum_i \mathbf{r}_i \times \mathbf{F}_i \tag{8.17.12}$$

where i=1 and 2 denote the two spheres. x component of the moment is evaluated as

$$M_x = \sum_i \left(yF_{z,i} - zF_{y,i} \right)$$

$$= 2\left(\frac{b}{2}\right)\sin\theta\sin\phi\zeta\left(\frac{b}{2}\right)\left[-\sin\theta j_\theta\right] - 2\left(\frac{b}{2}\right)\cos\theta\zeta\left(\frac{b}{2}\right)$$

$$\times\left[\cos\theta\sin\phi j_\theta + \sin\theta\cos\phi\, j_\phi - g\sin\theta\cos\phi\right]$$

$$= 2\left(\frac{b}{2}\right)^2\zeta\left[-\sin\phi j_\theta + \sin\theta\cos\phi\, j_\phi - g\sin\theta\cos\phi\right] \qquad (8.17.13)$$

M_y and M_z are likewise obtained.

In the two-dimensional space, the force which acts on the first spheres $F_{y,1}$ is evaluated, in reference to Eq. (8.17.10) with putting $\theta=\pi/2$, as

$$F_{y,1} = \zeta\left(\frac{b}{2}\right)\left[\cos\phi j_\phi - g\cos\phi\right] = \zeta\left(\frac{b}{2}\right)\cos\phi\left[j_\phi - g\right] = F_{y,2} \qquad (8.17.14)$$

Similarly, from Eq. (8.17.9),

$$F_{x,1} = -\zeta\left(\frac{b}{2}\right)\sin\phi j_\phi = F_{x,2} \qquad (8.17.15)$$

The moment about z axis is given by

$$M = F_{y,1}x_1 + F_{y,2}x_2 + F_{x,1}y_1 + F_{y,2}y_2 = \frac{\zeta b^2}{2}\left(g\cos^2\phi - j_\phi\right) \qquad (8.17.16)$$

In the steady state, we have

$$j_\phi = g\cos^2\phi \qquad (8.17.17)$$

which agrees with Eq. (8.16.22).

<<Problem 8-18> Two-dimensional steady shear flow of solution of dumbbell-like molecule (III): Probability density

The probability density $f(\phi,t)$ for the two-dimensional flow of a dumbbell-like molecule is given by a set of equations

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial\phi}\left(j_\phi f\right) \qquad (8.18.1a)$$

$$j_\phi f = \dot{\phi} f - D\frac{\partial f}{\partial \phi} \qquad (8.18.1b)$$

(by putting $\theta=\pi/2$ and $j_\theta=0$ in Eqs. (8.16.7)-(8.16.9) and $\dot{\phi}=g\cos^2\phi$ (from Eq. (8.16.22)). Let's express f as a power series of g as

$$f = \frac{1}{2\pi}\left[\, 1 + f_1 g + f_2 g^2 + f_3 g^3 + \cdots\right] \qquad (8.18.2)$$

Here 2π comes from the normalization condition when

$$f_1 = f_2 = f_3 = \cdots = 0 \qquad (8.18.3a)$$

that is,

$$\int_0^{2\pi} f\, d\phi = 1, \quad \int_0^{2\pi} f_r g^r\, d\phi = 0\; (r = 1,2,3,\cdots) \qquad (8.18.3b)$$

Derive f_1 and f_2 in the steady state

$$\frac{\partial f}{\partial t} = 0 \qquad (8.18.4)$$

Answer

Using Eq. (8.18.1b), Eq. (8.18.1a) is rewritten as

$$\begin{aligned}
\frac{\partial f}{\partial t} &= -\frac{\partial}{\partial \phi}\left(j_\phi f\right) \\
&= -\frac{\partial}{\partial \phi}\left[\frac{\dot{\phi}}{2\pi}\left(1 + f_1 g + f_2 g^2 + \cdots\right) - \frac{D}{2\pi}\frac{\partial}{\partial \phi}\left(1 + f_1 g + f_2 g^2 + \cdots\right)\right] \\
&= -\frac{1}{2\pi}\left[\left(-2\sin\phi\cos\phi - D\frac{\partial^2 f_1}{\partial \phi^2}\right)g + \left(-2\sin\phi\cos\phi f_1 + \cos^2\phi\frac{\partial f_1}{\partial \phi} - D\frac{\partial^2 f_2}{\partial \phi^2}\right)g^2 + \cdots\right]
\end{aligned}$$

(8.18.5)

From the steady state condition $\partial f/\partial t=0$, all the coefficients of g, g^2,... must be zero. For the coefficient of g,

$$- 2\sin\phi\cos\phi - D\frac{\partial^2 f_1}{\partial\phi^2} = 0 \tag{8.18.6}$$

The solution of this equation is

$$f_1 = \frac{\sin 2\phi}{4D} + c_1\phi + c_2 \tag{8.18.7}$$

f_1 at $\phi=0$ and $\phi=2\pi$ should be the same, then $c_1=0$. From the normalization condition

$$\int_0^{2\pi} f_1\, d\phi = 0 \tag{8.18.8}$$

$c_2=0$. Thus we have

$$f_1 = \frac{\sin 2\phi}{4D} \tag{8.18.9}$$

For the coefficient of g^2, we have

$$-2\sin\phi\cos\phi f_1 + \cos^2\phi\frac{\partial f_1}{\partial\phi} - D\frac{\partial^2 f_2}{\partial\phi^2} = 0 \tag{8.18.10}$$

Substitution of Eq. (8.18.9) for f_1 in Eq. (8.18.10) and rearrangement yields

$$\frac{\partial^2 f_2}{\partial\phi^2} = -\frac{1}{4D^2}\left[\sin^2 2\phi + 2\cos^2\phi - 4\cos^4\phi\right] \tag{8.18.11}$$

Integration of Eq. (8.18.11) over ϕ yields

$$\frac{\partial f_2}{\partial\phi} = -\frac{1}{(4D)^2}\left(\sin 4\phi + 2\sin 2\phi + c_3''\right) \tag{8.18.12}$$

$$f_2 = -\frac{1}{(4D)^2}\left[\frac{\cos 4\phi}{4} + \cos 2\phi + c_3''\phi + c_4\right] \tag{8.18.13}$$

Since f_2 should be the same at $\phi=0$ and 2π, $c_3''=0$. Using the normalization condition, $c_4=0$. Then we have

$$f_2 = -\frac{1}{(4D)^2}\left[\frac{\cos 4\phi}{4} + \cos 2\phi\right] \tag{8.18.14}$$

Substitution of Eqs. (8.18.9) and (8.18.14) in Eq. (8.18.2) yields

$$f=\frac{1}{2\pi}\left[1+\left(\frac{g}{4D}\right)\sin 2\phi-\left(\frac{g}{4D}\right)^2\left(\frac{\cos 4\phi}{4}+\cos 2\phi\right)\right] \tag{8.18.15}$$

The probability density f is given as a function of 2ϕ for various values of g/4D in Fig. 8-18. Such a relationship was first derived by Boeder.(See P. Boeder, Z. Phys. **75**, 258 (1932))

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* The diffusion equation for dumbbell-like molecule in three dimensional case is given in <<Problem 8-45>>

<<Problem 8-19> Two-dimensional steady shear flow of solution of dumbell-like molecule (IV):Viscous dissipation

Pure shear flow of viscous fluids with shear velocity g induces heat of ηg^2 per unit volume and unit time (See Eq. (8.15.3)). The viscosity of the solution η is related to the viscosity of pure solvent η_0 as

$$\eta g^2 = \eta_0 g^2 + \Delta q \tag{8.19.1}$$

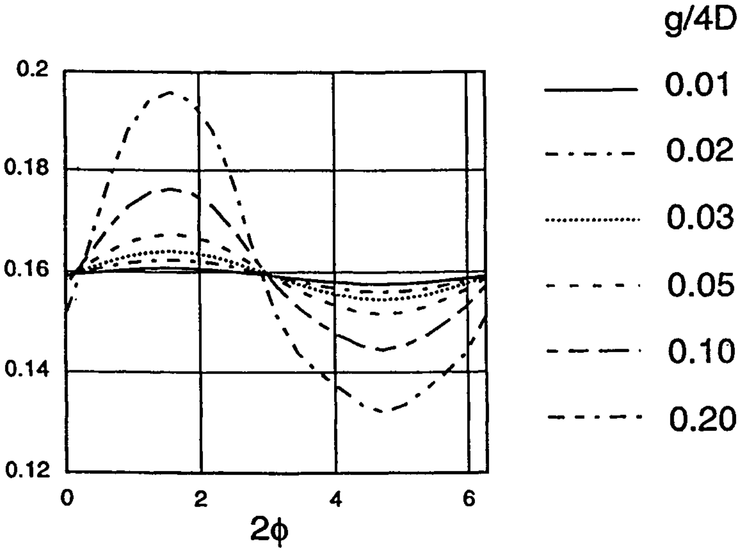

Fig. 8-18 Probability density as a function of 2ϕ

This equation means that the solution generates heat more than the solvent by Δq. Consider a solution which contains N dumbbell-like molecules per unit volume. The force on the spheres of the dumbbell-like molecules exerted by solvent is -**F** whose components are given by Eqs. (8.17.9)- (8.17.11). Thus the work done per unit volume by the solution is larger than that by solvent by -$N(\mathbf{F}_1\mathbf{v}_1^0+\mathbf{F}_2\mathbf{v}_2^0)$. Here the subscripts 1 and 2 denote two spheres of the dumbbell-like molecule. In the two-dimensional flow, the motions of the two spheres are the same, that is, $\mathbf{F}_1\mathbf{v}_1^0=\mathbf{F}_2\mathbf{v}_2^0$. Then we have

$$\Delta q = -N\int_0^{2\pi} f(\phi)\left(\mathbf{F}_1\mathbf{v}_1^0 + \mathbf{F}_2\mathbf{v}_2^0\right) d\phi = -N\int_0^{2\pi} f(\phi)\left(F_{y1}v_{y1}^0 + F_{y2}v_{y2}^0\right) d\phi$$

$$= -4N\int_0^{\frac{\pi}{2}} 2f(\phi)F_{y1}v_{y1}\, d\phi \qquad (8.19.2)$$

Evaluate Δq using $f(\phi)$, $F_{y,1}$ and $v_{y,1}$ obtained in <<Problem 8-17>> and <<Problem 8-18>>.

Answer

From Eqs. (8.17.14) and (8.17.17), we have

$$F_{y1} = \zeta\left(\frac{b}{2}\right)\cos\phi\left[j_\phi - g\right] = \zeta\left(\frac{b}{2}\right)\cos\phi\; g\left[\cos^2\phi - 1\right] \qquad (8.19.3)$$

In Eq. (8.16.11), x=-(bcosϕ)/2 for the present problem. Then we have

$$v_{y1}^0 = -\left(\frac{b}{2}\right)g\cos\phi \qquad (8.19.4)$$

From Eqs. (8.19.3) and (8.19.4),

$$F_{y1}v_{y1}^0 = \zeta\left(\frac{b}{2}\right)^2 g^2\cos^2\phi\left[1 - \cos^2\phi\right] \qquad (8.19.5)$$

Substitution of Eqs. (8.18.15) and (8.19.5) in Eq. (8.19.2) yields

$$\Delta q = \frac{8N}{2\pi}\int_0^{\frac{\pi}{2}} \left[1 + \left(\frac{g}{4D}\right)\sin 2\phi - \left(\frac{g}{4D}\right)^2\left(\frac{1}{4}\cos 4\phi + \cos 2\phi\right)\right]$$

$$\times\zeta\left(\frac{b}{2}\right)^2 g^2\cos^2\phi\left[1-\cos^2\phi\right]d\phi$$

$$=\frac{8\mathcal{N}}{2\pi}\zeta\left(\frac{b}{2}\right)^2 g^2\int_0^{\frac{\pi}{2}}\left[\cos^2\phi-\cos^4\phi+\left(\frac{g}{4D}\right)\cos^2\phi\sin 2\phi\right.$$

$$\left.-\left(\frac{g}{4D}\right)\cos^4\phi\sin 2\phi-\left(\frac{g}{4D}\right)\frac{\cos^2\phi\sin 4\phi}{4}-\left(\frac{g}{4D}\right)^2\cos^4\phi\sin 2\phi\right]d\phi \tag{8.19.6}$$

and then

$$\Delta q=\frac{\mathcal{N}b^2\zeta g^2}{\pi}\left[\left(\frac{\pi}{4}-\frac{3\pi}{16}\right)+\left(\frac{g}{4D}\right)\left[\frac{1}{2}-\frac{1}{3}\right]-\left(\frac{g}{4D}\right)^2\left(\frac{\pi}{8}\right)\right]$$

$$=\frac{\mathcal{N}b^2\zeta g^2}{16}\left[1+\frac{16}{6\pi}\left(\frac{g}{4D}\right)-2\left(\frac{g}{4D}\right)^2\right] \tag{8.19.7}$$

<<Problem 8-20>> Limiting viscosity number of solution of dumbbell-like molecule (I): Estimated from heat dissipation

The viscosity of a solution is related to the viscosity of the solvent as

$$\eta=\eta_0+\frac{\Delta q}{g^2} \tag{8.19.1}$$

The **limiting viscosity number** is defined by

$$[\eta]=\lim_{c\to 0}\frac{\eta-\eta_0}{\eta_0 C} \tag{8.20.1}$$

Evaluate $[\eta]$ using Eq. (8.19.7).

Answer

From Eqs. (8.19.1) and (8.19.7),

$$\eta - \eta_0 = \frac{\Delta q}{g^2} = \frac{\mathcal{N}b^2\zeta}{16}\left[1 + \left(\frac{g}{4D}\right)\frac{16}{6\pi} - 2\left(\frac{g}{4D}\right)^2\right] \tag{8.20.2}$$

Substitution of Eq. (8.20.2) in Eq. (8.20.1) yields

$$[\eta] = \lim_{C\to 0}\frac{\eta - \eta_0}{\eta_0 C} = \lim_{C\to 0}\frac{\mathcal{N}b^2\zeta}{16\eta_0 C}\left[1 + \left(\frac{g}{4D}\right)\frac{16}{6\pi} - 2\left(\frac{g}{4D}\right)^2\right] \tag{8.20.3}$$

Using the relationship $\mathcal{N}$=N$_A$/(M/C), Eq. (8.20.3) is further rewritten as

$$[\eta] = \frac{N_A b^2\zeta}{16\eta_0 M}\left[1 + \frac{16}{6\pi}\left(\frac{g}{4D}\right) - \left(\frac{g}{4D}\right)^2\right] = \frac{N_A b^2\zeta}{2\eta_0 M}\left[\frac{1}{8} + \frac{1}{3\pi}\left(\frac{g}{4D}\right) - \frac{1}{4}\left(\frac{g}{4D}\right)^2\right] \tag{8.20.4}$$

Eq. (8.20.4) indicates that a dumbbell-like molecule solution is non-Newtonian.

<<Problem 8-21>> Limiting viscosity number of solution of dumbbell-like molecule (II): From the ratio of shear stress to shear rate

Consider a surface S with unit area in a solution. Let's denote the normal vector of the surface as ν. The plus side and the minus side of S are defined as the side where ν has the plus sign and the minus sign, respectively. Denote the unit vector along the molecular axis (θ,ϕ) as **e**. The total number of molecules with the molecular axis (θ,ϕ) among the molecules which pass through the surface S is the total number of molecules having the molecular axis (θ,ϕ) in the volume of the cylinder surrounded by the dashed line in Fig. 8-21, that is, $|\nu \mathbf{l}|\, b\mathcal{N}f$. Here $|\nu \mathbf{l}|b$ is the height of the cylinder. Let's denote the force that an arbitrary molecule exerts on the surface of the fluid from the minus side to the plus side as **F**. Thus the force induced by a dumbbell-like molecule from the plus side to
the minus side is given by the integration of

$$-\mathbf{F}|\nu \mathbf{l}|b\,\mathcal{N}f(\theta,\phi) \tag{8.21.1}$$

over all the directions, that is,

$$-\mathcal{N}b\int\int|\mathbf{vl}|\mathbf{F}f(\theta,\phi)\sin\theta\,d\theta d\phi \tag{8.21.2}$$

If we denote the total stress on the surface S as σ_v and the corresponding stress for the fluid without the dumbbell-like molecule as σ_v^0, we have

$$\sigma_v-\sigma_v^0=-\mathcal{N}b\int\int\mathbf{F}f(\theta,\phi)\sin\theta\,d\theta d\phi \tag{8.21.3}$$

Now we take $\mathbf{v}$ axis in the same direction as x axis so that $(\mathbf{vl})=\sin\theta\cos\phi$. Thus, the shear stress σ_{xy}, the y component of the stress on the surface perpendicular to x axis is given by

$$\sigma_{xy}-\sigma_{xy}{}^0=-\mathcal{N}b\int\int F_y f(\theta,\phi)\sin^2\theta\cos\phi\,d\theta d\phi \tag{8.21.4}$$

Since η is defined by

$$\sigma_{xy}=\eta\frac{\partial v^0}{\partial x}=\eta g \tag{8.21.5}$$

$\eta-\eta^0$ is expressed as

$$\eta-\eta^0=-\left(\frac{\mathcal{N}b}{g}\right)\int\int F_y f\sin^2\theta\cos\phi\,d\theta d\phi \tag{8.21.6}$$

Evaluate the **viscosity coefficient η for the solution of dumbbell-like molecules in two-dimensional space.**

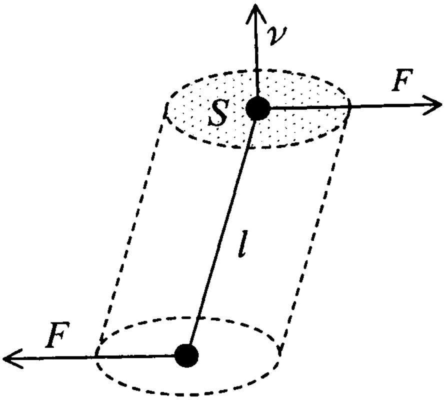

Fig. 8-21 Stress on the surface of an arbitrary volume element in a fluid

Answer

In two-dimensional space, Eq. (8.21.6) reads

$$\eta - \eta^0 = -\left(\frac{\mathcal{N}b}{g}\right)\int F_y f \cos\phi \, d\phi \tag{8.21.7}$$

Using Eqs. (8.18.15) and (8.19.3), we have

$$\eta - \eta^0 = \frac{\mathcal{N}b^2\zeta}{16}\left\{1 + \frac{16}{6\pi}\left(\frac{g}{4D}\right) - \frac{1}{4}\left(\frac{g}{4D}\right)^2\right\} \tag{8.21.8}$$

Eq. (8.21.8) agrees with Eq. (8.20.3). Thus we can confirm that η calculated from the viscous dissipation induced by fluid of unit volume per unit time is the same as the ratio of the shear stress to the shear velocity.

<<Problem 8-22>> Definition of solution viscosities

In physical chemistry of polymer solutions, relative increase in viscosity of dilute solution induced by dissolving solute is more important than the viscosity itself. Describe the definition of (1) **relative viscosity**$^{1)}$ or **viscosity ratio**$^{2)}$, (2) **specific viscosity**$^{1)}$, (3) **reduced viscosity**$^{1)}$ or **viscosity number**$^{2)}$, (4) **inherent viscosity**$^{1)}$ and (5) **limiting viscosity number**$^{2)}$ or **intrinsic viscosity**$^{1)}$

Answer

Let's denote the viscosity of solvent and solution as η_0 and η, respectively.

$$(1)\ \eta_r = \frac{\eta}{\eta_0} \tag{8.22.1}$$

$$(2)\ \eta_{sp} = \frac{\eta}{\eta_0} - 1 = \eta_r - 1 \tag{8.22.2}$$

$$(3)\ \frac{\eta_{sp}}{C} \tag{8.22.3}$$

where C is the mass concentration.

$$(4)\ \frac{\ln \eta_r}{C} \tag{8.22.4}$$

$$(5)\ [\eta] = \lim_{C\to 0}\frac{\eta_{sp}}{C} \tag{8.22.5}$$

or

$$[\eta] = \lim_{C \to 0} \frac{\ln \eta_r}{C} \tag{8.22.6}$$

The unit of $[\eta]$ is volume/weight (usually $100\mathrm{cm}^3/\mathrm{g}$[1] or cm^3/g[2]). $[\eta]$ defined by Eqs. (8.22.5) and (8.22.6) are sometimes denoted as $[\eta]_H$(Huggins) and $[\eta]_K$ (Kraemer), respectively.

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[1] L. H. Cragg, *J. Colloid Sci.* **1**, 261 (1946); [2] International Union of Pure and Applied Chemistry, *J. Polym. Sci.* **8**, 257 (1952)

* The concept of specific viscosity was proposed by Staudinger-Heuer in 1930 (See H. Staudinger and W. Heuer, *Ber. dtsch. chem. Ges.* **63**, 222 (1930)). They understood η_{sp} as 'die Viscositäts-Erhöhung', die in einem Lösungsmittel durch den gelösten Stoff hervorgerufen wird'

<<Problem 8-23>> Determination of relative viscosity by viscometer

When a viscous fluid flows in a capillary viscometer, η is determined from the time t required for the fluid falling by a certain distance as

$$\begin{aligned}\eta &= \rho\left(C_1 t - \frac{C_2}{t}\right)\\ &= \rho C_1\left(t - \frac{C_2}{C_1 t}\right)\end{aligned} \tag{8.23.1}$$

where ρ is the density of the solution and C_1 and C_2 are the apparatus constants which mainly depend on the dimension of the viscometer. Derive the relationship between η_r and t.

Answer

From the definition

$$\eta_r = \frac{\eta}{\eta_0} \tag{8.22.1}$$

Substitution of Eq. (8.23.1) for η in Eq. (8.22.1) yields

$$\eta_r = \frac{\eta}{\eta_0}$$

$$= \left(\frac{C_1\rho}{C_1\rho_0}\right)\left(\frac{t - C_2/C_1 t}{t - C_2/C_1 t_0}\right) \tag{8.23.2}$$

where ρ_0 and t_0 are the density and the falling time of solvent. In the usual condition of dilute polymer solutions

$$\begin{aligned} &\rho/\rho_0 \cong 1 \\ &t >> C_2/C_1 t, \\ &t_0 >> C_2/C_1 t_0 \end{aligned} \tag{8.23.3}$$

Thus we have

$$\eta_r = \frac{t}{t_o} \tag{8.23.4}$$

Therefore, measurements of the flowing time in a capillary tube t allows us to determine η_r.

---

* Concept of limiting viscosity number as $\lim_{C\to 0} \eta_{sp} / C$ or $\lim_{C\to 0}(\ln \eta_r) / C$ was formed when η_{sp}/C for numerous polymer solutions was observed experimentally to show concentration dependence. $[\eta]$ was considered that it represents the contribution of a polymer molecule to solution viscosity. In 1937 Staudinger used Z_η for $\lim_{c\to 0} \eta_{sp} / C$ of cellulose nitrate solutions (H. Staudinger and M. Sorkin, *Ber. dtsch. chem. Ges.* **70**, 1993 (1937)). In 1938 E. O. Kraemer named $[\eta]$ 'intrinsic viscosity' and in1944 G. V. Schulz named $[\eta]$ 'Viscositätszahl' (E. O. Kraemer, *Ind. Eng. Chem.* **30**, 1200 (1938); G. V. Schulz, *Z. Elektrochem.* **50**, 122 (1944)). In 1945 I. Sakurada proposed 'limiting viscosity number' for $[\eta]$ (I. Sakurada, *Kobunshi Kagaku (Chem. High Polym. Japan)* **2**, 253 (1945)). Note that $[\eta]$ is not viscosity, but just a number. In German industry, k in Fikentscher-Mark equation (Eq. (8.26.2)) was utilized as 'Eigen viscosität'.

<<Problem 8-24>> Huggins' plot and Kraemer's plot (I)

Limiting viscosity number $[\eta]$ is defined by

$$[\eta] = \lim_{C\to 0} \frac{\eta_{sp}}{C} \tag{8.22.4}$$

$$[\eta] = \lim_{C\to 0} \frac{\ln \eta_r}{C} \tag{8.22.5}$$

Prove $[\eta]$ defined by Eqs. (8.22.4) and (8.22.5) are the same.

Answer

From Eq. (8.22.2),

$$\eta_r = 1 + \eta_{sp} \tag{8.24.1}$$

The logarithm of Eq. (8.24.1) is expanded in a Taylor series as

$$\frac{\ln \eta_r}{C} = \frac{\eta_{sp}}{C} - \left(\frac{1}{2}\right)\left(\frac{\eta_{sp}^{\ 2}}{C}\right) + \left(\frac{1}{3}\right)\left(\frac{\eta_{sp}^{\ 3}}{C}\right) - \left(\frac{1}{4}\right)\left(\frac{\eta_{sp}^{\ 4}}{C}\right) + \cdots \tag{8.24.2}$$

When the concentration tends to 0, η_{sp} tends to 0 and η_{sp}/C approaches a constant. Then

$$\lim_{C\to 0}\frac{\eta_{sp}^{\ 2}}{C} = \lim_{C\to 0}\frac{\eta_{sp}^{\ 3}}{C} = \cdots = \lim_{C\to 0}\frac{\eta_{sp}^{\ n}}{C} = 0 \tag{8.24.3}$$

Thus we have

$$\lim_{C\to 0}\frac{\ln \eta_r}{C} = \lim_{C\to 0}\frac{\eta_{sp}}{C} \equiv [\eta] \tag{8.24.4}$$

<<Problem 8-25>> Huggins' plot and Kraemer's plot (II)

The concentration dependences of the quantities η_{sp}/C and $\ln\eta_r/C$ are generally expressed as

$$\frac{\eta_{sp}}{C} = \frac{\eta_r - 1}{C} = [\eta]\left\{1 + k_1[\eta]C + k_1'([\eta]C)^2 + \cdots\right\} \tag{8.25.1}$$

$$\ln\frac{\eta_r}{C} = [\eta]\left\{1 + k_2[\eta]C + k_2'([\eta]C)^2 + \cdots\right\} \tag{8.25.2}$$

respectively. Derive the relationship among the coefficients

$$k_1 - k_2 = \frac{1}{2} \tag{8.25.3}$$

$$k_2' - k_1' + k_1 = \frac{1}{3} \tag{8.25.4}$$

Answer

From Eq. (8.24.2),

$$\frac{\ln \eta_r}{C} = \frac{\eta_{sp}}{C}\left\{1-\left(\frac{1}{2}\right)\left(\frac{\eta_{sp}}{C}\right)C+\left(\frac{1}{3}\right)\left(\frac{\eta_{sp}}{C}\right)^2 C^2-\left(\frac{1}{4}\right)\left(\frac{\eta_{sp}}{C}\right)^3 C^3+\cdots\right\} \tag{8.25.5}$$

Substitution of Eq. (8.25.1) for η_{sp}/C in Eq. (8.25.5) yields

$$\frac{\ln \eta_r}{C} = [\eta]\left[1+\left(k_1-\frac{1}{2}\right)[\eta]C+\left(k_1'-k_1+\frac{1}{3}\right)\left\{[\eta]C\right\}^2+\cdots\right] \tag{8.25.6}$$

Comparing the coefficients of C and C^2 in Eqs. (8.25.2) and (8.25.6), we have

$$k_1 - \frac{1}{2} = k_2 \tag{8.25.7}$$

$$k_1' - k_1 + \frac{1}{3} = k_2' \tag{8.24.8}$$

---

* When higher order terms in Eq. (8.25.1) is negligible, we have

$$\frac{\eta_{sp}}{C} = [\eta]\left\{1 + k_1[\eta]C\right\} \tag{8.25.9}$$

This equation is called the **Huggins' equation** (See M. L. Huggins, *J. Am. Chem. Soc.* **64**, 2716 (1942)). $[\eta]$ and k_1 are determined from the intercept at C→ 0 and the slope, respectively,of the plot of η_{sp}/C vs. C. This plot is called the **Huggins' plot** and the coefficient k_1 is called the **Huggins' coefficient**. The notation k' is used in place of k_1, frequently. When higher order terms in Eq. (8.25.2) is negligible, we have the **Kraemer's equation** (See E. O. Kraemer, *Ind. Eng. Chem.* **30**, 1200 (1938))

$$\ln\frac{\eta_r}{C} = [\eta]\left\{1 + k_2[\eta]C\right\} \tag{8.25.10}$$

Table 8-25 Comparison of calculated values of $\ln\eta_r$ and the summation $\Sigma[(-1)^{i+1}/i]\,\eta_{sp}^{\,i}$

η_r	$\ln\eta_r$	η_{sp}	η_{sp}^2	η_{sp}^3	η_{sp}^4	η_{sp}^5	η_{sp}^6
1.2	0.1823	0.200	0.180	0.1827	0.1823	0.1824	0.1824
1.3	0.2624	0.300	0.255	0.2640	0.2620	0.2615	0.2614
1.4	0.3365	0.400	0.320	0.3413	0.3347	0.3368	0.3361
1.6	0.4700	0.600	0.420	0.4840	0.4552	0.4690	0.4621
1.8	0.5878	0.800	0.480	0.6507	0.5483	0.6138	0.5801

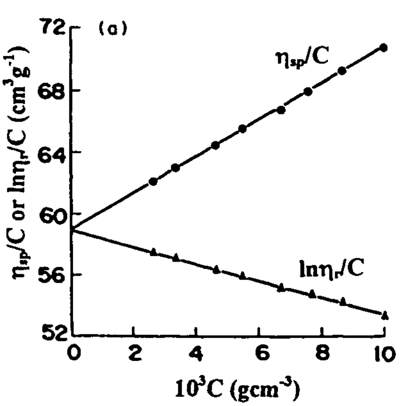

Fig. 8-25 Evaluation of intrinsic viscosity for solutions of poly(*t*-butyl acrylate) in toluene at 25°C by Huggins plot and Kraemer plot, which yields $[\eta]_H=[\eta]_K=59.0\text{cm}^3\text{g}^{-1}$, $k_H=0.340$ and $k_K=0.158$ (See P.A.Lovell, Dilute solution viscometry, in *Comprehensive Polymer Science*, Eds. C.Booth and C.Price eds., Pergamon, Oxford, 1989, vol.1, p185)

$[\eta]$ is determined from the intercept of the plot for $\ln\eta_r/C$ vs. C **(Kraemer's plot)**.
Table 8-25 shows the comparison of the left-hand side and the right-hand side of Eq. (8.25.5).
Figure 8-25 shows the Huggins plot and Kraemer plot for poly(t-butyl acrylate) in toluene.

<<Problem 8-26>> Empirical functional form of the concentration dependence of solution viscosity

A number of empirical equation have been proposed for the concentration dependence of solution viscosity. For example,

(1) **Arrhenius**

$$\ln \eta_r = [\eta]C \tag{8.26.1}$$

(2)**Fikentscher-Mark**

$$\eta_{sp} = \frac{[\eta]C}{1 - k[\eta]C} \tag{8.26.2}$$

(3)**Staudinger-Heuer**

$$\ln\frac{\eta_{sp}}{C} = \ln[\eta] + aC \tag{8.26.3}$$

(4)**Baker**

$$\eta_r = \left(1 + [\eta]\frac{C}{k}\right)^k \tag{8.26.4}$$

Comparing Eqs. (8.26.1)-(8.26.4) with the **Huggins' equation**

$$\frac{\eta_{sp}}{C} = [\eta] + k'[\eta]^2 C \tag{8.25.9}$$

evaluate k' for (1) to (4) (See Note in <<Problem 8-25>>).

Answer

(1): From Eq. (8.26.1),

$$\ln\left(1 + \eta_{sp}\right) = \eta_{sp} - \left(\frac{1}{2}\right)\eta_{sp}{}^2 + \cdots = [\eta]C \tag{8.26.5}$$

Eq. (8.26.5) is rewritten as

$$\eta_{sp} = [\eta]C + \left(\frac{1}{2}\right)\eta_{sp}{}^2 + \cdots = [\eta]C + \left(\frac{1}{2}\right)\left([\eta]C\right)^2 + \cdots \tag{8.26.6}$$

Thus we find

$$k' = 0.5 \tag{8.26.7}$$

(2): When $1 \gg k[\eta]C$, the denominator of the right-hand side of Eq. (8.26.2) is expanded in a Taylor series as

$$\eta_{sp} = [\eta]C + k([\eta]C)^2 + k^2([\eta]C)^3 + \cdots \tag{8.26.8}$$

Comparing Eq. (8.26.8) with Eq. (8.25.9), we find

$$k' = k \tag{8.26.9}$$

(3): Eq. (8.26.3) is rewritten as

$$\eta_{sp} = [\eta]\, C\, e^{aC} \tag{8.26.10}$$

When $aC \ll 1$, we have

$$e^{aC} = 1 + aC + \left(\frac{1}{2}\right)(aC)^2 + \cdots \tag{8.25.11}$$

Substitution of Eq. (8.26.11) for e^{aC} in Eq. (8.26.10) yields

$$\eta_{sp} = [\eta]\left\{C + aC^2 + \left(\frac{a^2}{2}\right)C^3 + \cdots\right\} \tag{8.26.12}$$

Comparing Eq. (8.26.12) with Eq. (8.25.9), we find

$$k' = \frac{a}{[\eta]} \tag{8.26.13}$$

(4): Eq. (8.26.4) is expanded as

$$\eta_r - 1 = \eta_{sp} = [\eta]C + \left(\frac{k-1}{2}\right)([\eta]C)^2 \tag{8.26.14}$$

Comparing Eq. (8.26.14) with Eq. (8.25.9), we find

$$k' = \frac{k-1}{2} + \cdots \tag{8.26.15}$$

Coefficients of the term C^2 in Eqs. (8.26.1)-(8.26.4) are proportional to $[\eta]^2$.

Thus, Eqs. (8.26.1)-(8.26.4) are equivalent to the Huggins equation when C is small. (See S.F.Arrhenius; *Z.phys.Chem.* **1**,285(1887), H.Staudinger and W.Heuer, *Z.phys.Chem.* **A171**, 129 (1934); H.Fikentscher and H.Mark, *Kolloid-Z.* **49**, 135 (1930), F.Baker, *J.Chem.Soc.(London)* **103**, 1653 (1913))

<<Problem 8-27>> Einstein's viscosity equation: Rigid sphere model

Derive Einstein's viscosity equation (A. Einstein, *Ann. Phys.* **19**, 289 (1906); *ibid.* **34**, 591 (1911))

$$\eta = \eta_0(1+2.5\phi) \tag{8.27.1}$$

using the following assumptions. Here ϕ is the volume fraction of the solute.

1. The solute is in the form of rigid spherical particles

2 The solution is regarded as a continuous field, and there exists no specific interaction between solvent molecules and solute particles.

3. The solution is so dilute that the hydrodynamic interaction between particles is negligible.

4. The solution is incompressible.

5. Flow is sufficiently slow and the Stokes equation is valid for this fluid.

6. The velocity of the flow on the surface of these particles is zero (i.e., perfectly non-free draining).

Answer

We consider particles in a simple laminar shear flow (**Couette flow**) for which velocity, in the absence of the particles, is expressed as

$$\mathbf{v}^0 = \begin{pmatrix} 0 \\ gx \\ 0 \end{pmatrix} \tag{8.27.2}$$

The field $\mathbf{v}^0$ may be divided into two parts: rotational flow $\mathbf{v}_r$ and deformational flow $\mathbf{v}'$, that is,

$$\mathbf{v}^0 = \mathbf{v}_r + \mathbf{v}' \tag{8.27.3}$$

where

$$\mathbf{v}_r = \begin{pmatrix} \frac{-gy}{2} \\ \frac{gx}{2} \\ 0 \end{pmatrix} \tag{8.27.4}$$

and

$$\mathbf{v} = \begin{pmatrix} \frac{gy}{2} \\ \frac{gx}{2} \\ 0 \end{pmatrix} \tag{8.27.5}$$

A particle with radius a placed at the origin of Cartesian coordinate rotates along the z axis with an angular velocity g/2. An increase in viscosity of this solution arises from the deformational flow. However, an introduction of a particle with finite volume brings about an additional local disturbance, and this effect can be treated by replacing the sphere with the equivalent forces in the fluid. To reproduce the pertubational flow due to the presence of the particle at the origin, we introduce a doublet force at points infinitely near the origin. According to Oseen, a positive force at (x=0, y=-ε, z=0) and a negative force at (x=0, y=+ε, z=0) gives rise to velocity such that

$$\mathbf{v}_I = A\begin{pmatrix} -\frac{y}{r^3} - \frac{3x^2y}{r^5} \\ \frac{x}{r^3} - \frac{3xy^2}{r^5} \\ \frac{-3xyz}{r^5} \end{pmatrix} \tag{8.27.6}$$

and

$$\mathbf{v}_{II} = A\begin{pmatrix} \frac{y}{r^3} - \frac{3x^2y}{r^5} \\ -\frac{x}{r^3} - \frac{3xy^2}{r^5} \\ -\frac{3xyz}{r^5} \end{pmatrix} \tag{8.27.7}$$

respectively. Here A is an undetermined constant relating to the strength of the doublet and r is the distance from the origin. By the requirement to represent correctly the initial unperturbed velocity, the third velocity field $\mathbf{v}_{III}$, which is derived from the potential ϕ through Eq. (8.27.8), is added to the two velocity fields above.

$$\mathbf{v}_{III} = \nabla\phi \tag{8.27.8}$$

The potential ϕ in the form

$$\phi = \frac{B\partial^2\left(\frac{1}{r}\right)}{\partial x \partial y} \tag{8.27.9}$$

yields

$$\mathbf{v}_{III} = B\begin{pmatrix} \frac{3y}{r^5} - \frac{15x^2y}{r^7} \\ \frac{3x}{r^5} - \frac{15xy^2}{r^7} \\ -\frac{15xyz}{r^7} \end{pmatrix} \tag{8.27.10}$$

Superposing these three velocity fields, we choose a suitable relation between the constants A and B at r=a, as

$$B = -\frac{2Aa^2}{5} \tag{8.27.11}$$

Then, on the surface of the sphere, the perturbed velocity $\mathbf{v}'$ becomes

$$\mathbf{v}' = -\frac{6A}{5a^3}\begin{pmatrix} y \\ x \\ 0 \end{pmatrix} \tag{8.27.12}$$

Comparing this with Eq. (8.27.5), we conclude that the choice of A should be such that

$$-\frac{6A}{5a^3} = \frac{g}{2} \tag{8.27.13}$$

At large distance from the origin, the effect of the sphere should vanish and the third velocity field $\mathbf{v}_{\mathrm{III}}$ is relatively small compared to $\mathbf{v}_{\mathrm{I}}$ and $\mathbf{v}_{\mathrm{II}}$. Thus, a combination of the fields $\mathbf{v}_{\mathrm{I}}$ and $\mathbf{v}_{\mathrm{II}}$ yields the pertubation

$$\mathbf{v}' = \begin{pmatrix} \dfrac{x^2y}{r^5} \\ (\dfrac{5ga^3}{2})\dfrac{xy^2}{r^5} \\ \dfrac{xyz}{r^5} \end{pmatrix} \tag{8.27.14}$$

Energy dispersion per unit volume and unit time in this solution ($=\eta g^2$) is attributed to the frictional force in the original solvent flow ($\eta_0 g^2$) and to that due to the particles with number density n. Neglecting hydrodynamic interaction between the particles, we simply superpose the energy dispersion arising from individual particles. Then the energy equation is

$$\eta g^2 = \eta_0 g^2 + 2n\int\int\left(\frac{5ga^3}{2}\right)\left(\frac{xy^2}{r^5}\right)(h_0 g)dxdy \tag{8.27.15}$$

Carrying the integration over all the space of the fluid, we obtain the specific viscosity η_{sp} as

$$\eta_{sp} = \left(\frac{5n}{2}\right)\left(\frac{4\pi a^3}{3}\right) \tag{8.27.16}$$

where $4\pi a^3 n/3$ is the product of concentration C (g/cm^3) and the specific volume v of the solute. Finally we arrive at the **Einstein's equation.**

$$\eta=\eta_0(1+2.5\phi) \tag{8.27.1}$$

(See A. Ishihara, *Adv. Polym. Sci.* **5**, 531 (1968); K. Kamide and M. Saito, *Determination of Molecular Weight*, (ed. by A.R.Cooper), p103, Wiley-Interscience, New York, 1989). (See also <<Problem 8-15>>)

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* Einstein's equation is applied for spherical molecules and branched molecules.
Examples are
(1) natural rubber latex
(2) polystyrene produced by emulsion polymerization in aqueous solution
(3) aqueous solution of saccharose
(4) glucose pentaacetate, cellobiose octaacetate etc.
(5) egg albumin
(6) phenol resin
(7) glycogen and its derivatives
(8) amylopectine
(See I. Sakurada, *Polymer Chemistry (Kobunshi Kagaku Gairon)*, Kobunshi Kagaku Kankokai (1948))

* The coefficients of higher order terms than ϕ in Eq. (8.27.1) were calculated by Guth and Simha (E. Guth and R. Simha, Kolloid Z. 74, 266 (1936)) as $\eta=\eta_0(1+2.5\phi+14.1\phi^2+...)$ and Vand (V. Vand, J. Phys. & Colloid Chem. 52, 277 (1949)) as $\eta=\eta_0(1+2.5\phi+7.349\phi^2+...)$.

<<Problem 8-28>> Molecular weight dependence of [η] (I): Unpenetrable sphere formed by chain polymer or linear polymer forming sphere

Using Einstein's equation

$$\eta=\eta_0(1+2.5\phi) \tag{8.27.1}$$

derive the equation

$$[\eta]=\lim_{c\to 0}\frac{\eta-\eta_0}{\eta_0 c}=K_m M^{0.5} \tag{8.28.1}$$

for chain polymer solutions where η and η_0 are the viscosities of solution and solvent, respectively, M the molecular weight of the polymer and K_m a constant.

Answer

A chain polymer in a solution can be regarded as a spherical coil with diameter d which is roughly approximated as the root mean square end-to-end distance of the chain. That is,

$$d^2 \cong \left\langle R^2 \right\rangle = nb^2 \tag{8.28.2}$$

where n is the number of segments of the chain polymer and b the segment length, respectively. The volume of the coil V_e is estimated as

$$V_e = \left(\frac{4\pi}{3}\right)\left(\frac{d}{2}\right)^{3/2} \cong \left(\frac{2\pi}{3\cdot 2^{1/2}}\right)\left(nb^2\right)^{3/2} \tag{8.28.3}$$

When C gram of polymer with the molecular weight M is dissolved in a solvent to make 100 cc solution, the number of polymer in the solution is

$$\frac{C}{M/N_A} = \frac{CN_A}{M} \tag{8.28.4}$$

and the total volume of polymers in the solution is $(2\pi/(3 \cdot 2^{1/2}))(nb^2)^{3/2} \times (N_A/M)C$, where N_A is Avogadro's number. Then the volume fraction of polymer is

$$\phi = \left(\frac{1}{100}\right)\left(\frac{2\pi}{3\cdot 2^{0.5}}\right)\left(nb^2\right)^{1.5}\left(\frac{N_A}{M}\right)C \tag{8.28.5}$$

Using the monomer molecular weight m=M/n, Eq. (8.28.5) is rewritten as

$$\phi = \left(\frac{1}{100}\right)\left(\frac{2\pi}{3\cdot 2^{0.5}}\right)\left(\frac{N_A b^3}{m^{1.5}}\right)M^{0.5}C \tag{8.28.6}$$

Substitution of Eq. (8.28.6) for ϕ in Eq. (8.27.1) yields

$$[\eta] = \frac{\pi N_A b^3}{60\cdot 2^{0.5} m^{1.5}} M^{0.5} \tag{8.28.7}$$

Comparing Eqs. (8.28.1) and (8.28.7), we find

$$K_m = \frac{\pi N_A b^3}{60\cdot 2^{0.5} m^{1.5}} \tag{8.28.8}$$

Thus [η] of linear polymer solutions is proportional to $M^{0.5}$ when Einstein's viscosity relationship is applicable. If we take account of the excluded volume effect, the power in Eq. (8.28.1) is larger than 0.5. (See W. Kuhn, *Kolloid Z.* **68**, 2 (1934)).

<<**Problem 8-29**>> **Angular velocity of molecular chain in steady flow**

Show that the angular velocity of molecular chains is given by

$$\Omega = \frac{g}{2} \tag{8.29.1}$$

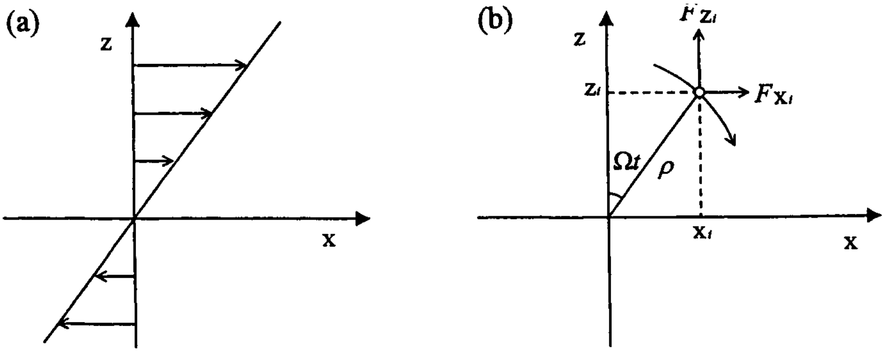

Fig. 8-29 Chain polymer molecule in a shear flow

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* In case of spherical molecules,

$$V_e = M/(\rho/N_A) \tag{8.28.9}$$

(ρ: density of solute), then,

$$\phi = V_e C N_A/100M = C/100\rho \tag{8.28.10}$$

Combination of Eqs. (8.27.1) and (8.28.10) gives

$$\eta_{sp}/C = 2.5/100\rho = 0.025/\rho \tag{8.28.11}$$

Eq. (8.28.11) indicates that if a polymer molecule is spherical, [η] is constant, irrespective of M.

for the steady flow of chain polymer solutions.

Answer

Let's take a pearl-necklace model and number the small spheres as 0,1,2..., n from one end. If we denote the coordinate of *i* th sphere as (x_i,y_i,z_i), the velocity of solvent at the location of *i* th sphere is given by

$$v_{xi} = gz_i,\ v_{zi} = 0,\ v_{yi} = 0 \tag{8.29.2}$$

as shown in Fig. 8-29. When the molecule rotates along y axis with the angular velocity Ω, *i* th sphere likewise rotates with the same angular velocity. Then the position of *i* th sphere is expressed as

$$x_i = \rho\sin\Omega t,\ z_i = \rho\cos\Omega t,\ y_i = 0 \tag{8.29.3}$$

and its velocity is given by

$$u_{xi} = \frac{dx_i}{dt} = \Omega\rho\cos\Omega t = \Omega z_i$$

$$u_{zi} = \frac{dz_i}{dt} = -\Omega\rho\sin\Omega t = -\Omega x_i$$

$$u_{yi} = \frac{dy_i}{dt} = 0 \tag{8.29.4}$$

The velocity difference between *i* th sphere and solvent is given by

$$v_{xi} - u_{xi} = gz_i - \Omega z_i,\ -u_{zi} = \Omega x_i \tag{8.29.5}$$

Friction force is proportional to the velocity difference and is given by

$$F_{xi} = \zeta(v_{xi} - u_{xi}) = \zeta(g - \Omega)z_i,\ F_{zi} = -\zeta u_{zi} = \zeta\Omega x_i \tag{8.29.6}$$

where ζ is the friction constant. The moment to rotate *i* th sphere from z axis to x axis (i.e., in the direction of Ω) is z_iF_{xi} (distance x force) and the moment to rotate it from x axis to z axis is x_iF_{zi}. Then the moment to rotate *i* th sphere along y axis is given by

$$M_i = z_iF_{xi} - x_iF_{zi} \tag{8.29.7}$$

where the plus sign of the moment denotes the same direction as Ω. Substitution of Eq. (8.29.6) for F_{xi} and F_{zi} in Eq. (8.29.7) yields

$$M_i = \zeta(g - \Omega)z_i^2 - \zeta\Omega x_i^2 \tag{8.29.8}$$

The moment for the total chain is the sum of the moment for each sphere, so we have

$$M = \sum_{i=0}^{n} M_i = \zeta(g - \Omega)\sum_{i=0}^{n} z_i^2 - \zeta\Omega\sum_{i=0}^{n} x_i^2 \tag{8.29.9}$$

Since small spheres distribute randomly about the center of gravity of the chain polymer, we have

$$\sum_{i=0}^{n} x_i^2 = \sum_{i=0}^{n} y_i^2 = \sum_{i=0}^{n} z_i^2 = \frac{1}{3}\left(\sum_{i=0}^{n} S_i^2\right) \tag{8.29.10}$$

where S_i is the distance between *i* th sphere and the center of gravity of the molecule. Substitution of Eq. (8.29.10) in Eq. (8.29.9) yields

$$M = \zeta(g - 2\Omega)\left(\frac{1}{3}\sum_{i=0}^{n} S_i^2\right) \tag{8.29.11}$$

For the steady flow, M must be zero in Eq. (8.29.11). Then we find

$$g - 2\Omega = 0 \tag{8.29.12}$$

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* In this case it is assumed that the molecule is spherically symmetrical (about the center of gravity).

<<Problem 8-30>> Molecular weight dependence of [η] (II): Free draining random coil molecules

Derive the relationship

$$[\eta] = K_m M \tag{8.30.1}$$

for free draining random coil molecules, using the results in <<Problem 8-29>>.

Answer

Substitution of

$$\Omega = \frac{g}{2} \tag{8.29.12}$$

in equations

$$F_{xi} = \zeta(g - \Omega)z_i$$
$$F_{zi} = \zeta\Omega x_i \tag{8.29.6}$$

yields

$$F_{xi} = \frac{\zeta g z_i}{2}$$
$$F_{zi} = \frac{\zeta g x_i}{2} \tag{8.30.2}$$

for the force for *i* th sphere in the steady flow. The solvent exerts the force given by Eq. (8.30.2) on *i* th sphere and flows with the velocity

$$v_{xi} = g z_i \tag{8.29.2}$$

---

* Eq. (8.29.2) means that there is no hydrodynamic interference between two small spheres arbitrarily chosen (i. e. completely free draining).

Thus the work done by the solvent on *i* th sphere per unit time is

$$F_{xi}v_{xi} = \frac{\zeta g^2 z_i^2}{2} \tag{8.30.3}$$

and finally dissipates as a frictional heat. The total work done by the solvent on the chain molecule is

$$\sum_{i=0}^{n} F_{xi}v_{xi} = \frac{\zeta g^2}{2}\sum_{i=0}^{n} z_i^2 \tag{8.30.4}$$

where

$$\sum_{i=0}^{n} z_i^2 = \frac{1}{3}\sum_{i=0}^{n} s_i^2 \tag{8.30.5}$$

If there are N_1 chain polymers in unit volume, the dissipation energy caused by the presence of solutes is given by

$$w_2 = \frac{\zeta \mathcal{N}_1 g^2}{6} \sum_{i=0}^{n} S_i^2 \tag{8.30.6}$$

On the other hand, the dissipation energy of pure solvent is given by

$$w_1 = \eta_0 g^2 \tag{8.15.3}$$

Thus the total dissipation energy per unit volume of the solution is

$$w = w_1 + w_2 = \eta_0 g^2 + \frac{\zeta \mathcal{N}_1 g^2}{6} \sum_{i=0}^{n} S_i^2 \tag{8.30.7}$$

Since the radius of gyration $\langle S^2 \rangle$ for random coil chains is given by

$$\sum_{i=0}^{n} S_i^2 = \left(\frac{n+1}{6}\right) nb^2 \cong \frac{n^2 b^2}{6} \tag{6.9.15'}$$

for n>>1, Eq. (8.30.7) is rewritten as

$$w = \eta_0 g^2 + \frac{\zeta \mathcal{N}_1 g^2 n^2 b^2}{36} \tag{8.30.8}$$

Comparing the definition

$$w = \eta g^2 \tag{8.15.3}$$

with Eq. (8.30.8), we find

$$\eta = \eta_0 + \frac{\zeta \mathcal{N}_1 n^2 b^2}{36} \tag{8.30.9}$$

If we express the concentration C in g/100cc, the number of molecules of polymer per 1 cc is given by

$$\mathcal{N}_1 = \frac{N_A C}{100M} \tag{8.30.10}$$

The degree of polymerization is

$$n = \frac{M}{m} \tag{8.30.11}$$

Substitution of Eqs. (8.30.10) and (8.30.11) in Eq. (8.30.9) yields

$$\eta = \eta_0 + \frac{\zeta N_A b^2 MC}{3600m^2} \tag{8.30.12}$$

Then we have

$$[\eta] = \lim_{C \to 0} \frac{\eta - \eta_0}{\eta_0 C} = \frac{\zeta N_A b^2 M}{3600\eta_0 m^2} \tag{8.30.13}$$

Thus the coefficient K_m in Eq. (8.30.1) is given by

$$K_m = \frac{\zeta N_A b^2}{3600\eta_0 m^2} \tag{8.30.14}$$

If the **Stokes' law** is applicable, then

$$\zeta = 6\pi a \eta_0 \tag{8.13.15}$$

is valid for this solution, and Eq. (8.30.14) is further rewritten as

$$K_m = \frac{\pi a N_A b^2}{600m^2} \tag{8.30.15}$$

---

* It should be noted that Eq. (8.30.13) has been derived on the assumption that the flow inside the chain molecule is the same as that outside, that is, complete free draining. (See M.L. Huggins, *J. Phys. Chem.* **42**, 911 (1938), *ibid* **43**, 439 (1939), *J. Appl. Phys.* **10**, 700 (1939); P. Debye, *J. Chem. Phys.* **14**, 636 (1946); H. A. Kramers, *J. Chem. Phys.* **14**, 415 (1946); N. Saito, *Polymer Physics*, Chap. 6, 40-3, Syoka-bo, 1959)) On the other hand, Eq. (8.28.1) was derived on the assumption that the solvent molecules do not pass through the coil, that is, **complete non-free draining**. For the pearl-necklace model of chain polymers,

$$[\eta] \propto M^{0.5} \quad \text{(complete non–free draining) : Rigid sphere} \tag{8.30.16}$$

$$[\eta] \propto M \quad \text{(complete free draining) : Pearl necklace} \tag{8.30.17}$$

The exponent of M depends on the degree of free draining. Debye-Bueche and Kirkwood-Riseman introduced the concept of partially free draining and showed that the power a in the equation $[\eta]=KM^a$ is in the range between 0.5 and 1. (See P. Debye and A.M.Bueche, *J. Chem. Phys.* **16**, 573 (1948); J.G.Kirkwood and J.Riseman, *J. Chem. Phys.* **16**, 565 (1948)).

* Eq.(8.30.1) coincides with **Staudinger's viscosity equation.** In 1930 Staudinger and Heuer (H. Staudinger and W. Heuer, *Ber. dtsch. chem. Ges.* **63**, 222 (1930)) studied the viscosity of solutions for linear polymers (six whole polystyrene samples, prepared by thermal polymerization method (75~240°C)(molecular weight 3500~ca. 2000)) in benzene and found that η_{sp}/C of linear polymer (Faden-Molekülen) is proportional to M, that is,

$$\frac{\eta_{sp}}{C} = K_m M \qquad (8.30.18)$$

Staudinger and Nodzu (H. Staudinger and R. Nodzu, *Ber. dtsch. chem. Ges.* **63**, 721 (1930)) also studied in the same year the viscosity of low molecular weight linear molecules (four paraffin fractions, isolated by fractional distillation under high vacuum (at 0.1mmHg) (M_n by melting point depression method in benzene; 336~744), dotricontane and pentatriacontane in tetrachlorocarbon, confirming Eq. (8.30.18). Staudinger and Heuer stated that 'Auf Grund dieser Gleichung kann man das vorhandene Beobachtungsmaterial daraufhin prüfen, ob in gleichkonzentrierten Lösungen verschidener gewicht zunimmt, dah proportional M ist'. This equation is one of the approximate equations of Eq. (8.30.1). He and his colleagues then studied solutions of cellulose derivatives and high molecular weight polystyrenes and concluded that Eq. (8.30.18) also holds for these solutions. However, for most polymer solutions, the relationship between [η] and the molecular weight is rather expressed as

$$[\eta] = K_m M^a \qquad 0.5 \le a \le 1 \qquad (8.30.19)$$

This relationship was theoretically derived by Kuhn in 1934 and empirically proposed by Mark (1938), Houwink (1941) and Sakurada (1940), independently. Now, Eq. (8.30.19) is called **Mark-Houwink-Sakurada equation** or **Kuhn-Mark-Houwink-Sakurada equation** (See W. Kuhn, *Kolloid Z.* 68, 9 (1934); *Angew. Chem.* 49, 860 (1936); H. Mark, *Der feste Korper*, p.103, Leipzig (1938); R. Houwink, *J. prakt. Chem.* **157**, 15 (1941) and I. Sakurada, *Nihon Kagakusenikenkyusho Koensyu (Proc. Symp. Japan Textile Res. Lab.)*, **5**, 33 (1940)). Sakurada derived Eq. (8.30.19) from very systematic analysis on experimental data of twelve synthetic polymer-solvent systems. The concept established by Staudinger that the molecular weight of solute molecules can be determined by a viscosity law is, however, still meaningful. It's instructive to note that Staudinger assumed polymers to be rod-like in the solution. This is obviously unrealistic because the limiting viscosity number of solutions of rod-like molecules with $l/d \gg 1$ is expressed as $[\eta]=(1/16)(l/d)^2\phi/100=K_m M^2$, since $l \propto M$ and d and ϕ are independent of M. Here l, d and ϕ are the length and the diameter of the crosssection and the volume fraction of the rod-like molecule. This misunderstanding came from his wrong idea; (1) polymers become crystals having the same crystal lattice, independently of the molecular weight. If low molecular weight polymers were semiflexible and the high molecular weight polymer were a coil, the same crystal lattice should not be obtained. (2) the viscosity law holds regardless of molecular weight. Thus linear polymers should have the same shape, irrespective of molecular weight. It may not be possible to change their shape from rod to flexible coil when molecular weight is increased. (See I. Sakurada, *Kobunshi Kagaku Gairon*,

Table 8-30.1 The parameters K_m and *a* in the Mark-Houwink-Sakurada equation for polymer solutions (K. Kamide and M. Saito, in *Determination of Molecular Weight*, Ed. A. R. Cooper, John Wiley & Sons, New York, Chap. 8, p168)

Polymer	Solvent	Temperature (°C)	K_m (cm^3/g) ($\times 10^3$)	*a*	Number of Samples	Molecular Weight Range ($\times 10^{-4}$)
Polybutadiene	Benzene	30	8.5	0.78	4	15–50
	Cyclohexane	30	11.2	0.75	4	15–50
Polychloroprene	Butanone	25	113	0.5	7	15–300
	Toluene	30	20.2	0.73	12	14–580
Polyethylene (high density)	Trichlorobenzene	135	71.1	0.67	8	0.4–90
	Decalin	135	62	0.7	11	2–104
	Diphenyl ether	161	295	0.5	6	2–104
Polypropylene (atactic)	Decalin	135	11.0	0.80	6	2–62
Polyacrylonitrile	Dimethylformamide	20	46.6	0.71	36	7–170
		25	52	0.69	7	5–52
(atactic)	Dimethyl sulfoxide	25	153	0.60	4	11–52
	85% Aqueous ethylene carbonate	25	256	0.49	7	5–52
	55% HNO_3	25	342	0.50	7	5–52
	67% HNO_3	25	122	0.62	7	5–52
(high meso)	Dimethyl sulfoxide	25	204	0.58	8	7–78
	57% HNO_3	25	363	0.50	7	7–78
	67% HNO_3	25	217	0.57	8	7–78
Acrylonitrile–methylacrylate copolymer	Dimethylformamide	25	21.3	0.74	9	5–53
	51% HNO_3	25	152	0.50	9	5–53
	80% HNO_3	25	62	0.68	9	5–53
Poly(methylacrylate)	Butanone	20	3.5	0.81	13	6–240

Poly(methyl methacrylate)	Acetone	25	5.3	0.73	7	2–78
	Benzene	25	5.5	0.76	11	2–740
	4-Heptanone	33.8	48	0.50	5	1–172
Poly(vinyl chloride)	Cyclohexanone	25	13.8	0.78	28	1–12
	Tetrahydrofuran	25	16.3	0.77	23	2–30
Polystyrene (linear atactic)	Benzene	25	7.8	0.75	12	40–6000
	Butanone	25	39	0.58	16	1–180
	Cyclohexane	34.5	88.	0.50	16	1–6000
	Toluene	25	10.5	0.73	6	16–100
Polyimino(1-oxohexamethylene) (nylon 6)	Conc. H_2SO_4	20–35	3.32[a]	0.78	—[b]	0.1–10
Polyoxydimethylsilylene	Bromocyclohexane	29.0	74	0.50	5	3.3–106
Cellulose	Cadoxen	25	38.5	0.76	9	1–95
	6 wt% Aqueous LiOH	25	27.8	0.79	6	4–19
	Iron sodium tartrate	25	53.1	0.78	10	0.6–64
Cellulose triacetate (2.92)[c]	Dimethylacetamide	25	26.4	0.75	10	6–69
	Trifluoroacetic acid	25	39.6	0.71	8	6–69
	Acetone	25	28.9	0.76	9	6–64
	Trichloromethane	25	45.4	0.65	7	6–69
	Dichloromethane	20	24.7	0.70	7	6–69
Cellulose diacetate (2.46)[c]	Dimethylacetamide	25	13.4	0.82	5	5–27
	Acetone	25	133	0.62	9	6–27
Carboxymethyl cellulose (1)[c]	NaCl (limit of infinite ion strength)	25	1.9	0.6	4	14–106
Amylose	Dimethyl sulfoxide	25	1.25	0.87	9	22–310
Amylose triacetate	Nitromethane	22.5	8.5	0.73	12	14–310

[a] Established using viscosity-average molecular weight.

[b] Obtained by analysis of literature data.

[c] Degree of substitution.

Kobunshi Kagaku Kyokai, 1948, p261)

* Although Mark-Houwink-Sakurada equation is an empirical equation, this relationship is valid for a wide range of molecular weight. The linearity in the plot of log[η] vs. logM for high molecular weight range can be improved by measuring the viscosity at low shear rate. A typical example is shown in Fig. 8-30.1. Empirical values of the exponent *a* and the coefficient K_m are summarized in Table 8-30.1.

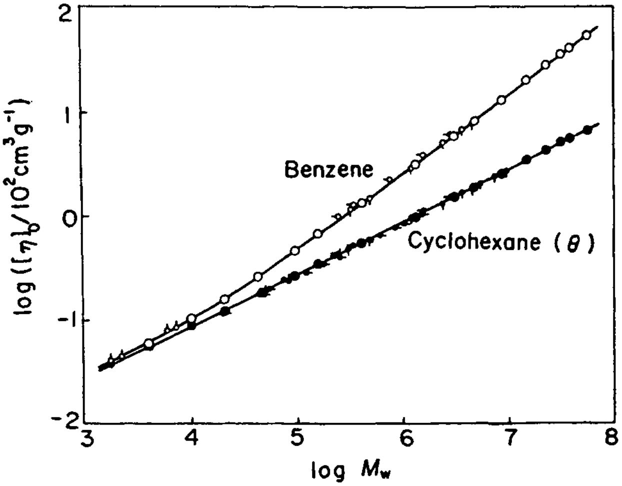

Fig. 8-30.1 Log-log plot of limiting viscosity number for polystyrene solutions against weight-average molecular weight. ○benzene at 25° and 30°C; ●, cyclohexane at θ temperature; (○, ● data of Einaga et al.[1]; ó, ♦ Altares et al.[2]; ●-, Berry[3] ;ọ,●, Fukuda et al.[4]; -○, -● Yamamoto et al.[5]) (See Y. Einaga, Y. Miyaki and H. Fujita, *J. Polym. Sci. Polym. Phys. Ed.* **17**, 2103 (1979))

[1]Y. Einaga, Y. Miyaki and H. Fujita, *J. Polym. Sci. Polym. Phys. Ed.* **17**, 2103 (1979), [2] T. A. Altares, D.P.Wyman and V.R.Alten, *J. Polym. Sci.* **A2**, 4533 (1964), [3] G.C.Berry, *J. Chem. Phys.* **46**, 1338 (1967), [4] M. Fukuda, M. Fukutomi, Y. Kato and H. Yamakawa, *J. Polym. Sci., Polym. Phys. Ed.* **12**, 871 (1974), [5]A. Yamamoto, M. Fujii, G. Tanaka, and H. Yamakawa, *Polym. J.* **2**, 799 (1971).

* For well-fractionated polymer homologues in a series of solvents, K_m is related to a as shown in Fig. 8-30.2. Thus experimental relationships are classified into two groups. One group is amorphous polymers and another group is crystalline polymers with poor flexibility. Flory's lattice theory cannot be applied for the latter group. (See T.Kawai, K.Kamide, *J. Polym. Sci.* **54**, 343 (1961))

* The power a in Eq. (8.30.19) for different theoretical model is summarized in Table 8-30.2. The value of a in the viscosity equation could be evaluated from the free draining effect or the excluded volume effect.

* For molecular weight as low as 10^3-10^4, the power a in Eq. (8.30.19) reduces to 0.5 even in good solvents. In Flory-Fox equation (See <<Problem 8-32>>)

$$[\eta] = KM^{1/2}\alpha^3 \qquad (6.18.1)$$

the swelling coefficient α decreases with decreasing molecular weight (α^5-law, α^3-law etc.) For $M=10^3$-10^4 and $\alpha \sim 1$, we have

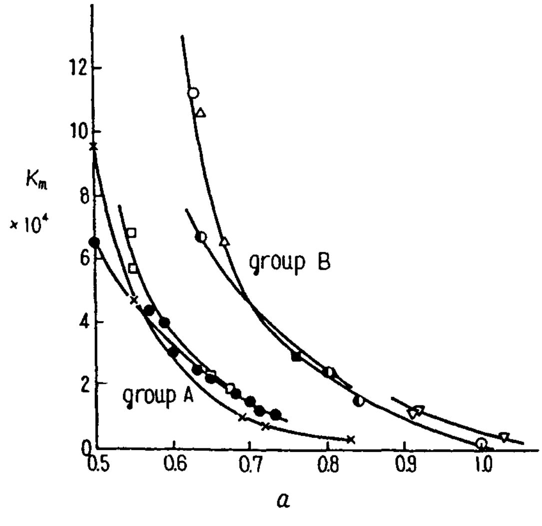

Fig. 8-30.2 Experimental relationships between K_m and a for various polymers in various solvents. ○ polyvinylchloride at 20°C, △ polybutadiene at 25°C, ◑ polyvinylalchohol at 30°C, ▽ cellulose nitrate at 25°C □ polyvinylpyrrolidone at 25°C, ● polystyrene at 25°C, × polymethylmethacrylate at 25°C, ■▲ polyacrylonitrile at 30°C. (See T. Kawai, K. Kamide, *J. Polym. Sci.* **54**, 343 (1961))

Table 8-30.2 The value of the parameter *a* in Eq. (8.30.19) for various theoretical model

a	Theoretical Model	Scientist
0	sphere	Einstein
0.5	pearl-necklace model (non-free draining)	Kuhn
0.5~1	identical sphere of Gaussian coil or partially free draining	Flory-Fox Kirkwood-Riseman
1	pearl-necklace model (free draining)	Huggins, Debye
2	rod	Kuhn

Table 8-30.3 Typical examples of K_s and K_θ

polymer	$10^3 K_s$	$10^3 K_\theta$
polydimethylcyloxane	0.75	0.75-0.80
polyisobutyrene	1.3	1.1

$$[\eta] = KM^{1/2} \tag{8.30.20}$$

approximately. To distinguish K for low molecular weight polymers in good solvents from that for high molecular weight polymers in θ solvents, we denote the former as K_s and the latter as K_θ.

$$K_s \cong K_\theta \tag{8.30.21}$$

Validity of Eq. (8.30.21) is confirmed by experiments (Table 8-30.3). Thus K_θ can be approximately estimated by determining the viscosity law for extremely small molecular weight polymers in good solvents even when we cannot find θ solvent. (See C. Rossi, U. Bianchi, E. Bianchi, *Makromol. Chem.* **41**, 31 (1960))

* Free draining effect is remarkable for low molecular weight regime, so the power *a* should be larger in this regime. But this expectation is not often true in experiments. It is also noted that the effect of end functional groups should not be neglected.

<<Problem 8-31>> Molecular weight dependence of [η] (III): Linear polymer Gaussian chain with hydrodynamic interaction (Kirkwood-

Riseman theory)

Consider a linear polymer molecule consisting of a number of segments n in a laminar flow for which the velocity field is expressed by the equation

$$\mathbf{v}^0 = \begin{pmatrix} 0 \\ g\,x \\ 0 \end{pmatrix} \qquad (8.27.2)$$

Assume that the polymer segment is hydrodynamically regarded as a material point, i.e., the effect of drainage on the surface of the segment is negligible, in contrast with the case of Einstein's theory. Derive the **expression for the relationship between solution viscosity and molecular weight** for linear polymer solutions with hydrodynamic interaction.

Answer

The origin of the coordinate is set at the center of mass of this molecule, and the radius vector of *i* th segment is $\mathbf{r}_i$. In the low velocity field, a frictional force $\mathbf{F}_i$ at the location of the *i* th segment with the velocity $\mathbf{u}_i$ is given, using the solvent velocity $\mathbf{v}_i$, as

$$\mathbf{F}_i = \zeta\left(\mathbf{u}_i - \mathbf{v}_i\right) \qquad (8.31.1)$$

Here ζ is the friction constant. On the other hand, the flow field at the *i* th segment is perturbed as a result of the frictional forces exerted by other segments. This is the **hydrodynamic interation**. As shown in the perturbed velocity $\mathbf{v}'_j$ at the *i* th segment, which arises from the frictional force $\mathbf{F}_j$ due to the *j*th segment, is derived by Oseen as

$$\mathbf{v}'_j = \mathbf{T}_{ij}\mathbf{F}_j \qquad (8.31.2)$$

with

$$\mathbf{T}_{ij} = \frac{1}{8\pi\eta_0}\left[\frac{\mathbf{I}}{r_{ij}} + \frac{\mathbf{r}_{ij}\mathbf{r}_{ij}}{r_{ij}^{\,3}}\right] \qquad (8.31.3)$$

where **I** is a unit tensor, $\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$, r_{ij} is the absolute value of vector $\mathbf{r}_{ij}$ (See <<Problem 8-13>> Eq. (8.13.1)). The Oseen tensor $\mathbf{T}_{ij}$ is a symmetric tensor. The sum of the initial unperturbed velocity and the perturbed velocity due to all other segments is $\mathbf{v}'_i$, which is given by

$$\mathbf{v}_i' = \mathbf{v}_i^0 + \zeta\sum_{j=1}^{n}{}' \mathbf{T}_{ij}\left(\mathbf{u}_i - \mathbf{v}_j\right) \tag{8.31.4}$$

Then the frictional force $\mathbf{F}_i$ is

$$\mathbf{F}_i = -\zeta\left(\mathbf{v}_i - \mathbf{u}_i\right) - \zeta\sum_{j=1}^{n}{}' \mathbf{T}_{ij}\mathbf{F}_j \tag{8.31.5}$$

When we neglect the deformation of the chain molecules in the flow field, all the segments rotate around the origin with the same angular velocity g/2 (Refer to Eq. (8.29.1)). The velocity difference $\mathbf{v}_i^0$-$\mathbf{u}_i$ is deduced as

$$\mathbf{v}_i^0 - \mathbf{u}_i = \frac{g}{2}\begin{pmatrix} y_i \\ x_i \\ 0 \end{pmatrix} \tag{8.31.6}$$

The energy dissipation per unit volume and unit time due to the presence of a molecule in an instantaneous conformation is

$$-\sum_{i=1}^{n}\mathbf{F}_i\mathbf{v}_i^0$$

where $\mathbf{F}_i$ works in the opposite direction to the flow. Neglecting hydrodynamic interactions between molecules and averaging $\Sigma\mathbf{F}_i\mathbf{v}_i^0$ over all the possible configurations of a molecule, we obtain the viscosity of the solution which contains N molecules per unit volume in the form

$$\eta g^2 = \eta_0 g^2 - Ng\sum_{i=0}^{n}\left\langle \mathbf{F}_i\mathbf{v}_i^0\right\rangle \tag{8.31.7}$$

Specific viscosity is

$$\frac{\eta_{sp}}{C} = -\frac{N_A}{\eta_0 Mg}\sum_{i=0}^{n}\left\langle \mathbf{F}_i\mathbf{v}_i^0\right\rangle \tag{8.31.8}$$

where N_A is Avogadro's number and M is the molecular weight of the polymer. Using Eqs. (8.27.2), (8.31.5) and (8.31.6), the vector inner product on the right-hand side of Eq. (8.31.8) may be rewritten as

$$\left\langle \mathbf{F}_i \mathbf{v}_i^{\mathbf{0}} \right\rangle = -\frac{\zeta g\left\langle x_i x_i \right\rangle}{2} - \zeta \sum_{j=0}^{n}{}' \left\langle \left(\mathbf{T}_{ij} \mathbf{F}_j \right)_y x_i \right\rangle \tag{8.31.9}$$

Kirkwood and Riseman introduced an approximation on the Oseen tensor, the so-called **preaverage assumption**, such that

$$\left\langle \left(\mathbf{T}_{ij} \mathbf{F}_j \right)_y x_i \right\rangle = \left\langle \left(\left\langle \mathbf{T}_{ij} \right\rangle \mathbf{F}_j \right)_y x_i \right\rangle \tag{8.31.10}$$

When the radial distribution function of the segments in the polymer is assumed to be Gaussian and the number of segments is sufficiently large, $<\mathbf{T}_{ij}>$ and $<x_i x_j>$ are readily calculated in the form

$$\left\langle \mathbf{T}_{ij} \right\rangle = \frac{I}{\left(6\pi^3\right)^{1/2} \left| i - j \right|^{1/2} a' \eta_0} \tag{8.31.11}$$

and

$$\left\langle x_i x_i \right\rangle = \left(\frac{a'^2}{9n} \right) \left[3i^2 - 3ni + n^2 \right] \tag{8.31.12}$$

where a' is the bond length (See Note). If we assume that $\mathbf{F}_j$ is a function with the same form as $\mathbf{F}_i$ and the summation Σ' in Eq. (8.31.9) can be converted to a definite integral, then Eq. (8.31.9) becomes the **second kind of Fredholm integral equation**. Here we define a function $\phi(x,x)$ as

$$\phi(x,x) = -\left(\frac{18}{n a'^2 \zeta} \right) \left\langle \mathbf{F}_i \mathbf{v}_i^{\mathbf{0}} \right\rangle \tag{8.31.13}$$

Then Eq. (8.31.9) is reduced to (See Note)

$$\phi(x,x) = f(x,x) - \lambda \int_{-1}^{1} \frac{\phi(x,t)}{\left| x - t \right|^{1/2}} dt \tag{8.31.14}$$

where

$$x = \frac{2i}{n} - 1 \tag{8.31.15}$$

$$f(x,x) = \frac{3x^2 + 1}{4} \qquad (8.31.16)$$

and

$$\lambda = \frac{\zeta n^{1/2}}{\left(6\pi^3\right)^{1/2} \eta_0 a'} \qquad (8.31.17)$$

Using the function $\phi(x,x)$, the limiting viscosity number $[\eta]$ may be written in the form

$$[\eta] = \left(\frac{N_A \zeta a'^2}{36\eta_0 m}\right) n F(\lambda) \qquad (8.31.18)$$

$$F(\lambda) = \int_{-1}^{1} \phi(x;\lambda) dx \qquad (8.31.19)$$

where m is the molecular weight of a segment. The integral equation (8.31.14) is solved with the aid of the Fourier expansion. Fourier series of the functions ϕ and f are

$$\phi(x,x) = \sum_{-\infty}^{\infty} \phi_k e^{i\pi kx} \qquad (8.31.20)$$

and

$$f(x,x) = \sum_{-\infty}^{\infty} f_k e^{i\pi kx} \qquad (8.31.21)$$

Eq. (8.31.14) leads to a set of linear equations for the Fourier coefficients ϕ_k and f_k such as

$$\phi_k + \lambda \sum \alpha_{ks} \phi_s = f_k \qquad (8.31.22)$$

$$\left(k=0,\pm1,\pm2,\right)$$

where

$$\alpha_{ks} = \frac{1}{2}\int \frac{\exp\left\{i\pi\left(st-kx\right)\right\}}{\left|x-t\right|^{1/2}}dxdt \tag{8.31.23}$$

The matrix component α_{ks} is given by

$$\alpha_{00} = \frac{8\cdot 2^{1/2}}{3}$$

$$\alpha_{k0} = \left(-1\right)^{k+1}4\pi^{1/2}\frac{S\left(2\pi\left|k\right|\right)}{\left(2\pi\left|k\right|\right)^{3/2}}$$

$$\alpha_{kk} = 4\pi^{1/2}\left[\frac{C\left(2\pi\left|k\right|\right)}{\left(2\pi\left|k\right|\right)^{3/2}} + \frac{S\left(2\pi\left|k\right|\right)}{2\left(2\pi\left|k\right|\right)^{3/2}}\right]$$

$$\alpha_{ks} = \frac{2\left(-1\right)^{s-k}}{\pi^{1/2}\left(s-k\right)}\left[\frac{kS\left(2\pi\left|k\right|\right)}{\left|k\right|\left(2\pi\left|k\right|\right)^{1/2}} - \frac{sS\left(2\pi\left|s\right|\right)}{\left|s\right|2\left(2\pi\left|s\right|\right)^{1/2}}\right] \tag{8.31.24}$$

where

$$C\left(x\right) = \int_0^x \frac{\cos t}{\left(2\pi t\right)^{1/2}}dt \tag{8.31.25}$$

and

$$S\left(x\right) = \int_0^x \frac{\sin t}{\left(2\pi t\right)^{1/2}}dt \tag{8.31.26}$$

Following Kirkwood and Riseman, here we employ an approximation for α_{sk} which is valid for large k and s:

$$\alpha_{sk} = \left(2/\left|k\right|\right)^{1/2}\delta_{ks} \quad \text{for} \quad k \neq 0 \tag{8.31.27}$$

Then we readily obtain $\phi(x;\lambda)$ in the form

$$\phi(x;\lambda) = \sum_k \frac{f_k(x)\exp(i\pi kx)}{1+\lambda\left(2/|k|\right)^{1/2}} \tag{8.31.28}$$

with

$$f_k(x) = \left(\frac{3}{4\pi^2 k^2}\right)\exp(-i\pi kx) + (-1)^k\frac{3ix}{4\pi k} \tag{8.31.29}$$

Finally [η] in Eq. (8.31.18) becomes

$$[\eta] = \frac{N_A\zeta a'^2}{36\eta_0 m}nF(X) \tag{8.31.30}$$

where

$$F(X) = \frac{6}{\pi^2}\sum_k \frac{1}{k^2\left(1+X/k^{1/2}\right)} \tag{8.31.31}$$

with

$$X = n^{1/2}\lambda \tag{8.31.32}$$

Eq. (8.31.31) is the Kirkwood-Riseman function. F(X)=1 at X=0 (i.e., no hydrodynamic interaction between segments; completely free draining) and Eq. (8.31.31) reduces to, at the limit of X=0,

$$[\eta] = \frac{N_A\zeta a'^2 n}{36\eta_0 m} = \frac{N_A\zeta a'^2 n^2}{36\eta_0 M} = \frac{N_A\zeta n}{6\eta_0 M}\left\langle S^2\right\rangle_0 \;(\mathrm{at}\; X=0) \tag{8.31.31)'}$$

In deriving Eq. (8.31.31)', Eqs. (6.5.6) and (6.9.1) are used. At X=∞ (non-free draining), XF(X)=1.588 is obtained. X (or λ) is called the draining parameter (See J. G. Kirkwood and J. Riseman, *J. Chem. Phys.* **16**, 565 (1948)).

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* Eq. (8.31.11) is derived as follows.

We put $\mathbf{r}_{ij}=\mathbf{r}=(x_1,x_2,x_3)$ and $|\mathbf{r}_{ij}|=r$. Then Eq. (8.31.3) is expressed as

$$\langle T_{ij}\rangle=\frac{1}{8\pi\eta_0}\left[\left\langle\frac{1}{r}\right\rangle+\left\langle\frac{rr}{r^3}\right\rangle\right] \tag{8.31.33}$$

The second term of [ ] in the right-hand side of Eq. (8.31.33) is rewritten as

$$\left\langle\frac{rr}{r^3}\right\rangle=\left\langle\frac{1}{r^3}\begin{pmatrix} x_1^2 & & \vdots \\ & x_2^2 & \\ \vdots & & x_3^2 \end{pmatrix}\right\rangle \tag{8.31.34}$$

Using the relationship

$$\left\langle\frac{x_i x_j}{r^3}\right\rangle=\left\langle\frac{x_i^2}{r^3}\right\rangle\delta_{ij}=\frac{1}{3}\left\langle\frac{1}{r}\right\rangle \tag{8.31.35}$$

Eq. (8.31.33) is reduced to

$$\langle T_{ij}\rangle=\frac{1}{6\pi\eta_0}\left\langle\frac{1}{r}\right\rangle \tag{8.31.36}$$

Now we assume the Gaussian distribution $f(\mathbf{r}_{ij})[\equiv f(\mathbf{r})]$ for the distribution of bonds between *i* th bond and *j* th bond, as

$$f(r)=\left(\frac{3}{2\pi|i-j|a'^2}\right)^{3/2}\exp\left(-\frac{3r^2}{2|i-j|a'^2}\right) \tag{8.31.37}$$

Then

$$\left\langle\frac{1}{r}\right\rangle=\int_0^\infty\left(\frac{1}{r}\right)f(r)\,dr \tag{8.31.38}$$

Since 1/r does not depend on θ and ϕ of the polar coordinate,

$$\begin{aligned}\left\langle\frac{1}{r}\right\rangle&=\int_0^\infty\left(\frac{1}{r}\right)f(r)4\pi r^2\,dr\\ &=4\pi\left(\frac{3}{2\pi|i-j|a'^2}\right)^{3/2}\int_0^\infty r\exp\left(-\frac{3r^2}{2\pi|i-j|a'^2}\right)dr\\ &=-2\sqrt{\frac{b}{\pi}}\exp\left(-br^2\right)\Big|_0^\infty\\ &=\left(\frac{6}{\pi|i-j|}\right)^{1/2}a'^{-1} \qquad\qquad b\equiv\frac{3}{2|i-j|a'^2}\end{aligned} \tag{8.31.39}$$

Thus we have Eq. (8.31.11).

* Eq. (8.31.12) is derived as follows.
For isotropic systems, we have

$$\langle x_i x_i \rangle = \frac{1}{3} \langle r_i r_i \rangle \tag{8.31.40}$$

Let's change the origin to the first bond and denote the vector connecting the origin and the center of gravity as $\mathbf{r}_G$. The position vector of *i* th bond $\mathbf{r}_i'$ is related with $\mathbf{r}_i$ as $\mathbf{r}_i = \mathbf{r}_i' - \mathbf{r}_G$.
From the definition

$$r_G = \frac{\sum r'_j}{n} \tag{8.31.41}$$

we have

$$r_i = r'_i - \frac{\sum r'_j}{n} \tag{8.31.42}$$

and

$$\langle r_i \cdot r_i \rangle = \langle r_i'^2 \rangle - 2 \left\langle \frac{r'_j \left(\sum r'_j \right)}{n} \right\rangle + \left\langle \frac{\left(\sum r'_j \right)^2}{n^2} \right\rangle \tag{8.31.43}$$

Then we denote the position vector of *k* th bond when the first bond is put at the origin as $\mathbf{a}_k'$ and the absolute value of $\mathbf{a}_k'$ as a'. We have

$$\left\langle r'_i \cdot \left(\sum r'_j \right) \right\rangle = \left\langle \left(\sum^{i} a'_k \right) \cdot \left(\sum_j \left(\sum_{m=1}^{j} a'_m \right) \right) \right\rangle \tag{8.31.44}$$

Using the relationship

$$\langle a'_k \cdot a'_m \rangle = \delta_{km} a'^2 \tag{8.31.45}$$

we have

$$\begin{aligned} \left\langle r'_i \cdot \left(\sum_i^n r'_j \right) \right\rangle &= \sum_{k=1}^{i} k a'^2 + (n-i)\, i a'^2 = \frac{i(i+1)}{2} a'^2 + (n-i)\, i a'^2 \\ &= \frac{1}{2} \left[-i^2 + (2n+1)\, i \right] a'^2 \end{aligned} \tag{8.31.46}$$

and

$$\left\langle \sum_{j=1}^{n} \left(r_i' \cdot \sum_{j=1}^{n} r_j' \right) \right\rangle = \sum_{i=1}^{n} \frac{1}{2}\left[-i^2+(2n+1)\,i \right] a'^2 \tag{8.31.47}$$

The sum of the arithmetical progression is calculated as

$$\sum_{i=1}^{n} i^2 = \frac{n(n+1)(2n+1)}{6} \tag{8.31.48}$$

Eqs. (8.31.46) and (8.31.47) are reduced to

$$\left\langle \left(\sum r_j \right)^2 \right\rangle = \left[-\frac{n(n+1)(2n+1)}{12} + \frac{n(n+1)(2n+1)}{4} \right] a'^2 \tag{8.31.49}$$

and

$$\left\langle r_i'^2 \right\rangle = i a'^2 \tag{8.31.50}$$

respectively. Substitution of Eqs. (8.31.46), (8.31.47), (8.31.49) and (8.31.50) in Eq. (8.31.43) yields

$$\begin{aligned} \left\langle r_i \cdot r_i \right\rangle &= a'^2 \left[i - \frac{-i^2+(2n+1)\,i}{n} + \frac{2n(n+1)(2n+1)}{12n^2} \right] \\ &= a'^2 \left[\frac{i^2 - i - ni}{n} + \frac{(n+1)(2n+1)}{6n} \right] \\ &= \frac{a'^2}{3n}\left[3i^2 - 3i - 3ni + \frac{1}{2}\left(2n^2+3n+1 \right) \right] \end{aligned} \tag{8.31.51}$$

When n is sufficiently large and the higher order terms of n can be neglected, Eq. (8.31.51) is reduced to

$$\left\langle r_i \cdot r_i \right\rangle = \frac{a'^2}{3n}\left[3i^2 - 3ni + n^2 \right] \tag{8.31.52}$$

Then we have

$$\left\langle x_i x_i \right\rangle = \frac{a'^2}{9n}\left[3i^2 - 3ni + n^2 \right] \tag{8.31.12}$$

* Eq. (8.31.14) is derived as follows.
Substitution of Eq. (8.31.11) in Eq. (8.31.9) yields

$$\left\langle F_i v_i^0 \right\rangle = -\frac{\zeta g}{2}\left\langle x_i x_i \right\rangle - \frac{\zeta}{\left(6\pi^3\right)^{1/2} a'\eta_0} \sum \frac{1}{|i-j|^{1/2}} \left\langle F_{jy} \cdot x_i \right\rangle \tag{8.31.53}$$

From Eq. (8.27.2),

$$\left\langle F_i v_i^0 \right\rangle = \left\langle F_{iy} \cdot g x_i \right\rangle \tag{8.31.54}$$

From the definition

$$\varphi_{ij} = \frac{18}{na'^2 \zeta g}\left\langle F_{iy} \cdot x_j \right\rangle \tag*{(8.31.13)'}$$

Eq. (8.31.53) is rewritten as

$$\varphi_{ii} = \frac{9}{na'^2}\left\langle x_i x_i \right\rangle + \frac{\zeta}{\left(6\pi^3\right)^{1/2} a'\eta_0} \sum_j \frac{\varphi_{ji}}{|i-j|^{1/2}} \tag{8.31.55}$$

Substitution of Eq. (8.31.12) in Eq. (8.31.55) yields

$$\varphi_{ii} = \frac{1}{n^2}\left(3\, i^2 - 3\, ni + n^2\right) + \frac{\zeta}{n\left(6\pi^3\right)^{1/2} a'\eta_0} \sum_j \frac{\varphi_{ji}}{|i-j|^{1/2}} \tag{8.31.56}$$

Now we rewrite Eq. (8.31.56) by putting

$$\varphi_{j,i} = \varphi(x, y) \tag{8.31.57}$$

$$x = \frac{2\,i}{n} - 1 \quad (-1<x<1) \tag{8.31.58}$$

$$t = \frac{2\,j}{n} - 1 \quad (-1<t<1) \tag{8.31.59}$$

$$x = \frac{\zeta\, n^{1/2}}{\left(6\pi^3\right)^{1/2} \eta_0\, a'} \tag{8.31.60}$$

If n is sufficiently large, the sum of the second term in the right-hand side of Eq. (8.31.56) is replaced by integration. The first term in the right-hand side of Eq. (8.31.56) is calculated as

$$f(x) = \frac{3\, x^2 + 1}{4} \tag{8.31.61}$$

Substitution of Eqs. (8.31.57)-(8.31.61) in Eq. (8.31.56) yields Eq. (8.31.14).

* An attempt to take into account the draining effect on the surface of the segments was made by Edwards and Oliver in the course of the derivation of the sedimentation coefficient. The problems involved in the preaveraging the Oseen tensor are reviewed by Yamakawa (See H. Yamakawa, *Modern Theory of Polymer Solutions*, Harper & Row, 1971). An improvement on

Table 8-31.1 Comparison of the Debye-Buche (BD), Kirkwood-Riseman (KR) and Kurata-Yamakawa (KY) theories

Model	Deriving Method	Theoretical Expression for [η]
Chain segment disperses in sphere of hydrodynamic diameter R_g; solvent molecule can pass through the sphere	Rigorous solution	$[\eta]=\left(\frac{4}{3}\right)\pi R_g^3\phi(x)/M$ $\phi(x)=\frac{0.025[1+(3/x^3)-(3/x)\coth x]}{1+(10/x^2)[1+(3/x^3)-(3/x)\coth x]}$
Pearl necklace model (link length a') hydrodynamic interaction between pearls is considered using Oseen's method	Approximate solution	$[\eta]=\frac{\zeta N_A a'^2 n F_0(x)}{36\eta_0 m}$ $F_0(x)=\left(\frac{6}{\pi}\right)\sum\frac{1}{k^2(1+X/k^{1/2})}$ $X=\frac{\zeta n^{1/2}}{(6\pi^3)\eta_0 a'}$
Pearl necklace model, based on the KR theory; excluded volume effect is taken into account	Approximate solution	$F(X)=F_0[1+p(X)z-\cdots]$, where p is a function of X X; draining effect parameter $=\zeta n^{1/2}/\left\{(6\pi^3)^{1/2}a'\eta_0\right\}$ ζ; friction coefficient per segment, a'; the length of a link, η_0; viscosity coefficient of solvent and n; number of segment

(See K.Kamide and M. Saito, in *Determination of molecular weight* Ed. A. R. Cooper, Wiley-Interscience, New York, 1989, Chap. 8, p150)

Table 8-31.2 Comparison of the Debye-Buche (DB), Kirkwood-Riseman (KR) and Kurata-Yamakawa (KY) theories. X is the draining effect parameter defined by $\zeta n^{1/2}/\{(6\pi^3)^{1/2}a'\eta_0\}$, where ζ denotes the friction coefficient per a segment and a' the length of a link. (K. Kamide and M. Saito, in *Determination of Molecular Weight*, Ed. A.R.Cooper, Wiley-Interscience, New York, (1989), Chap. 8, p152)

	Debye-Büche		Kirwood-Riseman			Kurata-Yamakawa		
x	$\phi(x)$	a	X	$XF_0(X)$	a	X	$XF_0(X)$	a
0	0.000	1.000	0	0.000	1.000	0	0.000	1.000
1	0.0947	0.973	0.1	0.092	0.963	0.1	0.073	0.963
2	0.327	0.910	0.3	0.242	0.905	0.3	0.192	0.905
3	0.600	0.839	0.5	0.358	0.862	0.5	0.284	0.862
4	0.857	0.778	1.0	0.564	0.791	1.0	0.447	0.791
5	1.07	0.731	1.5	0.700	0.746	2.0	0.634	0.715
6	1.25	0.693	2.5	0.875	0.691	3.0	0.742	0.674
7	1.40	0.664	3.5	0.984	0.66	4.0	0.812	0.647
8	1.52	0.642	4.0	1.024	0.647	5.0	0.864	0.632
9	1.62	0.625	5.0	1.090	0.632	10.0	0.999	0.583
10	1.72	0.611	10	1.260	0.583	20.0	1.110	0.552
20	2.10	0.549	50	1.486	0.524	50.0	1.178	0.524
∞	2.50	0.500	∞	1.588	0.500	∞	1.259	0.500

the solution of Eq. (8.31.14) was carried out by Kirkwood , Zwanzig, and Plock (See A. Ishihara, *Adv. Polym. Sci.* **5**, 531 (1968); K. Kamide and M. Saito, *Determination of Molecular Weight*, Ed. A.R.Cooper, Wiley-Interscience, New York, 1989, Chap. 8).

*Kurata and Yamakawa improved Kirkwood-Riseman theory, in which Gaussian chain was assumed for polymer chain without the excluded volume effect, taking into consideration the segment distribution of polymer chain with the excluded volume effect. They obtained the equation

$$[\eta]=\pi^{3/2}N_A[XF(X)]X_{\to\infty}(nb'^2/6)^{3/2}\alpha^{2.43}/M \qquad (8.31.62)$$

for n>>1 and X→∞. Eq. (8.31.62) is compared with Eq. (8.30.18). (See H. Kurata and H. Yamakawa, *J. Chem. Phys.* **29**, 311 (1958))

* Table 8-31.1 and 8-31.2 are the comparison of various theoretical models.

<<Problem 8-32>> Flory constant K (I)

Consider a solution with volume V which consists of n_2 solutes and n_1 solvents. If the solute molecules can be regarded as spheres with the volume v_e, Einstein's viscosity equation (Refer to Eq. (8.27.1)) is expressed as

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta} = 2.5\left(\frac{n_2}{V}\right)v_e \tag{8.32.1}$$

Chain molecules are coil-like in the solution and the solvent in the coil moves associated with the coil. In other words, the velocity of the solvent near the center of the polymer coil is close to the velocity of the polymer itself. Thus the polymer coil is approximated as a rigid sphere with an effective radius R_e. This sphere is called the **hydrodynamically equivalent sphere**. The volume of the sphere is

$$v_e = \left(\frac{4\pi}{3}\right)R_e^{\,3} \tag{8.32.2}$$

For flexible polymer solutions, the limiting viscosity number is semi-empirically related to the molecular weight M as

$$[\eta] = KM^{1/2}\alpha^3 \tag{6.18.1}$$

with

$$K = \Phi_0\left(\frac{\langle R^2\rangle_0}{M}\right)^{3/2} \tag{6.18.2}$$

At θ

$$[\eta] \propto M^{1/2}$$

The parameter K is often called the **Flory constant**. Derive Eq. (6.18.1) based on Eqs. (8.32.1) and (8.32.2).

Answer

The ratio n_2/V in Eq. (8.32.1) is related to the ratio of mass concentration C (g/100cc) and molecular weight M, C/M, as

$$\frac{n_2}{V} = \frac{N_A C}{100M} \tag{8.32.3}$$

Then Eq. (8.32.1) is rewritten as

$$\frac{\eta_{sp}}{C} = \frac{2.5N_A v_e}{100M} \tag{8.32.4}$$

or

$$[\eta] = \lim_{c\to 0}\frac{\eta_{sp}}{C} = \frac{2.5N_A v_e}{100M} \tag{8.32.5}$$

Substitution of Eq. (8.32.2) in Eq. (8.32.5) yields

$$[\eta] = \frac{2.5N_A}{100}\left(\frac{4\pi}{3}\right)\left(\frac{R_e{}^3}{M}\right) \tag{8.32.6}$$

The radius of the hydrodynamically equivalent sphere R_e is considered to be proportional to the radius of gyration $<S^2>^{1/2}$ as

$$R_e{}^3 = k\langle S^2\rangle^{3/2} = k\langle S^2\rangle_0{}^{3/2}\alpha^3 \tag{8.32.7}$$

where α is a swelling coefficient. From Eqs. (8.32.6) and (8.32.7), we have

$$\begin{aligned}[\eta] &= \frac{2.5N_A}{100}\left(\frac{4\pi}{3}\right)k\left(\frac{\langle S^2\rangle_0}{M}\right)^{3/2} M^{1/2}\alpha^3 \\ &= \Phi'\left(\frac{\langle S^2\rangle_0}{M}\right)^{3/2} M^{1/2}\alpha^3 \end{aligned} \tag{8.32.8}$$

where

$$\Phi' = \frac{2.5N_A}{100}\left(\frac{4\pi}{3}\right)k \tag{8.32.9}$$

If the polymer chain is approximated by a Gaussian chain, the radius of gyration is related to the mean square end-to-end distance as

$$\langle S^2\rangle_0 = \frac{1}{6}\langle R^2\rangle_0 \tag{6.9.1}$$

Then Eq. (8.32.8) is rewritten as

$$[\eta] = \Phi\left(\frac{\langle R^2\rangle_0}{M}\right)^{3/2} M^{1/2}\alpha^3 \tag{8.32.10}$$

where

$$\Phi = \frac{\Phi_0'}{6^{3/2}} \tag{8.32.11}$$

Φ is a universal constant and does not depend on the kind of polymer and solvent, and temperature. Using the definition of K in Eq. (6.18.2), (8.32.10) is rewritten into the **Flory-Fox equation** (6.18.1), in which the relationship

$$\alpha = \alpha_s = \frac{\langle S^2\rangle^{1/2}}{\langle S^2\rangle_0^{\ 1/2}} = \alpha_R = \frac{\langle R^2\rangle^{1/2}}{\langle R^2\rangle_0^{\ 1/2}} \tag{8.32.12}$$

is assumed. The radius of the hydrodynamically equivalent sphere depends on the excluded volume rather than the statistical extension. Thus, α of this problem
should be regarded as a physical quantity defined by

$$\alpha_\eta^{\ 3} = \frac{[\eta]}{[\eta]_\theta} \tag{8.32.13}$$

Then Eq. (6.18.1) should be written as

$$[\eta] = KM^{1/2}\alpha_\eta^{\ 3} \tag{8.32.14}$$

Eq. (8.32.14) is compared with

$$[\eta] = KM^{1/2}\alpha_s^{\ 2.43} \tag{8.32.15}$$

which was derived by Kurata and Yamakawa.
(See P.J.Flory, *J.Phys. Colloid Chem.* **53**, 197 (1949); T.G Fox, Jr., *J. Polym. Sci.* **5**, 745 (1950); M.Kurata and H.Yamakawa, *J.Chem.Phys.* **29**, 311 (1958); M.Kurata, H.Yamakawa and H.Utiyama, *Makromol. Chem.* **34**, 139 (1959))

<<Problem 8-33>> Flory constant K (II)

The coefficient K_m in **Mark-Houwink-Sakurada equation** (Eq. (8.30.19)) agrees with the **Flory constant** K in Eq. (6.18.2) for polymers in θ solvent. Discuss the meaning of determining K empirically.

Answer

If Φ_0 (i.e., $\Phi_0 \equiv \Phi$ at θ) is known, the ratio of the mean square end-to-end distance for the ideal conformation $\langle R^2 \rangle_0$ and the molecular weight M can be determined from the equation

$$K = \Phi_0 \left(\frac{\langle R^2 \rangle_0}{M} \right)^{3/2} \qquad (6.18.2)$$

This ratio is calculated statistically from Eq. (6.6.35) as

$$\frac{\langle R^2 \rangle_0}{M} = \frac{nb^2}{M} \frac{1-\cos\theta}{1+\cos\theta} \frac{1+\langle \cos\phi \rangle}{1-\langle \cos\phi \rangle} = \frac{b^2}{m_0} \frac{1-\cos\theta}{1+\cos\theta} \frac{1+\langle \cos\phi \rangle}{1-\langle \cos\phi \rangle} \qquad (8.33.2)$$

where b is the segment length, n the number of segments, m_0 the molecular weight of a segment, θ the bond angle and ϕ the rotation angle about bonds. $\langle R^2 \rangle_0$ for chain molecules with freely rotating bonds (freely rotating chains) ($\langle \cos\phi \rangle = 0$ (See Eq. (8.33.5)), $\langle R^2 \rangle_{0f}$, is given by

$$\frac{\langle R^2 \rangle_{0f}}{M} = \frac{b^2}{m_0} \frac{1-\cos\theta}{1+\cos\theta} \qquad (8.33.3)$$

The ratio of $\langle R^2 \rangle_0^{1/2}$ and $\langle R^2 \rangle_{0f}^{1/2}$ is called the **characteristic ratio** or **steric hindrance factor** σ. It depends only on the degree of rotational steric hindrance $\langle \cos\phi \rangle$. From Eqs. (8.33.2) and (8.33.3), we have

$$\sigma \equiv \frac{\langle R^2 \rangle_0^{1/2}}{\langle R^2 \rangle_{0f}^{1/2}} = \frac{1+\langle \cos\phi \rangle}{1-\langle \cos\phi \rangle} \qquad (8.33.4)$$

where

$$\langle \cos\phi \rangle = \int_0^{2\pi} \cos\phi\, e^{-V(\phi)/kT} d\phi \Big/ \int_0^{2\pi} e^{-V(\phi)/kT} d\phi \qquad (8.33.5)$$

Thus we can estimate the potential for the internal rotation V(ϕ) from σ or from K.

<<Problem 8-34>> Viscosity parameter Φ

From Eqs. (8.32.8) and (8.32.11), [η] is written as

$$[\eta] = 6^{3/2}\Phi\frac{\langle S^2\rangle^{3/2}}{M} \tag{8.34.1}$$

Coefficient Φ_0 is defined as Φ in the unperturbed state and experimentally evaluated by using the relationship

$$[\eta]_\theta = 6^{3/2}\Phi_0\frac{\langle S^2\rangle_0^{\ 3/2}}{M} \tag{8.34.2}$$

Derive the relationship between Φ and Φ_0:

$$\Phi = \Phi_0\left(\frac{\alpha_\eta}{\alpha_s}\right)^3 \tag{8.34.3}$$

Answer

From Eqs. (8.32.13) and (8.34.2),

$$[\eta] = [\eta]_\theta\alpha_\eta{}^3 = 6^{3/2}\Phi_0\frac{\langle S^2\rangle_0^{\ 3/2}}{M}\ \alpha_\eta{}^3 \tag{8.34.4}$$

α_s is defined by

$$\langle S^2\rangle^{3/2} = \alpha_s\langle S^2\rangle_0^{\ 3/2} \tag{6.14.27}$$

Substitution of Eq. (6.14.27) in Eq. (8.34.1) yields

$$[\eta] = 6^{3/2}\Phi\frac{\langle S^2\rangle_0^{\ 3/2}}{M}\ \alpha_s{}^3 \tag{8.34.5}$$

Then from Eqs. (8.34.4) and (8.34.5), we have Eq. (8.34.3).

---

* Comparing Eq. (8.32.15) with Eq. (8.32.16), we find

Table 8-34.1 Typical experimental values of Φ at or near $T=\theta$ for polystyrene in cyclohexane.

authors	θ solvent	$M_w \times 10^{-6}$/g mol	$\Phi \times 10^{-23}$/mol^{-1}
Krigbaum-Carpenter [1]	cyclohexane	3.2	1.85
McIntyre et al. [2]	cyclohexane, 35℃	4.0	1.76
Berry[3]	cyclohexane, 34.8℃	0.62-1.6	2.6-2.9
Cowie-Cussler[4]	cyclohexane, 35℃	0.21-1.0	1.7-2.1
Yamamoto et al. [5]	cyclohexane, 34.6℃	0.34-2.9	2.4-2.6
McIntyre et al.[6]	cyclohexane, 35.4℃	27-44	1.5-2.0
Einaga et al. [7]	cyclohexane, 34.5℃	8.8-57	2.2-2.4
Miyaki et al. [8]	cyclohexane, 34.5℃	6.5	2.55

[1] W.R.Krigbaum and D.K.Carpenter, *J. Phys. Chem.* **59**, 1166 (1955).

[2] D.McIntyre, A.Wilms, L.C.Williams and L.Mandelkern, *J. Phys. Chem.* **66**, 1932 (1962).

[3] G.C.Berry, *J. Chem. Phys.* **44**, 4550 (1966); **46**, 1338 (1967).

[4] J.M.G.Cowie and E.L.Cussler, *J. Chem. Phys.* **46**, 4886 (1967).

[5] A. Yamamoto, M. Fujii, G.Tanaka and H.Yamakawa, *Polym. J.* **2**, 799 (1971).

[6] D.McIntyre, L.J.Fetters and E.Slagowski, *Science* **176**, 1041 (1972).

[7] Y.Miyaki, Y.Einaga and H.Fujita, *Macromolecules* **11**, 1180 (1978); Y.Einaga, Y.Miyaki and H.Fujita, *J. Polym. Sci., Polym. Phys. Ed.* **17**, 2103 (1979).

[8] Y. Miyaki, Y. Einaga, H. Fujita and M. Fukuda, *Macromolecules* **13**, 588 (1980).

Table 8-34.2 The parameters K_m and a in the Mark-Houwink-Sakurada equation and the exponent a_Φ, for solutions of cellulose and its derivatives. (See K. Kamide and M. Saito, *Adv. Polym. Sci.* **83**, 1 (1987))

Polymer («F»)	Solvent	$\frac{K_m \times 10^2}{cm^3\,g^{-1}}$	a	a_Φ
Cellulose	Cadoxen	0.0338	0.77	0.304
	FeTNa[a]	0.0531	0.775	0.429
Cellulose acetate(2.92)	TFA[b]	3.96	0.70_6	—
	DMAc[c]	2.64	0.75	0.106
	Acetone	2.89	0.75_5	—
	TCM[d]	4.54	0.64_6	—
	DCM[e]	2.47	0.70_4	—
Cellulose acetate(2.46)	DMAc	1.34	0.82	0.23
	Acetone	0.13	0.616	0.716
	THF[f]	0.51_3	0.68_8	0.105
Cellulose acetate(1.75)	DMAc	9.58	0.65	0.12
Cellulose acetate(0.49)	Formamide	20.9	0.60	—
	Water	20.9	0.60	—
	DMSO[g]	17.1	0.61	—
	DMAc	19.1	0.60	0.103
Cellulose nitrate(2.91)	Acetone	0.76	0.903	0.379
Cellulose nitrate(2.55)	Acetone	0.48	0.916	0.274
Cellulose tricaproate	DMF[h]	0.245	0.5	0.377
	1-Cl—N[i]	0.17	0.51	0.377
Cellulose tricarbanilate	Acetone	1.43×10^{-3}	0.91	0.21
	Dioxane	8.13×10^{-4}	0.97	0.462
Methylcellulose(2.3)	Water	0.316	0.55	0.464
Hydroxyethyl cellulose(0.88)	Water	8.62×10^{-3}	0.87	0.608
Ethyl hydroxy-ethyl cellulose ($-OC_2H_4$; 0.84; $-OC_2H_5$; 0.56)	Water	0.037	0.8	0.688
Sodium cellulose xantate(0.78)	1 M NaOH	2.47	0.679	0.568
Sodium carboxy methyl cellulose(1)	NaCl ($I \rightarrow \infty$)	0.19	0.60	0.192

[a] Iron sodium tartrate; [b] trifluoroacetic acid; [c] N,N-dimethylacetamide; [d] trichloromethane; [e] dichloromethane; [f] tetrahydrofuran; [g] dimethylsulphoxide; [h] N,N-dimethylformamide; [i] 1-chloronaphthalene

$$\alpha_\eta^3 = \alpha_s^{2.43} \tag{8.34.6}$$

and

$$\Phi = \Phi_0 \alpha_s^{-0.57} \tag{8.34.7}$$

Eq. (8.34.5) indicates that Φ decreases with increasing α_s.

* Eq. (8.34.3) was derived by **Ptitsyn-Eisner** (O. B. Ptitsyn and Yu. E. Eizner, *Zh. Fiz. Khim.* **32**, 2464 (1958); O. B. Ptitsyn and Yu. E. Eizner,*Zh. Tekhn. Fiz.* **29**, 1117 (1959)) and **Kurata-Yamakawa** (M. Kurata and H. Yamakawa, *J. Chem. Phys.* **29**, 311 (1958)) independently. The theoretical value of Φ_0 is much different from the experimental values Φ=2.1~2.2 x 10^{21}. The latter values of Φ could be obtained only when we assumed α=1.5 and Φ_0=2.87 x 10^{21}. The disagreement of Φ and Φ_0 may come from (1) polydispersity of polymer, (2) solvent property (good solvent is used frequently in experiment) and (3) free draining effect $\Phi_0(X)/\Phi_0(\infty)=(\pi^{3/2}N_A/6^{3/2}\ 100)/2.87\times10^{21}\ [X\Phi(X)]=X\Phi(X)/1.588$ (Kirkwood-Riseman) (See Table 8-31.1, Eq. (8.31.31) and M. Kurata and H. Yamakawa, *J. Chem. Phys.* **29**, 311 (1958)). Typical experimental values of Φ are summarized in Table 8-34.1. The molecular weight dependence of Φ is approximated by the following empirical equation:

$$\Phi = K_\phi M^{a_\phi} \tag{8.34.8}$$

where K_ϕ and a_ϕ are parameters characteristic of the system. a_ϕ is given by $a_\phi=[\nu(X)-\varepsilon(3-n(X))]_{Av}$. It is clear that for X~0, a_ϕ is essentially zero and $a_\phi\sim\Delta$. (See <<Problem 8-40>>-<<8-44>>). Values for K_m, a and a_ϕ for cellulose and cellulose-derivative solutions are summarized in Table 8-34.2.

<<Problem 8-35>> Upper limit of the exponent in Mark-Houwink-Sakurada equation

Estimate the upper limit of the exponent a in **Mark-Houwink-Sakurada equation**

$$[\eta] = K_m M^a \tag{8.30.19}$$

from the **Flory-Fox viscosity equation**

$$[\eta] = KM^{1/2}\alpha_\eta^3 \tag{8.32.15}$$

Answer

For convenience, we approximate

$$\alpha_\eta \cong \alpha_s \qquad (8.35.1)$$

The molecular weight dependence of α_s was derived theoretically by many scientists. For example, Flory derived the equation

$$\alpha_s^5 - \alpha_s^3 = 2C_M\psi_1\left(1 - \frac{\theta}{T}\right)M^{1/2} \qquad (6.13.30)$$

Kurata and Yamakawa proposed the equation

$$\alpha_s^3 - 1 = 1.91Z \qquad (6.15.10)$$

with

$$Z = \beta n^{1/2}\left(\frac{3}{2\pi b^2}\right)^{3/2} \propto M^{1/2} \qquad (5.20.3)$$

using Fixman's equation (Eq. (6.15.1)). If

$$\alpha_s >> 1$$

we have

$$\alpha_s^5 \propto M^{1/2} \qquad \text{(Flory)} \qquad (8.35.2)$$

and

$$\alpha_s^3 \propto M^{1/2} \qquad \text{(Fixman)} \qquad (8.35.3)$$

respectively. If we define ε as

$$\alpha_s^3 \propto M^\varepsilon \qquad (8.35.4)$$

the exponent a in Eq. (8.30.19) is related to ε as

$$a = 0.5 + \varepsilon \qquad (8.35.5)$$

Thus the upper limit of a is 0.8 and 1.0 for Eqs. (8.35.2) and (8.35.3), respectively. If we use a more strict relationship

$$\alpha_\eta^3 = \alpha_s^{2.43} \qquad (8.34.7)$$

in place of Eq. (8.35.1), we have

$$\alpha_\eta{}^3 \propto M^{0.243}$$
$$\varepsilon = 0.243 \tag{8.35.6}$$

from Eq. (8.35.2) and

$$\alpha_\eta{}^3 \propto M^{0.243/6}$$
$$\varepsilon = 0.405 \tag{8.35.7}$$

from Eq. (8.35.3). Thus we find

$a = 0.743$ (Flory)

or

$a = 0.905$ (Fixman)

We note that the empirical value of a is often larger than 0.8 (See Table 8-34.2).

<<Problem 8-36>> Theoretical relations between two parameters in Mark-Houwink-Sakurada equation (I)

Derive the relationship between K_m and a in the equation

$$[\eta] = K_m M^a \tag{8.30.19}$$

using the Flory-Fox viscosity equation

$$[\eta] = KM^{1/2}\alpha^3 \tag{6.18.1}$$

and the excluded volume equation proposed by Flory

$$\alpha_s{}^5 - \alpha_s{}^3 = 2C_M\psi_1\left(1 - \frac{\theta}{T}\right)M^{1/2} \tag{6.13.30}$$

Answer

From Eqs. (8.30.19) and (6.18.1), we have

$$\alpha^3 = \left(\frac{K_m}{K}\right)M^{a-1/2} \equiv AM^\beta \tag{8.36.1}$$

Substitution of Eq. (8.36.1) for α in Eq. (6.13.30) yields

$$1+\left\{\frac{2C_M\Psi_1\left(1-\frac{\theta}{T}\right)M^{1/2-\beta}}{A}\right\}=\left(AM^{\beta}\right)^{2/3} \tag{8.36.2}$$

Taking logarithm of Eq. (8.36.2) and differentiating it with respect to logM, we have

$$\beta=\frac{1}{\left\{10/3+\left(4/3\right)\left(A/x\right)\right\}} \tag{8.36.3}$$

where

$$x=2C_M\Psi_1\left(1-\frac{\theta}{T}\right)M^{1/2-\beta} \tag{8.36.4}$$

Then Eq. (8.36.2) is rewritten as

$$1+\frac{x}{A}=A^{2/3}M^{2\beta/3} \tag{8.36.5}$$

$M^{2\beta/3}$ is only slightly dependent on M for $0<\beta<0.3$ (the upper limit in the Flory theory) and can be expanded in a series of $\Delta M=M-M_0$ as

$$M^{2\beta/3}=M_0^{2\beta/3}\left\{1+\frac{2\beta}{3}\left(\frac{\Delta M}{M}\right)+\cdots\right\}\cong M_0^{2\beta/3} \tag{8.36.6}$$

Here M_0 is a parameter determined by the mean values of M (such as M_n and M_w...) and can be approximated by $(M_1M_2)^{1/2}$ where M_1 and M_2 are the upper and lower limits of the molecular weight of polymers used for determining Eq. (8.30.19). From Eqs. (8.36.3), (8.36.5) and (8.36.6), we have

$$A^{2/3}=\left(\frac{K_m}{K}\right)^{2/3}=\frac{\left\{\left(\frac{4}{3}\right)\left(\frac{1}{\beta}-\frac{10}{3}\right)^{-1}+1\right\}}{M_0^{2\beta/3}} \tag{8.36.7}$$

or

$$-\ln K_m + \frac{2}{3}\ln\left\{\left(\frac{4}{3}\right)\left(\frac{1}{\beta} - \frac{10}{3}\right)^{-1} + 1\right\} = \beta \ln M_0 - \ln K \tag{8.36.8}$$

Comparing Eqs. (8.36.1) and (6.18.1), we have

$$\beta = a - \frac{1}{2} \tag{8.36.9}$$

Thus we find

$$\frac{K_m}{K} = \frac{\left\{\left(\frac{4}{3}\right)\left(\frac{1}{a - 0.5} - \frac{10}{3}\right)^{-1} + 1\right\}^{\frac{3}{2}}}{M_0{}^{a-0.5}} \tag{8.36.10}$$

(See T. Kawai and R. Naito, *J. Appl. Polym. Sci.* **3**, 232 (1960); T. Kawai and K. Kamide, *J. Polym. Sci.* **54**, 343 (1961))

<<Problem 8-37>> Theoretical relations between two parameters in Mark-Houwink-Sakurada equation (II)

Derive the relationship between K_m and a for

(1) Kurata-Yamakawa viscosity equation

$$[\eta] = KM^{1/2}\alpha^{2.43} \tag{8.32.15}$$

and Kurata-Yamakawa-Roig excluded volume equation

$$\alpha^3 - \alpha = \left(1 + \frac{\alpha^{-2}}{3}\right)^{-3/2} C'Z \tag{6.17.11}$$

(2)Flory-Fox viscosity equation

$$[\eta] = KM^{1/2}\alpha^3 \tag{6.18.1}$$

and Kurata-Yamakawa-Roig excluded volume equation [Eq. (6.17.11)]

(3) Flory-Fox viscosity equation (Eq. (6.18.1)) and Fixman excluded volume equation

$$\alpha^3 - 1 = 2Z \tag{6.15.1}$$

Answer

(1) Eq. (6.17.11) is rewritten as

$$\alpha^3 - \alpha = C''M^{1/2} \tag{8.37.1}$$

where C'' is a parameter which is roughly independent of molecular weight; for $\alpha > 1.5$, the error is less than 20%. From Mark-Houwink-Sakurada equation

$$[\eta] = K_m M^a \tag{8.30.19}$$

and Eq. (8.32.15), we have

$$\alpha^{2.43} = AM^{\beta} \tag{8.37.2}$$

and then

$$\alpha^3 = A^{3/2.43}M^{3\beta/2.43} \tag{8.37.3}$$

From Eqs. (8.37.1) and (8.37.3), we have

$$A^{2/2.43}M^{2\beta/2.43} = 1 + A^{-1/2.43}C''M^{1/2-\beta/2.43} \tag{8.37.4}$$

Differentiating the logarithm of Eq. (8.37.4) with respect to logM yields

$$\beta = \left\{ \frac{6}{2.43} + \frac{4}{2.43}\left(\frac{A^{1/2.43}}{x} \right) \right\}^{-1} \tag{8.37.5}$$

with

$$x = C''M^{\left(1/2 - \beta/2.43\right)} \tag{8.37.6}$$

From Eqs. (8.37.4) and (8.37.6), we have

$$1 + \frac{x}{A^{1/2.43}} = A^{2/3}M^{2\beta/2.43} \tag{8.37.7}$$

If we use the approximation

$$M^{2\beta/2.43} \cong M_0^{\;2\beta/2.43} \tag{8.37.8}$$

we find

$$\left(\frac{K_m}{K}\right)^{2/2.43} = \frac{\left\{1+\left(\frac{4}{2.43}\right)\left(\frac{1}{a-0.5}-\frac{10}{3}\right)^{-1}\right\}}{M_0^{2(a-0.5)/2.43}} \tag{8.37.9}$$

where M_0 is defined by $(M_1M_2)^{1/2}$, M_1 and M_2 are the upper and lower limit of the molecular weights used in the experiment (See K. Kamide and M. Saito, *Determination of Molecular Weight*, Ed. A.R.Cooper, John Wiley-Interscience, New York, 1989, Chap. 8).

(2): Similarly we find

$$\left(\frac{K_m}{K}\right)^{2/3} = \frac{\left\{1+\left(\frac{4}{3}\right)\left(\frac{1}{a-0.5}-2\right)^{-1}\right\}}{M_0^{2\beta/3}} \tag{8.37.10}$$

(3):Similarly we find

$$-\ln K_m + \ln\left\{1+2\left(\frac{1}{a-0.5}-2\right)^{-1}\right\} = -\ln K + (a-0.5)\ln M_0 \tag{8.37.11}$$

(See K.Kamide and T.Kawai, *Kobunshi Kagaku (Chem. High Polymers)* **20**, 512 (1963); K.Kamide and W.R.Moore, *Kobunshi Kagaku (Chem. High Polymers)* **21**, 682 (1964))

<<Problem 8-38>> Flory-Fox-Schaefgen equation

Flory-Fox-Schaefgen proposed the equation

$$\frac{[\eta]^{2/3}}{M^{1/3}} = K^{2/3} + 2C_M\psi_1\left(1-\frac{\theta}{T}\right)K^{5/3}\frac{M}{[\eta]} \tag{8.38.1}$$

for estimating the Flory constant K from $[\eta]$ of polymers in a good solvent: $K^{2/3}$ can be determined from the intercept in the plot of $[\eta]^{2/3}/M^{1/3}$ vs. $M/[\eta]$. (See P.J.Flory and T.G.Fox, *J. Am. Chem. Soc.* **73**, 190 (1951)) Derive Eq. (8.38.1).

Answer

According to the Flory-Fox theory, molecular weight dependence of $[\eta]$ is expressed as

$$[\eta] = KM^{1/2}\alpha^3 \tag{6.18.1}$$

where

$$K = \Phi_0\left(\frac{\langle R^2\rangle_0}{M}\right)^{3/2} \tag{6.18.2}$$

Here α is the expansion factor which is related to M as

$$\alpha^5 - \alpha^3 = 2C_M\psi_1\left(1 - \frac{\theta}{T}\right)M^{1/2} \tag{6.13.30}$$

where

$$C_M = \frac{27}{2^{5/2}\pi^{3/2}}\left(\frac{\bar{v}^2}{N_A V_0}\right)\left(\frac{\langle R^2\rangle_0}{M}\right)^{-3/2} \tag{6.13.26}$$

Here $\bar{v}$ is the partial specific volume of the polymer and V_0 is the molar volume of the solvent. Eq. (6.18.1) is rewritten as

$$\begin{aligned} \alpha^3 &= [\eta]/KM^{1/2} \\ \alpha^5 &= [\eta]^{5/3}/K^{5/3}M^{5/6} \end{aligned} \tag{8.38.2}$$

Substitution of Eq. (8.38.2) in Eq. (6.13.30) yields

$$\alpha^5 - \alpha^3 = \frac{[\eta]^{5/3}}{K^{5/3}M^{5/6}} - \frac{[\eta]}{KM^{1/2}} = 2C_M\psi_1\left(1 - \frac{\theta}{T}\right)M^{1/2} \tag{8.38.3}$$

From Eq. (8.38.3), we finally obtain

$$\frac{[\eta]^{5/3}}{M^{5/6}} = \frac{[\eta]}{M^{1/2}}K^{2/3} + 2C_M\psi_1\left(1 - \frac{\theta}{T}\right)K^{5/3}M^{1/2} \tag{8.38.4}$$

Eq. (8.38.4) is readily converted to Eq. (8.38.1).

<<Problem 8-39>> Flory constant K (III)

Summarize the equations for various models for determining Flory constant K.

Answer

Table 8-39 collects the methods for determining K.

<<Problem 8-40>> Evaluation of parameters in Mark-Houwink-Sakurada equation by Kurata-Yamakawa theory

According to Kurata-Yamakawa theory (See M. Kurata and H. Yamakawa, *J. Chem. Phys.* **29**, 311 (1958)), limiting viscosity number $[\eta]$ is given by

$$[\eta] \fallingdotseq \Phi_0(X_0)\alpha_s^{\{-3-n(X)\}}\frac{XF(X)}{X_0F_0(\infty)}\left(\frac{\langle R^2\rangle_0}{M}\right)^{3/2} M^{1/2}\alpha_s^{\ 3} \tag{8.40.1}$$

with

$$\Phi_0(X) = 2.283\cdot 10^{21} XF_0(X) \tag{8.40.2}$$

$$X = \left(\frac{1}{2}\right)\left(\frac{6}{\pi}\right)^{1/2}\left(\frac{b}{a'}\right)n^{1/2} = k_X M^{1/2} \tag{8.40.3}$$

$$\alpha_s = \frac{\langle S^2\rangle^{1/2}}{\langle S^2\rangle_0^{\ 1/2}} \tag{6.12.52}$$

Here, n(X) and F(X) are functions of **draining parameter** X. a' and b are the length and the diameter of the crosssection of a segment, respectively. Eq. (8.40.3) is obtained by rewriting Eq. (8.31.32). X_0 is defined as X which satisfies the equation

$$\nu(X_0) = \varepsilon\{3-n(X_0)\} \tag{8.40.4}$$

with

$$\varepsilon = d\ln\alpha_s/d\ln M \cong \alpha \tag{8.40.5}$$

Derive the expression for the exponent *a* in Mark-Houwink-Sakurada equation

Table 8-39 Methods for determining Flory constant K using experimental data of $[\eta]$ and M

Scientist (year)	Equation
Flory-Fox-Schaefgen[1]	$[\eta]^{2/3}M^{-1/3}=K^{2/3}+K^{5/3}C_MM[\eta]^{-1}$
Kawai-Kamide[2]	$K_m/K=\{4/3[1/(a-0.5)-10/3]^{-1}+1\}^{3/2}/M_0^{(a-0.5)}$
Kurata-Stockmayer[3]	$[\eta]^{2/3}M^{-1/3}=K^{2/3}+0.363\ \Phi_0B[g(\alpha_\eta)M^{2/3}[\eta]^{-1/3}$ $;\ g(\alpha_\eta)=g\ \alpha_\eta^{\ 3}(3\ \alpha_\eta^{\ 2}+1)^{-3/2}$
Burchand[4],Stockmayer-Fixman[5]	$[\eta]=KM^{1/2}+0.5\ \Phi_0BM;\ \alpha_\eta<1.5$
Bodanecky[6]	$[\eta]/M^{1/2}=0.80K+0.65Kk^{0.7}M^{0.35};\ Z=kM^{1/2}$
Inagaki-Suzuki-Kurata[7]	$([\eta]/M^{1/2})^{4/5}=0.786K^{4/5}+0.950K^{4/5}k^{2/3}M^{1/3};\ \alpha>1.4$
Cowie[8]	$[\eta]/M^{1/2}=(\Phi(\varepsilon)/\Phi_0)K+0.9166(\Phi(\varepsilon)/\Phi_0)Kk^{7/10}M^{7/20}$ $\Phi(\varepsilon)=\Phi_0(1-2.63\ \varepsilon+3.86\ \varepsilon^2),a=(1+3\ \varepsilon)/2$ $\alpha=1.2\sim2.5$
Kamide-Moore[9]	$-\log K_m+\log[1+2\{(a-1/3)^{-1}-2\}^{-1}]=\log K+(a-1/2)\log M_0$
Kamide-Miyazaki[10]	$[\eta]/M^{1/2+a_\Phi+3a_2/2}=6^{3/2}K_\Phi K_0^{3/2}+0.66K_\Phi BM^{(1-3\ a_2)/2}$
Kamide-Saito[11]	$\log K_m+\log(1-3\ a_2/2(1-a+a_\Phi)+(3/2)\log 6+K_\Phi$ $=-(3/2)\log K_0+(a-1/2-a_\Phi-3a_2/2)\log M_0$

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1) P.J.Flory, T.G Fox, Jr., *J. Am. Chem. Soc.* **73**, 1904 (1951). 2) T.Kawai and K. Kamide, *J. Polym. Sci.* **54**, 343 (1961). 3) M. Kurata and W.H.Stockmayer, *Adv. Polym. Sci.* **3**, 196 (1963). 4) W.Burchard, *Makromol. Chem.* **50**, 20 (1961). 5) W.H.Stockmayer and M.Fixman, *J. Polym. Sci. C* **1**, 137 (1963). 6) M.Bodanecky, *J. Polym. Sci. B* **3**, 201 (1965). 7) H. Inagaki, H. Suzuki and M. Kurata, *J. Polym. Sci. C* **15**, 409 (1966). 8) J.M.G.Cowie, *Polymer* **7**, 487 (1966), 9) K. Kamide and W.R.Moore, *J.Polym.Sci. B* **2**, 809 (1964). 10) K.Kamide and Y.Miyazaki, *Polym. J.* **10**, 409 (1978). 11) K. Kamide and M. Saito, *Eur. Polym. J.* **17**, 1049 (1981).

$$[\eta] = K_m M^{a} \tag{8.30.19}$$

using Eq. (8.40.1).

Answer

From Eq. (8.30.19),

$$a = \frac{d \ln[\eta]}{d \ln M} \tag{8.40.6}$$

Using Eq. (8.40.1), the differentiation is performed as

$$a = \frac{d \ln\Phi_0}{d \ln M} + \left\{-3 - n\left(X_0\right)\right\}\frac{d \ln\alpha_s}{d \ln M} + d \ln\left(\frac{XF(X)}{X_0F_0(\infty)}\right)/d \ln M$$
$$+ 1.5 d \ln\left(\frac{\left\langle R^2\right\rangle_0}{M}\right)/d \ln M + 0.5 + 3\frac{d \ln\alpha_s}{d \ln M} \tag{8.40.7}$$

If we define

$$\nu(X) = \frac{1}{2}\left(\frac{dXF_0(X)}{d \ln X}\right) = \frac{d \ln XF_0(X)}{d \ln M} \tag{8.40.8}$$

$$a_2 = \frac{d \ln\left(\frac{\left\langle R^2\right\rangle_0}{M}\right)}{d \ln M} \tag{8.40.9}$$

Eq. (8.40.7) is rewritten as

$$\begin{aligned} a &= \varepsilon\left\{-3 - n\left(X_0\right)\right\} + \nu\left(X_0\right) + \nu(X) - \nu\left(X_0\right) + 1.5a_2 + 0.5 + 3\varepsilon \\ &= 0.5 + \Delta + a_1 + 1.5a_2 \\ &= 0.5 + \nu(X) + n(X)\varepsilon + 1.5a_2 \end{aligned} \tag{8.40.10}$$

with

$$\Delta = \nu(X) - \nu\left(X_0\right) \tag{8.40.11}$$

$$a_1 = 3\varepsilon \tag{8.40.12}$$

Thus Δ and a_1 express the contribution of the free draining and the excluded volume to a, respectively.

<<Problem 8-41>> Molecular weight dependence of sedimentation coefficient (I)

Sedimentation coefficient of polymer solutions s_0 is related to the molecular weight of the polymer M as

$$s_0 = K_s M^{a_s} \tag{8.41.1}$$

Relate the exponent a_s in Eq. (8.41.1) to a in the equation

$$[\eta] = K_m M^{a} \tag{8.30.19}$$

and the degree of free draining.

Answer

s is expressed as

$$s = \frac{M(1 - \bar{v}\rho)}{\xi} = M(1 - \bar{v}\rho)6^{-1/2}P^{-1}\left(\frac{\langle S^2\rangle_0}{M}\right)^{-1/2} M^{1/2}\alpha_s^{-1} \tag{8.41.2}$$

with

$$P = P_0(X)\alpha_s^{-\{1-m(X)\}} \tag{8.41.3}$$

$$X = \left(\frac{1}{2}\right)\left(\frac{6}{\pi}\right)^{1/2}\left(\frac{b}{a'}\right)n^{1/2} \tag{8.40.3}$$

$$\alpha_s = \frac{\langle S^2\rangle^{1/2}}{\langle S^2\rangle_0^{1/2}} \cong \frac{\langle R^2\rangle^{1/2}}{\langle R^2\rangle_0^{1/2}} \tag{8.41.4}$$

where $\bar{v}$ is the partial specific volume and ρ the density. From the above equations, we have

$$a_s = \frac{d\,\ln s}{d\,\ln M} = 1 - \frac{d\,\ln P}{d\,\ln M} - \frac{1}{2}d\,\ln\left(\frac{\langle S^2\rangle_0}{M}\right)/d\,\ln M + 0.5 - \frac{d\,\ln\alpha_s}{d\,\ln M} \tag{8.41.5}$$

$$\varepsilon \equiv \frac{d\ \ln\alpha_s}{d\ \ln M} \tag{8.41.6}$$

and

$$a_4 \equiv \frac{d\ln P}{d\ln M} = \frac{d\ln P_0(X)}{d\ln M} - \{1 - m(X)\}\varepsilon = \mu(X) - \{1 - m(X)\}\varepsilon \tag{8.41.7}$$

Putting

$$a_2 \equiv \frac{d\ln\left(\frac{\langle S^2\rangle_0}{M}\right)}{d\ln M} \tag{8.41.8}$$

and substituting Eqs. (8.41.6)-(8.41.8) in Eq. (8.41.5), we have

$$a_s = a - a_4 - 0.5a_2 - \varepsilon \tag{8.41.9}$$

From <<Problem 8-40>>

$$a = 0.5 + \nu(X) + 1.5a_2 + n(X)\varepsilon \tag{8.40.11}$$

From Eqs. (8.41.9) and (8.40.11),

$$3a_s + a - 2.0 = \Delta - 3a_4 = \nu(X) - 3a_4 - \{3 - n(X)\}\varepsilon \tag{8.41.10}$$

and then from Eq. (8.41.7),

$$3a_s + a - 2.0 = \nu(X) - 3\mu(X) + \{n(X) - 3m(X)\}\varepsilon \tag{8.41.11}$$

(See K.Kamide, *Makromol. Chem.* **128**, 197 (1969))

<<Problem 8-42>> Molecular weight dependence of sedimentation coefficient (II)

The coefficients a_s and a were experimentally determined as 0.29 and 1.01, respectively, for the system cellulose trinitrate in ethylacetate and 0.285 and 1.00, respectively, for the system cellulose trinitrate in acetone. Calculate X, ν(X) and ε from these data.

Answer

X_0 and ε are determined from the equation

$$\nu(X_0) = \varepsilon\{3 - n(X_0)\} \tag{8.40.5}$$

Then $\nu(X)$ can be calculated by substituting X_0 and ε thus obtained in Eq. (8.41.11). For the system cellulose trinitrate in ethylacetate $X=0.725$, $\nu(X)=0.326$, $X_0=18$ and $\varepsilon=0.271$ and for the system cellulose trinitrate in acetone $X=0.66$, $\nu(X)=0.335$, $X_0=22$ and $\varepsilon=0.286$.

<<Problem 8-43>> Molecular weight dependence of diffusion coefficient (I)

Diffusion coefficient D_0 depends experimentally on molecular weight M as

$$D_0 = K_\beta M^{-\beta} \tag{8.43.1}$$

According to Kurata-Yamakawa theory, the exponent β in Eq. (8.43.1) is given by

$$\beta = \mu(X) + m(X)\varepsilon + 0.5a_2 + 0.5 \tag{8.43.2}$$

Relate the exponent β in Eq. (8.43.2) to a in

$$[\eta] = K_m M^a \tag{8.30.19}$$

and the free draining effect.

Answer

From <<Problem 8-40>>,

$$a = 0.5 \pm \nu(X) + 1.5a_2 + n(X)\varepsilon \tag{8.40.11}$$

Combining Eqs. (8.43.2) and (8.40.11), we have

$$a - 3\beta + 1 = \nu(X) - 3\mu(X) + \{n(X)\text{-}3m(X)\}\varepsilon \tag{8.43.3}$$

Then we can calculate X from β and a.

<<Problem 8-44>> Molecular weight dependence of diffusion coefficient (II)

Mayerhoff determined β and a for cellulose trinitrate (N=13.8%) in acetone as 0.675 and 1.00, respectively. Calculate X, $\nu(X)$ and ε for this system.

Answer

On the assumption of Gaussian distribution of the molecular chain, $a_2=0$. Using Eq. (8.40.11), we have

$$X = 1.13,\ \nu(X) = 0.278,\ \varepsilon = 0.113$$

Substitution of these values in the equation

$$\nu(X_0) = \varepsilon\left\{3 - n(X_0)\right\} \tag{8.40.5}$$

yields $X_0=12$.

<<Problem 8-45>> Two-dimensional steady shear flow of solution of dumbbell-like molecule (V)

The diffusion equation for dumbbell-like molecules of Eqs. (8.16.7)-(8.16.9) in <<Problem 8-16>> is rewritten in the steady state ($\partial f/\partial t=0$) as

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 f}{\partial\phi^2}$$
$$=\frac{g}{D}\left\{\frac{\sin 2\theta\sin 2\phi}{4}\frac{\partial f}{\partial\theta}+\cos^2\phi\frac{\partial f}{\partial\phi}-\frac{3}{2}\sin^2\theta\sin 2\phi f\right\} \tag{8.45.1}$$

Let's express the probability density $f(\theta,\phi)$ as a series of g as

$$f(\theta,\phi)=f_0(\theta,\phi)+\left(\frac{g}{D}\right)f_1(\theta,\phi)+\left(\frac{g}{D}\right)^2 f_2(\theta,\phi)+\left(\frac{g}{D}\right)^3 f_3(\theta,\phi)+\cdots \tag{8.45.2}$$

Derive the expression for the coefficients $f_1(\theta,\phi)$, $f_2(\theta,\phi)$ and $f_3(\theta,\phi)$.

Answer

Substituting Eq. (8.45.2) for $f(\theta,\phi)$ in Eq. (8.45.1) and comparing the coefficients of (g/D), $(g/D)^2$, $(g/D)^3$ ... in both sides, we obtain a set of differential equations as

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f_0}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 f_0}{\partial\phi^2}=0 \tag{8.45.3}$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f_1}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 f_1}{\partial\phi^2}$$
$$=\frac{\sin 2\theta\sin 2\phi}{4}\frac{\partial f_0}{\partial\theta}+\cos^2\phi\frac{\partial f_0}{\partial\phi}-\frac{3}{2}\sin^2\theta\sin 2\phi\, f_0 \tag{8.45.4}$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f_2}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 f_2}{\partial\phi^2}$$
$$=\frac{\sin 2\theta\sin 2\phi}{4}\frac{\partial f_1}{\partial\theta}+\cos^2\phi\frac{\partial f_1}{\partial\phi}-\frac{3}{2}\sin^2\theta\sin 2\phi\, f_1 \tag{8.45.5}$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f_3}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 f_3}{\partial\phi^2}$$
$$=\frac{\sin 2\theta\sin 2\phi}{4}\frac{\partial f_2}{\partial\theta}+\cos^2\phi\frac{\partial f_2}{\partial\phi}-\frac{3}{2}\sin^2\theta\sin 2\phi\, f_2 \tag{8.45.6}$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f_4}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 f_4}{\partial\phi^2}$$
$$=\frac{\sin 2\theta\sin 2\phi}{4}\frac{\partial f_3}{\partial\theta}+\cos^2\phi\frac{\partial f_3}{\partial\phi}-\frac{3}{2}\sin^2\theta\sin 2\phi\, f_3 \tag{8.45.7}$$

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The solution of the first equation is used to solve the second equation and the solution of the second equation is used to solve the third equation and so on, successively. This method is called the **successive approximation method.** When g=0, we have $f(\theta,\phi)=f_0(\theta,\phi)$. In this case, the direction of the principal axis of the dumbbell-like molecules is completely random. As usual, we put f_0 as a constant (for normalization, f_0 is the reciprocal of the integral of $\sin\theta d\theta d\phi$ all over the direction).

$$f_0=\frac{1}{4\pi} \tag{8.45.8}$$

Then Eq. (8.45.4) is rewritten as

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f_1}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 f_1}{\partial\phi^2}=-\frac{3}{2}\sin^2\theta\sin 2\phi\frac{1}{4\pi} \tag{8.45.9}$$

The first step to solve Eq. (8.45.9) is to solve the following homogeneous equation.

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f_l}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 f_l}{\partial\phi^2}=0 \qquad (8.45.10)$$

Eq. (8.45.10) is the Laplace equation for r=const. expressed in the polar coordinate. Putting f_l as

$$f_l=\Theta_l(\theta)\,\Phi_l(\phi) \qquad (8.45.11)$$

and using the separation of variables, we have

$$\frac{\sin\theta}{\Theta_l}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta_l}{\partial\theta}\right)+\frac{1}{\Phi_l}\frac{\partial^2\Phi_l}{\partial\phi^2}=0 \qquad (8.45.12)$$

Putting

$$\frac{1}{\Phi_l}\frac{\partial^2\Phi_l}{\partial\phi^2}=-m^2 \quad (=\text{const}) \qquad (8.45.13)$$

we have a set of equations

$$\frac{\partial^2\Phi_l}{\partial\phi^2}=-m^2\Phi_l \qquad (8.45.14.a)$$

$$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta_l}{\partial\theta}\right)-m^2\Theta_l=0 \qquad (8.45.14.b)$$

From Eq. (8.45.14a),

$$\Phi_l=e^{\pm im\phi} \qquad (8.45.15)$$

or

$$\Phi_l=\cos m\phi \quad \text{or} \quad \sin m\phi \qquad (8.45.16)$$

Here the equation $\Phi_l(\phi+2\pi)=\Phi(\phi)$ must be satisfied. Thus, m=0 or integers. Putting $x=\cos\theta$ in Eq. (8.45.14b), we have

$$\frac{\partial\Theta_l(\theta)}{\partial\theta}=\frac{d\Theta_l(x)}{dx}\frac{dx}{d\theta}=-\sin\theta\frac{d\Theta_l(x)}{dx} \qquad (8.45.17)$$

Eq. (8.45.17) is further rewritten as

$$\left(1-x^2\right)\frac{d^2\Theta_l}{dx^2}-2x\frac{d\Theta_l}{dx}-\frac{m^2}{1-x^2}\Theta_l=0 \qquad (8.45.18)$$

Eq. (8.45.18) is **associated Legendre function**

$$\left(1-x^2\right)\frac{d^2y}{dx^2}-2x\frac{dy}{dx}+\left[l\left(l+1\right)-\frac{m^2}{1-x^2}\right]y=0 \tag{8.45.19}$$

in case of l=0. Eq. (8.45.18) is rewritten as

$$\frac{d^2\Theta_l}{dx^2}-\frac{2x}{1-x^2}\frac{d\Theta_l}{dx}-\frac{m^2}{1-x^2}\Theta_l=0 \tag{8.45.20}$$

The second and the third terms in the left-hand side have a singular point of the first order and the second order, respectively, at x=± 1. To avoid the singular point, we put

$$\Theta_l(x)=\left(1-x^2\right)^{\frac{m}{2}}Y_l(x) \tag{8.45.21}$$

Then Eq. (8.45.18) is rewritten as

$$\left(1-x^2\right)^{\frac{m}{2}}\left[\left(1-x^2\right)\frac{d^2Y_l}{dx^2}-2\left(m+1\right)x\frac{dY_l}{dx}-m\left(m+1\right)Y_l\right]=0 \tag{8.45.22}$$

or

$$\left(1-x^2\right)\frac{d^2Y_l}{dx^2}-2\left(m+1\right)x\frac{dY_l}{dx}-m\left(m+1\right)Y_l=0 \tag{8.45.23}$$

Introducing a new variable

$$z=1-x \tag{8.45.24}$$

Eq. (8.45.23) is rewritten as

$$z\left(2-z\right)\frac{d^2Y_l(z)}{dz^2}+2\left(m+1\right)\left(1-z\right)\frac{dY_l(z)}{dz}-m\left(m+1\right)Y_l\left(z\right)=0 \tag{8.45.25}$$

$Y_l(z)$ is expanded as a series of z as

$$Y_l\left(z\right)=\sum_{\lambda=1}^{\infty}a_\lambda z^{k+\lambda}=a_0z^k+a_1z^{k+1}+a_2z^{k+2}+\cdots \tag{8.45.26}$$

Substitution of Eq. (8.45.26) in Eq. (8.45.25) yields

z^{k-1} : $2a_0k\left(k+m\right)=0$

z^k : $2\left(k+1\right)\left(k+m+1\right)a_1-\left(k+m\right)\left(k+m+1\right)a_0=0$

$$\begin{aligned} z^{k+1} &: \ 2(k+2)(k+m+2)\,a_2-(k+m+1)(k+m+2)a_1=0 \\ z^{k+2} &: \ 2(k+3)(k+m+3)\,a_3-(k+m+2)(k+m+3)a_2=0 \\ z^{k+3} &: \ \cdots\cdots\cdots\cdots\cdots \end{aligned} \tag{8.45.27}$$

Since the lowest order of z is k, $a_0 \neq 0$ and then

$$k(k+m)=0 \tag{8.45.28}$$

Therefore, k=0 or k=-m. For k=0, Y_l is not finite and physically meaningless. For k=-m,

$$a_0 \neq 0$$

$$a_0 = a_1 = a_2 = a_3 = \cdots\cdots\cdots = 0$$

Then we have a finite solution as

$$Y_l(z) = a_0(1-x)^{-m} \tag{8.45.29}$$

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* If we introduce a variable z=1+x instead of z=1-x in Eq. (8.45.24), we have $Y_l(z)= a_0(1+x)^{-m}$. However, both the second and the third terms in Eq.(8.45.14b) have singular points of the first order of (1-x) or (1+x). Thus, either $(1-x)^{-m}$ or $(1+x)^{-m}$ is satisfactory as the solution. The final solution is independent of the choice of the variable z.

Then we proceed to finding a particular solution of Eq. (8.45.9). If we put

$$f_l = \Theta_l(\theta)\sin 2\phi \qquad m=2 \tag{8.45.30}$$

Eq. (8.45.30) satisfies Eq. (8.45.9). Then the differential equation is reduced to

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\,\Theta_l}{\partial\theta}\right)-\frac{2^2}{\sin^2\theta}\Theta_l=-\frac{3}{8\pi}\sin^2\theta \tag{8.45.31}$$

Putting

$$x=\cos\theta \tag{8.45.32}$$

Eq. (8.45.31) is rewritten as

$$\left(1-x^2\right)\frac{d^2\Theta_l}{dx^2}-2x\frac{d\Theta_l}{dx}-\frac{2^2}{1-x^2}\Theta_l=-\frac{3}{8\pi}\left(1-x^2\right) \tag{8.45.33}$$

Eq. (8.45.18) is the homogeneous equation of Eq. (8.45.33). Substitution of

$$\Theta_1(x) = \left(1 - x^2\right) Y_1(x) \tag{8.45.34}$$

in Eq. (8.45.33) yields

$$\left(1 - x^2\right)\left[\left(1 - x^2\right)\frac{d^2Y_1}{dx^2} - 6x\frac{dY_1}{dx} - 6Y_1\right] = -\frac{3}{8\pi}\left(1 - x^2\right)$$

$$\left(1 - x^2\right)\frac{d^2Y_1}{dx^2} - 6x\frac{dY_1}{dx} - 6Y_1 = -\frac{3}{8\pi} \tag{8.45.35}$$

The homogeneous equation for Eq. (8.45.35) is

$$\left(1 - x^2\right)\frac{d^2Y_1}{dx^2} - 6x\frac{dY_1}{dx} - 6Y_1 = 0 \tag{8.45.36}$$

and the solution of Eq. (8.45.36) is

$$Y_1 = a_0\left(1 - x\right)^{-2} \tag{8.45.37}$$

Using the solution of the homogeneous equation (8.45.36)

$$y_1 = \left(1 - x\right)^{-2} \tag{8.45.38}$$

Y_1 is expressed as

$$Y_1 = C(x)y_1 \tag{8.45.39}$$

Eq. (8.45.35) is rewritten as

$$\frac{d^2Y_1}{dx^2} - \frac{6x}{1 - x^2}\frac{dY_1}{dx} - \frac{6Y_1}{1 - x^2} = -\frac{3}{8\pi}\frac{1}{1 - x^2} \tag{8.45.40}$$

Substitution of Eq. (8.45.39) in Eq. (8.45.40) yields

$$y_1\left[\frac{d^2C}{dx^2} + \left\{-\frac{6x}{1 - x^2} + 2\frac{1}{y_1}\frac{dy_1}{dx}\right\}\frac{dC}{dx}\right] = -\frac{3}{8\pi}\frac{1}{1 - x^2}$$

$$\frac{d^2C}{dx^2} + \left\{-\frac{6x}{1 - x^2} + \frac{d\ln y_1^2}{dx}\right\}\frac{dC}{dx} = -\frac{3}{8\pi}\frac{1}{1 - x^2}\frac{1}{y_1} \tag{8.45.41}$$

The integration of the coefficient of dC/dx in the left-hand side of Eq. (8.45.41) is calculated as

$$Z=\int\left\{-\frac{6x}{1-x^2}+\frac{d\ln y_1^2}{dx}\right\}dx=\ln\left(1-x^2\right)^3 y_1^2 \qquad (8.45.42)$$

Therefore, Eq. (8.45.41) is rewritten as

$$e^z\frac{d^2C}{dx^2}+e^z\frac{dZ}{dx}\frac{dC}{dx}=-\frac{3}{8\pi}\frac{1}{1-x^2}\frac{1}{y_1}e^z \qquad (8.45.43)$$

Eq. (8.45.43) is reduced to

$$\frac{d}{dx}\left\{e^z\frac{dC}{dx}\right\}=-\frac{3}{8\pi}\frac{1}{1-x^2}\frac{1}{y_1}e^{\ln\left(1-x^2\right)^3 y_1^2}=-\frac{3}{8\pi}\frac{1}{1-x^2}\frac{\left(1-x^2\right)^3}{y_1}y_1^2$$

$$=-\frac{3}{8\pi}\left(1-x^2\right)^2\left(1-x^2\right)^{-2}=-\frac{3}{8\pi}\left(1+x\right) \qquad (8.45.44)$$

The integration of Eq. (8.45.44) yields

$$\frac{dC}{dx}=\frac{1}{e^{\ln\left(1-x^2\right)^3 y_1^2}}\left[-\int\frac{3}{8\pi}\left(1+x\right)dx+C_0\right]$$

$$=\frac{\left(1-x\right)^4}{\left(1-x^2\right)^3}\left[-\frac{3}{8\pi}\frac{\left(1+x\right)^3}{3}+C_0\right]=-\frac{1}{8\pi}\left(1-x\right) \qquad (8.45.45)$$

where C_0 is chosen as 0, since $dC/dx=0$ when $x=1$ ($\theta=0$). Further integration yields

$$C=-\frac{1}{8\pi}\int\left(1-x\right)dx+C_{00}=\frac{1}{2}\frac{1}{8\pi}\left(1-x\right)^2 \qquad (8.45.46)$$

where C_{00} is chosen as 0, since $C=0$ when $x=1$ ($\theta=0$).
Substitution of Eq. (8.45.46) in Eq. (8.45.38) yields

$$Y_1=\frac{1}{16\pi} \qquad (8.45.47)$$

Substitution of Eq. (8.45.47) in Eq. (8.45.34) yields

$$\Theta_1=\frac{1}{16\pi}\left(1-x^2\right)=\frac{1}{16\pi}\sin^2\theta \qquad (8.45.48)$$

Substitution of Eq. (8.45.48) in Eq. (8.45.30) yields

$$f_1(\theta,\phi)=\frac{1}{16\pi}\sin^2\theta\,\sin 2\phi=\frac{1}{4\pi}\,\frac{1}{4}\sin^2\theta\,\sin 2\phi \qquad (8.45.49)$$

Substitution of Eq. (8.45.49) in Eq. (8.45.5) yields

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f_2}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 f_2}{\partial\phi^2}=\frac{1}{16\pi}\,\frac{\sin 2\theta\,\sin 2\phi}{4}\,2\sin\theta\cos\theta\,\sin 2\phi$$

$$+\frac{1}{16\pi}\sin^2\theta\left(2\cos 2\phi\right)\cos^2\phi-\frac{3}{2}\frac{1}{16\pi}\sin^2\theta\,\sin 2\phi\,\sin^2\theta\,\sin 2\phi$$

$$=\frac{1}{16\pi}\sin^2\theta-\frac{5}{4}\frac{1}{16\pi}\sin^4\theta+\frac{1}{16\pi}\sin^2\theta\cos 2\phi+\frac{5}{4}\,\frac{1}{16\pi}\sin^4\theta\cos 4\phi \qquad (8.45.50)$$

Now we express f_2 as

$$f_2=f_{21}+f_{22}+f_{23} \qquad (8.45.51)$$

and Eq. (8.45.50) is rewritten as

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f_{21}}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 f_{21}}{\partial\phi^2}=\frac{1}{16\pi}\left(\sin^2\theta-\frac{5}{4}\sin^4\theta\right) \qquad (8.45.52.a)$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f_{22}}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 f_{22}}{\partial\phi^2}=\frac{1}{16\pi}\sin^2\theta\cos 2\phi \qquad (8.45.52.b)$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f_{23}}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 f_{23}}{\partial\phi^2}=\frac{1}{16\pi}\,\frac{5}{4}\sin^4\theta\cos 4\phi \qquad (8.45.52.c)$$

Then we put

$$x=\cos\theta \qquad (8.45.53)$$

$$f_{21}=\Theta_{21}(x)\cos 0\phi=\Theta_{21}(x) \qquad (8.45.54.a)$$

$$f_{22}=\Theta_{22}(x)\cos 2\phi \qquad (8.45.54.b)$$

$$f_{23}=\Theta_{23}(x)\cos 4\phi \qquad (8.45.54.c)$$

Eqs. (8.45.52.a)-(8.45.52.c) are reduced to

$$\frac{d}{dx}\left\{\left(1-x^2\right)\frac{d\Theta_{21}}{dx}\right\}=\frac{1}{16\pi}\left\{\left(1-x^2\right)-\frac{5}{4}\left(1-x^2\right)^2\right\} \qquad (8.45.55.a)$$

$$\frac{d}{dx}\left\{\left(1-x^2\right)\frac{d\Theta_{22}}{dx}\right\}-\frac{2^2}{1-x^2}\Theta_{22}=\frac{1}{16\pi}\left(1-x^2\right) \tag{8.45.55.b}$$

$$\frac{d}{dx}\left\{\left(1-x^2\right)\frac{d\Theta_{22}}{dx}\right\}-\frac{4^2}{1-x^2}\Theta_{23}=\frac{1}{16\pi}\left(\frac{5}{4}\right)\left(1-x^2\right)^2 \tag{8.45.55.c}$$

Eqs. (8.45.55.b) and (8.45.55.c) have the same functional form as

$$\frac{d}{dx}\left\{\left(1-x^2\right)\frac{d\Theta}{dx}\right\}-\frac{m^2}{1-x^2}\Theta=A\left(1-x^2\right)^n \tag{8.45.56}$$

Referring to the calculation procedure for Eq. (8.45.30), we put

$$\Theta=\left(1-x^2\right)^{\frac{m}{2}}Y(x) \tag{8.45.57}$$

Eq. (8.45.56) is reduced to

$$\frac{d^2Y}{dx^2}-\frac{2x\left(m+1\right)}{1-x^2}\frac{dY}{dx}-\frac{m\left(m+1\right)}{1-x^2}Y=A\left(1-x^2\right)^{n-\frac{m}{2}-1} \tag{8.45.58}$$

Then we put

$$Y=C(x)y=C(x)(1-x)^{-m} \tag{8.45.59}$$

Eq. (8.45.58) is reduced to

$$\frac{d^2C}{dx^2}+\left\{\frac{2x\left(m+1\right)}{1-x^2}+2\frac{1}{y}\frac{dy}{dx}\right\}\frac{dC}{dx}=A\left(1-x^2\right)^{n-\frac{m}{2}-1}\frac{1}{y} \tag{8.45.60}$$

The integration for the coefficient of dC/dx is calculated as

$$Z=\int\left\{-\frac{2x\left(m+1\right)}{1-x^2}+2\frac{1}{y}\frac{dy}{dx}\right\}dx=\ln\left\{\left(1-x^2\right)^{m+1}y^2\right\} \tag{8.45.61}$$

The integrant is rewritten as

$$\left\{-\frac{2x\left(m+1\right)}{1-x^2}+2\frac{1}{y}\frac{dy}{dx}\right\}=\frac{dZ}{dx} \tag{8.45.62}$$

Eq. (8.45.60) is reduced to

$$\frac{d}{dx}\left\{e^{z}\frac{dC}{dx}\right\}=A\left(1-x^{2}\right)^{n-\frac{m}{2}-1}\frac{e^{z}}{y}$$

$$\frac{dC}{dx}=A\frac{1}{e^{z}}\int\left(1-x^{2}\right)^{n-\frac{m}{2}-1}\frac{e^{z}}{y}dx+C_{0}\frac{1}{e^{z}} \tag{8.45.63}$$

Then we obtain

$$C=A\int\left[\frac{1}{e^{z}}\int\left(1-x^{2}\right)^{n-\frac{m}{2}-1}\frac{e^{z}}{y}\right]dx+C_{0}\int\frac{dx}{e^{z}}+C_{00} \tag{8.45.64}$$

From Eqs. (8.45.59) and (8.45.61),

$$e^{z}=\frac{\left(1-x^{2}\right)^{m+1}}{\left(1-x\right)^{2m}}=\frac{\left(1+x\right)^{m+1}}{\left(1-x\right)^{m-1}} \tag{8.45.65}$$

Thus we have

$$\begin{aligned}C=A&\int\left[\frac{\left(1-x\right)^{m-1}}{\left(1+x\right)^{m+1}}\int\left(1+x\right)^{n+\frac{m}{2}}\left(1-x\right)^{n-\frac{m}{2}}dx\right]dx\\&+C_{0}\int\frac{\left(1-x\right)^{m-1}}{\left(1+x\right)^{m+1}}dx+C_{00}\end{aligned} \tag{8.45.66}$$

From Eqs. (8.45.57), (8.45.59) and (8.45.66), we have

$$\Theta=\frac{\left(1-x^{2}\right)^{\frac{m}{2}}}{\left(1-x\right)^{m}}C\left(x\right) \tag{8.45.67}$$

The first equation of Eq. (8.45.55) is integrated as

$$\int\left\{\left(1-x^{2}\right)-\frac{5}{4}\left(1-x^{2}\right)^{2}\right\}dx=-\frac{x}{4}\left(1-x^{2}\right)^{2} \tag{8.45.68}$$

Then we have

$$\begin{aligned}f_{21}=\Theta_{21}&=-\frac{1}{16\pi}\frac{1}{4}\int\left(1-x^{2}\right)x\,dx+C_{0}\int\frac{dx}{1-x^{2}}+C_{00}\\&=\frac{1}{4\pi}\left(\frac{1}{4}\right)^{2}\frac{1}{4}\left(1-x^{2}\right)^{2}+C_{0}\ln\sqrt{\frac{1+x}{1-x}}+C_{00}\end{aligned} \tag{8.45.69}$$

Here, C_0 is 0, since f_{21} must be finite when $x=1$ ($\theta=0$). Then

$$f_{21} = \frac{1}{4\pi}\left(\frac{1}{4}\right)^3\left(1-x^2\right)^2 + C_{00} \tag{8.45.70}$$

From the normalization condition

$$\iint f(\theta,\phi)\sin\theta\, d\theta\, d\phi = 1 \tag{8.45.71}$$

or

$$f_0 = \frac{1}{4\pi} \tag{8.45.8}$$

$$\iint f_0 \sin\theta\, d\theta\, d\phi = 1 \tag{8.45.72}$$

and

$$\iint f_i(\theta,\phi)\sin\theta\, d\theta\, d\phi = 0 \tag{8.45.73}$$

f_{22} and f_{23} are 0 due to the terms $\cos 2\phi$ or $\cos 4\phi$.

$$\iint f_{22}\sin\theta\, d\theta\, d\phi = 0 \tag{8.45.74.a}$$

$$\iint f_{23}\sin\theta\, d\theta\, d\phi = 0 \tag{8.45.74.b}$$

The coefficient C_{00} in Eq. (8.45.70) is determined by the normalization condition (total integration of f_{21} affords zero):

$$\int_0^{2\pi}\int_0^{\pi} f_{21}\sin\theta\, d\theta\, d\phi = \frac{1}{4\pi}\left(\frac{1}{4}\right)^2 \int_0^{2\pi} d\phi \int_{-1}^{1}\left(1-x^2\right)^2 dx + C_{00}\,4\pi = 0 \tag{8.45.75}$$

Then we obtain

$$C_{00} = -\frac{1}{4\pi}\left(\frac{1}{4}\right)^3 \frac{1}{2}\int_{-1}^{1}\left\{1-2x^2+4x^4\right\}dx = -\frac{1}{4\pi}\left(\frac{1}{4}\right)^2 \frac{2}{15} \tag{8.45.76}$$

Substitution of Eq. (8.45.76) for C_{00} in Eq. (8.45.70) yields

$$f_{21} = \frac{1}{4\pi}\left(\frac{1}{4}\right)^2\left\{\frac{1}{4}\left(1-x^2\right)^2 - \frac{2}{15}\right\} = \frac{1}{4\pi}\left(\frac{1}{4}\right)^2\left\{\frac{1}{4}\sin^4\theta - \frac{2}{15}\right\} \tag{8.45.77}$$

Eq. (8.45.55b) shows that f_{22} is calculated from Eq. (8.45.56) by replacing the parameters as

$$A = \frac{1}{16\pi} \quad , m = 2 \quad , n = 1$$

From Eq. (8.45.66),

$$C_{22}(x) = -\frac{1}{4\pi}\left(\frac{1}{4}\right)^2 \frac{2}{3}(1-x)^2 + C_0 \frac{x}{(1+x)^2} + C_{00} \tag{8.45.78}$$

Substitution of Eq. (8.45.78) for C_{22} in Eq. (8.45.67) yields

$$\Theta_{22} = -\frac{1}{4\pi}\left(\frac{1}{4}\right)^2 \frac{2}{3}\left(1-x^2\right) + C_0 \frac{x}{1-x^2} + C_{00} \frac{1+x}{1-x} \tag{8.45.79}$$

The integration constants C_0 and C_{00} are determined so that Θ_{22} is finite when $x = \pm 1$ as

$$C_0 = 0 \qquad C_{00} = 0$$

Then we have

$$\Theta_{22} = -\frac{1}{4\pi}\left(\frac{1}{4}\right)^2 \frac{2}{3}\left(1-x^2\right) = \frac{1}{4\pi}\left(\frac{1}{4}\right)^2 \left[-\frac{2}{3}\sin^2\theta\right] \tag{8.45.80}$$

Substitution of Eq. (8.45.80) for Θ_{22} in Eq. (8.45.55b) yields

$$f_{22} = \frac{1}{4\pi}\left(\frac{1}{4}\right)^2 \left[-\frac{2}{3}\sin^2\theta \cos 2\phi\right] \tag{8.45.81}$$

Similarly, f_{23} is calculated from Eq. (8.45.55b) by replacing the parameters as

$$A = \frac{1}{16\pi}\frac{5}{4}, \qquad m = 4 \ , \qquad n = 2$$

The integration constants C_0 and C_{00} are determined so that Θ_{22} is finite in Eq. (8.45.67) when $x = \pm 1$ as

$$C_0 = 0 \qquad C_{00} = 0$$

Then we have

$$C(x) = \frac{1}{16\pi} \cdot \frac{5}{4} \cdot \left(-\frac{1}{5 \cdot 4}\right)(1-x)^4 \tag{8.45.82}$$

Substitution of Eq. (8.45.82) in Eq. (8.45.68) yields

$$\Theta_{23} = \frac{1}{4\pi}\left(\frac{1}{4}\right)^2\left[-\frac{1}{4}\left(1-x^2\right)^2\right] = \frac{1}{4\pi}\left(\frac{1}{4}\right)^2\left[-\frac{1}{4}\sin^4\theta\right] \tag{8.45.83}$$

$$f_{23} = \frac{1}{4\pi}\left(\frac{1}{4}\right)^2\left[-\frac{1}{4}\sin^4\theta\cos 4\phi\right] \tag{8.45.84}$$

Substitution of Eqs. (8.45.77), (8.45.81) and (8.45.84) in Eq. (8.45.51) yields

$$f_2 = \frac{1}{4\pi}\left(\frac{1}{4}\right)^2\left[-\frac{2}{15} + \frac{1}{4}\sin^4\theta - \frac{2}{3}\sin^2\theta\cos 2\phi - \frac{1}{4}\sin^4\theta\cos 4\phi\right] \tag{8.45.85}$$

Substitution of Eq. (8.45.85) in Eq. (8.45.6) yields

$$\begin{aligned}
&\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f_3}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 f_3}{\partial\phi^2} \\
&= \frac{1}{4\pi}\left(\frac{1}{4}\right)^2\Bigg[\frac{\sin 2\theta\sin\phi}{4}\Bigg\{\sin^3\theta\cos\theta - \frac{3}{4}\sin\theta\cos\theta\cos 2\phi \\
&\quad -\sin^3\theta\cos\theta\cos 4\phi\Bigg\} + \cos^2\phi\left\{\frac{4}{3}\sin^2\theta\sin 2\phi + \sin^4\theta\sin 4\phi\right\} \\
&\quad -\frac{3}{2}\sin^2\theta\sin 2\phi\left\{-\frac{2}{15} + \frac{1}{4}\sin^4\theta - \frac{2}{3}\sin^2\theta\cos 2\phi - \frac{1}{4}\sin^4\theta\cos 4\phi\right\}\Bigg] \\
&= \frac{1}{4\pi}\left(\frac{1}{4}\right)^2\Bigg[\left\{\frac{13}{15}\sin^2\theta\sin 2\phi + \sin^4\theta\sin 2\phi - \frac{21}{16}\sin^6\theta\sin 2\phi\right\} \\
&\quad + \frac{4}{3}\sin^4\theta\sin 4\phi + \frac{7}{16}\sin^6\theta\sin 6\phi\Bigg]
\end{aligned} \tag{8.45.86}$$

Eq. (8.45.86) is rewritten as

$$f_3 = f_{31} + f_{32} + f_{33} + f_{34} + f_{35} \tag{8.45.87}$$

$$f_{31} = \Theta_{31}\sin 2\phi \tag{8.45.88.a}$$

$$f_{32} = \Theta_{32}\sin 2\phi \tag{8.45.88.b}$$

$$f_{33} = \Theta_{33}\sin 2\phi \tag{8.45.88.c}$$

$$f_{34} = \Theta_{34}\sin 4\phi \tag{8.45.88.d}$$

$$f_{35} = \Theta_{35} \sin 6\phi \tag{8.45.88.e}$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta_{31}}{\partial\theta}\right)+\frac{2^2}{\sin^2\theta}\Theta_{31}=\frac{1}{4\pi}\left(\frac{1}{4}\right)^2\left(\frac{13}{15}\right)\sin^2\theta$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta_{32}}{\partial\theta}\right)+\frac{2^2}{\sin^2\theta}\Theta_{32}=\frac{1}{4\pi}\left(\frac{1}{4}\right)^2\sin^4\theta$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta_{33}}{\partial\theta}\right)+\frac{2^2}{\sin^2\theta}\Theta_{33}=\frac{1}{4\pi}\left(\frac{1}{4}\right)^2\left(-\frac{21}{16}\right)\sin^6\theta$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta_{34}}{\partial\theta}\right)+\frac{4^2}{\sin^2\theta}\Theta_{34}=\frac{1}{4\pi}\left(\frac{1}{4}\right)^2\left(\frac{4}{3}\right)\sin^6\theta$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta_{35}}{\partial\theta}\right)+\frac{6^2}{\sin^2\theta}\Theta_{35}=\frac{1}{4\pi}\left(\frac{1}{4}\right)^2\left(\frac{7}{16}\right)\sin^2\theta \tag{8.45.89}$$

Putting

$x = \cos\theta$

Eq. (8.45.90) is rewritten as

$$\frac{d}{dx}\left\{\left(1-x^2\right)\frac{d\Theta_{31}}{dx}\right\}-\frac{2^2}{1-x^2}\Theta_{31}=\frac{1}{4\pi}\left(\frac{1}{4}\right)^2\left(\frac{13}{15}\right)\left(1-x^2\right) \tag{8.45.90.a}$$

$$\frac{d}{dx}\left\{\left(1-x^2\right)\frac{d\Theta_{32}}{dx}\right\}-\frac{2^2}{1-x^2}\Theta_{32}=\frac{1}{4\pi}\left(\frac{1}{4}\right)^2\left(1-x^2\right)^2 \tag{8.45.90.b}$$

$$\frac{d}{dx}\left\{\left(1-x^2\right)\frac{d\Theta_{33}}{dx}\right\}-\frac{2^2}{1-x^2}\Theta_{33}=\frac{1}{4\pi}\left(\frac{1}{4}\right)^2\left(-\frac{21}{16}\right)\left(1-x^2\right)^3 \tag{8.45.90.c}$$

$$\frac{d}{dx}\left\{\left(1-x^2\right)\frac{d\Theta_{34}}{dx}\right\}-\frac{4^2}{1-x^2}\Theta_{34}=\frac{1}{4\pi}\left(\frac{1}{4}\right)^2\left(\frac{4}{3}\right)\left(1-x^2\right)^2 \tag{8.45.90.d}$$

$$\frac{d}{dx}\left\{\left(1-x^2\right)\frac{d\Theta_{35}}{dx}\right\}-\frac{6^2}{1-x^2}\Theta_{35}=\frac{1}{4\pi}\left(\frac{1}{4}\right)^2\left(\frac{7}{16}\right)\left(1-x^2\right)^3 \tag{8.45.90.e}$$

where

$$\Theta_{31}=\left(1-x^2\right)\left(1-x\right)^{-2}C_{31}\left(x\right) \tag{8.45.91.a}$$

$$\Theta_{32}=\left(1-x^2\right)\left(1-x\right)^{-2}C_{32}\left(x\right) \tag{8.45.91.b}$$

$$\Theta_{33}=\left(1-x^2\right)\left(1-x\right)^{-2}C_{33}\left(x\right) \tag{8.45.91.c}$$

$$\Theta_{34} = \left(1 - x^2\right)^2 \left(1 - x\right)^{-4} C_{34}\left(x\right) \qquad (8.45.91.d)$$

$$\Theta_{31} = \left(1 - x^2\right)^3 \left(1 - x\right)^{-6} C_{35}\left(x\right) \qquad (8.45.91.e)$$

The functions C_{31}, C_{32}, C_{33}, C_{34} and C_{35} are obtained using Eq. (8.45.67). From Eq. (8.45.90a),

$$A = \frac{1}{4\pi}\left(\frac{1}{4}\right)^2\left(\frac{13}{15}\right), \quad m = 2, \quad n = 1$$

Then we have

$$C_{31} = \frac{1}{4\pi}\left(\frac{1}{4}\right)^3\left(-\frac{26}{45}\right)\left(1 - x\right)^2$$

From Eqs. (8.45.88a) and (8.45.91a), we have

$$f_{31} = \frac{1}{4\pi}\left(\frac{1}{4}\right)^3\left(-\frac{26}{45}\right)\sin^2\theta \sin 2\phi \qquad (8.45.92.a)$$

From Eq. (8.45.90b),

$$A = \frac{1}{4\pi}\left(\frac{1}{4}\right)^2, \quad m = 2, \quad n = 2$$

Then we have

$$C_{32} = \frac{1}{4\pi}\left(\frac{1}{4}\right)^3\left\{-\frac{3}{5} + \frac{1}{5}x^2\right\}\left(1 - x\right)^2$$

From Eqs. (8.45.88b) and (8.45.91b), we have

$$f_{32} = \frac{1}{4\pi}\left(\frac{1}{4}\right)^3\left\{-\frac{3}{5}\sin^2\theta \sin 2\phi + \frac{1}{5}\sin^2\theta\cos^2\theta\sin 2\phi\right\} \qquad (8.45.92.b)$$

Similarly, for C_{33}

$$A = \frac{1}{4\pi}\left(\frac{1}{4}\right)^2\left(-\frac{21}{16}\right), \quad m = 2, \quad n = 3$$

$$C_{33} = \frac{1}{4\pi}\left(\frac{1}{4}\right)^3\left\{\frac{33}{40} - \frac{9}{20}x^2 + \frac{1}{8}x^4\right\}\left(1 - x\right)^2$$

$$f_{33} = \frac{1}{4\pi}\left(\frac{1}{4}\right)^3\left\{\frac{33}{40}\sin^2\theta \sin 2\phi - \frac{9}{20}\sin^2\theta\cos^2\theta\sin 2\phi\right.$$

$$\left. + \frac{1}{8}\sin^2\theta \cos^4\theta \sin 2\phi \right\} \tag{8.45.92.c}$$

For C_{34},

$$A = \frac{1}{4\pi}\left(\frac{1}{4}\right)^2\left(\frac{4}{3}\right), \quad m = 4, \quad n = 2$$

$$C_{34} = \frac{1}{4\pi}\left(\frac{1}{4}\right)^3\left(-\frac{4}{15}\right)(1-x)^4$$

$$f_{34} = \frac{1}{4\pi}\left(\frac{1}{4}\right)^3\left(-\frac{4}{15}\right)\sin^4\theta \sin 4\phi \tag{8.45.92.d}$$

For C_{35},

$$A = \frac{1}{4\pi}\left(\frac{1}{4}\right)^2\left(\frac{7}{16}\right), \quad m = 6, \quad n = 3$$

$$C_{35} = \frac{1}{4\pi}\left(\frac{1}{4}\right)^3\left(-\frac{1}{24}\right)(1-x)^6$$

$$f_{35} = \frac{1}{4\pi}\left(\frac{1}{4}\right)^3\left(-\frac{1}{24}\right)\sin^6\theta \sin 6\phi \tag{8.45.92.e}$$

Substituting Eq. (8.45.92) in Eq. (8.45.87), we finally obtain

$$\begin{aligned} f_3 = \frac{1}{4\pi}\left(\frac{1}{4}\right)^3 \Bigg[& -\frac{26}{45}\sin^2\theta \sin 2\phi + \frac{9}{40}\sin^2\theta \sin 2\phi \\ & - \frac{1}{4}\sin^2\theta \cos^2\theta \sin 2\phi + \frac{1}{8}\sin^2\theta \cos^4\theta \sin 2\phi \\ & - \frac{4}{15}\sin^4\theta \sin 4\phi - \frac{1}{24}\sin^6\theta \sin 6\phi \Bigg] \end{aligned} \tag{8.45.93}$$

Chapter 9 Molecular weight and molecular weight distribution

<<Problem 9-1>> Definition of average molecular weight

Synthetic polymers are mixtures of polymers with different degrees of polymerization (or molecular weights) even if the chemical compositions are the same, since the growth and termination reaction of polymerization as well as the polymer degradation are stochastic processes. The degree of polymerization n (or molecular weight M) is expressed with the average degree of polymerization (or molecular weight) and the **degree of polymerization distribution (or molecular weight distribution)**. Let's denote the number fraction and the weight fraction of the polymer with the degree of polymerization being in the range n and n+dn as $f_n(n)dn$ and $f_w(n)dn$, respectively. From the normalization condition,

$$\int_0^\infty f_n(n)\,dn = 1 \tag{9.1.1}$$

and

$$\int_0^\infty f_w(n)\,dn = 1 \tag{9.1.2}$$

$f_w(n)$ is related to $f_n(n)$ as

$$f_w(n) = nf_n(n) \tag{9.1.3}$$

Express the terms **(1) *m* th moment μ_m, (2) mean μ_1, (3) variance σ^2, (4) average of the distribution $\overline{n_i}$, (5) number-average (6) weight-average and (7) z-average degree of polymerization and molecular weight**, using $f_n(n)$ and $f_w(n)$.

Answer

(1) *m* th moment

$$\mu_m = \int_0^{\infty} n^m f_m(n)\, dn = \sum_n n^m f_m(n) \tag{9.1.4}$$

(2) mean

$$\mu_1 = \int_0^{\infty} n f_n(n) dn = \sum_n n f_n(n) \tag{9.1.5}$$

(3) variance

$$\sigma^2 = \int_0^{\infty} \left(n - \mu_1\right)^2 f_n(n)\, dn$$

$$= \int_0^{\infty} n^2 f_n(n)\, dn - 2\mu_1 \int_0^{\infty} n f_n(n)\, dn + \mu_1^2 \int_0^{\infty} f_n(n)\, dn \ = \mu_2 - \mu_1^2 \tag{9.1.6}$$

(4) average

$$\bar{n}_i = \frac{\int_0^{\infty} n^i f_n(n) dn}{\int_0^{\infty} n^{i-1} f_n(n) dn} = \frac{\sum_n n^i f_n(n)}{\sum_n n^{i-1} f_n(n)} = \frac{\int_0^{\infty} n^{i-1} f_w(n) dn}{\int_0^{\infty} n^{i-2} f_w(n) dn} = \frac{\sum_n n^{i-1} f_w(n)}{\sum_n n^{i-2} f_w(n)} = \frac{\mu_i}{\mu_{i-1}} \tag{9.1.7}$$

(5) number-average degree of polymerization

$$n_n = \frac{\int_0^{\infty} n f_n(n) dn}{\int_0^{\infty} f_n(n) dn} = \frac{\int_0^{\infty} f_w(n) dn}{\int_0^{\infty} \frac{f_w(n)}{n} dn} = \mu_1 \tag{9.1.8}$$

(6) weight-average degree of polymerization

$$n_w = \frac{\int_0^\infty n^2 f_n(n)dn}{\int_0^\infty n f_n(n)dn} = \frac{\int_0^\infty n f_w(n)dn}{\int_0^\infty f_w(n)dn} = \frac{\mu_2}{\mu_1} \qquad (9.1.9)$$

(7) z-average degree of polymerization

$$n_z = \frac{\int_0^\infty n^3 f_n(n)dn}{\int_0^\infty n^2 f_n(n)dn} = \frac{\int_0^\infty n^2 f_w(n)dn}{\int_0^\infty n f_w(n)dn} = \frac{\mu_3}{\mu_2} \qquad (9.1.10)$$

(5') number-average molecular weight

$$M_n = \int_0^\infty M f_n(M)\, dM = 1/\int_0^\infty \frac{f_w(M)}{M}\, dM \qquad (9.1.11)$$

(6') weight-average molecular weight

$$M_w = \frac{\int_0^\infty M^2 f_n(M)\, dM}{\int_0^\infty M f_n(M)\, dM} = \int_0^\infty M f_w(M)\, dM \qquad (9.1.12)$$

(7') z-average molecular weight

$$M_z = \frac{\int_0^\infty M^3 f_n(M)\, dM}{\int_0^\infty M^2 f_n(M)\, dM} = \frac{\int_0^\infty M^2 f_w(M)\, dM}{\int_0^\infty M f_w(M)\, dM} \qquad (9.1.13)$$

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* Staudinger proposed 'Makromolekül' as a nomenclature for extremely large molecules which are formed by covalent bonds (See H. Staudinger and J. Fritschi, *Helv. Chim. Acta* **5**, 785 (1922)). He described as early as 1926 that macromolecular compounds are mixtures of molecules with similar chemical structure, but different size (See H. Staudinger, *Ber. dtsch. chem. Ges.* **59**, 3019 (1926))

* The variance of $f_n(n)$, σ^2, is related to the average as

$$\sigma^2 = n_w n_n - n_n^2 \tag{9.1.14}$$

and the variance of $f_w(n)$, σ_w^2, is related to the average as

$$\sigma_w^2 = n_z n_w - n_w^2 \tag{9.1.15}$$

Schulz proposed a parameter defined by

$$u = \frac{n_w}{n_n} - 1 \tag{9.1.16}$$

as a measure of the inhomogeneity of the degree of polymerization (**Schulz polymolecularity index**). u agrees with the square of the parameter C defined by

$$C = \frac{\sigma}{\mu_1} \tag{9.1.17}$$

as

$$C^2 = \frac{\sigma^2}{\mu_1^2} = \frac{n_w n_n - n_n^2}{n_n^2} = u \tag{9.1.18}$$

u depends on the average degree of polymerization as well as the width of the distribution as

$$u = \frac{n_w}{n_n} - 1 = \frac{\sigma^2}{n_n^2} \tag{9.1.19}$$

* **Polymolecularity index** as a measure of the width of the molecular weight distribution was first proposed by Schulz in 1939. (See G.V.Schulz, *Z. Phys. Chem.* **B43**, 25 (1939)) u is the head character of **Uneinheitlichkeit**. In general, a ratio of the moments of different degrees gives a measure of the width of the distribution.

<<Problem 9-2>> Schulz polymolecularity index

Show that **Schulz polymolecularity index** u (Eq.(9.1.16)) depends on the average degree of polymerization as well as the width of the distribution.

Answer

Let's consider two distributions with the same width of the distribution and the different average degree of polymerization n_n, say,

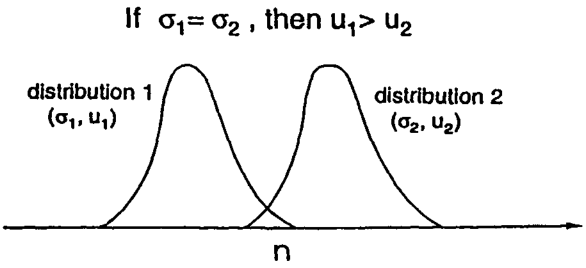

Fig. 9-2 Schulz polymolecularity index and the variance of molecular weight distribution

$$n_{n,1} < n_{n,2} \tag{9.2.1}$$

Then from Eq.(9.1.19)

$$u_1 = \left(\frac{\sigma}{n_{n,1}}\right)^2 > \left(\frac{\sigma}{n_{n,2}}\right)^2 = u_2 \tag{9.2.2}$$

Even if the widths of the distributions are the same, u_l increases with decreasing n_n, as shown in Fig. 9-2. Thus when u is used as a measure of the width of the distribution, the same n_n is the prerequisite condition.

<<Problem 9-3>> Average degree of polymerization (I)

Show the relationship between the average degrees of polymerization

$$n_n \leq n_v \leq n_w \leq n_z \tag{9.3.1}$$

and derive the required condition for the equality

$$n_n = n_v = n_w = n_z \tag{9.3.2}$$

in Eq. (9.3.1), where n_v is the viscosity-average degree of polymerization.

Answer

From Eq. (9.1.6),

$$\mu_2 \geq \mu_1^2 \tag{9.3.3}$$

then

$$n_n \leq n_w \tag{9.3.4}$$

From Eqs. (9.1.9) and (9.1.10), $n_z/n_w = \mu_3\mu_1/\mu_2^2$.

In general,

$$\mu_3\mu_1 \ge \mu_2^2 \tag{9.3.5}$$

then

$$n_w \le n_z \tag{9.3.6}$$

n_v is defined by

$$n_v = \left[\frac{\int_0^\infty n^{a+1} f_n(n)\,dn}{\int_0^\infty n f_n(n)\,dn}\right]^{1/a} \tag{9.3.7}$$

Here, a is the exponent in Mark-Houwink-Sakurada equation Eq. (8.30.19). If a=1, Eq. (9.3.7) agrees with Eq. (9.1.9), that is,

$$n_v(a=1) = n_w \tag{9.3.8}$$

If a=-1,

$$n_v = \left[\frac{\int_0^\infty f_n(n)\,dn}{\int_0^\infty n f_n(n)\,dn}\right]^{-1} = \left[\frac{\int_0^\infty n f_n(n)\,dn}{\int_0^\infty f_n(n)\,dn}\right] \tag{9.3.9}$$

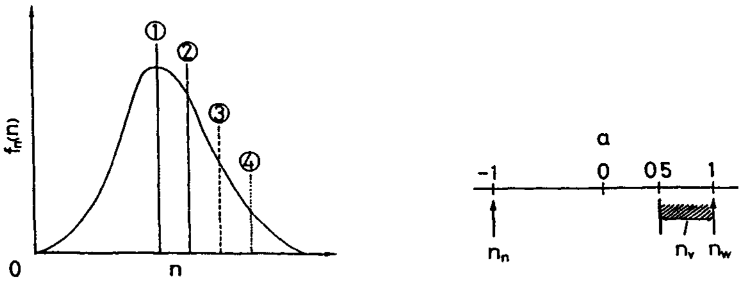

Fig. 9-3 Relationship among various average degrees of polymerization. ①, ②, ③ and ④ corresponds to n_n, n_w, n_v and n_z, respectively.

that is,

$$n_v(a=-1)=n_n \qquad (9.3.10)$$

Experiments show $0.5<a<1.0$. Thus, from Eqs. (9.3.8) and (9.3.10), we have

$$n_n \le n_v \le n_w \qquad (9.3.11)$$

as illustrated in Fig. 9-3. It should be noted that Eqs. (9.3.8) and (9.3.10) are valid irrespective of the width of the distribution of the degree of polymerization. If the polymer is monodisperse (consisting of polymers with a single molecular weight),

$$\mu_n = n^n \qquad (9.3.12)$$

Then we have

$$\frac{n_w}{n_n}=\frac{\mu_2}{\mu_1{}^2}=\frac{n^2}{(n)^2}=1 \qquad (9.3.13)$$

and

$$\frac{n_z}{n_w}=\frac{\mu_3\mu_1}{\mu_2{}^2}=\frac{n^3 n}{(n^2)^2}=1 \qquad (9.3.14)$$

Eq. (9.3.2) holds in this special case.

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* The scientists who first noticed that the molecular weight of polymer depends on the method for determining it are Lansing and Kraemer (See W.D.Lansing and E.O.Kraemer, *J.Am.Chem.Soc.* **57**, 1369 (1935)). The experimental fact that the molecular weights determined by viscometry was always larger than those determined from the freezing point and the osmotic pressure attracted their attention. Afterwards, Schulz named the average degree of polymerization determined by viscometry the weight-average one and that determined from osmometry the mean. (See G.V.Schulz, *Z. phys. Chem.* **B32**, 27 (1936))) In 1930s, the molecular weight determined by viscometry was regarded as the weight-average one, though that is not generally true as shown in this problem (See W.H.Carothers, *Trans.Farad.Soc.* **32**, 39 (1936)). Referring to the experimental fact $0.5<a<1.0$, n_v is close to n_w.

* Physical meaning of n_v (Eq. (9.3.9)) varies, depending on the kind of average degree of polymerization (n_n or n_w) employed for establishing Eq. (8.30.19) (See A. Kotera, *Science* **27**, 38 (1957)).

<<Problem 9-4>> Average degree of polymerization (II)

Consider a mixture of ten molecules with n=100 and five molecules with n=1000. Calculate n_n, n_w and n_z.

Answer

From Eq. (9.1.8),

$$n_n = \sum nf_n(n) = 100 \times \frac{5}{10+5} + 1000 \times \frac{5}{10+5} = 400 \tag{9.4.1}$$

From Eq. (9.1.9),

$$n_w = \frac{\sum n^2 f_n(n)}{\sum nf_n(n)} = \frac{(100)^2 \times \frac{10}{10+5} + (1000)^2 \times \frac{5}{10+5}}{100 \times \frac{5}{10+5} + 1000 \times \frac{5}{10+5}} = 850 \tag{9.4.2}$$

From Eq. (9.1.10),

$$n_z = \frac{\sum n^3 f_n(n)}{\sum n^2 f_n(n)} = \frac{(100)^3 \times \frac{10}{10+5} + (1000)^3 \times \frac{5}{10+5}}{(100)^2 \times \frac{5}{10+5} + (1000)^2 \times \frac{5}{10+5}} = 982 \tag{9.4.3}$$

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* This sample calculation was used in a paper of Carothers (See W.H.Carothers, *Trans.Farad.Soc.* **32**, 39 (1936)). He pointed out that the relationship between [η] and M for monodisperse polymer samples is not correct for polydisperse ones so that the determinaition of M by the viscosity method is not reliable. However, the effect of polydispersity on the viscosity equation can be precisely corrected, as shown later.

<<Problem 9-5-a>> Condensation polymerization (I)

Suppose the probability of condensation reaction p be independent of the degree of polymerization in **condensation polymerization**. The probability that n-1 condensation reactions occur successively to make a polymer where the degree of polymerization n is p^{n-1} and the probability that the condensation reaction terminates after the final step is 1-p. Since the probability of independent events is the product of the probability of each event, the expected value for the number of n-mer N_n after the polymerization reaction process is $Np^{n-1}(1-p)$, where N is the total number of molecules after the polymerization. Thus the number fraction of n-mer is

$$f_n(n) = \frac{N_n}{N} = p^{n-1}(1 - p) \tag{9.5.1}$$

If the total number of monomers before the polymerization is N_0,

$$N = N_0(1 - p) \tag{9.5.2}$$

The weight of the polymer is proportional to the degree of polymerization. Thus the weight fraction of n-mer is

$$f_w(n) = \frac{nN_n}{N_0} = np^{n-1}(1 - p)^2 \tag{9.5.3}$$

Determine number- and weight-average molecular weights M_n and M_w as functions of p.

Answer

M_n and M_w are given by

$$M_n = m_0\sum_{n=1}^{\infty} np^{n-1}(1 - p) = \frac{m_0}{1 - p} \tag{9.5.4}$$

and

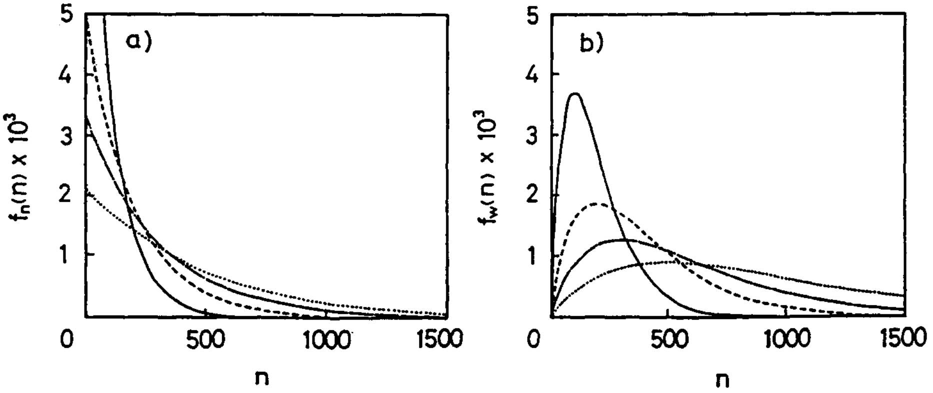

Fig. 9-5 Schulz-Flory distribution function for n_n=100 (solid line), 200 (broken line), 500 (chain line) and 1000 (dot line)

$$M_w = m_0 \sum_{n=1}^{\infty} n^2 p^{n-1}(1-p)^2 = m_0\left\{(1+p)/(1-p)\right\} \tag{9.5.5}$$

respectively, where m_0 is the molecular weight of a monomer. Here we use the relationships

$$\sum_{n=1}^{\infty} np^{n-1} = \frac{1}{(1-p)^2} \tag{9.5.6}$$

and

$$\sum_{n=1}^{\infty} n^2 p^{n-1} = \frac{1+p}{(1-p)^3} \tag{9.5.7}$$

Eq. (9.5.3) also holds for polymers obtained in the steady state of initiation reaction, growth reaction and termination reaction in the **addition polymerization** and the termination reaction by disproportionation and for polymers produced by a random degradation reaction. The molecular weight distribution of the latter polymers is the **most probable distribution.** Figure 9-5 shows $f_n(n)$ in Eq. (9.5.1) and $f_w(n)$ in Eq. (9.5.3) for various n_n.

<<Problem 9-5-b>> Condensation polymerization (II)

Derive the **expression for z-average and viscosity-average degree of polymerization** for the probability of condensation reaction p.

Answer

z-average degree of polymerization defined by (See i=3 in Eq. (9.1.7))

$$n_z = \frac{\sum n^3 f_n(n)}{\sum n^2 f_n(n)} \tag{9.5.8}$$

is expressed as

$$n_z = \frac{\sum n^3 p^{n-1}(1-p)}{\sum n^2 p^{n-1}(1-p)} \tag{9.5.9}$$

Here, we use the relationship

$$\sum n^3 p^{n-1} = \frac{d}{dp}\left[p\sum n^2 p^{n-1}\right] \tag{9.5.10}$$

From Eq. (9.5.7), we have

$$p\sum n^2 p^{n-1} = \frac{p(1+p)}{(1-p)^3} \tag{9.5.11}$$

Differentiation of Eq. (9.5.11) with respect to p yields

$$\frac{d}{dp}\left[p\sum n^2 p^{n-1}\right] = \frac{\{(1+p)+p\}(1-p)^3 - 3(1-p)^2(-1)\,p\,(1+p)}{(1-p)^6}$$

$$= \frac{1+4p+p^2}{(1-p)^4} \tag{9.5.12}$$

Substitution of Eqs. (9.5.7) and (9.5.12) in Eq. (9.5.9) yields

$$n_z = \frac{(1+4p+p^2)}{(1-p)^4} \Big/ \frac{(1+p)}{(1-p)^3} = \frac{1+4p+p^2}{(1+p)(1-p)} \tag{9.5.13}$$

Viscosity-average degree of polymerization is defined by

$$n_v = \left[\frac{\sum n^{1+a} f_n(n)}{\sum n f_n(n)}\right]^{1/a}$$

From Eqs. (9.3.7) and (9.5.1), we have

$$n_v = \left[\frac{\sum n^{1+a} p^{n-1}(1-p)}{\sum n p^{n-1}(1-p)}\right]^{1/a} = \left[\frac{\sum n^{1+a} p^{n-1}}{\sum n p^{n-1}}\right]^{1/a} \tag{9.5.14}$$

Using the relationship

$$\sum n p^{n-1} = \frac{1}{(1-p)^2} \tag{9.5.15}$$

Eq. (9.5.14) is rewritten as

$$n_v = \left[\sum n^{1+a} p^{n-1} (1 - p)^2\right]^{1/a} \tag{9.5.16}$$

The right-hand side of Eq. (9.5.16) is calculated as follows. For convenience, sum is replaced by integral as

$$\sum_{n=1}^{\infty} n^{1+a} p^{n-1} = \int_0^{\infty} n^{1+a} p^{n-1} dn = \frac{1}{p}\int_0^{\infty} n^{1+a} p^n dn \tag{9.5.17}$$

Putting $p^n = X$ ($p<1$),

$$n = \frac{\ln X}{\ln p}, \quad dn = \frac{1}{\ln p}\frac{dX}{X} \tag{9.5.18}$$

Substitution of Eq. (9.5.18) in Eq. (9.5.17) yields

$$\begin{aligned} \frac{1}{p}\int_0^{\infty} n^{1+a} p^n dn &= \frac{1}{p}\int_1^0 \left(\frac{\ln X}{\ln p}\right)^{1+a} X \frac{dX}{X \ln p} \\ &= \frac{1}{p}\frac{(-1)}{(-\ln p)^{2+a}}\int_1^0 (-\ln X)^{1+a} dX \end{aligned} \tag{9.5.19}$$

Putting

$$X = \exp(-z), \quad dX = -X dz \tag{9.5.20}$$

Eq. (9.5.19) is further reduced to

$$\begin{aligned} \frac{1}{p}\int_0^{\infty} n^{1+a} p^n dn &= \frac{1}{p}\frac{(-1)}{(-\ln p)^{2+a}}\int_0^{\infty} z^{1+a} \exp(-z)\, dz \\ &= \frac{1}{p}\frac{(-1)}{(-\ln p)^{2+a}}\Gamma(2+a) \end{aligned} \tag{9.5.21}$$

where $\Gamma(h)$ is the Gamma function

$$\Gamma(h) = \int_0^{\infty} z^{h-1} \exp(-z)\, dz \tag{9.5.22}$$

Substitution of Eq. (9.5.21) in Eq. (9.5.16) yields

$$n_v = \left[\frac{1}{p} \frac{1}{\left(-\ln p\right)^{2+a}} \Gamma\left(2+a\right) \left(1-p\right)^2 \right]^{1/a} \tag{9.5.23}$$

For p~1,

$$-\ln p = 1 - p \tag{9.5.24}$$

Then Eq. (9.5.23) is rewritten as

$$n_v = \left[\frac{1}{p} \frac{\Gamma\left(2+a\right)}{\left(-\ln p\right)^{a}} \right]^{1/a} \tag{9.5.25}$$

From Eqs. (9.5.4) and (9.5.24), we have

$$n_n = \frac{1}{-\ln p} \tag{9.5.26}$$

If we approximate 1/p~1, Eq. (9.5.25) is reduced to

$$n_v = \left[n_n{}^{a} \Gamma\left(2+a\right) \right]^{1/a} = n_n \Gamma\left(2+a\right)^{1/a} \tag{9.5.27}$$

---

* Gamma function defined by

$$\Gamma(s) = \int_0^\infty e^{-x} x^{s-1}\, dx \quad (s>0) \tag{9.5.28}$$

converges. Putting $x=t^2$, we have

$$\Gamma(s) = 2\int_0^\infty e^{-x^2} x^{2s-1}\, dx \quad (s>0) \tag{9.5.29}$$

Then we can deduce a recursion equation as

$$\Gamma\left(s+1\right) = \int_0^\infty e^{-x} x^{s} dx = \lim_{\varepsilon \to 0} \int_\varepsilon^1 e^{-x} x^{s} dx + \lim_{b \to \infty} \int_1^b e^{-x} x^{s} dx$$

$$= \lim_{\varepsilon \to 0} \left(\left[-e^{-x} x^{s} \right]_\varepsilon^1 + s\int_\varepsilon^1 e^{-x} x^{s-1} dx \right) + \lim_{b \to \infty} \left(\left[-e^{-x} x^{s} \right]_1^b + s\int_1^b e^{-x} x^{s-1} dx \right)$$

$$= -e^{-1} + s\int_0^1 e^{-x}x^{s-1}dx + e^{-1} + s\int_1^\infty e^{-x}x^{s-1}dx = s\int_0^\infty e^{-x}x^{s-1}dx = s\Gamma(s) \tag{9.5.30}$$

For s=1 and 1/2, we have

$$\Gamma(1) = \int_0^\infty e^{-x}dx = 1 \tag{9.5.31}$$

and

$$\Gamma\left(\frac{1}{2}\right) = 2\int_0^\infty e^{-x^2}dx = \sqrt{\pi} \tag{9.5.32}$$

The important properties of Gamma function are summarized as follows.

(1)

$$\Gamma(1) = 1\ ,\ \Gamma\left(\frac{1}{2}\right) = \sqrt{\pi} \tag{9.5.33}$$

(2) when n is a natural number,

$$\Gamma(n+1) = n! \tag{9.5.34}$$

(3)

$$\Gamma(s+1) = s\Gamma(s) \tag{9.5.35}$$

$\Gamma(s)$ becomes very large when $s \to \infty$. Stirling's law of

$$\lim_{s \to \infty} \frac{\Gamma(s+1)}{s^{s+1/2}e^{-s}} = \sqrt{2\pi} \tag{9.5.36}$$

is well known.

<<Problem 9-6>> Condensation polymerization (III)

Show that the weight distribution function for condensation reaction

$$f_w(n) = np^{n-1}(1 - p)^2 \tag{9.5.3}$$

is approximated by the exponential distribution function

$$f_w(n) = \frac{1}{(n_n)^2}\, n \exp(-n/n_n) \tag{9.6.1}$$

when $p^{-1} \sim 1$

Answer

From Eqs. (9.5.24) and (9.5.26),

$$n_n = \frac{1}{-\ln p} = \frac{1}{1-p} \tag{9.6.2}$$

Eq. (9.6.2) is rewritten as

$$p = \exp\left(-1/n_n\right) \tag{9.6.3}$$

and then

$$p^n = \exp\left(-n/n_n\right) \tag{9.6.4}$$

From Eq. (9.6.2),

$$\left(1-p\right)^2 = \frac{1}{\left(n_n\right)^2} \tag{9.6.5}$$

Substitution of Eqs. (9.6.4) and (9.6.5) in Eq. (9.5.3) yields

$$f_w(n) = p^{-1} n \frac{1}{\left(n_n\right)^2} \exp\left(-n/n_n\right) = p^{-1} \frac{1}{\left(n_n\right)^2} n \exp\left(-n/n_n\right) \tag{9.6.6}$$

Thus, if we approximate $p^{-1} \sim 1$ in Eq. (9.6.6), Eq. (9.5.3) agrees with Eq. (9.6.1).

<<Problem 9-7>> Condensation polymerization (IV)

Show the value of n at the maximum, n_{max}, of the most probable weight distribution function

$$f_w(n) = n(1-p)^2 p^{n-1} \tag{9.5.3}$$

agrees with the number-average degree of polymerization, that is,

$$n_{max} = n_n \tag{9.7.1}$$

Answer

Differentiation of Eq. (9.5.3) with respect to n yields

$$\frac{df_w(n)}{dn} = (1 - p)^2 p^{n-1} + n(1 - p)^2 p^{n-1} / \ln p \tag{9.7.2}$$

At the maximum of $f_w(n)$, $df_w(n)/dn=0$. Then,

$$1 + \frac{n_{max}}{\ln p} = 0 \tag{9.7.3}$$

Compared with the relationship

$$-\frac{1}{\ln p} = n_n \tag{9.6.2}$$

Eq. (9.7.1) is derived.

<<Problem 9-8>> Molecular weight distribution function (I)

Schulz showed that the weight distribution function is given by

$$f_w(n) = (- \ln p)^2 n p^n \tag{9.8.1}$$

in some cases (Refer to Eq. (9.16.4)). Compare this equation with the Kuhn-Schulz-Flory distribution function

$$f_w(n) = n p^{n-1} (1 - p)^2 \tag{9.5.3}$$

Answer

ln(1+x) is expanded in a Taylor series as

$$\ln(1 + x) = \sum_{n=1}^{\infty} \frac{x}{n!} \tag{9.8.2}$$

When $x \ll 1$,

$$\ln(1 + x) \propto x \tag{9.8.3}$$

Putting $x=p-1$ ($p \sim 1$) in Eq. (9.8.3), we have

$$\ln p \approx p - 1 \tag{9.8.4}$$

Substitution of Eq. (9.8.4) in Eq. (9.8.1) yields

$$f_w(n) = (1 - p)^2 n p^n \tag{9.8.5}$$

When $n \gg 1$, Eq. (9.8.1) agrees with Eq. (9.5.3).

---

*Schulz distribution function defined by

$$f_w(n) = \left(-\ln p\right)^2 n p^n \tag{9.8.1}$$

or

$$f_n(n) = \left(-\ln p\right) p^n \tag{9.8.6}$$

is generalized as

$$f_w(n) = \left(-\ln p\right)^{k+1} n^k p^n / \Gamma(k+1) \tag{9.8.7}$$

or

$$f_n(n) = \left(-\ln p\right)^k n^{k-1} p^n / \Gamma(k) \tag{9.8.8}$$

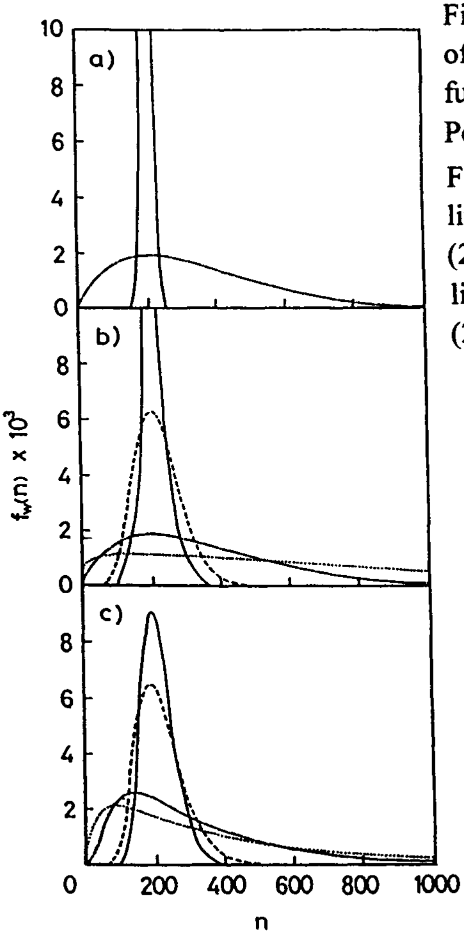

Fig. 9-8.1 Distribution of the degree of polymerization for various distribution functions for n_n=200. a) solid line, Poisson (n_w/n_n=1.005); chain line Schulz-Flory (1.995), b) Schulz-Zimm: solid line (1.05), dashed line (1.1), chain line (2.0) , dot line (5.0), c) Wesslau: solid line (1.05), dashed line (1.1), chain line (2.0) , dot line (5.0)

where Γ(k+1) in Eq. (9.8.7) and Γ(k) in Eq. (9.8.8) are the normalization constants. This distribution function is called the **Schulz-Zimm distribution function**, which is also expressed as

$$f_n(M) = AM^z \exp(-\beta M) \tag{9.8.9}$$

and

$$f_w(M) = \frac{a^{h+1}}{\Gamma(h+1)} \exp(-aM) M^h \tag{9.8.10}$$

with

$$z = h = k \tag{9.8.11}$$

and

$$\beta = a = \{1/(-\ln p)\} M_0 \tag{9.8.12}$$

* Schulz derived Eqs. (9.8.7) and (9.8.8) for **radical polymerization**. Twelve years later, Zimm used these equations for taking account of polydispersity in the analysis of light

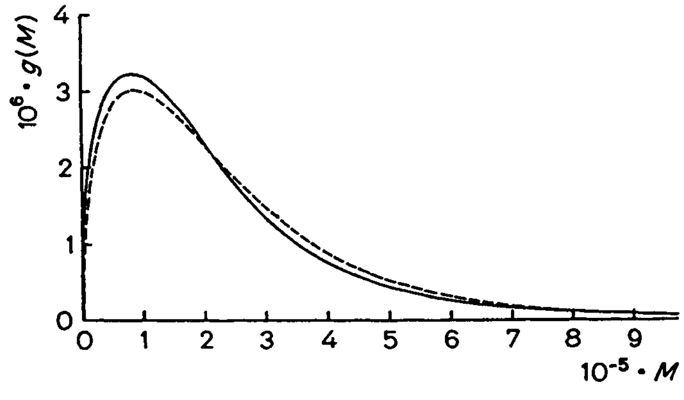

Fig. 9-8.2 Molecular weight distribution curve g(M), measured by gel permeation chromatography (full line) of the original polymer produced by radical polymerization, as compared with that of the model polymer having a Schulz-Zimm distribution with M_w=24.0x10^4 and M_w/M_n=2.80 (broken line). (See K. Kamide, Y. Miyazaki and T. Abe, *Makromol. Chem.* **177**, 485 (1976))

scattering (See G.V.Schulz, *Z.phys.Chem.* **B43**, 25 (1939); B.H.Zimm, *J.Chem.Phys.* **16**, 1093 (1948)).

* Figure 9-8.1 shows the comparison of typical molecular weight distributions, and Fig. 9-8.2 shows an example of the comparison of an observed distribution with a model calculation.

* (1) **Poisson distribution** (See for example, S. M. Ross, *Introduction to Probability Models*, Academic Press, San Diego, 1972)

$$f_w(X) = (X_n)^{X-1}\exp(-X_n) / (X-1)! \qquad (9.8.13)$$

where X is the degree of polymerization

(2) **Schulz-Zimm distribution** (Refer to Eq. (9.8.19))

$$f_w(X) = \frac{y^{h+1}}{\Gamma(h+1)} X^h \exp(-yX) \qquad (9.8.14)$$

where

$$y = h / X_n \qquad (9.8.15)$$

and

$$h = \left(\frac{X_w}{X_n} - 1\right)^{-1} \qquad (9.8.16)$$

(3) **Wesslau distribution** (See H. Wesslau, *Makromol. Chem.* **20**, 111 (1956))

$$g(X) = \frac{1}{X\beta\sqrt{\pi}} \exp\left\{-\frac{1}{\beta^2}\left(\frac{\ln X}{X_0}\right)^2\right\} \qquad (9.8.17)$$

where

$$\beta^2 = 2 \ln X_w / X_n \qquad (9.8.18)$$

and

$$X_0 = X_w / \exp\left(\frac{\beta^2}{4}\right) \qquad (9.8.19)$$

(See <<Problem 9-12>>)

<<Problem 9-9>> Molecular weight distribution function (II)

Calculate the degree of polymerization at the maximum of Schulz-Zimm distribution $f_n(n)$ and $f_w(n)$.

Answer

From Eq. (9.8.8),

$$\frac{\partial f_n(n)}{\partial n} = \frac{(-\ln p)^k}{\Gamma(k)} n^{k-2} p^n (k - 1 + n \ln p) \tag{9.9.1}$$

The value of n which satisfies the condition $\partial f_n(n)/\partial n=0$ is

$$n_{max} = -\frac{k-1}{\ln p} \tag{9.9.2}$$

For k=1 (i.e., the most probable distribution), we have

$$n_{max} = 0 \tag{9.9.3}$$

Similarly, from Eq. (9.8.7),

$$\frac{\partial f_w(n)}{\partial n} = \frac{(-\ln p)^{k+1}}{\Gamma(k+1)} n^{k-1} p^n (k + n \ln p) \tag{9.9.4}$$

The value of n which satisfies the condition $\partial f_w(n)/\partial n=0$ is

$$n_{max} = -\frac{k}{\ln p} \tag{9.9.5}$$

For k=1, we have

$$n_{max} = -\frac{1}{\ln p} = n_n \tag{9.9.6}$$

(Eq. (9.9.6) agrees with Eq. (9.7.1))

---

* Using the relationship Eq. (9.10.5) in <<Problem 9-10>>, n_{max} of $f_n(n)$ (Eq. (9.9.2)) is expressed as

$$n_{max} = \frac{(k-1)n_n}{k} \tag{9.9.7}$$

and n_{max} of $f_w(n)$ (Eq. (9.9.5)) is reduced to

$$n_{max} = n_n \tag{9.9.8}$$

<<Problem 9-10>> Average degree of polymerization for Schulz-Zimm distribution

For the **Schulz-Zimm distribution function**

$$f_n(n) = (-\ln p)^k n^{k-1} p^n / \Gamma(k) \tag{9.8.8}$$

and

$$f_w(n) = (-\ln p)^{k+1} n^k p^n / \Gamma(k+1) \tag{9.8.7}$$

derive n_n, n_w, n_z and n_v.

Answer

(1) n_n

From Eq. (9.1.8),

$$n_n = \int_0^\infty n f_n(n)\, dn \tag{9.10.1}$$

Substitution of Eq. (9.8.8) for $f_n(n)$ in Eq. (9.10.1) yields

$$n_n = \frac{(-\ln p)^k}{\Gamma(k)} \int_0^\infty n^k p^n\, dn \tag{9.10.2}$$

Putting $p^n=X$ ($n=\ln X/\ln p$ and $dn=1/\ln p\ dX/X$), we have

$$\int_0^\infty n^k p^n dn = \int_1^0 \frac{(\ln X)^k}{(\ln p)^k} \frac{X}{\ln p} \frac{dX}{X} = \frac{1}{(\ln p)^{k+1}} \int_1^0 (\ln X)^k dX \tag{9.10.3}$$

Putting $\ln X=-z$ ($X=\exp(-z)$ and $dX/X=-dz$), we have

$$\frac{1}{(\ln p)^{k+1}} \int_1^0 (\ln X)^k dX = \frac{-1}{(\ln p)^{k+1}} \int_0^\infty (-z)^k \exp(-z)\, dz$$

$$= \frac{1}{(-\ln p)^{k+1}} \Gamma(k+1) \tag{9.10.4}$$

Substitution of Eqs. (9.10.3) and Eq. (9.10.4) in Eq. (9.10.2) yields

$$n_n = \frac{(-\ln p)^k}{(-\ln p)^{k+1}} \frac{\Gamma(k+1)}{\Gamma(k)} = \frac{k}{-\ln p} \tag{9.10.5}$$

(2) n_w
From Eq. (9.1.9),

$$n_w = \int_0^\infty n f_w(n)\, dn \tag{9.10.6}$$

Substitution of Eq. (9.8.7) for $f_w(n)$ in Eq. (9.10.6) yields

$$\begin{aligned} n_w &= \int_0^\infty n(-\ln p)^{k+1} n^k p^n / \Gamma(k+1)\, dn \\ &= \frac{(-\ln p)^{k+1}}{\Gamma(k+1)} \int_0^\infty n^{k+1} p^n\, dn \end{aligned} \tag{9.10.7}$$

The integral in Eq. (9.10.7) is calculated in reference to Eqs. (9.10.3) and (9.10.4) as

$$\int_0^\infty n^{k+1} p^n\, dn = \frac{1}{(-\ln p)^{k+2}} \Gamma(k+2) \tag{9.10.8}$$

Substitution of Eq. (9.10.8) in Eq. (9.10.7) yields

$$n_w = \frac{(-\ln p)^{k+1}}{(-\ln p)^{k+2}} \frac{\Gamma(k+2)}{\Gamma(k+1)} = \frac{k+1}{-\ln p} \tag{9.10.9}$$

(3) n_z
From Eq. (9.1.10),

$$n_z = \int_0^\infty n^3 f_n(n)\, dn \Big/ \int_0^\infty n^2 f_n(n)\, dn \tag{9.10.10}$$

Substitution of Eq. (9.8.8) for $f_n(n)$ in Eq. (9.10.10) yields

$$n_z=\int_0^{\infty}\frac{n^3(-\ln p)^k n^{k-1}p^n}{\Gamma(k)}\,dn\bigg/\int_0^{\infty}\frac{n^2(-\ln p)^k n^{k-1}p^n}{\Gamma(k)}\,dn \tag{9.10.11}$$

The numerator of Eq. (9.10.11) is calculated as

$$\int_0^{\infty}\frac{(-\ln p)^k n^{k+2}p^n}{\Gamma(k)}\,dn=\frac{(-\ln p)^k}{\Gamma(k)}\int_0^{\infty}n^{k+2}p^n\,dn=\frac{(-\ln p)^k}{\Gamma(k)}\frac{\Gamma(k+3)}{(-\ln p)^{k+3}}$$

$$=\frac{(k+2)(k+1)}{(-\ln p)^3} \tag{9.10.12}$$

and the denominator of Eq. (9.10.11) is calculated as

$$\int_0^{\infty}\frac{(-\ln p)^k}{\Gamma(k)}n^{k+1}p^n\,dn=\frac{k+1}{(-\ln p)^2} \tag{9.10.13}$$

Substitution of Eqs. (9.10.12) and (9.10.13) in Eq. (9.10.11) yields

$$n_z=\frac{(k+2)(k+1)}{(-\ln p)^3}\frac{(-\ln p)^2}{(k+1)}=\frac{k+2}{-\ln p} \tag{9.10.14}$$

(4) n_v

From Eq. (9.3.7),

$$n_v=\left[\int_0^{\infty}n^{1+a}f_n(n)\,dn\bigg/\int_0^{\infty}nf_n(n)\,dn\right]^{1/a} \tag{9.10.15}$$

Substitution of Eq. (9.8.8) for $f_n(n)$ in Eq. (9.10.15) yields

$$n_v=\left[\int_0^{\infty}n^{1+a}\frac{(-\ln p)^k}{\Gamma(k)}n^{k-1}p^n\,dn\bigg/\int_0^{\infty}n\frac{(-\ln p)^k}{\Gamma(k)}n^{k-1}p^n\,dn\right]^{1/a} \tag{9.10.16}$$

The numerator and the denominator in the bracket of Eq. (9.10.16) are calculated as

$$\int_0^{\infty} \frac{(-\ln p)^k}{\Gamma(k)} n^{a+k} p^n \, dn = \frac{(-\ln p)^k}{\Gamma(k)} \frac{\Gamma(a+k+1)}{(-\ln p)^{a+k+1}} \tag{9.10.17}$$

and

$$\int_0^{\infty} \frac{(-\ln p)^k}{\Gamma(k)} n^k p^n \, dn = \frac{(-\ln p)^k}{\Gamma(k)} \frac{\Gamma(k+1)}{(-\ln p)^{k+1}} \tag{9.10.18}$$

respectively. Substitution of Eqs. (9.10.17) and (9.10.18) in Eq. (9.10.16) yields

$$\begin{aligned} n_v &= \left[\frac{(-\ln p)^k}{\Gamma(k)} \frac{\Gamma(a+k+1)}{(-\ln p)^{a+k+1}} \frac{\Gamma(k)}{(-\ln p)^k} \frac{(-\ln p)^{k+1}}{\Gamma(k+1)} \right]^{1/a} \\ &= \frac{1}{-\ln p} \left\{ \frac{\Gamma(a+k+1)}{\Gamma(k+1)} \right\}^{1/a} \end{aligned} \tag{9.10.19}$$

Using Eq. (9.10.5), Eq. (9.10.19) is further rewritten as

$$n_v = \frac{n_n}{k} \left\{ \frac{\Gamma(a+k+1)}{\Gamma(k+1)} \right\}^{1/a} \tag{9.10.20}$$

We summarize the expressions for n_n, n_w,n_z and n_v for the Schulz-Zimm distribution as

$$n_n = \frac{k}{-\ln p} \tag{9.10.5}$$

$$n_w = \frac{k+1}{-\ln p} \tag{9.10.9}$$

$$n_z = \frac{k+2}{-\ln p} \tag{9.10.14}$$

$$n_v = \frac{n_n}{k}\left\{\frac{\Gamma(a+k+1)}{\Gamma(k+1)}\right\}^{1/a} \tag{9.10.20}$$

For Schulz-Zimm distribution function $f_w(n)$ (Eq. (9.8.11)), we have

$$n_n = \frac{z}{\beta} \tag{9.10.21}$$

$$n_w = \frac{z+1}{\beta} \tag{9.10.22}$$

$$n_z = \frac{z+2}{\beta} \tag{9.10.23}$$

$$n_v = \frac{1}{\beta}\left\{\frac{\Gamma(a+z+1)}{\Gamma(z+1)}\right\}^{1/a} \tag{9.10.24}$$

Using Eqs. (9.10.5), (9.10.9), (9.10.14), we have

$$n_n:n_w:n_z = k:k+1:k+2 \tag{9.10.25}$$

For k=1 (the most probable distribution), we have

$$n_n:n_w:n_z = 1:2:3 \tag{9.10.26}$$

The parameter k reflects the width of the distribution and p depends on the size of the molecules. The polymolecularity index u is related to k as

$$u = \frac{n_w}{n_n} - 1 = \frac{k+1}{k} - 1 = \frac{1}{k} \tag{9.10.27}$$

for the Schulz-Zimm distribution function. When k=1, the Schulz-Zimm distribution is called the most probable distribution (Refer to Eq. (9.5.3)).

<<Problem 9-11>> Average degree of polymerization for the most probable distribution

Calculate the ratio $n_n:n_v:n_w$ for the most probable distribution for a=0.5 and 0.8.

Answer

Putting k=1 in Eqs. (9.10.5), (9.10.20), and (9.10.9), we have

$$n_n = -1/\ln p \tag{9.11.1}$$

$$n_v = n_n \left[\frac{\Gamma(2+a)}{\Gamma(2)} \right]^{1/a} = n_n\, \Gamma(2+a)^{1/a} \tag{9.11.2}$$

$$n_w = -2/\ln p = 2\, n_n \tag{9.11.3}$$

For a=0.5, using the numerical value $\Gamma(2+0.5)^{1/0.5}$=1.766 we have n_n:n_v:n_w=1:1.766:2.0. For a=0.8, using the numerical value $\Gamma(2+0.8)^{1/0.8}$=1.974, we have n_n:n_v:n_w=1:1.974:2.0.

<<Problem 9-12>> Average degree of polymerization for Wesslau distribution

Normal distribution function is expressed as

$$f_w(n) = \frac{\exp\left\{-\left(n - n_m\right)^2 / 2\sigma^2\right\}}{(2\pi)^{1/2}\sigma} \tag{9.12.1}$$

where

$$\sigma^2 = \int_{-\infty}^{+\infty} \left(n - n_m\right)^2 f_w(n)\, dn \tag{9.12.2}$$

and n_m is the median of the distribution. If we replace n by ln n, we have another distribution function

$$f_w(\ln n) = \frac{\exp\left\{-\left(\ln n - \ln n_m\right)^2 / 2\sigma^2\right\}}{(2\pi)^{1/2}\sigma} \tag{9.12.3}$$

which is called the **log-normal distribution** (or **Wesslau distribution**). Eq. (9.12.3) satisfies the normalization condition

$$\int_0^{\infty} f_w(\ln n)\, d(\ln n) = 1 \tag{9.12.4}$$

If the normalization condition

$$\int_0^\infty f_w(n)\,dn = 1 \tag{9.12.5}$$

is used in place of Eq. (9.12.4), we have

$$f_w(n) = \frac{\exp\left\{-\left(\ln n - \ln n_m\right)^2 / 2\sigma^2\right\}}{n\left(2\pi\right)^{1/2}\sigma} \tag{9.12.6}$$

Derive the expression for n_n, n_w, n_v, and n_z for Eq. (9.12.6).

Answer

For convenience, we put

$$t = \frac{\ln n - \ln n_m}{\sigma} \tag{9.12.7}$$

and then

$$\left.\begin{aligned} n &= n_m e^{\sigma t} \\ dn &= n_m \sigma e^{\sigma t} dt \end{aligned}\right\} \tag{9.12.8}$$

Eq. (9.12.6) is rewritten as

$$f_w(n)\,dn = f_w(t)\,dt = \frac{\exp\left(-\frac{t^2}{2} + \sigma t\right)}{\left(2\pi\right)^{1/2} e^{\sigma t}}\,dt \tag{9.12.9}$$

(1) n_n

From Eqs. (9.1.8) and (9.12.6), we have

$$\left(n_n\right)^{-1} = \int_0^\infty \frac{f_w(n)\,dn}{n} = \int_0^\infty \frac{\exp\left\{-\left(\ln n - \ln n_m\right)^2 / 2\sigma^2\right\}}{n^2\left(2\pi\right)^{1/2}\sigma}\,dn$$

$$= \int_{-\infty}^{\infty} \frac{1}{(2\pi)^{1/2}\sigma} \frac{\exp\left(-t^2/2\right) n_m \sigma e^{\sigma t}}{(n_m)^2 e^{2\sigma t}} dt = \int_{-\infty}^{\infty} \frac{1}{(2\pi)^{1/2}} \frac{1}{n_m} \exp\left(-t^2/2 - \sigma t\right) dt$$

(9.12.10)

The exponential term in the integrant is rewritten as

$$\int_{-\infty}^{\infty} \exp\left(-t^2/2 - \sigma t\right) dt = \exp\left(\sigma^2/2\right) \int_{-\infty}^{\infty} \exp\left\{-\left(\frac{t}{\sqrt{2}} + \frac{\sigma}{\sqrt{2}}\right)^2\right\} dt \qquad (9.12.11)$$

Putting $X = t/\sqrt{2} + \sigma/\sqrt{2} (dt = \sqrt{2} dX)$, we perform integration as

$$\int_{-\infty}^{\infty} \exp\left(-\frac{t^2}{2} - \sigma t\right) dt = \exp\left(\sigma^2/2\right) \int_{-\infty}^{\infty} \left[\exp\left(-X^2\right)\right] \sqrt{2}\, dX$$

$$= \sqrt{2} \exp\left(\sigma^2/2\right) \int_{-\infty}^{\infty} \exp\left(-X^2\right) dX = \sqrt{2\pi} \exp\left(\sigma^2/2\right) \qquad (9.12.12)$$

where we use the relationship

$$\int_{-\infty}^{\infty} \exp\left(-\beta X^2\right) dX = \sqrt{\frac{\pi}{\beta}} \qquad (9.12.13)$$

Then Eq. (9.12.10) is further rewritten as

$$n_n = n_m \exp\left(-\sigma^2/2\right) \qquad (9.12.14)$$

(2) n_w

From Eqs. (9.1.9) and (9.12.6), we have

$$n_w = \int_0^{\infty} nf_w(n)\,dn = \int_{-\infty}^{\infty} \frac{n_m \exp(\sigma t)\exp\left\{-t^2/2+\sigma t\right\} n_m}{(2\pi)^{1/2} n_m \exp(\sigma t)}\,dt$$

$$= \int_{-\infty}^{\infty} \frac{n_m \exp\left\{-t^2/2+\sigma t\right\}}{(2\pi)^{1/2}}\,dt = \frac{\exp(\sigma^2/2)\,n_m}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} \exp\left\{-\left(\frac{t}{\sqrt{2}}+\frac{\sigma}{\sqrt{2}}\right)^2\right\} dt$$

$$= \frac{n_m \exp(\sigma^2/2)}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} e^{-X}\sqrt{2}\,dX = \frac{n_m \exp(\sigma^2/2)(2\pi)^{1/2}}{(2\pi)^{1/2}}$$

$$= n_m \exp(\sigma^2/2) \qquad (9.12.15)$$

(3) n_z
From Eqs. (9.1.10), (9.12.9) and (9.12.15), we have

$$n_z = \frac{\int_0^{\infty} n^2 f_w(n)\,dn}{\int_0^{\infty} nf_w(n)\,dn} = \frac{\int_{-\infty}^{\infty} {n_m}^2 \exp(\sigma t)\exp\left\{-t^2/2+\sigma t\right\} dt}{(2\pi)^{1/2} n_m \exp(\sigma^2/2)}$$

$$= \frac{n_m \exp(2\sigma^2)}{(2\pi)^{1/2}\exp(\sigma^2/2)} \int_{-\infty}^{\infty} \exp(-X^2)\sqrt{2}\,dX = n_m \exp\left(\frac{3}{2}\sigma^2\right) \qquad (9.12.16)$$

(4) n_v
From Eqs. (9.10.15) and (9.12.9), we have

$$n_v = \left[\int_0^{\infty} n^a f_w(n)\,dn\right]^{1/a} = \left[\int_{-\infty}^{\infty} \frac{{n_m}^a \exp(a\sigma t)\exp\left(-\frac{t^2}{2}+\sigma t\right)}{(2\pi)^{1/2} n_m \exp(\sigma t)}\,dt\right]^{1/a}$$

$$= \left[\frac{n_m{}^{a}}{(2\pi)^{1/2}} \int_{-\infty}^{\infty} \exp\left\{ -\frac{t^2}{2} + a\sigma t \right\} dt \right]^{1/a}$$

$$= \left[\frac{n_m^{a}}{(2\pi)^{1/2}} \exp\left(\frac{a^2\sigma^2}{2} \right) \int_{-\infty}^{\infty} \exp\left\{ -\left(\frac{t}{\sqrt{2}} + \frac{a\sigma}{\sqrt{2}} \right)^2 \right\} dt \right]^{1/a}$$

$$= n_m \exp\left(\frac{a\sigma^2}{2} \right) \qquad (9.12.17)$$

n_m is defined as the value of n when the cumulative distribution $I_w(n)$ takes the value 0.5. Wesslau proposed Eq. (9.12.2) for describing the molecular weight distribution of polyethylene (See H.Wesslau, *Makromol. Chem.* **20**, 111 (1956)).

<<Problem 9-13>> Average degree of polymerization for Lansing-Kraemer distribution

For the distribution function

$$f_w(n) = \frac{1}{\beta\sqrt{\pi}\, n_n} \exp\left\{ -\left(\frac{1}{\beta} \ln \frac{n}{n_0} \right)^2 \right\} \qquad (9.13.1)$$

derive the expression for n_n,n_w and n_v. This distribution function is called the **Lansing-Kraemer distribution function** (See W.D.Lansing and E.O.Kraemer, *J.Am.Chem.Soc.* **57**, 1369 (1935)).

Answer

(1)n_n

From Eqs. (9.1.8) and (9.13.1), we have

$$\frac{1}{n_n}=\frac{\displaystyle\int_0^\infty \frac{f_w(n)}{n}\,dn}{\displaystyle\int_0^\infty f_w(n)\,dn}=\frac{\displaystyle\int_0^\infty \frac{1}{n}\exp\left\{-\left(\frac{1}{\beta}\ln\frac{n}{n_0}\right)^2\right\}dn}{\displaystyle\int_0^\infty \exp\left\{-\left(\frac{1}{\beta}\ln\frac{n}{n_0}\right)^2\right\}dn} \tag{9.13.2}$$

Putting

$$\frac{1}{\beta}\ln\frac{n}{n_0}=x$$

$$\left.\begin{aligned} n&=n_0\exp(\beta x)\\ dn&=\beta n\,dx=\beta n_0\exp(\beta x)\,dx\end{aligned}\right\} \tag{9.13.3}$$

then Eq. (9.13.2) is rewritten as

$$\frac{1}{n_n}=\frac{\beta\displaystyle\int_{-\infty}^{\infty}\exp\left(-x^2\right)dx}{n_0\beta\displaystyle\int_{-\infty}^{\infty}\exp\left(-x^2\right)\exp(\beta x)\,dx}=\frac{\displaystyle\int_{-\infty}^{\infty}\exp\left(-x^2\right)dx}{n_0\displaystyle\int_{-\infty}^{\infty}\exp\left\{-\left(x-\frac{1}{2}\beta\right)^2\right\}\exp\left(\frac{1}{4}\beta^2\right)dx}$$

$$=\frac{1}{n_0\exp\left(\frac{1}{4}\beta^2\right)}\frac{\displaystyle\int_{-\infty}^{\infty}\exp\left(-x^2\right)dx}{\displaystyle\int_{-\infty}^{\infty}\exp\left\{-\left(x-\frac{1}{2}\beta\right)^2\right\}dx}=\frac{1}{n_0\exp\left(\frac{1}{4}\beta^2\right)}\frac{\sqrt{\pi}}{\sqrt{\pi}}$$

$$=\frac{1}{n_0\exp\left(\frac{1}{4}\beta^2\right)} \tag{9.13.4}$$

We finally find

$$n_n = n_0 \exp\left(\frac{1}{4}\beta^2\right) \tag{9.13.5}$$

(2) n_w

Similarly from Eqs. (9.1.9) and (9.13.1), we have

$$n_w = \frac{\int_0^\infty n f_w(n)\, dn}{\int_0^\infty f_w(n)\, dn} = \frac{\int_0^\infty n \exp\left\{-\left(\frac{1}{\beta}\ln\frac{n}{n_0}\right)^2\right\} dn}{\int_0^\infty \exp\left\{-\left(\frac{1}{\beta}\ln\frac{n}{n_0}\right)^2\right\} dn}$$

$$= n_0 \frac{\exp\left(\beta^2\right)}{\exp\left(\beta^2/4\right)} \frac{\int_{-\infty}^\infty \exp\left\{-(x-\beta)^2\right\} dx}{\int_{-\infty}^\infty \exp\left\{-\left(x-\frac{1}{2}\beta\right)^2\right\} dx} = n_0 \exp\left(\frac{3}{4}\beta^2\right) \tag{9.13.6}$$

(3)n_v

From Eqs. (9.10.15) and (9.13.1),

$$n_v = \left[\frac{\int_0^\infty n^a f_w(n)\, dn}{\int_0^\infty f_w(n)\, dn}\right]^{1/a} = \left[\frac{n_0{}^{a+1}\beta \int_{-\infty}^\infty \exp(a\beta x)\exp\left(-x^2\right)\exp(\beta x)\, dx}{n_0\beta\exp\left(\frac{1}{4}\beta^2\right)}\right]^{1/a}$$

$$= n_0 \left[\frac{\exp\left(\frac{1+a}{2}\right)^2\beta^2}{\exp\left(\frac{1}{4}\beta^2\right)} \int_{-\infty}^\infty \exp\left\{-\left(x-\frac{1+a}{2}\right)^2\right\} dx\right]^{1/a} = n_0\left[\exp\left\{\frac{a}{2}\left(1+\frac{a}{2}\right)\beta^2\right\}\right]^{1/a}$$

$$= n_0 \exp\left\{\left(\frac{2+a}{4}\right)\beta^2\right\} \tag{9.13.7}$$

The ratio of the weight- and the number average molecular weight is a function of only β as

$$\frac{n_w}{n_n} = \frac{n_0 \exp\left(\frac{3}{4}\beta^2\right)}{n_0 \exp\left(\frac{1}{4}\beta^2\right)} = \exp\left(\frac{1}{2}\beta^2\right) \tag{9.13.8}$$

From Eqs. (9.12.14) and (9.12.15), we have

$$\frac{n_w}{n_n} = \frac{\exp\left(\frac{1}{2}\sigma^2\right)}{\exp\left(-\frac{1}{2}\sigma^2\right)} \tag{9.13.9}$$

From Eqs. (9.12.15), (9.12.17) and (9.13.9), we have

$$\frac{n_w}{n_v} = \frac{\exp\left(\frac{\sigma^2}{2}\right)}{\exp\left(\frac{a\,\sigma^2}{2}\right)} \tag{9.13.10}$$

---

* According to Lansing-Kraemer, β is called the homogeneity coefficient,. The maximum of $f_w(n)$ decreases with increasing β.

<<Problem 9-14>> Average degree of polymerization for general log-normal distribution

For the distribution function

$$f_w(n) = An^m \exp\left\{-\frac{1}{\beta}\left(\ln\frac{n}{n_0}\right)^2\right\} \tag{9.14.1}$$

derive the expression for n_n, n_w, and n_v.

Answer

(1) n_n

From Eqs. (9.1.8) and (9.14.1), we have

$$\frac{1}{n_n} = \frac{\int_0^\infty \frac{1}{n} f_w(n)\, dn}{\int_0^\infty f_w(n)\, dn} = \frac{\int_0^\infty A n^{m-1} \exp\left\{ -\frac{1}{\beta}\left(\ln \frac{n}{n_0}\right)^2 \right\} dn}{\int_0^\infty A n^{m} \exp\left\{ -\frac{1}{\beta}\left(\ln \frac{n}{n_0}\right)^2 \right\} dn} \tag{9.14.2}$$

Putting

$$x = \frac{1}{\beta} \ln \frac{n}{n_0}$$

$$\left.\begin{aligned} n &= n_0 \exp(\beta x) \\ dn &= \beta n_0 \exp(\beta x)\, dx \end{aligned}\right\} \tag{9.14.3}$$

we have

$$\frac{1}{n_n} = \frac{\int_{-\infty}^{\infty} n_0{}^m \exp(m\beta x) \exp(-x^2)\, dx}{\int_{-\infty}^{\infty} n_0{}^{m+1} \exp\{(m+1)\beta x\} \exp(-x^2)\, dx}$$

$$= \frac{1}{n_0} \frac{\exp\left(\frac{m^2}{4}\right)}{\exp\left\{\frac{(m+1)^2}{4}\beta^2\right\}} \frac{\int_{-\infty}^{\infty} \exp\left\{ -\left(x - \frac{m\beta}{2}\right)^2 \right\} dx}{\int_{-\infty}^{\infty} \exp\left\{ -\left(x - \frac{(m+1)\beta}{2}\right)^2 \right\} dx}$$

$$= \frac{1}{n_0}\exp\left(-\frac{2m+1}{4}\beta^2\right) \tag{9.14.4}$$

We finally find

$$n_n = n_0\exp\left(\frac{2m+1}{4}\beta^2\right) \tag{9.14.5}$$

(2) n_w

From Eqs. (9.1.9) and (9.14.1), we have

$$n_w = \frac{\int_0^\infty n f_w(n)\,dn}{\int_0^\infty f_w(n)\,dn} = \frac{\int_0^\infty An^{m-1}\exp\left\{-\frac{1}{\beta}\left(\ln\frac{n}{n_0}\right)^2\right\}dn}{\int_0^\infty An^{m}\exp\left\{-\frac{1}{\beta}\left(\ln\frac{n}{n_0}\right)^2\right\}dn} \tag{9.14.6}$$

Similarly to Eq. (9.14.3), we have

$$n_w = \frac{n_0{}^{m+2}\exp\left(\frac{(m+2)^2}{4}\right)}{n_0{}^{m+1}\exp\left\{\frac{(m+1)^2}{4}\beta^2\right\}}\,\frac{\int_{-\infty}^{\infty}\exp\left\{-\left(x-\frac{(m+2)\beta}{2}\right)^2\right\}dx}{\int_{-\infty}^{\infty}\exp\left\{-\left(x-\frac{(m+1)\beta}{2}\right)^2\right\}dx}$$

$$= n_0\exp\left(\frac{2m+3}{4}\beta^2\right) \tag{9.14.7}$$

(3) n_v

From Eqs. (9.10.15) and (9.14.1), we have

$$n_v = \left[\frac{\int_0^{\infty} n^{a} f_w(n)\, dn}{\int_0^{\infty} f_w(n)\, dn} \right]^{\frac{1}{a}} = \left[\frac{\int_0^{\infty} n^{m+a} \exp\left\{ -\frac{1}{\beta}\left(\ln \frac{n}{n_0} \right)^2 \right\} dn}{\int_0^{\infty} n^{m} \exp\left\{ -\frac{1}{\beta}\left(\ln \frac{n}{n_0} \right)^2 \right\} dn} \right]^{\frac{1}{a}} \tag{9.14.8}$$

Using Eq. (9.14.3), Eq. (9.14.8) can be rearranged into

$$n_v = \left[\frac{n_0^{\,m+1+a}}{n_0^{\,m+1}} \, \frac{\exp\left\{ \frac{(m+1+a)^2 \beta^2}{4} \right\}}{\exp\left\{ \frac{(m+1)^2}{4} \beta^2 \right\}} \, \frac{\int_{-\infty}^{\infty} \exp\left\{ -\left(x - \frac{m+1+a}{2} \beta \right)^2 \right\} dx}{\int_{-\infty}^{\infty} \exp\left\{ -\left(x - \frac{(m+1)\beta}{2} \right)^2 \right\} dx} \right]^{\frac{1}{a}}$$

$$= n_0 \exp \frac{(2m+2+a)}{4} \beta^2 \tag{9.14.9}$$

From Eqs. (9.14.5) and (9.14.7),

$$\frac{n_w}{n_n} = \frac{\exp\left(\frac{2m+3}{4} \beta^2 \right)}{\exp\left(\frac{2m+1}{4} \beta^2 \right)} = \exp\left(\frac{\beta^2}{2} \right) \tag{9.14.10}$$

Similarly, from Eqs. (9.14.7) and (9.14.9), we have

$$\frac{n_w}{n_v} = \exp\left(\frac{1-a}{4}\beta^2\right) = \exp\left\{\left(\frac{1-a}{2}\right)\left(\frac{\beta^2}{2}\right)\right\} = \left(\frac{n_w}{n_n}\right)^{\frac{1-a}{2}} \tag{9.14.11}$$

---

* The distribution function Eq. (9.14.1) agrees with Lansing-Kraemer distribution function Eq. (9.13.1) for n=0 and Wesslau distribution function Eq. (9.12.6) for n=-1. Eq. (9.14.1) is the most general log-normal distribution function (See C.Mussa IV, *J.Appl.Polym. Sci.* **1**, 300 (1959); W.F.Espenscheid, M.Kerker and E.Matijevic, *J.Phys.Chem.* **68**, 3093 (1964)).

<<Problem 9-15>> Average degree of polymerization for Poisson distribution

Calculate **n_n, n_w and n_z for the polymer with Poisson molecular weight distribution function** defined by (Refer to Eq. (9.8.13))

$$f_n(n) = \{\exp(-v)\} v^{n-1}/(n-1)! \tag{9.15.1}$$

Answer

(1) From Eqs. (9.1.8) and (9.15.1),

$$n_n = \sum_{n=1}^{\infty} n f_n(n) = \exp(-v) \sum_{n=1}^{\infty} n v^{n-1}/(n-1)!$$

$$= \exp(-v)(1+v)\exp(v) = 1 + v \tag{9.15.2}$$

where

$$\sum f_n(n) = \sum \exp(-v) v^{n-1}/(n-1)! = \exp(-v) \sum v^{n-1}/(n-1)!$$

$$= \exp(-v)\exp(v) = 1 \tag{9.15.3}$$

and

$$\sum n v^{n-1}/(n-1)! = (1+v)\exp(v) \tag{9.15.4}$$

(2) From Eqs. (9.1.9) and (9.15.1),

$$n_w = \frac{\sum_{n=1}^{\infty} n^2 f_n(n)}{\sum_{n=1}^{\infty} n f_n(n)} = \frac{\exp(-v) \sum_{n=1}^{\infty} n^2 v^{n-1}/(n-1)!}{\exp(-v) \sum_{n=1}^{\infty} n v^{n-1}/(n-1)!} = \frac{(1 + 3v + v^2)\exp(v)}{(1+v)\exp(v)}$$

$$= \frac{1 + 3\nu + \nu^2}{1 + \nu} = \frac{\left(1 + \nu\right)^2}{1 + \nu} + \frac{\nu}{1 + \nu} \cong 1 + \nu \qquad (9.15.5)$$

From Eqs. (9.15.2) and (9.15.5), we have

$$n_w = n_n + \frac{\nu}{1 + \nu} \simeq n_n + 1 \qquad (9.15.6)$$

for $\nu >> 1$.

(3) From Eqs. (9.1.10) and (9.15.1),

$$n_z = \frac{\sum_{n=1}^{\infty} n^3 f_n(n)}{\sum_{n=1}^{\infty} n^2 f_n(n)} = \frac{\sum_{n=1}^{\infty} n^3 \nu^{n-1} / \left(n - 1\right)!}{\sum_{n=1}^{\infty} n^2 \nu^{n-1} / \left(n - 1\right)!} \qquad (9.15.7)$$

Using the relationship

$$\sum_{n=1}^{\infty} n^3 \nu^{n-1} / \left(n - 1\right)! = \frac{d}{d\nu}\left[\nu \sum_{n=1}^{\infty} n^2 \nu^{n-1} / \left(n - 1\right)!\right] \qquad (9.15.8)$$

we have

$$\sum_{n=1}^{\infty} n^3 \nu^{n-1} / \left(n - 1\right)! = \frac{d}{d\nu}\left[\nu\left(1 + 3\nu + \nu^2\right)\exp\left(\nu\right)\right]$$

$$= \left(1 + 7\nu + 6\nu^2 + \nu^3\right)\exp\left(\nu\right) \qquad (9.15.9)$$

Substitution of Eq. (9.15.9) in Eq. (9.15.7) yields

$$n_z = \frac{\left(1 + 7\nu + 6\nu^2 + \nu^3\right)\exp \nu}{\left(1 + 3\nu + \nu^2\right)\exp \nu} = \frac{1 + 7\nu + 6\nu^2 + \nu^3}{1 + 3\nu + \nu^2} \cong 6 + \nu \qquad (9.15.10)$$

From Eq. (9.15.6),

$$\frac{n_w}{n_n} = 1 + \frac{\nu}{\left(1 + \nu\right)^2} = 1 + \frac{\nu}{n_n^{\,2}} \qquad (9.15.11)$$

<<Problem 9-16>> Molecular weight distribution for equilibrium condensation polymerization

Consider an equilibrium state of a solution which contains monomers, dimers, trimers and solvent in condensation polymerization. In this case, both polymerization and degradation occur simultaneously (**equilibrium polymerization**). Let's denote the concentration of r-mer and solvent as C_r and C_w, respectively. Then from the law of mass action,

$$\frac{C_2 C_w}{C_1^2} = K_2 \tag{9.16.1}$$

and

$$\frac{C_3 C_w}{C_2 C_1} = K_3 \tag{9.16.2}$$

If we assume the equilibrium constants K_2, K_3... be independent of the degree of polymerization, then

$$K = K_2 = K_3 = \cdots \tag{9.16.3}$$

Show that the weight distribution function is given by

$$f_w(n) = n\,(\ln\alpha)^2 \alpha^n \tag{9.16.4}$$

Answer

The number of moles of i-mer N_i is related to C_i as

$$N_i = C_i V \tag{9.16.5}$$

where V is the total volume of the system. From Eqs. (9.16.1) and (9.16.3),

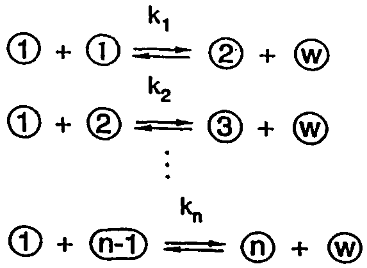

Fig. 9-16 Equilibrium condensation polymerization reaction

$$K = \frac{C_2C_w}{C_1^2} = \frac{N_2N_w}{N_1^2} \tag{9.16.6}$$

From Eqs. (9.16.2) and (9.16.3),

$$K = \frac{C_3C_w}{C_2C_1} = \frac{N_3N_w}{N_2N_1} \tag{9.16.7}$$

In general,

$$K = \frac{N_nN_w}{N_{n-1}N_1} \tag{9.16.8}$$

From Eq. (9.16.6),

$$N_2 = \frac{KN_1^2}{N_w} \tag{9.16.9}$$

From Eq. (9.16.7),

$$N_3 = \frac{KN_1N_2}{N_w} = \left(\frac{KN_1}{N_w}\right)^2 N_1 \tag{9.16.10}$$

From Eq. (9.16.8), the number of moles of n-mer is

$$N_n = \frac{N_1N_{n-1}}{N_w} = \left(\frac{KN_1}{N_w}\right)^{n-1} N_1 \tag{9.16.11}$$

If we put

$$\frac{KN_1}{N_w} = \alpha \tag{9.16.12}$$

Eq. (9.16.11) is rewritten as

$$N_n = N_1\alpha^{n-1} \tag{9.16.13}$$

$f_n(n)$ is proportional to N_n as

$$f_n(n) = (\text{const.})_n\, \alpha^{n-1} \tag{9.16.14}$$

Similarly,

$$f_w(n) = (\text{const.})_w\, n\alpha^{n-1} \tag{9.16.15}$$

From the normalization condition

$$\sum_{n=1}^{\infty} f_w(n) = 1 = \left(\text{const.}\right)_w \sum_{n=1}^{\infty} n\alpha^{n-1} \tag{9.16.16}$$

$$\left(\text{const.}\right)_w = \frac{1}{\sum_{n=1}^{\infty} n\alpha^{n-1}} = \frac{1}{1 + 2\alpha + 3\alpha^2 + \cdots} \tag{9.16.17}$$

When $\alpha<1$,

$$\left(\text{const.}\right)_w \cong (1 - \alpha)^2 \tag{9.16.18}$$

Substitution of Eq. (9.16.18) in Eq. (9.16.15) yields

$$f_w(n) = (1 - \alpha)^2 n\alpha^{n-1} \tag{9.16.19}$$

Approximating

$$1 - \alpha \cong \ln \alpha \tag{9.16.20}$$

and $n \sim n-1 >> 1$, we have Eq. (9.16.4).
(See G.V.Schulz, *Z. phys. Chem.* **A182**, 127 (1938).)

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* From the normalization condition

$$\sum_{n=1}^{\infty} f_n(n) = 1 = \left(\text{const.}\right)_n \sum_{n=1}^{\infty} \alpha^{n-1} \tag{9.16.21}$$

$$\left(\text{const.}\right)_n = \frac{1}{\sum_{n=1}^{\infty} \alpha^{n-1}} = \frac{1}{1 + \alpha + \alpha^2 + \cdots} \tag{9.16.22}$$

Since the right hand side of Eq. (9.16.22) is equal to the series expansion of $(1-\alpha)$,

$$\left(\text{const.}\right)_n \cong 1 - \alpha \tag{9.16.23}$$

From Eqs. (9.16.23) and (9.16.14),

$$f_n(n) = (1 - \alpha)\, \alpha^{n-1} \tag{9.16.24}$$

<<Problem 9-17>> Molecular weight distribution for radical polymerization

Derive the **Schulz-Zimm molecular weight distribution function;**

$$f_n(n) = \frac{(-\ln\alpha)^k}{(k-1)!} n^{k-1} \alpha^n \tag{9.8.8}$$

and

$$f_w(n) = \frac{(-\ln\alpha)^{k+1}}{k!} n^k \alpha^n \tag{9.8.7}$$

based on the mechanism of radical polymerization.

Answer

Let's denote the growth reaction rate as v_B and the termination reaction rate as v_C and the ratio of these two rates as x:

$$\frac{v_C}{v_B} = x \tag{9.17.1}$$

If the probability that the growth reaction occurs on an arbitrary radical be w_B and the probability that the termination reaction occurs on the same radical be w_C, we have

$$\frac{v_C}{v_B} = \frac{w_C}{w_B} = x \tag{9.17.2}$$

From the definition,

$$w_B + w_C = 1 \tag{9.17.3}$$

or

$$w_B = 1 - w_C = \frac{1}{1+x} \tag{9.17.4}$$

If $x \ll 1$, then

$$w_B \cong 1 - x = \alpha \tag{9.17.5}$$

Thus the probability of finding n-mer is proportional to α^n. Let's denote the degree of connectivity, i.e., the number of the primary molecular chain in the reaction as k.

(a) **Case of k=2**

In general, the molecule with the degree of polymerization n is produced by the reaction of x-mer and (n-x)-mer, where x takes the value between 1 (monomer) and n-1. If we denote the distribution function of the primary molecular chain as $f_n^P(x)$,

$$f_n^P(x) = \text{const.}\ \alpha^x \tag{9.17.6}$$

$$f_n^P(n - x) = \text{const.}\ \alpha^{n-x} \tag{9.17.7}$$

Thus the distribution function of n-mer is

$$f_n(n) \propto f_n^P(x) f_n^P(n - x) = \text{const}'.\ \alpha^x \alpha^{n-x} \tag{9.17.8}$$

If n>>1,

$$f_n(n) = \text{const}'.\ \sum_{x=1}^{n} f_n(n,x) = \text{const}'.\ \sum_{x=1}^{n} \alpha^x\ \alpha^{n-x} = \text{const}'.\ n\ \alpha^n \tag{9.17.9}$$

From the normalization condition

$$\int_0^\infty f_n(n)\, dn = \text{const}'.\ \int_0^\infty n\alpha^n dn = 1 \tag{9.17.10}$$

then we have

$$\text{const}'. = \frac{1}{\displaystyle\int_0^\infty n\alpha^n\, dn} = (\ln\alpha)^2 \tag{9.17.11}$$

---

* Using the relationship

$$\int_0^\infty \alpha^n\, dn = \left.\frac{\alpha^n}{\ln\alpha}\right|_0^\infty \tag{9.17.12}$$

we have

$$\int_0^\infty n\alpha^n\, dn = \left.\frac{n\alpha^n}{\ln\alpha} - \frac{\alpha^n}{\ln\alpha^2}\right|_0^\infty \tag{9.17.13}$$

and then

$$\int_0^\infty n\alpha^n\, dn = \frac{1}{(\ln\alpha)^2} \tag{9.17.14}$$

Substitution of Eq. (9.17.11) in Eq. (9.17.9) yields

$$f_n(n) = (\ln \alpha)^2 \cdot n \cdot \alpha^n \tag{9.17.15}$$

Similarly from Eq. (9.17.9),

$$f_w(n) = \text{const}''.\ n\ f_n(n) = \text{const}'''.\ n^2\alpha^n \tag{9.17.16}$$

From the normalization condition

$$\int_0^\infty f_w(n)\, dn = \text{const}'''.\int_0^\infty n^2\, \alpha^n\, dn = 1 \tag{9.17.17}$$

we have

$$\text{const}'''. = -\frac{(\ln \alpha)^3}{2} \tag{9.17.18}$$

From Eqs. (9.17.16) and (9.17.17),

$$f_w(n) = -\frac{(\ln \alpha)^3}{2} \cdot n^2 \cdot \alpha^n \tag{9.17.19}$$

(b) Case of k=3

Suppose the primary molecular chains x_1-mer, x_2-mer and n-x_1-x_2-mer react to produce an r-mer. In reference to Eqs. (9.17.6) and (9.17.7),

$$f_n^P(x_1) = \text{const.}\ \alpha^{x_1} \tag{9.17.20}$$

$$f_n^P(x_2) = \text{const.}\ \alpha^{x_2} \tag{9.17.21}$$

$$f_n^P(n - x_1 - x_2) = \text{const.}\ \alpha^{n - x_1 - x_2} \tag{9.17.22}$$

Thus,

$$f_n(n, x_1, x_2) = \text{const}'.\ \alpha^{x_1} \cdot \alpha^{x_2} \cdot \alpha^{n-x_1-x_2} \tag{9.17.23}$$

$$f_n(n) = \sum_{x_1=1}^{n} \sum_{x_2=1}^{n} f_n(n, x_1, x_2) = \text{const}'.\sum_{x_1=1}^{n} \sum_{x_2=1}^{n} \alpha^n = \text{const}'.\ n^2 \cdot \alpha^n \tag{9.17.24}$$

From the normalization condition,

$$\text{const}'. = -\frac{(\ln \alpha)^3}{2} \tag{9.17.25}$$

Then we have

$$f_n(n) = -\frac{(\ln \alpha)^3}{2} \cdot n^2 \cdot \alpha^n \tag{9.17.26}$$

$$f_w(n) = \frac{(\ln \alpha)^4}{3 \cdot 2} \cdot n^3 \cdot \alpha^n \tag{9.17.27}$$

From Eqs. (9.17.15), (9.17.19), (9.17.26) and (9.17.27), Eqs. (9.8.8) and (9.8.7) are easily derived. In Table 9-18 polymerization methods and corresponding model distribution functions are summarized.

<<Problem 9-18>> Viscosity-average molecular weight

The coefficients K_m and a in the Mark-Houwink-Sakurada viscosity equation

$$[\eta] = K_m M^a \tag{8.30.19}$$

are the constants in a certain temperature range for given polymer/solvent systems. a is usually in the range between 0.5-1. The molecular weight determined from Eq. (8.30.19) is called the **viscosity-average molecular weight** M_v. Discuss what kind of average molecular weight M_v stands for.

Answer

The intrinsic viscosity $[\eta]$ is defined by

$$[\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{C} \tag{8.22.3}$$

where

$$\eta_{sp} = \eta_r - 1 = \frac{\eta}{\eta_0} - 1 \tag{8.22.1}$$

η_r, η and η_0 are the relative viscosity and the viscosities of the solution and solvent, respectively and C is the concentration. If concentration dependence of η_{sp} is negligible,

$$\eta_{sp} = C \lim_{c \to 0} \frac{\eta_{sp}}{C} = C[\eta] \tag{9.18.1}$$

For i th component, Eqs. (8.30.19) and (9.18.1) read

$$\eta_{sp,i} = K_m C_i M_i^{a} \tag{9.18.2}$$

where C_i and M_i are the concentration and the molecular weight, respectively, of *i* th component. Since the total η_{sp} is the sum of η_{sp} of each component, $\eta_{sp,i}$,

$$\eta_{sp} = \sum_i \eta_{sp,i} \tag{9.18.3}$$

Substitution of Eq. (9.18.2) for $\eta_{sp,i}$ in Eq. (9.18.3) yields

$$\eta_{sp} = \sum_i K_m M_i^{a} C_i = K_m \sum_i M_i^{a} C_i \tag{9.18.4}$$

From Eqs. (8.30.19) and (9.18.1),

$$\eta_{sp} = K_m \left(M_v\right)^{a} C \tag{9.18.5}$$

where

$$C = \sum_i C_i \tag{9.18.6}$$

is the total polymer concentration. By comparing Eqs. (9.18.4) and (9.18.5), we have

$$K_m \left(M_v\right)^{a} C = K_m \left(M_v\right)^{a} \sum C_i = K_m \sum M_i^{a} C_i \tag{9.18.7}$$

Then Eq. (9.18.7) is rewritten as

$$M_v = \left[\frac{\sum_i C_i M_i^{a}}{\sum_i C_i} \right]^{\frac{1}{a}} \tag{9.18.8}$$

C_i is related to the weight fraction of i-mer, $f_w(M_i)$, as

$$C_i = \left(\sum_i C_i \right) f_w(M_i) \tag{9.18.9}$$

Substitution of Eq. (9.18.9) for C_i in Eq. (9.18.8) yields (Refer also to Eq. (9.3.7))

Table 9-18 Polymerization method and model distribution function

Most probable distribution	radical polymerization condensation polymerization
Schulz-Zimm distribution	radical polymerization step polymerization
Logarithmic-normal distribution (Wesslau distribution)	Ziegler polymerization
Poisson distribution	living polymerization (ex. Base-catalyzed polymerization of ethylene-oxide)

$$M_v = \left[\frac{\sum_i \left(\sum_i c_i \right) f_w(M_i)\, M_i^{a}}{\sum_i \left(\sum_i c_i \right) f_w(M_i)} \right]^{\frac{1}{a}} = \left[\frac{\sum_i f_w(M_i) M_i^{a}}{\sum_i f_w(M_i)} \right]^{\frac{1}{a}} = \left[\sum_i f_w(M_i)\, M_i^{a} \right]^{\frac{1}{a}}$$

$$= \left[\int_0^\infty M^{a} f_w(M)\, dM \right]^{\frac{1}{a}} = \left[\frac{\int_0^\infty M^{a+1}\, f_n(M)\, dM}{\int_0^\infty M\, f_n(M)\, dM} \right]^{\frac{1}{a}} \tag{9.18.10}$$

Similarly, the viscosity-average degree of polymerization is expressed as

$$n_v = \left[\int_0^\infty n^{a}\, f_w(n)\, dn \right]^{\frac{1}{a}} = \left[\frac{\int_0^\infty n^{a+1}\, f_n(n)\, dn}{\int_0^\infty n\, f_n(n)\, dn} \right]^{\frac{1}{a}} \tag{9.18.11}$$

Eq. (9.18.11) is rewritten as

$$n_v = \left[\frac{\mu_{a+1}}{\mu_1}\right]^{\frac{1}{a}} \tag{9.18.12}$$

where μ_a is a th moment of the degree of polymerization.

<<Problem 9-19>> Effect of molecular weight distribution on Mark-Houwink-Sakurada equation (I): Schulz-Zimm type

The **limiting viscosity number** $[\eta]$ **of polydisperse polymer solutions** is related to the molecular weight distribution function $f_w(M)$ as

$$[\eta] = \int_0^\infty [\eta]_M f_w(M)\, dM \Big/ \int_0^\infty f_w(M)\, dM \tag{9.19.1}$$

where $[\eta]_M$ is the limiting viscosity number of the component with the molecular weight M. Evaluate the effect of molecular weight distribution on the Mark-Houwink-Sakurada equation

$$[\eta] = K_m M^a \tag{8.30.19}$$

which was obtained for monodisperse polymer solutions. Assume **Schulz-Zimm molecular weight distribution function**

$$f_w(M) = \frac{\alpha^{h+1}}{\Gamma(h+1)} \exp(-\alpha M)\, M^h \tag{9.8.14}$$

Answer

Substitution of $[\eta]$ for Eq. (8.30.19) in $[\eta]_M$, Eq. (9.19.1) is rewritten as

$$[\eta] = \int_0^\infty [\eta]_M f_w(M)\, dM = \int_0^\infty K_m M^a f_w(M)\, dM \tag{9.19.2}$$

where

$$\int_0^\infty f_w(M)\, dM = 1 \tag{9.19.3}$$

(See Eq. (9.1.2)) Substitution of Eq. (9.8.14) for $f_w(M)$ in Eq. (9.19.2) yields

$$[\eta] = K_m \int_0^\infty \frac{\alpha^{h+1}}{\Gamma(h+1)} \exp(-\alpha M)\, M^{h+a}\, dM$$

$$= K_m \frac{\alpha^{h+1}}{\Gamma(h+1)} \int_0^\infty \exp(-\alpha M)\, M^{h+a}\, dM \tag{9.19.4}$$

Putting $\alpha M = X$, we have

$$\int_0^\infty \exp(-X) \left(\frac{X}{\alpha}\right)^{h+a} \frac{dX}{\alpha} = \frac{1}{\alpha^{h+a+1}} \int_0^\infty \exp(-X)\, X^{h+a}\, dX$$

$$= \frac{\Gamma(h+a+1)}{\alpha^{h+a+1}} \tag{9.19.5}$$

Substitution of Eq. (9.19.5) in Eq. (9.19.4) yields

$$[\eta] = K_m \frac{\alpha^{h+1}}{\Gamma(h+1)} \cdot \frac{\Gamma(h+a+1)}{\alpha^{h+a+1}} = \frac{K_m}{\alpha^a} \cdot \frac{\Gamma(h+a+1)}{\Gamma(h+1)} \tag{9.19.6}$$

Using the relationships for Schulz-Zimm distribution function

$$M_w = \frac{h+1}{\alpha} \tag{9.10.22)'$$

$$M_n = \frac{h}{\alpha} \tag{9.10.21)'$$

Eq. (9.19.6) is rewritten as

$$[\eta] = K_m \cdot \frac{1}{(h+1)^a} \cdot \frac{\Gamma(h+a+1)}{\Gamma(h+1)} \cdot (M_w)^a \tag{9.19.7}$$

or

$$[\eta] = K_m \cdot \frac{1}{h^a} \cdot \frac{\Gamma(h+a+1)}{\Gamma(h+1)} \cdot (M_n)^a \tag{9.19.8}$$

Using the relationship

$$\Gamma(h+a+1) = (h+a)\,\Gamma(h+a) \tag{9.19.9}$$

Eqs. (9.19.7) and (9.19.8) are further rewritten as

$$[\eta] = K_m \cdot \frac{(h+a)\,\Gamma(h+a)}{(h+1)^a\,\Gamma(h+1)} \cdot (M_w)^a \tag{9.19.10}$$

$$[\eta] = K_m \cdot \frac{(h+a)\,\Gamma(h+a)}{h^a\,\Gamma(h+1)} \cdot (M_n)^a \tag{9.19.11}$$

(See S. Matsumoto and K. Ohyanagi, *Kobunshi Kagaku (Chem. High Polymers)* **17**, 1 (1960)).

<<Problem 9-20>> Effect of molecular weight distribution on Mark-Houwink-Sakurada equation (II): Logarithmic-normal type

Estimate the effect of molecular weight distribution for logarithmic-normal type (Refer to Eqs. (9.13.1) and (9.14.1))

$$f_w(M) = AM\exp\left\{-\frac{1}{\beta}\left(\ln\frac{M}{M_0}\right)^2\right\} \tag{9.20.1}$$

on the Mark-Houwink-Sakurada equation.

Answer

Substitution of Eq. (9.20.1) for $f_w(M)$ in Eq. (9.19.1) yields

$$[\eta] = \frac{K_m \displaystyle\int_0^\infty AM^{a+1}\exp\left\{-p^2\left(\ln\frac{M}{M_0}\right)^2\right\}dM}{\displaystyle\int_0^\infty AM\exp\left\{-p^2\left(\ln\frac{M}{M_0}\right)^2\right\}dM} \tag{9.20.2}$$

The integration is performed to give

$$\frac{\displaystyle\int_0^\infty M^{a+1}\exp\left\{-p^2\left(\ln\frac{M}{M_0}\right)^2\right\}dM}{\displaystyle\int_0^\infty \exp\left\{-p^2\left(\ln\frac{M}{M_0}\right)^2\right\}dM}=\left\{M_0\exp\left(\frac{4+a}{4}\right)\beta^2\right\}^a \tag{9.20.3}$$

Substitution of Eq. (9.20.3) in Eq. (9.20.2) yields

$$[\eta]=K_m\left\{M_0\exp\left(\frac{4+a}{4}\right)\beta^2\right\}^a \tag{9.20.4}$$

Using the relationship for logarithmic-normal distribution function

$$M_w=M_0\exp\left(\frac{5}{4}\beta^2\right) \tag{9.20.5}$$

$$M_n=M_0\exp\left(\frac{3}{4}\beta^2\right) \tag{9.20.6}$$

we have the ratio of M_w and M_n as

$$\frac{M_w}{M_n}=\exp\left(\frac{\beta^2}{2}\right) \tag{9.20.7}$$

Then Eq. (9.20.4) is rewritten as

$$\begin{aligned}[\eta]&=K_m\left\{M_0\exp\left(\frac{5}{4}\beta^2\right)\right\}^a\left\{M_0\exp\left(-\frac{1}{4}+\frac{a}{4}\right)\beta^2\right\}^a\\&=K_m\left\{M_0\exp\left(\frac{5}{4}\beta^2\right)\right\}^a\left\{\exp\frac{\beta^2}{2}\right\}^{\frac{a(a-1)}{2}}=K_m(M_w)^a\left(\frac{M_w}{M_n}\right)^{\frac{a(a-1)}{2}}\end{aligned} \tag{9.20.8}$$

or

$$[\eta]=K_m\left\{M_0\exp\left(\frac{3}{4}\beta^2\right)\right\}^a\left\{\exp\left(\frac{1+a}{4}\beta^2\right)\right\}^a$$

$$= K_m \left(M_n \right)^a \left\{ \exp\left(\frac{\beta^2}{2} \right) \right\}^{\frac{a(1+a)}{2}} = K_m \left(M_n \right)^a \left(\frac{M_w}{M_n} \right)^{\frac{a(1+a)}{2}} \tag{9.20.9}$$

Thus we finally obtain

$$[\eta] = K_m \cdot \left(\frac{M_w}{M_n} \right)^{\frac{a(a-1)}{2}} \cdot \left(M_w \right)^a \tag{9.20.10}$$

and

$$[\eta] = K_m \cdot \left(\frac{M_w}{M_n} \right)^{\frac{a(1+a)}{2}} \cdot \left(M_n \right)^a \tag{9.20.11}$$

(See R. Koningsveld and A.F.Tuijnman, *Makromol. Chem.* **38**, 39 (1966))

<<Problem 9-21>> Effect of molecular weight distribution on Mark-Houwink-Sakurada equation (III)

Demonstrate that the Mark-Houwink-Sakurada equation

$$[\eta] = K_{m,w} M_w^{\,a} \tag{8.30.17'}$$

is not affected by the molecular weight distribution if we use M_w as the molecular weight in case of $a=1$. Assume Schulz-Zimm and logarithmic-normal distribution functions.

Answer

For Schulz-Zimm distribution, we have

$$[\eta] = K_m \cdot \frac{\left(a + h \right) \Gamma\left(a{+}h \right)}{\left(h + 1 \right)^a \Gamma\left(h{+}1 \right)} \cdot \left(M_w \right)^a \tag{9.19.10}$$

For logarithmic-normal distribution, we have

$$[\eta] = K_m \left(\frac{M_w}{M_n} \right)^{\frac{a(a-1)}{2}} \cdot \left(M_w \right)^a \tag{9.20.10}$$

When a=1, both equations (9.19.10) and (9.20.10) are reduced to

$$[\eta]=K_m\left(M_w\right) \tag{9.21.1}$$

Thus the equation

$$K_{m,w}=K_m \tag{9.21.2}$$

holds irrespective of the value of $M_w/M_n(=h)$.

<<Problem 9-22>> Effect of molecular weight distribution on Mark-Houwink-Sakurada equation (IV)

Draw log-log plot of $[\eta]$ vs. M for M_w/M_n=1,2,5,10 and 20 and for a=0.5 and 0.8 using Schulz-Zimm distribution function.

Answer

For Schulz-Zimm distribution function, we have

$$[\eta]=\frac{K_m}{(h+1)^a}\frac{\Gamma(h+a+1)}{\Gamma(h+1)}\cdot M_w^{\,a} \tag{9.19.7}$$

$$[\eta]=K_m\frac{1}{h^a}\frac{\Gamma(h+a+1)}{\Gamma(h+1)}\cdot M_n^{\,a} \tag{9.19.8}$$

$$\frac{M_w}{M_n}=\frac{h+1}{h}=1+\frac{1}{h} \tag{9.8.16'}$$

---

* For Wesslau distribution function, we have

$$[\eta]=K_m\left(\frac{M_w}{M_n}\right)^{\frac{a(a-1)}{2}}\cdot\left(M_w\right)^a \tag{9.20.10}$$

$$[\eta]=K_m\left(\frac{M_w}{M_n}\right)^{\frac{a(a+1)}{2}}\cdot\left(M_n\right)^a \tag{9.20.11}$$

Figure 9-22 shows the relationship between $[\eta]$ and M_w or M_n for various M_w/M_n. For convenience of calculation, we put $K_m=1\times10^{-3}$ for a=0.5 and $K_m=1\times10^{-4}$ for a=0.8. a and K_m have a negative correlation (See T, Kawai and K. Kamide, *J. Polym. Sci.* **54**, 343 (1961)). At constant M_w, $[\eta]$ decreases with increasing the width of the distribution. On the other hand, at a constant M_n, $[\eta]$ increases with increasing the width of the distribution. The effect of the width of the molecular weight distribution on the viscosity equation is larger when M_n is used than when M_w is used. The effect of the width of the distribution increases with increasing a. Thus we should use M_w in order not to be affected by the width of the molecular weight distribution. Empirically, polymer samples can be regarded as homogeneous if $M_w/M_n<1.1$. In this discussion we assumed the width of the molecular weight distribution was constant for all over the molecular weight range. If the width of the distribution increases with increasing the average molecular weight, we cannot regard a as a constant.

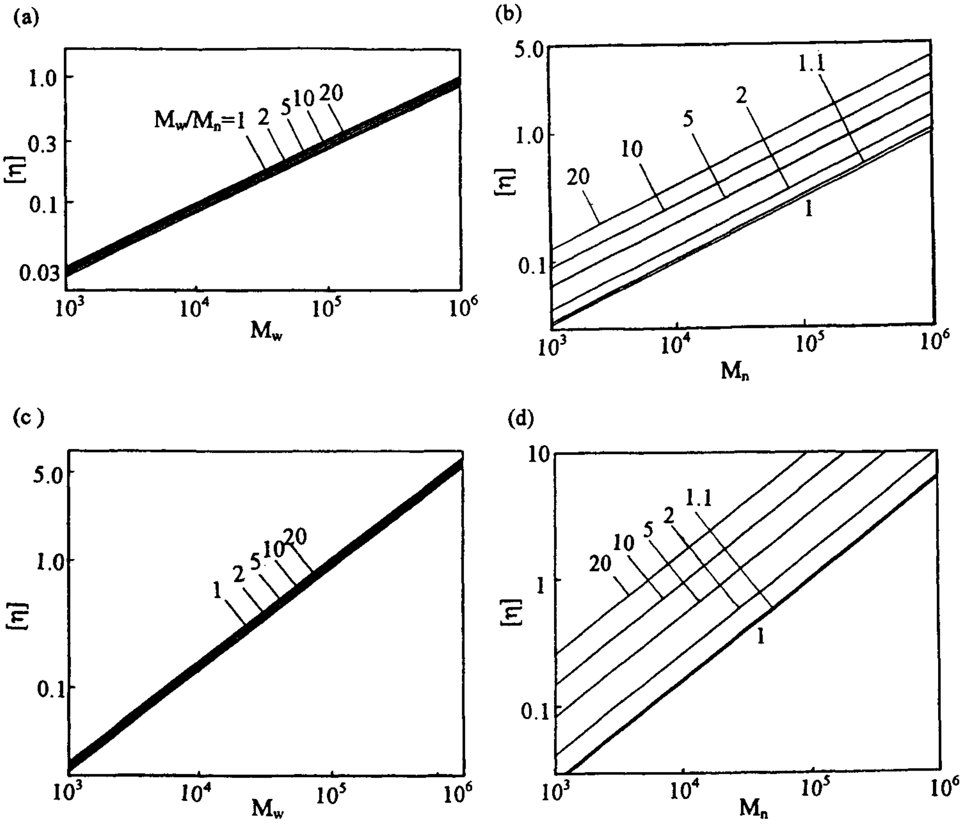

Fig. 9-22 Log-log plots for intrinsic viscosity vs. weight- or number-average molecular weight for the polymer with Schulz-Zimm molecular weight distribution. (a) and (b); a=0.5, (c) and (d); a=0.8 in Mark-Houwink-Sakurada equation.

<<Problem 9-23>> Effect of molecular weight distribution on viscosity parameter Φ

According to Flory's theory , [η] is related to the mean square end-to-end distance $<R^2>$ and the molecular weight M as

$$[\eta] = \Phi \frac{\langle R^2 \rangle^{3/2}}{M} \tag{6.18.2)'}$$

where Φ is called the universal parameter. Discuss the effect of the molecular weight distribution on Φ.

Answer

From the definition,

$$[\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{C} \tag{8.22.5}$$

If we denote [η], R^2 and M of *i* th component as $[\eta]_i$, R_i^2 and M_i, we have

$$\eta_{sp} = \sum_i \eta_{sp,i} = \sum_i \frac{\Phi \langle R_i^2 \rangle^{3/2} \cdot C_i}{M_i} = \Phi \sum_i \frac{\langle R_i^2 \rangle^{3/2} \cdot C_i}{M_i} \tag{9.23.1}$$

The number average of $<R^2>^{3/2}$ is defined by

$$\left\langle \langle R^2 \rangle^{3/2} \right\rangle_n = \frac{\sum_i \left\{ \langle R_i^2 \rangle^{3/2} \cdot C_i / M_i \right\}}{\sum_i \frac{C_i}{M_i}} \tag{9.23.2}$$

Using Eq. (9.23.2), Eq. (9.23.1) is rewritten as

$$\eta_{sp} = \Phi \left\langle \langle R^2 \rangle^{3/2} \right\rangle_n \sum_i \frac{C_i}{M_i} \tag{9.23.3}$$

Using the relationship

$$M_n = \frac{\sum_i C_i}{\sum_i \left(C_i / M_i \right)} \tag{9.23.4}$$

Eq. (9.23.3) is further rewritten as

$$\eta_{sp} = \Phi \left\langle \left\langle R^2 \right\rangle^{3/2} \right\rangle_n \cdot \frac{\sum_i C_i}{M_n} = \Phi \left\langle \left\langle R^2 \right\rangle^{3/2} \right\rangle_n \cdot \frac{C}{M_n} \qquad (9.23.5)$$

Thus,

$$\lim_{C \to 0} \frac{\eta_{sp}}{C} = [\eta] = \Phi \left\langle \left\langle R^2 \right\rangle^{3/2} \right\rangle_n / M_n \qquad (9.23.6)$$

If we use the number-average for $<R^2>^{3/2}$ and M in Eq. (6.18.2)', then Φ is not affected by the molecular weight distribution.

---

* $<R^2>^{3/2}$ and M can be empirically determined by the light scattering method (dissymmetry method and Zimm plot). $<R^2>^{3/2}$ determined from the dissymmetry method is expressed as

$$\left\langle R^2 \right\rangle_d = \sum_i R_i^2 \cdot N_i \cdot M_i^2 / \sum_i N_i \cdot M_i^2 = \sum_i \left(\frac{\left\langle R^2 \right\rangle_0}{M} \right) \cdot \alpha^2 M_z \qquad (9.23.7)$$

where $<R_0^2>$ and α are the unperturbed mean square end-to-end distance and the swelling coefficient, respectively. M determined from the Zimm plot is the weight-average one. Now we can define a correction parameter q by

$$[\eta] = (\Phi / q) \left\langle R^2 \right\rangle_d^{3/2} / M_w \qquad (9.23.8)$$

By comparing Eqs. (9.23.6) and (9.23.8), we have the parameter q as

$$q = \left\langle R^2 \right\rangle_d^{3/2} \cdot M_n / \left\langle \left\langle R^2 \right\rangle^{3/2} \right\rangle_n \cdot M_w \qquad (9.23.9)$$

Using the relationship

$$R^2 \propto M \qquad (9.23.10)$$

Eq. (9.23.11) is further rewritten as

$$q \cong M_z^{3/2} \cdot M_n / M_n^{3/2} \cdot M_w \qquad (9.23.11)$$

(See S. Newman, W. R. Krigbaum, C.Laugier, P.J.Flory, *J.Polym.Sci.* **14**, 459 (1954))

<<Problem 9-24>> Effect of molecular weight distribution on Flory-Fox equation

Derive the equation

$$[\eta] = 6^{3/2}\Phi\left\langle \langle S^2\rangle^{3/2} / M \right\rangle_w \qquad (8.32.8)''$$

for polydisperse polymer solutions based on the Flory-Fox equation and show Eq. (8.32.8)'' agrees with Eq. (9.23.6).

Answer

From Eq. (9.23.1)'' for *i* th component,

$$\eta_{sp,i} = \Phi\langle R_i^2\rangle^{3/2} C_i / M_i \qquad (9.24.1)$$

Using the relationship

$$\langle S^2\rangle = \frac{1}{6}\langle R^2\rangle \qquad (6.9.1)$$

Eq. (9.24.1) is rewritten as

$$\eta_{sp,i} = 6^{3/2}\,\Phi\,\langle S_i^2\rangle^{3/2} C_i / M_i \qquad (9.24.2)$$

Thus we have

$$[\eta] = \lim_{C\to 0}\frac{\eta_{sp}}{C} \cong \frac{6^{3/2}\Phi\sum\limits_i \left\{\langle S_i^2\rangle^{3/2}/M_i\right\}C_i}{\sum\limits_i C_i} = 6^{3/2}\Phi\left\langle \frac{\langle S^2\rangle^{3/2}}{M}\right\rangle_w \qquad (8.32.8)''$$

Eq. (8.32.8)'' is further rewritten as

$$[\eta] = 6^{3/2}\,\Phi\frac{\sum\limits_i \langle S_i^2\rangle^{3/2}\cdot n_i}{\sum\limits_i n_i M_i} = 6^{3/2}\,\Phi\frac{\sum\limits_i \langle S_i^2\rangle^{3/2}\cdot n_i}{\sum\limits_i n_i}\cdot\frac{\sum\limits_i n_i}{\sum\limits_i n_i M_i}$$

$$= 6^{3/2}\,\Phi\left\langle\langle S^2\rangle^{3/2}\right\rangle_n / M_n \qquad (9.24.3)$$

which agrees with Eq. (9.23.6) (See L.D. Moore, *J. Polym. Sci.* **36,** 155

(1959)).

<<Problem 9-25>> Correction parameter q for viscosity parameter Φ

If weight- and z-average values are used for <R^2> and M, respectively, **the correction parameter q for the Flory viscosity parameter Φ** is defined by (Refer to (9.23.8))

$$q_w^{-1} = \frac{[\eta] M_w}{\langle R^2 \rangle_w^{3/2} \Phi} \tag{9.25.1}$$

and

$$q_z^{-1} = \frac{[\eta] M_z}{\langle R^2 \rangle_z^{3/2} \Phi} \tag{9.25.2}$$

Evaluate q_w and q_z for

(1) Schulz-Zimm distribution

$$f_w(M) = \frac{\alpha^{h+1}}{\Gamma(h+1)} \exp(-\alpha M) M^h \tag{9.8.10}$$

and

(2) Lansing-Kraemer distribution

$$f_w(M) = \frac{1}{\beta\sqrt{\pi}\, M_n} \exp\left\{ -\left(\frac{1}{\beta} \ln \frac{M}{M_0} \right)^2 \right\} \tag{9.13.1}$$

on the assumption of an approximate equation

$$R^2 = k\, M \tag{9.25.3}$$

Answer

Comparing Eq. (9.25.1) or (9.25.2) with the equation

$$[\eta] = \Phi \left\langle \langle R^2 \rangle^{3/2} \right\rangle_n / M_n \tag{9.23.6}$$

we have

$$q_w = \left(M_n / M_w\right)\left\{\left(\left\langle R^2\right\rangle_w\right)^{3/2} / \left\langle\left\langle R^2\right\rangle^{3/2}\right\rangle_n\right\} \tag{9.25.4}$$

and

$$q_z = \left(M_n / M_z\right)\left\{\left(\left\langle R^2\right\rangle_z\right)^{3/2} / \left\langle\left\langle R^2\right\rangle^{3/2}\right\rangle_n\right\} \tag{9.25.5}$$

(1) For Schulz-Zimm distribution,

$$\frac{M_w}{M_n} = \frac{h+1}{h} \tag{9.25.6a}$$

and

$$\frac{M_z}{M_n} = \frac{h+2}{h} \tag{9.25.6b}$$

Number average of 3/2 power of R^2 is expressed as

$$\left\langle\left\langle R^2\right\rangle^{3/2}\right\rangle_n = k^{3/2}\left\langle M^{3/2}\right\rangle_n$$

$$= k^{3/2}\frac{\displaystyle\int_0^\infty M^{3/2}\frac{f_w(M)}{M}\,dM}{\displaystyle\int_0^\infty \frac{f_w(M)}{M}\,dM} = k^{3/2}\frac{\displaystyle\int_0^\infty M^{1/2}f_w(M)\,dM}{\displaystyle\int_0^\infty \frac{f_w(M)}{M}\,dM} \tag{9.25.7}$$

For the distribution function of Eq. (9.8.10), we have

$$\int_0^\infty M^{1/2}f_w(M)\,dM = \int_0^\infty \frac{\alpha^{h+1}}{\Gamma(h+1)}\exp(-\alpha M)\,M^{h+1/2}\,dM$$

$$= \frac{\alpha^{h+1}}{\Gamma(h+1)}\cdot\frac{1}{\alpha^{h+3/2}}\int_0^\infty \exp(-x)\left(\frac{x}{\alpha}\right)^{h+1/2} d\left(\frac{x}{\alpha}\right)$$

$$= \frac{1}{\Gamma(h+1)\alpha^{1/2}}\,\Gamma\left(h+\frac{3}{2}\right) = \frac{M_n^{1/2}}{h^{1/2}}\,\frac{\Gamma\left(h+\frac{3}{2}\right)}{\Gamma(h+1)} \tag{9.25.8}$$

and

$$\int_0^\infty \frac{f_w(M)}{M}\,dM = \int_0^\infty \frac{\alpha^{h+1}}{\Gamma(h+1)}\exp(-\alpha M)\,M^{h-1}dM$$

$$= \frac{\alpha^{h+1}}{\Gamma(h+1)}\,\frac{1}{\alpha^h}\int_0^\infty \exp(-x)\,x^{h-1}\,dx$$

$$= \frac{\alpha}{\Gamma(h+1)}\,\Gamma(h) = \frac{\alpha}{h} = M_n^{-1} \tag{9.25.9}$$

Substitution of Eqs. (9.25.8) and (9.25.9) in Eq. (9.25.7) yields

$$\left\langle \left\langle R^2 \right\rangle^{3/2} \right\rangle_n = k^{3/2}\frac{\Gamma\left(h+\frac{3}{2}\right)}{\Gamma(h+1)\,\alpha^{1/2}}\,\frac{x}{\alpha} = k^{3/2}\frac{\Gamma\left(h+\frac{3}{2}\right)}{\alpha^{1/2}\Gamma(h+1)}\cdot M_n$$

$$= k^{3/2}\frac{\Gamma\left(h+\frac{3}{2}\right)}{\Gamma(h+1)}\cdot\frac{1}{h^{1/2}}\cdot\left(M_n\right)^{3/2} \tag{9.25.10}$$

Taking weight average of Eq. (9.25.3), we have

$$\left\langle R^2 \right\rangle_w^{\;3/2} = k^{3/2}\left(M_w\right)^{3/2} \qquad \text{with } k = l^2/m_0^2 \tag{9.25.11}$$

Eq. (9.25.4) is rewritten as

$$q_w = \frac{M_n}{M_w}\,\frac{k^{3/2}\left(M_w\right)^{3/2}\Gamma(h+1)\,h^{1/2}}{k^{3/2}\Gamma\left(h+\frac{3}{2}\right)\left(M_n\right)^{3/2}} = \left(\frac{M_w}{M_n}\right)^{1/2}\frac{\Gamma(h+1)}{\Gamma\left(h+\frac{3}{2}\right)}\cdot h^{1/2}$$

$$= \frac{(h+1)^{1/2}\Gamma(h+1)}{\Gamma\left(h+\frac{3}{2}\right)} \tag{9.25.12}$$

Similarly, taking z-average of Eq. (9.25.3), we have

$$\langle R^2\rangle_z^{\ 3/2} = k^{3/2}\left(M_z\right)^{3/2} \tag{9.25.13}$$

Eq. (9.25.5) is rewritten as

$$\begin{aligned} q_z &= \frac{M_n}{M_z}\,\frac{k^{3/2}\left(M_z\right)^{3/2}\Gamma(h+1)\,h^{1/2}}{k^{3/2}\Gamma\left(h+\frac{3}{2}\right)\left(M_n\right)^{3/2}} = \left(\frac{M_z}{M_n}\right)^{1/2}\frac{\Gamma(h+1)}{\Gamma\left(h+\frac{3}{2}\right)}\cdot h^{1/2} \\ &= \frac{(h+2)^{1/2}\Gamma(h+1)}{\Gamma\left(h+\frac{3}{2}\right)} \end{aligned} \tag{9.25.14}$$

(2) For Lansing-Kraemer distribution,

$$\frac{M_w}{M_n} = \exp\left(\frac{\beta^2}{2}\right) \tag{9.13.8}$$

$$\frac{M_z}{M_n} = \exp\left(\beta^2\right) \tag{9.25.15}$$

$$M_z = \exp\left(\frac{5}{4}\,\beta^2\right) \tag{9.25.16}$$

and

$$\int_0^{\infty} M^{1/2} f_w(M)\,dM = \int_0^{\infty} \frac{1}{\beta\sqrt{\pi}\,M_n}\exp\left\{-\left(\frac{1}{\beta}\ln\frac{M}{M_0}\right)^2\right\} M^{1/2}\,dM \tag{9.25.17}$$

Putting $1/\beta \ln M/M_0 = x$,

$$\left.\begin{aligned} M &= M_0\exp(\beta x) \\ dM &= \beta\,M_0\exp(\beta x)\,dx \end{aligned}\right\} \tag{9.25.18}$$

and substituting Eq. (9.25.18) in Eq. (9.25.17), we have

$$\int_0^\infty M^{1/2} f_w(M)\, dM = \frac{1}{\beta\sqrt{\pi}\, M_n} \int_{-\infty}^{\infty} \exp\left(-x^2\right) M_0^{1/2} \exp\left(\frac{\beta}{2}x\right) \beta M_0 \exp(\beta x)\, dx$$

$$= \frac{1}{\beta\sqrt{\pi}\, M_n} \cdot \beta M_0^{3/2} \int_{-\infty}^{\infty} \exp\left(-x^2 + \frac{3}{2}\beta x\right) dx$$

$$= \frac{\beta M_0^{3/2}}{\beta\sqrt{\pi}\, M_n} \int_{-\infty}^{\infty} \exp\left(\frac{3}{4}\beta^2\right) \exp\left\{-\left(x - \frac{3}{4}\beta\right)^2\right\} dx$$

$$= \frac{M_0^{3/2}}{\sqrt{\pi}\, M_n} \cdot \exp\left(\frac{3}{4}\beta^2\right)\sqrt{\pi} = \frac{M_0^{3/2}}{M_n} \exp\left(\frac{3}{4}\beta^2\right) \qquad (9.25.19)$$

Thus, the number- and weight-average in Eq. (9.25.4) are expressed as

$$\left\langle \left\langle R^2 \right\rangle^{3/2} \right\rangle_n = k^{3/2} \frac{M_0^{3/2} \exp\left(\frac{3}{4}\beta^2\right)}{M_n} \cdot M_n = k^{3/2} M_0^{3/2} \exp\left(\frac{3}{4}\beta^2\right)$$

$$= k^{3/2} \left(M_n\right)^{3/2} \exp\left(\frac{3}{8}\beta^2\right) \qquad (9.25.20)$$

and

$$\left\langle R^2 \right\rangle_w^{3/2} = k^{3/2} \left(M_w\right)^{3/2} = k^{3/2} M_0^{3/2} \exp\left(\frac{3}{4}\beta^2 \frac{3}{2}\right) \qquad (9.25.21)$$

respectively. Thus we find

$$q_w = \frac{M_n}{M_w} \frac{k^{3/2} \left(M_w\right)^{3/2}}{k^{3/2} \left(M_n\right)^{3/2} \exp\left(\frac{3}{8}\beta^2\right)} = \left(\frac{M_w}{M_n}\right)^{1/2} \exp\left(-\frac{3}{8}\beta^2\right)$$

$$= \exp\left(\frac{\beta^2}{2}\right) \cdot \exp\left(-\frac{3}{8}\beta^2\right) = \exp\left(\frac{1}{8}\beta^2\right) \qquad (9.25.22)$$

and

$$q_z = \frac{M_n}{M_z}\,\frac{k^{3/2}\left(M_z\right)^{3/2}}{k^{3/2}\left(M_n\right)^{3/2}\exp\left(\frac{3}{8}\beta^2\right)} = \left(\frac{M_z}{M_n}\right)^{1/2}\exp\left(-\frac{3}{8}\beta^2\right)$$
$$= \exp\left(\beta^2\right)\cdot\exp\left(-\frac{3}{8}\beta^2\right) = \exp\left(\frac{5}{8}\beta^2\right) \qquad (9.25.23)$$

<<Problem 9-26>> Effect of molecular weight distribution on parameter $q_{w,z}$

Evaluate the effect of molecular weight distribution on the parameter defined by

$$q_{w,z} = \frac{\left\langle R^2\right\rangle_z^{3/2}\Phi}{[\eta]M_w} \qquad (9.26.1)$$

for Schulz-Zimm distribution.

Answer

Comparing Eq. (9.26.1) with Eq. (9.23.6),

$$q_{w,z} = \left(\frac{M_n}{M_w}\right)\left(\frac{\left\langle R^2\right\rangle_z^{3/2}}{\left\langle\left\langle R^2\right\rangle^{3/2}\right\rangle_n}\right) \qquad (9.26.2)$$

Substitution of Eq. (9.25.13) for $\langle R^2\rangle_z^{3/2}$ and Eq. (9.25.10) for $\langle\langle R^2\rangle^{3/2}\rangle_n$ in Eq. (9.26.2) yields

$$q_{w,z} = \left(\frac{M_n}{M_w}\right)\frac{k^{3/2}M_z^{3/2}\Gamma(h+1)h^{1/2}}{k^{3/2}\Gamma(h+3/2)M_n^{3/2}} = \left(\frac{M_n}{M_w}\right)\left(\frac{M_z}{M_n}\right)^{3/2}\frac{\Gamma(h+1)h^{1/2}}{\Gamma(h+3/2)}$$
$$= \frac{h}{(h+1)}\,\frac{(h+2)^{3/2}}{h^{3/2}}\,\frac{\Gamma(h+1)}{\Gamma(h+3/2)}\,h^{1/2} = \frac{(h+2)^{3/2}\Gamma(h+1)}{(h+1)\Gamma(h+3/2)} \qquad (9.26.3)$$

<<Problem 9-27>> q_w and $q_{w,z}$ for Schulz-Zimm distribution (I)

In <<Problem 9-25>> we assumed $\langle R^2\rangle \propto M$. This assumption is only applicable at θ-state. On the assumption of more general relationship

$$R^2 = k\,M^{1+\varepsilon} \tag{9.27.1}$$

evaluate q_w and $q_{w,z}$ for Schulz-Zimm molecular weight distribution.

Answer

From the definition

$$\left\langle \langle R^2\rangle^{3/2}\right\rangle_n = k^{3/2}\frac{\int_0^\infty M^{1.5+1.5\varepsilon}\frac{f_w(M)}{M}dM}{\int_0^\infty \frac{f_w(M)}{M}dM} = k^{3/2}\frac{\int_0^\infty M^{0.5+1.5\varepsilon}f_w(M)dM}{(M_n)^{-1}} \tag{9.27.2}$$

For Schulz-Zimm distribution function,

$$\begin{aligned}\int_0^\infty M^{0.5+1.5\varepsilon} f_w(M)\,dM &= \int_0^\infty \frac{\alpha^{h+1}}{\Gamma(h+1)}\exp(-\alpha M)\,M^{h+0.5+1.5\varepsilon}dM \\ &= \frac{\alpha^{h+1}}{\Gamma(h+1)}\cdot\frac{\Gamma(h+1.5+1.5\varepsilon)}{\alpha^{h+1.5+1.5\varepsilon}} = \frac{\Gamma(h+1.5+1.5\varepsilon)}{\Gamma(h+1)\,\alpha^{0.5+1.5\varepsilon}} \\ &= \frac{(M_n)^{1/2}}{h^{1/2}\alpha^{1.5\varepsilon}}\frac{\Gamma(h+1.5+1.5\varepsilon)}{\Gamma(h+1)}\end{aligned} \tag{9.27.3}$$

Then we have

$$\left\langle \langle R^2\rangle^{3/2}\right\rangle_n = k^{3/2}\frac{\Gamma(h+1.5+1.5\varepsilon)}{h^{0.5}\alpha^{1.5\varepsilon}\Gamma(h+1)}(M_n)^{3/2} = k^{3/2}\frac{\Gamma(h+1.5+1.5\varepsilon)}{h^{0.5+1.5\varepsilon}\Gamma(h+1)}(M_n)^{3(1+\varepsilon)/2} \tag{9.27.4}$$

Similarly,

$$\left\langle R^2\right\rangle_w = \int_0^\infty \left\langle R^2\right\rangle f_w(M)\,dM = k\int_0^\infty M^{1+\varepsilon} f_w(M)\,dM$$

$$= k\,\frac{\Gamma(h+\varepsilon+2)}{h^{1+\varepsilon}\,\Gamma(h+1)}\,M_n^{1+\varepsilon} \tag{9.27.5}$$

or

$$\left\langle R^2\right\rangle_w^{3/2} = k^{3/2}\,\frac{1}{h^{1.5(1+\varepsilon)}}\left\{\frac{\Gamma(h+\varepsilon+2)}{\Gamma(h+1)}\right\}^{3/2} M_n^{1.5(1+\varepsilon)} \tag{9.27.6}$$

Substitution of Eqs. (9.27.4) and (9.27.6) in Eq. (9.25.4) yields

$$q_w = \left(\frac{M_n}{M_w}\right)\left\{\frac{M_n^{1.5(1+\varepsilon)}}{M_n^{1.5(1+\varepsilon)}}\right\}\left\{\frac{h^{0.5+1.5\varepsilon}}{h^{1.5(1+\varepsilon)}}\right\}\left\{\frac{\Gamma(h+2+\varepsilon)}{\Gamma(h+1)}\right\}^{3/2}\cdot\frac{\Gamma(h+1)}{\Gamma(h+1.5+1.5\varepsilon)}$$

$$= \frac{1}{(h+1)}\left\{\frac{\Gamma(h+2+\varepsilon)}{\Gamma(h+1)}\right\}^{3/2}\cdot\frac{\Gamma(h+1)}{\Gamma(h+1.5+1.5\varepsilon)} \tag{9.27.7}$$

Similarly,

$$\left\langle R^2\right\rangle_z = \frac{\int_0^\infty \left\langle R^2\right\rangle M\,f_w(M)\,dM}{\int_0^\infty M\,f_w(M)\,dM} = \frac{k\int_0^\infty M^{2+\varepsilon} f_w(M)\,dM}{M_z}$$

$$= k\,\frac{\Gamma(h+3+\varepsilon)}{h^{1+\varepsilon}(h+1)\,\Gamma(h+1)}\left(M_n\right)^{1+\varepsilon} \tag{9.27.8}$$

or

$$\left\langle R^2\right\rangle_z^{3/2} = \frac{k^{3/2}}{h^{1.5(1+\varepsilon)}}\left\{\frac{\Gamma(h+3+\varepsilon)}{\Gamma(h+2)}\right\}^{3/2}\left(M_n\right)^{1.5(1+\varepsilon)} \tag{9.27.9}$$

Here we use the relationship

$$(h+1)\,\Gamma(h+1) = \Gamma(h+2) \tag{9.27.10}$$

Substitution of Eqs. (9.27.4) and (9.27.9) in Eq. (9.26.2) yields

$$q_{w,z} = \frac{1}{h+1}\left\{\frac{\Gamma(h+3+\varepsilon)}{\Gamma(h+2)}\right\}^{3/2}\left\{\frac{\Gamma(h+1)}{\Gamma(h+1.5+1.5\varepsilon)}\right\} \qquad (9.27.11)$$

Eqs. (9.27.7) and (9.27.11) agree with Eqs. (9.25.12) and (9.26.3), respectively, when $\varepsilon \to 0$. The power a in the Mark-Houwink-Sakurada equation

$$[\eta] = K_m M^a \qquad (8.30.19)$$

is related to ε as

$$\varepsilon = \frac{a - 0.5}{1.5} \qquad (9.27.12)$$

The upper limit of ε is around 1/3.

<<Problem 9-28>> q_w and $q_{w,z}$ for Schulz-Zimm distribution (II)

Plot the correction parameters q_w, q_z and $q_{w,z}$ as a function of M_w/M_n for Schulz-Zimm distribution function.

Answer

For Schulz-Zimm distribution function,

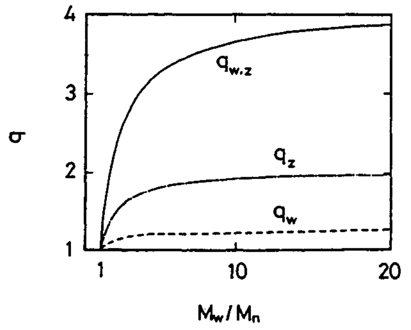

Fig. 9-28 The parameters q_w, q_z and $q_{w,z}$ as a function of molecular weight distribution index

$$q_w = \frac{1}{h+1}\left\{\frac{\Gamma(h+2+\varepsilon)}{\Gamma(h+1)}\right\}^{3/2}\frac{\Gamma(h+1)}{\Gamma(h+1.5+1.5\varepsilon)} \qquad (9.27.7)$$

$$q_z = \frac{1}{h+2}\left\{\frac{\Gamma(h+3+\varepsilon)}{\Gamma(h+2)}\right\}^{3/2}\left\{\frac{\Gamma(h+1)}{\Gamma(h+1.5+1.5\varepsilon)}\right\} \qquad (9.28.1)$$

$$q_{w,z} = \frac{1}{h+1}\left\{\frac{\Gamma(h+3+\varepsilon)}{\Gamma(h+2)}\right\}^{3/2}\left\{\frac{\Gamma(h+1)}{\Gamma(h+1.5+1.5\varepsilon)}\right\} \qquad (9.27.11)$$

Here the expression of q_z is derived in reference to <<Problem 9-27>>. The parameter h is related to M_w/M_n as

$$\frac{n_w}{n_n} = \frac{M_w}{M_n} = 1 + \frac{1}{h} \qquad (9.25.6a)$$

Fig.9-28 is a plot for ε=0.2(a=0.8).

<<Problem 9-29>> Sedimentation coefficient and diffusion coefficient for polydisperse polymer solution (I)

Molecular weight M_{SD} can be determined from the **sedimentation coefficient s_0** and the **diffusion coefficient D_0** using the **Svedberg equation**

$$M_{sD} = \frac{RTs_0}{D_0\left(1 - \bar{v}\rho\right)} \qquad (9.29.1)$$

where ρ is the specific gravity of solvent and $\bar{v}$ is the partial specific volume.

(1) When the polymer has a molecular weight distribution, *n* th power of diffusion coefficient ${}_nD_{mix}$ calculated from *2n* th moment of diffusion curve is equal to the *n* th moment of the weight distribution curve of diffusion coefficient as

$${}_nD^n_{mix} = \frac{\sum_i w_i D_i^n}{\sum_i w_i} \qquad (9.29.2)$$

where w_i is the weight of the monodisperse polymer with the diffusion coefficient D_i. The corresponding sedimentation coefficient is expressed as

$$ {}_n s^n_{mix} = \frac{\sum_i w_i s_i^n}{\sum_i w_i} \tag{9.29.3}$$

(2) The molecular weight dependences of the sedimentation coefficient and the diffusion coefficient are given by

$$ s_i = K_s M_i^{1-\gamma} \tag{9.29.4}$$

and

$$ D_i = K_D M_i^{-\gamma} \tag{9.29.5}$$

respectively. Here, K_S, K_D and γ are the constants which depend on the combination of polymer/solvent and temperature. Evaluate the **effect of molecular weight distribution on M_{SD}**.

Answer

Substitution of Eqs. (9.29.2) and (9.29.3) in s_0 and D_0 of Eq. (9.29.1) yields

$$ {}_nM_{sD} = \left(\frac{RT}{1-v\rho}\right)\left(\frac{\sum_i w_i s_i^n}{\sum_i w_i}\right)^{1/n} \Bigg/ \left(\frac{\sum_i w_i D_i^n}{\sum_i w_i}\right)^{1/n} \tag{9.29.6}$$

The subscript n in ${}_nM_{SD}$ denotes that *n* th moments of s and D are used in the calculation of molecular weight M_{SD}. Substitution of Eqs. (9.29.4) and (9.29.5) in Eq. (9.29.6) yields

$$ {}_nM_{sD} = \left(\frac{RT}{1-\bar{v}\rho}\right)\frac{K_s}{K_D}\left\{\frac{\sum_i w_i M_i^{n(1-\gamma)} \Big/ \sum_i w_i}{\sum_i w_i M_i^{-n\gamma} \Big/ \sum_i w_i}\right\}^{1/n} \tag{9.29.7}$$

s_0 and D_0 are related to the friction coefficient f_0 as

$$s_0 = \frac{M\left(1 - \bar{v}\rho\right)}{f_0} \tag{9.29.8}$$

$$D_0 = \frac{RT}{f_0} \tag{9.29.9}$$

Here the subscript 0 denotes the extrapolated value at the infinitely diluted solution. Then

$$\frac{RT}{\left(1 - \bar{v}\rho\right)} \frac{K_S}{K_D} = 1 \tag{9.29.10}$$

Substitution of Eq. (9.29.10) in Eq. (9.29.7) yields

$${}_n M_{sD} = \left\{ \frac{\sum\limits_i w_i M_i^{n(1-\gamma)}}{\sum\limits_i w_i M_i^{-n\gamma}} \right\}^{1/n} = \left\{ \frac{\sum\limits_i f_w\left(M_i\right) M_i^{n(1-\gamma)}}{\sum\limits_i f_w\left(M_i\right) M_i^{-n\gamma}} \right\}^{1/n} \tag{9.29.11}$$

---

* The sedimentation coefficient is defined by

$$s = \frac{dx/dt}{\omega^2 x} \tag{9.29.12}$$

where x is the distance from the rotational axis, t the time and ω the angular velocity. From the equation of motion of a single solute molecule, Eq.(9.29.8) is derived. (See N. Yamada and H. Matsuda, *Kobunshi Kagaku* **18**, 110 (1961); T. Svedberg, *Kolloid-Z. Eng.* **-Bd. 36**, 53 (1925)).

<<Problem 9-30>> Sedimentation coefficient and diffusion coefficient for polydisperse polymer solution (II)

The **sedimentation coefficient** s_0 determined by the usual sedimentation experiment and the **diffusion coefficient** D_0 determined by the moment method are the weight-average ones. Show

$$M_{SD} = M_w \quad \text{when} \quad \gamma = 0 \tag{9.30.1}$$

and

$$M_{SD} = M_n \quad \text{when} \quad \gamma = 1 \tag{9.30.2}$$

Answer

From the result of <<Problem 9-29>>,

$$_{n}M_{SD}=\left\{\frac{\sum_{i} w_{i} M_{i}^{n(1-\gamma)}}{\sum_{i} w_{i} M_{i}^{-n\gamma}}\right\}^{1/n} \tag{9.30.3}$$

From Eqs. (9.29.2) and (9.29.3), n=1 corresponds to the weight average as

$$_{1}M_{SD}=M_{SD}=\frac{\sum_{i} w_{i} M_{i}^{1-\gamma}}{\sum_{i} w_{i} M_{i}^{-\gamma}} \tag{9.30.4}$$

Then we have

$$M_{SD}=\frac{\sum_{i} w_{i} M_{i}}{\sum_{i} w_{i}}=\frac{\sum_{i} f_{w}(M_{i}) M_{i}}{\sum_{i} f_{w}(M_{i})}=M_{w} \quad \text{when} \quad \gamma=0 \tag{9.30.5}$$

and

$$M_{SD}=\frac{\sum_{i} w_{i}}{\sum_{i}\left(\frac{w_{i}}{M_{i}}\right)}=\frac{\sum_{i} f_{w}(M_{i})}{\sum_{i}\left\{\frac{f_{w}(M_{i})}{M_{i}}\right\}}=M_{n} \quad \text{when} \quad \gamma=1 \tag{9.30.6}$$

<<Problem 9-31>> Radius of gyration for polymer solution with Schulz-Zimm molecular weight distribution (I)

Derive the relationship between weight- and z-average radius of gyration, $<S^2>_w$ and $<S^2>_z$, for polymers with Schulz-Zimm molecular weight distribution.

Answer

$<S^2>$ of monodisperse polymers is expressed as

$$\langle S^2\rangle=k_S M^{1+\beta} \tag{9.31.1}$$

Substituting Eq. (9.31.1) in the Flory-Fox viscosity equation

$$[\eta] = 6^{3/2}\Phi\left\langle S^2\right\rangle^{3/2} / M \tag{8.34.1}$$

and comparing with the Mark-Houwink-Sakurada equation

$$[\eta] = K_m M^a \tag{8.30.19}$$

we have

$$\left(M^{1+\beta}\right)^{3/2} / M = M^a \tag{9.31.2}$$

Then

$$1 + 3\beta = 2a \tag{9.31.3}$$

Here β is a correction for the excluded volume effect. $<S^2>_z$ is defined by

$$\left\langle S^2\right\rangle_z = \frac{\int_0^\infty \left\langle S^2\right\rangle M\, f_w(M)\, dM}{\int_0^\infty M\, f_w(M)\, dM} \tag{9.31.4}$$

For Schulz-Zimm molecular weight distribution function

$$f_w(M) = \frac{a^{h+1}}{\Gamma(h+1)} \exp(-aM)\, M^h \tag{9.8.10}$$

we have

$$\left\langle S^2\right\rangle_z = \frac{\int_0^\infty k_s M^{2+\beta} \frac{a^{h+1}}{\Gamma(h+1)} \exp(-aM)\, M^h\, dM}{\int_0^\infty \frac{a^{h+1}}{\Gamma(h+1)} \exp(-aM)\, M^{h+1}\, dM}$$

$$= \frac{k_s a^{h+1}}{\Gamma(h+1)} \frac{\int_0^\infty M^{2+\beta+h} \exp(-aM)\, dM}{(h+1)/a}$$

$$= \frac{k_s a^{h+1}}{\Gamma(h+1)} \frac{\Gamma(3+\beta+h)}{a^{3+\beta+h}} \cdot \frac{a}{h+1} = \frac{k_s \Gamma(3+\beta+h)}{a^{\beta+2}\Gamma(h+2)} \tag{9.31.5}$$

$<S^2>_w$ is defined by

$$\langle S^2 \rangle_w = \frac{\int_0^\infty \langle S^2 \rangle f_w(M)\, dM}{\int_0^\infty f_w(M)\, dM} \tag{9.31.6}$$

Substitution of Eqs. (9.31.1) and (9.8.10) in Eq. (9.31.6) yields

$$\langle S^2 \rangle_w = \frac{\int_0^\infty k_s M^{1+\beta} \frac{a^{h+1}}{\Gamma(h+1)} \exp(-aM)\, M^h\, dM}{\int_0^\infty \frac{a^{h+1}}{\Gamma(h+1)} \exp(-aM)\, M^{h+1}\, dM}$$

$$= \frac{k_s a^{h+1}}{\Gamma(h+1)} \frac{\Gamma(2+\beta+h)}{a^{2+\beta+h}} = \frac{k_s \Gamma(2+\beta+h)}{a^{\beta+1}\Gamma(h+1)} \tag{9.31.7}$$

The ratio of Eqs. (9.31.5) and (9.31.7) is obtained as

$$\frac{\langle S^2 \rangle_z}{\langle S^2 \rangle_w} = \frac{\Gamma(3+\beta+h)\,\Gamma(h+1)}{\Gamma(h+2)\,\Gamma(2+\beta+h)} = \frac{2+\beta+h}{h+1} \tag{9.31.8}$$

or

$$\langle S^2 \rangle_w = \frac{1+h}{2+\beta+h} \cdot \langle S^2 \rangle_z \tag{9.31.9}$$

Using Eq. (9.31.3), Eq. (9.31.9) is further rewritten as

$$\langle S^2 \rangle_w = \langle S^2 \rangle_z \frac{1+h}{\frac{5}{3} + \frac{2a}{3} + h} \tag{9.31.10}$$

$<S^2>_z$ can be determined from the light scattering method. If the exponent *a* is known, we can evaluate $< S^2>_w$ from $< S^2>_z$. For θ-state (a=0.5), we have

$$\left\langle S^2 \right\rangle_w = \left\langle S^2 \right\rangle_z \frac{1+h}{2+h} \qquad (9.31.11)$$

<<Problem 9-32>> Radius of gyration for polymer solution with Schulz-Zimm molecular weight distribution (II)

Derive the relationship between $<S_0{}^2>_w$ and $<S_0{}^2>_z$ for Schulz-Zimm distribution function. Here $<S_0{}^2>$ is the mean square radius of gyration for the ideal conformation.

Answer

Substitution of β=0 for the ideal conformation in Eq. (9.31.10) yields

$$\left\langle S_o{}^2 \right\rangle_w = \left\langle S_o{}^2 \right\rangle_z \frac{1+h}{2+h} \qquad (9.32.1)$$

For the most probable distribution (M_w/M_n=2 or h=1), the coefficient (1+h)/(2+h) is 2/3.

<<Problem 9-33>> Chemical potential of mixing for polydisperse polymer solution

Entropies of mixing and chemical potentials for monodisperse polymer solutions are given by

$$\Delta S_0 = -R\left\{ \ln\left(1-\phi_1\right) + \left(1-\frac{1}{n}\right)\phi_1 \right\} \qquad (3.8.3)$$

$$\Delta S_1 = -R\left\{ \left(1-n\right)\phi_0 + \ln\left(1-\phi_0\right) \right\} \qquad (3.8.4)$$

$$\Delta\mu_0 = RT\left\{ \ln\left(1-\phi_1\right) + \left(1-\frac{1}{n}\right)\phi_1 + \chi\,\phi_1{}^2 \right\} \qquad (3.11.3)$$

$$\Delta\mu_1 = RT\left\{ \ln\left(1-\phi_0\right) - \left(n-1\right)\phi_0 + \chi\, n\, \phi_0{}^2 \right\} \qquad (3.12.2)$$

where the subscripts 0 and 1 denote solvent and polymer, respectively. Derive the corresponding expressions for polydisperse polymer solutions.

Answer

Consider a process to make a polymer solution by melting crystallized polymer molecules and mixing the polymer in a solvent (See Fig. 9-33). Let's denote the number of moles of polymer molecules with the degree of polymerization n
and the volume fraction as N_n and f_n , respectively.

$$\left.\begin{aligned} & N_1 = \sum_n N_n \\ & \phi_1 = \sum_n \phi_n = \frac{\sum\limits_n n N_n}{N_0 + \sum\limits_n nN_n} \end{aligned}\right\} \qquad (9.33.1)$$

where N_1 and ϕ_1 denote the number of moles of molecules and the volume fraction of the overall polymer. Similarly to <<Problem 3-6>>,

$$\begin{aligned} S = & -k\left[N_0 \ln \phi_0 + \sum_n N_n \ln\left(\frac{\phi_n}{n}\right)\right] \\ & + k\sum_n \left[N_n \ln z + N_n(n-2)\ln(z-1) - N_n \ln \sigma\right] \end{aligned} \qquad (9.33.2)$$

which corresponds to Eq. (3.6.4). The entropy of mixing is calculated as

$$\Delta S = S - S(N_0 = 0) - S(N_1 = N_2 = \cdots = 0) \qquad (9.33.3)$$

The increase in entropy for dissolving amorphous polydisperse polymers in a

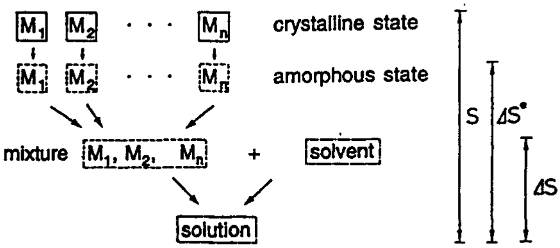

Fig. 9-33 Entropy of mixing for monodisperse polymer solution

solvent is given by

$$\Delta S = -k[N_0 \ln \phi_0 + N_1 \ln \phi_1] \tag{3.7.6}$$

The partial molar entropy is given by

$$\begin{aligned}
\Delta S_0 = \frac{\partial \Delta S}{\partial N_0} = -R & \left[\ln \phi_0 + N_0 \frac{N_0 + \sum_n nN_n}{N_0} \frac{\left(N_0 + \sum_n nN_n - N_0 \right)}{\left(N_0 + \sum_n nN_n \right)^2} \right. \\
& \left. + \sum_n N_n \frac{N_0 + \sum_n nN_n}{\sum_n nN_n} \frac{\left(- \sum_n nN_n \right)}{\left(N_0 + \sum_n nN_n \right)^2} \right] \\
= -R & \left[\ln \phi_0 + \frac{\sum_n nN_n}{N_0 + \sum_n nN_n} - \frac{\sum_n N_n}{\sum_n nN_n} \frac{\sum_n nN_n}{N_0 + \sum_n nN_n} \right] \\
= -R & \left[\ln \phi_0 + \phi_1 - \frac{1}{n_n} \phi_1 \right] = -R \left[\ln\left(1 - \phi_1\right) + \left(1 - \frac{1}{n_n}\right) \phi_1 \right]
\end{aligned} \tag{9.33.4}$$

where

$$n_n = \frac{\sum_n nN_n}{\sum_n N_n} \tag{9.33.5}$$

Thus ΔS_0 for polydisperse polymer solutions is obtained by replacing n by n_n in ΔS_0 for monodisperse polymer solutions. The heat of mixing for monodisperse polymer solutions is given by

$$\Delta H = \frac{BN_0 nN_1}{N_0 + nN_1} \tag{9.33.6}$$

For polydisperse polymer solutions, Eq. (9.33.6) is replaced by

$$\Delta H = \frac{BN_0 \sum_n nN_n}{N_0 + \sum_n nN_n} \tag{9.33.7}$$

The partial molar enthalpy is given by

$$\Delta H_0 = \frac{\partial \Delta H}{\partial N_0} = B \frac{\sum_n nN_n \left(N_0 + \sum_n nN_n \right) - N_0 \sum_n nN_n}{\left(N_0 + \sum_n nN_n \right)^2}$$

$$= B \left(\frac{\sum_n nN_n}{N_0 + \sum_n nN_n} \right)^2 = B\phi_1^{\,2} \tag{9.33.8}$$

Using the expressions for ΔS_0 in Eq. (9.33.4) and ΔH_0 in Eq. (9.33.8), the chemical potential of mixing is given by

$$\Delta\mu_0 = \Delta H_0 - T\Delta S_0 = RT\left\{ \ln\left(1 - \phi_1\right) + \left(1 - \frac{1}{n_n}\right)\phi_1 + \frac{B}{RT}\phi_1^{\,2} \right\}$$

$$= RT\left\{ \ln\left(1 - \phi_1\right) + \left(1 - \frac{1}{n_n}\right)\phi_1 + \chi\,\phi_1^{\,2} \right\} \tag{9.33.9}$$

To derive the expression for $\Delta\mu_n$, we need to derive the expression for

$$\Delta S^* = S - \sum_n S\left(N_0{=}0,\ N_{n'}{=}0\ \left(n'{\neq}n\right)\right) \tag{9.33.10}$$

instead of ΔS. Here, $N_{n'} = 0$ means that the number of moles of polymer except for *n'* th polymer is zero. Substitution of Eq. (9.33.2) in Eq. (9.33.10) yields

$$\Delta S^{*} = -R\left(N_0 \ln \phi_0 + \sum_n N_n \ln \phi_n\right) \tag{9.33.11}$$

From Eq. (9.33.11),

$$\Delta S_n^{*} = \frac{\partial \Delta S^{*}}{\partial N_n} = -R\left\{\ln \phi_n - (n-1) + \phi_1 n\left(1 - \frac{1}{n_n}\right)\right\} \tag{9.33.12}$$

From Eq. (9.33.7),

$$\Delta H_n = \frac{\partial \Delta H}{\partial N_n} = Bn(1 - \phi_1)^2 \tag{9.33.13}$$

Then we have

$$\begin{aligned}\Delta\mu_n &= RT\left\{\ln \phi_n - (n-1) + \phi_1 n\left(1 - \frac{1}{n_n}\right) + \frac{B}{RT} n\left(1 - \phi_1\right)^2\right\} \\ &= RT\left\{\ln \phi_n - (n-1) + \phi_1 n\left(1 - \frac{1}{n_n}\right) + \chi n\left(1 - \phi_1\right)^2\right\}\end{aligned} \tag{9.33.14}$$

Eq. (9.33.14) is reduced to Eq. (3.12.2) for n_n=n.

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