Problems of Polymer Science by the late Professor Hiroshi Fujita
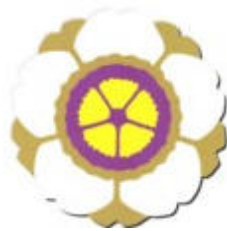
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1 Molecular Weight Distribution and Average Molecular Weights

[Problem A1]

Select at random an unreacted functional group in the polycondensation of a bifunctional monomer. Let p denote the probability that the other end (functional group) of that monomer unit has condensed. It is assumed that p is independent of the length to which end that monomer unit is attached. Show that when p is very close to unity, the number distribution of length j chains, f_j, is represented by

$$f_j = \frac{1}{\langle j \rangle_n} \exp\left(-\frac{j}{\langle j \rangle_n}\right) \tag{1.1}$$

where $\langle j \rangle_n$ denotes the number-average degree of polymerization of the polycondensate.

[Solution A1]

The probability that the chain consists of at least j monomer units is given by p^{j-1}. The probability that any particular group is not condensed is $1-p$. Hence the probability that the chain is limited to exactly j monomer units is $p^{j-1}(1 - p)$. If there were N_m° monomer molecules at the beginning of the polycondensation, the total number of molecules remaining is $N_m^\circ(1 - p)$. Therefore, the number of chains consisting of j monomer units, N_j, is expressed by

$$N_j = N_m^\circ p^{j-1}(1 - p) \tag{1.2}$$

Thus

$$f_j = \frac{N_j}{\text{total number of molecules in the system}}$$
$$= \frac{p^{j-1}(1-p)^2}{\sum_{j=1}^{\infty} p^{j-1}(1-p)^2} = (1-p)p^{j-1} \tag{1.3}$$

The number-average degree of polymerization, $\langle j \rangle_n$, is defined by

$$\langle j \rangle_n = \sum_{j=1}^{\infty} j f_j \tag{1.4}$$

Substitution of Eq.(1.3) gives

$$\langle j \rangle_n = \frac{1}{1-p} \tag{1.5}$$

Solving this for p and putting the result in Eq.(1.3), one gets

$$f_j = \frac{1}{\langle j \rangle_n} \left(1 - \frac{1}{\langle j \rangle_n}\right)^{j-1} \tag{1.6}$$

If p is close to unity, $\langle j \rangle_n$ is very large. For this case, the approximation

$$f_j \to \frac{1}{\langle j \rangle_n} \left(1 - \frac{1}{\langle j \rangle_n}\right)^{\langle j \rangle_n (j / \langle j \rangle_n)}$$
$$\to \frac{1}{\langle j \rangle_n} \exp\left(-\frac{j}{\langle j \rangle_n}\right) \tag{1.7}$$

holds if j is not comparable to unity.

[Problem A2]

Show that in the copolymerization process of a monomer A and a monomer B, the molar concentrations, $[M_A]_t$ and $[M_B]_t$, of unreacted monomers A and B in the system at time t obey the equation

$$\frac{\mathrm{d}[M_A]_t}{\mathrm{d}[M_B]_t} = \frac{[M_A]_t}{[M_B]_t} \frac{r_A[M_A]_t + [M_B]_t}{[M_A]_t + r_B[M_B]_t} \tag{1.8}$$

Here r_A and r_B are defined by

$$r_A = \frac{k_{AA}}{k_{AB}}, \qquad r_B = \frac{k_{BB}}{k_{BA}} \tag{1.9}$$

where k_{xy} (x, y =A, B) denotes the rate constant for the addition of a monomer y to the chain with a monomer x as its active end unit.

[Solution A2]

The rates of change of $[M_A]_t$ and $[M_B]_t$ may be expressed by

$$\frac{\mathrm{d}[M_A]_t}{\mathrm{d}t} = -k_{AA}[M_A]_t[P_A^*]_t - k_{BA}[M_A]_t[P_B^*]_t \tag{1.10}$$

$$\frac{\mathrm{d}[M_B]_t}{\mathrm{d}t} = -k_{AB}[M_B]_t[P_A^*]_t - k_{BB}[M_B]_t[P_B^*]_t \tag{1.11}$$

where $[P_A^*]_t$ denotes the molar concentration of copolymers which have the monomer A as its active end unit, with the corresponding interpretation for $[P_B^*]_t$. We have the additional condition

$$k_{BA}[M_A]_t[P_B^*]_t = k_{AB}[M_B]_t[P_A^*]_t \tag{1.12}$$

because in a long copolymer chain the sequences of A monomers only and those of B monomers only appear alternately. division of Eq.(1.10) by Eq.(1.11), with the consideration of Eq.(1.12), leads to the desired expression for $\mathrm{d}[M_A]_t/\mathrm{d}[M_B]_t$.

[Comments]

The quantities r_A and r_B are called the reactivity ratios of monomers A and B, respectively. Equation (1.12) is strictly valid for infinitely long

copolymer chains. When this equation holds, the system is said to be in the statistically steady (or stationary) state.

If we put

$$\frac{d[M_A]_t}{d[M_B]_t} = f, \qquad \frac{[M_A]_t}{[M_B]_t} = \rho \tag{1.13}$$

the relation for f given in the problem may be rewritten in the form

$$\frac{\rho(f-1)}{f} = \frac{\rho^2}{f} r_A - r_B \tag{1.14}$$

In the initial period of copolymerization, in which the rates of conversion are low, ρ may be replaced in a good approximation by its initial value ρ_0, which can be varied by changing the amounts of the monomers fed into the system. For the approximation $\rho = \rho_0$ the value of f should be independent of time, as can be seen from Eq.(1.14), and it may be determined by measuring the average composition of the copolymers produced in the initial period of copolymerization. In this way, we may obtain values of f for a series of different values of ρ_0, and may plot them in the form of $\rho_0(f-1)/f$ versus ρ_0^2/f. according to Eq.(1.14), the resulting data points shoul follow a straight line, and r_B and r_A may be evaluated from the intercept and the slope of the line, respectively. This type of plot is called the Fineman-Ross plot.
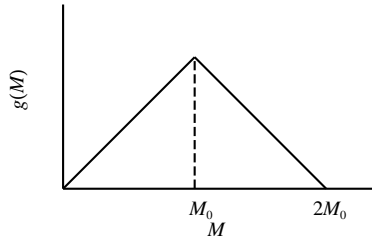
[Problem A3]

Calculate M_n, M_w, and M_z for a sample whose $g(M)$, the weight distribution of M, is represented by a triangle as shown above.

[solution A3]

$g(M)$ may be represented by

$$g(M) = \begin{cases} AM & (0 < M < M_0) \\ -AM + 2AM_0 & (M_0 < M < 2M_0) \\ 0 & (2M_0 < M) \end{cases}$$

The factor A is to be determined from the condition that $\int_0^\infty g(M)\mathrm{d}M = 1$, giving $A = 1/M_0^2$. Thus

$$\begin{aligned} M_n &= \frac{\int_0^\infty g(M)\mathrm{d}M}{\int_0^\infty \frac{g(M)}{M}\mathrm{d}M} \\ &= \frac{M_0}{2\ln 2} = 0.721 M_0 \end{aligned} \tag{1.15}$$

$$\begin{aligned} M_w &= \frac{\int_0^\infty Mg(M)\mathrm{d}M}{\int_0^\infty g(M)\mathrm{d}M} \\ &= M_0 \end{aligned} \tag{1.16}$$

$$\begin{aligned} M_z &= \frac{\int_0^\infty M^2 g(M)\mathrm{d}M}{\int_0^\infty Mg(M)\mathrm{d}M} \\ &= \frac{7M_0}{6} \end{aligned} \tag{1.17}$$

[Problem A4]

Obtain the expressions for M_n, M_v, and M_w of a polymer sample with the (weight) distribution of molecular weight M given by

$$g(M) = \frac{\exp(-\beta^2/4)}{M^*\beta\sqrt{\pi}}\exp\left\{-\frac{[\ln(M/M^*)]^2}{\beta^2}\right\} \tag{1.18}$$

where M^* and β are adjustable (positive) parameters. M_v is the viscosity-average molecular weight defined by

$$M_v = \left[\int_0^\infty g(M)M^\alpha \mathrm{d}M\right]^{1/\alpha} \tag{1.19}$$

[Solution A4]

Let us calculate

$$M_k = \left[\int_0^\infty g(M)M^k \mathrm{d}M\right]^{1/k} \tag{1.20}$$

$k = -1$, α, and 1 correspond to M_n, M_v, and M_w, respectively. Putting

$$M = M^* \mathrm{e}^x \tag{1.21}$$

we obtain

$$M_k = M^*\left[\frac{\exp(-\beta^2/4)}{\beta\sqrt{\pi}}\right]^{1/k}\left\{\int_{-\infty}^\infty \exp\left[(k+1)x - \frac{x^2}{\beta^2}\right]\mathrm{d}x\right\}^{1/k} \tag{1.22}$$

Since

$$\int_{-\infty}^\infty \exp\left[(k+)x - \frac{x^2}{\beta^2}\right]\mathrm{d}x = \exp\left[\frac{\beta^2(k+1)^2}{4}\right]$$

$$\times \int_{-\infty}^\infty \exp\left[-\left(\frac{x}{\beta} - \frac{\beta(k+1)}{2}\right)^2\right]\mathrm{d}x$$

$$= \sqrt{\pi}\beta\exp\left[\frac{\beta^2(k+1)^2}{4}\right] \tag{1.23}$$

$$M_k = M^* \exp\left[\frac{\beta^2(k+2)}{4}\right] \tag{1.24}$$

Thus

$$M_n = M^* \exp\left(\frac{\beta^2}{4}\right) \tag{1.25}$$

$$M_v = M^* \exp\left(\frac{\beta^2(2+\alpha)}{4}\right) \tag{1.26}$$

$$M_w = M^* \exp\left(\frac{3\beta^2}{4}\right) \tag{1.27}$$

Hence

$$\frac{M_v}{M_n} = \exp\left[\frac{\beta^2(1+\alpha)}{4}\right] \tag{1.28}$$

$$\frac{M_w}{M_n} = \exp\left(\frac{\beta^2}{2}\right) \tag{1.29}$$

$$\frac{M_v}{M_w} = \exp\left[-\frac{\beta^2(1-\alpha)}{4}\right] \tag{1.30}$$

For example, when $\beta = 1$, i.e., $M_w/M_n = 1.649$,

$$\frac{M_v}{M_w} = 0.88_2 \quad \text{for } \alpha = 0.5 \tag{1.31}$$

$$\frac{M_v}{M_w} = 0.951 \quad \text{for } \alpha = 0.8 \tag{1.32}$$
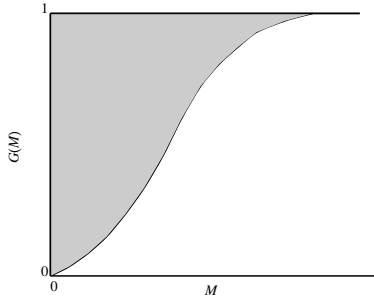
[Comments]

The $g(M)$ defined by Eq.(1.18) is usually called the logarithmic normal distribution of M. For this distribution function

$$M_z = M^* \exp\left(\frac{5\beta^2}{4}\right), \quad M_{z+1} = M^* \exp\left(\frac{7\beta^2}{4}\right), \cdots \tag{1.33}$$

and

$$\frac{M_w}{M_n} = \frac{M_z}{M_w} = \frac{M_{z+1}}{M_z} = \frac{M_{z+2}}{M_{z+1}} = \cdots \tag{1.34}$$

[Problem A5]

Suppose that the curve in the figure represents the integral weight distribution of molecular weights for a polymeric substance. Prove that the area of the shaded region is equal to the weight-average molecular weight of the substance.

[Solution A5]

$$M_w = \int_0^\infty M g(M) \mathrm{d}M \tag{1.35}$$

where $g(M)$ is the differential weight distribution of M. Since $g(M) = \mathrm{d}G(M)/\mathrm{d}M$ [$G(M)$ is the integral weight distribution of M], Eq.(1.35) may be written

$$M_w = \int_0^1 M \mathrm{d}G(M) \tag{1.36}$$

where one has considered tha fact that $M = 0$ and ∞ correspond to $G = 0$ and 1, respectively. One easily sees that the integral in Eq.(1.36) represents the area of the shaded region in the above graph.

[Problem A6]

Show that M_w/M_n and M_z/M_w are measures of the spreads of $f(M)$ and $g(M)$, respectively. Here $f(M)$ and $g(M)$ are the number and weight distributions of molecular weight M in a given polymer sample.

[Solution A6]

From its definition one finds that M_n represents the centroid of an $f(M)$ curve. Hence the standard deviation of $f(M)$, σ_n, may be defined by

$$\sigma_n^2 = \int_0^\infty (M - M_n)^2 f(M) \mathrm{d}M \tag{1.37}$$

and the ratio σ_n/M_n may be regarded as a measure of the spread of $f(M)$. From Eq.(1.37) it follows that

$$
\begin{aligned}
\frac{\sigma_n^2}{M_n^2} =& \frac{1}{M_n^2} \int_0^\infty M^2 f(M) \mathrm{d}M \\
& \frac{2}{M_n} \int_0^\infty M f(M) \mathrm{d}M + \int_0^\infty f(M) \mathrm{d}M \\
=& \frac{M_w}{M_n} - 1
\end{aligned}
\tag{1.38}
$$

Hence

$$\frac{\sigma_n}{M_n} = \left(\frac{M_w}{M_n} - 1 \right)^{1/2} \tag{1.39}$$

which indicates that M_w/M_n is an appropriate measure of the spread of $f(M)$.

In a similar way, one can show that

$$\frac{\sigma_w}{M_w} = \left(\frac{M_z}{M_w} - 1 \right)^{1/2} \tag{1.40}$$

where σ_w is the standard deviation of $g(M)$, defined as

$$\sigma_w^2 = \int_0^\infty (M - M_w)^2 g(M) \mathrm{d}M \tag{1.41}$$

Hence, M_z/M_w is a measure of the spread of $g(M)$.

[Problem A7]

Show for any polydisperse sample of polymer that

$$M_n < M_w < M_z < M_{z+1} < \cdots \qquad (1.42)$$

[Solution A7]

Define A and B by

$$A = (\sum_{i=1}^{N} G_i M_i^{m+1})(\sum_{i=1}^{N} g_i M_i^{m-1}) \qquad (1.43)$$

$$B = (\sum_{i=1}^{N} g_i M_i^{m})^2 \qquad (1.44)$$

where N is the total number of different molecular wights in the sample, g_i is the weight fraction of the $i-$th component with molecular weight M_i, and m is an arbitrary number. It can be shown easily that

$$A - B = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} g_i g_j (M_i M_j)^m f(M_i/M_j) \qquad (1.45)$$

where

$$f(x) = \left(\sqrt{x} - \frac{1}{\sqrt{x}}\right)^2 \qquad (1.46)$$

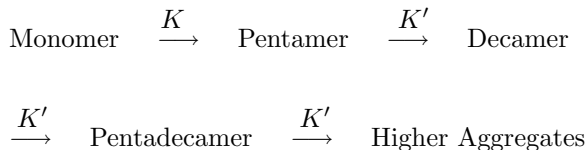The function $f(x)$ is positive for all positive x, except at $x = 1$. This means that $A > B$ for any polydisperse sample. In other words,

$$\frac{\sum_{i=1}^{N} g_i M_i^{m+1}}{\sum_{i=1}^{N} g_i M_i^{m}} > \frac{\sum_{i=1}^{N} g_i M_i^{m}}{\sum_{i=1}^{N} g_i M_i^{m-1}} \qquad (1.47)$$

unless the sample is monodisperse. By putting successively $m = -1$, 0, 1, $2, \cdots$ we obtain from Eq.(1.47) the desired in equalities.

[Problem A8]

A protein called hemocyanin self-associates to a pentamer. The pentamers then tend to stack on each other to produce elongated particles.

$$\text{Monomer} \quad \xrightarrow{K} \quad \text{Pentamer} \quad \xrightarrow{K'} \quad \text{Decamer}$$

$$\xrightarrow{K'} \quad \text{Pentadecamer} \quad \xrightarrow{K'} \quad \text{Higher Aggregates}$$

Obtain the expression for the weight-average molecular weight M_w of a mixture of the monomer protein and these aggregates of it, assuming the ideal association for any pair of the successive species and also the associations between aggregates to be indefinite and isodesmic.

[Solution A8]

The equilibrium relation between the monomer and the pentamer is

$$c_5 = Kc_1^5 \tag{1.48}$$

where c_1 and c_5 are the molar concentrations of the monomers and the pentamer, respectively, and K is the molar equilibrium constant between these two species. Denoting the molar concentration of the aggregate consisting of i pentamers stacked by $c_{5(i)}$, we have a series of equilibrium relations:

$$c_{5(i+1)} = K'c_{5(i)} \quad (i = 1, 2, \cdots) \tag{1.49}$$

Combination of Eqs.(1.48) and (1.49) gives

$$c_{5(i)} = (K')^{i-1}(K)^i(c_1^5)^i \quad (i = 1, 2, \cdots) \tag{1.50}$$

The total molar concentration, C, of the mixture is expressed by

$$\begin{aligned} C =& c_1 + c_{5(1)} + c_{5(2)} + c_{5(3)} + \cdots \\ =& C_1 + \sum_{i=1}^{\infty} (K')^{i-1}(K)^i(c_1)^{5i} \end{aligned} \tag{1.51}$$

The sum can be evaluated to give (with the assumption $KK'c_1^5 < 1$)

$$C = \left(1 + \frac{Kc_1^4}{1 - KK'c_1^5}\right)c_1 \tag{1.52}$$

The required M_w is represented by

$$M_w = \frac{M_1^2 c_1 + \sum_{i=1}^{\infty}(5M_1 i)^2 c_{5(i)}}{M_1 c_1 + \sum_{i=1}^{\infty}(5M_1 i)c_{5(i)}} \tag{1.53}$$

where M_1 is the molecular weight of the monomer. Introduction of Eq.(1.50) into Eq.(1.53), followed by evaluation of the sums, yields

$$M_w = M_1 \frac{1 + \frac{25KC_1^4(1+KK'c_1^5)}{(1-KK'c_1^5)^3}}{1 + \frac{5Kc_1^4}{(1-KK'c_1^5)^2}} \tag{1.54}$$

Equation (1.54)) combined with Eq.(1.52) determines M_w as a funtion of C, but this functional relation cannot be obtained explicitely, because Eq.(1.52) cannot be solved for c_1 in analytical way.

[Problem A9]

Find the number-average degree of polymerization as a function of time when a monodisperse sample undergoes random scission. Assume that each chain is not broken at more than one position at the same time.

[Solution A9]

The molar concentration of j-mer at time t is denoted by $[P_j]_t$. Then the rate of change in $[P_j]_t$ is represented by

$$\frac{\mathrm{d}[P_j]_t}{\mathrm{d}t} = -k(j-1)[P_j]_t + 2k \sum_{m=j+1}^{n} [P_m]_t \quad (j = 1, 2, \cdots, n) \quad (1.55)$$

where k is the rate constant for scission of a bond, and n is the degree of polymerization of the given monodisperse sample. The first term on the right hand side of Eq.(1.55) represents the rate of diappearance of j-mers, and the second term is the rate of formation of j-mers from any m-mer $(m > j)$. Note that a j-mer molecule can be formed in two different ways by rupture of a sequence of j bonds from either end of an m-mer. The initial conditions for the system of Eqs.(1.55) are

$$[P_j]_0 = 0 \quad \text{for } j < n \tag{1.56}$$

The desired solutions to Eqs.(1.55) can be obtained in elementary way, giving

$$[P_n]_t = [P_n]_0 \exp[-k(n-1)t] \tag{1.57}$$

$$[P_j]_t = [P_n]_0 \exp[-k(j-1)t][1 - \exp(-kt)]$$
$$\times \{2 + (n-1-j)[1 - \exp(-kt)]\} \quad (j < n) \tag{1.58}$$

The total molar concentration $[P]_t$ at time t is given by

$$[P]_t = [P_n]_t + \sum_{j=1}^{n-1} [P_j]_t \tag{1.59}$$

Substitution of Eqs.(1.57) and (1.58) gives

$$[P]_t = [P_n]_0[x + n(1 - x)] \tag{1.60}$$

where

$$x = \exp(-kt) \tag{1.61}$$

The number-average degree of polymerization $P_n(t)$ at time t is represented by

$$P_n(t) = \frac{\sum_{j=1}^n j[P_j]_t}{[P]_t} \tag{1.62}$$

Substituting Eqs.(1.57) and(1.58), we find that

$$P_n = \left[\frac{e^{-kt}}{n} + (1 - e^{-kt})\right]^{-1} \tag{1.63}$$

which gives $P_n = n$ at $t = 0$ and $P_n = 1$ at $t = \infty$. These limiting values of P_n would have been anticipated intuitively.

[Problem A10]

Suppose that addition polymerization initiated by a monofunctional reagent proceeds without termination. Obtain the expression for the distribution of polymerization degrees at time t from the start of reaction. It is assumed that the initiation of polymerization takes place instantly.

[Solution A10]

The polymerization reaction is represented schematically by

$$L_j + M \quad \xrightarrow{k} \quad L_{j+1}$$
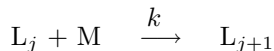
where L_j represents the polymer chain with the degree of polymerization j, M represents the monomer, and k is the reaction constant.

The molar concentration of $j-$mer and monomers at time t are denoted by $[P_j]_t$ and $[M]_t$, respectively. Then by simple physical considerations we obtain

$$\frac{\mathrm{d}[P_1]_t}{\mathrm{d}t} = -k[M]_t[P_1]_t \tag{1.64}$$

$$\frac{\mathrm{d}[P_j]_t}{\mathrm{d}t} = -k[M]_t([P_j]_t - [P_{j-1}]_t) \quad (j = 2, 3, \cdots) \tag{1.65}$$

$$\frac{\mathrm{d}[M]_t}{\mathrm{d}t} = -k[M]_t \sum_{j=1}^{\infty}[P_j]_t \tag{1.66}$$

The initial conditions for this system of kinetic equations are

$$[P_1]_0 = [I], \quad [P_j]_0 = 0 \;\; (j > 1) \tag{1.67}$$

with $[I]$ being the molar concentration of initiators.

For simplicity, it is assumed that k is independent of time. Then it can be shown easily that the system of equations above subject to the conditions (1.67) is given by

$$[P_j]_t = [I]\frac{\mathrm{e}^{-\theta}\theta^{j-1}}{(j-1)!} \quad (j = 1, 2, \cdots) \tag{1.68}$$

$$[M]_t = [M]_0 \left(1 - \frac{[I]}{[M]_0} \theta \right) \tag{1.69}$$

with

$$\theta = \frac{[M]_0}{[I]} (1 - e^{-k[I]t}) \tag{1.70}$$

The $[M]_0$ represents the molar concentration of monomers initially fed into the reaction vessel.

The mole fraction of j-mers is given by

$$f_j(t) = \frac{[P_j]_t}{\sum_{j=1}^{\infty} [P_j]_t} \tag{1.71}$$

Substitution of Eq.(1.68) yields

$$f_j(t) = \frac{e^{-\theta} \theta^{j-1}}{(j-1)!} \tag{1.72}$$

which is the desired distribution of polymerization degrees at time t.

The number-average and weight-average degrees of polymerization at time t are denoted by $P_n(t)$ and $P_w(t)$, respectively. These are expressed in terms of $f_j(t)$ as

$$P_n(t) = \sum_{j=1}^{\infty} j f_j(t) \tag{1.73}$$

$$P_w(t) = \frac{\sum_{j=1}^{\infty} j^2 f_j(t)}{\sum_{j=1}^{\infty} j f_j(t)} \tag{1.74}$$

Introduction of Eq.(1.72) gives

$$P_n(t) = 1 + \theta \tag{1.75}$$

$$P_w(t) = 1 + \theta + \frac{\theta}{1+\theta} \tag{1.76}$$

Hence

$$\frac{P_w(t)}{P_n(t)} = 1 + \theta(1+\theta)^2 \tag{1.77}$$

Equation (1.70) indicates that θ approaches $[M]_0/[I]$ as t goes infinity. Thus we get for polymerization equilibrium

$$P_n(\infty) = 1 + \frac{[M]_0}{[I]} \tag{1.78}$$

$$P_w(\infty) = 1 + \frac{[M]_0}{[I]} + \frac{[M]_0}{[I] + [M]_0} \tag{1.79}$$

$$\frac{P_w(\infty)}{P_n(\infty)} = 1 + \frac{[M]_0[I]}{([I] + [M]_0)^2} \tag{1.80}$$

and also

$$f_j(\infty) = e^{-[M]_0/[I]} \frac{([M]_0/[I])^{j-1}}{(j-1)!} \tag{1.81}$$

This equation gives a very narrow distribution of j if $[M]_0/[I] \gg 1$. For example, for $[M]_0/[I] = 100$, $P_n(\infty) = 101$, $P_w(\infty) = 102$, and $P_w(\infty)/P_n(\infty) = 1.01$.

[Comments]

The distribution of j represented by the form of Eq.(1.72) or (1.81) is called Poisson's distribution. The present problem refers to the kinetics of ideal "living" polymerization.

2   Polymer Chain Characteristics

[Problem B1]

Show that the square radius of gyration, S^2, for a molecule consisting of n identical segments is expressed by

$$S^2 = \frac{1}{n^2} \sum_{i=1}^{n-1} \sum_{j>i}^{n} \mathbf{R}_{ij}^2 \tag{2.1}$$

where $\mathbf{R}_{ij}$ is the vector connecting the i-th segment to the j-th one.

[Solution B1]

S^2 is defined by

$$S^2 = \frac{1}{n} \sum_{i=1}^{n} \mathbf{S}_i^2 \tag{2.2}$$

where $\mathbf{S}_i$ is the distance vector between the center of gravity of the molecule and the i-th segment, and then a set of $\mathbf{S}_1$, $\mathbf{S}_2$, $\cdots$, $\mathbf{S}_n$ satisfies the condition

$$\sum_{i=1}^{n} \mathbf{S}_i = 0 \tag{2.3}$$

From Eq.(2.3) one obtains

$$\sum_{i=1}^{n} \sum_{j=1}^{n} \mathbf{S}_i \cdot \mathbf{S}_j = 0 \tag{2.4}$$

Since

$$\mathbf{S}_i \cdot \mathbf{S}_j = \frac{1}{2}(\mathbf{S}_i^2 + \mathbf{S}_j^2 - \mathbf{R}_{ij}^2) \tag{2.5}$$

One gets

$$0 = \frac{n}{s} \sum_{i=1}^{n} \mathbf{S}_i^2 + \frac{n}{2} \sum_{j=1}^{n} \mathbf{S}_j^2 - \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} \mathbf{R}_{ij}^2 \qquad (2.6)$$

or

$$\sum_{i=1}^{n} \mathbf{S}_i^2 = \frac{1}{2n} \sum_{i=1}^{n} \sum_{j=1}^{n} \mathbf{R}_{ij}^2 = \frac{1}{n} \sum_{i=1}^{n-1} \sum_{j>i}^{n} \mathbf{R}_{ij}^2 \qquad (2.7)$$

Note that $\mathbf{R}_{ij} = 0$ for $i = j$. Substitution of Eq.(2.7) into Eq.(2.2) leads to the desired relation (2.1).

[Comments]

Taking average of Eq.(2.1) over all possible configurations of the molecule, one obtains

$$\langle S^2 \rangle = \frac{1}{n^2} \sum_{i=1}^{n-1} \sum_{j>i}^{n} \langle R_{ij}^2 \rangle \qquad (2.8)$$

This is very often used in the statistics of chain molecules, either linear or branched. For example, if the chain is freely jointed with bonds of length b,

$$\begin{aligned} \langle S^2 \rangle &= \frac{b^2}{n^2} \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} (j-i) \\ &= \frac{b^2}{2n^2} \sum_{i=1}^{n-1} i(i+1) \\ &= \frac{nb^2}{6} \left(1 - \frac{1}{n^2} \right) \end{aligned} \qquad (2.9)$$

[Problem B2]

We have a linear chain which consists of $n + 1$ identical segments (small spheres) connected by bonds of length b. Assume that the bonds are jointed freely. Then show that the mean square of $\mathbf{S}_j$, the distance from the center of gravity of the chain to the j-th segment, is expressed by

$$\langle S_j^2 \rangle = \frac{1}{3} nb^2 \left[1 - \frac{3j(n-j)}{n^2} \right] \tag{2.10}$$

if n is sufficiently large.

[Solution B2]

We have

$$\mathbf{S}_j - \mathbf{S}_i = \sum_{k=i+1}^{j} \mathbf{r}_k \quad \text{for } j > i \tag{2.11}$$

$$\mathbf{S}_j - \mathbf{S}_i = - \sum_{k=j+1}^{i} \mathbf{r}_k \quad \text{for } j < i \tag{2.12}$$

where $\mathbf{r}_k$ is the k-th bond vector. By definition

$$\sum_{i=0}^{n} \mathbf{S}_i = 0 \tag{2.13}$$

From Eqs.(2.11), (2.12), and (2.13) it follows that

$$\mathbf{S}_j = \sum_{i=1}^{n} \psi_{ji} \mathbf{r}_i \tag{2.14}$$

where

$$\psi_{ji} = H(j - i) + \frac{i}{n + 1} - 1 \tag{2.15}$$

with

$$H(x) = 1 \ (x > 0), \quad H(x) = 0 \ (x < 0) \tag{2.16}$$

With Eq.(2.14

$$\langle \mathbf{S}_j^2 \rangle = \langle (\sum_{i=1}^{n} \psi_{ji} \mathbf{r}_i)^2 \rangle$$

$$= b^2 \sum_{i=1}^{n} \psi_{ij}^2 \qquad (2.17)$$

because $\langle \mathbf{r}_i^2 \rangle = b^2$ and $\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle = 0$ $(i \neq j)$ for freely jointed chains. Introducing Eq.(2.15) into Eq.(2.17) and replacing the sum by an integral under the assumption $n \gg 1$, we obtain

$$\langle \mathbf{S}_j^2 \rangle = \frac{1}{3} n b^2 \left[1 - \frac{3j(n-j)}{n^2} \right] \qquad (2.18)$$

which is the required expression.

[Comments]

From Eq.(2.18) we find that

$$\langle \mathbf{S}_0^2 \rangle = \langle \mathbf{S}_n^2 \rangle = \frac{nb^2}{3} \qquad (\text{maxima of } \langle \mathbf{S}_j^2 \rangle) \qquad (2.19)$$

$$\langle \mathbf{S}_{n/2}^2 \rangle = \frac{nb^2}{12} \qquad (\text{minimum of } \langle \mathbf{S}_j^2 \rangle) \qquad (2.20)$$

Thus, on average, the chain ends are found at the most remote places from the center of gravity, while the center of the chain is located nearest to the center of gravity.

Also we find that

$$\langle S^2 \rangle = \frac{1}{n+1} \sum_{j=0}^{n} \langle \mathbf{S}_j^2 \rangle$$

$$\simeq \frac{1}{n} \int_0^n \langle \mathbf{S}_j^2 \rangle \mathrm{d}j$$

$$= \frac{nb^2}{6} \qquad (2.21)$$

[Problem B3]

For a linear chain containing $N + 1$ segments connected by N bonds of length b, show that

$$\langle S^2 \rangle = \frac{1}{N+1} \sum_{p=1}^{N} \left(1 - \frac{p}{N+1} \right) \langle \mathbf{R}_{0p}^2 \rangle \tag{2.22}$$

if the internal rotation about each bond is independent. Here $\mathbf{R}_{0p}$ is the vector connecting the 0-th segment to the p-th segment.

[Solution B3]

We use the general expression

$$\langle S^2 \rangle = \frac{1}{(N+1)^2} \sum_{i=0}^{N-1} \sum_{j=i+1}^{N} \langle \mathbf{R}_{ij}^2 \rangle \tag{2.23}$$

For the chain under consideration, $\langle \mathbf{R}_{ij}^2 \rangle$ for pairs of i and j with $|j - i|$ fixed are all equal, and there are $N + 1 - p$ pairs of i and j which satisfy the constraint $j - i = p > 0$. From these two facts we may rewrite Eq.(2.23) as follows:

$$\langle S^2 \rangle = \frac{1}{(N+1)^2} \sum_{p=1}^{N} (N + 1 - p) \langle \mathbf{R}_{0p}^2 \rangle$$

$$= \frac{1}{N+1} \sum_{p=1}^{N} N \left(1 - \frac{p}{N+1} \right) \langle \mathbf{R}_{0p}^2 \rangle \tag{2.24}$$

which is the desired formula. Note that this equation does not hold for chains which involve interdependent bond rotations or which undergo excluded-volume effects, because $\langle \mathbf{R}_{ij}^2 \rangle$ in these chains depend on individual values of i and j, i.e., not a function only of $|j - i|$.

[Problem B4]

Find the expression for $\langle S^2 \rangle$ of a chain composed of N thin rods of length L which are connected by universal joints.

[Solution B4]

The vector $\mathbf{R}_n$ from a chain end (the origin) to a point in the n-th bond (rod) is represented by

$$\mathbf{R}_n = L \sum_{j=1}^{n-1} \mathbf{u}_j + L x_n \mathbf{u}_n \tag{2.25}$$

where $\mathbf{u}_j$ is the unit vector for the j-th bond, and x_n is the fractional variable. Applying Eq.(2.25) to the general relation for $\langle S^2 \rangle$, we obtain

$$\langle S^2 \rangle = \frac{L^2}{2N^2} \sum_{n=1}^{N} \sum_{m=1}^{N} \int_0^1 \int_0^1 \langle (\mathbf{R}_n - \mathbf{R}_m)^2 \rangle \mathrm{d}x_n \mathrm{d}x_m \tag{2.26}$$

Ths may be rewritten

$$\langle S^2 \rangle = \frac{L^2}{2N^2} \sum_{n=1}^{N} A_N + \frac{L^2}{N^2} \sum_{n=1}^{N-1} \sum_{m>n}^{N} A_{mn} \tag{2.27}$$

where

$$A_n = \int_0^1 \int_0^1 (x_n - x'_n)^2 \mathrm{d}x_n \mathrm{d}x'_n \tag{2.28}$$

$$A_{nm} = \int_0^1 \int_0^1 \langle v_{nm}^2 \rangle \mathrm{d}x_n \mathrm{d}x_m \tag{2.29}$$

with

$$\mathbf{v}_{nm} = x_n \mathbf{u}_n - x_m \mathbf{u}_m - \sum_{k=n}^{m-1} \mathbf{u}_k \quad (m > n) \tag{2.30}$$

It can be shown that

$$A_n = \frac{1}{6}, \quad A_{nm} = m - n - \frac{1}{3} \quad (m > n) \tag{2.31}$$

where use has been made of tha fact that $\langle \mathbf{u}_n \cdot \mathbf{u}_n \rangle = 1$ and $\langle \mathbf{u}_n \cdot \mathbf{u}_m \rangle = 0$ ($n \neq m$). With Eq.(2.31), Eq.(2.27) becomes

$$\langle S^2 \rangle = \frac{L^2}{6} \left(N - 1 + \frac{1}{2N} \right) \tag{2.32}$$

[Comments]

When $N = 1$, Eq.(2.32) gives $\langle S^2 \rangle_{N=1} = L^2/12$, which is the well-known formula for straight rods. For $N = 2$ the chain is called a once-broken rod, and Eq.(2.32) gives $\langle S^2 \rangle_{N=2} = 5L^2/24$. Thus the mean square radius of gyration for a once-broken rod is 5/8 of that for a straight rod of equal total length.

[Problem B5]

For a freely jointed chain consisting of n bonds of length b, show that if $n \gg 1$,

$$\langle x_i x_j \rangle = \frac{1}{9} n b^2 \left[1 - \frac{3}{2n}(i + j + |i - j|) + \frac{3}{2n^2}(i^2 + j^2) \right] \qquad (2.33)$$

Here x_i is the x-coordinate of the vector $\mathbf{S}_i$ which connects the center of gravity of the chain to its i-th segment (or bead).

[Solution B5]

It is obvious that $\langle x_i x_j \rangle = \langle y_i y_j \rangle = \langle z_i z_j \rangle$. Hence

$$\langle x_i x_j \rangle = \frac{1}{3} \langle x_i x_j + y_i y_j + z_i z_j \rangle$$

$$= \frac{1}{3} \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$$

$$= \frac{1}{6} [\langle \mathbf{S}_i^2 \rangle + \langle \mathbf{S}_j^2 \rangle - \langle \mathbf{R}_{ij}^2 \rangle] \qquad (2.34)$$

For the chain considered

$$\langle \mathbf{S}_i^2 \rangle = \frac{1}{3} n b^2 \left[1 - \frac{3i(n - i)}{n^2} \right] \qquad (2.35)$$

$$\langle \mathbf{R}_{ij}^2 \rangle = b^2 |i - j| \qquad (2.36)$$

Thus

$$\langle x_i x_j \rangle = \frac{1}{6} \left[\frac{2nb^2}{3} - \frac{i(n - i)b^2}{n} - \frac{j(n - j)b^2}{n} - |i - j|b^2 \right]$$

$$= \frac{nb^2}{9} \left[1 - \frac{3}{2n}(i + j + |i - j|) + \frac{3}{2n^2}(i^2 + j^2) \right] \qquad (2.37)$$

which is the required formula.

[Problem B6]

Suppose that a linear chain of n identical bonds is divided into two subchains I and II, which contain m and $n-m$ bonds, respectively. Show that, with $x = (m+1)/(n+1)$,

$$\langle \mathbf{L}^2 \rangle = \frac{1}{x(1-x)} [\langle S^2 \rangle - x\langle S^2 \rangle_I - (1-x)\langle S^2 \rangle_{II}] \qquad (2.38)$$

where L is the distance between the centers of gravity of subchains I and II, and $\langle S^2 \rangle$, $\langle S^2 \rangle_I$, and $\langle S^2 \rangle_{II}$ are the mean-square radii of gyration of the entire chain, subchain I, and subchain II, respectively.

[Solution B6]

One may rewrite the genaral expression

$$\langle S^2 \rangle = \frac{1}{2(n+1)^2} \sum_{i=0}^{n} \sum_{j=0}^{n} \langle \mathbf{R}_{ij}^2 \rangle \qquad (2.39)$$

in the form

$$\langle S^2 \rangle = \frac{1}{2(n+1)^2} [\sum_{i=0}^{m} \sum_{j=0}^{m} \langle \mathbf{R}_{ij}^2 \rangle + \sum_{i=m+1}^{n} \sum_{j=m+1}^{n} \langle \mathbf{R}_{ij}^2 \rangle + 2 \sum_{i=0}^{m} \sum_{j=m+1}^{n} \langle \mathbf{R}_{ij}^2 \rangle \qquad (2.40)$$

But

$$\frac{1}{2} \sum_{i=0}^{m} \sum_{j=0}^{m} \langle \mathbf{R}_{ij}^2 \rangle = (m+1)^2 \langle S^2 \rangle_I \qquad (2.41)$$

$$\frac{1}{2} \sum_{i=m+1}^{n} \sum_{j=m+1}^{n} \langle \mathbf{R}_{ij}^2 \rangle = (n-m)^2 \langle S^2 \rangle_{II} \qquad (2.42)$$

and

$$\sum_{i=0}^{m} \sum_{j=m+1}^{n} \langle \mathbf{R}_{ij}^2 \rangle = \sum_{i=0}^{m} \sum_{j=m+1}^{n} \langle (\mathbf{L} + \mathbf{S}_j^{II} - \mathbf{S}_i^{I})^2 \rangle \qquad (2.43)$$

Since

$$\sum_{i=0}^{m} \mathbf{S}_i^{I} = 0, \qquad \sum_{j=m+1}^{n} \mathbf{S}_j^{II} = 0,$$

$$\sum_{i=0}^{m} \sum_{j=m+1}^{n} \mathbf{S}_j^{II} \cdot \mathbf{S}_i^{I} = (\sum_{i=0}^{m} \mathbf{S}_i^{I}) \cdot (\sum_{j=m+1}^{n} \mathbf{S}_j^{II}) = 0 \qquad (2.44)$$

Eq.(2.43) becomes

$$\sum_{i=0}^{m} \sum_{j=m+1}^{n} \langle \mathbf{R}_{ij}^2 \rangle = (m+1)(n-m)(\langle \mathbf{L}^2 \rangle \langle S^2 \rangle_I + \langle S^2 \rangle_{II}) \qquad (2.45)$$

where one has used the relations $\langle S^2 \rangle_I = (m+1)^{-1} \sum_{i=0}^{m} \langle \mathbf{S}_i^{I2} \rangle$ and $\langle S^2 \rangle_{II} = (n-m)^{-1} \sum_{j=m+1}^{n} \langle \mathbf{S}_i^{II2} \rangle$.

With Eqs.(2.41), (2.42), and (2.45), Eq.(2.40) gives

$$\langle S^2 \rangle = \left(\frac{m+1}{n+1} \right)^2 \langle S^2 \rangle_I + \left(\frac{n-m}{n+1} \right)^2 \langle S^2 \rangle_{II}$$
$$+ \frac{(m+1)(n-m)}{(n+1)^2} [\langle S^2 \rangle_I + \langle S^2 \rangle_{II} + \langle \mathbf{L}^2 \rangle] \qquad (2.46)$$

whence

$$\langle \mathbf{L}^2 \rangle = \frac{1}{x(1-x)} [\langle S^2 \rangle - x \langle S^2 \rangle_I - (1-x) \langle S^2 \rangle_{II}] \qquad (2.47)$$

with $x = (m+1)/(n+1)$.

[Comments]

If the chain is Gaussian and both m and $n - m$ are sufficiently large, Eq.(2.38) gives an interesting relation:

$$\langle \mathbf{L}^2 \rangle = \sqrt{2} \langle S^2 \rangle^{1/2} \qquad (2.48)$$

For such a chain one has

$$\langle S^2 \rangle = \frac{nb^2}{6}, \qquad \langle S^2 \rangle_I = \frac{mb^2}{6}, \qquad \langle S^2 \rangle_{II} = \frac{(n-m)b^2}{6} \qquad (2.49)$$

where b is the length of a bond. Hence

$$\langle S^2 \rangle_I = x \langle S^2 \rangle, \qquad \langle S^2 \rangle_{II} = (1-x) \langle S^2 \rangle \qquad (2.50)$$

Substitution of these into Eq.(2.38) leads to Eq.(2.48).

[Problem B7]

For a polymer molecule composed of n identical units, show that

$$\langle \mathbf{S}_j^2 \rangle = \frac{1}{n}(\sum_{i=1}^{j} \langle \mathbf{R}_{ij}^2 \rangle + \sum_{i=j+1}^{n} \langle \mathbf{R}_{ji}^2 \rangle) - \langle S^2 \rangle \tag{2.51}$$

Here $\mathbf{S}_j$ is the vector connecting the center of gravity of the polymer to its j-th unit, $\mathbf{R}_{ij}$ is the vector connecting the i-th to the j-th units, and $\langle S^2 \rangle$ is the mean-square radius of gyration of the polymer.

[Solution B7]

From chain geometry one readily write down the expressions:

$$\mathbf{S}_i \cdot \mathbf{S}_j = \frac{1}{2}(\mathbf{S}_i^2 + \mathbf{S}_j^2 - \mathbf{R}_{ij}^2) \quad \text{for } j \geq i \tag{2.52}$$

$$\mathbf{S}_i \cdot \mathbf{S}_j = \frac{1}{2}(\mathbf{S}_i^2 + \mathbf{S}_j^2 - \mathbf{R}_{ji}^2) \quad \text{for } j < i \tag{2.53}$$

Summing both sides over i, one gets

$$\sum_{i=1}^{n} \mathbf{S}_i^2 + n\mathbf{S}_j^2 - \sum_{i=1}^{j} \mathbf{R}_{ij}^2 - \sum_{i=j+1}^{n} \mathbf{R}_{ji}^2 = 0 \tag{2.54}$$

because $\mathbf{S}_i$ satisfies the condition for the center of gravity that

$$\sum_{i=1}^{n} \mathbf{S}_i = 0 \tag{2.55}$$

Taking average over all possible conformations, Eq.(2.52) gives

$$\langle \mathbf{S}_j^2 \rangle = \frac{1}{n}(\sum_{i=1}^{j} \langle \mathbf{R}_{ij}^2 \rangle + \sum_{i=j+1}^{n} \langle \mathbf{R}_{ji}^2 \rangle) - \frac{1}{n}\sum_{i=1}^{n} \langle \mathbf{S}_i^2 \rangle \tag{2.56}$$

Use of the definition, $\langle S^2 \rangle = (1/n)\sum_{i=1}^{n}\langle \mathbf{S}_i^2 \rangle$, for mean-square radius of gyration, leads to Eq.(2.51).

[Problem B8]

Find the expression for $\langle S^2 \rangle$ of a block copolymer of A-B type, assuming that each block is sufficiently long and may be treated as freely jointed.

[Solution B8]

Apply the general expression for $\langle S^2 \rangle$ of copolymers of general type, i.e.,

$$\langle S^2 \rangle = \frac{1}{M^2} \sum \sum_{j>i} m_i m_j \langle \mathbf{R}_{ij}^2 \rangle \tag{2.57}$$

where $M = \sum_i m_i$ = total mass of a molecule. For our copolymer we have

$$\sum \sum_{j>i} m_i m_j \langle \mathbf{R}_{ij}^2 \rangle = N_A^2 m_A^2 \langle S^2 \rangle_A + N_B^2 m_B^2 \langle S^2 \rangle_B$$

$$+ \sum_{p_A=1}^{N_A} \sum_{q_B=1}^{N_B} m_A m_B \langle \mathbf{R}_{p_A q_B}^2 \rangle \tag{2.58}$$

where N_A and $\langle S^2 \rangle_A$ denote the number of segments contained in and the mean-square radius of gyration for the isolated A block, respectively, with the corresponding definitions of N_B and $\langle S^2 \rangle_B$. Now, $\langle \mathbf{R}_{p_A q_B}^2 \rangle$ may be written

$$\langle \mathbf{R}_{p_A q_B}^2 \rangle = (N_A - p_A) b_A^2 + (q_B - 1) b_B^2 + b_{AB}^2 \tag{2.59}$$

because both A and B blocks are assumed to behave like freely jointed chains. Here $b_A = \overline{A - A}$, $b_B = \overline{B - B}$, and $b_{AB} = \overline{A - B}$.

Substitution of Eq.(2.59) gives for $N_A \gg 1$ and $N_B \gg 1$

$$\sum_{p_A=1}^{N_A} \sum_{q_B=1}^{N_B} m_A m_B \langle \mathbf{R}_{p_A q_b}^2 \rangle = m_A m_B \left(\frac{N_A^2 N_B}{2} b_A^2 + \frac{N_B^2 N_A}{2} b_B^2 \right) \tag{2.60}$$

Thus

$$\langle S^2 \rangle = \frac{1}{(m_A N_A + m_B N_B)^2} \left[\frac{m_A^2 N_A^3}{6} b_A^2 + \frac{m_B^2 N_B^3}{6} b_B^2 \right.$$

$$\left. + \frac{m_A m_B}{2} (N_A^2 N_B b_A^2 + N_B^2 N_A b_B^2) \right] \tag{2.61}$$

where the well-known formula ($\langle S^2 \rangle = Nb^2/6$) has been used for $\langle S^2 \rangle_A$ and $\langle S^2 \rangle_B$. If the masses of the blocks A and B are denoted by M_A and M_B, respectively, Eq.(2.61) may be written

$$\langle S^2 \rangle = \frac{1}{6(M_A + M_B)^2}[M_A(M_A + 3M_B)N_A b_A^2 + M_B(M_B + 3M_A)N_B b_B^2]$$
(2.62)

[Problem B9]

Show that the mean-square radius of gyration, $\langle S^2 \rangle_b$, of a branched chain molecule which containes no ring portion is represented by

$$\langle S^2 \rangle_b = \frac{b^2}{n^2} \left(\frac{n}{2} \sum_{k=1}^{p} n_k^2 - \frac{1}{3} \sum_{k=1}^{p} n_k^3 + \sum_{(k,j)} n_k n_{kj} n_j \right) \qquad (2.63)$$

if each subchain, i.e., a portion of the chain between adjacent branch points or between a chain end and its adjacent branch point, behaves as a random-flight chain of bond length b. In Eq.(2.63), n is the total number of beads in the chain, n_k is the number of beads contained in the k-th subchain $(k = 1, 2, \cdots, p)$, and n_{kj} is the number of beads in the chains intervening between the k-th and j-th subchains. The symbol (k, j) means the sum taken over all different combinations of k and j $(k \neq j)$.

Equation (2.63) is called Kataoka's formula for branched chain molecules.

[Solution B9]

The general expression

$$\langle S^2 \rangle = \frac{1}{2n^2} \sum_{\text{all combinations of } \alpha \text{ and } \beta} \sum \langle \mathbf{r}_{\alpha\beta}^2 \rangle \qquad (2.64)$$

holds for branched molecules as well. If beads α and β belong to the same subchain, say the k-th chain, one obtains by using the knowledge about random-flight linear chains

$$\frac{1}{2} \sum_{\text{fixed } k} \sum \langle \mathbf{r}_{\alpha\beta}^2 \rangle \simeq \frac{b^2 n_k^3}{6} \qquad (2.65)$$

When beads α and β belong to different chains, say the k-th and j-th subchains, respectively, one obtains

$$\frac{1}{2} \sum_{\text{fixed } k \text{ and } j} \sum \langle \mathbf{r}_{\alpha\beta}^2 \rangle \simeq \sum_{f=1}^{n_k} \sum_{g=1}^{n_j} (n_{kj} + f + g) \qquad (2.66)$$

where f and g are new parameters to count the beads on the k-th and j-th subchains, respectively, with $f = 1$ and $g = 1$ assigned to their teminal beads. The double sum in Eq.(2.66) may be evaluated to give

$$\frac{1}{2} \sum_{\text{fixed } k \text{ and } j} \sum \langle \mathbf{r}_{\alpha\beta}^2 \rangle b^2 \left[n_k n_{kj} n_j + n_k \frac{n_j(n_j + 1)}{2} + n_j \frac{n_k(n_k + 1)}{2} \right]$$

$$\simeq b^2 \left[n_k n_{kj} n_j + \frac{n_k n_j^2 + n_j n_k^2}{2} \right] \tag{2.67}$$

It should be noted that the symbol $\simeq$ in Eqs.(2.65), (2.66), and (2.67) implies "being valid for large n_k, n_j, and n_{kj}."

With Eqs.(2.65) and (2.67), Eq.(2.64) gives for $\langle S^2 \rangle_b$

$$\langle S^2 \rangle_b = \frac{b^2}{n^2} \left[\frac{1}{6} \sum_{k=1}^{p} n_k^3 + \frac{1}{2} \sum_{(k,j)} (n_k n_j^2 + n_j n_k^2) + \sum_{(k,j)} n_k n_{kj} n_j \right] \tag{2.68}$$

where $\sum_{(k,j)}$ stnds for the sum over all different combinations of k and j with $k \neq j$. Since

$$\frac{1}{6} \sum_{k=1}^{p} n_k^3 + \frac{1}{2} \sum_{(k,j)} (n_k n_j^2 + n_j n_k^2)$$

$$= \frac{1}{2} \sum_{j=1}^{p} n_j \sum_{k=1}^{p} n_k^2 - \frac{1}{2} \sum_{k=1}^{p} n_k^3 + \frac{1}{6} \sum_{k=1}^{p} n_k^3$$

$$= \frac{n}{2} \sum_{k=1}^{p} n_k^2 - \frac{1}{3} \sum_{k=1}^{p} n_k^3 \quad (\sum_{k=1}^{p} n_k = n) \tag{2.69}$$

Eq.(2.68) can be written

$$\langle S^2 \rangle_b = \frac{b^2}{n^2} \left(\frac{n}{2} \sum_{k=1}^{p} n_k^2 - \frac{1}{3} \sum_{k=1}^{p} n_k^3 + \sum_{(k,j)} n_k n_{kj} n_j \right) \tag{2.70}$$

which is Kataoka's formula.

The g factor is defined by

$$g \equiv \frac{\langle S^2 \rangle_b}{\langle S^2 \rangle_l} \tag{2.71}$$

where $\langle S^2 \rangle_l$ denotes the mean square radius of gyration of a linear chain with the same number of beads and the same bond length as the branched chain. Since

$$\langle S^2 \rangle_l \simeq \frac{nb^2}{6} \tag{2.72}$$

one obtains

$$g = \frac{6}{n^3} \left(\frac{n}{2} \sum_{k=1}^{p} n_k^2 - \frac{1}{3} \sum_{k=1}^{p} n_k^3 + \sum_{(k,j)} n_k n_{kj} n_j \right) \tag{2.73}$$

[Problem B10]

Use Kataoka's formula for branched molecule to derive the g factor for a star molecule consisting of p equal random-flight chains.

[Solution B10]

For star molecules Kataoka'4 formula (2.73) in [Problem B9] gives

$$g = \frac{6}{n^3}\left(\frac{n}{2}\sum_{k=1}^{p} n_k^2 - \frac{1}{3}\sum_{k=1}^{p} n_k^3\right) \tag{2.74}$$

because $n_{kj} = 0$ for $k \neq j$. For the regular star considered here

$$n_k = \frac{n}{p} \tag{2.75}$$

Hence Eq.(2.74) becomes

$$g = \frac{3}{p}\left(1 - \frac{2}{3p}\right)$$
$$= \frac{3p - 2}{p^2} \tag{2.76}$$

This gives $g = 1$ for $p = 1$ and 2 as should be expected. $g = 7/9$ for $p = 3$, $g = 5/8$ for $p = 4$, and so forth.

[Problem B11]

Calculate the g factor averaged over an assembly of star molecules each of which sonsists of p branches of statistically varying lengths. It is assumed that each branch behaves like a random-flight chain.

[Solution B11]

Using Kataoka's equation (2.63) presented in [Problem B9], one obtains for the desired g

$$g = \frac{6}{n^3}\left(\frac{n}{2}\sum_{k=1}^{p}\langle n_k^2\rangle_{np} - \frac{1}{3}\sum_{k=1}^{p}\langle n_k^3\rangle_{np}\right) \qquad (2.77)$$

where $\langle n_k^2\rangle_{np}$ stands for the average of n_k^2 over all values of n_k possible under fixed n $(=\sum_{k=1}^{p} n_k)$ and p, with a similar definition of $\langle n_k^3\rangle_{np}$.

Since

$$\langle n_k^2\rangle_{np} = \frac{2}{p(p+1)}n^2 \qquad (2.78)$$

$$\langle n_k^3\rangle_{np} = \frac{6}{p(p+1)(p+2)}n^3 \qquad (2.79)$$

Eq.(2.77) becomes

$$g= 6\left[\frac{1}{p+1} - \frac{2}{(p+1)(p+2)}\right]$$

$$= \frac{6p}{(p+1)(p+2)} \qquad (2.80)$$

It would be of interest to this with Eq.(2.76) in [Problem B10].

[Problem B12]

Given a linear chain whose repeat unit is the type -X-Y-, derive the expression for $\langle \mathbf{R}^2 \rangle$ under the assumption of free rotation about each of the bonds. $\overline{X - Y} = b_1$, $\overline{Y - X} = b_2$, $\angle XYX = \theta_1$, $\angle YXY = \theta_2$.

[Solution B12]

The total number (even) of the bonds is denoted by n. Then, under the assumption made in the problem, we find that

$$\sum_{j>i}\sum \langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle = \sum_{l=1}^{2}\sum_{m=1}^{2}\sum_{k=0,\,l<2k+m}^{n/2-1}\left(\frac{n}{2}-k\right)\langle \mathbf{r}_l \cdot \mathbf{r}_{2k+m}\rangle \qquad (2.81)$$

This may be written

$$\sum_{j>i}\sum \langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle = \frac{n}{2}\langle \mathbf{r}_1 \cdot \mathbf{r}_2\rangle + \sum_{k=1}^{n/2-1}\left(\frac{n}{2}-k\right)[\langle \mathbf{r}_1 \cdot \mathbf{r}_{2k+1}\rangle$$
$$+ \langle \mathbf{r}_2 \cdot \mathbf{r}_{2k+1}\rangle + \langle \mathbf{r}_1 \cdot \mathbf{r}_{2k+2}\rangle + \langle \mathbf{r}_2 \cdot \mathbf{r}_{2k+2}\rangle] \quad (2.82)$$

Since for freely rotating bonds

$$\langle \mathbf{r}_1 \cdot \mathbf{r}_2 \rangle = b_1 b_2 r_1, \qquad \langle \mathbf{r}_1 \cdot \mathbf{r}_{2k+1}\rangle = b_1^2(\gamma_1\gamma_2)^k$$
$$\langle \mathbf{r}_1 \cdot \mathbf{r}_{2k+2}\rangle = b_1 b_2(\gamma_1\gamma_2)^k\gamma_1, \qquad \langle \mathbf{r}_2 \cdot \mathbf{r}_{2k+1}\rangle = b_1 b_2(\gamma_1\gamma_2)^{k-1}\gamma_2$$
$$\langle \mathbf{r}_2 \cdot \mathbf{r}_{2k+2}\rangle = b_2^2(\gamma_1\gamma_2)^k,$$

where $\gamma_i = -\cos\theta_i$ $(i = 1, 2)$, Eq.(2.82) becomes

$$\sum_{j>i}\sum \langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle = \frac{n}{2}b_1 b_2\gamma_1 + \left[b_1 b_2\left(\gamma_1 + \frac{1}{\gamma_1}\right)\right.$$
$$\left. + b_1^2 + b_2^2\right]\sum_{k=1}^{n/2-1}\left(\frac{n}{2}-k\right)(\gamma_1\gamma_2)^k \qquad (2.83)$$

Evaluating the sum, we arrive at

$$\sum_{j>i}\sum \langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle = \frac{n}{2}\left\{b_1 b_2\gamma_1 + \left[b_1 b_2\left(\gamma_1 + \frac{1}{\gamma_1}\right) + b_1^2 + b_2^2\right]\frac{\gamma_1\gamma_2}{1-\gamma_1\gamma_2}\right\}$$

$$-\left[b_1 b_2\left(\gamma_1 + \frac{1}{\gamma_1}\right) + b_1^2 + b_2^2\right]$$

$$\times \frac{\gamma_1 \gamma_2 [1 - (\gamma_1 \gamma_2)^{n/2}]}{(1 - \gamma_1 \gamma_2)^2} \tag{2.84}$$

If this is substituted into

$$\langle \mathbf{R}^2 \rangle = \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle$$

$$= \frac{n}{2} \langle r_1^2 \rangle + \frac{n}{2} \langle r_2^2 \rangle + 2 \sum \sum_{j>i} \langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle$$

$$= \frac{n}{2} (b_1^2 + b_2^2) + 2 \sum \sum_{j>i} \langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle \tag{2.85}$$

the desired expression for $\langle \mathbf{R}^2 \rangle$ is obtained.

[Comments]

For the special case $Y = X$, we have $\theta_1 = \theta_2 \equiv \theta$ and $b_1 = b_2 \equiv b$. Then, Eq.(2.85) with Eq.(2.84) gives

$$\langle \mathbf{R}^2 \rangle = n\left[b^2 + \frac{2b^2\gamma}{1 - \gamma}\right] - \frac{2b^2\gamma(1 - \gamma^n)}{(1 - \gamma)^2} -$$

$$= nb^2\left[\left(\frac{1 + \gamma}{1 - \gamma}\right) - \frac{2\gamma(1 - \gamma^n)}{n(1 - \gamma)^2}\right] \quad (\gamma = -\cos\theta) \tag{2.86}$$

[Problem B13]

Compute the characteristic ratio for unperturbed linear polymethylene chains at 140 °C, assuming the rotational isomer model in which (1) internal rotations about successive bonds are independent, (2) bonds are not allowed to take the *cis* conformation, and (3) the difference in potential energy, $\Delta\epsilon$, between the *gauche* and *trans* conformation is 500 cal/mol.

[Solution B13]

Under the condition (1) and for the reason that the internal rotation about each bond is symmetric about the *trans* conformation, the characteristic ratio C_∞ is

$$C_\infty \equiv \frac{\langle R^2 \rangle}{Nl^2} = \left(\frac{1 - \cos\theta}{1 + \cos\theta}\right)\left(\frac{1 + \langle \cos\phi \rangle}{1 - \langle \cos\phi \rangle}\right) \qquad (2.87)$$

where θ is the valence angle, and $\langle \cos\phi \rangle$ is given, with the conditions (2) and (3), by

$$\langle \cos\phi \rangle = \frac{\int_{-\pi}^{\pi} \cos\phi \exp[-u(\phi)/kT]\mathrm{d}\phi}{\int_{-\pi}^{\pi} \exp[-u(\phi)/kT]\mathrm{d}\phi}$$

$$= \frac{1 - \tau}{1 + 2\tau} \qquad (2.88)$$

where

$$\tau = \exp(-\Delta\epsilon/kT) \qquad (2.89)$$

Thus

$$C_\infty = \left(\frac{1 - \cos\theta}{1 - \cos\theta}\right)\left(\frac{2 + \tau}{3\tau}\right) \qquad (2.90)$$

Substituting $\cos\theta = -1/3$ (appropriate for hydrocarbon chains) $\Delta\epsilon = 500$ cal/mol, and $T = 140 + 273$ K, we obtain

$$C_\infty = 3.11 \qquad (2.91)$$

This value is far off the experimental values of C_∞ which range from 6 to 7.

[Problem B14]

For Gaussian chains in which the distribution function, $P(\mathbf{R})$, of the end-to-end vector $\mathbf{R}$ is represented by

$$P(\mathbf{R}) = \left(\frac{3}{2\pi nb^2} \right)^{3/2} \exp\left(-\frac{3\mathbf{R}^2}{2nb^2} \right) \tag{2.92}$$

with n = total number of bonds and b= length of a bond, show that

$$\langle \mathbf{R}^{2p} \rangle = \frac{(2p+1)!}{p!} \left(\frac{nb^2}{6} \right)^p \qquad (p = 1, 2, \cdots) \tag{2.93}$$

and

$$\langle |\mathbf{R}|^{-1} \rangle = \left(\frac{6}{\pi nb^2} \right)^{1/2} \tag{2.94}$$

[Solution B14]

To derive the result (2.92) it is convenient to use the generating (or characteristic) function $Q(\mathbf{s})$, which is the Fourier transform (three-dimensional) of $P(\mathbf{R})$. Thus

$$Q(\mathbf{s}) = \int P(\mathbf{R}) \exp(i\mathbf{s} \cdot \mathbf{R}) d\mathbf{R} \tag{2.95}$$

Expanding $\exp(i\mathbf{s} \cdot \mathbf{R})$ in powers of $i\mathbf{s} \cdot \mathbf{R}$, we obtain

$$Q(\mathbf{s}) = \sum_{k=0}^{\infty} \frac{1}{k!} \int (i\mathbf{s} \cdot \mathbf{R})^k P(\mathbf{R}) d\mathbf{R} \tag{2.96}$$

But

$$\int (\mathbf{s} \cdot \mathbf{R})^k P(\mathbf{R}) d\mathbf{R} = \frac{s^k}{2} \int_0^\pi (\cos \theta)^k \sin \theta d\theta \int_0^\infty R^k P(R) 4\pi R^2 dR$$

$$= \frac{s^k}{k+1} \langle R^k \rangle \qquad (k = 2p)$$

$$= 0 \qquad (k = 2p+1)$$

because

$$\langle \mathbf{R}^k \rangle = 4\pi \int R^{k+2} P(\mathbf{R}) d\mathbf{R}$$

Thus

$$Q(\mathbf{s}) = \sum_{p=0}^{\infty} \frac{(-1)^p}{(2p+1)!} \langle \mathbf{R}^{2p} \rangle s^{2p} \tag{2.97}$$

On the other hand, direct substitution of the given $P(\mathbf{R})$ into Eq.(2.94) yields

$$Q(\mathbf{s}) = 2\pi \int_0^\infty \int_0^\pi \left(\frac{3}{2\pi n b^2} \right)^{3/2} \exp\left(-\frac{3R^2}{2nb^2} + isR\cos\theta \right) R^2 \sin\theta \, dR d\theta$$

$$\left(\frac{3}{2\pi n b^2} \right)^{3/2} \frac{4\pi}{s} \int_0^\pi \exp\left(-\frac{3R^2}{2nb^2} \right) \sin(sR) R dR$$

$$= \exp\left(-\frac{nb^2}{6} s^2 \right)$$

$$= \sum_{p=0}^{\infty} \frac{(-1)^p}{p!} \left(\frac{nb^2}{6} \right)^p s^{2p} \tag{2.98}$$

where use has been made of the formula:

$$\int_0^\infty x e^{-x^2} \sin(bx) dx = \frac{\sqrt{\pi}}{4} b e^{-b^2/4} \tag{2.99}$$

Comparison of Eqs.(2.97) and (2.98) gives Eq.(2.93).

The calculation of $\langle |\mathbf{R}|^{-1} \rangle$ goes as follows:

$$\langle |\mathbf{R}|^{-1} \rangle = 4\pi \int_0^\infty R \left(\frac{3}{2\pi n b^2} \right)^{3/2} \exp\left(-\frac{3R^2}{2nb^2} \right) dR$$

$$= \left(\frac{6}{\pi n b^2} \right)^{1/2} \tag{2.100}$$

[Problem B15]

Suppose we have a linear chain which consists of two Gaussian chains 1 and 2. The chain 1 contains n_1 bonds of length b_1 and the chain 2 contains n_2 bonds of length b_2. Obtain the expression for $P(\mathbf{R})$, the distribution function of end-to-end vector $\mathbf{R}$ for the composite chain.

[Solution B15]

The distribution function $P_i(\mathbf{R}_i)$ for end-to-end vector $\mathbf{R}_i$ of the i-th subchain $(i = 1, 2)$ is given by

$$P_i(\mathbf{R}_i) = \left(\frac{3}{2\pi n_i b_i^2}\right)^{3/2} \exp\left(-\frac{3\mathbf{R}_i^2}{2n_i b_i^2}\right) \qquad (2.101)$$

The generating function $Q(\mathbf{s})$ of the composite chain is

$$Q(\mathbf{s}) = \int P(\mathbf{R})\exp(i\mathbf{R}\cdot\mathbf{s})\mathrm{d}\mathbf{R}$$
$$= [\int P_1(\mathbf{R}_1)\exp(i\mathbf{R}_1\cdot\mathbf{s})\mathrm{d}\mathbf{R}_1][\int P_2(\mathbf{R}_2)\exp(i\mathbf{R}_2\cdot\mathbf{s})\mathrm{d}\mathbf{R}_2] \qquad (2.102)$$

Substitution of Eq.(2.101) gives

$$Q(\mathbf{s}) = \exp[-(n_1 b_1^2 + n_2 b_2^2)\mathbf{s}^2/6] \qquad (2.103)$$

Hence

$$P(\mathbf{R}) = \left[\frac{3}{2\pi(n_1 b_1^2 + n_2 b_2^2)}\right]^{3/2} \exp\left[-\frac{3\mathbf{R}^2}{2(n_1 b_1^2 + n_2 b_2^2)}\right] \qquad (2.104)$$

It follows from this expression that

$$\langle\mathbf{R}^2\rangle = n_1 b_1^2 + n_2 b_2^2 = \langle\mathbf{R}_1^2\rangle + \langle\mathbf{R}_2^2\rangle \qquad (2.105)$$

[Comments]

For a linear chain which is composed of m freely jointed chains containing n_i bonds of length b_i $(i = 1, 2, \cdots, m)$ we have

$$P(\mathbf{R}) = \left(\frac{3}{2\pi n\langle b^2\rangle}\right)^{3/2} \exp\left(-\frac{3\mathbf{R}^2}{2n\langle b^2\rangle}\right) \qquad (2.106)$$

where

$$\langle \mathbf{R}^2 \rangle = \sum_{i=1}^{m} \langle \mathbf{R}_i^2 \rangle, \qquad n = \sum_{i=1}^{m} n_i, \qquad \langle b^2 \rangle = \frac{1}{n} \sum_{i=1}^{m} n_i b_i^2 \qquad (2.107)$$

[Problem B16]

For linear and single-ring Gaussian chains, each containing n bonds of length b, show that if $n \gg 1$,

$$\langle S^2 \rangle_r = \frac{1}{2} \langle S^2 \rangle_l \tag{2.108}$$

Here r and l indicate ring and linear chains, respectively.

[Solution B16]

The distribution function $P(\mathbf{R}_{ij})$ for the ring chain, where $\mathbf{R}_{ij}$ in the vector connecting the i-th segment to the j-th segment, is given by

$$P(\mathbf{R}_{ij}) = C\exp\left[-\frac{3\mathbf{R}_{ij}^2}{2b^2|j-i|}\right]\exp\left[-\frac{3\mathbf{R}_{ij}^2}{2b^2(n-|j-i|)}\right] \tag{2.109}$$

with C being a proportionality constant. The C may be determined from the normalization condition

$$\int P(\mathbf{R}_{ij}) d\mathbf{R}_{ij} = 1 \tag{2.110}$$

Thus

$$P(\mathbf{R}_{ij}) = \left(\frac{3}{2\pi b^2 \beta}\right)^{3/2} \exp\left(-\frac{3\mathbf{R}_{ij}^2}{2b^2\beta}\right) \tag{2.111}$$

where

$$\beta = |j-i|\left(1 - \frac{|j-i|}{n}\right) \tag{2.112}$$

With Eq.(2.111)

$$\langle \mathbf{R}_{ij}^2 \rangle = \int \mathbf{R}_{ij}^2 P(\mathbf{R}_{ij}) d\mathbf{R}_{ij} = \beta b^2 \tag{2.113}$$

Introduction into the general expression $\langle S^2 \rangle = (n+1)^{-2}\sum_{j>i}\sum\langle R_{ij}^2 \rangle$ gives, after the sum is replaced by an integral,

$$\langle S^2 \rangle_r = \frac{1}{12}nb^2 \tag{2.114}$$

In the same approximation, we have

$$\langle S^2 \rangle_l = \frac{1}{6}nb^2 \tag{2.115}$$

From Eqs.(2.114) and (2.115) the desired relation between $\langle S^2 \rangle_r$ and $\langle S^2 \rangle_l$ follows.

[Problem B17]

Show that

$$\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle_r = \frac{nb^2}{12} - \frac{1}{2}|j - i|\left(1 - \frac{|j - i|}{n}\right)b^2 \qquad (2.116)$$

for a flexible Gaussian ring polymer composed of n ($\gg 1$) units of bond length b. Here $\mathbf{S}_i$ is the vector connecting the i-th unit to the center of gravity of the polymer.

[Solution B17]

The mean-square distance between the i-th and the j-th units $\langle \mathbf{R}_{ij}^2 \rangle_r$ and the mean square radius of gyration of the ring $\langle S^2 \rangle_r$ are given by

$$\langle \mathbf{R}_{ij}^2 \rangle_r = (j - i)\left(1 - \frac{j - i}{n}\right)b^2 \qquad (j \geq i) \qquad (2.117)$$

$$\langle \mathbf{R}_{ij}^2 \rangle_r = (i - j)\left(1 - \frac{i - j}{n}\right)b^2 \qquad (i > j) \qquad (2.118)$$

$$\langle S^2 \rangle_r = \frac{1}{12}nb^2 \qquad (2.119)$$

If Eqs.(2.117), (2.118), and (2.119) are introduced into the general relation

$$\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle = \frac{1}{2}[\langle \mathbf{S}_i^2 \rangle + \langle \mathbf{S}_j^2 \rangle - \langle \mathbf{R}_{ij}^2 \rangle] \qquad (2.120)$$

one gets the desired equation (2.116). Note that $\langle \mathbf{S}_j^2 \rangle = \langle S^2 \rangle$.

[Problem B18]

In order to maintain a flexible chain undergoing microbrownian motion at a given end-to-end distance R it is necessary to pull the chain ends in the direction $\mathbf{R}$ by a certain force $\mathbf{K}$. Show for a Gaussian chain consisting of n equal bonds of length b that $\mathbf{K}$ is given by

$$\mathbf{K} = \frac{3kT}{\langle R^2 \rangle} \mathbf{R} \tag{2.121}$$

where T is the absolute temperature, k is Boltzmann's constant, and $\langle R^2 \rangle = nb^2$.

[Solution B18]

Let the internal energy and entropy of the chain be denoted by E and S, respectively. Then applying the first and second law of thermodynamics one can write the relation

$$dE = TdS + \mathbf{K} \cdot d\mathbf{R} \tag{2.122}$$

This gives

$$K = -T\left(\frac{\partial S}{\partial R}\right)_E \tag{2.123}$$

The Boltzmann equation for S in the present case reads

$$S = k \ln W(E, \mathbf{R}) \tag{2.124}$$

where $W(E, \mathbf{R})$ designates the number of chain configurations realizable at an energy E and an end-to-end distance $\mathbf{R}$. Substitution of Eq.(2.124) for S in Eq.(2.123) gives

$$\mathbf{K} = -kT\left(\frac{\partial \ln W}{\partial \mathbf{R}}\right)_E \tag{2.125}$$

Because W is proportional to $P(E, \mathbf{R})$, the distribution function of $\mathbf{R}$ at an energy level E, and since for the chain stated in the problem, $P(E, \mathbf{R})$ is given by

$$P(E, \mathbf{R}) = \left(\frac{3}{2\pi\langle R^2 \rangle}\right)^{3/2} \exp\left(-\frac{3R^2}{2\langle R^2 \rangle}\right) \tag{2.126}$$

Eq.(2.125) yields

$$\mathbf{K} = -kT\left(\frac{\partial \ln P}{\partial \mathbf{R}}\right)_E$$
$$= \left(\frac{3kT}{\langle R^2 \rangle}\right)\mathbf{R} \qquad (2.127)$$

which is the desired expression (2.121).

[Comments]

Equation (2.127) indicates that a Gaussian chain behaves like a spring whose elastic modulus is $3kT/\langle R^2 \rangle$.

[Problem B19]

A Gaussian chain consisting of n equal bonds of length b is atretched at its ends to keep the end-to-end distance at a given value $\mathbf{R}$. Show that the distribution of θ and ϕ for any constituent bond is given by

$$f(\theta, \phi) = \frac{3R}{4\pi nb\sinh(3R/nb)}\exp\left(\frac{3R\cos\theta}{nb}\right) \qquad (2.128)$$

Here θ is the angle between $\mathbf{r}$ and $\mathbf{R}$, with $\mathbf{r}$ being the vector representing the bond considered, ϕ is the rotational angle of $\mathbf{r}$ about the direction of $\mathbf{R}$, and $f(\theta, \phi)\sin\theta d\theta d\phi$ is the probability that the orientation is found between (θ, ϕ) and $(\theta + d\theta, \phi + d\phi)$.

[Solution B19]

The probability that the chain has a particular configuration $\{\mathbf{r}_i\}$ (which represents a set of $\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_n$, with $\mathbf{r}_i$ being the vector for the i-th bond) is proportional to

$$w(\mathbf{r}_1)w(\mathbf{r}_2)\cdots w(\mathbf{r}_n)\exp\left(\frac{\mathbf{K}\cdot\mathbf{R}}{kT}\right) \qquad (\mathbf{R} = \sum_{i=1}^{n}\mathbf{r}_i) \qquad (2.129)$$

where kT has the usual meaning, and $w(\mathbf{r}_i)$ designates the probability density of the i-th bond. For the chain under consideration $w(\mathbf{r}_i) = \delta(|\mathbf{r}_i| - b)/4\pi b^2$, where δ is Dirac's delta function.

From these considerations it follows that the distribution of θ_i and ϕ_i (these are θ and ϕ for the i-th bond), $f(\theta_i, \phi_i)$ is given by

$$f(\theta_i, \phi_i) = C\exp\left(\frac{Kb\cos\theta_i}{kT}\right) \qquad (K = |\mathbf{K}|) \qquad (2.130)$$

where C is defined by

$$C^{-1} = \int_0^{2\pi}\int_0^{\pi}\exp\left(\frac{Kb\cos\theta_i}{kT}\right)\sin\theta_i d\theta_i d\phi_1$$
$$= \left(\frac{4\pi kT}{Kb}\right)\sinh\left(\frac{Kb}{kT}\right) \qquad (2.131)$$

Thus

$$f(\theta, \phi) = \frac{Kb\exp(Kb\cos\theta/kT)}{4\pi kT\sinh(Kb/kT)} \qquad (2.132)$$

where subscript i has been omitted because Eq.(2.130) holds for any constituent bond in the chain. According to Eq.(2.121) in [Problem B18], one gets for Gaussian chains

$$K = \left(\frac{3kT}{\langle R^2 \rangle}\right)R = \left(\frac{3kT}{nb^2}\right)R \qquad (2.133)$$

Hence Eq.(2.132) is written

$$f(\theta, \phi) = \frac{3R}{4\pi nb\sinh(3R/nb)}\exp\left(\frac{3R\cos\theta}{nb}\right) \qquad (2.134)$$

which agrees with Eq.(2.128).

[Problem B20]

Suppose that the curve represents a wormlike chain. Let s be the contour length of the chain from its one end to a point P and let $\mathbf{u}(s)$ be the unit vector representing the tangent to the chain at P. Show that if $s > s'$,

$$\langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle = \exp\left(-\frac{s-s'}{q}\right) \qquad (2.135)$$

where $\langle \cdots \rangle$ designates the average over all possible configurations of the chain and q is the persistence length of the chain.

[Solution B20]

For a freely rotating chain consisting of n equal bonds of length b the statistical average of $\mathbf{r}_i \cdot \mathbf{r}_j$ $(j > i)$ is represented by

$$\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle = b^2 (-\cos\theta)^{j-i} \qquad (2.136)$$

where $\mathbf{r}_i$ is the vector for the i-th bond and θ is the bond angle. Let b and θ tend, respectively to 0 and π in such a way that $b/(1 + \cos\theta)$ remains finite, say q. Also let i and j go to infinity so that bi and bj remain at s' and s, respectively. Then the chain tends to a wormlike chain with a persistence length q, and Eq.(2.136) becomes

$$\langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle = \lim_{b \to 0}\left(1 - \frac{b}{q}\right)^{(s-s')/b} = \mathrm{e}^{-(s-s')/q} \qquad (2.137)$$

which is the required expression (2.135). Note that, in this derivation, $\mathbf{r}_i/b$ goes to $\mathbf{u}(s)$ as $b \to 0$. Though Eq.(2.135) is subject to the condition $s > s'$, one can show that

$$\langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle = \exp\left(-\frac{|s-s'|}{q}\right) \qquad (2.138)$$

regardless of the relative magnitude of s to s'.

[Comments]

The quantity $\langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle$ represents the correlation of the tangents to a continuous space curve at two different points on it when the curve is subject to thermal motion. The present problem shows that this correlation for wormlike chains vanishes exponentially with $|s - s'|$, with the rate of decrease becoming slower for larger q. This implies that the persisting length q is a measure of the stiffness of wormlike chains. The chain with infinite q represents a rigid straight rod, while the chain with zero q is regarded as perfectly flexible.

[Problem B21]

Consider two different points P and P', on a wormlike chain. The contour lengths of the chain measured from its one end 0 to P and P' are denoted by s and s'. Take the cartesian system (x, y, z) in such a way that the z-axis is parallel to the tangent to the chain at 0. The polar angles reffering to this coordinate system of the tangent vectors, $\mathbf{u}(s)$ and $\mathbf{u}(s')$, at P and P' are denoted by (θ, ϕ) and (θ', ϕ'), respectively. According to Saito, et al., the probability density (or Green's function) $G(s, \theta, \phi; s', \theta', \phi')$ for the condition that $\mathbf{u}(s)$ has an orientation specified by (θ, ϕ) and, at the same time, $\mathbf{u}(s')$ has an orientation specified by (θ', ϕ') is represented by

$$G(s, \theta, \phi; s', \theta', \phi') = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \exp\left[-\frac{n(n+1)(s-s')}{2q}\right]$$
$$\times [Y_{nm}(\theta, \phi)Y_{nm}(\theta', \phi') + Y'_{nm}(\theta, \phi)Y'_{nm}(\theta', \phi')] \qquad (2.139)$$

if $s > s'$. Here q is the persistence length of the chain, and

$$Y_{nm}(\theta, \phi) = \left[\frac{2n+1}{2\pi(1+\delta_{m,0})}\frac{(n-m)!}{(n+m)!}\right]^{1/2} P_n^m(\cos\theta)\cos(m\phi) \quad (2.140)$$

$$Y'_{nm}(\theta, \phi) = \left[\frac{2n+1}{2\pi(1+\delta_{m,0})}\frac{(n-m)!}{(n+m)!}\right]^{1/2} P_n^m(\cos\theta)\sin(m\phi) \quad (2.141)$$

with $\delta_{m,0} = 1$ ($m = 0$) and $\delta_{m,0} = 0$ ($m \geq 1$) and $P_n^m(z)$ being the associated Legendre polynomial of z.

Using Saito's formula for $G(s, \theta, \phi; s', \theta', \phi')$, show that

$$\langle \mathbf{u}(s) \cdot \mathbf{u}(0) \rangle = \exp\left(-\frac{s}{q}\right) \qquad (2.142)$$

$$\langle [\mathbf{u}(s) \cdot \mathbf{u}(0)][\mathbf{u}(s') \cdot \mathbf{u}(0)] \rangle = \frac{2}{3}\left[\exp\left(-\frac{s+2s'}{q}\right) + \frac{1}{2}\exp\left(-\frac{s-s'}{q}\right)\right]$$
$$(s > s') \qquad (2.143)$$

where $\langle \cdots \rangle$ designates the average over all possible configurations of the chain.

[Solution B21]

$$\langle \mathbf{u}(s) \cdot \mathbf{u}(0) \rangle = \int_0^{2\pi} \int_0^{\pi} \cos\theta\, G(s,\theta,\phi;0,0,0)\sin\theta \mathrm{d}\theta \mathrm{d}\phi \qquad (2.144)$$

From Eq.(2.139) one gets

$$G(s,\theta,\phi;0,0,0) = \sum_{n=0}^{\infty}\sum_{m=0}^{\infty}\exp\left[-\frac{n(n+1)}{2q}\right]Y_{nm}(\theta,\phi)Y_{nm}(0,0) \qquad (2.145)$$

because $Y'_{nm}(0,0) = 0$. With Eq.(2.145), Eq.(2.144) can be written

$$\langle \mathbf{u}(s) \cdot \mathbf{u}(0) \rangle = \sum_{n=0}^{\infty}\left(\frac{2n+1}{2}\right)\exp\left[-\frac{n(n+1)s}{2q}\right]\int_{-1}^{1}xP_n^0(x)P_n^0(1)\mathrm{d}x \qquad (2.146)$$

Since

$$\int_{-1}^{1}xP_n^0(x)P_n^0(1)\mathrm{d}x = \int_{-1}^{1}xP_n(x)P_n(1)\mathrm{d}x$$
$$= \int_{-1}^{1}xP_n(x)\mathrm{d}x = \frac{2}{3} \quad (n=1) \qquad (2.147)$$

$$\int_{-1}^{1}xP_n^0(x)P_n^0(1)\mathrm{d}x = \int_{-1}^{1}xP_n(x)P_n(1)\mathrm{d}x$$
$$= \int_{-1}^{1}xP_n(x)\mathrm{d}x = 0$$
$$(n=0 \ \text{and} \ n\geq 1) \qquad (2.148)$$

where P_n denotes the Legendre polynomial of order n, Eq.(2.146) reduces to

$$\langle \mathbf{u}(s) \cdot \mathbf{u}(0) \rangle = \exp\left(-\frac{s}{q}\right) \qquad (2.149)$$

which is Eq.(2.142).

Next one can write for $\langle [\mathbf{u}(s) \cdot \mathbf{u}(0)][\mathbf{u}(s') \cdot \mathbf{u}(0)] \rangle$

$$\langle [\mathbf{u}(s) \cdot \mathbf{u}(0)][\mathbf{u}(s') \cdot \mathbf{u}(0)] \rangle = \int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi}\int_0^{\pi}\cos\theta\cos\theta'$$
$$\times G(s',\theta',\phi';0,0,0)G(s,\theta,\phi;s',\theta',\phi')\sin\theta\sin\theta' \mathrm{d}\theta \mathrm{d}\theta' \mathrm{d}\phi \mathrm{d}\phi' (2.150)$$

Performing the integrations with respect to θ and ϕ, this becomes

$$\langle[\mathbf{u}(s)\cdot\mathbf{u}(0)][\mathbf{u}(s')\cdot\mathbf{u}(0)]\rangle = \int_0^{2\pi}\int_0^{\pi}\cos\theta'\sin\theta'G(s',\theta',\phi';0,0,0)$$
$$\times e^{-(s-s')/q}P_1(\cos\theta')d\theta'd\phi'l \qquad (2.151)$$

Substitution for $G(s',\theta',\phi';0,0,0)$ from Eq.(2.145) gives

$$\langle[\mathbf{u}(s)\cdot\mathbf{u}(0)][\mathbf{u}(s')\cdot\mathbf{u}(0)]\rangle = \sum_{n=0}^{\infty}\left(\frac{2n+1}{2}\right)\exp\left[-\frac{n(n+1)s'}{2q}\right]$$
$$\times\exp\left(-\frac{s-s'}{q}\right)\int_{-1}^{1}x^2P_n(x)\mathrm{d}x$$
$$=\frac{2}{3}\left[\exp\left(-\frac{3s'}{q}-\frac{s-s'}{q}\right)+\frac{1}{2}\exp\left(-\frac{s-s'}{q}\right)\right]$$
$$=\frac{2}{3}\left[\exp\left(-\frac{2+2s'}{q}\right)+\frac{1}{2}\exp\left(-\frac{s-s'}{q}\right)\right] \quad (2.152)$$

which is Eq.(2.143). For $s' = 0$ this reduces to Eq.(2.149), as should be expected.

[Comments]

Equation (2.139) may also be written in a more compact form as

$$G(s,\theta,\phi;s',\theta',\phi') = \frac{1}{2\pi}\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}\left(\frac{2n+1}{1+\delta_{m,0}}\right)\frac{(n-m)!}{(n+m)!}\exp\left[-\frac{n(n+1)(s-s')}{2q}\right]$$
$$\times P_n^m(\cos\theta)P_n^m(\cos\theta')\cos[m(\phi-\phi')] \qquad (2.153)$$

[Problem B22]

For a continuous chain with contour length L subjected to thermal motion, let $\langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle$ be the average correlation between unit tangent vectors of the chain, $\mathbf{u}(s)$ and $\mathbf{u}(s')$, at two points characterized by contour lengths s and s'. Show that the mean-square end-to-end distance of the chain, $\langle \mathbf{R}^2 \rangle$, is given by

$$\langle \mathbf{R}^2 \rangle = 2 \int_0^L (L - s) \langle \mathbf{u}(s) \cdot \mathbf{u}(0) \rangle \mathrm{d}s \tag{2.154}$$

if $\langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle$ depends only on $|s - s'|$. Apply Eq.(2.153) to wormlike chains. for which $\langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle = \exp(-|s - s'|/q)$ (see Eq.(2.135) in [Problem B20]).

[Solution B22]

The end-to-end distance, $\mathbf{R}$, of the chain under consideration is represented by

$$\mathbf{R} = \int_0^L \mathbf{u}(s) \mathrm{d}s \tag{2.155}$$

This may be derived by considering the limiting form of

$$\mathbf{R} = \sum_{i=1}^n \mathbf{r}_i \qquad |\mathbf{r}_i| = b \tag{2.156}$$

as $b \to 0$ and $n \to \infty$ but nb remains at a finite value L. With Eq.(2.155) one gets

$$\langle \mathbf{R}^2 \rangle = \int_0^L \int_0^L \langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle \mathrm{d}s \mathrm{d}s' \tag{2.157}$$

Now if $\langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle$ is dependent only on $|s - s'|$, Eq.(2.157) may be written, with $f(|s - s'|) = \langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle$, as

$$\begin{aligned}
\langle \mathbf{R}^2 \rangle &= \int_0^L \int_0^L f(|s - s'|) \mathrm{d}s \mathrm{d}s' \\
&= \int_0^L \left[\int_0^{s'} f(|s - s'|) \mathrm{d}s \right] \mathrm{d}s' \\
&\quad + \int_0^L \left[\int_{s'}^L f(|s - s'|) \mathrm{d}s \right] \mathrm{d}s'
\end{aligned} \tag{2.158}$$

Since

$$\int_0^L \left[\int_{s'}^L f(|s-s'|)\mathrm{d}s \right] \mathrm{d}s' = \int_0^L \left[\int_0^s f(|s-s'|)\mathrm{d}s' \right] \mathrm{d}s \qquad (2.159)$$

Eq.(2.158) becomes

$$\langle \mathbf{R}^2 \rangle = 2 \int_0^L \left[\int_0^{s'} f(|s-s'|)\mathrm{d}s \right] \mathrm{d}s' \qquad (2.160)$$

which is in turn written, with the substitution $s' - s = \xi$, as

$$
\begin{aligned}
\langle \mathbf{R}^2 \rangle &= 2 \int_0^L \left[\int_0^{s'} f(|\xi|)\mathrm{d}\xi \right] \mathrm{d}s' \\
&= 2 \int_0^L \left(\int_\xi^L \mathrm{d}s' \right) f(|\xi|)\mathrm{d}\xi \\
&= 2 \int_0^L (L-\xi)f(|\xi|)\mathrm{d}\xi \qquad (2.161)
\end{aligned}
$$

Because $f(|\xi|) = \langle \mathbf{u}(\xi) \cdot \mathbf{u}(0) \rangle$, Eq.(2.161) is equivalent to Eq.(2.154).

Substituting $f(|\xi|) = \exp(-|\xi|/q)$ into Eq.(2.161), one obtains for wormlike chains

$$
\begin{aligned}
\langle R^2 \rangle &= 2 \int_0^L (L-\xi)\exp\left(-\frac{\xi}{q}\right)\mathrm{d}\xi \\
&= 2q^2 \left(\frac{L}{q} - 1 + \mathrm{e}^{-L/q} \right) \qquad (2.162)
\end{aligned}
$$

[Problem B23]

Show that the mean-square radius of gyration for a wormlike chain, $\langle S^2 \rangle$, is expressed in terms of L and q as

$$\langle S^2 \rangle = \frac{q^2}{3}\left[\frac{L}{q} - 3 + 6\left(\frac{q}{L}\right)^2 \left(1 - \mathrm{e}^{-L/q}\right) \right] \qquad (2.163)$$

where L and q sre the contoue length and persistence length of the chain, respectively.

[Solution B23]

The general formula for discrete chains

$$\langle S^2 \rangle = \frac{1}{(n+1)^2} \sum_{i=0}^{n} \sum_{j>i}^{n} \langle R_{ij}^2 \rangle \qquad (2.164)$$

may be written for a continuous space curve as

$$\langle S^2 \rangle = \frac{1}{L^2} \int_0^L \left(\int_{s'}^L \langle [\mathbf{R}(s',s)]^2 \rangle \mathrm{d}s \right) \mathrm{d}s' \qquad (2.165)$$

where $\mathbf{R}(s',s)$ is the vector connecting two points on the curve which are characterized by contour lengths s' and s, respectively, with $s' < s$. For wormlike chains one may use for $\langle [\mathbf{R}(s',s)]^2 \rangle$ Eq.(2.162) in [Problem B22], with L replaced by $s - s'$. Thus the desired $\langle S^2 \rangle$ can be obtained from

$$\langle S^2 \rangle = \frac{2q^2}{L^2} \int_0^L \int_{s'}^L \left[\frac{s - s'}{q} - 1 + \exp\left(-\frac{s - s'}{q}\right) \right] \mathrm{d}s\,\mathrm{d}s' \qquad (2.166)$$

Performing the integration, one obtains Eq.(2.163).

[Problem B24]

Show that the persistence length q of s wormlike chain is the limit of $\langle R_t \rangle$ for infinite L, where $\langle R_t \rangle$ denotes the statistical average of the projection of $\mathbf{R}$, the end-to-end distance of the chain, on the direction tangential to the chain at its end, and L is the contour length of the chain.

[Solution B24]

$\mathbf{R}$ is represented by

$$\mathbf{R} = \int_0^L \mathbf{u}(s)\mathrm{d}s \tag{2.167}$$

where $\mathbf{u}(s)$ is the unit tangent to the chain at a point characterized by contour length s. $R_t = \mathbf{R} \cdot \mathbf{u}(0)$. Hence

$$\langle R_t \rangle = \int_0^L \langle \mathbf{u}(s) \cdot \mathbf{u}(0) \rangle \mathrm{d}s \tag{2.168}$$

For wormlike chains $\langle \mathbf{u}(s) \cdot \mathbf{u}(0) \rangle = \exp(-s/q)$. Therefore Eq.(2.168) becomes

$$\langle R_t \rangle = \int_0^L \exp\left(-\frac{s}{q}\right) = q\left[1 - \exp\left(-\frac{L}{q}\right)\right] \tag{2.169}$$

whence it follows that

$$\lim_{L \to 0} \langle R_t \rangle = q \tag{2.170}$$

This gives an interpretation of q.

[Problem B25]

For a wormlike chain with contour length L and persistence length q, show that

$$\langle R_t^2 \rangle = \frac{2q^2}{3}\left\{ \frac{L}{q} - \frac{1}{3}\left[1 - \exp\left(-\frac{3L}{q} \right) \right] \right\} \qquad (2.171)$$

where R_t is the projection of the end-to-end distance $\mathbf{R}$ on the tangent to the chain at its one end.

Hint: Use eq.(2.143) in [Problem B21].

[Solution B25]

$$R_t = \mathbf{R} \cdot \mathbf{u}(0) = \int_0^L \mathbf{u}(s) \cdot \mathbf{u}(0)\mathrm{d}s \qquad (2.172)$$

where $\mathbf{u}(s)$ is the unit tangent vector of the chain at contour length s. Hence

$$\langle R_t^2 \rangle = \int_0^L \int_0^L \langle [\mathbf{u}(s) \cdot \mathbf{u}(0)][\mathbf{u}(s') \cdot \mathbf{u}(0)] \rangle \mathrm{d}s\mathrm{d}s' \qquad (2.173)$$

Introducing Eq.(2.143) in the Hint into Eq.(2.173), one obtains

$$
\begin{aligned}
\langle R_t^2 \rangle &= \frac{4}{3}\int_0^L \int_{s'}^L \left[\exp\left(-\frac{s+2s'}{q} \right) + \frac{1}{2}\exp\left(-\frac{s-s'}{q} \right) \right] \mathrm{d}s\mathrm{d}s' \\
&= \frac{4}{3}\int_0^L \left[\exp\left(-\frac{2s'}{q} \right) + \frac{1}{2}\exp\left(\frac{s'}{q} \right) \right]\mathrm{d}s' \int_{s'}^L \exp\left(-\frac{s}{q} \right)\mathrm{d}s \\
&= \frac{4q}{3}\int_0^L \left[\exp\left(-\frac{s'}{q} \right) - \exp\left(-\frac{L}{q} \right) \right] \\
&\quad \times \left[\exp\left(-\frac{2s'}{q} \right) + \frac{1}{2}\exp\left(\frac{s'}{q} \right) \right]\mathrm{d}s' \\
&= q^2\left\{ \frac{2}{3}\left(\frac{L}{q} \right) - \frac{2}{9}\left[1 - \exp\left(-\frac{3L}{q} \right) \right] \right\}
\end{aligned} \qquad (2.174)
$$

[Problem B26]

Suppose a flexible polymer chain which undergoes excluded volume effects and assume that the potential, w_{km}, of mean forces acting between the k-th and m-th segments is expressed by

$$w_{km} = \beta kT\delta(\mathbf{R}_{km}) \qquad (2.175)$$

where $\mathbf{R}_{km}$ is the distance between the two segments considered, δ is the delta function, β is the excluded volume per segment, and kT has the usual meaning. Show that the partition function of the chain with its end-to-end vector $\mathbf{R}$ given, $Z(\mathbf{R})$, is represented by

$$Z(\mathbf{R}) = Z_0(\mathbf{R})\exp\left[-\sum_{k>m}\sum\int_0^\beta P(\xi;0_{km}|\mathbf{R})\mathrm{d}\xi\right] \qquad (2.176)$$

Here $Z_0(\mathbf{R})$ denotes the $Z(\mathbf{R})$ for the unperturbed chain in which $\beta = 0$, and $P(\xi;0_{km}|\mathbf{R})$ is the probability of contact of the k-th and m-th segments in a hypothetical chain in which the end-to-end vector takes the assigned value $\mathbf{R}$ and the excluded volume of each segment has a value of ξ.

[Solution B26]

Let $Z(\mathbf{R})$ for the hypothetical chain be denoted by $Z(\xi;\mathbf{R})$. Then

$$Z(\xi;\mathbf{R}) = \int \exp[-\xi\sum_{k>m}\sum\delta(\mathbf{R}_{km})]\mathrm{d}\{\mathbf{r}\}/\mathrm{d}\mathbf{R} \qquad (2.177)$$

where $\{\mathbf{r}\}$ is a short-hand notation for representing the configuration of the chain, and $\mathrm{d}\mathbf{R}$ put in the denominator indicates that the integral with respect to $\{\mathbf{r}\}$ should be made subject to the condition thet $\mathbf{R}$ is fixed. Logarithmic differentiation of Eq.(2.177) with respect to ξ gives

$$\frac{\mathrm{d}\ln Z(\xi;R)}{\mathrm{d}\xi} = -\frac{1}{Z(\xi;R)}\int\sum_{k>m}\sum\delta(\mathbf{R}_{km})\exp[-\xi\sum_{k>m}\sum\delta(\mathbf{R}_{km})]\frac{\mathrm{d}\{\mathbf{r}\}}{\mathrm{d}\mathbf{R}}$$

$$= -\sum_{k>m}\sum P(\xi;0_{km}|\mathbf{R}) \qquad (2.178)$$

Integration yields

$$Z(\beta; \mathbf{R}) = Z(0; \mathbf{R})\exp\left[-\sum_{k>m}\sum\int_0^\beta P(\xi; 0_{km}|\mathbf{R})\mathrm{d}\xi\right] \qquad (2.179)$$

Since $Z(\beta; \mathbf{R})$ and $Z(0; \mathbf{R})$ correspond to $Z\mathbf{R})$ and $Z_0(\mathbf{R})$ in Eq.(2.176), respectively, Eq.(2.179) is the required formula.

[Comments]

An equation in which $\mathbf{R}$ in Eq.(2.176) is replaced by S, the radius of gyration of the chain, also holds. These equations for $Z(\mathbf{R})$ and $Z(S)$ serve as the convenient bases for working out various approximations to the linear expansion factors, α_R and α_S, of perturbed chains.

[Problem B27]

Apply the Wang-Uhlenbeck-Fixman theorem to derive the bivariate distribution function $P(0_{ij}, \mathbf{R})$ of a flexible chain composed of n $(n \gg 1)$ identical units of bond length b. Here $\mathbf{R}$ is the end-to-end vector of the chain and 0_{ij} means that the distance R_{ij} between i and j is zero. Thus, $P(0_{ij}, \mathbf{R})$ is the probability density of finding that the end-to-end vector is $\mathbf{R}$ and at the same time units i and j are in contact.

[Solution B27]

Consider the case of $s = 2$ in the Wang-Uhlenbeck-Fixman theorem and equate $\mathbf{R}_{ij}(j \geq i)$ to Φ_1 and $\mathbf{R}$ to Φ_2. Then

$$\Phi_2 = \mathbf{R} = \sum_{j=1}^{n} \mathbf{r}_j \tag{2.180}$$

and

$$\Phi_1 = \mathbf{R}_{ij} = \sum_{k=1}^{n} \psi_{2k} \mathbf{r}_k \tag{2.181}$$

with

$$\psi_{2k} = 1 \quad \text{for} \ i < k < j$$
$$= 0 \quad \text{otherwise} \tag{2.182}$$

Hence, the elements of the 2×2 matrix $\mathbf{C}$ are found to be

$$c_{11} = n \tag{2.183}$$

$$c_{12} = c_{21} = \sum_{k=1}^{n} \psi_{2k} = j - i \tag{2.184}$$

$$c_{22} = \sum_{k=1}^{n} (\psi_{2k})^2 = j - i \tag{2.185}$$

and the determinant $|\mathbf{C}|$ and the cofactors c^{kl} are given by

$$|\mathbf{C}| = (j - i)(n - j + i) \tag{2.186}$$

$$c^{11} = j - i \tag{2.187}$$

$$c^{12} = c^{21} = i - j \tag{2.188}$$

$$c^{22} = n \tag{2.189}$$

Eqs.$(2.186) - (2.189)$ yields

$$P(\mathbf{R}_{ij}, \mathbf{R}) = \left(\frac{3}{2\pi b^2}\right) \left[\frac{1}{(j-i)(n-j+i)}\right]^{3/2} \exp\left\{-\frac{3}{2b^2(j-i)(n-j+i)}\right.$$
$$\times [(j-i)\mathbf{R}^2 - 2(j-i)\mathbf{R} \cdot \mathbf{R}_{ij} + n\mathbf{R}_{ij}^2] \right\} \tag{2.190}$$

When $\mathbf{R}_{ij} = 0$, this reduces to

$$P(0_{ij}, \mathbf{R}) = \left(\frac{3}{2\pi b^2}\right)^3 \left[\frac{1}{(j-i)(n-j+i)}\right]^{3/2} \exp\left[-\frac{3\mathbf{R}^2}{2b^2(n-j+i)}\right] \tag{2.191}$$

which is the desired expression.

[Comments]

The distribution function $P(0_{ij})$ can be obtained by integrating $P(0_{ij}, \mathbf{R})$ over $\mathbf{R}$;

$$P(0_{ij}) = \int P(0_{ij}, \mathbf{R}) d\mathbf{R} \tag{2.192}$$

Substitution of Eq.(2.191) gives

$$P(0_{ij}) = \left(\frac{3}{2\pi b^2}\right)^3 (j-i)^{-3/2} \tag{2.193}$$

which, as expected, agrees with the expression obtained by putting $\mathbf{R}_{ij} = 0$ in the Gaussian distribution function for $P(\mathbf{R}_{ij})$:

$$P(\mathbf{R}_{ij}) = \left[\frac{3}{2\pi b^2(j-i)}\right]^{3/2} \exp\left[-\frac{3\mathbf{R}_{ij}^2}{2(j-i)b^2}\right] \tag{2.194}$$

[Problem B28]

Show that the expansion factor α_R $[= \langle \mathbf{R}^2 \rangle^{1/2}/\langle \mathbf{R}^2 \rangle_0^{1/2}]$ of a flexible linear chain with a very small excluded volume is expressed by

$$\alpha_R^2 = 1 + \frac{4}{3}z + \cdots \tag{2.195}$$

where z is the excluded-volume parameter.

Hint: Use Eq.(2.175) in [Problem B26] for the potential of mean forces.

[Solution B28]

From the definition

$$\langle \mathbf{R}^2 \rangle = \int \mathbf{R}^2 P(\mathbf{R}) \mathrm{d}\mathbf{R} \tag{2.196}$$

where $P(\mathbf{R})$ denotes the distribution function for the end-to-end vector $\mathbf{R}$ of the chain in the perturbed state. With Eq.(2.177) in [Problem B26], one finds that $P(\mathbf{R})$ is represented by

$$P(R) = C \int \delta(\mathbf{R} - \sum_{j=i}^n \mathbf{r}_j) \exp[-\beta \sum_{i<j}^n \delta(\mathbf{R}_{ij})] [\prod_{j=1}^n \tau_j(\mathbf{r}_j)] \mathrm{d}\mathbf{r}_1 \cdots \mathrm{d}\mathbf{r}_n \tag{2.197}$$

with the normalization constant C and the bond probability $\tau_j(\mathbf{r}_j)$ for bond j. Expanding $\exp[-\beta \sum_{i<j} \delta(\mathbf{R}_{ij})]$ in powers of β, one gets

$$\begin{aligned} P(R) =& C \int \delta(\mathbf{R} - \sum_{j=1}^n \mathbf{r}_j) [\prod_{j=1}^n \tau_j(\mathbf{r}_j)] \mathrm{d}\mathbf{r}_1 \cdots \mathrm{d}\mathbf{r}_n \\ &- \beta \sum_{i<j} \int (\mathbf{R} - \sum_{j=1}^n \mathbf{r}_j) \delta(\mathbf{R}_{ij}) [\prod_{j=1}^n \tau_j(\mathbf{r}_j)] \mathrm{d}\mathbf{r}_1 \cdots \mathbf{r}_n + \cdots \\ =& C[P_0(\mathbf{R}) - \beta \sum_{i<j} P_0(0_{ij}, \mathbf{R}) + \cdots] \end{aligned} \tag{2.198}$$

where the subscript zero refers to the unperturbed state. The constant C can be determined from the normalization condition $\int P(\mathbf{R}) \mathrm{d}\mathbf{R} = 1$, yielding

$$C^{-1} = 1 - \beta \sum_{i<j} P_0(0_{ij}) + \cdots \tag{2.199}$$

where use has been made of Eq.(2.192) in [Problem B27].

Substitution of Eq.(2.198) with Eq.(2.199) and the expressions for $P_0(\mathbf{R})$, $P_0(0_{ij})$, and $P_0(\mathbf{R}, 0_{ij})$ (see [Problem B27]) into Eq.(2.196), followed by integration, gives

$$\langle R^2 \rangle = \langle R^2 \rangle_0 + \beta \left(\frac{3}{2\pi b^2} \right)^{3/2} b^2 \sum_{i<j} (j-i)^{-1/2} + \cdots \qquad (2.200)$$

with

$$\langle R^2 \rangle = nb^2 \qquad (2.201)$$

In terms of α_R^2 and z, Eq.(2.200) may be written

$$\alpha_R^2 = 1 + zn^{-3/2} \sum_{i<j} (j-i)^{-1/2} + \cdots \qquad (2.202)$$

Approximating the sums by integrals,

$$\sum_{i<j} (j-i)^{-1/2} = \frac{4}{3} n^{3/2} \qquad (2.203)$$

Introduction of this into Eq.(2.202) leads to Eq.(2.195).

[Problem B29]

The partition function $Z(\mathbf{R})$ of a perturbed flexible chain with a given end-to-end distance $\mathbf{R}$ is represented by Eq.(2.176) in [Problem B26]. Show that the expansion factor α_R satisfies the relation

$$\alpha_R^5 - \alpha_R^3 = \left(\frac{2\pi}{3}\right)^{1/2} z \tag{2.204}$$

if the following approximations are used: (1) ξ in the equation (2.176) is replaced by the maximum value β and (2) $P(\beta; 0_{kl}|\mathbf{R})$ is replaced by the unperturbed $P_0(0_{kl}|\mathbf{R})$ with the bond length expanded by a factor α_R.

Hint: Evaluate the integral

$$I = \frac{\int_0^\infty x^4 e^{-f(x)} dx}{\int_0^\infty x^2 e^{-f(x)} dx} \tag{2.205}$$

by use of the Hermans-Overbeek approximation in which I is equated to the value of x at which $x^3 e^{-f(x)}$ becomes maximum.

[Solution B29]

Under the assumption stated in Problem, $Z(\mathbf{R})$ is given by

$$Z(\mathbf{R}) = Z_0(\mathbf{R}) \exp[-\beta \sum_{i<j} P(0_{ij}|\mathbf{R})] \tag{2.206}$$

with

$$P(0_{ij}|\mathbf{R}) = \frac{P(0_{ij}, \mathbf{R})}{P(\mathbf{R})}$$
$$= \left(\frac{3}{2\pi\alpha_R^2 b^2}\right)^{3/2} \left[\frac{n}{(j-i)(n-j+1)}\right]^{3/2}$$
$$\times \exp\left[-\frac{3(j-i)\mathbf{R}^2}{2n(n-j+1)\alpha_R^2 b^2}\right] \tag{2.207}$$

[see Eq.(2.191) in [Problem B27] for $P(0_{ij}, \mathbf{R})$]. Hence

$$\langle R^2 \rangle = \frac{\int \mathbf{R}^2 Z(\mathbf{R}) d\mathbf{R}}{\int Z(\mathbf{R}) d\mathbf{R}}$$

$$= \frac{\int_0^\infty R^4 P_0(\mathbf{R})\exp[-\beta \sum_{i<j} P(0_{ij}|\mathbf{R})]\mathrm{d}R}{\int_0^\infty R^2 P_0(\mathbf{R})\exp[-\beta \sum_{i<j} P(0_{ij}|\mathbf{R})]\mathrm{d}R} \qquad (2.208)$$

with

$$P_0(\mathbf{R}) = \left(\frac{3}{2\pi n b^2}\right)^{3/2} \exp\left(-\frac{3\mathbf{R}^2}{2nb^2}\right) \qquad (2.209)$$

Therefore, α_R^2 $[= \langle \mathbf{R}^2\rangle/\langle \mathbf{R}^2\rangle_0]$ is given by

$$\alpha_R^2 = \frac{\int_0^\infty x^4 \exp\left\{-\frac{3}{2}x^2 - \frac{nz}{\alpha_R^3}\sum_{i<j}\left[\frac{1}{(j-i)(n-j+1)}\right]^{3/2}\exp\left[-\frac{3x^2(j-i)}{\alpha_R^2(n-j+i)}\right]\right\}\mathrm{d}x}{\int_0^\infty x^2 \exp\left\{-\frac{3}{2}x^2 - \frac{nz}{\alpha_R^3}\sum_{i<j}\left[\frac{1}{(j-i)(n-j+1)}\right]^{3/2}\exp\left[-\frac{3x^2(j-i)}{\alpha_R^2(n-j+i)}\right]\right\}\mathrm{d}x}$$

$$(2.210)$$

By applying the Hermans-Overbeek approximation to Eq.(2.210), one can derive

$$\alpha_R^5 - \alpha_R^3 = nz \sum_{i<j} \frac{1}{(j-i)^{1/2}(n-j+i)^{5/2}}\exp\left[-\frac{3(j-i)}{2(n-j+i)}\right] \quad (2.211)$$

If the double sum in this equation is approximated by integrals,

$$\sum_{i<j} \frac{1}{(j-i)^{1/2}(n-j+i)^{5/2}}\exp\left[-\frac{3(j-i)}{2(n-j+i)}\right]$$

$$\simeq \int_0^n \frac{1}{t^{1/2}(n-t)^{3/2}}\exp\left[-\frac{3t}{2(n-t)}\right]\mathrm{d}t$$

$$= \frac{1}{n}\int_0^\infty \frac{1}{\sqrt{\xi}}e^{-3\xi/2}\mathrm{d}\xi = \frac{1}{n}\left(\frac{2\pi}{3}\right)^{1/2} \qquad (2.212)$$

which is inserted into Eq.(2.210) to give the desired expression, Eq.(2.204).

[Comments]

(1) For small values of z, Eq.(2.204) is expanded to give

$$\alpha_R^2 = 1 + \left(\frac{2\pi}{3}\right)^{1/2} z + \cdots \qquad (2.213)$$

The coefficient $(2\pi/2)^{1/2}$ is slightly larger than the corresponding value of $4/3$ in Eq.(2.195) in [Problem B28]. This difference may be ascribed to

the Hermans-Overbeek approximation employed. Thus one may replace $(2\pi/3)$ in Eq.(2.204) by $4/3$. The resulting equation is referred to as the modified Flory equation. On the other hand, the equation originally derived by Flory with a mean-molecular field approximation has the value of 2.60 for this coefficient.

(2) Equation (2.204) indicates that α_R^5 becomes proportional to z as z increases and hence that in an extremely good solvent $\langle R^2 \rangle$ is proportional to $M^{1.2}$ (M: molecular weight of the chain). For this reason Eq.(2.204) is referred to as of the fifth-power type.

[Problem30]

Show that $N(n)$, the number of observationally distinguishable $n(ads)$ (types of sequence containing n monomer units), is represented by $2^{n-2}+2^{m-1}$, where $m = n/2$ if n is even and $m = (n-1)/2$ if n is odd.

[Solution B30]

The total number of $n(ads)$ is n^{n-1}, because there are $n-1$ pairs of adjacent monomer units in a succession of n monomer units and each pair can be of either meso type or racemic type. However, not all of these $n(ads)$ are observationally distinguishable. For example, the pentads $mmrm$ and $mrmm$ (m: designates a meso diad and r a racemic diad) are observationally equivalent. A simple consideration indicates that

$$2N(n) = 2^{n-1} + S(n) \tag{2.214}$$

where $S(n)$ is the number of $n(ads)$ which are symmetric in the distribution of m and r, such as $mmrmm$, $mrrrm$, $rmmmr$ in the case of hexads. One finds that $S(n)$ is given by 2^m if $m = n/2$ for even n and $m = (n-1)/2$ for odd n. Thus

$$N(n) = 2^{n-2} + 2^{m-1} \tag{2.215}$$

which is the required expression for $N(n)$.

For exmple, when $n = 5$ (pentads), $m = 2$ and $N(n) = 2^3 + 2 = 10$.

[Problem B31]

Suppose a stereoregular polymer chain long enough for the end effects to be ignored. Define P_{xy} $(x, y = i, s)$ as the probanility that a monomer adds in the y form to the chain with a monomer of the x form as its active end unit. Show that if the penultimate effect is not taken into consideration, the number-average and weight-average sequence lengths, $\langle i \rangle_n$ and $\langle i \rangle_w$, are represented by

$$\langle i \rangle_n = \frac{1}{p_{is}}, \qquad \langle i \rangle_w = \frac{2}{p_{is}} - 1 \qquad (2.216)$$

[Solution B31]

$$\langle i \rangle_n = \frac{\sum_{k=0}^{\infty}(k+1)p_{si}(p_{ii})^k p_{is}}{\sum_{k=0}^{\infty} p_{si}(p_{ii})^k p_{is}} \qquad (2.217)$$

$$\langle i \rangle_w = \frac{\sum_{k=0}^{\infty}(k+1)^2 p_{si}(p_{ii})^k p_{is}}{\sum_{k=0}^{\infty}(k+1)p_{si}(p_{ii})^k p_{is}} \qquad (2.218)$$

The calculation of the sums gives

$$\langle i \rangle_n = \frac{1}{1 - p_{ii}} \qquad (2.219)$$

$$\langle i \rangle_w = \frac{2}{1 - p_{ii}} - 1 \qquad (2.220)$$

Since $p_{ii} + p_{is} = 1$, Eqs.(2.219) and (2.220) give the desired formulas.

[Problem B32]

Show that the average fraction $\langle f(t) \rangle$ of bonds of *trans* conformation in an infinitely long polyethylene chain is given by

$$\langle f(t) \rangle = \frac{1 - \lambda_2}{\lambda_1 - \lambda_2} \tag{2.221}$$

Here λ_1 and λ_2 $(\lambda_1 > \lambda_2)$ are the eigenvalue of the matrix $\mathbf{U}$ given by

$$\mathbf{U} = \begin{pmatrix} 1 & \sigma & \sigma \\ 1 & \sigma\psi & \sigma\omega \\ 1 & \sigma\omega & \sigma\psi \end{pmatrix} \tag{2.222}$$

with $\omega \simeq 0$ and $\psi \simeq 1$.

[Solution B32]

The average fraction of bonds of *trans* conformation is given by

$$\langle f(t) \rangle = \lim_{n \to \infty} \frac{1}{n-2} \sum_{i=2}^{n-1} \langle f_i(t) \rangle \tag{2.223}$$

with

$$\langle f_i(t) \rangle = Z_n^{-1} (1\ 0\ 0) \mathbf{U}^{i-2} \begin{pmatrix} 1 & 0 & 0 \\ 1 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} \mathbf{U}^{n-i-1} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \tag{2.224}$$

where $\langle f_i(t) \rangle$ denotes the probability that the i-th bond is in *trans* conformation regardless of the state of other bonds. Since

$$\begin{pmatrix} 1 & 0 & 0 \\ 1 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} (1\ 0\ 0) \tag{2.225}$$

Eq.(2.224) may be rewritten

$$\langle f_i(t) \rangle = Z_n^{-1} Z_i Z_{n-i+1} \tag{2.226}$$

by use of the expression of Z_n given by

$$Z_n = \left(\frac{\lambda_1 - \sigma}{\lambda_1 - \lambda_2} \right) \lambda_1^n + \left(\frac{\sigma - \lambda_2}{\lambda_1 - \lambda_2} \right) \lambda_2^n \qquad (2.227)$$

Substituting this into Eq.(2.226), $\langle f_i(t) \rangle$ becomes

$$\langle f_i(t) \rangle = \frac{1 - \lambda_2}{\lambda_1 - \lambda_2} \left\{ 1 + \frac{\lambda_1 - 1}{1 - \lambda_2} \left[\left(\frac{\lambda_2}{\lambda_1} \right)^{i-1} + \left(\frac{\lambda_2}{\lambda_1} \right)^{n-i} \right] \right.$$
$$\left. + \left(\frac{\lambda_1 - 1}{1 - \lambda_2} \right)^2 \left(\frac{\lambda_2}{\lambda_1} \right)^{n-1} \right\} \left[1 + \frac{\lambda_1 - 1}{\lambda_2} \left(\frac{\lambda_2}{\lambda_1} \right)^{n-1} \right]^{-1} \qquad (2.228)$$

Substitution of this equation into Eq.(2.223), followed by summation, gives the desired expression (2.221). Note that

$$\lambda_1 = \frac{1}{2}\{1 + \sigma(1 + \omega) + [(1 - \sigma(1 + \omega))^2 + 8\sigma]^{1/2}\} \qquad (2.229)$$

$$\lambda_2 = \frac{1}{2}\{1 + \sigma(1 + \omega) - [(1 - \sigma(1 + \omega))^2 + 8\sigma]^{1/2}\} \qquad (2.230)$$

$$\lambda_3 = \sigma(1 - \omega) \qquad (2.231)$$

when $\psi = 1$.

[Problem B33]

Compute $\langle f(t) \rangle$ at 413.16 K with $E_g = 500$ cal/mol and $E_{g^+}E_{g^-} = 2500$ cal/mol, and then compare it with $\langle f(t) \rangle$ for the corresponding independent rotation chain. Note that $\sigma = \exp(-E_g/RT)$ and $\sigma\omega = \exp(-E_{g^+}E_{g^-}/RT)$ and assume that $\psi = 1$.

[Solution B33]

$$\sigma\psi = \sigma = \exp\left(-\frac{500}{1.987 \times 413.16}\right)$$

$$= 0.544 \tag{2.232}$$

$$\sigma\omega = \exp\left(-\frac{2500}{1.987 \times 413.16}\right) = 0.0476 \tag{2.233}$$

Hence,

$$\lambda_1 = 1.86, \qquad \lambda_2 = -0.267 \tag{2.234}$$

(see Eqs.(2.229) and (2.230) in [Problem B32] for the expression of λ_1 and λ_2). Introducing these values of λ_1 and λ_2 into Eq.(2.221) in [Problem B32], one obtains

$$\langle f(t) \rangle = 0.596 \tag{2.235}$$

If all the bonds undergo independent rotation, the statistical weight matrix is written

$$\mathbf{U}_0 = \begin{pmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma \\ 1 & \sigma & \sigma \end{pmatrix} \tag{2.236}$$

since all the elements are determined by statistical weights of a paticular bond considered, regardless of the conformational state of the preceding bond. The eigenvalues of the $\mathbf{U}_0$ are easily found to be

$$\lambda_1 = 1 + 2\sigma, \qquad \lambda_2 = \lambda_3 = 0 \tag{2.237}$$

Hence, $\langle f(t) \rangle_0$ for independent rotation is given by

$$\langle f(t) \rangle_0 = \frac{1}{1 + 2\sigma} = 0.479 \tag{2.238}$$

which is about 20 % smaller than the $\langle f(t) \rangle$.

[Problem B34]

Show that the average fraction $\langle f(3t)\rangle$ of ttt triads in an infinitely long polyethylene chain is given by

$$\langle f(3t)\rangle = \frac{\langle f(t)\rangle}{\lambda_1^2} \tag{2.239}$$

where $\langle f(t)\rangle$ is defined in [Problem B32].

[Solution B34]

One can express $\langle f(3t)\rangle$ in terms of $\mathbf{U}$ as

$$\langle f(3t)\rangle = \lim_{n\to\infty} \frac{1}{(n-4)Z_n} \sum_{i=3}^{n-2} (1\ 0\ 0)\mathbf{U}^{i-3} \begin{pmatrix} 1 & 0 & 0 \\ 1 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}^3 \mathbf{U}^{n-i-2} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \tag{2.240}$$

Since

$$\begin{pmatrix} 1 & 0 & 0 \\ 1 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}^3 = \begin{pmatrix} 1 & 0 & 0 \\ 1 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} (1\ 0\ 0) \tag{2.241}$$

Eq.(2.240) is written

$$\langle f(3t)\rangle = \lim_{n\to\infty} \frac{1}{(n-4)Z_n} \sum_{i=3}^{n-2} Z_{i-1}Z_{n-i} \tag{2.242}$$

Substituting Eq.(2.227) in [Problem B32] and evaluating the sum, one arrives at the desired expression, Eq.(2.239).

[Problem B35]

Write down all possible conformations of a polypeptide chain of $N = 6$ and confirm Eq.(2.227) in [Problem B32] for the partition function Z_N.

[Solution B35]

The possible conformations for this chain may be enumerated as

Conformation	Statistical weight
$chhhhc$	σs^2
$cchhhc$	σs
$chhhcc$	σs
$cccccc$	1

Here the above statistical weight for each conformation is expressed by the product of the respective statistical weights defined for the joint conformations. For example, the conformation $chhhhc$ gives $1 \cdot \sqrt{\sigma} \cdot s \cdot s \cdot \sqrt{\sigma} \cdot 1$. Since the partition function Z_6 is the sum of the indicated statistical weights,

$$Z_6 = 1 + 2\sigma s + \sigma s^2 \tag{2.243}$$

On the other hand,

$$Z_6 = (0\,0\,0\,1\,0\,0\,1) \begin{pmatrix} s & 0 & 0 & 0 & \sqrt{\sigma} & 0 & 0 \\ 0 & 0 & \sqrt{\sigma} & 0 & 0 & 0 & 0 \\ s & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \sqrt{\sigma} & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 1 \\ 1 \end{pmatrix} \tag{2.244}$$

Carrying out the multiplication of the matrices, one actually finds that Eq.(2.244) agrees with Eq.(2.243).

[Problem B36]

In the simplified model of Zimm and Bragg, the partition function Z_N for an α-helix-forming polypeptide composed of N residues is represented by

$$Z_N = (1\ 1)\mathbf{M}^{N-3} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{2.245}$$

with the transition probability matrix $\mathbf{M}$ given by

$$\mathbf{M} = \begin{pmatrix} 1 & 1 \\ s\sigma & s \end{pmatrix} \tag{2.246}$$

Here the statistical weight σs is assigned to every residue of h which follows a coiled residue (c). Express the Z_N in terms of the eigenvlues λ_1 and λ_2 for the matrix $\mathbf{M}$.

[Solution B36]

The $\mathbf{M}$ may be diagonalized by an appropriate matrix $\mathbf{A}$ such that

$$\mathbf{A}^{-1}\mathbf{M}\mathbf{A} = \Lambda = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix} \tag{2.247}$$

The eigenvalues λ_1 and λ_2 ($\lambda_1 > \lambda_2$) satisfy

$$|\mathbf{M} - \lambda_k \mathbf{E}| = 0 \quad (k = 1, 2) \tag{2.248}$$

where $\mathbf{E}$ is 2×2 unit matrix and $|\cdots|$ denotes the determinant. Thus one finds that λ_1 and λ_2 are the roots of the characteristic equation

$$(\lambda_k - s)(\lambda_k - 1) = \sigma s \tag{2.249}$$

Now, one has from Eq.(2.247)

$$\mathbf{M}\mathbf{A} = \mathbf{A}\Lambda \tag{2.250}$$

$$\mathbf{M} = \mathbf{A}\Lambda\mathbf{A}^{-1} \tag{2.251}$$

Introduction of Eq.(2.251) into Eq.(2.245) yields

$$Z_N = (1\ 1)\mathbf{A}\Lambda\mathbf{A}^{-1}\mathbf{A}\Lambda\mathbf{A}^{-1}\cdots\mathbf{A}\Lambda\mathbf{A}^{-1}\begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$= (1\ 1)\mathbf{A}\Lambda^{N-3}\mathbf{A}^{-1}\begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$= A_{11}^{-1}(A_{11} + A21)\lambda_1^{N-3} + A_{21}^{-1}(A_{21} + A_{22})\lambda_2^{N-3} \quad (2.252)$$

The $(1, k)$ element, A_{1k}, of $\mathbf{A}$ can be determined from

$$\mathbf{M}\begin{pmatrix} A_{1k} \\ A_{2k} \end{pmatrix} = \lambda_k \begin{pmatrix} A_{1k} \\ A_{2k} \end{pmatrix} \qquad (k = 1, 2) \qquad (2.253)$$

which is rewritten

$$A_{1k} + A_{2k} = \lambda_k A_{1k} \qquad (2.254)$$

$$\sigma s A_{1k} + 2 A_{2k} = \lambda_k A_{2k} \qquad (2.255)$$

One may put $A_{1k} = 1$, since the value of either A_{1k} or A_{2K} may be assigned arbitrarily. Thus, solving either Eq.(2.254) or Eq.(2.255) with respect to A_{2k}, one gets

$$A_{2k} = \lambda_k - 1$$

$$\text{or} \quad \frac{\sigma s}{\lambda_k - s} \qquad (2.256)$$

Note that $\lambda_k - 1 = \sigma s/(\lambda_k - 2)$ on account of Eq.(2.249). Eq.(2.256) allows $\mathbf{A}$ to be written

$$\mathbf{A} = \begin{pmatrix} 1 & 1 \\ \lambda_1 - 1 & \lambda_2 - 1 \end{pmatrix} \qquad (2.257)$$

The inverse of $\mathbf{A}$ is given by

$$\mathbf{A}^{-1} = \begin{pmatrix} A^{11} & A^{21} \\ A^{12} & A^{22} \end{pmatrix}/|\mathbf{A}| \qquad (2.258)$$

with A^{kl} being the cofactors of $\mathbf{A}$. Since $|\mathbf{A}| = \lambda_2 - \lambda_1$, $\mathbf{A}^{-1}$ is found to be

$$\mathbf{A}^{-1} = \frac{1}{\lambda_2 - \lambda_1}\begin{pmatrix} \lambda_2 - 1 & -1 \\ 1 - \lambda_1 & 1 \end{pmatrix} \qquad (2.259)$$

Substituting the values of necessary elements of $\mathbf{A}$ and $\mathbf{A}^{-1}$ into Eq.(2.251), one obtaines

$$Z_N = \frac{1}{\lambda_2 - \lambda_1}[(\lambda_2 - 1)\lambda_1^{N-2} + (1 - \lambda_1)\lambda_2^{N-2}] \qquad (2.260)$$

If the relation $\lambda_1 + \lambda_2 = 1 + s$, which follows from Eq.(2.249), is inserted into Eq.(2.260), Eq.(2.260) becomes

$$Z_N = \frac{\lambda_1 - s}{\lambda_1 - \lambda_2}\lambda_1^{N-2} + \frac{s - \lambda_2}{\lambda_1 - \lambda_2}\lambda_2^{N-2} \qquad (2.261)$$

[Comments]

The present model (by B. H. Zimm and J. K. Bragg) does not precisely take into account the features of actual α-helix-forming polypeptides. However, various results derived from Eq.(2.261) are of practical values, because this equation is a very good approximation to Z_N derived on the basis of more accurate models.

[Problem B37]

With use of the expression for Z_N and $\mathbf{M}$, show that the average fraction θ_N of intact hydrogen bonds formed in a polypeptide chain consisting of N residues is represented by

$$\theta_N = \frac{1}{N-4} \frac{\partial \ln Z_N}{\partial \ln s} \tag{2.262}$$

[Solution B37]

Form the definition of s it follows that θ_N is equal to the average number of residues in the state specified by s relative to the total number of residues $N-4$ capable of forming a hydrogen bond. Thus θ_N may be expressed by

$$\theta_N = \frac{1}{N-4} \sum_{i=3}^{N-2} \langle \theta_i \rangle \tag{2.263}$$

where $\langle \theta_i \rangle$ denotes the average probability that residue i is in the state specified by s regardless of the state of other residues. This definition of $\langle \theta_i \rangle$ gives

$$\langle \theta_i \rangle = \frac{1}{Z_N} [\mathbf{e}_1 \mathbf{M}_2 \mathbf{M}^{i-3} \mathbf{P}_i \mathbf{M}^{N-i-2} \mathbf{M}_{N-1} \mathbf{e}_N] \tag{2.264}$$

with

$$Z_N = \mathbf{e}_1 \mathbf{M}_2 \mathbf{M}^{N-4} \mathbf{M}_{N-1} \mathbf{e}_N \tag{2.265}$$

Here the matrix $\mathbf{P}_i$ is given by

$$\mathbf{P}_i = \begin{pmatrix} s & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ s & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \tag{2.266}$$

because residue i is in the state of s. Since

$$\frac{\partial \mathbf{M}}{\partial s} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \tag{2.267}$$

the $\mathbf{P}_i$ is rewritten

$$\mathbf{P}_i = s\frac{\partial \mathbf{M}}{\partial s} \tag{2.268}$$

Introduction of Eq.(2.264) together with Eq.(2.268) into Eq.(2.263) yields

$$\theta_N = \frac{s}{(N-4)Z_N}\left[\mathbf{e}_1\mathbf{M}_2\mathbf{M}^{i-3}\frac{\partial \mathbf{M}}{\partial s}\mathbf{M}^{N-i-2}\mathbf{M}_{N-1}\mathbf{e}_N\right] \tag{2.269}$$

Since

$$\frac{\partial \mathbf{M}\mathbf{M}'}{\partial s} = \mathbf{M}\frac{\partial \mathbf{M}'}{\partial s} + \frac{\partial \mathbf{M}}{\partial s}\mathbf{M}' \tag{2.270}$$

and since $\mathbf{e}_1$, $\mathbf{M}_2$, $\mathbf{M}_{N-i}$, and $\mathbf{e}_N$ are independent of s, Eq.(2.269) may be rewritten

$$\begin{aligned}\theta_N &= \frac{2}{(N-4)Z_N}\mathbf{e}_1\mathbf{M}_2\left[\sum_{i=3}^{N-2}\left(\mathbf{M}^{i-3}\frac{\partial \mathbf{M}}{\partial s}\mathbf{M}^{N-i-2}\right)\right]\mathbf{M}_{N-1}\mathbf{e}_N \\ &= \frac{s}{(N-4)Z_N}\left[\mathbf{e}_1\mathbf{M}_2\frac{\partial(\mathbf{M})^{N-4}}{\partial s}\mathbf{M}_{N-1}\mathbf{e}_N\right] \\ &= \frac{s}{(N-4)Z_N}\frac{\partial}{\partial s}(\mathbf{e}_1\mathbf{M}_2\mathbf{M}^{N-4}\mathbf{M}_{N-1}\mathbf{e}_N) \end{aligned} \tag{2.271}$$

Substitution of Eq.(2.265) into the last equation (2.271) leads to Eq.(2.262).

[Problem B38]

On the simplified Zimm-Bragg model, show that the average fraction of hydrogen bonds formed in an infinitely long polypeptide is one half at the mid point of the helix-coil transition.

[Solution B38]

The average fraction of hydrogen bonds, θ_∞, in an infinitely long chain may be calculated with use of Eq.(2.262) in [Problem B37]. Introducing Eq.(2.261) for Z_N in [Problem B36] into this equation and going to $N = \infty$, one obtains

$$\theta_\infty = \frac{s}{\lambda_1}\frac{\partial \lambda_1}{\partial s} \tag{2.272}$$

The $\partial \lambda_1/\partial s$ can be calculated from the characteristic equation (2.249) in [Problem B36]

$$(\lambda_1 - s)(\lambda_1 - 1) = \sigma s \tag{2.273}$$

to give

$$\frac{\partial \lambda_1}{\partial s} = \frac{\lambda_1 - 1 + \sigma}{2\lambda_1 - 1 - s} \tag{2.274}$$

Substitution of this equation into Eq.(2.272) gives

$$\theta_\infty = \frac{2}{\lambda_1}\frac{\lambda_1 - 1 + \sigma}{2\lambda_1 - 1 - s} \tag{2.275}$$

At the transition point at which $s = 1$, the larger root of Eq.(2.273) is given by (smaller one corresponds to λ_2)

$$\lambda_1 = 1 + \sqrt{\sigma} \tag{2.276}$$

Introducing Eq.(2.276) together with $s = 1$ into Eq.(2.275), one finds that

$$\theta_\infty = \frac{1}{2} \tag{2.277}$$

[Comments]

Strictly speaking, θ_N is slightly different from the average fraction of α-helical conformations f_N when N is finite. However, the difference is so small that one may equate θ_N to f_N unless N is too small.

[Problem B39]

With the simplified Zimm-Bragg model, show (1) that the average number of helical sections $\langle g \rangle$ in an infinitely long polypeptide chain is given by

$$\langle g \rangle = \frac{N\sigma s}{2\lambda_1 - 1 - s} \tag{2.278}$$

and (2) that at the transition point the average number of residues in one helical section is equal to $1/\sqrt{\sigma}$.

Hint: $\langle g \rangle$ equals the average number of residues which have the statistical weight σs.

[Solution B39]

(1) With the aid of the hint and by analogy with Eq.(2.262) for θ_N in [Problem B37], one may express $\langle g \rangle$ as

$$\langle g \rangle = \frac{\partial \ln Z_N}{\partial \ln \sigma} \tag{2.279}$$

Introduction of Eq.(2.261) in [Problem B36] into Eq.(2.279) gives for infinitely large N

$$\langle g \rangle = \frac{N\sigma}{\lambda_1} \frac{\partial \lambda_1}{\partial \sigma} \tag{2.280}$$

The $\partial \lambda_1 / \partial \sigma$ is calculated to give

$$\frac{\partial \lambda_1}{\partial \sigma} = \frac{s}{2\lambda_1 - s - 1} \tag{2.281}$$

Substitution of this into Eq.(2.280) gives Eq.(2.278).

(2) Since at the mid point of the transition, $s = 1$ and $\lambda_1 = 1 + \sqrt{\sigma}$ (see [Problem B38]), Eq.(2.278) reduces to

$$\langle g \rangle = \frac{1}{2} N \sqrt{\sigma} \tag{2.282}$$

The solution to [Problem B38] indicates that the average number of residues in the α-helical conformation is equal to $N/2$ at the transition point. Thus the corresponding average number of residues in one helical section is $(N/2)/\langle g \rangle \ (= 1/\sqrt{\sigma})$.

3   Polymer Solutions

[Problem C1]

In most cases of practical interest, especially in dealing with polyelectrolytes or biopolymers, the components of macromolecular solutions are didided into two groups, depending on whether they are diffusible or not through an appropriate semi-permeable membrane. For a thermodynamic treatment of such solutions it is very useful to choose as the state variables the temperature T, the volume V, the chemical potentials of the diffusible components, μ_0, μ_1, $\cdots$, μ_d, and the moles of the non-diffusible, i.e., macromolecular components n_{d+1}, n_{d+2}, $\cdots$, n_{d+r}. Show that the appropriate characteristic function B for this choice of variables is

$$B(T, V, \mu_0, \mu_1, \cdots, \mu_d, n_{d+1}, n_{d+2}, \cdots, n_r)$$
$$= A(T, V, n_0, n_1, \cdots, n_r) - \sum_{i=0}^{d} n_i \mu_i \tag{3.1}$$

where $r + 1$ denotes the total number of components in the system, and A is the Helmholtz free energy of the system.

[Solution C1]

The task is to show that the equilibrium condition for the system is given by

$$(\delta B)_{T, V, \mu_0, \cdots, \mu_d, n_{d+1}, \cdots, n_r} = 0 \tag{3.2}$$

where δ denotes small virtual displacements.

From the definition of B it follows that

$$\delta B = \delta A - \sum_{i=0}^{d} \mu_i dn_i - \sum_{i=0}^{d} n_i d\mu_i \qquad (3.3)$$

If this is combined with the familiar relation

$$\delta A = -SdT - pdV + \sum_{i=0}^{r} \mu_i dn_i \qquad (3.4)$$

where S and p are the entropy and pressure of the system, we obtain

$$\delta B = -SdT - pdV + \sum_{i=d+1}^{r} \mu_i dn_i - \sum_{i=0}^{d} n_i d\mu_i \qquad (3.5)$$

Equation (3.2) immediately follows from this equation.

Equation (3.5) may be used to derive the following relations:

$$S = -\left(\frac{\partial B}{\partial T}\right)_{V,\mu_0,\mu_1,\cdots,\mu_d,n_{d+1},n_{d+2},\cdots,n_r} \qquad (3.6)$$

$$p = -\left(\frac{\partial B}{\partial V}\right)_{T,\mu_0,\mu_1,\cdots,\mu_d,n_{d+1},n_{d+2},\cdots,n_r} \qquad (3.7)$$

$$n_i = -\left(\frac{\partial B}{\partial \mu_i}\right)_{T,V,\mu_0,\cdots,\mu_{i-1},\mu_{i+1},\cdots,\mu_d,n_{d+1},\cdots,n_r}$$
$$(0 \leq i \leq d) \qquad (3.8)$$

$$\mu_i = -\left(\frac{\partial B}{\partial n_i}\right)_{T,V,\mu_0,\cdots,\mu_d,n_{d+1},\cdots,n_{d+i-1},n_{d+i+1},\cdots,n_r}$$
$$(d+1 \leq i \leq r) \qquad (3.9)$$

The Gibbs-Duhem relation gives

$$V dp - \sum_{i=d+1}^{r} n_i d\mu_i = 0 \quad (T, \mu_0, \mu_1, \cdots, \mu_d = \text{const}) \qquad (3.10)$$

[Comments]

The word dyalysis is given to the procedure by which the chemical potentials of all diffusible components in a given solution are fixed at desired values. This can be done by bringing the solution to osmotic equilibrium against a solution (dialyzate) which consists of all of the diffusible components at a desired composition and is held at a desired pressure.

[Problem C2]

Find the relationship between the practical activity coefficient γ_i^∞ appropriate for the molality scale and the one y_i^∞ appropriate for the mass concentration scale.

[Solution C2]

The chemical potential of component i may be written

$$\mu_i = \mu_{im}^\infty + RT \ln \gamma_i^\infty m_i \tag{3.11}$$

or

$$\mu_i = \mu_{ic}^\infty + RT \ln y_i^\infty c_i \tag{3.12}$$

Hence

$$\mu_{im}^\infty - \mu_{ic}^\infty = RT \ln \left(\frac{y_i^\infty c_i}{\gamma_i^\infty m_i} \right) \tag{3.13}$$

One has the relation

$$c_i = \frac{m_i M_i}{v_M} \tag{3.14}$$

where M_i is the molecular weight of component i and v_M denotes the volume of the solution per one kilogram of the principal solvent chosen here as component 0. With Eq.(3.14), Eq.(3.13) becomes

$$\mu_{im}^\infty - \mu_{ic}^\infty = RT \ln \left(\frac{y_i^\infty}{\gamma_i^\infty} \right) \left(\frac{M_i}{v_M} \right) \tag{3.15}$$

Now let all concentrations of the components other than component 0 approach zero. Then $y_i^\infty \to 1$ and $\gamma_i^\infty \to 1$, and v_M tends to $1000/\rho_0^0$, where ρ_-^0 is the density of component 0 in the pure state at given temperature and pressure. Thus

$$\mu_{im}^\infty - \mu_{ic}^\infty = RT \ln \left(\frac{M_i \rho_o^0}{1000} \right) \tag{3.16}$$

This is substituted back into Eq.(3.13) to give

$$\frac{y_i^\infty c_i}{\gamma_i^\infty m_i} = \frac{M_i \rho_0^0}{1000} \tag{3.17}$$

This is the required relation between y_i^∞ and γ_i^∞. Note that v_M may be expressed

$$v_M = 1000v_0 + \sum_{i=1}^{q} m_i M_i v_i \qquad (3.18)$$

where $q + 1$ is the number of components in the solution and v_i is the partial specific volume of component i.

[Problem C3]

Show that the partial specific volume, v_i, of component i ($i = 1, 2, \cdots, q$) in a $q + 1$ component solution is represented by

$$v_i = \frac{1}{M_i} \left(\frac{\partial v_M}{\partial m_i} \right)_{T,p,m_{k \neq i}} \tag{3.19}$$

where v_M is the volume of the solution per one kilogram of component 0 chosen as the principal solvent, and M_i and m_i are the molecular weight and molality of component i.

[Solution C3]

$$v_i = \frac{1}{M_i} \left(\frac{\partial V}{\partial n_i} \right)_{T,p,n_{k \neq i}} \tag{3.20}$$

where V is the total volume of the solution and n_i is the moles of component i. By definition $V(1000/n_0 M_0) - v_M$ and $m_i = n_i(1000/n_0 M_0)$. Hence Eq.(3.20) becomes for $i \geq 1$

$$v_i = \frac{1}{M_i} \left(\frac{\partial v_M}{\partial m_i} \right)_{T,p,m_{k \neq i}} \tag{3.21}$$

which is Eq.(3.19).

[Problem C4]

Prove that the partial specific volume v_i of any component in an incompressible solution consisting of a single solvent (component 0) and q different solutes (component $1, 2, \cdots, q$) becomes independent of the composition if the practical activity coefficient y_i^∞ of that component does not vary with pressure.

[Solution C4]

When the solution is incompressible, one can write for v_i

$$v_i = \left(\frac{\partial \mu_i}{\partial p}\right)_{T, \{c\}} \qquad (i = 0, 1, \cdots, q) \tag{3.22}$$

where $\{c\}$ stands for the set of $c_1, c_2, \cdots, c_q$. This equation is written, because the composition of an incompressible system is determined in terms of $\{c\}$. The chemical potential μ_i is expressed in the form

$$\mu_i = \mu_i^\infty(T, p) + RT \ln[y_i^\infty(T, p, \{c\})]c_i \tag{3.23}$$

with y_i^∞ defined as $\lim_{\{c\} \to 0} y_i^\infty = 1$.

Introducing Eq.(3.23) into Eq.(3.22), one obtains

$$v_i = \left(\frac{\partial \mu_i^\infty}{\partial p}\right)_T \tag{3.24}$$

if y_i^∞ is independent of p. Thus, under the imposed conditions, v_i becomes independent of $\{c\}$, and actually takes the value at infinite dilution of the solution (i.e., at the limit of $\{c\} \to 0$), because μ_i^∞ represents μ_i at this limit. $(\partial \mu_i^\infty / \partial p)_T$ is denoted by the symbol v_i^0.

[Problem C5]

For a solution of $q + 1$ components, show that

$$\frac{1}{M_i}\left(\frac{\partial \mu_i}{\partial c_j}\right)_{T,\mu_0,c_{k\neq j}} = \frac{1}{M_j}\left(\frac{\partial \mu_j}{\partial c_i}\right)_{T,\mu_0,c_{k\neq i}}$$
$$(i, k, j = 1, 2, \cdots, q) \qquad (3.25)$$

Apply Eq.(3.9) in [Problem C1].

[Solution C5]

Equation (3.9) cited gives

$$\mu_i = \left(\frac{\partial B}{\partial n_i}\right)_{T,V,\mu_0,n_{k\neq i}} \qquad (k, i = 1, 2, \cdots, q) \qquad (3.26)$$

Hence

$$\left(\frac{\partial \mu_i}{\partial n_j}\right)_{T,V,\mu_0,n_{k\neq j}} = \left(\frac{\partial \mu_j}{\partial n_i}\right)_{T,V,\mu_0,n_{k\neq i}} \qquad (j = 1, 2, \cdots, q) \qquad (3.27)$$

But

$$\left(\frac{\partial \mu_i}{\partial n_j}\right)_{T,V,\mu_0,n_{k\neq j}} = \frac{M_j}{V}\left(\frac{\partial \mu_i}{\partial c_j}\right)_{T,\mu_0,c_{k\neq j}} \qquad (3.28)$$

Thus, Eq.(3.27) yields

$$\frac{1}{M_i}\left(\frac{\partial \mu_i}{\partial c_j}\right)_{T,\mu_0,c_{k\neq j}} = \frac{1}{M_j}\left(\frac{\partial \mu_j}{\partial c_i}\right)_{T,\mu_0,c_{k\neq i}} \qquad (3.29)$$

which is the required equation.

[Problem C6]

Derive

$$\left(\frac{\partial \rho}{\partial c_i}\right)_{T,\mu_0,c_{k\neq i}} = 1 - v_i^0 \rho_0 \qquad (i,k = 1,2,\cdots,q) \qquad (3.30)$$

for an incompressible solution of $q+1$ components in which the practical activity coefficient y_i^∞ of all components are independent of pressure p. Here ρ is the density of the solution, v_i^0 is the partial specific volume of the i-th component at the limit of $\{c\}[= (c_1, c_2, \cdots, c_q)] \to 0$, and ρ_0 is the density of the 0-th component in the pure state, i.e., $1/v_0^0$.

[Solution C6]

The density, an intensive quantity, can be described in terms of the set of state variables $T, p, \{c\}$. Hence one may write the relation

$$(\mathrm{d}\rho)_{T,c_{k\neq j}} = \left(\frac{\partial \rho}{\partial c_j}\right)_{T,p,c_{k\neq j}} \mathrm{d}c_j + \left(\frac{\partial \rho}{\partial p}\right)_{T,\{c\}} \mathrm{d}p$$

$$(j,k = 1,2,\cdots,q) \qquad (3.31)$$

whence

$$\left(\frac{\partial \rho}{\partial c_j}\right)_{T,\mu_0,c_{k\neq j}} = \left(\frac{\partial \rho}{\partial c_j}\right)_{T,p,c_{k\neq j}} + \left(\frac{\partial \rho}{\partial p}\right)_{T,\{c\}}\left(\frac{\partial p}{\partial c_j}\right)_{T,\mu_0,c_{k\neq j}} \qquad (3.32)$$

For incompressible solutions $(\partial \rho/\partial p)_{T,\{c\}} = 0$. Hence

$$\left(\frac{\partial \rho}{\partial c_j}\right)_{T,\mu_0,c_{k\neq j}} = \left(\frac{\partial \rho}{\partial c_j}\right)_{T,p,c_{k\neq j}} \qquad (3.33)$$

Eliminating c_0 from the two relations $\rho = \sum_{i=0}^{q} c_i$ and $\sum_{i=0}^{q} v_i c_i = 1$, one gets

$$\rho = \frac{1}{v_0} + \sum_{i=1}^{q}\left(1 - \frac{v_i}{v_0}\right)c_i \qquad (3.34)$$

Under the incompressibility of the solution and the imposed condition on y_i^∞, v_i $(i = 1,2,\cdots,q)$ becomes independent of $\{c\}$ and equal to v_i^0.

(See [Problem C4]). Therefore, in this case,

$$\left(\frac{\partial \rho}{\partial c_j}\right)_{T,p,c_{k \neq j}} = 1 - v_i^0 \rho_0 \quad (\rho_0 = 1/v_0^0) \tag{3.35}$$

This is substituted into Eq.(3.33) to give the required relation (3.30).

[Problem C7]

The practical activity coefficient y_i^∞ of the i-th component in a $q+1$ component solution may be treated as a function of the variables T, μ_0, and $\{c\}$, where $\{c\}$ denotes a set of $c_1, c_2, \cdots, c_q$ and μ_0 is the chemical potential of the 0-th component. For dilute solutions in which $c_1, c_2, \cdots, c_q$ are all small, $\ln y_i^\infty(T, \mu_0, \{c\})$ may be expanded in a Taylor series as

$$\ln y_i^\infty(T, \mu_0, \{c\}) = M_i\left(\sum_{j=1}^q A_{ij}c_j + \frac{1}{2}\sum_{j=1}^q\sum_{k=1}^q A_{ijk}c_jc_k + \cdots\right) \quad (3.36)$$

where M_i is the molecular weight of the i-th component. The coefficients $A_{ij}, A_{ijk}, \cdots$ are functions of T and μ_0. Show that $A_{ij}, A_{ijk}, \cdots$ are invariant for the exchange of their subscripts. Thus

$$A_{ij} = A_{ji} \quad (3.37)$$

$$A_{ijk} = A_{jik} = A_{jki} = A_{ikj} = \cdots \quad (3.38)$$

[Solution C7]

From

$$\mu_i = \mu_i^\infty(T, \mu_0) + RT\ln c_i y_i^\infty(T, \mu_0, \{c\}) \quad (3.39)$$

and the relation (see [Problem C5])

$$\frac{1}{M_i}\left(\frac{\partial\mu_i}{\partial c_j}\right)_{T,\mu_0,c_{k\neq j}} = \frac{1}{M_j}\left(\frac{\partial\mu_j}{\partial c_i}\right)_{T,\mu_0,c_{k\neq i}} \quad (3.40)$$

one obtains

$$\frac{1}{M_i}\left(\frac{\partial\ln y_i^\infty}{\partial c_j}\right)_{T,\mu_0,c_{k\neq j}} = \frac{1}{M_j}\left(\frac{\partial\ln y_j^\infty}{\partial c_i}\right)_{T,\mu_0,c_{k\neq i}} \quad (3.41)$$

Substituting Eq.(3.36) for $\ln y_i^\infty$ and the correaponding expression for $\ln y_j^\infty$ and then letting all of $c_1, c_2, \cdots, c_q$ tend to zero, one finds

$$A_{ij} = A_{ji} \quad (3.42)$$

Partial diggerentiation of Eq.(3.41) with respect to c_k gives

$$\frac{1}{M_1}\frac{\partial^2 \ln y_i^\infty}{\partial c_k \partial c_j} = \frac{1}{M_j}\frac{\partial^2 \ln y_j^\infty}{\partial c_k \partial c_i} \tag{3.43}$$

where, for simplicity, the subscripts to be fixed in each differentiation has not been indicated. Again, introducing the Taylor series for $\ln y_i^\infty$ and $\ln y_j^\infty$ and taking the limit $c_1, c_2, \cdots, c_q \to 0$, one obtains

$$A_{ijk} + A_{ikj} = A_{jik} + A_{jki} \tag{3.44}$$

Since j and k in Eq.(3.36) are dummy indices, it is obvious that $A_{ijk} = A_{ikj}$. Similarly, $A_{jik} = A_{jki}$. Thus

$$A_{ijk} = A_{jik} \tag{3.45}$$

which indicates that the first two indices of A_{ijk} are interchangeable. The fact that $A_{ijk} = A_{ikj}$ implies that the last two indices of A_{ijk} are also interchangeable. From these results it follows that A_{ijk} is invarient for the exchange of its subscripts.

The above-mentioned properties of $A_{ij}, A_{ijk}, \cdots$ play an important role in solving various subsequent problems in which the Taylor expansion for $\ln y_i^\infty(T, \mu_0, \{c\})$ appears, but they will not be specifically mentioned in those problems.

[Problem C8]

The practical activity coefficient y_i^∞ of the i-th component in a solution of $q+1$ components may be considered a function of either a set of variables $(T, \mu_0, \{c\})$ or a set of variables $(T, p, \{c\})$. Here $\{c\} = (c_1, c_2, \cdots, c_q)$. For dilute solutions one may expand $\ln y_i^\infty$ as

$$\ln y_i^\infty(T, \mu_0, \{c\}) = M_i \left(\sum_{j=1}^q A_{ij}c_j + \frac{1}{2} \sum_{j=1}^q \sum_{k=1}^q A_{ijk}c_jc_k + \cdots \right) \quad (3.46)$$

$$\ln y_i^\infty(T, p, \{c\}) = M_i \left(\sum_{j=1}^q B_{ij}c_j + \frac{1}{2} \sum_{j=1}^q \sum_{k=1}^q B_{ijk}c_jc_k + \cdots \right) \quad (3.47)$$

where M_i is the molecular weight of the i-th component. Show that if the pressure dependence of $\ln y_i^\infty$ is negligible, there are relations

$$A_{ij} = B_{ij} + \frac{v_i^0}{M_j} \tag{3.48}$$

$$A_{ijk} = B_{ijk} + v_i^0 B_{jk} + \frac{v_i^0 v_j^0}{M_k} \tag{3.49}$$

where v_i^0 is the partial specific volume of the i-th component at the limit of $\{c\} \to 0$.

[Solution C8]

If μ_i us treated as a function of T, p, and $\{c\}$, one can write the relation

$$(\mathrm{d}\mu_i)_T = \sum_{j=1}^q \left(\frac{\partial \mu_i}{\partial c_j} \right)_{T,p,c_{k\neq j}} \mathrm{d}c_j + \left(\frac{\partial \mu_i}{\partial p} \right)_{T,\{c\}} \mathrm{d}p$$

$$(i = 1, 2, \cdots, q) \tag{3.50}$$

which gives

$$\left(\frac{\partial \mu_i}{\partial c_j} \right)_{T,\mu_0,c_{k\neq j}} = \left(\frac{\partial \mu_i}{\partial c_j} \right)_{T,p,c_{k\neq j}} + \left(\frac{\partial \mu_i}{\partial p} \right)_{T,\{c\}} \left(\frac{\partial p}{\partial c_j} \right)_{T\mu_0,c_{k\neq j}} \tag{3.51}$$

Using $\mu_i = \mu_i^\infty(T,p) + RT \ln y_i^\infty(T,p,\{c\}) c_i$ and assuming that $y_i^\infty(T,p,\{c\})$ does not depend on p, one finds

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,\{c\}} = \left(\frac{\partial \mu_i^\infty(T,p)}{\partial p}\right) T = M_i v_i^0 \qquad (3.52)$$

From the Gibbs-Duhem relation $(dp)_{T,\mu_0} = \sum_{i=1}^{q}(c_i/M_i)(d\mu_i)_{T,\mu_0}$ it follows that

$$\left(\frac{\partial p}{\partial c_j}\right)_{T,\mu_0,c_{k\neq j}} = \sum_{k=1}^{q} \frac{c_k}{M_k}\left(\frac{\partial \mu_k}{\partial c_j}\right)_{T,\mu_0,c_{k\neq j}} \qquad (3.53)$$

Thus, Eq.(3.51) can be written, subject to the assumption made above for $y_i^\infty(T,p,\{c\})$,

$$\left(\frac{\partial \mu_i}{\partial c_j}\right)_{T,\mu_0,c_{k\neq j}} = \left(\frac{\partial \mu_i}{\partial c_j}\right)_{T,p,c_{k\neq j}} + M_i v_i^0 \sum_{k=1}^{q} \frac{c_k}{M_k}\left(\frac{\partial \mu_k}{\partial c_j}\right)_{T,\mu_0,c_{k\neq j}} \qquad (3.54)$$

From Eqs.(3.46) and (3.47) one gets

$$\frac{1}{M_i}\left(\frac{\partial \mu_i}{\partial c_j}\right)_{T,\mu_0,c_{k\neq j}} = RT\left(\frac{\delta_{ij}}{M_i c_i} + A_{ij} + \sum_{k=1}^{q} A_{ijk} c_k + \cdots\right) \qquad (3.55)$$

$$\frac{1}{M_i}\left(\frac{\partial \mu_i}{\partial c_j}\right)_{T,p,c_{k\neq j}} = RT\left(\frac{\delta_{ij}}{M_i c_i} + B_{ij} + \sum_{k=1}^{q} B_{ijk} c_k + \cdots\right) \qquad (3.56)$$

where δ_{ij} is Kronecker's delta. In deriving Eqs.(3.55) and (3.56), one has considered tha fact that A_{ijk} and B_{ijk} are invariant for the exchange of j and k, because these subscripts are dummy indices. Introduction of Eqs.(3.55) and (3.56) into Eq.(3.54) gives

$$A_{ij} + \sum_{k=1}^{q} A_{ijk} c_k + \cdots = B_{ij} + \sum_{k=1}^{q} B_{ijk} c_k + \cdots$$

$$+ v_i^0\left(\frac{1}{M_j} + \sum_{k=1}^{q} A_{kj} c_k + \cdots\right) \qquad (3.57)$$

Therefore,

$$A_{ij} = B_{ij} + \frac{v_i^0}{M_j} \qquad (3.58)$$

$$A_{ijk} = B_{ijk} + v_i^0 A_{kj} \qquad (3.59)$$

Equation (3.58) agrees with Eq.(3.48). Because $A_{ij} = A_{ji}$ (see [Problem C7]), Eq.(3.59) may be written, with insertion of Eq.(3.58),

$$A_{ijk} = B_{ijk} + v_i^0 B_{kj} + \frac{v_i^0 v_k^0}{M_j} \qquad (3.60)$$

which is equivalent to Eq.(3.49).

[Problem C9]

For a solution of $q + 1$ components, show that, in general,

$$\frac{1}{M_i}\left(\frac{\partial \mu_i}{\partial c_j}\right)_{T,p,c_{k\neq j}} \neq \frac{1}{M_j}\left(\frac{\partial \mu_j}{\partial c_i}\right)_{T,p,c_{k\neq i}}$$
$$(i, j, k = 1, 2, \cdots, q) \tag{3.61}$$

[Solution C9]

Since μ_i is regarded as a function of T, p, and $\{c\}(= c_1, c_2, \cdots, c_q)$, one can write the expression

$$(\mathrm{d}\mu_i)_T = \sum_{i=1}^{q}\left(\frac{\partial \mu_i}{\partial c_j}\right)_{T,p,c_{k\neq j}} \mathrm{d}c_j + \left(\frac{\partial \mu_i}{\partial p}\right)_{T,\{c\}} \mathrm{d}p \tag{3.62}$$

whence

$$\frac{1}{M_i}\left(\frac{\partial \mu_i}{\partial c_j}\right)_{T,p,c_{k\neq j}} = \frac{1}{M_i}\left(\frac{\partial \mu_i}{\partial c_j}\right)_{T,\mu_0,c_{k\neq j}} - \frac{1}{M_i}\left(\frac{\partial \mu_i}{\partial p}\right)_{T,\{c\}}\left(\frac{\partial p}{\partial c_j}\right)_{T,\mu_0,c_{k\neq j}} \tag{3.63}$$

A similar expression for $M_j^{-1}(\partial \mu_j/\partial c_i)_{T,p,c_{k\neq j}}$ may be obtained by exchanging the subscripts i and j. Subtracting it from Eq.(3.63) and using the relation (3.25) in [Problem C5], one obtains

$$\frac{1}{M_i}\left(\frac{\partial \mu_i}{\partial c_j}\right)_{T,p,c_{k\neq j}} - \frac{1}{M_j}\left(\frac{\partial \mu_j}{\partial c_i}\right)_{T,p,c_{k\neq i}}$$
$$= \frac{1}{M_j}\left(\frac{\partial \mu_j}{\partial p}\right)_{T,\{c\}}\left(\frac{\partial p}{\partial c_i}\right)_{T,\mu_0,c_{k\neq i}} - \frac{1}{M_i}\left(\frac{\partial \mu_i}{\partial p}\right)_{T,\{c\}}\left(\frac{\partial p}{\partial c_j}\right)_{T,\mu_0,c_{k\neq j}} \tag{3.64}$$

The Gibbs-Duhem relation gives $(\mathrm{d}p)_{T,\mu_0} = \sum_{i=1}^{q}(c_i/M_i)(\mathrm{d}\mu_i)_{T,\mu_0}$. Hence

$$\left(\frac{\partial p}{\partial c_i}\right)_{T,\mu_0,c_{k\neq i}} = \sum_{m=1}^{q}\frac{c_m}{M_m}\left(\frac{\partial \mu_m}{\partial c_i}\right)_{T,\mu_0,c_{k\neq i}} \tag{3.65}$$

Using this and the relation (eq.(3.25) quated above, one can write Eq.(3.64) as

$$\frac{1}{M_i}\left(\frac{\partial \mu_i}{\partial c_j}\right)_{T,p,c_{k\neq j}} - \frac{1}{M_j}\left(\frac{\partial \mu_j}{\partial c_i}\right)_{T,p,c_{k\neq i}}$$

$$= \frac{1}{M_i M_j} \left[\left(\frac{\partial \mu_j}{\partial p} \right)_{T,\{c\}} \sum_{m=1}^{q} c_m \left(\frac{\partial \mu_i}{\partial c_m} \right)_{T,\mu_0,c_{k \neq m}} \right.$$

$$\left. - \left(\frac{\partial \mu_i}{\partial p} \right)_{T,\{c\}} \sum_{m=1}^{q} c_m \left(\frac{\partial \mu_j}{\partial c_m} \right)_{T,\mu_0,c_{k \neq m}} \right] \qquad (3.66)$$

The right-hand side of this equation does not vanish identically. To show it one may consider a certain special case, for example, the solution which is incompressible and in which the practical activity coefficient $y_i^{\infty}(i = 1, 2, \cdots, q)$ regarded as a function of T, μ_0, and $\{c\}$ is unity. For such a solution

$$\left(\frac{\partial \mu_i}{\partial p} \right)_{T,\{c\}} = M_i v_i \qquad (3.67)$$

$$c_m \left(\frac{\partial \mu_i}{\partial c_m} \right)_{T,\mu_0,c_{k \neq m}} = \begin{cases} RT & (m = i) \\ 0 & (m \neq i) \end{cases}$$

where v_i^0 is the partial specific volume of the i-th component, and hence Eq.(3.66) becomes

$$\frac{1}{M_i} \left(\frac{\partial \mu_i}{\partial c_j} \right)_{T,p,c_{k \neq j}} - \frac{1}{M_j} \left(\frac{\partial \mu_j}{\partial c_i} \right)_{T,p,c_{k \neq i}} = RT \left(\frac{v_j}{M_i} - \frac{v_i}{M_j} \right) \qquad (3.68)$$

The right-hand side vanishes only when $v_j M_j = v_i M_i$, i.e., the partial molar volumes of the i-th and j-th components are equal. Thus one may state that, as the in equality (3.61) indicates, the subscripts i and j in $M_i^{-1}(\partial \mu_i / \partial c_j)_{T,p,c_{k \neq j}}$ are not exchangeable in general.

[Problem C10]

A solution which contains a protein (component 2) and a simple electrolyte (component 1) in water (component 0) is brought to osmotic equilibrium against a large volume of a dyalyzate (component 0 + component 1) held at constant pressure p'. Find the expression for the osmotic pressure π set up in the protein solution.

[Solution C10]

Regardless of the protein concentration, the chemical potentials, μ_0 and μ_1, of the components 0 and 1 in the protein solution are held constant at osmotic equilibrium, because this equilibrium is established when μ_0 and μ_1 become equal to μ_0' and μ_1', respectively. (the prime indicates the quantity of the dialyzate), and both μ_0' and μ_1' are fixed under the experimental conditions specified in the problem. Thus the Gibbs-Duhem relation at constant temperature gives

$$V\mathrm{d}p - C_2\mathrm{d}\mu_2 = 0 \tag{3.69}$$

When applied to the protein solution. Here V and p are the volume and pressure of the protein solution, respectively, and C_2 is the molar concentration of the protein component. It should be noted that $\mathrm{d}\mu_2$ in Eq.(3.69) is concerned with constant T, μ_0, and μ_1. Since $p = \pi + p'$ with constant p', $\mathrm{d}p = \mathrm{d}\pi$. Thus Eq.(3.69) gives

$$\pi = \int_0^{C_2} C_2\left(\frac{\partial\mu_2}{\partial C_2}\right)_{T,\mu_0,\mu_1}\mathrm{d}C_2 \tag{3.70}$$

where the integration constant has been determined from the condition that $\pi \to 0$ as $C_2 \to 0$.

For practical purposes it is convenient to write Eq.(3.70) as

$$\pi = \frac{1}{M_2}\int_0^{c_2} c_2\left(\frac{\partial\mu_2}{\partial c_2}\right)_{T,p',c_1'}\mathrm{d}c_2 \tag{3.71}$$

by considering tha fact that μ_0 and μ_1 depend on p' and c_1', under the present condition of osmotic equilibrium. Here c_2 and M_2 are the mass

concentration and molecular weight of the protein component, respectively. Thus, by use of Eq.(3.71) we can, in principle, determine μ_2 as a function of c_2, p', and c_1' from experiments in which π is measured as a function of c_2 for a variety of combination of p' and c_1'.

We may write $\mu_2(T, c_2; p', c_1')$ in the form

$$\mu_2(T, c_2; p', c_1') = \mu_2^\infty(T; p', c_1') + RT \ln y_2^\infty(T, c_2; p', c_1')c_2 \qquad (3.72)$$

where the activity coefficient y_2^∞ is defined in such a way that it tends to unity as $c_2 \to 0$. The $\ln y_2^\infty$ may be expanded in powers of c_2 as

$$\ln y_2^\infty = M_2 \left[A_2(T; p', c_1')c_2 + \frac{1}{2}A_3(T; p', c_1')c_2^2 + \cdots \right] \qquad (3.73)$$

Introduction of Eq.(3.72) with Eq.(3.73) into Eq.(3.71) yields

$$\frac{\pi}{RT} = \frac{c_2}{M_2} + A_2'(T; p', c_1')c_2^2 + A_3'(T; p', c_1')c_2^3 + \cdots \qquad (3.74)$$

where $A_2' = (1/2)A_2$, $A_3' = (1/3)A_3$, $\cdots$. It is to be observed that the virial coefficients $A_2', A_3', \cdots$ here refer to the variables T, p', and c_1' and that plots of $\pi/c_2 RT$ versus c_2 at fixed p' and c_1' allow M_2 to be evaluated when exprapolated to infinite dilution of the protein component, no matter what interactions may be involved between the protein and the supporting electrolyte.

[Comments]

The present problem is concerned with experiments done with a classic osmometer of the U-tube type. In modern high-speed osmometers, the pressure p' ia varied so that the pressure p of the protein solution is kept constant, regardless of the osmotic pressure set up.

[Problem C11]

Suppose a polymer solute (component 2) dissolved in a mixture of two solvents (component 0 and 1). Show that the molecular weight M_2 of the polymer component can be evaluated by the van't Hoff relation

$$\lim_{c_2 \to -} \frac{\pi}{c_2 RT} = \frac{1}{M_2} \tag{3.75}$$

where π is the osmotic pressure of the solution against the mixed solvent (component 0+1) and c_2 is the mass concentration of the polymer.

[Solution C11]

The terms "inner phase" and "outer phase" are used to describe the phase containing no polymer, respectively, which are separated by a semipermeable membrane. It is asumed that the entire system is held at constant temperature and that the outer phase id held at constant pressure p'. Osmotic pressure is reached when the following conditions are satisfied:

$$\mu_0' = \mu_0 \tag{3.76}$$

$$\mu_1' = \mu_1 \tag{3.77}$$

where μ denotes the chemical potential and the prime refers to the outer phase. Since p' is held constant, it follows from Eqs.(3.76) and (3.77) that

$$d\mu_0 = d\mu_1 = 0 \tag{3.78}$$

for any small change dc_2 in the mass concentration of component 2. Small changes in p in p (pressure in the inner phase) and μ_2 which accompany the change dc_2 are denoted by dp and $d]\mu_2$. When Eq.(3.78) holds, these are related to one another by

$$(dp)_{T,\mu_0,\mu_1} = \frac{c_2}{M_2}(d\mu_2)_{T,\mu_0,\mu_1} \tag{3.79}$$

which follows from the Gibbs-Duhem relation for constant temperature. Integarating Eq.(3.79) one gets

$$\pi = p - p' = \int_0^{c_2} \frac{c_2}{M_2} \left(\frac{\partial \mu_2}{\partial c_2} \right)_{T, \mu_0, \mu_1} dc_2 \tag{3.80}$$

which follows from the Gibbs-Duhem relation for constant temperature. Integrating Eq.(3.80) one gets

$$\pi = p - p' = \int_0^{c_2} \frac{c_2}{M_2} \left(\frac{d\mu_2}{dc_2} \right)_{T, \mu_0, \mu_1} dc_2 \tag{3.81}$$

where the integration constant has been determined from the condition that when $c_2 = 0$, the inner and outer phases are equalized in pressure.

Now, one may write for μ_2

$$\mu_2 = \mu_2^\infty(T, \mu_0, \mu_1) + RT \ln y_2(T, \mu_0, \mu_1) c_2 \tag{3.82}$$

where the activity coefficient y_2 is defined in such a way that it tends to unity as c_2 goes to zero. Introduction of Eq.(3.82) into Eq.(3.81) gives

$$\pi = \frac{RT}{M_2} \left[c_2 + \int_0^{c_2} c_2 \left(\frac{\partial \ln y_2}{\partial c_2} \right)_{T, \mu_0, \mu_1} dc_2 \right] \tag{3.83}$$

For dilute solutions one may write

$$\ln y_2(T, \mu_0, \mu_1, c_2) = A_2(T, \mu_0, \mu_1) c_2 + \mathcal{O}(c_2^2) \tag{3.84}$$

Hence Eq.(3.83) becomes

$$\pi = \frac{c_2 RT}{M_2} \left[1 + \frac{c_2}{2} A_2(T, \mu_0, \mu_1) + \mathcal{O}(c_2^2) \right] \tag{3.85}$$

Therefore

$$\lim_{c_2 \to p} \frac{\pi}{c_2 RT} = \frac{1}{M_2} \tag{3.86}$$

[Comments]
(1) For a polydisperse maclomolecular solute the M_2 in Eq.(3.75) may be replaced by the number-average molecular weight M_n.

(2) This problem tells an important fact that the conventional osmotic pressure method allows correct M_n of macromolecular solute to be determined even if a mixed solvent is used. This feature is contrasted to the light-scattering method in which the use of s mixed solvent generally gives only an apparent (weight-average) molecular weight involving the effect of preferential adsorption of one particular solvent onto the macromolecule.

[Problem C12]

A solution which consists of q different macromolecular solutes (designated components 1, 2, $\cdots$, q) and a solvent (component 0) is separated from the solvent by a semi-permeable membrane and brought to osmotic equilibrium under either of the following two conditions: (i) the "outer" solvent phase is held at a constant pressure and (ii) the "inner" solution phase is held at a constant pressure. Derive the expressions for the osmotic pressures, π^* and π, which are set up in cases (i) and (ii), assuming that the solution is dilute.

[Solution C12]

[Case (i)]

The condition for osmotic equilibrium of the system under consideration is

$$\mu_0 \text{ for the inner phase} = \mu_0 \text{ for the outer phase}$$

where μ_0 denotes the chemical potential of component 0. In case (i), the pressure of the outer phase is held constant, so that μ_0 for the outer phase = constant. Thus

$$d\mu_0(T, p, c_1, c_2, \cdots, c_q) = 0 \tag{3.87}$$

for any changes which occur in the mass concentrations $c_1, c_2, \cdots, c_q$ of the inner solution phase. With eq.(3.87) one gets from the Gibbs-Duhem relation

$$(dp)_{T,\mu_0} = \sum_{i=1}^{q} \frac{c_i}{M_i} (d\mu_i) T, \mu_0 \tag{3.88}$$

for a smalll change in p which accompanies a small variation of the composition in the inner solution phase. Since the pressure of the outer phase is held constant, the pressure increment in inner phase, dp, becomes equal to $d\pi^*$. Therefore Eq.(3.88) gives

$$\pi^* = \sum_{i=1}^{q} \sum_{j=1}^{q} \int_{\{0\}}^{\{c\}} \frac{c_i}{M_i} \left(\frac{\partial \mu_i}{\partial c_j} \right)_{T,\mu_0,c_{k \neq j}} dc_j \tag{3.89}$$

where $\{c\}$ stands for a set of $c_1, c_2, \cdots, c_q$ and $\{0\} = (0, 0, \cdots, 0)$. One should not confuse c_i in $\{c\}$ with c_i in the integrand, the latter being the variable of integration.

Now, according to [Problem C8], one has for dilute solutions of $q + 1$ components

$$\frac{1}{M_i}\left(\frac{\partial \mu_i}{\partial c_j}\right)_{T,\mu_0,c_{k\neq j}} = RT\left(\frac{\delta_{ij}}{c_i M_i} + A_{ij} + \sum_{k=1}^{q} A_{ijk}c_k + \cdots\right) \quad (3.90)$$

where δ_{ij} is Kronecker's delta, and A_{ij}, $A_{ijk}, \cdots$ are the coefficients in the Taylor expansion for $\ln y_i^\infty(T, \mu_0, \{c\})$:

$$\ln y_i^\infty(T, \mu_0, \{c\}) = M_i\left(\sum_{j=1}^{q} A_{ij}c_j + \frac{1}{2}\sum_{j=1}^{q}\sum_{k=1}^{q} A_{ijk}c_jc_k + \cdots\right) \quad (3.91)$$

Introducing Eq.(3.90) into Eq.(3.89), one obtains the desired expression for π^* in the form

$$\pi^* = RT\left(\sum_{i=1}^{q}\frac{c_i}{M_i} + \frac{1}{2}\sum_{i=1}^{q}\sum_{j=1}^{q} A_{ij}c_1c_j + \frac{1}{3}\sum_{i=1}^{q}\sum_{j=1}^{q}\sum_{k=1}^{q} A_{ijk}c_ic_jc_k + \cdots\right) \tag{3.92}$$

Note that, in deriving this, one has used the relations

$$\sum_{i=1}^{q}\sum_{j=1}^{q} A_{ij}c_i\mathrm{d}c_j = \frac{1}{2}\sum_{i=1}^{q}\sum_{j=1}^{q} A_{ij}\mathrm{d}(c_ic_j) \tag{3.93}$$

$$\sum_{i=1}^{q}\sum_{j=1}^{q}\sum_{k=1}^{q} A_{ijk}c_ic_k\mathrm{d}c_j = \frac{1}{3}\sum_{i=1}^{q}\sum_{j=1}^{q}\sum_{k=1}^{q} A_{ijk}\mathrm{d}(c_ic_jc_k) \tag{3.94}$$

which follow from the invariance of A_{ij} and A_{ijk} for the exchange of indices.

Equation (3.92) is called the virial expansion for π^*. It shoud be observed that its derivation contains no approximation.

[Case (ii)]

In this case, Eq.(3.87) does not apply, and one must resort to

$$\mu_0 \text{ for the inner phase} = \mu_0 \text{ for the outer phase}$$

to find the desired expression for π. Since $\pi = p - p'$ (p = pressure of the outer solvent phase), the starting equation is written

$$\mu_0(T, p, \{c\}) = \mu_0^0(T, p - \pi) \tag{3.95}$$

where the superacript 0 indicates the pure solvent, i.e., the liquid in the outer phase. In Eq.(3.95), T and p are treated as given constants, and one must try to express π in terms of a Taylor series of $\{c\}$. For this to be done two approximations need to be introduced. One is that the solution is incompressible and the other is that the pressure dependence of $y_i^\infty(T, p, \{c\})$ is negligible. Here $y_i^\infty(T, p, \{c\})$ is the practical activity coefficient of the i-th macromolecular component appropriate for T, p, and $\{c\}$ chosen as the set of state variables.

One can write the expression

$$\mu_0^0(T, p) - \mu_0^0(T, p - \pi) = M_0 \int_{p-\pi}^{p} v_0^0(T, \xi) \mathrm{d}\xi \tag{3.96}$$

where $v_0^0(T, \xi)$ is the specific volume of the pure solvent at temperature T and pressure ξ. If, as assumed above, the solution is incompressible, v_0^0 is independent of pressure. Hence Eq.(3.96) gives

$$\mu_0^0(T, p - \pi) = \mu_0^0(T, p) - M_0 v_0^0 \pi \tag{3.97}$$

in which v_0^0 may be evaluated at the atmospheric pressure. Introduction of Eq.(3.97) into Eq.(3.95) gives

$$\pi = -\frac{1}{M_0 v_0^0}[\mu_0(T, p, \{c\}) - \mu_0^0(T, p)] \tag{3.98}$$

which is the well-known formula in thermodynamics.

To proceed further one differentiates Eq.(3.98) at constant T and p, giving

$$(\mathrm{d}\pi)_{T,p} = -\frac{1}{M_0 v_0^0}[\mathrm{d}\mu_0(T, p, \{c\})]_{T,p} \tag{3.99}$$

Using the Gibbs-Duhem relation at constant T and p, this equation may be transformed to

$$(\mathrm{d}\pi)_{T,p} = \frac{1}{c_0 v_0^0} \sum_{i=1}^{q} \frac{c_i}{M_i} (\mathrm{d}\mu_i)_{T,p}$$

$$= \frac{\sum_{i=1}^{q} \sum_{j=1}^{q} (c_i/M_i)(\partial \mu_i/\partial c_j)_{T,p,c_{k \neq j}} \mathrm{d}c_j}{1 - \sum_{i=1}^{q} c_i v_i} \qquad (3.100)$$

where the relation $c_0 v_0 + c_1 v_1 + \cdots + c_q v_q = 1$ (v_i is the partial specific volume of the i-th component) has been inserted.

As has been shown in [Problem C8], one has for dilute solutions in which all of $c_1, c_2, \cdots, c_q$ are small

$$\frac{1}{M_i} \left(\frac{\partial \mu_i}{\partial c_j} \right)_{T,p,c_{k \neq j}} = RT \left(\frac{\delta_{ij}}{c_i M_i} + B_{ij} + \sum_{k=1}^{q} B_{ijk} c_k + \cdots \right) \qquad (3.101)$$

where $B_{ij}, B_{ijk}, \cdots$ are the coefficients in the Taylor expansion for $\ln y_i^{\infty}$:

$$\ln y_i^{\infty}(T, p, \{c\}) = M_i \left(\sum_{j=1}^{q} B_{ij} + \frac{1}{2} \sum_{j=1}^{q} \sum_{k=1}^{q} B_{ijk} c_j c_k + \cdots \right) \qquad (3.102)$$

Introducing Eq.(3.101) into Eq.(3.100) and expanding $(1 - \sum_{i=1}^{q} c_i v_i)^{-1}$ in powers of c_i, one obtains

$$
\begin{aligned}
(\mathrm{d}\pi)_{T,p} = {} & RT \left(\sum_{i=1}^{q} \frac{\mathrm{d}c_i}{M_i} + \sum_{i=1}^{q} \sum_{j=1}^{q} B_{ij} c_i \mathrm{d}c_j + \sum_{i=1}^{q} \sum_{j=1}^{q} \sum_{k=1}^{q} B_{ijk} c_i c_k \mathrm{d}c_j + \cdots \right) \\
& \times \left\{ 1 + \sum_{i=1}^{q} c_i v_i^0 + \sum_{i=1}^{q} \sum_{j=1}^{q} \left[v_i^0 v_j^0 + \left(\frac{\partial v_i}{\partial c_j} \right)^0 \right] c_i c_j + \cdots \right\} \\
= {} & RT \left\{ \sum_{i=1}^{q} \frac{\mathrm{d}c_i}{M_i} + \sum_{i=1}^{q} \sum_{j=1}^{q} \left(B_{ij} + \frac{v_i^0}{M_j} \right) c_i \mathrm{d}c_j + \sum_{i=1}^{q} \sum_{j=1}^{q} \sum_{k=1}^{q} \left[B_{ijk} \right. \right. \\
& \left. \left. + \frac{v_i^0 v_k^0}{M_j} + \frac{1}{M_j} \left(\frac{\partial v_i}{\partial c_k} \right)^0 + B_{kj} v_i^0 \right] c_i c_k \mathrm{d}c_j + \cdots \right\} \qquad (3.103)
\end{aligned}
$$

where the superscript 0 indicates the limit of infinite dilution, i.e., the state in which all of $c_1, c_2, \cdots, c_q$ are reduced to zero.

Integrating Eq. (3.103) from infinite dilution to a given composition, one gets

$$\pi = RT \Bigg\{ \sum_{i=1}^{q} \frac{c_i}{M_i} + \sum_{i=1}^{q} \sum_{j=1}^{q} \left(B_{ij} + \frac{v_i^0}{M_j} \right) \int_0^{\{c\}} c_i dc_j$$
$$+ \sum_{i=1}^{q} \sum_{j=1}^{q} \sum_{k=1}^{q} \left[B_{ijk} + \frac{v_i^0 v_k^0}{M_j} + \frac{1}{M_j} \left(\frac{\partial v_i}{\partial c_k} \right)^0 + B_{kj} v_i^0 \right]$$
$$\times \int_o^{\{c\}} c_i c_k dc_j + \cdots \Bigg\} \qquad (3.104)$$

To step further one must introduce the approximation that $y_i^\infty(T, p, \{c\})$ does not depend on p. Then, as has been shown in [Problem C8], there are relations

$$B_{ij} + \frac{v_i}{M_j} = A_{ij} \qquad (3.105)$$

$$B_{ijk} + \frac{v_i^0 v_k^0}{M_j} + B_{kj} v_i^0 = A_{ijk} \qquad (3.106)$$

and also $(\partial v_i / \partial c_k)^0$ vanishes. Hence Eq.(3.104) becomes

$$\pi = \sum_{i=1}^{q} \frac{c_i}{M_i} + \frac{1}{2} \sum_{i=1}^{q} \sum_{j=1}^{q} A_{ij} c_i c_j$$
$$+ \frac{1}{3} \sum_{i=1}^{q} \sum_{j=1}^{q} \sum_{k=1}^{q} A_{ijk} c_i c_j c_k + \cdots \qquad (3.107)$$

where the invariance of A_{ij} and A_{ijk} for the interchange of dummy indices has been used. Equation (3.107) is the virial expansion for π, subject to the two approximations made, and it is seen that this expression agrees with the virial expansion for π^* at least up to the third power of solute concentrations.

[Comments]
(1) Classical U-tube osmometers measure π^*, while modern automatic osmometers are designed so as to measure π. It is important to notice from the above developed analysis that, strictly speaking, π^* is not

equal to π. However, the approximations made above, i.e., pressure-independence of ρ (solution density) and of $y_i^\infty(T, p, \{c\})$, apply almost rigorously under usual experimental conditions for osmotic pressure measurements on macromolecular solutions.

(2) When the solution is quasi-binary, i.e., is consists of a solvent and a polymer solute polydisperse in molecular weight, one can write

$$c_i = cg_i \tag{3.108}$$

where c is the total solute concentration and g_i is the weight fraction of the i-th polymer solute of molecular weight M_i. With Eq.(3.108), Eq.(3.92) for π^* (or Eq.(3.107) for π) may be written

$$\pi^*(\text{or } \pi) = cRT\left(\frac{1}{M_n} + A_2 c + A_3 c^2 + \cdots\right) \tag{3.109}$$

where M_n is the number-average molecular weight of the dissolved polymer $(= 1/\sum_{i=1}^{q} g_i/M_i)$, and $A_2, A_3, \cdots$ are the second, third, $\cdots$ osmotic virial coefficients of the system, defined by

$$A_2 = \frac{1}{2}\sum_{i=1}^{q}\sum_{j=1}^{q} g_i g_j A_{ij} \tag{3.110}$$

$$A_3 = \frac{1}{3}\sum_{i=1}^{q}\sum_{j=1}^{q}\sum_{k=1}^{q} g_i g_j g_k A_{ijk} \tag{3.111}$$

Equation (3.109) indicates that plots of π/cRT versus c give M_n^{-1} and A_2 from their ordinate intercept and initial slope. For flexible polymers in good solvent it is often advantageous to use a graph in which $(\pi^*/cRT)^{1/2}$ is plotted against c, because by so doing one can take the effect of the $A_3 c^2$ term approximately into account. On this graph, the ordinate intercept and initial slope are equal to $M_n^{-1/2}$ and $M_n^{1/2}A_2/2$, respectively.

[Problem C13]

For a solution which contains a macromolecular solute (component 2) in a mixture of two solvents (components 0 and 1), show that

$$\left(\frac{\partial m_1}{\partial m_1}\right)_{T,p,\mu_1} = -\left(\frac{\partial \mu_1}{\partial m_2}\right)_{T,p,m_1} \Big/ \left(\frac{\partial \mu_1}{\partial m_1}\right)_{T,p,m_2} \tag{3.112}$$

$$\left(\frac{\partial m_1}{\partial m_2}\right)_{T,\mu_1,\mu_2} = -\left(\frac{\partial \mu_1}{\partial m_2}\right)_{T,p,m_1} \Big/ \left(\frac{\partial \mu_1}{\partial m_1}\right)_{T,p,m_2}$$
$$-M_1 v_1 \left(\frac{\partial p}{\partial m_2}\right)_{T,\mu_1} \Big/ \left(\frac{\partial \mu_1}{m_1}\right)_{T,p,m_2} \tag{3.113}$$

where M_1, v_1, μ_1, and m_1 are the molecular weight, partial specific volume, chemical potential, and molality of component 1 (a secondary solvent), and m_2 is tha molality of component 2. These molalities are defined as the moles of the respective components per one kilogram of component 0 (a principal solvent).

[Solution C13]

Since μ_1 may be regarded as a function of T, p, m_1, and m_2, one can write at constant T

$$d\mu_1 = \left(\frac{\partial \mu_1}{\partial m_1}\right)_{T,p,m_2} dm_1 + \left(\frac{\partial \mu_1}{\partial m_2}\right)_{T,p,m_1} dm_2 + \left(\frac{\partial \mu_1}{\partial p}\right)_{T,m_1,m_2} dp \tag{3.114}$$

Hence

$$0 = \left(\frac{\partial \mu_1}{\partial m_1}\right)_{T,p,m_2} \left(\frac{\partial m_1}{\partial m_2}\right)_{T<\mu_0,\mu_1} + \left(\frac{\partial \mu_1}{m_2}\right)_{T,p,m_1} + v_1 M_1 \left(\frac{\partial p}{\partial m_2}\right)_{T,\mu_0,\mu_1} \tag{3.115}$$

where the relation $(\partial \mu_1/\partial p)_{T,m_1,m_2} = v_1 M_1$ has been inserted. Equation (3.115) may be rearranged to give Eq.(3.113).

It also follows from Eq.(3.114) that

$$0 = \left(\frac{\partial \mu_1}{\partial m_1}\right)_{T,p,m_2} \left(\frac{\partial m_1}{\partial m_2}\right)_{T,p,\mu_1} + \left(\frac{\partial \mu_1}{\partial m_2}\right)_{T,p,m_1} \tag{3.116}$$

which can be put in the form of Eq.(3.112).

[Comments]

The quantity $(\partial m_1/\partial m_2)_{T,p,\mu_1}$ often appears in thermodynamic analyses of a macromolecular solute in a binary mixed solvent (principal solvent + secondary solvent), and usually it is designated by:

$$\Gamma = \left(\frac{\partial m_1}{\partial m_2}\right)_{T,p,\mu_1} \tag{3.117}$$

If there is no thermodynamic interaction between components 1 and 2, $(\partial\mu_1/\partial m_2)_{T,p,m_1}$ should vanish. Then, according to Eq.(3.112), Γ may vanish, because $(\partial\mu_1/\partial m_1)_{T,p,m_2}$ generally remains at a nonzero value. Thus Γ may be regarded as ameasure for the thermodynamic interaction between components 1 and 2, at constant T, p, and μ_1.

On the other hand, from the form of Eq.(3.117) one may consider Γ to be the moles of component 1 that must be added to the solution containing one kilogram of component 0 in order to keep μ_1 constant when the content of component 2 is increased by one mole at given temperature and pressure. It is misleading to interpret Γ as the moles of component 1 bound on one mole of component 2 at constant T, p, and μ_1 in the solution containing one kilogram of component 0. Therefore, the term "binding coefficient"or "preferential adsorption coefficient"of component 2 for component 1 that is often assigned to Γ is conceptually incorrect. One may properly refer to Γ as the thermodynamic interaction parameter for a pair of components 1 and 2 st constant T, p, and μ_1. Similarly, the quantity Γ^* defined by

$$\Gamma^* = \left(\frac{\partial m_1}{\partial m_2}\right)_{T,\mu_1,\mu_1} \tag{3.118}$$

may be called the thermodynamic interaction parameter for the same pair of components at constant T, μ_0, and μ_1.

[Problem C14]

According to the classic Flory-Huggins theory of polymer solutions, the entropy of mixing, $\Delta_M S$, of binary solutions consisting of a slovent (component 0) and a monodisperse polymer of P degrees of polymerization (component 1) is given by

$$\Delta_M S = -R(n_0 \ln \phi_0 + n_1 \ln \phi_1) \tag{3.119}$$

where n_i and ϕ_i $(i = 0, 1)$ are moles and the apparent volume fraction of component i, with ϕ_i defined by

$$\phi_0 = 1 - \phi_1. \qquad \phi_1 = \frac{Pn_1}{n_0 + Pn_1} \tag{3.120}$$

If this solution is regarded as ideal, its entropy of mixing, $\Delta_M^* S$ is

$$\Delta_M^* S = -R(n_0 \ln x_0 + n_1 \ln x_1) \tag{3.121}$$

where x_i is the mole fraction of component i; thus

$$x_0 = 1 - x_1, \qquad x_1 = \frac{n_1}{n_0 + n_1} \tag{3.122}$$

Evaluate the ratios $\Delta_M S / \Delta_M^* S$ at $\phi = 0.1$ and 0.5 for the case of $P = 1000$.

[Solution C14]

From Eqs.(3.120) and (3.122)

$$x_1 = \frac{\phi_1}{P - (P-1)\phi_1} \tag{3.123}$$

$$\frac{n_1}{n_0} = \frac{\phi_1}{P(1 - \phi_1)} \tag{3.124}$$

Hence $\Delta_M S / \Delta_M^* S$ may be written

$$\frac{\Delta_M S}{\Delta_M^* S} = \frac{\left[\ln(1 - \phi_1) + \frac{\phi_1}{P(1-\phi_1)} \ln \phi_1 \right]}{\left[\ln \frac{P(1-\phi_1)}{P-(P-1)\phi_1} + \frac{\phi_1}{P(1-\phi_1)} \ln \frac{\phi_1}{P-(P-1)\phi_1} \right]} \tag{3.125}$$

For $P = 1000$ and $\phi_1 = 0.1$,

$$\frac{\Delta_M S}{\Delta_M^* S} = 94.1 \tag{3.126}$$

For $P = 1000$ and $\phi_1 = 0.5$,

$$\frac{\Delta_M S}{\Delta_M^* S} = 87.7 \tag{3.127}$$

These values illustrate how anomalously the mixing entropy of polymer solutions deviates from the ideal solution value. This deviation comes from a greater internal freedom of flexible polymer chains.

[Problem C15]

By use of the Flory-Huggins expression of the Gibbs free energy of mixing, $\Delta_m G$, for polydisperse solution, obtain the chemical potential, μ_i, of the i-th component ($i = 1, 2, \cdots, q$) in the undiluted polymer mixture. Assume that the interaction parameter χ is independent of composition.

[Solution C15]

The relevant expression for $\Delta_m G$ is

$$\Delta_m G = RT[n_0 \ln \phi_0 + \sum_{i=1}^{q} n_i \ln \phi_i + (n_0 + \sum_{i=1}^{q} P_i n_i)\chi\phi_0\phi] \qquad (3.128)$$

where n_0 and ϕ_0 are the moles and apparent volume fraction of the solvent (component 0), n_i and ϕ_i are the corresponding quantities of the i-th polymer component, and ϕ is equal to $1 - \phi_0$, i.e., the total apparent volume fraction of the solute components. The definition of ϕ_i is

$$\phi_i = \frac{P_i n_i}{n_0 + \sum_{j=1}^{q} P_j n_j} \qquad (3.129)$$

with P_j being the degree of polymerization of the j-th polymer component. From Eq.(3.128), with consideration of Eq.(3.129), we get

$$\mu_i - \mu_i^0 = \left(\frac{\partial \Delta_m G}{\partial n_i}\right)_{T,p,n_{j\neq i}}$$

$$= RT\left[\ln \phi_i - (P_i - 1) + P_i\left(1 - \frac{1}{P_n}\right)\phi\right.$$

$$\left. + P_i\chi(1 - \phi)^2\right] \qquad (3.130)$$

where P_n is the number-average degree of polymerization defined by

$$P_n = \frac{\sum_{i=1}^{q} P_i n_i}{\sum_{i=1}^{q} n_i} \qquad (3.131)$$

and μ_i^0 is the value of μ_i in the pure state of the i-th polymer component.

For the undiluted polymer, $\phi = 1$ and $\phi_i = P_i n_i / \sum_{j=1}^{q} P_j n_j = w_i$, where w_i is the weight fraction of the i-th component in the polymer mixture, so that Eq.(3.130) reduces to

$$\mu_i = \mu_i^0 + RT \left[\ln w_i + \ln \left(\frac{P_i}{P_n} \right) + 1 - \frac{P_i}{P_n} \right] \qquad (3.132)$$

The second term on the right-hand side of Eq.(3.132) represents the effect arisen from the mixing of polymers of different chain length.

[Comments]

Note that the $\Delta_m G$ of the Flory-Huggins theory is not for the process

a solvent + a polymer solid

but for the process

a solvent + mutually isolated polymer components of different P

[Problem C16]

According to Gibbs, the spinodal of a system consisting of $q + 1$ components is given by the equation

$$|\boldsymbol{\mu}| \equiv \begin{vmatrix} \mu_{11} & \mu_{12} & \cdots & \mu_{1q} \\ \mu_{21} & \mu_{22} & \cdots & \mu_{2q} \\ \vdots & \vdots & \ddots & \vdots \\ \mu_{q1} & \mu_{q2} & \cdots & \mu_{qq} \end{vmatrix} = 0 \qquad (3.133)$$

where

$$\mu_{ij} = \left(\frac{\partial \mu_i}{\partial m_j} \right)_{T,p,m_k} \qquad (3.134)$$

with μ_i and m_i being the chemical potential and molality of the i-th component, respectively. Show that Eq.(3.133) is equivalent to

$$|\mathbf{G}_n| \equiv \begin{vmatrix} G_{11} & G_{12} & \cdots & G_{1q} \\ G_{21} & G_{22} & \cdots & G_{2q} \\ \vdots & \vdots & \ddots & \vdots \\ G_{q1} & G_{q2} & \cdots & G_{qq} \end{vmatrix} = 0 \qquad (3.135)$$

where

$$G_{ij} = \left(\frac{\partial^2 G_n}{\partial x_i \partial x_j} \right)_{T,p,x_k} \qquad (3.136)$$

with

$$G_n = \sum_{i=0}^{q} x_i \mu_i \qquad (3.137)$$

and x_i being the mole fraction of the i-th component. Note that G_n is the mean molar Gibbs free energy of the system.

[Solution C16]

Using the relation $x_i = m_i / \sum_{j=0}^{q} m_j$, one finds that

$$\mu_{ij} = \sum_{k=1}^{q} \left(\frac{\partial \mu_i}{\partial x_k} \right)_{x_l} \left(\frac{\partial x_k}{\partial m_j} \right)_{m_k}$$

$$= \frac{1}{\sum_{k=0}^{q} m_k} \left[\left(\frac{\partial \mu_i}{\partial x_j} \right)_{x_l} - \sum_{k=1}^{q} x_k \left(\frac{\partial \mu_i}{\partial x_k} \right)_{x_l} \right] \qquad (3.138)$$

where the subscripts T, p have been omitted for simplicity. Equation (3.137) can be rewritten

$$G_n = (1 - \sum_{i=1}^{q} x_i)\mu_0 + \sum_{i=1}^{q} x_i\mu_i \qquad (3.139)$$

Differentiation with respect to x_j gives

$$\frac{\partial G_n}{\partial x_j} \equiv G_j = \mu_j - \mu_0 \qquad (3.140)$$

where the Gibbs-Duhem relation $\sum_{i=0}^{q} x_i(\partial\mu_i/\partial x_j)_{T,p,x_k} = 0$ has been used. Thus Eq.(3.139) may be written

$$\mu_i = G_n + G_i - \sum_{k=1}^{q} x_k G_k \qquad (3.141)$$

This is differentiated with respect to x_j to give

$$\left(\frac{\partial \mu_i}{\partial x_j}\right)_{x_k} = G_j + G_{ij} - G_j - \sum_{k=1}^{q} x_k G_{kj}$$

$$= G_{ij} - \sum_{k=1}^{q} x_k G_{kj} \qquad (3.142)$$

Substitution of Eq.(3.142) into Eq.(3.138) gives

$$\mu_{ij} = \frac{G_{ij} - \sum_{k=1}^{q} x_k G_{kj} - \sum_{k=1}^{q} x_k G_{ik} + \sum_{k=1}^{q} \sum_{h=1}^{q} x_k x_h G_{kh}}{\sum_{k=0}^{q} m_k} \qquad (3.143)$$

If one defines $q \times q$ matrices, $\boldsymbol{\mu}$, $\mathbf{G}_n$, $\mathbf{x}$, and $\mathbf{E}$ as

$$\boldsymbol{\mu} \equiv \begin{pmatrix} \mu_{11} & \mu_{12} & \cdots & \mu_{1q} \\ \mu_{21} & \mu_{22} & \cdots & \mu_{2q} \\ \vdots & \vdots & \ddots & \vdots \\ \mu_{q1} & \mu_{q2} & \cdots & \mu_{qq} \end{pmatrix} \qquad (3.144)$$

$$\mathbf{G}_n \equiv \begin{pmatrix} G_{11} & G_{12} & \cdots & G_{1q} \\ G_{21} & G_{22} & \cdots & G_{2q} \\ \vdots & \vdots & \ddots & \vdots \\ G_{q1} & G_{q2} & \cdots & G_{qq} \end{pmatrix} \qquad (3.145)$$

$$\mathbf{x} \equiv \begin{pmatrix} x_1 & x_1 & \cdots & x_1 \\ x_2 & x_2 & \cdots & x_2 \\ \vdots & \vdots & \ddots & \vdots \\ x_q & x_q & \cdots & x_q \end{pmatrix} \tag{3.146}$$

$$\mathbf{E} \equiv \begin{pmatrix} 1 & 0 & \cdots & 0 \\ 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & 1 \end{pmatrix} \tag{3.147}$$

Eq.(3.143) may be put in a compact form as

$$\begin{aligned} \boldsymbol{\mu} =& (\sum_{k=0}^{q} m_k)^{-1}(\mathbf{G}_n - \mathbf{x}^T\mathbf{G}_n - \mathbf{G}_n\mathbf{x} + \mathbf{x}^T\mathbf{G}_n\mathbf{x}) \\ =& (\sum_{k=0}^{q} m_k)^{-1}(\mathbf{E} - \mathbf{x}^T)\mathbf{G}_n(\mathbf{E} - \mathbf{x}) \end{aligned} \tag{3.148}$$

where $\mathbf{x}^T$ is the transposed matrix of $\mathbf{x}$. Thus

$$|\boldsymbol{\mu}| = (\sum_{k=0}^{q} m_k)^{-1}|\mathbf{E} - \mathbf{x}^T||\mathbf{G}_n||\mathbf{E} - \mathbf{x}| = 0 \tag{3.149}$$

Since $|\mathbf{E} - \mathbf{x}| \neq 0$ and $|\mathbf{E} - \mathbf{x}| \neq 0$, $(|\mathbf{E} - \mathbf{x}^T| = |\mathbf{E} - \mathbf{x}| = 1 - \sum_{i=1}^{q} x_i$, as one may easily show.) it follows that

$$|\mathbf{G}_n| = 0 \tag{3.150}$$

which is the required result.

[Comments]

In theoretical treatments of polymer solutions,the more appropriate composition variables are not the mole fractions but the apparent volume fractions of the components. For quasi-binary solutions which contain a single solvent (component 0) and a polydisperse polymer solute that consists of component $1, 2, \cdots, q$ of the degrees of polymerization

$P_1, P_2, \cdots, P_q$, respectively, the apparent volume fraction ϕ_i is defined by

$$\phi_i = \frac{P_i n_i}{n_0 + \sum_{j=1}^{q} P_j n_j} \tag{3.151}$$

One may define a mean Gibbs free energy of the system by

$$G_\phi = \frac{G}{n_0 + \sum_{j=1}^{q} P_j n_j} \tag{3.152}$$

and may regard this as a function of $\phi_1, \phi_2, \cdots, \phi_q$ (note that $\phi_1 + \phi_2 + \cdots + \phi_q = 1$). By the same operation as above, it can be shown that the spinodal of the system is given by

$$|\mathbf{G}_\phi| \equiv \begin{vmatrix} G_{11} & G_{12} & \cdots & G_{1q} \\ G_{21} & G_{22} & \cdots & G_{2q} \\ \vdots & \vdots & \ddots & \vdots \\ G_{q1} & G_{q2} & \cdots & G_{qq} \end{vmatrix} = 0 \tag{3.153}$$

where G_{ij} is defined as

$$G_{ij} = \left(\frac{\partial^2 G_\phi}{\partial \phi_i \partial \phi_j} \right)_{T,p,\phi_k} \tag{3.154}$$

[Problem C17]

For quasi-binary solutions which consist of a solvent (component 0) and a polydisperse polymer solute (component $1, 2, \cdots, q$ depending on the degrees of polymerization of the constituting polymer chains) one may define a mean Gibbs free energy G_ϕ by

$$G_\phi = \frac{G}{n_0 + \sum_{i=1}^{q} P_i n_i} \qquad (3.155)$$

Here G is the Gibbs free energy of the system, n_i is the mole of the i-th component, and P_i is the degree of polymerization of the same component. Accoring to the Flory-Huggins formalism, the function G_ϕ is expressed by

$$G_\phi = G_\phi^0 + RT \left[(1 - \phi) \ln(1 - \phi) + \sum_{i=1}^{q} \frac{\phi_i}{P_i} \ln \phi_i + \chi(1 - \phi)\phi \right] \quad (3.156)$$

where ϕ_i is the apparent volume fraction of the i-th component defined by

$$\phi_i = \frac{P_i n_i}{n_0 + \sum_{j=1}^{q} P_j n_j} \qquad (3.157)$$

ϕ is defined by

$$\phi = \sum_{i=1}^{q} \phi_i \qquad (3.158)$$

χ is the parameter assumed to depend on ϕ, T (temperature), and p (pressure), and G_ϕ^0 is a reference value of G_ϕ depending only on T and p.

Show that the spinodal of the Flory-Huggins quasi-binary system is given by

$$\frac{1}{1 - \phi} + \frac{1}{P_w \phi} - 2X - \phi \left(\frac{\partial X}{\partial \phi} \right) = 0 \qquad (3.159)$$

where P_w is the weight-average degree of polymerization of the polymer solute, and X is defined by

$$X = \chi - (1 - \phi) \frac{\partial \chi}{\partial \phi} \qquad (3.160)$$

[Solution C17]

As shown in [Problem C16], the spinodal is calculated from the equation:

$$\begin{vmatrix} G_{11} & G_{12} & \cdots & G_{1q} \\ G_{21} & G_{22} & \cdots & G_{2q} \\ \vdots & \vdots & \ddots & \vdots \\ G_{q1} & G_{q2} & \cdots & G_{qq} \end{vmatrix} = 0 \tag{3.161}$$

where

$$G_{ij} = \left(\frac{\partial^2 G_\phi}{\partial \phi_i \partial \phi_j} \right)_{T,p,\phi_k} \tag{3.162}$$

Substitution of Eq.(3.156) into Eq.(3.162) yields

$$G_{ij} = RT \left[\frac{1}{1-\phi} - 2X - \phi \frac{\partial X}{\partial \phi} \right] \quad (i \neq j) \tag{3.163}$$

$$G_{ii} = RT \left[\frac{1}{1-\phi} - 2X - \psi \frac{\partial X}{\partial \phi} + \frac{1}{P_i \phi_i} \right] \tag{3.164}$$

Thus Eq.(3.161) assumes the form

$$|\mathbf{L}_n| \equiv \begin{vmatrix} L + L_1 & L & \cdots & L \\ L & L + L_2 & \cdots & L \\ \vdots & \vdots & \ddots & \vdots \\ L & L & \cdots & L + L_q \end{vmatrix} = 0 \tag{3.165}$$

with

$$L = \frac{1}{1-\phi} - 2X - \phi \frac{\partial X}{\partial \phi} \tag{3.166}$$

$$L_i = \frac{1}{P_i \phi_i} \tag{3.167}$$

One may expand the determinant $|\mathbf{L}|$ by use of the formula:

$$\begin{vmatrix} A + a_1 & B + b_1 & \cdots \\ A + a_2 & B + b_2 & \cdots \\ \cdots & \cdots & \cdots \\ A + a_q & B + b_q & \cdots \end{vmatrix} = \begin{vmatrix} a_1 & b_1 & \cdots \\ a_2 & b_2 & \cdots \\ \cdots & \cdots & \cdots \\ a_q & b_q & \cdots \end{vmatrix}$$

$$+A\begin{vmatrix} 1 & b_1 & \cdots \\ 1 & b_2 & \cdots \\ \cdots & \cdots & \cdots \\ a_q & b_q & \cdots \end{vmatrix} + B\begin{vmatrix} a_1 & 1 & \cdots \\ a_2 & 1 & \cdots \\ \cdots & \cdots & \cdots \\ a_q & 1 & \cdots \end{vmatrix} + \cdots \qquad (3.168)$$

Then

$$|\mathbf{L}| = (\prod_{i=1}^{q} L_i)(L \sum_{i=1}^{q} L_i^{-1} + 1) = 0 \qquad (3.169)$$

Inserting Eqs.(3.166) and (3.167), one gets the desired equation for the spinodal,

$$\frac{1}{1-\phi} + \frac{1}{P_w \phi} - 2X - \phi \frac{\partial X}{\partial \phi} = 0 \qquad (3.170)$$

where

$$P_w = \frac{\sum_{i=1}^{q} P_i^2 n_i}{\sum_{i=1}^{q} P_i n_i} \qquad (3.171)$$

[Problem C18]

A polypeptide is supposed to take only two conformations, α-helix and random coil, depending on the conditions of surrouding temperature and solvent. Define ΔH and ΔS as the enthalpy and entropy of the system in which the polypeptide assumes the helical conformation, relative to those of the same system in which the polypeptide helix is disrupted to random coil. The ΔH and ΔS thus defined are called the transition enthalpy and transition entropy, respectively. Show that if $\Delta H > 0$ and $\Delta S > 0$ in a given solvent, the polypeptide undergoes a conformational change from random coil to α-helix as the temperature is raised.

[Solution C18]

The transition free energy ΔG defined by

$$\Delta G = \Delta H - T\Delta S \tag{3.172}$$

with T being the absolute temperature, is positive below and negative above the temperature T_c determined by the relation:

$$T_c = \left(\frac{\Delta H}{\Delta S} \right)_{T=T_c} \tag{3.173}$$

provided that, as assumed in the problem, $\Delta H > 9$ and $\Delta S > 0$. This means that for $T < T_c$ the polypeptide chain favors random coil conformation, and for $T_c < T$ it tends to assume the α-helix. Note that ΔH and ΔS are, in general, functions of temperature. The T_c is usually referred to as the transition temperature of the system. When $\Delta H < 0$ and $\Delta S < 0$, the polypeptide conformation changes from α-helix to random coil as T increases.
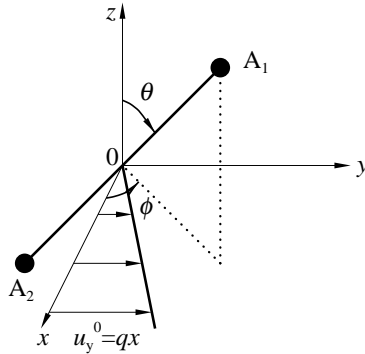
[Problem C19]

Consider a dumbell-type molecule in a simple shear flow of solvent, which is represented by (see the figure above)

$$\mathbf{u}^0 = \left\{ \begin{array}{l} u_x^0 = 0 \\ u_y^0 = qx \\ u_z^0 = 0 \end{array} \right.$$

with the origin of (x, y, z) coordinates fixed at the center of gravity of the molecule. Show that if the shear rate q relative to the rotational diffusion coefficient, Θ, of the dumbell is sufficiently small, the molecule rotates, on time average, at an angular speed equal to $q/2$ about the z-axis.

[Solution]

The dumbell is subject to two forces at each of its two beads A_1 and A_2. One is the hydrodynamic drag due to applied shear flow, and the other is the fluctuating forcs due to irregular collision of the solvent molecules. Thus the motion of the dumbell must be described according to the theory of Brownian motion. Clearly, it is convenient to use the polar coordinates (θ, ϕ) for the description of this motion. Let the probability that the orientation of the dumbell at a given time t is

found in the angular regions $(\theta, \theta + d\theta)$ and $(\phi, \phi + d\phi)$ be denoted by $(1/4\pi)\rho(\theta, \phi, t) \sin \theta d\theta d\phi$. According to the theory of Brownian motion, ρ satisfies the differential equation

$$\frac{\partial \rho}{\partial t} = -\mathrm{div}(\mathbf{j}\rho) \tag{3.174}$$

where $\mathbf{j}$ is the flux of probability density for the bead A_1. In terms of polar coordinates, Eq.(3.174) may be written

$$\frac{\partial \rho}{\partial t} = -\frac{2}{b \sin \theta} \frac{\partial}{\partial \theta}(j_\theta \rho \sin \theta) - \frac{2}{b \sin \theta} \frac{\partial}{\partial \phi}(j_\phi \rho) \tag{3.175}$$

where b is the distance between the two beads A_1 and A_2, and j_θ and j_ϕ are the θ and ϕ components of $\mathbf{j}$, respectively, so that

$$j_\theta = \frac{b}{2}\left(\frac{d\theta}{dt} - \Theta \frac{\partial \ln \rho}{\partial \theta}\right) \tag{3.176}$$

$$j_\phi = \frac{b}{2}\left(\sin \theta \frac{d\phi}{dt} - \frac{\Theta}{\sin \theta}\frac{\partial \ln \rho}{\partial \phi}\right) \tag{3.177}$$

In these equations, $d\theta/dt$ and $d\phi/dt$ have such meaning that $(b/2)(d\theta/dt)$ and $(b/2)\sin\theta(d\phi/dt)$ are the velocities in the θ and ϕ directions that the bead A_1 would aquire from applied shear flow of solvent if the Brownian fluctuating force were absent.

To calculate $d\theta/dt$ and $d\phi/dt$ it is assumed for simplicity that the hydrodynamic disturbance caused by the bead A_2 at the position of the bead A_1 is negligible and also that the moment of inertia of the molecule is negligibly small. Then, one finds that

$$\frac{d\theta}{dt} = \frac{q}{4}\sin 2\theta \sin 2\phi, \qquad \frac{d\phi}{dt} = q\cos^2\phi \tag{3.178}$$

Substitution of Eqs.(3.176) and (3.177), with Eq.(3.178), into Eq.(3.175) yields

$$\begin{aligned}
\frac{\partial \rho}{\partial t} =&\, \Theta\left[\frac{1}{\sin \theta}\frac{\partial}{\partial \theta}\left(\sin \theta \frac{\partial \rho}{\partial \theta}\right) + \frac{1}{\sin^2 \theta}\frac{\partial^2 \rho}{\partial \phi^2}\right]\\
&- q\left[\frac{1}{4}\sin 2\theta \sin 2\phi \frac{\partial \rho}{\partial \theta} + \cos^2 \phi \frac{\partial \rho}{\partial \phi} - \frac{3\rho}{2}\sin^2 \theta \sin 2\phi\right] \tag{3.179}
\end{aligned}$$

For the present problem one may be interested only in the steady-state solution to this partial differential equation. For the steady state $\partial\rho/\partial t = 0$, so that Eq.(3.179) reduces to

$$\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\rho}{\partial\theta}\right) + \frac{1}{\sin\theta}\frac{\partial^2\rho}{\partial\phi^2}$$
$$-\frac{q}{\Theta}\left[\frac{1}{4}\sin\theta\sin 2\theta\sin 2\phi\frac{\partial\rho}{\partial\theta} + \sin\theta\cos^2\phi\frac{\partial\rho}{\partial\phi}\right.$$
$$\left. -\frac{3\rho}{2}\sin^3\theta\sin 2\phi\right] = 0 \tag{3.180}$$

One must solve this with the auxiliary conditions that

$$\frac{1}{4\pi}\int_0^\pi\int_0^{2\pi}\rho\sin\theta\mathrm{d}\theta\mathrm{d}\phi = 1 \tag{3.181}$$

and that $\rho(\theta,\phi) = \rho(\pi-\theta,\phi)$ and $\rho(\theta,\phi) = (\theta,\phi+\pi)$.

The derivation of the appropriate solution to Eq.(3.180) is left for [Problem C21], which gives

$$\rho = 1 + \frac{q}{\Theta}\sin^2\theta\sin 2\phi + \mathcal{O}\left(\frac{q^2}{\Theta^2}\right) \tag{3.182}$$

Substituting this, together with Eq.(3.178), into Eqs.(3.176) and (3.177), one gets

$$j_\theta = \frac{bq}{12}\left(\frac{q}{\Theta}\right)\left[\sin 2\theta\cos 2\phi + \mathcal{O}\left(\frac{q}{\Theta}\right)\right] \tag{3.183}$$

$$j_\phi = \frac{bq}{4}\left[1 + \mathcal{O}\left(\frac{q}{\Theta}\right)\right]\sin\theta \tag{3.184}$$

Therefore, one sees that when $q/\Theta \ll 1$, $j_\theta \simeq 0$ and $j_\phi \simeq (bq/4)sin\theta$. In other words, the dumbell rotates at a constant angular speed $q/2$ about the z-axis (the axis perpendicular to the plane of applied shear flow), keeping the angle relative to the z-axis at a certain value. From this conclusion it follows that when $q/\Theta \ll 1$, the x, y, z components, v_x, v_y, v_z, of the average valocity of the bead A_1 are

$$\mathbf{v}^0 = \begin{cases} v_x = -\frac{q}{2}y \\ v_y = \frac{q}{2}x \\ v_z = 0 \end{cases}$$

[Comments]

It can be shown that the conclusions derived above hold even when there are hydrodynamic interactions between the two beads of the dumb-ell.

[Problem C20]

Derive Eq.(3.178) in [Problem C19], i.e.,

$$\frac{d\theta}{dt} = \frac{q}{4} \sin 2\theta \sin 2\phi, \qquad \frac{d\phi}{dt} = q \cos^2 \phi \qquad (3.185)$$

[Solution C20]

Referring to the figure given in [Problem C19], one sees that the θ and ϕ components $(v_{1\theta}, v_{1\phi})$ of the velocity of the bead A_1 are written

$$v_{1\theta} = \frac{\theta}{2} \frac{d\theta}{dt}, \qquad v_{1\phi} = \frac{b}{2} \sin \theta \frac{d\phi}{dt} \qquad (3.186)$$

and that the θ and ϕ components $(u_{1\theta}^0, u_{1\phi}^0)$ of the fluid valocity at the position A_1 are represented by

$$u_{1\theta}^0 = \frac{bq}{2} \sin \theta \cos \theta \sin \phi \cos \phi, \qquad u_{1\phi}^0 = \frac{bq}{2} \sin \theta \cos^2 \phi \qquad (3.187)$$

if hydrodynamic disturbances caused by the bead A_2 are ignored. Then, in the absence of Brownian motion, the θ and ϕ components $(F_{1\theta}, F_{1\phi})$ of the force that the fluid flow excerts on the bead A_1 are given by

$$F_{1\theta} = -\zeta(v_{1\theta} - u_{1\theta}^0) = -\zeta \frac{b}{2} \left(\frac{d\theta}{dt} - \frac{q}{4} \sin 2\theta \sin 2\phi \right) \qquad (3.188)$$

$$F_{1\phi} = -\zeta(v_{1\phi} - u_{1\phi}^0) = -\zeta \frac{b}{2} \sin \theta \left(\frac{d\phi}{dt} - q \cos^2 \phi \right) \qquad (3.189)$$

where ζ is the friction factor of the bead A_1.

In a similar way, one can write the θ and ϕ components $(F_{2\theta}, F_{2\phi})$ of the force that the fluid flow excerts on the bead A_2, and one finds that $F_{2\theta} = F_{1\theta}$ and $F_{2\phi} = F_{1\phi}$.

To the approximation that the moment of inertia of the molecule may be neglected, the moment of the dumbell about any axis that passes through the center of gravity 0 can be set equal to zero. From this it follows that

$$\frac{b}{2} F_{1\theta} + \frac{b}{2} F_{2\theta} = 0 \qquad (3.190)$$

$$\frac{b}{2} \sin \theta F_{1\phi} + \frac{b}{2} \sin \theta F_{2\phi} = 0 \qquad (3.191)$$

Since $F_{1\theta} = F_{2\theta}$ and $F_{1\phi} = F_{2\phi}$, one gets

$$F_{1\theta} = 0, \qquad F_{1\phi} = 0 \qquad (3.192)$$

Substitution of these conditions into Eqs.(3.188) and (3.189) leads to the desired equation (3.185).

[Problem C21]

Solve the differential equation for $\rho(\theta, \phi)$

$$\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial\rho}{\partial\theta}\right) + \frac{1}{\sin\theta}\frac{\partial^2\rho}{\partial\phi^2}$$

$$-\frac{q}{\Theta}\left[\frac{1}{4}\sin\theta\sin 2\theta\sin 2\phi\frac{\partial\rho}{\partial\theta} + \sin\theta\cos^2\phi\frac{\partial\rho}{\partial\phi}\right.$$

$$\left.-\frac{3\rho}{2}\sin^3\theta\sin 2\phi\right] = 0$$

$$(0 \le \theta \le \pi; \;\; 0 \le \phi \le 2\pi) \tag{3.193}$$

with the conditions that

$$\frac{1}{4\pi}\int_0^\pi\int_0^{2\pi}\rho\sin\theta\mathrm{d}\theta\mathrm{d}\phi = 1 \tag{3.194}$$

and that $\rho(\pi - \theta, \phi) = \rho(\theta, \phi)$ and $\rho(\theta, \phi + \pi) = \rho(\theta, \phi)$.

Hint: Expand ρ in powers of θ and ϕ.

[Solution C21]

Assume for $\rho(\theta, \phi)$ the series in q/Θ such that

$$\rho(\theta, \phi) = \rho_0(\theta, \phi) + \frac{q}{\Theta}\rho_1(\theta, \phi) + \left(\frac{q}{\Theta}\right)^2\rho_2(\theta, \phi) + \cdots \tag{3.195}$$

and substitute this into Eq.(3.193). After collecting terms of the same power of q/Θ, one obtains a set of equations:

$$\left(\frac{q}{\Theta}\right)^0 : \quad \frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\rho_0}{\partial\theta}\right) + \frac{1}{\theta}\frac{\partial^2\rho_0}{\partial\phi^2} = 0 \tag{3.196}$$

$$\left(\frac{q}{\Theta}\right)^1 : \quad \frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\rho_1}{\partial\theta}\right) + \frac{1}{\sin\theta}\frac{\partial^2\rho_1}{\partial\phi^2} = \frac{1}{4}\sin\theta\sin 2\theta\sin 2\phi\frac{\partial\rho_0}{\partial\theta}$$

$$+ \sin\theta\cos^2\phi\frac{\partial\rho_0}{\partial\phi} - \frac{3\rho_0}{2}\sin^3\theta\sin 2\phi \tag{3.197}$$

$$\left(\frac{q}{\Theta}\right)^2 : \quad \frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial \rho_2}{\partial \theta}\right) + \frac{1}{\sin\theta}\frac{\partial^2 \rho_2}{\partial \phi^2} = \frac{1}{4}\sin\theta \sin 2\theta \sin 2\phi \frac{\partial \rho_1}{\partial \theta}$$

$$+ \sin\theta \cos^2\phi \frac{\partial \rho_1}{\partial \phi} - \frac{3\rho_0}{2}\sin^3\theta \sin 2\phi \quad (3.198)$$

$$\cdots\cdots\cdots$$

Also from the auxiliary conditions given above and Eq.(3.195) one obtains

$$\frac{1}{\pi}\int_0^{\pi/2}\int_0^{\pi} \rho_0 \sin\theta d\theta d\phi = 1 \qquad (3.199)$$

$$\int_0^{\pi/2}\int_0^{\pi} \rho_i \sin\theta d\theta d\phi = 0 \quad (i \geq 1) \qquad (3.200)$$

It is a simple matter to see that

$$\rho_0 = 1 \qquad (3.201)$$

satisfies Eqs.(3.196) and (3.199). Thus Eq.(3.197) becomes

$$\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial \rho_1}{\partial \theta}\right) + \frac{1}{\sin\theta}\frac{\partial^2 \rho_1}{\partial \phi^2} = -\frac{3}{2}\sin^3\theta \sin 2\phi \qquad (3.202)$$

By inspection one finds that this equation has a solution of the form $\rho_1 = f(\theta)\sin 2\phi$ and that this particular form satisfies the required condition $\rho_1(\theta, \phi + \pi) = \rho_1(\theta, \phi)$ and Eq.(3.200). The equation to be satisfied by $f(\theta)$ is

$$\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{df}{d\theta}\right) - 4f = -\frac{3}{2}\sin^4\theta \qquad (3.203)$$

If one puts $f = f_1 + (1/4)\sin^2\theta$, Eq.(3.203) yields

$$\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{df_1}{d\theta}\right) - 4f_1 = 0 \qquad (3.204)$$

which may be transformed to

$$\frac{d^2 f_1}{dz^2} - 4f_1 = 0 \qquad (3.205)$$

by the substitution

$$z = \int \frac{d\theta}{\sin \theta} = -\frac{1}{2} \ln \frac{1 + \cos \theta}{a - \cos \theta} \tag{3.206}$$

The genaral solution to Eq.(3.205) is $f_1 = C_1 \exp(2z) + C_2 \exp(-2z)$, or

$$f_1 = C_1 \frac{1 - \cos \theta}{1 + \cos \theta} + C_2 \frac{1 + \cos \theta}{1 - \cos \theta} \tag{3.207}$$

This solution diverges at $\theta = 0$ or π. Hence one must discard it. Thus the desired expression for ρ_1 is

$$\rho_1 = \frac{1}{4\pi} \sin^2 \theta \sin 2\phi \tag{3.208}$$

In a similar way, one can show that the desired expression for ρ_2 is given by

$$\rho_2 = \frac{1}{16} \left(-\frac{2}{3} \sin^2 \theta \cos 2\phi + \frac{1}{4} \sin^4 \theta - \frac{2}{15} - \frac{1}{4} \sin^4 \theta \cos 4\phi \right) \tag{3.209}$$

The derivation is left for the reader.

Thus, correct to the order of $(q/\Theta)^2$, $\rho(\theta, \phi)$ is expressed as

$$\begin{aligned} \rho(\theta, \phi) = &1 + \frac{q}{4\Theta} \sin^2 \theta \sin 2\phi \\ &+ \left(\frac{q}{4\Theta} \right)^2 \left(-\frac{2}{3} \sin^2 \theta \cos 2\phi + \frac{1}{4} \sin^4 \theta - \frac{2}{15} - \frac{1}{4} \sin^4 \theta \cos 4\phi \right) \\ &+ \mathcal{O}\left(\frac{q^3}{\Theta^3} \right) \end{aligned} \tag{3.210}$$

This result tells that when there is a bunch of dumbell molecules in a simple shear flow of solvent, the distribution of orientation of the molecules becomes maximum in the direction $\theta = \pi/2$ and $\phi = \pi/4$, provided $q/\Theta \ll 1$.

[Problem C22]

Average the Oseen tensor for hydrodynamic interactions

$$\mathbf{T}_{ij} = \frac{1}{8\pi\eta_0 R_{ij}}\left(\mathbf{E} + \frac{\mathbf{R}_{ij}\mathbf{R}_{ij}}{R_{ij}^2}\right) \quad (R_{ij} = |\mathbf{R}_{ij}|) \tag{3.211}$$

when the distribution of $\mathbf{R}_{ij}$ is Gaussian, i.e.,

$$P(\mathbf{R}_{ij}) = \left(\frac{3}{2\pi b^2|i-j|}\right)^{3/2}\exp\left(-\frac{3\mathbf{R}_{ij}^2}{2b^2|i-j|}\right) \tag{3.212}$$

[Solution C22]

$$\langle\mathbf{T}_{ij}\rangle = \frac{1}{8\pi\eta_0}\left(\langle\frac{1}{R_{ij}}\rangle\mathbf{E} + \langle\frac{\mathbf{R}_{ij}\mathbf{R}_{ij}}{R_{ij}^3}\rangle\right) \tag{3.213}$$

where

$$\langle\frac{1}{R_{ij}}\rangle = 4\pi\int_0^\infty R_{ij}P(R_{ij})\mathrm{d}R_{ij} \tag{3.214}$$

$$\langle\frac{\mathbf{R}_{ij}\mathbf{R}_{ij}}{R_{ij}^3}\rangle$$
$$= \begin{pmatrix} \langle\frac{(x_i-x_j)^2}{R_{ij}^3}\rangle & \langle\frac{(x_i-x_j)(y_i-y_j)}{R_{ij}^3}\rangle & \langle\frac{(x_i-x_j)(z_i-z_j)}{R_{ij}^3}\rangle \\ \langle\frac{(y_i-y_j)(x_i-x_j)}{R_{ij}^3}\rangle & \langle\frac{(y_i-y_j)^2}{R_{ij}^3}\rangle & \langle\frac{(y_i-y_j)(z_i-z_j)}{R_{ij}^3}\rangle \\ \langle\frac{(z_i-z_j)(x_i-x_j)}{R_{ij}^3}\rangle & \langle\frac{(z_i-z_j)(y_i-y_j)}{R_{ij}^3}\rangle & \langle\frac{(z_i-z_j)^2}{R_{ij}^3}\rangle \end{pmatrix} \tag{3.215}$$

It is easily found that all the cross-terms in this matrix are zero, while

$$\langle(x_i-x_j)^2/R_{ij}^3\rangle = \langle(y_i-y_j)^2/R_{ij}^3\rangle = \langle(z_i-z_j)^2/R_{ij}^3\rangle$$
$$= \frac{1}{3}\langle[(x_i-x_j)^2 + (y_i-y_j)^2 + (z_i-z_j)^2]/R_{ij}^3\rangle$$
$$= \frac{1}{3}\langle R_{ij}^2/R_{ij}^3\rangle = \frac{1}{3}\langle R_{ij}^{-1}\rangle \tag{3.216}$$

Hence

$$\langle\frac{\mathbf{R}_{ij}\mathbf{R}_{ij}}{R_{ij}^3}\rangle = \frac{1}{3}\langle\frac{1}{R_{ij}}\rangle\mathbf{E} \tag{3.217}$$

Thus

$$\langle \mathbf{T}_{ij} \rangle = \frac{1}{8\pi\eta_0} \left(1 + \frac{1}{3} \right) \langle \frac{1}{R_{ij}} \rangle \mathbf{E} = \frac{1}{6\pi\eta_0} \langle \frac{1}{R_{ij}} \rangle \mathbf{E} \qquad (3.218)$$

Substitution of Eq.(3.212) into Eq.(3.214) gives

$$\langle \frac{1}{R_{ij}} \rangle = \frac{\sqrt{6}}{\sqrt{\pi}b|i-j|^{1/2}} \qquad (3.219)$$

Therefore

$$\langle \mathbf{T}_{ij} \rangle = \left(\frac{1}{6^{1/2}\pi^{3/2}b\eta_0} \right) \frac{\mathbf{E}}{|i-j|^{1/2}} \qquad (3.220)$$

[Problem C23]

Show that from the series expansion of η_{sp}/c in powers of the solute concentration c

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c + k''[\eta]^3 c^2 + k'''[\eta]^4 c^3 + \cdots \qquad (3.221)$$

one obtains

$$\frac{2(\eta_{sp} - \ln \eta_{rel})]^{1/2}}{c} = [\eta] + K'[\eta]\, 2c + K''[\eta]^3 c^2 + \cdots \qquad (3.222)$$

where

$$K' = k' - \frac{1}{3} \qquad (3.223)$$

$$K'' = k'' - \frac{2}{3}k' + \frac{7}{36} \qquad (3.224)$$

[Solution C23]

Since $\eta_{rel} = \eta_{sp} + 1$, one obtains

$$\begin{aligned}
\ln \eta_{rel} =& \ln[1 + [\eta]c + k'[\eta]^2 c^2 + k''[\eta]^3 c^3 + k''''[\eta]^4 c^4 + \cdots] \\
=& [\eta]c + k'[\eta]^2 c^2 + k''[\eta]^3 c^3 + k''''[\eta]^4 c^4 x + \cdots \\
& - \frac{1}{2}\{[\eta]^2 c^2 + 2k'[\eta]^3 c^3 + (k'^2[\eta]^4 + 2k''[\eta]^4)c^4 + \cdots\} \\
& + \frac{1}{3}\{[\eta]^3 c^3 + 3k'[\eta]^4 c^4 + \cdots\} - \frac{1}{4}[\eta]^4 c^4 + \mathcal{O}(c^5) \qquad (3.225)
\end{aligned}$$

Thus

$$\begin{aligned}
2(\eta_{sp} - \ln \eta_{rel}) =& [\eta]^2 c^2 + \left(2k' - \frac{2}{3}\right)[\eta]^3 c^3 \\
& + \left(k'^2 + 2k'' - 2k' + \frac{1}{2}\right)[\eta]^4 c^4 + \mathcal{O}(c^5) \qquad (3.226)
\end{aligned}$$

Hence

$$\begin{aligned}
\frac{[2(\eta_{sp} - \ln \eta_{rel})]^{1/2}}{c} =& \left\{[\eta]^2 + \left(2k' - \frac{2}{3}\right)[\eta]^3 c \right. \\
& \left. + \left(2k'' + k'^2 - 2k' + \frac{1}{2}\right)[\eta]^4 c^2 + \mathcal{O}(c^3)\right\}^{1/2} \\
=& [\eta] + \left(k' - \frac{1}{3}\right)[\eta]^2 c + \left(k'' - \frac{2}{3}k' + \frac{7}{36}\right)[\eta]^3 c^2 + \mathcal{O}(c^4) \qquad (3.227)
\end{aligned}$$

which is the desired formula.

[Comments]

In manu cases with good solvents, k' is close to $1/3$, and hence one can expect that plots of $[2(\eta_{sp} - \ln \eta_{rel})]^{1/2}/c$ versus c should exhibit a small inclination at low concentrations, the behavior which makes the extrapolation of the plots to infinite dilution easier. If $k' = 1/3$, the coefficient K'' vanishes for $k'' = 1/36$.

[Problem C24]

Show that the intrinsic viscosity, $[\eta]$, of a flexible macromolecule may be calculated from

$$[\eta] = -\frac{N_A}{M\eta_0 q} \sum_{i=1}^{n} \langle F_{iy} x_i \rangle \qquad (3.228)$$

where N_A is Avogadro's number, M is the molecular weight of the molecule, η_0 is the viscosity coefficient of the solvent, F_{iy} is the y-component of the force $\mathbf{F}_i$ which the i-th segment $(i = 1, 2, \cdots, n)$ of the molecule excerts on the surrouding fluid when the molecule is placed in a simple shear flow of solvent that is represented by

$$\mathbf{u}^0 = \begin{cases} u_x^0 = 0 \\ u_y^0 = qx \\ u_z^0 = 0 \end{cases}$$

with the center of gravity of the molecule taken at the origin of (x, y, z) coordinates, and x_i is the x-coordinate of the i-th segment. The symbol $\langle \cdots \rangle$ means to take average over all possible configurations of the macromolecular chain.

[Solution C24]

As is illustrated in the figure, one suppose two parallel plates between which the solvent is filled. In order to produce the simple shear flow mentioned, one must shear them with the valocities $qh/2$ and $-qh/2$, where h is the distance between the plates. The work done in unit time is

$$w_0 = \eta_0 q^2 h A \qquad (3.229)$$

where A is the area of one plate.

When the macromolecule is placed in the solvent, with its center of gravity (more correctly, its center of fluid resistence) at the midway between the two plates, the molecule tends to rotate about the center of gravity, and this dissipates part of the energy supplied to the fluid by
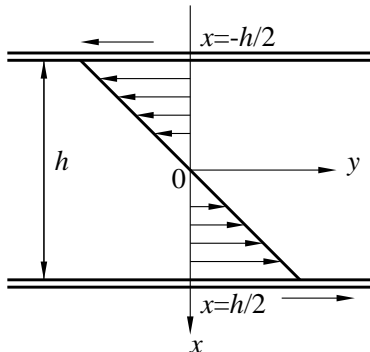
shearing the plates in opposite direction, because the molecular rotation experiences frictional resistence from the solvent. Consequently, an additional energy must be supplied on plates in order for the original shear rate to be maintained by the fluid. The work to be done in unit time in the presence of the macromolecule is

$$w = \eta q^2 hA \qquad (3.230)$$

where η is the viscosity of the solution. The additional energy is therefore expressed by $w - w_0 = (\eta - \eta_0)q^2 hA$. It can be equated to the sum of $-\mathbf{F}_i \cdot \mathbf{u}_i^0$ over all segments of the macromolecular solute, where $\mathbf{u}_i^0$ is the value of $\mathbf{u}^0$ at the position of the i-th segment. Thus one gets

$$\frac{\eta - \eta_0}{\eta_0} = -\frac{1}{\eta_0 q^2 hA} \sum_{i=1}^{n} \mathbf{F}_i \cdot \mathbf{u}_i^0 \qquad (3.231)$$

which may be rewritten

$$[\eta] = \lim_{c \to 0} \frac{\eta - \eta_0}{\eta_0 c} = -\frac{N_A}{\eta_0 qM} \sum_{i=1}^{n} \mathbf{F}_{iy} x_i \qquad (3.232)$$

where $c = M/(N_A hA)$ is the mass concentration of the macromolecular solute. This equation refers to a particular instantaneous configuration of the molecule. The actual $[\eta]$ is given by Eq.(3.232) averaged over all possible configurations of the molecular chain. In this way, Eq.(3.228) is derived.

[Comments]

Equation (3.228) may also apply for rigid macromolecules. In this case, $\langle \cdots \rangle$ means an orientational average.

[Problem C25]

Derive the Kirkwood-Riseman equation basic to the calculation of the friction coefficient of macromolecules.

[Solution C25]

Let the segments (or beads) of a macromolecular chain be numbered $1, 2, \cdots, n$, and let the center of gravity of the chain be moved at a constant velocity $\mathbf{u}^0$ in a solvent at rest. Neglecting the inertia of each segment, the force $\mathbf{F}_i$ that the i-th segment exerts on its surrounding liquid is expressed by

$$\mathbf{F}_i = \zeta(\mathbf{u}^0 - \mathbf{v}'_i) \tag{3.233}$$

Here ζ is the frictional factor of a segment, and $\mathbf{v}'_i$ is the fluid velocity which is produced at the position of the i-th segments by the forces acting on all other segments. The $\mathbf{v}'_i$ is given by

$$\mathbf{v}'_i = \sum_{j=1, j \neq 1}^{n} \frac{1}{8\pi\eta_0} \left(\frac{\mathbf{E}}{R_{ij}} + \frac{\mathbf{R}_{ij}\mathbf{R}_{ij}}{R_{ij}^3} \right) \cdot \mathbf{F}_j \quad (R_{ij} = |\mathbf{R}_{ij}|) \tag{3.234}$$

where η_0 is the viscosity coefficient of the solvent, $\mathbf{E}$ is the 3×3 unit matrix, $\mathbf{R}_{ij}$ is the distance vector between the i-th and j-th segments. The term multiplied by $\mathbf{F}_j$ in the sum is usually called Oseen's tensor for hydrodynamic interactions. Substitution of Eq.(3.234) into Eq.(3.233), followed by averaging over all possible configurations of the chain, yields

$$\langle \mathbf{F}_i \rangle = \zeta \mathbf{u}^0 - \frac{\zeta}{8\pi\eta_0} \sum_{j=1, j \neq i}^{n} \langle \left(\frac{\mathbf{E}}{R_{ij}} + \frac{\mathbf{R}_{ij}\mathbf{R}_{ij}}{R_{ij}^3} \right) \cdot \mathbf{F}_j \rangle$$
$$(i = 1, 2, \cdots, n) \tag{3.235}$$

The Kirkwood-Riseman formalism approximates $\langle \cdots \rangle$ in the sum by

$$\langle \frac{\mathbf{E}}{R_{ij}} + \frac{\mathbf{R}_{ij}\mathbf{R}_{ij}}{r_{ij}^3} \rangle \langle \mathbf{F}_j \rangle \tag{3.236}$$

Then Eq.(3.235) becomes

$$\langle \mathbf{F}_i \rangle = \zeta \mathbf{u}^0 - \frac{\zeta}{6\pi\eta_0} \sum_{j=i,j\neq i}^{n} \langle \frac{1}{R_{ij}} \rangle \langle \mathbf{F}_j \rangle \quad (1,2,\cdots,n) \tag{3.237}$$

(See [Problem C22]) This gives a set of linear simultaneous equations for n average forces $\langle \mathbf{F}_1 \rangle$, $\langle \mathbf{F}_2 \rangle$, $\cdots$, $\langle \mathbf{F}_n \rangle$. The average total force $\langle \mathbf{F} \rangle$ required to drag the chain with a given velocity $\mathbf{u}^0$ is given by

$$\langle \mathbf{F} \rangle = \sum_{i=1}^{n} \langle \mathbf{F}_i \rangle \tag{3.238}$$

The friction coefficient of the chain, Ξ, is then calculated from

$$\Xi = \frac{\langle \mathbf{F} \rangle}{\mathbf{u}^0} \tag{3.239}$$

It is convenient to define ψ_i buy

$$\langle \mathbf{F}_i \rangle = \zeta \psi_i \mathbf{u}^0 \tag{3.240}$$

Then, Eq.(3.237) may be written

$$\psi_i = 1 - \frac{\zeta}{6\pi\eta_0} \sum_{j=1,j\neq i}^{n} \langle \frac{1}{R_{ij}} \rangle \psi_j \quad (i=1,2,\cdots,n) \tag{3.241}$$

and Ξ may be expressed as

$$\Xi = \zeta \sum_{i=1}^{n} \psi_i \tag{3.242}$$

[Comments]

For linear chains in which the distribution of $\mathbf{R}_{ij}$ is Gaussian, one gets (see [Problem C22])

$$\langle \frac{1}{R_{ij}} \rangle = \frac{6^{1/2}}{\pi^{1/2} b |i-j|^{1/2}} \tag{3.243}$$

Hence Eq.(3.241) becomes

$$\psi_i = 1 - h^* \sum_{j=1, j \neq 1}^{n} \frac{\psi_j}{|i-j|^{1/2}} \quad (i = 1, 2, \cdots, n) \tag{3.244}$$

where

$$h^* = \frac{\zeta}{(6\pi^3)^{1/2} b \eta_0} \tag{3.245}$$

[Problem C26]

According to Einstein, the intrinsic viscosity $[\eta]$ of a spherical particle is proportional to the specific volume of the particle. Flory and Fox assumed that this proportionality would hold for polymer molecules if the essentially spherical domain occupied by the molecule is to be impermeable to solvent flow. Derive from this assumption that $[\eta]$ of homologous polymers increase lineraly with $M^{1/2}$ at the theta point, where M is the molecular weight of the polymer.

[Solution C26]

Because the radius of the spherical polymer coil may be assumed to be proportional to $\langle S^2 \rangle^{1/2}$, we may write, according to Flory and Fox,

$$[\eta] = K \frac{\langle S^2 \rangle^{3/2}}{M} \tag{3.246}$$

with K being constant. At the theta point, $\langle S^2 \rangle$ varies linearly with M for a series of homologous polymers. Thus $[\eta] \propto M^{1/2}$.

[Comments]

If $\langle S^2 \rangle$ at the theta point is denoted by $\langle S^2 \rangle_0$, Eq.(3.246) may be rewritten

$$[\eta] = K' \left(\frac{\langle S^2 \rangle}{\langle S^2 \rangle_0} \right)^{3/2} M^{1/2} \tag{3.247}$$

or

$$[\eta] = K' \alpha_S^3 M^{1/2} \tag{3.248}$$

with α_S being defined by

$$\alpha_S = \left(\frac{\langle S^2 \rangle}{\langle S \rangle_0} \right)^{1/2} \tag{3.249}$$

The dimension-less quantity α_S is called the linear expansion factor of the polymer coil referring to the radius of gyration. The new constant K' is often expressed in terms of the Flory viscosity constant Φ as

$$K' = \left(\frac{\langle S^2 \rangle_0}{6M} \right)^{3/2} \Phi \tag{3.250}$$

It has been predicted theoretically and verified experimentally that, in actual systems, Φ is not a constant but decreases with increasing α_S. However, no exact information is as yet available about the dependence of Φ on α_S.

[Problem C27]

Compute the Flory-Mandelkern-Scheraga parameter β for rigid spherical particles.

[Solution C27]

If $[\eta]$ is expressed in dl/g, β is defined by

$$\beta \equiv \frac{N_A \eta_0 [s_0][\eta]^{1/3}}{(100)^{1/3} M^{2/3}} \tag{3.251}$$

where s_0 is the sedimentation coefficient. For rigid spheres

$$[s_0] = \frac{M}{f_0 N_A} = \frac{M}{6\pi\eta_0 N_A a} \tag{3.252}$$

$$[\eta] = 2.5\left(\frac{4\pi N_A a^3}{3M}\right) \tag{3.253}$$

where a is the radius of the sphere. Introduction of Eqs.(3.252) and (3.253) into Eq.(3.251) yields $\beta = 2.11 \times 10^6$.

[Problem C28]

For the spring-bead model for a polymer chain confirm the relations:

$$\sum_{i=1}^{n}(x_i - x_{i-1})^2 = \mathbf{x}^T \mathbf{A} \mathbf{x} \tag{3.254}$$

$$\sum_{i=1}^{n}(x_i - x_{i-1})(y_i - y_{i-1}) = \mathbf{x}^T \mathbf{A} \mathbf{y} \tag{3.255}$$

where

$$\mathbf{x} = \begin{pmatrix} x_0 \\ x_1 \\ \vdots \\ x_n \end{pmatrix} \tag{3.256}$$

$$\mathbf{y} = \begin{pmatrix} y_0 \\ y_1 \\ \vdots \\ y_n \end{pmatrix} \tag{3.257}$$

$$\mathbf{A} = \begin{pmatrix}
1 & -1 & 0 & 0 & \cdots & 0 & 0 & 0 \\
-1 & 2 & -1 & 0 & \cdots & 0 & 0 & 0 \\
0 & -1 & 2 & -1 & \cdots & 0 & 0 & 0 \\
0 & 0 & -1 & 2 & \cdots & 0 & 0 & 0 \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & 0 & \cdots & -1 & 2 & -1 \\
0 & 0 & 0 & 0 & \cdots & 0 & -1 & 1
\end{pmatrix} \tag{3.258}$$

and $\mathbf{x}^T$ designates the transpose of $\mathbf{x}$. The $\mathbf{A}$ is a $(n+1) \times (n+1)$ matrix, with $n+1$ being the number of beads (hence n is the number of springs) in the chain.

Hint: It is not easy to go from the left-hand to the right-hand side in either Eq.(3.254) and(3.255), but the reverse is a simple matter.

[Solution C28]

$$\mathbf{x}^T \mathbf{A} = (x_0 \ x_1 \ \cdots \ x_n)\mathbf{A}$$
$$= (x_0 - x_1 \ - x_0 + 2x_x - x_2 \ - x_1 + 2x_2 - x_3 \ \cdots$$
$$- x_{n-1} + x_n) \tag{3.259}$$

Hence

$$\mathbf{x}^T \mathbf{A} \mathbf{x} = x_0^2 - x_1 x_0 - x_0 x_1 + 2x_1^2 - x_2 x_1 - x_1 x_2 + 2x_2^2 - x_3 x_2 - x_2 x_3$$
$$+ \cdots - x_{n-i} x_n + x_n^2$$
$$= (x_0^2 - 2x_0 x_1 + x_1^2) + (x_1^2 - 2x_1 x_2 + x_2^2) + \cdots$$
$$+ (x_{n-i}^2 - 2x_{n-1} x_n + x_n^2)$$
$$= \sum_{i=1}^n (x_i - x_{i-1})^2 \tag{3.260}$$

Try a similar operation to confirm Eq.(3.255).

[Problem C29]

The $(n + 1) \times (n + 1)$ matrix $\mathbf{A}$ defined below plays a central role in the Rouse-Zimm theory for the dynamics of linear polymer chains:

$$
\mathbf{A} = \begin{pmatrix}
1 & -1 & 0 & 0 & \cdots & 0 & 0 & 0 \\
-1 & 2 & -1 & 0 & \cdots & 0 & 0 & 0 \\
0 & -1 & 2 & -1 & \cdots & 0 & 0 & 0 \\
0 & 0 & -1 & 2 & \cdots & 0 & 0 & 0 \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & 0 & \cdots & -1 & 2 & -1 \\
0 & 0 & 0 & 0 & \cdots & 0 & -1 & 1
\end{pmatrix} \tag{3.261}
$$

Show that the k-th eigenvalue λ_k $(k = 1, 2, \cdots, n + 1)$ of $\mathbf{A}$ is given by

$$
\lambda_k = 4 \sin^2 \left[\frac{k\pi}{2(n+1)} \right] \tag{3.262}
$$

[Solution C29]

The eigenvector for $\mathbf{A}$ is designated by $\mathbf{p}$. Then

$$
\mathbf{Ap} - \lambda\mathbf{p} = 0 \tag{3.263}
$$

where λ is the eigenvalue. If $n + 1$ elements of $\mathbf{p}$ are denoted by p_1, p_2, $\cdots$, p_{n+1}, Eq.(3.263) may be written

$$
(1 - \lambda)p_1 - p_2 = 0 \tag{3.264}
$$

$$
- p_1 + (2 - \lambda)p_2 - p_3 = 0 \tag{3.265}
$$

$$
\cdots\cdots\cdots
$$

$$
- p_{j-1} + (2 - \lambda)p_j - p_{j+1} = 0 \tag{3.266}
$$

$$
\cdots\cdots\cdots
$$

$$- p_{n-1} + (2 - \lambda)p_n - p_{n+1} = 0 \tag{3.267}$$

$$- p_n + (1 - \lambda)p_{n+1} = 0 \tag{3.268}$$

To solve this set of difference equations one sets $p_j = Cz^{j-1}$ and substitutes it into Eqs.(3.265)−(3.267). Then one gets

$$- 1 + (2 - \lambda)z - z^2 = 0 \tag{3.269}$$

The roots of this quadratic equation are denoted by z_1 and z_2. Then

$$z_1 + z_2 = 2 - \lambda, \quad z_1 z_2 = 1 \tag{3.270}$$

and

$$p_j = C_1 z_1^{j-1} + C_2 z_2^{j-1} \tag{3.271}$$

where C_1 and C_2 are constants. If Eq.(3.271) is put into Eqs.(3.264) and (3.268),

$$(1 - \lambda - z_1)C_1 + (1 - \lambda - z_2)C_2 = 0 \tag{3.272}$$

$$[(1 - \lambda)z_1^n - z_1^{n-1}]C_1 + [(1 - \lambda)z_2^n - z_2^{n-1}]C_2 = 0 \tag{3.273}$$

For these two equations to have nonzero roots of C_1 and C_2 it is necessary that the condition

$$(1 - \lambda - z_1)(1 - \lambda - z_2^{-1})z_2^n - (1 - \lambda - z_2)(1 - \lambda - z_1^{-1})z_1^n = 0 \tag{3.274}$$

is satisfied. Using the relations $1 - \lambda - z_1 = z_2 - 1 = (1 - z_1)/z_1$ and $1 - \lambda - z_2 = z_1 - 1$ which follow from Eqs.(3.270), one may rewrite Eq.(3.274) as

$$\left(\frac{1 - z_1}{z_1}\right)^2 z_1^{-n} = (z_1 - 1)^2 z_1^n \tag{3.275}$$

whence

$$z_1 = 1 \quad \text{or} \quad z_1^{2n+2} = 1 \tag{3.276}$$

Thus

$$z_1 = \exp\left(\frac{\pi i}{n+1}k\right) \quad (k = 0, 1, \cdots, n + 1) \tag{3.277}$$

This is substituted into Eq.(3.270) to give

$$\lambda_k = 2 - \exp\left(\frac{\pi i}{n+1}k\right) - \exp\left(-\frac{\pi i}{n+1}k\right)$$

$$= 2\left(1 - \cos\frac{k\pi}{n+1}\right) = 4\sin^2\frac{k\pi}{2(n+2)} \tag{3.278}$$

The case $k = 0$ should be discarded, because, in this case, $\lambda = 0$ and hence one obtains the trivial eigenvector $\mathbf{p} = 0$ from Eq.(3.263). In this way one finds that the eigenvalues of $\mathbf{A}$ are given by Eq.(3.262).

[Comments] Equations (3.264) and (3.268) are the boundary conditions for the set of $n - 1$ difference equations given by Eqs.(3.265)−(3.267). The constants C_1 and C_2 in Eq.(3.271), the the general solutions to this set of equations, must be determined in such a way that these boundary conditions are satisfied. Equations (3.272) and (3.273) are the expressions for this requirement.

[Problem C30]

Calculate the intrinsic viscosity of a dumbell-type molecule consisting ot two beads 1 and 2 connected by a rigid bond of length b, by using the Kirkwood-Riseman formalism with the preaveraged Oseen tensor for hydrodynamic interactions.

[Solution C30]

Let the molecule be placed in a simple shear flow of shear rate q which is represented by

$$\mathbf{u}^0 = \begin{cases} u_x^0 = 0 \\ u_y^0 = qx \\ u_z^0 = 0 \end{cases}$$

with the origin of (x, y, z) taken at the center of the bond connecting the two beads. According to the Kirkwood-Riseman theory, the fluid valocity $\mathbf{u}(1)$ at the position of the bead 1 is represented by

$$\mathbf{u}(1) = \mathbf{u}^0(1) + \frac{1}{8\pi\eta_0}\left(\frac{\mathbf{E}}{b} + \frac{\mathbf{bb}}{b^3}\right) \cdot \mathbf{F}(2) \qquad (3.279)$$

where $\mathbf{u}^0(1)$ is the value of $\mathbf{u}^0$ at the bead 1, η_0 is the viscosity coefficient of the fluid, $\mathbf{E}$ is the 3×3 unit tensor, $\mathbf{bb}$ is the dyadic of the vector $\mathbf{b}$ which represents the direction from the bead 2 to the bead 1, and $\mathbf{F}(2)$ is the force that the bead 2 exerts on the fluid. It is physically obvious that

$$\mathbf{F}(2) = -\mathbf{F}(1) \qquad (3.280)$$

where $\mathbf{F}(1)$ is the force that the bead 1 exerts on the fluid. If the friction coefficient of either bead is denoted by ζ, $\mathbf{F}(1)$ is expressed by

$$\mathbf{F}(1) = \zeta[\mathbf{v}(1) - \mathbf{u}(1)] \qquad (3.281)$$

with $\mathbf{v}(1)$ being the velocity of the bead 1. Substitution of Eq.(3.279), with consideration of Eq.(3.280), gives

$$\mathbf{F}(1) = \zeta[\mathbf{v}(1) - \mathbf{u}^0(1)] + \frac{\zeta}{8\pi\eta_0}\left(\frac{\mathbf{E}}{b} + \langle\frac{\mathbf{bb}}{b^3}\rangle\right) \cdot \mathbf{F}(1) \qquad (3.282)$$

where $\langle \cdots \rangle$ indicates the averaging over all orientations of the molecule. Since

$$\mathbf{bb} = 4 \begin{pmatrix} x^2 & xy & xz \\ yx & y^2 & yz \\ zx & zy & z^2 \end{pmatrix} \tag{3.283}$$

and since $\langle xy \rangle = \langle yx \rangle = \langle xz \rangle = \langle zx \rangle = \langle yz \rangle = \langle zy \rangle = 0$ and $\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle = b^2/12$, we have

$$\langle \mathbf{bb} \rangle = \frac{1}{3} \begin{pmatrix} b^2 & 0 & 0 \\ 0 & b^2 & 0 \\ 0 & 0 & b^2 \end{pmatrix} \tag{3.284}$$

Thus, with

$$\mathbf{v}(1) = \begin{pmatrix} v_x(1) \\ v_y(1) \\ v_z(1) \end{pmatrix}, \qquad \mathbf{F}(1) = \begin{pmatrix} F_x(1) \\ F_y(1) \\ F_z(1) \end{pmatrix} \tag{3.285}$$

we obtain from Eq.3.282)

$$\begin{pmatrix} F_x(1) \\ F_y(1) \\ F_z(1) \end{pmatrix} = \zeta \begin{pmatrix} v_x(1) \\ v_y(1) - qx \\ v_z(1) \end{pmatrix} + \frac{\zeta}{6\pi\eta_0 b} \begin{pmatrix} F_x(1) \\ F_y(1) \\ F_z(1) \end{pmatrix} \tag{3.286}$$

which gives

$$F_y(1) = \frac{\zeta[v_y(1) - qx]}{\left(1 - \frac{\zeta}{6\pi\eta_0 b}\right)} \tag{3.287}$$

The required intrinsic viscosity $[\eta]$ is calculated from

$$[\eta] = -\frac{\langle J \rangle N_A}{M \eta_0 q} \tag{3.288}$$

where N_A is Avogadro's number, M is the molecular weight of the dumbell, and $\langle J \rangle$ is given by

$$\langle J \rangle = \langle F_y(1)x(1) \rangle + \langle F_y(2)x(2) \rangle \tag{3.289}$$

Since, by Eq.(3.280), $F_y(2) = -E_y(1)$, and also since $x(2) = -x(1)$, Eq.(3.289) may be written, after introduction of Eq.(3.287),

$$\langle J \rangle = \frac{2\zeta[\langle xv_y(1) \rangle - q\langle x^2 \rangle]}{\left(1 - \frac{\zeta}{6\pi\eta_0 b}\right)} \tag{3.290}$$

As has been shown in [Problem C19],

$$\langle xv_y(1) \rangle = \frac{q}{2}\langle x^2 \rangle \tag{3.291}$$

Hence, with $\langle x^2 \rangle = b^2/12$, we have

$$\langle J \rangle = -\frac{\zeta q b^2}{12} \Big/ \left(1 - \frac{\zeta}{6\pi\eta_0 b}\right) \tag{3.292}$$

Thus,

$$[\eta] = \frac{\zeta N_A b^2}{12 M \eta_0} \Big/ \left(1 - \frac{\zeta}{6\pi\eta_0 b}\right) \tag{3.293}$$

[Problem C31]

Apply the Kirkwood-Riseman formalism to derive the expression for the translational friction coefficient Ξ_r of a flexible Gaussian ring composed of $n(\gg 1)$ segments of length b.

Hint: Replace the equation for ψ_j [Eq.(3.241) in [Problem C25]] by an integral equation for $\psi(y)$, and then expand $\psi(y)$ in a Fourier series.

[Solution C31]

The statistical average $\langle R_{ij}^{-1}\rangle$ (R_{ij}: distance between segments i and j) for Gaussian rings may be obtained by using Eq.(2.111) in [Problem B16] as

$$\langle\frac{1}{R_{ij}}\rangle = \left(\frac{6}{\pi b^2}\right)^{1/2}\left[\frac{n}{|j-i|(n-|j-i|)}\right]^{1/2} \tag{3.294}$$

Substituting this equation into Eq.(3.241) in [Problem C25] and approximating the sum by an integral, one obtains the integral equation

$$\psi(x) = 1 - h\int_{-1}^{1}\frac{\psi(y)}{[|y-x|(1-|y-x|)]^{1/2}}\mathrm{d}y \tag{3.295}$$

with

$$h = \frac{\zeta\sqrt{n}}{(6\pi^3)^{1/2}b\eta_0} \tag{3.296}$$

and

$$x = \frac{2i}{n} - 1, \quad y = \frac{2j}{n} - 1 \tag{3.297}$$

where ζ and η_0 have the same meaning as given in [Problem C25]. Then, Eq.(3.242) for Ξ in [Problem C25] is expressed by

$$\Xi_r = \frac{\zeta n}{2}\int_{-1}^{1}\psi(x)\mathrm{d}x \tag{3.298}$$

Now, one may expand $\psi(y)$ in a Fourier series as

$$\psi(y) = \frac{\alpha_0}{2} + \sum_{k=1}^{\infty}[\alpha_k\cos(\pi ky) + \beta_k\sin(\pi ky)] \tag{3.299}$$

Introduction of this equation into Eq.(3.295) gives

$$\frac{\alpha_0}{2} + \sum_{k=1}^{\infty}[\alpha_k \cos(\pi k x) + \beta_k \sin(\pi k x)]$$

$$= 1 - h\left\{\frac{\alpha_0}{2}I(0)(x) + \sum_{k=1}^{\infty}[\alpha_k I_k(x) + \beta_k H_k(x)]\right\} \quad (3.300)$$

with

$$I_0(x) = \int_{-1}^{1} \frac{1}{[|y-x|(2-|y-x|)]^{1/2}} dy \quad (3.301)$$

$$I_k(x) = \int_{-1}^{1} \frac{\cos(\pi k y)}{[|y-x|(2-|y-x|)]^{1/2}} dy \quad (3.302)$$

$$H_k(x) = \int_{-1}^{1} \frac{\sin(\pi k y)}{[|y-x|(2-|y-x|)]^{1/2}} dy \quad (3.303)$$

These integrals are then evaluated to give

$$I_0(x) = \int_{-1}^{1} \frac{d\xi}{\sqrt{1-\xi^2}} = \pi \quad (3.304)$$

$$I_k(x) = (-1)^k \int_{-1}^{1} \frac{\cos[k\pi(\xi-x)]}{\sqrt{1-\xi^2}} d\xi$$

$$= (-1)^k \pi \cos(k\pi x) J_0(k\pi) \quad (k \gg 1) \quad (3.305)$$

$$H_k(x) = (-1)^k \sin(k\pi x) J_0(k\pi) \quad (k \gg 1) \quad (3.306)$$

where J_0 is the Bessel function of zeroth order defined by

$$J_0(z) = \frac{2}{\pi} \int_0^1 \frac{\cos(z\xi)}{\sqrt{1-\xi^2}} d\xi \quad (3.307)$$

Substitution of Eqs.(3.304)−(3.306), followed by comparison of both sides for each k, gives

$$\alpha_0 = \frac{2}{1+\pi h} \quad (3.308)$$

$$\alpha_k = \beta_k = 0 \quad \text{(for } k \gg 1) \quad (3.309)$$

With these values, Eq.(3.299) for $\psi(y)$ becomes

$$\psi(y) = \frac{1}{1 + \pi h} \tag{3.310}$$

Introduction of this equation into Eq.(3.298), followed by integration, yields the desired equation for Ξ_r:

$$\Xi_r = \frac{n}{1 + \pi h} \tag{3.311}$$

[Comments]

If $h \gg 1$, Eq.(3.311) becomes

$$\Xi_r = \frac{n^{1/2}}{(6\pi)^{1/2} b \eta_0} \tag{3.312}$$

which indicates that the translational friction coefficient is proportional to the square root of molecular weight of the sample.

[Problem C32]

Show that the Kirkwood-Riseman approach gives the intrinsic viscosity $[\eta]_r$ of a flexible Gaussian ring

$$[\eta]_r = \frac{\zeta N_A n^2 b^2}{12\pi^2 M\eta_0} \sum_{k=1}^{\infty} \frac{1}{k^2[1 + \pi h(-1)^k J_0(k\pi)]} \tag{3.313}$$

with

$$h = \frac{\zeta n^{1/2}}{(6\pi^3)^{1/2} b\eta_0} \tag{3.314}$$

Here N_A is Avogadro's number, ζ is the friction constant of a segment, n is the number of segments in the ring, b is the bond length, M is the molecular weight, η_0 is the viscosity of solvent, and J_0 denotes the Bessel function of zeroth order.

Hint: Follow a procedure similar to that employed for evaluating the translational friction coefficient of a flexible ring (see [Problem C31]). One may find the expressions for $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle_r$ and $\langle R_{ij}^{-1} \rangle$ from [Problem B17] and [Problem C31].

[Solution C32]

Substitution of the expressions for $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle_r$ and $\langle R_{ij}^{-1} \rangle$ into the Kirkwood-Riseman rquation, followed by replacement of the sum by an integral, leads to the integral equation

$$\phi(x,y) = -Af(x,y) - h \int_{-1}^{1} \frac{\phi(t,y)}{[|x-t|(2-|x-t|)]^{1/2}} dt \tag{3.315}$$

with

$$A = \frac{\zeta qnb^2}{48} \tag{3.316}$$

$$f(x,y) = \frac{2}{3} - |x-y|(2 - |x-y|) \tag{3.317}$$

$$x = \frac{2i}{n} - 1, \qquad y = \frac{2j}{n} - 1 \tag{3.318}$$

and h defined by Eq.(3.314). At the same time, one finds that Eq.(3.228) in [Problem C24] is rewritten

$$[\eta]_r = -\frac{nN_A}{2M\eta_0 q}\int_{-1}^{1}\phi(x,x)\mathrm{d}x \tag{3.319}$$

Let $\phi(t, y)$ be expanded in a Fourier series as

$$\phi(t,y) = \frac{\alpha_0}{2} + \sum_{k=1}^{\infty}[\alpha_k(y)\cos(k\pi t) + \beta_k(y)\sin(k\pi t)] \tag{3.320}$$

Introduction of this equation into Eq.(3.315), followed by integration, gives

$$\begin{aligned}
&\frac{\alpha_0(y}{2}(1+\pi h) + \sum_{k=1}^{\infty}[1+\pi h(-1)^k J_0(k\pi)] \\
&\times[\alpha_k(y)\cos(k\pi x) + \beta_k(y)\sin(k\pi x)] \\
&= -Af(x,y)
\end{aligned} \tag{3.321}$$

The coefficients $\alpha_k(y)$ and $\beta_k(y)$ can be determined by

$$\begin{aligned}
\alpha_k(y) &= \frac{-A}{1+\pi h(-1)^k J_0(k\pi)}\int_{-1}^{1}f(x,y)\cos(k\pi x)\mathrm{d}x \\
&(k = 0,1,\cdots,\infty)
\end{aligned} \tag{3.322}$$

$$\begin{aligned}
\beta_k(y) &= \frac{-A}{1+\pi h(-1)^k J_0(k\pi)}\int_{-1}^{1}f(x,y)\sin(k\pi x)\mathrm{d}x \\
&(k = 0,1,\cdots,\infty)
\end{aligned} \tag{3.323}$$

with $f(x, y)$ given by Eq.(3.317). These integrals are evaluated to give

$$\alpha_0(y) = 0 \tag{3.324}$$

$$\alpha_k(y) = \frac{-A}{1+\pi h(-1)^k J_0(k\pi)}\left(\frac{2}{k\pi}\right)^2\cos(k\pi y) \quad (k = 1,2,\cdots,\infty) \tag{3.325}$$

$$\beta_k(y) = \frac{-A}{1 + \pi h(-1)^k J_0(k\pi)} \left(\frac{2}{k\pi}\right)^2 \sin(k\pi y) \ \ (k = 1, 2, \cdots, \infty)$$

$$(3.326)$$

Substitution of these coefficients back into Eq.(3.320) gives

$$\phi(x, x) = -\frac{4A}{\pi^2} \sum_{k=1}^{\infty} \frac{1}{k^2[1 + \pi h(-1)^k J_0(k\pi)]} \qquad (3.327)$$

Finally, introducing this into Eq.(3.319), one arrives at Eq.(3.313).

In the non-draining limit $(h \gg 1)$, Eq.(3.313) reduces to

$$[\eta]_r = \frac{N_A(nb^2)^{3/2}}{2\sqrt{6}\pi^{3/2}M} \sum_{k=1}^{\infty} \frac{(-1)^k}{k^2 J_0(k\pi)} \qquad (3.328)$$

which indicates that $[\eta]_r$ is proportional to $M^{1/2}$.

[Problem C33]

Evaluate the sum $\sum_{k=1}^{\infty}(-1)^k/[k^2 J_0(k\pi)]$ which appears in the expression for the intrinsic viscosity $[\eta]_r$ of a flexible ring in the non-draining limit, and estimate the ratio of $\eta]_r$ to the intrinsic viscosity $[\eta]_l$ of the corresponding linear chains. The $[\eta]_l$ derived from the Kirkwood-Riseman equation is given by

$$[\eta]_l = 2.87 \times 10^{23}\frac{(nb^2)^{3/2}}{M} \tag{3.329}$$

[Solution C33]

The sum may be evaluated with the aid of the tabulated values of $J_0(k\pi)$ for small values of k and by use of the asymptotic form of $(-1)^k/[k^2 J_0(k\pi)] \simeq \pi/k^{3/2} + 1/(8k^{5/2})$ for large values of k.

For example

$$\sum_{k=1}^{50} \frac{(-1)^k}{k^2 J_0(k\pi)} = 7.514 \tag{3.330}$$

$$\sum_{k=51}^{100} \left(\frac{\pi}{k^{3/2}} + \frac{1}{8k^{5/2}}\right) = 0.258 \tag{3.331}$$

$$\sum_{k=101}^{\infty} \left(\frac{\pi}{k^{3/2}} + \frac{1}{8k^{5/2}}\right) \simeq \int_{101}^{\infty} \frac{\pi}{k^{3/2}}\mathrm{d}k = 0.625 \tag{3.332}$$

Hence,

$$\sum_{k=1}^{\infty} \frac{(-1)^k}{k^2 J_0(k\pi)} = 8.397 \tag{3.333}$$

Introducing this value into Eq.(3.327) in [Ptoblem C32], one gets

$$[\eta]_r = 1.854 \times 10^{23}\frac{(nb^2)^{3/2}}{M} \tag{3.334}$$

Thus, the ratio $[\eta]_r/[\eta]_l$ becomes

$$\frac{[\eta]_r}{[\eta]_l} = 0.646 \tag{3.335}$$

which predicts a decrease of about 35 %.

[Problem C34]

Show that the polarizability tensor $\boldsymbol{\alpha}$ of a molecule whose principal axes of polarization, denoted by 1, 2, and 3, have polarizabilities $\alpha_\parallel$, $\alpha_\perp$, and $\alpha_\perp$ is represented by

$$
\boldsymbol{\alpha} = \begin{pmatrix}
(\alpha_\parallel - \alpha_\perp)l_1^2 + \alpha_\perp & (\alpha_\parallel - \alpha_\perp)l_1 m_1 & (\alpha_\parallel - \alpha_\perp)l_1 n_1 \\
(\alpha_\parallel - \alpha_\perp)m_1 l_1 & (\alpha_\parallel - \alpha_\perp)m_1^2 + \alpha_\perp & (\alpha_\parallel - \alpha_\perp)m_1 n_1 \\
(\alpha_\parallel - \alpha_\perp)n_i l_1 & (\alpha_\parallel - \alpha_\perp)n_1 m_1 & (\alpha_\parallel - \alpha_\perp)n_1^2 + \alpha_\perp
\end{pmatrix}
\tag{3.336}
$$

when the axis 1 has direction cosines l_1, m_1, and n_1 relative to the laboratory-fixed Cartesian coordinates x, y, and z.

[Solutions C34]

Denote the dipole moments induced in the direction of the axes 1, 2, and 3 by p_1, p_2, and p_3, respectively, and denote the x, y, and z components of the electric vector of incident light by E_x, E_y, and E_z, respectively. Then one gets

$$
p_1 = (l_1 E_x + m_1 E_y + n_1 E_z)\alpha_\parallel
\tag{3.337}
$$

$$
p_2 = (l_2 E_x + m_2 E_y + n_2 E_z)\alpha_\perp
\tag{3.338}
$$

$$
p_3 = (l_3 E_x + m_3 E_y + n_3 E_z)\alpha_\perp
\tag{3.339}
$$

where l_i, m_i, and n_I $(i = 1, 2, 3)$ are direction cosines of the axis i relative to the x, y, and z axes, respectively.

The x, y, and z components, p_x, p_y, and p_z, of the induced dipole moment are expressed in terms of p_1, p_2, and p_3 as follows:

$$
p_x = p_1 l_1 + p_2 l_2 + p_3 l_3
\tag{3.340}
$$

$$
p_y = p_1 m_1 + p_2 m_2 + p_3 m_3
\tag{3.341}
$$

$$
p_z = p_1 n_1 + p_2 n_2 + p_3 n_3
\tag{3.342}
$$

Introduction of Eqs.(3.337) through (3.339) into these equations gives

$$p_x = [\alpha_\parallel l_1^2 + \alpha_\perp (l_2^2 + l_3^2)]E_x + [\alpha_\parallel l_1 m_1 + \alpha_\perp (l_2 m_2 + l_3 m_3)]E_y$$
$$+ [\alpha_\parallel l_1 n_1 + \alpha_\perp (l_2 n_2 + l_3 n_3)]E_z \qquad (3.343)$$

$$p_y = [\alpha_\parallel l_1 m_1 + \alpha_\perp (l_2 m_2 + l_3 m_3)]E_x + [\alpha_\parallel m_1^2 + \alpha_\perp (m_2^2 + m_3^2)]E_y$$
$$+ [\alpha_\parallel m_1 n_1 + \alpha_\perp (m_2 n_2 + m_3 n_3)]E_z \qquad (3.344)$$

$$p_z = [\alpha_\parallel l_1 n_1 + \alpha_\perp (l_2 n_2 + l_3 n_3)]E_x + [\alpha_\parallel n_1 m_1 + \alpha_\perp (n_2 m_2 + n_3 m_3)]E_y$$
$$+ [\alpha_\parallel n_1^2 + \alpha_\perp (n_2^2 + n_3^2)]E_z \qquad (3.345)$$

Hence if one write

$$\mathbf{p} = \boldsymbol{\alpha} \cdot \mathbf{E} \qquad (3.346)$$

or

$$\begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix} \qquad (3.347)$$

it follows that

$$\alpha_{xx} = \alpha_\parallel l_1^2 + \alpha_\perp (l_2^2 + l_3^2) \qquad (3.348)$$

$$\alpha_{yy} = \alpha_\parallel m_1^2 + \alpha_\perp (m_2^2 + m_3^2) \qquad (3.349)$$

$$\alpha_{zz} = \alpha_\parallel n_1^2 + \alpha_\perp (n_2^2 + n_3^2) \qquad (3.350)$$

$$\alpha_{xy} = \alpha_{yx} = \alpha_\parallel l_1 m_1 + \alpha_\perp (l_2 m_2 + l_3 m_3) \qquad (3.351)$$

$$\alpha_{yz} = \alpha_{zy} = \alpha_\parallel n_1 m_1 + \alpha_\perp (n_2 m_2 + n_3 m_3) \qquad (3.352)$$

$$\alpha_{xz} = \alpha_{zx} = \alpha_\parallel l_1 n_1 + \alpha_\perp (l_2 n_2 + l_3 n_3) \qquad (3.353)$$

Since $l_1^2 + l_2^2 + l_3^2 = 1$, $m_1^2 + m_2^2 + m_3^2 = 1$, $n_1^2 + n_2^2 + n_3^2 = 1$, $l_1 m_1 + l_2 m_2 + l_3 m_3 = 0$, $l_1 n_1 + l_2 n_2 + l_3 n_3 = 0$, $n_1 m_1 + n_2 m_2 + n_3 m_3 = 0$, these expressions reduce to

$$\alpha_{xx} = (\alpha_\parallel - \alpha_\perp)l_1^2 + \alpha_\perp \qquad (3.354)$$

$$\alpha_{yy} = (\alpha_{\parallel} - \alpha_{\perp})m_1^2 + \alpha_{\perp} \tag{3.355}$$

$$\alpha_{zz} = (\alpha_{\parallel} - \alpha_{\perp})n_1^2 + \alpha_{\perp} \tag{3.356}$$

$$\alpha_{xy} = \alpha_{yx} = (\alpha_{\parallel} - \alpha_{\perp})l_1 m_1 \tag{3.357}$$

$$\alpha_{yz} = \alpha_{zy} = (\alpha_{\parallel} - \alpha_{\perp})n_1 m_1 \tag{3.358}$$

$$\alpha_{xz} = \alpha_{zx} = (\alpha_{\parallel} - \alpha_{\perp})l_1 n_1 \tag{3.359}$$

which gives the desired expression (3.336

[Comments]

Equation (3.336) may be decomposed into two parts as

$$\boldsymbol{\alpha} = \boldsymbol{\alpha}_I + \boldsymbol{\alpha}_A \tag{3.360}$$

where

$$\boldsymbol{\alpha}_I = \alpha_{\perp}\mathbf{E} = \alpha_{\perp}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{3.361}$$

$$\boldsymbol{\alpha}_A = (\alpha_{\parallel} - \alpha_{\perp})\begin{pmatrix} l_1^2 & l_1 m_1 & l_1 n_1 \\ m_1 l_1 & m_1^2 & m_1 n_1 \\ n_1 l_1 & n_1 m_1 & n_1^2 \end{pmatrix} \tag{3.362}$$

$\boldsymbol{\alpha}_I$ and $\boldsymbol{\alpha}_A$ represents, respectively, the optical isotropy and anisotoropy of the molecule considered. It is this latter part of $\boldsymbol{\alpha}$ that is responsible for birefringent behavior of the molecule in shear flow.
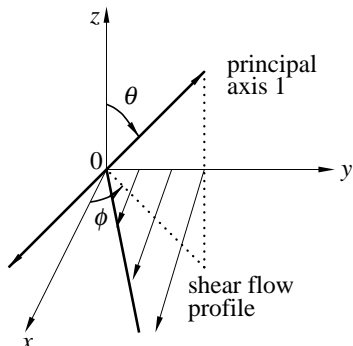
[Problem C35]

In the usual concentric cylinder apparatus for studying flow birefringence of dilute solutions, show that the extinction angle χ is given by

$$\tan 2\chi = \frac{\langle \sin 2\phi \sin^2 \theta \rangle}{\langle \cos 2\phi \sin^2 \theta \rangle} \tag{3.363}$$

when the principal polarizabilities of the solute molecule are $\alpha_\parallel$, $\alpha_\perp$, and $\alpha_\perp$ for the principal axes of polarization 1, 2, and 3. In Eq.(3.363), θ and ϕ are the polar angles which define the orientation of the principal axis 1 with respect to the x, y, z axes taken in such a way that the x axis is in the direction of shear flow at the point considered and the z axis is in the direction of incident light (see the figure), and $\langle \cdots \rangle$ designates an appropriate average over all orientations of the solute subject to shear flow.

Hint: Apply Eq.(3.336) in [Problem C34].

[Solution C35]

Incident light is plane polarized. The x and y components of its electric vector **E** are denoted by E_x and E_y, and the x, v, and z components of the dipole moment **p** induced in the solute molecule are denoted by p_x,

p_y, and p_z. Then

$$\begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix} = \boldsymbol{\alpha} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix} \tag{3.364}$$

Substituting Eq.(3.336) in [Problem C34] for the polarizability tensor $\boldsymbol{\alpha}$ and considering the fact that $l_1 = \cos\phi\sin\theta$ and $m_1 = \sin\phi\sin\theta$, one obtains, after orientational averaging,

$$p_x = \tau_{11}E_x + \tau_{12}E_y \tag{3.365}$$

$$p_y = \tau_{12}E_x + \tau_{22}E_y \tag{3.366}$$

where

$$\tau_{11} = (\alpha_\parallel - \alpha_\perp)\langle\cos^2\phi\sin^2\theta\rangle + \alpha_\perp \tag{3.367}$$

$$\tau_{22} = (\alpha_\parallel - \alpha_\perp)\langle\sin^2\phi\sin^2\theta\rangle + \alpha_\perp \tag{3.368}$$

$$\tau_{12} = (\alpha_\parallel - \alpha_\perp)\langle\sin\phi\cos\phi\sin^2\theta\rangle \tag{3.369}$$

From Eqs.(3.365) and (3.365) together with $E_x^2 + E_y^2 = E^2$ $(E = |\mathbf{E}|)$, it follows that

$$\beta_{11}p_x^2 - 2\beta_{12}p_xp_y + \beta_{22}p_y^2 = E^2 \tag{3.370}$$

where

$$\beta_{11} = \frac{\tau_{22}^2 + \tau_{12}^2}{(\tau_{11}\tau_{22} - \tau_{12}^2)^2} \tag{3.371}$$

$$\beta_{22} = \frac{\tau_{11}^2 + \tau_{12}^2}{(\tau_{11}\tau_{22} - \tau_{12}^2)^2} \tag{3.372}$$

$$\beta_{12} = \frac{\tau_{12}(\tau_{11} + \tau_{22})}{(\tau_{11}\tau_{22} - \tau_{12}^2)^2} \tag{3.373}$$

Equation (3.370) represents an ellipse described by the projection of the orientation-averaged $\mathbf{p}$ on the $x - y$ plane.

Now one takes a new (x', y') coordinate system, i.e., the x' and y' axes are chosen in the directions of the principal axes of this ellipse. Then, one can write

$$p_x = p_{x'}\cos\chi - p_{y'}\sin\chi \tag{3.374}$$

$$p_y = p_{x'} \sin \chi - p_{y'} \cos \chi \qquad (3.375)$$

where χ is taken to be the smaller one of the two angles that the y axis makes with the principal axes of the ellipse. Introduction of Eqs.(3.374) and (3.375) into Eq.(3.370) gives

$$
\begin{aligned}
&(\beta_{11} \cos^2 \chi + \beta_{22} \sin^2 \chi - 2\beta_{12} \cos \chi \sin \chi)(p_{x'})^2 \\
&+(\beta_{11} \sin^2 \chi + \beta_{22} \cos^2 \chi + 2\beta_{12} \cos \chi \sin \chi)(p_{y'})^2 \\
&-2[(\beta_{11} - \beta_{22}) \cos \chi \sin \chi + \beta_{12}(\cos^2 \chi - \sin^2 \chi)]p_{x'}p_{y'} \\
&= E^2 \qquad (3.376)
\end{aligned}
$$

The term multiplied by $p_{x'}p_{y'}$, must be vanish, because the x' and y' axes are the principal axes of the ellipse considered. Thus one obtains

$$\tan 2\chi = -\frac{2\beta_{12}}{\beta_{11} - \beta_{22}} \qquad (3.377)$$

Extinction occurs when the plane of polarization of incident light coincides with the $z - y'$ plane, because then the transmitted light is stopped by the analyzer. Thus the χ defined by Eq.(3.377) is equal to the extiction angle. Substitution of Eqs.(3.371) through (3.373) into this equation yields

$$\tan 2\chi = \frac{2\tau_{12}}{\tau_{11} - \tau_{22}} \qquad (3.378)$$

which is found to be equivalent to Eq.(3.363) when Eqs.(3.367) through (3.369) are inserted.

[Problem C36]

In [Problem C35], show that $\Delta\alpha$, the difference between the principal polarizabilities of the ellipse that the orientation-average **p** describes on the plane of shear flow ($x - y$ plane), is given by

$$\Delta\alpha = \frac{2\tau_{12}}{\sin 2\chi} \tag{3.379}$$

where χ is the extinction angle and τ_{12} is given by Eq.(3.369) in the same problem.

[Solution C36]

When χ is the extinction angle, Eq.(3.376) in [Problem C35] becomes, with $p_{x'} = \alpha_{x'} E$ and $p_{y'} = \alpha_{y'} E$,

$$\frac{\alpha_{x'}^2}{a^2} + \frac{\alpha_{y'}^2}{b^2} = 1 \tag{3.380}$$

where

$$a = (\beta_{11} \cos^2 \chi + \beta_{22} \sin^2 \chi - 2\beta_{12} \cos \chi \sin \chi)^{-1/2} \tag{3.381}$$

$$b = (\beta_{11} \sin^2 \chi + \beta_{22} \cos^2 \chi + 2\beta_{12} \cos \chi \sin \chi)^{-1/2} \tag{3.382}$$

Equation (3.380) indicates that $\Delta\alpha$ is represented by

$$\Delta\alpha = a - b \tag{3.383}$$

Substituting Eqs.(3.371) through (3.373) in [Problem C35] for β_{11}, β_{22}, and β_{12} and considering that χ is related to τ_{11}, τ_{22}, and τ_{12} by Eq.(3.378) in the same problem, one obtains

$$a = \frac{\cos 2\chi(\tau_{11}\tau_{22} - \tau_{12}^2)}{\tau_{22} \cos^2 \chi - \tau_{11} \sin^2 \chi} \tag{3.384}$$

$$b = \frac{\cos 2\chi(\tau_{11}\tau_{22} - \tau_{12}^2)}{\tau_{11} \cos^2 \chi - \tau_{22} \sin^2 \chi} \tag{3.385}$$

Therefore

$$\Delta\alpha = \frac{-\cos 2\chi(\tau_{11}\tau_{22} - \tau_{12}^2)(\tau_{11} - \tau_{22})}{(\tau_{11}^2\tau_{22}^2)\cos^2\chi\sin^2\chi - \tau_{11}\tau_{22}(\cos^4\chi + \sin^4\chi)} \quad (3.386)$$

But, using $\tan 2\chi = 2\tau_{12}/(\tau_{11} - \tau_{22})$,

$$(\tau_{11}^2 + \tau_{22}^2)\cos^2\chi\sin^2\chi - \tau_{11}\tau_{22}(\cos^2\chi + \sin^4\chi)$$
$$= (\tau_{11} - \tau_{22})^2\cos^2\chi\sin^2\chi - \tau_{11}\tau_{22}(\cos^2\chi - \sin^2\chi)^2$$
$$= (\tau_{12} - \tau_{11}\tau_{22})\cos^2 2\chi \quad (3.387)$$

Equation (3.386) becomes

$$\Delta\alpha = \frac{\tau_{11} - \tau_{22}}{\cos 2\chi} \quad (3.388)$$

or

$$\Delta\alpha = \frac{2\tau_{12}}{\sin 2\chi} \quad (3.389)$$

which is the required formula (3.379).

One may eliminates χ from Eq.(3.389) by use of the relation $\tan 2\chi = 2\tau_{12}/(\tau_{11} - \tau_{22})$, yielding

$$\Delta\alpha = [(\tau_{11} - \tau_{22})^2 + 4\tau_{12}^2]^{1/2} \quad (3.390)$$
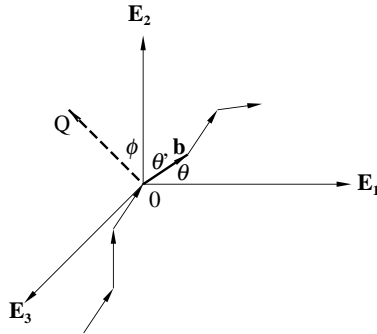
[Problem C37]

Suppose that a Gaussian chain of n equal bonds, each having polar-izabilities α_1 and α_2 in the directions parallel and perpendicular to its axis, is fixed at its end, with R as the end-to-end distance. Show that the polarizabilities of the chain in the directions paralle and perpendicular to end-to-end distance vector $\mathbf{R}$ $(R = |\mathbf{R}|)$ are represented by

$$\alpha_\parallel = \frac{n(\alpha_1 + 2\alpha_2)}{3} + (\alpha_1 - \alpha_2)\frac{2\mathbf{R}^2}{5\langle \mathbf{R}^2 \rangle} \tag{3.391}$$

$$\alpha_\perp = \frac{n(\alpha_1 + 2\alpha_2)}{3} - (\alpha_1 - \alpha_2)\frac{\mathbf{R}^2}{5\langle \mathbf{R}^2 \rangle} \tag{3.392}$$

Hint: Apply Eq.(3.336) in [Problem C34].

[Solution C37]

In the figure above, let $\mathbf{E}_1$ and $\mathbf{E}_2$ be the unit vectors parallel and perpendicular to $\mathbf{R}$. Denote the angle between $\mathbf{b}$ (the bond vector) and $\mathbf{E}_1$ by θ and denote the angle between $\mathbf{b}$ and $\mathbf{E}_2$ by θ'. Then $\alpha_\parallel$ and $\alpha_\perp$ are represented by

$$\begin{aligned}\alpha_\parallel &= n\langle \alpha_1 \cos^2 \theta + \alpha_2 \sin^2 \theta \rangle \\ &= n\langle \alpha_2 + (\alpha_1 - \alpha_2) \cos^2 \theta \rangle \end{aligned} \tag{3.393}$$

$$\alpha_\perp = n\langle \alpha_1 \cos^2 \theta' + \alpha_2 \sin^2 \theta' \rangle$$
$$= n\langle \alpha_2 + (\alpha_1 - \alpha_2) \cos^2 \theta' \rangle \tag{3.394}$$

where $\langle \cdots \rangle$ designates the average taken over orientations of $\mathbf{b}$ which are possible under the condition that the end-to-end distance of the chain is fixed at R.

Equation (3.393) is derived as follows. Suppose that $\mathbf{E}_1$ is an electric field vector. Then there is induced a dipole moment of $E_1 \alpha_1 \cos \theta$ in the direction of $\mathbf{b}$ and a dipole moment of $E_1 \alpha_2 \sin \theta$ in the direction perpendicular to $\mathbf{b}$. These give a dipole moment $E_1(\alpha_1 \cos^2 \theta + \alpha_2 \sin^2 \theta)$ in the direction of $\mathbf{E}_1$. This moment averaged over orientations of the bond is $E_1 \langle \alpha_1 \cos^2 \theta + \alpha_2 \sin^2 \theta \rangle$, which is the same for all n bonds of the chain so that the chain as a whole has a dipole moment of $E_1 n \langle \alpha_1 \cos^2 \theta + \alpha_2 \sin^2 \theta \rangle$ in the direction of $\mathbf{E}_1$, i.e., that of $\mathbf{R}$. Thus $\alpha_\parallel$ is represented by Eq.(3.393). Equation (3.394) may be obtains in a similar way.

The orientation of $\mathbf{b}$ is characterized by a pair of angle θ and ϕ. Here ϕ is defined as the angle that $\overrightarrow{OQ}$ in the figure makes with $\mathbf{E}_2$. $\overrightarrow{OQ}$ is the line along which the plane formed by $\mathbf{b}$ and $\mathbf{E}_1$ intersects with the plane formed by $\mathbf{E}_2$ and $\mathbf{E}_3$ (the vector normal to both $\mathbf{E}_1$ and $\mathbf{E}_2$). Since $\cos \theta' = \cos \phi \sin \theta$, Eq.(3.394) may be written

$$\alpha_\perp = n\langle \alpha_1 + (\alpha_1 - \alpha_2) \cos^2 \phi \sin^2 \theta \rangle \tag{3.395}$$

Now, let the probability that $\mathbf{b}$ assumes an orientation between (θ, ϕ) and $(\theta + d\theta, \phi + d\phi)$ subject to a given R be denoted by $f(\theta, \phi)d\theta d\phi$. Then Eqs.(3.393) and (3.395) are expreaaed as

$$\alpha_\parallel = n\left[\alpha_2 + (\alpha_1 - \alpha_2) \int_0^{2\pi} \int_0^{\pi} \cos^2 \theta f(\theta, \phi) \sin \theta d\theta d\phi\right] \tag{3.396}$$

$$\alpha_\perp = n\left[\alpha_2 + (\alpha_1 - \alpha_2) \int_0^{2\pi} \int_0^{\pi} \sin^3 \theta \cos^2 \phi f(\theta, \phi) d\theta d\phi\right] \tag{3.397}$$

According to Eq.(3.336) in [Problem C34], $f(\theta, \phi)$ for Gaussian chains is represented by

$$f(\theta, \phi) = \frac{3R}{4\pi nb\text{sinh}(3R/nb)}\exp\left(\frac{3R\cos\theta}{nb}\right) \tag{3.398}$$

Hence

$$\int_0^{2\pi}\int_0^{\pi} \cos^2\theta\sin\theta f(\theta, \phi)\mathrm{d}\theta\mathrm{d}\phi = 1 + \frac{2(1 - \beta\text{coth}\beta)}{\beta^2} \tag{3.399}$$

$$\int_0^{2\pi}\int_0^{\pi} \sin^3\theta\cos^2\phi f(\theta, \phi)\mathrm{d}\theta\mathrm{d}\phi = -\frac{2(1 - \beta\text{coth}\beta)}{\beta^2} \tag{3.400}$$

where

$$\beta = \frac{3R}{nb} = \frac{3R}{\sqrt{n}\langle R^2\rangle^{1/2}} \tag{3.401}$$

Note that $\langle \mathbf{R}^2\rangle = nb^2$ for Gaussian chains consisting of n equal bond of length b.

One may impose the condition $R \ll nb$ or $\beta \ll 1$ for Gaussian chains. For $\beta \ll 1$

$$1 + \frac{1(1 - \beta\text{coth}\beta)}{\beta^2} = 1 + \frac{2}{\beta^2}\left(1 - 1 - \frac{\beta^2}{3} + \frac{\beta^4}{45} + \cdots\right)$$

$$= \frac{1}{3} + \frac{2\beta^2}{45} + \mathcal{O}(\beta^4) \tag{3.402}$$

$$-\frac{1(1 - \beta\text{coth}\beta)}{\beta^2} = -\frac{1}{\beta^2}\left(1 - 1 - \frac{\beta^2}{3} + \frac{\beta^4}{45} + \cdots\right)$$

$$= \frac{1}{3} - \frac{\beta^2}{45} + \mathcal{O}(\beta^4) \tag{3.403}$$

Therefore

$$\alpha_{\|} = n\left[\alpha_2 + (\alpha_1 - \alpha_2)\left(\frac{1}{3} + \frac{2\beta^2}{45}\right)\right]$$

$$= \frac{n(\alpha_1 + 2\alpha_2)}{3} + \frac{2}{5}(\alpha_1 - \alpha_2)\frac{\mathbf{R}^2}{\langle \mathbf{R}^2\rangle} \tag{3.404}$$

$$\alpha_\perp = n\left[\alpha_2 + (\alpha_1 - \alpha_2)\left(\frac{1}{3} - \frac{\beta^2}{45}\right)\right]$$
$$= \frac{n(\alpha_1 + 2\alpha_2)}{3} - \frac{1}{5}(\alpha_1 - \alpha_2)\frac{\mathbf{R}^2}{\langle\mathbf{R}^2\rangle} \qquad (3.405)$$

where terms higher than (β^2) have been neglected in comparison to unity. Equations (3.404) and (3.405) are the required expressions.

[Comments]

From Eqs.(3.404) and (3.405) one gets

$$\alpha_\parallel - \alpha_\perp = \frac{3}{5}(\alpha_1 - \alpha_2)\frac{\mathbf{R}^2}{\langle\mathbf{R}^2\rangle} \qquad (3.406)$$

which sows how the optical anisotropy of the chain as a whole, i.e., $\alpha_\parallel - \alpha_\perp$, is related to the optical anisotropy of its constituent bonds, i.e., $\alpha_1 - \alpha_2$, when the end-to-end distance of the chain is fixed at a given value R. When the chain ends are not fixed but allowed to move freely, Eq.(3.406) no longer holds, because Eq.(3.398) for Gaussian chains is not always obeyed.

[Problem C38]

A dilute solution of flexible polymers represented by a Gaussian spring model is subjected to a flow birefringence experiment in a conventional concentric cylinder apparatus. Show that the extinction angle, χ, for the solution is expressed by

$$\tan 2\chi = \frac{2\langle \mathbf{x}^T \mathbf{A} \mathbf{x} \rangle}{\langle \mathbf{x}^T \mathbf{A} \mathbf{x} \rangle - \langle \mathbf{y}^T \mathbf{A} \mathbf{y} \rangle} \tag{3.407}$$

when the $x - y$ plane is taken perpendicular to the incident beam of plane-polarized light, with the x axis in the direction of stream lines of shear flow. Here $\mathbf{x}^T \mathbf{A} \mathbf{x}$ etc have the meaning found in [Problem C28], and $\langle \cdots \rangle$ designates an appropriate average over configurations of the polymer solute subject to shear flow.

Hint: Apply Eq.(3.360) in [Problem C34] to the individual Gaussian springs, with $\alpha_\parallel$ and $\alpha_\perp$ as given by Eqs.(3.391) and (3.392) in [Problem C37].

[Solution C38]

If the equations stated in the Hint are applied to the i-th spring, one obtains for its polarizability tensor $\boldsymbol{\alpha}_i$

$$\boldsymbol{\alpha}_i = \left[n_0 \left(\frac{\alpha_1 + 2\alpha_2}{3} \right) - (\alpha_1 - \alpha_2) \frac{\mathbf{r}_i^2}{5n_0 b^2} \right] \begin{pmatrix} l & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \frac{3(\alpha_1 - \alpha_2)}{5n_0 b^2}$$

$$\times \begin{pmatrix} (x_i - x_{i-1})^2 & (x_i - x_{i-1})(y_i - y_{i-1}) & (x_i - x_{i-1})(z_i - z_{i-1}) \\ (y_i - y_{i-1})(x_i - x_{i-1}) & (y_i - y_{i-1})^2 & (y_i - y_{i-1})(z_i - z_{i-1}) \\ (z_i - z_{i-1})(x_i - x_{i-1}) & (z_i - z_{i-1})(y_i - y_{i-1}) & (z_i - z_{i-1})^2 \end{pmatrix}$$

It is assumed here that each Gaussian spring consists of n_0 equal bonds, each having length b and polarizxabilities α_1 and α_2 in the directions parallel and perpendicular to its axis. $\mathbf{r}_i$ is the end-to-end distanxe vector of the i-th Gaussian spring, and $x_i - x_{i-1}$, $y_i - y_{i-1}$, and $z_i - z_{i-1}$ are the x, y, and z components of $\mathbf{r}_i$.

Summing up the above equation over n springs constituting the chain and averaging the sum over configurations of the chain possible in a given shear flow, one gets for the average plarizability tensor $\langle\boldsymbol{\alpha}\rangle$ of the polymer solute

$$\boldsymbol{\alpha} = n\left[n_0\left(\frac{\alpha_1 + 2\alpha_2}{3}\right) - \frac{\alpha_1 - \alpha_2}{5}\right]\begin{pmatrix} l & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$+ \frac{3(\alpha_1 - \alpha_2)}{5n_0 b^2}\begin{pmatrix} \langle\mathbf{x}^T\mathbf{A}\mathbf{x}\rangle & \langle\mathbf{x}^T\mathbf{A}\mathbf{y}\rangle & \mathbf{x}^T\mathbf{A}\mathbf{z}\rangle \\ \langle\mathbf{y}^T\mathbf{A}\mathbf{x}\rangle & \langle\mathbf{y}^T\mathbf{A}\mathbf{y}\rangle & \mathbf{y}^T\mathbf{A}\mathbf{z}\rangle \\ \langle\mathbf{z}^T\mathbf{A}\mathbf{x}\rangle & \langle\mathbf{z}^T\mathbf{A}\mathbf{y}\rangle & \mathbf{z}^T\mathbf{A}\mathbf{z}\rangle \end{pmatrix} \quad (3.408)$$

where

$$\langle\mathbf{x}^T\mathbf{A}\mathbf{x}\rangle = \sum_{i=1}^{n}\langle(x_i - x_{i-1})^2\rangle \quad (3.409)$$

$$\langle\mathbf{x}^T\mathbf{A}\mathbf{y}\rangle = \langle\mathbf{y}^T\mathbf{A}\mathbf{x}\rangle = \sum_{i=1}^{n}\langle(x_i - x_{i-1})(y_i - y_{i-1})\rangle \quad (3.410)$$

etc and $\langle\cdots\rangle$ denote the above-mentioned average.

Up to this point the Gaussian coordinate system (x, y, z) can be taken arbitrarily. Now, let the $x - y$ plane be chosen perpendicularily to the direction of incident plane-polarized light, with the x-axis parallel to the stream lines of applied shear flow. Then by proceeding in exactly the same way as in [Problem C35], with $\langle\boldsymbol{\alpha}\rangle$ substituted for $\boldsymbol{\alpha}$, one can obtain

$$\tan 2\chi = \frac{2\tau_{12}}{\tau_{11} - \tau_{22}} \quad (3.411)$$

where

$$\tau_{11} = P + Q\langle\mathbf{x}^T\mathbf{A}\mathbf{x}\rangle \quad (3.412)$$

$$\tau_{22} = P + Q\langle\mathbf{y}^T\mathbf{A}\mathbf{y}\rangle \quad (3.413)$$

$$\tau_{12} = Q\langle\mathbf{x}^T\mathbf{A}\mathbf{y}\rangle \quad (3.414)$$

with

$$P = n\left[n_0\left(\frac{\alpha_1 + 2\alpha_2}{3}\right) - \frac{\alpha_1 - \alpha_2}{5}\right] \quad (3.415)$$

$$Q = \frac{3(\alpha_1 - \alpha_2)}{5 n_0 n^2} \tag{3.416}$$

Substitution of Eqs.(3.412) through (3.414) into Eq.(3.411) gives the required expression (3.407).

[Comments]

(1) Equation (3.390) in [Problem C36] holds for the present case with τ_{11}, τ_{22}, and τ_{12} given by Eqs.(3.412) through (3.414). Thus,

$$\Delta\alpha = Q[(\langle \mathbf{x}^T \mathbf{A} \mathbf{x} \rangle - \langle \mathbf{y}^T \mathbf{A} \mathbf{y} \rangle)^2 + 4\langle \mathbf{x}^T \mathbf{A} \mathbf{y} \rangle^2]^{1/2} \tag{3.417}$$

The magnitude pf birefringence of the solution, $\Delta\mathbf{n}$, is defined as the product of $\Delta\alpha$ and the number of solute molecules per cm^3 of the solution. Thus

$$\Delta\mathbf{n} = \frac{N_a c}{M} \Delta\alpha \tag{3.418}$$

where c is the mass concentration of the solute, M is its molecular weight, and N_A is Avogadro's number.

(2) In order to evaluate the averages $\mathbf{x}^T \mathbf{A} \mathbf{x}$, etc, one must know the probability density ρ that the chain assumes a given configuration when it is placed in a simple shear flow.
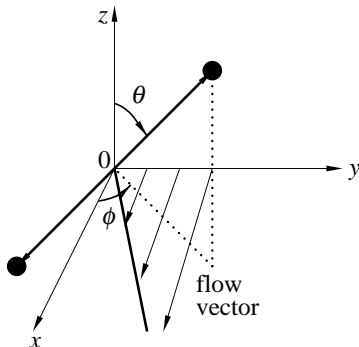
[Problem C39]

The orientation distribution function $\rho(\theta, \phi)$ for a dumbell-type molecule in a simple shear flow is given by

$$\rho(\theta, \phi) = \frac{1}{4\pi}\left[1 + \frac{q}{4\Theta}\sin^2\theta\sin 2\phi + \left(\frac{q}{4\Theta}\right)^2\left(-\frac{2}{3}\sin^2\theta\cos 2\phi\right.\right.$$

$$\left.\left. +\frac{1}{4}\sin^4\theta - \frac{2}{15} - \frac{1}{4}\sin^4\theta\cos 4\phi\right) + \mathcal{O}\left(\frac{q^3}{\Theta^3}\right)\right] \qquad (3.419)$$

where q is the rate of shear, Θ is the rotary diffusion coefficient of the molecule, and θ and ϕ are the polar angles of the molecular axis which are defined as shown in the figure above. Deduce that the extinction angle χ for the solution is represented by

$$\chi = \frac{\pi}{4} - \frac{1}{12}\left(\frac{q}{\Theta}\right) + \cdots \qquad (3.420)$$

[Solution C39]

One may apply Eq.(3.363) in [Problem C35], because the molecule under consideration is supposed to be optically symmetric about its axis. The task is to evaluate

$$I_1 = \langle \sin 2\phi \sin 2\theta \rangle$$

$$= \int_0^{2\pi}\int_0^\pi \sin^3\theta \sin 2\phi\rho(\theta, \phi)\mathrm{d}\theta\mathrm{d}\phi \qquad (3.421)$$

$$I_2 = \langle \cos 2\phi \sin 2\theta \rangle$$

$$= \int_0^{2\pi} \int_0^\pi \sin^3 \theta \cos 2\phi \rho(\theta, \phi) \mathrm{d}\theta \mathrm{d}\phi \tag{3.422}$$

Substitution of Eq.(3.419) gives

$$I_1 = \frac{q}{15\Theta} + \cdots \tag{3.423}$$

$$I_2 = \frac{1}{90} \left(\frac{q}{\Theta} \right)^2 + \cdots \tag{3.424}$$

Hence one gets

$$\tan 2\chi = \frac{6}{(q/\Theta)} \left[1 + \mathcal{O}\left(\frac{q}{\Theta} \right) \right] \tag{3.425}$$

Thus it follows that χ tends to $\pi/4$ (45°) for vanishing shear rates. Hence one may assume the expansion

$$\chi = \frac{\pi}{4} + A_1 \left(\frac{q}{\Theta} \right) + A_2 \left(\frac{q}{\Theta} \right)^2 + \cdots \tag{3.426}$$

With this, one obtains

$$\tan 2\chi = \tan \left[\frac{\pi}{2} + 2A_1 \left(\frac{q}{\Theta} \right) + 2A_2 \left(\frac{q}{\Theta} \right)^2 + \cdots \right]$$

$$= -\cot \left[2A_1 \left(\frac{q}{\Theta} \right) + 2A_2 \left(\frac{q}{\Theta} \right)^2 + \cdots \right]$$

$$= -\frac{1}{2A_1(q/\Theta)} + \cdots \tag{3.427}$$

where one has used tha formula

$$x \cot x = 1 - \frac{x^2}{3} - \cdots \quad (\text{for } |x| < \pi) \tag{3.428}$$

From Eqs.(3.425) and (3.427)

$$-\frac{1}{2A_1} \left[1 + \mathcal{O}\left(\frac{q}{\Theta} \right) \right] = 6 \left[1 + \mathcal{O}\left(\frac{q}{\Theta} \right) \right] \tag{3.429}$$

which gives

$$A_1 = -\frac{1}{12} \tag{3.430}$$

This is introduced into Eq.(3.426) to give the required equation (3.420).

[Comments]

The series (3.420) ought to consist only of terms which are odd powers of q/Θ, as can be argued from a simple physical consideration, which is left for the reader. In fact, for rigid molecules represented by an ellipsoid of revolution

$$\chi = \frac{\pi}{4} - \frac{1}{12}\left(\frac{q}{\Theta}\right) + \frac{1}{1296}\left(\frac{q}{\Theta}\right)^3\left[1 + \frac{24}{25}\left(\frac{p^2-1}{p^2+1}\right) + \cdots\right] + \cdots \tag{3.431}$$

where p is the axial ratio of the ellopsoid. Note that the coefficient for q/Θ is the same as that for dumbell-type molecules. Equation (3.431) may be used to evaluate Θ from the initial slope of χ plotted against q. In this case, the theoretical requirement that χ approach to $\pi/4$ as q tends to zero will help determine the initial slope of the plot.

4   Polymer Characterization

[Problem D1]

Light scattering measurements on a monodisperse polystyrene sample of molecular weight 43.3×10^4 in cyclohexane at the theta temperature (34.5 °C) gave 180 Å for $\langle S^2 \rangle^{1/2}$.

(1) Compute the conformation factor σ for polystyrene. $\overline{C - C} = 1.54$ Å, and $\angle CCC = 109.5°$.

(2) How much is $\langle R^2 \rangle$ for a monodisperse polystyrene of molecular weight 10^6 in the same solvent at the same temperature?

[Solution D1]

(1)

$$\langle S^2 \rangle_f = \frac{1}{6} n l^2 \left(\frac{1 - \cos \theta}{1 + \cos \theta} \right)$$

$$= \frac{1}{6} \times \frac{43.3 \times 10^4}{104} \times \frac{1 + (1/3)}{1 - (1/3)} \times (1.54)^2$$

$$= 6.58 \times 10^3 \tag{4.1}$$

$$\sigma = 2.22 \tag{4.2}$$

(2)

$$\langle \mathbf{R}^2 \rangle = 6 \left(\frac{100}{43.3} \right) \times 2.22^2 \times 6.58 \times 10^3$$

$$= 4.49 \times 10^4 \tag{4.3}$$

Hence

$$\langle R^2 \rangle^{1/2} = 212 \times 10^{-8} \ \text{(cm)} \tag{4.4}$$

[Problem D2]

Osmotic pressure measurements on a polyisobutylene fraction in toluene at 30 °C gave the data below. Determine M_n and A_2.

Polymer concentration (c)	Osmotic head (h)
g/dl	cm
1.046	5.120
0.893	3.448
0.652	2.195
0.389	0.930

The density of toluene at 30 °C is 0.8577 g/cm^3.

[Solution D2]

In order to take the effect of the third virial coefficient approximately into account it is convenient to analyze the given data in terms of $(\pi/cRT)^{1/2}$ versus c, where π is the osmotic pressure and RT has the usual meaning. The intercept and slope of the plot may be equated to $M_n^{-1/2}$ and $(1/2)M_n^{1/2}A_2$, respectively, and yield

$$M_n = 2.20 \times 10^5, \quad A_2 = 7.54 \times 10^{-4}(\text{mol cm}^3/\text{g}^2) \qquad (4.5)$$

This value of A_2 indicates that toluene at 30 °C is a good solvent for polyisobutylene. It is instructive that benzene is a poor solvent for this polymer and that, in fact, the polyisobutylene-benzene system has the theta temperature at about 24 °C.

[Problem D3]

Two samples, A and B, of a given polymer were mixed at the ratio $1 : 1$ by weight, and a number-average molecular weight of 20×10^4 was obtained osmotically for the mixed sample. Next, the two samples were mixed at the weight ratio $1 : 3$, and the resulting mixture was found to have a number-average molecular weight of 16.2×10^4. Use these data to find the number-average molecular weights, $M_n(A)$ and $M_n(B)$, of the samples A and B.

[Solution D3]

We can write the equations:

$$\frac{1}{20 \times 10^4} = \frac{0.5}{M_n(A)} + \frac{0.5}{M_n(B)} \tag{4.6}$$

$$\frac{1}{16.2 \times 10^4} = \frac{0.25}{M_n(A)} + \frac{0.75}{M_n(B)} \tag{4.7}$$

From these equations we obtain

$$M_n(A) = 37.7 \times 10^4, \qquad M_n(B) = 13.6 \times 10^4 \tag{4.8}$$

[Problem D4]

Consider a small region of fixed volume V in a large volume of one-component liquid equilibriated at temperature T^0 and chemical potential μ^0. Derive the expression for the density fluctuation $\langle (\Delta\rho)^2 \rangle^{1/2}$. Here $\Delta\rho$ denotes the deviation of the density ρ in this region from the average (thermodynamic equilibrium) balue $\langle \rho \rangle$.

[Solution D4]

According to statistical mechanics, the probability w that the region considered has an energy E, an entropy S, and n moles of the liquid molecules ia given by

$$w = C\exp\left(-\frac{E - ST^0 - n\mu^0}{kT^0}\right) \tag{4.9}$$

where C is a normalization constant. This expression may be readily written down if one considers that the states realizable in the region form a grand canonical ensemble. Define ΔE, ΔS, and Δn by

$$\Delta E = E - \langle E \rangle, \quad \Delta S = S - \langle S \rangle, \quad \Delta n = n - \langle n \rangle \tag{4.10}$$

with $\langle E \rangle$, $\langle S \rangle$, and $\langle n \rangle$ being the average (equilibrium) values of E, S, and n, respectively, Then, Eq.(4.9) may be put in the form

$$w = C'\exp\left(-\frac{\Delta E - T^0\Delta S - \mu^0\Delta n}{kT^0}\right) \tag{4.11}$$

where C' is a new constant independent of ΔE, ΔS, and Δn.

Now, one may choose S, V, and n as independent variables to descirbe the state of the region. Then ΔE may be expanded in powers of ΔS, ΔV, and Δn. Since $\Delta V = 0$ in the present case, the expansion is

$$
\begin{aligned}
\Delta E =& \left(\frac{\partial E}{\partial S}\right)^0 \Delta S + \left(\frac{\partial E}{\partial n}\right)^0 \Delta n \\
&+ \frac{1}{2}\left[\left(\frac{\partial^2 E}{\partial S^2}\right)^0 (\Delta S)^2 + 2\left(\frac{\partial^2 E}{\partial S \partial n}\right)^0 \Delta S \Delta n + \left(\frac{\partial^2 E}{\partial n^2}\right)^0 (\Delta n)^2\right] \\
&+ \cdots
\end{aligned}
\tag{4.12}
$$

where the superscript 0 indicates that the derivatives are to be evaluated at the equilibrium state, and the variables to be fixed in these differenciations have been omitted for simplicity. Introducing Eq.(4.12) into Eq.(4.11) and using the relations $\partial E/\partial S = T$ and $\partial E/\partial n = \mu$, one obtains

$$w = C'\exp\left\{-\left[\left(\frac{\partial T}{\partial S}\right)^0 \Delta S + \left(\frac{\partial T}{\partial n}\right)^0 \Delta n\right]\Delta S/2kT^0\right.$$
$$\left.-\left[\left(\frac{\partial \mu}{\partial S}\right)^0 \Delta S + \left(\frac{\partial \mu}{\partial n}\right)^0 \Delta n\right]\Delta S/2kT^0\right\} \quad (4.13)$$

where terms higher than the second power in ΔS and Δn have benn ignored in order to limit oneself to the leading terms. In a similar approximation, Eq.(4.13) may be written

$$w = C'\exp\left(-\frac{\Delta T\Delta S + \Delta\mu\Delta n}{2kT^0}\right) \quad (4.14)$$

with ΔT and $\Delta\mu$ being the fluctuations of temperature and chemical potential of the small region considered, i.e.,

$$\Delta T = T - T^0, \quad \Delta\mu = \mu - \mu^0 \quad (4.15)$$

Note that except for V, all other thermodynamic quantities of the region fluctuate from time to time about the average (equilibrium) values which are determined by T^0, V, and μ^0.

One may change the set of independent variables from (S, V, n) to (T, V, n). Then, since $\Delta V = 0$,

$$\Delta S = \left(\frac{\partial S}{\partial T}\right)^0 \Delta T + \left(\frac{\partial S}{\partial n}\right)^0 \Delta n + \cdots \quad (4.16)$$

$$\Delta\mu = \left(\frac{\partial \mu}{\partial T}\right)^0 \Delta T + \left(\frac{\partial \mu}{\partial n}\right)^0 \Delta n + \cdots \quad (4.17)$$

Introducing Eqs.(4.16) and (4.17) into Eq.(4.14), neglecting terms higher than the second power of ΔT and Δn, and using the relations than the relations

$$\frac{\partial S}{\partial T} = -\frac{\partial^2 A}{\partial T^2} = \frac{1}{T}\frac{\partial E}{\partial T} = \frac{C_V}{T} \quad (4.18)$$

$$\frac{\partial S}{\partial n} = -\frac{\partial^2 G}{\partial n \partial T} = -\frac{\partial \mu}{\partial T} \tag{4.19}$$

(all refering to constant V), one gets

$$w = C' \exp\left\{-\left[\frac{C_V^0}{T^0}(\Delta T)^2 + \left(\frac{\partial \mu}{\partial n}\right)^0 (\Delta n)^2\right]/2kT^0\right\} \tag{4.20}$$

Thus

$$\langle(\Delta n)^2\rangle = \frac{\int_{-\infty}^{\infty} w(\Delta n)^2 \mathrm{d}(\Delta n)}{\int_{-\infty}^{\infty} w \mathrm{d}(\Delta n)}$$

$$= \frac{\int_{-\infty}^{\infty} \exp\left[-\left(\frac{\partial \mu}{\partial n}\right)^0 x^2/2kT^0\right] x^2 \mathrm{d}x}{\int_{-\infty}^{\infty} \exp\left[-\left(\frac{\partial \mu}{\partial n}\right)^0 x^2/2kT^0\right] \mathrm{d}x}$$

$$= \frac{kT^0}{(\partial \mu/\partial n)_{T,V}^0} \tag{4.21}$$

where, in the last equation, the variables to be fixed in differentiating μ with respect to n have been indicated for clarity. Since it can be shown that

$$\left(\frac{\partial \mu}{\partial n}\right)_{T,V}^0 = \frac{(\partial \mu/\partial p)_{T,V}^0}{(\partial \mu/\partial p)_{T,V}^0} = \frac{V/\langle n\rangle}{V[\partial(n/V)/\partial p]_{T,V}^0} = \frac{V}{\kappa^0 \langle n\rangle^2} \tag{4.22}$$

where κ is the isothermal compressibility of the liquid defined as

$$\kappa = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_{T,V} \qquad (\rho = Mn/V) \tag{4.23}$$

with M being the molecular weight. Eq.(4.21) is written

$$\langle(\Delta n)^2\rangle = \frac{k\kappa^0 T^0 \langle n\rangle^2}{V} \tag{4.24}$$

which gives

$$\langle(\Delta n)^2\rangle^{1/2} = \left(\frac{k\kappa^0 T^0 \langle \rho\rangle^2}{V}\right)^{1/2} \tag{4.25}$$

or

$$\frac{\langle(\Delta \rho)^2\rangle^{1/2}}{\langle \rho\rangle} = \left(\frac{k\kappa^0 T^0}{V}\right)^{1/2} \tag{4.26}$$

Thus $\langle(\Delta\rho)^2\rangle^{1/2}$ tends to vanish as V becomes large.

[Comments]

When the liquid is a multicomponent solution, it can be shown by a similar analysis that w is given as follows:

$$w = C'\exp\left(-\frac{C_V^0}{2kT^0}(\Delta T)^2 - \frac{1}{2kT^0}\sum_{i=0}^{q}\sum_{j=0}^{q}\mu_{ij}^0\Delta n_i\Delta n_j\right) \qquad (4.27)$$

Here $q+1$ is the number of components in the system, μ_{ij} stands for

$$\mu_{ij}^0 = \left(\frac{\partial\mu_i}{\partial n_j}\right)_{T,V,n_{k\neq j}}^0 \qquad (4.28)$$

abd Δn_j is defined by

$$\Delta n_j = n_j - \langle n_j\rangle \qquad (j = 0, 1, \cdots, q) \qquad (4.29)$$

Using Eq.(4.27), one finds that

$$\langle\Delta n_i\Delta n_j\rangle = \frac{\int_{-\infty}^{\infty} w\Delta n_i\Delta n_j\mathrm{d}(\Delta n_i)\mathrm{d}(\Delta n_j)}{\int_{-\infty}^{\infty} w\mathrm{d}(\Delta n_i)\mathrm{d}(\Delta n_j)}$$

$$= \frac{kT(\Delta_A)_{ij}}{|A|} \qquad (4.30)$$

where $|A|$ is the determinant of $q+1$ order whose elements are μ_{ij}^0, and $(\Delta_A)_{ij}$ is the cofactor for the element $(i.j)$ in this determinant. Thus the Δn's of different components are correlated with one another.

[Problem D5]

Show that light scattering measurements on a binary copolymer $(\alpha+\beta)$ in a single solvent yield, at infinite dilution, an apparent molecular weight M_{app} defined by

$$M_{app} = M_w \left[1 + 2\frac{\Delta\phi}{\langle\psi\rangle}\sigma + \left(\frac{\Delta\psi}{\langle\psi\rangle}\right)^2 \delta^2\right] \tag{4.31}$$

when the sample is heterogeneous both in molecular weight and composition. In Eq.(4.31), M_w is the weight-average molecular weight of the sample,

$$\Delta\psi = \psi_\alpha - \psi_\beta \tag{4.32}$$

$$\langle\psi\rangle = \psi_\alpha\langle h_\alpha\rangle + \psi_\beta\langle h_\beta\rangle \tag{4.33}$$

$$\sigma = \frac{1}{M_w}\sum_i g_i M_i \Delta h_i \tag{4.34}$$

$$\delta^2 = \frac{1}{M_w}\sum_i g_i M_i(\Delta h_i)^2 \tag{4.35}$$

and

$$\Delta h_i = h_{\alpha i} - \langle h_\alpha\rangle \tag{4.36}$$

where ψ_α and ψ_β are the specific refractive index increments of homopolymers α and β in the given solvent, respectively, g_i is the weight fraction of the i-th component of molecular weight M_i, $h_{\alpha i}$ $(= 1 - h_{\beta i})$ is the weight fraction of the monomer α in the i-th component, and $\langle h_\alpha\rangle$ is the weight fraction of the monomer averaged over the sample, i.e.,

$$\langle h_\alpha\rangle = \sum_i h_{\alpha i} g_i \tag{4.37}$$

[Solution D5]

Let $R_i(0)$ and ψ_1 be the Rayleigh ratio at zero scattering angle and the specific refractive index of the i-th component in the given solvent. Then at very low concentrations

$$\frac{R_i(0)}{K} = (\psi_i)^2 cg_i M_i \tag{4.38}$$

where c is the total mass concentration of the copolymer. Summation of Eq.(4.38) over all solute components gives

$$M_{app} \equiv \frac{R(0)}{K\langle\psi\rangle^2 c} = \sum_i \frac{(\psi_i)^2}{\langle\psi\rangle^2} g_i M_i \qquad (4.39)$$

where $R(0) = \sum_i R_i(0)$, ψ_i may be written

$$\psi_i = \psi_\alpha h_{\alpha i} + \psi_\beta h_{\beta i} \qquad (4.40)$$

The right-hand side of Eq.(4.36) may also be expressed by $\langle h_\beta \rangle - h_{\beta i}$, because $h_{\alpha i} + h_{\beta i} = 1$, and hence $\sum_i h_{\alpha i} g_i + \sum_i h_{\beta i} g_i = \sum_i g_i = 1$, or $\langle h_\alpha \rangle + \langle h_\beta \rangle = 1$. Thus Eq.(4.40) becomes

$$\psi_i = \Delta\psi\Delta h_i + \langle\psi\rangle \qquad (4.41)$$

where Eqs.(4.32) and (4.33) have been used. With this, Eq.(4.39) is written

$$M_{app} = \sum_i g_i M_i + \frac{2\Delta\psi}{\langle\psi\rangle} \sum_i g_i M_i \Delta h_i$$
$$+ \left(\frac{\Delta\psi}{\langle\psi\rangle}\right)^2 \sum_i g_i M_i (\Delta h_i)^2 \qquad (4.42)$$

which may be brought to the form of Eq.(4.31) by noting $M_w = \sum_i g_i M_i$ and the definition of σ and δ^2.

[Problem D6]

Find the intraparticle scattering function $P_1(\theta)$ for regid particles containing n scattering points.

[Solution D6]

For rigid particles, $P_{ij}(\mathbf{r}^{\alpha\beta}) = \delta(\mathbf{r}^{\alpha\beta} - \mathbf{r}_{ij})$, so that their $P_1(\theta)$ may be written

$$P_1(\theta) = \frac{1}{n^2} \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \exp(i\mathbf{s} \cdot \mathbf{r}_{ij}) \rangle_{\mathrm{OR}} \qquad (4.43)$$

where $\langle \cdots \rangle_{\mathrm{OR}}$ denotes the average taken over all orientations of the particle.

$$\langle \exp(i\mathbf{s} \cdot \mathbf{r}_{ij}) \rangle_{\mathrm{OR}} = \frac{1}{2} \int_{0}^{\pi} \exp(isr_{ij} \cos \phi_{ij}) \sin \phi_{ij} \mathrm{d}\phi_{ij}$$

$$= \frac{\sin(sr_{ij})}{sr_{ij}} \qquad (r_{ij} = |\mathbf{r}_{ij}|) \qquad (4.44)$$

Hence

$$P_1(\theta) = \frac{1}{n^2} \sum_{i=1}^{n} \sum_{j=1}^{n} \frac{\sin(sr_{ij})}{sr_{ij}} \qquad (4.45)$$

[Problem D7]

Show for Gaussian polymer coils that Berry's square-root method is advantageous over the method of Zimm for evaluation of M_w and $\langle S^2 \rangle$ from light scattering data. In Berry's square-root plot, values of $(K^*c/R_\theta)^{1/2}$, instead of K^*c/R_θ in the Zimm plot, are plotted against $\sin^2(\theta/2)$.

[Solution D7]

At infinite dilution, the intensity of light, $R_{\theta,i}$, scattered by polymer species i at a scattering angle θ, is represented by

$$R_{\theta,i} = K^* c_i M_i P_i(\theta) \qquad (4.46)$$

where c_i, M_i, and $P_i(\theta)$ are the mass concentration, molecular weight, and particle scattering function of the species i, respectively. The total intensity R_θ scattered from a polydisoerse polymer at infinite dilution is the sum of $R_{\theta,i}$ over all species. Thus

$$R_\theta = \sum_i R_{\theta,i} = k^* \sum_i c_i M_i P_i(\theta) \qquad (4.47)$$

For Gaussian coils, $P_i(\theta)$ is rxpressed by Debye equation

$$P_i(\theta) = \frac{2}{x_i^2}(e^{-x_i} - 1 + x_i) \qquad (4.48)$$

where

$$x_i = \langle S^2 \rangle_i u, \qquad u = \left(\frac{4\pi}{\lambda}\right)^2 \sin^2(\theta/2) \qquad (4.49)$$

and λ is the wavelength of the incident light in solution.

Expanding $P_i(\theta)$ in powers of x_i and introducing the series into Eq.(4.47), one obtains

$$\frac{R_\theta}{K^*c} = M_w\left(1 - \frac{1}{3M_w}\sum_i w_i M_i x_i + \frac{1}{12M_w}\sum_i w_i M_i x_i^2 - \cdots\right) \qquad (4.50)$$

where $c = \sum_i c_i$ and $w_i = c_i/c$. Introducing Eqs.(4.49), Eq.(4.50) may be written

$$\frac{K^*c}{R_\theta} = \frac{1}{M_w}\left(1 + \frac{1}{3}\langle S^2\rangle_z u + \frac{1}{36}\langle S^2\rangle_z^2 u^2 + \cdots\right) \qquad (4.51)$$

where

$$\langle S^2\rangle_z = \frac{1}{M_w}\sum_i w_i M_i \langle S^2\rangle_i \qquad (4.52)$$

Taking the square-root of Eq.(4.51),

$$\left(\frac{K^*c}{R_\theta}\right)^{1/2} = \left(\frac{1}{M_w}\right)^{1/2}\left[1 + \frac{1}{6}\langle S^2\rangle_z u + \mathcal{O}(u^3)\right] \qquad (4.53)$$

Equation (4.53) contains no term in u^2, differing from Eq.(4.51). Thus plots of $(K^*c/R_\theta)^{1/2}$ versus $\sin^2(\theta/2)$ exhibit a less curvature at small scattering angles than do plots of K^*c/R_θ versus $\sin^2(\theta/2)$, and hence facilitate the determination of M_w and $\langle S^2\rangle_z$ by extrapolating to $\sin^2(\theta/2) = 0$.

[Comments]

Experimentally, it is known that the Debye equation for $P(\theta)$ is closely obeyed by non-gaussian coils unless x exceeds about 4. Berry's square-root method is, therefore, widely used in the analysis of scattering data, regardless of the non-ideality of given solutions.

[Problem D8]

Evaluate M_w and $\langle S^2 \rangle^{1/2}$ from the following data for a polystyrene sample in cyclohexane at 34.5 °C (Θ) by employing the Berry's square-root plot.

θ/degree	$(K^*c/R_\theta) \times 10^8$ $\mathrm{g}^{-1}\mathrm{mol}$	θ/degree	$(K^*c/R_\theta) \times 10^8$ $\mathrm{g}^{-1}\mathrm{mol}$
15	7.14	45	11.9
17.5	7.35	60	16.1
20	7.60	75	21.2
22.5	7.90	90	26.7
25	8.17	105	32.4
27.5	8.50	120	37.6
30	8.91	135	42.0
33.5	9.49	142.5	44.3
37.5	10.2	150	46.0

$\lambda_0 = 5.461 \times 10^{-1}$ cm, $n_0 = 1.5201$.

[Solution D8]

$$M_w = 1.50 \times 10^7 \tag{4.54}$$

$$\langle S^2 \rangle^{1/2} = 1.16 \times 10^{-5} \ \text{cm} \tag{4.55}$$

[Problem D9]

Show for Gaussian polymer chains that the number-average molecular weight M_n can be evaluated from the asymptote of K^*c/R_θ at large values of the scattering vector u.

[Solution D9]

The Debye equation for $P_i(\theta)$ at large values of x_i (say $x_i > 3$) may be approximated by

$$P_i(\theta) = -\frac{1}{x_i^2} + \frac{1}{x_i} \tag{4.56}$$

Substituting Eq.(4.56) into Eq.(4.47) in [Problem D8],

$$\frac{R_\theta}{K^*c} = \frac{1}{u^2}\left(-\sum_i \frac{w_i M_i}{\langle S^2 \rangle_i^2} + u\sum_i \frac{w_i M_i}{\langle S^2 \rangle_i}\right) \tag{4.57}$$

where u is defined by Eq.(4.49) in [Problem D8], and $c = \sum_i c_i$ and $w_i = c_i/c$.

For a monodisperse Gaussian coil, one may write

$$\langle S^2 \rangle_i = KM_i \tag{4.58}$$

where K is a constant characteristic of a given polymer-solvent pair. With Eq.(4.58), Eq.(4.57) is rewritten

$$\left(\frac{R_\theta}{K^*c}\right)u^2 = -\frac{(2/K^2)}{M_n} + \left(\frac{2}{K}\right)u \tag{4.59}$$

which indicates that $(R_\theta/K^*c)u^2$ (at infinite dilution) plotted against u should follow a straight line at large values of u. Values of M_n and K can be obtained from the intercept at $u = 0$ and the slope of the straight line. It should be noted that K in Eq.(4.59) is independent of molecular weight distribution.

[Problem D10]

Obtain the values of M_n, M_w/M_n, and K for a polystyrene sample from the data given in [Problem D8], by using Eq.(4.59) in [Problem D9].

[Solution D10]

$$M_n = 1.32 \times 10^7 \tag{4.60}$$

$$\frac{M_w}{M_n} = 1.14 \tag{4.61}$$

$$K = 8.3 \times 10^{-18} \ \ \mathrm{cm}^2 \tag{4.62}$$

[Problem D11]

Show that the turbidity τ of ideal gases for natural light is expressed by

$$\tau = \frac{128\pi^5}{3\lambda_0^4}\alpha^2\nu \qquad (4.63)$$

where λ_0 is the wavelength of the incident beam in vacuum, α is the polarizability of the gas molecule, and ν is the number density of the gas. With Eq.(4.63), compute τ of air at 0 °C and 1 atm for $\lambda_0 = 5890$ Å(Na-D line), knowing that the refractive index of air for this wavelength is 1.000292.

[Solution D11]

The intensity $i(r,\theta)$ of natural light scattered from a molecule of ideal gas at a scattering angle θ and at a distance r from the position of the molecule is given by

$$i(r,\theta) = \frac{8\pi^4}{\lambda_0^4}\alpha^2\left(\frac{1+\cos^2\theta}{r^2}\right)I \qquad (4.64)$$

where I is the intensity of the incident beam. Therefore when natural light of intensity I travels a distance $\mathrm{d}x$ in an ideal gas, there occurs a decrease $-\mathrm{d}I$ which is given by

$$
\begin{aligned}
-\,\mathrm{d}I &= \int_0^{2\pi}\int_0^{\pi} i(r,\theta)r^2\sin\theta\mathrm{d}\theta\mathrm{d}\phi\mathrm{d}x \\
&= \nu\frac{8\pi^4}{\lambda_0^4}I\alpha^2\int_0^{2\pi}\int_0^{\pi}(1+\cos^2\theta)\sin\theta\mathrm{d}\theta\mathrm{d}\phi\mathrm{d}x \\
&= \frac{128\pi^5}{3\lambda_0^4}\alpha^2\nu I\mathrm{d}x \qquad (4.65)
\end{aligned}
$$

where ν is the number density of molecules in the gas. By definition we have for τ

$$\tau = -\frac{1}{I}\frac{\mathrm{d}I}{\mathrm{d}x} \qquad (4.66)$$

Subsitution of Eq.(4.65) gives the required formula (4.63).

For air at 0 °C and at 1 atm, $\nu=$ Avogadro's number$/22.4 \times 10^3 = 2.69 \times 10^{19}$ cm^{-3}. Electromagnetic theory tells that n^2 ($n=$ refractive index) $= 1 + 4\pi\nu\alpha$. Using these, we obtain for the air in question

$$\alpha = 1.73 \times 10^{-24} \ \text{cm}^3 \tag{4.67}$$

$$\tau = 0.87 \times 10^{-7} \ \text{cm}^{-1} \tag{4.68}$$

This value of τ implies that the D-line of Na must run about 115 km in air of 0 °C and 1 atm for its intensity to diminish to $1/e$ ($=0.37$) of the initial value.

[Problem D12]

Show that the Debye formula for $P_1(\theta)$ of Gaussian chains can be put in the form:

$$\frac{1}{P_1(\theta)} = 1 + \frac{2s^2}{3}\langle S^2\rangle Z(w) \qquad (4.69)$$

where

$$Z(w) = \frac{1}{P_1(\theta)w^2}\int_0^w P_1(\theta)w\mathrm{d}w \qquad (4.70)$$

with

$$w = \sin^3(\theta/2) \qquad (4.71)$$

[Solution D12]

With $u = s^2\langle S^2\rangle$, the Debye formula for $P_1(\theta)$ may be written

$$P_1(\theta) = \frac{2}{u^2}(u - 1 + \mathrm{e}^{-u}) \qquad (4.72)$$

This is multiplied by u^2 and then integrated from $u = 0$ to $u = u$. The result is

$$\int_0^u P_1(\theta)u^2\mathrm{d}u = 1\left(1 - u - \mathrm{e}^{-u} + \frac{u^2}{2}\right) \qquad (4.73)$$

From Eqs.(4.72) and (4.73) we find that

$$\frac{1}{P_1(\theta)} = 1 + \frac{1}{u^2 P_1(\theta)}\int_0^u P_1(\theta)u^2\mathrm{d}u \qquad (4.74)$$

If w is defined by

$$w = \sin^3(\theta/2) \qquad (4.75)$$

u may be written

$$u = \frac{16\pi^2}{\lambda^2}\langle S^2\rangle w^{2/3} \qquad (4.76)$$

since $s = (4\pi/\lambda)\sin(\theta/2)$. By the substitution (4.76), Eq.(4.74) is immediately brought to the form asked in the problem.

[Comments]

Both s and $Z(w)$ can be evaluated for a series of θ values from measurements of $P_1(\theta)$. Thus one can determine $\langle S^2 \rangle$ as the slope of a plot of $1/P_1(\theta)$ versus $s^2 Z(w)$. It can be shown by an extension of the present analysis that the initial tangent of this plot gives $\langle S^2 \rangle_z$ for polymer samples polydisperse in molecular weight.

[Problem D13]

suppose a small particle whose principal polarizabilities are α_1, α_2, and α_3 and whose orientation in space is such that the direction cosines of the i-th principal axis of polarization ($i = 1, 2, 3$) with respect to the laboratory-fixed Cartesian coordinates x, y, and z are l_i, m_i, and n_i. Light travelling in the z-direction impinges on this particle. Then there are induced in the directions of the three principal axes of polarization dipole moments whose strength p_1, p_2, and p_3 are given by

$$p_1 = \alpha_1(l_1 E_x + m_1 E_y), \quad p_2 = \alpha_2(l_1 E_x + m_2 E_y),$$
$$p_3 = \alpha_3(l_3 E_x + m_3 E_y) \tag{4.77}$$

where E_x and E_y are the x and y components of the electric vector of incident light. Therefore, the x, y, and z components, p_x, p_y, and p_z, of the dipole moment $\mathbf{p}$ induced in the particle are represented by

$$p_x = (l_1^2\alpha_1 + l_2^2\alpha_2 + l_3^2\alpha_3)E_x + (l_1 m_1\alpha_1 + l_2 m_2\alpha_2 + l_3 m_3\alpha_3)E_y \tag{4.78}$$

$$p_y = (l_1 m_1\alpha_1 + l_2 m_2\alpha_2 + l_3 m_3\alpha_3)E_x + (m_1^2\alpha_1 + m_2^2\alpha_2 + m_3^2\alpha_3)E_y \tag{4.79}$$

$$p_z = (l_1 n_1\alpha_1 + l_2 n_2\alpha_2 + l_3 n_3\alpha_3)E_x + (n_1 m_1\alpha_1 + n_2 m_2\alpha_2 + n_3 m_3\alpha_3)E_y \tag{4.80}$$

Show that $\langle p_x^2\rangle$, $\langle p_y^2\rangle$, and $\langle p_z^2\rangle$, the orientation averages of p_x^2, p_y^2, and p_z^2, are given by

$$\langle P_x^2\rangle = \left(A^2 + \frac{4}{5}B^2\right)E_x^2 + \frac{3}{5}B^2 E_y^2 \tag{4.81}$$

$$\langle P_y^2\rangle = \frac{3}{5}B^2 E_x^2 + \left(A^2 + \frac{4}{5}B^2\right)E_y^2 \tag{4.82}$$

$$\langle p_z^2\rangle = \frac{3}{5}B^2(E_x^2 + E_y^2) \tag{4.83}$$

where

$$A = \frac{\alpha_1 + \alpha_2 + \alpha_3}{3} \tag{4.84}$$

$$B = \frac{(\alpha_1 - \alpha_2)^2 + (\alpha_2 - \alpha_3)^2 + (\alpha_3 - \alpha_1)^2}{18} \tag{4.85}$$

A represents a mean polarizability of the particle, and B is a measure of optical anisotropy of the particle.

[Solution D13]

$$
\begin{aligned}
\langle p_x^2 \rangle =&[\langle l_1^4 \rangle \alpha_1^2 + \langle l_2^4 \rangle \alpha_2^2 + \langle l_3^4 \rangle \alpha_3^2 \\
&+2\langle l_1^2 l_2^2 \rangle \alpha_1 \alpha_2 + 2\langle l_2^2 l_3^2 \rangle \alpha_2 \alpha_3 + 2\langle l_3^2 l_1^2 \rangle \alpha_3 \alpha_1]E_x^2 \\
&+[\langle l_1^2 m_1^2 \rangle \alpha_1^2 + \langle l_2^2 m_2^2 \rangle \alpha_2^2 + \langle l_3^2 m_3^2 \rangle \alpha_3^2 \\
&+2\langle l_1 m_1 l_2 m_2 \rangle \alpha_1 \alpha_2 + 2\langle l_2 m_2 l_3 m_3 \rangle \alpha_2 \alpha_3 + 2\langle l_3 m_3 l_1 m_1 \rangle \alpha_3 \alpha_1]E_y^2 \\
&+[\langle l_1^3 m_1 \rangle \alpha_1^2 + \langle l_2^3 m_2 \rangle \alpha_2^2 + \langle l_3^3 m_3 \rangle \alpha_3^2 \\
&+(\langle l_1^2 l_2 m_2 \rangle + \langle l_1 l_2^2 m_1 \rangle)\alpha_1 \alpha_2 + (\langle l_2^2 l_3 m_3 \rangle + \langle l_2 l_3^2 m_2 \rangle)\alpha_2 \alpha_3 \\
&+(\langle l_1^2 l_3 m_3 \rangle + \langle l_3^2 l_1 m_1 \rangle)\alpha_1 \alpha_3]E_x E_y
\end{aligned}
\tag{4.86}
$$

One obtains

$$
\langle l_1^4 \rangle = \langle l_2^4 \rangle = \langle l_3^4 \rangle = \frac{1}{5}
\tag{4.87}
$$

$$
\begin{aligned}
\langle l_1^2 l_2^2 \rangle =&\langle l_2^2 l_3^2 \rangle = \langle l_3^2 l_1^2 \rangle = \langle l_1^2 m_1^2 \rangle \\
=&\langle l_2^2 m_2^2 \rangle = \langle l_3^2 m_3^2 \rangle = \frac{1}{15}
\end{aligned}
\tag{4.88}
$$

$$
\langle l_1 m_1 l_2 m_2 \rangle = \langle l_2 m_2 l_3 m_3 \rangle = \langle l_3 m_3 l_1 m_1 \rangle = -\frac{1}{30}
\tag{4.89}
$$

and all the averages appearing in the expression multiplied by $E_x E_y = 0$.

Hence Eq.(4.86) becomes

$$
\begin{aligned}
\langle p_x^2 \rangle =&\left[\frac{1}{5}(\alpha_1^2 + \alpha_2^2 + \alpha_3^2) + \frac{2}{15}(\alpha_1 \alpha_2 + \alpha_2 \alpha_3 + \alpha_3 \alpha_2)\right]E_x^2 \\
&+\left[\frac{1}{15}(\alpha_1^2 + \alpha_2^2 + \alpha_3^2) - \frac{1}{15}(\alpha_1 \alpha_2 + \alpha_2 \alpha_3 + \alpha_3 \alpha_1)\right]E_y^2 \\
=&\left\{\frac{1}{9}(\alpha_1 + \alpha_2 + \alpha_3)^2 + \frac{2}{45}[(\alpha_1 - \alpha_2)^2 + (\alpha_2 - \alpha_3)^2 + (\alpha_3 - \alpha_1)^2]\right\}E_x^2 \\
&+\frac{1}{30}[(\alpha_1 - \alpha_2)^2 + (\alpha_2 - \alpha_3)^2 + (\alpha_3 - \alpha_1)^2]E_y^2
\end{aligned}
\tag{4.90}
$$

which may be expressed in terms of A and B as

$$\langle p_x^2 \rangle = \left(A^2 + \frac{4}{5}B^2 \right) E_x^2 + \frac{3}{5}B^2 E_y^2 \qquad (4.91)$$

This is the required expression (4.81). The derivation of Eqs.(4.82) and (4.83) can be made in a similar way.
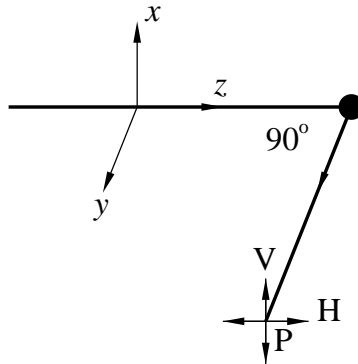
[Problem D14]

Unpolarized light impinges on a small and optically anisotropic particle, and one observes the intensity of scattered light at a point which sees the particle at $90°$ to the direction of the incident beam (see the figure above). The component of the observed intensity in the direction of incident light and that in the direction perpendicular to the plane containing incident and scattered light are denoted by H_u and V_u, respectively. Here the subscript u indicates that the incident beam is unpolarized.

Show that if the particle can assume all orientation by thermal agitation, the quantity ρ_u defined by

$$\rho_u = \frac{H_u}{V_u} \tag{4.92}$$

is represented by

$$\rho_u = \frac{6B^2}{5A^2 + 7B^2} \tag{4.93}$$

where

$$A = \frac{1}{3}(\alpha_1 + \alpha_2 + \alpha_3) \tag{4.94}$$

$$B = \frac{1}{18}[(\alpha_1 - \alpha_2)^2 + (\alpha_2 - \alpha_3)^2 + (\alpha_3 - \alpha_1)^2] \tag{4.95}$$

with α_1, α_2, and α_3 being the principal polarizabilities of the particle. ρ_u is called the degree of depolarization for unpolarized light.

[Solution D14]

Using the general theory of light scattering by small particles, one can write

$$H_u \propto \langle \overline{p_z^2} \rangle, \qquad V_u \propto \langle \overline{p_x^2} \rangle \qquad (4.96)$$

Here $\langle \overline{p_x^2} \rangle$ and $\langle \overline{p_z^2} \rangle$ are the orientation averages of the squares of the x and z components of the dipole moment induced in the particle by incident light, with the Cartesian coordinates x, y, z taken as indicated in the figure, and the upper bar designates the time average. The proportionality factors in the above expressions are identical. Thus

$$\rho_u = \frac{\langle \overline{p_z^2} \rangle}{\langle \overline{p_x^2} \rangle} \qquad (4.97)$$

Substitution for $\langle p_z^2 \rangle$ and $\langle p_x^2 \rangle$ from [Problem D13] gives

$$\rho_u = \frac{(3/5)B^2(\overline{E_x^2} + \overline{E_y^2})}{\{[A^2 + (4/5)B^2]\overline{E_x^2} + (3/5)B^2\overline{E_y^2}\}} \qquad (4.98)$$

For unpolarized incident light $\overline{E_x^2} = \overline{E_y^2}$. Hence Eq.(4.98) becomes

$$\rho_u = \frac{6B^2}{5A_2 + 7B^2} \qquad (4.99)$$

which is the required equation (4.93).

From Eq.(4.99) one finds that if the particle is optically isotropic, i.e., $\alpha_1 = \alpha_2 = \alpha_3$ so that $B = 0$, $\rho_u = 0$, which means that scattered light is vertically (i.e., in the direction od the x axis) polarized at 90° scattering angle. Experimental values of ρ_u for benzene are about 0.42.

[Problem D15]

In [Problem D14], let one consider the case in which incident light has unit intensity and is polarized vertically (in the direction of the y axis). The subscript v or h is given to H and V, such as H_v and V_h, depending on wether incident light is polarized vertically or horizontally. Then show that

$$\rho_h \equiv \frac{H_h}{V_h} = 1 \tag{4.100}$$

and

$$H_v = V_h \tag{4.101}$$

The latter is called the Krishnan relationship.

[Solution D15]

Since $E_x = 0$ for horizontally polarized incident light, one gets

$$H_h \propto \langle \overline{p_z^2} \rangle = \frac{3}{5} B^2, \qquad V_h \propto \langle \overline{p_x^2} \rangle = \frac{3}{5} B^2 \tag{4.102}$$

where the fact $E_y^2 = 1$ for this incident beam has been used. Hence $\rho_h = 1$.

One also gets for vertically polarized incident light of unit intensity

$$H_v \propto \langle \overline{p_z^2} \rangle = \frac{3}{5} B^2 \tag{4.103}$$

which is compared with V_h in Eq.(4.102) to give $H_v = V_h$, the Krishnan relationship.

[Problem D16]

Derive the intraparticle scattering factor $P_1(\theta)$ for a continuous spherical shell of radius a and thickness b.

[Solution D16]

The general expression for $P_1(\theta)$ of rigid particle is

$$P_1(\theta) = \langle \frac{1}{n^2} \sum_{i=1}^{n} \sum_{j=1}^{n} \exp(i\mathbf{s} \cdot \mathbf{r}_{ij}) \rangle \qquad (4.104)$$

where n is the total number of scattering points in the particle, $\mathbf{r}_{ij}$ is the distance between i-th and j-th scattering points, $\mathbf{s}$ is the scattering vector, and $\langle \cdots \rangle$ designates the average with respect to the orientation of the particle. Let $\mathbf{S}_I$ be the distance between the center of mass of the particle and the i-th scattering point. Then $\mathbf{r}_{ij} = \mathbf{S}_j - \mathbf{S}_i$. Hence Eq.(4.104) becomes

$$P_1(\theta) = \langle \frac{1}{n^2} \sum_{i=1}^{n} \sum_{j=1}^{n} \exp(i\mathbf{s} \cdot \mathbf{S}_j)\exp(-i\mathbf{s} \cdot \mathbf{S}_i) \rangle \qquad (4.105)$$

For spherical particles this may be written

$$P_1(\theta) = \langle \frac{1}{n} \sum_{i=1}^{n} \exp(-i\mathbf{s} \cdot \mathbf{S}_i) \rangle \langle \frac{1}{n} \sum_{j=1}^{n} \exp(i\mathbf{s} \cdot \mathbf{S}_j) \rangle$$

$$= \left[\frac{1}{n} \sum_{i=1}^{n} \frac{\sin(sS_i)}{sS_i} \right]^2 \qquad (s = |\mathbf{s}|) \qquad (4.106)$$

If the distribution of scattering points is uniform and continuous, Eq.(4.106) may be replaced by

$$P_1(\theta) = \left[\frac{1}{n} \int_0^a \frac{\sin(sS)}{sS} \rho(S) 4\pi S^2 \mathrm{d}S \right] \qquad (4.107)$$

where a is the radius of the sphere, and $\rho(S)$ is the number density of scattering points at radius S.

For the present spherical shell

$$\rho(S) = \frac{n}{(4\pi/3)[a^3 - (a-b)^3]} \qquad (a-b < S < a) \qquad (4.108)$$

$$\rho(S) = 0 \qquad (0 < S < a - b) \qquad (4.109)$$

Hence Eq.(4.107) gives

$$P_1(\theta) = \left[\frac{3}{b^3 - 3b^2a + 3ba^2} \int_{a-b}^{a} \frac{\sin(sS)}{sS} S^2 \mathrm{d}S \right]$$
$$= \left\{ \frac{3}{s^3(b^3 - 3b^2a + 3ba^2)} [\sin(as) - \sin(a - b)s \right.$$
$$\left. -as\cos(as) + (a-b)s\cos(a-b)s] \right\}^2 \qquad (4.110)$$

which is the desired result.

If the shell is infinitely thin, Eq.(4.110) reduces to

$$p_1(\theta) = \left[\frac{\sin(as)}{as} \right]^2 \qquad (4.111)$$

If $b = a$, i.e., there is no hollow part inside the particle, Eq.(4.110) becomes

$$P_1(\theta) = \left\{ \frac{3}{(as)^3} [\sin(as) - as\cos(as)] \right\}^2 \qquad (4.112)$$

[Problem D17]

Show that the particle scattering function $P_1(\theta)$ of a once broken rod which consists of two thin rods of equal length L connected by a universal joint is given by

$$P_1(\theta) = \frac{\mathrm{Si}(u)}{u} + \frac{1}{2}\left[\frac{\mathrm{Si}(u)}{u}\right]^2 - 2\left[\frac{\sin(u/2)}{u}\right]^2 \qquad (4.113)$$

where

$$u = sL \qquad (4.114)$$

$$\mathrm{Si}(u) = \int_0^u \frac{\sin z}{z}dz \qquad (4.115)$$

with s being the magnitude of the scattering vector.

[Solution D17]

Equation (4.45) in [Problem D6] can be applied to a broken rod averaged over all orientation with the angle between the two rods fixed at a constant vlue, say θ. In the limit of continuous scattering points, one thus obtains

$$P_1(\theta) = \frac{2}{(2L)^2}(I_1 + I_2) \qquad (4.116)$$

where

$$I_1 = \int_0^L \int_0^L \frac{\sin s(x - y)}{s(x - y)}dxdy \qquad (4.117)$$

$$I_2 = \frac{1}{2}\int_0^L \int_0^L \int_0^\pi \frac{\sin(s\sqrt{x^2 + y^2 - 2xy\cos\theta})}{s\sqrt{x^2 + y^2 - 2xy\cos\theta}}\sin\theta d\theta dxdy \qquad (4.118)$$

Here x (or y) is the distance from the universal joint to a given point on either rod. Note that I_1 and I_2 represent the contributions from pairs of scattering points (characterized by x and y) which are located on the same and different rods, respectively.

Since

$$\int_0^L \int_0^L \frac{\sin s(x - y)}{s(x - y)}dxdy = 2\int_0^L (L - t)\frac{\sin st}{st}dt \qquad (4.119)$$

I_1 is readily evaluated as

$$I_1 = \frac{2L^2}{u}\mathrm{Si}(u) - \left[\frac{2L\sin(u/2)}{u}\right]^2 \tag{4.120}$$

where $\mathrm{Si}(u)$ is the sine-integral function defined by Eq.(4.115).

Next, I_2 may be rewritten

$$\begin{aligned}
I_2 &= \int_0^L \mathrm{d}x \int_0^x \mathrm{d}y \int_0^p i\frac{\sin(s\sqrt{x^2+y^2-2xyt})}{s\sqrt{x^2+y^2-2xyt}}\mathrm{d}t \\
&= \int_0^L \frac{\mathrm{d}x}{sx} \int_0^x \frac{\mathrm{d}y}{sy} \int_{s(x-y)}^{s(x+y)} \sin\xi\mathrm{d}\xi
\end{aligned} \tag{4.121}$$

Hence one gets

$$I_2 = \left[\frac{L}{u}\mathrm{Si}(u)\right]^2 \tag{4.122}$$

Introducing Eqs.(4.120) and (4.122) into Eq.(4.116), one comes to the desired expression.

[Comments]

Replacing $2/(2L)^2$ in Eq.(4.116) by $1/L^2$ and putting I_2 equal to zero, one obtains the expression for the particle scattering function of a thin straight rod of length L:

$$P_1(\theta) = \frac{1}{u}\mathrm{Si}(2u) - \left(\frac{\sin u}{u}\right)^2 \tag{4.123}$$

with

$$u = \frac{L}{2}s \tag{4.124}$$

[Problem D18]

Show that the particle scattering function $P_1(\theta)$ for an infinitely thin circular disc of redius a is represented by

$$P_1(\theta) = \frac{2}{u^2}\left[1 - \frac{J_1(2u)}{u}\right]$$ (4.125)

where J_1 is the Bessel function of first order, and

$$u = as = \frac{4\pi a}{\lambda}\sin\left(\frac{\theta}{2}\right)$$ (4.126)

Hint: The following series expansions of $[J_1(z)]^2$ and $J_1(2z)$ may be used if necessary:

$$[J_1(z)]^2 = \sum_{m=0}^{\infty}(-1)^m\frac{(2m+1)!!}{m!(m+2)!(2m+2)!!}z^{2m+2}$$ (4.127)

$$J_1(2z) = \sum_{m=0}^{\infty}(-1)^m\frac{z^{2m+1}}{m!(m+1)!}$$ (4.128)

[Solution D18]

Application of Eq.(4.45) in [Problem D6] to the disc (the scattering points distribute continuously and uniformly) yields

$$P_1(\theta) = \frac{1}{(\pi a^2)^2}\langle Q^2\rangle_{\text{or}}$$ (4.129)

with

$$Q = \int e^{i\mathbf{s}\cdot\mathbf{r}}d\mathbf{r}$$ (4.130)

where $\langle\cdots\rangle_{\text{or}}$ denotes the average over all possible orientations of the disc and the integration $d\mathbf{r}$ goes over all its surface. Let the direction of $\mathbf{s}$ be chosen as tha z-axis in the laboratory-fixed coordinates (x,y,z) and let coordinates (ξ,η,ζ) fixed in the disc be defined. In the (ξ,η,ζ)

coordinates, the ξ- and η-components of $\mathbf{s}$ are thus given by $\sin\phi$ and 0, respectively. Hence, Q is written in terms of the coordinates (ξ, η, ζ) as

$$Q = \int_{-a}^{a} \mathrm{d}\xi \int_{-\sqrt{a^2-\xi^2}}^{\sqrt{a^2-\xi^2}} e^{is\xi\sin\phi} \mathrm{d}\eta \qquad (4.131)$$

which, upon integration over η, gives

$$Q = 2a^2 \int_0^{\pi} \cos(u\sin\phi\cos\beta)\sin^2\beta \mathrm{d}\beta \qquad (4.132)$$

where use has been made of the definition of u ($u = as$). The integral representation of J_1 allows Eq.(4.132) to be written

$$Q = \frac{2\pi a^2}{u\sin\phi} J_1(u\sin\phi) \qquad (4.133)$$

With this expression of Q, the $P_1(\theta)$ is now written

$$P_1(\theta) = \frac{2}{u^2} \int_0^{\pi} \frac{1}{\sin\phi} [J_1(u\sin\phi)]^2 \mathrm{d}\phi \qquad (4.134)$$

Introduction of Eq.4.127) into Eq.(4.134), followed by integration, yields

$$P_1(\theta) = \frac{2}{u^2} \sum_{m=0}^{\infty} (-1)^m \frac{u^{2m+2}}{(m+2)!(m+1)!} \qquad (4.135)$$

Since

$$\sum_{m=0}^{\infty} (-1)^m \frac{u^{2m+2}}{(m+2)!(m+1)!} = \sum_{m=0}^{\infty} -(-1)^m \frac{u^{2m}}{(m+1)!m!}$$

$$= 1 - \sum_{m=0}^{\infty} \frac{(-1)^m u^{2m}}{(m+1)!m!} \qquad (4.136)$$

use of Eq.(4.128) leads to the desired expression, Eq.(4.125).

[Problem D19]

Show that the particle scattering function $P_1(\theta)$ for a randomly oriented circular disc is represented by

$$P_1(\theta) = \frac{2}{u^2}\left[1 - \frac{J_1(2u)}{u}\right] \qquad (4.137)$$

where J_1 is the Bessel function of first order, and

$$u = \frac{4\pi a}{\lambda}\sin(\theta/2) = sa \qquad (4.138)$$

with a being the radius of the disc.

[Solution D19]

One may apply Eq.(4.45) in [Problem D6] by going to the limit where the scattering points distribute continuously and uniformly over an infinitely thin circular region of radius a. Such a limiting form of Eq.(4.45) gives

$$P_1(\theta) = \frac{4\pi}{(\pi a^2)^2}\int_0^\pi \mathrm{d}\phi \int_0^a x\mathrm{d}x \int_0^{R(\phi,x)}\frac{\sin(sy)}{sy}y\mathrm{d}y \qquad (4.139)$$

where ϕ, x, y, and $R(\phi, x)$ have the meaning as seen from the figure. It is easily shown that R is related to x and ϕ by

$$R^2 + 2Rx\cos\phi + x^2 - a^2 = 0 \qquad (4.140)$$

Equation (4.139) gives

$$P_1(\theta) = \frac{4}{\pi a^4 s^2}\left(\frac{\pi a^2}{2} - F\right) \qquad (4.141)$$

where

$$F = \int_0^\pi \mathrm{d}\phi \int_0^a x\cos(sR)\mathrm{d}x \qquad (4.142)$$

Considering the fact that the upper and lower limits of x in Eq.(4.142), $x = a$ and $x = 0$, correspond, respectively, to $R = 0$ and $R = a$ for
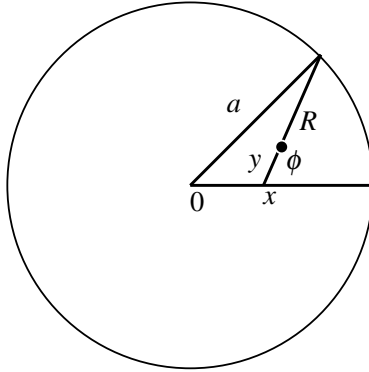
$0 < \phi < \pi/2$ and to $R = -2a\cos\phi$ and $R = a$ for $\pi/2 < \phi < \pi$, one may transform Eq.(4.142) to

$$F = \int_0^{\pi/2} d\phi \int_a^0 \cos(sR)G_1(R,\phi)dR$$
$$+ \int_0^{\pi/2} d\phi \int_a^{2a\cos\phi} \cos(sR)G_2(R,\phi)dR \qquad (4.143)$$

where

$$G_1(R,\phi) = R\cos 2\phi - \cos\phi\left[2\sqrt{a^2 - R^2\sin^2\phi} - \frac{a^2}{\sqrt{a^2 - R^2\sin^2\phi}}\right]$$
$$(4.144)$$

$$G_2(R,\phi) = R\cos 2\phi + \cos\phi\left[2\sqrt{a^2 - R^2\sin^2\phi} - \frac{a^2}{\sqrt{a^2 - R^2\sin^2\phi}}\right]$$
$$(4.145)$$

Equation (4.143) may be rewritten

$$F = \int_0^{\pi/2} d\phi \int = 0^{2a\cos\phi} G_2(R,\phi)\cos(sR)dR \qquad (4.146)$$

because

$$\int_0^{\pi/2} d\phi \int_a^0 R\cos 2\phi \cos(sR)dR = 0 \qquad (4.147)$$

Now, by use of the formula

$$\int_0^{\pi/2}\left[\int_0^{2a\cos\phi} f(\phi,r)dr\right] = \int_0^{2a}\left[\int_0^{\cos^{-1}(r/2a)} f(\phi,r)d\phi\right]dr \qquad (4.148)$$

one finds that

$$\int_{-}^{\pi/2} \mathrm{d}\phi \int_{0}^{2a\cos\phi} R\cos 2\phi \cos(sR)\mathrm{d}R = 4a^2 \int_{0}^{1} \xi^2 \sqrt{1-\xi^2}\cos(2u\xi)\mathrm{d}\xi \tag{4.149}$$

$$\int_{0}^{\pi/2} \mathrm{d}\phi \int_{0}^{2a\cos\phi} \left[2\sqrt{a^2 - R^2\sin^2\phi} - \frac{a^2}{\sqrt{a^2 - R^2\sin^2\phi}} \right] \cos\phi \cos(sR)\mathrm{d}R$$
$$= 2a^2 \int_{0}^{1} (1 - 2\xi^2)\sqrt{1-\xi^2}\cos(2u\xi)\mathrm{d}\xi \tag{4.150}$$

Hnece

$$F = 2a^2 \int_{0}^{1} \sqrt{1-\xi^2}\cos(2u\xi)\mathrm{d}\xi \tag{4.151}$$

Substitution of $\xi = \cos\theta$ changes this to

$$F = 2a^2 \int_{0}^{\pi/2} \sin^2\theta \cos(2u\cos\theta)\mathrm{d}\theta$$
$$= a^2 \int_{0}^{\pi} \sin^2\theta \cos(2u\cos\theta)\mathrm{d}\theta \tag{4.152}$$

Since

$$J_1(z) = \frac{z/2}{\sqrt{\pi}\gamma(3/2)} \int_{0}^{p} i\cos(z\cos\theta)\sin^2\theta\mathrm{d}\theta \tag{4.153}$$

Eq.(4.152) becomes

$$F = \frac{\pi a^2}{2u} J_1(2u) \tag{4.154}$$

This is introduced into Eq.(4.142) to give the desired formula (4.137).

[Problem D20]

Suppose a solution which contains a (monodisperse) macromolecular solute (component 2) in a mixture of two solvents (component 0 and 1). Let component 0 be called the principal solvent. According to Stockmayer, the turbidity, τ, of this solution over that of the principal solvent at given temperature T and pressure p is represented by

$$\tau = RTHv_M \frac{\sum_{i=1}^{2} \sum_{j=1}^{2} \Psi_i \Psi_j \Delta_{ij}}{|\mu_{ij}|} \tag{4.155}$$

where v_M is the volume of the solution containing one kilogram of the principal solvent,

$$H = \frac{32\pi^3 \tilde{n}^2}{3\lambda_0^4 N_A} \tag{4.156}$$

$$\Psi_i = \left(\frac{\partial \tilde{n}}{\partial m_1}\right)_{T,p,m_{k\neq i}} \tag{4.157}$$

and

$$\mu_{ij} = \left(\frac{\partial \mu_i}{\partial \mu_j}\right)_{T,p,m_{k\neq j}} \tag{4.158}$$

In these expressions, λ_0 is the wavelength of the incident light in vacuum, $\tilde{n}$ is the refractive index of the solution, m_i is the molality of component i, μ_i is the chemical potential of the same component, and Δ_{ij} is the cofactor for the element μ_{ij} in the determinant $|\mu_{ij}| = \mu_{11}\mu_{22} - \mu_{12}\mu_{21}$.

Derive the expression for $\Delta\tau_c$, the difference between the turbidity of the solution and that of the solvents (component 0 and 1) mixed in the same proportion without polymer, valid for the case in which the concentration of the polymer is very low.

[Solution D20]

The quantities associated with the "mixed" solvent containing no polymer are distinguished by the superscript zero. Then Eq.(4.155) gives

$$\tau_0 = RTH^0 v_M^0 \frac{(\Psi_1^0)^2}{\mu_{11}} \tag{4.159}$$

Hence

$$\Delta\tau = RTHv_M \frac{\Psi_1^2\mu_{22} - 2\Psi_1\Psi_2\mu_{12} + \Psi_2^2\mu_{11}}{\mu_{11}\mu_{22} - (\mu_{12})^2} - RTH^0v_M^0 \frac{(\Psi_1^0)^2}{\mu_{11}^0} \quad (4.160)$$

where the relationship $\mu_{12} = \mu_{21}$ (the proof is left to the reader) has been used.

For solution very dilute in the polymer component one may replace H, v_M, μ_{11}, and Ψ_1 by H^0, v_M^0, μ_{11}^0, and Ψ_1^0, whist one may approximate μ_{12}, μ_{22}, and Ψ_2 by their limiting forms for vanishing small m_2. Then Eq.(4.160) becomes for very low polymer concentrations

$$\frac{\Delta\tau_c}{RTH^0v_M^0} = \frac{\{(\Psi_2)_0 - [(\mu_{12})_0/\mu_{11}^0]\Psi_1^0\}^2}{(\mu_{22})_0 - [(\mu_{12})_0^2/\mu_{11}^0]} \quad (4.161)$$

where the subscript zero indicates the value for $m_2 \rightarrow 0$.

If one expresses μ_i as

$$\mu_i = \mu_i^\infty(T,p) + RT\ln\gamma_i^\infty(T,p,m_1,m_2)m_i \quad (i=1,2) \quad (4.162)$$

with γ_i^∞ defined so that it tends to unity as both m_1 and m_2 simultaneously approaches zero, one gets

$$\mu_{ii} = RT\frac{1 + \beta_{ii}m_i}{m_i} \quad (4.163)$$

$$\mu_{ij} = RT\beta_{ij} \quad (i \neq j) \quad (4.164)$$

with

$$\beta_{ij} = \left(\frac{\partial\ln\gamma_i^\infty}{\partial m_j}\right)_{T,p,m_{k\neq j}} \quad (4.165)$$

Introducing Eqs.(4.163) and (4.164) into Eq.(4.161), one obtains

$$\frac{\Delta\tau_c}{RTH^0v_M^0} = \left[(\Psi_2)_0 - \frac{m_1(\beta_{12})_0}{1 + \beta_{11}^0m_1}\Psi_1^0\right]^2 m_2 \quad (4.166)$$

or

$$\frac{\Delta\tau_c}{RTH^ov_M^0} = \left[(\Psi_2)_0 - \frac{(\mu_{12})_0}{\mu_{11}^0}\Psi_1^0\right]^2 m_2 \quad (4.167)$$

Since $\mu_{11}^0 = (\mu_{11})_0$,

$$\frac{(\mu_{12})_0}{\mu_{11}^0}\left[\frac{(\partial\mu_1/\partial m_2)_{T,p,m_1}}{(\partial\mu_1/\partial m_1)_{T,p,m_2}}\right]_0 = -\left[\left(\frac{\partial m_1}{\partial m_2}\right)_{T,p,\mu_1}\right]_0 \tag{4.168}$$

where Eq.(3.112) in [Problem C13] has been used. Hence Eq.(4.167) may be written

$$\frac{\Delta\tau_c}{RTH^0 v_M^0} = [(\psi_1)_0 + \Gamma_0\Psi_1^0]^2 m_2 \tag{4.169}$$

where

$$\Gamma_0 = \lim_{m_2\to 0}\Gamma = \lim_{m_2\to 0}\left(\frac{\partial m_1}{\partial m_2}\right)_{T,p,\mu_1} \tag{4.170}$$

(see [Problem C13] for Γ).

Now one defines $\Psi_1^{(g)}$ and $\Psi_2^{(g)}$ by

$$\Psi_1^{(g)} = \left(\frac{\partial\tilde{n}}{\partial g_1}\right)_{T,p,g_2}, \qquad \Psi_2^{(g)} = \left(\frac{\partial\tilde{n}}{\partial g_2}\right)_{T,p,g_1} \tag{4.171}$$

where g_1 and g_2 are the grams of components 1 and 2 containing in one kilogram of component 0. These refractive index increments are the quantities that are measured by actual experimental procedures, and are related to Ψ_1 and Ψ_1 by

$$\Psi_1 = M_1\Psi_1^{(g)}, \qquad \Psi_2 = M_2\Psi_2^{(g)} \tag{4.172}$$

Introducing Eq.(4.172) into (4.169) and using the relation $m_i = c_i v_M/M_i$, one obtains

$$\frac{\Delta\tau_c}{RTH^0(v_M^0)^2} = M_2(\Psi_2^{(g)})_0^2\left[1 + \frac{M_1}{M_2}\Gamma_0\frac{(\Psi_1^{(g)})^0}{(\Psi_2^{(g)})_0}\right]^2 c_2 \tag{4.173}$$

Thus if $(\Psi_1^{(g)})^0 = 0$ or $\Gamma_0 = 0$, one can evaluate M_2, the molecular weight of the polymer solute from the intercept of a plot of $\Delta\tau_c/RTH^0(v_M^0)^2 \times (\Psi_2^{(g)})_0^2 c_2$ versus c_2. Note that $(\Psi_1^{(g)})^0 = 0$ means that the principal and secondary solvents have an identical refractive index. Such solvents are called isorefractive.

[Problem D21]

Let $A(t)$ be a quantity that fluctuates irregularly with time t. A typical example of $A(t)$ is a succession of small displacements that a particle in liquid undergoes due to thermal collision of other particles. In general, there will be a correlation between the values of A at two times t and $t + \tau$. As a measure of this correlation one may consider a function 0f τ which is defined by

$$C(\tau) = \lim_{T \to 0} \frac{1}{T} \int_0^T A(t) A(t + \tau) dt \quad (\tau \geq 0) \tag{4.174}$$

The $C(\tau)$ thus defined is called the autocorrelation function for A. Show that

$$C(0) \geq C(\tau) \tag{4.175}$$

[Solution D21]

Suppose that the time axis is divied into discrete intervals Δt in such a way that $t = j\Delta t$, $\tau = n\Delta t$, $T = N\Delta t$, and $t + \tau = (j + n)\Delta t$ and suppose further that A varies very little over the time interval Δt. Then Eq.(4.174) is equivalent to

$$C(\tau) = \lim_{N \to \infty} \frac{1}{N} \sum_{j=1}^{N} a_j A_{j+n} \tag{4.176}$$

and

$$C(0) = \lim_{N \to \infty} \frac{1}{N} \sum_{j=1}^{N} A_j^2 \tag{4.177}$$

Now, according to Schwarz's inequality,

$$\left(\sum_{j=1}^{N} A_j B_j\right)^2 \leq \left(\sum_{j=1}^{N} A_j^2\right)\left(\sum_{j=1}^{N} B_j^2\right) \tag{4.178}$$

If one takes $B_j = A_{j+n}$, divides both sides by N^2, goes to the limit $N \to \infty$, and then refers to Eqs.(4.176) and (4.177), one gets

$$[C(\tau)]^2 \leq C(0) \times \lim_{N \to \infty} \frac{1}{N} \sum_{j=1}^{N} A_{j+n}^2 \tag{4.179}$$

But

$$\lim_{N\to\infty} \frac{1}{N} \sum_{j=1}^{N} A_{j+n}^2 = \lim_{N\to\infty} \frac{1}{N} \sum_{i=1}^{N} A_i^2$$

$$+ \lim_{N\to\infty} \frac{1}{N} \left(\sum_{i=N+1}^{N+n} a_i^2 - \sum_{i=1}^{n} A_i^2 \right)$$

$$= \lim_{N\to\infty} \frac{1}{N} \sum_{i=1}^{N} A_i^2 = C(0) \qquad (4.180)$$

Hence Eq.(4.179) becomes

$$[C(\tau)]^2 \leq [C(0)]^2 \qquad (4.181)$$

Since $C(\tau)$ is real, this is equivalent to the desired result $C(\tau) \leq C(0)$.

[Problem D22]

If the time dependent variation of a quantity $A(t)$ is stationary and ergodic, show that the autocorrelation function for A, $C(\tau)$, is represented by

$$C(\tau) = \langle A(0)A(\tau) \rangle \tag{4.182}$$

where $\langle \cdots \rangle$ designates the ensemble average, i.e.,

$$\langle A(0)A(\tau) \rangle = \int_0^\infty \int_0^\infty P_0^\tau(A_1, A_2)A_1 A_2 \mathrm{d}A_1 \mathrm{d}A_2 \tag{4.183}$$

with $P_0(A_1, A_2)$ being the probability density for obtaining specified value A_1 and A_2 for A from measurements at time 0 and τ, respectively.

[Solution D22]

The definition of $C(\tau)$ is

$$C(\tau) = \lim_{T \to \infty} \frac{1}{T} \int_0^T A(t)A(t+\tau)\mathrm{d}t \tag{4.184}$$

Since the process is ergodic,

$$\lim_{T \to \infty} \frac{1}{T} \int_0^T A(t)A(t+\tau)\mathrm{d}t = \langle A(t)A(t+\tau) \rangle$$

$$= \int_0^\infty \int_0^\infty P_t^{t+\tau}(A_1, A_2)A_1 A_2 \mathrm{d}A_1 \mathrm{d}A_2 \tag{4.185}$$

where $P_t^{t+\tau}(A_1, A_2)$ represents the probability density for obtaining values A_1 and A_2 at times t and $t+\tau$, respectively. When the process is stationary, the probability density $P_t^{t+\tau}$ does not change with t. hence

$$P_t^{t+\tau}(A_1, A_2) = P_0^\tau(A_1, A_2) \tag{4.186}$$

With Eqs.(4.186) and (4.183), Eq.(4.185) becomes

$$\lim_{T \to \infty} \frac{1}{T} \int_0^T A(t)A(t+\tau)\mathrm{d}t = \langle A(0)A(\tau) \rangle \tag{4.187}$$

This is substituted into Eq.(4.184) to give the desired expression (4.182).

[Comments]

From Eq.(4.182) one gets

$$C(0) = \langle A(0)^2 \rangle \tag{4.188}$$

which means that $C(0)$ is the ensemble average (mean value) of $A(0)^2$. Equation (4.182) also gives

$$C(\infty) = \langle A(0)A(\infty) \rangle \tag{4.189}$$

Physically, one can expect that $A(0)$ and $A(\tau)$ become uncorrelated as τ increases indefinitely. This means that $P_0(A_1, A_2)$ may be represented by

$$P_0^\tau(A_1, A_2) = P_0(A_1)P_\tau(A_2) \tag{4.190}$$

in the limit $\tau \to \infty$. Here $P_\tau(A_2)$ denotes the probability density for obtaining a value of A_2 for A from measurement at time τ. When the process is stationary, $P_\tau(A_2)$ may be equated to $P_0(A_2)$. Thus for $\tau \to \infty$ one obtains

$$P_0^\tau(A_1, A_2) = P_0(A_1)P_0(A_2) \tag{4.191}$$

Hence

$$\langle A(0)A(\infty) \rangle = \int_0^\infty \int_0^\infty P_0(A_1)P_0(A_2)A_1 A_2 \mathrm{d}A_1 \mathrm{d}A_2$$
$$= \left(\int_0^\infty P_0(A_1)A_1 \mathrm{d}A_1 \right)^2 = \langle A(0) \rangle^2 \tag{4.192}$$

Thus

$$C(\infty) = \langle A(0) \rangle^2 \tag{4.193}$$

From Eqs.(4.188) and (4.189) one finds that $C(\tau)$ changes from $\langle A(0)^2 \rangle$ to $\langle A(0) \rangle^2$ as τ increases from zero to infinity. Details of this τ dependence of the autocorrelation function are a very important subject of both theoretical and experimental studies, being a reflection of the physical process which gives rise to fluctuations of the quantity A with time.

Often it is convenient to use the normalized autocorrelation function $g(\tau)$ which ia defined by

$$g(\tau) = \frac{\langle A(0)A(\tau)\rangle - \langle A(0)\rangle^2}{\langle A(0)^2\rangle - \langle A(0)\rangle^2} \qquad (4.194)$$

This function varies from 1 to 0 as τ increases from zero to infinity.

[Problem D23]

According to the theory of dynamic scattering, the field (or first-order) autocorrelation function $G_1(\tau)$ for light scattered from a fixed volume containing N identical spherical particles is represented by

$$G_1(\tau) = \langle \sum_{j=1}^{N} A e^{-i\mathbf{q}\cdot\mathbf{r}_j(0)} \sum_{k=1}^{N} A e^{-i\mathbf{q}\cdot\mathbf{r}_k(\tau)} \rangle e^{-i\omega_0\tau} \qquad (4.195)$$

if the system is stationary. Here A is the time-independent scattering amplitude of each particle, ω_0 is the ferequency of the incident beam of light, $\mathbf{r}_k(\tau)$ is the position of the k-th particle at time τ, and $\mathbf{q}$ is the scattering vector. The symbol $\langle \cdots \rangle$ designates the ensemble average over all particles in the volume considered.

Show that if the concentration of the particles is very low, $G_1(\tau)$ is written

$$G_1(\tau) = NA^2 e^{-i\omega_0\tau} \int C_s(\mathbf{R},\tau) e^{i\mathbf{q}\cdot\mathbf{R}} d\mathbf{R} \qquad (4.196)$$

where $C_s(\mathbf{R},\tau)$ is the conditional probability density that a particle located at the origin at time 0 will be found at the position $\mathbf{R}$ at time τ.

[Solution D23]

For very dilute solutions the positions of the different scattering particles will be uncorrelated. Hence

$$\langle e^{-i\mathbf{q}\cdot\mathbf{r}_j(0)} \times e^{i\mathbf{q}\cdot\mathbf{r}_k(\tau)} \rangle = 0 \qquad (j \neq k) \qquad (4.197)$$

and Eq.(4.195) becomes

$$G_1(\tau) = A^2 \sum_{j=1}^{N} \langle e^{i\mathbf{q}\cdot[\mathbf{r}_j(\tau)-\mathbf{r}_j(0)]} \rangle e^{-i\omega_0\tau} \qquad (4.198)$$

Since the N particles are identical, Eq.(4.198) may be written (dropping the now unnecessary subscript j)

$$G_1(\tau) = A^2 N e^{-i\omega_0\tau} \langle \exp\{i\mathbf{q} \cdot [\mathbf{r}(\tau) - \mathbf{r}(0)]\} \rangle \qquad (4.199)$$

$\mathbf{r}(\tau) - \mathbf{r}(0)$ represents the displacement that a given particle suffers for a time interval τ. The definition of $C_s(\mathbf{R}, \tau)$ is

$$\exp\{i\mathbf{q} \cdot [\mathbf{r}(\tau) - \mathbf{r}(0)]\} = \int C_s(\mathbf{R}, \tau)\exp(i\mathbf{q} \cdot \mathbf{R})\mathrm{d}\mathbf{R} \qquad (4.200)$$

Substitution of Eq.(4.200) into Eq.(4.199) yields Eq.(4.196).

$C_s(\mathbf{R}, \tau)$ is called the "self" part of the van Hove space-time correlation function.

[Problem D24]

Find the power spectrum $S(\omega)$ of an autocorrelation function $C(\tau)$ which is represented by

$$c(\tau) = C(0)e^{-|\tau|/\tau_c} \qquad (4.201)$$

where τ_c is a positive characteristic time constant or relaxation time.

[Solution D24]

$$S(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} C(\tau)e^{i\omega\tau} d\tau \qquad (\omega \geq 0) \qquad (4.202)$$

Substituting Eq.(4.201), one gets

$$S(\omega) = \frac{1}{2\pi} \left(\int_0^{\infty} C(0)e^{-\tau/\tau_c + i\omega\tau} d\tau + \int_0^{\infty} C(0)e^{-\tau/\tau_c - i\omega\tau} d\tau \right)$$

$$= \frac{C(0)}{\pi} \int_0^{\infty} e^{-\tau/\tau_c} \cos\omega\tau d\tau \qquad (4.203)$$

Using the formula

$$\int_0^{\infty} e^{-ax} \cos(bx) dx = \frac{a}{a^2 + b^2} \qquad (a > 0) \qquad (4.204)$$

Eq.(4.203) becomes

$$S(\omega) = \frac{[C(0)/\pi]\tau_c^{-1}}{\tau_c^{-2} + \omega^2}$$

$$= \frac{[C(0)/\pi]\Gamma}{\Gamma^2 + \omega^2} \qquad (4.205)$$

where

$$\gamma = \frac{1}{\tau_c} \qquad (4.206)$$

The $S(\omega)$ represented by Eq.(4.205) is called single Lorentzian.

Let $\omega_{1/2}$ be the value of ω at which $S(\omega)$ becomes one-half of its value at $\omega = 0$. It follows from Eq.(4.205) that

$$\omega_{1/2} = \Gamma(= \tau_c^{-1}) \qquad (4.207)$$

Hence one can determine τ_c by knowing $\omega_{1/2}$ if $S(\omega)$ is a single Lorentzian. In general, $\omega_{1/2}$ is called the half width of a power spectrum.

[Problem D25]

The space-time correlation function $C_s(\mathbf{R}, \tau)$ defined in [Problem D23] or [Problem D24] satisfies the diffusion equation

$$\frac{\partial C_s}{\partial \tau} = D_T \nabla^2 C_s \qquad (4.208)$$

and the initial condition $C_s(\mathbf{R}, 0) = \delta(\mathbf{R})$, where D_T is the translational diffusion coefficient of the particle undergoing Brownian motion, and δ is the delta function. The solution to Eq.(4.208) subject to this initial condition is given by

$$C_s(\mathbf{R}, \tau) = \left(\frac{1}{4\pi D_T \tau}\right)^{3/2} \exp\left(-\frac{R^2}{4D_T \tau}\right) \qquad (4.209)$$

Derive the field autocorrelation function $G_1(\tau)$ and the power spectrum $S(\omega)$ for very dilute solution of identical spherical particles.

[Solution D25]

$G_1(\tau)$ is obtained by substituting Eq.(4.209) into Eq.(4.196) in [Problem D23]. Thus

$$\begin{aligned}
G_1(\tau) =& NA^2 e^{-i\omega_0 \tau} \left(\frac{1}{4\pi D_T \tau}\right)^{3/2} \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} \left\{ \exp\left(-\frac{R^2}{4D_T \tau}\right) \right. \\
& \times \left. e^{iqR\cos\theta} R^2 \sin\theta \,d\theta \,d\phi \,dR \right\}
\end{aligned} \qquad (4.210)$$

$$\begin{aligned}
\int\int\int \{\cdots\} &= \frac{2\pi}{iq} \int_0^{\infty} (e^{iqR} - e^{-iqR}) R \exp\left(-\frac{R^2}{4D_T \tau}\right) dR \\
&= \frac{4\pi}{q} \int_0^{\infty} R\sin(qR)\exp\left(-\frac{R^2}{4D_T \tau}\right) dR \\
&= \frac{2\pi}{q} \int_0^{\infty} \sin(q\sqrt{x})\exp\left(-\frac{x}{4D_T \tau}\right) dx \\
&= 8\pi^{3/2}(D_T \tau)^{3/2}\exp(-q^2 D_T \tau) \qquad (4.211)
\end{aligned}$$

where use has been made of the formula:

$$\int_0^\infty e^{-ax} \sin(b\sqrt{x}) dx = \frac{\sqrt{\pi} b}{2a^{3/2}} \exp\left(-\frac{b^2}{4a}\right) \tag{4.212}$$

Thus

$$G_1(\tau) = NA^2 e^{-i\omega_0\tau} e^{-q^2 D_T \tau} \tag{4.213}$$

The power spectrum $S(\omega)$ is calculated from

$$S(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} G_1(|\tau|) e^{i\omega\tau} d\tau \tag{4.214}$$

Substituting Eq.(4.213), one gets

$$\begin{aligned}
S(\omega) &= \frac{NA^2}{2\pi} \int_{-\infty}^{\infty} \exp(-q^2 D_T |\tau|) \exp(i\omega\tau - i\omega_0\tau) d\tau \\
&= \frac{NA^2}{\pi} \int_0^\infty \exp(-q^2 D_T \tau) \cos(\omega - \omega_0)\tau d\tau \\
&= \frac{(NA^2/\pi)(q^2 D_T)}{(\omega - \omega_0)^2 + (q^2 D_T)^2}
\end{aligned} \tag{4.215}$$

Since $G_1(0) = NA^2$, this may be written

$$S(\omega) = \frac{[G_1(0)/\pi](q^2 D_T)}{(\omega - \omega_0)^2 + (q^2 D_T)^2} \tag{4.216}$$

It folloows that

$$\frac{S(\omega)}{S(\omega_0)} = \frac{(q^2 D_T)^2}{(\Delta\omega)^2 + (q^2 D_T)^2} \qquad (\Delta\omega = \omega - \omega_0) \tag{4.217}$$

Hence $\Delta\omega_{1/2}$. the value of $\Delta\omega$ for which $S(\omega)/S(\omega_0) = 1/2$, is given by

$$\Delta\omega_{1/2} = q^2 D_T \tag{4.218}$$

which indicates that a plot of $\Delta\omega_{1/2}$ versus q^2 gives a straight line with a slope D_T.

[Problem D26]

For a stationary time variation of $E(t)$, the electric field of scattered light impinging the photomultiplier cathode as a detector one defines the normalized first-order (or heterodyne) and second-order (homodyne) autocorrelation functions $g_1(\tau)$ and $g_2(\tau)$ by

$$g_1(\tau) = \frac{\langle E^*(0)E(\tau)\rangle}{\langle I\rangle} \tag{4.219}$$

$$g_2(\tau) = \frac{\langle E^*(0)E(0)E^*(\tau)E(\tau)\rangle}{\langle I\rangle^2} \tag{4.220}$$

where E^* is the complex conjugate of E and $\langle I\rangle$ is the average field intensity defined by

$$\langle I\rangle = \langle E^*(0)E(0)\rangle \tag{4.221}$$

$\langle\cdots\rangle$ designates an appropriate ensemble average.

Show that if $E(t)$ obeys Gaussian statistics, $g_2(\tau)$ is related to $g_1(\tau)$ by

$$g_2(\tau) = |g_1(\tau)|^2 + 1 \tag{4.222}$$

This is called the Siegert relation.

[Solution D27]

Consider a quantity $G(\tau)$ defined by

$$G(\tau) = E^*(0)E(\tau)E(0)E^*(\tau) - \langle E^*(0)E(\tau)\rangle\langle E(0)E^*(\tau)\rangle \tag{4.223}$$

which varies irregularly but stationarily with time τ. From the condition of stationarity one can write the relation

$$\langle G(\tau)\rangle = \langle G(0)\rangle \tag{4.224}$$

which is equivalent to

$$\langle I\rangle^2 g_2(\tau) - \langle I\rangle^2|g_1(\tau)|^2 = \langle I\rangle^2 g_2(0) - \langle I\rangle^2 g_1(0)^2 \tag{4.225}$$

or

$$g_2(\tau) - |g_1(\tau)|^2 = g_2(0) - 1 \qquad (4.226)$$

Now

$$g_2(0) = \frac{\langle [E^*(0)E(0)]^2 \rangle}{\langle E^*(0)E(0) \rangle^2} \qquad (4.227)$$

Let $E(0)$ be expressed in terms of its real and imaginary parts as

$$E(0) = E_+(0) + iE_-(0) \qquad (4.228)$$

Then

$$\begin{aligned}
\langle [E^*(0)E(0)]^2 \rangle &= \langle E_+(0)^4 \rangle + 2\langle E_+(0)^2 E_-(0)^2 \rangle + \langle E_-(0)^4 \rangle \\
&= 2[\langle E_+(0)^4 \rangle + \langle E_+(0)^2 E_-(0)^2 \rangle] \qquad (4.229)
\end{aligned}$$

$$\langle E^*(0)E(0) \rangle^2 = 4\langle E_+(0)^2 \rangle^2 \qquad (4.230)$$

where one has considered the fact that $\langle E_+(0)^2 \rangle = \langle E_-(0)^2 \rangle$ and $\langle E_+(0)^4 \rangle = \langle E_-(0)^4 \rangle$.

The condition that $E(t)$ obeys Gaussian statistics means that $E_+(0)$ has the probability of occurence given by

$$P(E_+(0)) = \frac{1}{\sqrt{2\pi\langle E_+(0)^2 \rangle}} \exp\left[-\frac{E_+(0)^2}{2\langle E_+(0)^2 \rangle} \right] \qquad (4.231)$$

and that the same expression can be written for $P(E_-(0))$. Since $E_+(0)$ and $E_-(0)$ are statistically independent,

$$\langle E_+(0)^2 E_-(0)^2 \rangle = \int_{-\infty}^{\infty} x^2 P(x) \mathrm{d}x \int_{-\infty}^{\infty} y^2 P(y) \mathrm{d}y \qquad (4.232)$$

with $x = E_+(0)$ and $y = E_-(0)$. With Eq.(4.231) for P, Eq.(4.232) gives

$$\langle E_+(0)^2 E_-(0)^2 \rangle = \langle E_+(0)^2 \rangle^2 \qquad (4.233)$$

where the fact that $\langle E_+(0)^2 \rangle = \langle E_-(0)^2 \rangle$ has been used. Next

$$\langle E_+(0)^2 \rangle = \int_{-\infty}^{\infty} x^2 P(x) \mathrm{d}x = 3\langle E_+(0)^2 \rangle^2 \qquad (4.234)$$

Hence

$$\langle [E^*(0)E(0)]^2 \rangle = 8\langle E_+(0)^2 \rangle^2 \qquad (4.235)$$

which, together with Eq.(4.230), is introduced into Eq.(4.227) to give

$$g_2(0) = 2 \qquad (4.236)$$

Thus Eq.(4.226) becomes

$$g_2(\tau) = |g_1(\tau)|^2 + 1 \qquad (4.237)$$

which is the Siegert relation.

[Comments]

  In practice, the Siegert relation is often used to obtain $|g_1(\tau)|$ from homodyne-beat light scattering experiments which allow $g_2(\tau)$ to be evaluated.

[Problem D27]

Prove that the intrinsic viscosity $[\eta]$ of a mixture of macromolecules in a given solvent is expressed by

$$[\eta] = \sum_{i=1}^{N} [\eta]_i w_i \qquad (4.238)$$

where $[\eta]_i$ ia the intrinsic viscosity of the i-th component in the given solvent, w_i is the weight fraction of the same component, and N is the number of the components in the mixture.

[Solution D27]

At very low concentrations c of the mixture, the rotations of solute molecules in shear flow do not interfere with each other, and the energy dissipations due to them are additive. Then the specific viscosity of the mixture η_{sp} becomes the sum of the intrinsic viscosities of the individual components, i.e.,

$$\eta_{sp} = \sum_{i=1}^{N} (\eta_{sp})_i \qquad (4.239)$$

because specific viscosity is a measure of the rate of energy dissipation due to the viscous flow of a solute component. For very small c, and hence for small concentrations c_1 of the individual components we may write

$$(\eta_{sp})_i = [\eta]_i c_1 \qquad (i = 1, 2, \cdots, N) \qquad (4.240)$$

Substitution of Eq.(4.240) into Eq.(4.239), followed by division by c, gives

$$\frac{\eta_{sp}}{c} = \sum_{i=1}^{N} [\eta]_i \frac{c_i}{c} \qquad (4.241)$$

If c is allowed to approach zero, Eq.(4.241) tends to the required relation (4.238), since $\eta_{sp}/c \to [\eta]$ and $c_i/c \to w_i$ as $c \to 0$.

[Problem D28]

Evaluate the coefficient K and the exponent ν of the Mark-Houwink-Sakurada equation from the intrinsic viscosity $[\eta]$ data given below for polyisobutylene.

$M_w \times 10^{-6}$	$[\eta]/g^{-1}dl$ n-heptane 25.0°C	$[\eta]/g^{-1}dl$ benzene 25.0°C
0.160	0.712	0.451
0.252	0.945	0.555
0.391	1.30	0.705
0.815	2.14	1.03
1.46	3.27	1.34
3.19	5.75	2.01
4.70	7.48	2.40

[Solution D28]

In n-heptane at 25.0 °C,

$$[\eta] = 1.63 \times 10^{-1} M_w^{0.70} \qquad (4.242)$$

In benzene at 25.0 °C,

$$[\eta] = 1.12 \times 10^{-3} M_w^{0.50} \qquad (4.243)$$

where $[\eta]$ is given in dl/g.

[Problem D29]

Evaluate the conformation factor σ and the binary cluster integral β for polyisobutylene in n-heptane at 25.0 °C from the data given in [Problem D28]. The conformation factor σ is defined by

$$\sigma = \left(\frac{\langle S^2 \rangle_0}{\langle S^2 \rangle_{0f}} \right)^{1/2} \tag{4.244}$$

where $\langle S^2 \rangle_{0f}$ is the mean square redius of gyration for the unperturbed freely rotating chain. Use the Stockmayer-Fixman plot and the equation

$$\frac{[\eta]}{M_w^{1/2}} = K + 0.346\Phi_0(\beta/M_0^2)M_w^{1/2} \quad ([\eta]/[\eta]_0 < 1.6) \tag{4.245}$$

$$K = \Phi_0 \left(\frac{6\langle S^2 \rangle_0}{M_w} \right)^{3/2} \tag{4.246}$$

where Φ_0 is Flory's viscosity constant and M_0 is the molecular weight of monomer. Assume 2.65×10^{23} (cgs) for Φ_0.

[Solution D29]

From the intercept at $M_w^{1/2} = 0$ of the Stockmayer-Fixman plot, one gets

$$\frac{\langle S^2 \rangle_0}{M_w} = 9.39 \times 10^{-18} \ \text{cm}^2 \tag{4.247}$$

With $\langle S^2 \rangle_{0f}/M = 2.79 \times 10^{-18} \ \text{cm}^2$,

$$\sigma = 1.83 \tag{4.248}$$

The binary cluster integral β of s polyisobutylene monomer in n-heptane at 25.0 °C is estimated as $14 \times 10^{-24} \ \text{cm}^3$, from the initial slope of the plot.

[Problem D30]

Show that the radius a or the molecular weight M of rigid spherical particles may be evaluated from a quantity similar to the Flory-Mandelkern-Scheraga parameter β, by using the translational diffusion coefficient D_0 at infinite dilution in place of the intrinsic sedimentation coefficient $[s_0]$.

[Solution D30]

If $[\eta]$ is expressed in dl/g, β is defined by

$$\beta = \frac{N_A \eta_0 [s_0][\eta]^{1/3}}{(100)^{1/3} M^{2/3}} \tag{4.249}$$

For rigid spheres

$$[s_0] = \frac{M}{6\pi\eta_0 N_A a} = \frac{D_0 M}{RT} \tag{4.250}$$

$$[\eta] = 2.5 \frac{(4/3)\pi a^3 N_A}{M} \tag{4.251}$$

[Problem D31]

One-dimensional diffusion of a homogeneous solute in a single solvent is governed by the differential equation

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}[D(c)\frac{\partial c}{\partial x}] \tag{4.252}$$

where t is the time, x is the distance in the direction of diffusion, c is the mass concentration of the solute, and $D(c)$ is a function of c called the (mutual) diffusion coefficient for the binary solution considered. Experimentalists are interested in evaluating $D(c)$ from measurement of the distribution of c or $\partial c/\partial x$ (concentration gradient) in a diffusion cell as a function of time. The experiment for this purpose is usually done by allowing solute molecules to diffuse from the initial inhomogeneous distribution represented by

$$c = c^0 \quad (-\infty < x < 0, t = 0) \tag{4.253}$$

$$c = 0 \quad (0 < x < \infty, t = 0) \tag{4.254}$$

where c^0 is the mass concentration of the solute in the given solution.

(1) Show that Eq.(4.252) and condition (4.253) and (4.254) are transformed to

$$-2z\frac{dc}{dz} = \frac{d}{dz}[D(c)\frac{dc}{dz}] \tag{4.255}$$

$$c = c^0 \quad (z = -\infty) \tag{4.256}$$

$$c = 0 \quad (z = \infty) \tag{4.257}$$

where

$$z = \frac{x}{2t^{1/2}} \tag{4.258}$$

(Boltzmann's transformation)

(2) Show that if D is independent of c, Eq.(4.255) subject to condition (4.256) and (4.257) can be solved to give

$$\frac{\partial c}{\partial x} = -\frac{c^0}{2(\pi Dt)^{1/2}}\exp\left(-\frac{x^2}{4Dt}\right) \tag{4.259}$$

(3) Show that plots of $(A/H)^2$ versus t give a straight line whose slope is equal to $4\pi D$, where A is the area under the $\partial c/\partial x$ versus x curve, and H is the maximum height of the curve.

[Solution D31]

(1)

$$\frac{\partial}{\partial t} = \frac{\partial z}{\partial t}\frac{\mathrm{d}}{\mathrm{d}z} = -\frac{x}{4t^{3/2}}\frac{\mathrm{d}}{\mathrm{d}z} \tag{4.260}$$

$$\frac{\partial}{\partial x} = \frac{1}{2t^{1/2}}\frac{\mathrm{d}}{\mathrm{d}z}, \quad \frac{\partial}{\partial x}[D(c)\frac{\partial}{\partial x}] = \frac{1}{4t}\frac{\mathrm{d}}{\mathrm{d}z}[D(c)\frac{\mathrm{d}}{\mathrm{d}z}] \tag{4.261}$$

Hence Eq.(4.252) becomes

$$-\frac{x}{4t^{3/2}}\frac{\mathrm{d}c}{\mathrm{d}z} = \frac{1}{4t}\frac{\mathrm{d}}{\mathrm{d}z}[D(c)\frac{\mathrm{d}c}{\mathrm{d}z}] \tag{4.262}$$

or

$$-2z\frac{\mathrm{d}c}{\mathrm{d}z} = \frac{\mathrm{d}}{\mathrm{d}z}[D(c)\frac{\mathrm{d}c}{\mathrm{d}z}] \tag{4.263}$$

which is Eq.(4.255). For $x > 0$, $z \to \infty$ as $t \to 0$, while for $x < 0$, $z \to -\infty$ as $t \to 0$. Therefore condition (4.253) and (4.254) is equivalent to condition (4.256) and (4.257).

(2) If D is independent of c, Eq.(4.263) is written

$$-2z\frac{\mathrm{d}c}{\mathrm{d}z} = D\frac{\mathrm{d}^2c}{\mathrm{d}z^2} \tag{4.264}$$

or

$$-2z = D\frac{\mathrm{d}^2c/\mathrm{d}z^2}{\mathrm{d}c/\mathrm{d}z} = D\frac{\mathrm{d}}{\mathrm{d}z}\left(\ln\frac{\mathrm{d}c}{\mathrm{d}z}\right) \tag{4.265}$$

Integration gives

$$-z^2 + \alpha = D\ln\left(\frac{\mathrm{d}c}{\mathrm{d}z}\right) \tag{4.266}$$

or

$$\frac{\mathrm{d}c}{\mathrm{d}z} = \beta\mathrm{e}^{-z^2/D} \tag{4.267}$$

where α and β are integration constants. Equation (4.267) is integrated to give

$$c = \beta \int^z e^{-z^2/D} dz + \gamma \qquad (4.268)$$

where γ is a constant. Applying condition (4.256) and (4.257), Eq.(4.268) yields

$$c = c^0 \left[1 - \frac{1}{\sqrt{\pi}} \int_{-\infty}^{z/\sqrt{D}} e^{-y^2} dy \right] \qquad (4.269)$$

where one has used the formula

$$\int_{-\infty}^{\infty} e^{-y^2} dy = \sqrt{\pi} \qquad (4.270)$$

From Eq.(4.269) one gets

$$\frac{\partial c}{\partial x} = -\frac{c^0}{\sqrt{\pi D}} e^{-z^2/D} \frac{\partial z}{\partial x} = -\frac{c^0}{2\sqrt{\pi Dt}} e^{-x^2/(4Dt)} \qquad (4.271)$$

which is Eq.(4.259).

(3) One finds from Eq.(4.271) that

$$A = | \int_{-\infty}^{\infty} \frac{\partial c}{\partial x} dx | = \frac{c^0}{2\sqrt{\pi Dt}} \int_{-\infty}^{\infty} e^{-x^2/4Dt} dx$$

$$= \frac{c^0}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-y^2} dy = c^0 \qquad \left(y = \frac{x}{2\sqrt{Dt}} \right) \qquad (4.272)$$

$$H = | \left(\frac{\partial c}{\partial x} \right)_{\text{max}} | = \frac{c^0}{2\sqrt{\pi Dt}} \qquad (4.273)$$

Hence

$$\left(\frac{A}{H} \right)^2 = 4\pi Dt \qquad (4.274)$$

which indicates that $(A/H)^2$ plotted against t gives a straight line with a slope equal to $4\pi D$. This theoretical consequence provides a convenient way of evaluating D, when D is independent of c. One usually calls it the height-area ratio method for D.

[Problem D32]

When the solute is heterogeneous, consisting of q different components, the height-area ratio method yields a certain average diffusion coefficient $\langle D \rangle$. Obtain the expression for $\langle D \rangle$ in terms of the diffusion coefficients of individual solute components.

[Solution D32]

If the mass concentration and diffusion coefficient (assumed to be concentration-independent) are denoted by c_i and D_i, respectively, one obtains

$$\frac{\partial c_i}{\partial x} = -\frac{c^0}{2\sqrt{piD_it}}\exp\left(-\frac{x^2}{4D_it}\right) \tag{4.275}$$

(See Eq.(4.271) in [Problem D31]). Here c_i^0 is the mass concentration of component i in the initial given solution. From Eq.(4.275) it follows that

$$A = \sum_{i=1}^{q} A_i = \sum_{i=1}^{q} c_i^0 \tag{4.276}$$

$$H = \sum_{i=1}^{q} H_i = \sum_{i=1}^{q} \frac{c_i^0}{2\sqrt{\pi D_it}} \tag{4.277}$$

where A_i and H_i denote the area and maximum height of the concentration gradient curve ($\partial c_i / \partial x$ versus x) for component i. Hence

$$\left(\frac{A}{H}\right) = \left[\frac{\sum_{i=1}^{q} c_i^0}{\sum_{i=1}^{q}(c_i^0/2\sqrt{\pi D_it})}\right]^2$$

$$= 4\pi t\left(\frac{\sum_{i=1}^{q} g_i}{\sum_{i=1}^{q} g_i/\sqrt{D_i}}\right)^2 \tag{4.278}$$

where g_i is the weight fraction of component i in the given solution, i.e., $g_i = c_i^0/(c_1^0 + c_2^0 + \cdots + c_q^0)$. If Eq.(4.278) is equated to $4\pi t\langle D \rangle$ and if $\sum_{i=1}^{q} g_i = 1$ is considered, one finds

$$\langle D \rangle = \left(\sum_{i=1}^{q} \frac{g_i}{\sqrt{D_i}}\right)^{-2} \tag{4.279}$$

which is the desired expression for $\langle D \rangle$.

[Comments]

When the solute is a homologous series of flexible linear polymers, one may empirically assume the form

$$D_i = K M_i^{-\alpha} \tag{4.280}$$

where M_i is the molecular weight of component i, and K and α are empirical constants depending on the polymer species, the solvent, and temperature. In this case, the measurement of $\langle D \rangle$ allows evaluation of an average molecular weight M_D

$$M_D = \left(\sum_{i=1}^{q} g_i M_i^{\alpha/2} \right)^{2/\alpha} \tag{4.281}$$

For example, when the solvent is a theta solvent for the polymer, $\alpha = 1/2$, so that

$$M_D = \left(\sum_{i=1}^{q} g_i M_i^{1/4} \right)^{4} \tag{4.282}$$

[Problem D33]

The average number density of molecules in a small volume V of a one-component liquid equilibriated at temperature T and pressure p is denoted by $\langle \nu \rangle$. Then

$$\langle \nu \rangle \kappa k t - 1 = \langle \nu \rangle \left[\frac{1}{V} \int \int_V g_2(i,j) \mathrm{d}(i) \mathrm{d}(j) \right] \qquad (4.283)$$

where κ is the isothermal compressibility of the liquid, and $g_2(i,j)$ is the pair-correlation function. Derive this Ornstein-Zernike relation.

[Solution D33]

Let thew total molecules in the entire system be numbered $1, 2, \cdots, N_t$ and let the instantaneous position of the i-th molecule be denoted by $\mathbf{r}_i$. Then the number of molecules, N, in the small volume V is expressed by

$$N = \sum_{i=1}^{N_t} m(\mathbf{r}_i) \qquad (4.284)$$

if one uses a position function $m(\mathbf{r}_i)$ defined as

$$m(\mathbf{r}) = 1 \quad (\mathbf{r} \text{ in } V) \qquad (4.285)$$

$$m(\mathbf{r}) = 0 \quad (\text{otherwise}) \qquad (4.286)$$

Noting the property $[m(\mathbf{r})]^2 = m(\mathbf{r})$, one gets

$$N^2 = \sum_{i=1}^{N_t} m(\mathbf{r}_i) + \sum_{i=1}^{N_t} \sum_{j=1, i \neq j}^{N_t} m(\mathbf{r}_i) m(\mathbf{r}_j) \qquad (4.287)$$

In terms of Eq.(4.284) and the one-body distribution function $F_1(i)$, the statistical average of N, $\langle N \rangle$, is expressed as

$$\begin{aligned}
\langle N \rangle &= \frac{1}{V_t} \sum_{i=1}^{N_t} \int_{V_t} m(\mathbf{r}_i) F_1(i) \mathrm{d}(i) \\
&= \frac{N_t}{V_t} \int_V F_1(i) \mathrm{d}(i) \\
&= \frac{N_t V}{V_t} \qquad (4.288)
\end{aligned}$$

where V_t is the volume of the entire system.

Next, using Eq.(4.287) and the two-body distribution function $F_2(i,j)$, $\langle N^2 \rangle$ may be expressed as

$$
\begin{aligned}
\langle N^2 \rangle &= \langle N \rangle + \frac{1}{V_t^2} \sum_{i=1, i \neq j}^{N_t} \sum_{j=1}^{N_t} \int \int_{V_t} m(\mathbf{r}_i) m(\mathbf{r}_j) F_2(i,j) \mathrm{d}(i) \mathrm{d}(j) \\
&= \langle N \rangle + \frac{N_t^2}{V_t^2} \int \int_V F_2(i,j) \mathrm{d}(i) \mathrm{d}(j) \qquad (4.289)
\end{aligned}
$$

where $N_t - 1$ is approximated by N_t. In terms of $\langle \nu \rangle$ $(= \langle N \rangle / V)$ and $\langle \nu^2 \rangle$ $(= \langle N^2 \rangle / V^2)$, this equation is transformed to

$$
\langle \nu^2 \rangle - \langle \nu \rangle^2 = \frac{\langle \nu \rangle}{V} \left\{ 1 + \frac{\langle \nu \rangle}{V} \left[\int_V F_2(i,j) \mathrm{d}(i) \mathrm{d}(j) - V^2 \right] \right\} \qquad (4.290)
$$

where Eq.(4.288) has been used. Since

$$
\frac{1}{V} \int_V F_1(i) \mathrm{d}(i) = 1 \qquad (4.291)
$$

and since $\langle (\Delta \nu)^2 \rangle = \langle (\nu - \langle \nu \rangle)^2 \rangle = \langle \nu^2 \rangle - \langle \nu \rangle^2$, one obtains from Eq.(4.290)

$$
\begin{aligned}
\langle (\Delta \nu)^2 \rangle &= \frac{\langle \nu \rangle}{V} \left(1 + \frac{\langle \nu \rangle}{V} \left\{ \int \int_V [F_2(i,j) - F_1(i) F_1(j)] \mathrm{d}(i) \mathrm{d}(j) \right\} \right) \\
&= \frac{\langle \nu \rangle}{V} \left(1 + \frac{\langle \nu \rangle}{V} \int \int_V g_2(i,j) \mathrm{d}(i) \mathrm{d}(j) \right) \qquad (4.292)
\end{aligned}
$$

If this is compared to the known expression

$$
\langle (\Delta \nu)^2 \rangle = \frac{\langle \nu \rangle^2 \kappa k T}{V} \qquad (4.293)
$$

one finds that

$$
\langle \nu \rangle \kappa k T - 1 = \langle \nu \rangle \left[\frac{1}{V} \int \int_V g_2(i,j) \mathrm{d}(i) \mathrm{d}(j) \right] \qquad (4.294)
$$

which is the Ornstein-Zernike relation.

[Problem D34]

Let $(x_1, x_2, \cdots, x_p)$ be a set of p non-negative variable subjected to the constraint

$$\sum_{i=1}^{p} x_i = n \tag{4.295}$$

It is assumed that all of these sets appear at equal probability. Show that if $\alpha_1, \alpha_2, \cdots, \alpha_p > -1$,

$$\langle x_1^{\alpha_1} x_2^{\alpha_2} \cdots x_p^{\alpha_p} \rangle_{np} = \frac{\Gamma(\alpha_1 + 1)\Gamma(\alpha_2 + 1)\cdots\Gamma(\alpha_p + 1)\gamma(p)}{\Gamma(\alpha_1 + \alpha_2 + \cdots + \alpha_p + p)} n^{\alpha_1 + \alpha_2 + \cdots + \alpha_p} \tag{4.296}$$

where $\langle \cdots \rangle$ denotes the average under fixed n and p.

[Solution D34]

For simplicity the average to be evaluated is designated by A. Then one can write

$$A = \frac{\int_0^n dx_{p-1} \int_0^{n-x_{p-1}} dx_{p-2} \cdots \int_0^{n-\sum_{i=2}^{p-1} x_i} x_1^{\alpha_1} x_2^{\alpha_2} \cdots (n - \sum_{k=1}^{p-1} x_k)^{\alpha_p} dx_1}{\int_0^n dx_{p-1} \int_0^{n-x_{p-1}} dx_{p-2} \cdots \int_0^{n-\sum_{i=2}^{p-1}} dx_1}$$

$$= n^{\alpha_1 + \alpha_2 + \cdots + \alpha_p} I / J \tag{4.297}$$

where

$$I = \int_0^1 d\xi_{p-1} \int_0^{1-\xi_{p-}} d\xi_{p-2} \cdots \int_0^{1-\sum_{i=2}^{p-1} \xi_i} \xi_1^{\alpha_1} \xi_2^{\alpha_2} \cdots (1 - \sum_{k=1}^{p-1} \xi_k)^{\alpha_p} d\xi_1 \tag{4.298}$$

$$J = \int_0^1 d\xi_{p-1} \int_0^{1-\xi_{p-1}} d\xi_{p-2} \cdots \int_0^{1-\sum_{i=1}^{p-1} \xi_i} d\xi_1 \tag{4.299}$$

Since J is equal to I for $\alpha_1 = \alpha_2 = \cdots = \alpha_p = 0$, one may calculate I only.

Now

$$I = \int_0^1 \xi_{p-1}^{\alpha_{p-1}} d\xi_{p-1} \int_0^{1-\xi_{p-1}} \xi_{p-2}^{\alpha_{p-2}} d\xi_{p-2} \cdots \int_0^{t_2} \xi_1^{\alpha_1} (t_2 - \xi_1)^{\alpha_p} d\xi_1 \tag{4.300}$$

with $t_2 = 1 - \sum_{i=2}^{p-1} \xi_i$. Since if α_1 and $\alpha_p > -1$

$$\int_0^{t_2} \xi_1^{\alpha_1} 8t_2 - \xi_1)^{\alpha_p} d\xi_1 = (t_2)^{\alpha_1 + \alpha_p + 1} B(\alpha_1 + 1, \alpha_p + 1) \qquad (4.301)$$

where B denotes the beta function, I becomes

$$I = \int_0^1 \xi_{p-1}^{\alpha_{p-1}} d\xi_{p-1} \cdots \int_0^{t_3} \xi_2^{\alpha_2} (t_3 - \xi_2)^{\alpha_1 + \alpha_p + 1} B(\alpha_1 + 1, \alpha_p + 1) d\xi_2 \tag{4.302}$$

with $t_3 = 1 - \sum_{i=3}^{p-1} \xi_i = t_2 + \xi_2$. Applying Eq.(4.301), Eq.(4.302) becomes

$$I = \left[\int_0^1 \xi_{p-1}^{\alpha_{p-1}} d\xi_{p-1} \cdots \int_0^{t_4} \xi_3^{\alpha_3} (t_4 - \xi_3)^{\alpha_1 + \alpha_2 + \alpha_p + 2} d\xi_3 \right] \\ \times B(\alpha_1 + 1, \alpha_p + 1) B(\alpha_2 + 1, \alpha_1 + \alpha_p + 2) \tag{4.303}$$

Proceeding in a similar way, one finally gets

$$\begin{aligned} I =& B(\alpha_1 + 1, \alpha_p + 1) B(\alpha_2 + 1, \alpha_1 + \alpha_p + 2) B(\alpha_3 + 1, \alpha_1 + \alpha_2 + \alpha_p + 3) \\ & \times \cdots B(\alpha_{p-1} + 1, \alpha_1 + \alpha_2 + \cdots + \alpha_{p-2} + \alpha_p + p - 1) \\ =& \frac{\Gamma(\alpha_1 + 1)\Gamma(\alpha_2 + 1) \cdots \Gamma(\alpha_p + 1)}{\Gamma(\alpha_1 + \alpha_2 + \cdots + \alpha_{p-1} + \alpha_p + p)} \end{aligned} \tag{4.304}$$

Hence

$$J = \frac{\Gamma(1)\Gamma(1) \cdots \Gamma(1)}{\Gamma(p)} = \frac{1}{\Gamma(p)} \tag{4.305}$$

Therefore, Eq.(4.297), with Eqs.(4.304) and (4.305), gives

$$A = n^{\alpha_1 + \alpha_2 + \cdots + \alpha_p} \frac{\Gamma(p)\Gamma(\alpha_1 + 1)\Gamma(\alpha_2 + 1) \cdots \Gamma(\alpha_p + 1)}{\Gamma(\alpha_a + \alpha_2 + \cdots + \alpha_p + p)} \tag{4.306}$$

which is the desired formula. This formula finds its useful applications in the statistics of branched chains.

[Problem D35]

When $\Psi(x_1, x_2, \cdots, x_n)$ defined by

$$\Psi = \sum_{i=1}^{n} \sum_{j=1}^{n} a_{ij} x_i x_j \qquad (a_{ij} = a_{ji}) \qquad (4.307)$$

is positive definite, i.e., greater than zero for any set of real $x_1, x_2, \cdots, x_n$, evaluate

$$I = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-\beta\Psi/2} dx_1 dx_2 \cdots dx_n \qquad (4.308)$$

$$I' = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} x_i x_j e^{-\beta\Psi/2} dx_1 dx_2 \cdots dx_n \qquad (4.309)$$

where $\beta = 1/(kT) > 0$.

[Solution D35]

Define Matrices $\mathbf{x}$ and $\mathbf{A}$ by

$$\mathbf{x} \equiv \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{pmatrix} \qquad \mathbf{A} \equiv \begin{pmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n} \\ \cdots & \cdots & \cdots & \cdots \\ a_{n1} & a_{n2} & \cdots & a_{nn} \end{pmatrix} \qquad (4.310)$$

Then Ψ may be written

$$\Psi = \mathbf{x}^T \mathbf{A} \mathbf{x} \qquad (4.311)$$

where $\mathbf{x}^T$ is the transpose of $\mathbf{x}$, i.e.,

$$\mathbf{x}^T = (x_1 \ \ x_2 \ \ \cdots \ \ x_n) \qquad (4.312)$$

Because $\mathbf{A}$ is symmetric $(a_{ij} = a_{ji})$ it can be transformed into a diagonal matrix Λ by an appropriate orthogonal matrix $\mathbf{L}$ [which is a matrix such that $\mathbf{L}^T\mathbf{L} = \mathbf{L}\mathbf{L}^T = \mathbf{E}$ (unit matrix)]. Thus

$$\mathbf{L}^T \mathbf{A} \mathbf{L} = \Lambda = \begin{pmatrix} \lambda_1 & 0 & \cdots & 0 \\ 0 & \lambda_2 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & \lambda_n \end{pmatrix} \qquad (4.313)$$

Let a new column vector $\boldsymbol{\xi}$

$$\boldsymbol{\xi} = \begin{pmatrix} \xi_1 \\ \xi_2 \\ \vdots \\ \xi_n \end{pmatrix} \tag{4.314}$$

be introduced by the transformation

$$\boldsymbol{\xi} = \mathbf{L}^T \mathbf{x} \tag{4.315}$$

Since $\mathbf{L}$ is orthgonal, this gives

$$\mathbf{x} = \mathbf{L}\boldsymbol{\xi} \tag{4.316}$$

This is introduced into Eq.(4.311) to give

$$\Psi = (\mathbf{L}\boldsymbol{\xi})^T \mathbf{A}(\mathbf{L}\boldsymbol{\xi}) = \boldsymbol{\xi}^T \mathbf{L}^T \mathbf{A} \mathbf{L}\boldsymbol{\xi} = \boldsymbol{\xi}^T \Lambda \boldsymbol{\xi} = \sum_{i=1}^{n} \lambda_i \xi_i^2 \tag{4.317}$$

where Eq.(4.313) has been inserted. The Jacobian J for the transformation (4.316) is

$$J = \begin{vmatrix} \frac{\partial x_1}{\partial \xi_1} & \frac{\partial x_1}{\partial \xi_2} & \cdots & \frac{\partial x_1}{\partial \xi_n} \\ \frac{\partial x_2}{\partial \xi_1} & \frac{\partial x_2}{\partial \xi_2} & \cdots & \frac{\partial x_2}{\partial \xi_n} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial x_n}{\partial \xi_1} & \frac{\partial x_n}{\partial \xi_2} & \cdots & \frac{\partial x_n}{\partial \xi_n} \end{vmatrix} = |\mathbf{L}| \tag{4.318}$$

Since $|\mathbf{L}^T| = |\mathbf{L}|$ and $|\mathbf{E}| = 1$, it follows from $\mathbf{L}^T \mathbf{L} = \mathbf{E}$ that $|\mathbf{L}| = 1$. Thus $J = 1$. Hence, with Eq.(4.316), I is written

$$\begin{aligned} I &= \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-(\beta/2) \sum_{i=1}^{n} \lambda_i \xi_i^2} d\xi_1 d\xi_2 \cdots d\xi_n \\ &= \prod_{i=1}^{n} \int_{-\infty}^{\infty} e^{-\beta \xi_i^2 \lambda_i/2} d\xi_i \\ &= \left(\frac{2\pi}{\beta}\right)^{n/2} \prod_{i=1}^{n} \left(\frac{1}{\lambda_i}\right)^{1/2} \end{aligned} \tag{4.319}$$

Now, $\lambda_1, \lambda_2, \cdots, \lambda_n$ are the roots of the characteristic equation

$$|\mathbf{A} - \lambda\mathbf{E}| = \begin{vmatrix} a_{11} - \lambda & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} - \lambda & \cdots & a_{2n} \\ \cdots & \cdots & \cdots & \cdots \\ a_{n1} & a_{n2} & \cdots & a_{nn} - \lambda \end{vmatrix} = 0 \qquad (4.320)$$

One of the root-coefficient relations for algebric equations yields

$$\lambda_1\lambda_2\cdots\lambda_n = |\mathbf{A}| \qquad (4.321)$$

Thus Eq.(4.319) may be written

$$I = \left(\frac{2\pi}{\beta}\right)^{n/2} |\mathbf{A}|^{-1/2} \qquad (4.322)$$

From Eq.(4.316) one gets

$$x_i = \sum_{k=1}^{n} L_{ik}\xi_k \qquad (4.323)$$

where L_{ik} denotes the (i, k) element of $\mathbf{L}$. With Eqs.(4.317) and (4.323), I' may be written

$$\begin{aligned} I' &= \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \left(\sum_{k=1}^{n} L_{ik}\xi_k \sum_{h=1}^{n} L_{jh}\xi_h\right) \\ &\quad \times \exp\left(-\beta/2 \sum_{m=1}^{n} \lambda_m \xi_m^2\right) \mathrm{d}\xi_1 \mathrm{d}\xi_2 \cdots \mathrm{d}\xi_n \\ &= \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \left(\sum_{k=1}^{n} L_{ik}L_{jk}\xi_k^2\right) \\ &\quad \times \exp\left(-\beta/2 \sum_{m=1}^{n} \lambda_m \xi_m^2\right) \mathrm{d}\xi_1 \mathrm{d}\xi_2 \cdots \mathrm{d}\xi_n \\ &= \sum_{k=1}^{n} L_{ik}L_{jk} \frac{1}{\beta\lambda_k} \left(\frac{2\pi}{\beta}\right)^{n/2} \prod_{m=1}^{n} \left(\frac{1}{\lambda_m}\right)^{1/2} \\ &= \frac{1}{\beta|\mathbf{A}|^{1/2}} \left(\frac{2\pi}{\beta}\right)^{n/2} \sum_{k=1}^{n} \frac{L_{ik}L_{jk}}{\lambda_k} \qquad (4.324) \end{aligned}$$

where Eq.(4.321) has been used.

It follows from Eq.(4.313) that

$$\mathbf{L}\Lambda^{-1}\mathbf{L}^T\mathbf{A}\mathbf{L}\mathbf{L}^T\mathbf{A}^{-1} = \mathbf{L}\Lambda^{-1}\Lambda\mathbf{L}^T\mathbf{A}^{-1} \tag{4.325}$$

or

$$\mathbf{L}\Lambda^{-1}\mathbf{L}^T = \mathbf{A}^{-1} \tag{4.326}$$

Because

$$\Lambda^{-1} = \begin{pmatrix} \lambda_1^{-1} & 0 & \cdots & 0 \\ 0 & \lambda_2^{-1} & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & \lambda_n^{-1} \end{pmatrix} \tag{4.327}$$

Eq.(4.326) is written

$$\sum_{k=1}^{n} \frac{L_{jk}L_{ik}}{\lambda_k} = \frac{\Delta_{ij}}{|\mathbf{A}|} \tag{4.328}$$

where Δ_{ij} is the cofactor for the (i,j) element of $\mathbf{A}$. By virtue of Eq.(4.328), one can put Eq.(4.324) in the form:

$$I' = \frac{\Delta_{ij}}{\beta|\mathbf{A}|^{3/2}} \left(\frac{2\pi}{\beta}\right)^{n/2} \tag{4.329}$$

Equations (4.322) and (4.329) are the final results, which express I and I' in terms of β and the elements of $\mathbf{A}$.

[Comments]

The development presented above assumes that all the roots λ_1, λ_2, $\cdots$, λ_n are real and positive. This is justified by the condition that Ψ is positive definite.

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