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Statistical Mechanical Theory of Semidilute Polymer Solutions†

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ABSTRACT: Semidilute poor solvent polymer solution is investigated by the method of Ursell–Mayer cluster expansion. Series and ring-form diagrams are considered for polymers to calculate the osmotic equation of state of the solution, and this equation is shown to be the same as obtained by Edwards by a different method. The static structure factor, which is the Fourier transform of the correlation function of the system, is also calculated in the same approximation; the first term of this factor corresponds to the Jannink–de Gennes result by the random phase approximation. The osmotic compressibility equation, which connects the osmotic pressure and the correlation function, is considered to check the consistency of our results and confirm the validity of the present approximation. Effects of the excluded volume on the equation of state and on the structure factor are investigated up to the first order of the excluded volume parameter z. It is shown that the excluded volume does not affect the osmotic equation of state as well as the structure factor in this approximation.

I. Introduction

We study the semidilute poor solvent polymer solutions based upon the virial expansion theory.[1-3] The semidilute region of polymer solution is defined by Edwards[4] as

$$nv \ll \frac{V}{N} < \kappa_0^{-3} < (nb^2)^{3/2} \tag{I.1}$$

where n is the number of monomer units in a polymer, b is the bond length, N is the number of polymers in solution, V is the volume of the system, v is the excluded volume defined for binary interaction between monomer pairs, and κ_0 is the inverse of the screening length defined by

$$\kappa_0 = \left(\frac{12nvN}{b^2V}\right)^{1/2} \tag{I.2}$$

The region defined by eq I.1 is the same as the semidilute tricritical region (region III in their paper) defined by Daoud and Jannink.[5] In this region, we do not have to rely on the renormalization group (RG) calculations based on the field-theoretic formalism, which is very useful in the theory of good solvent solutions.

The osmotic equation of state in this region was first obtained by Edwards;[4] the equation includes the "Debye–Hückel" term, which represents the fact that the interactions between polymers are screened by the existence of other polymers. Nevertheless, this equation differs completely from that derived by Daoud and Jannink[5] by means of scaling arguments. Moore[6] pointed out this discrepancy and explained that the expression given by Edwards is valid provided that the ternary cluster integral is very small. Furthermore, in the case when the ternary cluster integral (v_2) was assumed to be neglected, Moore obtained the Edwards' "Debye–Hückel" term as a correction to the virial expansion of the osmotic pressure by means of the RG calculation.

In section II, the Saitô theory for solutions, developed by using "grand" canonical ensemble, is first outlined; then it is shown, in the same case where $v_2 = 0$, that this osmotic equation of state is also obtained by summing series and ring-form diagrams, each of which has a single intermolecular interaction between two polymers (see Figure 1) in the formalism of grand partition function.

In the present paper the effect of the ternary interactions, which becomes important to investigate solution properties of polymers at Θ-temperature, is neglected. The effect of these three-body terms on the solution properties of semidilute polymer solution will be discussed in our forthcoming paper.

The structure factor for semidilute polymer solution was first obtained by Jannink and de Gennes[7] using a random phase approximation (RPA), and it was compared with experiments after certain renormalization in small-angle neutron scattering (SANS) by Daoud et al.[8] and in small-angle X-ray scattering (SAXS) by Okano et al.[9] In section III, we calculate the structure factor of the solution by summing diagrams like those given in Figure 1 and show that when the contribution from the ring-form diagrams (Figure 1b) to the structure factor is small compared with that from the series diagrams (Figure 1a) we have the Jannink–de Gennes result.[7]

Recently, des Cloizeaux[10] presented a systematic way to calculate the osmotic pressure and the density correlation function of the semidilute poor solvent solution following grand canonical ensemble formalism in polydisperse systems. The basic idea of his paper is similar to ours and his result for the osmotic pressure including the effect of one-loop diagrams corresponds to Moore's results and ours; moreover, the density correlation function that des Cloizeaux obtained corresponds to the first term of our correlation function, which is given by taking ac-

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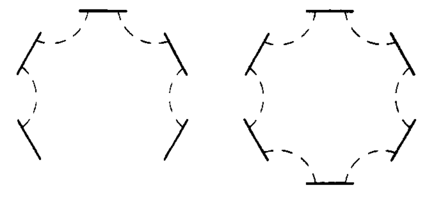

Figure 1. (a) A series diagram and (b) a ring-form diagram.

count of series-connected diagrams as shown in section III.

In section IV, the osmotic compressibility equation, which gives a connection between the osmotic pressure and the correlation function of the solution, is considered to confirm the consistency between the results obtained in sections II and III; the contribution from the "Debye–Hückel" term to the osmotic equation of state corresponds to that from the ring-form diagrams to the correlation function.

In section V, based upon the McMillan–Mayer theory in grand canonical formalism, the effects of the intramolecular interactions on the osmotic equation of state as well as on the static structure factor are examined by assuming that the same binary interactions can be adopted also for the intramolecular interactions.

Finally, the validity of the assumptions adopted in sections II and III is discussed in section VI.

II. Osmotic Equation of State

1. Osmotic Pressure of Polymer Solutions in "Grand" Canonical Ensemble. The virial expansion of the osmotic pressure can be derived by the method of grand partition function by McMillan and Mayer[1,2] or by the method of semi-grand partition function by Saitô.[3] The latter theory has the advantage of having a structure quite similar to the theory of imperfect gases in canonical ensemble, and the present paper will be developed by following this method; thus a brief introduction to this theory is in order.

When we consider the osmotic pressure of solutions, the ensemble, called the semi-grand canonical ensemble,[11] in which the chemical potential of the solvent, μ_0, is held constant, may be preferable to the usual canonical ensemble since the number of the solvent molecules, N_0, changes by passing through a membrane separating solvent and solute phases. Let us consider solutions of one solute species. The partition function, $Z_N(T,V,\mu_0)$, of the semi-grand canonical ensemble is related to the partition function, $Z_N(T,V,N_0)$ of the canonical ensemble by

$$Z_N(T,V,\mu_0) = \sum_{N_0} Z_N(T,V,N_0)\lambda_0^{N_0} \qquad \text{(II.1)}$$

where $\lambda_0 = \exp(\mu_0/k_BT)$ is the absolute activity of the solvent. The thermodynamic function defined by $\mathcal{F} = -k_BT \ln Z_N$ has the following properties:

$$\mathcal{F} = F - \mu_0 N_0 \qquad \text{(II.2)}$$

$$d\mathcal{F} = -S\,dT - p\,dV - N_0\,d\mu_0 + \mu\,dN \qquad \text{(II.3)}$$

$$p = -\left(\frac{\partial \mathcal{F}}{\partial V}\right)_{T,\mu_0,N} = k_BT\left(\frac{\partial \ln Z_N}{\partial V}\right)_{T,\mu_0,N} \qquad \text{(II.4)}$$

where S, p, and $F = -k_BT \ln Z_N$ are entropy, pressure, and Helmholtz free energy, respectively. On the other hand, the osmotic pressure, π_{os}, is defined as the pressure difference between solute and solvent phases which have the same solvent chemical potential:

$$\pi_{os} = k_BT\left(\frac{\partial \ln Z_N^*(T,V,\mu_0)}{\partial V}\right)_{T,\mu_0,N} \qquad \text{(II.5)}$$

where

$$Z_N^*(T,V,\mu_0) = Z_N(T,V,\mu_0)/Z_0(T,V,\mu_0) \qquad \text{(II.6)}$$

This $Z_N^*(T,V,\mu_0)$ is to be compared with the partition function $Z_N(T,V)$ in a canonical ensemble which is usually used in the theory of imperfect gases and is given by

$$Z_N(T,V) = \frac{1}{N!h^{fN}}\int\cdots\int \exp\left[-\frac{E(N)}{k_BT}\right] d\tau_N \qquad \text{(II.7)}$$

where h is Planck's constant, f is the number of degrees of freedom of a solute molecule, $E(N)$ is the total energy of N molecules, and $d\tau_N$ is the volume element of the phase space of N molecules.

Now let us define a new function, $Q(N)$, by

$$\frac{1}{N!h^{fN}}\exp\left(-\frac{Q(N)}{k_BT}\right) = \left\{\sum_{N_0}\frac{\lambda_0^{N_0}}{N_0!N!h^{f_0N_0+fN}}\int\cdots\int \exp\left(-\frac{E(N_0,N)}{k_BT}\right) d\tau_{N_0}\right\}\Bigg/ \left\{\sum_{N_0}\frac{\lambda_0^{N_0}}{N_0!h^{f_0N_0}}\int\cdots\int \exp\left(-\frac{E(N_0)}{k_BT}\right) d\tau_{N_0}\right\} \qquad \text{(II.8)}$$

In general, the total energy $E(N_0,N)$ can be expressed as a sum of potential energy $U'(N_0,N)$ and kinetic energy $T(N_0,N)$; the latter is a sum of kinetic energies of individual molecules. Then

$$E(N_0,N) = U'(N_0,N) + T(N_0) + T(N) \qquad \text{(II.9)}$$

Thus, $Q(N)$ can be written

$$Q(N) = U(N) + T(N) \qquad \text{(II.10)}$$

where $U(N)$ is defined by

$$\exp\left(-\frac{U(N)}{k_BT}\right) = \left\{\sum_{N_0}\frac{\lambda_0^{N_0}}{N_0!h^{f_0N_0}}\int\cdots\int \exp\left(-\frac{T(N_0) + U'(N_0,N)}{k_BT}\right) d\tau_{N_0}\right\}\Bigg/ \left\{\sum_{N_0}\frac{\lambda_0^{N_0}}{N_0!h^{f_0N_0}}\int\cdots\int \exp\left(-\frac{T(N_0) + U'(N_0)}{k_BT}\right) d\tau_{N_0}\right\} \qquad \text{(II.11)}$$

The function $U(N)$ has the following properties:

(1) $U(N)$ is a function of the configurational coordinates of solute molecules only.

(2) $U(N) = 0$ in the case $N = 0$.

(3) If we denote by grad_s the differentiation with respect to the configurational coordinates of solute molecules, we have

$$-\text{grad}_s\, U(N) = \left\{\sum_{N_0}\frac{\lambda_0^{N_0}}{N_0!h^{f_0N_0}}\int\cdots\int \{-\text{grad}_s\, U'(N_0,N)\} \times \exp\left(-\frac{T(N_0) + U'(N_0,N)}{k_BT}\right) d\tau_{N_0}\right\}\Bigg/ \left\{\sum_{N_0}\frac{\lambda_0^{N_0}}{N_0!h^{f_0N_0}}\int\cdots\int \exp\left(-\frac{T(N_0) + U'(N_0,N)}{k_BT}\right) d\tau_{N_0}\right\} \qquad \text{(II.12)}$$

This means that $U(N)$ is the average potential, i.e., the potential of mean force among N molecules in a solution of given solvent activity.

(4) $Z_N{}^*$ is given by

$$Z_N{}^* = \frac{C(T)^N}{N!h^{fN}}\int\ldots\int\exp\left(-\frac{U(N)}{k_{\mathrm{B}}T}\right)\,\mathrm{d}\{N\} \quad \text{(II.13)}$$

where $C(T)$ comes from the kinetic energy part of $Z_N{}^*$ and $\mathrm{d}\{N\}$ is the volume element in configuration space.

We may include a constant term in $U(N)$ so as to have the property

$$\lim_{V\to\infty}\frac{1}{V^N}\int\ldots\int F_N(1,2,\ldots,N)\,\mathrm{d}\{N\} = 1 \quad \text{(II.14)}$$

where

$$F_N(1,2,\ldots,N) = \exp(-U(N)/k_{\mathrm{B}}T) \quad \text{(II.15)}$$

This constant term to be added to the original $U(N)$ contributes a constant factor to $Z_N{}^*$, but it has nothing to do with the calculation of the osmotic pressure. Hence, we can omit it.

Define successively g functions as follows:

$$F_N(1,2,\ldots,N) = \sum_{(N=\sum m_in_i)}\prod_{i=1}^{k} g_{n_i}(\{n_i\}) \quad \text{(II.16)}$$

where $(N = \sum m_in_i)$ means that N molecules are divided into several groups among which a group with supscript i has n_i molecules; further, there are m_i groups, each of which has n_i molecules and contributes a factor g_{n_i}. The summation means the sum over all the ways of division of N molecules into such groups as mentioned above. We introduce the cluster integrals by

$$b_m = \frac{1}{m!V}\int\ldots\int g_m(\{m\})\,\mathrm{d}\{m\} \quad \text{(II.17)}$$

Then $Z_N{}^*$ is expressed by

$$Z_N{}^* = \frac{C(T)^N}{N!h^{fN}}\sum_{(N=\sum m_in_i)}\frac{N!}{\prod_i m_i!(n_i!)^{m_i}}\prod_i(Vn_i!b_{n_i})^{m_i} \quad \text{(II.18)}$$

where the factor $N!/\prod_i m_i!(n_i!)^{m_i}$ is the number of terms which give the same integral $\prod_i(Vn_i!b_{n_i})^{m_i}$.

This function, if the summation with respect to N is taken, yields the "grand" partition function related to osmotic pressure (of course, it is different from the usual grand canonical partition function related to pressure):

$$\Xi = \sum_N Z_N{}^*\lambda^N = \sum_N\frac{C(T)^N\lambda^N}{h^{fN}}\sum_{(N=\sum m_in_i)}\frac{\prod_i(Vb_{n_i})^{m_i}}{\prod_i m_i!} = \exp\Bigl(\sum_n Vb_nz'^n\Bigr) \quad \text{(II.19)}$$

where $z' = C(T)\lambda/h^f$ is the fugacity. Again the osmotic pressure π_{os} is given by

$$\pi_{\mathrm{os}} = \frac{k_{\mathrm{B}}T}{V}\ln\Xi = k_{\mathrm{B}}T\sum_n b_nz'^n \quad \text{(II.20)}$$

Equation II.20 with the condition

$$\rho = \langle N\rangle/V = \sum_n nb_nz'^n \quad \text{(II.21)}$$

yields

$$\pi_{\mathrm{os}} = k_{\mathrm{B}}T\rho\left[1 - \sum_{m=1}^{\infty}\frac{m}{m+1}\beta_m\rho^m\right] = k_{\mathrm{B}}T\rho + k_{\mathrm{B}}T\frac{\partial W}{\partial V} \quad \text{(II.22)}$$

where k_{B} is the Boltzmann constant, T is the absolute temperature, and ρ is the average density of solution; W is the contribution to the free energy of the system from intramolecular and intermolecular interactions between monomers of polymers

$$W = \sum_{m=1}^{\infty}\frac{1}{m+1}V\beta_m\rho^{m+1} \quad \text{(II.23)}$$

This equation may be called the osmotic equation of state and is identical with that obtained for the pressure of an imperfect gas except that here the irreducible integrals, β_m's, are functionals of the potentials of average force between solute molecules only and the presence of the solvent appears only implicitly as the potentials of average force of the solute molecules are influenced by the presence of the solvent. Further, we assume that these potentials of average force can be expanded by Mayer's f functions; that is, we assume binary interactions to act between pairs of monomeric units.

For polymer solutions, the potential energy $U(N)$ is expressed as a sum of potential energies of "short-range" interactions, U_{S}, and of "long-range" interactions, U_{L}, where the "distance" is defined along a contour length of a chain. The "short-range" interaction means the nearest-neighbor intrachain interaction between monomers of a polymer molecule and the function U_{S} leads to the distribution function P defined in eq II.27. The "long-range" interaction means the interaction between "distant" monomers, and, if U_{L} can be assumed to be a sum of potentials of binary interactions, we can expand the factor $\exp(-U_{\mathrm{L}}/k_{\mathrm{B}}T)$ by the product of f functions.

The irreducible integral β_m is then given by

$$\beta_m = \frac{1}{m!V}V^{m+1}\langle\textstyle\sum\prod f\rangle_{\mathrm{c},m+1} = \frac{1}{m!V}\int\ldots\int\sum{}^{(\mathrm{s})}\prod fP(\{m+1\})\,\mathrm{d}\{m+1\} \quad \text{(II.24)}$$

where f's are Mayer's f functions for intramolecular and intermolecular pairs of monomers and $\sum^{(\mathrm{s})}$ means that the summation is taken over all possible irreducible diagrams composed of $m + 1$ polymers. The average $\langle\ldots\rangle_{\mathrm{c},m+1}$ stands for the cumulant average, and the ordinary average $\langle\ldots\rangle_{m+1}$ for $m + 1$ polymers defined by

$$\langle A\rangle_{m+1} = \frac{1}{V^{m+1}}\int\ldots\int AP(\{m+1\})\,\mathrm{d}\{m+1\} \quad \text{(II.25)}$$

where

$$\{m+1\} = (1)\ldots(m+1) \quad \text{(II.26a)}$$

$$\mathrm{d}\{m+1\} = \mathrm{d}(1)\ldots\mathrm{d}(m+1) \quad \text{(II.26b)}$$

and (α) denotes all the coordinates of the monomeric units of the αth polymer and the distribution function P is assumed to be the product of the Gaussian function

$$P(\{m+1\}) = \prod_{\alpha=1}^{m+1}\prod_{i=1}^{n-1}\left(\frac{3}{2\pi b^2}\right)^{3/2}\exp[-3|\mathbf{r}_i{}^{(\alpha)} - \mathbf{r}_{i+1}{}^{(\alpha)}|^2/2b^2] \quad \text{(II.27)}$$

where $\mathbf{r}_i{}^{(\alpha)}$ denotes the coordinates of the ith unit of the αth polymer. Hereafter, to make the calculation possible we assume that the f function is given by the Dirac δ function:

$$f(\mathbf{r}) = (-v)\delta(\mathbf{r}) \quad \text{(II.28)}$$

where $|v|$ is small in poor solvent.

To calculate the cumulant average in eq II.24, we must rewrite it in terms of the ordinary averages defined by eq II.25. It is easy to show that cumulant averages of dis-

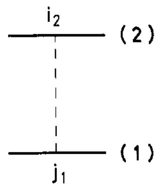

Figure 2. An irreducible series-connected diagram.

connected clusters consisting of intermolecular f functions can be neglected. For example, if $f(\mathrm{I})$ and $f(\mathrm{II})$ are statistically independent, i.e., $\langle f(\mathrm{I})f(\mathrm{II})\rangle_4 = \langle f(\mathrm{I})\rangle_2\langle f(\mathrm{II})\rangle_2$, we have

$$\langle f(\mathrm{I})f(\mathrm{II})\rangle_{c,4} = 0$$

where each of I and II stands for the difference of the position vectors of monomers belonging to different molecules. However, if they are statistically dependent like they are in a ring-form diagram (see Figure 1b), we get

$$\langle f(\mathrm{I})f(\mathrm{II})\rangle_{c,2} = \langle f(\mathrm{I})f(\mathrm{II})\rangle_2 \tag{II.29}$$

in the limit of $V \to \infty$, since the product of the ordinary averages of intermolecular f functions can be neglected in this limit. On the other hand, if one of the f functions in eq II.29 is an intramolecular f function, f_0, we can estimate roughly that the averages, $\langle f_0 f\rangle_2$ and $\langle f_0\rangle_1\langle f\rangle_2$, have the same order with respect to V. Note that the product of the ordinary averages of intramolecular f functions cannot be neglected even in the limit of $V \to \infty$. Therefore, we must calculate explicitly cumulant averages of intramolecular f functions;[12] the cumulant expansion of the product of ordinary averages of intermolecular and intramolecular f functions is considered precisely in section V where the self-interaction effect of a molecule on the osmotic pressure is investigated.

2. Calculation of the Osmotic Pressure in "Grand" Canonical Ensemble. According to the Saitô theory developed in the previous subsection, the irreducible integral β_m defined by eq II.24 has to be calculated to obtain the osmotic pressure of solutions. Let us first consider the case where the effect of the intramolecular interactions is neglected. Although it is possible to consider many connected series diagrams like that shown in Figure 1a, the diagram shown in Figure 2 is a unique irreducible diagram; other types of diagrams like trees which are reducible do not contribute to W, the free energy of the system. The integral β_1 calculated for this diagram is given by

$$\beta_1 = \frac{1}{V}\sum_{i_2,j_1}\int\int f(\mathbf{r}_{j_1}{}^{(1)} - \mathbf{r}_{i_2}{}^{(2)})P((1),(2))\ \mathrm{d}(1)\ \mathrm{d}(2) \tag{II.30}$$

Making use of the Fourier series expansion of the Gaussian function included in $P((1),(2))$

$$\left(\frac{3}{2\pi b^2}\right)^{3/2} \exp\left[-\frac{3|\mathbf{r}_i{}^{(1)} - \mathbf{r}_{i+1}{}^{(1)}|^2}{2b^2}\right] = \frac{1}{V}\sum_{\mathbf{q}}\exp[i\mathbf{q}(\mathbf{r}_i{}^{(1)} - \mathbf{r}_{i+1}{}^{(1)})]\ \exp\left[-\frac{b^2}{6}\mathbf{q}^2\right] \tag{II.31}$$

and definition of the f function (eq II.28), we obtain

$$\beta_1 = (-v)\sum_{i_2,j_1}1 = -n^2v \tag{II.32}$$

Therefore, W_{series}, the contribution from the series diagrams to the free energy of the system, is given by

$$W_{\text{series}} = {}^1\!/_2 V\beta_1\rho^2 = -{}^1\!/_2 n^2vV\rho^2 \tag{II.33}$$

Then, let us consider the ring-form diagrams like those shown in Figure 1b. The integral β_{m-1}, calculated for the ring-form irreducible diagram composed of m polymers, is

$$\beta_{m-1} = \frac{(m-1)!}{2V}\ \frac{1}{(m-1)!}\sum_{i_1,j_1}\cdots\sum_{i_m,j_m}\int\cdots\int \mathrm{d}(1)\ldots\mathrm{d}(m)\ f(\mathbf{r}_{j_1}{}^{(1)} - \mathbf{r}_{i_2}{}^{(2)})\ldots f(\mathbf{r}_{j_m}{}^{(m)} - \mathbf{r}_{i_1}{}^{(1)})\left\{\prod_{i=1}^{n-1}\left(\frac{3}{2\pi b^2}\right)^{3/2}\times \exp\left[-\frac{3|\mathbf{r}_i{}^{(1)} - \mathbf{r}_{i+1}{}^{(1)}|^2}{2b^2}\right]\right\}\cdots\left\{\prod_{j=1}^{n-1}\left(\frac{3}{2\pi b^2}\right)^{3/2}\times \exp\left[-\frac{3|\mathbf{r}_i{}^{(m)} - \mathbf{r}_{i+1}{}^{(m)}|^2}{2b^2}\right]\right\} = \frac{1}{2V}(-v)^m\sum_{\mathbf{q}}\{a_0(\mathbf{q})\}^m \tag{II.34}$$

where $a_0(\mathbf{q})$ is the intramolecular structure factor $G_0(\mathbf{q},n)$, i.e., the structure factor of a single molecule

$$q_0(\mathbf{q}) = G_0(\mathbf{q},n) = \sum_{ij}\exp\left[-\frac{b^2}{6}|j - i|\mathbf{q}^2\right] \tag{II.35}$$

and for the wave range, $(nb^2/6)^{-1} \ll q^2 \ll b^{-2}$, it is given approximately by

$$a_0(q) = 12n/b^2q^2 \tag{II.36}$$

Substituting eq II.34 into eq II.23, we have W_{ring}, the contribution from the ring-form diagrams to the free energy of the system,

$$W_{\text{ring}} = \sum_{m=1}^{\infty}\frac{1}{m+1}\rho^{m+1}\left(\frac{1}{2}(-v)^{m+1}\sum_{\mathbf{q}}\{a_0(\mathbf{q})\}^{m+1}\right) = \sum_{\mathbf{q}}\sum_{m=2}^{\infty}\frac{1}{2m}\rho^m(-v)^m\{a_0(\mathbf{q})\}^m = \frac{1}{2}\sum_{\mathbf{q}}[-\ln\{1 + \rho va_0(\mathbf{q})\} + \rho va_0(\mathbf{q})] \tag{II.37}$$

where use is made of the equality

$$\ln(1 + x) = \sum_{m=1}^{\infty}\frac{1}{m}(-1)^{m-1}x^m \tag{II.38}$$

Furthermore, replacing the sum by the integral with respect to $\mathbf{q}$, we obtain

$$W_{\text{ring}} = \frac{V}{2}\int\frac{\mathrm{d}\mathbf{q}}{(2\pi)^3}\left[-\ln\left(1 + \frac{\kappa_0{}^2}{q^2}\right) + \frac{\kappa_0{}^2}{q^2}\right] = \frac{V}{12\pi}\kappa_0{}^3 \tag{II.39}$$

where $q = |\mathbf{q}|$ and κ_0 is the inverse of the screening length defined by eq I.2.

From eq II.33 and eq II.39 we obtain

$$W = W_{\text{series}} + W_{\text{ring}} = -\frac{n^2v}{2}V\rho^2 + \frac{V}{12\pi}\left(\frac{12nv}{b^2}\rho\right)^{3/2} \tag{II.40}$$

Substituting eq II.40 into eq II.22, we finally obtain the osmotic pressure in the present approximation for polymers

$$\pi_{\text{os}} = k_{\text{B}}T\rho\left[1 + \frac{n^2v}{2}\rho - \frac{3^{1/2}}{\pi}\left(\frac{nv}{b^2}\right)^{3/2}\rho^{1/2}\right] \tag{II.41}$$

The third term is of a Debye–Hückel form; that is, the interaction between polymers is screened by the presence of other polymers. To see this screening effect by the presence of other molecules more closely we calculate the effective f function in Appendix A.

The expression II.41 corresponds to Edwards' result except for the discrepancy between our third term and his third term. As Moore pointed out[6] we also think that this discrepancy is due to a trivial error in the calculation going from eq 3.16 to eq 3.17 in Edwards' paper.[4]

des Cloizeaux calculated the osmotic pressure by considering irreducible diagrams to one-loop order in a polydisperse system and obtained the same expression as eq II.41 in the case of a monodisperse system. The feature of his method is similar to that of our theory in the present section except the point that in des Cloizeaux's theory the elimination of the short-range divergences is inevitable when replacing the sums with respect to monomers by the integral; on the other hand, in our calculation the contribution from a diagram to the free energy of the system is obtained by actually summing monomeric units of the diagram and there is no difficulty of divergence in the calculation (see also section V).

III. Static Structure Factor

In this section, we first calculate the molecular distribution function $g_2(\mathbf{r},\mathbf{r}')$ of the polymer solution based on the "grand" canonical ensemble formalism considered in the previous subsection. The calculation method of the function is quite similar to that of the radial distribution function of imperfect gases based on the grand canonical ensemble formalism except for the fact that we consider here the potential of the average forces acting on solute molecules only instead of the actual potential of forces acting on gas molecules.

1. Molecular Distribution Function $g_2(\mathbf{r},\mathbf{r}')$. Suppose that there is a region (volume V) in solution which includes N molecules; the molecular density $\rho(\mathbf{r})$ at point $\mathbf{r}$ in this region is defined as

$$\rho(\mathbf{r}) = \frac{1}{n}\sum_{\alpha=1}^{N}\sum_{i=1}^{n}\delta(\mathbf{r} - \mathbf{r}_i^{(\alpha)}) \tag{III.1}$$

where n is the number of monomeric units per molecule and

$$N = \int_V \rho(\mathbf{r})\,\mathrm{d}\mathbf{r} \tag{III.2}$$

Since the number (N) of molecules changes in the grand canonical ensemble treatment, we may define the average density of the molecules

$$\langle\rho(\mathbf{r})\rangle = \langle N\rangle/V = \rho \tag{III.3}$$

Because of molecular interactions, the distribution of molecules is not completely random, and the molecular distribution function is defined by the density-density correlation function of the system

$$\langle\rho(\mathbf{r})\rho(\mathbf{r}')\rangle = \frac{1}{n^2}\langle\sum_{\alpha\beta}\sum_{ij}\delta(\mathbf{r} - \mathbf{r}_i^{(\alpha)})\delta(\mathbf{r}' - \mathbf{r}_j^{(\beta)})\rangle = \rho^2 g_2(\mathbf{r},\mathbf{r}') \tag{III.4}$$

where summation is taken for all values of α and β ($1 \leq \alpha, \beta \leq N$) except for the cases where both of the conditions $\alpha = \beta$ and $i = j$ are satisfied; since a polymer molecule has a structure (i.e., many monomeric units are connected to build up a molecule), we have to sum up also the cases where $\alpha = \beta$ unless th condition $i = j$ is satisfied.

The Fourier transform of the correlation function gives the static structure factor of the system, which can be measured by experimental methods such as light, neutron, and X-ray scattering.

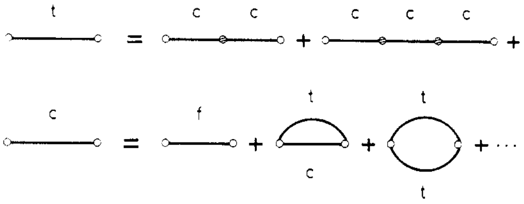

Figure 3. Correlation functions $t(\mathbf{r},\mathbf{r}')$ and $c(\mathbf{r},\mathbf{r}')$.

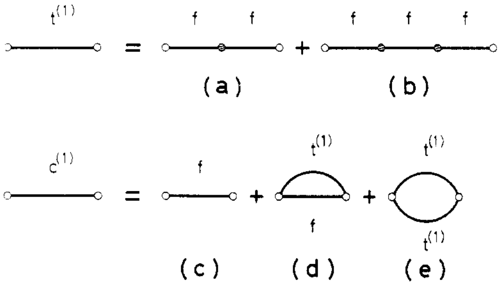

Figure 4. First iteration terms of correlation functions $t(\mathbf{r},\mathbf{r}')$ and $c(\mathbf{r},\mathbf{r}')$.

By making use of the f-function expansion, we can rewrite eq III.4 in the form of a fugacity expansion

$$\rho^2 g_2(\mathbf{r},\mathbf{r}') = \frac{1}{n^2\Xi}\sum_N \frac{1}{N!}(z')^N \int\ldots\int \exp\left(-\frac{U_L}{k_B T}\right) \times \sum_{\alpha\beta}\sum_{ij}\delta(\mathbf{r} - \mathbf{r}_i^{(\alpha)})\delta(\mathbf{r} - \mathbf{r}_j^{(\beta)})P(\{N\})\,\mathrm{d}\{N\} = \frac{1}{n^2\Xi}\sum_N \frac{1}{N!}(z')^N \sum_{\alpha\beta}\sum_{ij}\int [1 + \sum\prod f]\delta(\mathbf{r} - \mathbf{r}_i^{(\alpha)})\delta(\mathbf{r} - \mathbf{r}_j^{(\beta)})P(\{N\})\,\mathrm{d}\{N\} \tag{III.5}$$

We here make use of the topological reduction method of Stell[13] to obtain the function $g_2(\mathbf{r},\mathbf{r}')$ as a power series of the average density ρ from the fugacity expansions (eq III.5). To make the calculation more tractable let us use again the ring-form approximation in performing the calculation. Although the ring-form approximation is much simpler than the more general hypernetted chain approximation which Stell and other workers discussed, the former may be sufficient for the present purpose to obtain the $g_2(\mathbf{r},\mathbf{r}')$ function in poor solvent. Let us define another correlation function $h_2(\mathbf{r},\mathbf{r}')$ which is related to $g_2(\mathbf{r},\mathbf{r}')$ by

$$h_2(\mathbf{r},\mathbf{r}') = g_2(\mathbf{r},\mathbf{r}') - 1 \tag{III.6}$$

where $h_2(\mathbf{r},\mathbf{r}')$, if multiplied by ρ^2, is well-known as a Mayer cluster function; $h_2(\mathbf{r},\mathbf{r}')$ consists of two parts

$$h_2(\mathbf{r},\mathbf{r}') = t(\mathbf{r},\mathbf{r}') + c(\mathbf{r},\mathbf{r}') \tag{III.7}$$

where $c(\mathbf{r},\mathbf{r}')$ is the Ornstein–Zernike direct correlation function. The functions $t(\mathbf{r},\mathbf{r}')$ and $c(\mathbf{r},\mathbf{r}')$ are given by the iterative method shown in Figure 3, where black circles stand for ρ and white circles stand for 1-circle labeled by $\mathbf{r}$ and $\mathbf{r}'$; for the first iteration terms in the ring-form approximation they are expressed in diagrams as shown in Figure 4. In the case of polymer solution each term a–e in Figure 4 should be modified to express intermolecular interactions between polymers; then, the diagrams contributing to the functions $t^{(1)}$ and $c^{(1)}$ are given in Figures 5 and 6, respectively.

We have to consider two different types of diagrams for $t^{(1)}$; that is, one in which white circles are located on different molecules (Figure 5a) and another in which white circles are located on the same molecule (Figure 5b). As we do not consider the effect of the intramolecular interactions in the present section, the necessary diagrams to be considered to calculate $c^{(1)}$ are expressed in Figure 6; cases c, d, and e correspond to the diagrams c, d, and

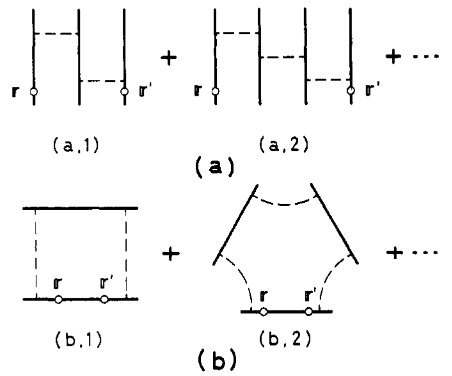

Figure 5. Diagrams contributing to the $t^{(1)}$ function: (a) series-connected diagrams; (b) ring-form diagrams.

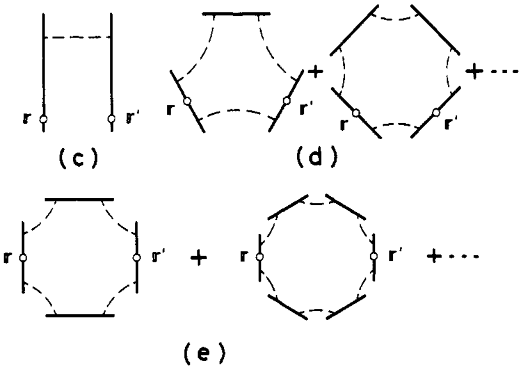

Figure 6. Diagrams contributing to the $c^{(1)}$ function: (c) a series-connected diagram; (d and e) ring-form diagrams.

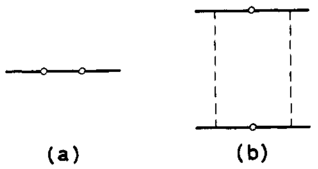

Figure 7. (a) A diagram which gives the structure factor of a single molecule and (b) a ring-form diagram which gives the first term (i.e., $l = 0$ term) of the expansion in eq III.15.

e in Figure 4, respectively. Moreover, we have to consider the following terms, shown in Figure 7, especially for the case of polymer solutions, which do not appear in the theory of imperfect gases.

For example, the contribution to the $h_2(\mathbf{r},\mathbf{r}')$ function from the diagram shown in Figure 5a.1 is given explicitly as

$$\frac{1}{n^2}\,\frac{3!}{2}\,2\,\frac{1}{3!}\,\rho\sum_{ij}\,\sum_{i_1 j_a}\,\sum_{i_b j_1}\int \mathrm{d}\{\mathbf{r}^a\}\,\mathrm{d}\{\mathbf{r}^1\}\,\mathrm{d}\{\mathbf{r}^b\}f(\mathbf{r}_{i_1} - \mathbf{r}_{j_a})f(\mathbf{r}_{i_b} - \mathbf{r}_{j_1})\delta(\mathbf{r} - \mathbf{r}_i)\delta(\mathbf{r}' - \mathbf{r}_j)P((a),(1),(b)) \tag{III.8}$$

where the coefficient (3!/2)(2) gives the number of ways of arranging three molecules (named a, 1, and b) in series and deciding molecules on which the points $\mathbf{r}$ and $\mathbf{r}'$ should be located. By making use of the Fourier series expansion of the Gaussian function $P((a),(1),(b))$ in volume V (i.e., eq II.27) and the definition of the f function, eq II.28, we obtain

$$\frac{(-\upsilon)^2}{n^2}\rho\frac{1}{V}\sum_{\mathbf{q}} e^{-i\mathbf{q}(\mathbf{r}-\mathbf{r}')}\{a_0(\mathbf{q})\}^3 \tag{III.9}$$

In general, the contribution to the h_2 function from the higher order terms of the series diagram connected by $m + 1$ f functions as shown in Figure 8 is then just

$$\frac{(-\upsilon)^{m+1}}{n^2}\rho^m\frac{1}{V}\sum_{\mathbf{q}} e^{-i\mathbf{q}(\mathbf{r}-\mathbf{r}')}\{a_0(\mathbf{q})\}^{m+2} \qquad (\text{for } m \geq 1) \tag{III.10}$$

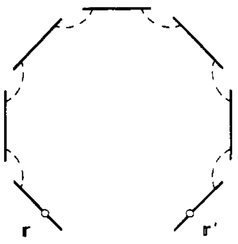

Figure 8. A connected series diagram where $\alpha \neq \beta$.

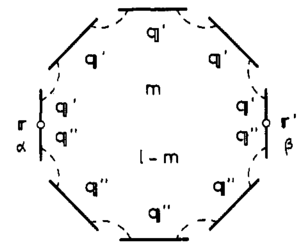

Figure 9. A ring-form diagram including $l + 2$ molecules where $\alpha \neq \beta$.

The diagram shown in Figure 6c corresponds to the $m = 0$ case in the expansion of series diagrams (Figure 5a); the contribution from this diagram to $h_2(\mathbf{r},\mathbf{r}')$ is, therefore, given by simply taking $m = 0$ in eq III.10.

The contribution to $h_2(\mathbf{r},\mathbf{r}')$ from all series-connected diagrams, i.e., Figures 5a and 6c, is given by

$$\frac{1}{n^2}\,\frac{1}{V}\sum_{\mathbf{q}} e^{-i\mathbf{q}(\mathbf{r}-\mathbf{r}_i)}\sum_{m=0}^{\infty}(-\upsilon)^{m+1}\rho^m\{a_0(\mathbf{q})\}^{m+2} = \frac{1}{n^2}\,\frac{1}{V}\sum_{\mathbf{q}} e^{-i\mathbf{q}(\mathbf{r}-\mathbf{r}')}\frac{(-\upsilon)\{a_0(\mathbf{q})\}^2}{1 + \upsilon\rho a_0(\mathbf{q})} \tag{III.11}$$

The diagram shown in Figure 7a gives the intramolecular structure factor of a single molecule; in the theory of imperfect gases, this term corresponds to the perfect gas term without interactions. The contribution to $h_2(\mathbf{r},\mathbf{r}')$ from this diagram is

$$\frac{1}{n^2}\,\frac{1}{\rho}\,\frac{1}{V}\sum_{\mathbf{q}} e^{-i\mathbf{q}(\mathbf{r}-\mathbf{r}')}a_0(\mathbf{q}) \tag{III.12}$$

which gives a term proportional to ρ in the expression of the density–density correlation function $\langle\rho(\mathbf{r})\rho(\mathbf{r}')\rangle$.

Adding eq III.12 to eq III.11, we obtain the contribution to $h_2(\mathbf{r},\mathbf{r}')$ from all connected series diagrams:

$$\frac{1}{n^2}\,\frac{1}{V}\sum_{\mathbf{q}} e^{-i\mathbf{q}(\mathbf{r}-\mathbf{r}')}\left[\frac{(-\upsilon)\{a_0(\mathbf{q})\}^2}{1 + \upsilon\rho a_0(\mathbf{q})} + \frac{1}{\rho}a_0(\mathbf{q})\right] = \frac{1}{n^2\rho}\,\frac{1}{V}\sum_{\mathbf{q}} e^{-i\mathbf{q}(\mathbf{r}-\mathbf{r}')}\frac{a_0(\mathbf{q})}{1 + \upsilon\rho a_0(\mathbf{q})} \tag{III.13}$$

and if $a_0(\mathbf{q}) \simeq 12n/(b^2\mathbf{q}^2)$ (eq II.36), eq III.13 is given by a function of the screened-coulomb type

$$\frac{12}{nb^2\rho}\,\frac{1}{V}\sum_{\mathbf{q}} e^{-i\mathbf{q}(\mathbf{r}-\mathbf{r}')}\frac{1}{\mathbf{q}^2 + \kappa_0^2} = \frac{3}{\pi nb^2\rho}\,\frac{e^{-\kappa_0|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|} \tag{III.14}$$

Furthermore, we have to consider also the contribution from ring-form diagrams like those shown in Figure 6d,e. One may consider a general term of the connected ring-form term including $l + 2$ polymers which is shown in Figure 9; the calculation of the contribution to $h_2(\mathbf{r},\mathbf{r}')$ from this diagram yields

$$\frac{(l + 1)!}{2}\,{}_{l+2}C_1\frac{\rho^l}{(l + 2)!}\,\frac{(-\upsilon)^{l+2}}{n^2} \times \frac{1}{V^2}\sum_{m=0}^{l}\sum_{\mathbf{q}'}\sum_{\mathbf{q}''} e^{-i(\mathbf{q}'-\mathbf{q}'')(\mathbf{r}-\mathbf{r}')}\{a_0(\mathbf{q}')\}^m\{a_0(\mathbf{q}'')\}^{l-m}\{B(\mathbf{q}',\mathbf{q}'')\}^2 \tag{III.15}$$

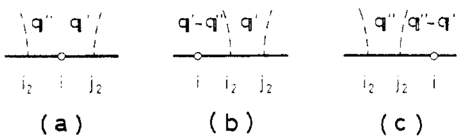

Figure 10. Diagrams contributing to $B(\mathbf{q}',\mathbf{q}'')$.

where the coefficient $[(l+1)!/2]\,{}_{l+2}C_1$ gives the number of ways of arranging $l+2$ molecules in a circular form and deciding a molecule on which the point $\mathbf{r}$ should be located; the case where l is equal to 0 corresponds to the diagram shown in Figure 7b, and $B(\mathbf{q}',\mathbf{q}'')$ consists of three terms, each of which corresponds to each of the three cases in Figure 10 (first term from (a), second term from (b), and third term from (c))

$$B(\mathbf{q}',\mathbf{q}'') = 2\sum_{i_2\le i<j_2}\exp\left[-\frac{i-i_2}{6}b^2\mathbf{q}''^2 - \frac{j_2-i}{6}b^2\mathbf{q}'^2\right] + 2\sum_{i\le i_2<j_2}\exp\left[-\frac{i_2-i}{6}b^2(\mathbf{q}'-\mathbf{q}'')^2 - \frac{j_2-i_2}{6}b^2\mathbf{q}'^2\right] + 2\sum_{i_2<j_2\le i}\exp\left[-\frac{j_2-i_2}{6}b^2\mathbf{q}''^2 - \frac{i-j_2}{6}b^2(\mathbf{q}''-\mathbf{q}')^2\right] \quad \text{(III.16)}$$

On the other hand, by taking the sum of eq III.15 with respect to l, we can obtain the contribution from all the connected ring-form diagrams of Figure 9 type:

$$\frac{1}{n^2}\sum_{l=0}^{\infty}\rho^l\frac{(-\upsilon)^{l+2}}{2}\;\frac{1}{V^2}\sum_{\mathbf{q}'}\sum_{\mathbf{q}''}e^{-i(\mathbf{q}'-\mathbf{q}'')(\mathbf{r}-\mathbf{r}')}\frac{\{a_0(\mathbf{q}'')\}^{l+1}-\{a_0(\mathbf{q}')\}^{l+1}}{a_0(\mathbf{q}'')-a_0(\mathbf{q}')} \times \{B(\mathbf{q}',\mathbf{q}'')\}^2 = \frac{1}{n^2}\;\frac{1}{2V^2}\sum_{\mathbf{q}'}\sum_{\mathbf{q}''}e^{-i(\mathbf{q}'-\mathbf{q}'')(\mathbf{r}-\mathbf{r}')}(-\upsilon)^2\frac{\{B(\mathbf{q}',\mathbf{q}'')\}^2}{[1+\upsilon\rho a_0(\mathbf{q}')][1+\upsilon\rho a_0(\mathbf{q}'')]} \quad \text{(III.17)}$$

The value of $B(\mathbf{q}',\mathbf{q}'')$ is obtained approximately

$$B(\mathbf{q}',\mathbf{q}'') \cong \frac{2n}{a'a''} + \frac{2n}{ca'} + \frac{2n}{a''c} = 2\frac{a'+a''+c}{a'a''c}n \quad \text{(III.18)}$$

where

$$a' = b^2\mathbf{q}'^2/6 \quad \text{(III.19a)}$$

$$a'' = b^2\mathbf{q}''^2/6 \quad \text{(III.19b)}$$

$$c = b^2(\mathbf{q}'-\mathbf{q}'')^2/6 \quad \text{(III.19c)}$$

Furthermore, if we may assume that

$$a' + a'' + c \cong 2c$$

we obtain

$$B(\mathbf{q}',\mathbf{q}'') \cong \frac{4n}{a'a''} = \frac{1}{n}a_0(\mathbf{q}')a_0(\mathbf{q}'') \quad \text{(III.20)}$$

Substituting eq III.20 into eq III.17, we obtain approximately the expression of this contribution as follows:

$$\frac{9}{2\pi^2n^2\rho^2}\left(\frac{1-e^{-\kappa_0|\mathbf{r}-\mathbf{r}'|}}{b^2|\mathbf{r}-\mathbf{r}'|}\right)^2 \quad \text{(III.21)}$$

where use is made of the relation

$$\frac{1}{V}\sum_{\mathbf{q}}e^{-i\mathbf{q}(\mathbf{r}-\mathbf{r}')}\frac{\{a_0(\mathbf{q})\}^2}{1+\upsilon\rho a_0(\mathbf{q})} = \left(\frac{12n}{b^2}\right)^2\frac{1-e^{-\kappa_0|\mathbf{r}-\mathbf{r}'|}}{4\pi\kappa_0{}^2|\mathbf{r}-\mathbf{r}'|} \quad \text{(III.22)}$$

Expression III.21 also includes a function of the screened-coulomb type but it is not dominant to eq III.14 since, if the appropriate range

$$\kappa_0|\mathbf{r}-\mathbf{r}'| \lesssim 1$$

is taken into account, the ratio of eq III.21 to eq III.14 is small:

$$\frac{3}{2\pi}\frac{|\mathbf{r}-\mathbf{r}'|}{nb^2}\kappa_0{}^2\frac{1}{\rho} < \frac{3}{2\pi}\frac{|\mathbf{r}-\mathbf{r}'|}{nb^2\kappa_0} < \frac{3}{2\pi} < 1 \quad \text{(III.23)}$$

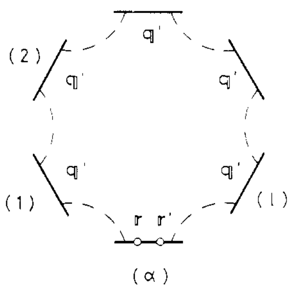

Figure 11. A ring-form diagram including $l+1$ molecules where $\alpha = \beta$.

We may consider, furthermore, the contribution to $h_2(\mathbf{r},\mathbf{r}')$ from another connected ring-form diagram where both of the points $\mathbf{r}$ and $\mathbf{r}'$ (small circles) are located on the same molecule as shown in Figure 11, representing a higher order term of the diagram (b.2) of Figure 5; this yields a correlation function which is related to the intramolecular structure factor of a single molecule. The calculation of the contribution to $h_2(\mathbf{r},\mathbf{r}')$ from such a diagram consisting of $l+1$ molecules yields

$$\frac{1}{(l+1)!}\;\frac{1}{n^2}\rho^{l-1}\frac{l!}{2} \times {}_{l+1}C_1(-\upsilon)^{l+1}\frac{1}{V^2}\sum_{\mathbf{q}'}\sum_{\mathbf{q}''}e^{-i\mathbf{q}''(\mathbf{r}-\mathbf{r}')}\{a_0(\mathbf{q}')\}^l\{e^{i\mathbf{q}'(\mathbf{r}-\mathbf{r}')}D_1(\mathbf{q}',\mathbf{q}'') + D_2(\mathbf{q}',\mathbf{q}'')\} \quad \text{(III.24)}$$

where the coefficient $(l!/2)\,{}_{l+1}C_1$ gives the number of ways of arranging $l+1$ molecules in a circular form and deciding a molecule on which the points $\mathbf{r}$ and $\mathbf{r}'$ should be located and

$$D_1(\mathbf{q}',\mathbf{q}'') = 2\sum_{i_1\le i<j\le j_1}\exp\left[-\frac{j_1-j}{6}b^2\mathbf{q}'^2 - \frac{j-i}{6}b^2\mathbf{q}''^2 - \frac{i-i_1}{6}b^2\mathbf{q}'^2\right] + 2\sum_{i\le i_1<j_1\le j}\exp\left[-\frac{j-j_1}{6}b^2(\mathbf{q}''-\mathbf{q}')^2 - \frac{j_1-i_1}{6}b^2\mathbf{q}'^2 - \frac{i_1-i}{6}b^2(\mathbf{q}''-\mathbf{q}')^2\right] + 2\sum_{i_1\le i<j_1\le j}\exp\left[-\frac{j-j_1}{6}b^2(\mathbf{q}''-\mathbf{q}')^2 - \frac{j_1-i}{6}b^2\mathbf{q}''^2 - \frac{i-i_1}{6}b^2\mathbf{q}'^2\right] + 2\sum_{i\le i_1<j\le j_1}\exp\left[-\frac{j_1-j}{6}b^2\mathbf{q}'^2 - \frac{j-i_1}{6}b^2\mathbf{q}''^2 - \frac{i_1-i}{6}b^2(\mathbf{q}''-\mathbf{q}')^2\right] \quad \text{(III.25)}$$

and

$$D_2(\mathbf{q}',\mathbf{q}'') = 2\sum_{i_1<j_1\le i<j}\exp\left[-\frac{j-i}{6}b^2\mathbf{q}''^2 - \frac{j_1-i_1}{6}b^2\mathbf{q}'^2\right] + 2\sum_{i<j\le i_1<j_1}\exp\left[-\frac{j_1-i_1}{6}b^2\mathbf{q}'^2 - \frac{j-i}{6}b^2\mathbf{q}''^2\right] \quad \text{(III.26)}$$

are given by sums of contributions from each case of the diagrams shown in Figure 12 (diagrams a–d define $D_1(\mathbf{q},\mathbf{q}')$ and diagrams e and f define $D_2(\mathbf{q},\mathbf{q}')$). If the appropriate

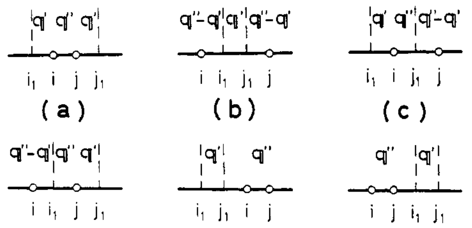

Figure 12. Diagrams contributing to $D_1(\mathbf{q}',\mathbf{q}'')$ and $D_2(\mathbf{q}',\mathbf{q}'')$.

range of $\mathbf{q}'$ and $\mathbf{q}''$ is taken into account, one may obtain approximately

$$D_1(\mathbf{q}',\mathbf{q}'') \cong 2\left(\frac{n}{a'^2a''} + \frac{n}{c^2a''} + \frac{2n}{a'a''c}\right) = \frac{2n}{a''}\left(\frac{1}{a'} + \frac{1}{c}\right)^2 \tag{III.27}$$

$$D_2(\mathbf{q}',\mathbf{q}'') \cong 2\left(\frac{n^2}{2a'a''} + \frac{n^2}{2a''a'}\right) = \frac{2n^2}{a'a''} \tag{III.28}$$

A comparison between eq III.27 and III.28 yields the fact that $D_2(\mathbf{q}',\mathbf{q}'')$ is dominant over $D_1(\mathbf{q}',\mathbf{q}'')$:

$$e^{i\mathbf{q}'(\mathbf{r}-\mathbf{r}')}D_1(\mathbf{q}',\mathbf{q}'') \cong e^{i\mathbf{q}'(\mathbf{r}-\mathbf{r}')}\frac{2n}{a''}\left(\frac{a'+c}{a'c}\right)^2 \ll D_2(\mathbf{q}',\mathbf{q}'') = \frac{2n^2}{a'a''} \tag{III.29}$$

Substituting $D_2(\mathbf{q}',\mathbf{q}'') \cong a_0(\mathbf{q}')a_0(\mathbf{q}'')/2$ into eq III.24 and taking a sum with respect to l ($l \geq 1$), we obtain approximately

$$\frac{1}{n^2}\sum_{l=1}^{\infty}\rho^{l-1}\frac{(-\upsilon)^{l+1}}{2}\,\frac{1}{V^2}\sum_{\mathbf{q}'}\sum_{\mathbf{q}''}e^{-i\mathbf{q}''(\mathbf{r}-\mathbf{r}')}\{a_0(\mathbf{q}')\}^l\,{}^1\!/_2\,a_0(\mathbf{q}')a_0(\mathbf{q}'') = \frac{1}{n^2\rho^2}\,\frac{1}{4V^2}\sum_{\mathbf{q}'}\sum_{\mathbf{q}''}e^{-i\mathbf{q}''(\mathbf{r}-\mathbf{r}')}\frac{\{\upsilon\rho a_0(\mathbf{q}')\}^2}{1+\upsilon\rho a_0(\mathbf{q}')}a_0(\mathbf{q}'') = \frac{1}{n^2}\,\frac{{\kappa_0}^3}{4\pi\rho^2}\,\frac{1}{4V}\sum_{\mathbf{q}''}e^{-i\mathbf{q}''(\mathbf{r}-\mathbf{r}')}a_0(\mathbf{q}'') \tag{III.30}$$

where use is made of the relation

$$\frac{1}{V}\sum_{\mathbf{q}}\frac{\{\upsilon\rho a_0(\mathbf{q})\}^2}{1+\upsilon\rho a_0(\mathbf{q})} = \frac{{\kappa_0}^3}{4\pi} \tag{III.31}$$

Expression III.30 is similar to eq III.12, a part of the first term of the expansion, in its $\mathbf{r} - \mathbf{r}'$ dependence. We may neglect eq III.30 since the ratio of eq III.30 to eq III.12 is small:

$$\frac{{\kappa_0}^3}{16\pi}\Big/\rho < \frac{1}{16\pi} \ll 1$$

From eq III.21, the contribution from ring-form diagrams can then be obtained as

$$\frac{9}{2\pi^2n^2\rho^2}\left(\frac{1-e^{-\kappa_0|\mathbf{r}-\mathbf{r}'|}}{b^2|\mathbf{r}-\mathbf{r}'|}\right)^2 \tag{III.32}$$

Finally, the contribution to the correlation function $h_2(\mathbf{r},\mathbf{r}')$ from connected series diagrams (eq III.14) and that from connected ring-form diagrams (eq III.32) is obtained:

$$h_2(\mathbf{r},\mathbf{r}') = \frac{3}{\pi nb^2\rho}\,\frac{e^{-\kappa_0|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} + \frac{9}{2\pi^2n^2\rho^2}\left(\frac{1-e^{-\kappa_0|\mathbf{r}-\mathbf{r}'|}}{b^2|\mathbf{r}-\mathbf{r}'|}\right)^2 \tag{III.33}$$

The density–density correlation function $g_2(\mathbf{r},\mathbf{r}')$ is given by eq III.6, and for large separation, $|\mathbf{r} - \mathbf{r}'| \rightarrow \infty$

$$h_2(\mathbf{r},\mathbf{r}') \rightarrow 0; \qquad g_2(\mathbf{r}-\mathbf{r}') \rightarrow 1$$

2. Static Structure Factor. The static structure factor, $S(\mathbf{q})$, of the present system is the Fourier transform of the density–density correlation function:

$$S(\mathbf{q}) = \int e^{i\mathbf{q}\cdot\mathbf{r}}[g_2(\mathbf{r}) - 1]\,\mathrm{d}\mathbf{r} = \int e^{i\mathbf{q}\cdot\mathbf{r}}h_2(\mathbf{r})\,\mathrm{d}\mathbf{r} \tag{III.34}$$

where $h_2(\mathbf{r} - \mathbf{r}') = h_2(\mathbf{r},\mathbf{r}')$. Substituting eq III.33 into eq III.34, we obtain

$$S(\mathbf{q}) = S_{\text{series}}(\mathbf{q}) + S_{\text{ring}}(\mathbf{q}) = \int e^{i\mathbf{q}\cdot\mathbf{r}}\left\{\frac{3}{\pi nb^2\rho}\,\frac{e^{-\kappa_0r}}{r} + \frac{9}{2\pi^2n^2\rho^2}\left(\frac{1-e^{-\kappa_0r}}{r}\right)^2\right\}\mathrm{d}\mathbf{r} \tag{III.35}$$

where $S_{\text{series}}(\mathbf{q})$ is the contribution to $S(\mathbf{q})$ from the series diagrams

$$S_{\text{series}}(\mathbf{q}) = \frac{1}{n^2\rho}\,\frac{a_0(\mathbf{q})}{1+\upsilon\rho a_0(\mathbf{q})} \tag{III.36}$$

The contribution to $S(\mathbf{q})$ from the ring-form diagram, $S_{\text{ring}}(\mathbf{q})$, is given by eq III.17:

$$S_{\text{ring}}(\mathbf{q}) = \int\mathrm{d}\mathbf{r}\; e^{i\mathbf{q}\cdot\mathbf{r}}\frac{1}{2n^2V^2}\sum_{\mathbf{q}'}\sum_{\mathbf{q}''}e^{-i(\mathbf{q}'-\mathbf{q}'')\cdot\mathbf{r}}(-\upsilon)^2\frac{1}{1+\upsilon\rho a_0(\mathbf{q}')} \times \frac{1}{1+\upsilon\rho a_0(\mathbf{q}'')}\{B(\mathbf{q}',\mathbf{q}'')\}^2 = \frac{(-\upsilon)^2}{2n^2}\,\frac{1}{V}\sum_{\mathbf{q}''}\frac{1}{1+\upsilon\rho a_0(\mathbf{q}'')} \times \frac{1}{1+\upsilon\rho a_0(\mathbf{q}+\mathbf{q}'')}\{B(\mathbf{q}''+\mathbf{q},\,\mathbf{q}'')\}^2 \tag{III.37}$$

Then we obtain

$$S(\mathbf{q}) = \frac{1}{n^2\rho}\,\frac{a_0(\mathbf{q})}{1+\upsilon\rho a_0(\mathbf{q})} + \frac{(-\upsilon)^2}{2n^2}\,\frac{1}{V}\sum_{\mathbf{q}'}\frac{1}{1+\upsilon\rho a_0(\mathbf{q}')}\,\frac{1}{1+\upsilon\rho a_0(\mathbf{q}+\mathbf{q}')}\{B(\mathbf{q}',\,\mathbf{q}'+\mathbf{q})\}^2 \tag{III.38}$$

and if $(nb^2/6)^{-1} \ll \mathbf{q}^2 \ll b^{-2}$, we have

$$S(\mathbf{q}) = \frac{1}{n^2\rho^2\upsilon}\,\frac{{\kappa_0}^2}{\mathbf{q}^2+{\kappa_0}^2} + \frac{(-\upsilon)^2}{2n^2}\,\frac{1}{V}\sum_{\mathbf{q}'}\frac{\mathbf{q}'^2}{\mathbf{q}'^2+{\kappa_0}^2}\,\frac{(\mathbf{q}+\mathbf{q}')^2}{(\mathbf{q}+\mathbf{q}')^2+{\kappa_0}^2}\{B(\mathbf{q}',\,\mathbf{q}'+\mathbf{q})\}^2 \tag{III.39}$$

If the second term can be neglected with respect to the first term in eq III.39, we obtain

$$S(\mathbf{q}) = \frac{12}{nb^2\rho}\,\frac{1}{q^2+{\kappa_0}^2} \tag{III.40}$$

Jannink and de Gennes[7] have obtained eq III.40 by random phase approximation; des Cloizeaux obtained a result similar to that of eq III.40 by zero-loop approximation. This Lorentzian form is also shown to be in good agreement with experiment.[8,9] In the derivation of the second term of eq III.39 in the structure factor we assumed that $a' + a'' \cong c$, which means that two variables, $\mathbf{q}$ and $\mathbf{q}'$, are orthogonal; otherwise, a correction term must be introduced in the expression of the second term, the determination of which required further experimental studies and calculations.

In section IV, we will not make use of this approximate expression, but use is made of the original expression of

$S(\mathbf{q})$, i.e., eq III.38. Consequently, the discussion in the following section is exact.

IV. Osmotic Compressibility Equation

In the theory of fluids it is known that the correlation function $g_2(\mathbf{r})$ is related to the compressibility of the system by the compressibility equation

$$\rho \int [g_2(\mathbf{r}) - 1]\, d\mathbf{r} = \rho\kappa_T k_B T - 1 \qquad \text{(IV.1)}$$

where κ_T is the isothermal compressibility defined by the pressure of the system:

$$\kappa_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T \qquad \text{(IV.2)}$$

By making use of the Mayer cluster expansion method we have obtained the osmotic pressure in section II and the static structure factor in section III. In this section let us check the validity of these results by eq IV.1; then, κ_T stands for the osmotic compressibility of the polymer solution. The expression of the osmotic pressure in the grand canonical ensemble was obtained in eq II.41 and, when differentiated with respect to density ρ, it gives

$$\left(\frac{\partial \pi_{os}}{\partial \rho}\right) = k_B T\left[1 + vn^2\rho - \frac{3(3^{1/2})}{2\pi}\left(\frac{vn}{b^2}\right)^{3/2}\rho^{1/2}\right] \qquad \text{(IV.3)}$$

Then the right-hand side of eq IV.1 is

$$\rho\kappa_T k_B T - 1 = \left[1 + vn^2\rho - \frac{3(3^{1/2})}{2\pi}\left(\frac{vn}{b^2}\right)^{3/2}\rho^{1/2}\right]^{-1} - 1$$

and it is given approximately for $n^2 v\rho \ll 1$ as

$$-vn^2\rho + \frac{3(3^{1/2})}{2\pi}\left(\frac{vn}{b^2}\right)^{3/2}\rho^{1/2} \qquad \text{(IV.4a)}$$

and for $n^2 v\rho \gg 1$ as

$$(n^2\rho)^{-1}\left[v^{-1} + \frac{3(3^{1/2})}{2\pi}\,\frac{(nv)^{-1/2}}{b^3}\rho^{-1/2}\right] \qquad \text{(IV.4b)}$$

The left-hand side of eq IV.1 is given by the static structure factor, $S(\mathbf{q})$, at $\mathbf{q} = \mathbf{0}$

$$\rho \int [g_2(\mathbf{r}) - 1]\, d\mathbf{r} = \rho S(\mathbf{q} = \mathbf{0}) \qquad \text{(IV.5)}$$

The structure factor $S(\mathbf{q})$ includes the single-molecule term whose contribution to $S(\mathbf{q})$ was calculated by considering the diagram shown in Figure 7a; this term corresponds to the van't Hoff term (i.e., the term, $\rho k_B T$, on the right-hand side of eq II.41) in the virial expansion of the osmotic pressure; then, this should be excluded from the factor $S(\mathbf{q})$ if one wants to compare the result with that of osmotic pressure by eq IV.1. So, let us define a factor $S^*(\mathbf{q})$ which is given by simply subtracting eq III.12 from eq III.38; we have

$$S^*(\mathbf{q}) = \frac{1}{n^2}\,\frac{(-v)\{a_0(\mathbf{q})\}^2}{1 + v\rho a_0(\mathbf{q})} + \frac{(-v)^2}{2n^2}\,\frac{1}{V}\sum_{\mathbf{q}'}\frac{1}{1 + v\rho a_0(\mathbf{q}')}\,\frac{1}{1 + v\rho a_0(\mathbf{q} + \mathbf{q}')}\{B(\mathbf{q}', \mathbf{q}' + \mathbf{q})\}^2 \qquad \text{(IV.6)}$$

Then the left-hand side of eq IV.1 is rewritten as

$$\rho \int [g_2^*(\mathbf{r}) - 1]\, d\mathbf{r} = \rho S^*(\mathbf{q} = \mathbf{0}) \qquad \text{(IV.7)}$$

where the single-molecule term is also subtracted in the expression of a correlation function $g^*_2(\mathbf{r})$. From eq IV.6, we obtain

$$\rho S^*(\mathbf{q} = \mathbf{0}) = \frac{(-v)\rho n^2}{1 + v\rho n^2} + \frac{(-v)^2\rho}{2n^2}\,\frac{1}{V}\sum_{\mathbf{q}'}\left\{\frac{B(\mathbf{q}',\mathbf{q}')}{1 + v\rho a_0(\mathbf{q}')}\right\}^2 \qquad \text{(IV.8)}$$

where use is made of the definition (eq II.35) of $a_0(\mathbf{q})$ at $\mathbf{q} = \mathbf{0}$

$$a_0(\mathbf{q} = \mathbf{0}) = \sum_{ij} 1 = n^2 \qquad \text{(IV.9)}$$

Note that to obtain $\rho S(\mathbf{q} = \mathbf{0})$ we must not simply use in eq III.38 the expression $a_0(\mathbf{q}) = 12n/(b^2\mathbf{q}^2)$, which is valid only between the limited range of $\mathbf{q}$, i.e., $(nb^2/6)^{-1} \ll q^2 \ll b^{-2}$. It is easily seen from the definition (III.16) that

$$B(\mathbf{q}',\mathbf{q}') = 2\sum_{i}\sum_{i_2<j_2}\exp\left[-\frac{j_2 - i_2}{6}b^2\mathbf{q}'^2\right] = na_0(\mathbf{q}') \qquad \text{(IV.10)}$$

Then the left-hand side of eq IV.1 turns out to be

$$\rho S^*(\mathbf{q} = \mathbf{0}) = \frac{(-v)\rho n^2}{1 + v\rho n^2} + \frac{\rho}{2}\,\frac{1}{V}\sum_{\mathbf{q}'}\left\{\frac{va_0(\mathbf{q}')}{1 + v\rho a_0(\mathbf{q}')}\right\}^2 = \frac{(-v)\rho n^2}{1 + v\rho n^2} + \left(\frac{12nv}{b^2}\right)^2\rho\frac{1}{16\pi\kappa_0} \cong (-v)n^2\rho + \frac{3(3^{1/2})}{2\pi}\left(\frac{nv}{b^2}\right)^{3/2}\rho^{1/2} \qquad \text{(IV.11)}$$

which is identical with eq IV.4a and where use is made of the relation

$$\frac{1}{V}\sum_{\mathbf{q}}\left\{\frac{va_0(\mathbf{q})}{1 + v\rho a_0(\mathbf{q})}\right\}^2 = \left(\frac{12nv}{b^2}\right)^2\frac{1}{8\pi\kappa_0} \qquad \text{(IV.12)}$$

Even though we have used a simpler approximation than the general HNC approximation to obtain the osmotic pressure of solution and the correlation function of the system, we find that these two results satisfy the compressibility equation and are, therefore, consistent with each other; the third term of the osmotic pressure (the "Debye–Hückel" term in eq II.41) given by the ring-form diagram corresponds to the third term of the correlation function (last term of the screened-coulomb type in eq III.33).

On the other hand, Moore[6] obtained the structure factor $S(\mathbf{q})$ of semidilute polymer solution by a renormalization group calculation and, in the limit of $\mathbf{q} \to \mathbf{0}$, if a trivial error made in his eq 2.23 is corrected, it was shown that in three dimensions

$$S(\mathbf{0}) = v^{-1} + \frac{3(3^{1/2})}{2\pi}\,\frac{(vn)^{-1/2}}{b^3}\rho^{-1/2} \qquad \text{(IV.13)}$$

which is consistent with eq IV.4b. Which relation holds for semidilute solution, $n^2 v\rho \gg 1$ or $n^2 v\rho \ll 1$, cannot be answered from the Edwards definitions of semidilute solution. In other words, either relation is valid for appropriate ranges of relevant variables.

V. Effect of Intramolecular Interactions

It is now believed that the excluded volume effect of one polymer molecule disappears in the bulk amorphous polymers. This may be the case for semidilute polymer solutions since, as Edwards mentioned,[4] the effect of other chains is to weaken the self-interaction of a chain and make

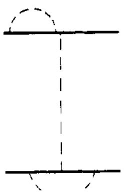

Figure 13. An irreducible series diagram which includes intramolecular interactions.

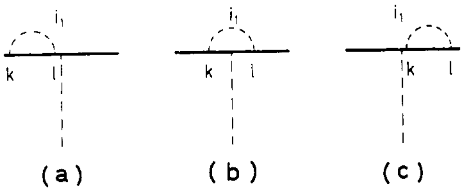

Figure 14. Combinations of an intermolecular interaction and an intramolecular interaction when (a) $k < l \le i_1$, (b) $k \le i_1 < l$, and (c) $i_1 \le k < l$.

its configuration close to that of a random walk. Therefore, by making use of the cluster expansion method, we investigate the effect of the intramolecular interactions on the osmotic equation of state, structure factor, and the correlation length up to the first order of the excluded volume parameter z defined by eq V.21; this is because each molecule has at most one intramolecular interaction. It should be noted again that we have to express cumulant averages explicitly by the product of averages of intermolecular and intramolecular f functions; furthermore, we assume that the intramolecular f function, f_0, is also given by the same form as $f(\mathbf{r})$ in eq II.28:

$$f_0(\mathbf{r}) = (-v)\delta(\mathbf{r}) \qquad \text{(V.1)}$$

Let us define a contribution from intermolecular and intramolecular interactions between monomeric units of polymers to the free energy of the system by W' especially when the self-interaction effect is considered. Again we will consider series and ring-form diagrams to calculate W' and therefore assume that

$$W' \simeq W'_{\text{series}} + W'_{\text{ring}} \qquad \text{(V.2)}$$

where W'_{series} and W'_{ring} are contributions to W' from series and ring-form diagrams, respectively.

1. **Calculation of W'_{series}.** An example of the irreducible series diagram including intramolecular interactions is shown in Figure 13. As each molecule is assumed to have at most one intramolecular interaction, one may consider the following three cases, corresponding to combinations of intermolecular and intramolecular interactions in a single molecule as shown in Figure 14. The expressions of the intramolecular structure factors are given by $a^{(\alpha)}(\mathbf{q})$, $a^{(\beta)}(\mathbf{q})$, and $a^{(\gamma)}(\mathbf{q})$, corresponding to cases a, b, and c in Figure 14, respectively:

$$a^{(\alpha)}(\mathbf{q}) = \sum_{k<l\le i_1} \exp\left[-\frac{l-k}{6}b^2\mathbf{q}^2\right] \qquad \text{(V.3a)}$$

$$a^{(\beta)}(\mathbf{q}) = \sum_{k\le i_1<l} \exp\left[-\frac{l-k}{6}b^2\mathbf{q}^2\right] \qquad \text{(V.3b)}$$

$$a^{(\gamma)}(\mathbf{q}) = \sum_{i_1\le k\le l} \exp\left[-\frac{l-k}{6}b^2\mathbf{q}^2\right] \qquad \text{(V.3c)}$$

Then one may consider the following three diagrams (see Figure 15) which contribute to W'_{series} and obtain cumulant averages of the interactions.

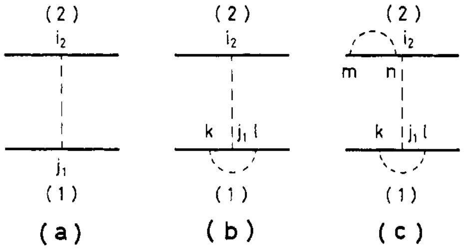

Figure 15. Irreducible series diagrams contributing to W'_{series} where (a) no, (b) one, and (c) two intramolecular interactions are included.

(a) Case Where Neither of the Molecules Has an Intramolecular Interaction (Figure 15a). This case is the same as that considered in section II. We have

$$\sum_{j_1,i_2} \langle f(\mathbf{r}_{j_1}{}^{(1)} - \mathbf{r}_{i_2}{}^{(2)})\rangle_{\text{c},2} = \sum_{j_1,i_2} \langle f(\mathbf{r}_{j_1}{}^{(1)} - \mathbf{r}_{i_2}{}^{(2)})\rangle_2 = \frac{(-v)}{V}n^2 \qquad \text{(V.4)}$$

(b) Case Where One of the Molecules Has an Intramolecular Interaction (Figure 15b). The well-known cumulant expansion formula leads to

$$\sum_{j_1,i_2}\sum_{k,l} \langle f_0(\mathbf{r}_k{}^{(1)} - \mathbf{r}_l{}^{(1)}) f(\mathbf{r}_{j_1}{}^{(1)} - \mathbf{r}_{i_2}{}^{(2)})\rangle_{\text{c},2} = \sum\sum \langle f_0(\mathbf{r}_k{}^{(1)} - \mathbf{r}_l{}^{(1)}) f(\mathbf{r}_{j_1}{}^{(1)} - \mathbf{r}_{i_2}{}^{(2)})\rangle_2 - \sum \langle f_0(\mathbf{r}_k{}^{(1)} - \mathbf{r}_l{}^{(1)})\rangle_1 \sum \langle f(\mathbf{r}_{j_1}{}^{(1)} - \mathbf{r}_{i_2}{}^{(2)})\rangle_2 = \frac{(-v)^2}{V^2}n\sum_{\mathbf{q}} a'(\mathbf{q}) - \tilde{G}_1(0,n)\frac{(-v)}{V}n^2 \qquad \text{(V.5)}$$

where

$$a'(\mathbf{q}) \equiv a^{(\alpha)}(\mathbf{q}) + a^{(\beta)}(\mathbf{q}) + a^{(\gamma)}(\mathbf{q}) = \frac{n}{2}a_0(\mathbf{q}) \qquad \text{(V.6)}$$

and

$$\tilde{G}_1(0,n) \equiv \sum_{k<l} \langle f_0(\mathbf{r}_k{}^{(1)} - \mathbf{r}_l{}^{(1)})\rangle_1 = \frac{(-v)}{V}\sum_{k<l}\sum_{\mathbf{q}} \exp\left[-\frac{l-k}{6}b^2\mathbf{q}^2\right] = \frac{(-v)}{V}\frac{1}{n}\sum_{\mathbf{q}} a'(\mathbf{q}) \qquad \text{(V.7)}$$

Substitution of eq V.7 into eq V.5 yields

$$\sum_{j_1,i_2}\sum_{k,l} \langle f_0(\mathbf{r}_k{}^{(1)} - \mathbf{r}_l{}^{(1)}) f(\mathbf{r}_{j_1}{}^{(1)} - \mathbf{r}_{i_2}{}^{(2)})\rangle_{\text{c},2} = 0 \qquad \text{(V.8)}$$

We have no contribution from this diagram to W'_{series}.

(c) Case Where Each of the Molecules Has an Intramolecular Interaction (Figure 15c). In this case, we obtain

$$\sum_{j_1,i_2}\sum_{k,l}\sum_{m,n} \langle f_0(\mathbf{r}_k{}^{(1)} - \mathbf{r}_l{}^{(1)}) f_0(\mathbf{r}_m{}^{(2)} - \mathbf{r}_n{}^{(2)}) f(\mathbf{r}_{j_1}{}^{(1)} - \mathbf{r}_{i_2}{}^{(2)})\rangle_{\text{c},2} = \sum\sum\sum \langle f_0(1) f_0(2) f(1,2)\rangle_2 - \sum \langle f_0(1)\rangle_1 \sum\sum \langle f_0(2) f(1,2)\rangle_2 - \sum \langle f_0(2)\rangle \sum\sum \langle f_0(1) f(1,2)\rangle - \sum\sum \langle f_0(1) f_0(2)\rangle_2 \sum \langle f(1,2)\rangle_2 + 2\sum \langle f_0(1)\rangle_1 \sum \langle f_0(2)\rangle_1 \sum \langle f(1,2)\rangle_2 = \frac{(-v)}{V}\left\{\frac{(-v)^2}{V^2}\sum_{\mathbf{q}} a'(\mathbf{q}) - \tilde{G}_1(0,n)\frac{(-v)}{V}n\right\}^2 = 0 \qquad \text{(V.9)}$$

where $f_0(1)$, $f_0(2)$, and $f(1,2)$ are abbreviations for $f_0(\mathbf{r}_k{}^{(1)} - \mathbf{r}_l{}^{(1)})$, $f_0(\mathbf{r}_m{}^{(2)} - \mathbf{r}_n{}^{(2)})$, and $f(\mathbf{r}_{j_1}{}^{(1)} - \mathbf{r}_{i_2}{}^{(2)})$, respectively. We have no contribution from this diagram to W'_{series} again.

It is clear from eq V.4, V.8, and V.9 that the irreducible cluster integral β_1' is not affected by the intramolecular interactions and, therefore, we obtain

$$W'_{\text{series}} = W_{\text{series}} = -\frac{vn^2}{2}V\rho^2 \qquad \text{(V.10)}$$

2. **Calculation of W'_{ring}.** Let us consider an irreducible ring-form diagram consisting of m molecules and l intramolecular interactions as shown in Figure 16. The irre-

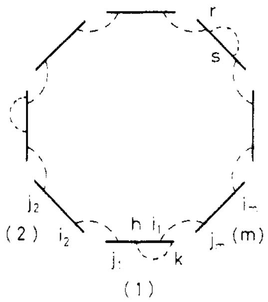

Figure 16. An irreducible ring-form diagram consisting of m molecules and l intramolecular interactions.

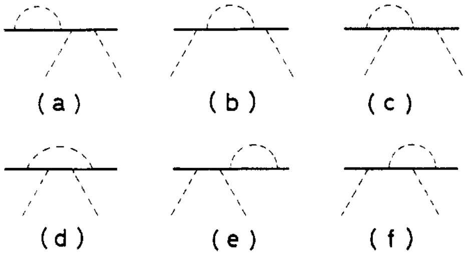

Figure 17. Combinations of two intermolecular interactions and an intramolecular interaction when (a) $k < l \leq i < j$, (b) $i \leq k < l \leq j$, (c) $k \leq i < l \leq j$, (d) $k \leq i < j \leq l$, (e) $i < j \leq k < l$, and (f) $i \leq k < j \leq l$.

ducible integral $\beta'_{m-1,l}$ defined in eq II.24 can be written for this diagram

$$V\beta'_{m-1,l} = \frac{(m-1)!}{2}\frac{1}{(m-1)!}V^m\sum\ldots\sum\langle f_0(1)\ldots f_0(l)f(1,2)\ldots f(m,1)\rangle_{\mathrm{c},m} = \tfrac{1}{2}V^m\sum_{i_1,j_1}\ldots\sum_{i_m,j_m}\sum_{h,k}\ldots\sum_{r,s}\langle f_0(1)\ldots f_0(l)f(1,2)\ldots f(m,1)\rangle_{\mathrm{c},m} \qquad \text{(V.11)}$$

To calculate the cumulant average in eq V.11 one needs to obtain the intramolecular structure factor first; and, since each molecule in the ring-form diagram is connected to other molecules by two intermolecular f functions, one has to consider the following six cases corresponding to combinations of intermolecular and intramolecular interactions as shown in Figure 17. The structure factors $a^{(\mathrm{a})}(\mathbf{q})$ to $a^{(\mathrm{f})}(\mathbf{q})$ corresponding to cases a–f in Figure 17, respectively, are calculated as follows:

$$a^{(\mathrm{a})}(\mathbf{q}) = a^{(\mathrm{e})}(\mathbf{q}) = 2(-\upsilon)\sum_{k<l\leq i<j}\frac{1}{V}\sum_{\mathbf{q}'}\exp\left[-\frac{l-k}{6}b^2\mathbf{q}'^2\right]\exp\left[-\frac{j-i}{6}b^2\mathbf{q}^2\right] \qquad \text{(V.12)}$$

$$a^{(\mathrm{b})}(\mathbf{q}) = 2(-\upsilon)\sum_{i\leq k<l\leq j}\frac{1}{V}\sum_{\mathbf{q}'}\exp\left[-\frac{l-k}{6}b^2\mathbf{q}'^2\right] \times \exp\left[-\frac{j-i-l+k}{6}b^2\mathbf{q}^2\right] \qquad \text{(V.13)}$$

$$a^{(\mathrm{c})}(\mathbf{q}) = a^{(\mathrm{f})}(\mathbf{q}) = 2(-\upsilon)\sum_{k\leq i<l\leq j}\frac{1}{V}\sum_{\mathbf{q}'}\exp\left[-\frac{i-k}{6}b^2\mathbf{q}'^2\right] \times \exp\left[-\frac{l-i}{6}b^2(\mathbf{q}+\mathbf{q}')^2\right]\exp\left[-\frac{j-l}{6}b^2\mathbf{q}^2\right] \qquad \text{(V.14)}$$

$$a^{(\mathrm{d})}(\mathbf{q}) = 2(-\upsilon)\sum_{k\leq i<j\leq l}\frac{1}{V}\sum_{\mathbf{q}'}\exp\left[-\frac{i-k}{6}b^2\mathbf{q}'^2\right] \times \exp\left[-\frac{j-i}{6}b^2(\mathbf{q}+\mathbf{q}')^2\right]\exp\left[-\frac{l-j}{6}b^2\mathbf{q}'^2\right] \qquad \text{(V.15)}$$

Performing the summation with respect to $\mathbf{q}'$ and then to i, j, k, and l by taking notice of their orders as directed in each case of Figure 17, we obtain

$$a^{(\mathrm{a})}(\mathbf{q}) = a^{(\mathrm{e})}(\mathbf{q}) = \left\{-n\upsilon' + \frac{8}{3}z + \frac{2}{a}(1-3a)\upsilon'\right\}a_0(\mathbf{q}) \qquad \text{(V.16)}$$

$$a^{(\mathrm{b})}(\mathbf{q}) = (-n\upsilon' + z)a_0(\mathbf{q})\mathcal{O}((n^2b^2\mathbf{q}^2)^{-1}) \qquad \text{(V.17)}$$

$$a^{(\mathrm{c})}(\mathbf{q}) = a^{(\mathrm{f})}(\mathbf{q}) = (-n\upsilon' + z)a_0(\mathbf{q})\mathcal{O}((n^2b^2\mathbf{q}^2)^{-1}) \qquad \text{(V.18)}$$

$$a^{(\mathrm{d})}(\mathbf{q}) = \left\{-\frac{4}{3}z - 2\left(1+\frac{2}{a}\right)\upsilon'\right\}a_0(\mathbf{q}) \qquad \text{(V.19)}$$

with

$$\upsilon' = \left(\frac{3}{2\pi b^2}\right)^{3/2}\upsilon \qquad \text{(V.20)}$$

and

$$z = \upsilon' n^{1/2} \qquad \text{(V.21)}$$

The factors $a^{(\mathrm{b})}(\mathbf{q})$, $a^{(\mathrm{c})}(\mathbf{q})$, and $a^{(\mathrm{f})}(\mathbf{q})$ can be ignored since we assume that $(nb^2/6)^{-1} \ll q^2 \ll b^{-2}$.

As shown in Appendix B, we can rewrite the cumulant average in eq V.11 by the sum of products of the ordinal averages. Thus we have

$$\sum_{i_1,j_1}\ldots\sum_{i_m,j_m}\sum_{h,k}\ldots\sum_{r,s}\langle f_0(1)\ldots f_0(l)f(1,2)\ldots f(m,1)\rangle_{\mathrm{c},m} = \frac{(-\upsilon)^m}{V^m}\sum_{\mathbf{q}}{}_mC_l\{a_0(\mathbf{q})\}^{m-l}\{a''(\mathbf{q}) - \tilde{G}_1(0,n)a_0(\mathbf{q})\}^l \qquad \text{(V.22)}$$

where

$$a''(\mathbf{q}) \equiv a^{(\mathrm{a})}(\mathbf{q}) + a^{(\mathrm{b})}(\mathbf{q}) + a^{(\mathrm{c})}(\mathbf{q}) + a^{(\mathrm{d})}(\mathbf{q}) + a^{(\mathrm{e})}(\mathbf{q}) + a^{(\mathrm{f})}(\mathbf{q}) \qquad \text{(V.23)}$$

Substituting eq V.22 into eq V.11 and making the summation with respect to l, we obtain the irreducible integral β'_{m-1}:

$$V\beta'_{m-1} = \sum_{l=0}^{m}\frac{(-\upsilon)^m}{2}\sum_{\mathbf{q}}{}_mC_l\{a_0(\mathbf{q})\}^{m-l}\{a''(\mathbf{q}) - \tilde{G}_1(0,n)a_0(\mathbf{q})\}^l = \frac{(-\upsilon)^m}{2}\sum_{\mathbf{q}}\{a(\mathbf{q}) - \tilde{G}_1(0,n)a_0(\mathbf{q})\}^m \qquad \text{(V.24)}$$

where we write

$$a(\mathbf{q}) \equiv a_0(\mathbf{q}) + a''(\mathbf{q}) \qquad \text{(V.25)}$$

This factor $a(\mathbf{q})$ can be rewritten by eq V.16, V.19, and V.23 to give

$$a(\mathbf{q}) \simeq (1 - 2n\upsilon' + 4z)a_0(\mathbf{q}) \qquad \text{(V.26)}$$

Since eq V.7 gives another expression of $\tilde{G}_1(0,n)$

$$G_1(0,n) = \sum_{k<l}\langle f_0(\mathbf{r}_k{}^{(1)} - \mathbf{r}_l{}^{(1)})\rangle_1 = -2n\upsilon' + 4z\left\{1 + \mathcal{O}\left(\frac{1}{n}\right)\right\} \qquad \text{(V.27)}$$

we have the result

$$V\beta'_{m-1} = \frac{(-\upsilon)^m}{2}\sum_{\mathbf{q}}\{a_0(\mathbf{q})\}^m \qquad \text{(V.28)}$$

Therefore we obtain

$$W'_{\mathrm{ring}} = W_{\mathrm{ring}} = \frac{V}{12\pi}\kappa_0{}^3 \qquad \text{(V.29)}$$

Equations V.10 and V.29 show that the osmotic equation of state is not altered in the presence of the self-interaction

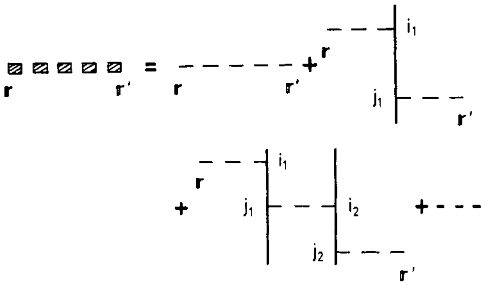

Figure 18. Diagrams necessary to calculate the effective interaction.

effect of a chain (see eq II.41).

In a similar way it can be shown that the structure factor and the correlation length in the presence of intramolecular interactions are also identical with eq III.38 and κ_0^{-1}, respectively. Alternatively, this fact may be proved by making use of the compressibility equation given in section IV. The above calculations based on simple approximations suggest that the effect of self-interaction of a polymer does not alter the solution properties of semidilute poor solvent solutions, but whether this view can be accepted or not requires further investigation.

VI. Discussion

We have shown that the osmotic equation of state for semidilute poor solvent polymer solutions has a term which is proportional to $\rho^{3/2}$ as derived by Edwards[4] in the case where the ternary cluster integral is small ($v_2 = 0$). In the same approximation, taking account of the series and the ring-form diagrams we obtained the structure factor; the contribution of the series diagram yields the structure factor in Lorentzian form first derived by Jannink and de Gennes[7] and that of the ring-form diagram gives a correction term to this Lorentzian term. The conditions of the validity of this approximation are as follows: (i) $nv\rho \ll 1$, which means that the total excluded volume of a polymer molecule is less than the volume per polymer molecule and is obtained by the ratio of the diagram composed of $m + 1$ polymers to that of m polymers in eq II.34, and (ii) $(nb^2)^{3/2}\rho > 1$, which means that the volume of a polymer molecule is larger than the volume per molecule. Furthermore, for the validity of expression II.41, the second term must be smaller than 1 (i.e., (iii) $1 > (n^2 v/2)\rho$); from (ii) and (iii), we show that the excluded volume parameter z, defined by eq V.20 and V.21, is smaller than 1 and furthermore that the third term of eq II.41 is smaller than the second term; this guarantees the approximation adopted here.

Appendix A. Effective *f* Function

To see the screening effect of the interaction with other polymers more closely, we calculate the effective f function, $\bar{f}$, by summing series diagrams as shown in Figure 18. The effective f function is given by

$$\bar{f}(\mathbf{r} - \mathbf{r}') = -v\delta(\mathbf{r} - \mathbf{r}') + \sum_{m=1}^{\infty} f_m(\mathbf{r} - \mathbf{r}') \qquad (A.1)$$

where

$$f_m(\mathbf{r} - \mathbf{r}') = \rho^m \sum_{i_1 j_1} \cdots \sum_{i_m j_m} \int \cdots \int f(\mathbf{r} - \mathbf{r}_{i_1}) f(\mathbf{r}_{j_1} - \mathbf{r}_{i_2}) \ldots f(\mathbf{r}_{j_m} - \mathbf{r}') P(\{m\})\, \mathrm{d}\{m\} \qquad (A.2)$$

In a similar way as we did in the calculation of β_m, we obtain

$$f_m(\mathbf{r} - \mathbf{r}') = (-v)^{m+1} \rho^m \frac{1}{V} \sum_{\mathbf{q}} e^{-i\mathbf{q}(\mathbf{r}-\mathbf{r}')} \{a_0(\mathbf{q})\}^m \qquad (A.3)$$

Substitution of eq A.3 into eq A.1 yields

$$\bar{f}(\mathbf{r} - \mathbf{r}') = -v\delta(\mathbf{r} - \mathbf{r}') + \frac{v\kappa_0^2}{4\pi|\mathbf{r} - \mathbf{r}'|} e^{-\kappa_0|\mathbf{r}-\mathbf{r}'|} \qquad (A.4)$$

This equation clearly shows the screening effect with the screening length κ_0^{-1}. After certain renormalization the screening length has been shown to be in good agreement with the neutron scattering experiment.[8]

Appendix B. Proof of the Equality (V.22)

In this appendix we prove the equality

$$\sum \ldots \sum \langle f_0(1) f_0(2) \ldots f_0(l) f_m \rangle_{c,m} = \frac{(-v)^m}{V^m} {}_mC_l \sum_{\mathbf{q}} \{a_0(\mathbf{q})\}^{m-l} \{a''(\mathbf{q}) - \tilde{G}_1(0,n) a_0(\mathbf{q})\}^l \qquad (B.1)$$

by the inductive method, where f_m is the abbreviation for the product of f functions:

$$f_m \equiv f(1,2) f(2,3) \ldots f(m,1) \qquad (B.2)$$

1. Case Where *l* = 1. The cumulant average of the product of one f_0 and f_m is calculated as follows:

$$\sum \ldots \sum \langle f_0(1) f_m \rangle_{c,m} = \sum \ldots \sum \langle f_0(1) f_m \rangle_m - \sum \langle f_0(1) \rangle_1 \sum \ldots \sum \langle f_m \rangle_m = \frac{(-v)^m}{V^m} \sum_{\mathbf{q}} [\{a_0(\mathbf{q})\}^{m-1} a''(\mathbf{q}) - \tilde{G}_1(0,n) \{a_0(\mathbf{q})\}^m] = \frac{(-v)^m}{V^m} \sum_{\mathbf{q}} \{a_0(\mathbf{q})\}^{m-1} \{a''(\mathbf{q}) - \tilde{G}_1(0,n) a_0(\mathbf{q})\} \qquad (B.3)$$

where $a''(\mathbf{q})$ and $\tilde{G}_1(0,n)$ are defined by

$$a''(\mathbf{q}) \equiv a^{(a)}(\mathbf{q}) + a^{(b)}(\mathbf{q}) + a^{(c)}(\mathbf{q}) + a^{(d)}(\mathbf{q}) + a^{(e)}(\mathbf{q}) + a^{(f)}(\mathbf{q}) \qquad (B.4)$$

and

$$\tilde{G}_1(0,n) \equiv \sum \langle f_0(1) \rangle_1 \qquad (B.5)$$

respectively. We can obtain the same result as eq B.3 for each case of $\sum \ldots \sum \langle f_0(i) f_m \rangle_{c,m}$ ($i = 2, \ldots, m$). Multiplying eq B.3 by this number of ways, ${}_mC_1$, we find that the equality B.1 is satisfied in the case where $l = 1$.

2. Case Where *l* Is an Arbitrary Integer (2 ≤ *l* ≤ *m*). We will show that the equality (B.1) is satisfied under the assumption that this equality is valid up to the case where l is equal to $l - 1$. The cumulant expansion of the moment of multivariables is given by the following formula:

$$\langle x_1 x_2 \ldots x_M \rangle = \sum_{(B.6)} \prod_i \{\langle x_1^{m_{i1}} x_2^{m_{i2}} \ldots x_M^{m_{iM}} \rangle_c\}^{k_i}$$

where $\sum_{(B.6)}$ means the sum over all possible sets of k_i under the condition that

$$\sum_i k_i m_{ij} = 1 \qquad \text{(both } k_i \text{ and } m_{ij} \text{ are 0 or 1)} \qquad (B.6)$$

Therefore, we have

$$\langle f_0(1) f_0(2) \ldots f_0(l) f_m \rangle_{c,m} = \langle f_0(1) \ldots f_0(l) f_m \rangle_m - \sum_{k=1}^{l} {}_lC_k \{\langle f_0(1) \rangle_1\}^k \langle f_0(k+1) \ldots f_0(l) f_m \rangle_{c,m} \qquad (B.7)$$

Substitution of eq B.7 and the assumption for k ($1 \le k \le l - 1$)

$$\sum \ldots \sum \langle f_0(k+1) \ldots f_0(l) f_m \rangle_{c,m} = \frac{(-v)^m}{V^m} \sum_{\mathbf{q}} \{a_0(\mathbf{q})\}^{m-l+k} \{a''(\mathbf{q}) - \tilde{G}_1(0,n) a_0(\mathbf{q})\}^{l-k} \qquad (B.8)$$

into the left-hand side of eq B.1 yields

$$\sum\ldots\sum\langle f_0(1)f_0(2)\ldots f_0(l)f_m\rangle_{\mathrm{c},m} = \frac{(-\upsilon)^m}{V^m}\sum_{\mathbf{q}}\{a_0(\mathbf{q})\}^{m-l}[\{a''(\mathbf{q})\}^l - \sum_{k=1}^{l}{}_lC_k\{\tilde{G}_1(0,n)a_0(\mathbf{q})\}^k\{a''(\mathbf{q}) - \tilde{G}_1(0,n)a_0(\mathbf{q})\}^{l-k}] = \frac{(-\upsilon)^m}{V^m}\sum_{\mathbf{q}}\{a_0(\mathbf{q})\}^{m-l}[\{a''(\mathbf{q})\}^l - \sum_{k=1}^{l}\sum_{p=0}^{l-k}{}_lC_k\,{}_{l-k}C_p(-1)^{l-k-p}\{\tilde{G}_1(0,n)a_0(\mathbf{q})\}^{l-p}\{a''(\mathbf{q})\}^p] \quad \text{(B.9)}$$

Changing the order of the summations from $\sum_{k=1}^{l}\sum_{p=0}^{l-k}$ to $\sum_{p=0}^{l-1}\sum_{k=1}^{l-p}$ and making use of the equality

$$\sum_{k=1}^{l-p}{}_lC_k\,{}_{l-k}C_p(-1)^{l-k} = -{}_lC_p(-1)^l \quad \text{(B.10)}$$

we obtain

$$\sum\ldots\sum\langle f_0(1)\ldots f_0(l)f_m\rangle_{\mathrm{c},m} = \frac{(-\upsilon)^m}{V^m}\sum_{\mathbf{q}}\{a_0(\mathbf{q})\}^{m-l}[\{a''(\mathbf{q})\}^l + \sum_{p=0}^{l-1}(-1)^{l-p}{}_lC_p\{\tilde{G}_1(0,n)a_0(\mathbf{q})\}^{l-p}\{a''(\mathbf{q})\}^p] = \frac{(-\upsilon)^m}{V^m}\sum_{\mathbf{q}}\{a_0(\mathbf{q})\}^{m-l}\{a''(\mathbf{q}) - \tilde{G}_1(0,n)a_0(\mathbf{q})\}^l \quad \text{(B.11)}$$

Multiplying eq B.11 by the number of ways selecting l molecules out of m molecules, ${}_mC_l$, gives the right-hand side of eq B.1.

With the cases 1 and 2 we have proved the equality B.1.

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Theory of Homopolymer Retention in Semidilute Solutions Using Liquid Chromatography

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ABSTRACT: A previously developed theory of fractionation of flexible homopolymers by gradient elution high-performance liquid chromatography (HPLC) is extended to include intermolecular polymer–polymer interactions and hence be applicable to polymer solutions of finite concentration. The analysis predicts that in favorable mobile-phase solvent environments, the retention time or capacity factor should increase with polymer loading. The theory also suggests the potential utilization of HPLC to obtain osmotic second virial coefficients and hence average molecular volumes of flexible polymer molecules in dilute solution. Also briefly considered is the possibility of verification by HPLC of the osmotic pressure equation of state in semidilute polymer solutions where scaling concepts are applicable. Chromatographic measurements of osmotic second virial coefficients are expected to become more difficult as the degree of polymerization increases, and equation of state measurements in semidilute solutions would require careful operational selection of the mobile-phase composition to achieve low polymer retention at relatively high loading of polymeric solute.

I. Introduction

The transition between infinitely dilute solutions of isolated flexible polymer molecules to semidilute solutions where different polymer molecules begin to interpenetrate substantially occurs in good solvents for a volume fraction of chain monomers given by $\Phi \sim M^{-0.8}$, where M is the degree of polymerization.[1] Thus departures from infinite dilution can be anticipated for small values of Φ when M is large (e.g., when $10^3 \leq M \leq 10^5$, $4 \times 10^{-3} \geq \Phi \geq 1 \times 10^{-4}$). High-performance liquid chromatography (HPLC) has been successfully applied to the reversed-phase fractionation of polystyrene homopolymers using gradient elution with mixed methylene chloride–methanol mobile phases,[2] and a theoretical interpretation of the separation process has been introduced on the basis of assumption of infinite dilution of polymer solute.[3] Preliminary HPLC measurements of the retention time of polystyrene homopolymers distributed between a chemically bonded C-18 stationary phase and a methylene chloride–methanol mixed mobile phase indicate that the retention increases with the amount of polymer loaded into the column.[4] The polystyrene samples had M values in the range $600 \leq M \leq 8600$ and, assuming a molar volume for styrene monomers of 125 cm^3/mol, Φ values in the range $3 \times 10^{-4} < \Phi < 3 \times 10^{-2}$. Thus for the higher polymer loadings $\Phi > M^{-0.8}$, which indicates these samples were semidilute. The purpose of the present analysis is to extend a recent theory of HPLC homopolymer fractionation[3] to include intermolecular polymer–polymer interactions.

In section II we apply the McMillan–Mayer theory[3,5] to dilute (but not infinitely dilute) polymer solutions and scaling theory[1] to semidilute polymer solutions to derive

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