Concentration Dependence of Equilibrium Chain Properties in Dilute Polymer Solutions

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ABSTRACT: The concentration dependence of single-chain equilibrium properties such as the radius of gyration R_G, the hydrodynamic radius R_H, and the static structure factor $S_S(q)$ of a labeled chain in a dilute solution is due, in the first order in concentration, to the deformation of the labeled chain, both in size and in shape, when it experiences a binary encounter. We calculate the concentration correction in R_G, R_H, and $S_S(q)$ using two-chain Monte Carlo calculations of Olaj et al. to quantify the intramolecular deformations in a pair. The magnitude of the correction turns out to be less than a few percent. The concentration dependence of the static structure factor $S(q;C)$, including the interference effects, is also calculated using the pair distribution function obtained in the above Monte Carlo calculations, without resorting to the single-contact approximation for the excluded volume interaction between two chains. The results for $S^{-1}(q;C)$ are compared with the Zimm plot. The initial slope of $S^{-1}(q;C)$ as a function of q^2 in the good solvent limit is found to depend on concentration appreciably while it is known to be independent of concentration in the single-contact approximation.

Introduction

The main purpose of this paper is to investigate the concentration dependence of single-chain equilibrium properties in the lowest order in concentration. Specifically, we consider a labeled chain in the presence of other identical chains in a dilute solution. A single-chain property is defined in general as a function $Z(\mathbf{S})$, which depends on the positions $\mathbf{S} = \{\mathbf{S}_1, \mathbf{S}_2, ..., \mathbf{S}_N\}$ of the monomers of the labeled chain relative to its center of mass. Other internal variables such as the bond vectors $\mathbf{b} = \{\mathbf{b}_1, \mathbf{b}_2, ..., \mathbf{b}_{N-1}\}$ could also be used to specify Z. The equilibrium average of Z is defined as

$$\langle Z\rangle_{\psi(\mathbf{S};C)} = \int d\mathbf{S}\; Z(\mathbf{S})\psi(\mathbf{S};C) \tag{1}$$

where $\psi(\mathbf{S};C)$ is the equilibrium monomer distribution of the labeled chain in the presence of others at a specific concentration C (C being the number of molecules per unit volume). The concentration dependence of $\psi(\mathbf{S};C)$, in the lowest order in polymer concentration, can be displayed as[1]

$$\psi(\mathbf{S};C) = \psi(\mathbf{S}) + C\int d^3R\; G(R)[\psi(\mathbf{S}|\mathbf{R}) - \psi(\mathbf{S})] \tag{2}$$

where $\psi(\mathbf{S})$ and $\psi(\mathbf{S}|\mathbf{R})$ denote, respectively, the intramolecular distribution of the labeled chain when it is isolated and when it is forming a pair with a center-of-mass separation distance R. Here, $G(R)$ is the pair distribution function of polymers in the infinite dilution limit and is related to the intermolecular interaction potential $U(R)$ by

$$G(R) = \exp[-U(R)/k_BT] \tag{3}$$

k_BT being the temperature in energy units.

The equilibrium average of Z can be written by the use of (2) in (1) as

$$\langle Z\rangle_{\psi(\mathbf{S};C)} = \langle Z\rangle_{\psi(\mathbf{S})} + C\int d^3R\; G(R)[\langle Z\rangle_{\psi(\mathbf{S}|\mathbf{R})} - \langle Z\rangle_{\psi(\mathbf{S})}] \tag{4}$$

which is the starting equation in the present work.

In many cases, the single-chain property can be expressed as a sum of pairs

$$Z(\mathbf{S}) = \sum_{i,j=1}^{N} Z(\mathbf{S}_{ij}) \tag{5}$$

where $\mathbf{S}_{ij} = \mathbf{S}_i - \mathbf{S}_j$ is the vector distance of two monomers on the labeled chain. Hence, we only need the distributions $\psi_{ij}(\mathbf{S})$ and $\psi_{ij}(\mathbf{S}|\mathbf{R})$ of $\mathbf{S} = \mathbf{S}_{ij}$ in an isolated chain and in a chain forming a pair.

The conditional distribution $\psi_{ij}(\mathbf{S}|\mathbf{R})$ takes into account the deformation of the labeled chain both in shape and in size when it is in a pair. Olaj et al.[2-4] have investigated deformations of two identical chains as a function of their center-of-mass separation distance under both Θ and good solvent conditions with two-chain Monte Carlo calculations. In particular, they obtained the variations of the radius of gyration and the end-to-end distance along parallel and perpendicular directions to the pair axis.

In order to make use of this information, we represent the distribution of $\mathbf{S}$ as a product of two Gaussian distributions for its parallel and transverse components to the axis of the pair:

$$\psi_{ij}(\mathbf{S}|\mathbf{R}) = \left(\frac{3}{2\pi\langle S_{ij}^2\rangle}\right)^{3/2}\frac{1}{\epsilon_\parallel\epsilon_\perp^2}\exp\left[-\frac{3S^2}{2\langle S_{ij}^2\rangle}\left(\frac{1-\mu^2}{\epsilon_\perp^2}+\frac{\mu^2}{\epsilon_\parallel^2}\right)\right] \tag{6}$$

where $\cos^{-1}\mu$ is the angle between $\mathbf{S}$ and the axis of the pair. The quantity $\langle S_{ij}^2\rangle$ denotes the equilibrium average of $|S_{ij}^2|$ for a single isolated chain. The quantities $\epsilon_\parallel^2(R)$ and $\epsilon_\perp^2(R)$ account for the deformation in the shape of the labeled chain in a pair when the separation distance is R. They are defined as the mean squares of the parallel and perpendicular components of the end-to-end vector $\mathbf{R}_N$ of the chain, normalized such that $\epsilon_\parallel^2(\infty) = \epsilon_\perp^2(\infty) = 1$. The assumption that $\epsilon_\parallel^2(R)$ and $\epsilon_\perp^2(R)$ are independent of i and j implies a proportional deformation of all chain sections. The variation of $\epsilon_\parallel^2(R)$, $\epsilon_\perp^2(R)$, and $G(R)$ with the separation distance R has been obtained by Olaj et al.[4] numerically.

We have investigated explicitly the concentration dependence of the radius of gyration R_G, the hydrodynamic radius R_H, and the static structure factor $S_S(q;C)$ of a labeled chain as an application of the above formalism. In the case of the concentration dependence of R_G, our general formalism in eq 4 reproduces the method used by Olaj et al.[4]

In addition to the self part of the static structure factor $S(q;C)$, we have also obtained the interference term $S_I(q;C)$, which involves the joint intramolecular segment distribution $\psi(\mathbf{S}_1,\mathbf{S}_2|\mathbf{R})$ of two chains forming a pair with a separation distance R. By approximating this function as a product $\psi(\mathbf{S}_1|\mathbf{R})\psi(\mathbf{S}_2|\mathbf{R})$, we have obtained an expression for $S(q;C)$ in the lowest order in concentration and for all

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q values in terms of $G(R)$, $\epsilon_{\parallel}(R)$, and $\epsilon_{\perp}(R)$. This approximation differs from the single-contact approximation used by Zimm[5] originally to handle the excluded volume interaction between two chains. The variation of $S(q;C)$ and $S^{-1}(q;C)$ as function of qR_G is plotted for a few values of concentration and compared to the results obtained with the single-contact approximation.

Radius of Gyration

The choice of Z as

$$Z = \frac{1}{2N^2}\sum_{i,j=1}^{N}|\mathbf{S}_i - \mathbf{S}_j|^2$$

in (4) gives the concentration dependence of the radius of gyration (or rather of its square) of a labeled chain. The result can be displayed as

$$R_G^2(C) = R_G^2(1 + K_G C_V) \tag{7}$$

where C_V is the polymer concentration as a volume fraction; i.e., $C_V = (4\pi/3)R_G^3 C$. R_G is the radius of gyration for an isolated chain, and

$$K_G = 3\int_0^\infty dX\, X^2 G(X)\frac{\Delta R_G^2(X)}{R_G^2} \tag{8}$$

In (8), $X = R/R_G$ and $\Delta R_G^2(X) = R_G^2(X) - R_G^2$, where $R_G^2(X)$ denotes the radius of gyration of the labeled chain in a pair with a separation distance R and satisfies $R_G(\infty) = R_G$. Equation 8 was first obtained by Olaj et al. (eq 5 of ref 4). The interesting feature of (7) and (8) is that the functions $G(X)$ and $\Delta R_G^2(X)/R_G^2$ needed to calculate K_G are also available numerically from two-chain Monte Carlo computations on lattices.[3,4] Using the numerical results reported by Olaj et al.,[4] we have calculated $K_G = 0.0192$ (4-way lattice) and $K_G = 0.0356$ (5-way lattice) under Θ conditions and $K_G = -0.0862$ (4-way lattice) and $K_G = -0.0930$ (5-way lattice) in the good solvent limit. Equations 7 and 8 are identical with those given by Olaj et al.,[4] except for the definition of the volume fraction.

One could derive an expression for the quantity $R_G^2(R)$ by performing the ensemble average $\langle Z\rangle_{\psi(\mathbf{S}|\mathbf{R})}$ in (4) using the modeled distribution function $\psi_{ij}(\mathbf{S}|\mathbf{R})$ in (6):

$$R_G^2(R) = \frac{1}{2N^2}\sum_{i,j=1}^{N}\langle S_{ij}^2\rangle_{\psi(\mathbf{S}|\mathbf{R})} = R_G^2\epsilon^2(R) \tag{9}$$

where

$$\epsilon^2(R) = \frac{\epsilon_\perp^3}{\epsilon_\parallel}\int_0^1 d\mu\,\frac{1}{[1 + \mu^2(\epsilon_\perp^2/\epsilon_\parallel^2 - 1)]^{5/2}}$$

which can be reduced to

$$\epsilon^2(R) = (2\epsilon_\perp^2 + \epsilon_\parallel^2)/3 \tag{10}$$

Substitution of (10) into (4) leads to the following expression for K_G in terms of the deformation of the end-to-end distance, viz., $\Delta H^2(R) = \epsilon^2(R) - 1$:

$$K_G = 3\int_0^\infty dX\, X^2 G(X)\Delta H^2(X) \tag{11}$$

Using the values of $\Delta H^2(X)$ also calculated by Olaj et al.,[4] one finds $K_G = 0.0167$ (4-way lattice) and $K_G = 0.0377$ (5-way lattice) under Θ conditions and $K_G = -0.1100$ (4-way lattice) and $K_G = -0.1269$ (5-way lattice) for the good solvent limit. The agreement between these values and those given above provides a check of the validity of the form $\psi_{ij}(\mathbf{S}|\mathbf{R})$ introduced in (6).

The significance of these results is more qualitative than quantitative because the concentration correction even in the good solvent limit turns out to be less than a few percent. However, it is still interesting to find that the radius of gyration tends to increase with concentration under Θ conditions, whereas it decreases in the good solvent limit. The physical origin of this behavior lies in that, according to the Monte Carlo calculations,[4] $\Delta H^2(X)$ in (11) is positive for small separation distances and negative for large distances in the good solvent limit. Since distant pairwise encounters are more numerous as indicated by the weighting factor $X^2G(X)$, the decrease in the size of the molecules predominates, resulting in a decrease of the radius of gyration with concentration in good solvents. In the case of Θ solvents, $\Delta H^2(X)$ is again positive for small distances but oscillates between negative and positive values a few times when the separation distance is increased. Although there is a possibility that these oscillations may be an artifact due to some computational reasons, there is no physical reason, to our knowledge, to reject them as such. Furthermore, the pair distribution function $G(X)$ is larger than in the good solvent case for short distances. The net result is that K_G is slightly positive under Θ conditions. The accuracy of the numerical estimates of K_G does not seem to be reliable because of the statistical uncertainty in $\epsilon_\parallel^2(R)$ and $\epsilon_\perp^2(R)$ at large separation distances, where the weighting factor $X^2G(X)$ is more important than at shorter distances. The large discrepancy between 4-way and 5-way cubic lattice results under Θ conditions may be an indication of this uncertainty.

The decrease of $R_G^2(C)$ with increasing concentration in good solvents is in qualitative agreement with ref 6 and with the results obtained by Sanchez and Lohse,[7] who expressed K_G as $K_G \sim -A_2M^2$. We should, however, mention that the positive (and small) slope K_G at the Θ temperature may be due to the fact that Olaj's Θ temperature (with 50-mers) is below the Flory temperature. In the former case the Θ condition is defined as the point where the $N^{1/2}$ power law for R_G is obeyed. $A_2 = 0$ defines the Θ temperature in the long-chain limit.

First Cumulant and Hydrodynamic Radius

Another single-chain property is the first cumulant, defined as

$$\Omega_S(q;C) = -\lim_{t\to 0}\frac{d}{dt}\ln S_S(q,t;C) \tag{12}$$

where $S_S(q,t;C)$ is the intermediate scattering function for the labeled chain. In the small-q limit, it reduces to $\Omega_S(q\to 0;C) = q^2D_{0S}(C)$, where

$$D_{0S}(C) = \langle Z\rangle_{\psi(\mathbf{S};C)} \tag{13}$$

with

$$Z = \frac{k_BT}{\xi N}\left[1 + \frac{\xi}{6\pi\eta}\frac{1}{N}\sum_{i,j=1}^{N}{}'\frac{1}{|\mathbf{S}_i - \mathbf{S}_j|}\right] \tag{14}$$

The Oseen tensor appears as an averaged quantity (over angles) because $\psi(\mathbf{S};C)$ is spherically symmetric even in the presence of other chains. The quantity $D_{0S}(C)$ can be interpreted as the concentration-dependent short-time self-diffusion coefficient of a chain. Indeed, in the zero concentration limit, the translational diffusion coefficient D of a polymer is related to the short-time diffusion coefficient D_0 by $D = D_0 - D_1$, where D_1 is a correction term accounting for the coupling between internal modes and diffusion of the center of mass.[8-10] The magnitude of D_1 relative to D_0 for a Gaussian chain with preaveraged Oseen tensor is 1.68%. At finite concentrations, the self-diffusion and mutual (or cooperative) diffusion coefficients deviate

from each other due to the difference in their concentration dependences. In this paper, we focus our attention on the concentration dependence of D_{0S} (short-time self-diffusion coefficient) only and drop the subscript zero for notational convenience. The concentration dependence of the mutual diffusion coefficient was discussed elsewhere.[1,11] Since a working definition of the hydrodynamic radius R_H of a chain is usually taken as

$$R_H^{-1} = \frac{1}{N^2} \sum_{i,j=1}^{N}{}' \left\langle \frac{1}{R_{ij}} \right\rangle$$

we may also interpret $D_S(C)$ as $D_S(C) \sim R_H^{-1}(C)$ for large N and investigate the concentration dependence of the hydrodynamic radius using (13).

Substitution of (14) into (4) yields

$$D_S(C) = D_S\left[1 + C \int d^3R\, G(R) \left[\frac{D_S(R) - D_S}{D_S} \right] \right] \quad (15)$$

where

$$D_S(R) = \frac{k_B T}{\xi N}\left[1 + \frac{\xi}{6\pi\eta} \frac{1}{N} \sum_{i,j=1}^{N}{}' \left\langle \frac{1}{S_{ij}} \right\rangle_{\psi(\mathbf{S}|\mathbf{R})} \right] \quad (16)$$

and

$$D_S = \frac{k_B T}{\xi N}\left[1 + \frac{\xi}{6\pi\eta} \frac{1}{N} \sum_{i,j=1}^{N}{}' \left\langle \frac{1}{S_{ij}} \right\rangle_{\psi(\mathbf{S})} \right] \quad (17)$$

Here, D_S corresponds to Kirkwood's approximation for the translational diffusion coefficient[12] in the zero concentration limit. The quantity $D_S(R)$ can be interpreted as the short-time translational diffusion coefficient of the center of mass of the labeled chain when it forms a pair with another molecule at a separation distance R. It can be calculated numerically as a function of R using the two-chain Monte Carlo results given by Olaj et al.,[4] similarly to the calculation of $R_G^2(R)$. To our knowledge, such calculations have not yet been reported in the literature. Therefore, we proceed by performing the averages over the modeled distribution function $\psi_{ij}(\mathbf{S}|\mathbf{R})$ in (6), and find

$$\left\langle \frac{1}{S_{ij}} \right\rangle = \left(\frac{6}{\pi} \right)^{1/2} \frac{1}{\langle S_{ij}^2 \rangle^{1/2}} h(R) \quad (18)$$

where

$$h(R) = \frac{1}{(\epsilon_\perp^2 - \epsilon_\parallel^2)^{1/2}} \tan^{-1}\left(\frac{\epsilon_\perp^2}{\epsilon_\parallel^2} - 1 \right)^{1/2}; \qquad \epsilon_\perp^2 > \epsilon_\parallel^2$$

$$h(R) = \frac{1}{(\epsilon_\parallel^2 - \epsilon_\perp^2)^{1/2}} \tanh^{-1}\left(1 - \frac{\epsilon_\perp^2}{\epsilon_\parallel^2} \right)^{1/2}; \qquad \epsilon_\perp^2 < \epsilon_\parallel^2 \quad (19)$$

Substitution of (18) into D_S and $D_S(R)$ leads to

$$\frac{D_S(R) - D_S}{D_S} = \left(1 - \frac{k_B T}{\xi N D_S} \right)(h(R) - 1) \quad (20)$$

Expressing the concentration dependence of $D_S(C)$ as

$$D_S(C) = D_S(1 + K_{DS}^G C_V)$$

we obtain the coefficient K_{DS}^G

$$K_{DS}^G = \left[1 - \frac{k_B T}{\xi N D_S} \right] 3 \int_0^\infty dX\, X^2 G(X)[h(X) - 1] \quad (21)$$

where $X = R/R_G$ is a normalized intermolecular distance and C_V is measured in volume fraction. If we define C_V using a hydrodynamic volume as $C_V = (4\pi/3)R_H^3 C$, K_{DS}^G is replaced by $K_{DS}^H = K_{DS}^G (R_G/R_H)^3$. We have calculated both K_{DS}^G and K_{DS}^H using the two-chain Monte Carlo data for $G(X)$, $\epsilon_\parallel^2(X)$, and $\epsilon_\perp^2(X)$ for 4-way and 5-way cubic lattices under Θ and good solvent conditions. We have also used $R_H/R_G = 0.665$ under Θ conditions[13] and $R_H/R_G = 0.537$ for good solvent conditions[14] to convert K_{DS}^G to K_{DS}^H.

	4-way		5-way	
	Θ	good	Θ	good
K_{DS}^G	−0.0025	0.0722	−0.0154	0.0794
K_{DS}^H	−0.0086	0.4663	−0.0525	0.5129

If deviations from spherical deformation are such that $\epsilon_\parallel^2 \simeq \epsilon_\perp^2$, a simpler and physically more interpretable result is obtained from (19) by expanding $\tan^{-1} X$ and $\tanh^{-1} X$ for small arguments

$$h(R) = \frac{1}{3\epsilon_\parallel}\left(4 - \frac{\epsilon_\perp^2}{\epsilon_\parallel^2} \right) \quad (22)$$

Introducing $\Delta H^2 = (\Delta H_\parallel^2 + 2\Delta H_\perp^2)/3$ given in terms of the perturbations $\Delta H_\parallel^2 = \epsilon_\parallel^2 - 1$ and $\Delta H_\perp^2 = \epsilon_\perp^2 - 1$ that are calculated by Olaj et al.,[4] one obtains

$$K_{DS}^G = -\frac{3}{2}\left(1 - \frac{k_B T}{\xi N D_S} \right) \int_0^\infty dX\, X^2 G(X) \Delta H^2(X) \quad (23)$$

ΔH^2 is a measure of the overall change in the end-to-end distance of the labeled chain as a function of the separation distance. This simplified result provides a cruder estimate for K_{DS}^G than the one presented above but lends itself better to physical interpretation than the original form in (21) (see discussion at the end of the previous section).

Equation 23 was used by one of us[1] to calculate $D_S(C)$ by assuming that $\psi(\mathbf{S}|\mathbf{R})$ is an isotropic Gaussian chain with an $\mathbf{R}$-dependent radius of gyration. This assumption is tantamount to letting $\epsilon_\parallel^2(R) = \epsilon_\perp^2(R) = \epsilon^2(R)$ in (6) for all separation distances, with the implication that the deformation of the labeled chain is spherical. It leads to $h(R) = 1/\epsilon(R)$ in (19), which is equivalent to assuming that $D_S(R)/D_S = R_N/R_N(R)$ for all R (R_N being the end-to-end distance). In ref 1, K_{DS} was calculated with $\epsilon^2(R) = R_G^2(R)/R_G^2$ and by ignoring the decrease in size at large separation distance. Furthermore, $G(R)$ was obtained from $\exp(-U(R)/k_B T)$ with a uniform-sphere model for the intermolecular interaction potential $U(R)$. At the Θ temperature, $U(R) = 0$ ($G(R) = 1$) according to this model, so that it puts more weight on close encounters than the Monte Carlo value of $G(R)$ used in the present work. This and the neglect of the decrease in size at large distances led to $K_{DS}^H = -1.063$ under Θ conditions and $K_{DS}^H = -0.187$ for the good solvent case. Although it predicted the correct trend from Θ to good solvent, it represents a cruder estimation of the numerical value of K_{DS}^H than the calculation presented here. The latter includes a more detailed description of binary encounters and makes use of the Monte Carlo results for both $U(R)/k_B T$ and size changes in parallel and perpendicular directions consistently.

Equation 21 indicates that, because of the first bracket, the short-time self-diffusion coefficient becomes independent of concentration in the Rouse limit. We also notice in (21) that K_{DS} vanishes when there is no deformation in the monomer distribution in a molecule during binary encounters, e.g., hard spheres. However, the long-time self-diffusion coefficient can still be concentra-

tion dependent[15] through the correction term D_1 which has not been considered in this paper.

Before leaving this section, we should mention that several works have shown that for finite-length chains at infinite dilution, the Θ dimensions are slightly larger than ideal.[16-18]

Single-Chain Static Structure Factor

The concentration dependence of the static structure factor of the labeled chain is obtained by choosing

$$Z = \frac{1}{N^2}\sum_{i,j=1}^{N} \exp(i\mathbf{q}\cdot\mathbf{S}_{ij})$$

in (4) as

$$S_S(q;C) = S_S(q) + C\int d^3R\; G(R)[S_{ps}(\mathbf{q}|\mathbf{R}) - S_S(q)] \quad (24)$$

where

$$S_S(q) = \frac{1}{N^2}\sum_{i,j=1}^{N} \langle \exp(i\mathbf{q}\cdot\mathbf{S}_{ij})\rangle_{\psi(\mathbf{S})} \quad (25)$$

and

$$S_{ps}(\mathbf{q}|\mathbf{R}) = \frac{1}{N^2}\sum_{i,j=1}^{N} \langle \exp(i\mathbf{q}\cdot\mathbf{S}_{ij})\rangle_{\psi(\mathbf{S}|\mathbf{R})} \quad (26)$$

The quantities $S_S(q)$ and $S_{ps}(\mathbf{q}|\mathbf{R})$ are, respectively, the static structure factors of an isolated molecule and of a molecule in an isolated pair with a separation distance R. $S_{ps}(\mathbf{q}|\mathbf{R})$ is readily available for Gaussian chains, as we assumed for $\psi_{ij}(\mathbf{S}|\mathbf{R})$ in (6), in the form of a Debye function with an $\mathbf{R}$-dependent argument:

$$S_{ps}(\kappa|\mathbf{X}) = 2\frac{[e^{-\kappa^2(X)} + \kappa^2(\mathbf{X}) - 1]}{\kappa^4(\mathbf{X})} \quad (27a)$$

where $\mathbf{X} = \mathbf{R}/R_G$ and

$$\kappa^2(\mathbf{X}) = \kappa^2\epsilon_\perp{}^2(X) + \kappa^2\alpha^2[\epsilon_\parallel{}^2(X) - \epsilon_\perp{}^2(X)] \quad (27b)$$

with $\kappa = \mathbf{q}R_G$ and $\cos^{-1}\alpha$ the angle between κ and the separation distance $\mathbf{X}$. $S_S(q)$ is the limit of $S_{ps}(\kappa|\mathbf{X})$ as $X \to \infty$. Combining these results, one finds in terms of volume fraction C_V

$$S_S(\kappa;C) = S_S(\kappa) + C_V T(\kappa) \quad (28a)$$

where

$$T(\kappa) = \frac{3}{4\pi}\int d^3X\; G(X)[S_{ps}(\kappa|\mathbf{X}) - S_S(\kappa)] \quad (28b)$$

The $\mathbf{X}$ integration in (28b) is performed numerically by using the Monte Carlo results for $\epsilon_\perp{}^2(X)$, $\epsilon_\parallel{}^2(X)$, and $G(X)$. These results are presented together with those for the interference term to be discussed next.

Static Structure Factor

Although it is not a single-chain property, we also consider the interference term in the static structure factor

$$S(q;C) = S_S(q;C) + S_I(q;C)$$

in order to investigate the concentration dependence of $S(q;C)$ as a whole. By definition

$$S_I(q;C) = \frac{N_P - 1}{N^2}\sum_{i,j=1}^{N} \langle e^{i\mathbf{q}\cdot(\mathbf{R}_{12}+\mathbf{S}_{1i2j})}\rangle_{\psi(\mathbf{S}_1,\mathbf{S}_2,\mathbf{R}_{12};C)} \quad (29)$$

where N_P is the number of chains in the system of volume V, $\mathbf{R}_{12}$ is the vector distance between the centers of mass of the molecules in a pair, $\mathbf{S}_{1i2j} = \mathbf{S}_{1i} - \mathbf{S}_{2j}$, and $\psi(\mathbf{S}_1,\mathbf{S}_2,\mathbf{R}_{12};C)$ is the concentration-dependent joint distribution function of the intramolecular coordinates $\mathbf{S}_1$ and $\mathbf{S}_2$ and the centers of mass of the molecules in the pair.

We need this two-molecule distribution function only in the infinite dilution limit because S_I is already proportional to N_P/V. Separating the pair distribution function $\psi(\mathbf{R}_{12}) = G(\mathbf{R}_{12})/V^2$ as

$$\psi(\mathbf{S}_1,\mathbf{S}_2,\mathbf{R}_{12}) = \frac{1}{V^2}G(\mathbf{R}_{12})\psi_C(\mathbf{S}_1,\mathbf{S}_2|\mathbf{R}_{12})$$

where $\psi_C(\mathbf{S}_1,\mathbf{S}_2|\mathbf{R}_{12})$ is the conditional joint intramolecular distribution function of molecules in an isolated pair with a separation distance $\mathbf{R}_{12}$, we can express $S_I(q;C)$ as

$$S_I(q;C) = C\int d^3R\; G(R)e^{i\mathbf{q}\cdot\mathbf{R}}S_{pd}(\mathbf{q}|\mathbf{R}) \quad (30)$$

where

$$S_{pd}(\mathbf{q}|\mathbf{R}) = \frac{1}{N^2}\sum_{i,j=1}^{N} \langle \exp(i\mathbf{q}\cdot\mathbf{S}_{1i2j})\rangle_{\psi_C(\mathbf{S}_1,\mathbf{S}_2|\mathbf{R})} \quad (31)$$

Since $\psi_C(\mathbf{S}_1,\mathbf{S}_2|\mathbf{R})$ approaches the product $\psi(\mathbf{S}_1)\psi(\mathbf{S}_2)$ of single-chain monomer distributions $\psi(\mathbf{S}_1)$ and $\psi(\mathbf{S}_2)$ as $R \to \infty$, (31) reduces for large separation distances to

$$S_{pd}(\mathbf{q}|\mathbf{R}) \to |\rho_M(q)|^2 \quad (32)$$

where $\rho_M(q)$ is the characteristic function of the monomer distribution function $\rho_M(\mathbf{S}) = (1/N)\sum_{i=1}^{N}\langle\delta(\mathbf{S} - \mathbf{S}_i)\rangle$ about the center of mass.

$S_I(q;C)$ can be cast into the following form:

$$S_I(q;C) = C\int d^3R\; [G(R) - 1]e^{i\mathbf{q}\cdot\mathbf{R}}S_{pd}(\mathbf{q}|\mathbf{R}) + C\int d^3R\; e^{i\mathbf{q}\cdot\mathbf{R}}[S_{pd}(\mathbf{q}|\mathbf{R}) - |\rho_M(q)|^2] + C|\rho_M(q)|^2\delta(\mathbf{q}) \quad (33)$$

The last term is the usual central peak that vanishes for $q \neq 0$ and will be dropped henceforth.

In order to calculate $S_{pd}(\mathbf{q}|\mathbf{R})$ in (33) explicitly, we introduce the separability assumption, which is the only assumption, to proceed further

$$\psi_C(\mathbf{S}_1,\mathbf{S}_2|\mathbf{R}) \simeq \psi(\mathbf{S}_1|\mathbf{R})\psi(\mathbf{S}_2|\mathbf{R}) \quad (34)$$

where $\psi(\mathbf{S}|\mathbf{R})$ is the $\mathbf{R}$-dependent intramolecular distribution function defined earlier in (6). Furthermore, assuming (as is usually done) that the monomer density distribution about the center of mass is Gaussian, we obtain $S_{pd}(\mathbf{q}|\mathbf{R})$ in dimensionless variables as

$$S_{pd}(\kappa|\mathbf{X}) \simeq \exp[-\kappa^2(\mathbf{X})/3] \quad (35)$$

where $\kappa^2(\mathbf{X})$ is defined in (27b). The assumption of a Gaussian monomer distribution about the center of mass is not essential. One may use the sum of the distributions of the individual monomers[19] instead, without any significant numerical improvement. Substitution of (35) into (33) for $q \neq 0$ yields

$$S_I(\kappa;C) = -C_V F(\kappa)$$

where

$$F(\kappa) = \frac{3}{4\pi}\int d^3X\; [1 - G(X)]e^{i\kappa\cdot\mathbf{X}}e^{-\kappa^2(\mathbf{X})/3} + \frac{3}{4\pi}\int d^3X\; e^{i\kappa\cdot\mathbf{X}}[e^{-\kappa^2/3} - e^{-\kappa^2(\mathbf{X})/3}] \quad (36)$$

Using (28) and (36) in

$$S(\kappa;C_V) = S_S(\kappa;C_V) - C_V F(\kappa) \quad (37)$$

we have calculated the static structure factor numerically as function of κ for various values of concentration. Although we do not have to commit ourselves to a particular shape for the single-chain static structure factor in the theoretical formulation, we use a Debye function to generate our plots even in the good solvent limit. The renormalization calculations reported by Ohta et al.[20] indi-

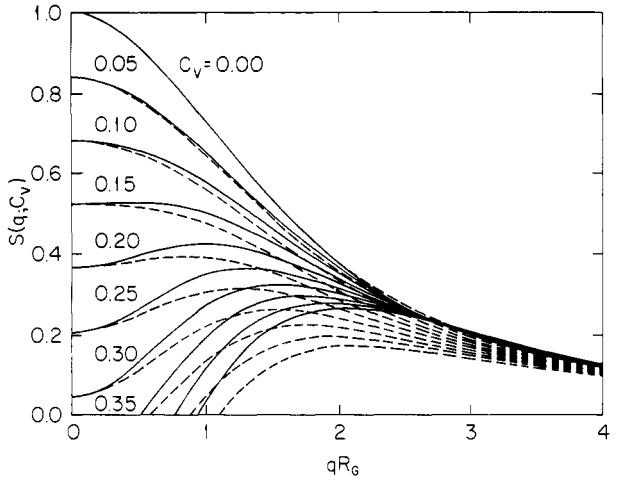

Figure 1. $S(q;C)$ vs. qR_G for various values of concentration C_V. Solid curves represent eq 37; dashed curves represent eq 38.

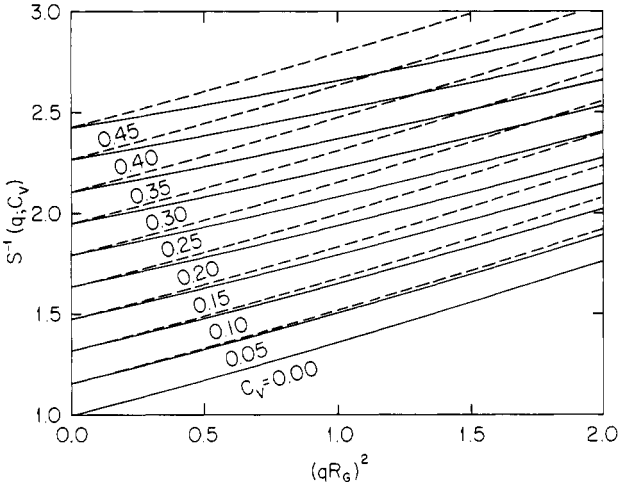

Figure 2. $S^{-1}(q;C)$ vs. $(qR_G)^2$ for various values of concentration C_V. Solid curves represent eq 39; dashed curves represent eq 40.

cate that the Debye form with swollen R_G reproduces the calculated single-chain static structure factor for athermal chains up to $q^2R_G^2 \simeq 60$ very closely. Other models can be used, such as the completely swollen chain model (Peterlin[21] and Akcasu and Benmouna[22] among others) or models based on the blob hypothesis, if the single-chain static structure factor is needed as a function of temperature. The results are presented in Figure 1. The dashed curves are calculated from Zimm's[5] result based on the single-contact approximation, viz.

$$S(\kappa;C) = S_S(\kappa) - 2A_2MC_MS_S^2(\kappa) \quad (38)$$

where A_2 is the second virial coefficient, M is the molecular weight, and C_M is the mass concentration of polymers. We have adjusted the value of A_2 so that both models take the same value $S(q;C)$ at $q = 0$. We point out that single-chain properties in general and $S_S(q;C)$ in particular become independent of concentration in the single-contact approximation because this approximation leads to $\psi(\mathbf{S};C) \simeq \psi(\mathbf{S})$ in the lowest order in concentration.

Figure 2 represents $S^{-1}(q;C)$ calculated from

$$S^{-1}(\kappa;C_V) = S_S^{-1}(\kappa;C_V) + C_VF(\kappa)S_S^{-2}(\kappa;C_V) \quad (39)$$

in solid curves and from

$$S^{-1}(\kappa;C) = S_S^{-1}(\kappa) + 2A_2MC_M \quad (40)$$

in dashed curves. It was shown by Zimm[5] in the single-contact approximation for the intermolecular interaction

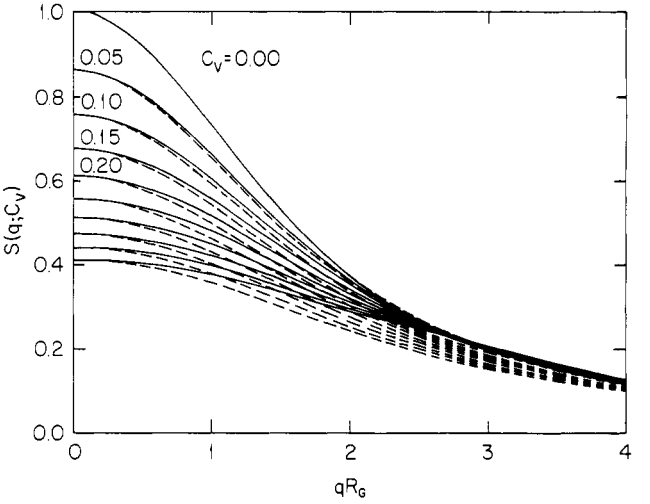

Figure 3. $S(q;C)$ vs. qR_G for various values of concentration C_V. Solid curves use the inverse of eq 39; dashed curves use the inverse of eq 40.

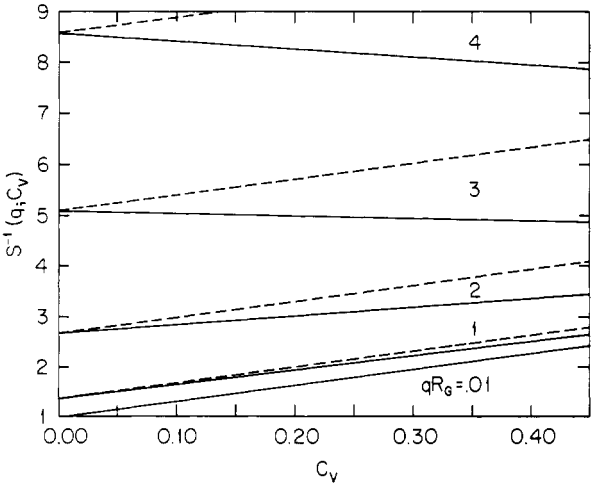

Figure 4. $S^{-1}(q;C)$ vs. C_V for various values of qR_G using eq 39 and 40.

that expression 39 is a better approximation for $S(\kappa;C_V)$ at higher concentrations than its reciprocal, expression 37. The important difference between (39) and (40) is that the initial slope of $S^{-1}(\kappa;C_V)$ vs. κ^2 is independent of concentration in Zimm's formula whereas it slightly decreases with concentration in (39). One finds, for example, that the change in the initial slope as a function of κ^2 is about 25% in the good solvent limit when the concentration is $C_V = 0.25$. This effect appears to be large enough to affect the accuracy of the extraction of the radius of gyration from $S(q;C)$ data in good solvents, especially in the case of large radius of gyration and high concentration.

In Figure 3 we plot $S(q;C_V)$ using the inverse of eq 39 and 40 that involve the reciprocal approximation. When the concentration is increased, these curves show less structure than those obtained by using eq 37 and 38. Finally, using (39) and (40), we plot $S^{-1}(\kappa;C_V)$ vs. C_V for different values of qR_G in Figure 4. One sees that the deviation becomes appreciable for large values of qR_G.

Discussion

It is shown that single-chain equilibrium properties such as the radius of gyration, the hydrodynamic radius, and the single-chain static structure factor depend on concentration in dilute solutions as a result of the deformation, both in size and in shape, of two molecules experiencing a binary encounter. The magnitude of this dependence,

however, is smaller than a few percent in all cases, so it is not expected to be of any experimental significance. In the single-contact approximation, this concentration dependence disappears because the intramolecular segment distributions of the molecules in a pair are not perturbed in this approximation.

The numerical calculations are based on the two-chain Monte Carlo results of Olaj and co-workers[2-4] for $G(R)$, $\epsilon_{\parallel}(R)$, and $\epsilon_{\perp}(R)$ obtained by considering a chain with 50 steps on a cubic lattice, under both Θ and good solvent conditions. Therefore, the accuracy of the numerical estimates of the initial slopes of the single-chain properties as a function of concentration presented in this paper is restricted by the statistical accuracy of the computer results, especially at large separation distances. Furthermore, it is assumed that the shape of the functions $G(R)$, $\epsilon_{\parallel}(R)$, and $\epsilon_{\perp}(R)$ when they are expressed in terms of the normalized separation distance R/R_G is independent of molecular weight. It is desirable to check the validity of this assumption by repeating the two-chain Monte Carlo calculations with longer chains. As an independent test, we have calculated the interpenetration function

$$\psi = \frac{1}{2\pi^{1/2}} \int_0^\infty dX\, X^2(1 - G(X)) \qquad (41)$$

using the computer data for $G(X)$ and found $\psi = 0.29$, which is in fair agreement with experimental[19,23] as well as theoretical[24] values for the limit of the interpenetration function as the excluded volume parameter z goes to infinity. The discrepancy is perhaps due to the fact that the chain length is not sufficiently long (50-mers) and hence one is not quite in the large-z region. Extension of two-chain Monte Carlo calculations from Θ and good solvent conditions to intermediate solvents and parametrization of the pair distribution $G(R)$ at different temperatures are also desirable in the study of concentration dependence of static and dynamic chain properties in dilute solutions in general.

The concentration dependence of the static structure factor has also been studied by using two-chain Monte Carlo results without resorting to the single-contact approximation, and it was found that the shape of $S^{-1}(q;C)$ as a function of q^2 changes slightly with concentration, whereas it is independent in the conventional Zimm theory. The change seems to be large enough in the good solvent limit to be observed experimentally.

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Experimental Determination of the Temperature–Concentration Diagram of Daoud and Jannink in Two-Dimensional Space by Surface Pressure Measurements

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ABSTRACT: Surface pressure (π)–surface concentration (Γ) isotherms of poly(methyl acrylate) monolayers at the air–water interface were measured as functions of molecular weight and temperature in the vicinity of the Θ temperature. The crossover Γ^* between the dilute and semidilute regimes and the crossover Γ^{**} between the semidilute and concentrated regimes were determined. The π, Γ^*, Γ^{**}, and second virial coefficient A_2 data were compared with the theoretical predictions of Daoud and Jannink based on scaling concepts in two-dimensional space. The temperature dependences of these measured quantities were in good agreement with the theory, whereas the molecular weight dependence of these values did not agree with the theoretical calculations of Daoud and Jannink. A temperature–concentration diagram in two-dimensional space was drawn with the experimental results.

The scaling theories proposed by de Gennes[1] and the recently developed techniques of small-angle neutron scattering[2] and quasi-elastic light scattering[3] are making clear the thermodynamic, static, and dynamic properties of polymer solutions in the semidilute and concentrated (gel) regimes.

Daoud and Jannink[4] presented a temperature–concentration diagram of polymer solutions based on de Gennes'

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