Concentration Effects on the Dynamic Structure Factor in Polymer Solutions

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ABSTRACT: Concentration and momentum transfer dependence of the characteristic frequency Ω associated with the dynamic structure factor for coherent scattering from polymer solutions is investigated. In the case of scattering from a single labeled chain among other identical chains the results are: In the Rouse limit and in the intermediate q region, Ω behaves as q^4 with a concentration-dependent proportionality constant below a crossover momentum q^*, and as $q^{11/3}$ above q^* with a concentration-independent proportionality constant. In the Zimm limit, Ω displays a transition from $\sim 0.053q^3$ for $q < q^*$ to $\sim 0.071q^3$ for $q > q^*$, when the Oseen tensor is unscreened. When hydrodynamic screening is included, Ω behaves as q^4 for $q < q^*$ with a concentration-dependent proportionality constant. The case of scattering from identical chains is investigated only for small q and dilute solutions. We found that the diffusion coefficient $D(c)$ increases with concentration c in a good solvent and decreases in a poor solvent. Expressing $D(c)$ as $D(c) = D(0)[1 + \phi(N)c]$, we have discussed the variation of $\phi(N)$ as a function of temperature. We have also shown that $\phi(N) \sim N^{0.8}$ in a good solvent and $\phi(N) \sim N^{0.5}$ in a poor solvent.

I. Introduction

In this paper we investigate the concentration effects on the dynamic structure factor in dilute and semidilute polymer solutions in the cases of coherent scattering from a single labeled chain in the presence of other chemically identical chains and scattering from identical chains in solution. In an accompanying paper (henceforth referred to as 1), we discussed the temperature effects on the dynamic structure factor in a dilute solution by introducing a characteristic frequency Ω as the slope of the normalized intermediate scattering function $S(q,t)$ for short times, and investigating its dependence in momentum transfer and temperature. In the present work we focus our attention on the concentration dependence of Ω at a fixed temperature. The concentration dependence is taken into account by adopting a model proposed by Farnoux et al.[2,3] for the equilibrium distribution of the vector distance between monomer pairs belonging to the same chain. The dynamics of the polymer solution is assumed to be governed by Kirkwood's generalized diffusion equation for the distribution function of monomer positions. It is shown in 1 that $S(q,t)$ behaves exponentially for short times as $S(q,t) \simeq \exp[-\Omega t]$ so that Ω can be obtained in principle from the linear portion of log $S(q,t)$ vs. time for small t if $S(q,t)$ is measured directly by light scattering. If it is $S(q,\omega)$ that is measured directly as in the case of neutron scattering, then Ω can be determined from the large ω-behavior of $S(q,w)$. However, Ω can also be estimated crudely as the measured half-width of $S(q,\omega)$,[4,5] with increasing accuracy for small and large q values. (For intermediate values of q, Ω is about 60% larger than the true width[4,5] although it has the correct qualitative behavior for all values of q.)

The concentration effects obtained in this paper depend strongly on the equilibrium and dynamical models adopted for the calculation of Ω. The results are in agreement with those predicted by the dynamical scaling theory[6-8] for small concentrations and away from the gellike region. We regard the model calculations presented in this paper only as a first attempt to reproduce the predictions of the dynamical scaling theory starting from a dynamical equation. Other models can also be used within the same mathematical framework presented in this paper for the calculation of Ω and the range of validity of the results can be extended to other regions in the $q - (1/\xi)$ plane.

II. Theory

The characteristic frequency is given in general (see 1 or ref 4 and 5) by

$$\Omega(q) = \langle \rho^* \mathcal{L} \rho \rangle / \langle \rho^* \rho \rangle \tag{1}$$

where $\langle[...]\rangle$ denotes the equilibrium average of the quantity [...] over the equilibrium distribution ψ_0 in monomer position space, and $\mathcal{L}$ is in general the dynamical operator introduced in 1, which we take here to be the adjoint of Kirkwood's Fokker–Planck operator

$$\mathcal{L} = -\sum_{\alpha,m} \sum_{\beta,n} [(\nabla_{\alpha m} log\ \psi_0) \cdot \mathbf{D}_{\alpha m,\beta n} \cdot \nabla_{\beta n} + \mathbf{D}_{\alpha m,\beta n} : \nabla_{\alpha m} \nabla_{\beta n}] \tag{2}$$

where α and β designate different chains in the solution, and m and n refer to the monomers in the αth and βth chains. $\mathbf{D}_{jk}$ is the diffusion tensor

$$\mathbf{D}_{jk} = (1/\beta)[\mathbf{T}_{jk} + (1/\xi_0)\mathbf{I}\delta_{jk}] \tag{3}$$

where $\mathbf{T}_{jk}$ is the Oseen tensor which is given for $j \neq k (\mathbf{T}_{jj} = 0)$ by

$$\mathbf{T}_{jk} = (1/8\Pi\eta_0 R_{jk}^3)[\mathbf{I}R_{jk}^2 + \mathbf{R}_{jk}\mathbf{R}_{jk}] \tag{4}$$

In these definitions ξ_0 and η_0 are respectively the friction coefficient per monomer and the viscosity of the solvent, and β is the inverse temperature $\beta = (1/k_B T)$. Different models for the hydrodynamic interaction can be accomodated in the calculation of Ω through $\mathbf{T}_{jk}$. For example, the screening effect due to other chains on the hydrodynamic interaction between monomer pairs will be taken into account by replacing the conventional bare Oseen tensor defined in (3) by its screened version, as proposed by Freed and Edwards,[9] with a concentration-dependent screening length.

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The ρ in (1) denotes, in general, the density of the scattering centers in Fourier space. In the case of single labeled chain in the presence of other chemically identical chains in solution we take ρ to be the density of monomers belonging to the labeled chain only:

$$\rho_1 = \sum_{m=1}^{N} e^{i\mathbf{q}\cdot\mathbf{R}_{1m}}$$

Then the characteristic frequency reduces to:

$$\Omega(q,c) = \frac{\sum_{m,n} \langle \mathbf{D}_{m,n} e^{i\mathbf{q}\cdot(\mathbf{R}_n - \mathbf{R}_m)} \rangle : \mathbf{qq}}{\sum_{m,n} \langle e^{i\mathbf{q}\cdot(\mathbf{R}_n - \mathbf{R}_m)} \rangle} \tag{5}$$

where $\mathbf{q}$ is the wave vector and c is the monomer concentration which is implicite in ψ_0. In the case of identical chains in solution, ρ denotes the total monomer density

$$\rho = \sum_{\alpha,n} e^{i\mathbf{q}\cdot\mathbf{R}_{\alpha n}}$$

and Ω becomes:

$$\Omega(q,c) = \frac{\mathbf{qq}:\sum_{m,n}[\langle D_{1m,1n} e^{i\mathbf{q}\cdot(\mathbf{R}_{1n}-\mathbf{R}_{1m})}\rangle + (n_{\mathrm{p}} - 1)\langle \mathbf{D}_{1m,2n} e^{i\mathbf{q}\cdot(\mathbf{R}_{2n}-\mathbf{R}_{1m})}\rangle]}{\sum_{m,n}[\langle e^{i\mathbf{q}\cdot(\mathbf{R}_{1n}-\mathbf{R}_{1m})}\rangle + (n_{\mathrm{p}} - 1)\langle e^{i\mathbf{q}\cdot(\mathbf{R}_{2n}-\mathbf{R}_{1m})}\rangle]} \tag{6}$$

Here n_{p} is the number of chains in the entire system.

Equations 5 and 6 constitute the starting point for the calculation of the characteristic frequency in model chain solutions. Two points are to be made at this stage: The first is that the diffusion tensor is a function of the vector difference of monomer positions so that one needs only $P_{11}(\mathbf{R}_{mn})$, which is the distribution function of the vector spacing between monomer pairs belonging to the same chain, to calculate $\Omega(q,c)$ in the case of a single-labeled chain. In the case of identical chains in solution one also needs $P_{12}(\mathbf{R}_{mn})$ which is the distribution of vector distance between monomer pairs belonging to two different chains. The second point is that the calculation of the characteristic frequency which is a dynamical property of polymer solution, has been reduced in (5) and (6) to the calculation of *equilibrium averages*.

III. Single-Labeled Chain

Following Farnoux et al.[2,3] we model $P_{11}(\mathbf{R}_{mn})$ such that its characteristic function is given by

$$\langle e^{i\mathbf{q}\cdot\mathbf{R}_{nm}} \rangle \simeq e^{-(q^2/6)\langle |\mathbf{R}_{nm}|^2 \rangle} \tag{i}$$

$$\langle |\mathbf{R}_{nm}|^2 \rangle = |m - n|^{2\nu} l^2 \qquad \text{for } |m - n| \leq N_{\mathrm{c}} \tag{iia}$$

$$\langle |\mathbf{R}_{nm}|^2 \rangle = \frac{|m - n|}{N_{\mathrm{c}}} \xi^2 \qquad \text{for } |m - n| \geq N_{\mathrm{c}} \tag{iib}$$

where N_{c} is a concentration-dependent cutoff introduced to take into account the screening effect due to other chains on the excluded volume interaction between the monomers of the labeled chain. When $|m - n| \geq N_{\mathrm{c}}$ the excluded volume interaction is screened so that the chain is treated as a Gaussian chain with a statistical length $\xi = lN_{\mathrm{c}}^{\nu}$ and number of segments $|m - n|/N_{\mathrm{c}}$. The value of N_{c}, which is the number of segments forming a chain with excluded volume effects, is given by:[2]

$$N_{\mathrm{c}} = (m_0/l^3 N_{\mathrm{A}})^{5/4} c^{-5/4}$$

where m_0 is the molecular weight per monomer, N_{A} is the Avogadro's number, and c is the concentration.

Substitution of this equilibrium chain model into (5) yields:

$$\Omega(q,c) = \frac{q^2}{\beta\xi_0}\left\{1 + A_1\left[F\left(\frac{1-\nu}{2\nu},a_1\right) - \frac{z}{a_1^{1/2\nu}}F\left(\frac{2-\nu}{2\nu},a_1\right)\right] + A_2\int_{z^{1/2}}^{1} \mathrm{d}u\, e^{-a_2u^2}(1 - u^2)\right\} \times \left\{\frac{N_{\mathrm{c}}}{\nu a_1^{1/2\nu}}\left[F\left(\frac{1}{2\nu},a_1\right) - \frac{z}{a_1^{1/2\nu}}F\left(\frac{1}{\nu},a_1\right)\right] + 1 + \frac{2N}{a_2}\left[(1 - z)e^{-za_2} + \frac{1}{a_2}(e^{-a_2} - e^{-za_2})\right]\right\}^{-1} \tag{7}$$

where $F(\mu,a_1) \equiv \gamma(\mu,a_1) - \gamma(\mu,a_1/N_{\mathrm{c}}^{2\nu})$; $A_1 = BN_{\mathrm{c}}^{1-\nu}/(2\nu a_1^{(1-\nu)/2\nu})$; $B = (2/\pi(6\pi)^{1/2})(\xi_0/\eta_0 l)$; $z = (N_{\mathrm{c}}/N)$; $A_2 = 2B(N)^{1/2}N_{\mathrm{c}}^{(1-2\nu)/2}$; $a_1 = (q^2\xi^2/6)$; $a_2 = (a_1/z)$; and $\gamma(\mu,x)$ is the incomplete γ function.[11] The calculations involved in the derivation of (7) are very similar to those presented in the appendix of 1.

The long chain limit of $\Omega(q,c)$ is obtained from (7) with $z = 0$ and $ql(N)^{1/2} >> 1$. Its variation with concentration and momentum transfer in this limit in various asymptotic regions is presented below:

i. Rouse limit

$$\Omega(q,c) = \frac{\nu}{6^{1/2\nu}\Gamma(1/2\nu)}\left(\frac{k_{\mathrm{B}}T}{\xi_0}\right) l^{1/\nu} q^{2+1/\nu} \qquad \text{for } q > q^* \tag{8}$$

$$\Omega(q,c) = \frac{1}{12}\left(\frac{k_{\mathrm{B}}T}{N_{\mathrm{c}}\xi_0}\right)\xi^2 q^4 \qquad \text{for } q < q^* \tag{9}$$

where $\Gamma(z)$ is the Γ function and

$$q^* = 6^{1/2}/\xi$$

It is observed that there is a crossover in the q dependence at a value q^*. Since $\xi \sim c^{-3/4}$ the crossover momentum increases with concentration as $c^{3/4}$. Below the crossover point, the behavior of Ω as a function of q is that of an unperturbed Gaussian chain (cf. eq 14a of 1) with a statistical length ξ and a friction coefficient per segment $N_{\mathrm{c}}\xi_0$. Above q^* it varies with q for $\nu = {}^3/_5$ as

$$\Omega(q,c) = 0.12\left(\frac{k_{\mathrm{B}}T}{\xi_0 l^2}\right)(ql)^{11/3}$$

which is characteristic of a chain with excluded volume interaction. This behavior was predicted by De Gennes[6] on the basis of scaling arguments. It is also noted that the proportionality constant in the power law for $q < q^*$ depends on concentration as $1/c^{1/4}$ whereas it is a constant for $q > q^*$.

ii. Zimm limit

$$\Omega(q,c) = \frac{1}{6\pi(\pi)^{1/2}}\frac{\Gamma[(1 - \nu)/2\nu]}{\Gamma(1/2\nu)}\left(\frac{k_{\mathrm{B}}T}{\eta_0 l^3}\right)(ql)^3 \qquad \text{for } q > q^* \tag{10a}$$

$$\Omega(q,c) = \frac{1}{6\pi}\left(\frac{k_{\mathrm{B}}T}{\eta_0 l^3}\right)(ql)^3 \qquad \text{for } q < q^* \tag{10b}$$

The numerical values of the coefficients in (10a) and (10b) for $\nu = {}^3/_5$ are respectively 0.071 and 0.053. We observe that in the Zimm limit the characteristic frequency obeys a third-power law both below and above the crossover point. For $q < q^*$ the coefficient in (10) is the same as that obtained for an unperturbed Gaussian chain with preaveraged Oseen tensor (cf. eq 14b of 1). When q is increased past the crossover point the coefficient increases from 0.053 to 0.071 although the q^3 dependence remains unchanged. It is noted also that the coefficients are independent of concentration for both $q > q^*$ and $q < q^*$. It should be recalled here that the above results are based on a model in which the hydrodynamic interactions are included through the unscreened Oseen tensor (cf. eq 4). The behavior of Ω in the intermediate q region for $q < q^*$ is sensitive to the screening effects. To demonstrate this point we crudely assume[20] that the hydrodynamic interaction between monomers of the labeled chains extends only over a monomer spacing for which $|m - n| \leq N_c$, i.e., $\mathbf{T}_{mn} = 0$ for $|m - n| \geq N_c$. In such a model, the term proportional to A_2 in (7) is not present so that (10b) is replaced by:

$$\Omega(q,c) = \frac{k_BT}{12}\frac{q^4\xi^2}{\xi_0^B} \tag{11}$$

where we have introduced

$$\xi_0^B = 6\pi\eta_0 R_H \tag{12}$$

and

$$R_H = \frac{\pi}{2(6\pi)^{1/2}}(1 - \nu)\xi \tag{13}$$

The result in (11) is equivalent to that obtained in the Rouse limit (cf. eq 14a or 1) for an unperturbed Gaussian chain with a statistical length ξ and a friction coefficient per segment (or blob) ξ_0^B. Equation 12 defines a hydrodynamic radius R_H for a blob through Stoke's formula. The results in this section are obtained in the long chain limit. For a finite N, we shall shortly see that R_H depends also on z (see eq 18).

iii. Small q region. In the limit of $ql(N)^{1/2} << 1$ the characteristic frequency can be written as $\Omega(q,c) = D(c)q^2$. We obtain the concentration-dependent diffusion coefficient from (7) as

$$D(c) = \frac{k_BT}{N\xi_0} + \frac{k_BT}{N\eta_0}\frac{2}{(6\pi)^{1/2}\pi}\left[\frac{\xi^{(1-\nu)/\nu}}{l^{1/\nu}}\left(\frac{1}{1-\nu} - \frac{z}{2-\nu}\right) + 2\frac{(NN_c)^{1/2}}{\xi}\left(\frac{2}{3} - z^{1/2} + \frac{1}{3}z^{3/2}\right)\right] \tag{14}$$

In the dilute limit we have $N = N_c$, $z = 1$, and $\xi = N^\nu l$ so that $D(c)$, for sufficiently large N (Zimm limit), reduces to

$$D(0) = \frac{2}{(6\pi)^{1/2}\pi}\frac{1}{(1-\nu)(2-\nu)}\frac{k_BT}{\eta_0 lN^\nu} \tag{15}$$

In the semidilute regime with sufficiently small $z = (N_c/N)$ the third term in (14) dominates:

$$D(c) = \frac{8}{3\pi(6\pi)^{1/2}}\frac{k_BT}{\eta_0}\frac{1}{\xi(N/N_c)^{1/2}} \tag{16}$$

This result corresponds to the diffusion coefficient of a Gaussian chain with a statistical length ξ and number of segments (or blobs) N/N_c (cf. eq 15 of 1). The diffusion coefficient in this regime is also sensitive to the screening effects in hydrodynamic interaction between monomers. Adopting again the same screened Oseen tensor model as in expression 11 (here it means dropping the third term in eq 14) along with the assumption that the first term in (14) is small as compared to the second (Zimm limit) we get:

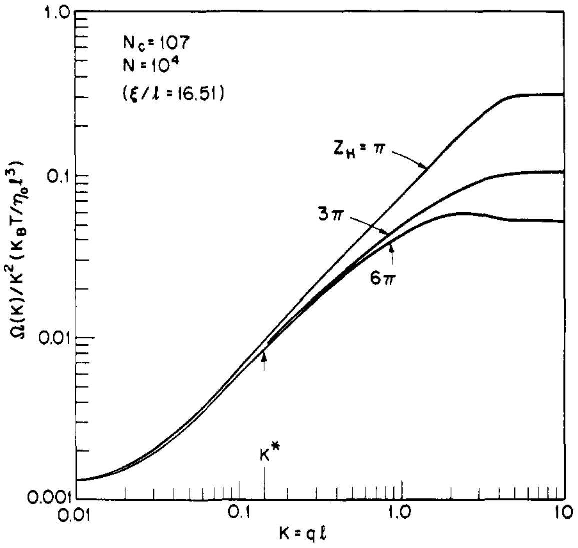

Figure 1. Variation of the normalized characteristic frequency with momentum transfer at the concentration corresponding to a crossover value of $\kappa^* = 0.148$, and for various values of $z_H = (\xi_0/\eta_0 l)$.

$$D(c) = \frac{2}{\pi(6\pi)^{1/2}}\frac{k_BT}{\eta_0}\frac{1}{(N/N_c)\xi}\left(\frac{1}{1-\nu} - z\frac{1}{2-\nu}\right) \tag{17}$$

This result may be interpreted as the diffusion coefficient of a chain in the free-draining limit, which consists of (N/N_c) segments and a friction coefficient per segment $6\pi\eta_0 R_H$ where

$$R_H = \xi\frac{\pi}{2(6\pi)^{1/2}}\frac{(1-\nu)(2-\nu)}{(2-\nu) - z(1-\nu)} \tag{18}$$

Observe that if we let $z = 0$ in the above expression we recapture (13) which was obtained in the long chain limit, i.e., $N \to \infty$.

The large q limit of $\Omega(q,c)$ for which $ql >> 1$ always yields $\Omega(q) = (k_BT/\xi_0)q^2$ at any concentration.

The variation of $\Omega(q,c)$ as a continuous function of $\kappa = ql$ can be presented conveniently by introducing a normalized characteristic frequency as

$$\frac{\Omega(\kappa)}{\kappa^2/(k_BT/\eta_0 l^3)} = \frac{1}{z_H}G(z_H,\kappa,N,\xi/l) \tag{19}$$

where the explicit form of G can be obtained by comparing (19) with (7).

In Figure 1 we plotted[21] the normalized characteristic frequency as a function of κ and for various values of $z_H = (\xi_0/\eta_0 l)$, at a concentration corresponding to $N_c = 107$ (or $\xi/l = 16.51$).

To illustrate the effect of hydrodynamic screening we also plotted the curve corresponding to $z = 3\pi$ on Figure 2 together with the curve obtained using the screened Oseen tensor.

We observe that for $q < q^*$, the characteristic frequency behaves approximately as q^3 in the case of the bare Oseen tensor and as q^4 in the presence of hydrodynamic screening. This is consistent with the prediction of (11) in the intermediate q region with $N \to \infty$.

In plotting the curves in Figures 1 and 2 we have used, following Farnoux,[2] $l = 2.54$ Å, $m_0 = 104$, and $N = 10^4$. Although these values represent polystyrene, it is not clear that 2.54 Å is a realistic value for l. We have also assumed arbitrarily $\xi_0 = 3\pi\eta_0 l$. These two parameters may have to

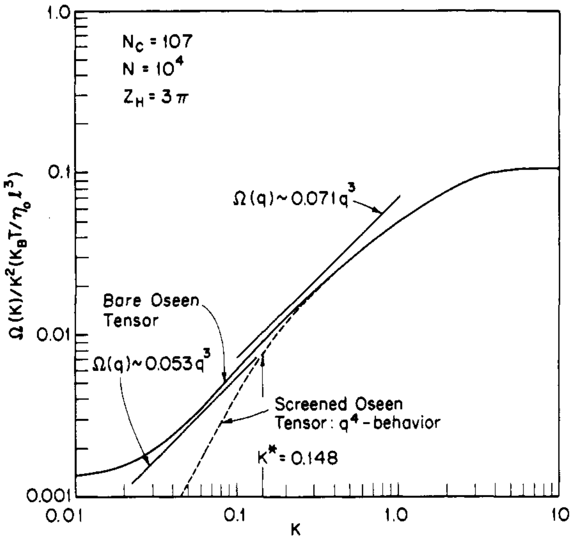

Figure 2. Variation of the normalized characteristic frequency with momentum transfer at constant concentration and for $z_H = 3\pi$ with hydrodynamic screening (dotted line) and without hydrodynamic screening (solid line).

be adjusted in the analysis of actual experimental data to obtain a better fit as explained in ref 5. At any rate, the crossover at $q^*l = 0.148$ and the transition from $\Omega \sim 0.053q^3$ to $\Omega \sim 0.071q^3$ is clearly demonstrated in Figure 2 with these set of parameters.

IV. Identical Chains

In this section we present the calculation of the characteristic frequency in the case of scattering from identical chains in solution. Due to the complexity in obtaining the distribution of the vector distance between two monomers belonging to different polymers which is needed in this case, we consider only the small q limit and dilute solutions. Under these conditions the characteristic frequency Ω given by (6) may be written as $\Omega = D(c)q^2$ where $D(c)$ is the concentration-dependent diffusion coefficient which may be displayed as

$$D(c) = D(0)[1 + \phi(N)c] \tag{20}$$

In (20), c is the polymer concentration, and $\phi(N)$ is the molecular weight dependent proportionality constant. Our main task is to obtain $\phi(N)$ and compare it with the previous theoretical results. The conclusion of this section is relevant to light-scattering experiments in the small q region.

We start with the general expression for the characteristic frequency given by (6) and introduce the following approximations:

$$e^{i\mathbf{q}\cdot(\mathbf{R}_{1n}-\mathbf{R}_{1m})} \approx 1 \tag{21a}$$

and

$$e^{i\mathbf{q}\cdot(\mathbf{R}_{2n}-\mathbf{R}_{1m})} \approx e^{i\mathbf{q}\cdot(\mathbf{R}_2-\mathbf{R}_1)} \tag{21b}$$

where $\mathbf{R}_1$ and $\mathbf{R}_2$ denote the position of the center of mass of the polymers 1 and 2. These approximations are justified in the small q limit where the wavelength of the momentum transfer is much larger than the size of the solute molecules, so that $|\mathbf{q}\cdot(S_{1n} - S_{2m})| << 1$ holds. Here $\mathbf{S}_{1n}$ and $\mathbf{S}_{2n}$ denote the positions of the monomers relative to the center of mass of each molecule. The magnitude of $|\mathbf{q}\cdot(\mathbf{R}_2 - \mathbf{R}_1)|$ in (21b) is not always small as compared to unity even in the limit of $\mathbf{q} \to 0$ because $|\mathbf{R}_2 - \mathbf{R}_1|$ may be of the order of the linear dimension of the sample. We shall let $q \to 0$ only after we take the thermodynamic limit of $V \to \infty$, $n_p \to 0$ keeping the polymer number density n_p/V constant. This procedure eliminates divergences which would appear if q is set equal to zero at the outset.

Choosing the z axis parallel to $\mathbf{q}$ and using the approximations in (21) we obtain the diffusion coefficient from (6) as

$$D(c) = \frac{\sum_{m,n} \langle D^{33}(\mathbf{S}_{mn}) \rangle_c + n_p \sum_{m,n} \langle D^{33}(\mathbf{R}_{12} + \mathbf{S}_{1n} - \mathbf{S}_{2m}) e^{i\mathbf{q}\cdot\mathbf{R}_{12}} \rangle_0}{N^2[1 + n_p\langle \exp(i\mathbf{q}\cdot\mathbf{R}_{12}) \rangle_0]} \tag{22}$$

Since we are interested in the concentration dependence in the lowest order, the equilibrium averages in the terms proportional to n_p in (22) involve the equilibrium distribution in the infinite dilution limit as implied by the subscripts in $\langle ... \rangle_0$. The equilibrium distribution model adopted in the previous section for the calculation of $\langle D^{33}(\mathbf{S}_{mn}) \rangle_c$, however, also becomes independent of concentration in the dilute regime where the screening length exceeds the molecular size. Hence, the first term in the numerator of (22) is the zero-concentration limit of the diffusion coefficient which was already calculated in (15). We reproduce the latter here as

$$D(0) = k_BT/6\pi\eta_0 R_H \tag{23}$$

where R_H is the equivalent hydrodynamic radius

$$R_H = \frac{\pi}{2(6\pi)^{1/2}}(1 - \nu)(2 - \nu)lN^\nu \tag{24}$$

(Note that (24) is identical to (18) with $z = 1$ and $\xi = N^\nu l$). The concentration dependence of $D(c)$ can be displayed as

$$D(c) = D(0)\frac{1 - ck_2}{1 - ck_1} \tag{25}$$

where c is the concentration in mass per unit volume. Then k_1 may be shown to be

$$k_1 = \frac{N_A}{M} \int d^3x [1 - e^{-\beta V(x)}] \tag{26}$$

where N_A is the Avogadro's number, M is the molecular weight of the polymer, and $V(x)$ is the intermolecular potential for a pair of solute molecules in infinite dilution limit. Clearly k_1 is proportional to the osmotic second virial coefficient.[12]

The k_2 in (25) is obtained from (22) as

$$k_2 = -\frac{V}{N^2}\frac{N_A}{M} 6\pi\eta_0 R_H \sum_{m,n} \langle T^{33}(\mathbf{R}_{12} + \mathbf{S}_{1n} - \mathbf{S}_{2m}) e^{i\mathbf{q}\cdot\mathbf{R}_{12}} \rangle \tag{27}$$

where we have replaced D^{33} by the Oseen tensor for only different chains are involved in (27). We shall first present a simple calculation of k_2 by approximating $T^{33}(\mathbf{R}_{12} + \mathbf{S}_{1n} - \mathbf{S}_{2m})$ in (27) by $T^{33}(\mathbf{R}_{12})$. This approximation is expected to be valid in the good solvent limit in which the molecules may be regarded as hard spheres with no penetration into each other so that $|\mathbf{R}_{12}| > |\mathbf{S}_{1n} - \mathbf{S}_{2m}|$ holds. Then (27) becomes

$$k_2 = \frac{N_A}{M} 4\pi R_H \int_0^\infty dX X e^{-KX} [1 - e^{-\beta V(X)}] \tag{28}$$

where we have used

$$\int d^3x T^{33}(x) e^{i\mathbf{q}\cdot x} = 0$$

before taking the limit of $\mathbf{q} \to 0$. Both in (26) and (28) we have replaced the intermolecular pair correlation function $g(x)$ by its zero-concentration limit, i.e., $\exp[-V(X)] - 1$.

In (28) the directional integration of $T^{33}(X)$ has been performed. The quantity K in (28) is the inverse screening length associated with the hydrodynamic interaction between molecules. We shall let $K = 0$ in the following calculations.

In order to evaluate (26) and (28) one needs the intermolecular pair potential. As a model calculation we shall use hard sphere potential, i.e., $V(X) = +\infty$ for $0 \leq X \leq 2\bar{S}$ and $V(X) = 0$ for $X > 2\bar{S}$. The hard sphere radius $\bar{S}$ is related to the second virial coefficient and can be calculated from

$$\bar{S} = \left[\frac{3(\pi)^{1/2}}{4}\psi\right]^{1/3} R_G \qquad (29)$$

where R_G is the radius of gyration and ψ is a function of the excluded volume parameter $\bar{z}$. Various approximate forms of $\psi(\bar{z})$ are discussed by Yamakawa[12] (in fact, (29) is obtained by combining eq 21.17 and IVA.5 in this reference).

Using the hard sphere potential in (26) and (28) we obtain $\phi(N) = (k_1 - k_2)$ in (20) as

$$\phi_m(N) = \frac{N_A}{M}\left(\frac{4\pi}{3}R_H{}^3\right)\left(\frac{\bar{S}}{R_H}\right)^2\left[8\left(\frac{\bar{S}}{R_H}\right) - 6\right] \qquad (30)$$

when c is in mass per unit volume, and as

$$\phi_v(N) = \left(\frac{\bar{S}}{R_H}\right)^2\left[8\left(\frac{\bar{S}}{R_H}\right) - 6\right] \qquad (31)$$

when c is measured as volume fraction with a volume $(4\pi R_H{}^3/3)$ per polymer.

Discussion. (a) If the hydrodynamic and hard sphere radii are taken to be the same, (31) yields $\phi_v(N) = 2$, which is the result obtained by Altenberger and Deutch[13] for hard spheres. Pyun and Fixman[14] found $\phi_v(N) = 0.84$ in the hard sphere limit of their calculations. Yamakawa's[12,15] work on the friction coefficient may be written as

$$\phi_v(N) = 3.2(\bar{S}/R_H)^3 - 1 \qquad (32)$$

which yields 2.2 when $\bar{S} = R_H$. Burger's[12,17] result is $\phi_v(N) = 1.2$.

(b) The equivalent hard sphere radius is not constant and diminishes as the solvent becomes poorer, and vanishes at the Θ temperature. Its value in a very good solvent can be obtained from (29) using the asymptotic value of $\psi(\bar{z})$ as $\bar{z} \to \infty$, which is given by Yamakawa[12] (cf. eq 21.17 and 20.82 therein) as $\psi(\infty) = 1/1.828$. The result is $\bar{S} \simeq 0.9R_G$. The radius of gyration and the hydrodynamic radius are calculated from $R_G = N^{\nu}l[2(1 + \nu)(1 + 2\nu)]^{-1/2}$ and (24), respectively, as $R_G = 0.377\,N^{\nu}l$ and $R_H = 0.202N^{\nu}l$ for $\nu = {}^3/_5$. Substituting these values into (31) we find $\phi_v(N) \simeq 21$ (Yamakawa's formula yields $\phi_v(N) \simeq 14$). The value of $\phi_v(N)$ decreases as the solvent becomes poorer and vanishes when $\bar{S} \simeq 0.75R_H$ (Yamakawa's result is $\bar{S} \simeq 0.68R_H$). Although (31) is not expected to be quantitatively correct as the solvent becomes poorer, it predicts the diffusion coefficient to increase with concentration in a good solvent, and to decrease when the solvent is sufficiently poor. The molecular weight dependence $\phi_m(N)$ in a good solvent follows from (30) as $N^{0.8}$ since $R_H \sim N^{0.6}$ and $M \sim N$. In the poor solvent limit[22] $\phi_m(N) \sim N^{0.5}$. The slope $\mathrm{d}D(c)/\mathrm{d}c$ which is equal to $D(0)\phi_m(N)$ is then proportional to $N^{0.2}$ in a good solvent, and independent of N in the poor solvent limit.

The above predictions in the case of a good solvent are in agreement with the results of the light-scattering experiments by Adam and Delsanti.[18] The independence of the negative slope of the molecular weight in a poor solvent has been demonstrated recently by Han[19] in his light-scattering experiments.

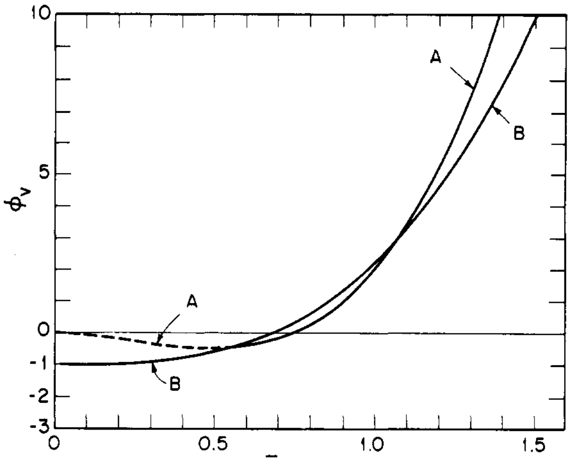

Figure 3. Variation of $\phi_v(N)$ in $D(c) = D(0)[1 + \phi_v(N)c]$ with $x = \bar{S}/R_H$ (the concentration c is in volume fraction, $4\pi R_H{}^3/3$ being the volume per polymer). The curves A and B represent respectively eq 31 and 32.

(c) The variation of $\phi_v(N)$ as a function of $x \equiv \bar{S}/R_H$ is plotted in Figure 3. The curve A is obtained from (31) and the curve B from (32). It is observed that ϕ_v vanishes, according to (31), at the Θ temperature where $x = 0$. The experiment on the other hand predicts a nonvanishing negative slope near the Θ temperature. This discrepancy is due to the approximation $T^{33}(\mathbf{R}_{12} + \mathbf{S}_{1n} - \mathbf{S}_{2m}) \simeq T^{33}(\mathbf{R}_{12})$ introduced in (27). When the Θ temperature is approached the molecules are interpenetrable and $|\mathbf{R}_{12}| > |\mathbf{S}_{1n} - \mathbf{S}_{2m}|$ can no longer be valid. Since k_1 in (26) vanishes at the Θ temperature, $\phi(N) = -k_2$ at $\mathbf{T} = \Theta$. The calculation of k_2 is identical to the calculation of the concentration dependence of the frictional coefficient $f(c) = f(\mathrm{o})[1 + ck_2 + \ldots]$, which was subject to several earlier investigations.[12-16] Yamakawa's[15] original calculations predicted a vanishing k_2 at the Θ temperature (eq 32 without −1). Pyun and Fixman[14] predicted first time a nonvanishing k_2 at $T = \Theta$, which is equal to $k_2 = 2.23$, provided the effective radius of the interpenetrable soft spheres in his calculations is interpreted as R_H of the present approach. The last term in (32) was introduced by Yamakawa[12] on the basis of conservation of the solution volume in any volume element in the system when switching from the actual polymer velocity to the drift velocities.

The concentration dependence of the diffusion coefficient near the Θ temperature can be investigated in the present approach by relaxing the approximation of $T^{33}(\mathbf{R}_{12} + \mathbf{S}_{1n} - \mathbf{S}_{2m}) \simeq T^{33}(\mathbf{R}_{12})$ in (27). In this case the calculation of the equilibrium averages requires the knowledge of the joint distribution, $\phi(\mathbf{R}_1,\mathbf{R}_2;\mathbf{S}_1{}^N,\mathbf{S}_2{}^N)$, of the inter- and intramolecular coordinates. This distribution can be decomposed as

$$\psi = \psi_{12}(\mathbf{R}_1,\mathbf{R}_2)\psi_1(\mathbf{S}_1{}^N)\psi_2(\mathbf{S}_2{}^N) + \psi_{12}(\mathbf{R}_1,\mathbf{R}_2)[\psi_c(\mathbf{S}_1{}^N,\mathbf{S}_2{}^N|\mathbf{R}_1,\mathbf{R}_2) - \psi_1(\mathbf{S}_1{}^N)\psi_2(\mathbf{S}_2{}^N)] \qquad (33)$$

where ψ_c is the conditional monomer distribution when the centers of masses of each molecule are located at $\mathbf{R}_1$ and $\mathbf{R}_2$. Yamakawa[15] in his original calculation of the friction coefficient retained only the first term in (33) assuming that the intermolecular and intramolecular distributions are independent, i.e., $\psi_c = \psi_1\psi_2$. Pyun and Fixman[14] pointed out that the concentration independence of the friction coefficient at the Θ point was due to the neglect of the correlations in Yamakawa's work.

A calculation of the diffusion coefficient based on (33) including the correlations of inter- and intramolecular distributions will be presented in a subsequent paper together with the recent data on the concentration dependence of $D(c)$ obtained by light-scattering experiments.[19]

V. Discussions

In this paper we investigated the concentration dependence of the characteristic frequency in all regions of the momentum transfer in the case of coherent scattering from a single labeled chain among other chains in a good solvent. We have demonstrated the existence of a crossover momentum transfer q^* in the q dependence of the characteristic frequency Ω in the semidilute regime and examined its asymptotic behavior above and below q^*. These results are relevant, in particular, to the interpretation of neutron scattering experiments.

We have investigated the concentration dependence of Ω in the case of scattering from identical chains only for small momentum transfers and in the dilute regime. We have shown that the diffusion coefficient increases with concentration in a good solvent whereas it decreases in a poor solvent. We have determined the slope of $D(c)$ as a function of the second virial coefficient. These results are directly applicable to the interpretation of light-scattering experiments.

Since entanglement is not included in the dynamical model, the results of this paper are expected to be valid for all q values in dilute solutions, and for $q\xi \geq 1$, and in the vicinity of the crossover line $q\xi \approx 1$ in semidilute solutions. In these regions the results are in agreement with the predictions of the dynamical scaling approach.

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(20) Adelman recently showed[10] that the screened Oseen tensor has an R^{-2} decay. It is quite long ranged, and the simple cutoff model we use here is probably cruder than it would be in the case of an exponentially decaying Oseen tensor.[9] However, our purpose here is to investigate the effect of hydrodynamic screening on the dynamic structure factor only qualitatively, and to demonstrate how the hydrodynamic screening can be included in the present calculation of the characteristic frequency.
(21) Figures 1 and 2 are plotted using the original expression 5 of $\Omega(q,c)$ involving summations, rather than (7) which is obtained by approximating these summations by integrations (cf. Appendix of 1).
(22) Here we anticipate the result that ϕ_γ approaches a constant at the Θ temperature as discussed in (c).

Dynamic Flow Birefringence and Flow Dichroism of Block-Copolymer Molecules in Solution with Application to the Free-Draining Limit

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ABSTRACT: The dynamic flow birefringence and the flow dichroism of block-copolymer molecules in solution have been calculated by modifying the bead-spring model theory of Zimm to take into account the existence of dissimilar segments in block copolymers. The expressions for the birefringence and the dichroism properties have been found to be the same as those for homopolymers except that the contributions of normal modes are weighted by generally different factors. Some calculated results in the free-draining limit are given to illustrate how the inhomogeneity in segmental optical properties is expected to affect the flow birefringence and the flow dichroism.

Recently, there has been much interest in the theoretical investigation of the dynamics of block copolymers. For example, Hall and DeWames,[1] Shen and Hansen,[2] Stockmayer and Kennedy,[3] and Wang and DiMarzio[4] have all discussed the dynamics of free-draining block copolymers. In our previous papers,[5,6] we have extended the bead-spring model theory of Zimm[7] to treat the viscoelasticity and the translational diffusion of non-free-draining block copolymers in dilute solutions. In this paper the bead-spring model is again used to discuss the flow birefringence and the flow dichroism of block copolymers in solution. In treating the viscoelasticity and the translational diffusion of block copolymers,[4-6] we have taken into account the differences in flexibility and