Temperature Effects on the Dynamic Structure Factor in Dilute Polymer Solutions

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ABSTRACT: A characteristic frequency Ω, associated with the dynamic structure factor, is introduced as the slope of the normalized intermediate scattering function $S(q,t)$ for short times, and its variation with momentum transfer and temperature is investigated in dilute polymer solutions. The existence of a cross-over in the q dependence of Ω at a temperature-dependent q^* is discussed.

I. Introduction

In this paper we discuss the temperature effects on coherent scattering from dilute polymer solutions. More specifically, we introduce a characteristic frequency associated with the dynamic structure factor, and investigate its variation with momentum transfer and temperature in the case of a single chain in a good solvent.

In our earlier work[1,2] we calculated the characteristic frequency for a Gaussian and a freely jointed chain in a Θ solvent ignoring the excluded volume effects. In this paper we extend these calculations to good solvents by taking into account the excluded volume effects in terms of the "screening length" concept introduced by Edwards[3] and extended by Daoud et al.[4]

The behavior of the characteristic frequency in the presence of excluded volume effects has recently been studied by DeGennes[5,6] and Daoud and Jannink[7] from the point of view of scaling laws. These laws predict the critical exponents in the simple power laws obeyed by various polymer properties as a function of momentum transfer, temperature, and concentration in certain ranges of these variables. However they do not provide precise numerical coefficients, nor do they yield information in the transition regions where the simple power laws are not obeyed. Such detailed information can be obtained by actually solving the dynamical equations describing the time evolution of the polymer in solution. One of the purposes of this paper is to present the predictions of such a dynamical theory using a specific chain model. However, it is the mathematical framework we wish to emphasize in this paper, rather than the consequences of the specific model we use. The latter can always be improved by resorting to more sophisticated models within the same computational frame work.

II. Theory

The time evolution of the polymer in solution is assumed to be governed by the following dynamical equation

$$\partial\psi/\partial t = \mathcal{D}\psi \tag{1}$$

where $\psi(R_1,...,R_N,t)$ is the distribution of the polymer segments, and $\mathcal{D}$ is the dynamical operator which will be taken in this paper as Kirkwood's diffusion operator. Other choices are allowed in the general theory as long as $\mathcal{D}$ is time independent. It is shown elsewhere[1,8,9] that any dynamical property $\mathbf{A}$ depending on polymer configuration satisfies an adjoint dynamical equation

$$\frac{\partial}{\partial t}\mathbf{A} = -\mathcal{L}\mathbf{A} \tag{2}$$

where the adjoint operator is defined, for any arbitrary dynamical variable B, by

$$\mathcal{D}(\psi_0 B) = -\psi_0(\mathcal{L}B) \tag{3}$$

where $\psi_0(R_1,...,R_N)$ is the equilibrium distribution. When $\mathcal{D}$ is chosen to be Kirkwood's diffusion operator $\mathcal{L}$ becomes

$$\mathcal{L} = -\sum_{j,k}[\nabla_j \log \psi_0 \cdot \mathbf{D}_{jk} \cdot \nabla_k + \mathbf{D}_{jk}:\nabla_j\nabla_k] \tag{4}$$

where ∇_j is the gradient operator with respect to the coordinate of the jth monomer, and $\mathbf{D}_{jk}$ is the configuration-dependent diffusion tensor. Summation over j,k runs through all the monomers.

The dynamical property $\mathbf{A}$ is in general a vector quantity whose components $\mathbf{A}_\mu$ $(\mathbf{R}_1,...,\mathbf{R}_N)$ are the dynamical variables of interest in a given problem. They are constructed in such a way that their equilibrium average vanishes, i.e., $\langle A_\mu \rangle = 0$. Since we are interested in the monomer density–time correlation function in the description of coherent scattering, we choose the monomer density in Fourier space as the relevant dynamical variable

$$\rho = \sum_j e^{i\mathbf{q}\cdot\mathbf{R}_j} \tag{5}$$

The normalized scattering function

$$S(q,t) = \langle \rho^* e^{-t\mathcal{L}} \rho \rangle / \langle \rho^* \rho \rangle \tag{6}$$

satisfies the following equation of motion

$$\frac{\partial}{\partial t} S(q,t) = -\Omega S(q,t) + \int_0^t \mathrm{d}u\, \phi(q,u) S(q,t-u) \tag{7}$$

which is obtained from (2) using the Zwanzig–Mori projection operator technique.[10,11] Here $\Omega(q)$ is the relaxation frequency obtained in the derivation of (7) as

$$\Omega(q) = \langle \rho^* \mathcal{L} \rho \rangle / \langle \rho^* \rho \rangle \tag{8}$$

and $\phi(q,t)$ is the memory kernel accounting for the non-Markovian nature of the evolution of $S(q,t)$. The explicite form of $\phi(q,t)$ is given elsewhere[1] and will not be needed here.

Equation 7 indicates that $S(q,t)$ behaves as an exponential function for short times, and the initial slope of $S(q,t)$ is determined by $\Omega(q)$. It is noted that the time reversibility would require the first time derivative of $S(q,t)$ to vanish at $t = 0$. This does not happen here because

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dynamical eq 1 is a diffusion equation and does not obey time reversibility. It is a Markovian description of the dynamics of polymer in solution, in which memory effects associated with the dynamics of the solvent are neglected. Therefore (1) and (7) are valid for times larger than such memory time.

The dynamic structure factor $S(q,\omega)$ follows from (7) as

$$S(q,\omega) = 2Re[S + \Omega - \tilde{\phi}(s)]^{-1}_{s=i\omega} \tag{9}$$

where $\tilde{\phi}(s)$ is the Laplace transform of $\phi(t)$. We observe in (9) that $S(q,\omega)$ becomes a Lorentzian with a half-width Ω when the memory function is neglected. A quantitative evaluation of the effect of $\tilde{\phi}(s)$ on $\Omega(q)$ as well as on the shape of $S(q,\omega)$ is very difficult in realistic chain models[12] and will not be attempted here. Suffice it to mention that $\tilde{\phi}(s)$ accounts for deviation of $S(q,\omega)$ from Lorentzian for small ω and makes the true half-width somewhat smaller than Ω in the intermediate momentum transfer range $qR >> 1$ and $ql << 1$ where R is the end-to-end distance and l is the statistical segment length.

The half-width in this q region was calculated by Dubois-Violette and DeGennes[13] for an unperturbed Gaussian chain in the Zimm limit with preaveraged Oseen tensor as $0.030(k_BT/\eta_0)q^3$ where k_BT and η_0 are the temperature and viscosity of the solvent, respectively. In an earlier work[1] we calculated Ω for the same chain model and in the same q region as $0.053(k_BT/\eta_0)q^3$.[22] For small ($qR << 1$) and large ($ql >> 1$) values of q the half-width is correctly given by Ω. Reference 2 compares Ω, with some success, to the experimental half-widths obtained in coherent neutron scattering from dilute polymer solutions by fitting a Lorentzian to the experimental $S(q,\omega)$ in the large q region. Although the half-width of the quasi-elastic peak provides a crude estimate of Ω with increasing accuracy for small and large q values, we do not wish to imply, by the above arguments, that Ω is to be interpreted as the half-width. The true meaning of Ω is apparent from (7), i.e.,

$$\Omega = -\lim_{t\to 0} \frac{d}{dt} \log S(q,t) \tag{10}$$

which shows that Ω can be determined precisely from the measured short-time behavior of log $S(q,t)$, or from the large ω behavior of $S(q,\omega)$, provided these limits are experimentally accessible.

One may, however, interprete Ω as a characteristic frequency in the sense of dynamic scaling. Let us assume for a moment that $S(q,t)$ can be scaled through a change of variable $t \to t\omega_c$ in such a way that

$$S(q,t) = f(\omega_c t) \tag{11}$$

where $f(x)$ is a shape function which is independent of q. Then any frequency proportional to ω_c serves as a characteristic frequency. If we require $|f'(0)| = 1$ as a particular choice, then ω_c becomes the initial slope of $S(q,t)$. We see from (10) that Ω coincides with this definition of frequency. In ref 13 and 14 it is shown for an unperturbed Gaussian chain that $S_{coh}(q,t)$ can indeed be scaled for sufficiently large times in the intermediate q region with a characteristic frequency

$$\omega_c = \frac{1}{3\pi} \frac{k_BT}{\xi_0} q^4 l^2 \tag{12}$$

in the Rouse limit, and

$$\omega_c = \frac{1}{6\pi 2^{1/2}} \frac{k_BT}{\eta_0} q^3 \tag{13}$$

in the Zimm limit with preaveraged Oseen tensor. (In (12), ξ_0 is the friction coefficient per segment.) In the same q region Ω yields[1]

$$\Omega = \frac{1}{12} \frac{k_BT}{\xi_0} q^4 l^2 \qquad \text{Rouse limit} \tag{14a}$$

and

$$\Omega = \frac{1}{6\pi} \frac{k_BT}{\eta_0} q^3 \qquad \text{Zimm limit} \tag{14b}$$

which are proportional to the characteristic frequencies in (12) and (13).

For small values of q for which $qR << 1$, $S(q,t)$ is an exponential function of t with a decay constant Dq^2 where D is the diffusion coefficient which is given by Yamakawa[15] as $D = 0.192(k_BT/\eta_0 l N^{1/2})$ for an unperturbed Gaussian chain. In this limit Dq^2 is the natural choice for the characteristic frequency. In ref 1, Ω was calculated in this limit as $\Omega = Dq^2$ with

$$D = 0.195 \frac{k_BT}{\eta_0} \frac{1}{lN^{1/2}} \tag{15}$$

which is in excellent agreement with the previous result. As a last limiting case we computed Ω in ref 1 in the large q limit as $\Omega = (k_BT/\xi_0)q^2$ which corresponds again to a simple diffusion of segments with a diffusion coefficient $D = (k_BT/\xi_0)$.

In general one may define a characteristic frequency w_c by expressing $S(q,t)$ as

$$S(q,t) = f(qL,\omega_c t) \tag{16}$$

where L is a characteristic length such as R, and requiring that the shape function $f(qL,x)$ for a fixed x is a slowly varying function of qL. In this general case identification of a characteristic frequency is not straightforward. If we require $|f_x'(qL,0)| = 1$ as before, then w_c again coincides with Ω which is defined by (10).

We conclude from these observations that Ω can be interpreted as a characteristic frequency even when the scaling property (11) is not strictly obeyed, and may be used to compare the predictions of theoretical dynamical models for polymers in solution with experimental data insofar as it is a measurable quantity. Similar arguments were used by Kawasaki[16] in the discussion of dynamics of critical fluctuations.

III. Calculation of the Characteristic Frequency

Substitution of (4) and (5) into (8) yields

$$\Omega(q,t) = \frac{\sum_{m,n} \langle \mathbf{D}_{mn} e^{i\mathbf{q}\cdot\mathbf{R}_{mn}} \rangle : \mathbf{qq}}{\sum_{m,n} \langle e^{i\mathbf{q}\cdot\mathbf{R}_{mn}} \rangle} \tag{17}$$

Since the diffusion tensor $\mathbf{D}_{mn}$ depends[15] on the vector distance $\mathbf{R}_{mn} = \mathbf{R}_m - \mathbf{R}_n$ between the mth and nth monomers the calculation of the equilibrium averages appearing in (17) does not require the full knowledge of the equilibrium distribution $\psi_0(\mathbf{R}_1,...,\mathbf{R}_N)$. It is sufficient to know only the equilibrium distribution function of the vector distance $\mathbf{R}_{mn}$. Following Farnoux[17] and Daoud et al.,[7,18] we model this distribution function in such a way that its characteristic function reads as

$$\langle e^{i\mathbf{q}\cdot\mathbf{R}_{mn}} \rangle \simeq e^{-(\mathbf{q}2/6)\langle|\mathbf{R}_{mn}|2\rangle} \tag{18}$$

which implies a Gaussian distribution for $\mathbf{R}_{mn}$ with

$$\langle|\mathbf{R}_{mn}|^2\rangle = l^2|m-n| \qquad \text{for } |m-n| \le N_\tau \tag{19a}$$

$$\langle|\mathbf{R}_{mn}|^2\rangle = l_s{}^2|m-n|^{2\nu} \qquad \text{for } |m-n| \ge N_\tau \tag{19b}$$

Here N_τ is a temperature-dependent cutoff introduced by Daoud[18] to separate Gaussian and excluded-volume regimes. Its temperature dependence is taken to be

$$N_\tau \simeq 1/\tau^2 \tag{20}$$

where

$$\tau = (T - \Theta)/\Theta \tag{21}$$

and Θ is the theta temperature. The continuity of $\langle|\mathbf{R}_{mn}|^2\rangle$ at $|m - n| = N_\tau$ determines the "swollen" statistical segment length as

$$l_s = l\tau^{2\nu-1} \tag{22}$$

one may also introduce a "temperature-dependent" screening length ξ_τ similar to the "concentration-dependent" screening length discussed by Daoud et al.[4,17,18] as

$$\xi_\tau = lN_\tau^{1/2} \tag{23}$$

Then, ξ_τ would be a measure of distance beyond which the excluded volume interaction between monomers becomes important. A somewhat similar expression for $\langle|\mathbf{R}_{nm}|^2\rangle$ was used long ago by Peterlin[19] to calculate the end-to-end distance of a macromolecule in a good solvent, i.e.,

$$\langle|\mathbf{R}_{mn}|^2\rangle \sim |m - n|^{1+\epsilon}$$

where $1 + \epsilon = 1.25$, slightly differs from Flory's value $2\nu = 1.2$ which we adopt in this paper.

We emphasize at this point once more than (17) allows the calculation of the characteristic frequency using other dynamical and equilibrium models than adapted in (18) and (19).

Using (18) and (19) in (17), and the conventional expression of the diffusion tensor with preaveraged Oseen tensor[15] we obtain after some calculations (see Appendix)

$$\Omega(q,\tau) = \frac{q^2}{\beta\xi_0}\left\{1 + A_1\left[\left(\gamma\left(\frac{1-\nu}{2\nu},a_2\right) - \gamma\left(\frac{1-\nu}{2\nu},a_1\right)\right) - \frac{z}{a_1^{1/2\nu}}\left(\gamma\left(\frac{2-\nu}{2\nu},a_2\right) - \gamma\left(\frac{2-\nu}{2\nu},a_1\right)\right)\right] + A_2\int_{N_\tau^{-1/2}}^{1}\mathrm{d}u(1 - zu^2)e^{-a_1u^2}\right\}\left\{1 + \frac{N_\tau}{\nu a_1^{1/2\nu}}\left[\left(\gamma\left(\frac{1}{2\nu},a_2\right) - \gamma\left(\frac{1}{2\nu},a_1\right)\right) - \frac{z}{a_1^{1/2\nu}}\left(\gamma\left(\frac{1}{\nu},a_2\right) - \gamma\left(\frac{1}{\nu},a_1\right)\right)\right] + \frac{2N_\tau}{a_1}(e^{-a_1/N_\tau} - e^{-a_1}) + \frac{2N_\tau^2}{Na_1}\left(e^{-a_1} + \frac{e^{-a_1}}{a_1} - \frac{e^{a_1/N_\tau}}{N_\tau} - \frac{e^{-a_1/N_\tau}}{a_1}\right)\right\}^{-1} \tag{24}$$

where

$$A_1 = \frac{BN_\tau^{1/2}}{2ra_1^{(1-\nu)/2\nu}}; \qquad B = \frac{2}{(6\pi)^{1/2}\pi}\left(\frac{\xi_0}{\eta_0 l}\right)$$

$$A_2 = 2BN\tau^{1/2}$$

$$a_1 = \frac{q^2\xi_\tau^2}{6}; \qquad a_2 = \frac{a_1}{z^{2\nu}}; \qquad z = \frac{N_\tau}{N}$$

and $\gamma(\mu,x)$ is the incomplete γ function.[20]

We now discuss the behavior of $\Omega(q,\tau)$ in various asymptotic regions.

1. Large q region ($ql >> 1$): In this limit (24) yields $\Omega = (k_BT/\xi_0)q^2$ which is the usual result corresponding to the segmental motion.

2. Intermediate q region ($qR >> 1$, $ql << 1$): This region is also the long chain limit. The variation of $\Omega(q,\tau)$ with q in Rouse and Zimm limits is found from (24) as follows

(a) Rouse limit

$$\Omega(q,\tau) = \frac{1}{12}\left(\frac{k_BT}{\xi_0 l^2}\right)(ql)^4 \qquad \text{for } q > q^* \tag{25a}$$

$$\Omega(q,\tau) = \frac{\nu}{6^{1/2\nu}\Gamma\left(\frac{1}{2\nu}\right)}\left(\frac{k_BT}{\xi_0 N_\tau\xi_\tau^2}\right)(q\xi_\tau)^{2+(1/\nu)} \qquad \text{for } q < q^* \tag{25b}$$

where $\Gamma(x)$ is the usual Γ function. We observe that there is a crossover in the q dependence at $q^* = 6^{1/2}/\xi_\tau$. Below q^*, $\Omega \sim q^{11/3}$ for $\nu = {}^3/_5$ which is the q dependence of a perturbed chain whose statistical length is ξ_τ, and friction coefficient per segment is $\xi_0 N_\tau$. Above q^* the q dependence of Ω is that of an unperturbed Gaussian chain with a statistical length l (see eq 14a).

(b) Zimm limit

$$\Omega(q,\tau) = \frac{1}{6\pi}\left(\frac{k_BT}{\eta_0 l^3}\right)(ql)^3 \qquad \text{for } q > q^* \tag{26a}$$

$$\Omega(q,\tau) = \frac{1}{6\pi\pi^{1/2}}\,\frac{\Gamma([1-\nu]/2\nu)}{\Gamma(\frac{1}{2}\nu)}\left(\frac{k_BT}{\eta_0\xi_\tau^3}\right)(q\xi_\tau)^3 \qquad \text{for } q < q^* \tag{26b}$$

We observe that $\Omega \sim q^3$ both above and below the crossover regardless of the value of the critical exponent ν. The proportionality constant is independent of τ. The numerical values of the coefficients in (26a) and (26b) are respectively 0.053 and 0.071 for $\nu = {}^3/_5$. The behavior of Ω for $q > q^*$ is the same as that of an unperturbed Gaussian chain with preaveraged Oseen tensor (see eq 14b).

3. Small q region ($qR << 1$): In this region the wavelength of the momentum transfer is larger than the size of the chain. The characteristic frequency reduces to $\Omega = D(\tau)q^2$ which represents the relaxation of the translational diffusion of the chain as a whole. Using

$$\gamma(\mu,x) = \int_0^x \mathrm{d}t\ e^{-t}t^{\mu-1} \rightarrow x^\mu/\mu \qquad \text{as } x \rightarrow 0 \tag{27}$$

we obtain from (24)

$$D(\tau) = \frac{k_BT}{N\xi_0} + \frac{2}{(6\pi)^{1/2}\pi}\,\frac{k_BT}{N^{1/2}\eta_0 l}z^{1/2}\left[2\left(1 - \frac{z}{3}\right) + \frac{1}{1-\nu}\left(\frac{1}{z^{1-\nu}} - 1\right) - \frac{1}{(2-\nu)}\left(\frac{1}{z^{1-\nu}} - z\right)\right] \tag{28}$$

We distinguish two limiting cases: (a) Θ solvent ($\tau = 0$, $N_\tau = N$, $z = 1$). Ignoring the Rouse term in (28) we obtain

$$D(0) = \frac{8}{3\pi(6\pi)^{1/2}}\left(\frac{k_B\Theta}{\eta_0 l}\right)\frac{1}{N^{1/2}} \tag{29}$$

which is the diffusion coefficient of an unperturbed Gaussian chain with a statistical length l and number of segments N (see eq 15). (b) Good solvent ($N >> N_\tau$ or z

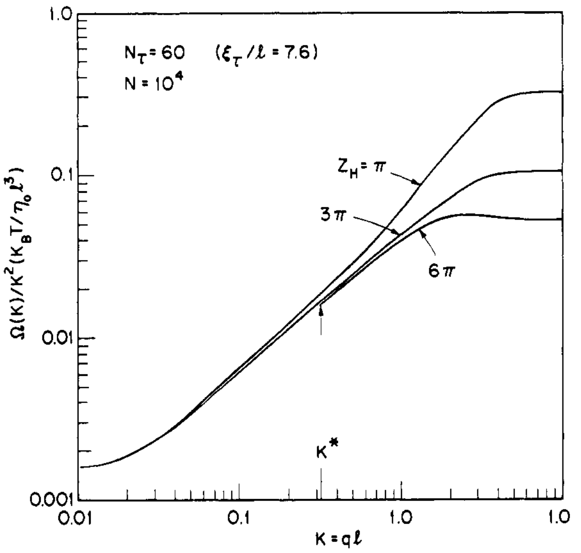

Figure 1. Variation of the normalized characteristic frequency with momentum transfer at a temperature corresponding to N_τ = 60 and for various values of $z_H = (\xi_0/\eta_0 l)$.

<< 1). In the high-temperature limit $z \ll 1$, the third and fourth terms in (28) dominate:

$$D(\tau) = \frac{2}{(6\pi)^{1/2}\pi(1-\nu)(2-\nu)}\left(\frac{k_BT}{\eta_0\xi_\tau}\right)\frac{1}{(N/N_\tau)^\nu} \quad (30)$$

This result corresponds to the diffusion coefficient of a perturbed chain of statistical length ξ_τ and number of segments (or blobs) N/N_τ. In the limit of large τ, $N_\tau \rightarrow 1$ and $\xi_\tau \rightarrow l$ and (30) reduces to

$$D(\infty) = \frac{2}{(6\pi)^{1/2}\pi(1-\nu)(2-\nu)}\left(\frac{k_BT}{\eta_0 l}\right)\frac{1}{N^\nu} \quad (31)$$

which is the diffusion coefficient in a good solvent.

The variation of $\Omega(q,\tau)$ as a continuous function of q can be presented conveniently in terms of dimensionless parameters as

$$\frac{\Omega(q,\tau)}{K^2(k_BT/\eta_0 l^3)} = \frac{1}{z_H}F(z_H,K,N,\xi_\tau/l) \quad (32)$$

where $K = ql$, and

$$z_H = (\xi_0/\eta_0 l) \quad (33)$$

which measures the relative strength of the hydrodynamic interaction between monomers as compared to the frictional drag. The explicite form of F can be obtained by comparing (32) and (24). In Figure 1 we plotted the normalized characteristic frequency[23] as a function of $K = ql$ for various values of z_H ($z_H = 3\pi$ corresponds to Stoke's law assuming that the beads are hard spheres of radius $l/2$) and $N = 10^4$ at a temperature corresponding to $N_\tau = 60$ or $\xi_\tau/l \simeq 7.6$.

The crossover which is expected to occur at $K^* \simeq 0.32$ is not clearly discernable. This is probably due to the leveling off of $\Omega(q)$ in the lower and higher transition regions, which obscures the predicted assymptotic form $\Omega(q) = 0.071(k_BT/\eta_0)q^3$ (good solvent behavior) below K^* and $\Omega(q) = 0.053(k_BT/\eta_0)q^3$ (Gaussian behavior) above K^*.

Figures 2 and 3 show the normalized characteristic frequency as a function of q for a good solvent ($\xi_\tau = l$ and $N_\tau = 1$) and a Θ solvent ($\xi_\tau = lN^{1/2}$ and $N_\tau = N$), respectively.

The behavior of $\Omega(q)$ in a Θ solvent was also presented earlier both in the case of a Gaussian chain[1] and a freely jointed chain.[2]

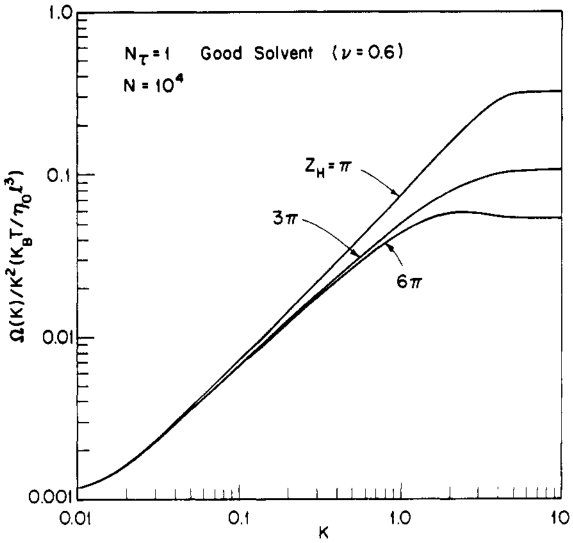

Figure 2. Variation of the normalized characteristic frequency with momentum transfer in the case of a good solvent (N_τ = 1) and for various values of $z_H = (\xi_0/\eta_0 l)$.

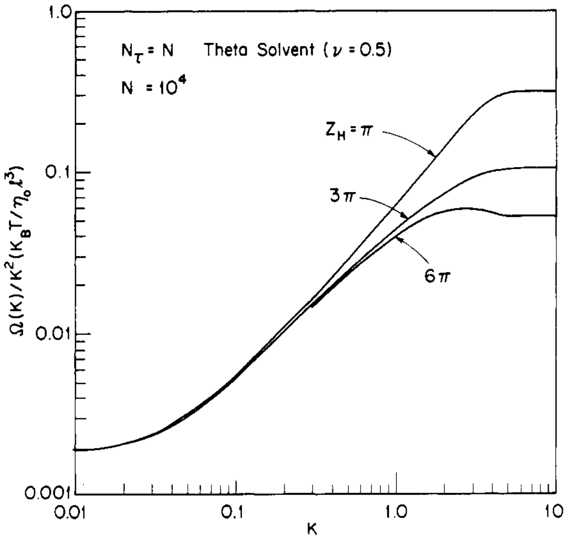

Figure 3. Variation of the normalized characteristic frequency with momentum transfer in the case of Θ solvent (N_τ = N) and for various values of $z_H = (\xi_0/\eta_0 l)$.

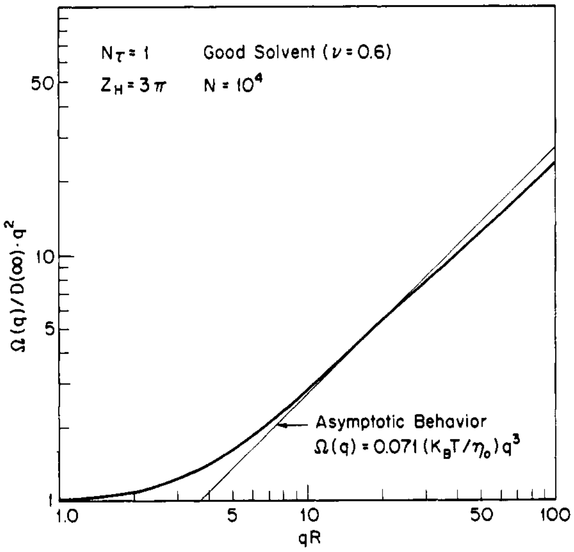

Figure 4. Variation of the normalized characteristic frequency for a good solvent (N_τ = 1) in the transition region from small to intermediate q values.

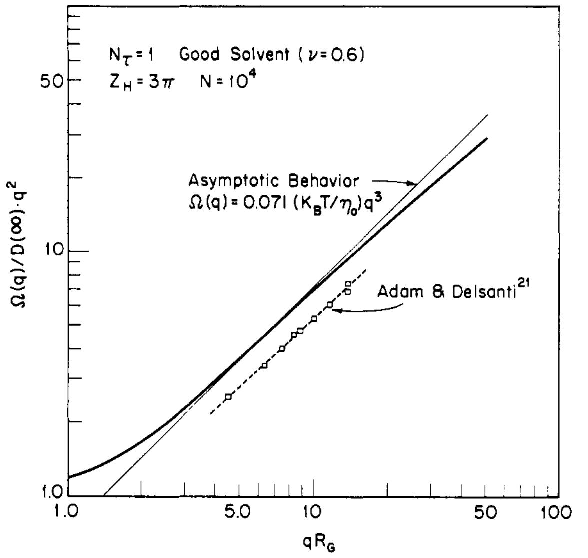

Figure 5. Variation of the normalized characteristic frequency for a good solvent as a function of qR_G in the light-scattering region. The dotted line gives the experimental data for the normalized characteristic frequency as reported by Adam and Delsanti[21] for solutions of polystyrene ($M_w = 24 \times 10^6$) in benzene ($c = 5.54 \times 10^{-4}$ g/cm^3) (these data are multiplied by $2^{1/2}$, see text).

In Figure 4 we plotted $\Omega(q)/D(\infty)\cdot q^2$ again for a good solvent in the transition region from small to intermediate q values as a function of qR where R is the end-to-end distance, i.e., $R = N^{\nu}l$. In this region, which is accessible in light-scattering experiments,[21] the behavior of $\Omega(q)$ is not influenced appreciably by the values of z_H and is determined mainly by lN^{ν}. We observe that $\Omega(q)$ does not obey strictly a simple power law in any appreciable q region as seen from Figure 4 as well as Figures 2 and 3.

In Figure 5 we plotted $\Omega(q)/D(\infty)\cdot q^2$ as a function of qR_G where R_G is the radius of gyration. Also shown on this figure are the experimental data reported by Adam and Delsanti[21] obtained by light scattering from polystyrene ($M_w = 24 \times 10^6$) in benzene ($c = 5.54 \times 10^{-4}$ g/cm^3). We have multiplied their data by $2^{1/2}$ since they measured the characteristic frequency by fitting $S(q,t)$ to the expression provided by De Gennes and Dubois-Violette (see eq 13 and 14b). The dotted line through the experimental points, which is obtained by shifting the calculated solid curve downward, is plotted to demonstrate the agreement between the theoretical and the experimental slopes.

IV. Conclusions

In this paper we have introduced a characteristic frequency as

$$\Omega = \frac{\langle \rho^* \mathcal{L} \rho \rangle}{\langle \rho^* \rho \rangle}$$

which is the initial slope of the normalized scattering function $S(q,t)$ and can be obtained experimentally by plotting log $S(q,t)$ vs. time t. We have investigated the variation of Ω as a function of momentum transfer and temperature and discussed the crossover behavior at relatively high temperatures. We think that this microscopic approach to the discussion of dynamic scaling has several attractive features: (a) the characteristic frequency is expressed solely in terms of equilibrium averages; (b) the dynamical and equilibrium properties of the polymer in solution enter in the expression of Ω through the dynamical operator $\mathcal{L}$ and the equilibrium distribution ψ_0, respectively (different dynamic and equilibrium models are readily accomodated by specifying $\mathcal{L}$ and ψ_0, as illustrated in this paper); and (c) Ω remains a well-defined quantity even in the transition q regions where simple power laws are not obeyed and may be useful in testing the validity of various dynamic and equilibrium chain models, insofar as it can be determined experimentally, by comparing theoretical predictions to measured data in a larger range of momentum transfer.

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Appendix. Derivation of Equation 24

Comparing eq 8 and 17 yields:

$$\langle \rho^* \mathcal{L} \rho \rangle = \sum_{m,n} \langle \mathbf{D}_{mn} e^{i\mathbf{q}\cdot\mathbf{R}_{mn}} \rangle : \mathbf{qq} \tag{A}$$

$$\langle \rho^* \rho \rangle = \sum_{m,n} \langle e^{i\mathbf{q}\cdot\mathbf{R}_{mn}} \rangle \tag{B}$$

Using the preaveraged Oseen tensor approximation in (A) we get:

$$\langle \rho^* \mathcal{L} \rho \rangle = \frac{Nq^2}{\beta\xi_0} + \frac{1}{\beta} \sum_{m \neq n} \langle \mathbf{T}_{mn} \rangle \langle e^{i\mathbf{q}\cdot\mathbf{R}_{mn}} \rangle : \mathbf{qq}$$

where

$$\mathbf{T}_{mn} = \mathbf{I} \frac{1}{(6\pi)^{1/2}\pi\eta_0} \frac{1}{\langle |\mathbf{R}_{mn}|^2 \rangle^{1/2}} \qquad (m \neq n)$$

Using eq 18 and 19 gives:

$$\langle \rho^* \mathcal{L} \rho \rangle = \frac{Nq^2}{\beta\xi_0} \left\{ 1 + B \left[\sum_{n=1}^{N_\tau - 1} \left(1 - \frac{n}{N}\right) \frac{e^{-(q^2l^2/6)n}}{n^{1/2}} + N^{(2\nu-1)/2} \sum_{n=N_\tau}^{N-1} \left(1 - \frac{n}{N}\right) \frac{e^{-(q^2\xi_\tau^2/6)(n/N\tau)^{2\nu}}}{n^{\nu}} \right] \right\} \tag{A1}$$

where

$$B = \frac{2}{(6\pi)^{1/2}\pi} \left(\frac{\xi_0}{\eta_0 l} \right)$$

Replacing sums by integrals it is easy to verify the following results:

$$\sum_{n=1}^{N_\tau - 1} \left(1 - \frac{n}{N}\right) \frac{e^{-q^2l^2/6}}{n^{1/2}} \simeq 2(N_\tau)^{1/2} \int_{N_\tau^{-1/2}}^{1} \mathrm{d}u (1 - zu^2) e^{-a_1u^2}$$

and

$$\sum_{n=N_\tau}^{N-1} \left(1 - \frac{n}{N}\right) \frac{e^{-(q^2\xi_\tau^2/6)(n/N_\tau)^{2\nu}}}{n^{\nu}} \simeq \frac{N_\tau^{1-\nu}}{2\nu a_1^{(1-\nu)/2\nu}} \left\{ \left(\gamma\left(\frac{1-\nu}{2\nu}, a_2\right) - \gamma\left(\frac{1-\nu}{2\nu}, a_1\right) \right) - \frac{z}{a_1^{1/2\nu}} \left(\gamma\left(\frac{2-\nu}{2\nu}, a_2\right) - \gamma\left(\frac{2-\nu}{2\nu}, a_1\right) \right) \right\}$$

where $a_1 = q^2\xi_\tau^2/6$; $a_2 = a_1/z^{2\nu}$; $z = (N_\tau/N)$; and $\gamma(\mu,a) = \int_0^a \mathrm{d}x\, x^{\mu-1}e^{-x}$. Substituting these results into (Al) gives:

$$\langle \rho^* \mathcal{L} \rho \rangle = \frac{Nq^2}{\beta\xi_0} \left\{ 1 + A_1 \left[\left(\gamma\left(\frac{1-\nu}{2\nu}, a_2\right) - \gamma\left(\frac{1-\nu}{2\nu}, a_1\right) \right) - \frac{z}{a_1^{1/2\nu}} \left(\gamma\left(\frac{2-\nu}{2\nu}, a_2\right) - \gamma\left(\frac{2-\nu}{2\nu}, a_1\right) \right) \right] + A_2 \int_{N_\tau^{-1/2}}^{1} \mathrm{d}u\, (1 - zu^2) e^{-a_1u^2} \right\} \tag{A2}$$

where

$$A_1 = \frac{BN_\tau^{1/2}}{2\nu a_1^{(1-\nu)/2\nu}}; \qquad A_2 = 2BN_\tau^{1/2}$$

Similarly we can verify that (B) transforms as follows:

$$\langle\rho^*\rho\rangle \simeq N + \sum_{m\neq n} e^{-(q^2/6)\langle|\mathbf{R}_{mn}|^2\rangle} = N + 2N\left\{\sum_{n=1}^{N_\tau-1}\left(1-\frac{n}{N}\right)e^{-(q^2l^2/6)n} + \sum_{n=N_\tau}^{N-1}\left(1-\frac{n}{N}\right)e^{-(q^2\xi_\tau^{\,2}/6)(n/N_\tau)^{2\nu}}\right\} \tag{B1}$$

Using the same integral approximation as in the previous calculations we get:

$$\sum_{n=1}^{N_\tau-1}\left(1-\frac{n}{N}\right)e^{-(q^2l^2/6)n} \simeq \frac{N_\tau}{a_1}(e^{-a_1/N_\tau} - e^{-a_1}) + \frac{N_\tau^{\,2}}{Na_1}\left(e^{-a_1} + \frac{e^{-a_1}}{a_1} - \frac{e^{-a_1/N_\tau}}{N_\tau} - \frac{e^{-a_1/N_\tau}}{a_1}\right)$$

and

$$\sum_{n=N_\tau}^{N-1}\left(1-\frac{n}{N}\right)e^{-(q^2\xi_\tau^2/6)(n/N_\tau)^{2\nu}} \simeq \frac{N_\tau}{2\nu a_1^{\,1/2\nu}}\left[\left(\gamma\left(\frac{1}{2\nu},a_2\right) - \gamma\left(\frac{1}{2\nu},a_1\right)\right) - \frac{z}{a_1^{\,1/2\nu}}\left(\gamma\left(\frac{1}{\nu},a_2\right) - \gamma\left(\frac{1}{\nu},a_1\right)\right)\right]$$

Substituting these into (B1) we get:

$$\langle\rho^*\rho\rangle = N + \frac{2NN_\tau}{a_1}(e^{-a_1/N_\tau} - e^{-a_1}) + \frac{2N_\tau^{\,2}}{a_1}\left(e^{-a_1} + \frac{e^{-a_1}}{a_1} - \frac{e^{-a_1/N_\tau}}{N_\tau} - \frac{e^{-a_1/N_\tau}}{a_1}\right) + \frac{NN_\tau}{\nu a_1^{\,1/2\nu}}\left[\left(\gamma\left(\frac{1}{2\nu},a_2\right) - \gamma\left(\frac{1}{2\nu},a_1\right)\right) - \frac{z}{a_1^{\,1/2\nu}}\left(\gamma\left(\frac{1}{\nu},a_2\right) - \gamma\left(\frac{1}{\nu},a_1\right)\right)\right] \tag{B2}$$

The ratio of (A2) by (B2) gives eq 24.

References and Notes

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(22) In ref 1, Ω was calculated without preaveraging the Oseen tensor as $0.055(k_BT/\eta_0)q^3$, in the intermediate q region. The difference between preaveraging and not preaveraging becomes more pronounced for larger values of q and preaveraging always yields smaller values for Ω.

(23) In plotting the curves in Figures 1–5 we have used the original expressions of $\langle\rho^*\mathcal{L}\rho\rangle$ and $\langle\rho^*\rho\rangle$ involving summations as given by eq A1 and B1 in the appendix. The analytical expression of $\Omega(q)$ in (24) is obtained by approximating summations by integrals. These two expressions of $\Omega(q)$ differ from each other at most by 10% about $ql \simeq 1$ and by a gradually decreasing amount for larger and smaller values of ql.