$T_m(n,p)$ with n and p, while defining the free energy balance in molar quantities (cf. eq 3, 4, 10, and 11) as

$$\Delta F_c(l,T) - \sum_e(n) = 0 \quad \text{(A1)}$$

where

$$\sum_e(n) = 2\sigma_{e,e}(n) + 2n\sigma_{e,f} \quad \text{(A2)}$$

$\sigma_{e,e}(n)$ is the surface free energy of one chain end in the surface of a crystal made of n-times folded chains, and $2\sigma_{e,f}$ is the surface free energy of one chain fold (occupying two lattice sites, cf. Figure 2b). Hence

$$[p\Delta H_f/T_m(\infty)][T_m(\infty) - T_m(n,p)] - RT_m(n,p) \ln p = \sum_e(n) + RT_m(n,p) \ln C \equiv \sum_e^+(n) \quad \text{(A3)}$$

in which C^{-1} is the number of monomer units in the statistical segment.[15]

The analysis, at an average temperature $\bar{T} = 61.2$ °C, in the melting range of the various fractions considered, yields the following results

$$2\sigma_{e,e}(0) + R\bar{T} \ln C = 1.57 \text{ kcal/mol}$$

$$2\sigma_{e,e}(n \geq 1) + R\bar{T} \ln C = 2.15 \text{ kcal/mol}$$

$$2\sigma_{e,f} = 1.38 \text{ kcal/mol}$$

from which one can easily derive the various molar surface free energies $\sum_e^+(n)$. In most cases it was necessary to account for the temperature dependence of $\sum_e^+(n,T) = \sum_e^+(n,\bar{T})[1 - \alpha(T - \bar{T})]$ with $\alpha \simeq 1.3 \times 10^{-2}$ K^{-1}. (The conversion factor is 1 kcal/mol = 32.5 erg cm^{-2}.)

References and Notes

(1) J. I. Lauritzen, Jr., and J. D. Hoffman, *J. Chem. Phys.*, **31**, 1680 (1959); *J. Res. Natl. Bur. Stand., Sect. A*, **64**, 73 (1960).
(2) J. D. Hoffman and J. I. Lauritzen, Jr., *J. Res. Natl. Bur. Stand., Sect. A*, **65**, 297 (1961).
(3) F. C. Frank and M. Tosi, *Proc. R. Soc. London, Ser. A*, **263**, 323 (1961).
(4) A. Keller, *Philos. Mag.*, **2**, 1171 (1957).
(5) J. D. Hoffman, G. T. Davis, and J. I. Lauritzen, Jr., in "Treatise on Solid State Chemistry", Vol. 3, N. B. Hannay, Ed., Plenum Press, New York, 1976, Chapter 7, pp 497–614.
(6) D. M. Sadler and A. Keller, *Macromolecules*, **10**, 1128 (1977).
(7) A. J. Kovacs and A. Gonthier, *Kolloid Z. Z. Polym.*, **250**, 530 (1972).
(8) A. J. Kovacs, A. Gonthier, and C. Straupe, *J. Polym. Sci., Part C*, **50**, 283 (1975).
(9) A. J. Kovacs, C. Straupe, and A. Gonthier, *J. Polym. Sci., Part C*, **59**, 31 (1977).
(10) A. J. Kovacs and C. Straupe, *Faraday Discuss. Chem. Soc.*, in press.
(11) J. P. Arlie, P. Spegt, and A. Skoulios, *Makromol. Chem.*, **99**, 160 (1966); **104**, 212 (1967).
(12) Y. Takahashi and H. Tadokoro, *Macromolecules*, **6**, 672 (1973).
(13) C. P. Buckley and A. J. Kovacs, *Prog. Colloid Polym. Sci.*, **58**, 44 (1975).
(14) C. P. Buckley and A. J. Kovacs, *Colloid Polym. Sci.*, **254**, 695 (1976).
(15) P. J. Flory and A. Vrij, *J. Am. Chem. Soc.*, **85**, 3548 (1963).
(16) F. Pierson, Thesis, Faculté des Sciences, Université de Strasbourg, 1968.
(17) J. I. Lauritzen, Jr., and J. D. Hoffman, *J. Appl. Phys.*, **44**, 4340 (1973).
(18) I. C. Sanchez and E. A. Dimarzio, *J. Chem. Phys.*, **55**, 893 (1971).
(19) C. P. Buckley, *Polymer*, in press.
(20) J. J. Labaig, Thesis, University Louis Pasteur Strasbourg, 1978.
(21) J. D. Hoffman, G. S. Ross, L. Frolen, and J. I. Lauritzen, Jr., *J. Res., Natl. Bur. Stand., Sect. A*, **79**, 671 (1975).
(22) J. I. Lauritzen, Jr., private communication, 1975.
(23) J. A. Koutsky, A. G. Walton, and E. Baer, *J. Appl. Phys.*, **38**, 1832 (1967).
(24) R. L. Miller in "Flow-Induced Crystallization", R. L. Miller, Ed., Gordon and Breach, London, 1979.
(25) Shear viscosity measurements of molten PEO fractions[16] show that chain entanglements occur for molecular weights larger than about 7000.
(26) The apportionating of this entropy is not compulsory, since it can also be assumed to be entirely lost during the attachment of the first stem.[19] In the present context both assumptions lead to similar results.
(27) Experimental data do not suggest any molecular weight dependence for β, since the maximum of the growth rate (reached at room temperature) is independent of p[7,8] (cf. Figure 1).
(28) Or, they should involve a *fixed* fractional length ($^1/_2 < l/L < 1$) over the entire temperature range of interest, which appears to be an unrealistic assumption, since l/L must approach unity as T approaches $T_m(0,p)$.

The Effect of Preaveraging the Oseen Tensor on the Characteristic Frequency in Good Solvents

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ABSTRACT: The characteristic frequency $\Omega(q)$ for linear polymer chains is calculated as a function of temperature, for all values of q, without *preaveraging* the Oseen tensor. It is found that the preaveraging does not affect the overall qualitative behavior of $\Omega(q)$ as a function of q, but it introduces non-negligible numerical errors. In particular, in the intermediate q region and for good solvents the ratio $z(q) \equiv \Omega(q)/(k_BT/\eta_0)q^3$ is found to be 0.0789 instead of 0.071 which was previously calculated by using the preaveraged Oseen tensor. The ratio $z(q)$ is investigated in detail as a function of q.

The purpose of this paper is to investigate the effects of preaveraging the Oseen tensor on the characteristic frequency (or first cumulant) $\Omega(q)$ of the coherent scattering function $S(q,t)$ in a good solvent and to study the variation of $\Omega(q)/q^3$ with molecular weight and the type of polymer. $\Omega(q)$ was first calculated by Akcasu and Gurol[1] for a linear single unperturbed Gaussian chain without preaveraging the Oseen tensor. By comparing their results with those obtained by preaveraging the Oseen tensor, they concluded that the effect of preaveraging is to predict a lower value for $\Omega(q)$, with the difference being largest in the vicinity of $qa = 1$ and vanishing as $qa \to 0$. Akcasu and Higgins[2] later obtained $\Omega(q)$ for a freely jointed chain with nonpreaveraged Oseen tensor again in a Θ solvent. Burchard et al.[3] extended these calculations to branched polymers in a Θ solvent and showed that the error resulting from preaveraging may be as large as 40% in such polymers. More recently, Akcasu and Benmouna[4] considered

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the effects of temperature and concentration on $\Omega(q)$ by using the preaveraged Oseen tensor. In the present paper we repeat the calculation of $\Omega(q)$ without preaveraging the Oseen tensor, for a single linear Gaussian chain, as a function of temperature and in particular in the good solvent limit.

Theory

The starting point for the calculation of $\Omega(q)$ is given by the following expression[1]

$$\Omega(q) = \frac{\sum_{nm} \langle \mathbf{D}_{nm} e^{i\mathbf{q}\cdot\mathbf{R}_{nm}} \rangle : \mathbf{qq}}{\sum_{n,m} \langle e^{i\mathbf{q}\cdot\mathbf{R}_{nm}} \rangle} \tag{1a}$$

where

$$\mathbf{D}_{nm} = k_B T[\mathbf{T}_{nm} + (1/\xi_0)\mathbf{I}\delta_{nm}] \tag{1b}$$

and

$$\mathbf{T}_{nm} = \frac{1}{8\pi\eta_0 R_{nm}{}^3}[\mathbf{I}R_{nm}{}^2 + \mathbf{R}_{nm}\mathbf{R}_{nm}] \tag{1c}$$

ξ_0 is the friction coefficient per segment, η_0 is the viscosity of the solvent, and $\mathbf{R}_{nm} \equiv \mathbf{R}_n - \mathbf{R}_m$. Since $\mathbf{D}_{nm}$ is a function of $\mathbf{R}_{nm}$ only, it is sufficient to know the equilibrium distribution of $\mathbf{R}_{nm}$ which we assume to be Gaussian.

$$P(\mathbf{R}_{nm}) = \left(\frac{3}{2\pi\langle R_{nm}{}^2\rangle}\right)^{3/2} \exp\left(-\frac{3}{2\langle R_{nm}{}^2\rangle} R_{nm}{}^2\right) \tag{2a}$$

Temperature effects are incorporated through $\langle R_{nm}{}^2\rangle$, using the blob model of chain statistics,

$$\langle R_{nm}{}^2\rangle = |n-m|a^2 \qquad \text{if } |n-m| < N_\tau \tag{2b}$$

and

$$\langle R_{nm}{}^2\rangle = \left(\frac{|n-m|}{N_\tau}\right)^{2\nu} \xi_\tau{}^2 \qquad \text{if } |n-m| > N_\tau \tag{2c}$$

where $N_\tau \sim \tau^{-2}$ and $\xi_\tau{}^2 = N_\tau a^2$; a is the unit segment length (for more details on these aspects, we refer the reader to ref 4 and the references listed therein). Combining eq 1 and 2 we obtain the first cumulant as a function of momentum transfer q and reduced temperature $\tau \equiv (T-\Theta)/T$ as

$$\Omega(q,\tau) = q^2\frac{k_B T}{\xi_0}\left\{1 + \frac{3}{2}\frac{B}{\alpha^{1/2}}\mathscr{I}_N(q,\tau)\right\}\cdot\left\{1 + \frac{2}{\alpha}H_N(q,\tau)\right\}^{-1} \tag{3a}$$

where

$$\mathscr{I}_N(q,\tau) \equiv \alpha\sum_{n=1}^{N_\tau-1}\left(1-\frac{n}{N}\right)X_n{}^{-2} \times \left[-X_n{}^{-1} + (2 + X_n{}^{-2})e^{-X_n{}^2}\int_0^{X_n} dt\, e^{t^2}\right] + \alpha\sum_{n=N_\tau}^{N-1}\left(1-\frac{n}{N}\right)Y_n{}^{-2}\left[-Y_n{}^{-1} + (2 + Y_n{}^{-2})e^{-Y_n{}^2}\int_0^{Y_n} dt\, e^{t^2}\right] \tag{3b}$$

$$H_N(q,\tau) \equiv \alpha\sum_{n=1}^{N_\tau-1}\left(1-\frac{n}{N}\right)e^{-X_n{}^2} + \alpha\sum_{n=N_\tau}^{N-1}\left(1-\frac{n}{N}\right)e^{-Y_n{}^2} \tag{3c}$$

and

$$\alpha \equiv (q^2a^2/6)$$
$$X_n{}^2 \equiv \alpha n$$
$$Y_n{}^2 \equiv (\alpha n^{2\nu}/N_\tau{}^{2\nu-1}) \qquad (\nu = {}^3/_5)$$
$$B \equiv ({}^1/_6{}^{1/2}\pi^{3/2})(\xi_0/\eta_0 a)$$

These results become identical with those obtained by Akcasu and Gurol[1] when $N_\tau = N$, i.e., in the absence of excluded volume effects.

To discuss the various limiting cases of $\Omega(q,\tau)$ analytically, we approximate the sums by integrals[10] so that eq 3b,c become, respectively

$$\mathscr{I}_N(q,\tau) \simeq \int_\alpha^{xK^2} du\left(1-\frac{u}{K^2}\right)\frac{1}{u}\times\left[-\frac{1}{u^{1/2}} + \left(2+\frac{1}{u}\right)e^{-u}\int_0^{u^{1/2}} e^{t^2}\,dt\right] + \frac{(xK^2)^{1-(1/2\nu)}}{2\nu}\int_{xK^2}^{K^2/x^{2\nu-1}} du\left(1-\frac{x}{(xK^2)^{1/2\nu}}u\right)\frac{1}{u^{2-(1/2\nu)}}\times\left[-\frac{1}{u^{1/2}} + \left(2+\frac{1}{u}\right)e^{-u}\int_0^{u^{1/2}} dt\, e^{t^2}\right] \tag{4a}$$

and

$$H_N(q,\tau) \simeq \int_\alpha^{xK^2} du\left(1-\frac{u}{K^2}\right)e^{-u} + \int_{xK^2}^{K^2} du\left(1-\frac{u}{K^2}\right)e^{-u^{2\nu}(xK^2)^{1-2\nu}} \tag{4b}$$

where $K^2 \equiv \alpha N$ and $x \equiv N_\tau/N$. If we let $x = 1/N$, the first integral in eq 4a and 4b vanishes and we obtain the good solvent limit. In the Θ solvent case $x = 1$ and it is the second integral which vanishes. Note that if we set $\nu = {}^1/_2$ in these equations, we recapture the Θ solvent limit.[1] In this paper, we focus our attention on the temperature dependence of $\Omega(q)$, and in particular on the good solvent limit. In this limit eq 4a and 4b become, respectively

$$\mathscr{I}_N{}^{\text{good}}(q) = \frac{\alpha^{1/2}}{2\nu N^{\nu-1}}K_\nu{}^{1-1/\nu}\int_\alpha^{K_\nu{}^2} du\times\left(1-\frac{u}{K_\nu{}^{1/\nu}}\right)\frac{1}{u^{2-(1/2\nu)}}\left[-\frac{1}{u^{1/2}} + \left(2+\frac{1}{u}\right)e^{-u}\int_0^{u^{1/2}} dt\, e^{t^2}\right] \tag{5a}$$

and

$$H_N{}^{\text{good}}(q) = N\alpha\int_{1/N(\approx 0)}^1 du\,(1-u)e^{-u^{2\nu}K_\nu{}^2} \tag{5b}$$

where

$$K_\nu{}^2 \equiv (1/3)(1+\nu)(1+2\nu)q^2R^2g(\nu) \tag{5c}$$

with

$$Rg(\nu) \equiv aN^\nu[2(1+\nu)(1+2\nu)]^{-1/2} \tag{5d}$$

Substituting (5) in (3a) we obtain Ω in the good solvent limit as a function of q. We distinguish three q regions: in the region where $qa \ll 1$ but qRg is finite we let $\alpha \to 0$ in (5a) and obtain

$$\frac{\Omega(q)}{q^2D(\nu)} = \frac{3(1-\nu)(2-\nu)}{16\nu}K_\nu{}^{(1-\nu)/\nu}\int_0^{K_\nu{}^2} du\times\left(1-\frac{u}{K_\nu{}^{1/\nu}}\right)\frac{1}{u^{2-(1/2\nu)}}\times\left[-\frac{1}{u^{1/2}} + \left(2+\frac{1}{u}\right)e^{-u}\int_0^{u^{1/2}} dt\, e^{t^2}\right]\cdot\left(\int_0^1 du\,(1-u)e^{-u^{2\nu}K_\nu{}^2}\right)^{-1} \tag{6a}$$

where

$$D(\nu) = \frac{k_B T}{\eta_0 Rg(\nu)}\{\pi(1-\nu)(2-\nu)[3\pi(1+\nu)(1+2\nu)]^{1/2}\}^{-1} \quad (6b)$$

This form of the normalized Ω, which depends only on qRg, is suitable for interpreting light-scattering experiments. Furthermore, it contains both the good and Θ solvent limits by letting $\nu = {}^3/_5$ and ${}^1/_2$, respectively.

In the low q region where $qRg \ll 1$ holds, eq 3a reduces to $\Omega(q,\tau) = D(\tau)q^2$, where $D(\tau)$ is the temperature-dependent diffusion coefficient. The expression of $D(\tau)$ obtained from (3a) is identical with that derived by Benmouna and Akcasu, using the preaveraged Oseen tensor (see eq 28 of ref 4a), and hence will not be reproduced here. It reduces to $D(\nu)$ in (6b) in both good ($\nu = {}^3/_5$) and Θ solvent ($\nu = {}^1/_2$) limits. The fact that the diffusion coefficient is not affected by preaveraging the Oseen tensor is not surprising because in the small q limit $\Omega(q)$ depends on $\langle \mathbf{T}_{nm} \rangle$ only, as can be seen from eq 1. If we take the limit $\alpha \to 0$ and $K \to \infty$ in (4) we obtain Ω in the intermediate q region. In this region, $\Omega(q)$ as a function of q displays a crossover at $q = q^* \equiv 6^{1/2}/\xi_\tau$, just as it does when it is calculated with the preaveraged Oseen tensor. In the Rouse limit ($B = 0$) in which the Oseen tensor is not present, Ω varies with q as q^4 when $q \ll q^*$ and as $q^{11/3}$ when $q \gg q^*$ as discussed elsewhere.[4] In the Zimm limit where hydrodynamic interaction plays a dominant role, we find

$$\Omega(q) = 0.0625\frac{k_B T}{\eta_0}q^3 \quad (\Theta \text{ solvent}) \text{ if } q \gg q^* \quad (7a)$$

and

$$\Omega(q) = 0.0789\frac{k_B T}{\eta_0}q^3 \quad (\text{good solvent}) \text{ if } q \ll q^* \quad (7b)$$

Equation 7a is obtained from eq 3 after substituting $\mathcal{J}_N(q,\tau)$ given by eq 4a in the limit $\alpha \to 0$ and $(q/q^*) \to \infty$. In this limit $\mathcal{J}_N(q,\tau)$ becomes

$$\int_0^\infty \frac{du}{u}\left[-\frac{1}{u^{1/2}} + \left(2 + \frac{1}{u}\right)e^{-u}\int_0^{u^{1/2}} dt\, e^{t^2}\right] = \frac{\pi(\pi^{1/2})}{2} \quad (8)$$

This integral was calculated for the first time by Stockmayer.[7] We reproduce this calculation in Appendix A as a special case when $\nu = {}^1/_2$. Equation 7b is obtained by the same procedure, but now we let $(q/q^*) \to 0$ and $K \to \infty$. In this limit $\mathcal{J}_N(q,\tau)$ becomes

$$\int_0^\infty \frac{du}{u^{2-(1/2\nu)}}\left[-\frac{1}{u^{1/2}} + \left(2 + \frac{1}{u}\right)e^{-u}\int_0^{u^{1/2}} dt\, e^{t^2}\right] \quad (9)$$

which is evaluated in Appendix A as 3.965 for $\nu = {}^3/_5$. It is interesting to recall the corresponding expressions of Ω in the case of the preaveraged Oseen tensor:

$$\Omega(q) = 0.053\frac{k_B T}{\eta_0}q^3 \quad (\Theta \text{ solvent}) \text{ if } q \gg q^* \quad (10a)$$

and

$$\Omega(q) = 0.071\frac{k_B T}{\eta_0}q^3 \quad (\text{good solvent}) \text{ if } q \ll q^* \quad (10b)$$

These results show that $\Omega(q)$ is about 15% lower in the Θ solvent and 10% lower in the good solvent limits when the Oseen tensor is preaveraged.

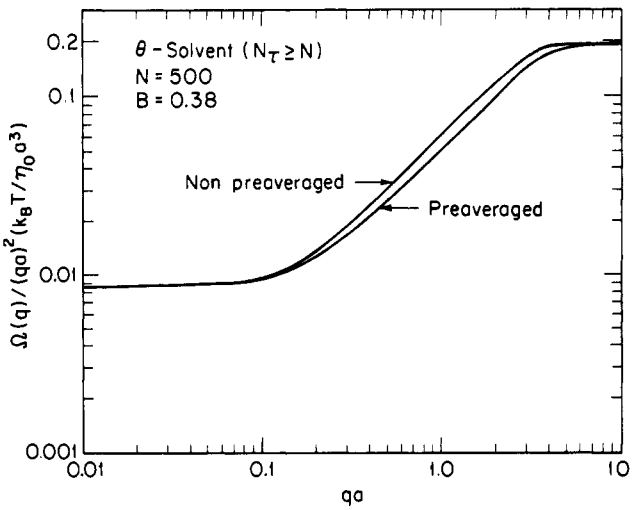

Figure 1. Variation of $\Omega(q)/q^2(k_BT/\eta_0)$ with (qa) under Θ conditions with the preaveraged and the nonpreaveraged Oseen tensor. Note that the maximum difference (15%) is reached at $qa \simeq 1$.

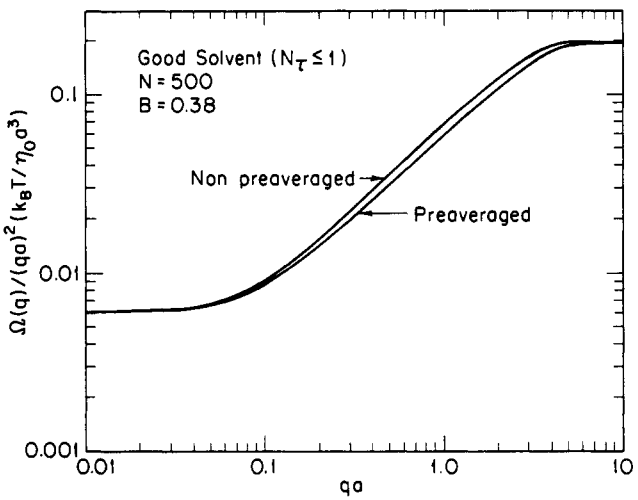

Figure 2. Variation of $\Omega(q)/q^2(k_BT/\eta_0)$ with (qa) under good solvent conditions with the preaveraged and the nonpreaveraged Oseen tensor. Note that the maximum difference (11%) is reached at $qa \simeq 1$.

In the upper transition region where $K_\nu \to \infty$ and α is finite, the normalized Ω can be obtained from eq 3a and 5 as

$$\frac{\Omega(q)}{q^2\frac{k_B T}{\xi_0}} = \left[1 + {}^3/_4 B[\alpha^{(\nu-1)/2\nu}/\nu] \times \int_\alpha^\infty \frac{du}{u^{2-(1/2\nu)}}\left(-\frac{1}{u^{1/2}} + \left(2 + \frac{1}{u}\right)e^{-u}\int_0^{u^{1/2}} e^{t^2}\,dt\right)\right] \Big/ [1 + [\alpha^{-1/2\nu}/\nu][\Gamma(1/2\nu) - \gamma(1/2\nu,\alpha)]] \quad (11)$$

where $\gamma(\mu,x)$ is the incomplete γ function of argument x and order μ.[5] This form can be used in the interpretation of neutron-scattering data. Note that $\Omega(q)$ depends only on qa and B, the draining parameter, in this q region.

At higher values of $q(\alpha \gg 1)$ eq 11 reduces to the usual segmental diffusion relaxation frequency[1,4] $\Omega(q) = (k_BT/\xi_0)q^2$.

Numerical Results

We calculated $\Omega(q)$ numerically by using its original expression (eq 3) and plotted $\Omega(q)/q^2(k_BT/\eta_0)$ vs. qa in

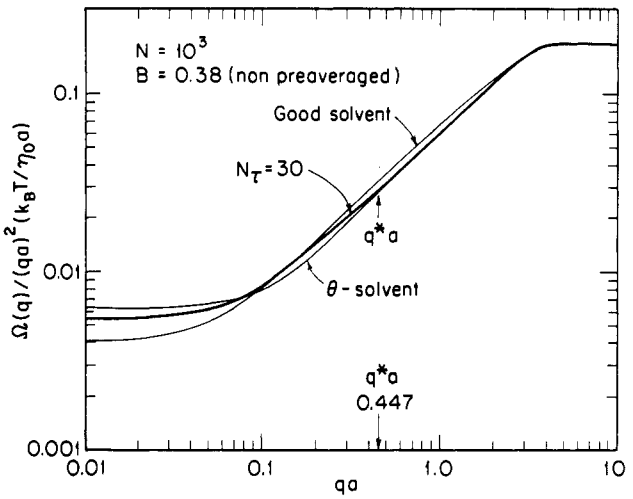

Figure 3. Variation of $\Omega(q)/q^2(k_BT/\eta_0)$ with (qa) in good solvent, Θ solvent, and for an intermediate temperature corresponding to $N_\tau = 30$ with the nonpreaveraged Oseen tensor. This figure illustrates the tendency to a crossover from good to Θ solvent conditions when q is increased from $q < q^*$ to $q > q^*$.

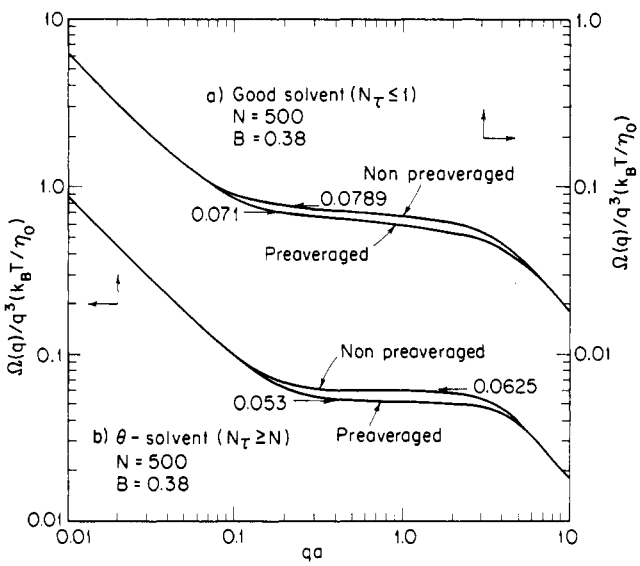

Figure 4. Variation of $z(q) \equiv \Omega(q)/q^3(k_BT/\eta_0)$ with (qa) under good (curve a) and Θ (curve b) solvent conditions with the preaveraged and the nonpreaveraged Oseen tensor.

Figures 1–3 in Θ and good solvent limits as well as at an intermediate temperature corresponding to $N_\tau = 30$. In Figures 1 and 2 we have also included the curves corresponding to the preaveraged Oseen tensor for comparison. One observes that preaveraging the Oseen tensor does not change the qualitative behavior of $\Omega(q)$ vs. q, but only affects its numerical values in certain q regions. In Figure 3 one may observe the tendency for crossover at $q = q^*$ from good solvent behavior when $q < q^*$ to Θ solvent behavior when $q > q^*$. This tendency is more pronounced for longer chains. However, due to the effect of the translational and segmental diffusion at low and high q regions, respectively, the asymptotic behaviors of good and Θ solvent limits, i.e., $\Omega \sim 0.0789q^3$ and $\Omega \sim 0.0625q^3$, are not quite attained. Consequently the crossover may not be discernable in an actual experiment, even when q^* is adjusted, by choosing the temperature properly, to fall in the intermediate q range. However, its effect may still be observable in the form of a smaller exponent than 3 when the experimental Ω in the intermediate q region is fitted to a simple power law q^α. Note that concentration crossover would lead to an exponent slightly larger than

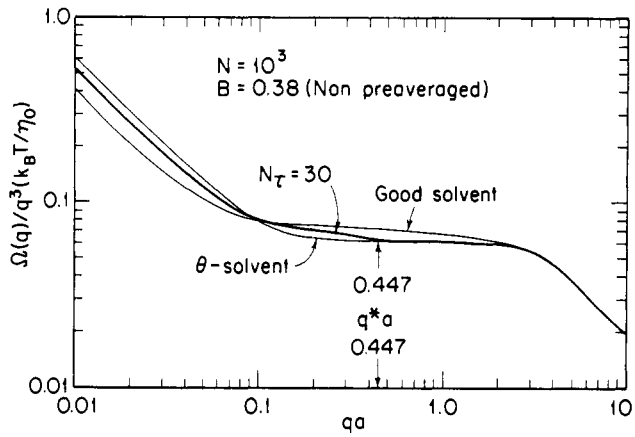

Figure 5. Variation of $z(q) \equiv \Omega(q)/q^3(k_BT/\eta_0)$ with (qa), using the nonpreaveraged Oseen tensor, in good solvent, Θ solvent, and for an intermediate temperature correponding to $N_\tau = 30$. This figure also illustrates the tendency to a crossover from good to Θ conditions when q is increased from $q < q^*$ to $q > q^*$.

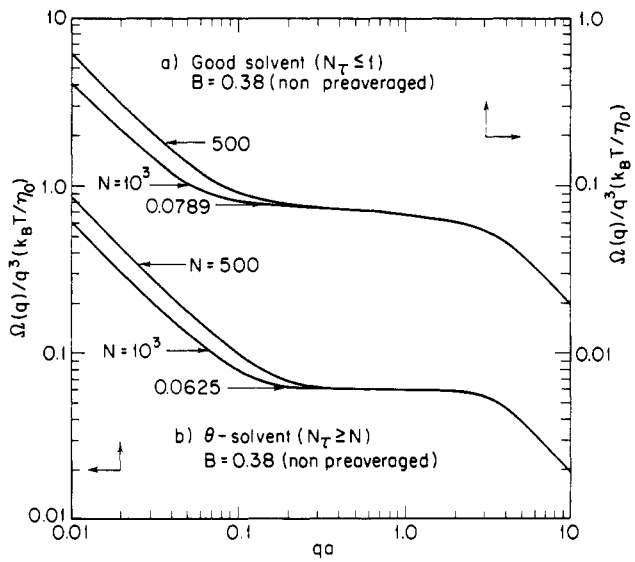

Figure 6. Variation of $z(q) \equiv \Omega(q)/q^3(k_BT/\eta_0)$ with (qa), using the nonpreaveraged Oseen tensor, in good (curve a) and Θ (curve b) solvent conditions for two values of N. This figure illustrates the effect of molecular weight on $z(q)$.

3, because the crossover in this case is from $\Omega \sim 0.0625q^3$ (Θ solvent behavior) to $\Omega \sim 0.0789q^3$ (good solvent behavior), as shown previously[4b] by using the preaveraged Oseen tensor.

Since in the recent neutron spin echo experiments[6] particular attention was given to the variation of $z(q) \equiv \Omega(q)/q^3(k_BT/\eta_0)$ as a function of q, we plotted the latter in Figures 4 and 5, using the expression of $\Omega(q)$ in Θ and good solvent limits as well as for $N_\tau = 30$. The curves in (4a) and (4b) depict the effect of preaveraging on this ratio in various q regions. In Figure 5, the effect of temperature crossover on $z(q)$ is illustrated. One observes, again, that the plateau corresponding to $\Omega \sim q^3$ behavior is replaced by a smooth transition from 0.0789 to 0.0625. In order to investigate the effect of molecular weight, we plotted $z(q)$ in Figure 6 for various values of N. It is seen that $z(q)$ is not affected by N in the intermediate and large q regions. Figure 7 shows the variation of $z(q)$ as a function of qRg to illustrate that it is a function of qRg only in the small and intermediate q regions. We note that $z(q)$ decreases with molecular weight for a fixed q in this region of q. Figure 8 illustrates the dependence of $z(q)$ on the draining parameter B in the q region relevant to neutron scattering.

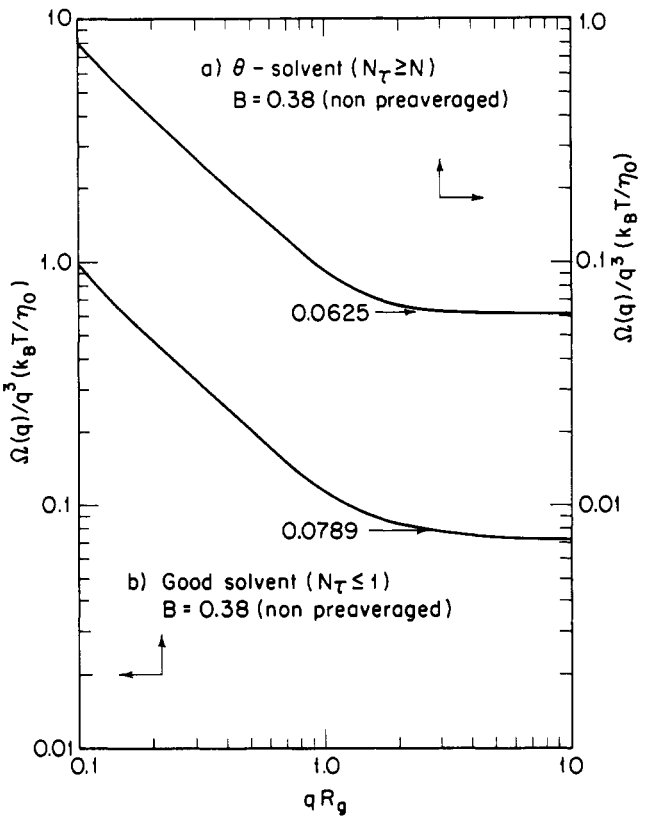

Figure 7. Variation of $z(q) \equiv \Omega(q)/q^3(k_BT/\eta_0)$ with (qRg) in the q region relevant to light-scattering experiments. Curve a corresponds to Θ solvent and curve b corresponds to good solvent conditions, with the nonpreaveraged Oseen tensor. $z(q)$ is a function of Rg only in this q region.

One observes that for a fixed q, $z(q)$ may decrease or increase, when the segment length is increased, depending on the value of B. The effect of increasing B is to uniformly decrease $z(q)$ for a fixed qa. The continuous transition to Rouse behavior, i.e., $\Omega = 0.12(k_BT/\xi_0a^2)\cdot(qa)^{11/3}$ as B approaches zero, is to be noted. The conclusion is that the analytical expression of $z(q)$ contains "a" and "B" as two adjustable parameters. Figure 8 simply explores the theoretically possible behaviors of $z(q)$ as a function of "a" and "B" in the neutron-scattering q region, whether or not these curves may be used to explain the experimental data. However, these possibilities offered by the theory should be taken into consideration whenever one is not strictly in the asymptotic region.

Discussion

In this paper we investigated the effect of preaveraging the Oseen tensor on the characteristic frequency Ω under various solvent conditions and in particular for good solvents. We found that preaveraging introduces a numerical error in Ω as large as 10% for linear chains in good solvents. Clearly this is not negligible in the interpretation of an actual experiment. We have also examined the effects of molecular weight and draining parameter B on the quantity $z(q) \equiv \Omega(q)/q^3(k_BT/\eta_0)$ which has been subject to recent experimental discussions. It is clear that $z(q)$ tends to a universal constant which we calculate in this paper as 0.0789 in good solvent and 0.0625 in Θ solvent, only in the asymptotic intermediate q region where both limits $qa \to 0$ and $qRg \to \infty$ hold. We have explored the direction of deviation of this quantity from its universal value outside the asymptotic region. We have found that in the neutron-scattering region, $z(q)$ is sensitive to the segmental length (a) as well as to the draining parameter (B), but not

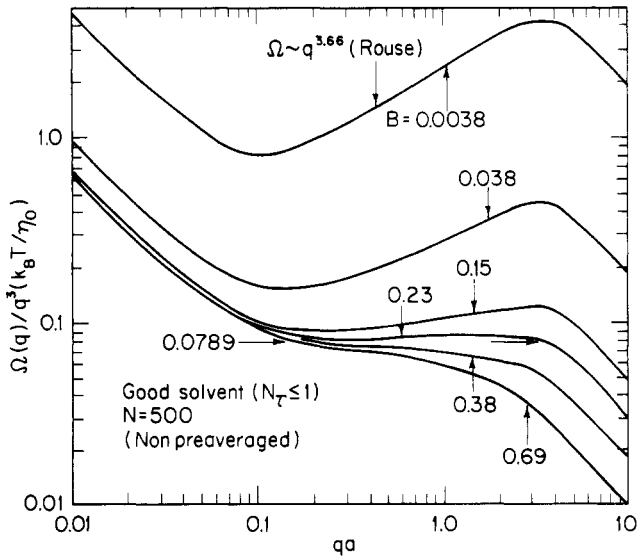

Figure 8. Variation of $z(q) \equiv \Omega(q)/q^3(k_BT/\eta_0)$ with (qa) in good solvent conditions, using the nonpreaveraged Oseen tensor, and for various values of the draining parameter B. This figure illustrates the effect of the type of polymer molecule on $z(q)$.

to the molecular weight. In the lower transition region, $z(q)$ is found to depend only on Rg as shown in Figure 7. These theoretical predictions may shed some light on the dependence of $z(q)$ on the type of polymer molecule as reported by Richter et al.[6] in their neutron-spin echo experiments. We were not able to make more quantitative remarks on their results because the characteristic frequency (or linewidth) in ref 6 was obtained by fitting Dubois-Violette and de Gennes'[8] asymptotic shape function even in qa regions where the conditions $qa \ll 1$ and $qRg \gg 1$ are not satisfied. The quantity extracted by this procedure coincides with the characteristic frequency Ω (within a factor of $2^{1/2}$ due to a different definition of the characteristic frequency). However, this quantity is not interpretable once the asymptotic conditions are not fulfilled in the experiment. The characteristic frequency Ω (or first cumulant of $S(q,t)$) which we have been using to interpret the scattering data[1,4,9] remains interpretable for all values of qa and qRg, at least within the limitations of chain models adopted for specific calculations.[2] The conclusions of this and our previous work are applicable only if the experiment measures the characteristic frequency consistently, using the shape function appropriate to the conditions of the experiment (see ref 9 for more details on this subject).

Finally, we further showed that the crossover phenomenon may also contribute to the deviation of $z(q)$ from its plateau value, even in the intermediate q region. One should notice that this effect varies with the molecular weight, at a given temperature for which the crossover value q^* is essentially fixed, because the relative position of q^* with respect to the intermediate q region changes with molecular weight due to the interference of translational motion (see Figure 6).

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Appendix

The calculation of the integral in (9) can be written as

$$\mathcal{J}_1 + 2\mathcal{J}_2 \qquad \text{(A1)}$$

where

$$\mathcal{J}_1 = \int_0^\infty \frac{du}{u^{3-(1/2\nu)}} e^{-u} \int_0^{u^{1/2}} dt\, e^{t^2} - \int_0^\infty \frac{du}{u^{(5/2)-(1/2\nu)}} \tag{A2}$$

and

$$\mathcal{J}_2 = \int_0^\infty \frac{du}{u^{2-(1/2\nu)}} e^{-u} \int_0^{u^{1/2}} dt\, e^{t^2} \tag{A3}$$

with a simple transformation, we can write $\mathcal{J}_1$ as

$$\mathcal{J}_1 = \int_0^\infty \frac{du}{u^{3-(1/2\nu)}} \int_0^{u^{1/2}} dt\, (e^{(t^2-u)} - 1)$$

or, by a change of variables, $t = z\,(u^{1/2})$

$$\mathcal{J}_1 = \int_0^\infty \frac{du}{u^{(5/2)-(1/2\nu)}} \int_0^1 dz\, (e^{-u(1-z^2)} - 1)$$

where it is easy to verify that

$$\int_0^1 dz\, (e^{-u(1-z^2)} - 1) = \int_0^1 dz\, u(z^2 - 1) \int_0^1 dy\, e^{-yu(1-z^2)}$$

Substituting this result into $\mathcal{J}_1$ we obtain

$$\mathcal{J}_1 = -\int_0^1 dz(1 - z^2) \int_0^1 dy \int_0^\infty du \frac{e^{-yu(1-z^2)}}{u^{(3/2)-(1/2\nu)}}$$

or

$$\mathcal{J}_1 = -\int_0^1 dz\, (1 - z^2)^{(3/2)-(1/2\nu)} \cdot \int_0^1 \frac{dy}{y^{(1/2\nu)-(1/2)}} \int_0^\infty du \frac{e^{-u}}{u^{(3/2)-(1/2\nu)}}$$

which reduces to

$$\mathcal{J}_1 = -\frac{2\nu}{(3\nu - 1)} \Gamma\left(\frac{1}{2\nu} - \frac{1}{2}\right) \int_0^1 \frac{dz}{(1 - z^2)^{(1/2\nu)-(3/2)}}$$

By using the change of variable $z = \sin\Theta$, $\mathcal{J}_1$ becomes

$$\mathcal{J}_1 = -\frac{2\nu}{(3\nu - 1)} \Gamma\left(\frac{1}{2\nu} - \frac{1}{2}\right) \int_0^{\pi/2} d\Theta\, (\cos\Theta)^{4-(1/\nu)} \tag{A4}$$

Now consider $\mathcal{J}_2$ in (A3) where we let $t = z(u^{1/2})$

$$\mathcal{J}_2 = \int_0^1 dz \int_0^\infty du \frac{e^{-u(1-z^2)}}{u^{(3/2)-(1/2\nu)}}$$

Transforming u to y as follows, $u(1 - z^2) = y$, we obtain

$$\mathcal{J}_2 = \Gamma\left(\frac{1}{2\nu} - \frac{1}{2}\right) \int_0^1 \frac{dz}{(1 - z^2)^{(1/2\nu)-(1/2)}}$$

and by letting $z = \sin\Theta$, $\mathcal{J}_2$ reduces to

$$\mathcal{J}_2 = \Gamma\left(\frac{1}{2\nu} - \frac{1}{2}\right) \int_0^{\pi/2} d\Theta\, (\cos\Theta)^{2-(1/\nu)} \tag{A5}$$

(i) Θ Solvent Case ($\nu = {}^1/_2$). In this case, it is easy to calculate $\mathcal{J}_1$ and $\mathcal{J}_2$ from eq A4 and A5, respectively. The results are

$$\mathcal{J}_1 = -\frac{\pi(\pi^{1/2})}{2}$$

and

$$\mathcal{J}_2 = \frac{\pi(\pi^{1/2})}{2}$$

Substituting these results into (A1) we arrive at the result which was first derived by Stockmayer[7] (see eq 8):

$$\mathcal{J}_1 + 2\mathcal{J}_2 = \pi(\pi^{1/2})/2$$

(ii) Good Solvent Case ($\nu = {}^3/_5$). Combining (A4) and (A5) with (A1) we have

$$\mathcal{J}_1 + 2\mathcal{J}_2 = -\frac{3}{2}\Gamma\left(\frac{1}{3}\right) \int_0^{\pi/2} d\Theta\, (\cos\Theta)^{7/3} + 2\Gamma\left(\frac{1}{3}\right) \int_0^{\pi/2} d\Theta\, (\cos\Theta)^{1/3}$$

and using the numerical results

$$\int_0^{\pi/2} d\Theta\, (\cos\Theta)^{7/3} = 0.7392$$

$$\int_0^{\pi/2} d\Theta\, (\cos\Theta)^{1/3} = 1.293$$

$$\Gamma({}^1/_3) = 2.6789^{(5)}$$

We obtain

$$\mathcal{J}_1 + 2\mathcal{J}_2 = 3.965$$

References and Notes

(1) Z. Akcasu and H. Gurol, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 1 (1976).
(2) Z. Akcasu and J. Higgins, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 1745 (1977).
(3) W. Burchard, M. Schmidt, and W. Stockmayer, *Macromolecules*, in press.
(4) (a) M. Benmouna and Z. Akcasu, *Macromolecules*, **11**, 1187 (1978); (b) Z. Akcasu and M. Benmouna, *ibid.*, **11**, 1193 (1978).
(5) I. S. Gradhteyn and I. M. Ruzhik, Eds., "Tables of Integrals, Series and Products", Academic Press, New York, 1965.
(6) D. Richter, J. Hayter, R. Mezei, and B. Ewen, *Phys. Rev. Lett.*, **41**, 1484 (1978).
(7) W. Stockmayer, private communication.
(8) E. Dubois-Violette and P. G. deGennes, *Physics (Long Island City, N.Y.)*, **3**, 181 (1967).
(9) Z. Akcasu, M. Benmouna, and C. Han, *Polymer*, to be published.
(10) Note that in the numerical computations we have used the exact sums rather than the integral representation.