VI. Conclusions

The diffusive nature of the orientation relaxation in flexible polymers introduces in the orientation autocorrelation function features that can be accounted for only by specific models. Synchrotron-excited fluorescence polarized decay provides a basis for an extensive discussion of available theories. In spite of good curve fitting capability, the empirical Williams–Watts expression should be discarded, because of too large variations of best-fit parameters upon changes in the fitting window. Valeur, Jarry, Geny, and Monnerie's model fits the data only in the long-time region and should be discarded for a precise short-time analysis.

The theoretical weakness of the VJGM model demonstrated here experimentally for the first time was overcome later by Jones and Stockmayer and by Bendler and Yaris. Indeed, our results clearly demonstrate the practical importance of these improvements: both models account satisfyingly for the orientational motions of polystyrene in solutions of various viscosities and using several fitting windows. But both models are also difficult to interpret because of arbitrary truncation procedures. On the other hand, the model recently proposed by Hall and Helfand, which relies on clear molecular assumptions, does not fit as well to the experiments. Using some empirical considerations and qualitative theoretical arguments, one can propose an expression for the orientational autocorrelation function closely related to Hall and Helfand's model, but more adapted to fluorescence decay experiments. In the case of polystyrene, this expression fits to the data as well as the BY and JS models, while keeping the attractive molecular basis of the HH model. Nevertheless, further theoretical work seems necessary to understand the exact physical meaning of this modification imposed by experiment.

Registry No. Polystyrene (homopolymer), 9003-53-6.

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Concentration Dependence of the First Cumulant as a Function of Momentum Transfer

Boualem Hammouda

Department of Nuclear Engineering, The University of Michigan,
Ann Arbor, Michigan 48109

A. Ziya Akcasu*,†

Center for Material Sciences, National Bureau of Standards, Washington, DC 20234.
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ABSTRACT: Zimm's single-contact approximation is used to derive an expression for the concentration dependence of the first cumulant for dilute polymer solutions. The concentration dependence coefficient is found to decrease as a function of momentum transfer. This means that the concentration effect on the first cumulant is less important for smaller portions of polymer chains.

Introduction

A good deal of effort has been generated to study the concentration dependence of static as well as dynamic quantities characterizing polymer molecules in solution. Theoretical investigations tend to concentrate on the calculation of the concentration correction (in dilute solutions, for example) for directly measurable quantities, namely, the static structure factor or the dynamic structure factor and quantities that are related to them such as the first cumulant considered here.

In the case of the static structure factor $S(q)$, Zimm's[1] single-contact approximation is probably the first ap-

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[†] Permanent address: Department of Nuclear Engineering, The University of Michigan.

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proximation that has been used to derive a simple expression for the concentration correction coefficient. This coefficient is proportional to the second virial coefficient and can be extracted experimentally either by curve fitting or by the Zimm plot if low enough q data are available.

The first cumulant $\Omega(q)$ can be obtained from dynamic light or neutron scattering measurements. Some models present a concentration dependence of the short-time diffusion coefficient $D = \lim_{q\to 0} \Omega(q)/q^2$ to linear order in concentration, which can be used to interpret light scattering data in the Guinier range. In order to interpret dynamic light or neutron scattering experiments in the intermediate q range, however, one needs an expression for the concentration dependence of $\Omega(q)$ without restriction to the small-q range. In this paper, we use Zimm's single-contact approximation to determine the concentration dependence of $\Omega(q)$ in dilute solutions for all values of q.

First Cumulant and Generalized Mobility

The single-contact approximation was introduced by Zimm to model excluded volume interactions between chains. This approximation was applied to the static structure factor

$$S(q,C) = \frac{1}{Nn^2}\sum_{\alpha\alpha'}^{N}\sum_{jj'}^{n}\langle \exp(i\mathbf{q})\cdot(\mathbf{R}_{\alpha\alpha'} + \mathbf{S}_{\alpha j\alpha' j'})\rangle \qquad (1)$$

to obtain its concentration dependence for dilute polymer solutions as

$$S(q,C) \simeq S_s(q)[1 - k_s(q)C] \qquad (2)$$

where $k_s = \chi n^2 S_s(q)$ and $S_s(q)$ is the normalized single-chain static structure factor. In these equations N and n are the number of polymers in the solution and the number of monomers in each polymer, respectively. $\mathbf{R}_\alpha$ is the position of the center of mass of the αth polymer, $\mathbf{S}_{\alpha j}$ is the position of the jth monomer about this center of mass, and $\mathbf{S}_{\alpha j\alpha' j'} = \mathbf{S}_{\alpha j} - \mathbf{S}_{\alpha' j'}$. Equation 2 is sometimes also presented in the form

$$S^{-1}(q,C) \simeq S_s^{-1}(q)(1 + k_s(q)C) \qquad (3)$$

used in the conventional Zimm plot.

In this paper, we also use the single-contact approximation to obtain the concentration dependence of the first cumulant $\Omega(q)$. The latter can be written in terms of the q-dependent mobility $\mu(q)$ as[2]

$$\Omega(q) = q^2 k_B T\frac{\mu(q)}{S(q)} \qquad (4)$$

Since the concentration dependence of $S(q)$ is already known, we concentrate, in this paper, on the concentration dependence of $\mu(q)$, which is defined explicitly as

$$\mu(q,C) = \frac{1}{Nn^2}\sum_{\alpha\alpha'}^{N}\sum_{jj'}^{n}\left\langle \frac{\mathbf{q}\cdot\bar{\bar{D}}(\mathbf{R}_{\alpha\alpha'} + \mathbf{S}_{\alpha j\alpha' j'})\cdot\mathbf{q}}{q^2} e^{i\mathbf{q}\cdot(\mathbf{R}_{\alpha\alpha'}+\mathbf{S}_{\alpha j\alpha' j'})}\right\rangle \qquad (5)$$

where $\bar{\bar{D}}$ is the diffusion tensor[3]

$$\bar{\bar{D}}(\mathbf{R}_{AB}) = \frac{k_B T}{\xi}(\bar{\bar{I}}\delta_{AB} + \xi(1 - \delta_{AB})\bar{\bar{T}}(\mathbf{R}_{AB})) \qquad (6)$$

and $\bar{\bar{T}}(\mathbf{R}_{AB})$ is the Oseen tensor for hydrodynamic interaction

$$\bar{\bar{T}}(\mathbf{R}_{AB}) = \frac{1}{8\pi\eta R_{AB}}\left(\bar{\bar{I}} + \frac{\mathbf{R}_{AB}\mathbf{R}_{AB}}{R_{AB}^2}\right) \qquad (7)$$

For simplicity, $\mathbf{q}$ is often taken along the z direction so that $\mathbf{q}\cdot\bar{\bar{T}}\cdot\mathbf{q} = q^2 T_{33}$.

To make the concentration dependence explicit, we separate the α sums over single-chain ($\alpha' = \alpha$) and interference ($\alpha' \neq \alpha$) parts:

$$\mu(q,C) = \frac{1}{n\xi}\left(1 + \frac{\xi}{n}\sum_{jj'}^{n}{}'\langle T_{33}(\mathbf{S}_{1j1j'})e^{i\mathbf{q}\cdot\mathbf{S}_{1j1j'}}\rangle_{\Psi_1}(\mathbf{R}_1,\mathbf{S}_1)\right) + \frac{N}{n^2}\sum_{jj'}^{n}\langle T_{33}(\mathbf{R}_{12} + \mathbf{S}_{1j2j'})e^{i\mathbf{q}\cdot(\mathbf{R}_{12}+\mathbf{S}_{1j2j'})}\rangle_{\Psi_2}(\mathbf{R}_1,\mathbf{S}_1,\mathbf{R}_2,\mathbf{S}_2) \qquad (8)$$

As we have indicated, the first and second ensemble averages are over the one-chain Ψ_1 and two-chain Ψ_2 distribution functions, respectively. We should note that Ψ_1 is also concentration dependent due to the deformation of the chain in the presence of others. The estimate of this concentration dependence shows that, in general, single-chain properties are very insensitive to concentration effects.[4] Actually, within the framework of the single-contact approximation, the concentration dependence of single-chain properties disappears completely. Ψ_2 is also to be calculated in the zero-concentration limit because the term involving the second ensemble average in $\mu(q,C)$ is already proportional to concentration.

Introducing the Fourier transform $\tilde{T}_{33}(\mathbf{K})$ of the Oseen tensor and the radial distribution for a pair of molecules $g(R)$, the first term in eq 8 can be written as

$$\mu(q) = \frac{1}{n\xi} + \frac{1}{(2\pi)^3}\int \mathrm{d}^3K\ \tilde{T}_{33}(\mathbf{K} - \mathbf{q})\left(S_s(\mathbf{K}) - \frac{1}{n}\right) \qquad (9)$$

which is the generalized mobility in the infinite dilution limit.

To evaluate the second term in eq 8, one needs the explicit form of the two-chain distribution function Ψ_2. In the single-contact approximation, Ψ_2 is given by

$$\Psi_2(\mathbf{R}_1,\mathbf{S}_1,\mathbf{R}_2,\mathbf{S}_2) \simeq \Psi_1(\mathbf{R}_1,\mathbf{S}_1)\Psi_1(\mathbf{R}_2,\mathbf{S}_2)(1 - \chi\sum_{k,l}^{n}\delta(\mathbf{R}_{12} + \mathbf{S}_{1k2l})) \qquad (10)$$

where χ is the excluded volume parameter for contacts between two monomers of two separate chains and is given by the binary cluster integral.[5] Using this expansion and performing $\mathbf{R}_{12}$ integration, one obtains

$$\mu(q,C) = \mu(q) - C\frac{\chi n^2}{(2\pi)^3}\int \mathrm{d}^3K\ \tilde{T}_{33}(\mathbf{K} - \mathbf{q})\left(S_s(\mathbf{K}) - \frac{1}{n}\right)^2 \qquad (11)$$

The term $1/n$ has been subtracted to keep contributions only from $k \neq i$ and $l \neq j$ in the summation and thus not to include hydrodynamic interaction between two monomers located at the same position as a result of the single-contact approximation. Expanding $\mu(q,C)$ as

$$\mu(q,C) = \mu(q)(1 - k_\mu(q)C) \qquad (12)$$

one can identify the concentration coefficient $k_\mu(q)$ as

$$k_\mu(q) = \chi n^2\frac{I_2(q)}{I_1(q)} \qquad (13)$$

where we have introduced the following q-dependent integrals:

$$I_{1,2}(q) = \int \mathrm{d}^3K\ \tilde{T}_{33}(\mathbf{K} - \mathbf{q})\left(S_s(\mathbf{K}) - \frac{1}{n}\right)^{1,2} \qquad (14)$$

The angular integrations are performed analytically in Appendix I and the K integrations are done numerically by assuming a form for $S_s(K)$. We would like to mention,

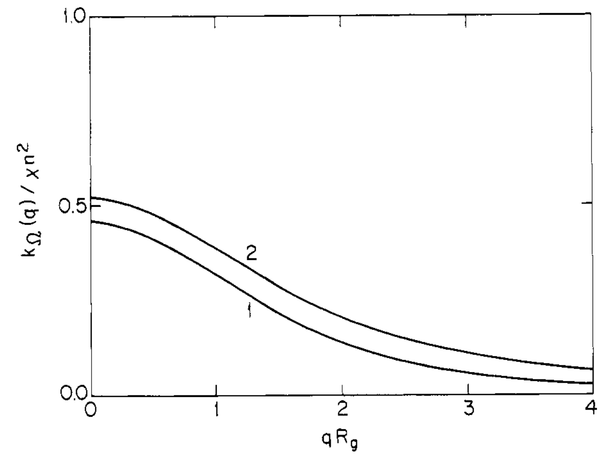

Figure 1. Variation of the normalized concentration coefficient $k_\Omega(q)/\chi n^2$ as a function of the normalized momentum transfer qR_g using (1) a Debye function and (2) the fully swollen Gaussian chain model with $\nu = 0.6$.

however, that the theoretical formulas containing $S_s(K)$ are general and not restricted to a particular shape for the static structure factor. In the present paper, we use a Debye function for $S_s(K)$ known to be valid for Θ solvents. The calculations reported by Ohta et al.[6] show that the Debye function with swollen R_g is a fairly good approximation up to large values of its argument $x = KR_g$ for good solvents as well. However, one should remember that the Debye function goes to $1/x^2$ for very large x, whereas $S_s(x)$ goes to $1/x^{1/\nu}$, where ν is the excluded volume exponent taken to be $\nu = 0.6$ for good solvents. Other models such as the completely swollen chain model (Peterlin[7] and Akcasu and Benmouna[8] among others) or those based on the blob hypothesis can be used if $S_s(K)$ is needed as a function of temperature.

The concentration dependence of the first cumulant in dilute polymer solutions follows from eq 4 as

$$\Omega(q,C) = \Omega(q)(1 + k_\Omega(q)C) \qquad (15)$$

where

$$k_\Omega(q) \simeq k_s(q) - k_\mu(q)$$

or

$$k_\Omega(q) \simeq \chi n^2\left(S_s(q) - \frac{I_2(q)}{I_1(q)}\right) \qquad (16)$$

The excluded volume parameter χ can be related to the second virial coeefficient A_2, to the interpenetration function ψ, or to the dimensionless radius of influence $X = \bar{s}/R_H$ (normalized with respect to the hydrodynamic radius):

$$n^2\chi \simeq 2M_w^2A_2/N_{Av} \simeq (4\pi)^{3/2}R_g^3\psi \simeq \frac{32\pi}{3}X^3R_H^3 \qquad (17)$$

where N_{Av} is Avogadro's number, M_w is the molecular weight, and R_g is the radius of gyration.

Results and Conclusions

The plot of $k_\Omega(q)/\chi n^2$ in Figure 1 shows that as q increases, the concentration dependence decreases and ultimately vanishes for large enough q values. This q dependence of $k_\Omega(q)/\chi n^2$ is expected because smaller portions of the chain are probed by the scattering radiation as q increases. Since $k_\Omega(q)/\chi n^2$ is positive, the plateau[9] of $\Omega(q)/q^3$ in the intermediate q range is shifted upward for good solvents with increasing concentration but not uniformly. This nonuniform variation remains to be seen experimentally. In the case of Θ solvents, where $A_2 = 0$, the single-contact approximation would imply $\chi = 0$ and hence $k_\Omega(q) = 0$ for all values of q. However, this conclusion cannot be true, at least in the small-q limit, where $\Omega(q)/q^2$ approaches the short-time diffusion coefficient

$$D(C) = D(1 + k_DC) \qquad (18)$$

with $k_\Omega(q \to 0) = k_D$ and

$$k_D = \chi n^2\left(1 - \frac{2}{\pi}\int_0^\infty du \left[S_s(u) - \frac{1}{n}\right]^2\right) \qquad (19)$$

where $u = KR_H$. It is known both theoretically and experimentally that the diffusion coefficient decreases with increasing concentration, i.e., $k_D < 0$, under the Θ condition. This discrepancy is due to the inadequacy of the single-contact approximation near the Θ temperature, where the interpenetration of chains is important.

When the concentration dependence in eq 18 is measured in terms of hydrodynamic volume fraction $C_v = {}^4/_3\pi R_H^3C$, k_D becomes

$$k_D^v = 8X^3\left(1 - \frac{2}{\pi}\int_0^\infty du \left[S_s(u) - \frac{1}{n}\right]^2\right) \qquad (20)$$

where X was defined before. This expression is yet another estimate for the concentration coefficient of the collective diffusion coefficient. In order to compare eq 20 with the previous estimates, we calculated k_D^v as $k_D^v = 3.77X^3$ using the Debye form of $S_s(K)$ (see eq 16 and Appendix II) and as $k_D^v = 4.16X^3$ using the fully swollen Gaussian chain model with $\nu = 0.6$. The latter estimate is, of course, pertinent only to the good solvent limit. These results should be compared with $k_D^v = 3.2X^3 - 1$ due to Yamakawa[5] and $k_D^v = X^2(8X - 6)$ by Akcasu and Benmouna.[8] We observe that when $X = 1$, which is a typical value in good solvents, one obtains $k_D^v = 3.77$, 2.2, and 2, respectively. Since experimental results[10,11] seem to suggest smaller values than $k_D^v = 2$ in the vicinity of $X = 1$, we conclude that eq 20 based on the single-contact approximation overestimates the concentration correction to the small-q limit of $\Omega(q)$. One would expect that the same trend be true for all values of q.

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Appendix I

In this appendix, we perform the angular integrations involved in $I_{1,2}(q)$. Recall the Fourier transform of the Oseen tensor:

$$\tilde{T}_{33}(\mathbf{K} - \mathbf{q}) = \frac{1}{\eta}\,\frac{1}{K^2 + q^2 - 2Kq\cos\theta}[1 - \cos^2\alpha] \qquad (21)$$

where θ is the angle between $\mathbf{K}$ and $\mathbf{q}$ and α is the angle between $\mathbf{K} - \mathbf{q}$ and $\mathbf{q}$. The azimuthal integration in $I_{1,2}(q)$ is trivially done:

$$I_{1,2}(q) = \frac{2\pi}{\eta}\int_{-1}^{1}d(\cos\theta)\int_0^\infty dK\,\frac{K^2}{K^2 + q^2 - 2Kq\cos\theta}[1 - \cos^2\alpha]\left(S_s(K) - \frac{1}{n}\right)^{1,2} \qquad (22)$$

We use the angular relation

$$1 - \cos^2\alpha = \frac{K^2}{K^2 + q^2 - 2Kq\cos\theta}[1 - \cos^2\theta] \qquad (23)$$

and perform the Θ integration straightforwardly to obtain

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$$I_{1,2}(q) = \frac{2\pi}{\eta}\int_0^\infty \mathrm{d}K \left(\frac{K}{2q}\,\frac{K^2+q^2}{q^2}\ln\frac{|K+q|}{|K-q|} - \frac{K^2}{q^2} \right) \times \left(S_\mathrm{s}(K) - \frac{1}{n} \right)^{1,2} \quad (24)$$

The small-q limit of this expression can be checked by expanding the logarithm in the q/K smallness parameter

$$I_{1,2}(q \to 0) = \frac{8\pi}{3\eta}\int_0^\infty \mathrm{d}K \left(S_\mathrm{s}(K) - \frac{1}{n} \right)^{1,2} \quad (25)$$

These integrals are evaluated analytically in the next appendix for Gaussian chains.

Appendix II

We assume a Gaussian chain model for $S_\mathrm{s}(K)$

$$S_\mathrm{s}(K) = \frac{1}{n^2}\sum_{i,j}^{n} e^{-(K^2l^2/6)|i-j|} \quad (26)$$

where l is the statistical length, introduce a dimensionless variable $x = Kl(n/6)^{1/2} = KR_\mathrm{g}$, and use the general identity (valid for $j \neq i$)

$$\sum_{i,j}^{n} A(|i-j|) = 2\sum_{i}^{n}(n-i)A(i) \quad (27)$$

to manipulate $I_1(q \to 0)$ to the form

$$I_1(q \to 0) = \frac{16\pi}{3\eta n^2 R_\mathrm{g}}\int_0^\infty \mathrm{d}x \sum_{i}^{n} e^{-x^2 i/n}(n-i) \quad (28)$$

We approximate the summation by an integration to find

$$I_1(q \to 0) = \frac{32\pi^{3/2}}{9\eta R_\mathrm{g}} \quad (29)$$

and similarly for $I_2(q \to 0)$

$$I_2(q \to 0) = \frac{8\pi}{3\eta}\,\frac{1}{n^4 R_\mathrm{g}}\int_0^\infty \mathrm{d}x \left(\sum_{i,j}^{n} e^{-x^2|i-j|/n} - \frac{1}{n} \right) \times \left(\sum_{k,l}^{n} e^{-x^2|k-l|/n} - \frac{1}{n} \right) = \frac{768\pi^{3/2}}{945\eta R_\mathrm{g}}(8(2^{1/2}) - 9) \quad (30)$$

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Incorporation of Excluded Volume into the Multiple-Scattering Theory of the Concentration Dependence of Polymer Dynamics

Karl F. Freed*

Institute for Theoretical Physics, University of California, Santa Barbara, California 93106, and The James Franck Institute and the Department of Chemistry, The University of Chicago, Chicago, Illinois 60637.

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ABSTRACT: A formal multiple-scattering solution is provided for the polymer chain dynamics, the fluid velocity field, etc., for a system of polymers at nonzero concentration with excluded volume. The analysis proceeds by the introduction of operators describing the dynamical contributions of excluded volume interactions to the polymer force constants. We evaluate the average of the fluid velocity field over the conformations of all polymers because this average velocity field may be utilized to compute the concentration-dependent dynamical viscosity and because related quantities can be used to evaluate the concentration-dependent polymer friction coefficients. The final results are in a form that bears a one-to-one correspondence with terms in the multiple-scattering expansion for Gaussian chains, thereby providing a general prescription for converting these former multiple-scattering expressions into ones incorporating excluded volume exactly. A set of preaveraging-type approximations is introduced. The simplest is shown to yield a dynamic intrinsic viscosity of the Rouse–Zimm form, but with excluded volume dependent hydrodynamic and force constant matrices. A microscopic prescription is provided for calculating the latter, while the former has been evaluated elsewhere by renormalization group methods. The same analysis, applied here to derive the excluded volume dependent viscosity, can readily be utilized to consider concentration-dependent quantities using either the concentration expansion or effective medium methods.

I. Introduction

The theory of the concentration dependence of the hydrodynamics of solutions of polymer chains has been presented in a multiple-scattering formalism based on either the pure solvent or an effective medium reference.[1-8] The former is useful for the development of a concentration expansion of the viscoelastic and frictional properties[8] of polymer solutions, and applications to a number of these properties have been given.[5,8] Of particular note is the theory of the leading concentration dependence of the relaxation times of the individual polymer modes,[5] which is in excellent agreement with recent experiments by Lodge and Schrag[9] except for some slight difference in the overall numerical factor and discrepancies at higher frequencies.[9] Improved calculations of these features are currently in progress. The effective medium representation,[1-3] on the other hand, is useful in describing the full concentration dependence, displaying the crossover from Zimm-like

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*Address correspondence to the author at The University of Chicago.

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