through time may be ignored; $10 < CL^3 < 50$ current theories inadequate—diffusion in a maze with cages appearing and disappearing with time; $50 < CL^3 < 500$ caging theories reasonable; $500 < CL^3$ Doi and Edwards dependence valid for infinitely thin rigid rods.

Generalization of the averages done in this paper to anisotropic solutions is expected to be complex but would be of immense value since a flowing system will be partially aligned by the flow. An incorporation of the effects of flexibility, polydispersity, and finite thickness of the molecules should also be of interest in treating the case of real physical molecules. Experimental work is needed especially in finding the variation in behavior with the flexibility parameter.

Also, the onset of semidilute behavior should be sought and characterized in the region $20 < CL^3 < 50$ by either experimental methods or by dynamic modeling of cage rearrangement, or both.

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Concentration-Dependent Translational Friction Coefficients of Polymers with Excluded Volume Effect in Dilute Solutions

Mark DeMeuse

Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616

M. Muthukumar*[†]

Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003. *Received September 7, 1984*

ABSTRACT: Using a multiple scattering approach, we obtain explicit expressions for the leading concentration dependence of self-friction and cooperative translational friction coefficients of a flexible polymer chain with arbitrary excluded volume interaction. Employing Fixman's radial distribution function for the polymer chains, we find $k_s/[\eta]$ for the self-friction coefficient to change smoothly from 0.75 at Θ temperature to 0.45 in very good solutions, while for the cooperative friction coefficient the corresponding change is from 0.75 to 1.85. Comparison of our calculated results with the available experimental data is also presented.

I. Introduction

The translational friction coefficient, f_t, of a polymer molecule in dilute solutions at a concentration c is given by

$$f_t = f_t^{(0)}(1 + k_s c + ...) \qquad (1.1)$$

where $f_t^{(0)}$ is the infinite-dilution friction coefficient. Experimentally both $f_t^{(0)}$ and k_s, which are used to characterize the polymers, are easily obtainable quantities as the intercept and the initial slope, respectively, of a plot of f_t vs. c. The calculation of $f_t^{(0)}$ of an isolated flexible chain in a hydrodynamic medium is a well-understood old problem and is reviewed in the literature.[1,2] When many chains are present, the intrachain hydrodynamic interaction is considerably modified.[3-5] Due to the long-ranged nature of the hydrodynamic interaction, the calculation of the extent of this modification and the value of k_s is not straightforward and has attracted considerable interest.[3-11]

There have been many previous attempts in the literature to calculate k_s. Yamakawa,[6] by assuming that the polymers obey random-flight statistics, has provided an extension of the Kirkwood–Riseman theory for $f_t^{(0)}$. The resulting formula predicts $k_s = 0.2[\eta]$ at the Θ temperature, where $[\eta]$ is the intrinsic viscosity. A formula for extrapolating to the good-solution limit is provided in terms of A_2, the second virial coefficient. Unfortunately, reliance on existing experimental data is needed to obtain the dependence of k_s on the solvent quality. Pyun and Fixman[7] treated the problem for interpenetrable spheres. They obtained $k_s = 0.45[\eta]$ under Θ conditions. They also provide an extrapolation formula to the hard-sphere limit, which is assumed to correspond to the good-solvent case. Following Pyun and Fixman's work, there have been numerous investigations[8] reported in the literature to calculate k_s for a suspension of spheres. The most important

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[†] Alfred P. Sloan Research Fellow.

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of these is due to Batchelor,[8] who treated the two-sphere hydrodynamics exactly. Also, Freed[9] obtained a value of $k_s = [\eta]$, a totally different result from that obtained by Yamakama. Recently, Perico and Freed[10] calculated k_s numerically for very short chains with full chain dynamics and extrapolated the results to obtain a value of $0.58[\eta]$ in the long-chain limit. These results were obtained under Θ conditions. It is suggested[11] that these results can be extended to good solvents by utilizing the Peterlin method[1] of scaled force constants, but these models require further investigation.

There are also a number of experimental investigations regarding the value of k_s. Most recent of these is due to Mulderije.[12] Working with the system polystyrene in cyclohexane, he obtained $k_s = 0.75[\eta]$. In that investigation, a thorough review of the various other measurements[13-15] of k_s at the Θ temperature is also provided. All of these investigations result in $k_s/[\eta]$ values ranging between 0.7 and 0.8. The ratio $k_s/[\eta]$ is known to be large for good solutions. Thus, there has been a great deal of interest both theoretically and experimentally in the concentration-dependent friction coefficient. There does not appear to be any satisfactory theory to describe the crossover behavior from the Θ solution to the very good solution limit. This is the task set for the present investigation.

Recently we have derived a multiple scattering formalism[16] to obtain the transport coefficients of polymer solutions as cluster expansions in concentration by generalizing the Kirkwood–Riseman model to account for the interchain hydrodynamic interaction. The great value of our multiple scattering formalism is that it can also be applied to good solutions. The formulas presented are general and are valid for any strength of the excluded volume effect. In addition to recovering the familiar Kirkwood–Riseman result for $f_t^{(0)}$, our earlier calculation based on this method gives $k_s = 0.75[\eta]$ under Θ conditions[17,18] which is thus in very good agreement with the experimental data of Mulderije. In the present investigation, the previous results are generalized to include the good-solution behavior. We provide a general crossover formula for k_s for any arbitrary strength of the excluded volume interaction ranging from Θ to very good solution conditions.

The outline of this paper is as follows. Section II contains a summary of the important results and also summarizes the assumptions of the present model. Section III contains an explicit calculation of the concentration-dependent cooperative translational friction coefficient. The self-friction coefficients are examined in section IV. A summary of the results and a comparison of the calculations with experimental data are presented in section V.

II. Basic Equations

There are two types of friction coefficients distinguishable in a noninfinitely dilute polymer solution: (1) the tracer or self-friction coefficient, which corresponds to the motion of a labeled molecule surrounded by solvent molecules and the other solute molecules; and (2) the cooperative friction coefficient, which corresponds to the friction coefficient per polymer molecule in a solution of N interacting polymers immersed in a solvent. Recently,[17] explicit expressions for the concentration dependence of both the self-friction and cooperative friction coefficients using a multiple scattering cluster expansion method have been derived. In that investigation, the self-friction and cooperative friction coefficients are shown to be the same in the Θ solvent, at least to leading order in concentration. The derived equations are general and are valid for both good and Θ solutions. In an accompanying paper,[18] the formalism is specialized to Θ solutions and the explicit calculations of the leading concentration-dependent terms are presented. It is the interest of the present investigation to generalize those previous results to include the excluded volume interactions.

The basic assumptions of the cluster theory are the following: (i) The size of a solvent molecule is much smaller in comparison with that of a polymer chain so that the solvent can be treated as a hydrodynamic continuum. The solvent is assumed to obey the linearized Navier–Stokes equation, while the polymer obeys a Langevin equation for the bean and spring model. (ii) The polymer concentration is lower than the overlap concentration so that the virial series in concentration is valid. (iii) For such low concentrations, the chains are assumed to be rigid with respect to the translational diffusion of the center of mass and the rotational motion of the chains. (iv) The dynamics of the chains and the solvent are coupled by the no-slip boundary condition.

In addition to these ingredients, some specific way of treating the excluded volume effect must be developed. The excluded volume effect manifests itself in two ways. A polymer chain possesses a short-ranged intramolecular excluded volume effect due to the exclusion to multiple occupancy of space by two or more segments of the polymer. Also, in polymer solutions at finite concentrations, a concentration-dependent intermolecular excluded volume effect can also be present.

First, as shown by Muthukumar and Edwards,[19] the mean squared end-to-end distance of the polymer chain, $\langle R^2 \rangle$, becomes renormalized from Ll under Θ solvent conditions to Ll_1 when the excluded volume effect is present. Here, L is the contour length of the polymer chain and l is the Kuhn step length. l_1 is an effective step length and is, in general, a function of the strength of the excluded volume effect, the contour length of the chain, and the monomer density.[19] Since, in the present calculations, only the low-concentration region is being explored, the monomer density dependence of l_1 can be ignored. l_1 is, then, a function of two variables. It should be noted that this form of the excluded volume effect manifests itself even in the infinite-dilution limit. Thus, the infinite-dilution friction coefficient is different here than under Θ solvent conditions. This will be clearly demonstrated later.

The second way that the excluded volume effect appears is only present at nonzero concentrations. At nonzero concentrations, the effective potential energy of interaction between two polymer chains must be considered. Under Θ solution conditions, this is zero. In a good solution, however, the average polymer–polymer and polymer–solvent interactions do not cancel each other and the potential energy is not zero. In the present formalism, this is expressed through the radial distribution function for two polymer molecules, designated $g(r)$. Under Θ solution conditions, $g(r) = 1$, for all r.

The system to be considered is a suspension of N chains each with n Kuhn segments immersed in a solvent. A shown previously,[16-18] the translational self-friction coefficient is given by

$$f_{t,s} = \langle \sum_{i,j=1}^{n} \mathbf{G}^{(\alpha)^{-1}}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha j}) \rangle \tag{2.1}$$

In this equation, $\mathbf{S}_{\alpha i}$ is the position vector of the ith bead with respect to the center of mass for the α chain. The angular brackets denote the averaging over the distribution of the centers of mass of all the chains and the distribution of beads i and j of chain α. $\mathbf{G}^{(\alpha)^{-1}}$ appearing in eq 2.1 is given by

$$\mathbf{G}^{(\alpha)^{-1}}(\mathbf{S}_{\alpha i},\mathbf{S}_{\alpha j}) = \mathbf{G}_\alpha^{-1}(\mathbf{A}_{\alpha i},\mathbf{S}_{\alpha j}) + \sum_{\substack{\beta=1\\ \beta\neq\alpha}}^{N} \sum_{i'pp'j'} \mathbf{G}_\alpha^{-1}(\mathbf{S}_{\alpha i},\mathbf{S}_{\alpha i'})\cdot \mathbf{G}(\mathbf{R}_{\alpha i'},\mathbf{R}_{\beta p})\cdot\bar{\mathbf{T}}_\beta(\mathbf{S}_{\beta p},\mathbf{S}_{\beta p'})\cdot\mathbf{G}(\mathbf{R}_{\beta p'},\mathbf{R}_{\alpha j'})\cdot\mathbf{G}_\alpha^{-1}(\mathbf{S}_{\alpha j'},\mathbf{S}_{\alpha j}) + \ldots \tag{2.2}$$

where

$$\sum_{p=1}^{n} \mathbf{G}_\alpha^{-1}(\mathbf{S}_{\alpha i},\mathbf{S}_{\alpha p})\cdot\mathbf{G}_\alpha(\mathbf{S}_{\alpha p},\mathbf{S}_{\alpha j}) = \mathbf{1}\delta_{ij} \tag{2.3}$$

$\mathbf{G}(r)$ appearing in eq 2.2 is the Oseen tensor given by

$$\mathbf{G}(\mathbf{r}) = \int \frac{d^3k}{(2\pi)^3}\,\mathbf{G}(\mathbf{k})\exp(i\mathbf{k}\cdot\mathbf{r}) \tag{2.4}$$

with

$$\mathbf{G}(\mathbf{k}) = (\mathbf{1} - k^{-2}\mathbf{kk})/\eta_0 k^2 \tag{2.5}$$

where η_0 is the pure-solvent viscosity.

$\bar{\mathbf{T}}_\beta$ appearing in eq 2.2 is the single-chain scattering operator. It corresponds to the modification of an incident viscosity field into a force field by means of interchain hydrodynamic interactions involved with chain β. Within the preaveraging approximation,[1] which is used throughout this work, $\bar{\mathbf{T}}_\beta$ is given by (for details, see ref 17)

$$\bar{\mathbf{T}}_\beta(\mathbf{S}_{\beta i},\mathbf{S}_{\beta j}) = \mathbf{G}_\beta^{-1}(\mathbf{S}_{\beta i},\mathbf{S}_{\beta j}) - \sum_{pp'=1}^{n} \mathbf{G}_\beta^{-1}(\mathbf{S}_{\beta i},\mathbf{S}_{\beta p})\cdot\mathbf{g}_\mathrm{t}^{-1}\cdot\mathbf{G}_\beta^{-1}(\mathbf{S}_{\beta p'},\mathbf{S}_{\beta j}) + \sum_{p,p'} \mathbf{G}_\beta^{-1}(\mathbf{S}_{\beta i},\mathbf{S}_{\beta p}) \times \mathbf{S}_{\beta p}\cdot\mathbf{g}_\mathrm{r}^{-1}\cdot\mathbf{S}_{\beta p'} \times \mathbf{G}_\beta^{-1}(\mathbf{S}_{\beta p'},\mathbf{S}_{\beta j}) \tag{2.6}$$

where g_t and g_r are the same as $f_\mathrm{t}^{(0)}$ and $f_\mathrm{r}^{(0)}$, the infinite-dilution translational and rotational friction coefficients, respectively.

The expression for the translational cooperative friction coefficient is

$$f_{\mathrm{t,c}}^{-1} = \langle \mathbf{g}_\mathrm{t}^{-1} + \sum_{\beta\neq\alpha} [\mathbf{g}_\mathrm{t}^{-1}\cdot\mathbf{G}_\alpha^{-1}(\mathbf{S}_{\alpha i},\mathbf{S}_{\alpha j}) - \mathbf{1}]\cdot\mathbf{G}(\mathbf{R}_{\alpha i} - \mathbf{G}_{\beta j})\cdot\mathbf{g}_\mathrm{t}^{-1}\cdot \mathbf{G}_\beta^{-1}(\mathbf{S}_{\beta i'},\mathbf{S}_{\beta j'}) - \sum_{\substack{\beta\neq\alpha\\ \gamma\neq\beta}} \mathbf{g}_\mathrm{t}^{-1}\cdot\mathbf{G}_\alpha^{-1}\cdot\mathbf{G}_{\alpha\beta}\cdot\bar{\mathbf{T}}_\beta\cdot\mathbf{G}_{\beta\gamma}\cdot\mathbf{G}_\gamma^{-1}\cdot\mathbf{g}_\mathrm{t}^{-1} + \ldots\rangle \tag{2.7}$$

The result that the cross-frictional terms vanish within the preaveraging approximation is utilized in obtaining eq 2.7.

The expressions for the self-friction and cooperative translational friction coefficients given by eq 2.1 and 2.7 are general and their concentration dependence can be explicitly calculated to any desired order of concentration and for any given strnegth of the excluded volume effect. In the present work, terms contributing to $O(c^2)$ are not considered. The first two concentration-dependent terms are considered in the calculation of the cooperative friction coefficient while only the leading term for the self-friction coefficient is considered. The algebraic details involved in the evaluation of these terms are presented in the following sections.

III. Cooperative Friction Coefficient

The translational friction coefficient at infinite dilution, $f_\mathrm{t}^{(0)}$, is the leading term of f_t which is given by

$$f_\mathrm{t}^{(0)} = \langle \sum_{ij} \mathbf{G}^{-1}(\mathbf{S}_i,\mathbf{S}_j)\rangle \tag{3.1}$$

If we convert the summations in eq 3.1 to integrals with the changes of variables $x = (2i/n) - 1$, $y = (2j/n) - 1$, the result is obtained that

$$f_\mathrm{t}^{(0)} = (n^2/4)\int_{-1}^{1}\mathrm{d}x\int_{-1}^{1}\mathrm{d}y\,\langle G^{-1}(x,y)\rangle \tag{3.2}$$

Expanding $\langle G^{-1}(x,y)\rangle$ in double Fourier series

$$\langle G^{-1}(x,y)\rangle = \sum_{\mu=-\infty}^{\infty}\sum_{\mu'=-\infty}^{\infty} G_{\mu\mu'}^{-1}\exp[-i\pi\mu x + i\pi\mu' y] \tag{3.3}$$

$f_\mathrm{t}^{(0)} = n^2 G_{00}^{-1}$. The various $G_{\mu\mu}^{-1}$ are obtained by inverting $G_{\mu\mu}$, using eq 2.3. In general, $G_{\mu\mu}$ is given by[16,17]

$$G_{\mu\mu'} = \tfrac{1}{4}\int_{-1}^{1}\mathrm{d}x\int_{-1}^{1}\mathrm{d}y\,\exp(i\pi\mu x - i\pi\mu' y)/\eta_0[3ll_1(\mu)\pi^3 n|x - y|]^{1/2} \tag{3.4}$$

$$\begin{aligned} &= 8(2^{1/2})h/3 \qquad \mu = 0 = \mu' \\ &= h\delta_{\mu\mu'}(2/|\mu|^{1/2}) \qquad \mu \neq 0 \end{aligned} \tag{3.5}$$

where

$$h = 1/\eta_0[12\pi^3 nll_1(\mu)]^{1/2} \tag{3.6}$$

l appearing in these equations is the Kuhn step length. $l_1(\mu)$ is the mode-dependent effective step length. l_1 and its dependence on the polymer mode label have already been discussed in great detail elsewhere.[5,19,20] The reader is referred to those earlier works for complete details.

From eq 2.3 it follows that

$$G_{\mu\mu}^{-1} = 1/n^2 G_{\mu\mu} \tag{3.7}$$

Inserting this expression for G_{00} from eq 3.5 into eq 3.7 yields

$$f_\mathrm{t}^{(0)} = 1/G_{00} = 3/8(2^{1/2})h \tag{3.8}$$

Examining eq 3.6 for h along with eq 3.8 for $f_\mathrm{t}^{(0)}$, we see that the infinite-dilution translational friction coefficient has been calculated as a function of excluded volume effect. As shown elsewhere,[21] l_1 depends on the excluded volume effect as

$$(l_1/l)^{5/2} - (l_1/l)^{3/2} = 1.144z \tag{3.9}$$

where z is the usual dimensionless excluded volume parameter given by $z = (^3/_{2\pi})^{3/2} w L^{1/2}/l^{3/2}$. L is the contour length of the polymer chain. wl^2 is the angular averaged binary cluster integral for a pair of segments and represents the strength of the excluded volume effect. It includes that net results of polymer–solvent effects and is temperature dependent.

Equations 3.9, 3.8, and 3.6 predict that at the Θ solution limit

$$f_\mathrm{t}^{(0)} \propto M^{1/2} \tag{3.10}$$

where M is the molecular weight of the polymer. In the limit of a very good solution, eq 3.9 predicts $l_1 \propto M^{1/5}$. The present formulas, then, predict

$$f_\mathrm{t}^{(0)} \propto M^{0.6} \tag{3.11}$$

Both eq 3.10 and 3.11 have been confirmed by experiment.[13] It should also be noted that the present formalism provides the transition behavior of $f_\mathrm{t}^{(0)}$ from one limit to the other.

Now the second term in eq 2.7 must be examined. This term was shown[17] to vanish in the case of a Θ solution because a term containing the factor of $g(r) - 1$ appears. Since $g(r) = 1$ at the Θ temperature, this term made no contribution. In the case of a good solution, this term must be explicitly evaluated.

The term in question is

$$I_\mathrm{c} \equiv \sum_{\beta\neq\alpha}\left\langle \sum_{ipp'j}\left[\mathbf{g}_\mathrm{t}^{-1}\cdot\mathbf{G}_\alpha^{-1}(\mathbf{A}_{\alpha p},\mathbf{S}_{\alpha i}) - \frac{1}{n}\delta_{ip}\right]\cdot\mathbf{G}(\mathbf{R}_{\alpha i} - \mathbf{R}_{\beta j})\cdot [\mathbf{G}_\beta^{-1}(\mathbf{S}_{\beta j},\mathbf{S}_{\beta p'})\cdot\mathbf{g}_\mathrm{t}^{-1}]\right\rangle \tag{3.12}$$

Applying the δ function to the second term gives

$$\frac{1}{n}\sum_{\beta\neq\alpha}\left\langle\sum_{pp'j}\mathbf{G}(\mathbf{R}_{\alpha p}-\mathbf{R}_{\beta j})\cdot\mathbf{G}_{\beta}^{-1}(\mathbf{S}_{\beta j},\mathbf{S}_{\beta p'})\cdot\mathbf{g}_{\mathrm{t}}^{-1}\right\rangle \quad (3.13)$$

The angular brackets appearing in eq 3.13 mean that the quantity is to be ensemble averaged in the static limit over the positions of all the polymers. The spatial distribution function to be used is

$$P = Z_N^{-1}\exp[-\beta U_N([\mathbf{R}_\alpha^0])] \quad (3.14)$$

where U_N is the total potential energy for the N polymers, Z_N is the configuration integral $\int \mathrm{d}[R_\alpha^0]\exp[-\beta U_N([R_\alpha^0])$, and $\beta = 1/k_{\mathrm{B}}T$ with k_{B} being Boltzmann's constant, and T is the absolute temperature. Using the distribution function given in eq 3.14 and performing the indicated average makes the term from eq 3.13

$$\frac{N}{nV}\int \mathrm{d}\mathbf{r}\sum_{pp'j}\langle\mathbf{G}(\mathbf{r}+\mathbf{S}_{\alpha p}-\mathbf{S}_{\alpha j})\cdot\mathbf{G}_{\beta}^{-1}(\mathbf{S}_{\beta j},\mathbf{S}_{\beta p'})\rangle \quad (3.15)$$

where now the angular brackets imply that the averaging is over the polymer configuration. In obtaining eq 3.15 we have also made use of the fact that $N-1\approx N$ for very large N.

Now, the term

$$\sum_{\beta\neq\alpha}\left\langle\sum_{ipp'j}[\mathbf{g}_{\mathrm{t}}^{-1}\cdot\mathbf{G}_{\alpha}^{-1}(\mathbf{S}_{\alpha p},\mathbf{S}_{\alpha i})]\cdot\mathbf{G}(\mathbf{R}_{\alpha i}-\mathbf{R}_{\beta j})\cdot\mathbf{G}_{\beta}^{-1}(\mathbf{S}_{\beta j},\mathbf{S}_{\beta p'})\right\rangle \quad (3.16)$$

must be examined. Using eq 2.4 for $\mathbf{G}(\mathbf{R}_{\alpha i}-\mathbf{R}_{\beta j})$ and the fact that $\mathbf{R}_{\alpha i} = \mathbf{R}_\alpha^0 + \mathbf{S}_{\alpha i}$, one can write this equation as

$$\int\frac{\mathrm{d}^3k}{(2\pi)^3}\sum_{ipp'j}\mathbf{g}_{\mathrm{t}}^{-1}\cdot\mathbf{G}_{\alpha}^{-1}(\mathbf{S}_{\alpha p},\mathbf{S}_{\alpha i})\cdot\mathbf{G}(\mathbf{k})\cdot\exp[i\mathbf{k}\cdot(\mathbf{S}_{\alpha i}-\mathbf{S}_{\alpha j})]\cdot \mathbf{G}_{\beta}^{-1}(\mathbf{S}_{\beta j},\mathbf{S}_{\beta p'})\cdot\left\langle\sum_{\beta\neq\alpha}\exp[i\mathbf{k}\cdot(\mathbf{R}_\alpha^0-\mathbf{R}_\beta^0)]\right\rangle \quad (3.17)$$

Evaluation of the ensemble average appearing in eq 3.17 requires a knowledge of the two-polymer distribution function. In general, the n-particle distribution function is given by

$$g^{(n)}(\mathbf{R}_1^0,\ldots,\mathbf{R}_n^0) = \frac{V^nN!}{N^n(N-n)!}\frac{1}{Z_N}\int\prod_{\alpha=n+1}^{N}\mathrm{d}\mathbf{R}_\alpha^0\exp(-\beta U_N) \quad (3.18)$$

where V is the volume of the system and the configurational integral, Z_N, has previously been defined. Using eq 3.18, eq 3.17 reduces to

$$\frac{N}{V}\int\frac{\mathrm{d}^3k}{(2\pi)^3}\int\mathrm{d}\mathbf{r}\,g(\mathbf{r})\left\langle\sum_{ipp'j}\mathbf{g}_{\mathrm{t}}^{-1}\cdot \mathbf{G}_{\alpha}^{-1}(\mathbf{S}_{\alpha p},\mathbf{S}_{\alpha i})\cdot\mathbf{G}(\mathbf{k})\cdot\exp[i\mathbf{k}\cdot(\mathbf{r}+\mathbf{S}_{\alpha i}-\mathbf{S}_{\beta j})]\cdot\mathbf{G}_{\beta}^{-1}(\mathbf{S}_{\beta j},\mathbf{S}_{\beta p'})\right\rangle \quad (3.19)$$

where once again the angular brackets correspond to an average over the polymer configuration. Combining eq 3.19 and 3.15 produces the result (upon preaveraging)

$$I_{\mathrm{c}} = \frac{N}{Vf_{\mathrm{t}}^{(0)}}\int\frac{\mathrm{d}^3k}{(2\pi)^3}\int\mathrm{d}\mathbf{r}\left[g(\mathbf{r})\cdot \langle\mathbf{g}_{\mathrm{t}}^{-1}\rangle\cdot\left\langle\sum_{p,i}\mathbf{G}_{\alpha}^{-1}(\mathbf{S}_{\alpha p},\mathbf{S}_{\alpha i})\cdot\exp(i\mathbf{k}\cdot\mathbf{S}_{\alpha i})\right\rangle - \frac{1}{n}\left\langle\sum_{p}\exp(i\mathbf{k}\cdot \mathbf{S}_{\alpha p})\right\rangle\right]\cdot\mathbf{G}(\mathbf{k})\cdot\exp(i\mathbf{k}\cdot\mathbf{r})\cdot\left\langle\sum_{p'j}\exp(i\mathbf{k}\cdot\mathbf{S}_{\beta j})\mathbf{G}_{\beta}^{-1}(\mathbf{S}_{\beta j},\mathbf{S}_{\beta p'})\right\rangle \quad (3.20)$$

The only difference between the averages appearing in eq 3.20 and the averages calculated elsewhere[18] in the Θ solution calculations is that Ll, the mean squared end-to-end distance of the polymer, is to be replaced by Ll_1. In general, l_1 is a function of w, the strength of the excluded volume interaction, L, the contour length of the polymer chain, and the wave vector $\mathbf{k}$.

Edwards and Singh[18] have investigated the wave vector dependence of l_1. Their work contains formulas which provide the explicit dependence of l_1 on k. The calculations predict that l_1 is independent of k for small excluded volume effect and $l_1 \propto k^{-1/3}$ for large excluded volume effect. An extrapolation formula from one limit to the other is also provided. In the present investigation, as a first approximation, l_1 is assumed to be independent of the wave vector. It should be noted, however, that the formulas of Edwards and Singh could be incorporated into the present formalism without any conceptual difficulty. l_1 is left, then, as a function of only w and L. But the needed formula to express this dependence has already been given by eq 3.9. Thus, all of the necessary details are available.

Making the analogy with the Θ solution calculations,[17,18] one can easily evaluate the various averages appearing in eq 3.20. For example

$$\sum_{p,i}\langle\mathbf{G}_{\alpha}^{-1}(\mathbf{S}_{\alpha p},\mathbf{S}_{\alpha i})\exp(i\mathbf{k}\cdot\mathbf{S}_{\alpha i})\rangle = \sum_{p,i}\langle\mathbf{G}^{-1}(\mathbf{S}_p,\mathbf{S}_i)\rangle\langle\exp(i\mathbf{k}\cdot\mathbf{S}_i)\rangle = \sum_{p,i}\langle\mathbf{G}^{-1}(\mathbf{S}_p,\mathbf{S}_i)\rangle\exp(-k^2\langle\mathbf{S}_i^2\rangle/6) \quad (3.21)$$

Completely analogous to the Θ solution, $\langle S_i^2\rangle$ is given by[1,17,18]

$$\langle S_i^2\rangle = \frac{Ll_1}{3}\left[1-\frac{3i(n-i)}{n^2}\right] \quad (3.22)$$

If we insert eq 3.22 into eq 3.15 and go to continuous notation, eq 3.21 becomes

$$\sum_{p,i}\langle\mathbf{G}^{-1}(\mathbf{S}_p,\mathbf{S}_i)\exp(i\mathbf{k}\cdot\mathbf{S}_i)\rangle = 1f_{\mathrm{t}}^{(0)}\left(\frac{\pi}{3d}\right)^{1/2}\exp(-d/4)\,\mathrm{erf}\,(3d/4)^{1/2} \quad (3.23)$$

where $d = k^2Ll_1/1^8$ and erf is an error function.[19]

Using eq 3.22 and going to continuous notation we can also show that

$$\left\langle\sum_{p=1}^{n}\exp(i\mathbf{k}\cdot\mathbf{S}_{\alpha p})\right\rangle = n(\pi/3d)^{1/2}\exp(-d/4)\,\mathrm{erf}\,(3d/4)^{1/2} \quad (3.24)$$

Substituting both eq 3.23 and 3.24 into eq 3.20 and collecting the terms gives the result for the leading concentration-dependent term of the cooperative friction coefficient

$$I_{\mathrm{c}} = \frac{N}{V}\int\frac{\mathrm{d}^3k}{(2\pi)^3}\int\mathrm{d}\mathbf{r}\,[g(\mathbf{r})-1]\left(\frac{\pi}{3d}\right)\exp(-d/2)\times [\mathrm{erf}\,(3d/4)^{1/2}]^2\mathbf{G}(\mathbf{k})\exp(i\mathbf{k}\cdot\mathbf{r}) \quad (3.25)$$

Notice that this term vanishes for Θ solutions when $g(\mathbf{r}) = 1$. I_{c} must now be evaluated under non-Θ conditions.

In order to evaluate I_{c}, $\exp[i\mathbf{k}\cdot\mathbf{r}]$ can be expanded in spherical harmonics. That is[23]

$$\exp(i\mathbf{k}\cdot\mathbf{r}) = 4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{+l}(i)^lj_l(kr)Y_{lm}(\Omega_k)Y_{lm}^*(\Omega_{\mathrm{r}}) \quad (3.26)$$

where j_l are the spherical Bessel functions and Y_{lm} are the spherical harmonics. Substituting this expression into eq

3.25 and doing the simple angular integrals produces

$$I_c = \frac{N}{V}\,\frac{4}{3\pi\eta_0}\int_0^\infty \mathrm{d}k\,\exp(-k^2Ll_1/36)(6\pi/k^2Ll_1)\times [\mathrm{erf}\,(k^2Ll_1/24)^{1/2}]^2\int_0^\infty \mathrm{d}r\,r^2[g(r)-1]j_0(kr) \quad (3.27)$$

This is the general result for I_c, within the preaveraging approximation. In order to make further progress in the calculation, a functional form for $g(r)$, the radial distribution function for the polymers, must be supplied.

There must have been two major investigations in the literature of $g(r)$. Koyama[24-26] investigated numerically the concentration as well as the temperature dependence of $g(r)$. He used the integral equation of Born, Green, and Yvon[27] for $g(r)$ and the Flory–Krigbaum[2] potential for the intermolecular potential, $u(r)$. The result is obtained that in the limit of zero concentration $g(r)$ is given by

$$g(r) = \exp[-x_0\exp(-r^2)] \quad (3.28)$$

where x_0 is a measure of the strength of the excluded volume effect and is related to the parameter z. This formula is valid for the present calculations because one power of the concentration is already present in the formulas. Since the presence interest is in the term linear in concentration, the infinite-dilution value of $g(r)$ is adequate.

The problem with this form for $g(r)$ is that when it is substituted into eq 3.27, the integral over r cannot be performed analytically. In the present calculation, this would mean that a two-dimensional integral must be done numerically. While conceptually this can be done easily, it only makes the problem more complicated. Also, in later calculations, inability to perform the r integral analytically would result in a three-dimensional numerical integration. Thus, Koyama's form for $g(r)$, while being adequate, does not lend itself well to analytical calculations.

A form for $g(r)$ which does allow easy analytic calculations has been investigated by Fixman.[28] Working with the same Born–Green–Yvon equation as Koyama, he assumed that the radial distribution function can be written as

$$g(r) = 1 - a\exp(-br^2) \quad (3.29)$$

where a and b are parameters to be determined in a variational-type calculation. Koyama[26] compares the predictions of his formula with Fixman's, and under zero-concentration conditions very good agreement is found between the two formulas. Since Fixman's form for $g(r)$ is more easily handled in the calculations, it is used in the present calculations. More will be said about the parameters a and b and their relation to experimental observables later.

Substituting eq 3.29 into eq 3.27 allows the r integral to be done. The result is

$$I_c = -\frac{aN}{V}\,\frac{1}{3\pi\eta_0}\,\frac{\pi^{1/2}}{b^{3/2}}\int_0^\infty \mathrm{d}k\,\exp(-k^2/4b - k^2Ll_1/36)\frac{6\pi}{k^2Ll_1}[\mathrm{erf}\,(k^2Ll_1/24)^{1/2}]^2 \quad (3.30)$$

In the present notation, $b = 9.61\delta/Ll_1$, where a and δ are given as a function of the excluded volume effect by Fixman's[28] equations (72) and (73). Substituting this formula for b into eq 3.30 and changing to dimensionless variables, $x = k^2Ll_1/6$, produces

$$I_c = -\frac{aN}{V}\,\frac{4}{3\pi\eta_0}\,\frac{\pi^{1/2}}{4}\left(\frac{Ll_1}{9.61\delta}\right)^{3/2}(3/2Ll_1)^{1/2}P_1 \quad (3.31)$$

where P_1 is given by

$$P_1 = \int_0^\infty \frac{\mathrm{d}x}{x^{1/2}}\exp(-3x/19.22\delta)(\pi/x)\exp(-x/6)\times [\mathrm{erf}\,(x^{1/2}/2)]^2 \quad (3.32)$$

and must be evaluated numerically as a function of δ.

An expression for the infinite-dilution translational friction coefficient, $f_t^{(0)}$, under good-solution conditions has already been given by eq 3.8 along with eq 3.9. An expression for the intrinsic viscosity, $[\eta]$, valid for all strengths of the excluded volume effect, has recently been derived.[29] Using the results from eq 3.31 and 3.32 along with the definitions of the expansion factors, $\alpha^2 \equiv l_1/l$ and $\alpha^2(p) \equiv l_1(p)/l_1$ produces after some tedious algebra

$$I_c = -3c(6\pi^3)^{1/2}[\eta]a\alpha P_1/8f_t^{(0)}(9.61\delta)^{3/2}[\sum_{p=1}^{\infty}\alpha(p)/p^{3/2}] \quad (3.33)$$

Notice that in the limit of a Θ solution, $a = 0$, and this term vanishes. Also, when $\alpha(p)$ is independent of mode, $I_c \propto [\eta]/f_t^{(0)}$, exactly the same relationship as obtained under Θ solution conditions. What remains to be done is to evaluate P_1 as a function of δ and develop the formalism to relate Fixman's parameters to physical observables.

In order to relate a and δ to physical observables, reference must be made to Fixman's original paper[28] on the subject. There are four parameters in Fixman's treatment of the radial distribution function. The parameters a and δ have already been discussed. Fixman also defines a parameter, A, which is related to the usual Flory–Krigbaum parameter, x, by $A = (x\pi^{1/2})/4$. This parameter is a measure of the potential interacting between the two polymer molecules. It is directly related to the strength of the excluded volume interaction.

The other parameter in Fixman's formalism is v, which is directly proportional to the polymer concentration. Since, as mentioned earlier, the present interest is in the infinite-dilution limit of $g(r)$, v can be taken to be zero. This leaves three parameters to be specified.

Using the assumed form for $g(r)$, Fixman performs a variational calculation, assuming that the radial distribution function obeys the Born–Green–Yvon integral equation. This produces two equations relating his four parameters. Taking the zero concentration limit of those equations results in

$$I_2(a) + A(\delta/(1+\delta))^{3/2} = 0 \quad (3.34)$$

$$I_4(a) + (3A/2)(\delta/(1+\delta))^{5/2} = 0 \quad (3.35)$$

where, in general

$$I_m(a) = \int_0^\infty \mathrm{d}x\,x^m\ln[1 - a\exp(-x^2)]\exp(-x^2) \quad (3.36)$$

The calculated procedure, then, consists of assuming a particular value for A. In other words, a certain strength of the excluded volume effect is assumed. Equations 3.34 and 3.35 then become two equations in two unknowns which can be solved. What remains is relating A to a measurable quantity so that a reasonable range of volumes can be used.

Yamakawa[1] and Koyama,[25] both in discussing the Flory–Krigbaum potential, give

$$x = 3^{3/2}z/\alpha_s^3 \quad (3.37)$$

where z is the usual excluded volume parameter and α_s is the expansion factor for the mean squared radius of gyration. Substituting this formula into the previous formula for A and using the relation between α_s and z developed previously[21]

$$\alpha_s^5 - \alpha_s^3 = 1.159z \tag{3.38}$$

produces

$$A = 1.987(\alpha_s^2 - 1) \tag{3.39}$$

This formula relates A, the strength of the interpolymer potential, to an experimental parameter, α_s, the expansion factor for the mean squared radius of gyration.

Miyaki et al.[30] have measured α_s for poly(D-β-hydroxybutyrate) in trifluoroethanol. This system is expected to be very close to the very good solution limit. In fact, these workers showed that the solutions obey the relations $\langle S^2 \rangle^{1/2} \propto M^{0.60}$ and $A_2 \propto M^{-0.20}$, where $\langle S^2 \rangle$ is the mean squared radius of gyration of the polymer, A_2 is the second virial coefficient, and M is the polymer molecular weight. Both of these results are characteristics of being in the asymptotic limit of a very good solution.

The largest α_s measured by these workers is $\alpha_s = 2.4$. Substituting this value into eq 3.39 gives $A = 9.46$. This value of A, then, corresponds to the largest observed, experimental value of A. This means that A must be between 0 and 9.46.

Limits for A having been established now, values between these two limiting values can be substituted into eq 3.34 and 3.35. If one knows A, then, a and δ can be solved for. Having solved for a and δ, one knows all the information needed to calculate I_c from eq 3.33.

Knowing all of the parameters, one can then calculate I_c. Having obtained a value for I_c, one can solve for the concentration-dependent cooperative translational friction coefficient. This is obtained as

$$f_{t,c} = f_t^{(0)}\left\{1 + \frac{3}{8}ac(6\pi^3)^{1/2}\alpha[\eta]P_1/(9.61\delta)^{3/2}\sum_{p=1}^{\infty}\frac{\alpha(p)}{p^{3/2}}\right\} \tag{3.40}$$

Thus, the result from this first term is

$$k_s = \frac{3}{8}(6\pi^3)^{1/2}a\alpha[\eta]P_1/(9.61\delta)^{3/2}\sum_p\frac{\alpha(p)}{p^{3/2}} \tag{3.41}$$

As can clearly be seen from this result, $k_s/[\eta]$ is a function of the excluded volume effect. The excluded volume effect is present in the $a/\delta^{3/2}$ term. Also, it is present in the P_1 integral. Both of these terms are due to the radial distribution function. The other place where the excluded volume is present is in the terms contributing to α, the expansion factor. These terms are due to the expansion of the mean squared end-to-end distance, $\langle R^2 \rangle$.

Assuming a value for z, eq 3.38 can be used to calculate α_s. This value for α_s can, then, be substituted into eq 3.39 to yield a value of A. This value of A, when substituted into Fixman's equations, gives values for a and δ. This result completes the total characterization of Fixman's form for the radial distribution function.

Using the calculated values of a and δ as functions of z, one can calculate the parameter $k_s/[\eta]$ from eq 3.41 as a function of z. The formulas for the expansion factors, α and $\alpha(p)$, have been given elsewhere.[19,21]

Rather than displaying $k_s/[\eta]$ as a function of z, it is more desirable to display it as a function of α_s, the expansion factor of the mean squared radius of gyration. This is because α_s is an experimental quantity. z, on the other hand, is not directly observable by experiment. There have been several attempts to relate z to the temperature.[12] Each of these formulas produces a different result depending on the polymer–solvent system being examined. In the interest of keeping the results general, this approach is not attempted in the present investigation.

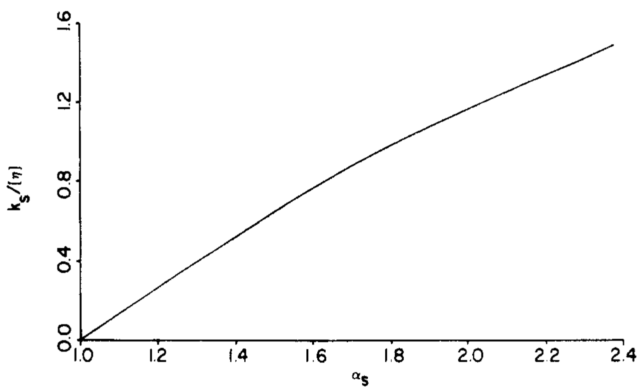

Figure 1. Calculated results for $k_s/[\eta]$ from the first term in the scattering series as a function of excluded volume.

The final result for the ratio $k_s/[\eta]$ is displayed in Figure 1. A definite plateau region in the values can be observed as α_s increases. This corresponds to approaching the very good solution limit of behavior. Also, notice that this formula predicts $k_s/[\eta] = 0$ at the Θ temperature. Thus, the correct limiting behaviors have been established.

A comparison of the extrapolation formula from one limit to the other with the experimental data cannot be made at this time. This is because the cooperative friction coefficient has only been partially evaluated at this time. In the case of the Θ solution calculations,[17,18] it was shown that the present term contributed nothing and it was the next term in the scattering series which made all of the contribution. In order to be consistent with those calculations, that term must be examined under good-solution conditions. That is the task set for the next section.

IV. Self-Friction Coefficient

The infinite-dilution self-friction coefficient is the same as the infinite-dilution cooperative friction coefficient. It is given by eq 3.8 along with eq 3.6. The first concentration-dependent term in the self-friction coefficient is given by the second term on the right-hand side of eq 2.2. This term also is the second term in the concentration-dependent cooperative friction coefficient.

With regard to the cooperative friction coefficient, an indication of the relative importance of the two terms can be obtained from a recent calculation due to Muthukumar and Freed.[31] These workers did a calculation similar to the present one except that they were interested in a suspension of spheres. Assuming that the spheres interact via a hard-sphere potential, they were able to show that the first term contributes approximately 80% of the total answer. The total answer, here, corresponds to an exact calculation done by Batchelor,[7] who treated the two-body hydrodynamics exactly. Similar to that calculation, it is expected that, in the present calculation, the dominant contribution to the cooperative friction coefficient will come from the term which has already been calculated. However, in order to be consistent with the previous calculation, the next term must be examined.

The term under consideration is the third term in eq 2.7 with $\beta \neq \alpha$. When this term is written with all of its indices, it is given by

$$I_t = \left\langle \sum_{\substack{\beta=1\\ \beta\neq\alpha}} \sum_{ii'pp'jj'} \mathbf{G}_\alpha^{-1}(\mathbf{S}_{\alpha i},\mathbf{S}_{\alpha j})\cdot\mathbf{G}(\mathbf{R}_{\alpha i},\mathbf{R}_{\beta p})\cdot\bar{\mathbf{T}}_\beta(\mathbf{S}_{\beta p},\mathbf{S}_{\beta p'})\cdot \mathbf{G}(\mathbf{R}_{\beta p'},\mathbf{R}_{\alpha j})\cdot\mathbf{G}_\alpha^{-1}(\mathbf{S}_{\alpha j},\mathbf{S}_{\alpha j'})\right\rangle \tag{4.1}$$

Performing the average over the centers of mass and using eq 3.18 for the radial distribution function reduces I_t to

$$I_{\mathrm{t}} = \frac{N}{V}\sum_{ii'pp'jj'}\int\frac{\mathrm{d}^3k}{(2\pi)^3}\int\frac{\mathrm{d}^3k'}{(2\pi)^3}\int\mathrm{d}\mathbf{r}\, g(\mathbf{r})\mathbf{G}_{\alpha}^{-1}(\mathbf{S}_{\alpha i},\mathbf{S}_{\alpha i'})\cdot \mathbf{G}(\mathbf{k})\cdot\bar{\mathbf{G}}_{\beta}(\mathbf{S}_{\beta p},\mathbf{S}_{\beta p'})\cdot\mathbf{G}(\mathbf{k}')\cdot\mathbf{G}_{\alpha}^{-1}(\mathbf{S}_{\alpha j},\mathbf{S}_{\alpha j'}) \exp[i\mathbf{r}\cdot(\mathbf{k}-\mathbf{k}')i\mathbf{k}\cdot (\mathbf{S}_{\alpha i'}-\mathbf{S}_{\beta p}) + ik'\cdot(\mathbf{S}_{\beta p'}-\mathbf{S}_{\alpha j})] \quad (4.2)$$

It is possible to write $g(\mathbf{r}) \exp[i\mathbf{r} - (\mathbf{k} - \mathbf{k}')]$ as

$$[g(\mathbf{r}) - 1] \exp[i\mathbf{r}\cdot(\mathbf{k} - \mathbf{k}')] + \exp[i\mathbf{r}\cdot(\mathbf{k} - \mathbf{k}')] \quad (4.3)$$

Using this result in eq 4.2 allows I_{t} to be split into two parts. These two terms are designated $I_{\mathrm{t}}^{(1)}$ and $I_{\mathrm{t}}^{(2)}$.

Using the preaveraging approximation and performing the average over the angles reduces $I_{\mathrm{t}}^{(1)}$ to

$$I_{\mathrm{t}}^{(1)} = \frac{N}{V\eta_0^2}\int\frac{\mathrm{d}^3k}{(2\pi)^3}\int\frac{\mathrm{d}^3k'}{(2\pi)^3}\int\mathrm{d}\mathbf{r}\,[g(\mathbf{r}) - 1] \exp[i\mathbf{r}\cdot(\mathbf{k}-\mathbf{k}')]\langle\sum_{ii'}\mathbf{G}_{\alpha}^{-1}(\mathbf{S}_{\alpha i},\mathbf{S}_{\alpha i'}) \exp(i\mathbf{k}\cdot\mathbf{S}_{\alpha i'})\rangle(2/3k^2)\cdot \langle\sum_{pp'}\exp(-i\mathbf{k}\cdot\mathbf{S}_{\beta p} + i\mathbf{k}'\cdot\mathbf{S}_{\beta p'})\bar{\mathbf{T}}_{\beta}(\mathbf{S}_{\beta p},\mathbf{S}_{\beta p'})\rangle(2/3k'^2)\cdot \langle\sum_{jj'}\mathbf{G}_{\alpha}^{-1}(\mathbf{S}_{\alpha j},\mathbf{S}_{\alpha j'}) \exp(-i\mathbf{k}'\cdot\mathbf{S}_{\alpha j'})\rangle \quad (4.4)$$

The first and third averages have already been calculated and are given by eq 3.23. The only term still to be evaluated is $\langle\sum\exp[i\mathbf{k}\cdot\mathbf{S}_{\beta p}]\cdot\bar{\mathbf{T}}_{\beta}(\mathbf{S}_{\beta p},\mathbf{S}_{\beta p'}) \exp[i\mathbf{k}' - \mathbf{S}_{\beta p}]\rangle$.

$\bar{\mathbf{T}}_{\beta}(\mathbf{S}_{\beta p},\mathbf{S}_{\beta p'})$, within the preaveraging approximation, has already been given by eq 2.6. When this is substituted into eq 4.4, three separate terms result. These correspond to the three terms contained in $\bar{\mathbf{T}}_{\beta}$. Physically, the first term corresponds to the translational motion, the second term corresponds to the center-of-mass motion of the polymer, and the third term represents the rotational motion of the polymer.

If we examine the first term which results from substituting $\bar{\mathbf{T}}_{\beta}$ into eq 4.4, it is found to contain a term which is given by

$$\langle\sum_{pp'}\mathbf{G}_{\beta}^{-1}(\mathbf{S}_{\beta p},\mathbf{S}_{\beta p'}) \exp[-i\mathbf{k}\cdot\mathbf{S}_{\beta p} + i\mathbf{k}'\cdot\mathbf{S}_{\beta p'}]\rangle \quad (4.5)$$

When we use the preaveraging approximation this can be written

$$\langle\sum_{pp'}\mathbf{G}_{\beta}^{-1}(\mathbf{S}_{\beta p'},\mathbf{S}_{\beta p})\rangle\langle\exp(-i\mathbf{k}\cdot\mathbf{S}_{\beta p} + i\mathbf{k}'\cdot\mathbf{S}_{\beta p'})\rangle \quad (4.6)$$

When the average is preformed with the bivariate distribution function,[2] eq 4.6 becomes

$$\sum_{pp'}\langle\mathbf{G}_{\beta}^{-1}(\mathbf{S}_{\beta p},\mathbf{S}_{\beta p'})\rangle \exp\left[-\left(\frac{ll_1}{6}\right)\times (c_{22}k^2 + 2c_{12}\mathbf{k}\cdot\mathbf{k}' + c_{11}k'^2)\right] \quad (4.7)$$

where $c_{11} = n/3 - p - p^2/n$, $c_{22} = n/3 - p' + p'^2/n$, and $c_{12} = -[(p^2/2n) + p/2n + p'^2/2n - p' + n/3]$. Going to continuous notation and representing $\langle G^{-1}(x,y)\rangle$ in terms of its Fourier transforms, eq 4.7 becomes

$$\frac{n^2}{4}\sum_{\mu=-\infty}^{\infty} G_{\mu\mu}^{-1}\int_{-1}^{1}\mathrm{d}x\int_{-1}^{1}\mathrm{d}y \exp\left[i\pi\mu(x - y) - \frac{k^2Ll_1}{72}(3x^2 + 1) - \frac{k'^2Ll_1}{72}(3y^2 + 1) + \frac{\mathbf{k}\cdot\mathbf{k}'}{3}f(x,y)\right] \quad (4.8)$$

where $f(x,y) = (nll_1/24)[3(x^2 + y^2) - 6|x - y| + 2]$. $G_{\mu\mu}^{-1}$ appearing in eq 4.8 are given by eq 3.5 and 3.7.

This result must be substituted back into eq 4.4, which would, then, produce the first term of $I_{\mathrm{t}}^{(1)}$. When we examine eq 4.4, it is seen to contain a term $\exp[i\mathbf{r}\cdot(\mathbf{k} - \mathbf{k}')]$. Expaning $\exp[i\mathbf{r}\cdot\mathbf{k})$ and $\exp[-i\mathbf{r}\cdot\mathbf{k}']$ in spherical harmonics allows the integral over the angles of r to be done. This results in

$$\int\mathrm{d}\Omega_{\mathrm{r}} \exp[i\mathbf{r}\cdot(\mathbf{k} - \mathbf{k}')] = (4\pi)^2\sum_{l=0}^{\infty}\sum_{m=-l}^{l} j_l(kr)j_l(kr')Y_{lm}(\Omega_k)Y_{lm}{}^*(\Omega_{k'}) \quad (4.9)$$

This means that the r integral has now been reduced to

$$\Phi_l(k,k') \equiv \int_0^{\infty}\mathrm{d}r\, r^2[g(r) - 1]j_l(kr)j_l(k'r) \quad (4.10)$$

Assuming Fixman's form for $g(r)$, i.e., $g(r) = 1 - a\exp(-br^2)$, this integral can be performed analytically. It results in

$$\Phi_l(k,k') = -\frac{\pi a}{(4kk')^{1/2}}\,\frac{1}{2b}\exp[-(k^2 + k'^2)/4\beta]I_{l+1/2}(kk'/2b) \quad (4.11)$$

where I_l is the modified spherical Bessel function of the first kind.[19]

All that is left is the integral over $\mathbf{k}$ and $\mathbf{k}'$. The angular integrals can be performed analytically by expanding the term involving $\exp[\mathbf{k}\cdot\mathbf{k}']$ in spherical harmonics. This produces a general result valid for any value of l, the spherical harmonic index. The result obtained is quite complex, however.

In this case, it is expected that the $l = 0$ term in the series is going to make the dominant contribution. This has been verified by Muthukumar and Freed[31] in the case of a suspension of spheres. As a further approximation, this term alone will be considered.

The term under examination is

$$\int\Omega_k\int\mathrm{d}\Omega_{k'} \exp\left[\frac{\mathbf{k}\cdot\mathbf{k}'}{3}f(x,y)\right]Y_{lm}(\Omega_k)Y_{lm}{}^*(\Omega_{k'}) \quad (4.12)$$

where the Y_{lm} terms come from eq 4.9. The important point to realize is that Y_{00} does not depend on the angles of $\mathbf{k}$ and $\mathbf{k}'$. Writing $\mathbf{k}\cdot\mathbf{k}'$ as $kk'\cos\theta$, where θ is the angle subtended by $\mathbf{k}$ and $\mathbf{k}'$, allows the double integral to be done trivially. This results in eq 4.12 becoming

$$\frac{6\pi}{kk'f(x,y)}\left[\exp\left(\frac{kk'f(x,y)}{3}\right) - \exp\left(\frac{-kk'f(x,y)}{3}\right)\right] \quad (4.13)$$

If we combine eq 4.13, 4.11, 4.8, and 3.23, write the result in terms of dimensionless parameters, $x = k^2Ll_1/6$ and $x' = k'^2Ll_1/6$, and use the previously derived results for $f_{\mathrm{t}}^{(0)}$ and $[\eta]$, the first term of $I_{\mathrm{t}}^{(1)}$ becomes

$$-cf_{\mathrm{t}}^{(0)}[\eta]\frac{3a}{64}\,\frac{\pi^{1/2}}{9.61\delta}\left[\alpha/\sum_{p=1}^{\infty}\frac{\alpha(p)}{p^{3/2}}\right]\times \int_0^{\infty}\mathrm{d}x\int_0^{\infty}\frac{\mathrm{d}x'}{(xx')^{3/4}}\exp\left[-\frac{3(x+x')}{19.22\delta} - \frac{(x+x')}{12}\right]\times \frac{\pi}{(xx')^{1/2}}I_{1/2}\left(\frac{3(xx')^{1/2}}{9.61\delta}\right)\operatorname{erf}\left(\frac{x^{1/2}}{4}\right)\times \operatorname{erf}\left(\frac{(x')^{1/2}}{4}\right)\sum_{\mu=1}^{\infty}\mu^{1/2}\int_{-1}^{1}\mathrm{d}y\int_{-1}^{1}\mathrm{d}y'\,\frac{24}{(xx')^{1/2}}e^{i\pi\mu(y-y)} [3(y^2 + y'^2) - 6|y - y'| + 2]^{-1}\left\{\exp\left[\frac{(xx')^{1/2}}{12}[3(y^2 + y'^2) - 6|y - y'| + 2]\right] - \exp\left[-\frac{(xx')^{1/2}}{12}[3(y^2 + y'^2) - 6|y - y'| + 2]\right]\right\}e^{-(x/12)(3y^2+1)-(x'/12)(3y'^2+1)} \quad (4.14)$$

Numerical results will be presented later.

A similar evaluation of the second and third terms from $\bar{\mathbf{T}}_\beta$ can be carried out. Focusing on the second term of $\bar{\mathbf{T}}_\beta$, it produces a term of

$$-\langle \sum_{ii'pp'} \mathbf{G}^{-1}(\mathbf{S}_i,\mathbf{S}_p)\cdot\mathbf{g}_t^{-1}\cdot\mathbf{G}^{-1}(\mathbf{S}_{p'},\mathbf{S}_j) \exp[-i\mathbf{k}\cdot\mathbf{S}_i + i\mathbf{k}'\cdot\mathbf{S}_j]\rangle \tag{4.15}$$

in the formula for $I_t^{(1)}$. Assuming preaveraging approximation, this term becomes

$$-\langle \sum_{ip}\mathbf{G}^{-1}(\mathbf{S}_i,\mathbf{S}_p) \exp(-i\mathbf{k}\cdot\mathbf{S}_i)\rangle\cdot\langle\mathbf{g}_t^{-1}\rangle\cdot \langle \sum_{p'j}\mathbf{G}^{-1}(\mathbf{S}_{p'},\mathbf{S}_j) \exp(i\mathbf{k}'\cdot\mathbf{S}_j)\rangle \tag{4.16}$$

All of the terms involved here are known. $\langle g_t^{-1}\rangle = 1/f_t^{(0)}$. The other two averages are given by eq 3.23. As before, $\exp[i\mathbf{r}\cdot(\mathbf{k}-\mathbf{k}')]$ can be expanded in spherical harmonics. This allows all of the integrals except the $\mathbf{k}$ and $\mathbf{k}'$ terms to be done analytically. The integrals over Ω_k and $\Omega_{k'}$ can be done trivially because the integrand is independent of angles. Doing the angular integrals and also the r integral, assuming Fixman's form for $g(r)$, and writing the result in terms of dimensionless variables, $f_t^{(0)}$ and $[\eta]$, produces

$$I_{t2}^{(1)} = 1\frac{9\pi^{7/2}ac}{64}\,\frac{\alpha f_t^{(0)}[\eta]}{(9.61\delta)}\left(\sum_{p=1}^{\infty}\frac{\alpha(p)}{p^{3/2}}\right)^{-1} \times \int_0^\infty \frac{\mathrm{d}x}{x^{7/4}}\int_0^\infty \frac{\mathrm{d}x'}{(x')^{7/4}} \exp\left[-\frac{3(x+x')}{19.22\delta} - \frac{(x+x')}{6}\right] I_{1/2}\left(\frac{3(xx')^{1/2}}{9.61\delta}\right)\left[\mathrm{erf}\left(\frac{x^{1/2}}{4}\right)\right]^2 \times \left[\mathrm{erf}\left(\frac{x'^{1/2}}{4}\right)\right]^2 \tag{4.17}$$

The double integral appearing in eq 4.17 must be performed numerically.

If we go through precisely the same analysis as was done for $I_{t2}^{(1)}$, the third term for $\bar{\mathbf{T}}_\beta$ can be inserted into eq 4.4 for $I_t^{(1)}$. Performing the angular integrals by using exactly the same technique as before of expanding the exponentials in spherical harmonics produces

$$\frac{\pi^{3/2}ac}{4}\,\frac{f_t^{(0)}[\eta]}{9.61\delta}\int_0^\infty \frac{\mathrm{d}x}{x^{5/4}}\int_0^\infty\frac{\mathrm{d}x'}{(x')^{5/4}} \times \exp\left[-\left(\frac{3}{19.22\delta}+\frac{1}{6}\right)(x + x')\right] I_{3/2}\left(\frac{3(xx')^{1/2}}{9.61\delta}\right)\left[\mathrm{erf}\left(\frac{x^{1/2}}{4}\right)\right]^2\left[\mathrm{erf}\left(\frac{x'^{1/2}}{4}\right)\right]^2 \tag{4.18}$$

This completes the derivation of $I_t^{(1)}$.

The term earlier designated as $I_t^{(2)}$ must now be evaluated. This is given as, assuming preaveraging approximation

$$I_t^{(2)} = \frac{N}{V}\int\frac{\mathrm{d}^3k}{(2\pi)^3}\langle\sum_{ii'}\mathbf{G}_\alpha^{-1}(\mathbf{S}_{\alpha i},\mathbf{S}_{\alpha i'}) \exp(i\mathbf{k}\cdot\mathbf{S}_{\alpha i})\rangle\cdot\mathbf{G}(\mathbf{k})\cdot \langle\sum_{pp'}\bar{\mathbf{T}}_\beta(\mathbf{S}_p,\mathbf{S}_{p'}) \exp[-i\mathbf{k}\cdot(\mathbf{S}_p-\mathbf{S}_{p'})]\rangle\cdot\mathbf{G}(\mathbf{k})\cdot \langle\sum_{jj'}\mathbf{G}_\alpha^{-1}(\mathbf{S}_j,\mathbf{S}_{j'}) \exp(-i\mathbf{k}\cdot\mathbf{S}_j)\rangle \tag{4.19}$$

When we substitute the expression for $\bar{\mathbf{T}}_\beta$ from eq 2.6, $\langle\sum_{pp'}\bar{\mathbf{T}}_\beta(\mathbf{S}_p,\mathbf{S}_{p'}) \exp[-i\mathbf{k}\cdot(\mathbf{S}_p-\mathbf{S}_{p'})]\rangle$ becomes

$$\langle\sum_{pp'}\bar{\mathbf{T}}_\beta(\mathbf{S}_p,\mathbf{S}_{p'}) \exp[-i\mathbf{k}\cdot(\mathbf{S}_p-\mathbf{S}_{p'})]\rangle \equiv T_1 + T_2 + T_3 \tag{4.20a}$$

where

$$T_1 = \langle\sum_{pp'}\mathbf{G}^{-1}(\mathbf{S}_p,\mathbf{S}_{p'}) \exp[-i\mathbf{k}\cdot(\mathbf{S}_p-\mathbf{S}_{p'})]\rangle \tag{4.20b}$$

$$T_2 = -\langle\sum_{ijpp'}\mathbf{G}^{-1}(\mathbf{S}_i,\mathbf{S}_p)\cdot\mathbf{g}_t^{-1}\cdot\mathbf{G}^{-1}(\mathbf{S}_{p'},\mathbf{S}_j) \exp[-i\mathbf{k}\cdot(\mathbf{S}_i-\mathbf{S}_j)]\rangle \tag{4.20c}$$

$$T_3 = \langle\sum_{ijpp'}\mathbf{G}^{-1}(\mathbf{S}_i,\mathbf{S}_p)\times\mathbf{S}_p\cdot\mathbf{g}_r^{-1}\cdot\mathbf{S}_{p'}\times \mathbf{G}^{-1}(\mathbf{S}_{p'},\mathbf{S}_j) \exp[-i\mathbf{k}\cdot(\mathbf{S}_i-\mathbf{S}_j)]\rangle \tag{4.20d}$$

Using the preaveraging approximation

$$T_1 = \sum_{i,j}\langle\mathbf{G}^{-1}(\mathbf{S}_i,\mathbf{S}_j)\rangle \exp(-k^2ll_1|i-j|/6) = \frac{n^2}{4}\int_{-1}^{1}\mathrm{d}x\int_{-1}^{1}\mathrm{d}y\ \langle G^{-1}(x,y)\rangle \exp(-k^2Ll_1|x-y|/12) \tag{4.21}$$

Expanding $\langle G^{-1}(x,y)\rangle$ in terms of its Fourier transform produces

$$T_1 = 1\frac{n^2}{4}\sum_{\mu=-\infty}^{\infty}G_{\mu\mu}^{-1}\left[\frac{4\epsilon}{\epsilon^2+\pi^2\mu^2} - \frac{2(\epsilon^2-\pi^2\mu^2)(1-e^{-2\epsilon})}{(\epsilon^2+\pi^2\mu^2)^2}\right] \tag{4.22}$$

where $\epsilon = k^2Ll_1/12$.

Using the preaveraging approximation, T_2 becomes

$$T_2 = -\langle\sum_{ip}\mathbf{G}^{-1}(\mathbf{S}_i,\mathbf{S}_p) \exp(-i\mathbf{k}\cdot\mathbf{S}_i)\rangle\cdot\langle\mathbf{g}_t^{-1}\rangle\cdot \langle\sum_{p'j}\exp(i\mathbf{k}\cdot\mathbf{S}_j)\mathbf{G}^{-1}(\mathbf{S}_{p'},\mathbf{S}_j)\rangle \tag{4.23}$$

All of the terms appearing here have already been evaluated. Using eq 3.23 for the first and third averages and $\langle\mathbf{g}_t^{-1}\rangle = f_t^{(0)-1}$ produces

$$T_2 = -1\frac{\pi}{3d}f_t^{(0)} \exp(-d/2)[\mathrm{erf}\ (3d/4)^{1/2}]^2 \tag{4.24}$$

where $d = k^2Ll_1/18$. Again, using the preaveraging approximation simplifies T_3 to give

$$T_3 = \langle\sum_{ip}\exp(-i\mathbf{k}\cdot\mathbf{S}_i)\mathbf{G}^{-1}(\mathbf{S}_i,\mathbf{S}_p)\times\mathbf{S}_p\rangle\cdot\langle\mathbf{g}_r^{-1}\rangle\cdot \langle\sum_{p'j}\exp(i\mathbf{k}\cdot\mathbf{S}_j)\mathbf{S}_{p'}\times\mathbf{G}^{-1}(\mathbf{S}_{p'},\mathbf{S}_j)\rangle \tag{4.25}$$

In evaluation of the first factor of eq 4.25, the Wang–Uhlenbeck theorem[1] is utilized. Noting that

$$\langle\exp(-i\mathbf{k}\cdot\mathbf{S}_{p'})\mathbf{S}_p\rangle = \frac{c_{12}ll_1i\mathbf{k}}{3}\exp(-k^2ll_1c_{22}/6) \tag{4.26}$$

where c_{12} and c_{22} are given after eq 4.7, and going to continuous notation, we obtain

$$\langle\sum_{ip}\exp(-i\mathbf{k}\cdot\mathbf{S}_i)\mathbf{G}^{-1}(\mathbf{S}_i,\mathbf{S}_p)\times\mathbf{S}_p\rangle = -B\mathbf{1}\times i\mathbf{k} \tag{4.27}$$

where

$$B = \frac{f_r^{(0)}}{2}\left(\frac{\pi}{3d}\right)^{1/2}\exp(-d/4)\ \mathrm{erf}\ (3d/4)^{1/2} \tag{4.28}$$

$f_r^{(0)}$ under non-Θ conditions is given by

$$f_r^{(0)} = \frac{2nll_1}{3\pi^2}\sum_{\mu=1}^{\infty}(2^{1/2}h\mu^{3/2})^{-1} \tag{4.29}$$

Similarly, the third factor of eq 4.25 becomes

$$-Bi\mathbf{k}\times\mathbf{1} \tag{4.30}$$

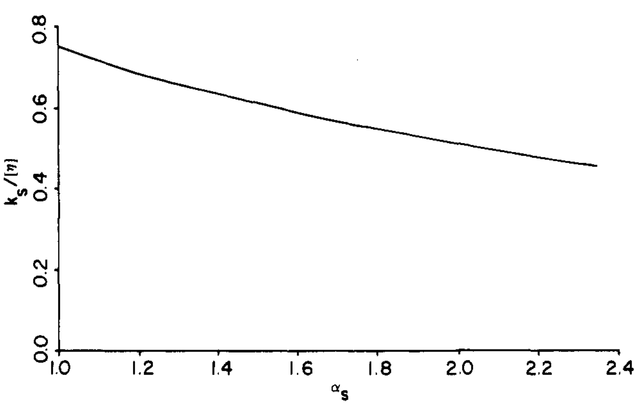

Figure 2. $k_s/[\eta]$ ratio for translational self-friction coefficient as a function of excluded volume.

Noting that $\langle \mathbf{g}_r^{-1}\rangle = 1/f_r^{(0)}$, we get from eq 4.25, 4.27, and 4.30

$$-T_3 = 1\frac{f_r^{(0)}}{6}\,\frac{\pi k^2}{3d}\,\exp(-d/2)[\mathrm{erf}\,(3d/4)^{1/2}]^2 \quad (4.31)$$

Insertion of eq 3.23 for the first and third terms in eq 4.19 and use of eq 2.5 for $\mathbf{G}(\mathbf{k})$ completes the evaluation of $I_t^{(2)}$. Writing the result in terms of $f_t^{(0)}$ and $[\eta]$ produces

$$I_t^{(2)} = \frac{3}{2}c\alpha\pi^{3/2}f_t^{(0)}[\eta]\left(\frac{3}{32}P_1 + P_2\right)\bigg/\sum_{p=1}^{\infty}\frac{\alpha(p)}{p^{3/2}} \quad (4.32)$$

where

$$P_1 = \int_0^{\infty}\frac{\mathrm{d}x}{x^{3/2}}\,A(x)\left[\frac{2}{x} - \frac{2}{x^2}(1 - e^{-x}) - A(x)\right]$$

$$P_2 = \int_0^{\infty}\frac{\mathrm{d}x}{x^{3/2}}\,A(x)\,\times \sum_{m=1}^{\infty}\mu^{1/2}\left\{\frac{x}{x^2 + 4\pi^2\mu^2} - \frac{(x^2 - 4\pi^2\mu^2)(1 - e^{-x})}{(x^2 + 4\pi^2\mu^2)^2} - \frac{xA(x)}{6\pi^2\mu^2}\right\} \quad (4.33)$$

with

$$A(x) = (\pi/x)\exp(-x/6)[\mathrm{erf}\,(x^{1/2}/4)]^2 \quad (4.34)$$

Numerical evaluation of the integrals produces

$$P_1 = 0.0373$$
$$P_2 = 0.2322 \quad (4.35)$$

The second concentration-dependent term for the cooperative friction coefficient and the leading term for the self-friction coefficient are obtained by combining eq 4.14, 4.17, 4.18, and 4.32. The calculational procedure presented earlier for the previous term can be employed again.

Since the term just calculated represents the leading term for the concentration-dependent self-friction coefficient, it will be displayed separately as a function of the experimental parameter, α_s. The data are displayed vs. α_s. The same value of α_s which was used previously to indicate the very good solution limit will be used here.

The calculated values are displayed in Figure 2. It is observed that the coefficient $k_s/[\eta]$ decreases from 0.75 at the Θ temperature to about 0.45 in the limit of a very good solution. As noted in the calculation of the cooperative friction coefficient, a definite plateau is noted in the limit of very good solution.

At the present time, there does not appear to be any experimental investigation of the concentration-dependent self-friction coefficient over a wide range of solvent conditions. The general trend of decreasing k_s has, however, been noted by both experimentalists,[32] and in a recent theoretical investigation.[33] When more extensive data become available, the present calculations are available for comparison.

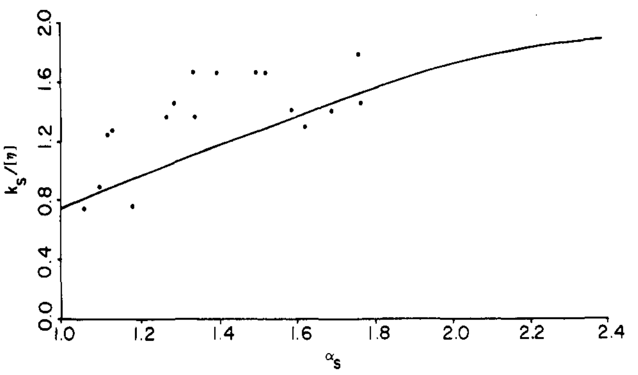

Figure 3. Comparison of results of present calculation for $k_s/[\eta]$ for cooperative translational friction coefficient with data of Petrus et al. (ref 34). The full line is the calculated result and the dots are the experimental data.

There have been investigations of the k_s value for the cooperative translational friction coefficient as a function of goodness of solution.[1] Most significant of these is due to Petrus and co-workers.[34] Working with the system polystyrene in cyclohexane, these workers simply varied the temperature of the solution and measured k_s at these various temperatures. They also compared their results with previous experimental data.

Figure 3 contains a comparison of the present calculations with the data contained in the Petrus paper. Reasonable agreement is found between the calculated values and the experimental data. As is often the case when a compilation of all the data is made, a good deal of scatter is noted in the data points. However, several key points can be noted. The experimental data begin at $k_s/[\eta] = 0.75$ at the Θ temperature as do the calculated results. This has already been noted. The experimental data indicate $k_s/[\eta]$ reaches a limiting value of 1.7–1.8 for very good solutions. The calculated value for a very good solution is $k_s/[\eta] = 1.85$. This is again in very good agreement. Qualitatively, at least, the present formulas also reproduce the transition behavior from the limit of Θ solution to very good solution.

V. Conclusions

In the present investigation, the translational self-friction and cooperative friction coefficients are calculated under differing goodness of the solvent. The calculations are specialized to calculate the first virial coefficient of the cluster expansion series of these transport coefficients. It is found that the self-friction and cooperative friction coefficients develop different concentration dependencies under these conditions. As shown previously, $k_s/[\eta]$ is 0.75 for both the self-friction and cooperative friction coefficients under Θ conditions. Using Fixman's radial distribution function, we have shown that, in the asymptotic limit of very good solutions, $k_s/[\eta]$ approaches 0.45 and 1.85, respectively, for the self-friction and cooperative friction coefficients. Explicit formulas are derived for the intermediate temperatures and are displayed graphically in Figures 2 and 3. Reasonable agreement between theory and experiment is observed.

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Determination of the Guest Radius of Gyration in Polymer Blends: Time-Resolved Measurements of Excitation Transport Induced Fluorescence Depolarization

M. D. Ediger,[†] **R. P. Domingue, K. A. Peterson, and M. D. Fayer***

Chemistry Department, Stanford University, Stanford, California 94305.
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ABSTRACT: An experimental study of polymer blend structure using electronic excitation transport induced fluorescence depolarization is presented. Copolymers of vinylnaphthalene and methyl methacrylate in poly(methyl methacrylate) (PMMA) and poly(ethyl methacrylate) (PEMA) hosts are examined. It is shown that recent theoretical treatments accurately describe the time dependence of the fluorescence depolarization caused by excitation transport among chromophores on isolated polymer coils. Analysis of the experimental results strongly suggests that if an appropriate pair correlation function is employed, quantitative determination of coil size (the root-mean-square radius of gyration, $\langle R_g^2 \rangle^{1/2}$) will be possible. Comparisons are made between the size of the copolymer in PMMA and PEMA hosts and in different molecular weight PMMA hosts. The technique is capable of examining blends in which the guest concentration is very small, a regime which is difficult to investigate with previous methods. When the concentration of copolymer in PEMA is increased, phase separation occurs and is manifested by an increased rate of fluorescence depolarization (increased rate of excitation transport) and a decreased fluorescence lifetime due to trapping.

I. Introduction

The nature of intermolecular interactions determines the microscopic structure of condensed phase systems. For a relatively small molecule with basically fixed molecular framework, the structure of an ensemble of molecules is, nonetheless, very complex, e.g., the structure of liquid water or the crystal structure of naphthalene. However, if the molecules of interest are macromolecules, the structural problem has an additional dimension of complexity. A polymer coil in a solution or in a solid polymer blend has a vast number of possible configurations. The interaction of a polymer coil with its environment determines its macroscopic structure, while the local structure (chain segment geometry) determines the nature of the coil–environment interactions. Thus, the problem of polymer structure involves an interplay between thermodynamic interactions and possible coil configurations. Understanding this interplay is of fundamental importance in understanding polymeric materials.

Polymer blends are also of tremendous technological importance. This is due in large part to the fact that the bulk properties of a blend can be carefully controlled by adjusting the composition of the various components. These properties are critically dependent on the mixing of blend components on a molecular level. Phase separation into domains of various compositions can occur as a result of unfavorable intermolecular interactions between the different polymers present. A very sensitive indicator

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[†] Permanent address: Department of Chemistry, University of Wisconsin, Madison, WI 53706.

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