at high molecular weights. The reason for the existence of a lower limit is basically the need to avoid anomalously high amorphous densities. It should be noted, as Frank[16] has pointed out, that the value depends on the tilt angle between the chain direction and normal to the fold surface. The above values assume no tilt, but at least some tilt is known to occur in, e.g., polyethylene, which if it occurred in *cis*-polyisoprene would further depress the lower limit.

Fringed-micelle-type chain exits from a crystal have been suggested (see ref 11) as having very high fold surface free energy σ_e due to chain overcrowding. However, if this problem is avoided by keeping above the lower limit of AR folding, such chain exits could have very low σ_e.

Considering the above arguments, as well as the very high molecular weight ($\bar{M}_w > 10^6$) of this polymer and the regime III crystallization process, it is possible that the AR fold fraction r is quite low and that this effect is responsible for the low σ_e values. If, as postulated above, σ_e is of the order of σ for a cilium or loose nonadjacent reentry fold, q is given by

$$q = (\sigma_e/r - \sigma_{e0})2A_0 \qquad (10)$$

instead of by eq 9, with σ_e being the effective (measured) surface free energy rather than that corresponding to an AR fold. Using Hoffman's "limiting" value of $r = 0.3$ gave $q \simeq 21.4$ kJ/mol = 5.1 kcal/mol at atmospheric pressure, which is a reasonable value for an essentially linear aliphatic chain, being slightly above that quoted for polyethylene.[11] This value would be even higher if r is lowered (by tilt) or if the heat of fusion is higher than the value used (6.4×10^7 (J/m^3)).

The high-pressure value of q, using $\sigma_e \simeq 0.035$ J/m^2 (see Figure 3) and $r = 0.3$ as before, was found to be 34.3 kJ/mol = 8.2 kcal/mol, which is an increase of ~60% over the low-pressure value.

6. Conclusions

The Lauritzen–Hoffman theory[11] was found to be suitable for the analysis of isobaric high-pressure crystallization kinetics data for *cis*-polyisoprene. The applicability of this theory is further justified by the similar σ_e values, and their pressure dependence, calculated from independent lamellar thickness data[6] and crystallization kinetics data.

The fold surface free energy σ_e for material crystallized under pressure increases suddenly between 0.5 and 1 kbar to a value significantly higher than that at low pressure. On the other hand, for material crystallized at atmospheric pressure, σ_e is practically independent of pressure.[6] A model involving a pressure-induced change in the fold conformation of a macromolecule in the crystal apparently satisfies these observations qualitatively. Several other possible explanations have been found to be inappropriate.

The σ_e values obtained for *cis*-polyisoprene are somewhat lower than typical values for other polymers, and the work of chain folding q, calculated as suggested by Hoffman et al.,[11] is unacceptably low. It is possible that this is because only a small fraction of the folds are of the adjacent reentry type.

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Registry No. Polyisoprene (homopolymer), 9003-31-0.

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Diffusion of Brownian Spheres in Semidilute Polymer Solutions

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ABSTRACT: We develop a theory of the dependence on polymer concentration of D/D_0, the diffusion coefficient of dilute Brownian spheres of radius R in a semidilute polymer solution relative to the pure solvent value. The result is $D/D_0 = \exp(-\kappa R)$, where κ is the screening constant of the semidilute polymer solution. For rodlike polymers, $\kappa = (\zeta_L n_L/\eta)^{1/2}$, with n_L and ζ_L the rod number density and friction coefficient, respectively, and η the fluid viscosity. For random coil polymers with Debye–Bueche screening, $\kappa = (\zeta_a n_a/\eta)^{1/2}$, with ζ_a and n_a the monomer friction and number density, respectively; thus $\kappa \sim n_a^{1/2}$. Other dependences of κ on n_a were obtained by Edwards and Freed and by de Gennes. Therefore, the above D/D_0 expression can serve as a probe of screening in the semidilute regime. Comparison with experiments for rod and coil solutions are made, and good agreement is found with the above D/D_0 expression with $\kappa R \sim n_a^{1/2}R$.

I. Introduction

In a dilute polymer solution the monomer density is very inhomogeneous since there are polymer–solvent and pure solvent regions. In the semidilute regime, where the polymer coils overlap extensively yet the monomer volume fraction $\phi \ll 1$, the monomer density is quite homogeneous. It has been suggested that it is useful to describe a semidilute polymer solution as a porous "sponge" through

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which the solvent flows.[1-3] As a probe of the dynamic response of semidilute polymer solutions, Brownian spheres have been added to polymer solutions and their diffusion D and sedimentation s coefficients measured as a function of polymer concentration. The results of two of these experiments[4,5] can be summarized as follows:

$$D/D_0 = \exp(-BRc^{1/2}) \tag{1.1}$$

where D (D_0) is the diffusion coefficient of the dilute Brownian spheres with (without) the polymer present, R is the Brownian sphere radius, c is the polymer concentration in g/mL, and B is a constant.

In this article we provide a derivation of this relation based on our recent calculation[6] for the following related problem. We considered the diffusion of Brownian spheres in the presence of randomly distributed, fixed spheres of number density n_a and radius a immersed in an incompressible Navier–Stokes fluid. The problem can be formulated by first averaging over the (random) configuration of the fixed spheres to obtain a new fluid whose velocity $\mathbf{V}(\mathbf{r})$ and pressure $P(\mathbf{r})$ satisfy

$$\begin{gathered} \eta\nabla^2\mathbf{V}(\mathbf{r}) - \kappa^2\mathbf{V}(\mathbf{r}) - \nabla P(\mathbf{r}) = \mathbf{F}(\mathbf{r}); \\ \nabla\cdot\mathbf{V}(\mathbf{r}) = 0 \end{gathered} \tag{1.2}$$

where η is the fluid's shear viscosity coefficient, $\kappa^{-1} = (\zeta n_a/\eta)^{-1/2}$ is a screening length related to ζ, the friction coefficient of a fixed sphere, and $\mathbf{F}(\mathbf{r})$ is a force to drive the fluid motion. The presence of the fixed spheres modifies the Navier–Stokes equation (eq 1.2 without the $\kappa^2\mathbf{V}$ term) to the screened Navier–Stokes equation of eq 1.2. Since in a semidilute solution the coils no longer are free to move with the solvent, they appear fixed with regard to the solvent motion. Thus, there is a correspondence between the fixed sphere and semidilute polymer solution.

On the basis of this analogy we will discuss the diffusion coefficient of Brownian spheres in two semidilute polymer solutions. The first is a solution made up of long rodlike polymers, and the second is a random coil solution. We separate the discussion since the nature of screening in rod and coil solutions may be different and the two experiments we cited are for these two cases.

In section III the calculation for rod solutions is carried out by solving for the friction coefficient of a Brownian sphere in a semidilute rod fluid described by a screened Navier–Stokes equation. An exact result valid for small $\kappa_L R$ is developed (κ_L is the rod solution screening constant). Then an approximate relation for larger $\kappa_L R$ is obtained and compared with experimental data.[5] In section IV the corresponding theory for coil solutions is developed. There are several[2,3,7,8] predictions for the concentration dependence of κ here and their consequences are reflected in the sphere friction coefficient. The measurement of the corresponding sphere diffusion and the sedimentation coefficients can help elucidate the nature of screening in semidilute polymer solutions. We conclude with a discussion of our results in section IV.

II. Rod Solutions

We consider a solution consisting of rodlike polymer molecules of number density n_L, dilute test spheres of radius R in an incompressible solvent described by the linearized Navier–Stokes equation (eq 1.2 *without* the κ^2 term). The polymer molecules are modeled as prolate ellipsoids of major (minor) axes L (b) with $L \gg b$.

If the rodlike polymers were fixed in space, that is, if they did *not* drift with the mean solvent velocity, then they would exert a frictional force on the fluid. In the semidilute regime it is hypothesized that the polymers form a transient network that impedes the flow of the solvent due to the hydrodynamic (Oseen) interactions of the monomers. The polymer network appears fixed to the solvent motion in this sense, and we may view the system as a porous material. On a coarse-grained scale, the fluid consisting of solvent and polymer is a "Debye–Bueche–Brinkman" (DBB) fluid[7] characterized by eq 1.2. The screening constant κ_L, which measures the resistance to fluid flow from the presence of the fixed rods, is related to the friction experienced by the rods. If the solution is dilute in rods, then κ_L^2 must be of the form

$$\kappa_L^2 = \zeta_L n_L/\eta \tag{2.1}$$

where ζ_L is the friction coefficient for one rod. At higher rod concentration a formal expression for κ_L^2 can be given by a multiple scattering expansion.[9] The one-rod friction coefficient ζ_L is[10]

$$\zeta_L = \frac{6\pi\eta(L/2)}{\ln(L/b)} \tag{2.2}$$

where we use the prolate-ellipsoid model for the rod and take $L \gg b$. The DBB fluid is thus defined by eq 1.2, 2.1, and 2.2.

The friction coefficient f for the Brownian particle is now obtained by following the usual Stokes law derivation for the drag on a fixed sphere of radius R with stick boundary condition,[11] with the alteration that we use the above DBB equation instead of the Navier–Stokes equation. The result is[2]

$$f = f_0(1 + \kappa_L R) \tag{2.3}$$

to lowest order in $\kappa_L R$. Since $\kappa_L \sim n_L^{1/2}$, the sphere friction coefficient is a nonanalytic function of the polymer concentration. The origin of this effect is as follows. A more microscopic derivation of eq 2.3 proceeds by considering the hydrodynamic interaction between the Brownian sphere and the fixed rods of number density n_L.[6] The sphere friction is obtained by summing over all the possible scatterings of the fluid from the sphere and the rods, with the rods in a given configuration. Then an average over the rod distribution function is carried out. Because the hydrodynamic interaction is given by the Oseen tensor $\mathbf{T} = (8\pi\eta r)^{-1}(\mathit{I} + \hat{r}\hat{r})$, the interaction is of long range $\sim 1/r$ and divergences are obtained when an expansion in rod density is attempted. Summing to all orders in rod concentration before configuration averaging eliminates these divergences and leads to the nonanalytic dependence on n_L. Summation of the most divergent series of terms, the "ring diagrams", familiar from Debye–Hückel theory, leads to eq 2.3. Only to this lowest order do the two calculations of f, via the DBB and via the just described microscopic approaches, agree.

The result of eq 2.3 is a "limiting law"; corrections can be generated but they are very complex and still limited to small $\kappa_L R$.[6] To obtain an expression for the friction f when $\kappa_L R$ is not small is a formidable task that we shall not attempt here. Rather, a phenomenological approach is adopted. We modify eq 2.3 to

$$\delta f = f\delta(\kappa_L R) \tag{2.4}$$

where by δf we denote an increment in f arising from a corresponding increment in $\kappa_L R$. [For a change from zero concentration we would have $\delta f = f - f_0 = f_0(\kappa_L R)$, which is eq 2.3.] Now we assert that δf is proportional to f itself. The solution of eq 2.4 is

$$f/f_0 = \exp(\kappa_L R) \tag{2.5}$$

which reduces to eq 2.3 for $\kappa_L R \ll 1$ of course. Since the screening constant κ_L given by eq 2.1 and 2.2 is proportional to $c^{1/2}$, with c the rod concentration in g/mL, the form of eq 2.5 agrees with the experimental observations of eq 1.1.

To assess the quantitative success of eq 2.5, the expression for $\kappa_L R$ is rewritten in terms of c as

$$\kappa_L R = \left(\frac{3\pi L N_A}{\ln (L/b) M} \right)^{1/2} R c^{1/2} \qquad (2.6)$$

with N_A Avogadro's number and M the rod molecular weight. The data we compare with were obtained by Jamieson et al.[5] in a study of xanthan biopolymers. As noted there, the data in the semidilute regime support an entangled network of long thin rods (L = 15 000 Å, b = 20 Å) of molecular weight 2.2 × 10^6. The Brownian particles are latex spheres with R = 1100 Å. Above a xanthan concentration of ~0.1% (w/v) the translational diffusion coefficient of the latex spheres is observed to be sharply reduced and the corresponding friction ratio $f/f_0 = D_0/D$ obeys eq 1.1 with a slope $S = BR = 75$. From eq 2.6 and the numbers cited above we obtain $S = 84$, in excellent agreement with these data.

III. Coil Solution

The DBB perspective was developed for the interior of a given polymer coil. The screening constant for the coil interior, which we now denote as κ_D, is

$$\kappa_D^2 = \zeta n_a^* / \eta = 6\pi n_a^* a \qquad (3.1)$$

where n_a^* is the monomer number density, "a" is the monomer radius, and we use the Stokes law monomer friction $\zeta = 6\pi\eta a$. This expression should be adequate for the dilute monomer density within the coil. In semidilute solution $\kappa^2 = \zeta n_a/\eta$, n_a is to be interpreted as the monomer density from any coil, and $n_a \geq n_a^*$, where we consider n_a^* as the characteristic number density denoting the lower limit of the semidilute regime. In this regime the monomer friction becomes concentration dependent, $\zeta \rightarrow \zeta(n_a)$.[3,8]

As noted in the previous section, even for rod (or sphere) suspensions the calculation of κ is difficult beyond the lowest orders. It is correspondingly more difficult for a semidilute polymer solution. Two predictions are given by Edwards and Freed[8] (EF) and by de Gennes.[3] EF noted that in the calculation of the monomer friction $\zeta(n_a)$ the monomer–monomer interactions of a given coil are not given by the Oseen tensor interaction, $T \sim 1/r$, as in dilute solution, but rather by an interaction in the medium with the other polymer coils present, i.e., by a screened Oseen interaction $T_s \sim e^{-\kappa r}/r$. The value of κ, which is connected to the monomer friction by $\kappa = (\zeta(n_a) n_a/\eta)^{1/2}$ is to be obtained self-consistently. The result is that $\kappa_{EF} \sim n_a$. Following this work, de Gennes[3] showed by a scaling analysis that when κ is calculated for a swollen chain rather than the ideal chain used in EF, the result is $\kappa_{DG} \sim n_a^{3/4}$. Thus, there are three predictions for κ in the semidilute regime for coils: $\kappa_D \sim n_a^{1/2}$, $\kappa_{EF} \sim n_a$, and $\kappa_{DG} \sim n_a^{3/4}$.

These results are readily incorporated in our theory. We still obtain

$$f/f_0 = \exp(\kappa R) \qquad (3.2)$$

where κ is the screening constant for the just described theories. Thus measurement of f/f_0 as a function of polymer concentration in the semidilute regime should provide a test of these different predictions on the nature of screening in polymer solutions.

Quite some time ago an extensive series of experiments were carried out on the sedimentation and diffusion of globular particles of varying sizes in the presence of hyaluronic acid (HA), a polysaccharide, for varying HA concentration.[4] Light scattering[12] and intrinsic viscosity[13] measurements indicate that HA is a random coil, with some degree of expansion, in solutions with not too low ionic strength. The HA molecular weight is (1.5–1.7) × 10^6 and the sphere radii varied from about 50 to 1000 Å. The experimental results were fit to the form

$$s/s_0 = A \exp(-kRc_{HA}^{1/2}) \qquad (3.3)$$

with c_{HA}, the HA concentration, in g/mL, R the sphere radius, k a constant, and A a constant that varied between 1 and 2. The s/s_0 ratios were measured for $c_{HA} \sim 10^{-4}$–10^{-2} g/mL, which should be in the semidilute regime for a 10^6 molecular weight coil. The constant A was determined by linear extrapolation of the data to $c_{HA} = 0$, and clearly, once below c_{HA}^*, there is no reason to expect the $c_{HA}^{1/2}$ dependence (see Discussion). Therefore, a value of A different from 1 is suspect. They also found that the diffusion coefficient ratio D/D_0 satisfied $(D/D_0)(s/s_0) = 1$ to experimental error, and we use the equality $s/s_0 = f_0/f$ to compare eq 3.3 with eq 3.2.

The noteworthy features in eq 3.3 are that the data support the $c_{HA}^{1/2}$ behavior in the semidilute regime and thus the κ_D form of screening. Also, the linear dependence of ln (s/s_0) on R is very well supported over the wide range of sphere sizes used. To estimate the slope k we write the theoretical relation of eq 3.2 with $\kappa = \kappa_D$ as

$$f/f_0 = \exp\{[(6\bar{v})^{1/2}/a] R c_{HA}^{1/2}\} \qquad (3.4)$$

with $\bar{v}$ the partial specific volume of the polymer and "a" the monomer radius. In obtaining eq 3.4 we define $l = n_a a$, the coil length density of *all* the coils, and note that $\pi a^2 l = c_{HA}\bar{v}$. Using the measured value $\bar{v} = 0.65$[14] and the inferred value a = 10 Å[4] yields $k = (6\bar{v})^{1/2}/a = 9.5 \times 10^6$. This is in reasonable agreement with $k \approx 16 \times 10^6$ obtained from experiment.

IV. Discussion

We have found that the Brownian motion of dilute spheres in a semidilute polymer solution can serve as a probe of the nature of hydrodynamic screening in the solution. In the semidilute regime Brownian motion occurs in a screened fluid and leads to eq 3.2. The concentration dependence of κ depends on the model chosen for the hydrodynamic screening, and this should be reflected in the measurement of diffusion and sedimentation coefficients.

Our prediction $f/f_0 = \exp(\kappa R)$ is obtained in the spirit of an effective medium calculation.[15] In this nonperturbative approach, designed for concentration regimes where small parameter expansions about zero concentration are no longer sensible, the diffusion process occurs in a medium characterized by the transport properties at the true concentration. Effective medium theories often do represent higher concentration results quite well, but they are of uncertain validity. With reference to the data of section III, it is possible that the expression $f/f_0 = \exp(\kappa R)$ is not correct and the screening constant changes its dependence on n_a to κ_{EF} or κ_{DG} in such a fashion to still agree with the data of section III. Thus, it is important to develop a theory for f/f_0 that is valid over a large range of κR so that the nature of screening in the semidilute regime can be more critically assessed. More systematic forms of effective medium theory are available[16] and we shall apply them to the current problem.

As κR gets smaller, we obtain $f/f_0 = 1 + \kappa R$, which is a rigorous result. Since the Brownian sphere radius R can be reduced for a given value of κ, the regime κR small can be obtained independently of changing the polymer concentration. This offers the possibility of probing the concentration dependence of κ in the regime where κR is small and $f/f_0 = 1 + \kappa R$ is the appropriate expression. Much of the data of section III is for κR small and the data support $\kappa \sim c^{1/2}$, the DBB screening form. It would be of use to have the experiments on rod solutions done for smaller values of R such that κR is also small.

The screening constant of eq 2.1 can be further interpreted by introducing an "equivalent rod" consisting of monomers of radius b and number density n_b such that $n_L L = n_b(2b)$. Then defining $\kappa_b = (6\pi n_b b)^{1/2}$ we obtain

$$\kappa_L = \kappa_b/[\ln (L/b)] \qquad (4.1)$$

κ_b is the screening constant for a dilute system of fixed, randomly distributed spheres of radius b and number density n_b.[9] Thus, there is a close connection between screening in rod and sphere solutions, the difference only manifest in the concentration-independent and slowly varying factor ln (L/b). For a random coil polymer the DBB screening constant κ_D is the same as that of a suspension of fixed spheres with the same radius as the monomer radius. (We have assumed a uniform monomer density in the coil; a more appropriate choice would be a $n_a(r)$, but in the semidilute regime the monomer density should again be uniform.) The point is that screening, at least for low monomer concentration, is dominated by the long-range hydrodynamic interaction and therefore is mainly determined by the density of (fixed) material, not geometric factors.

In dilute polymer solution we expect that

$$f/f_0 = 1 + \alpha c + ... \qquad (4.2)$$

where α is a constant; that is, a concentration expansion does exist. This should be the case when both species diffuse on comparable time scales. Then screening will be absent, the fluid will be characterized as a Navier–Stokes fluid, and the transport coefficients are analytic functions of polymer concentration.[17] With regard to the rod polymer experiment, for example, we note that the xanthan rod and latex sphere volumes are comparable. Thus, their respective diffusion coefficients are comparable, and f/f_0 should obey eq 4.2. To obtain the result of eq 2.3 it is crucial that the rods be fixed, at least on the time scale of the sphere diffusion. In polymer solutions the transition to "fixed" rods can occur at a small rod concentration since, using the criterion of filling the system with spheres of radius L leads to $c^* \sim 10^{-4}$% (w/v) for the cited experiment.[5] Intuitively, one expects the locking-up behavior of the rods to occur at a concentration considerably in excess of c^*, and all the data of Jamieson et al.[5] support this idea, but this still corresponds to a low polymer volume fraction. Thus we expect that the functional dependence of eq 4.2 would be hard to observe for this system; when c is large enough to measure a change in f/f_0, the transition to the $c^{1/2}$ behavior of eq 2.3 has taken place.

In addition to the three screening constant expressions we noted in section III, there are a variety of other predictions for different monomer density and solvent quality regimes. Edwards and Freed[8] obtain $\kappa \sim n_a^{1/2}$ at higher monomer density than their $\kappa \sim n_a$. Schaefer, Joanny, and Pincus[18] extend scaling and mean field arguments to locally stiff chains and obtain $\kappa \sim n_a^{3/4}$, $\sim n_a^{1/2}$, and $\sim n_a$ in semidilute good, semidilute marginal, and semidilute Θ solution, respectively. Experimental evidence for the semidilute good and semidilute marginal regime κ predictions has been obtained.[18,19] Muthukumar and Edwards,[20] with the use of self-consistent field theoretic techniques, find $\kappa \sim n_a^{3/4}$ for the semidilute poor-solvent regime and $\kappa \sim n_a$ for the semidilute good-solvent regime.

Lastly, we note that the experiments of Laurent et al.[4] and Jamieson et al.[5] have been interpreted in terms of a theory developed by Ogston et al.[21] In their approach a random walk of the Brownian particle is carried out in a space with holes whose size is characterized by the distribution of spherical spaces of radius R in a suspension of random fibers. The size of the random step is reduced by the presence of the fibers, and this reduction is mirrored in the reduction of the sphere diffusion coefficient. They obtain $D/D_0 = \exp(-\pi^{1/2}Rl^{1/2})$, where l is again the total polymer chain length density. Our result for the Debye screening case is the same except for the different coefficient. Their theory, which is purely geometric, does not rely on the concept of hydrodynamic screening, and therefore, in our view, does not identify the physical mechanism that is responsible for the $c^{1/2}$ behavior.

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