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Concentration Dependence of the Polymer Diffusion Coefficient

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The form of the concentration dependence of the polymer diffusion coefficient depends on the concentration of the polymer relative to the crossover concentration, c^*, between the dilute and semidilute regimes. At concentrations below c^* the diffusion is of a single polymer molecule. As the polymer concentration is increased the friction coefficient is increased, thus leading to a slowing down of the motion of individual molecules. A microscopic, hydrodynamic theory explains this behavior quite adequately.[1] As the polymer concentration approaches c^* the diffusion coefficient vs. concentration curve flattens out and, at concentrations above c^* but still in the semidilute regime, the diffusion coefficient becomes a linearly increasing function of the polymer concentration.[2] Typically, scaling approaches are employed to explain the behavior in the semidilute regime. By examining static correlations near the Θ temperature, Daoud and Jannink[3] have expressed the density–density correlation function in terms of a correlation length that is inversely proportional to the concentration. Brochard and de Gennes,[4] using dynamic scaling arguments for Θ conditions, have shown that the diffusion coefficient is inversely proportional to the correlation length and is therefore directly proportional to the concentration.

Combining the above descriptions leads to a picture that describes the experimentally observed concentration dependence of the polymer diffusion coefficient. At low concentrations the decrease of the translational diffusion coefficient is due to hydrodynamic interactions that increase the friction coefficient and thereby slow down the motion of the polymer chain. At high concentrations the system becomes an entangled network. The diffusion of the chains becomes a cooperative process, and the diffusion of the chains increases with increasing polymer concentration. This description requires two different expressions in the two concentration regimes. A microscopic, hydrodynamic theory should be capable of explaining the observed behavior at all concentrations. In this note we present such a microscopic interpretation.

Theory

The diffusion coefficient is related to a microscopic variable through a Green–Kubo relation

$$D = (1/3)\int_0^\infty \mathrm{d}t\ \langle \dot{A}(t)\dot{A}^+(0)\rangle \qquad (1)$$

where for diffusion the microscopic variable is the flux of the number of particles through an imaginary plane of unit area in the fluid. Thus, for diffusion $\dot{A}(t) = (\mathrm{d}x/\mathrm{d}N)\dot{N}(t)$, where $\dot{N}(t)$ is the flux of the number of particles through the plane at time t , and $\dot{N}(t)$ is a phase-space variable; that is, the flux will depend on both the positions and velocities of the polymer segments. Therefore, we can expand it in the variables $(\mathbf{x}_i, \mathbf{p}_i)$ and, using eq 1, obtain

$$D = \int_0^\infty \mathrm{d}t\ \langle \mathbf{v}_i(t)\mathbf{v}_i(0)\rangle + \int_0^\infty \mathrm{d}t\ (\mathrm{d}\mathbf{x}_i/\mathrm{d}N)^2(\mathrm{d}N/\mathrm{d}\mathbf{p}_i)^2\langle \mathbf{F}_i(t)\mathbf{F}_i(0)\rangle \qquad (2)$$

where we have used the repeated index convention. Noting that the velocities of the individual segments add up to the overall polymer velocity, we see that the first term in eq 2 gives simply the relation between the polymer diffusion coefficient and the velocity–velocity correlation function. A microscopic approach yields the Einstein relation[4] $D = k_\mathrm{b}T/f_0(1 + k_\mathrm{s}c)$, where k_b is Boltzmann's constant, T is the absolute temperature, f_0 is the friction coefficient at infinite dilution, k_s is a constant, and c is the polymer concentration. Because the forces on the individual segments are not additive, the second term in eq 2 must be left in terms of segment variables.

Following Ferrell,[5] the second term in eq 2 can be expressed as a Green–Kubo integral over a flux–flux correlation function. The transport is due to a velocity perturbation caused by two driving forces, the Brownian force and frictional force. The transport coefficient due to the segment–segment interaction can be calculated from the Kubo formula.[6]

$$\lambda = (1/k_\mathrm{b}T)\int\int\int_0^\infty \mathrm{d}\mathbf{r}_1\ \mathrm{d}\mathbf{r}_2\ \mathrm{d}(t_2 - t_1)\langle \mathbf{J}(\mathbf{r}_2,t_2)\mathbf{J}(\mathbf{r}_1,t_1)\rangle \qquad (3)$$

where $\mathbf{J}(\mathbf{r},t) = S(\mathbf{r},t)\mathbf{V}(\mathbf{r},t)$; $S(\mathbf{r},t)$ is the density fluctuation, and $\mathbf{V}(\mathbf{r},t)$ is the local velocity of the segment in the polymer solution. For simplicity,[5] we define the equal time density correlation function $G(\mathbf{r})$

$$G(\mathbf{r}_{12}) = \langle S(\mathbf{r}_1,0)S(\mathbf{r}_2,0)\rangle \qquad (4)$$

and the time-integrated velocity correlation tensor $A_{ij}(\mathbf{r})$

$$A_{ij}(\mathbf{r}_{12}) = \int_0^\infty \mathrm{d}t\ \langle V_i(\mathbf{r}_1,t)V_j(\mathbf{r}_2,0)\rangle \qquad (5)$$

Substituting $G(\mathbf{r})$ and $A_{ij}(\mathbf{r})$ into eq 3, we have

$$\lambda = (1/k_\mathrm{b}T)\int\int\int \mathrm{d}\mathbf{r}_1\ \mathrm{d}\mathbf{r}_2\ \mathrm{d}t\ \langle S(\mathbf{r}_2,t)\mathbf{V}(\mathbf{r}_2,t)S(\mathbf{r}_1,0)\mathbf{V}(\mathbf{r}_1,0)\rangle$$

$$\lambda = (1/k_\mathrm{b}T)\int\int\int \mathrm{d}\mathbf{r}_1\ \mathrm{d}\mathbf{r}_2\ \mathrm{d}t\ G(\mathbf{r}_{12})\langle \mathbf{V}(\mathbf{r}_2,t)\mathbf{V}(\mathbf{r}_1,0)\rangle$$

$$\lambda = (1/k_\mathrm{b}T)\int\int G(\mathbf{r}_{12})A(\mathbf{r}_{12})\ \mathrm{d}\mathbf{r}_1\ \mathrm{d}\mathbf{r}_2$$

$$\lambda = (V/k_\mathrm{b}T)\int G(\mathbf{r})A(\mathbf{r})\ \mathrm{d}\mathbf{r} \qquad (6)$$

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where $A(\mathbf{r})$ is the trace of A_{ij} and V is the volume of the system. The diffusion coefficient can be obtained by eq 1, that is, the flux divided by the thermodynamic driving force via

$$D = (1/3)\lambda k_b T \Big/ \left(V \int G(\mathbf{r})\, \mathrm{d}\mathbf{r} \right) = (1/3)\langle A \rangle_{\text{ave}} \quad (7)$$

Such a decomposition of the diffusion coefficient has previously been noted by Pattle et al.[7] Now we must evaluate $\langle A \rangle_{\text{ave}}$. The time-integrated velocity correlation function A_{ij} is due to the hydrodynamic interaction and can be described by the Oseen tensor. The Oseen tensor is related to the velocity perturbation caused by the hydrodynamic force, F. By checking units, we see that A is the Oseen tensor times the energy term, k_bT, or

$$A_{ij}(\mathbf{r}) = (k_b T / 8\pi\eta)(\delta_{ij}/r + r_i r_j / r^3) \quad (8)$$

where δ_{ij} is the Kronecker δ function. Obviously, the trace of $A_{ij}(\mathbf{r})$ is

$$A(\mathbf{r}) = k_b T / (2\pi\eta \mathbf{r}) \quad (9)$$

For now, we restrict our discussion to the Θ point, where the polymers in solution have a random coil distribution. Therefore, it is reasonable to say that in the semidilute regime at the Θ point the distribution of the segments in the solution is spherical. With this concept, the velocity of the diffusing segments at the Θ condition can be expressed as

$$\mathbf{V}_i(t)(4\pi (R_{ij})_{\text{ave}}{}^3/3) = \int_{\mathbf{r}<(R_{ij})_{\text{ave}}} \mathrm{d}\mathbf{r}\; \mathbf{V}(\mathbf{r},t) \quad (10)$$

Then the diffusion coefficient due to the hydrodynamic interaction between the segments in the polymer solution, that is, the mutual diffusion coefficient, is given by

$$\begin{aligned} D_{\text{mut}} &= (1/3) \int \mathrm{d}t\; \langle \sum_{i,j} \mathbf{V}_i(t) \mathbf{V}_j(0) \rangle = \\ &(1/3) \int\int\int \mathrm{d}t\; \mathrm{d}\mathbf{r}_1\; \mathrm{d}\mathbf{r}_2\; (3/4\pi R_{ij}{}^3)^2 \langle \mathbf{V}(\mathbf{r}_1,t)\mathbf{V}(\mathbf{r}_2,0)\rangle = \\ &(1/3) \int\int \mathrm{d}\mathbf{r}_1\; \mathrm{d}\mathbf{r}_2\; (3/4\pi R_{ij}{}^3)^2 \langle k_b T / 2\pi\eta R_{ij} \rangle = \\ &(1/3)[k_b T/(2\pi\eta \langle R_{ij}\rangle_{\text{ave}})] = (k_b T/6\pi\eta)\langle 1/R_{ij}\rangle_{\text{ave}} \quad (11) \end{aligned}$$

where we have used eq 9 and 10 and $\langle R_{ij} \rangle$ is the average distance between any two segments in the solution. Although the notation is perhaps misleading, we have chosen to write the expression in this form to correspond to the notation of Imai.[8] The transport is due to a velocity perturbation caused by some driving force. Diffusion of the segments is a result of the hydrodynamic force that can be described in terms of the Oseen tensor[8] with the solvent modeled as a continuum with viscosity, η_0. Thus, the second term in eq 2 can be written as the energy, k_bT, times the trace over the Oseen tensor. Averaging over the distribution of segment positions yields

$$D = k_b T / f_0 (1 + k_s c) + (k_b T / 6\pi\eta_0) \langle R_{ij} \rangle^{-1} \quad (12)$$

Typically the experimental data on the diffusion coefficient are normalized relative to the diffusion coefficient at infinite dilution, $D_0 = k_bT/f_0$, so that eq 12 will be most useful as

$$D/D_0 = (1 + k_s c)^{-1} + R_H \langle R_{ij} \rangle^{-1} \quad (13)$$

where the hydrodynamic radius $R_H = f_0/6\pi\eta_0$. Equation 13 is the general result of this paper.

The term $\langle R_{ij} \rangle$ has been evaluated by Imai for hydrodynamic interactions at the Θ point.[8] He has shown that

$$\langle R_{ij} \rangle^{-1} = (1/6\pi\eta_0)\langle T_{ij} \rangle = (\pi N b^2/9)c \quad (14)$$

where N is the number of segments and b is the segment bond length. Combining eq 13 and 14 with the experimental result for the hydrodynamic radius, $R_H = R_H' M^{1/2}$, where R_H' is a constant for a given polymer–solvent system, yields our final result, which is specific for Θ conditions.

$$D/D_0 = (1 + k_s c)^{-1} + 2.1014 \times 10^{15} R_H' b^2 N^{1/2} c_w / m^{1/2} \quad (15)$$

where c_w is expressed as a weight concentration (g/cm^3), $c_w = cM^{1/2}/m^{1/2}$, where m is the molecular weight of each segment and the bond length is given in angstroms.

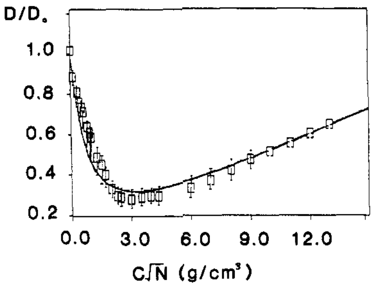

Figure 1. Normalized diffusion coefficient of different molecular weights of polystyrene at the Θ temperature, 34.5 °C. (□) Data taken from ref 9; the line is the theoretical curve.

Results and Discussion

We compare our theoretical expression with the experimentally measured values for the diffusion coefficient of polystyrene. The diffusion coefficient has been measured for polystyrene of various molecular weights in cyclohexane, using light scattering, by Munch, et al.[9] This study examined the concentration dependence of the diffusion coefficient over a wide range of molecular weights and at concentrations spanning the dilute–semidilute regimes. For polystyrene the hydrodynamic radius is given[10] by $R_H = 0.228M^{1/2}$ Å and the bond length is 3.124 Å.

The constant k_s is given by $k_s = (2mNA_2 - k_f - \bar{v})$, where A_2 is the second virial coefficient, k_f is the frictional hydrodynamic interaction parameter, and $\bar{v}$ is the partial specific volume of the polymer. At the Θ point, A_2 is identically zero and $\bar{v}$ is negligible compared to k_f. For polystyrene at the Θ point k_s is[9] 1.45 cm^3/g. The fit to the experimental points is given in Figure 1.

As can be seen in Figure 1, the microscopic expression for the diffusion coefficient, eq 15, correctly describes the shape of the diffusion coefficient curve over the dilute and semidilute concentration regimes. It is important to note that eq 15 contains no adjustable parameters. All of the constants in our microscopic expression have been independently measured by various experimental techniques. Thus, the description of the concentration dependence of the diffusion coefficient does not require a microscopic theory in the dilute regime and a scaling argument in the semidilute regime. A single microscopic approach is capable of explaining the observed behavior in both concentration regimes. It should also be stressed that even though eq 13 implies that both overall polymer and segmental diffusion contribute at all concentrations, except at concentrations near c^*, one term or the other dominates. Indeed, at concentrations near the crossover concentration both types of diffusional motion contribute to the measured diffusion coefficient. Thus, there is no sharp dividing line along the concentration axis, to be identified with c^*, that separates the different contributions to D/D_0. Equation 13 does yield an expression for a crossover concentration at which the two contributions are equal. Equating the two terms on the right-hand side of eq 13, noting that, at c^*, $k_sc \gg 1$, and solving for the concentration yield

$$c^* = \langle R_{ij} \rangle / k_s R_H \quad (16)$$

The crossover concentration calculated for polystyrene with this expression is in the range of the reported values.[9,11] Finally, the above discussion points out that c^* is not a sharp dividing line. It is therefore not physically meaningful to scale the concentration axis in a plot of D/D_0 vs. concentration divided by the crossover concentration. Equation 13 demonstrates that it is better to plot the relative diffusion coefficient vs. the weight concentration of the polymer, as was done by Munch et al.[9]

A similar decomposition of the diffusion coefficient into a linear relationship between the diffusion constant and the polymer concentration has been derived by Brochard et al.[12] While their equation was applied to diffusion in polymer–polymer melts it is applicable to polymer–simple molecular solvent systems if the degree of polymerization of one of the species is taken to be unity. While their result also predicts a linear relationship between the diffusion coefficient and the polymer concentration at concentrations well below and well above c^*, the same expression, but with different sets of constants, must be used. Our result is a single expression that is correct at all polymer concentrations.

Future work will involve comparison of eq 15 to measured diffusion coefficients for systems with a wide range of bond lengths and segmental molecular weights. Unfortunately, reliable data over a wide range of concentrations are difficult to obtain. We also hope to extend eq 13 to non-Θ conditions. At least superficially, eq 13 can be extended to non-Θ conditions by multiplying $\langle R_{ij} \rangle$ by an expansion parameter. Since it is known that the expansion parameter is greater than unity for good solvents and less than unity for poor solvents, eq 13 would predict that the slope of the D/D_0 vs. c_w line for $c_w > c^*$ would decrease in good solvents and increase in poor solvents, in agreement with predictions from scaling theory.[13] This is only superficial, since expansion parameters are functions of the polymer concentration and, therefore, for non-Θ solvents the diffusion coefficient curve at concentrations above the crossover concentration may no longer be linear.[14]

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Nonequilibrium Mechanical Response of a Cross-Linked Network

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Our understanding of the molecular mechanisms responsible for the nonequilibrium mechanical properties of a cross-linked network has recently been deepened by a theoretical model suggested by de Gennes.[1,2] In this analysis, each dangling chain and unattached chain in the network is confined by other chains in a virtual tube lying along the chain contour from which it is able to escape by a diffusion of its free end(s) along the chain contour. The escape of an unattached chain occurs by a "reptation" mechanism[1] involving the motion of both chain ends. The escape of a dangling chain occurs by a "retracing" mechanism[2] involving the motion of the free chain end toward the fixed chain end. In both cases, as a chain end passes out of a portion of the tube for the first time, that tube portion evaporates. The stress contribution of an unattached chain[3] or a dangling chain[4] is assumed to be proportional to the fraction of the tube that remains at time t.

When a cross-linked network is deformed, a dangling chain or an unattached chain deforms by virtue of its having distinct, localized entanglements at various positions along its chain contour. Using this picture, we can replace the evaporation of portions of the continuous tube in the de Gennes model by the dissolution of discrete entanglements as the free chain end(s) diffuse along the chain contour. Each disentanglement is obviously a barrier passage event, the precise nature of which depends on the specific character of the entanglement. The overall chain relaxation process is therefore a multiple barrier passage process.[5,6] This type of process has been modeled[7,8] in terms of a continuous-time random walk (CTRW) having a pausing-time distribution with a long time tail

$$\psi(t) \sim t^{-1-\alpha} \qquad 0 < \alpha \leqslant 1 \tag{1}$$

In the following sections, we will examine both the reptation and retracing mechanisms in terms of this CTRW model.

Reptation of an Unattached Chain

We have recently shown[9] that in the reptation process, the fraction of tube that has evaporated at time t equals the span at time t of a one-dimensional nearest-neighbor random walk and that the stress relaxation function at time t is given by

$$\phi(t) = f(L,t) = \int_0^L \left(1 - \frac{s}{L}\right) p(s,t)\, \mathrm{d}s \tag{2}$$

where $f(L,t)$ is the fraction of the tube that remains at time t, L is the chain contour length, and $p(s,t)$ is the probability density for the random walk to achieve a span s at time t.

We can rewrite eq 2 in the form

$$f(L,t) = \frac{1}{L} \int_0^L P(s,t)\, \mathrm{d}s \tag{3}$$

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