Application of the Blob Model to the Calculation of Cooperative and Self-Diffusion Coefficients in Polymer Solutions

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ABSTRACT: The concentration and temperature dependences of the cooperative and self-diffusion coefficients for semidilute polymer solutions are discussed by using the blob model. The blob model is shown to be particularly useful in describing the behavior of these quantities near the crossover from the semidilute good-solvent region to the semidilute Θ-solvent region of the temperature–concentration diagram. Universal plots for the cooperative and self-diffusion coefficients are proposed, and theoretical predictions are compared with experimental results from the literature.

1. Introduction

The blob model has proven to be useful in discussions of many different properties of polymer solutions since its introduction by Daoud et al.[1] and Farnoux et al.[2] Initially, it was used to investigate properties of semidilute solutions such as the mean-square end-to-end distance[1] and the static structure factor.[2] It has also been applied to calculations of the temperature and chain-length dependence of the radius of gyration,[2-4] the hydrodynamic radius,[3,4] and the intrinsic viscosity[4,5] of a polymer at infinite dilution.

One of the main advantages of the blob model is its ability to provide a simple interpretation of crossover effects. For example, in the dilute-solution case, the expansion factor for the radius of gyration of a polymer in a good solvent takes the Θ-solvent value when the molar mass is low, but it crosses over to good-solvent behavior as the molar mass is increased. Similarly, a crossover from semidilute good-solvent behavior to semidilute Θ-solvent behavior is expected when the concentration is increased from the overlap concentration C^* to a concentration C^{**}. These ideas were discussed theoretically by Daoud and Jannink[6] and have been applied to the interpretation of a wide variety of experiments.

One consequence of crossover effects, which can be explained by using the blob model, is the existence of effective exponents. The use of the blob model in the calculation of effective exponents for both cooperative and self-diffusion coefficients has already been described in the literature.[6,7] However, a more detailed analysis in the spirit of Akcasu and Han's[3] study of the dilute-solution radius of gyration and hydrodynamic radius has not previously been attempted. This paper describes how such an analysis can be performed.

2. Review of Dilute-Solution Results

The blob model has been applied to the quantitative calculation of the expansion factors for the radius of gyration and the hydrodynamic radius at infinite dilution by Akcasu and Han.[3] It is worthwhile to summarize the main features of their approach before extending it to semidilute properties.

We will assume that the Flory interaction parameter, χ, is related to the segment–segment excluded volume, v, by the relation

$$1 - 2\chi = v/a^3 \tag{1}$$

where a^3 is the volume of a polymer segment or solvent molecule (which are taken to be identical). The excluded volume can often be written in terms of the reduced temperature, $\tau = (T - \theta)/T$, as[3]

$$(v/a^3)^2 = \tau^2/k_1 \tag{2}$$

where k_1 is a constant, which is expected to depend insensitively on the solvent and monomer type.

In the blob model of chain statistics,[2] it is assumed that the mean-square distance between two segments separated by n segments along the chain is given by

$$R^2(n) = a^2 n \qquad n \le N_\tau \tag{3a}$$

$$R^2(n) = a^2 n^{2\nu} N_\tau^{1-2\nu} \qquad n > N_\tau \tag{3b}$$

where ν is the excluded-volume exponent ($\nu \approx {}^3/_5$) so that at small values of n the chain is Gaussian but at large values of n the chain is swollen. N_τ is a cut-off parameter reflecting solvent quality. It is related to temperature by

$$N_\tau = k_1/\tau^2 \tag{4}$$

Equation 3 indicates that if N_τ is greater than or equal to N, the total number of segments in the chain, the entire chain is Gaussian.

Expressed in terms of the polymer molar mass, N is equal to M/nA with n being the number of monomers per statistical segment and A the molar mass of a monomer. Therefore, the condition for the onset of swelling is that $\tau \ge \tau^*$ where

$$\tau^* = (k_1 nA/M)^{1/2} \tag{5}$$

When eqs 3a and 3b are substituted into the definition of the radius of gyration, the result is[3,4]

$$R_G^2 = a^2 N_\tau \left(\frac{2\nu - 1}{2(2\nu + 1)} x - \frac{2\nu - 1}{3(2\nu + 2)} x^2 + \frac{1}{(2\nu + 1)(2\nu + 2)} x^{-2\nu} \right) \tag{6}$$

where $x = N_\tau/N$.

With $\nu = {}^3/_5$ this becomes

$$R_G^2 = a^2 N_\tau (24x - 11x^2 + 75x^{-2\nu})/528 \tag{7}$$

In the dilute Θ region ($x \ge 1$), the blob model gives

$$R_G^2 = a^2 N/6 \tag{8}$$

for the radius of gyration.

Likewise, eqs 3a and 3b can be substituted into the Kirkwood equation for D_0 to give an equation for the hydro-

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dynamic radius[3,4]

$$R_H^{-1} = (12/[6\pi]^{1/2})a^{-1}N_\tau^{-1/2}\left(\frac{1-2\nu}{1-\nu}x + \frac{2\nu-1}{3(2-\nu)}x^2 + \frac{1}{(1-\nu)(2-\nu)}x^\nu\right) \quad (9)$$

which, with $\nu = {}^3/_5$, becomes

$$R_H^{-1} = (12/[6\pi]^{1/2})a^{-1}N_\tau^{-1/2}(-21x + 2x^2 + 75x^\nu)/42 \quad (10)$$

In the dilute Θ region, the blob model gives R_H as

$$R_H = ([6\pi]^{1/2}/16)aN^{1/2} \quad (11)$$

These results can be used to construct universal quantities, i.e., quantities that are expected to fall on a common curve when plotted against x regardless of solvent quality, molar mass, or monomer and solvent structure. The expansion factors α_S and α_H depend only on x and are therefore universal. To simplify the algebra, it is convenient to define the following quantities:

$$B = 24x - 11x^2 + 75x^{-2\nu} \quad (12)$$

$$G = -21x + 2x^2 + 75x^\nu \quad (13)$$

Then α_S and α_H are given by

$$\alpha_S = (Bx/88)^{1/2} \quad (14)$$

and

$$\alpha_H = x^{1/2}56/G \quad (15)$$

The relationship between $x = N_\tau/N$ and the experimentally accessible quantities M and τ can be written as

$$1/x = (\tau/\tau^*)^2 \quad (16)$$

where τ^* is given by eq 5. The value of the product k_1n appearing in eq 5 is expected to depend insensitively on the type of solvent and the structure of the monomer units. Akcasu and Han[3] determined that k_1n was equal to 4 for polystyrene in cyclohexane by matching the theoretical expression for α_S with experimental data in the large N/N_τ limit where the blob model is expected to be most accurate. They then used the same value to plot data for other solvents, although they left open the possibility of determining k_1n separately for each polymer–solvent pair.

3. Semidilute Solutions

When the blob model is applied to semidilute polymer solutions, the idea that ideal chain statistics exist within a group of N_τ segments (called a temperature blob) is maintained. In addition, the concept of thermodynamic screening is used to justify the assumption that each group of g segments (called a concentration blob) between interchain contact points behaves as a noninteracting unit.[2,6] Therefore, if a chain is made up of N/g concentration blobs, each of mean-square end-to-end length $\xi_R = aN_\tau^{1/2-\nu}g^\nu$, the total end-to-end distance is $\xi_R(N/g)^{1/2}$. Note that g varies with both the temperature (solvent quality) and concentration. The blob model for semidilute solutions can then be written as

$$R^2(n) = a^2n \qquad n \le N_\tau \quad (17a)$$

$$R^2(n) = a^2N_\tau^{1-2\nu}n^{2\nu} \qquad N_\tau < n \le g \quad (17b)$$

$$R^2(n) = a^2N_\tau^{1-2\nu}g^{2\nu-1}n \qquad n > g \quad (17c)$$

By analogy with the dilute-solution case, the radius of gyration of a blob, ξ_S, is given by eq 6 with N_τ/N replaced by N_τ/g. The hydrodynamic radius of a blob, ξ_H, is found by the same method from eq 9.

At semidilute concentrations, a universal quantity would be expected to fall on a master curve when plotted against $x = N_\tau/g$ regardless of concentration, solvent quality, molar mass, or monomer and solvent structure. To construct a universal quantity, we proceed by the same method as was used for the dilute case. For example, the expansion factor for the total mean-square end-to-end length of a polymer in the semidilute region is written as

$$\alpha_R = R/R(\theta) = [\xi_R(N/g)^{1/2}]/[\xi_{R\theta}(N/g_\theta)^{1/2}] \quad (18)$$

It is necessary to distinguish between g and g_θ because g depends on both concentration and temperature. The ratio g_θ/g must be written in terms of x before eq 18 can be developed. The critical concentration for overlap of polymer molecules is

$$c^* = \frac{N}{k_2R_G^3} \quad (19)$$

where k_2 is a parameter determined by experiment and c is the number density of segments ($C = cnAN_A$). At higher concentrations, the analogous relationship

$$c = \frac{g}{k_2\xi_S^3} \quad (20)$$

holds. Therefore, at a given concentration, we have

$$g_\theta/g = (\xi_{S\theta}/\xi_S)^3 \quad (21)$$

or

$$g_\theta/g = [88g_\theta/(BN_\tau)]^{3/2} \quad (22)$$

where eqs 7 and 8 have been used with R_G replaced by ξ_S and $x = N_\tau/g$ in the semidilute region. Substituting $N_\tau = xg$ in eq 22 gives

$$g_\theta/g = (Bx/88)^3 \quad (23)$$

This result can be used to find expressions for various universal quantities in the semidilute regime. One which will prove useful later is the universal ratio involving the radius of gyration of a blob

$$\xi_S/\xi_{S\theta} = 88/(Bx) \quad (24)$$

It is necessary to find a relationship between x and the experimental variables M, C, and τ before this equation can be used quantitatively. This has been done by Daoud and Jannink,[6] who showed that the ratio C/τ could be written as a function of x only. (Note that eq 14 of ref 6 contains a misprint; N_τ should be replaced by τ. Also, Daoud and Jannink appear to have assumed that $k_1 = k_2 = 6$ for their numercial calculations.) Here, we will follow their method to find a result that retains experimental factors so as to enable a direct comparison between theory and experiment.

The mass/volume concentration is $C = cnA/N_A$ and the reduced temperature, τ, is given by eq 4 so, with eqs 5 and 20, we find

$$C/\tau = \frac{C_\theta^*}{\tau^*}F(x) \quad (25)$$

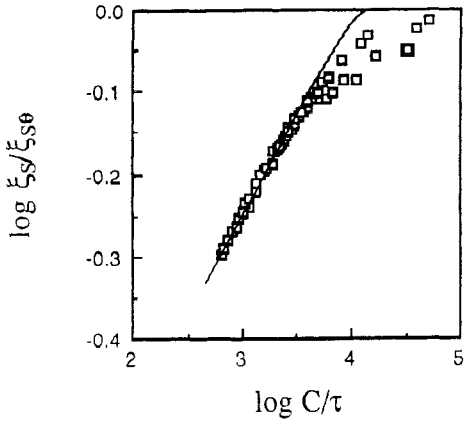

Figure 1. Ratio $\xi_S/\xi_{S\theta}$ plotted against C/τ. Experimental data were taken from the work of Cotton et al.[8] The curve was plotted by using eqs 24 and 25 and shifted horizontally to give the best agreement with the data, yielding $C_\theta^*/\tau^* = 14\,800$ kg m^{-3}.

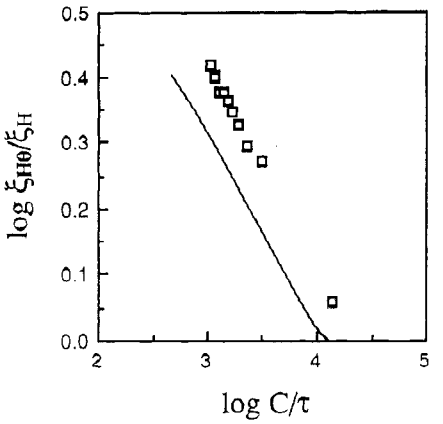

Figure 2. Universal plot for the blob hydrodynamic radius, ξ_H. Experimental points were taken from Adam and Delsanti,[9] and the curve was calculated by using the blob model (eq 28). The value of C_θ^*/τ^* was taken as 14 800 kg m^{-3}, which was obtained by matching theory and experiment in Figure 1.

where

$$C_\theta^* = M/(k_2 N_A R_{G\theta}^3) \tag{26}$$

and

$$F(x) = \frac{1}{x}(88/B)^{3/2} \tag{27}$$

On the C/C_θ^*–τ/τ^* plane, a given value of x corresponds to a straight line through the origin, the slope being given by $1/F(x)$. Slopes less than 1 correspond to $x > 1$ (semidilute θ) and slopes greater than 1 correspond to $x < 1$ (semidilute good).

We can use the same procedure to determine k_2 as was used by Akcasu and Han to determine k_1. First, data for a universal ratio involving a static property is plotted against C/τ on a log–log plot. Then the theoretical curve for the universal ratio as a function of $F(x)$ is plotted on the same axes. The shift factor on the log (C/τ) axis, which is required to give a good fit in the small x (small C/τ) region where the property obeys a power law, is recorded. This gives the value of C_θ^*/τ^*. If nk_1 is already known from a fit to dilute-solution data, the value of k_2 can be determined. We have done this in Figure 1 with the data of Cotton et al.[8] for $\xi_S/\xi_{S\theta}$ measured on polystyrene in deuterated cyclohexane. This procedure gives $C_\theta^*/\tau^* = 14\,800$ kg m^{-3}. The value of k_2 obtained from this result (0.13) seems low, but more experiments would need to be analyzed before a more informed discussion of this matter could be attempted. The value of nk_1 was taken as 4, which was obtained for undeuterated polystyrene in C_6H_{12}. Measurements of crossover effects made well inside the semidilute regime ($C/C_\theta^* > 3$, taking $k_2 = 1$) are rare and more work needs to be done in this area. The measurements of Cotton et al. concentrate on temperature crossover effects, corresponding to a variation of τ, while C is kept constant. Alternatively, concentration crossover effects could be studied by varying C while keeping τ constant.

4. Cooperative and Self-Diffusion Coefficients

The blob model can also be used to give a theoretical curve for the cooperative diffusion coefficient, $D_c = k_B T/6\pi\eta\xi_H$. We can define a universal quantity independent of temperature and viscosity effects as $D_c\eta T_\theta/D_{c\theta}\eta_\theta T$, which is equivalent to $\xi_{H\theta}/\xi_H$. This ratio is given by

$$\xi_{H\theta}/\xi_H = (xG/56)(B/88)^{3/2} \tag{28}$$

Taking $C_\theta^*/\tau^* = 14\,800$ kg m^{-3}, we obtain the curve shown in Figure 2. Also plotted are the data of Adam and Delsanti,[9] which show a similar slope. As has already been observed in the case of the hydrodynamic radius, dynamic properties approach the asymptotic power law behavior very slowly. Exact agreement between theory and experiment is not to be expected, because even in the dilute regime, the agreement between the blob model and experimental data for the hydrodynamic radius expansion factor is not particularly good.[3] This discrepancy need not be entirely attributed to a failure of the blob model. The Kirkwood equation for the hydrodynamic radius involves severe approximations in its treatment of hydrodynamic interactions (the draining effect). The blob model has the advantage of providing a useful unified framework for the interpretation of many different properties of polymer solutions.

Now we are in a position to apply the blob model to the analysis of crossover effects on the self-diffusion coefficient.

When hydrodynamic and static lengths are distinguished, the equation for the self-diffusion coefficient given by the combination of the reptation model and scaling arguments becomes[7]

$$D_S = \frac{k_B T}{18\eta\pi}\left(\frac{N}{g}\right)^{-2}\xi_H^{-1} \tag{29}$$

One approach to the investigation of crossover effects is to examine the effective exponents, which are found when data collected in the semidilute good to semidilute θ crossover region are force fitted to a power law.[6,7,10] True power law behavior is only expected in a θ solvent or in the asymptotic region for a good solvent.

For a θ solvent

$$\xi_S \sim g^{1/2} \tag{30}$$

whereas in the asymptotic region for a good solvent

$$\xi_S \sim g^{\nu} \tag{31}$$

with similar equations holding for ξ_H.

In the crossover region, the effective exponents of ξ_S and ξ_H are defined as

$$\nu_S = \frac{\partial \log \xi_S}{\partial \log g} = \frac{g}{\xi_S}\frac{\partial \xi_S}{\partial x}\frac{\partial x}{\partial g} \tag{32}$$

and

$$\nu_H = \frac{\partial \log \xi_H}{\partial \log g} = \frac{g}{\xi_H}\frac{\partial \xi_H}{\partial x}\frac{\partial x}{\partial g} \quad (33)$$

Callaghan and Pinder[7] determined the effective exponent for the concentration dependence of D_s by the following procedure. It was assumed that D_s could be written in terms of an effective exponent α as

$$D_S \sim C^{\alpha} \quad (34)$$

Equation 29 shows that, with $\xi_S \sim g^{\nu_S}$, D_S can also be written as

$$D_S \sim N^{-2}\xi_S^{2/\nu_S}\xi_H^{-1} \quad (35)$$

When eq 20 with $\xi_S \sim g^{\nu_S}$ and $\xi_H \sim g^{\nu_H}$ is used, it is found that

$$\xi_S \sim C^{\nu_S/(1-3\nu_S)} \quad (36)$$

and

$$\xi_H \sim C^{\nu_H/(1-3\nu_S)} \quad (37)$$

so the effective exponent is

$$\alpha = \frac{2-\nu_H}{1-3\nu_S} \quad (38)$$

The explicit formulas for ν_H and ν_S, which are found when ν is taken to be $^3/_5$, are

$$\nu_H = \frac{-21x + 4x^2 + 45x^{\nu}}{-21x + 2x^2 + 75x^{\nu}} \quad (39)$$

and

$$\nu_S = -\frac{12x - 11x^2 - 45x^{-2\nu}}{24x - 11x^2 + 75x^{-2\nu}} \quad (40)$$

Alternatively, it is possible to find an expression for the effective exponent α using the method of Daoud and Jannink,[6] who calculated the effective exponents for the concentration and temperature dependence of the cooperative diffusion coefficient in semidilute solutions.

The general scaling form of g is[6]

$$g \sim C^{-5/4}\tau^{-3/4}f(C/\tau) \quad (41)$$

so that

$$D_S \sim g^2\xi_H^{-1} \sim \tau^{-3}f(C/\tau) \quad (42)$$

In terms of effective exponents

$$D_S \sim C^{\alpha}\tau^{\beta} \quad (43)$$

Since we are insisting on a power law for D_S, the relationship between α and β can be found by comparing eqs 42 and 43 and assuming that $f(C/\tau)^z$, where z is as yet undetermined. This gives

$$\beta = -(3 + \alpha) \quad (44)$$

The effective expnent α is easily found by the following method. First, we write the effective exponent as

$$\alpha = \left(\frac{\partial \log D_S}{\partial \log C}\right)_{\tau} = \left(\frac{\partial \log D_S}{\partial \log g}\right)_{\tau}\left(\frac{\partial \log g}{\partial \log C}\right)_{\tau} \quad (45)$$

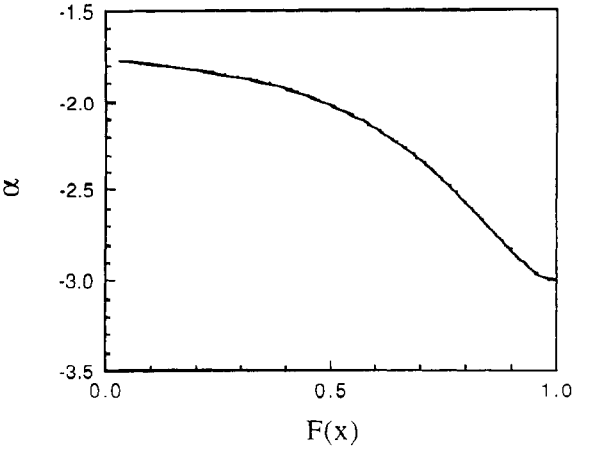

Figure 3. Effective exponent for the concentration dependence of the reptation self-diffusion coefficient according to the blob model. The horizontal axis is $F(x) = (C/C_\theta^*)/(\tau/\tau^*)$.

Then, since

$$D_S \sim \xi_S^{2/\nu_S}\xi_H^{-1} \quad (46)$$

we find

$$\left(\frac{\partial \log D_S}{\partial \log g}\right)_{\tau} = 2 - \nu_H \quad (47)$$

Daoud and Jannink[6] give an expression for the second factor in eq 45

$$\left(\frac{\partial \log g}{\partial \log C}\right)_{\tau} = \frac{24x - 11x^2 + 75x^{-2\nu}}{60x - 44x^2 - 60x^{-2\nu}} \quad (48)$$

Substitution of eqs 47 and 48 into eq 45 then gives the desired result

$$\alpha = (2 - \nu_H)\frac{24x - 11x^2 + 75x^{-2\nu}}{60x - 44x^2 - 60x^{-2\nu}} \quad (49)$$

Note that eqs 49 and 38 are equivalent. Both α and C/τ can be calculated as functions of x ($x = N_\tau/g$) so that α can then be plotted against C/τ, as is done in Figure 3.

We can define a universal quantity involving D_S by rearranging the right-hand side of eq 43 in terms of C/τ:

$$D_S \sim (C/\tau)^{3+\alpha}C^{-3} \quad (50)$$

Therefore

$$D_S C^3 \sim (C/\tau)^{3+\alpha} \quad (51)$$

is a function of C/τ only and is therefore universal.

It is also possible to construct a universal ratio involving the self-diffusion coefficient, D_S, by the method used for other properties above. If we remove the molar mass, temperature, and viscosity variations in D_S, the quantity we are left with is the reduced diffusion coefficient

$$D_S N^2 \eta T_\theta / D_{S\theta} N_\theta^2 \eta_\theta T = (g/g_\theta)^2(\xi_{H\theta}/\xi_H) \quad (52)$$

which can be written, by using previously calculated results, as

$$D_{red.} = (88/B)^{9/2}(G/56)/x^5 \quad (53)$$

This result is clearly dependent only on x and is plotted in Figure 4.

5. Discussion

The models for the cooperative and self-diffusion coefficients discussed here clearly suffer from several limitations. The usual derivations of the scaling laws for

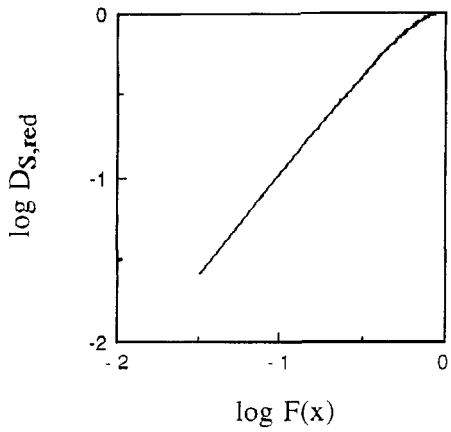

Figure 4. Universal plot for the reduced self-diffusion coefficient calculated by using the blob model.

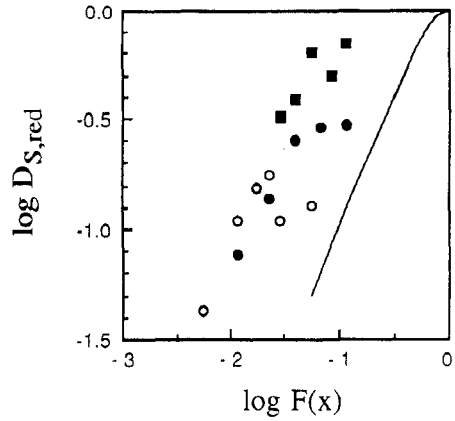

Figure 5. Comparison of the universal plot of Figure 4 with the data of Kim et al.[15] The molar masses of probe polymers (in kg mol^{-1}) were 1800 (○), 900 (●), and 390 (■).

the cooperative and self-diffusion coefficients[11] ignore the increase in local friction that occurs near the glass transition temperature. This effect is often described by using free-volume theory,[12] but it has not been included at all in this work. Experimental studies designed to test relationships derived by using scaling laws and the blob model have in recent times concentrated on solutions of high molar mass polymers so that a large semidilute region that is still relatively dilute in absolute terms is available and free-volume effects are minimized. This is true of the experimental data of Adam and Delsanti[9] plotted in Figure 2.

The derivation of eq 29 assumes that self-diffusion occurs by reptation alone. Recent experimental and theoretical studies have shown that other mechanisms such as Stokes–Einstein diffusion,[13] constraint release,[14] and contour length fluctuation[14] can contribute to the self-diffusion coefficient of a monodisperse polymer solution. However, reptation is expected to be the dominant mechanism for the self-diffusion of a probe chain in a matrix composed of much longer chains.

Equation 53 suggests that if the mechanism for diffusion is purely reptation, a universal plot should be obtained by plotting the reduced diffusion coefficient against $(C/C_\theta^*)/(\tau/\tau^*)$. The experimental data of Kim et al.[15] can be used to check the validity of eq 53. Kim et al.[15] measured D_S as a function of matrix molar mass P for different values of the probe molar mass N and matrix concentration. The value of D_S decreased and then became independent of P as P was increased to 3–4 times N. The extrapolated results of Kim et al.[15] probably satisfy the requirement for pure reptation, but $D_S(\theta)$ is unknown for the polystyrene–toluene system. One way of avoiding this problem would be to simply plot D_S/C^{-3} because D_S would be expected to scale as C^{-3} under Θ conditions. It is possible to do slightly better than that by using an approximate fit to Θ-solvent data collected in this laboratory.[16] The data in the power law region of the plot of log $(D_S M^2 \eta_0/T)$ against C can be approximately described by

$$\log (D_S M^2 \eta_0/T) = -1 - 3 \log C \qquad (54)$$

Taking $\theta = -41$ °C[3] for polystyrene in toluene and $C_\theta^*/\tau^* = 14\,800$ kg m^{-3}, the plot shown in Figure 5 is obtained. Data measured at concentrations below C^* have been omitted as have data for probe molar masses less than 100 000 g mol^{-1}. Figure 5 shows some interesting features. For each molar mass, the slope just above C^* is consistent with the asymptotic slope of the theoretical curve. This is in agreement with the −1.75 exponent expected for the concentration dependence of D_S in a good solvent. (Note that the asymptotic slope in Figure 5 is determined by log $D_S/D_S(\theta)$, giving −1.75 + 3 = 1.25.) As the concentration is increased, the curve for each molar mass flattens out, corresponding to a change in the effective exponent from −1.75 to −3. The concentration at which the change occurs increases with decreasing molar mass, a feature which was also noted by Callaghan and Pinder[7] in their work on the self-diffusion of polystyrene in good solvents with $N = P$. If the change in slope is due to crossover from the semidilute good to the semidilute Θ regions of the τ–C diagram, it would be expected to occur at the same concentration, C^{**}, for all molar masses. An alternative explanation is that the change in slope occurs due to a molar mass dependent increase in the effective local friction. Attempts have often been made to quantify the local friction effect by measuring the self-diffusion coefficient of a small molecule in the solution. Such measurements give a friction factor having a concentration dependence that is approximately independent of the polymer molar mass (provided that the molar mass is high enough for T_g to be essentially molar mass independent). However, the friction factor of a small probe molecule cannot give a completely adequate analogue of the effect of concentration on the effective friction on a polymer chain. Kim et al.[15] have pointed out that a small probe molecule is not equivalent to the hydrodynamically screened unit (blob), which determines dynamic behavior in the semidilute region. They estimated the concentration at which the effective local friction becomes important by plotting the value of D_S at C^* for each molar mass (obtained by interpolation of their data) against C. This assumes that the effective local friction does not depend on molar mass. The deviation of this quantity from power law behavior was taken as indicative of a deviation of the local effective viscosity from η_0. An alternative indirect measurement of the effective local friction might be possible by observing the deviation of the cooperative diffusion coefficient D_c from power law behavior with a plot similar to Figure 5. Such an investigation would be free of the extra complexities introduced by constraint release effects and contour length fuctuations that affect self-diffusion measurements.

Fleischer and Straube[17] have used a method similar to that described here in their discussion of self-diffusion in polystyrene–benzene solutions. It should be noted that the plot of α_H^{-1} for a blob appearing in their Figure 4 cannot be interpreted as $\xi_{H\theta}/\xi_H$ because it has the wrong asymptotic concentration dependence at low values of concentration. At low concentrations, this quantity would

be expected to decrease with increasing concentration with an exponent of $-1 + 0.75 = -0.25$. Their method is difficult to relate to previous work, whereas the one presented here follows directly from other studies that employ the blob model for the description of dilute[3] and semidilute[6] solutions.

Marmonier and Léger[18] have proposed a universal plot for the self-diffusion coefficient that differs from the one suggested by eq 53. They showed that a plot of D_S/D_0 against C/C^* for polystyrene in benzene reduced the data to a single universal curve, and they also gave a theoretical justification of the plot based on the scaling laws for a semidilute solution of a polymer in a good solvent. Later work[19] showed that Θ-solvent data collapsed to a different common curve when plotted in this way. It is therefore clear that such a plot is not universal with regard to changes in solvent quality, and it is also apparent from their theoretical arguments that this plot does not allow for the crossover from the semidilute good-solvent region to the semidilute Θ-solvent region.

Similar comments can be made regarding recently published renormalization group studies of diffusion.[20] Although renormalization group methods promise to provide improved theoretical predictions in the future, the studies of cooperative and self-diffusion coeficients are as yet restricted to the good-solvent limit and crossover effects have so far been neglected.

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