Universal Scaling Equation for Self-Diffusion by Macromolecules in Solution[†]

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ABSTRACT: A phenomenological scaling equation for the self-diffusion coefficient $D_s(c)$ of macromolecules in solution is obtained. The equation agrees with all modern studies of $D_s(c)$ of synthetic polymers and proteins. For each species, a single set of parameters suffices for all polymer concentrations up to the highest studied (in one case, the melt). $D_s(c)$ curves for large polymers in semidilute solution differ only numerically from $D_s(c)$ curves for low molecular weight polymers or globular proteins, the same functional form (and simple molecular weight dependences for parameters) describing all cases. When enough data are available, parameters obtained with only dilute ($c < c^*$) solution data predict $D_s(c)$ in semidilute and concentrated solutions. The scaling equation lacks c^x or M^{-2} scaling. Reptation is probably not important for polymer self-diffusion in solution.

Introduction

In the past decade, extensive studies have been made of self-diffusion by synthetic and natural macromolecules in dilute and concentrated solution. The self-diffusion coefficient D_s of a macromolecule depends strongly on macromolecule concentration c. For a homologous series of polymers, D_s depends systematically on polymer molecular weight M. Modern studies of polymer self-diffusion are reviewed by Tirrell;[1] ref 2 notes recent work on protein self-diffusion.

Studies of synthetic polymers have largely been motivated by the theoretical models of Edwards[3] and de Gennes.[4] These models divide random-coil polymer solutions into three regimes: dilute solutions (in which the spacing between polymer molecules is much larger than their radius of gyration R_G), semidilute solutions (in which neighboring polymer coils overlap), and concentrated solutions (melts and meltlike solutions dominated by polymer–polymer friction). The concentration separating the dilute and semidilute regimes is c^*; the concentration separating the semidilute and concentrated regimes is c_e.

In these models, polymer self-diffusion in each regime is proposed to occur by fundamentally different physical processes. In dilute solutions, polymer molecules move nearly independently of each other, D_s being determined primarily by R_G. In semidilute and concentrated solutions of high molecular weight polymers, self-diffusion is said to occur by reptation. In this process, each polymer molecule is contained in a "tube", the tube walls being formed by nearby polymer molecules. Diffusion of the tube perpendicular to its length is slow, so transverse diffusion of a polymer chain is inhibited by collisions with neighboring polymers in the tube walls. Motion along the length of the tube is not substantially inhibited by chain–chain collisions, so lateral diffusion (parallel to the tube axis) is relatively fast. A more detailed analysis gives[4]

$$D_s \sim M^{-2} \qquad (1)$$

as a signature (in semidilute solution) for reptation. Calculations of the concentration dependence of D_s in the semidilute regime find[4]

$$D_s \sim c^{-1.75} \qquad (2)$$

for good solvents, and[5]

$$D_s \sim c^{-3} \qquad (3)$$

for Θ solvents. In addition to de Gennes' model, Schaeffer et al.[6] advance a "marginal solvent" model for polymer dynamics, which includes reptation and a mean-field approximation for polymer excluded volume interactions, predicting $D_s \sim M^{-2}c^{-2.5}$.

The reptation concept is subject to several criticisms. In particular, the "walls" of the tube are made of the same type of polymer molecule as is found within the tube. Transverse diffusion of a portion of the tube wall and transverse diffusion of part of the polymer within the tube are the same physical process. These two transverse diffusion events should be characterized by the same diffusion coefficient, contrary to the reptation assumption that transverse tube diffusion is far slower than transverse polymer diffusion. Tube walls, which diffuse as rapidly as the polymers which they contain, cannot greatly hinder polymer motion. (Reptation has also been proposed for polymers in true gels, where the tube walls are actually immobile). Furthermore, in semidilute solution, tube ends have the same nature as tube walls, so chain–chain collisions should inhibit lateral ("reptatory") diffusion as well as transverse diffusion.

Literature data for D_s are treated below. Most studies of D_s are not grossly inconsistent with the predicted M^{-2} behavior. However, plots of log D_s against log c usually show smooth curves of progressively increasing curvature, not the straight lines predicted by eq 2 and 3. While these curves have tangents with the theoretical slopes −1.75 and −3, they also have tangents of every other slope[7] from 0 to −13. The varying slope has been explained by invoking a decrease in solvent quality with increasing polymer concentration, causing eq 3 to replace eq 2 near some concentration c_x. In the absence of numerical predictions for c_x, it is hard to demonstrate that this explanation is correct.

Our interest in polymer self-diffusion was inspired by our recent studies of the diffusion coefficient D_p of optical probes (polymer colloids and proteins) in solutions of synthetic polymers[8-14] and proteins.[15] D_p usually obeys a simple scaling law,[16] namely

$$D_p = D_0 \exp(-ac^\nu M^\gamma R^\delta) \qquad (4)$$

where D_0 is the probe diffusion coefficient in pure solvent, c and M are the concentration and molecular weight of the background polymer, R is the probe radius, and ν, γ, and δ are scaling coefficients. Experimentally[16] $\nu = 0.6$–1.0, $\gamma = 0.8 \pm 0.1$, and $\delta = 0$. These values are substantially inconsistent with theoretical[17-20] predictions $\gamma = 0$ and $\delta = 1$ for probe diffusion in open-coil polymer solutions.

Probe diffusion and macromolecule self-diffusion describe similar motions of large, colliding macromolecules. The primary hypothesis of this paper is that probe diffusion and self-diffusion also have the same fundamental mechanism. From this hypothesis, the scaling law for probe diffusion in a given system should be basically the same as the scaling law for self-diffusion in that system. The scaling equation for probe diffusion is eq 4. I therefore predict the scaling equation for macromolecule self-diffusion to be

$$D_s = D_0 \exp(-\alpha c^\nu) \tag{5}$$

D_0 is the diffusion coefficient of an isolated macromolecule. By comparison with eq 4, D_0 and the scaling coefficients α and ν are predicted to depend on M.

Experimentally, probe particles in polymer solutions obey the same scaling law as probe particles in protein solutions,[15] so the hypothesis predicts that polymer self-diffusion and protein self-diffusion follow the same equation—a unique scaling law for all macromolecules. Protein solutions lack distinct semidilute and dilute concentration regimes, so D_s of polymers should also not distinguish between "semidilute" and "dilute" solutions. In eq 5, a single set of parameters should suffice at all concentrations, dilute and semidilute, of a given polymer. There are no published results on probe diffusion in polymer melts or solutions of charged linear polyelectrolytes, branched polymers, or star polymers, so these systems are not treated further here.

The hypothesis does not specify how macromolecules move through concentrated solutions. However, *globular probe particles cannot reptate. If probe and polymer diffusion have the same mechanism, as is our hypothesis, reptation must not be important for polymer self-diffusion in solution.*

The remainder of this paper tests the hypothesis. The next section compares eq 5 with the experimental concentration dependence of D_s. A further section examines M^{-2} scaling, as implied by the reptation model. The discussion extracts the M dependence of α and ν, compares the findings with the reptation hypothesis, and proposes an image for self-diffusion which is consistent with the actual data.

Concentration Dependence of D_s

This section tests our scaling eq 5 against experimental studies by Brown et al.[21-23] Callaghan and Pinder,[24-27] Gros,[28] Hanley et al.,[29] Kitchen et al.,[30] von Meerwall et al.,[31,32] Wesson et al.,[7] Leger and co-workers,[33,34] Nemoto et al.,[35] Smith et al.,[36] Daivis et al.,[37] and Arunyawongsakorn et al.[38] The studies reviewed by Tirrell[1] are included.

Data analysis used a nonlinear least-squares fitting program given by Noggle.[39] Errors in D_s are generally a fixed fraction of its nominal value, so we minimized the fractional difference

$$\sum_{i=1}^{N} [(D_i - T_i)/D_i]^2$$

between experiment and theory. Here the sum is over all N data points, D_i is the experimental value of D_s at i, and T_i is the calculated value for D_s at the point i. Graphs of data and their fits appear below. In most cases, D_s was measured from figures in the original papers.

Our scheme of data analysis is fundamentally different from that of much previous work, in which plots of D_s against c (or $M^2 D_s$ against c) were subject to graphical analysis without apparent numerical support. The combination of numerical and graphical analysis is far more
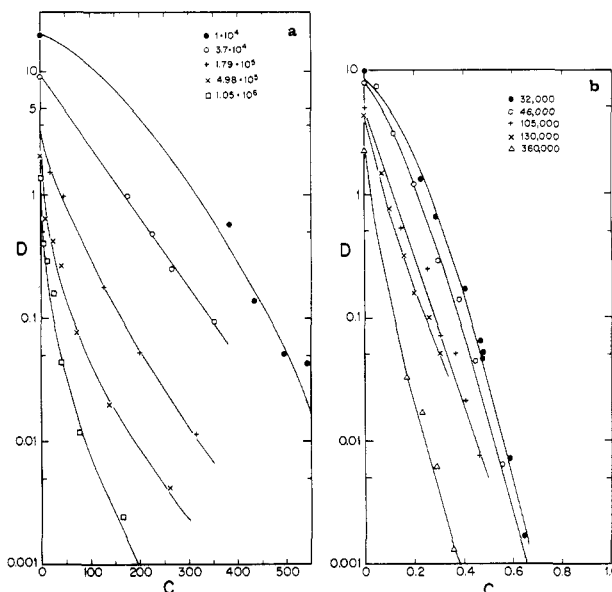
Figure 1. Self-diffusion of polystyrenes. D is in units 10^{-7} cm^2/s. Curves are fits to $D_s = D_0 \exp(-\alpha c^\nu)$. (a) gives von Meerwall et al.'s results[32] in tetrahydrofuran–hexafluorobenzene, with c in g/L, treating D_0 (here taken from ref 7) as known. (b) gives Wesson et al.'s results[7] in tetrahydrofuran, with c as the polymer weight fraction and D_0 as a free parameter.

demanding than is visual inspection of any graph. In particular, an obvious method for testing eq 5 would be to plot log (log (D)) against log c; eq 5 then gives a straight line of slope ν. This method fails with real data. The eye (and most simple fitting programs) customarily assumes that all error bars in a figure are of similar size. When this assumption is satisfied, the importance of a disagreement between a datum and a theoretical curve is the distance on the page between the point and the line. If error bars for different points are of very different size, a small distance between a curve and one point may represent a far worse failing of theory than a large difference between that curve and another point. In our case, the error in D is a given fraction of its total magnitude (say, 10% or 1%), so a figure showing log D has similar error bars for all points. In contrast, if log (log (D/D_0)) is plotted, the error bars diverge for small concentrations. Data in good agreement with eq 5 may not give a very straight line in plots of log (log (D/D_0)) against log c.

Table I gives all the numerical results. For each system, the concentration range is reported in units c/c^*. When possible c^* was calculated from R_G. Several relations between c^* and $[\eta]$ have been proposed; if R_G was unknown, $c^* = 1/[\eta]$ was used. In fitting eq 5, D_0 could be fixed (if its value were known) or used as a floating (free) parameter. When possible, both approaches were used. If D_s had been measured in dilute solution, floating or fixing D_0 gave similar answers. When data were only available for concentrated solutions (cf. Figure 3) extrapolations to c = 0 to determine D_0 were difficult.

Our detailed analyses find the following:

1. **Polystyrenes.** von Meerwall et al.[32] used pulsed-field gradient nuclear magnetic resonance (PFGNMR) to obtain D_s of polystyrenes in tetrahydrofuran (THF)–hexafluorobenzene (HFB), THF being the solvent and HFB being a tracer probe. Polymer molecular weights M ranged from 1×10^4 to 1.05×10^6, with M_w/M_n less than 1.2; c went as high as 550 g/L. D_s, which falls steeply with increasing c, extends over 4 orders of magnitude.

Figure 1a shows the experimental data, including estimates of D_0 interpolated from Wesson et al.'s work on the

Table I
Parameters from Fits to $D_s = D_0 \exp(-\alpha c^\nu)^a$

| system	ref	M(kD)	c*	$(c/c^*)_{least}$	$(c/c^*)_{most}$	$[D_0]$	α	ν	% RMS	D_0	α	ν	% RMS
polystyrene–THF–C₆F₆	32	10	0.45 g/L	0.85	1.6	[21.5]	6.9×10^{-4}	1.46	29	19.7	6.3×10^{-4}	1.47	24
		37	0.16 g/L	1.1	3.5	[10]	1.93×10^{-2}	0.99	8	9.16	1.24×10^{-2}	1.01	7
		179	0.046 g/L	0.46	9.3	[4.1]	0.106	0.70	9	3.55	8.26×10^{-2}	0.74	8
		498	0.021 g/L	0.48	12.4	[2.3]	0.36	0.52	16	2.55	0.386	0.51	16
		1050	0.011 g/L	0.58	15.2	[1.5]	0.55	0.49	24	4.02	1.09	0.38	22
polystyrene–THF	7	32	0.18 g/g	1.2	3.6	[10]	15.8	1.44	19	8.3	16.0	1.51	18
		46	0.135 g/g	0.4	4	[8]	15.7	1.32	17	8.3	15.6	1.30	17
		105	0.07 g/g	0.3	6.6	[5]	13.6	0.99	23	4.7	13.7	1.01	22
		130	0.06 g/g	1.2	5	[4.4]	12.2	0.83	14	4.6	12.2	0.82	14
		360	0.027 g/g	6	13	[2.3]	16.1	0.75	24	2.3	16.1	0.76	22
polystyrene–C₆H₁₂	7	130	0.06 g/g	0.5	2.5	[4.1]	8.2	0.60	4	2.4	11.4	0.89	1
polystyrene–C₆H₆	33	78	0.089 g/g	0.02	4.8	[5.9]	7.0	0.71	6	6.35	6.82	0.67	6
	34	123	0.062 g/L	0.13	8	[4.6]	0.071	0.68	17	9.0	0.22	0.51	6
	33	271	0.034 g/g	0.11	7.6	[3]	13.2	0.75	25	4.78	11.5	0.60	21
	33	598	0.018 g/g	0.13	14.1	[1.93]	12.7	0.54	23	2.32	12.3	0.50	22
	33	1230	0.015 g/g	1.3	30.5	[1.7]	14.2	0.53	16	3.5	13	0.42	6
	33	598; 1800	0.0076 g/g	1.3	30.5	[1.93]	14.4	0.52	29				
polystyrene–C₆D₆	27	110	68 g/L	0.6	3.4	[5.3]	0.11	0.68	7	3.6	0.058	0.79	6
		233	38 g/L	0.5	5.2	[3.3]	0.17	0.68	7	6.0	0.34	0.54	6
		350	27 g/L	0.4	6.9	[2.6]	0.20	0.65	8	4.1	0.33	0.57	7
polystyrene–CCl₄	25	2	∞			[28]	0.0072	0.99	10	24.7	0.0037	1.09	10
	27	110	68 g/L	0	4.1	[3.6]	0.078	0.75	12	3.23	0.062	0.78	12
	27	233	38 g/L	0	7.4	[2.3]	0.19	0.62	10	2.49	0.214	0.60	9
	27	350	27 g/L	0	8.1	[1.85]	0.21	0.63	9	1.86	0.213	0.63	9
polybutadiene–CCl₄	31	75	8.6 g/L	0.53	6	[2.8]	0.059	0.84	3	2.87	0.064	0.82	3
		90	7.4 g/L	0.56	5.8	[2.57]	0.119	0.74	2	2.54	0.115	0.75	2
human hemoglobin	28	1.6[b]	N/A	N/A	N/A	[8.25]	4.7×10^{-4}	1.49	17	6.53	6.3×10^{-5}	1.81	13
Lumbricus hemoglobin	28	45.6[b]	N/A	N/A	N/A	[1.30]	1.2×10^{-4}	1.78	11	1.14	1.1×10^{-5}	2.21	8
bovine serum albumin	30	2.56[b]	N/A	N/A	N/A	[6.22]	6.6×10^{-4}	1.42	7	5.81	8.4×10^{-5}	1.80	6
bovine serum albumin	38, 43	2.65[b]	N/A	N/A	N/A	[5.9]	4.7×10^{-6}	1.86		[5.9]	2.3×10^{-5}	[2.0]	
dextran–water	22	44	39 g/L	0.7	8.4	[9.86]	9.0	0.98	7	9.78	8.0	0.96	7
dextran–water	26	179		2.6 g/L	380 g/L	[2.4]	0.073	0.68	8	2.29	0.065	0.70	8
dextran–dextran–water	37	864; 20	96 g/L	0	1.8	[1.08]	0.0064	1.17	13	1.11	0.0071	1.15	13
poly(propylene oxide)–poly(propylene oxide)	36	32; 1	200 g/L	0	5					0.0523	3.89	0.66	6
polystyrene–poly(vinyl methyl ether)–o-fluorotoluene	29, 47	50; 60	25 g/L	2.0	16	[5.85]	0.107	0.65	4	7.37	0.146	0.61	3
		179; 60	25 g/L	1.0	15	[3.21]	0.126	0.68	23	1.52	0.036	0.87	19
		1050; 60	25 g/L	0.7	16	[1.29]	0.121	0.70	15	1.98	0.20	0.62	12
		1800; 60	25 g/L	0.4	4.0	[1.00]	0.196	0.61	21	0.70	0.085	0.77	20
poly(methyl methacrylate)–polystyrene–thiophenol		343; 44	0.036 g/g	0.28	4.7	[1.32]	0.21	0.91	3	1.56	0.32	0.77	1
		343; 186	0.013 g/g	0.26	7.0	[1.32]	0.46	0.80	3	1.43	0.54	0.74	2
		343; 775	0.005 g/g	0.20	34	[1.32]	0.89	0.65	7	1.16	0.78	0.69	6
	35	343; 8420	9.1×10^{-4} g/g	0.56	42	[1.32]	1.24	0.54	7	1.48	1.35	0.51	10

[a] Ref = reference, M = polymer molecular weight (when two molecular weights are listed, the first is the probe, while the second is the matrix), c/c^* = concentration in units of c^* (c^* from R_G[41] when possible; elsewise $c^* = 1/[\eta]$), brackets indicate that a parameter was fixed rather than being adjusted, and % RMS = percent root-mean-square fractional error in the best fit to the data. D has units 10^{-7} cm²/s, c has units g/L except for ref 7, 22, 33, and 36, for which c is the polymer weight fraction. N/A = not applicable. [b] M_s; see text.

same solvent.[7] Essentially all data are for $c > c^*$. The smooth curves are fits at each M, with D_0 held fixed. Floating D_0, besides slightly improving the RMS fit, usually has (Table I) only a modest effect on D_0, some effect on α, but little effect on ν. As seen in the figure, eq 5 describes measurements to within experimental error.

Polystyrenes in THF were also examined by Wesson et al.,[7] who employed forced Rayleigh scattering (FRS) to measure D_s of 4-(bromomethyl)azobenzene-labeled materials. Polystyrenes with M of 32 000, 46 000, 105 000, 130 000, and 360 000 were used; polymer weight fractions ranged from 0.048 to 0.648. Almost all measurements had $c > c^*$. Experimental data (and D_0 values which Wesson et al. based on the data of Mandema and Zeldenrust[40]) appear in Figure 1b. The curves in the figure refer to fits which retain D_0 as a free parameter. Table I shows that fixing D_0 only has small effects on the parameters α and ν. Agreement of the data with the scaling law is good, even

though D_s varies over 4 orders of magnitude.

Polystyrenes in CCl₄ were examined by von Meerwall et al.[31] and by Callaghan and Pinder.[24–27] von Meerwall et al.[31] used only dilute solutions (<60 g/L). Callaghan and Pinder[25,27] used PFGNMR to obtain $D_s(c)$ out to high concentrations (>200 g/L) for M = 2000, 1.1×10^5, 2.33×10^5, and 3.5×10^5. Their materials has $M_w/M_n < 1.1$. Figure 2 shows that the scaling law works well in dilute as well as concentrated solutions. Vertical arrows mark c^*; there is no evidence of a discontinuity between $c \ll c^*$ and $c \gg c^*$. Indeed, (Table II) it is possible to compute α and ν with only data on dilute ($c \, l \, c^*$) solutions; for the 233 000 and 350 000 amu polymers, there is excellent agreement between this fit and a fit made exclusively to high-concentration data. Floating D_0 has only a small effect on the fit, supporting the internal consistency of the small- and large-c data. von Meerwall et al.[31] also report results on polybutadiene–CCl₄. As seen in Table I, the
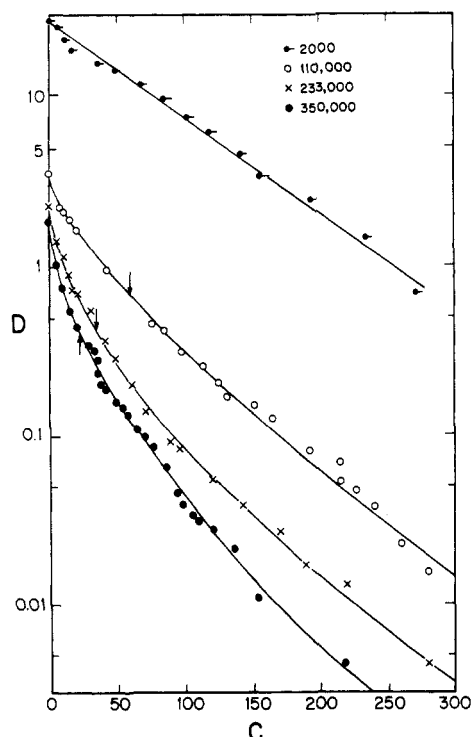
Figure 2. Self-diffusion of polystyrenes in CCl_4, from Callaghan and Pinder.[24-27] D has units 10^{-7} cm^2/s; c has units g/L. Curves are fits to $D_s = D_0 \exp(-\alpha c^\nu)$ using the measured value of D_0. Arrows indicate c^* from ref 27. Parameters (Table II) deduced exclusively at $c < c^*$ can predict D_s at $c > c^*$.

Table II
Fit of the Data of Callaghan and Pinder[25,27] on
Polystyrene–CCl_4 to $D = D_0 \exp(-\alpha c^\nu)$ Comparing
Parameters Obtained with All Data to Parameters
Obtained by Considering Only Results on Dilute ($c < c^*$)
Solutions[a]

$M(kD)$	all data	$c < c^*$
350	$\alpha = 0.211$	$\alpha = 0.221$
	$\nu = 0.627$	$\nu = 0.618$
	% RMS = 3.1	% RMS = 2.1
233	$\alpha = 0.192$	$\alpha = 0.186$
	$\nu = 0.617$	$\nu = 0.609$
	% RMS = 7.1	% RMS = 6.4
110	$\alpha = 0.0775$	$\alpha = 0.104$
	$\nu = 0.75$	$\nu = 0.67$
	% RMS = 6.2	% RMS = 2.8

[a] D_0 was fixed, not floated.

RMS error in the fit to this data is <3%.

Callaghan and Pinder[27] report D_s for polystyrenes (M = 1.10 × 10^5, 2.33 × 10^5, and 3.50 × 10^5) in perdeuterio-benzene. From Figure 3, the scaling law also describes these data. D_0 was estimated from Callaghan and Pinder's work on polystyrene–CCl_4 by correction for solvent viscosity. With D_0 fixed, α and ν show a smooth dependence on M. Since measurements were only made at large c, treating D_0 as unknown (and making the long extrapolation to $c = 0$) gave relatively more scattered results.

The early data of Hervet, Leger, and co-workers[33,34] on polystyrene–benzene appear in Table I. D_0 of the 78 000 amu species was obtained from a short linear extrapolation to $c = 0$; D_0 of the other species was computed by assuming $D_0 \sim M^{-0.55}$, in accord with Leger et al.'s assertion[34] that their data follow those of Adam and Delsanti.[41] Leger et al.'s data is unique in that it finds $dD_s/dc > 0$ at small c, a behavior not described by the scaling law nor seen in other studies of polystyrene solutions. With D_0 fixed, α, ν, and the RMS error are similar to those from fits to other
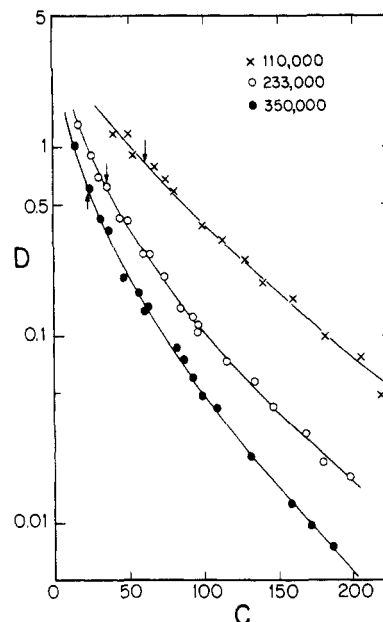
Figure 3. Self-diffusion of polystyrenes in perdeuteriobenzene, from Callaghan and Pinder[27]. D has units 10^{-7} cm^2/s; c is in g/L. Curves are fits to $D_s = D_0 \exp(-\alpha c^\nu)$, with D_0 as a free parameter.
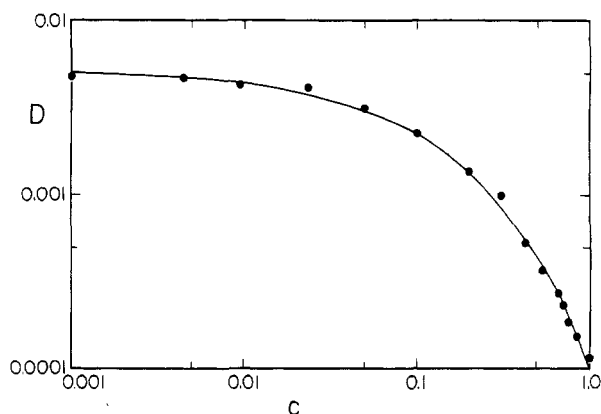
Figure 4. Diffusion of 33 600 amu poly(propylene oxide) through 1000 amu poly(propylene oxide). Line is a fit to $D_s = D_0 \exp(-\alpha c^\nu)$, with D_0 a free parameter. D_s has units 10^{-7} cm^2/s; c is the weight fraction of the large polymer.

polystyrene studies. Leger et al.[34] report $c^{-1.7}$ scaling of D_s, which is not consistent with our scaling form. Figure 5 of ref 34 shows that the reported $c^{-1.7}$ scaling includes a straight line through three data points, a straight line through four data points, and a straight line near data (on the 754 000 amu polymer) which is visibly curved. Table I also shows one of Leger et al.'s mixed systems (labeled 598 000 amu polymer in unlabeled 1.8 × 10^6 amu polymer). α and ν of the mixed system are different from α and ν for self-diffusion of the 598 000 amu polymer. As is apparent from ref 34, Figure 7, but contrary to Leger et al.'s description[34] of their own data, the 598 000 amu polymer diffuses through a matrix of larger polymer nearly twofold more slowly than it diffuses through itself.

Smith et al.[36] report work on 33 600 amu poly(propylene oxide), using low molecular weight poly(propylene oxide) ($M = 1000$) as the solvent. The vapor pressure of the smaller polymer is low, permitting the weight fraction of the large polymer to range from near zero all the way to the melt. For this system, the critical molecular weight for entanglement is 6000–7000, so M/M_c is 5 or more.[42] As seen in Figure 4, the scaling law fits D to within 6%, with no evidence of systematic deviations at large c, as would
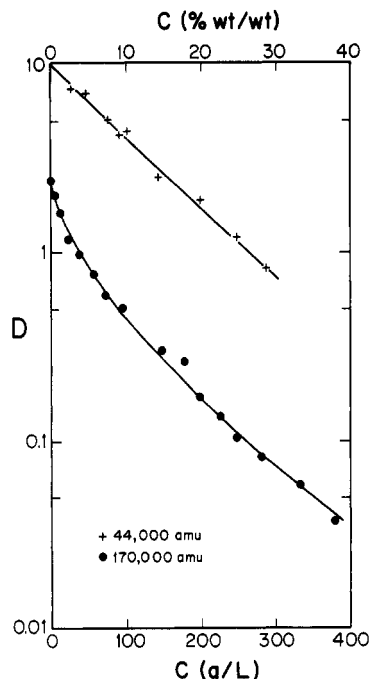
Figure 5. Self-diffusion of 44 000 amu[22] and 170 000 amu[26] dextran in water. Lines are fits to $D_s = D_0 \exp(-\alpha c^\nu)$.

Figure 6. Self-diffusion coefficient of human and *lumbricus terrestris* hemoglobins[28] and bovine serum albumin.[30] Lines represent fits to eq 5, keeping D_0 as a free parameter. D_s has units 10^{-7} cm^2/s; c is in g/L.

be expected if a crossover occurred to a distinct meltlike behavior.

2. Long-Chain Polymers in Water. Brown et al.[23] used PFGNMR to measure D_s of poly(ethylene oxide)–water. The poly(ethylene oxides) had $M = 7.3 \times 10^4$, 1.48 $\times 10^5$, 2.78 $\times 10^5$, and 6.61 $\times 10^5$ and $M_w/M_n = 1.02$–1.10. In the concentration range 0–20 g/L, log D_s is linear in c, consistent with eq 5 for $\nu = 1$. As c was never large, nonlinearities in log D_s–c plots could have been masked by experimental error, so $\nu \neq 1$ is not rigorously excluded. D_s of the 148 $\times 10^3$ amu polymer decreases more and more swiftly with increasing c, but there are not enough data points for a nonlinear fit.

Brown, Stilbs, and Johnsen[22] report D_s for dextran–water ($M_w = 64\,200$, $M_n = 44\,000$) at concentrations of 2.72–28.6 wt % at $T = 75$ °C. The fit (Table I, Figure 5) confirms that log D_s is virtually linear in c; we obtain $\nu = 0.96$, with <7% RMS fractional error. Dextran–water was also studied by Callaghan and Pinder,[26] who observed 1.7 $\times 10^5$ amu dextran for c as high as 375 g/L. Equation 5 describes the data well (8% RMS fractional error; Table I, Figure 5) with $\nu = 0.67$. Finally, Daivis et al.[37] report eht diffusion of dilute solutions of $M = 864\,000$ dextran through dilute to concentrated solutions of $M = 20\,400$ dextran. For D_0 fixed or allowed to float, the results of Daivis et al. fit reasonably well (13%) with $\nu = 1.15$ or so. ν shows a consistent inverse dependence on M of the matrix polymer, decreasing from 1.16 at 20 400 amu through 0.96 at $M = 64\,200$ to 0.67 at 170 000 amu.

3. Proteins. Gros[28] reports tracer diffusion studies on human and *lumbricus terrestris* hemoglobins for c up to 433 g/L. Equation 5 was fit separately to data on *lumbricus* hemoglobin and on human hemoglobin, with Gros' measurements[28] on human hemoglobin (taken only for c > 90 g/L) being supplemented by literature values[28] at lower c. D_0 could be obtained by extrapolation; there is reasonable agreement (Figure 6) with the scaling law.

Kitchen et al.[30] measured D_s of serum albumin with the open-capillary method. Figure 6 shows Kitchen et al.'s findings and our fit. While the points are somewhat scattered, the scaling law is adequate at all concentrations. More recently, Arunyawongsakorn et al.[38] used holographic
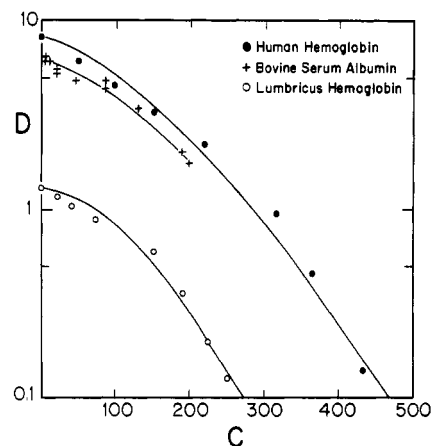
relaxation spectroscopy to study this system. For the concentration range 0–260 g/L, eq 5 (with D_0 fixed) describes the data for $\nu = 1.86$ or $\nu = 2$.[43]

4. Self-Diffusion in Mixtures. D_s determines the diffusion of a polymer probe through a background matrix of other polymer molecules. In the above, the probe polymer was chemically virtually identical with the matrix polymers. As an alternative, the probe and matrix polymers could be chemically distinct. In applying eq 5 to mixed systems, we find that D_0 refers to the probe, while c refers to the background matrix. Besides the aforementioned dextran–dextran–water results of Daivis et al.[37] mixed-polymer studies including the following:

Poly(ethylene oxide) in water–dextran was observed by Brown and Stilbs.[21] These authors identify their best results as those on poly(ethylene oxides) of $M_w = 7.3 \times 10^4$ and 2.78 $\times 10^5$ in dextrans of $M_w = 1.9 \times 10^4$, 1 $\times 10^5$, and 5.1 $\times 10^5$. While dextran concentrations were bounded above the miscibility limit of dextran with poly(ethylene oxide), measurements included both $c < c^*$ and $c > c^*$. A plot of log D_s against c gave a continuous, straight line, implying $\nu = 1$. There is no hint of a change in polymer dynamics near c^*, in agreement with our working hypothesis.

Hanley, Tirrel, and Lodge[29] used quasi-elastic light scattering spectroscopy (QELSS) to observe polystyrene in poly(vinyl methyl ether)–o-fluorotoluene. QELSS and related fluctuation techniques generally measure the mutual diffusion coefficient, not the tracer diffusion coefficient.[44] However, in a system in which only one, dilute, macromolecule species scatters light, the spectral line width yields a number which is indistinguishable from the self-diffusion coefficient of the scattering (probe) species in a pseudobinary probe–(mixed, polymeric solvent) system.[45,46] Here polystyrene was the probe, the other components being isorefractive and hence nonscattering. Polystyrenes of $M = 5.0 \times 10^4$, 1.79 $\times 10^5$, 1.05 $\times 10^6$, and 1.8 $\times 10^6$ were studied in poly(vinyl methyl ether) (PVME) solutions; the PVME had $M = 60\,000$ and $M_w/M_n \sim 3$. From the intrinsic viscosity and $c^* = 1/[\eta]$, $c^* \sim 25$ g/L for PVME (Hanley et al. use $c^* \sim 3/[\eta]$ and quote a larger c^*). Experiments included some points with $c < c^*$ and substantial data out to >300 g/L PVME. For three of the polystyrenes, D_0 was measured directly;[47] the fourth D_0 was extrapolated from a scaling law. Because of the substantial extrapolation from the smallest c studied to $c = 0$, fits with D_0 fixed are more stable than results which used D_0 as a free parameter. Excepting two outlier points, Hanley et
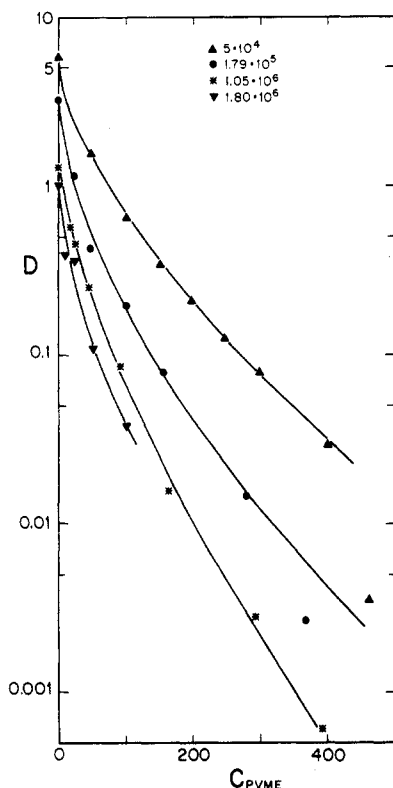
Figure 7. Diffusion of polystyrenes through poly(vinyl methyl ether)–o-fluorotoluene.[29] Lines are fits to the scaling law $D_s = D_0 \exp(-\alpha c^{\nu})$, using D_0 based on ref 7 and 47. D_s has units 10^{-7} cm^2/s; c (of poly(vinyl methyl ether)) is in g/L.

Table III
Parameters from Nonlinear Least-Squares Fits of Data with $c > c^*$ on Each Polymer–Solvent System to the Form $D_s = aM^b \exp(\alpha c^{\nu})$ for b either Allowed to Vary or Fixed at $b = -2$[a]

system	ref	a	b	α	ν	% RMSE
polystyrene–THF–HFB	32	6.02×10^5	-1.83	-16.4	0.78	32
		1.53×10^6	[−2]	-18.0	0.82	35
polystyrene–THF	7	1.82×10^5	-2.04	-16.1	1.36	25
		1.62×10^5	[−2]	-15.9	1.33	29
polystyrene–CCl$_4$	27	1.53×10^5	-1.78	-0.59	0.45	14
		2.53×10^5	[−2]	-0.35	0.53	20
polystyrene–C$_6$D$_6$	27	1.1×10^5	-1.71	-0.53	0.47	17
		1.24×10^5	[−2]	-0.15	0.66	21
polystyrene–PVME-oFT	29 47	4.85×10^3	-0.91	-0.99	0.36	

[a] Ref = reference, a, b, α, and ν are the fitting parameters, % RMSE is the root-mean-square fractional error in the fit, and brackets denote a parameter which was held fixed. M has units kilodaltons; units of c are as in the original references; D has units 10^{-7} cm^2/s.

Figure 8. Force fit of von Meerwall et al.'s[32] data (from Figure 1a) on polystyrene–THF–HFB for $c > c^*$ to eq 6. Agreement between data and theory has been forced; the theoretical form has too steep a slope for low molecular weights but has too shallow a slope for the highest molecular weight points. The solid line is obtained with b as an adjustable parameter; dashed line has b fixed at −2.

al.'s[29] results (Figure 7) are described well by eq 5.

Recently, Nemoto et al.[35] reported self-diffusion and sedimentation coefficients D_s and s of poly(methyl methacrylate) probes ($M = 343\,000$) in thiophenol. The matrix polymers were polystyrenes, with $M_w = 43\,900$, $186\,000$, $775\,000$, and 8.42×10^6. Nemoto et al. found that their data (both on D_s and on s) are described well by the functional form proposed here; reanalysis (Tabler I) finds RMS errors as small as 1%. It is noteworthy that ν depends substantially on matrix molecular weight and declines markedly (from 0.69 to 0.51) as one moves from $M_{probe} < M_{matrix}$(364-kilodalton polymer in 775-kilodalton polymer) to $M_{probe} \ll M_{matrix}$(343-kilodalton probe in 8420-kilodalton matrix).

5. Data Not Analyzed. We attempted to use every literature study which tested the proposed scaling law, rather than presenting a comparison with those results with which agreement is most satisfactory. We did not include the work of Amis and Han,[48,49] who measured D_s from a slow mode seen in quasi-elastic scattering spectra, because no theory predicts a slow mode, let alone shows that the slow mode reflects self-diffusion.

Molecular Weight Dependence of D_s

The preceeding section shows that a good representation for D_s, as a function of c and M, has been found. Here the reptation model is considered. This model predicts[4,5] that D_s depends on M only through a factor of M^{-2}. Plots of $D_s M^2$ against c should give a universal curve, valid for all large M and $c^* < c < c_e$. Equation 5 seemingly provides a reasonable form for the universal curve, allowing numerical tests of the reptation prediction. Combined measurements with $c > c^*$ for all polymer molecular weights for each system were fit to
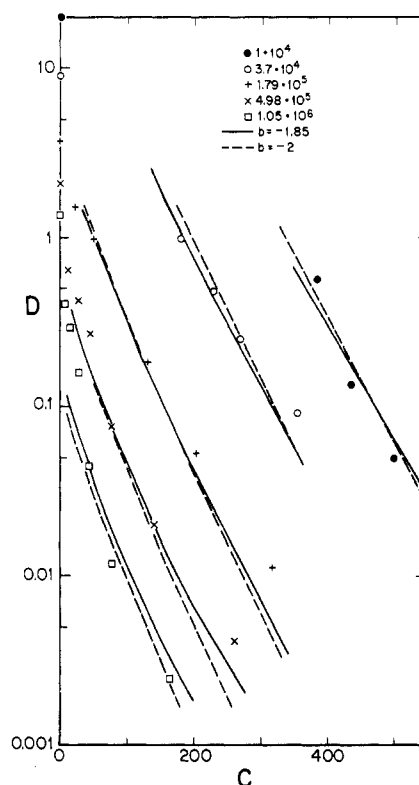
$$D_s = aM^b \exp(-\alpha c^{\nu}) \qquad (6)$$

where the fitting parameters a, b, α, and ν do not depend

on M. As a direct test of eq 1, fits were also made with eq 6 while holding b fixed as $b = -2$. Numerical results are in Table III.

von Meerwall et al.'s data[32] on polystyrene–THF (Figure 1) are largely confined to $c > c^*$. The five curves in Figure 1 are not self-similar: $D_s(c)$ becomes progressively more concave as M is increased, so curves for $D_s(c)$ cannot be superposed. The scaling-law prediction (eq 1) cannot be exact. A force fit to eq 6 still obtains $b = -1.85$, within 10% of the scaling-law prediction $b = -2$. Data with $c < c^*$ were not included in the least-mean-squares analysis. However, as seen in Figure 8, at low M eq 6 falls off more steeply with increasing c than does the experimental data. At high
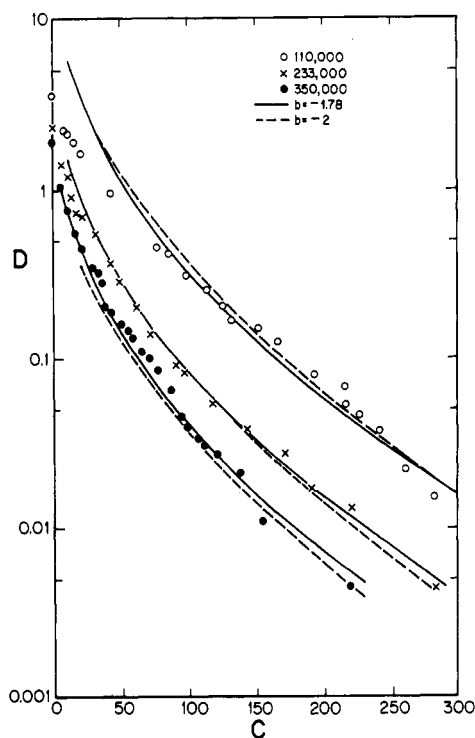
Figure 9. Force fit of Callaghan and Pinder's results[24-27] on polystyrene–CCl_4 to eq 6, using only the data points with $c > c^*$, with $b = -1.78$ or with b fixed (dashed line) at -2. There is mediocre agreement with theory, but cf. Figure 2. Equation 6 fails in the same way as seen in Figure 8.

M, eq 6 falls off much less quickly than does the data. For the 1 050 000 amu polystyrene, the experimental and theoretical lines cross at their midpoints but differ by as much as threefold at low c. If D_s had been measured over a different concentration range, the midpoint of the experimental curve would be in a different place. Moving the theoretical curve's midpoint to match the midpoint of a different experimental curve would change b. The calculated value of b thus seems to be an accident.

A fit of Wesson et al.'s data[7] on polystyrene–THF to eq 6 obtains $b = -2.04$, in excellent agreement with Wesson et al.'s observation that plotting M^2D against c puts all the data onto a single smooth curve. However, the RMS error in the fit to eq 6 is larger (0.29 vs. 0.07–0.24) than in the fits to eq 5.

Callaghan and Pinder[27] emphasize that their data on polystyrene–CCl_4 do not support the reptation model. Indeed, eq 6 matches their data best when $b = -1.78$, not the predicted $b = -2$. As seen in Figures 9 and 3, eq 6 is systematically worse at representing experiment than is eq 5. Callaghan and Pinder's results[25] on 2000 amu polystyrene were not included in the analysis against eq 6, because eq 6 is not expected to work for polymer chains which are too short to entangle.

Callaghan and Pinder's results (Figure 10) on polystyrene–perdeuteriobenzene[27] give $b = 1.71$, not the predicted -2.0. The error in the best fit to eq 6 is systematic. The equation accurately predicts $D_s(c)$ for 233 000 amu polystyrene but overestimates dD_s/dc of the 110 000 amu polymer and underestimates dD_s/dc of the 350 000 amu polymer.

The reptation model's M^{-2} prediction is sometimes interpreted as deriving one factor of M from the diffusing polymer and one factor of M from the background polymer. A probe of fixed M in solutions having various M_{matrix} would therefore obey

$$D_s \sim M_{matrix}^{-1} \qquad (7)$$
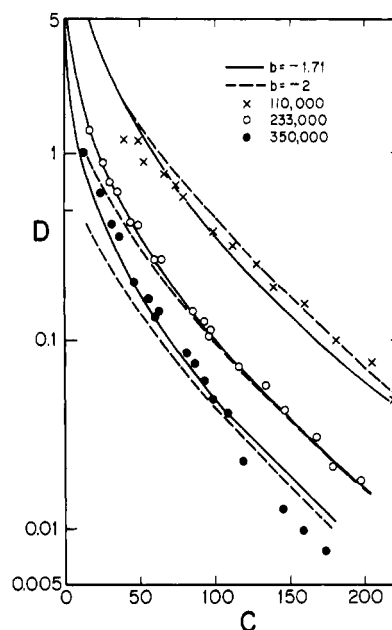
Figure 10. Force fit of Callaghan and Pinder's data[27] on polystyrene–perdeuteriobenzene to eq 6, obtaining $b = -1.71$ (solid line). Dashed line shows $b = -2$ (cf. Figure 3). Data for 233 000 amu polystyrene is fit well; results for the other polystyrenes show slopes systematically different from theory.

One could instead argue that eq 1 describes probe polymers in mixtures. Equation 1 was obtained by noting that the drag coefficient against reptatory motion is linear in M, so D for diffusion along the tube is $\sim M^{-1}$. For a polymer to reptate through its own length, so that the point initially occupied by one end of the chain is occupied by the other end of the chain, the polymer must diffuse through a distance (measured along its own contour length) $\sim M$. From the diffusion equation $x^2 = 2Dt$, the time T required for this displacement is $\sim M^3$. D_s measures not diffusion of a polymer along its own tortuous contour, but displacement of the polymer center of mass. A polymer which has diffused laterally through its own length will have moved its center of mass only by its end-to-end distance (up to constants, its radius of gyration $R_G \sim M^{1/2}$). The diffusion equation $R_G^2 \sim D_s T$ then gives $D_s \sim M^{-2}$, where at every step in the calculation M has been the probe molecular weight, not the matrix polymer molecular weight.

Brown and Stilb's[21] measurements on poly(ethylene oxide) probes in dextran–water show D_s depends on the matrix size far more weakly than $M_{dextran}^{-1}$. At fixed matrix concentration, a fivefold change in dextran molecular weight changes D_s by no more than 50%. D_s is rather more sensitive to probe molecular weight; at fixed concentration of a given dextran, D_s depends on M_{PEO}^{-a} with exponents a in the range 0.5–1.

For polystyrenes in poly(vinyl methyl ether)–*o*-fluorotoluene, a fit to eq 6 finds $b = -0.9$, close to the $b = -1$ implied by eq 7. Here M is the molar mass of probe, the molar mass of the background polymer being held fixed. Other parameters are in Table III. The RMS fractional error in the fit is >30%. While the 1.79×10^5 amu polymer follows eq 6 closely, the $M^{-0.9}$ dependence misses badly on the 5×10^4 amu polystyrene. Equation 6 gives approximate formal agreement with one interpretation of the reptation model, but (Figure 11) the fit of theory to the data is clearly forced.

In summary, from eq 6 the reptation model provides only a fair numerical approximation to reality. The exponent b is generally within 20% of the predicted values
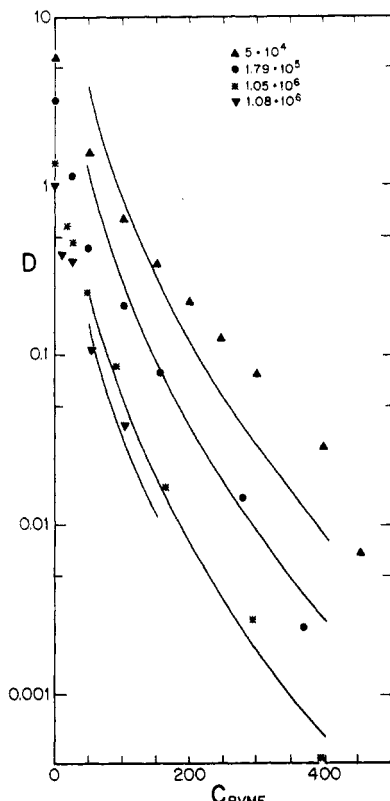
Figure 11. Force fit of Hanley et al.'s data on polystyrenes of various M in 60000 amu poly(vinyl methyl ether)-o-fluorotoluene to eq 6. c_{PVME} is the matrix polymer concentration. Curves are for $b = -0.9$. Compare with Figure 7.

Figure 12. Dependence of ν on the matrix polymer molecular weight M: (a) polystyrenes and dextrans, based on ref 7, 22, 24–27, and 32. (b) ν against effective molecular weight for all of Table I. The lines are $\nu \sim M^{-1/4}$. Abbreviations: PS = polystyrene, PB = polybutadiene, PVME = poly(vinyl methyl ether), PMMA = poly(methylmethacrylate), and THF = tetrahydrofuran. For proteins the effective molecular weight is fixed by particle size; see text.
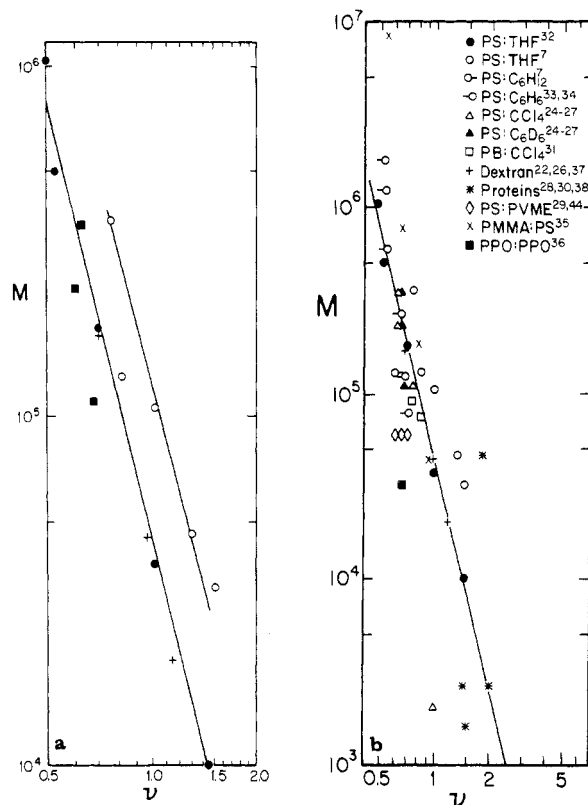
−2 and −1. If $b = -2.00$ is the definitive signature for reptation in semidilute solutions, this numerical disagreement could be unacceptable (though the similar disagreement between reptation and experiment in the relation $[\eta] \sim M^x$ is not generally seen as disabling the reptation model.) A more serious difficulty with eq 6 is qualitative. Contrary to theory, von Meerwall et al.,[32] Callaghan and Pinder,[27] and Brown and Stilbs[21] report $D_s(c)$ curves, for different polymer molecular weights, which are not superposable. The concentration dependence of D_s varies with the matrix polymer's molecular weight.

Discussion

From the preceding, our proposed scaling law (eq 5) correctly describes the concentration dependence of D_s. Good agreement is found with the entire modern literature on polymer and protein self-diffusion.

The proposed scaling law is not analytic in c. For spheres, there exist valid analytic expansions (with detailed hydrodynamic interactions) for D_s,[50–53] implying the existence of similar expansions for polymer chains. Equation 5 may therefore be an asymptotic expansion, not an exact result. Little of the available data has a random error under 5%. It would not be surprising that a form as simple as eq 5, with only three parameters, will not be satisfactory with high-precision measurements, when these become available. Such measurements will provide a considerably more demanding test if they include extensive results in dilute ($c < c^*$) as well as semidilute ($c > c^*$) solutions.

Equation 5 for D_s is more reliable than eq 4 for D_p, as there are a few cases in which the latter fails[13] but no cases in which the former fails. An element of chance may be involved. Recent data[54] indicate that eq 4 is more likely to fail in systems with especially wide molecular weight

distributions, while literature data on D_s largely involve monodisperse systems.

Molecular Weight Dependence. Equation 5 gives systematic information about the molecular weight dependence of D_s. We follow the two-step process previously[16] applied in interpreting eq 4 for D_p. First, measurements of D_p for each probe–polymer combination were fit to eq 4. Second, inspection of α and ν, as obtained from D_p, revealed that α depends on the molecular weight of the background polymer, but not on probe radius, a good representation being $\alpha \sim M^{0.8\pm0.1}$. For D_p, ν depends but weakly on M. We now repeat this process for D_s, finding that the molecular weight dependence of D_s appears through several parameters.

D_0 falls with increasing M. For random-coil polymers, D_0 scales as $D_0 \sim M^{-a}$ for $a = 0.5$–0.55, in agreement with standard results for dilute solutions.[41] Figures 1–6 show that the convexity of the $D_s(c)$ curves varies with M. At small M, the curves are concave downward; as M is increased, the curves flatten out and become convex upward. The convexity of $D_s(c)$ is determined by ν, which must depend on M. Figure 12a plots ν against M for the experiments on polystyrene and dextran solutions.[7,22,24–27,37] The visible linear relation indicates

$$\nu \sim (M/w)^{-1/4} \qquad (8)$$

to good accuracy. The straight lines are for intercepts $w = 45000$ and $w = 125000$, respectively.

Figure 12b extends this analysis to all of Table I, using when possible analyses in which D_0 was fixed. ν falls gradually with increasing M, changing from 1.46 for 1×10^4 amu polystyrene to 0.49 for 1×10^6 amu polystyrene

Table IV
Parameters from Nonlinear Least-Squares Fits of Data on Each Polymer–Solvent System to Eq 8^a

system	ref	α	ν	M_0	γ	% RMSE
polystyrene–THF–HFB	32	508	–15.6	54	–0.24	26
polystyrene–THF	7	517	–15.8	123	–0.29	25

^{a} Ref = reference, a, α, M_0, and γ are fitting parameters, % RMSE is the root-mean-square fractional error in the fit, and polymer masses are expressed in kilodaltons.

or 0.54 for 342 000 amu poly(methyl methacrylate) in 8.4 × 10^6 amu polystyrene. While 0.5 is a plausible large-M limit for ν, it is not apparent from separate analyses of ref 7, 33, or 35 that 0.5 is a limiting value, rather than being the smallest value which ν happens to have attained. Note that Nemoto et al.'s data (crosses, Figure 12b) lie virtually on a straight line out to $M = 8 \times 10^6$.

In the polystyrene–poly(vinyl methyl ether) study,[29,44] for fixed matrix molecular weight M_m, ν was largely independent of probe molecular weight M_p. Nemoto et al.'s data[35] at fixed M_p showed that ν depends strongly on M_m, in agreement with Leger et al.'s data[34] on labeled polystyrene in polystyrene matrices of varying M_m. In Figure 12b, M is therefore the matrix molecular weight.

Proteins were treated in the manner previously used for probes in protein solutions.[16] Each protein was assigned an effective molecular weight M_e, determined from the protein hydrodynamic radius R_h. M_e is the molecular weight of a random-coil polymer whose radius of gyration equals the hydrodynamic radius of the corresponding protein. M_e accounts for differences in describing molecular weights. The material within R_G of the center of mass of a random-coil polymer includes polymer and entrained solvent; M includes only the polymer. The material within R_G of the center of mass of a protein is predominantly polypeptide, all of which is included in M. A protein of given radius thus has a larger M than does a random-coil polymer molecule of the same radius.

M_e may appear artificial. Since $R_G \sim M^\gamma$, the vertical axis of Figure 12b could be labeled "R_G", indicating that ν depends on polymer size. The relative positions of the data points would shift only slightly, while eq 8 would become $\nu \sim (R_G/R_0)^{-1/2}$.

As ν depends on M, the dependence of a on M is determined by the units used for the concentration. Namely, a change of concentration units gives $c = kc'$, c and c' being the same physical concentration in two different systems of units, so

$$D_s = D_0 \exp(-\alpha c^\nu) = D_0 \exp(-\alpha(k^\nu)c'^\nu) \qquad (9)$$

On changing units from c to c', α is replaced with αk^ν, which depends on M through ν.

Finally, D_s for all c, for single studies reporting at least five values of M, was fit to

$$D_s = aM^{-1/2} \exp[\alpha c^{(M/M_0)^\gamma}] \qquad (10)$$

obtaining Table IV. RMS fractional errors are modestly lower than the error in the corresponding fits to the reptation model (eq 6), though eq 10 must describe all concentrations, while eq 6 only needs to match the data for $c > c^*$.

Reptation Model. Let us now compare our analysis with predictions based on the reptation model:

1. If reptation were important, polymer transport would proceed by different mechanisms at $c \ll c^*$ and $c \gg c^*$. Different mechanisms should result in different functional forms, or at least different numerical parameters, so there

should be some change in the behavior of $D_s(c)$ between dilute and nondilute solutions. As seen most vividly in Figure 2, one function with one set of parameters (D_0, α, ν) describes all solutions and concentrations. A single continuous curve passes near every data point, with no differences between the alleged "dilute" and "semidilute" regimes. Indeed, with enough dilute-solution data, measurements on dilute (nonreptating) solutions (Table II) predict D_s at all concentrations, including those large concentrations at which reptation is said to dominate.

2. Calculations based on reptation/scaling arguments[4-6] predict $D_s \sim c^x$ for x in the range –1.75 to –3. However, log–log plots of D_s against c rarely yield straight lines. D_s is actually fit well by an entirely different functional form—the "stretched exponential" $\exp(\alpha c^\nu)$.

3. For semidilute solutions, reptation gives an M^{-2} scaling rule for D_s. $D_s(c)$ depends on M through D_0, α, and ν, but efforts to extract an M^{-2} behavior succeed only by forcing the data.

4. For the movement of a polymer of mass M_p through matrix polymers of molar mass M_m, at $M_m > M_p$ the reptation model predicts D_s to be independent of M_m. For diffusing polymers in polymer solutions (though not melts[55,56] this prediction is not supported by experiment. At $M_m > M_p$, D_s of polymer molecules (though not small molecules) does depend on M_m.

5. Proteins cannot reptate. If polymers in semidilute solution moved by reptation, only by bizarre coincidence would $D_s(c)$ curves for reptating polymers have the same functional form (with compatible parameters) as $D_s(c)$ curves for nonreptating proteins or low molecular weight polymers. The forms are in fact quite similar.

The reptation/scaling models make a variety of predictions about polymer diffusion in solution, none of which are right. There is evidence for reptation in polymer melts, but the opposite is true in solution. On the basis of the available data, it is here concluded that *solution reptation probably does not exist*, at least on a major scale for systems heretofore studied. There is no experimental reason to suppose that solution reptation becomes important for self-diffusion if one goes to larger M; the results here do not rule out the possibility that small polymers diffusion through a matrix of large polymers do so by reptation.

The image of a semidilute polymer solution as a "pseudogel" may make it difficult to envision how polymers can diffuse other than by reptation. The following may be illuminating: It is clear that a sufficiently large force will rupture a real gel, let alone a weaker pseudogel, while objects driven by weaker forces can be restrained by gel structures. As an example of particle motion being restrained by a real gel, consider gel electrophoresis. Experiment and theory agree that the drug coefficient f of a particle in a true gel satisfies[57]

$$f = f_0 \exp(KR^2) \qquad (11)$$

f_0 being the drag coefficient at a fixed low gel concentration, R being the particle radius, and K increasing with increasing gel concentration. A true gel acts as a size filter, increasing f of large particles more than it increases f of small particles. Concentrated polymer solutions are said to be pseudogels, with polymer chains forming a transient mesh. Small probes, which fit through holes in the mesh, do not have their motion hindered, while probes too big to pass through the pseudogel lattice would find their motion blocked. In terms of eq 4, the polymer solution-evanescent gel analogy implies $\delta = 2$. Experimentally[8-16] probes in polymer solutions find $\delta = 0$. That is, the "pseudogel" structure of a polymer solution is simply too

weak to block the diffusion of probe particles. From the results here, the pseudogel structure is so weak that it cannot block self-diffusion either. Since the supposed pseudogel structure is unimportant to self-diffusion, it is not surprising that self-diffusion in entangling polymers does not differ from self-diffusion in systems which cannot form pseudogels. On the time and distance scales treated here, a polymer solution is not gellike. Studies of polymer chains in true gels say nothing about polymer motion in solution.

What forces, then, determine the self-diffusion coefficient? A partial answer is given by theoretical analyses of hard-sphere systems.[50-53] Hard spheres perform hindered Brownian motion, with each particle being slowed by hydrodynamic interactions and retarded (but not blocked) by collisions with neighbors. The same effects act on polymer chains. This proposal is similar to the factorization (1) of D_s into a monomer friction term $f(c)$ and a topological term $g(c,M)$, $f(c)$ arising from forces between each monomer and other polymer chains. In Tirrell's description, D_s and the monomer diffusion coefficient D_1 differ by a topological term $g(c,M)$, which incorporates reptation constraints. If reptation is unimportant, $g(c,M) = 1$; D_s and D_1 differ because they average over different radial distribution functions at different frequencies, not because polymer diffusion involves topological constraints.

Finally, our results support Kuhn's[58] assertion that theory and experiment are inherently coupled: a theoretical model dictates which data test its validity and which data are irrelevant. The reptation model does not apply in dilute ($c < c^*$) solutions, so experimental searches for M^{-2} behavior have oft elected not to study (irrelevant to them) dilute-solution behavior. The Edwards–de Gennes model emphasizes the importance of topological entanglements. Globular proteins cannot entangle, so studies of protein self-diffusion are irrelevant and do not appear in reviews on "polymer" self-diffusion, even though proteins are polymeric in nature. In contrast, our hypothesis—that proteins and random-coil polymers diffuse by the same mechanism—compels the comparison of D_s of proteins and random-coil polymers. Similarly, since there is no major difference between diffusion in "dilute" and "semidilute" regimes, D_s measurements with $c < c^*$ and $c > c^*$ must be considered on an equal footing.

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