Dynamics of Polymers in Concentrated Solutions: The Universal Scaling Equation Derived[†]

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ABSTRACT: A heuristic derivation of the universal scaling law for macromolecule self-diffusion is presented. Our model, which employs an entirely nonreptational description of polymer self-diffusion in solution, is consistent with our demonstration (Phillies, G. D. J. *Macromolecules* **1986**, *19*, 2367) that the entirety of the modern literature on polymer and protein self-diffusion in solution is described by the form $D_s = D_0 \exp(-\alpha c^\nu)$. The derivation correctly predicts ν at low and high polymer molecular weight, as well as the hitherto-unremarked M dependence of α.

Introduction

The objective of this paper is to sketch a new model for polymer dynamics in nondilute solutions. Relative to other treatments, the model emphasizes the importance of collective ("hydrodynamic") modes over local ("entanglement") modes. The focus is the single-chain (self-) diffusion coefficient D_s. As presented, the model does not necessarily describe polymer melts.

This calculation was motivated by our recent reexamination[1] of the phenomenology of polymer and biopolymer self-diffusion. In ref 1, we demonstrated that all modern studies of D_s in solution find the same dependence of D_s on polymer concentration, namely

$$D_s = D_0 \exp(-\alpha c^\nu) \tag{1}$$

where D_0 is the diffusion coefficient in the limit of small c, and α and ν are scaling parameters. The above expression, in which the concentration dependence is a stretched exponential, works to within experimental error at all polymer concentrations, a single set of parameters (D_0, α, ν) sufficing for measurements ranging from dilute solution up to the melt. (Reference 1 does not treat melt systems.) Equation 1 works equally well for high molecular weight polymers, low molecular weight polymers, and globular, nonentangling proteins.

The parameters α and ν vary from substance to substance. For a wide range of polymer molecular weights

$$\nu \sim M^{-1/4} \tag{2}$$

is observed. In the few cases[2,3] in which sufficient data are available, fits[1] of eq 1 to dilute-solution data obtain values for α and ν that are numerically indistinguishable from values for α and ν obtained by fitting eq 1 to data covering a complete range of concentrations. That is, once results are described by eq 1, there is no indication that the nature of polymer motion differs between dilute and semidilute solutions.

Equation 1 and its analysis are substantially different from predictions of the widely accepted scaling models[4-7] for polymer self-diffusion. The scaling models divide polymer solutions into several concentration regimes, the dominant mode of polymer motion changing qualitatively from regime to regime. In dilute solution, in which polymer chains are separated by distances much larger than their radius of gyration R_g, single chains diffuse as isolated, noninterpenetrating hydrodynamic ellipsoids. In the semidilute regime, in which polymer coils overlap, polymer self-diffusion is said to be dominated by the process of "reptation", in which polymer chains predominantly move parallel to their own backbones. For reptating polymers, detailed analyses predict

$$D_s \sim M^{-2} c^x \tag{3}$$

where x depends on solvent conditions and model-dependent constraints, but is in the range −1.75 to −3. Equation 3 is predicted not to be valid for dilute solution (indeed, it diverges as $c \to 0$) or for polymer chains that are smaller than the critical molar mass M_e for entanglement. The universal scaling law, eq 1, as verified by published measurements of D_s in polymer solutions, does not resemble the scaling models or eq 3. Reference 1 was led to conclude: "Reptation is probably not important for polymer self-diffusion in solution". This conclusion has not received unanimous acceptance.

A major criticism of ref 1 is that the universal scaling law (eq 1) was introduced in a totally phenomenological way. With appropriate choices of parameters α and ν, eq 1 can describe any of a wide variety of monotonic functions, so one could argue that the successes of eq 1 have no fundamental importance. The basis of ref 1 for introducing eq 1 was a proposed equivalence between polymer self-diffusion and optical probe diffusion in polymer solutions. Since the scaling law for probe diffusion[8] was itself obtained phenomenologically, an assertion of the equivalence of probe diffusion and self-diffusion is not a derivation of the scaling law from a model for polymer solutions.

To remove this criticism, a heuristic derivation of eq 1 is here presented. The derivation relies on fundamental assumptions concerning (i) the self-similar effect of infinitesimal concentration increments on D_s, (ii) the functional form for hydrodynamic interactions between mobile polymer chains, and (iii) the dependence of chain extension on polymer concentration. The assumptions differ significantly from those that have previously been used to treat this problem. The soundest defense of these assumptions, as seen below, is that they yield good agreement with experiment. The calculation obtains correctly the functional dependence of D_s on concentration, numerical values for ν, and a (hitherto-unremarked) dependence of α on M.

Derivation of the Scaling Law

The self-diffusion coefficient of a polymer molecule is related to its drag coefficient f by the Einstein relation

$$D_s = k_B T / f \tag{4}$$

At infinite dilution, $f = f_0$. At higher polymer concentrations, f and hence D_s depend on polymer concentration. It will be convenient to refer separately to the polymer molecule whose motions are observed (the "probe") and the other polymer molecules in solution (the "background polymers"). In a self-diffusion experiment, the probe and

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the background polymer molecules have identical dynamic properties.

Why does f depend on concentration? A moving probe molecule is accompanied by a wake—a flow—in the surrounding solution. (If the probe particle is moving under the influence of an outside force, as in a sedimentation experiment, one says that the probe induces the wake in the surrounding medium. If the probe is performing Brownian motion, there is still a wake, but the momentum in the wake came from thermal fluctuations in the surrounding medium, not from the Brownian particle, so that it would be incorrect to say that a Brownian particle induces a wake in the region around itself. Rather, stress fluctuations in the fluid induce local motions (eddies) in the liquid, the Brownian particles then being borne along by the displacements of the liquid.) Suppose as a gedanken experiment that some of the solvent is removed from the wake and replaced with a polymer molecule. Except on time scales so short that inertial effects are important, a suspended molecule moves with the surrounding flow. If at every point the polymer maintained precisely the velocity that the fluid would have had, at the same point, if the polymer were absent, then the polymer would have no effect on the fluid's flow pattern. Replacing some of the solvent with such a polymer would not change the probe's drag coefficient.

Real polymer molecules are somewhat rigid and have fixed contour lengths. If a polymer molecule is placed in the wake of a moving probe, the polymer cannot duplicate the motions that the solvent would have performed, at the points in space occupied by the polymer, in the polymer's absence. The polymer molecule therefore perturbs the probe's wake. In general, the perturbations travel back from the polymer to the probe and increase the probe's drag coefficient. (For a model suspension of hard spheres, these effects have been analyzed in detail by Mazur and van Saarloos.[9])

A central assumption of this paper is that *the ability of a polymer to perturb the probe's wake is proportional to the polymer's drag coefficient*. For a probe particle moving through a set of fixed obstacles, a problem previously analyzed by Cukier[10] and by Altenberger et al.,[11] this assumption is relatively transparent. In the fixed-obstacle problem, a probe at R sets up in the solvent a flow field $\mathbf{v}(\mathbf{r})$, described (in ref 10 and 11) by the Oseen tensor $\mathbf{T}$

$$\mathbf{v}(\mathbf{r}) = \mathbf{T}(\mathbf{r} - \mathbf{R})\cdot f\mathbf{v}_p(\mathbf{R}) \tag{5}$$

$\mathbf{v}_p(\mathbf{R})$ being the velocity of the probe. A fixed obstacle at $\mathbf{R}_1$ acts as a source of friction, exerting in first approximation a force $\mathbf{F}(\mathbf{R}_1)$ on the fluid. The force $\mathbf{F}(\mathbf{R}_1)$ creates an additional flow $d\mathbf{v}(\mathbf{r})$ in the solvent, $d\mathbf{v}(\mathbf{r})$ also being described by the Oseen tensor

$$d\mathbf{v}(\mathbf{r}) = \mathbf{T}(\mathbf{r} - \mathbf{R}_1)\cdot\mathbf{F}(\mathbf{R}_1) \tag{6}$$

The force $\mathbf{F}(\mathbf{R}_1)$ is determined by the total fluid velocity $\mathbf{V}(\mathbf{R}_1) = \mathbf{v}(\mathbf{R}_1) + d\mathbf{v}'(\mathbf{R}_1)$ ($d\mathbf{v}'$ being the perturbation of $\mathbf{V}$ at $\mathbf{R}_1$ due to sources of friction other than the source at $\mathbf{R}_1$) as

$$\mathbf{F}(\mathbf{R}_1) = f\mathbf{V}(\mathbf{R}_1) \tag{7}$$

Equation 7 applies specifically to fixed obstacles, i.e., obstacles that are held in place by an external potential, so that they can exert a net nonzero force on the solution. Increasing the drag coefficients of the fixed obstacles increases the forces that the obstacles exert on the fluid, hence increasing the flow induced by the obstacles at the location of the probe, thereby increasing the probe's apparent drag coefficient.

A probe particle in the presence of mobile obstacles, such as a suspension of polymer chains, presents a more subtle poblem than does a probe in the presence of fixed obstacles. Unlike fixed obstacles, which can retard a uniform ($v(r)$ = constant) flow, mobile obstacles move with a flow and have no effect on uniform fluid motion. Mobile obstacles do affect nonuniform flows. As shown in Kirkwood and Riseman's treatment,[12] a polymer in a shear field rotates. The rotation velocity of the polymer cannot everywhere match the local velocity of a fluid with uniform shear, so the rotating polymer exerts forces on the fluid, subject to the Newton law constraints that the net force and net torque exerted by a free-floating body must (absent inertial effects) vanish. Kirkwood and Riseman[12] demonstrate that the forces exerted by a polymer in a shear field are linear in the polymer's drag coefficient. An outside force that reduces the rotation speed of a polymer, such as a drag due to other polymers, increases the force parallel to the probe's motion that the polymer exerts on the fluid, thereby increasing the polymer's perturbation of the probe's wake. A drag on a polymer due to other polymers also increases that polymer's f. The ability of a polymer to retard a probe is thus related to the polymer's drag coefficient f in solution, and not to the polymer's drag coefficient f_0 in pure solvent. This approximation is central to our derivation of equation 1.

Let us now consider the effect of two infinitesimal concentration increments dc on f_0. The first increment increases f_0 by some amount $K\,dc$. K may be concentration dependent. From the above assumption, $K = a(c)f$. A second infinitesimal concentration increment affects f in two ways. First, polymers of the second increment act directly to retard the probe particle. Second, polymers of the second increment act on the polymers of the first increment, increasing their drag coefficients, thereby increasing the drag that the polymers of the first increment exert on the probe. f thus increases as

$$f_0 \rightarrow (f_0) + (af_0\,dc) \rightarrow (f_0 + af_0\,dc) + (a(f_0 + af_0\,dc)\,dc) \tag{8}$$

which may be regrouped as

$$f_0 \rightarrow f_0(1 + a\,dc) \rightarrow f_0(1 + a\,dc)^2 \tag{9}$$

Substituting $f(c) = f_0(1 + a\,dc)$ and $Df = f(c + dc) - f(c)$ gives a difference equation

$$Df/dc = af(c) \tag{10}$$

After the $dc \rightarrow 0$ limit, the integral of eq 10 is

$$f = f_0 \exp\left[\int_0^c dc\; a(c)\right] \tag{11}$$

or

$$D_s = D_{s0} \exp\left[-\int_0^c dc\; a(c)\right] \tag{12}$$

Equation 12 gives the concentration dependence of D_s in terms of an unknown function $a(c)$.

To obtain the function $a(c)$, we assume that the dominant dynamic interaction between polymer chains in solution is due to collective whole-polymer modes of the system; i.e., *chain–chain interactions are primarily hydrodynamic in nature*. This assumption is contrary to the assumption, made by scaling theories for polymer self-diffusion, that the dominant dynamic chain–chain interaction is the short-range contact force between small sections of nearby polymer molecules. What is the form of these hydrodynamic interactions? It is well-known that the basic excitations of a fluid are described by the fluid's Rayleigh–Brillouin spectrum, which reveals propagating momentum fluctuations (thermally excited sound waves) and nonpropagating energy ("entropy") fluctuations. However, at low frequency and long wavelength, the contributions of these fluctuations to the cross-diffusion coefficient are usually described by an approximation such as the Oseen tensor.[12] For spheres of radius a separated by a distance R, the Oseen tensor is a lowest-order ($(a/R)^1$) approximation, the full hydrodynamic interaction tensor being expressible as a power series in a/R. Although most treatments of polymer–polymer interactions have treated hydrodynamics at the Oseen level ($(a/R)^1$), the large literature on colloid dynamics (cf., e.g., ref 13 and references therein) has clearly established that the Oseen approximation is totally inadequate; to get reasonable agreement with experiment, one must carry the hydrodynamic interaction tensors out to the $(a/R)^5$ or $(a/R)^7$ level. While a polymer bead has a much smaller radius than do typical colloid particles, the distance of closest approach between two polymer chains is also much smaller than the distance of approach of two colloid particles, so polymer–polymer and colloid–colloid interactions involve similar values of a/R.

In the treatment of self-diffusion, the question of interest is the retardation of an object's motion by hydrodynamic interactions with other objects. For hard spheres, this problem's solution is presented by Mazur and van Saarlos,[9] namely

$$\mu_{ii} = \mu_{ii}^{\circ}\left(\mathbf{I} - \frac{15}{4}\sum_{j\neq i}\frac{ab^3}{r_{ij}^{4}}\hat{\mathbf{r}}_{ij}\hat{\mathbf{r}}_{ij}\right) \qquad (13)$$

where μ_{ii} is the mobility of a sphere, a and b are the radii of sphere i and its neighbor j, and $\hat{\mathbf{r}}_{ij}$ is the unit vector between i and j.

How comparable are the hydrodynamic interactions of hard spheres and polymer chains? While numerical coefficients will differ markedly, the hydrodynamic mechanism whereby which one polymer enhances another polymer's drag coefficient is basically similar to the mechanism that operates for hard spheres. We shall describe the mechanism for spheres and then argue that the replacement of spheres with chains will only alter numerical coefficients. Consider, for example, two nearby spheres 1 and 2, sphere 1 having a motion perpendicular to the spheres' line of centers. Sphere 1 establishes a wake in the surrounding fluid. Sphere 2 then tries to follow the motion of the liquid. Its velocity is an average of the fluid velocity over its surface. Since the wake's velocity falls off with distance from sphere 1, the fluid velocity at the surface of sphere 2 is different at different points. Sphere 2 can partially compensate for the velocity gradient in the fluid if it rotates. However, sphere 2 is not arbitrarily deformable; its surface velocity must differ from the velocity that the fluid would have had if sphere 2 were absent. While sphere 2 can exert (from momentum conservation) neither a net force nor a net torque on the fluid, the quadrapole moment of the force it exerts on the fluid is nonzero. The force quadrapole moment creates a second ("reflected") wake, which propagates back to sphere 1, retarding its motion.

If the spheres are replaced by polymer chains, only the technical details of this argument are changed. A sphere exerts a force on the fluid if the sphere's surface velocity does not match the velocity of the fluid. A polymer chain is porous; the force that a polymer exerts on a fluid is determined by the difference between the velocities of its component monomers and the velocities that the fluid would have had, at the same points within the polymer, if the polymer had been absent. Replacing a sphere with a polymer thus replaces a surface average with a volume average. Momentum conservation applies to polymers as well as to spheres, so the quadrapole moment of the polymer–solvent force creates the reflected wake. The dimensional (though not numerical) dependence of the wake on distance will be the same for polymer–polymer interactions as for the sphere–sphere interaction, because both have a quadrapolar form for the source. On identifying a and b with the radii of gyration of probe and background polymers, eq 13 suggests the approximation

$$f = f_0(1 + nQR_{ga}R_{gb}^{3}) \qquad (14)$$

for the thermally averaged chain–chain hydrodynamic interaction. Here n is the number density of background polymers, while Q is an average of an r^{-4} interaction over the monomer–monomer distribution of two chains. In terms of eq 9, $n \leftrightarrow \mathrm{d}c$ and $a \leftrightarrow QR_{ga}R_{gb}^{3}$.

The final approximation of the calculation is to estimate R_g with the "blob model" of Daoud et al.[14] For a large polymer in semidilute solution, this model predicts the radius of gyration R_g to scale as

$$R_g^{2} \sim Mc^{-x} \qquad (15)$$

for $x = {}^1/_4$. For long chains with $c < c^*$, $\mathrm{d}R_g/\mathrm{d}c < 0$ is also expected, though an exact concentration dependence was not predicted by ref 14. Daoud et al.'s discussion[14] implies that R_g is relatively concentration independent for short chains; i.e., $x = 0$ at low M.

Combining eq 12, 14, and 15 gives

$$D = D_0 \exp[-QMc^{1-2x}] \qquad (16)$$

for large chains. For small chains, a concentration independence of R_g would imply

$$D = D_0 \exp[-QMc] \qquad (17)$$

In combining eq 12 and 14, replacement of the number density n with the mass concentration c consumed a factor M_{polymer}^{+1}. In eq 16, the integral over $a(c)\,\mathrm{d}c$ approximated the unknown c dependence of R_g^{2} in dilute solution with the c^{-x} dependence found in semidilute solution. One could avoid this approximation by writing, for $c > c_+$

$$D = D' \exp[-QMc^{1-2x}] \qquad (18)$$

and

$$D' = D_0 \exp[-G] \qquad (19)$$

where

$$G = \int_0^{c_+} a(c)\,\mathrm{d}c - QMc_+^{1-2x} \qquad (20)$$

c_+ being the lowest concentration at which eq 15 is valid. At concentrations below c_+, D_s would deviate from a simple stretched-exponential form. Equations 15 and 16 implicitly approximate $G = 0$. Figure 2a of Lin et al.'s data[15] on particle diffusion in 3×10^5 amu poly(acrylic acid) exhibits the sort of transitions that would be seen if $G(c) \neq 0$ at low concentrations and if eq 18 were applicable at higher concentrations. As the dilute regime is small for large polymers, approximating $c_+ = 0$ may be less serious an error than ignoring the concentration dependence of Q.

If one identifies

$$\nu = 1 - 2x \qquad (21)$$

eq 16 and 17 have the same functional form as the phenomenological scaling law, eq 1.

Figure 1 of this paper tests eq 16 and 17 by plotting ν against polymer molecular weight for the data analyzed in ref 1 on random-coil polymers in good solvents.[16-31] As

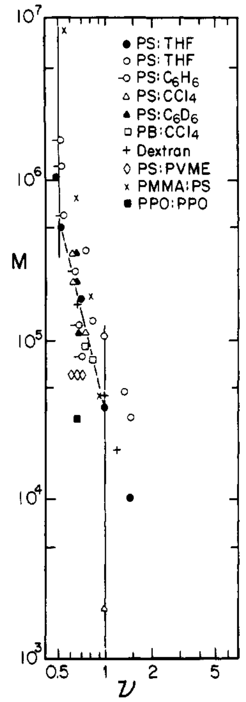

Figure 1. The dependence of ν on M for all random-coil polymers in good solvents treated in ref 1. Solid lines are the predicted high and low molecular weight limits $\nu = 0.5$ and $\nu = 1$; the dashed line is $\nu \sim M^{-1/4}$, adjusted to match the observed points. Abbreviations and original measurements of the data are as follows: PS:THF, polystyrene–tetrahydrofuran;[30,31] PS:C_6H_6, polystyrene–benzene;[24,25] PS:CCl_4, polystyrene–carbon tetrachloride;[17-20] PS:C_6D_6, polystyrene–perdeuteriobenzene;[17-20] PB:CCl_4, polybutadiene–CCl_4;[29] dextran;[16,19,21] PS:PVME, polystyrene diffusing through poly(vinyl methyl ether)–*o*-fluorotoluene;[23,28] PMMA:PS, poly(methyl methacrylate) diffusing through polystyrene–thiophenol;[26] PPO:PPO, poly(propylene oxide) diffusing through poly(propylene oxide).[27]

few of the measurements represented in Figure 1 were taken at low polymer concentration, these data are not sensitive to the approximations described by eq 18–20. The open and filled circles of Figure 1 both refer to polystyrene–tetrahydrofuran but were obtained with different physical techniques (pulsed field gradient NMR,[29] forced Rayleigh scattering[31]). The difference between the data sets has been noted previously and is not explained here.

In Figure 1, solid lines represent theoretical predictions for ν. At large M, $x = {}^1/_4$ and $\nu = {}^1/_2$. At small M, $x = 0$ and $\nu = 1$. For $M > 5 \times 10^5 kD$ and $M < 1 \times 10^5 kD$, respectively, the data show one to be in the predicted large (small, respectively) molecular weight limit. In the intermediate regime $5 \times 10^5 kD > M > 1 \times 10^5 kD$, ν appears to exhibit a transition from small-chain to blob-model chain statistics and scales as $\nu \sim M^{-1/4}$. Just as three molecular weight regimes are seen in Figure 1, previous work on probe diffusion in polymer solutions distinguished three molecular weight/concentration regimes.[8] The transition molecular weights between the three regimes were similar in the two cases.

If ν were dominated by the small-chain to blobbed-chain transition, eq 2 would be the crossover function linking the exponents in eq 16 and 17. There do not appear to be theoretical predictions for the crossover function with which our results could be compared.

Equations 14–17 show that α should scale as

$$\alpha \sim M^1 \tag{22}$$

where (on counting factors of a and b) M is the geometric mean of the molecular weight of the probe and background polymers. Equation 22 is predicted to be valid for all polymer molecular weights. Tests of eq 22 against the entire literature are delicate because our semiquantitative arguments do not identify appropriate concentration units for c. Since ν depends on M, a change in concentration units (e.g., from g/L to g/g) changes the M dependence of α. Specifically, if new and old concentration units are related by $c' = uc$

$$\alpha c^\nu = (\alpha u^{-\nu})(uc)^\nu = \alpha' c'^\nu \tag{23}$$

and α' depends on M through ν. For fixed ν, a change in concentration units changes α by a simple multiplicative constant. If ν differs from sample to sample, a change in concentration units would change each α by a different factor.

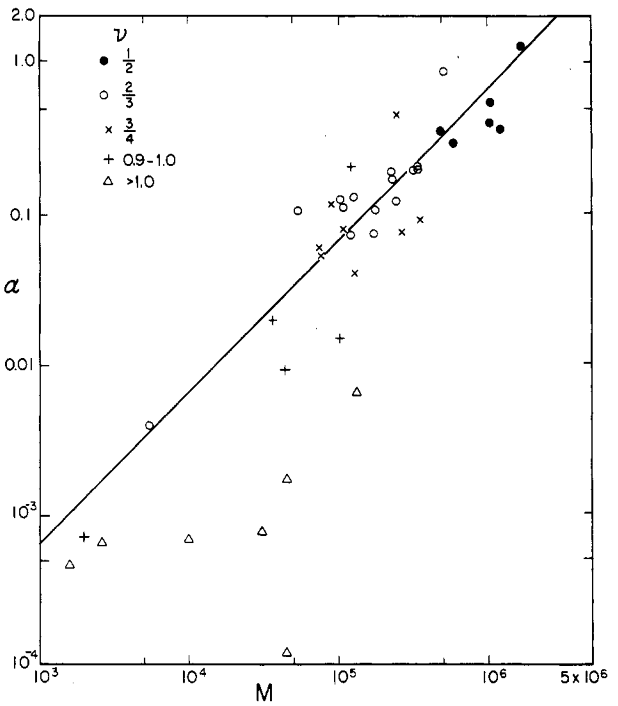

Figure 2. Correlation of the scaling law parameter α (eq 1) against polymer molecular weight M for data on all systems reviewed in ref 1. Solid line represents $\alpha \sim M^1$. Concentration units were converted to g/L with eq 23.

Figure 2 of this paper tests eq 22 by plotting log α against log M, using data from ref 1. For all points, concentration units were converted to g/L. The solid line represents eq 22. The agreement between the points and the model is quite good over more than 3 orders of magnitude in polymer molecular weight. As is apparent from the figure, it would be desirable to have additional data on both low and high molecular weight polymers. This desire may be contrasted with the dictates of the reptation model, which only suggests a requirement for additional data at very large polymer molecular weights.

Remarks

In summary, we have used straightforward ideas on dissipation, hydrodynamics, and polymer chain sizes to derive the universal scaling equation for polymer self-diffusion. The similarity argument sketched here provides a general way to obtain stretched-exponential forms from calculations of polymer dynamics. The assumptions used here are somewhat novel. However, they yield good agreement with experiment. In accord with experiment, the derivation predicts that α and ν values from dilute-solution measurements also describe concentrated solutions, though there can be deviations at very low concentration. The calculation correctly predicts the numerical value of ν and the relationships between α, ν, and M.

Since the derivation correctly predicts the molecular weight dependences of D_0, α, and ν, it correctly describes the molecular weight dependence of D_s, even though it does not have the M^{-2} dependence of reptation models. As shown in ref 1, the presently available experimental data on polymer solutions (we are not treating melts) can be described by algebraic forms other than M^{-2} scaling, so the absence of a factor M^{-2} from eq 1 does not mean that our model contradicts experiment.

The universal scaling law (1) is empirically valid at all concentrations from dilute solution up to the melt. How does eq 1 compare with data obtained in true melts? In a polymer melt, the space between any pair of chains is still filled with a liquid, albeit a highly viscoelastic one, so chain–chain interactions could remain "hydrodynamic" (i.e., dominated by collective modes) at melt-like concentrations. Since eq 13 refers to particles in a Newtonian fluid, it is not clear that our calculation of α and ν is valid at arbitrarily high concentrations.

The studies examined by ref 1 were largely performed on cold polymer solutions. These systems at the large-c limit are *not* melts; they are two-phase mixtures containing saturated solutions above bulk solid polymers. Our arguments can scarcely be supposed to survive analytic continuation across a phase transition, so (for most of the systems discussed in ref 1) the numerical findings cannot be extrapolated to compare with the $D_s \sim M^{-2}$ oft assumed to be found in melts. Equation 1 is not, however, inherently inconsistent with the melt behavior. If extrapolation of eq 1 to the melt concentration c_m satisfies the (transcendental) constraint

$$\alpha c_m^{\nu} = -2 \log M + \text{constant} \tag{24}$$

where α, ν, and c_m may all depend on M, then eq 1 predicts M^{-2} behavior in the melt.

One could argue that eq 1 does not agree with a supposed linear dependence of D_s on c in dilute solution, so that it cannot be the complete low-concentration form for D_s. However, eq 1 does agree well with experimental data on dilute solutions. Straight lines through the lowest concentration points of Figures 2, 4, 5, or 6 of ref 1 are indistinguishable, to within experimental error, from eq 1, even though eq 1 cannot be linearized around $c = 0$. While eq 1 is not analytic at $c = 0$, and hence cannot be represented by a power series of the form

$$D_0(1 + k_1 c + k_2 c^2 + ...) \tag{25}$$

eq 1 can be given a series expansion (over a limited domain not including $c = 0$) around some $c > 0$. The linear term in such an expansion is the observed linear slope of the data over a range of nonzero concentrations.

The arguments leading to eq 14 do not include any corrections for chain flexibility. Chain flexibility might be relatively most important to the case of a small probe polymer moving through a large background polymer. The wake of a probe falls off as a/R, so if $b \gg a$ only the nearby part of a background polymer would be sensibly perturbed by the probe. The background polymer would still hinder the probe, but if most of the background polymer was unperturbed by the probe, the actual size of the background polymer would not be significant. From chain flexibility, one might expect for $M_b \gg M_p$ that α and ν would be independent of M_b. Note that this argument depends on the relative magnitudes of a and b, and not their absolute magnitudes.

Kivelson[32] has emphasized the essential unity of transport parameters in fluids: the computation of the transport coefficients of a fluid can often be reduced to a difficult calculation of the viscosity from a microscopic model, followed by easy calculations of other parameters from the viscosity. Similarly, the model presented here for D_s could instead have been used to compute the viscosity. Use of the above approach should obtain stretched-exponential forms for the concentration dependences of other transport coefficients. Tests[33] of this expectation against literature data show that measurements of the viscosity, rotational diffusion coefficient, sedimentation coefficient, and other polymer transport properties are described accurately by stretched-exponential forms, even in cases in which the original papers reported that the measurements obeyed by power-law forms.

In our previous work on probe diffusion[8] and self-diffusion,[1] it was found that results on long-chain polymers and on globular proteins were consistent if each protein was assigned an effective (apparent) molecular weight M_a. M_a is the molecular weight of a random coil polymer whose radius of gyration is numerically equal to the hydrodynamic radius r_h of the polymer. If the analysis had been made in terms of hydrodynamic radii instead of molecular weights, the use of effective values for experimental quantities would have been unnecessary. Equations 12–15 explain the need for M_a rather than M. The relevant, fundamental physical parameter is the hydrodynamic radius, not the molecular weight; M_a is simply an obscure way to express r_h.

Our model differs from some other treatments of polymer self-diffusion in that it does not exhibit reptation. The assumed hydrodynamic interactions of nearby chains are those appropriate to freely rotating objects, so polymer motion perpendicular to the chain axes has been assumed to be substantial. The model also does not include hydrodynamic screening, as the interaction between a pair of polymer chains is assumed not to be changed by the presence of intervening polymers. Since reptation and hydrodynamic screening have been invoked so often, they may appear to be necessary parts of any model of polymer dynamics. The objective below is to argue that neither reptation nor hydrodynamic screening necessarily exists in polymer solutions.

The reptation model was originally introduced to treat diffusion of polymers through true cross-linked gels.[34] In a cross-linked gel, the gel chains are bonded to each other and to the container surfaces. Regardless of the time scale, gel chains do not diffuse far; they have true equilibrium positions. A polymer that collides with a gel chain cannot push the gel chain from its path; it must instead diffuse around the gel chain. A chain moving along its own length can crawl forward through holes in the mesh; this allowed diffusive motion is reptation. A chain that tries to move perpendicular to its contour will soon collide with nearby gel chains (the "tube"), blocking its further sideways motion. The polymer chain can float back and forth, but extensive longitudinal motion is prevented by the tube. In extending this polymer/gel model to a polymer solution, the assumption is made that the near-neighbors of a diffusing chain form a pseudogel, whose individual strands are as effective at blocking the longitudinal motions of the diffusing chain as was the true gel.

The pseudogel hypothesis suffers from several difficulties. Three arguments are now advanced, each indicating that the motion of a polymer through solution does not resemble the motion of a polymer through a gel:

First, in solution a polymer chain and its neighbors, being chemically identical, have the same hydrodynamic properties. The diffusion coefficient for the sideways motion of a section of polymer chain, whatever it is, must equal the diffusion coefficient for the sideways motion of a similar section of any of the chain's neighbors. The time scales for the sideways motion of a probe chain and of the polymer sections around it are therefore similar, contrary to the pseudogel model's hypothesis that the "tube" moves sideways far more slowly than does the chain of interest.

Second, the pseudogel model for a polymer solution treats the neighbors of a chain as rigid obstacles, beyond whose location the diffusing chain cannot pass. An obvious alternative is that a collision between a chain and one of its neighbors will displace the neighbor. The laws governing diffusion ensure that such displacements occur: Chains within tubes have the same hydrodynamic properties as chains in tube walls. Collisions between two bodies having the same drag coefficient create collective objects whose drag coefficients are less than twice the coefficient of either object separately. From the Einstein diffusion relation, the diffusion coefficient of the collective object is not zero; it can be no less than half the diffusion coefficient of either object separately. A diffusing chain that encounters one of its neighbors thus can diffuse beyond the original position of its neighbor, albeit at a reduced rate. (Note that Monte Carlo models of chain diffusion, which forbid chain displacements into occupied lattice sites, intrinsically assume that the diffusion coefficient of a two-chain collective object is zero. This assumption is inconsistent with the Einstein diffusion relation. Such Monte Carlo calculations cannot reliably test models for chain diffusion in solution.)

Third, the notion that polymer chains and their tubes of near neighbors move independently overlooks the existence of hydrodynamic interactions. These interactions arise because the random forces that drive Brownian motion are not totally uncorrelated. Instead, there exist *strong* correlations ("hydrodynamic interactions") between random forces on neighboring polymer chains. Hydrodynamic interactions cause the motion of a polymer to be accompanied by parallel motions of neighboring chains. Indeed, with stick boundary conditions, collisions between a chain and its neighbors do not occur; with stick boundary conditions the relative velocity of two bodies in contact is zero.[35]

The blob model of polymer dynamics describes direct and hydrodynamic interactions as being effective within a blob, but assumes that these interactions are screened over the distances between blobs.[36] In contrast to this description, eq 13 and 14 exhibit hydrodynamic interactions between complete molecules, without modification by other, intervening polymer molecules. Is there hydrodynamic screening in solution?

The term "hydrodynamic screening" takes its name from Debye screening of electrostatic forces. The Coulomb potential and the Oseen hydrodynamic interaction tensor are both $1/r$ interactions. In electrolyte solutions, correlations between the particle positions modify interparticle interactions, so that the pair correlations and the pair potential of average force in an electrolyte solution are $\exp(-kr)/r$ instead of $1/r$, k being the inverse Debye length. It is sometimes argued by analogy with the electrostatic potential that long-range hydrodynamic interactions are also screened, so that the $1/r$ Oseen interaction should be replaced in concentrated solutions by a short-range $\exp(-kr)/r$ interaction. The analogy is rather weak, as there are actually two $1/r$ potentials in nature, the electrostatic and the gravitational. In the last half-decade, Kandrup and co-workers[37] have analyzed the statistical mechanics of gravitating mass points (as experimentally realized by stars in galactic clusters). The statistical-mechanical behavior of charged and gravitating point masses are totally different, even though both are characterized by $1/r$ interactions. In particular, while electrostatic forces give density correlations that are proportional to $\exp(-kr)/r$, the density correlations due to gravity have the totally different form $\cos(k'r)/r$, k' being the inverse Jeans length. The assertion that hydrodynamic interactions must be exponentially screened "by analogy with the other long-range force" is not supportable, because one of the other long-range forces is not screened.

Detailed many-body calculations have been made on particle wakes in suspensions of fixed obstacles and on interactions in concentrated suspensions of mobile spheres. Cukier[10] and Altenberger et al.[11] both found that the wake of a particle moving through a system of fixed obstacles is subject to screening. The moving particle acts as a momentum source, while the fixed particles—as centers of friction—act as momentum sinks, removing momentum from the wake of the moving particle. In contrast, Beenakker and Mazur[38] have calculated the hydrodynamic interactions of mobile spheres, resumming the ring diagrams responsible (in the electrostatics problem) for Debye screening. Beenakker and Mazur demonstrate that many-body hydrodynamic interactions renormalize the hydrodynamic interaction tensors, weakening them by a multiplicative constant, but do not change the interaction range. These detailed hydrodynamic calculations find no evidence for hydrodynamic screening by mobile particles. Indeed, for suspensions of mobile pointlike particles, de Gennes has proven from translational invariance that hydrodynamic screening cannot occur.[36] These arguments suggest that the lack of hydrodynamic screening in eq 14 is not a serious difficulty for our model.

References and Notes

(1) Phillies, G. D. J. *Macromolecules* **1986**, *19*, 2367.
(2) Callaghan, P. T.; Pinder, D. N. *Macromolecules* **1984**, *17*, 431.
(3) Smith, B. A.; Mumby, S. J.; Samulski, E. T.; Yu, L.-P. *Macromolecules* **1986**, *19*, 470.
(4) Edwards, S. F. *J. Phys. A* **1975**, *8*, 1670.
(5) de Gennes, P.-G. *Macromolecules* **1976**, *9*, 594.
(6) Brochard, F.; de Gennes, P.-G. *Macromolecules* **1977**, *10*, 1157.
(7) Schaeffer, D. W.; Joanny, J. F.; Pincus, P. *Macromolecules* **1980**, *13*, 1280.
(8) Phillies, G. D. J.; Ullmann, G. S.; Ullmann, K.; Lin, T.-H. *J. Chem. Phys.* **1985**, *82*, 5242.
(9) Mazur, P.; van Saarloos, W. *Physica A: (Amsterdam)* **1982**, *115A*, 21.
(10) Cukier, R. I. *Macromolecules* **1984**, *17*, 252.
(11) Altenberger, A. R.; Dahler, J. S.; Tirrell, M. *J. Chem. Phys.* **1986**, *84*, 5122.
(12) Kirkwood, J. G.; Riseman, J. *J. Chem. Phys.* **1948**, *16*, 565.
(13) Carter, J. M.; Phillies, G. D. J. *J. Phys. Chem.* **1985**, *89*, 5118.
(14) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P.-G. *Macromolecules* **1975**, *8*, 804.
(15) Lin, T.-H.; Phillies, G. D. J. *Macromolecules* **1984**, *17*, 1686.
(16) Brown, W.; Stilbs, P.; Johnsen, R. M. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1771.
(17) Callaghan, P. T.; Pinder, D. N. *Macromolecules* **1980**, *13*, 1085.
(18) Callaghan, P. T.; Pinder, D. N. *Macromolecules* **1981**, *14*, 1334.
(19) Callaghan, P. T.; Pinder, D. N. *Macromolecules* **1983**, *16*, 968.
(20) Callaghan, P. T.; Pinder, D. N. *Macromolecules* **1984**, *17*, 431.
(21) Daivis, P.; Snook, I.; van Megen, W.; Preston, B. N.; Comper, W. D. *Macromolecules* **1984**, *17*, 2376.
(22) Gros, G. *Biophys. J.* **1978**, *22*, 453.
(23) Hanley, B.; Tirrell, M.; Lodge, T. *Polym. Bull.* **1985**, *14*, 437.
(24) Hervet, H.; Leger, L.; Rondelez, F. *Phys. Rev. Lett.* **1979**, *42*, 1681.
(25) Leger, L.; Hervet, H.; Rondelez, F. *Macromolecules* **1984**, *14*, 1732.
(26) Nemoto, N.; Inoue, T.; Makita, Y.; Tsunashima, Y.; Kurata, M. *Macromolecules* **1985**, *18*, 2516.
(27) Smith, B. A.; Mumby, S. J.; Samulski, E. T.; Yu, L.-P. *Macromolecules* **1986**, *19*, 470.
(28) Tirrell, M., private communication.

(29) von Meerwall, E. D.; Amis, E. J.; Ferry, J. D. *Macromolecules* **1983**, *16*, 1715.
(30) von Meerwall, E. D.; Amis, E. J.; Ferry, J. D. *Macromolecules* **1985**, *18*, 260.
(31) Wesson, J. A.; Noh, I.; Kitano, T.; Yu, H. *Macromolecules* **1984**, *17*, 782.
(32) Kivelson, D. Paper presented at the "Conference on Quasi-Elastic Light Scattering Spectroscopy—Ideas and Interpretations", Worcester, MA, June 1986.
(33) Peczak, P.; Phillies, G. D. J., in preparation.
(34) de Gennes, P.-G. *J. Chem. Phys.* **1971**, *55*, 572.
(35) Schurr, J. M. *Chem. Phys.* **1982**, *65*, 217.
(36) de Gennes, P.-G. *Macromolecules* **1976**, *9*, 594.
(37) Kandrup, H. E.; Kandrup, S. H. *Astrophys. J.* **1984**, *277*, 1.
(38) Beenakker, C. W. J.; Mazur, P. *Physica A: (Amsterdam)* **1984**, *126A*, 349.

Dynamic Mechanical Properties of Poly(γ-benzyl L-α-glutamate) Gels in Benzyl Alcohol

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ABSTRACT: The dependencies of the loss and storage moduli of solutions of poly(γ-benzyl L-glutamate) in benzyl alcohol on temperature, composition, and frequency are reported. It is found that the rheological behavior of the gel phase is dominated by kinetics and strongly depends on whether the gel is prepared from the high-temperature isotropic phase, biphasic phase, or the liquid crystalline phase.

Introduction

The growing demand for high-modulus fibers has resulted in the recent upsurge in the synthesis and production of liquid crystalline polymers. Due to their rigidity, rigid rodlike polymers tend to retain good orientation during spinning into fibers. In solution spinning, the polymer solution is extruded through a spinneret and the fibrils are drawn through a bath, called a coagulation bath, wherein the most important phenomenon, gelation, occurs. The strength of the fibers depends upon the gelation conditions.[1] Gelation is also an important phenomenon in many biological systems.[2-7] There are two distinct types of gels. In one, all the cross-links are chemically cross-linked and hence are permanent. In the other, the junction points are mobile in the sense that these cross-links will be continuously formed by physical entanglements and deformed. These physical cross-links make the gels thermoreversible, with the name suggesting that these gels go into solution on heating and the network is re-formed on cooling. In this work, we mainly focus our attention on such gels formed by the synthetic polypeptide poly(γ-benzyl L-α-glutamate) (PBLG) in the helicogenic solvent benzyl alcohol (BA).

The classic picture for the phase diagram of rigid rod polymers in solution is due to Onsager[8] and Flory,[9] showing three distinct phases depending upon the temperature and concentration (Figure 1). At sufficiently low concentration and high temperature, the solution is in the isotropic phase. Between the concentrations corresponding to the Robinson A[10,11] and the Robinson B[10,11] points and at high temperatures, the solution is in the narrow biphasic phase, wherein the isotropic and the liquid crystalline phases coexist. Beyond the concentrations corresponding to the Robinson B point and at high temperatures, the solution is in the pure liquid crystalline phase. At lower temperatures, all the phases go into the so-called wide biphasic phase. It is in this phase that the above-mentioned gelation occurs. Experimental results for the phase diagram for some rigid rodlike polymers in solution agree qualitatively[12,13] with Flory's theory, but many researchers have questioned the use of Flory's theory as a quantitative measure because of the assumptions involved in the development of the theory.[14] The effect of side-chain flexibility on phase equilibria was included in Flory's theory by Wee and Miller,[15] and later Flory and co-workers[16-22] incorporated polydispersity into their theoretical model to study its effect on the phase equilibrium. Miller et al.[12,13,15,23-27] made extensive studies on PBLG in various other solvents to arrive at the correct phase diagram based on their optical microscopic observations and their measurements of cholesteric pitch as a function of temperature by static light scattering. Sasaki et al.[28,29] and Ginzburg et al.[30] investigated the phase diagram for the PBLG–BA and PBLG–DMF systems, respectively. More basic than determining the phase boundaries are the questions concerning the definition and identification of the gel phase and the molecular origins of such a phase. These fundamental questions and the added complexity of the dynamics in each phase pose considerable difficulties to the successful development of a good theory that can describe the dynamics of such polymers in all phases. In this work, we attempt to make a systematic study of each phase for one such system, PBLG in benzyl alcohol, with the aim of understanding the dynamical behavior in each phase by performing oscillatory shear experiments. For this system, the isotropic and cholesteric phases are separated by a narrow biphasic region at higher temperatures. As the temperature is lowered, a gel phase is formed at all concentrations. Our goal is to establish the boundaries of the gel phase and to understand the nature of the gel phase.

Experimental Section

PBLG was purchased from Sigma Chemicals and the solutions were prepared by weighing the polymer and the solvent. The concentrations are expressed as weight percentage. The polymer (MW = 345 000) was dissolved by heating the solution to 70 °C with mechanical stirring. Rheological measurements were performed on a Rheometrics dynamical spectrometer fitted with parallel plates of 25-mm diameter. For the sinusoidal deformation, the applied stress (σ) and the strain (γ) are related by[31]

$$\sigma = \gamma[G' \sin(\omega t) + G'' \cos(\omega t)] \quad (1)$$

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