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Quantitative Prediction of α in the Scaling Law for Self-Diffusion[†]

George D. J. Phillies

Department of Physics, Worcester Polytechnic Institute, Worcester, Massachusetts 01609.

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ABSTRACT: The Kirkwood–Riseman picture of interacting polymer beads is used to calculate the parameter α of the universal scaling law $D_s = D_0 \exp(\alpha c^{\upsilon})$ for polymer self-diffusion. The previously predicted (Phillies, G. D. J. *Macromolecules* 1987, *20*, 558) behavior $\alpha \sim M^{-1}$, M being the polymer molecular weight, is confirmed. In contrast to previous work, the numerical prefactor of α is here obtained. For $M = 1.0 \times 10^6$ polystyrene in a good solvent, $\alpha = -2$, within calculational uncertainty of the experimental $\alpha = -0.7$ for this M. An extension of the universal scaling law to rotational diffusion is presented.

Introduction

The dependence of the self-diffusion coefficient D_s of random-coil polymers in good solvents upon polymer molecular weight M and concentration c has for the past decade been a topic of intense experimental and theoretial investigation.[1,2] Motivated by my laboratory's experimental studies[3] on the diffusion of spherical probe particles through polymer and protein solutions, I recently advanced a simple scaling law[4]

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

for D_s. Comparison[4] of the scaling law with the entirety of the then-available literature found eq 1 to be valid in every case, including good solvent systems of long polymers at semidilute and dilute concentrations, short polymers ($M <$ the critical molecular weight M_e for entanglement) at all concentrations, protein solutions, and polymers in θ solvents. For random-coil polymers in good solvents, D_0, α, and υ were all found to have simple correlations with M. More recently, a derivation of eq 1, based on the dominance of hydrodynamic forces over polymer entanglements, was obtained.[5] The derivation predicted the functional form of eq 1, numerical values for υ, and the M dependence of α, all of which were in good agreement with experiment.

A significant limitation of ref 5 is that it did not predict the numerical value of α, only its M dependence. This limitation is here removed, using a bead-spring picture of polymer chains to compute α. In a natural extension, the model is used to treat the rotational diffusion coefficient D_r of interacting polymer coils, including relations between D_r, c, and M.

Computation of α for Translational Diffusion

In this paper we discuss treatment of polymer chains in good solvents, using a refinement of the general dynamic model of Kirkwood and Riseman.[6] In this model, a polymer chain is represented as a sequence of N beads of radius a_0, the beads being separated by rigid or semirigid couplings ("springs"), which constrain the probable equilibrium configurations of the polymer beads. Bead–bead interactions include the following: (i) the rigid couplings (bonds) between adjoining monomers; (ii) hard-core "excluded volume" interactions, which prevent the beads from overlapping, thereby ensuring that chains cannot come closer to each other than a distance $2\alpha_0$ (in the original paper of Kirkwood and Riseman,[6] which only required $\langle r_{ij}^{-n} \rangle$ for $n = 1$, excluded volume interactions were not critical; with $n > 1$ (as arises here) such interactions will need to be treated explicitly); (iii) hydrodynamic interactions, which describe the wake set up by a polymer molecule acted on by an external force, and also the correlations between the random Brownian forces on different polymer beads. A moving bead, with velocity $\mathbf{v}_r$ relative to the solvent, applies a force $6\pi\eta\alpha\mathbf{v}_r$ on the solvent. The response of the solvent—a hydrodynamic interaction between a pair of beads—can be described by the Rotne–Prager hydrodynamic interaction tensor[7]

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$$\boldsymbol{T}_{\mathrm{rp}} = \frac{1}{8\pi\eta}\left[\frac{\boldsymbol{I} + \hat{r}\hat{r}}{r} + \frac{{a_0}^2}{r^3}\,\frac{\boldsymbol{I} - 3\hat{r}\hat{r}}{3}\right] \tag{2}$$

where η is the solvent viscosity, r is the distance between a pair of interacting beads, $\boldsymbol{I}$ is the identity tensor, and $\hat{}$ denotes the unit vector, so $\hat{r} = \mathbf{r}/r$ is the unit vector along the beads' line of centers, where $r = |\mathbf{r}|$. $\boldsymbol{T}_{\mathrm{rp}}$ is the zero-frequency Green's function for the fluid velocity induced at $\mathbf{r}$ by a unit force applied at the origin.

Most polymer calculations have limited themselves to the long-range $0(r^{-1})$ term of $\boldsymbol{T}_{\mathrm{rp}}$, namely, the Oseen tensor $\boldsymbol{T}$. Mazur[8] and co-workers have shown how $\boldsymbol{T}$ can extend to a higher order in a/r and include more than two beads; for other extensions of $\boldsymbol{T}$, note the results of Kynch,[9] Felderhof,[10] and Phillies.[11] Numerical calculations[12] on the drag coefficient of fixed configurations of spheres indicate that three- and four-body hydrodynamic interactions and the r^{-7} continuation of $\boldsymbol{T}_{\mathrm{rp}}$ largely cancel each other, so that calculations performed with $\boldsymbol{T}_{\mathrm{rp}}$ obtain nearly the same results as calculations performed with more elaborate forms for the hydrodynamic interaction tensors.

Because of hydrodynamic interactions, all beads do not make the same contribution to the total drag coefficient f_0 of a polymer. Deletion of a bead located near the core of a polymer has a smaller effect ("hydrodynamic screening") on f_0 than does deletion of a bead located near the periphery of the molecule. This variation in the contribution to f_0 of different beads is a consequence of the properties of $\boldsymbol{T}$, not a consequence of differences between different beads. All beads are initially assumed to have the same bare drag coefficient ζ.

The Kirkwood–Riseman description of interacting polymer beads will be used in the context of the hydrodynamic scaling model[5] for polymer self-diffusion. The model has previously been described in full and is summarized here:

(1) The effect of a concentration increment Δc on the mobility μ of a polymer chain is taken to be

$$\mu(c + \Delta c) = \mu(c) + A\Delta c \tag{3}$$

where the drag coefficient increment A is linearly proportional to $\mu(c)$.

(2) The dominant force between polymers in semidilute solution ($c > c^*$) is hydrodynamic. While polymers are subject to "topological" constraints, in that they cannot pass through each other, such constraints provide second-order corrections to the dynamics, not dominant forces. This assumption is precisely contrary to the assumption of the reptation-scaling models that topological constraints dominate all other forces. The dependence of A on polymer size can be obtained from hydrodynamic arguments; by comparison with results on spherical particles, $A \sim R_{\mathrm{ga}}{R_{\mathrm{gb}}}^3$, where R_{ga} is R_{g} of the diffusing polymer and R_{gb} is R_{g} of the other chains in solution.

(3) R_{g} falls with increasing polymer concentration, as described by the blob model of Daoud et al;[13] for $c > c^*$

$${R_{\mathrm{g}}}^2 \sim Mc^x \tag{4}$$

with $x = -{}^1/_4$. As is apparent from ref 13, Figure 6, this contraction begins at $c \ll c^*$, is perhaps one-third complete at the critical overlap concentration c^*, and continues all the way to the melt.

(4) Equation 3 is bootstrapped to large c via a self-similarity assumption, replacing

$$\mu(c + \Delta c) = \mu(c) + A\Delta c \rightarrow \mu(c) = \mu_0 \exp\left(\int_0^c \frac{A(c)\ \mathrm{d}c}{\mu_0}\right) \tag{5}$$

where μ_0 is the mobility of an isolated chain, contracted as per eq 4. A process similar to eq 5 has previously been used, e.g., by Adler and Freed,[14] where it was identified as a mean-field approximation.

(5) Since $D_{\mathrm{s}}(c) = k_{\mathrm{B}}T\mu(c)$, k_{B} being Boltzmann's constant and T the absolute temperature,

$$D_{\mathrm{s}}(c) = D_0 \exp\left(\int_0^c \frac{A(c)\ \mathrm{d}c}{\mu_0}\right) \tag{6}$$

Substitution of eq 2–5 into eq 6 gives $\int \mathrm{d}c\ A(c)/\mu_0 = \alpha c^{\upsilon}$ for $\alpha \sim M^1$ and $\upsilon = 1 - 2x$. The bootstrapping process must be performed separately at each concentration. $D_0 = k_{\mathrm{B}}T\mu_0$ refers to the diffusion coefficient of an isolated probe polymer which has been subject to the contraction described by eq 4. D_0 is therefore not a simple constant; instead, it should increase with c inversely to the contraction of R_{g}. This variation of D_0 with c, which is not a large effect, has been observed experimentally.[15]

The objective of this paper is to obtain $A(c)$, thereby replacing the proportionality symbols in steps 1–3 with equalities. The overall approach uses a generalization of Einstein's derivation of the Stokes–Einstein diffusion equation. To find the hydrodynamic interaction coefficient characteristic of a Brownian motion of a polymer in an equilibrium system, one treats the parallel problem in the nonequilibrium hydrodynamics of a polymer moving under the influence of an external force. Following Einstein, the hydrodynamic interaction coefficient obtained by solving the nonequilibrium problem is taken to be the same as the corresponding coefficient in the Brownian motion problem. Here the objective is to determine the retardation in the Brownian motion of a polymer chain by a second chain. The corresponding nonequilibrium problem is to treat the perturbation of the translational motion of a polymer chain by a second polymer chain, the first chain moving because it is subject to some uniform external force $\mathbf{F}$.

The hydrodynamic calculation is based on a method of reflections. The calculation consists of computing a series of velocities, each velocity leading in turn to the next. The first polymer has unperturbed mobility μ_0 and is subject to a uniform external force $\mathbf{F}$, giving its beads a velocity $\mathbf{V} = \mu_0\mathbf{F}$ with respect to the solvent. The drag ($\zeta\mathbf{V}$ by each bead) creates a flow field $\mathbf{v}_1(\mathbf{r})$ at a point $\mathbf{r}$ in the solvent. The second polymer responds to $\mathbf{v}_1(\mathbf{r})$, among other ways, by gaining a center-of-mass velocity $\mathbf{v}_2$ and average angular velocity ω_2 around its center. The second polymer furthermore creates an "echo" flow field $\delta\mathbf{v}(\mathbf{r})$. $\delta\mathbf{v}(\mathbf{r})$ acts back on the first polymer, giving it a velocity increment $\Delta\mathbf{v} = \boldsymbol{B}\cdot\mu_0\mathbf{V}$, where the interaction tensor $\boldsymbol{B}$ depends on $\mathbf{R}$. The second chain thus gives the first chain a perturbed mobility μ satisfying $\mu\cdot\mathbf{F} = \mathbf{V} + \Delta\mathbf{v}$. On averaging over the allowed positions $\mathbf{R}$ of the second chain, symmetry requires that $\mathbf{V}$ and $\langle\Delta\mathbf{v}\rangle$ be parallel, with the brackets $\langle\ \rangle$ denoting the ensemble average over $\mathbf{R}$. $\langle\boldsymbol{B}\rangle$ therefore acts on $\mathbf{V}$ as would a scalar, so

$$\langle\mu\cdot\mathbf{F}\rangle = \mu_0\mathbf{F}\cdot\boldsymbol{I}(1 + \langle\boldsymbol{B}\rangle) \tag{7}$$

By comparison with eq 3, $\langle\boldsymbol{B}\rangle$ gives the numerical prefactor $A(c)/\mu_0$ required to evaluate eq 6.

The original model of Kirkwood and Riseman[6] involved one polymer chain. Here there are two chains, whose centers of mass are separated by $\mathbf{R}$. The vectors from the centers of mass of the two chains to points within the chains will be denoted $\mathbf{s}_1$ and $\mathbf{s}_2$, respectively. $\mathbf{s}_1$ and $\mathbf{s}_2$ are field variables, not bead positions; they also serve as expansion parameters, with calculations being performed in their lowest non-zero order. The relaxation time for the bead positions is assumed to be much larger than the time required for the Oseen and Rotne–Prager tensors to become applicable. The distribution function for bead positions is taken to have its equilibrium form $g(s)$ at all interesting times. It is convenient to adopt a nonstandard normalization of $g(s)$, weighting $g(s)$ proportional to the friction factor of each bead, so

$$\int \mathrm{d}\mathbf{s}\; g(\mathbf{s}) = f_0 \tag{8a}$$

The radius of gyration follows

$$\langle R_g^2 \rangle = \int \mathrm{d}\mathbf{s}\; s^2 \tilde{g}(\mathbf{s}) \tag{8b}$$

with $f_0 = 1/\mu_0$ being the drag coefficient of an isolated chain. $\tilde{g}(\mathbf{s}) = g(\mathbf{s})/f_0$, the normalized drag coefficient distribution, is the conventional radial distribution function. For this work, only the second moment (eq 8b) of $g(s)$ is needed; eq 4 models the dependence of $g(s)$ on c.

Begin with the first polymer. Its beads exert on the solvent a force density $\tilde{g}(s) f_0 \mathbf{V}$, creating a total flow field $\mathbf{v}_1(\mathbf{r})$ at $\mathbf{r}$, namely

$$\mathbf{v}_1(\mathbf{r}) = \int \mathrm{d}\mathbf{s}_1\; \tilde{g}(\mathbf{s}_1) \boldsymbol{T}_{\mathrm{rp}}(\mathbf{r} - \mathbf{s}_1)\cdot f_0 \mathbf{V} \tag{9}$$

$\mathbf{r}$ and $\mathbf{s}_1$ are measured from the center of mass of the first polymer chain. For this calculation, the Oseen approximation to $\boldsymbol{T}_{\mathrm{rp}}$ suffices. Expanding $\boldsymbol{T}(\mathbf{r} - \mathbf{s}_1) = \boldsymbol{T}(\mathbf{r}) - (\mathbf{s}_1\cdot\nabla)\boldsymbol{T}(\mathbf{r})$, for the flow field of a single bead one has

$$\mathbf{v}_0(\mathbf{r} - \mathbf{s}_1) = \frac{3a}{4r}(\boldsymbol{I} + \hat{r}\hat{r})\cdot\mathbf{V} - \frac{3as_1}{4}[-\hat{s}_1\cdot\hat{r}\mathbf{V} + \hat{r}\cdot\mathbf{V}\hat{s}_1 + \hat{s}_1\cdot(\boldsymbol{I} - 3\hat{r}\hat{r})\cdot\mathbf{V}\hat{r}]/f_0 \tag{10}$$

where the relations $\mathrm{d}r/\mathrm{d}x = -x/r^3$, $\mathbf{s}\cdot\nabla(\hat{r}) = s\hat{s}\cdot(\boldsymbol{I} - \hat{r}\hat{r})/r$, and $\mathbf{s}\cdot\nabla(r^{-1}) = \mathbf{s}\cdot\hat{r}/r^2$ were employed, with $s = |\mathbf{s}|$ and $\hat{s} = \mathbf{s}/s$. The total flow field $\mathbf{v}_1(\mathbf{r})$ is obtained from eq 7a and 10 as $\int \mathrm{d}\mathbf{s}_1\, \tilde{g}(\mathbf{s}_1)\, \mathbf{v}_0(\mathbf{r})$. By spherical symmetry, terms odd in $\mathbf{s}_1$ vanish. Recalling how $g(\mathbf{s})$ is normalized, the total flow established at $\mathbf{r}$ by polymer 1 is

$$\mathbf{v}_1(\mathbf{r}) = \frac{3a}{4r}(\boldsymbol{I} + \hat{r}\hat{r})\cdot\mathbf{V} \tag{11}$$

the first correction for the size of the first polymer being neglected because it is of order s_1^2.

A second Taylor series expansion $\mathbf{v}_1(\mathbf{R} + \mathbf{s}_2) = \mathbf{v}_1(\mathbf{R}) + \mathbf{s}_2\cdot\nabla(\mathbf{v}_1(\mathbf{R}))$ establishes the flow field, at a point $\mathbf{s}_2$ with respect to the center of the second polymer, as

$$\mathbf{v}_1(\mathbf{R} + \mathbf{s}_2) = \frac{3a}{4R}(\boldsymbol{I} + \hat{R}\hat{R})\cdot\mathbf{V} + \frac{3as_2}{4R^2}[-\hat{s}_2\cdot\hat{R}\mathbf{V} + \hat{R}\cdot\mathbf{V}\hat{s}_2 + \hat{s}_2\cdot(\boldsymbol{I} - 3\hat{R}\hat{R})\cdot\mathbf{V}\hat{R}] \tag{12}$$

The effect of the second polymer on the solvent flow is tempered by the requirement that the polymer be subject to no net force or net torque. If the second polymer's center of mass motion and net rotation are denoted by $\mathbf{v}_2$ and ω_2, the zero force and zero torque conditions are

$$\int \mathrm{d}s_2\; f_0 g(\mathbf{s}_2)[\mathbf{v}_1(\mathbf{R} + \mathbf{s}_2) - \mathbf{v}_2] = 0 \tag{13a}$$

$$\int \mathrm{d}\mathbf{s}_2\; f_0 g(\mathbf{s}_2)[\mathbf{s}_2 \times (\mathbf{v}_1(\mathbf{R} + \mathbf{s}_2) - \omega_2 \times \mathbf{s}_2)] = 0 \tag{13b}$$

A polymer is not a rigid body. ω_2 corresponds to the rate of change in the lowest Rouse mode.

Internal deformations of the polymers occur on time scales shorter than that fixed by ω_2. These deformations are neglected, as a first approximation, because they supply high-frequency corrections to D_s. Neglect of internal deformations is most appropriate for polymer motions occurring over distances $> R_g$. If one polymer is made increasingly larger than the other, eventually the local motions of the larger polymer and the whole-body motions of the smaller polymer occur over the same distance and time scales. Once this condition is reached, internal deformations of the larger polymer must be included in the calculation. The model developed here is thus primarily applicable to polymer pairs of roughly equal molecular weights.

(While whole-body motions are M-dependent, local chain motions are not. If the ratio R_{ga}/R_{gb} is made increasingly different from unity, local chain motions will become increasingly important in a description of chain–chain dynamics. Increasing R_{ga}/R_{gb} will reduce the importance of M-dependent whole-chain contributions to chain dynamics, so when $R_{ga}/R_{gb} \gg 1$ or $R_{ga}/R_{gb} \ll 1$, the M dependence of D will be weaker than that predicted here or in ref 6.)

Taking into account that g only depends on $|\mathbf{s}_2|$, eq 13a becomes

$$\mathbf{v}_2 \int \mathrm{d}\mathbf{s}_2\; \tilde{g}(\mathbf{s}_2) = \int \mathrm{d}s_2\; s_2^2 \tilde{g}(s_2) \int \mathrm{d}\Omega_s \left[\frac{3a}{4R}(\boldsymbol{I} + \hat{R}\hat{R})\cdot \boldsymbol{V} + \frac{3as_2}{4R^2}\, O(\hat{s}_2^{\,1})\right] \tag{14}$$

On the right-hand side of the equation, terms odd in $\mathbf{s}_2$ vanish by symmetry, so

$$\mathbf{v}_2 = \frac{3a}{4R}(\boldsymbol{I} + \hat{R}\hat{R})\cdot\mathbf{V} \tag{15}$$

A more tedious calculation shows

$$\omega_2 = \frac{3aV}{4R^2}(\hat{V} \times \hat{R}) \tag{16}$$

The motion of polymer 2 relative to the fluid creates an additional fluid motion $\delta\mathbf{v}(\mathbf{r})$ (an "echo") near polymer 1, namely

$$\delta\mathbf{v}(\mathbf{r}) = \int \mathrm{d}\mathbf{s}_2\; \tilde{g}(\mathbf{s}_2)\boldsymbol{T}(\mathbf{s}_1 - \mathbf{R} - \mathbf{s}_2)\cdot f_0[\mathbf{v}_2 + \omega_2 \times \mathbf{s}_2 - \mathbf{v}_1(\mathbf{R} + \mathbf{s}_2)] \tag{17}$$

Substitute for $\mathbf{v}_2$, ω_2, and $\mathbf{v}_1$, and make Taylor series expansions in powers of $\mathbf{s}_1$ and $\mathbf{s}_2$. An average $\int \mathrm{d}\mathbf{s}_1\, g(\mathbf{s}_1)$-$\delta\mathbf{v}(\mathbf{s}_1)$ over polymer 1 eliminates Taylor series expansion terms which were odd in $\mathbf{s}_1$, so only $(\mathbf{s}_1)^0$ terms remain.

$$\delta\mathbf{v}(0) = \int \mathrm{d}\mathbf{s}_2\; \tilde{g}(\mathbf{s}_2) s_2^2 \frac{3a_2}{4R^2}\{-\hat{s}_2\cdot\hat{R}\boldsymbol{I} + \hat{s}_2\hat{R}\cdot\boldsymbol{I} + \hat{R}\hat{S}_2\cdot(\boldsymbol{I} - 3\hat{R}\hat{R})\}\cdot \left\{\frac{3a_1 V}{4R^2}\hat{R}\cdot\hat{V}(\boldsymbol{I} - 3\hat{R}\hat{R})\cdot\hat{s}_2\right\} \tag{18}$$

Here a_1 and a_2 are the hydrodynamic radii of the two polymers, from $f_0 = 6\pi\eta a$. The first term in braces arises from $\mathbf{s}_2\cdot\nabla(\boldsymbol{T}(\mathbf{R}))$; the second term in braces arises from $\omega_2 \times \mathbf{s}_2 - \mathbf{s}_2\cdot\nabla(\mathbf{v}_1(\mathbf{R}))$. By comparison with eq 7 and 8, $\boldsymbol{B}$ is

$$\boldsymbol{B} = \frac{-9a_1a_2R_{gb}^2}{8R^4}\hat{R}\hat{R} \tag{19}$$

Cannell et al.[16] note that a_i is roughly 30% smaller than R_{gi}, so $a_1a_2 \cong R_{ga}R_{gb}/2$. As predicted in ref 6, α has the same functional dependence on R_a, R_b, R, and $\hat{R}$ as does the corresponding term in the hydrodynamic interaction between two freely rotating, freely translating hard spheres. Only the numerical coefficient differs between the two cases.

Equation 19 gives $\boldsymbol{B}$ for the case that the second polymer is definitely at $\mathbf{R}$. Averaging $\mathbf{R}$ over all space (with cutoff $R > 2a_0$ due to the bead size), summing over the independent contributions of polymer chains 2, ..., N to the *linear* concentration dependence of $\boldsymbol{B}$, and substitution in eq 3–7 give

$$D_\mathrm{s} = D_0 \exp(\alpha c^\upsilon) \tag{20}$$

with

$$\alpha = -\frac{9}{16}\,\frac{R_\mathrm{ga}}{2a_0}\,\frac{4\pi}{3}\,\frac{{R_\mathrm{gb}}^3}{M_\mathrm{b}}\,\frac{1}{1-2x} \tag{21}$$

The average over R neglects the "correlation hole", the (small[13]) reduction in concentration of neighboring polymer chains within the interstices of a given chain. This neglect would not be appropriate if the polymer chains were replaced by protein molecules, whose distances of closest approach are of the same order of magnitude as their radii of gyration. Increasing the cutoff radius a_0 (in units of R_g) reduces α, so α should be smaller for proteins than for polymer chains of the same hydrodynamic radius, as is in fact observed (ref 5, Figure 2, triangular points).

The factor $1/M_\mathrm{b}$ appeared when the summation over chains 2, ..., N was replaced by an integral over the polymer mass concentration. The factor $1/(1 - 2x)$ arises from the $\int dc$ because R_g shrinks with increasing concentration; R_a and R_b are the hydrodynamic radii at $c = 1$. In some definitions $4\pi R_\mathrm{b}^3/3M = 1/c^*$, c^* being the critical overlap concentration, so

$$\alpha = -\frac{9R_\mathrm{ga}}{32a_0c^*(1-2x)} \tag{22}$$

Substitution of eq 4 into eq 21 gives $\alpha \sim (M_\mathrm{a}M_\mathrm{b})^{1/2}$, in complete agreement with the predictions of ref 6.

For 1×10^6 amu polystyrene, an average of literature values gives[5] $c^* \sim 20$ g/L, which determines R_a at c^* as 270 Å. If one follows a strict reading of the original paper of Kirkwood and Riseman,[6] as is not always done under modern conditions, the beads are interpreted as monomers, in which case a_0 may be estimated from an equivalent sphere having the mass and density of a polystyrene monomer, namely, $a_0 \sim 3.5$ Å. If one interprets the bead concept less literally, a pair of polymer chains can scarcely approach each other closer than the sum of their radii, so $a_0 \sim 3.5$ Å is still a lower bound, i.e., α is being given as an upper bound. At $M = 1 \times 10^6$, $x = {}^1/_4$, so $\alpha \cong -2$. The probable error in the estimate is at least a factor of 2.

By comparison, Figure 2 of ref 6 (which shows data on polymers in good solvents) finds $\alpha = -0.7$ for $M = 1 \times 10^6$. Within the uncertainties in the calculation and the spread in experimental values for α and c^*, there is good agreement between computed and measured values of α. As M is reduced from 1×10^6 to 1×10^5, x falls from ${}^1/_4$ to 0, so—over this range of M—α falls twofold in magnitude relative to its nominal M^1 dependence. The fractional difference between experimental and computed α values is thus smaller at low than at high M.

Concentration Dependence of D_R

In this section the concentration dependence of the rotational diffusion coefficient D_r of a random-coil polymer is computed. First, general arguments are employed to obtain a scaling equation for D_r and the M dependence of its parameters. The methods of the preceding section then determine quantitatively the numerical prefactors of the scaling equation.

D_r of random-coil polymers is expected to be experimentally accessible, though few measurements have been made. Pecora and collaborators[17-19] have published a detailed series of analyses of depolarized light scattering by optically anisotropic macromolecules. In their calculations, a polymer molecule is approximated as being divided into segments, each segment having its own polarizability tensor $\boldsymbol{E}$ and coordinate ρ_j relative to the polymer's center-of-mass $\mathbf{R}_\mathrm{e}$. If ϵ_0 and ϵ_f are the polarization vectors of the incident and scattered light, the scattering spectrum is

$$C(t) = \langle \sum_{i,j,l} \epsilon_f\cdot\boldsymbol{E}_j(0)\cdot\epsilon_0\epsilon_f\cdot\boldsymbol{E}_k(t)\cdot\epsilon_0 \exp[i\mathbf{q}\cdot(\rho_j(t) - \rho_i(0))] \exp[i\mathbf{q}\cdot(\mathbf{R}_l(t) - \mathbf{R}_l(0))]\rangle \tag{23}$$

with $\mathbf{q}$ being the scattering vector. Equation 23 applies to dilute solutions in which the relative positions of pairs of macromolecules are uncorrelated. To apply eq 23 to a bidisperse polymer system, the anisotropic probe polymer must be dilute, though the background ("matrix") polymer—which should not be anisotropic—may be concentrated.

For many polymers, eq 23 has substantial further simplifications. For $qR_\mathrm{g} \ll 1$, the intramolecular interference term $\exp[i\mathbf{q}(\rho_j - \rho_i)]$ is unimportant. On long (μs) time scales, side-chain orientations average away, so that each polymer segment may be approximated as having cylindrical symmetry. Center-of-mass diffusion contributes to $C(t)$ a factor $\exp(-Dq^2t)$, which may be eliminated by taking the $q \rightarrow 0$ limit or by measuring D from the polarized spectrum.

Orientation correlations within $\epsilon_f\cdot\boldsymbol{E}_j(0)\cdot\epsilon_0\epsilon_f\cdot\boldsymbol{E}_k(t)\cdot\epsilon_0$ are of several sorts. Self-correlations ($j = k$) largely reflect rapid local motions. Nearby subunits have equal time correlations extending over the polymer's persistence length. The slow relaxation of these correlations reflects motions of large sections of the molecule. Finally, specifying the end-to-end vector $\mathbf{R}$ of a long polymer constrains the orientation of each segment. $\mathbf{R}$ is the sum of the segmental end-to-end vectors $\mathbf{s}_j$, so specifying $\mathbf{R}$ ensures that $\overline{\mathbf{s}_j} = \mathbf{R}/N$, the average (denoted by the bar) being taken at fixed $\mathbf{R}$. The optical axis of symmetry of a cylindrically symmetric segment must parallel $\mathbf{s}_j$, so $C(t)$ decays like the molecular orientation correlation function $\langle\mathbf{R}(0)\cdot\mathbf{R}(t)\rangle$, whose relaxation time is governed by D_r. The slowest relaxation of the VH spectrum thus measures rotational diffusion of random-coil polymers containing anisotropic subunits.

Depolarized scattering by polymer solutions has been studied experimentally. Han and Yu[20] studied forward depolarized scattering by poly(n-hexyl isocyanate) and isotactic polystyrene, fitting spectra to one or more Lorentzians. Jones and Wang[21] observed a series of polyethylene glycols with M in the range 425–400, determining both M and c dependences. Bauer, Brauman, and Pecora[22] studied depolarized Rayleigh scattering by atactic polystyrenes. These studies each identified a slowest mode whose behavior was that expected for molecular reorientation or the longest wavelength Rouse–Zimm mode. When instrumental capabilities permitted, the studies also observed modes at higher frequencies. The higher frequency modes, which Bauer et al.[22] found to be independent of polymer molecular weight, were interpreted as local chain motions. Published data are thus consistent with the expected connection between depolarized scattering and molecular reorientation.

D_r and the rotational drag coefficient f_r are linked by an Einstein relation

$$D_\mathrm{r} = K_\mathrm{b}T/f_\mathrm{r} \tag{24}$$

In dilute solution, $f_\mathrm{r} \sim R_\mathrm{g}^3$. At elevated concentrations, interactions between neighboring polymer chains modify f_r, the effect of a concentration increment Δ_c being

$$f_r(c + \Delta c) = f_r(c) + A_r f_r(c)\Delta c \qquad (25)$$

assuming that the ability of the incremental polymers to alter f_r is proportional to their rotational drag coefficient at c.

A_r is estimated by comparison with established results on hard spheres. Mazur and van Saarloos[8] have shown that the decrease in a sphere's mobility due to the presence of a second sphere depends on the sphere radii as $R_a^3R_b^3$. Recalling $f_r = 1/\mu_r$, it is here assumed that A_r for random coils and for hard spheres has the same dependence on R_a and R_b. Conversion of eq 24 to a differential equation, integration, and application of eq 4 and 23 give

$$D_r = D_{r0}\exp(\alpha c^{\upsilon}) \qquad (26)$$

for $\upsilon = 1 - 3x$. Quantitatively, $\upsilon = 1$ would be predicted for small M, while $\upsilon = {}^1/_4$ is predicted at large M (though see eq 39 and following). Furthermore

$$\alpha \sim R_{ga}{}^3R_{gb}{}^3/M_b \sim (M_a{}^3M_b)^{1/2} \qquad (27)$$

the factor $1/M_b$ stemming from a conversion from number density to mass concentration. A reexamination[23] of the published literature on polymer rotational diffusion (albeit mostly in systems of rodlike polymers) finds good agreement with eq 26 in every case.

For a numerical computation of α, chain–chain forces are treated with a bead–spring model. The probe polymer has a rotational velocity Ω relative to the local solvent motion, so a polymer bead displaced by $\mathbf{s}_1$ from the polymer center-of-mass has imposed velocity $\mathbf{V}_1 = \Omega \times \mathbf{s}_1$. By analogy with eq 9, the flow field established by this polymer is

$$\mathbf{v}_1(\mathbf{r}) = \int \mathrm{d}\mathbf{s}_1\, \tilde{g}(\mathbf{s}_1) f_0 \boldsymbol{T}(\mathbf{r} - \mathbf{s}_1)\cdot\boldsymbol{\Omega} \times \mathbf{s}_1 \qquad (28)$$

Expansion of $\boldsymbol{T}$ in powers of $\mathbf{s}_1\cdot\nabla$ and retention of the lowest term in $\mathbf{s}_1$ not to be eliminated by the symmetry of $\tilde{g}(\mathbf{s}_1)$ give

$$\mathbf{v}_1(\mathbf{r}) = \frac{a_1 R_{ga}{}^2\Omega\hat{\Omega} \times \hat{r}}{2r^2} \qquad (29)$$

for the flow created at $\mathbf{r}$.

A second polymer centered at $\mathbf{R}$ responds to $\mathbf{v}_1(\mathbf{r})$ through translation, rotation, and higher order internal motions, which are neglected here. The translation and rotation velocities $\mathbf{v}_2$ and ω_2 follow from the zero force and zero torque conditions of eq 13. By expanding $\mathbf{V}_1(\mathbf{r})$ as a series in $(\mathbf{s}_2\cdot\nabla)^n$ around $\mathbf{R}$, eq 13b and 29 give

$$\omega_2 = -\frac{aR_{ga}{}^2\Omega\hat{\Omega}\cdot(\boldsymbol{I} - 3\hat{R}\hat{R})}{4R^3} \qquad (30)$$

From eq 30, if the rotation axis $\boldsymbol{\Omega}$ lies along the line of centers, the two chains rotate with the same sense (e.g., both clockwise). If $\boldsymbol{\Omega}$ is perpendicular to the line of centers, the two polymers rotate with opposite senses, i.e., if $\boldsymbol{\Omega}\cdot\mathbf{R} = 0$ then $\boldsymbol{\Omega}$ and ω_2 are antiparallel.

The motion of the second polymer with respect to the local flow field $\mathbf{v}_1(\mathbf{r})$ exerts a force on the solvent, thereby creating a second ("reflected") flow field

$$\mathbf{v}'(\mathbf{r}) = \int \mathrm{d}\mathbf{s}_2\, f_0\tilde{g}(\mathbf{s}_2)\boldsymbol{T}(\mathbf{r} - \mathbf{s}_2)\cdot[\mathbf{v}_2 + \omega_2 \times \mathbf{s}_2 - \mathbf{v}_1(\mathbf{R} + \mathbf{s}_2)] \qquad (31)$$

Here $\mathbf{s}_2$ and $\mathbf{r}$ are measured from the center of the second polymer. Expansion of $\boldsymbol{T}(\mathbf{r} - \mathbf{s}_2)$ and $\mathbf{v}_1(\mathbf{R} + \mathbf{s}_2)$ leads to further cancellations, namely, from eq 13a, $\mathbf{v}_2 - \mathbf{v}(\mathbf{R}) = 0$, while terms odd in $\mathbf{s}_2$ do not survive integration. An explicit value for $\mathbf{v}_2$ is not needed, so

$$\mathbf{v}'(\mathbf{r}) = -\frac{9a_1a_2R_{ga}{}^2R_{gb}{}^2\Omega}{16R^3r^2}[-2\hat{r}\cdot\hat{R}\hat{\Omega} \times \hat{R} + 2\hat{\Omega} \times \hat{R} - 2\hat{\Omega}\cdot\hat{R}\hat{R} \times \hat{r} + 2\hat{R}\hat{r}\cdot(\hat{\Omega} \times \hat{R}) - 6\hat{r}\hat{r}\cdot\hat{R}\hat{r}\cdot\hat{\Omega} \times \hat{R}] \qquad (32)$$

Since $\boldsymbol{\Omega}$ was defined relative to the local fluid motion, the effect of $\mathbf{v}'(\mathbf{r})$ on the first polymer follows from application of the zero torque condition. The local fluid motion around polymer 1 has a net rotation ω' given (noting that $\mathbf{r}$ of $\mathbf{v}'(\mathbf{r})$ has $\mathbf{r} = 0$ at chain 2) by

$$\int \mathrm{d}\mathbf{s}_1\, f_0\tilde{g}(\mathbf{s}_1)[\mathbf{s}_1 \times \mathbf{v}'(-\mathbf{R} + \mathbf{s}_1) - \mathbf{s}_1 \times (\omega' \times \mathbf{s}_1)] = 0 \qquad (33)$$

A final series expansion of $\mathbf{v}'$, followed by integration, gives

$$\omega' = -\frac{3R_{ga}{}^3R_{gb}{}^3}{32R^6}[2\boldsymbol{\Omega} - 3\boldsymbol{\Omega}\cdot\hat{R}\hat{R}] \qquad (34)$$

with a_1a_2 having been replaced by $R_{ga}R_{gb}/2$ as before. The induced fluid rotation at polymer 1 is opposite in sense to $\boldsymbol{\Omega}$; the second chain acts to retard the rotation of the first. The effect of adding another chain to the solution is determined by averaging eq 34 over the solution volume V, namely

$$\langle\omega'\rangle = V^{-1}\int_{R_0}^{\infty} R^2\,\mathrm{d}R \int \mathrm{d}\Omega\,\omega' \qquad (35)$$

with R_0 being the cutoff distance or

$$\langle\omega'\rangle = -\Omega\frac{3}{2048}\frac{4\pi}{3}\frac{R_{ga}{}^3R_{gb}{}^3}{R_0{}^3V} \qquad (36)$$

Simple mechanical considerations indicate that the cutoff distances for the translation and rotation problems are not the same. For translation, $R_0 = 2a_0$ is dictated by the distance of closest approach of two polymer chains. For rotation, R_0 is determined by the spatial pattern of two overlapping, displaced rotations. As long as two polymers are separated by a distance $R > R_a$ or R_b, their rotation vectors $\boldsymbol{\Omega}$ and ω are antiparallel. In the region of overlap, which lies (since $R > R_a$ or R_b) exclusively between the two centers, $\mathbf{s}_1$ and $\mathbf{s}_2$ are also antiparallel, so in this region beads of the two chains move on roughly parallel courses. However, if the polymers are separated by a distance $R < R_a$ or R_b, the overlap region extends beyond the center of each polymer. In this extended region, where $|\mathbf{s}_1| > R$ or $|\mathbf{s}_2| > R$, simple rotation of the two chains would cause their beads to move in antiparallel directions, a mode suppressed by the short-range components of $\boldsymbol{T}$. Replacement of whole-body rotation of chain 2 by local motions in which the two chains duplicate each other's displacements would substantially reduce the ability of the second chain to retard the first chain's motions, so that the chain–chain interaction of eq 34 is ineffective for $R < R_a$, giving $R_0 = R_a/2$ as the cutoff. This approximation is clearly not complete; for example, it neglects the extent to which the matrix polymers can increase the effective viscosity of the fluid within the volume occupied by the probe polymer.

Multiplying eq 25 by the torque $\tau = \Omega/\mu_r(c)$ gives

$$\tau\mu_r(c+\Delta c) = \Omega + A_r\Omega\Delta c \qquad (37)$$

Equation 36 refers to the addition of one matrix chain to the system, so $\Delta c = 1/V$; from eq 36 and 37

$$A_r = -\frac{3}{256}\left(\frac{R_{ga}}{R_0}\right)^3\frac{4\pi R_{gb}{}^3}{3M_b} \qquad (38)$$

Equation 38 is consistent with eq 26 and 27, *except* that the cutoff R_0 is concentration dependent. If R_a and R_b are assigned their values at $c = 1$, so $R_b(c) = R_b c^{x/2}$, it is predicted that

$$D_r = D_{r0} \exp(\alpha c^{v}) \tag{39}$$

for $v = 1 - 3x/2$ and

$$\alpha = -\frac{24}{256(1 - 3x/2)c^*} \tag{40}$$

For small M, $v = 1$; for large M, $v = {}^5/_8$. For an $M = 1 \times 10^6$ polymer one obtains $\alpha \cong 8 \times 10^{-3}$. There appear to be no data on random-coil polymers that are comparable with the calculated numbers.

Discussion

A method for computing the numerical prefactor α of the universal scaling equation has here been demonstrated. Agreement with experiment is obtained, to within experimental error. Experimentally, α ranges over more than 3 orders of magnitude as M is changed, so a coincidental agreement between data and computation is unlikely. The method was also applied to rotational diffusion, to predict how D_r depends on c and M. Experimental data on the rotational diffusion of random-coil polymers are, however, lacking.

Within the hydrodynamic scaling picture presented here, the self-diffusion of a star polymer is predicted to proceed by essentially the same mechanism as the self-diffusion of a linear polymer of the same size. α values of star and linear polymers of the same size should differ slightly from each other, because the bead distribution functions and correlation holes of star and linear polymers are not the same. (Exhibiting the magnitude of this difference would require a computation more detailed than the one presented here.) In contrast, the reptation scaling models predict for $c > c^*$ that linear and star polymers diffuse by different mechanisms (simple reptation and arm retraction), with D_s of a star polymer falling exponentially with M. Experiment strongly supports the near equality of α for similar star and linear polymers,[15,24] in agreement with the hydrodynamic scaling model.

The above calculation could have been performed while replacing the first polymer with an isolated monomer bead. While this replacement damps the utility of the "self-similarity" approximation, and while low-frequency hydrodynamics are probably inexact for the motions of small molecules, it would qualitatively be expected that a polymer matrix would have similar effects on the diffusion of a polymer chain and a single monomer bead. That is, the above model predicts that a polymer matrix will reduce the diffusion coefficient of small probe molecules. This reduction in D has been observed experimentally.[25] Under the cognomen "monomer friction effects", the observed effect of a polymer matrix on small molecule diffusion has been interpreted[25,24] as having important implications for D of polymer chains. The calculation here sustains this interpretation, in that the hydrodynamic retardations experienced by a probe polymer and a probe monomer have the same source and form.

There are several respects in which the above results are incomplete. At substantial algebraic cost, it would be possible to include higher order hydrodynamic interactions between beads on the two chains, so as to better the representation of the short-range hydrodynamic forces. Neglect of short-range forces is probably more serious for D_r than for D. The self-similarity ("bootstrapping") assumption employed to obtain the high-concentration forms for D needs a more detailed justification; nonseparable three- and four-body forces would be expected to lead to higher order corrections to eq 5 and 26. Finally, the model neglects the atomicity of matter, both in replacing the full bead–bead correlations with $g(\mathbf{s})$ and in treating the solvent as a continuum.

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