Dynamics of Semidilute Polymer Rods: An Alternative to Cages

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Brownian simulations of rods with variable diameter d show that the rotational friction constant β_{rot} is the same in the limit $d \to 0$ as for a probe rod in a system in which vicinal rods interact with the probe but not with each other. This agreement seems to rule out cage models. A model based on the rapid dissipation of cage forces accounts for the observed dependence of β_{rot} on concentration c, length L, and d.

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Brownian simulations of semidilute polymer rods were previously interpreted[1] on the basis of a modified Doi-Edwards (DE) cage model.[2] Discrepancies between the observed dependence of β_{rot} on c and L and DE predictions were rationalized in part through an assumed lack of ergodicity in the simulations[3] and, by implication, in experiments. However, ergodicity has now been verified by a comparison between structural statistics from Brownian and Monte Carlo equilibrium simulations. Agreement was found with no observed sensitivity to the Monte Carlo rules. Therefore, an alternative dynamical model has been devised and subjected to additional tests on rods with varying d, and on systems with special interactions. Support for the alternative model is reasonably strong. Conflict of the data with any frozen-cage model seems unambiguous.

The basis for the revised model lies in two conjectures that were inspired by the previous simulations[1] and have now been confirmed. The first is the proportionality of $\beta_{rot}-\beta^0_{rot}$ to cL^3 for very thin rods. β^0_{rot} is the dilute-solution value. The deviations from this proportionality that were observed[1] for large cL^3 were ascribed to effects of nonvanishing d, without direct evidence. The new data on systems with varying d confirm the interpretation for $24 \leq cL^3 \leq 146$. In terms of the factorization of a rotational diffusion constant into a mean square angular displacement θ^2 of a rod within a "cage," and a relaxation rate $1/\tau$, θ is inferred to be proportional to $1/(cL^3)^{1/2}$ for thin but noncrossing rods. In contrast, the DE model of a literal cage of nearest neighbors gives $\theta_{DE} \propto 1/cL^3$. In the related language of viscoelastic response,[1] $\beta_{rot}-\beta^0_{rot}$ factors into τ times an elastic force constant $K^T_0 \propto cL^3$, while $K^T_{DE} \propto (cL^3)^2$.

The second conjecture is that $\beta_{rot}-\beta^0_{rot}$ is strictly determined by independent binary interactions between a probe rod and each of its neighbors, for the Brownian model in the small-d limit. This is a plausible molecular interpretation of the proportionality between $\beta_{rot}-\beta^0_{rot}$ and cL^3 found for large cL^3. However, it might be objected that the proportionality has been verified only for large cL^3, and that independent binary interactions must be restricted to small cL^3 where a different proportionality constant would be found. A test of this objection by direct simulations on systems with very small cL^3 did not seem practical, because $\beta_{rot}-\beta^0_{rot}$ becomes too small to measure with any significant precision as cL^3 decreases below about 10. Moreover, a direct test of the second conjecture is possible. Simulations were performed on specially modified systems in which the probe rod interacts with all its neighbors, but the neighbors do not interact with each other. The same proportionality constant is found relating $\beta_{rot}-\beta^0_{rot}$ to cL^3 as applies to the fully interacting system in the limit of vanishing d. In this limit, therefore, secondary interactions of neighbors with each other have no influence on the relaxation of the probe.

An understanding of these observations, especially the second, must begin with a sharp distinction between (1) the propinquity of neighbors to a probe and (2) the torques exerted by neighbors on a probe. The physical significance of the elastic torque constants K^T_0 and K^T_{DE} can be understood as follows. An externally forced, "instantaneous," and small rotation ($< \theta_{DE}$) of a probe to a new fixed orientation initiates a perturbation in the system. The immediate neighbors no longer have an equilibrium distribution with respect to the probe, and a quasielastic free energy proportional to K^T_{DE} is stored in the "cage." [The meaning of "instantaneous" will be refined in the discussion that follows Eq. (1).] The instantaneous torque on the probe is a derivative of the induced free energy and is also proportional to K^T_{DE}. One channel which is available for the relaxation of elastic free energy is the DE mechanism of longitudinal diffusion, and this is the only channel easily imagined for the decay of propinquity in a system with large cL^3. However, a much faster mechanism is available for the short-time decay of torque. The elastic free energy, initially concentrated in the few neighbors that make up the "cage," can spread among a large set of neighbors by a process of rotational diffusion in which a typical neighbor rotates by no more than (roughly) θ_{DE} rad. The torque on the probe would initially decay very rapidly by this process, along with the local elastic

free-energy density. In the quantitative (but heuristic) calculation developed below, it is assumed that the initial decay of elastic free-energy density is due to a rotatory diffusion process controlled by $\beta^0_{\rm rot}$. Interactions between vicinal rods are presumed to have no effect either to help or to hinder the equilibration of vicinal rods with respect to the new position of the probe, in the vanishing-d limit. The rotational decay of free-energy density slows down only because the driving force for the diffusion process is the gradient of free-energy density, and this decreases in the course of time. Eventually longitudinal diffusion takes over as the fastest channel for the decay of torque as well as propinquity, and the long-time decay rate $1/\tau$ is computed just as in DE theory. However, the amplitude factor K^T_0 in this exponentially decaying component of torque is much less than the initial DE value $K^T_{\rm DE}$. The quantitative model of this effect will now be developed.

As shown previously,[1] the analysis is carried out in terms of a viscoelastic response function $K(t)$. The motion of one end of the probe rod is described on a spherical surface of radius $L/2$. Aside from the random Langevin force, the deterministic force acting in the tangent plane on an end bead is expressed as a frictional part $-\beta_e \mathbf{v}(t)$ ($\beta_e = 2^1$) and a force due to interactions with other rods:

$$\mathbf{F}(t) = -\beta_e \mathbf{v}(t) - \int_0^\infty K(t')\mathbf{v}(t-t')\,dt'. \qquad (1)$$

$K(t)$ is approximated by $K(t) = K_0 \exp(-Rt)$, where K_0 is an elastic force constant. The corresponding coefficient connecting the torque and angular velocity is designated $K^T(t) = K(t)L^2/4$. Likewise $\beta^T_e = \beta_e \times L^2/4$. For quasisteady motion,[4] rod-rod interactions add τK^T_0 to the dilute-solution value $\beta^0_{\rm rot} = \beta^T_e$, where $\tau = R^{-1}$; i.e., $\beta_{\rm rot} = \beta^T_e + \tau K^T_0$.

The alternative picture is introduced through a qualitative examination of $K^T(t)$ vs t (see Fig. 1). $K^T(0)$ is the mean square torque on a rod[5] (in units $K_B T = 1$) and will approach infinity as the potentials approach hard-core forms. Likewise the initial rate of decay will become infinite, and $K^T(t)$ should decay rapidly along curve 1 until caging forces come into play. Curve 2 illustrates the DE assumption that caging forces decay slowly, with a relaxation time proportional to the residence time of a vicinal rod in the neighborhood of the probe rod, i.e., to $L^2/D^0_{\parallel}$, where $D^0_{\parallel}$ is the longitudinal diffusion constant at $c = 0$. The intercept $K^T_{\rm DE}$ is the mean square torque produced by the cage rather than by the instantaneously acting hard-core forces. However, the DE assumption that cage forces relax only by longitudinal diffusion is now rejected with the observation that forces in dense media can propagate through space by cooperative interaction much more rapidly than the physical objects that generate the forces. It is supposed that as the probe rod rotates toward its immediate neighbors, comparably small rotations of the neighbors nearly suffice to equilibrate the neighbors with the new position of the probe, and further, that this equilibration procedes outward from the probe at substantially the same rate as unhindered angular diffusion of the rods.[6] This rate is estimated as $D^0_{\rm rot}/\Phi^2$, where Φ is the magnitude of the angular rotation through which the equilibration has propagated. The torque correlation will therefore continue to decrease rapidly, say along curve 3, until such time as Φ has increased sufficiently that $D^0_{\rm rot}/\Phi^2$ is comparable with the rate of cage breakup through longitudinal diffusion. The latter rate is $D^0_{\parallel}/(fL)^2$, where f is a parameter discussed below. The matching of rates occurs at $\Phi \propto f$; $\Phi = f\pi$ has been used.[7] Subsequent relaxation procedes along curve 4, with rate R similar to that of curve 2, but with intercept $K^T_0 \propto cL^3$ rather than the $K^T_{\rm DE} \propto (cL^3)^2$, for thin rods.

The detailed calculation is based on separate estimates of $\tau(f)$ and $K^T_0(f)$ and maximization of $\beta_{\rm rot}$ [or $\tau(f)K^T_0(f)$], with respect to f. This asserts minimum entropy production, in rough terms. A more formal variation basis exists.[8]

A conventional estimate is used for the relaxation time $\tau(f)$:

$$\tau(f) = (Lf)^2/2D^0_{\parallel}. \qquad (2)$$

Thus longitudinal diffusion through the distance fL is presumed to eliminate the contribution of a rod to the elastic restoring force.

K^T_0 is $\langle T^2 \rangle$. The torque $\mathbf{T}$ is calculated for the semiequilibrated state discussed above, through the sequence $\mathbf{T} \leftarrow p(\mathbf{s}) \leftarrow A[\delta(\mathbf{s})] = k_B T N(\delta(\mathbf{s}))$. Here $\mathbf{s}$ is a point on the surface of the probe, and $d + \delta(\mathbf{s})$ is the distance of closest approach of a vicinal rod to the

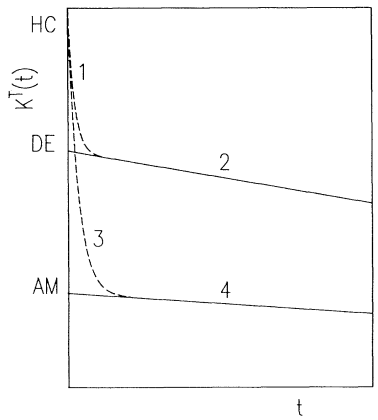

FIG. 1. Schematic illustration of the torque response function $K^T(t)$. The intercepts are HC [hard-core true $K^T(0)$], DE (Doi-Edwards $K^T_{\rm DE}$), and AM (alternative-model K^T_0).

probe. $N(\delta(\mathbf{s}))$ is the mean number of vicinal rods whose axes intersect the domain between d and $d+\delta(\mathbf{s})$, in the ensemble that describes a partial equilibration over azimuthal angles within domains of size $\Phi(f)=f\pi$. $p(\mathbf{s})$ is the pressure exerted on the probe by vicinal rods, and is a functional derivative of A with respect to $d\Sigma(\mathbf{s})\,\delta(\mathbf{s})$ at $\delta(\mathbf{s})=0$; $d\Sigma(\mathbf{s})$ is an element of area. A is the free energy of the system in the semiequilibrated state in which the azimuthal angle of each neighbor is averaged over a domain of size $\Phi(f)$. For fixed centers and polar angles of the neighbors, the mean number of vicinal rods that intersect any part of the shell of thickness $\delta(\mathbf{s})$ is

$$N=\int[\delta(\mathbf{s})/r\Phi]\sum q_i\delta(\mathbf{R}-\mathbf{R}_i)r\,dr\,dz\,d\phi, \qquad (3)$$

where q_i is a random variable equal to 1 if the azimuthal angle of vicinal rod i lies in an interval Φ adjacent to the probe, and 0 otherwise. The probability that the vicinal rod lies in any interval of size Φ is f. It is implied in Eq. (3), and useful in calculation of the necessary functional derivative, that a one-to-one correspondence exists between the position $\mathbf{s}$ on the surface of a probe and the coordinates of a vicinal rod. The latter are the cylindrical coordinates $\mathbf{R}=(r,z,\phi)$ of an end bead, a polar-orientational angle, and an azimuthal-angle interval of size Φ. Specifically, $d^{-1}d\Sigma(\mathbf{s})=dz\,d\phi$ (for small d, there is a constant 90° difference between ϕ and the corresponding angle of $\mathbf{s}$). A complete averaging of Eq. (3) at this stage gives known values[9] for $\langle p\rangle$ and $\langle N\rangle$.

Calculation of $\mathbf{T}$ and $\langle T^2\rangle$ gives

$$K_0^T(f)=Q[cL^3/12\pi f]\ln[(1-f)/f],$$

$$Q=1+\tfrac{1}{2}\pi cL^2d(1-2f)^2+\ldots. \qquad (4)$$

Q includes the (modified) first few terms of the osmotic virial expansion squared. Q gives an *ad hoc* account of the effect of finite d on the pressure or torque derived from (3). The series can be derived from the ensemble average used to calculate N, with certain assumptions. Note that the direct interaction between vicinal rods and the probe gives a neglected d-dependent correction factor $[1+O(d/L)]$ in K_0^T. $(1-2f)^2$ in the virial series and $(1-f)/f$ in the logarithm show the effect of suppression of rod ends due to longitudinal diffusion. The suppression seems reasonable. Without it, $\langle T^2\rangle$ would be infinite because azimuthal-angle preaveraging is ineffectual for vicinal rods whose ends are near the probe. The f^{-1} in front of the logarithm results from the azimuthal-angle restriction, which gives a factor f^{-2} in $\langle T^2\rangle$ from $1/\Phi^2$. This is partially compensated by the probability factor f that $q_i=1$.

The $\beta_{\rm rot}$ derived from Eqs. (2) and (4) fit the simulation data described previously, as well as values for higher and lower c and varying d, somewhat better than the previous formula.[1,10] Variational values of f range between about 0.1 and 0.2 ($f=0.22$ at $c=0$). $\beta_{\rm rot}/\beta_{\rm rot}^0$ vs d is shown in Fig. 2 for systems with full interactions between all rods, and for modified systems in which the vicinal rods interact with a probe rod but not with each other. The solid curves are the predictions of Eqs. (2) and (4). If caging played a significant role in the system with full interactions, the intercepts at $d=0$ should lie well above the open circles. In reality, it does not matter whether the vicinal rods are prohibited from crossing through each other in the limit $d\to 0$.

The effective hard-core diameters d are obtained from the continuous potentials $u(r)$ used in the simulations[1] through $u(d)=k_BT$ for rods crossing at right angles.

The "Brownian" simulations of Doi, Yamamoto, and Kano[11] seem to confirm the DE theory, contrary to this work. Probably, however, their algorithm fails to describe Brownian motion because of the extremely large time step that was used (200 to 400 times larger than in the present work). This made it necessary to impose arbitrary rules governing "collisions" which in effect extend the lifetime of cages. *Ad hoc* modification of the present Brownian dymanics equations, in attempted emulation of their procedures, gives similarly large increases in the rotational friction constants at high concentrations. The Frenkel and Maguire simulations[12] of rods obeying Newtonian dynamics also confirmed DE scaling of $\beta_{\rm rot}$. However, their model yields a divergence of $D_{\parallel}$ at high concentrations. This divergence, and perhaps other effects of elastic col-

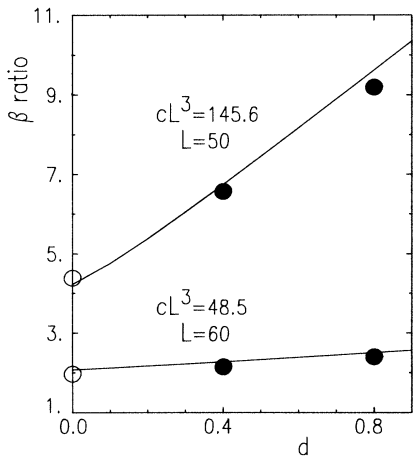

FIG. 2. Ratio $\beta_{\rm rot}/\beta_{\rm rot}^0$ vs rod diameter d. Curves are theoretical, Eqs. (2) and (4). Solid circles are simulation results for rods with finite diameter d, and open circles are results for the special system in which vicinal rods interact with a probe with $d=0.4$ but not with each other. Standard deviations are ca. 5% of the ordinates for $d>0$, and (5–10)% for $d=0$.

lisions, may limit the equilibration of Φ to very small values, as hypothesized in DE theory. See the discussion of Fig. 1.

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[3]Ergodicity was doubted because aged and unaged systems gave different cage sizes, and d was believed to be so small that aging was unnecessary. But the rapid increase in cage size of unaged systems at low c was later shown to occur also for aged (and Monte Carlo generated) systems, at slightly smaller c. Another false clue was the apparent correlation of $\beta_{\rm rot}$ with frozen cage sizes at large c. This correlation is now ascribed to the c^2 scaling of K_0^T in Eq. (4) for large cL^2d, which mimics frozen-cage scaling for $d=0$. The breakup of cages at small c is discussed by G. T. Keep and R. Pecora, Macromolecules **18**, 1167 (1985), and J. A. Odell, A. Keller, and E. D. T. Atkins, Macromolecules **18**, 1443 (1985).

[4]Definition of $\beta_{\rm rot}$ as an integral of the autocorrelation function is preferable to its interpretation as a steady-state coefficient. The distinction is here small (ca. 2% of $\beta_{\rm rot}/\beta_{\rm rot}^0-1$ at large c, 10% at small c).

[5]B. J. Berne, in *Statistical Mechanics,* edited by B. J. Berne (Plenum, New York, 1977), Part B, Chap. 5, and references there to Mori-Zwanzig projection theory. However, $K^T(0)=\langle T^2\rangle$ is an elementary result.

[6]Transverse diffusion of rod centers might well play a similar role to rotation in the relief of torques.

[7]Literal application of $D_{\rm rot}^0/\Phi^2=D_{\parallel}^0/(fL)^2$ would give $\Phi=f\sqrt{6}$ rather than $\Phi=f\pi$ for the three-bead friction model (Ref. 1), which has $D_{\parallel}^0=\frac{1}{3}$ and $D_{\rm rot}^0=1/\beta_{\rm rot}^0=2/L^2$. Such distinctions have little significance here [e.g., Eq. (2) has an uncertain proportionality factor]. $\Phi=f\pi$ was adopted because it gives a simple check of $\langle p\rangle$ and $\langle N\rangle$ from Eq. (4).

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[10]Doubling K_0^T and halving τ improves the $C(t)$ fit while leaving $\beta_{\rm rot}$ unchanged. For large t, the effect is only a constant shift in $\ln C(t)$, by about 0 to 0.02, depending on c.

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