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Brownian Dynamics of Nondilute Solutions of Rodlike Polymers. 1. Low Concentrations

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ABSTRACT: We report the results of Brownian dynamics simulations for solutions of rodlike polymers with an aspect ratio of 50 at moderate concentrations (5-50 rods/L^3, where L is the molecular length). Account for direct two-body interactions was sufficient for the description of the equilibrium properties over the range of concentrations we simulated. Correspondingly, the energy was adequately approximated by a density expansion through the second virial coefficient and the pair distribution function, which exhibited very weak concentration dependence, was well approximated by the Boltzmann factor. Despite the potentially nondiffusive character of rotation in concentrated systems of axisymmetric particles, the rotational motion could be described by a rotational diffusion equation in our simulations, due to the strong decorrelating effect of the solvent–polymer interaction. The translational diffusivity normal to the rod axis, despite its sharp decrease with concentration, did not freeze up to the highest concentration simulated, demonstrating in this way that the cage renewal mechanism postulated by the Doi–Edwards theory is inappropriate in this concentration regime. On the contrary, a model proposed by Fixman was found to be perfectly adequate since it reproduced very well our simulation results for the rotational diffusivity. These simulation results are the first to achieve quantitative agreement with experiment. The success of Fixman's model originates from the simple two-body nature of the polymer local structure and the strong solvent-induced decorrelation that weakens the intrinsically many-body character of the polymer–polymer interaction.

1. Introduction

The understanding of the dynamical behavior of concentrated polymer solutions and melts remains one of the major challenges of modern polymer physics. This behavior is complex due to the unique features of polymer molecules. Polymer molecules possess a large number of degrees of freedom associated with their intramolecular rotational and vibrational motions in addition to the global, translational degrees of freedom of their center of mass. Furthermore, the polymer chains are one dimensionally connected objects. The interplay between global and intramolecular motions, as well as the preservation of the chain connectivity, results in the entanglement effect,[1] which is believed to dominate the dynamical behavior of these systems.

Rodlike polymers differ from flexible polymers in many respects. Nevertheless, they are the simplest polymers where entanglements occur. As a matter of fact, the effect of entanglements is more dramatic for rodlike polymers than for flexible polymers because the rigidity of the molecule limits severely the motions that would allow disentanglement. Apart from their importance as the simplest systems of entangled polymer molecules, nondilute solutions of rodlike polymers have considerable interest on their own. There are many examples of polypeptides, polysaccharides, and polynucleotides that form helical structures which can be considered as rigid rods. Certain synthetic polyesters and polyamides form nematic liquid crystalline phases due to the molecular rigidity. These are molecules with important technological applicatons because they are capable of forming strong fibers and films.

The theoretical treatments of the entanglement effect for flexible and rodlike polymers have evolved along parallel paths. Doi and Edwards developed a theory of transport for nondilute solutions of rodlike polymers[2-4] conceptually analogous to the reptation theory for flexible polymers.[5-7] For both classes of polymers, the essence of the Doi–Edwards approach is to simplify the complex many-body problem by attempting to extract the dominant mode of motion. The Doi–Edwards theory for rodlike polymers (DET) is a semiempirical theory in that it postulates the underlying dynamics and, based on this, it predicts the molecular weight and concentration dependence of certain transport coefficients (primarily of the rotational diffusivity). The rodlike polymer is modeled as a completely rigid infinitely thin rod. Since the rods are infinitely thin, they can diffuse freely along their axes, whereas the motion normal to their axes and the rotational motion are severely restricted by the presence of neighboring rods. This restriction is conveniently visualized by imagining a sphere with its center at the center of a certain rod and with diameter equal to the rod length. By projecting the neighboring rods onto the spherical surface, we see that the rod is effectively confined in a cage. According to the original DET, *this cage is completely closed over extensive time intervals between cage breakups.* The cages occasionally dissolve as a result of the translational motion of the rods that form them or become ineffective because of the translational diffusion of the confined rod itself. The time between such events, however, is estimated by DET to be much larger than the time needed for the rod to equilibrate inside the cage (i.e. to explore the cage area by thermal motion). The orientational relaxation according to DET is accomplished by means of angular jumps with magnitude defined by the cage size and frequency essentially determined by the translational diffusivity of the rod along its axis, which according to DET retains its dilute solution value.

The comparison of DET predictions with experiment has met with limited success.[8-11] Refinements of DET[12-16] have improved agreement with experimental observations, although considerable discrepancies still remain. The issue of whether caging is the dominant mechanism by which entanglements influence the dynamical behavior is not only an open one but also one that cannot be answered directly by the available experimental techniques (dynamic light scattering, birefringence). Recently a generalized kinetic equation was derived for a suspension of rodlike Brownian particles.[17] This rigorous approach shows that rotational motion in nondilute solutions of rodlike polymers might not be a diffusive process.

The questions raised above can be answered only by direct microscopic tests. Molecular simulations are excellent tests of the microscopic dynamics of rodlike polymers in solutions since one can prescribe the ground rules

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for the simulation so that there is good correspondence with the situation described by the theory. Molecular dynamics simulations of a reasonably large system containing both polymer and solvent molecules being infeasible, one must either neglect the solvent entirely or simulate the polymer dynamics in an approximate, stochastic way. The primary challenge of any molecular simulation is to capture all the essential physics of the underlying molecular motion so that the resulting statistical regularities (macroscopic laws) are the same as those of the physical prototype. In this sense, results of molecular dynamics simulations that neglect the solvent altogether[18,19] must be interpreted with caution in the case of a solution. This is so, as explained in ref 19, since the polymer mobility is intrinsically different in the two cases. The conclusion in ref 19, from a study of solvent-free hard needles, is that the main prediction of DET, the inverse square concentration dependence of the rotational diffusivity, was confirmed only at concentrations substantially higher than the original DET anticipated (higher than 70 rods/L^3, where L is the rod length). Doi et al.[20] performed a dynamic Monte Carlo simulation, which could mimic the actual polymer dynamics more closely. However, the time step used in this simulation was too large. This has raised considerable objections,[16,21] since such a large time step artificially reduces the polymer mobility and favors the orientational relaxation mechanism suggested by DET (cage renewal) against all alternative mechanisms. This simulation confirmed DET predictions but only at concentrations higher than 80 rods/L^3.

It seems, therefore, that the concentration dependence of the rotational diffusivity predicted by DET was confirmed by the above studies[18-20] but only at concentrations higher than at least 70 rods/L^3. The results of these studies were in rough agreement with the theoretical predictions of improved versions of DET.[12,13] This leaves unexplored a large concentration regime (from 1 to 50 rods/L^3), where polymer–polymer interactions certainly cannot be neglected. The previous simulations certified the inadequacy of DET there, without providing detailed information, that could help in rationalizing the actual diffusion mechanism in this range of concentrations.

Even at higher concentrations the success of DET has not been established. Both the theory[3,6,12,13] and the simulations[18-20] modeled the rodlike polymer as an infinitely thin needle. This amounts to neglecting excluded volume effects on the dynamical properties. Such a simplification is acceptable when the volume fraction inaccessible to each rod because of the presence of the other rods is very small. For rodlike polymers with length L and diameter b in a solution of concentration c the excluded volume fraction is of the order of cL^2b and excluded volume effects can be ignored safely only when this fraction is very small. Therefore, the dynamics of rodlike polymers with finite width are expected to be very similar with those of infinitely thin needles when

$$cL^2b \ll 1 \qquad c \ll 1/L^2b \tag{1.1}$$

Typical values of the axial ratio L/b range from 30 to 100 for real polymers,[3,22] while the simulations of infinitely thin needles confirmed DET only for concentrations higher than 70–80 rods/L^3, i.e. exactly where excluded volume effects, present in real systems but absent from the simulated systems might be important. Although these simulations proved the validity of DET for infinitely thin needles, the relevance of their results to real polymers with realistic axial ratios is questionable.

Fixman[21] performed Brownian dynamics simulations for rodlike polymers with finite width ($L/b \approx 50$) for concentrations between 50 to 220 rods/L^3. His results were in complete disagreement with DET. These results implied a decrease of the rotational diffusivity for infinitely thin rods as the inverse first power of concentration, instead of the inverse square dependence predicted by DET. However, the number of particles used in this simulation and the simulation cell itself were very small so that the results may be statistically questionable. Furthermore, the lower concentration regime (1–50 rods/L^3) was not explored and the only quantity studied was the first rotational correlation function. The slight flexibility of the rodlike polymers in Fixman's simulations was extremely small, and we do not expect it to affect his results in any way.[23] Fixman[21] proposed a model in order to rationalize his simulation results. This model was supposed to be applicable for both high and low concentrations, but little evidence in support of it at low concentrations was presented. This model too will be tested by our simulation results.

The main objectives of the simulation to be developed here are designed to improve on the situation described above. We think that these objectives should be a detailed study of the lower concentration regime, between 1 and (L/b) rods/L^3, in an effort to rationalize the transport behavior there, which denied any satisfactory description up to date, and a thorough comparison of the simulation results for more concentrated solutions of rodlike polymers having finite width with the theoretical predictions (DET[2,3] and refinements of DET[12,13]).

In this paper we shall undertake only the first task. The second will be the theme of a future publication, currently in preparation.

2. The Molecular Model and Dynamics

We model the rodlike polymers as line particles interacting with each other via pairwise additive, purely repulsive forces. Almost nothing is known experimentally about the realistic functional form of the polymer intermolecular potential. We may expect, however, the macrosopic behavior to depend only on the gross features of the polymer–polymer interaction. We think that any sufficiently steep, purely repulsive, short-range potential will do, since it guarantees the uncrossability requirement and simulates the excluded volume interaction. Furthermore, for sufficiently thin rods, one expects the interaction energy to depend only on the minimum distance and the angle between the interacting molecules. A potential that meets the above requirements is the one employed by Fixman[21] in his simulations

$$U = \epsilon \exp[-(d/\sigma)^2]/\sin \alpha \tag{2.1}$$

where U is the energy of interaction, d is the minimum distance between the axes of the interacting rods, α is the rod–rod angle, ϵ is a parameter with the dimensions of energy, and σ is a parameter with the dimensions of length. We shall use this potential both for its simplicity and for purposes of comparison. Obviously, such a potential does not absolutely exclude rod–rod crossings. For sufficiently large ϵ values, however, crossings become extremely improbable. Throughout this work the value of ϵ, which determines the barrier for rod–rod crossing was set to (50/3) kT. This leads to a maximum probability for such crossings of the order of 10^{-7} to 10^{-6}. The length parameter determines the range of the intermolecular forces. An effective rod diameter b can be defined in a way analogous to that used for the definition of an effective hard-sphere diameter for point particles interacting via spherically symmetric continuous potentials.[24] We prefer, however, to identify the rod diameter with the distance where the potential barrier becomes three times larger than the kinetic energy of each rod (2.5 kT) for rods that are normal to each other. Obviously, this is a somewhat arbitrary definition, but its only purpose is to make the visualization easier and the terminology more familiar. A choice for $b = L/50$ yields a value of $\sigma = 0.03855L$. The potential we employ might be inappropriate at very high concentrations (200 rods/L^3 or higher) where nematic phase transition is about to occur.[1] A hard cylinder potential might be conceptually preferable, but we do not know of any physically realistic way to simulate the stochastic motion of bodies with discontinuous potentials.

As far as the interaction with the solvent is concerned, we model the rodlike polymers as Brownian particles with two friction centers (beads) each having a diameter equal to the effective rod diameter. The theory of Brownian motion,[25] apart from its success in describing a host of different phenomena, has been rigorously generalized[26-29] and can actually be deduced from statistical mechanics for particles with much larger mass than the solvent molecules.[30-32] As is well-known, there are two alternative ways to describe Brownian motion:[25,33] by means of the so-called Fokker–Planck equations,[25,34] partial differential equations describing the time evolution of the one-body probability density, or by means of the so-called Langevin equations,[25,34] equations of motion for the time evolution of the Brownian particles' momenta, where the interaction with the solvent consists of a systematic frictional force and a stochastic Langevin force. Our approximation amounts to describing the microscopic dynamics of the rodlike polymers as Brownian motion in an external field, the field originating from the polymer–polymer interactions. If the velocity fluctuations of the polymer molecules, *which are fluctuations caused by the incessant bombardment by solvent molecules*, decay over distances much smaller than the distances over which the intermolecular force changes appreciably, one can afford an even simpler description.[25,34] An integration over the momenta can be performed in this case and the Fokker–Planck equation reduces to the familiar diffusion or Smoluchowski equation[25] for the time evolution of the spatial probability density. This approximation is equivalent to the neglect of the acceleration terms in the Langevin equations. Such a condition is satisfied minimally in our case. This happens because the intermolecular forces change over distances comparable to the rod width, which although still larger, is not as much larger than the dimensions of the solvent molecules as the polymer length is.

For simulation purposes the Langevin equations are much more useful than the diffusion equation, since they can be employed to actually generate the trajectories of the Brownian particles.[35,36] Most theoretical work, however, has been done in terms of Fokker–Planck or diffusion equations.[1,37,38] The equivalence between the two descriptions has been established long ago for Langevin equations with linear noise terms.[25,34] The method for the derivation of the equivalent Langevin equations from the Fokker–Planck or diffusion equations and vice versa has been systematized in the general literature of noise and stochastic processes[39] and has been applied to polymer systems with or without rigid constraints or hydrodynamic interaction.[40,41]

Unfortunately, the situation is not nearly as simple for the nonlinear (both the deterministic and the stochastic terms are not linear) Langevin equation. The Langevin equation in this case is mathematically ill-defined. To assign some meaning to the Langevin equation one must complement it with an interpretive calculus for stochastic integration. This is a typical problem of stochastic differential equations with multiplicative noise. The two commonly used schemes for stochastic integration were developed by Ito and Stratanovich.[42] The Langevin equation along with Ito's rules for stochastic integration is equivalent to a certain Fokker–Planck equation, while the same Langevin equation along with Stratanovich's rules is equivalent to a different Fokker–Planck or diffusion equation. The above situation has been the source of considerable confusion. It has been beautifully presented and clarified by Van Kampen[33] and recently in closer connection to polymer systems by Tough et al.[43] In ref 43 it was shown that hydrodynamic interaction is a source of multiplicative noise in the Langevin equation for polymer systems without rigid constraints.

Ito's calculus for stochastic integration is simpler, while Stratanovich's is physically more appealing. The choice between them should of course not be based on mathematical convenience or physical intuition. Since the Fokker–Planck or diffusion equation provides a firm point of reference, one should complement the Langevin equations with the calculus, which recovers the original (and independently justified) diffusion equation.

The detailed derivation of the Langevin equations for a rigid dumbbell will be presented elsewhere[44] as a special case of a more general derivation applicable to models with *arbitrary rigid constraints. In ref 44 it is shown that* Stratanovich's calculus must be used in order to recover the special form of Kirkwood's diffusion equation appropriate for our model.[37,38] In the next section we simply present the first two moments of the increments of the rod's coordinates, which is actually all that is needed for simulation purposes. These moments are calculated from an integration of the Langevin equations over a short time interval, s. Such an integration needs to be exact up to first order in s, since only up to that order is an equivalence between Langevin and diffusion equations supposed to be established.[33,39]

In a dilute solution of rodlike particles the diffusivity parallel to the rod axis is larger than that normal to it (ref 1, Chapter 8). This anisotropy is a consequence of the hydrodynamic interactions among the various beads of the *same* molecule. In a concentrated solution one should consider the hydrodynamic interactions among beads of *different* molecules, as well. Unfortunately, this cannot be done in a consistent way during a simulation the reason being the long range character of hydrodynamic interactions. Having no way to account properly for the hydrodynamic interactions, we felt that it might be more appropriate to neglect them altogether than to consider selectively only those among the beads of the same molecule. We consider the neglect of hydrodynamic interactions to be the major weakness of our simulation. We note, however, that all earlier simulations[20,21] had to live with the same unpleasant situation. Of course, one might argue that hydrodynamic interactions are screened in concentrated solutions.[45] Although the screening can be rigorously shown to occur for a particle moving through fixed obstacles in a medium[46] or hydrodynamically interacting mobile Brownian particles in transient flows, it has been recently shown that screening is absent among hydrodynamically interacting *mobile* Brownian particles in steady flows or at equilibrium.[17,44]

3. The Simulation

The simulation technique we employ is now widely known as Brownian dynamics. It consists of the numerical integration of the stochastic equations of motion for a collection of Brownian particles.[35] If one neglects the

Table I
Units

physical quantity	unit
length	L
energy	kT
time	$\beta L^2/kT$
translational diffusivity	kT/β
rotational diffusivity	$kT/\beta L^2$
concentration	rods/L^3
angle	rads

inertial terms in the equations of motion, these become first-order differential equations in time. In this form the method has been used quite extensively for the study of complicated models for polymers in dilute solutions[48-51] or of interacting polymer molecules.[21,52] Various algorithms have been proposed for the integration of the stochastic equations,[37,53,54] and each one has its own advantages. In our algorithm the incremental displacements during a time step are random variables, calculated from the first-order integration of the stochastic equations of motion. These equations have almost the same form for a multibead rigid rod and for a rigid dumbbell except for numerical factors. The first two moments of the incremental displacements are

$$\langle \delta x_i(s) \rangle = Q^i(t)s/\beta \quad i = 1\text{–}3$$

$$\langle \delta \vartheta(s) \rangle = [Q^{\vartheta}(t) + 2kT \cot \vartheta / L^2]s/\beta$$

$$\langle \delta \varphi(s) \rangle = Q^{\varphi}(t)s/\beta \qquad (3.1)$$

$$\langle [\delta x_i(s)]^2 \rangle = kTs/\beta$$

$$\langle [\delta \vartheta(s)]^2 \rangle = 4kTs/\beta L^2$$

$$\langle [\delta \varphi(s)]^2 \rangle = 4kTs/\beta L^2 \sin^2 \vartheta \qquad (3.2)$$

where Q^i (i = 1–3) are the components of the intermolecular force exerted upon the rod under consideration by all other rods, Q^{ϑ} and Q^{φ} are the intermolecular torques, x_i (i = 1–3) are the coordinates of the rod's center of mass, ϑ and φ are the orientation angles of the rod, t and $t + s$ are the beginning and the end of the time step, k is Boltzmann's constant, T is the temperature, and β is the friction coefficent of a bead. During a time step the rods experience deterministic displacements and rotations given by eq 3.1, as well as random displacements and rotations. The magnitude of the latter is determined by generating random numbers with zero means and variances given by eq 3.2.

From a computational point of view, the combination of stiff potentials with a low order integration scheme poses serious difficulties. An extremely small time step must be used if spurious results, artifacts of the integration scheme, are to be avoided. Although physically the equivalence between the Langevin and diffusion equations holds only up to first order in time, computationally it might be advantageous to employ a higher order numerical integration scheme. Explicit higher order algorithms do not improve the situation considerably for very stiff potentials and, furthermore, are not quite as simple for stochastic equations as they are for regular deterministic equations.[53] The use of implicit methods is probably superior.[54]

Instead of any of the above we chose to follow a more physically motivated scheme similar to that used by Ceperley et al. in their simulations.[50] To appreciate the problem posed by a straightforward first-order numerical integration of the Langevin equations let us consider a simplified example. During one integration step a rod starting from a configuration of relatively low potential energy might get very close to other rods under the action of the random forces, thus increasing the system's potential energy significantly. In fact, this approach would be closer as a result of the low order integration scheme than what it would have been had the Langevin equations been integrated exactly. The reason is that in the numerical integration the rod does not experience the increasing repulsive forces from the other rods as it approaches them but rather is assigned a constant repulsive force corresponding to its initial configuration. Such an unphysically close approach can have two undesirable consequences. During the next time step the strongly interacting rods will be thrown far away from each other, since they will now experience the full strength of their repulsion, which would not have been so strong in the first place had the integration been exact. Furthermore, rod–rod crossings become more likely since the potential barrier against them is not the potential energy in contact but rather the potential energy at the beginning of the time step. Clearly, for a stiff potential an extremely small time step is needed in order to alleviate these problems. The method suggested in ref 50 is essentially a smart application of the standard Monte Carlo rejection scheme[55] in dynamical situation where movements leading to an unphysical increase of the potential energy are rejected a posteriori. There exists a conceptual difficulty associated with this method. Since the time advances even when a particle move is rejected, all diffusion processes will be slowed down by a factor which is comparable to the rejection ratio but whose exact value is not known. For a reasonably short time step, however, the rejection ratio is very low (at most 0.05 in our simulations). It is sensible, therefore, to slow down all motions by a factor exactly equal to the rejection ratio. Alternatively, one might consider this as an additional source of statistical uncertainty in our results for the diffusivities.

Finally, some simple geometrical tests and lists of nearest neighbors[56] are employed in order to reduce the number of rod–rod interactions that must be considered. The lists of nearest neighbors for rodlike particles are constructed by drawing a spherocylinder around each rod and listing the rods that pierce it.[19]

We performed simulations for six different concentrations, namely, 5, 10, 20, 30, 40, and 50 rods/L^3, where L is the rod length. The values of the various parameters used in these simulations are shown in Table II. As seen from this table long simulations were performed (typically, molecular dynamics and Brownian dynamics simulations have roughly 10^4 time steps). Such long simulations were necessary since a proper diffusive behavior originating from the disentanglement process is expected to take place over time intervals smaller but comparable to the time needed for the center of mass to diffuse one rod length (of the order of $\beta L^2/kT$), while the time step must be much smaller than $\beta b^2/kT$, where b is the rod width and β is the bead friction coefficient. These long simulations became feasible only by taking full advantage of the computational speed and the vector processing capabilities of the University of Minnesota CRAY-2 supercomputer. As a result of vectorization the computational speed was enhanced by a factor of 2–6 with better performance at the higher concentrations. An additional increase of the computational speed by a factor of roughly 2 came from the construction of lists of nearest neighbors and the employment of the preliminary geometrical tests, both of which reduced the number of pair interactions that had to be considered.

The initial purely random configurations were first relaxed by the standard Metropolis Monte Carlo method[55]

Table II
Simulation Parameters

concentration	5	10	20	30	40	50
no. of rods	91	93	187	281	371	463
side of simultn cell	2.63[a]	2.10[a]	2.10	2.10	2.10	2.10
spherocylinder radius	0.25	0.25	0.25	0.25[b]	0.25	0.25
time step	5×10^{-6}	5×10^{-6}	5×10^{-6}[c]	5×10^{-6}	5×10^{-6}	5×10^{-6}
no. of time steps	120 000	120 000	120 000	90 000	78 000	60 000
(CPU sec)/(time step)	0.019	0.021	0.051	0.092	0.137	0.197

[a] Periodic boundary conditions were employed. [b] A simulation with spherocylinder radius of 0.5 L was also performed. The results of the two simulations agreed very well with each other. [c] A simulation with time step 1.33×10^{-6} and duration 240 000 time steps was also performed. The results of the two simulations agreed very well with each other.

Table III
Average Potential Energy per Rod

concn	simulatn	eq 4.9	rejectn ratio
5	0.006 ± 0.001[a]	0.006	0.05
10	0.011 ± 0.002	0.012	0.010
20	0.024 ± 0.002	0.024	0.020
30	0.039 ± 0.002	0.036	0.032
40	0.049 ± 0.002	0.048	0.041
50	0.063 ± 0.002	0.060	0.051

[a] The uncertainties were determined by dividing the trajectories in equal parts of 10 000 time steps each and calculating the standard deviation of the average energies corresponding to these portions.

(100–1000 Monte Carlo moves for each particle). The potential energy of the initial purely random configuration was roughly 2 orders of magnitude higher than the equilibrium energy. Most of the relaxation (up to an energy 2–5 times higher than the equilibrium one) was achieved by the preliminary Monte Carlo simulation. Such a relaxation is much more efficiently performed with Monte Carlo because rod–rod crossings are allowed; therefore arbitrarily large Monte Carlo movements may be employed. The approach to equilibrium was very slow at the final stages, however. There, Brownian dynamics proved to be more efficient for equilibration purposes than Monte Carlo[57–59] (the energy relaxed to its equilibrium value after less than 100 time steps).

4. Results

The potential energy of interaction per rod as well as the rejection ratio are shown in Table III for the various concentrations simulated. The rejection ratio is indeed very small, as mentioned in the previous section, which permits us to deal heuristically with the problem it poses concerning the actual rate of time advancement. The interaction energy is also very small, especially compared to the mean rod kinetic energy, which should be 2.5 kT according to the equipartition theorem.[60] This is still one more indication that the topological constraint of uncrossability among the rods and not the precise form of the rod–rod intermolecular potential should dominate the rod dynamics in the concentration regime we examined.

i. Rotational Motion. There are several measures of the statistics of rotational motion.[19] The two most common are the mean square angle of rotation $\langle\theta^2(t)\rangle$ and the rotational diffusivity D_r.

The mean square angle is defined as follows

$$\langle\theta^2(t)\rangle = \langle\{\cos^{-1}[\mathbf{u}(0)\cdot\mathbf{u}(t)]\}^2\rangle \qquad \theta(t) = \mathbf{u}(0)\cdot\mathbf{u}(t) \quad (4.1)$$

where $\mathbf{u}(0)$ and $\mathbf{u}(t)$ are the orientation vectors of the rods at times 0 and t and the angular brackets denote an ensemble average. For simulation purposes the ensemble average is realized by averaging over the rodlike particles and over the initial times.

The rotational diffusivity is defined through the Debye equation,[61,62] which is the Smoluchowski (diffusion) equation for the rod's orientation. If the Debye equation holds, the probability that a rod with initial orientation $\mathbf{u}(0)$ will have an orientation $\mathbf{u}(t)$ at t is given from the solution of this equation[62]

$$F(\vartheta,\varphi,t) = \sum_{l=1}^{\infty}\left(\frac{2l+1}{4\pi}\right)P_l[\cos(\theta(t))]\exp[-l(l+1)D_r t] \quad (4.2)$$

where $P_l(x)$ is the Legendre polynomial of lth order. The angle θ given by eq 4.1 should not be confused with ϑ, the polar orientation angle relative to a fixed coordinate system. From eq 4.2 it follows that

$$\langle P_l[\cos\theta(t)]\rangle = \exp[-l(l+1)D_r t] \quad (4.3)$$

The rotational diffusivity can be calculated from the decay of the time correlation functions in eq 4.3. Customarily, one uses only the first two relations that follow from eq 4.3. In that case

$$D_{r1} = -(1/2)\ln\langle P_1[\cos\theta(t)]\rangle \qquad P_1(x) = x$$
$$D_{r2} = -(1/6)\ln\langle P_2[\cos\theta(t)]\rangle \qquad P_2(x) = 1.5x^2 - 0.5 \quad (4.4)$$

As mentioned above, D_{r1} and D_{r2} should be identical if a description in terms of the Debye equation is permissible. However, the applicability of the Debye equation for a solution of interacting rodlike polymers should be tested rather than accepted. Debye derived his equation[61] in a way that resembles closely Einstein's original derivation of the diffusion equation for spherically symmetric particles (ref 42, pp 3–6). Both derivations essentially describe the approach to equilibrium of an initially nonequilibrium density distribution of noninteracting Brownian particles. It is important to realize that the well-known assumption of completely uncorrelated consecutive displacements does not suffice for a diffusive description (i.e. in terms of a diffusion equation) of this motion. Such an assumption alone would lead to an integral equation (the Chapman–Kolmogorov equation) or an integrodifferential equation (the Master equation)[33] for the time evolution of the density distribution. A diffusive description results only at the cost of two additional assumptions, namely, that only very small displacements have any significant probability to occur during a random "jump" and that the nonequilibrium density distribution has a slow spatial variation. To state it more accurately, the spatial variation of the density distribution must occur over distances much larger than the magnitude of any "jump" that has a significant chance to take place.

All the above are very safe assumptions for a solution of large noninteracting spherically symmetric or axisymmetric Brownian particles. The microscopic process underlying a "jump" is a sequence of solvent–Brownian particle impacts sufficiently long so that the incremental displacements and rotations of the Brownian particle corresponding to two consecutive such sequences are completely uncorrelated. It is precisely because the angular and spatial displacements resulting from such sequences of solvent–Brownian particle impacts are still very small compared to the spatial and angular distances over which the density distribution changes, that the dynamics of Brownian particles in a dilute solution are diffusive.

For a solution of interacting Brownian particles, however, the situation is different. Superimposed on the diffusive process we just described are the Brownian particle–Brownian particle interactions. On a fine time scale between Brownian particle–Brownian particle collisions our picture is correct but on a longer time scale the Brownian particle–Brownian particle collisions constitute an additional mechanism that randomizes the configuration of the Brownian particles. One may be tempted to coarse grain even further, redefine the concept of a "jump", and say that a "jump" consists now of a sufficiently large number of Brownian particle–Brownian particle collisions so that the Brownian particle displacements and rotations corresponding to two subsequent "jumps" be completely uncorrelated. It is plausible that this would lead to a new diffusive process superimposed on the finer one for the case of spherically symmetric Brownian particles. The reason is that the "jump", although much larger than previously, has still a size comparable to the dimensions of the Brownian particle (say 10–100 times larger) while the density distribution is expected to vary macroscopically. For axisymmetric particles, however, as far as rotation is concerned, things are quite different. In the coarse of several Brownian particle–Brownian particle collisions each one of them might have rotated a large angle (comparable to π), and this angle cannot be considered as small on any scale. After all, if the distribution is to have any angular dependence this must occur in the interval from 0 to 2π.

Therefore, we see that the validity of the Debye equation is not guaranteed in our case. In fact, it is well-known that the Debye equation does not apply in different systems (dilute solutions of small molecules, gases of axisymmetric molecules, etc.), where the premises upon which this equation relies do not hold.[63] The molecular dynamics simulations for a gas of infinitely thin needles[18,19] showed unambiguously that the Debye equation is not appropriate at low concentrations for this system (lower than 30 rods/L^3). The possibility that rotation might not be diffusive for suspensions of interacting axisymmetric particles was demonstrated through a theoretical analysis by Altenberger and Dahler.[17] Chances for a diffusive character of rotation are worse if hydrodynamic interaction is considered since, being a longer range interaction, it acts essentially as a "memory storage" making the decorrelation more difficult and the angular intervals over which it occurs ("jumps") larger.

In summary, we may say that if the angle of rotation associated with a sufficiently long sequence of rod–rod collisions ("jump") is not very small, rotation will be intrinsically nondiffusive. The nondiffusive character, however, is weakened by the decorrelating effect of the random forces exerted by the solvent. As we shall discuss later this fact has very important consequences on the polymer dynamics. The solvent-induced decorrelation is certainly exaggerated in our simulation because of the neglect of hydrodynamic interactions. Whether the outcome of the two competing effects is a rotation noticeably nondiffusive is an open question, which will be answered in what follows.

In Figure 1 the quantities $-(^1/_2)\ \ln\ \langle P_1[\cos\,\theta(t)]\rangle$ and $-(^1/_6)\ \ln\ \langle P_2[\cos\,\theta(t)]\rangle$ have been plotted as functions of time for the concentrations of 10 and 50 rods/L^3. If the Debye equation is applicable in our case, both quantities are expected to grow linearly with time and the slopes of the two straight lines D_{r1} and D_{r2} must coincide (see eq 3.4). As we see from Figure 1 the growth is indeed linear, as much as one can tell for simulation results, at least over time intervals greater than 0.03 $\beta L^2/kT$. The correlation coefficients of the linear fits, excluding the first two points at the concentration of 10 rods/L^3 and the first three points at the concentration of 50 rods/L^3, were 0.999 78 and 0.998 98 for the first and second rotational correlation functions respectively for 10 rods/L^3 and 0.999 82 and 0.999 90 for 50 rods/L^3. Furthermore, the slopes of the two rotational correlation functions are statistically indistinguishable for both concentrations.

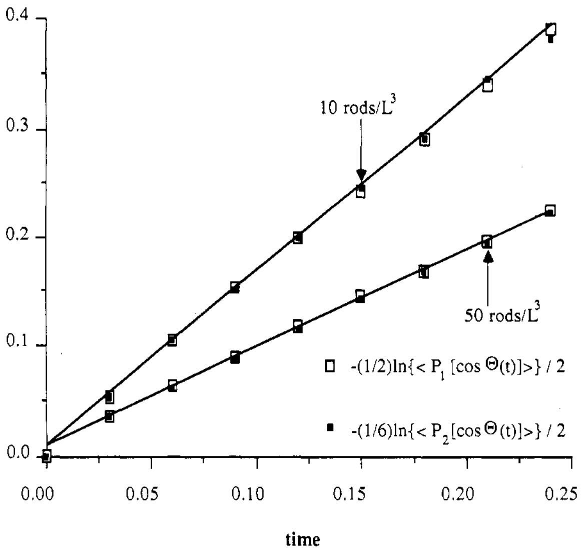

Figure 1. The time evolution of the logarithm of the first two rotational correlation functions at the concentrations of 10 and 50 rods/L^3.

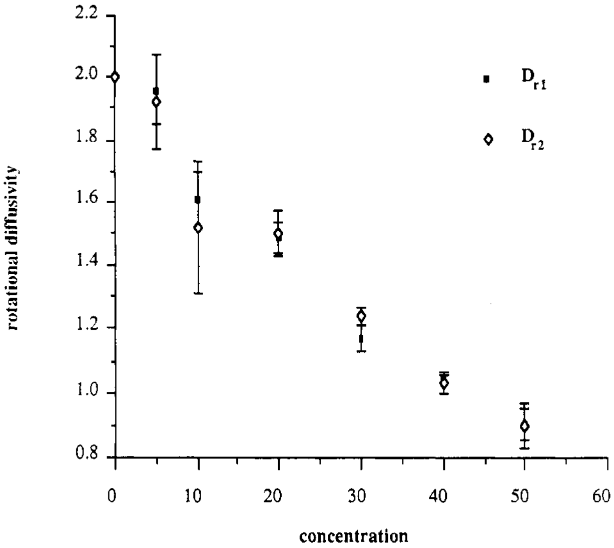

Figure 2. Rotational diffusivities, as calculated from the decay times of the first two rotational correlation functions, vs concentration.

In Figure 2 two "rotational diffusivities" calculated from eq 3.4 have been plotted vs concentration. In our units, the dilute solution rotational diffusivity is

$$D^{\circ}{}_{\mathrm{r}} = 2.0 \qquad (4.5)$$

As we see, D_{r1} and D_{r2} agree with each other within the limits of statistical uncertainty for all concentrations sim-

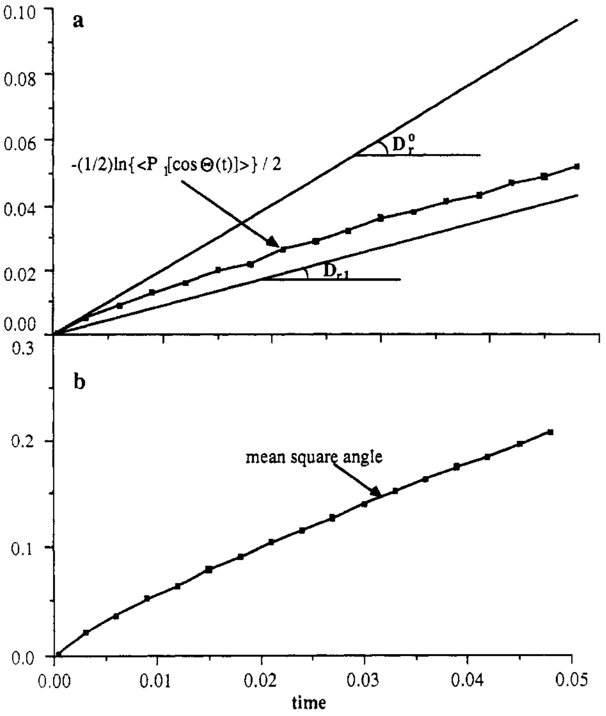

Figure 3. a. The first rotational correlation function at short times (concentration 50 rods/L^3). b. The mean square angle rotated at short times (concentration 50 rods/L^3).

ulated. We may conclude, therefore, that *rotation is a diffusive process* and that the Debye equation is valid over the range of concentrations we examined. This conclusion contradicts directly with the results of the molecular dynamics simulations we mentioned earlier.[18,19] It is clear that *the success of the Debye equation even at low concentrations is due to the strong decorrelating effect of the random force exerted by the solvent and not to the small angle of rotation associated with a "jump"*. Hence, things might be different if hydrodynamic interaction is included.

As discussed in the Introduction the main postulate of the original Doi–Edwards theory (DET)[2,3] is that the rods are confined in cages formed by their neighbors for extensive time intervals between cage breakups. Such a behavior would result to a plateau in the $-\ln \langle P_l[\cos(\theta(t)]\rangle$ and $\langle\theta^2(t)\rangle$ vs time curves. The plateau should appear when the angle rotated is roughly equal to the average cage size and must persist for a time comparable to the average lifetime of the cage. The theoretical estimates for these quantities can be obtained from the improved version of the DET developed by Keep and Pecora.[12] At the concentration of 50 rods/L^3 they esimate the angular cage size to be ~0.3 rad while the average lifetime of the cage must be from 0.01 to 0.2 $\beta L^2/kT$ with most probable value around 0.02 $\beta L^2/kT$. For this rotation angle the quantity $-(^1/_2)\ln\langle P_1[\cos\theta(t)]\rangle$ has a value of roughly 0.03. As seen in Figure 1 no plateau appears around this value or around any other value. In Figures 3a,b the short time behavior of $-(^1/_2)\ln\langle P_1[\cos\theta(t)]\rangle$ and of the mean square angle $\langle\theta^2(t)\rangle$ is shown for the same concentration of 50 rods/L^3. No evidence of plateau can be seen in any of these figures either. We may conclude, therefore, that complete caging does not occur up to a concentration of 50 rods/L^3. We should mention at this point that the theoretical prediction in ref 12 is that caging concepts should start being valid above a certain concentration somewhere between 20 and 50 rods/L^3. Our conclusion does not contradict other simulation results,[18-20] which agreed with the predictions of caging theories but only at concentrations higher than ours.

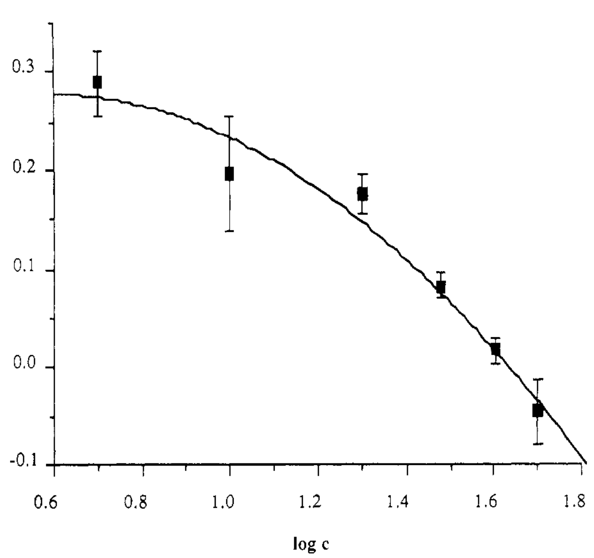

Figure 4. Logarithmic plot of the rotational diffusivity vs concentration. The rotational diffusivity is calculated from the decay time of the first rotational correlation function.

Apart from the proof or disproof of caging ideas, Figure 3a reveals some important aspects of the actual dynamics. For a short but observable time interval, the rod rotates as freely as it would in a dilute solution. There appears to exist, therefore, an initial amount of essentially unhindered rotation, as it is intuitively expected and in agreement with the picture of caging theories. Larger rotations become progressively more difficult but not extremely more difficult. As manifested by the decrease of the slope in Figure 3a, a relatively larger number of constraints must be overcome for the realization of larger rotations. This is about all, however, because the rod seems to be quite capable of doing so by slightly modifying its initial trajectory. In addition, the constraining rods themselves somehow clear the way, responding to the repulsive action of the rod under consideration. More important is the observation that the rod and its neighbors seem to have the time to explore most of their permissible mutual configurations and discover those that would facilitate the orientational relaxation. In the DET parlance, cages might form quite often as expected by a static analysis.[12] Their constraining capability, however, is not so severe as anticipated because of the ease with which they dissolve, i.e. their short lifetime. Furthermore, following the same line of thought, partially open cages are considerably less effective in constraining the motion, too.

Figure 4 is a logarithmic plot of the rotational diffusivity determined from the slope of the first rotational correlation function vs the concentration. Obviously it does not follow any power law and is not expected to do so even in the context of the improved versions of DET.[12,13] The continuous line is just a parabolic fit to which we attribute no greater significance than to demonstrate the failure of any power law and the increasingly stronger concentration dependence.

The only other simulation results for the same quantity and over the same concentration regime are presented in ref 20. Our values for the rotational diffusivity are systematically and significantly higher than the corresponding values in ref 20. In addition, the rotational diffusivities determined from our simulation agree quantitatively with experimental values of the same quantity[10] for rodlike polymers with length over width ratio similar to ours. All these can be seen in Figure 5 where the values of the rotational diffusivities from our simulation are compared with experimentally determined values and the simulation

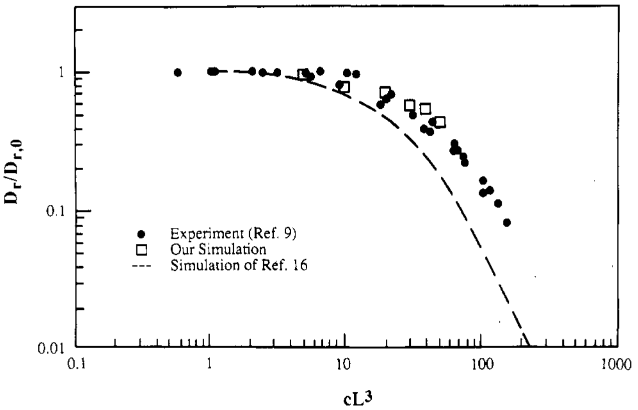

Figure 5. Comparison of the rotational diffusivities determined from our simulation with results from dynamic electric birefringence experiments on PBLG in *m*-cresol (ref 10 and 13) and the simulation results of ref 20.

results of ref 20. The experiments in ref 10 measured the dc component of the electric birefringence of poly(γ-benzyl-L-glutamate) (PBLG) in *m*-cresol under an ac electric field over a wide range of frequencies. The width of the rodlike molecules used in these experiments was 30–70 times smaller than their length. The persistence length of PBLG in *m*-cresol is approximately 100 nm.[64,65] Since the four different samples used in these experiments were monodisperse and the polymers in them had length 44, 51, 66, and 100 nm, the rodlike polymers were quite but not completely rigid. In ref 13 it is argued that no high frequency relaxation that can be attributed to the flexibility of the molecules was detected. The agreement between our simulation results and the experimental values as well as the absence of any leveling off of the data at high concentrations argue that no pronounced flexibility effects were present in these samples.

It seems that our comments about the effect of the large time step used in ref 20 (see Introduction) are confirmed by these comparisons. Indeed the time step used in ref 20 was 200 times larger than ours, which means that the average rotation angle during each time step was 14 times larger in the simulation of ref 20 than in our simulation. In agreement with the description of the rotational motion we presented earlier, such a large time step would both diminish the chances of a rod to escape from a partially open cage and decrease the ability of the system to discover collective configurations that would facilitate the orientational relaxation.

ii. Translational Motion. In a dilute solution the diffusivities in the directions parallel and normal to the rod axis are different as a result of the hydrodynamic interaction among the parts of the same rod. For the reasons explained in section 1, such an inherent anisotropy is not built in our model and the diffusivities in infinite dilution are the same both normal and parallel to the rod axis.

$$D^\circ = 0.5 \qquad \text{in all directions} \tag{4.6}$$

Therefore, any difference between the normal and parallel diffusivities in a concentrated solution will result exclusively from the fact that lateral motions are more hindered by the presence of other rods than motions parallel to the rod axis. To put it another way, any such difference, if observed, will demonstrate the selective effect of the intermolecular interactions on the various modes of motion. The strong, short-range, cylindrically symmetric intermolecular potential, which realizes the uncrossability feature of a slender rod, will produce interactions which suppress stronger the lateral modes and enhance the importance of the parallel mode in the total mobility.

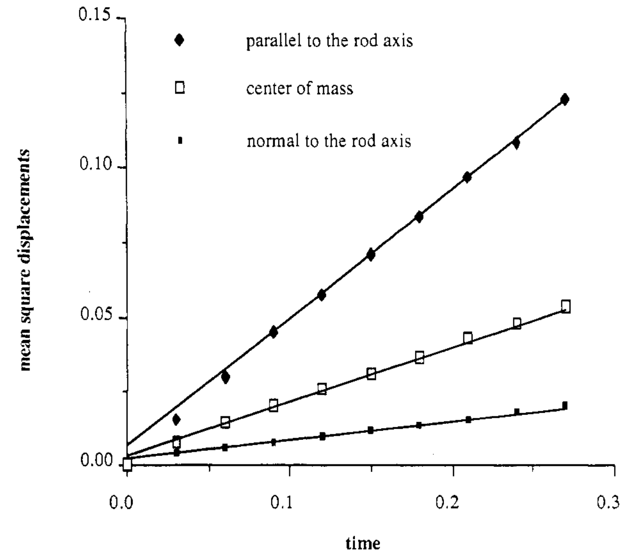

Figure 6. Mean square displacements normal and parallel to the rod axis for the concentration of 50 rods/L^3.

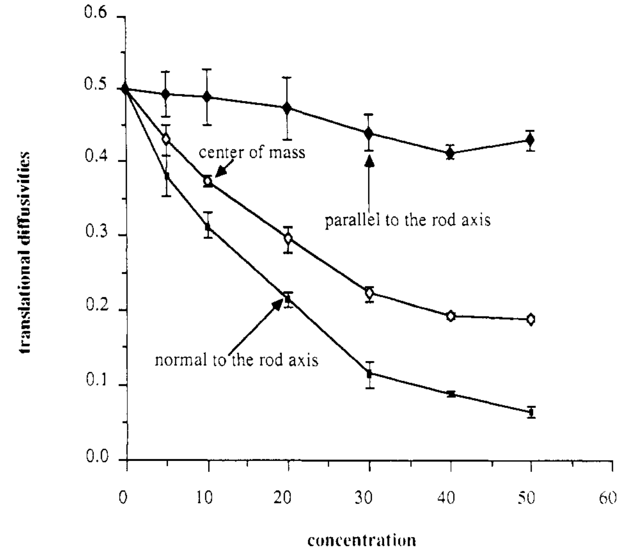

Figure 7. Center of mass diffusivity and diffusivities normal and parallel to the rod axis vs concentration.

Such a diminution of the normal diffusivity is indeed observed, as one would expect intuitively, and the effect becomes stronger at higher concentrations, again in agreement with intuition. The mean square displacements normal and parallel to the rod axis, as well as the mean square displacement of the center of mass are plotted as a function of time in Figure 6 for the concentration of 50 rods/L^3. Indeed, the diffusivity parallel to the rod axis is much larger. The rod can avoid the obstacles (neighboring rods) more effectively moving along its axis rather than normal to it, and the rod's neighbors can clear the way more easily by diffusing along their axes rather than normal to them.

This simple, intuitively obvious fact has been the primary motivation of DET (and of the reptation theory for flexible polymers). DET, however, adopts an extreme viewpoint, namely, that the diffusion parallel to the rod axis is completely unhindered and the diffusion normal to the rod axis is so strongly restricted that the diffusivity in this direction is practically zero (i.e. the normal mode freezes). As we see from Figure 7 the parallel diffusivity is indeed approximately equal to its dilute solution value although it exhibits a slight tendency to decrease (at the

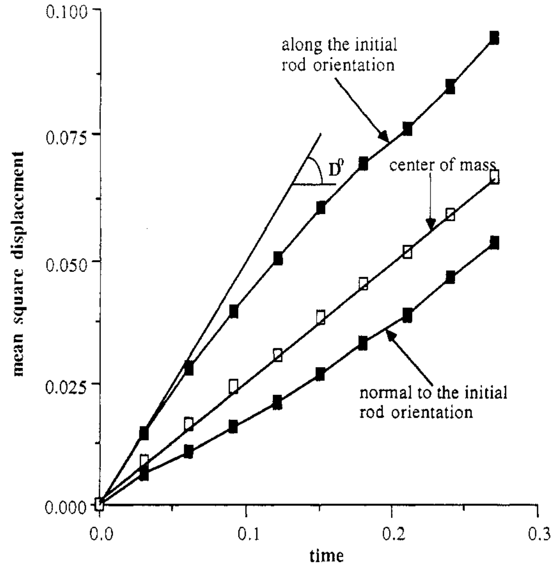

Figure 8. Mean square displacements normal and parallel to the *initial* rod orientation for the concentration of 30 rods/L^3.

two highest concentrations is 15–20% lower than the dilute solution value). The diffusivity normal to the rod axis decreases sharply with concentration, but it does not freeze up to the highest concentration simulated. The finite values of the normal diffusivity are a clear proof of the fact that *cage renewal is not the only, and possibly not even the dominant, rotational relaxation mechanism in the concentration range we examined.*

There are additional features of the translational diffusion mechanism, which are illuminating of the polymer dynamics. In Figure 8 the mean square displacements parallel and normal to the initial rod orienation have been plotted as a function of time for the concentration of 30 rods/L^3. At long times these mean square displacements grow linearly with time because the rod has forgotten its initial orientation. Therefore, the initial orientations have no special importance any longer, and the diffusivity along these directions is identical with the center of mass diffusivity. The shape of the mean square displacement curves parallel and normal to the initial rod orientation has some significance, too. Parallel to the rod axis the mean square displacement is convex before becoming linear, which simply reveals the fact that the convenience of the parallel movements is gradually lost, since the movement gets less and less parallel t the current rod orientation. Normal to the rod axis the mean square displacement is initially convex too, due to the relative freedom by which small scale normal displacements can take place. However, the rod cannot go too far moving normally to its orientation without experiencing a hindrance from its neighbors. Over longer times it rotates and the restriction becomes less effective along the normal direction to its initial orientation, which produces the concave shape. All these, although expected intuitively, have an important effect on the center of mass mobility. The two opposing effects cancel each other to a large extent resulting in an almost diffusive motion for the center of mass at very short times (~0.1 $\beta L^2/kT$). Normally, the center of mass motion is expected to be diffusive over times larger than $\beta L^2/kT$.

iii. The Pair Distribution Function. Since all theories and most of the simulations relevant to our problem employed an infinitely thin needle as a model for the rodlike polymer, static correlations among the configurations of neighboring polymer molecules were nonexistent and the pair distribution function was trivial.

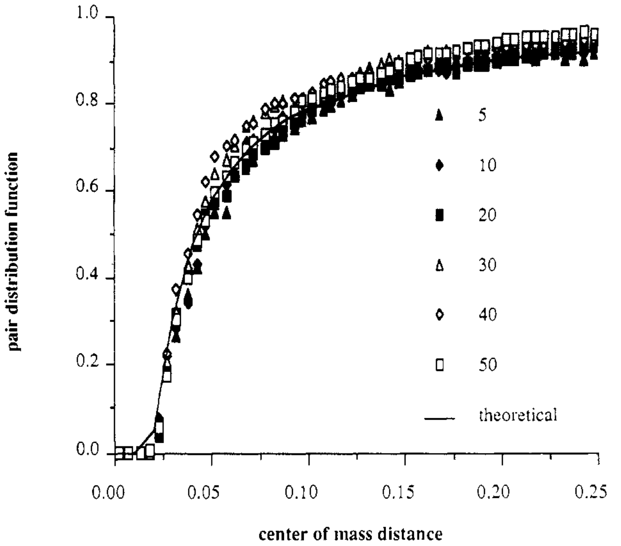

Figure 9. The rod–rod pair distribution function vs the center of mass distance of the pair at various concentrations. The continuous line is the approximate pair distribution function from eq 4.9.

Static properties are independent of the simulation dynamics (as long as the latter are ergodic). Therefore, our results for the pair distribution function would have been the same had hydrodynamic interaction been accounted for. Despite this advantage, the exact form of the pair distribution function will depend on the intermolecular potential used. Experience with simple fluids, however, suggests that the qualitative trends are the same and independent of the details of the intermolecular interaction. For example the pair distribution functions for hard spheres and Lennard-Jones fluids are quite similar.[60]

The rod–rod pair distribution function is plotted in Figure 9 as a function of the center of mass distance for all concentrations simulated. As we see, all curves grow monotonically a behavior reminiscent of that of weakly nonideal gases. The concentration dependence appears to be very weak and as a matter of fact, all curves practically overlap. It should be emphasized that the form of the pair distribution reflects as much the thin cylindrical shape as it reflects the weak and short-range ordering induced by the finite rod width. In this sense, the persistence of some negative correlation even over distances of 0.2L (ten times larger than the rod width) is due to the fact that there is still a slight chance for a pair with such a center of mass distance to have a minimum distance comparable to the rod diameter, adopting in this way an energetically unfavorable configuration. There seems to be a space free of neighbors over a distance of 0.02L around each rod. This is reassuring since it shows that our conjecture about the rod diameter made in section 2 was a successful one.

The shape of the pair distribution function with its monotonic increase with distance and the absence of any oscillations is very similar to that of pair distribution functions for weakly nonideal gases. It is tempting to try an expansion of the pair distribution function in powers of concentration

$$g = g_0 + cg_1 + c^2g_2 + ... \qquad (4.7)$$

where g is the rod–rod pair distribution function, c is the number concentration of polymers, and the term of order n in the expansion represents the contribution of $n + 2$ body interactions. The absence of significant concentration dependence (see Figure 9) suggests that the first term, which accounts for direct two-body interactions, make the

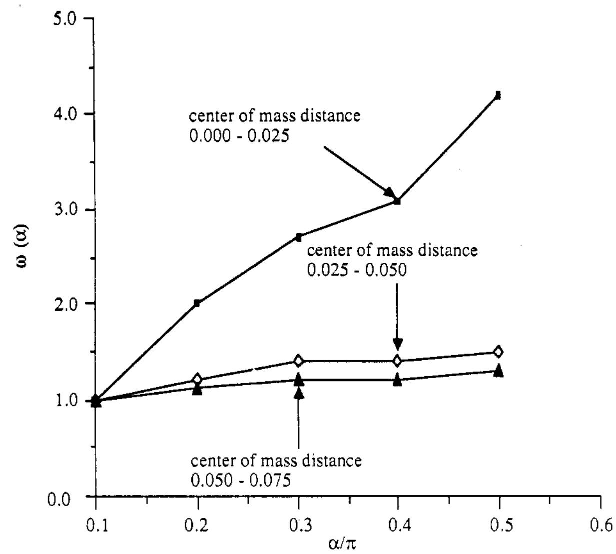

Figure 10. Angular dependence of the pair distribution function for the concentration of 40 rods/L^3.

dominant contribution to the value of g. We therefore approximate g as

$$g(\mathbf{r}_{12},\mathbf{u}_1,\mathbf{u}_2) \approx g_0(\mathbf{r}_{12},\mathbf{u}_1,\mathbf{u}_2) = \exp[-U(\mathbf{r}_{12},\mathbf{u}_1,\mathbf{u}_2)/kT] \quad (4.8)$$

i.e. a simple Boltzmann factor. In eq 4.8 U is the intermolecular potential given by eq 2.1, $\mathbf{r}_{12}$ is the vector connecting the centers of mass of the pair, and $\mathbf{u}_1$ and $\mathbf{u}_2$ are the orientation vectors of the pair. As we see from Figure 9 eq 4.8 is a very good approximation over the entire range of concentrations examined (5–50 rods/L^3). Using this approximate form of the pair distribution function, one can predict the average potential energy per rod u, at various concentrations.

$$u \approx (c/32\pi^2) \int g_0(\mathbf{r}_{12},\mathbf{u}_1,\mathbf{u}_2) U(\mathbf{r}_{12},\mathbf{u}_1,\mathbf{u}_2) \, d^3\mathbf{r}_{12} \, d^2\mathbf{u}_1 \, d^2\mathbf{u}_2 \quad (4.9)$$

An immediate consequence of our approximation is that u grows linearly with concentration. The theoretically predicted energies were compared to the ones determined by the simulation in Table III. The agreement is excellent up to the highest concentration of 50 rods/L^3.

For axisymmetric particles the pair distribution function has in principle some angular dependence. This dependence was integrated over in Figure 9 but is shown in Figure 10 for the concentration of 40 rods/L^3. The quantity ω plotted in Figure 10 is defined as

$$\omega(\alpha) = \{n(r_{12},\alpha)/[\cos(\alpha + \pi/10) - \cos(\alpha - \pi/10)]\}/\{n(r_{12},\pi/10)/[\cos(\pi/5) - 1]\} \quad (4.10)$$

where $n(r_{12},\alpha)$ is the number of pairs with center of mass distance r_{12} and angle α ($0 < \alpha < \pi/2$). Despite the poor statistics of this quantity, the qualitative trends are obvious. A significant angular dependence exists only among the small number of pairs that get closer than $0.025L$. For longer distances no angular dependence is observed. It seems, therefore, that the angular dependence too arises solely from direct two-body interactions.

iv. Rationalization. As we mentioned in the Introduction, experimental evidence,[8-11] molecular simulations[18-20] and theoretical analyses[12,13] all argue that DET is not valid for low concentrations (lower than 50–80 rods/L^3). In fact, it is fairly obvious in the original papers themselves[2,3] that DET is not appropriate at very low concentrations. The actual objective of our simulation, therefore, was not to certify the failure of DET in the lower concentration regime but rather to rationalize the dynamical behavior there.

Fixman[21] proposed a fundamentally different model in order to explain his simulation results. Although his model was expected to be appropriate for both high and low concentrations, the comparison of the model predictions with simulation results was done only for relatively high concentrations (higher than 50 rods/L^3). The basic premise of Fixman's model is that there exist two mechanisms for orientational relaxation. One is that proposed by DET, namely, translational diffusion of the rods along their axes. On a shorter time scale, however, the probe rod and its neighbors can perform slight rotations and translations normal to their axes that allow a certain initial relaxation. The tendency for such motions will be dominant at very short times as a result of the high free energy stored in the neighborhood of the probe owing to its close approach to its neighbors. Responding to the repulsion from its neighbors the probe will move fast toward the middle of the cage. Furthermore, the neighbors themselves will rotate, deforming the cage in a way that provides additional space for the rotation of the probe. These events will decrease significantly the extra free energy stored in the probe–neighbor system, and after a while the tendency of the probe to move further away from its neighbors and the tendency of the neighbors to deform the cage will be much weaker. Eventually, translational diffusion of the rods along their axes will become a faster (more efficient) channel for the release of the last remnants of extra free energy, and the cage renewal process will become the dominant mechanism for orientational relaxation. The relevance of caging ideas is recovered once more, but the cages we are talking about now are fundamentally different. It is not the hindrance posed by an equilibrium configuration of neighbors that matters but rather the hindrance posed by neighbors that have already done most of what is possible to provide free space for the rotation of the probe.

Arguments like that are certainly reasonable, but they appear to be of little value since any attempt to quantify them will require a detailed knowledge of both the structure and the dynamics of the probe–neighbor system. The situation is not nearly as hopeless as it might seem, however. As we pointed out in the previous subsection, knowledge of the second virial coefficient (i.e. account for direct two-body interactions) will suffice for the determination of the equilibrium properties and the local structure (pair distribution function) over the range of concentrations we simulated (see Figures 9 and 10 and Table IV). As a matter of fact, this has been a fairly common assumption for isotropic nondilute solutions of rodlike polymers[1] whose validity for very thin rods was first argued by Onsager.[66] Therefore, the local structure around a probe rod at a partially equilibrated state, where the probe–neighbor system has only partially released its extra free energy, can be determined in that context.[21]

The determination of the dynamics of the short time relaxation poses more serious problems. Fixman[21] adopts a simple viewpoint, i.e. "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 limit of vanishing rod width" (i.e. an "Enskog-like" approximation). Furthermore, short time rotations are assumed to be completely unhindered, i.e. until translational diffusion takes over as a faster channel for orientational relaxation, the rotational diffusivity retains essentially its dilute solution value. The first assumption, which is the most crucial, was tested directly in ref 19 and was found not be valid for a gas of needles without solvent. Chances are better in our case because of the strong, solvent-induced decorrelation which is responsible for a significant memory loss in between rod–rod collisions. Therefore, a neutral role of the interactions between neighbors in either enhancing or hindering the short time relaxation process seems more reasonable. The validity of this assumption for the concentration of 48.5 rods/L^3 has been tested directly by Fixman.[21] The second assumption is less defensible. In fact, if Fixman's model is taken literally, our simulation results prove that the assumption of completely unhindered short time rotations is not valid. The duration of the short time relaxation is calculated explicitly in Fixman's model. Our simulation results show that the "rotational diffusivity" during that time interval has values intermediate between the dilute solution value and the actual long time rotational diffusivity. These values are much closer to the long time rotational diffusivity than to the rotational diffusivity at infinite dilution, which implies that the short time rotations are themselves hindered to a certain extent. Nevertheless, we feel that this is not a crucial assumption. The model would retain the same form and would furnish the same results even if allowance was made for a lower (concentration dependent) short time rotational mobility (but of course still higher than the long time rotational mobility).

The final equation of Fixman's model for the rotational diffusivity is

$$\beta_r \equiv kT/D_r = \beta_r^\circ[1 + cL^3(24\pi R)^{-1}Qf \ln [(1-f)/f]] \tag{4.11}$$

where $Q = 1 + (\pi/2)cL^3(b/L)(1-2f)^2$, $R = \beta_r^\circ D_p^\circ/L^2kT$, β_r is the rotational friction constant, $\beta_r^\circ = \beta L^2/2$ is the rotational friction constant of a rigid dumbbell without hydrodynamic interaction at infinite dilution, $D_p^\circ = kT/2\beta$ is the translational diffusivity of a rigid dumbbell along its axis at infinite dilution, and β is the friction coefficient of the bead.

The quantity f is determined by maximizing β_r with respect to it. According to Fixman,[21] this maximization asserts minimum entropy production, i.e. that the system chooses the most probable combination of the two relaxation mechanisms (out of all the microscopically possible combinations) to release its extra free energy. This value of f has a direct physical significance in Fixman's model. It determines when the matching of the rates of the two relaxation mechanisms occurs. A translation of the rod over a distance fL along its axis suffices for the release of the cage-imposed constraint on the rod's rotation, while the slight rotational motions of the rod's neighbors over short times, i.e. as long as these rotations are more efficient in relaxing the free energy than translational diffusion along the rod axis, are of magnitude $\Phi \cong f\pi$.

The comparison between the predictions of Fixman's model and our simulation results is shown in Figure 11. The success of the model is impressive, especially in view of the simplicity of its assumptions. The predictions of the model agree with the simulation results well within the limits of statistical uncertainty for all concentrations we simulated. We should point out at this stage that the agreement with our simulation results implies a very good agreement with the experimental values of the rotational diffusivity of PBLG in *m*-cresol.[10] Because of the ambiguity about the equivalent hard cylinder diameter of our rodlike particles, we have also plotted in Figure 11 the predictions of Fixman's model for rods with length over width ratio of 30. The slightly larger diameter has little effect in the concentration regime we simulated, but the effect becomes more important at higher concentrations.

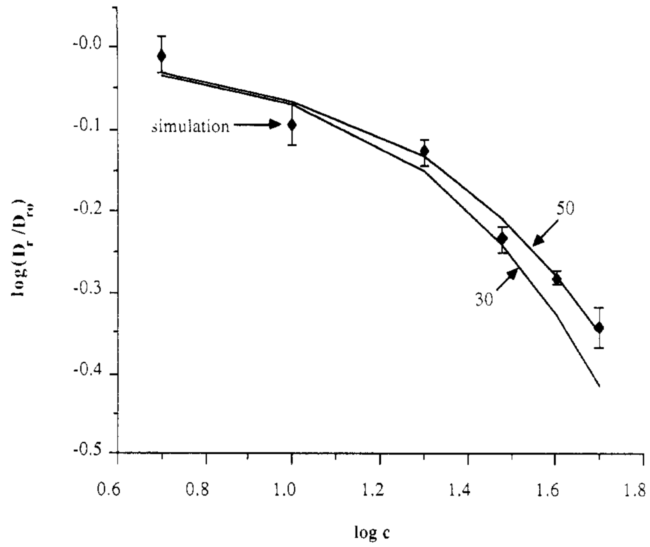

Figure 11. Comparison of our simulation results for the rotational diffusivity with the predictions of Fixman's model.[21] The model predictions for polymers with axial ratio equal to 30 is also shown (the axial ratio of our particles is estimated to be 50).

In summary, we think that Fixman's model provides a very appropriate description for the dynamics of nondilute solutions of rodlike polymers with finite width over the range of concentrations we simulated (5–50 rods/L^3) and as such it emerges as a most significant advance in our understanding of these systems since the development of the original DET. The model is insightful enough to discover the important trends of apparently very complicated dynamics by providing a self-consistent way to deal with dynamically deformable cages. Furthermore, it is very appealing both because of the simplicity of its final formulas and because of its ability to account for the finite molecular diameter removing in this way a major limitation present in DET and its improved versions.[9,10]

5. Conclusions

We performed Brownian dynamics simulations of moderately concentrated solutions of rodlike polymers (5–50 rods/L^3). The rodlike particles in our simulations had a length over width ratio of 50, which is typical of actual rodlike polymers. Aside from the issue of validity of the DET and caging ideas in general for sufficiently concentrated solutions, the DET approach is expected to be inappropriate for at least the lower part of the concentration regime we simulated.[12] Our simulation provided additional proof for the failure of caging ideas up to the highest concentration of 50 rods/L^3. This failure was demonstrated by the absence of any plateaus in the rotational correlation functions and more directly by the persistence of a finite and significant mobility of the rods normal to their axes.

The static properties of our systems were found to be very simple exhibiting none but the weakest deviations from ideality. These deviations are due solely to direct pair interactions. As a result of this, the polymer pair distribution function had very weak concentration dependence and was adequately approximated by the Boltzmann factor, while the potential energy values were quantitatively reproduced by density expansions through the second virial coefficient.

The dynamics, however, were anticipated to be very complex. In particular, subsequent rod–rod collisions were expected to be highly correlated. These considerations, however, were primarily based on geometrical arguments concerning the topological constraints on the rod's motion by the mere presence of its neighbors and ignored a major simplifying factor, namely, the strong solvent-induced decorrelation in between rod–rod collisions. In reality, the solvent–plymer impacts are responsible for a significant memory loss in between rod–rod collsions and a substantial decorrelation of the rod–rod collision sequences. Because of this decorrelation, rotation was found to be a diffusive process even at low concentrations, in sharp contrast to the strongly nondiffusive character of rotation in similar systems without solvent.[18,19]

A model proposed by Fixman[21] was found to reproduce very well our simulation results for the rotational diffusivities, the first simulation results in quantitative agreement with experimentally measured values of the same quantity for rodlike polymers with comparable to ours axial ratio. The basic premise of Fixman's model is the introduction of a short time relaxation mechanism that accounts for the slight rotations of a probe rod and its neighbors whenever they aproach very closely. These rotations allow for some initial relaxation before translational diffusion takes over and relaxes fully the probe's orientation by removing the constraints from its neighbors. Our simulation showed that the two major assumptions of Fixman's model are legitimate. The simple two-body nature of the local structure around the probe rod is a direct consequence of the two-body character of the static properties, while the neglect of interactions among the neighbors during the short time relaxation process is reasonable in view of the strong decorrelating effect of the solvent–polymer interaction during that process.

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References and Notes

(1) Doi, M.; Edwards, S. F. *Theory of Polymer Dynamics*; Clarendon: Oxford, 1986.
(2) Doi, M. *J. Phys.* (*Les Ulis, Fr.*) **1975**, *36*, 607.
(3) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday* Trans. *2* **1978**, *74*, 560.
(4) Kuzuu, N. Y.; Doi, M. *Polym. J.* (*Tokyo*) **1980**, *12*, 883.
(5) Edwards, S. F. *Proc. Phys. Soc., London* **1967**, *92*, 9.
(6) De Gennes, P. G. *J. Chem. Phys.* **1971**, *55*, 572.
(7) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1789; **1978**, *74*, 1802; **1978**, *74*, 1818; **1979**, *75*, 38.
(8) Maguire, J. F.; MacTague, J. P.; Rondelez, F. *Phys. Lett.* **1980**, *45*, 1891.
(9) Zero, K.; Pecora, R. *Macromolecules* **1982**, *15*, 87.
(10) Mori, Y.; Oocubo, N.; Hayakawa, R.; Wada, Y. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 2111.
(11) Odell, J. A.; Atkins, E. D. T.; Keller, A. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 289.
(12) Keep, G. T.; Pecora, R. *Macromolecules* **1985**, *18*, 1167.
(13) Teraoka, I.; Oocubo, N.; Hayakawa, R. *Phys. Rev. Lett.* **1985**, *55*, 2712.
(14) Jain, S.; Cohen, C. *Macromolecules* **1981**, *14*, 759.
(15) Fesciyan, S.; Dahler, J. S. *Macromolecules* **1982**, *15*, 517.
(16) Dahler, J. S.; Fesciyan, S.; Xystris, N. *Macromolecules* **1983**, *16*, 1673.
(17) Altenberger, A. R.; Dahler, J. S. *Mol. Phys.* **1987**, *60*, 1015.
(18) Frenkel, D.; Maguire, J. F. *Mol. Phys.* **1982**, *45*, 637.
(19) Magda, J. J.; Davis, H. T.; Tirell, M. *J. Chem. Phys.* **1986**, *85*, 6674.
(20) Doi, M.; Yamamoto, I.; Kano, F. *J. Phys. Soc. Jpn.* **1984**, *53*, 3000.
(21) Fixman, M. *Phys. Rev. Lett.* **1985**, *54*, 337; **1985**, *55*, 2429.
(22) Russo, P. S.; Langley, K. H.; Karasz, F. H. *J. Chem. Phys.* **1984**, *80*, 5312.
(23) Odijk, T. *Macromolecules* **1983**, *16*, 1340.
(24) Barker, J. A.; Henderson, D. *J. Chem. Phys.* **1967**, *47*, 2856.
(25) Chandrasekhar, S. *Rev. Mod. Phys.* **1943**, *15*, 1.
(26) Kirkwood, J. G. *J. Chem. Phys.* **1946**, *148*, 180.
(27) Green, M. S. *J. Chem. Phys.* **1952**, *20*, 1281.
(28) Zwanzig, R. *Phys. Rev.* **1961**, *124*, 983.
(29) Mori, H. *Prog. Theor. Phys.* **1965**, *33*, 423; **1965**, *34*, 399.
(30) Ross, J. *J. Chem. Phys.* **1956**, *24*, 375.
(31) Lebowitz, J. L.; Rubin, E. *Phys. Rev.* **1963**, *131*, 2381.
(32) Resibois, P.; Davis, H. T. *Physica* (*Amsterdam*) **1964**, *30*, 1077.
(33) Van Kampen, N. G. *Stochastic Processes in Physics and Astronomy*; North Holland: Amsterdam, 1981.
(34) Lord Rayleigh *Philos. Mag.* **1891**, *32*, 424.
(35) *Turk*, P.; Lentelme, F.; Friedman, H. *J. Chem. Phys* **1977**, *66*, 3039.
(36) Van Gunsteren, W. F.; Berendsen, H. J. C. *Mol. Phys.* **1982**, *45*, 637.
(37) Kirkwood, J. G. *Macromolecules*; Gordon and Breach: New York, 1967.
(38) Bird, R. B.; Hassager, O.; Armstrong, R. C.; Curtiss, C. F. *Dynamics of Polymeric Liquids. Kinetic Theory*, 2nd ed.; Wiley: New York, 1987; Vol. 2.
(39) Lax, M. *Rev. Mod. Phys.* **1966**, *38*, 541.
(40) Zwanzig, R. *Adv. Chem. Phys.* **1969**, *15*, 325.
(41) Fixman, M. *J. Chem. Phys.* **1978**, *69*, 1527.
(42) Gardiner, C. W. *Handbook of Stochastic Methods for Physics, Chemistry and Natural Scienes*; Springer-Verlag: Berlin, Heidelberg, 1983.
(43) Tough, R. J. A.; Pusey, P. N.; Lekkerkerker, H. N. W.; van der Broek, C. *Mol. Phys.* **1986**, *59*, 595.
(44) Bitsanis, I.; Davis, H. T.; Tirrell, M., to be submitted for publication.
(45) Freed, K. F.; Edwards, S. F. *J. Chem. Phys.* **1974**, *61*, 3626.
(46) Altenberger, A. R.; Tirrell, M.; Dahler, J. S. *J. Chem. Phys.* **1986**, *84*, 5122.
(47) Altenberger, A. R.; Dahler, J. S.; Tirrell, M. *Macromolecules* **1988**, *21*, 464.
(48) Fixman, M. *J. Chem. Phys.* **1978**, *69*, 1538.
(49) Dotson, P. J. *J. Chem. Phys.* **1983**, *79*, 5730.
(50) Ceperley, D.; Kalos, M. H.; Lebowitz, J. L. *Macromolecules* **1981**, *14*, 1472.
(51) Bishop, M.; Kalos, M. H.; Sokai, A. D.; Frisch, H. L. *J. Chem. Phys.* **1983**, *79*, 3496.
(52) Bishop, M.; Ceperley, D.; Frisch, H. L.; Kalos, M. H. *J. Chem. Phys.* **1982**, *76*, 1557.
(53) Helfand, E. *J. Chem. Phys.* **1978**, *69*, 1010.
(54) Fixman, M. *Macromolecules* **1986**, *19*, 1195.
(55) Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, M. N.; Teller, A. H.; Teller, E. *J. Chem. Phys.* **1953**, *21*, 1087.
(56) Verlet, L. *Phys. Rev.* **1967**, *159*, 98.
(57) Rossky, P. J.; Doll, J. D.; Friedman, H. L. *J. Chem. Phys.* **1978**, *69*, 4268.
(58) Rao, M.; Pangali, C.; Berne, B. J. *Mol. Phys.* **1979**, *37*, 1773.
(59) Rao, M.; Berne, B. J. *J. Chem. Phys.* **1979**, *71*, 129.
(60) McQuarrie, D. A. *Statistical Mechanics*; Harper and Row: New York, 1976.
(61) Debye, P. *Polar Molecules*; Dover: New York, 1929; Chapter V.
(62) Berne, B. J.; Pecora, R. *Dynamic Light Scattering*; Wiley: New York, 1976.
(63) Gordon, R. G. *J. Chem. Phys.* **1966**, *44*, 1830.
(64) Wada, A.; Kihara, H. *Polym. J.* (*Tokyo*) **1972**, *3*, 482.
(65) Tsuji, K.; Ohe, H.; Watanabe, H. *Polym. J.* (*Tokyo*) **1973**, *4*, 553.
(66) Onsager, L. *Ann. N.Y. Acad. Sci.* **1949**, *51*, 627.