Macromolecules 1990, 23, 1157-1165

Brownian Dynamics of Nondilute Solutions of Rodlike Polymers. 2. High Concentrations

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Received May 31, 1988; Revised Manuscript Received November 4, 1989

ABSTRACT: We report the results of Brownian dynamics simulations for solutions of rigid rodlike polymers with an aspect ratio of 50 at high concentrations (70-150 rods/L^3, where L is the molecular length). Many-body contributions to the static properties were found to be much weaker than direct two-body interactions up to the highest concentration simulated; therefore the local structure was mostly determined by independent binary interactions. Furthermore, the solvent-polymer impacts in between rod-rod collisions killed most of the temporal correlation of successive rod-rod collisions reducing in this way a highly correlated rod-rod collision sequence to a series of almostuncorrelated binary collisions. At sufficiently high concentrations (higher than 90 rods/L^3) the translational diffusivity normal to the rod axis froze, which proves the existence of completely closed cages. In this concentration regime our simulation results for the rotational diffusivity fall between the predictions of the Doi-Edwards theory for rods with finite diameter and those of Fixman's model. The discrepancy between Fixman's model and our simulation results at high concentrations probably originates from the very sharp decrease of the equilibrium cage size with concentration, which could make the short time relaxation mechanism introduced by Fixman inefficient.

1. Introduction

The distinctive feature of polymer molecules is their one-dimensional connectivity, which results in the uncrossability of the individual polymer chains. The need for the preservation of the chain connectivity along with the uncrossability requirement have a very interesting effect on the dynamics of concentrated polymer solutions and polymer melts; the topological constraints of uncrossability imposed upon a polymer chain by the presence of its neighbors suppress strongly large scale motions of the chain normal to its backbone, while the ability of the chain to perform motions more or less parallel to its backbone is hardly affected. This simple, intuitively obvious fact has been the major motivation of reptation theory.[1-3]

The simplest systems exhibiting the above feature are nondilute solutions of rodlike polymers. Therefore, it is no surprise that the theoretical treatments of the dynamics for concentrated systems of flexible and rodlike polymers have evolved along parallel paths. The counterpart of the reptation theory for rodlike polymers is the Doi-Edwards theory (DET).[4,5] The DET models the rodlike polymers as infinitely thin needles. According to this theory, for concentrations considerably higher than 1 rod/L^3 (L is the molecular length) each polymer molecule is confined inside a cage. The cage, the conceptual analog of the reptation theory tube, represents the collective topological constraint on the motion of the rod imposed by its neighbors. In the DET picture, the cages remain closed for extensive time intervals between cage breakups. Under such conditions, the only way orientational relaxation can be accomplished is if the cage dissolves by translational diffusion of the rods that form it along their axes or if it becomes ineffective because the confined rod itself escapes from the cage again by diffusing along its axis.

The DET is a heuristic theory since it identifies intuitively the dominant mode of motion. Furthermore, it is a qualitative theory since it does not result in concrete predictions of the cage sizes and the rotational diffusivity but only in power laws for the concentration dependence of these quantities.

It is clear that the DET is not adequate at low concentrations (comparable to 1 rod/L^3), where rod-rod interactions affect the dynamical behavior but caging is not expected to be complete and the closed cages that occasionally form might be so large and survive for such a short time that they do not impose any significant constraint on the rotation of the confined rod. The determination of the lowest concentration above which caging concepts are expected to be valid is a complicated statistical problem that was not resolved by the original DET.[4,5] Improved versions of the DET,[6,7] however, predicted that caging cannot be complete for concentrations lower than 20 rods/L^3 but that it is expected to be complete for concentrations higher than 50 rods/L^3. This prediction seems to overestimate the range of concentrations, where the DET is found to be valid. According to the results of molecular dynamics simulations for a gas of infinitely thin needles,[8,9] DET behavior occurs for concentrations higher than 70 rods/L^3. Earlier Monte Carlo simulations of a solution of infinitely thin needles[10] indicated that DET is valid only for concentrations higher than 80 rods/L^3. Therefore, it seems that even these simulations, which agree on the eventual validity, at least as far as concentration scaling is concerned, of the DET for concentrated systems of infinitely thin needles, disagree as to the precise concentration above which it is valid.

Up to now, there have been several experimental tests of the DET.[11-17] These experiments are tedious because the quantity of primary interest, the rotational diffusivity, cannot be measured easily. Furthermore, experimentally it is very hard to distinguish among the effects of different complicating factors (finite width, flexibility, polydispersity, thermodynamic effects), which makes it almost impossible to rationalize their influence on the dynamics. Due to these complications there is no clear experimental answer as to the validity of the DET at high concentrations.

Zero and Pecora[12] performed dynamic light scattering experiments on solutions of poly(γ-benzyl-L-glutamate) (PBLG) in 1,2-dichloroethane solvent. According to the

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0024-9297/90/2223-1157$02.50/0

authors, the polydispersity of their samples was higher than but close to 1.1 and the length-over-width ratio of their molecules ranged from 70 to 100. The length of the rodlike polymers in these experiments was estimated to be 1–1.5 times larger than the presistence length of the PBLG in the solvent used. The results agreed with the inverse square dependence of the rotational diffusivity on concentration (the major DET prediction) for concentrations higher than 70 rods/L^3. However, these results indicated that caging was less severe for longer molecules, probably as a result of the increased flexibility of the longer chains. Odell et al.[14] studied the response of poly(*p*-phenylenebenzthiazole) solutions to purely extensional flow fields. No estimate of the polydispersity or quantitative estimate of the molecular rigidity was reported. The results agreed with the DET in a rough qualitative way but only at extremely high concentrations (200 rods/L^3). Mori et al.[13,15] measured the dc component of the electric birefringence of PBLG in *m*-cresol under an ac electric field. Four samples with axial ratios from 30 to 70 were used in these experiments. Three of them were fractionated, but no estimate of their polydispersity was reported. The average molecular length in all four samples ranged from 0.44 to 1 persistence length, and, according to the authors, no high frequency relaxation that can be attributed to molecular flexibility was observed. Despite the authors' initial interpretation of their results,[13] these measurements agreed with the DET for concentrations higher than 80–100 rods/L^3.

There is yet another class of experimental studies, which furnished much more complex results and did not allow so direct a comparison with the DET.[16,17] Strong thermodynamic nonideality effects and considerable molecular flexibility resulted in a behavior profoundly different from the highly idealized theories and simulations. Thermodynamic effects may lead to an increase of the translational diffusivity with concentration,[16] while strong flexibility effects may result in a weak concentration dependence of the rotational diffusivity.[17]

For perfectly rigid rods with finite diameter, the original DET picture needs modification. Indeed, for rods with finite width the cage size must be reduced by a factor of b/L,[4] where b is the rod diameter. Such a correction will become important when the cage linear dimension becomes comparable to the rod width, and it will lead to a decrease of the rotational diffusivity stronger than the inverse second power of concentration. An estimate of the concentration above which the finite diameter effect becomes significant requires a theoretical prediction of the cage size. In the original DET[4,5] the cage size was estimated as the average distance between rods. A more quantitative estimate is that of Keep and Pecora,[6] which also assumes the basic DET picture. Experimentally, the finite diameter effect has been observed only at very high concentrations. The data in ref 12 indicate noticeable deviations from the inverse square concentration dependence only above 150–200 rods/L^3, while in ref 14 there is evidence of such deviations but only above 500 rods/L^3. No observable finite diameter effect was reported in ref 13 for molecules with axial ratio of 30 up to 150 rods/L^3.

Obviously, it would be very useful to examine the effects of various complicating factors (finite width, flexibility, polydispersity) separately. Although this is almost impossible to achieve experimentally, it is precisely what molecular simulations are meant to do. Fixman[18] performed a series of Brownian dynamics simulations for rodlike polymers with axial ratio of 42 over a wide range of concentrations (50–220 rods/L^3) and some additional simulations with axial ratios of 125 and 62.5 at 145.6 rods/L^3 and axial ratios of 150 and 75 at 48.5 rods/L^3 using quite realistic microscopic dynamics. However, the size of the systems used in these simulations (the side of the periodic box was equal to the rod length at the high concentrations simulated) does not allow as firm an establishment of some of the conclusions as one wishes. Fixman's results were in disagreement with the DET, since they exhibited a much weaker concentration dependence of the rotational diffusivity (for infinitely thin needles and finite diameter rods) than that predicted by the DET even at very high concentrations (higher than 150 rods/L^3).

Therefore it seems that the issue of validity of the DET at sufficiently high concentrations both for needles and for rods with finite width is still unresolved. Under these circumstances it would be premature to start dealing with the effects of flexibility and polydispersity or thermodynamic effects, when the validity of the DET concerning the basic connectivity and excluded volume effects for needles and for rigid rods is still in question.

In a recent publication[19] we presented the results of molecular simulations of rodlike polymers with finite width (axial ratio equal to 50) for concentrations ranging from 5 to 50 rods/L^3. The major conclusion of ref 19 was that a model developed by Fixman[18] in order to rationalize his high concentration results was very successful in describing quantitatively the dependence of the rotational diffusivity on concentration in the range of concentrations we simulated. Fixman studies the role of slight, short time rotations of the rods that deform the cages, creating in this way extra free space for the rotation of the confined rod. Even at concentrations where caging is expected to be complete based on a static analysis,[6] Fixman's approach indicates that the DET predictions might not be valid. It is the size of dynamically distorted cages (i.e. cages that have been deformed so as to allow additional free space for the rotation of the confined rod) and not the size of equilibrium cages that is relevant. Not only is the size of the dynamically distorted cages expected to be larger than that of undistorted (equilibrium) cages, but also its concentration dependence might be different as well. In particular, such a picture introduces explicitly the effect of local structure (and hence of the finite rod diameter) on the polymer dynamics. According to this model, the concentration dependence of the rotational diffusivity is slightly different for molecules with different axial ratios and this difference grows as the concentration increases.

Fixman's model relies on the simple, slightly nonideal character of the polymer–polymer pair distribution function even at relatively high concentrations, which is mostly determined by independent binary interactions alone. The validity of this assumption, which is also expected on theoretical grounds[20] for sufficiently thin rods, was confirmed in ref 19. A more drastic assumption is employed in order to handle the short time rod–rod collision dynamics. Interactions among neighboring rods are assumed to have no effect in either helping or hindering the short time relaxation of the confined rod. This is essentially the assumption of temporally uncorrelated binary collisions, and its inadequacy for a gas of infinitely thin needles was suggested in ref 8 and was demonstrated directly in ref 9. In particular, in ref 9 it was shown that successive rod–rod collisions are highly correlated, as manifested by the presence of a negative tail in the angular momentum autocorrelation function. Nevertheless, one

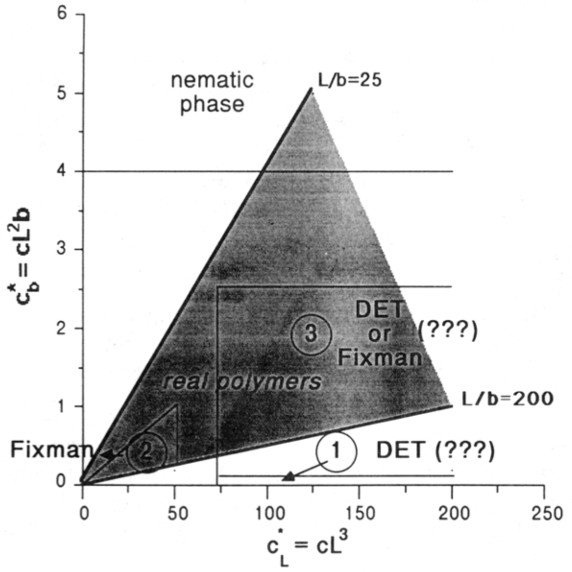

Figure 1. A diagram categorizing our knowledge of the dynamical behavior of rigid rodlike polymers with finite width. c^*_L is a measure of the hindrance to each rod's rotation because of the presence of its neighbors, and c^*_b is a measure of the importance of excluded volume effects.

of the major findings in ref 19 was that the solvent–polymer interaction (absent in a gas of needles) decorrelates strongly successive rod–rod collisions, thereby reducing a highly correlated rod–rod collision sequence to a series of almost uncorrelated binary collisions. This fact, as demonstrated in ref 19, makes rotation diffusive even at low concentrations and justifies, in the range of concentrations studied in that work,[19] the simple treatment of the rod–rod collision dynamics employed by Fixman.[18]

Rodlike polymer molecules are slender, strongly anisotropic objects. There are two natural units of volume for a nondilute system of such particles. The first is a cube with side equal to the rod length. The corresponding unit of concentration is the number of rods with centers of mass inside such a unit cube. Therefore, a natural dimensionless concentration can be defined as

$$c^*_L = cL^3 \tag{1.1}$$

where c is the number concentration and L is the length of the rodlike molecule. When $c^*_L > 1$, the motion of each rod is hindered by its neighbors and the microscopic dynamics are nontrivial.

The second natural unit of volume is the excluded volume per particle, which is roughly equal to L^2b (Onsager[20] found the exact value to be $\pi L^2b/2$ when $L \gg b$, where b is the rod width), and a natural dimensionless concentration may be defined as

$$c^*_b = cL^2b \tag{1.2}$$

Excluded volume effects on the static and dynamical properties can be ignored safely only when $c^*_b \ll 1$. The ratio of these two dimensionless concentrations, $c^*_L/c^*_b = L/b$, is the aspect ratio of the rod.

Our current knowledge of the dynamics of nondilute solutions of perfectly rigid rodlike polymers is summarized schematically in the space of these two parameters in Figure 1. A monodisperse solution of such particles with axial ratio L/b and at a concentration c is represented by a point in the plane. The abscissa of the point, $c^*_L = cL^3$, is a measure of the restriction imposed on the motion of each rod by the presence of its neighbors. The ordinate, $c^*_b = cL^2b$, is a measure of the importance of excluded volume effects on the rod dynamics. Solutions of a particular polymer are located on a line of slope b/L emanating from the origin. Actual rodlike polymers without strong flexibility effects have axial ratios ranging from about 20 to 200.[5,16] Therefore, the portion of the plane that is representative of a wide range of practical experiments is that with the dark shadow.

Figure 1 reveals how sketchy our knowledge of the behavior of real rodlike polymers is. We do know that when the excluded volume c^*_b exceeds 4 the system undergoes a phase transition[20,21] with the appearance of a mesophase (nematic liquid crystalline phase). Flory's estimate[22] for the appearance of a stable nematic phase is $c^*_b > 8$, but we think that Onsager's prediction should be more accurate, at least for rods as thin as those in our simulation. At low c^*_L, where the DET[4,5] and its improved versions[6,7] are known to be inadequate[8-17] (region 2 in Figure 1), Fixman's model[18] is quite accurate.[19] The validity of the DET both for needles and for molecules with realistic axial ratios at sufficiently high concentrations (regions 1 and 3 in Figure 1) is still an open question, especially in view of Fixman's simulation results.[18]

This overall picture is crucial in determining the major objective of our simulation, which is a thorough comparison of molecular simulation results for sufficiently concentrated solutions of rodlike polymers having realistic axial ratios with the predictions of DET and of Fixman's model.

2. The Simulation Method

For the study of the dynamics in a solution of large interacting rodlike particles the method of choice is Brownian dynamics.[23,24] The working equations are the Langevin equations of motion that describe the time evolution of the coordinates and momenta of the rodlike particles.[25-27] Rod–rod interactions are taken into account explicitly, while the interaction with the solvent molecules is accounted for in an approximate, stochastic way by separating the average force exerted by the solvent in the course of several solvent–rod collisions into a systematic friction force and a stochastic Langevin force. If the distances over which the correlation of the rods' velocities decays are much larger than the distances over which the rod–rod intermolecular potential changes appreciably, one can neglect the inertial terms in the Langevin equations.[25,26] In this case, the Langevin equations become first-order stochastic differential equations for the coordinates of the rodlike particles. Details of the simulation technique and of the working equations are given in ref 19.

As far as the interaction with the solvent is concerned, the rodlike polymer is modeled as a rigid dumbbell. For reasons explained in ref 19, hydrodynamic interaction is neglected both among the beads of the same molecule and those of different molecules. Therefore, the Langevin equations for a rigid dumbbell and those of a multibead rigid rod differ only by numerical factors that can be absorbed in the rotational and translational friction constants.

For the polymer–polymer interactions the rods are modeled as line particles interacting with each other via pairwise additive, cylindrically symmetric, purely repulsive forces. The rod–rod intermolecular potential we employed is identical with that used by Fixman[18] in his simulations

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

where U is the potential energy in kT, d is the minimum

Table I
Units

	units	important physical quantities in these units	
length	L	translational diffusivity at infinite dilution)	$D_0 = 0.5$
energy	kT	rotational diffusivity at infinite dilution)	$D_{r0} = 2.0$
translational diffusivity	kT/β	bead friction coefficient	$\beta = 1.0$
rotational diffusivity	kT/βL^2		
angle	rads		

Table II
Simulation Parameters

$c^*_L = cL^3$	70	90	110	130	150
no. of rods	649	833	1019	1203	1389
side of simulation cell[a]	2.1	2.1	2.1	2.1	2.1
time step[b]	5×10^{-6}	5×10^{-6}	5×10^{-6}	5×10^{-6}	5×10^{-6}
no. of time steps	60 000	54 000	54 000	54 000	54 000
(CPU s)/(time step)	0.350	0.549	0.728	1.014	1.372
rejection ratio	0.071	0.091	0.109	0.130	0.150

[a] Periodic boundary conditions were employed. [b] Two simulations with time step 1.33×10^{-6} and 5.00×10^{-6} at $c_L^* = 20$ were performed. Their results were in very good agreement.

distance between the axes of the interacting rods, α is the angle formed by the axes of the interacting rods, ϵ is an energy parameter that defines the potential barrier for rod–rod crossings, and σ is a length parameter that determines the range of the intermolecular potential. For all simulations the following values of the parameters were used:

$$\epsilon = 50/3\ \mathrm{kT} \qquad \sigma = 0.03855L \tag{2.2}$$

The above choices make rod–rod crossings extremely improbable (the probability for such crossings is $\approx 10^{-6}$) and result in an axial ratio

$$L/b \cong 50 \tag{2.3}$$

The units employed in our simulations are shown in Table I. The values of important physical quantities in these units are also shown in the same table.

The numerical method used for the integration of the Langevin equations of motion was presented in ref 19. As explained there, the combination of a stiff intermolecular potential with a low order integration scheme makes necessary the use of an extremely small time step. A significantly larger time step can be employed by a clever application of the Metropolis Monte Carlo rejection criterion in a dynamical situation.[28,29] According to this method, unphysically close approaches of rods, which are artifacts of the low order integration scheme, are rejected a posteriori. These rejections create a problem concerning the rate of time advancement.[19,28] To the extent that the number of movements rejected in this way is small, one is permitted to deal with this problem heuristically and assume that the rejections slow down all diffusion processes by a factor equal to the one minus the rejection ratio. The rejection ratio was 0.07 for $c^*_L = 70$ and 0.15 for $c^*_L = 150$ and grew linearly with concentration in our simulations.

The preparation of properly equilibrated initial configurations is a (computer) time-consuming task. The potential energy of an initial purely random configuration was typically 2–3 orders of magnitude higher than the potential energy of a fully equilibrated configuration. The usual Monte Carlo method[29] that allowed for rod–rod crossings was used to relax the energy up to a value roughly 5 times larger than the equilibrium value. The Monte Carlo method was inefficient during the final stages of the relaxation. At this point Brownian dynamics themselves were employed.[19,30–32] An initial portion of the simulation trajectory (up to 0.12 time unit or 24 000 time steps) was used only for equilibration purposes, and it was excluded from the calculation of the simulation averages (see Table II).

The parameters used in our simulations are contained in Table II. As we can see from this table, long simulations were needed in order to follow the long time disentanglement process and still describe the short time rod–rod collision dynamics with reasonable accuracy. Some of the simulation parameters, like the time step and the size of the spherocylinder drawn around each rod in order to construct the nearest neighbor lists,[9,33] were tested by comparison in ref 19.

We report here new simulations at five different concentrations: 70, 90, 110, 130, 150 rods/L^3. As expected, our simulations were quite time consuming. At the highest concentration simulated the CPU time needed on the University of Minnesota CRAY-2 Supercomputer for 54 000 time steps was almost 19 h. Such simulations became possible only by fully vectorizing our codes. The vectorization decreased the CPU time needs by a factor of 6–9. In the CRAY-2 (and other vector processing machines) the execution speed of a code can be enhanced considerably if special care is taken for its vectorization and its compatibility with the machine architecture. It is the realization of these limitations that made us choose such a simple integration scheme, avoiding more sophisticated and numerically more efficient but less compatible algorithms.

3. Results

i. Static Properties. For a solution of infinitely thin needles the excluded volume is zero at any concentration. Therefore, the thermodynamic properties are trivial and static correlations are absent altogether. This fact was used in the original DET[4,5] and its improved versions[6,7] in order to estimate the cage sizes. One can neglect static correlations when $c^*_b \ll 1$. For actual rodlike polymers, however, this corresponds to very low c^*_L values (see Figure 1), where caging concepts are not appropriate. On the other hand, at higher concentrations where caging concepts might be appropriate ($c^*_L > 50$) $c^*_b \approx 1$ for real rodlike polymers and static correlations cannot be neglected.

If static correlations are due entirely to binary interactions, the original DET picture is expected to survive with only minor modifications.[4] Indeed, it seems reasonable under these circumstances to simply decrease the angular cage size by b/L in order to account for the finite rod diameter. Many-body interactions, however, may alter the shape of the cages and the concentration dependence of the cage sizes. Many-body correlations introduce difficulties to Fixman's model[18] as well. Except for the obvious fact that the mean square torque on a rod cannot be calculated by using a second virial coefficient approximation, the assumption of uncorrelated binary collisions is questioned no matter how strong the solvent induced decorrelation might be.

The importance of many-body correlations can be assessed directly by studying the shape of the rod–rod pair distribution function at various concentrations (Fig-

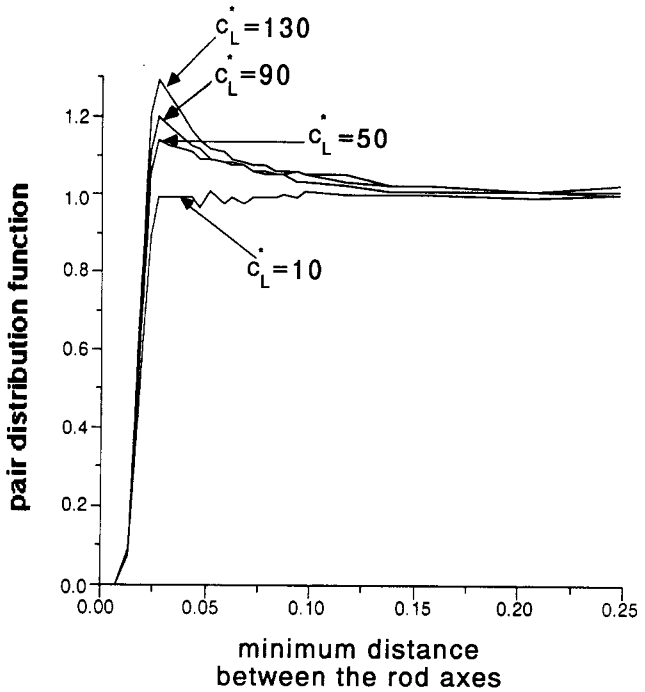

Figure 2. Rod–rod pair distribution function vs the minimum distance between the rods at various concentrations.

ure 2). If the static correlations are due exclusively to binary interactions, the pair distribution function would increase monotonically with distance. As we see from Figure 2, this is strictly true only at very low concentrations ($c^*_L < 10$). At higher concentrations the pair distribution function has a peak at approximately one rod diameter. This peak grows with increasing concentration manifesting in this way the increasing importance of many-body correlations. Nevertheless, the peak remains relatively weak up to the highest concentration simulated ($c^*_L = 150$). The shape of the pair distribution function is reminiscent of that in dense gases. In particular, the absence of any structure after the first shell of nearest neighbors (no multiple oscillations) allows an approximation of the static properties by means of a virial expansion in concentration and suggests that many-body effects although present are not overwhelming.

In Figure 3 we have plotted the potential energy per rod at the various concentrations simulated (the simulation results at low concentrations are from ref 19). The deviation of the actual energies from those predicted by a second virial approximation is a measure of the importance of many-body correlations. As we see from Figure 3, many-body contributions to the energy are negligible up to $c^*_L = 50$. At $c^*_L = 150$ they contribute 25% to the total energy. A third virial coefficient approximation of the potential energies is also shown in Figure 3. As we see, it agrees very closely with the simulation results up to the highest concentration examined. The value of the third virial coefficient that fits our results agrees within a factor of 5–10 with Onsager's theoretical estimate.[20] This is satisfactory in view of the very approximate character of Onsager's estimate and the difference in the molecular models (Onsager's prediction is for hard cylinders). Summarizing, we may say that four and higher body static correlations are negligible and three-body correlations are present but of lesser importance than the direct two-body interactions in our range of concentrations (c^*_L = 70–150) for the rodlike particles we simulated ($L/b = 50$).

The angular dependence of the pair distribution function is important as well. Although the statistics of this quantity are poor, the qualitative trend is clear. No significant angular dependence was observed except at distances so short that the rods interact directly. This observation, too, argues for the minor importance of many body effects.

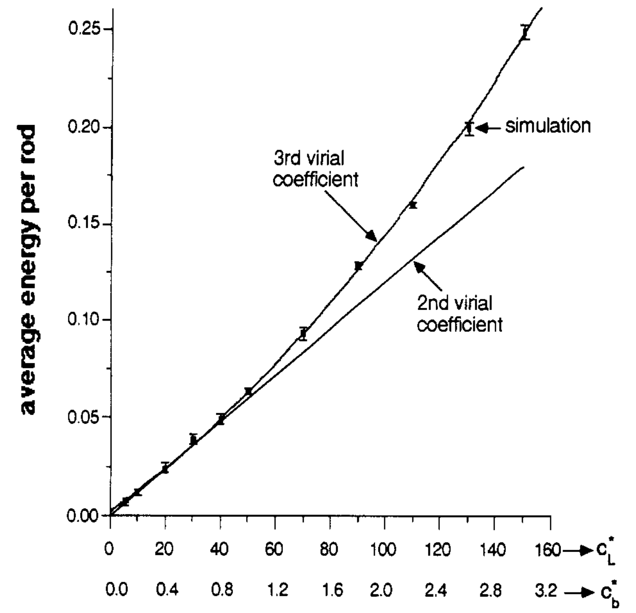

Figure 3. Comparison of the average potential energy per rod as determined from the simulation with the predictions of a second and a third virial coefficient approximation of the same quantity.

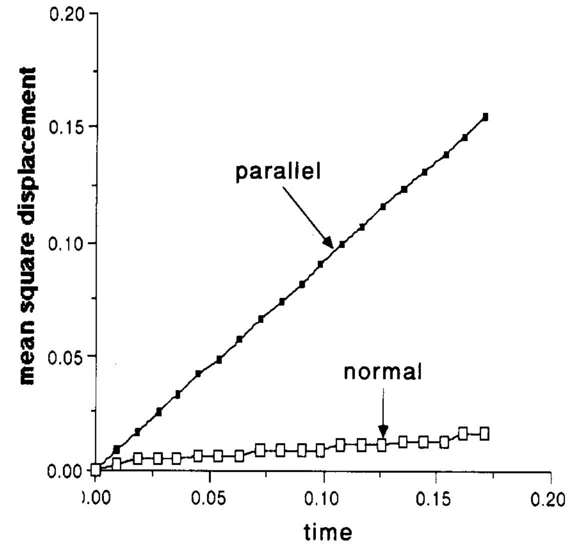

Figure 4. Mean square displacement parallel and normal to the rod axis vs time at $c^*_L = 110$.

ii. Translational Motion. In Figure 4 the mean square displacements parallel and normal to the rod axis are plotted vs time at the high concentration $c^*_L = 110$. The corresponding mean square displacements parallel and normal to the rod axis (Figure 4) and the diffusivities (Figure 5) are calculated by projecting the infinitesimal displacement of the rod on the unit vectors parallel and normal to the *current* rod orientation and not on those parallel and normal to the initial ($t = 0$) rod orientation. This distinction is important because the translational diffusivity parallel to the rod axis plotted in Figure 5 is a very different quantity from that studied in ref 8. In particular, the parallel translational diffusivity in Figure 5 will be independent of the amount of rod rotation and it cannot be expected to increase at high concentra-

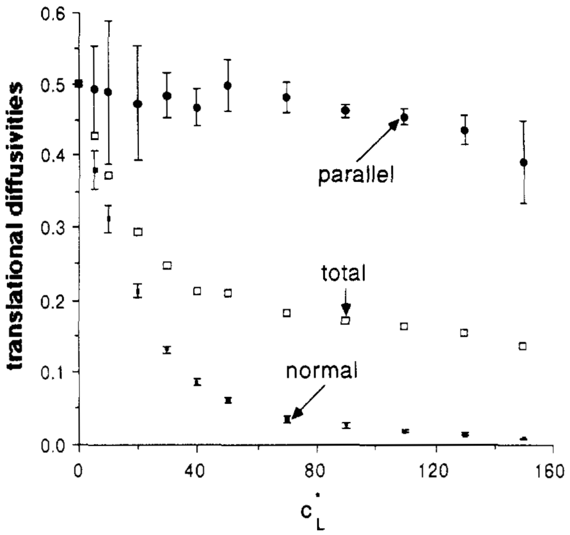

Figure 5. Translational diffusivities parallel and normal to the rod axis and the center of mass diffusivity vs. concentration.

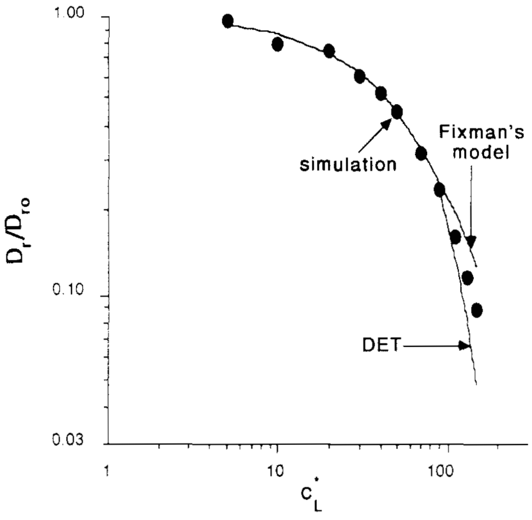

Figure 6. Comparison of the rotational diffusivities determined from the simulation with the predictions of Fixman's model[16] and of the DET for finite diameter rods[4,5] ($b/L = 0.02$).

tions as a result of the very slow decorrelation of the initial rod orientation.

As seen from Figure 4, all but the slightest normal displacements are severely hindered at this concentration. For times longer than 0.06 in our units (see Table I) the normal motion is diffusive but the slope (diffusivity) is 30 times smaller than the diffusivity parallel to the rod axis. Similar observations can be made from Figure 5, where the diffusivities normal and parallel to the rod axis, as well as the center of mass diffusivity are plotted vs concentration. For concentrations higher than $c^*_L = 90$ the mobility of the rod normal to its axis is at least 20 times lower than its mobility parallel to its axis. On the other hand, the diffusivity parallel to the rod axis remains within 80% of its dilute solution value. This suggests that the cage linear dimension is considerably larger than the rod diameter even at the highest concentration simulated.

The freezing of the normal mobility at sufficiently high concentrations is the most important finding of our simulation. It demonstrates that the short-range, cylindrically symmetric intermolecular forces, which realize the one-dimensional connectivity and uncrossability features of a slender rod, have highly selective effects on the various modes of motion. It offers a direct microscopic justification of the major assumption of the DET (and any "cage" theory for that matter), namely, that rods are indeed confined in cages.

Some of the earlier simulations[9,10] demonstrated the same point; however, the microscopic dynamics in these earlier studies differed in essential ways from those of actual rodlike polymer solutions (absence of solvent in ref 9 or an extremely large time step in ref 10). These differences were nontrivial and always in the direction of making the escape from partially open cages more difficult, casting doubt in this way on the generality of the result.[7,9,18] In view of that, an unambiguous proof of the formation of cages that are small enough to hinder strongly the motion normal to the rod axis and remain closed for extensive time intervals between cage breakups acquires special importance when it is found for a system with more realistic microscopic dynamics like ours.

iii. Rotational Motion. The proof of the existence of closed cages does not guarantee automatically the validity of the DET or its improved versions.[4-7] The common feature of these theories is that they estimate the cage size and its concentration dependence based on the equilibrium rod distribution. Furthermore, they all assume implicitly that the lifetime of the cages is a concentration independent quantity. It is not at all obvious why this should be the case.

On the other hand, Fixman's theory[18] predicts a different concentration dependence of the cage sizes. This is a result of the short time relaxation movements that distort the equilibrium cages and alter not only their sizes but also their concentration dependence, as well.

The rotational diffusivities at the various concentrations simulated (including those in ref 19) are plotted in Figure 6. Since the rodlike molecules in our simulation have a finite diameter, the infinitely thin needle prediction of the DET may not be applicable. In order to determine whether our results for the rotational diffusivity are in agreement with the DET for $c^*_L = 90$–150, we must assess the importance of finite diameter effects in the context of this theory. Before doing this, however, we note that finite molecular diameter effects cannot be extremely strong in our range of concentrations for rods with axial ratio of 50, like those in our simulation. Indeed, if that were the case, one would expect a significant reduction of the component of the translational diffusivity parallel to the rod axis from its dilute solution value ($D_0 = 0.5$). As we see from Figure 5, the parallel translational diffusivity is only 20% lower than its dilute solution value at the highest concentration simulated ($c^*_L = 150$).

Nevertheless, there is no quantitative theory predicting the effect of finite rod diameter on the parallel component of the translational diffusivity. Consequently, the very weak dependence of this quantity on concentration (in our range of parameters) does not necessarily prove that the finite molecular diameter has negligible influence on other quantities, like the rotational diffusivity, in the DET context.

According to DET,[4,5] the major effect of the finite rod diameter on the rotational diffusivity originates from the effective decrease of the angular jump after a cage breakup by a factor of b/a, where b is the rod width and a is the cage linear dimension. Therefore, the DET prediction for finite diameter rods is

$$D_r = A(1 - 2b/a)^2(c^*_L)^{-2} \tag{3.1}$$

where A is a numerical constant not determined by DET.

A quantitative estimate of the DET cage size was developed by Keep and Pecora.[6] Their analysis takes into account the effective increase of the cage size because of the small translational freedom of the rod center of mass normal to the rod axis. Keep and Pecora's predictions for the cage size is[6]

$$a = 13.0/[(c^*_L)^2 - 17.7c^*_L]^{1/2} \tag{3.2}$$

which yields $a = 0.092$ at $c^*_L = 150$. It is worth noting that Keep and Pecora's analysis is an improved DET analysis because it accepts the basic DET premise, namely, the existence of completely closed cages that survive over extensive time intervals between cage breakups and the validity of an equilibrium calculation of the cage sizes. Equation 3.2 is the only available quantitative estimate of the DET cage size and the one we shall use in eq 3.1.

The constant A in eq 3.1 can be determined by forcing eq 3.1 to reproduce our simulation result at the lowest concentration above which DET might be valid. From Figure 6 we see that this concentration is $c^*_L = 90$ (between $c^*_L = 70$ and $c^*_L = 90$ the apparent power law for the rotational diffusivity is $(c^*_L)^{-1.2}$ and DET is obviously inappropriate). The constant A determined in this way is

$$A = 6738 \tag{3.3}$$

The DET prediction for rods with $b = L/50$ shown in Figure 6 is calculated from eq 3.1–3.3. The prediction of Fixman's model[18] is also shown in the same figure. The simulation results fall between the two theoretical predictions.

iv. Discussion. The microscopic dynamics and the molecular model employed in our simulations are much more realistic than those used in some of the past simulations;[8,10] still, they are by no means identical with those of real rodlike polymer solutions. We think however, that the task of a molecular simulation is not to reproduce reality but rather to include enough physics in the rules governing the behavior of the simulation system so that the resulting statistical regularities (macroscopic laws) are identical with those of the physical prototype. Some of the physical assumptions, like the Brownian description of the rod dynamics, can be justified rigorously.[34,35] Others, like the ad hoc functional form of the intermolecular potential and the neglect of hydrodynamic interactions, are less defensible. This makes imperative the need to compare our simulation results with relevant experimental data.

Although the rods in our simulations have a finite diameter its effect does not appear to be very strong in our range of concentrations (Figure 6). Of course, experimental results on real rodlike polymers are also affected by the existence of a finite molecular width. In most experimental studies however, this effect was found to be weak, and, for simplicity, the experimental results have been analyzed quantitatively in terms of the original DET for infinitely thin needles.

According to DET for infinitely thin needles

$$D_r/D_{r0} = B(cL^3)^{-2} \tag{3.4}$$

for rods whose diameter is much smaller than the cage size. B was expected to be of order 1–10 in the original DET, but numerous experimental results, simulations, and theoretical analyses suggested that $B \gg 1$. From our simulation we get $B = 1945$. This is in good agreement with the experimental values of ref 12 (1070–1768). Recently, Keep and Pecora[17] presented new dynamic light scattering results. Although no firm conclusions for the concentration dependence of the rotational diffusivity were drawn in this work, the rotational diffusivity was found to decrease by a factor of 10–20 from its dilute solution value over a range of concentrations similar to ours for the more rigid polymers studied. As we can see from Figure 6, this again agrees qualitatively with our simulation results.

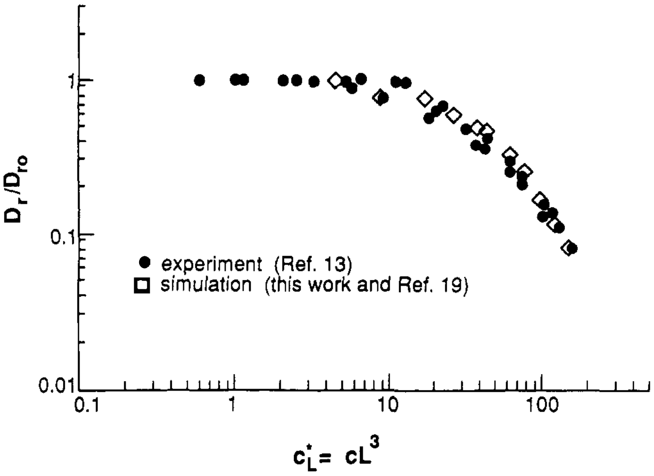

Figure 7. Comparison of the rotational diffusivities determined from the simulation with the results of dynamic electric birefringence experiments on PBLG in *m*-cresol.[13]

We think that the DEB measurements of ref 13 are the most directly comparable to our data. The axial ratio of the rodlike particles in these experiments (29, 34, 44, 67) spans ours (50). Furthermore, in these experiments no high-frequency relaxation that can be attributed to molecular flexibility was observed. The fact that the data for all four samples fall on the same curve further suggests the absence of strong flexibility effects. In any case, the polymer molecules in these samples were short enough (100, 66, 51, and 44 nm) compared with the persistence length of PBLG in *m*-cresol (100 nm[36,37]) to be quite rigid. Needless to say, the molecules in these experiments had finite flexibility that could have been significant under certain conditions (e.g., high-frequency viscoelastic experiments). Here we merely rely on the authors' arguments about the minor effect of flexibility on the particular set of data they presented. The comparison with the data of reference 13 is presented in Figure 7. The agreement is very close throughout the whole concentration range spanned by the experimental data and our simulation results ($1 < c^*_L < 150$).

Flexibility effects have been invoked frequently in order to explain the discrepancies between simulation and experiment. There is no doubt that strong flexibility effects were actually present in some experiments.[6,16,17] Nevertheless, the agreement between our simulation results and the experimental data of ref 13 suggests a complementary reason for the observed discrepancies.[10] Some of the earlier simulation results[8–10] underestimated the rotational diffusivities because they did not employ sufficiently realistic microscopic dynamics. The essence of the problem is illustrated schematically in Figure 8. In the absence of solvent (Figure 8a), the confined rod rotates freely until it reaches the boundaries of its cage. Such a mode of motion is not very efficient in taking advantage of small cage openings. In particular, the confined rod experiences repeated failures in its attempts to escape the cage because it samples more and more frequently similar pathways not allowing an escape. This type of repeated failure produces a strong temporal correlation of successive rod–rod collisions which manifests itself by the presence of a negative (backscattering) minimum in the angular momentum autocorrelation function after seven to eight rod–rod collisions.[9] The extremely large time step and the reflection rules employed in ref 10 resulted in a similarly inefficient behavior, despite the presence of solvent.

In contrast to this, our simulation dynamics will result in the behavior sketched in Figure 8b. The confined rod does not rotate freely between two successive attempts to escape from the cage, but it undergoes rotational Brownian motion. Such motions are obviously much more efficient in discovering cage openings. Brownian dynamics offers a more detailed account of the random, solvent-induced displacements, which are further enhanced by the repulsive interactions among rods that guide the escape from partially open cages and expand the cage openings.

As we discussed earlier, for sufficiently high concentrations ($c^*_L > 90$) the rotational diffusivities determined from our simulation fall between the DET predictions and those of Fixman's model (Figure 6). The novel feature of this model is the introduction of a short time relaxation mechanism that consists of small rotations of the rods forming the cage every time a confined rod approaches the boundaries of its cage. Obviously these short time rotations must be comparable to the average cage size, since the confining rods themselves experience topological constraints ("cages") imposed by their own neighbors. Such a restriction, although it is mentioned, it is not actually enforced in Fixman's model.[18] The size of the short time rotations is determined by a thermodynamic argument that maximizes the efficiency of the bimodal relaxation (short time rotations plus translational diffusion). Such an optimal behavior might not be possible at high concentrations, since it might require short time rotations of the confining rods so large than they can be accomplished only if the confining rods themselves violate their own topological constraints (escape from their own cages).

Some more confidence in the above comments is provided by the fact that the equilibrium cage size decreases much faster with concentration (roughly like the inverse first power) than the size of the short time rotations required by Fixman's model. Therefore, it is plausible that, after a critical concentration, the mechanism suggested by Fixman cannot be realized because it implies unphysically large rotations of the confining rods, rotations that can be accomplished only if the confined rods escape from their own cages.

The effectiveness of the short time rotations introduced by Fixman in expanding the relevant cage size explains why the trend to a more DET-like behavior (that is, stronger concentration dependence) occurs at the concentration $c^*_L = 90$, which is significantly higher than the concentration of complete caging as determined by the statistical analysis of Keep and Pecora[6] ($c^*_L = 50$).

4. Conclusions

We performed Brownian dynamics simulations of concentrated, isotropic solutions of rodlike polymers (70–150 rods/L^3). The rodlike particles in our simulation had finite width and an axial ratio of 50, which is typical of actual rodlike polymers.

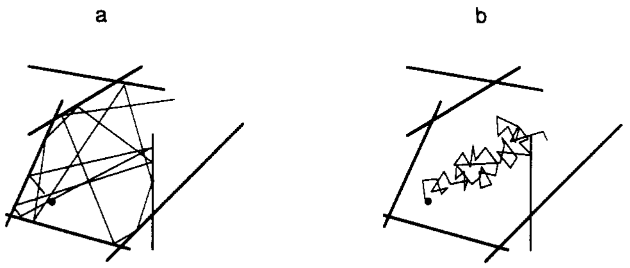

Figure 8. (a) The microscopic dynamics of a caged needle in a gas of infinitely thin needles without solvent.[8,9] (b) The microscopic dynamics of a caged rod in a solution of rodlike particles (this work and ref 19).

Our simulations provided three important pieces of information: Many-body effects contribute to the static properties much less than direct pair interactions up to the highest concentration we simulated (150 rods/L^3); therefore the local structure (pair distribution function) is mostly determined by independent binary interactions. The solvent–polymer impacts in between rod–rod collisions kill most of the temporal correlation of successive rod–rod collisions reducing in this way a highly correlated rod–rod collision sequence to a sequence of almost uncorrelated binary collisions. The mobilities of the rods normal to their axes practically freeze at sufficiently high concentrations. This fact is a direct proof of complete caging (Figures 4 and 5).

The first two points provide justification for a model developed by Fixman[16] in order to explain his simulation results. The predictions of Fixman's model agreed very well with our simulation results up to the concentration of 70 rods/L^3 [17] (Figure 6). At higher concentrations this model slightly but systematically overestimates the rotational diffusivities with the discrepancy growing as the concentration increases.

A possible explanation for the slight but systematic discrepancies between Fixman's model and our simulation results for concentrations higher than 70 rods/L^3 is that the size of the short time rotations, introduced by this model, exceeds the equilibrium cage size. In the concentration range from 70 to 90 rods/L^3, the nature of the concentration dependence of the cage sizes undergoes a transition. Probably, the actual short time rotations get smaller and smaller than those predicted by Fixman's model and, as a result of this, accomplish less and less in transforming the equilibrium cages into dynamically distorted cages of the sort envisioned by Fixman.

For concentrations higher than 90 rods/L^3 the rotational diffusivities determined from our simulations fall between those predicted by Fixman's model and those predicted by the DET for rods with finite diameter. It is possible that the cages have now hybrid features, intermediate between those of fully dynamically distorted cages (like those envisioned by Fixman) and equilibrium cages (like those introduced by DET).

Acknowledgment. This research was supported in part by grants from the National Science Foundation and the University of Minnesota Graduate School through a Doctoral Dissertation Fellowship awarded to I. Bitsanis. Our work could not have been undertaken and completeed without two generous allocations of computer time from the University of Minnesota Supercomputer Institute. The paper was significantly improved by a thorough and incisive review by two reviewers.

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Dynamic Behavior of Θ Solutions of Polystyrene Investigated by Dynamic Light Scattering

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Revised Manuscript Received August 9, 1989

ABSTRACT: Relaxation time distributions from dynamic light scattering (DLS) (obtained from the correlation curves using a Laplace inversion routine REPES), typically covering about 8 decades in relaxation time, have been determined for solutions of polystyrene in cyclohexane at 35 °C (Θ conditions) over a wide span of polymer concentrations from very dilute to far into the semidilute regime. The relaxation time distributions increase in complexity with increasing polymer concentration. The results from the semidilute solutions are compared to a theory developed by Brochard and de Gennes and are shown to agree only partially. The results indicate that DLS is a possible tool for the investigation of viscoelastic properties of semidilute polymer solutions.

Introduction

The scaling description of semidilute polymer solutions[1-3] has been a major inspiration of new ideas in the physics of static and dynamic properties of polymers in solution. It has led to predictions whose experimental verification required precisely the space and time resolution offered by light scattering and neutron scattering. A broad review that includes the application of dynamic light scattering (DLS) to this problem area is provided by ref 4.

A central prediction of the scaling theory for semidilute solutions in thermodynamically good solvents is that a single characteristic length exists in such systems and consequently only one dynamic process should be observed, characterized by a cooperative diffusion coefficient (D). Experimentally, it has been found, however, that although cooperative diffusion dominates in semidilute solutions in good solvents, other processes participate and give rise to deviations from a single exponential decay of the autocorrelation function of the scattered light. This effect, typified by low-frequency modes in the decay spectrum, becomes very pronounced with a decrease in solvent quality toward Θ conditions.[5-15]

Brochard and de Gennes[16,17] have developed scaling expressions for Θ systems. They propose two limiting regimes: at small scattering vectors (q) (such that $Dq^2 < T_r^{-1}$, where T_r is the characteristic disentanglement time for the chains or the terminal time from viscoelastic measurements) the restoring force for the concentration fluctuations, originating from the osmotic compressibility, leads to a cooperative diffusion coefficient that is linearly proportional to the polymer concentration. At scattering vectors (corresponding to $Dq^2 > T_r^{-1}$), they predict that the correlation function is bimodal. The fast mode characterizes the cooperative diffusion and the other mode, which is independent of the scattering vector, char-

0024-9297/90/2223-1165$02.50/0