Diffusion Coefficient Increases with Density in Hard Ellipsoid Liquid Crystals

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Molecular-dynamics simulations of highly nonspherical rodlike and platelike molecules reveal that one of the two diffusion coefficients in the nematic-liquid-crystal phase increases with density, reaches a maximum, and decreases, while the other coefficient decreases monotonically in the usual way. This effect seems to be associated with the density variation of the nematic order parameter near the phase transition. A kinetic theory based on isolated binary collisions significantly underestimates the diffusion coefficients, but partially accounts for the enhancement effect.

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The representation of molecular fluids by systems of hard ellipsoids is a natural extension of the venerable hard-sphere model which has been so useful in understanding the properties of atomic liquids.[1,2] Recent progress in the kinetic theory of hard convex bodies[3] and in molecular-dynamics simulation of such systems[4,5] has stimulated interest in the dynamical properties of molecular liquids and liquid crystals modeled in this way. Our interest in this paper is in fluids composed of hard ellipsoids of revolution, each having a symmetry axis of length $2a$ and two equal perpendicular axes of length $2b$. Efficient prescriptions exist[6,7] to determine whether or not two molecules overlap in a simulation, and the overall form of the phase diagram has already been determined by Monte Carlo techniques.[8] When the elongation $e=a/b$ is sufficiently different from unity, these systems form a nematic-liquid-crystal phase between the isotropic liquid and the crystal. Previous molecular-dynamics studies have shown the onset of the slowing down of collective reorientation on approaching the isotropic-nematic (I-N) transition,[9] and have tested the accuracy of kinetic theory for the translational and rotational diffusion coefficients in the isotropic phase.[10] In addition, the Frank elastic constants in the nematic phase have been determined.[11] These studies were confined to moderately nonspherical shapes, $e=2,3,\frac{1}{3}$. Ellipsoids with $e=2$ do not form a liquid crystal, and the nematic phases for $e=3,\frac{1}{3}$ are thermodynamically stable only over a narrow range of densities ρ, roughly between 70% and 80% of the close-packed density ρ_{cp}.

Here we report results for much more anisometric ellipsoids of revolution, with $e=10,5,0.2,0.1$. For these rodlike and platelike particles, the I-N transition occurs at a much lower density, as expected from the approximate theory of Onsager[12] and in accordance with the phase diagram determined to date,[8] so there is a much wider nematic range. In this Letter we focus on the density dependence of the translational diffusion coefficients within the nematic phase. Full technical details of our molecular-dynamics simulations have been given elsewhere,[5] so we present only a brief summary here. We use collision-by-collision dynamics with free flight between collisions; each forthcoming collision is detected by a method similar to that of Rebertus and Sando.[4] The collision dynamics are completely determined by the conditions that the ellipsoids are hard, smooth bodies, and that energy, linear momentum, and angular momentum are conserved. The molecules are taken to have unit mass m, distributed uniformly throughout the ellipsoid, and the molecular moment of inertia is calculated accordingly. However, the moment of inertia about the symmetry axis is set to zero, and the ellipsoids are treated dynamically as linear rotors with the angular velocity perpendicular to the axis at all times. The temperature

TABLE I. Nematic order parameters S, diffusion coefficients parallel ($D_{\parallel}$) and perpendicular ($D_{\perp}$) to the director, and the corresponding kinetic theory predictions ($D_{\parallel}^{E}$,$D_{\perp}^{E}$) for hard ellipsoids of various elongations e. In the isotropic phase parallel and perpendicular components are identical.

e	ρ/ρ_{cp}	S	$D_{\parallel}$	$D_{\perp}$	$D_{\parallel}^{E}$	$D_{\perp}^{E}$
10	0.20	0.0	0.452	0.452	0.173	0.173
10	0.25	0.06	0.338	0.338	0.120	0.120
10	0.30	0.597	0.921	0.154	0.229	0.084
10	0.35	0.803	1.564	0.110	0.488	0.071
10	0.50	0.934	1.531	0.052	0.782	0.040
10	0.60	0.948	1.380	0.029	0.870	0.032
5	0.40	0.0	0.205	0.205	0.097	0.097
5	0.45	0.0	0.159	0.159	0.074	0.074
5	0.50	0.28	0.196	0.107	0.075	0.052
5	0.55	0.730	0.380	0.056	0.192	0.042
5	0.60	0.822	0.337	0.040	0.206	0.033
5	0.65	0.868	0.258	0.027	0.183	0.026
0.2	0.40	0.16	0.171	0.171	0.104	0.104
0.2	0.45	0.33	0.105	0.180	0.059	0.114
0.2	0.50	0.700	0.042	0.200	0.037	0.149
0.2	0.55	0.775	0.030	0.176	0.029	0.155
0.2	0.60	0.849	0.019	0.153	0.021	0.148
0.2	0.65	0.884	0.014	0.108	0.017	0.122
0.1	0.20	0.06	0.337	0.337	0.223	0.223
0.1	0.30	0.740	0.077	0.590	0.063	0.393
0.1	0.35	0.833	0.048	0.580	0.048	0.429
0.1	0.50	0.939	0.014	0.361	0.022	0.407
0.1	0.60	0.961	0.007	0.236	0.013	0.296

T is chosen such that $k_BT=1$, k_B being Boltzmann's constant: This establishes a convenient time scale for the simulation.

In these simulations we employed truncated octahedral periodic boundary conditions. For $e=0.2,5$ we used a system size of $N=216$ molecules, while for $e=0.1,10$ we used $N=500$. We did not systematically investigate the dependence of our results on system size: Our primary concern is with the *density* variation of the diffusion coefficient for fixed N. Typical production run lengths were $(0.5\text{-}1.6)\times 10^6$ collisions, depending on density: Thus, the results were averaged over times $t_{\text{run}}\sim(2000\text{-}15000)t_c$, where t_c is the mean time between collisions per molecule. These run times are usually considered ample for the determination of single-particle properties, although we must bear in mind the slow fluctuations inherent in the nematic phase. We examined densities from just below the transition density ρ_{IN} (as indicated by the nematic order parameter) to $0.65\rho_{\text{cp}}$. For the weakly first-order I-N transition there will be a narrow coexistence region[8] around ρ_{IN}, but we have found no evidence of two-phase coexistence at the state points studied here. We have not yet located the solid-fluid transition for these systems, but the upper density limit $\rho=0.65\rho_{\text{cp}}$ is below the freezing density for all ellipsoid systems studied to date. The director and the nematic order parameter S were determined in a standard way.[13] Simulation averages of S appear in Table I. These values are plotted in Fig. 1, together with results of additional runs (not used for the diffusion coefficient calculation) close to the N-I transition.

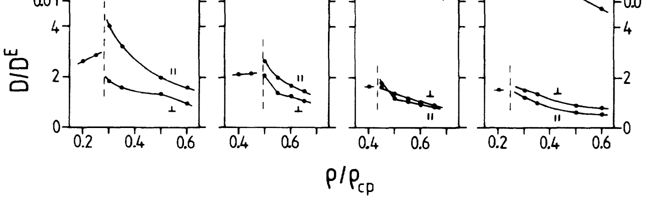

FIG. 1. Density variation, for each elongation e, of the nematic order parameter S; diffusion coefficients D parallel (∥) and perpendicular (⊥) to the director, on a logarithmic scale; and the ratios D/D^E, where D^E is the kinetic theory prediction. The lines are to guide the eye. The vertical broken line indicates the transition density ρ_{IN}.

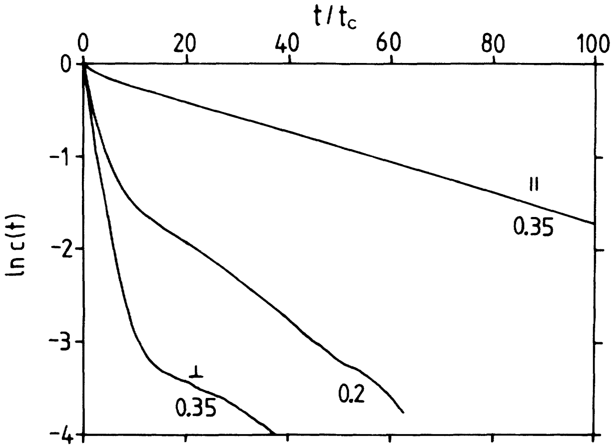

FIG. 2. Velocity autocorrelation functions $c(t)$, on a logarithmic scale, for prolate ellipsoids with $e=10$. Time is given in units of t_c, the mean time between collisions. We plot $c(t)$ for the isotropic phase at density $\rho/\rho_{\text{cp}}=0.2$, and for the nematic phase at $\rho/\rho_{\text{cp}}=0.35$ showing separate components parallel (∥) and perpendicular (⊥) to the director.

We calculated the center-of-mass velocity autocorrelation functions

$$c_\alpha(t)=\langle v_\alpha(0)v_\alpha(t)\rangle=\langle v_\alpha(t_0)v_\alpha(t_0+t)\rangle\,,$$

where α labels the Cartesian component, resolved in a system of axes based on the liquid-crystal director (the average preferred molecular orientation vector) defined at each time origin t_0. The director was seen to vary slightly during a simulation run, but remained essentially constant over the decay time of molecular velocities. Note that the chosen units of temperature and mass imply that $c_\alpha(0)=1$; i.e., the correlation functions are normalized.

In Fig. 2 we show, as illustrations, log-linear plots of the velocity autocorrelation functions for $e=10$ below and above the I-N transition. It is intended to analyze these time-dependent results in more detail in a later publication: Only a few important points will be made here. The velocity correlations extend to very long times, especially for $e=10$, even in the isotropic phase. We tentatively attribute this to the coupling of the velocity with slow molecular reorientation, *not* to coupling with the hydrodynamic vortex mode which gives rise to algebraic $t^{-3/2}$ long-time tails.[1] The decay seems to be exponential, not algebraic, at long times: We have not found any evidence for algebraic decay, which may be present but masked by other effects. Above the phase transition, in all cases, there is a clear distinction between the behavior of the velocity component $v_\parallel$ along the director and that of either of the two equivalent perpendicular components $v_\perp$. For the rodlike, prolate ellipsoids, after a very short initial decay, $c_\parallel(t)$ falls extremely slowly, over many tens of collision times. The function $c_\perp(t)$, in contrast, decays rapidly to a low value. For moderately low-density systems a small long-time decay is seen in this component. For the platelike, oblate ellipsoids similar observations apply, but with the behavior of $c_\perp(t)$ and $c_\parallel(t)$ interchanged. At the higher densities for oblate ellipsoids a negative "rebound" effect is observed in $c_\parallel(t)$.

Diffusion coefficients are related to the velocity autocorrelation function as follows:

$$D_\parallel = \int_0^\infty dt\, c_\parallel(t), \quad D_\perp = \int_0^\infty dt\, c_\perp(t) .$$

These integrals were calculated numerically from the measured correlation functions out to some maximum time $t_{\max}$; in all cases we took $t_{\max} > 50t_c$. As a check, we explicitly accumulated these integrals during the simulation via the functions $\langle v_a(0)[r_a(t) - r_a(0)]\rangle$, $0 \le t \le t_{\max}$, where $r_a(t)$ is a center-of-mass coordinate. We found good agreement with the results obtained from the numerical integration. In many cases the velocity autocorrelation function had not decayed to zero at $t = t_{\max}$, but in all cases an accurate exponential decay time τ_∞ could be determined from log-linear plots. Accordingly, a long-time correction was added to the integral on the assumption that, for $t > t_{\max}$, $c_a(t) = c_a(t_{\max})\exp[-(t - t_{\max})/\tau_\infty]$. The resulting values of $D_\parallel$ and $D_\perp$ appear in Table I. An Enskog-like kinetic theory, based on independent binary collisions, would predict exponential decay of the velocity autocorrelation functions at *all* times, $c_a^E(t) = \exp(-t/\tau_a^E)$, determined by the initial gradient.[14] The corresponding predictions for the diffusion coefficients, $D_\parallel^E$ and $D_\perp^E$, also appear in Table I.

We summarize our results in Fig. 1. Consider first the prolate cases $e = 5,10$. Understandably, in the aligned phase, the molecules find it easier to diffuse along the director, and indeed $D_\parallel$ just above the transition is larger than D in the isotropic phase just below. This result has been seen before, in studies[15] of the Berne-Pechukas model,[16] and in our own simulations[5] of hard ellipsoids with $e = 3$. However, as density is further increased, over almost the whole nematic range, the expected decrease in $D_\parallel$ due to the increased collision rate is offset by another effect. Close to the I-N transition $D_\parallel$ actually increases with density. This seems to be associated with the rise in the nematic order parameter: Presumably this reduces the contribution of decorrelating collisions parallel to the director. This enhancement of $D_\parallel$ seems not to have been observed before. At sufficiently high density $D_\parallel$ starts to decrease, and eventually negative rebound contributions can be seen in the associated correlation function, just as in the atomic fluid.

Turning to the oblate shapes $e = 0.1, 0.2$ (see Fig. 1), we see that $D_\perp$ behaves in a similar, if less dramatic, fashion. The platelike molecules slip more easily through the liquid crystal perpendicular to the director, and the increasing orientational ordering compensates for the tendency of the rising collision rate to reduce the diffusion coefficient.

We are unaware of any explicit theoretical prediction of these effects. The increase of $D_\parallel$ with density of rodlike molecules is reminiscent of the divergence of the longitudinal diffusion coefficient predicted by Doi and Edwards[17,18] and tested by simulation of the *isotropic* hard needle fluid.[19,20] The Doi-Edwards theory applies in the semidilute regime, and their idea of "tube dilation" associated with orientational ordering may be valid here. However, our systems are far from the appropriate scaling regime, and we see no simple scaling relation between D and ρ. A different theory, due to Doi,[18,21] described the rotational dynamics of rodlike molecules in dense isotropic and nematic phases, but does not address translational motion. It is well known that shear viscosities of rodlike polymers decrease with increasing concentration (and order parameter) in the nematic phase,[18] but this is associated with theories of rotational diffusion. In our simulations, in the nematic phase, reorientation is almost immeasurably slow.

Except at the highest densities, the Enskog predictions $D_\parallel^E$ and $D_\perp^E$ are gross underestimates. Nonetheless, $D_\parallel^E$ for the prolate molecules and $D_\perp^E$ for the oblate ones do increase with density above ρ_{IN}, rather more rapidly in fact than $D_\parallel$ and $D_\perp$. The ratio D/D^E is shown in Fig. 1: It is typically very large around the phase transition and *decreases* thereafter with increasing density. Thus, the observed dramatic density variation of the diffusion coefficients is a combination of two conflicting influences: the short-time isolated binary collision effects, dictating $D_\parallel^E$ and $D_\perp^E$, and the long-time correlations, which determine the ratios $D_\parallel/D_\parallel^E$ and $D_\perp/D_\perp^E$. The first of these should be easily understood, but the origins of the second are still unclear.

We should note that we have already reported[10] values of D/D^E as high as 1.57 for ellipsoids with $e = 2, 3, \frac{1}{3}$ in the *isotropic* phase. The results presented here for the isotropic phase just below the phase transition confirm and extend our previous observations: The enhancement is more dramatic (with D/D^E as high as 2.8 here) as the nonsphericity increases. Furthermore, for the prolate molecules at least, the ratio $D_\parallel/D_\parallel^E$ becomes even higher on entry into the nematic phase. This suggests that the enhancement D/D^E in the isotropic phase may be associated with translation of the prolate molecule along its symmetry axis, and the coupling of this motion with reorientation. It is worth repeating that the mechanism at work here seems to be different from (and presumably supplementary to) that giving rise to long-time tails and values of $D/D^E > 1$ in atomic liquids at medium and low densities.

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