Observation of Dynamical Precursors of the Isotropic-Nematic Transition by Computer Simulation

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We present the results of the first molecular-dynamics simulations of a molecular liquid, namely a system of prolate hard ellipsoids of revolution, near the isotropic-nematic liquid-crystal phase transition. Collective rotational motion in the isotropic phase slows down on approach to the transition. It is found that the most important contribution to the rotational slowing down is due to static correlations as measured by the second-rank Kirkwood factor g_2. The results suggest that the dynamic factor j_2 which occurs in the hydrodynamical theory of collective reorientation is small and negative.

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The study of the static and dynamic properties of liquid-crystal–forming fluids is an active and rewarding area of research. One particularly interesting aspect of this field is the study of pretransitional phenomena associated with phase transitions involving liquid-crystalline phases. On a microscopic level, the factors that determine the local structure and dynamics of a fluid in the vicinity of a liquid-crystalline phase are poorly understood. Despite this, very few computer simulations of even the simplest liquid-crystal–forming fluids, viz. nematogens, have been carried out. If we restrict our attention to systems with full translational and orientational degrees of freedom,[1] only two systems with continuous potentials seem to have been investigated.[2,3] In neither case was the thermodynamic stability of the nematic phase demonstrated by free-energy calculation. Recently, however,[4,5] the phase diagram of the hard-ellipsoid system has been investigated and shown to include nematic regions. The associated phase transitions were located by the computing of free energies. In view of the great simplicity of this model, and the interest in the kinetic theory and general dynamical properties of hard convex bodies,[6,7] it seems most suitable as a "benchmark" system for molecular liquids in both isotropic and nematic phases. We have commenced a program of molecular-dynamics simulations of this system. In this paper, we present the first results of this investigation: a study of molecular reorientation in the isotropic phase, on approach to the isotropic-nematic phase transition.

Our system consists of 144 hard ellipsoids of revolution, each with a symmetry axis of length $2a$ and two equal perpendicular axes of length $2b$. The ellipsoids are taken to have unit mass, distributed uniformly throughout the body, and moments of inertia are calculated accordingly. However, the moment of inertia about the symmetry axis is set equal to zero, and the ellipsoids are treated dynamically as linear rotors with no angular velocity about this axis. This choice is consistent with treating hard-ellipsoid collisions as smooth, in which case no change in this component of angular velocity can occur. It also guarantees that the moment of inertia about the perpendicular axes takes physically reasonable values over the whole range of ellipsoid anisometry, from the hard-line to the hard-plate limit. Between collisions, free flight occurs with constant linear and angular velocities. Collisions occur at the moment of contact of two ellipsoid surfaces: The collision dynamics are completely dictated by the hardness and smoothness criteria, and by conservation of total linear and angular momentum and energy. The temperature is fixed at $k_BT=1$ where k_B is Boltzmann's constant; this establishes a convenient time scale for the simulation.

Conventional microcanonical-ensemble molecular dynamics is used throughout. The simulation algorithm will be described in detail in a later publication. Suffice to say here that we adopted the basic approach of Rebertus and Sando,[8] which involves advancement of the configuration through a time step, detection of ellipsoid overlaps, and retrospective implementation of collision dynamics. To improve efficiency, we used a neighbor list.[9] At different stages in the program we found it convenient to use different (but exactly equivalent) formulations of the ellipsoid-overlap criterion.[10,11] The program was coded in such a way as to vectorize easily on a Cyber-205, and generated typically 10^6 collisions per hour of central processing unit time, the exact figure being slightly dependent on density.

Here we report the results of our simulations for prolate ellipsoids of elongation $a/b=2$ and 3, for a sequence of runs in the isotropic fluid phase with increasing density. At low density, $\rho \approx 0.5\rho_{cp}$ where $\rho_{cp}=\sqrt{2}/8ab^2$ is the close-packed density, about 10^5 collisions were allotted for equilibration following a change of state point, and a similar number were generated in the production runs.

At higher density, particularly close to the nematic phase boundary, these numbers were increased to $\sim 10^6$ collisions. The equations of state agreed well with those obtained from previous constant-volume and constant-pressure Monte Carlo simulations[5] using similar numbers of molecules. Details of collision rates, collision distributions, and compressibilities will be published elsewhere, along with an analysis of linear and angular velocity time-correlation functions and other properties. Here we wish to concentrate on the first- and second-rank orientational correlation functions, and specifically on the comparison between single-particle and collective correlation times, on approach to the isotropic phase boundary. These quantities are of special interest in the theory of spectroscopy and light scattering from molecular liquids.[12]

The normalized single-particle rank-L orientational correlation function $c_L^s(t)$ may be defined as

$$c_L^s(t) = \langle P_L(\mathbf{e}_i(0)\cdot\mathbf{e}_i(t))\rangle, \qquad (1)$$

where $\mathbf{e}_i(t)$ is a unit vector pointing along the axis of molecule i at time t and P_L is a Legendre polynomial. The analogous collective correlation function $c_L^c(t)$ is

$$c_L^c(t) = \frac{\sum_j\langle P_L(\mathbf{e}_i(0)\cdot\mathbf{e}_j(t))\rangle}{\sum_j\langle P_L(\mathbf{e}_i(0)\cdot\mathbf{e}_j(0))\rangle}. \qquad (2)$$

Both these quantities may be averaged over equivalent molecules i. The single-particle orientational variables entering into Eq. (1) are calculated in such a way as to maintain orthogonality, at all times, with the collective variables appearing in Eq. (2).

These functions of time are shown for various reduced densities ρ/ρ_{cp} in Fig. 1. Single-particle functions show exponential decay at long times, with limiting characteristic decay times τ_L^s obeying the relation $\tau_1^s \approx 3\tau_2^s$ as expected for rotational diffusion. Decay times increase steadily as the density is raised. It is interesting to compare $c_2^s(t)$ with the collective correlation function $c_2^c(t)$ [the first-rank functions $c_1^s(t)$ and $c_1^c(t)$ are identical]. The decay times τ_2^c are significantly longer than the corresponding τ_2^s, and become dramatically so on approach to the nematic-isotropic transition (at $\rho/\rho_{\text{cp}} \approx 0.69$ for $a/b=3$). This is shown in Fig. 2 where we plot the ratio τ_2^s/τ_2^c. For the case $a/b=3$, collective reorientation shows a critical slowing-down effect, and the rate goes to zero, apparently linearly, when the transition is reached. Similar behavior is observed for the case $a/b=2$, but here the nematic phase is preempted by freezing.

To examine this reorientational slowing down in more detail, we recall the expression

$$\tau_2^s/\tau_2^c = (1+j_2)/(1+g_c), \qquad (3)$$

where g_2 is the static second-rank Kirkwood factor

$$g_2 = \sum_{j\neq i} P_2(\mathbf{e}_i\cdot\mathbf{e}_j) = \frac{1}{N}\sum_i\sum_{j\neq i} P_2(\mathbf{e}_i\cdot\mathbf{e}_j) \qquad (4)$$

and j_2 is a dynamical quantity which can be expressed in terms of memory functions of the orientation.[12,13] (Often the symbol j_2 is used for our $1+j_2$.) In Fig. 2 we plot $(1+g_2)^{-1}$ and the average value of $1+j_2$ calculated from Eq. (3). The latter quantity is subject to large statistical errors. We could detect little systematic variation of j_2 with density. On the assumption that values calculated in different runs are independently and normally distributed, we estimate $1+j_2=0.92\pm0.05$ ($a/b=3$) and $1+j_2=0.74\pm0.16$ ($a/b=2$). It seems that a large part of the collective orientational slowing down

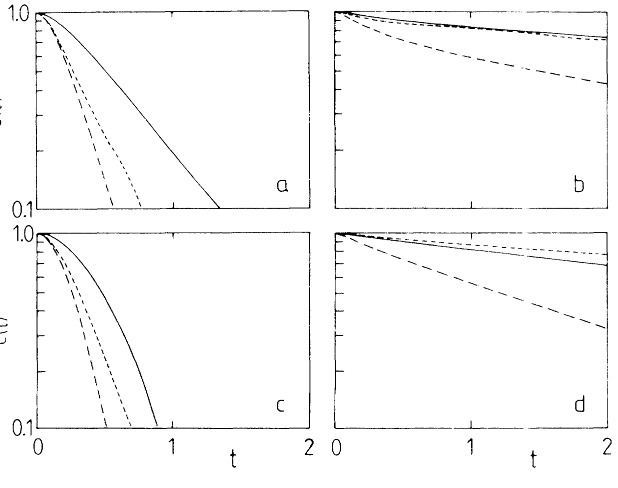

FIG. 1. Orientational time-correlation functions $c_1^s(t)$ (solid line), $c_2^s(t)$ (long dashes), and $c_2^c(t)$ (short dashes). (a) $a/b=2$, $\rho/\rho_{\text{cp}}=0.5$; (b) $a/b=2$, $\rho/\rho_{\text{cp}}=0.8$; (c) $a/b=3$, $\rho/\rho_{\text{cp}}=0.3$; (d) $a/b=3$, $\rho/\rho_{\text{cp}}=0.65$.

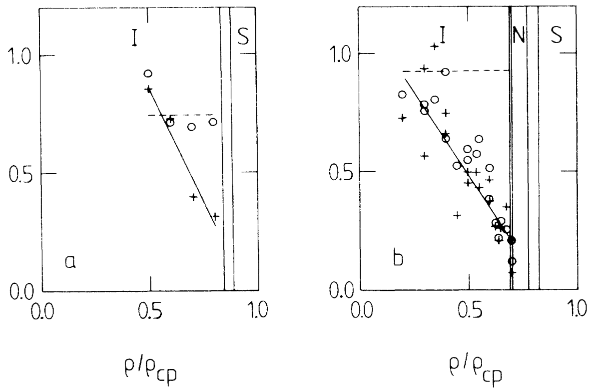

FIG. 2. Density dependence of the ratio of single-particle to collective times τ_2^s/τ_2^c (plusses) and the contribution $(1+g_2)^{-1}$ (circles). We show a linear least-squares fit to τ_2^s/τ_2^c (solid line) and the average value of $1+j_2$ (dashed line). The isotropic (I), nematic (N), and solid (S) regions are indicated, with two-phase regions delimited by vertical lines. (a) $a/b=2$, (b) $a/b=3$.

close to the isotropic-nematic transition for $a/b=3$ is associated with the $1+g_2$ term.

Although the hard-ellipsoid model is an idealization, it is interesting to compare our data for $a/b=3$ with the results of light-scattering experiments[14] on *p*-methoxybenzylidene-*n*-butylaniline (MBBA) which has a similar axial ratio. These experiments provided support for the mean-field prediction[15]

$$g_2^{-1} \propto \rho^* - \rho \qquad (5)$$

and for the hypothesis that g_2 diverges at a density ρ^* equal to that of the isotropic-nematic transition. Deviations from Eq. (5) seem to occur very close to the transition,[16] but the statistical limitations of our simulations make it difficult to test this. The experiments also allowed an estimate to be made of the dynamic quantity j_2, on the assumption that single-particle correlation times obey the Debye-Einstein relation[17]

$$\tau_2^s = v^* \eta / k_B T + \tau_2^0, \qquad (6)$$

where v^* is a molecular volume, η the shear viscosity, and τ_2^0 a constant. For solutions of MBBA in carbon tetrachloride, the experiments suggested $1+j_2 \approx 0.8$, decreasing to ≈ 0.7 for the neat nematogen. These results are in remarkable agreement with our estimates. However, in view of the above assumption, it is usual to set $j_2 \approx 0$ in the interpretation of experimental data.[14] Taken together, our simulation results for hard ellipsoids with $a/b=2$ and $a/b=3$ strongly suggest that j_2, although small, is negative. This would constitute the first *direct* evidence of a nonzero value of j_2.

We note in passing that the determination of collective orientational correlation parameters may often be subject to dramatic effects due to the simulation periodic boundary conditions.[18] These effects appear as oscillations in the function $g_2(r)$, defined as in Eq. (4) but with the sum restricted to molecules j lying within a "shell" at some distance from molecule i. For the hard-ellipsoid system, these effects are very small in both the isotropic and nematic phases[4,5]: $g_2(r)$ reaches a steady plateau value within one or two molecular diameters.

In conclusion, we have carried out the first molecular-dynamics simulations of a molecular fluid approaching an isotropic-nematic phase transition. Our results show clear evidence of pretransitional slowing down of collective molecular rotation, which seems to be closely linked with the growth in static structural correlations measured by the Kirkwood g_2 factor. The dynamic factor j_2 seems to be small, negative, and slowly varying with density. We should emphasize here that, despite these transition precursors, the isotropic-nematic transition is first order in this system,[5] albeit with a narrow coexistence range.

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[1] For simulations in which molecular translation or rotation is constrained see, e.g., G. R. Luckhurst and P. Simpson, Mol. Phys. **47**, 251 (1982); U. Fabbri and C. Zannoni, Mol. Phys. **58**, 763 (1986); D. Baalss and S. Hess, Phys. Rev. Lett. **57**, 86 (1986).

[2] J. Kushick and B. J. Berne, J. Chem. Phys. **64**, 1362 (1976); D. Decoster, E. Constant, and M. Constant, Mol. Cryst. Liq. Cryst. **97**, 263 (1983).

[3] G. R. Luckhurst and S. Romano, Proc. Roy. Soc. London, Ser. A **373**, 111 (1980).

[4] D. Frenkel, B. M. Mulder, and J. P. McTague, Phys. Rev. Lett. **52**, 287 (1984).

[5] D. Frenkel and B. M. Mulder, Mol. Phys. **55**, 1171 (1985).

[6] G. T. Evans, R. G. Cole, and D. K. Hoffman, J. Chem. Phys. **77**, 3209 (1982).

[7] R. G. Cole, D. R. Evans, and D. K. Hoffman, J. Chem. Phys. **82**, 2061 (1985).

[8] D. W. Rebertus and K. M. Sando, J. Chem. Phys. **67**, 2585 (1977).

[9] L. Verlet, Phys. Rev. **159**, 98 (1967).

[10] J. W. Perram, M. S. Wertheim, J. L. Lebowitz, and G. O. Williams, Chem. Phys. Lett. **105**, 277 (1984); J. W. Perram and M. S. Wertheim, J. Comput. Phys. **58**, 409 (1985).

[11] J. Vieillard-Baron, J. Chem. Phys. **56**, 4729 (1972).

[12] D. Kivelson and P. A. Madden, Ann. Rev. Phys. Chem. **31**, 523 (1980); S. J. Tsay and D. Kivelson, Mol. Phys. **29**, 1 (1975).

[13] B. J. Berne and R. Pecora, *Dynamic Light Scattering* (Wiley, New York, 1976), Chap. 12.

[14] T. D. Gierke and W. H. Flygare, J. Chem. Phys. **61**, 2231 (1974); G. R. Alms, T. D. Gierke, and W. H. Flygare, J. Chem. Phys. **61**, 4083 (1974).

[15] P. G. de Gennes, Mol. Cryst. Liq. Cryst. **12**, 193 (1971).

[16] H. Zink and W. H. de Jeu, Mol. Cryst. Liq. Cryst. **124**, 287 (1985).

[17] G. R. Alms, D. R. Bauer, J. I. Brauman, and R. Pecora, J. Chem. Phys. **59**, 5310 (1973).

[18] R. W. Impey, P. A. Madden, and D. J. Tildesley, Mol. Phys. **44**, 1319 (1981).