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Nematic order in nanoscopic liquid crystal droplets

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We have used atomistic molecular-dynamics simulations to model the detailed molecular configuration of 5CB (4-*n*-pentyl-4′-cyanobiphenyl) molecules in the form of a nanoscopic liquid crystal droplet in a vacuum microgravity environment. We find the equilibrium state of droplets consisting of as few as 26 or 50 molecules to exhibit significant nematic ordering. The shape of the droplets is also anisotropic, but there is little angular correlation between the nematic director and the long axis of the droplet. Some tendency to micelle formation is observed in droplets of 50 molecules. [S1063-651X(99)10407-0]

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I. INTRODUCTION

The order parameter in a nematic liquid crystal is an essentially macroscopic concept. The order-parameter tensor S_{ij} is formed as an average over a region assumed to contain a large number of molecules. In the various formulations [1,2] of elasticity theory for liquid crystal ordering, S_{ij} varies with position, but this variation must be small over molecular distances. As one approaches a disclination or other singularity in the director field, the concept of an order parameter breaks down.

These issues are of significance in the formation of very small droplets of liquid crystal. In the phase separation process that leads to the devices known as polymer-dispersed liquid crystals [3], droplets of submicrometer diameter may be created. There are then a number of questions that may be asked. Is there a critical size for nematic order to occur? What shape will a nanodroplet assume? To what extent will the polar ends of an assembly of asymmetric liquid crystal molecules tend to cluster?

To answer these questions we have performed a series of atomistic simulations of isolated droplets consisting of molecules of the nematic liquid crystal 5CB (4-*n*-pentyl-4′-cyanobiphenyl), each of which consists of 38 atoms. Assemblies of 26 and of 50 of these molecules were allowed to equilibrate at various temperatures and from various initial configurations, and the final shape and ordering were recorded. The effects of any polymer matrix were eliminated by considering only isolated droplets in a vacuum microgravity environment [4].

II. DETAILS OF THE SIMULATION

In commencing any simulation of the properties of liquid crystals, the initial choice to be made is between the use of fully atomistic models and simplified models of the Gay-Berne [5] or Lebwohl-Lasher [6] type. The great advantage of the simpler models is the small number of variables associated with each molecule. This number may vary from 2 (for the Lebwohl-Lasher model) to 10 (for a typical Gay-Berne system). In a fully atomistic model, on the other hand, there will be of the order of a few hundred variables to describe the state of each molecule when three position and three velocity coordinates are counted for each atom. The number of mesogens that can be included in a simulation is then very much smaller in the atomistic models than in the more primitive models. The precision of results for transition temperatures, order parameters, and other quantities of interest is thus much greater in the primitive models.

Despite this great disadvantage of the fully atomistic simulations, however, we choose to follow this path. The reason for this is that one cannot be certain that some of the qualitative features of the more realistic models are not essential for certain physical phenomena to occur. In our particular case, it may be that the polar nature or the flexibility of the molecule may play an important role in the behavior of microdroplets of liquid crystal. For this reason we will be limited to systems containing a comparatively small number of molecules. On the other hand, such nanoscopic systems may provide a host of new physical phenomena.

Molecular-dynamics simulations were performed with the aid of the commercial software package CERIUS^2 using the Dreiding force field [7]. The potential energy of an assembly of molecules is expressed as the sum of the contribution w_{val} of valence (or bonded) interactions and the contribution w_{nb} of nonbonded interactions. In fully atomistic molecular-dynamics simulations, the potential energy of the assembly of flexible 5CB molecules is given by [7–10]

$$W_{\mathrm{total}}=\sum_{\mathrm{bonds}\ i}\frac{1}{2}k_{b,i}(r_i-r_{i,0})^2+\sum_{\mathrm{angles}\ i}\frac{1}{2}k_{\theta,i}(\theta_i-\theta_{i,0})^2$$
$$+\sum_{\substack{\mathrm{torsion}\\ \mathrm{angles}\ i}}\frac{1}{2}k_{\phi,i}\{1-\cos(n_i[\phi_i-\phi_{i,0}])\} \qquad (1)$$
$$+\sum_{i<j}\left[\left(\frac{A_{ij}}{r_{ij}^{12}}-\frac{B_{ij}}{r_{ij}^{6}}\right)+\frac{q_iq_j}{4\pi\epsilon_0 r_{ij}}\right],$$

where $k_{b,i}$, $k_{\theta,i}$, and $k_{\phi,i}$ are force constants representing bond stretching, bond bending, and the rotational barrier for the ith bond, respectively; $r_{i,0}$, $\theta_{i,0}$, and $\phi_{i,0}$ are equilibrium values; the constants A and B are defining parameters of the Lennard-Jones model; and q is the electrostatic charge. Detailed explanations of each term are given in Ref. [9]. The potential energy function can be thought of as measuring how the energy of a particular molecular conformation varies from a hypothetical ideal geometry where all bonds, bond

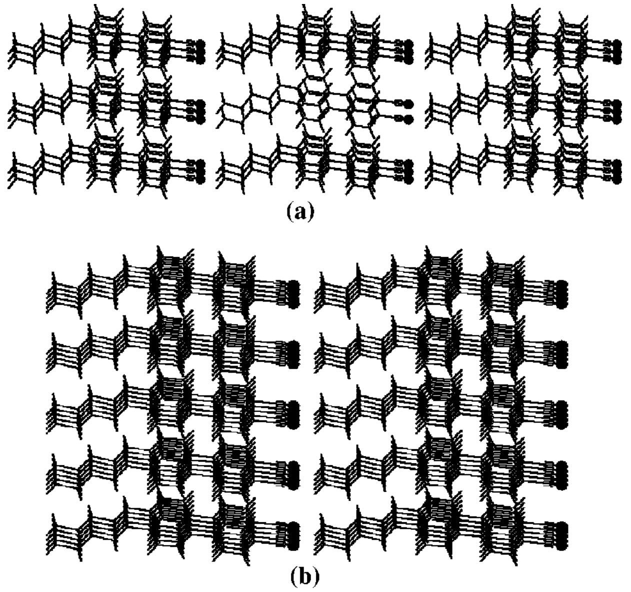

FIG. 1. Initial array configuration for (a) 26 molecules of 5CB and (b) 50 molecules of 5CB.

angles, etc. have their minimum energy [11]. While there is no term in the potential that directly refers to induced-dipole effects, it is believed that these are implicitly included in the other terms [12]. For polar molecules like 5CB, electrostatic forces are important, and the approach used to model the effects of these forces involves the use of partial charges. The partial charges for 5CB were taken from the work of Wilson and Allen on simulations of the bulk properties of 5CB [13].

Because the complexity of the model limits the length of computer runs to simulations of a few hundred picoseconds, it is important to verify whether equilibrium has been attained. It was consequently decided to run two parallel sets of simulations starting from diametrically opposite initial conditions. In one set (set A) the scalar order parameter was initially at its maximum value of unity, while in the other (set B) it was initially zero.

In set A, the starting point was a microcrystalline array in which all the molecules were aligned parallel to each other. In the smaller array shown in Fig. 1(a), which contained 26 molecules, the molecules formed a $3\times3\times3$ array from which the center molecule was removed. In the larger array of 50 molecules shown in Fig. 1(b) the center molecule was retained in a $5\times5\times2$ array. In all the illustrations the nitrogen atom has been shown as a black circle in order to aid the eye in seeing the location of the CN dipoles.

In set B, the molecules were initially configured as a ‘‘hedgehog,’’ in which the molecular axes radiated symmetrically from a common center point. For the smaller set of molecules, the 26 directions of cubic symmetry (1,0,0), (1,1,0) and (1,1,1) were occupied as in Fig. 2(a). In the larger array, which contained 50 molecules, the (2,1,0) orientations were also occupied as in Fig. 2(b). In this way the number of molecules in the corresponding sets A and B were equal, and a valid comparison of the degree of ordering in the final stages of the simulation for the two sets was possible.

The simulations were performed within a cell of sufficiently large size that no boundary effects occurred, thus making the simulation consistent with a free microgravity environment. The temperature was kept constant by rescaling the velocities at each molecular-dynamic time step [8]. The equations of motion were integrated with a time step $\Delta t = 2$ fs. In all simulations the position of each atom was recorded every 1 ps during runs totalling 350 ps. In order to study the temperature dependence of the orientational order and shape of a given droplet, simulations were performed at five different temperatures (120, 150, 200, 250, 300 K) for the case of 26 molecules and at three different temperatures (200, 250, 300 K) for the case of 50 molecules.

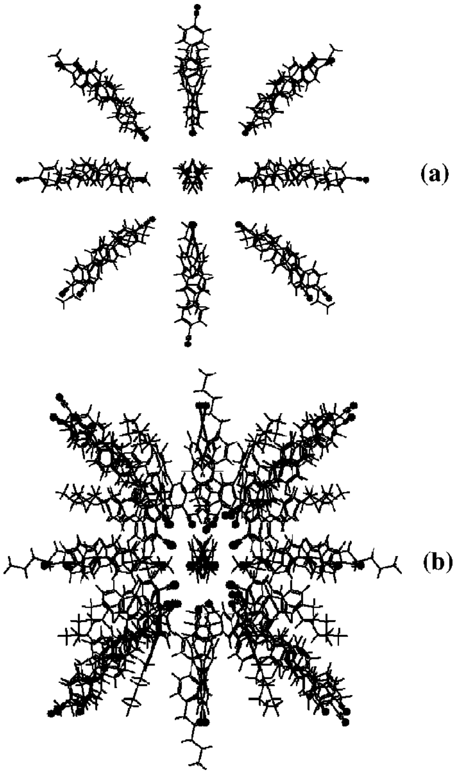

FIG. 2. Initial hedgehog configuration for (a) 26 molecules of 5CB and (b) 50 molecules of 5CB.

For a canonical ensemble like the system we were simulating, it is in principle only a question of time before equilibrium is attained. However, the length of time necessary for this to occur depends strongly on the temperature, and it was only in the case of the runs at 300 K that equilibrium appeared unequivocally to be achieved within the simulated real time of 350 ps. To overcome this problem we adopted a process of annealing. In this procedure the dynamics were first run at the chosen temperature for 0.3 ps. The temperature was then raised by successive increments of 20 K and run for further intervals of 0.3 ps until a temperature of 380 K or 390 K was reached. The system was then returned to its initial temperature in similar stages, completing one cycle of heating and cooling. This process was repeated for 30 cycles, by which time the energy at the lowest temperature in the cycle had generally ceased to change. At that point the simulation was continued at fixed temperature for a further 350 ps.

III. RESULTS AND DISCUSSION

The quantities in which we are primarily interested are the degree of nematic ordering and the average shape of the

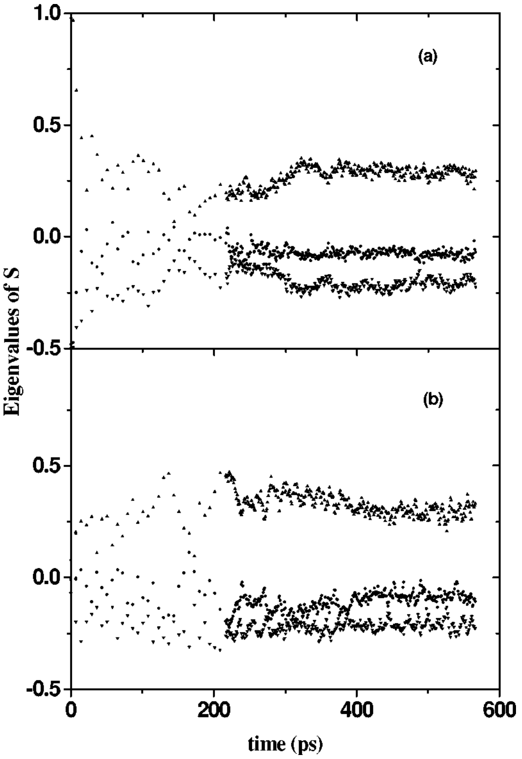

FIG. 3. Eigenvalues of the order-parameter tensor are shown as a function of time for 26 molecules at 150 K, and starting from (a) array and (b) hedgehog configurations.

droplet. To characterize the first of these two quantities we calculated the largest eigenvalues of the order-parameter tensor S_{ij}, which is defined in terms of the direction $\hat{r}$ of the molecular axes by the expression

$$S_{ij}=\frac{1}{2}\langle(3\hat{r}_i\hat{r}_j-\delta_{ij})\rangle. \tag{2}$$

Here $\langle\cdots\rangle$ represents an average over all the molecules in the assembly.

In models of the Gay-Berne type, the direction $\hat{r}$ of the molecular axis is unambiguous, apart from a possible minus sign. In atomistic models, however, the flexibility of the molecule permits a variety of definitions of $\hat{r}$. The method chosen here was to define the bond direction of the bond connecting the two benzene rings in 5CB as the axis of the molecule [9].

At each given temperature four different simulations, corresponding to the four initial configurations shown in Fig. 1 and Fig. 2, were performed. In order to interpret the results of these simulations we computed the eigenvalues of the tensor order parameter as a function of time for each temperature, given initial configuration, and number of molecules. As an example, Fig. 3(a) and Fig. 3(b) show the three eigenvalues of the order-parameter tensor as a function of time for 26 molecules at 150 K, starting, respectively, from the array and hedgehog configurations. The first 30 eigenvalues in each case are the result of the annealing process. In both cases, the eigenvalues for the last 150 ps indicate that we have reached a state that appears to be no longer varying with time. We then identify the order parameter with the average over this period of time of the largest eigenvalue. We see that the largest eigenvalue for the array configuration decreases from unity to 0.289±0.022 whereas for the hedgehog configuration it increases from zero to 0.293±0.028. The agreement between these two values confirms that equilibrium has been reached.

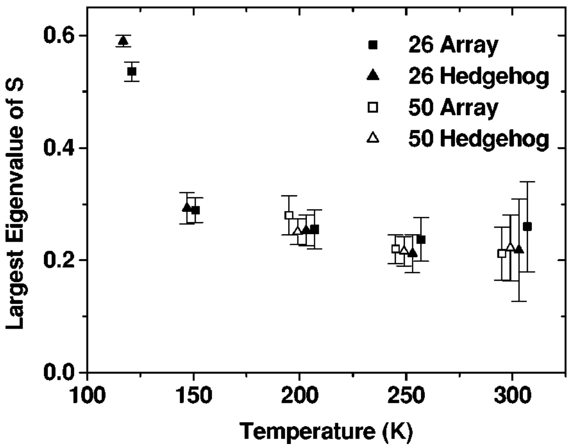

FIG. 4. The largest eigenvalue of the order-parameter tensor as a function of temperature for 26 and 50 molecules initially in the array and hedgehog configurations. The points at each temperature are displaced laterally for the sake of clarity.

The same procedure was applied for the other temperatures. The average values of the largest eigenvalue and their standard deviation as a function of temperature for the 26-molecule and 50-molecule droplets corresponding to the two initial configurations are summarized in Fig. 4. In all cases the largest eigenvalue increases as we reduce the temperature. Because 300 K lies close to the nematic-isotropic phase transition (305 K), the systems at this temperature show the largest standard deviation. As we reduce the temperature away from the vicinity of its critical value we observe the expected decrease in standard deviation. We also note the reduction in standard deviation that accompanies the increase in number of molecules from 26 to 50.

The fact that the order parameter determined in these simulations shows no observable dependence on the starting configuration and little dependence on the number of molecules encourages us to believe that our results are meaningful. However, it is also necessary to clarify that the observed order parameter is different from that which would be found in a totally random assembly of molecules. This we can do by making reference to the work of Doerr and Taylor [9], who showed that in a completely randomly oriented array of N molecules, the largest eigenvalue of the order-parameter tensor is expected to be close to $\sqrt{2/3N}$. This corresponds to values of 0.160 for a 26-molecule system, and 0.115 for a 50-molecule system.

Our second interest was in the average shape of a droplet. Figure 5 shows the distribution and orientation of 50 molecules of 5CB at the end of a simulation that had started from an array configuration, and which was run at $T=250$ K. The geometric anisotropy observed in this figure can be characterized in terms of the inertia tensor I, which is defined as

$$I_{\alpha\beta}=\sum_n\sum_i m_i(x_i^2\delta_{\alpha\beta}-x_{i\alpha}x_{i\beta}), \tag{3}$$

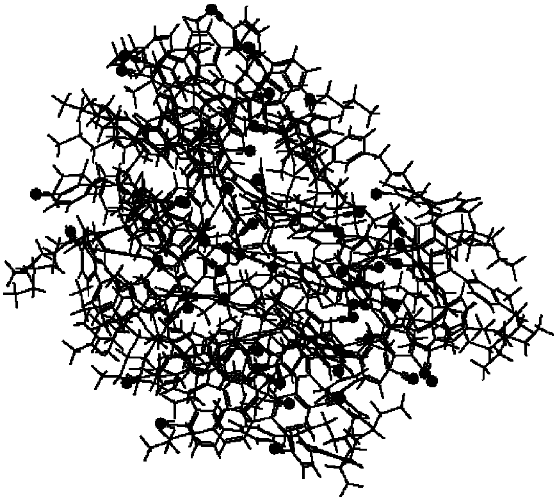

FIG. 5. Orientation of 50 molecules of 5CB at the end of a simulation that was run at 250 K and had started from an array configuration.

where the first sum is over all molecules in the system, the second sum is over all atoms in the molecule, and $\vec{x}_i$ and m_i are the position and mass of the ith atom in the nth molecule. For our particular problem we have either 26 or 50 molecules, and the number of atoms per molecule is always 38. In constructing the inertia tensor we took the mass of an atom to be its atomic mass.

By diagonalizing this tensor we obtain the three principal-axis vectors and the three corresponding principal moments of inertia I_{aa}, I_{bb}, and I_{cc}. Figures 6(a) and 6(b) show the three principal moments of inertia as a function of time for 26 molecules at 150 K, starting from, respectively, the array and hedgehog configurations. From these three values of the moments of inertia, one can gather the required information about the shape of the system by constructing an equivalent ellipsoid. This ellipsoid is defined to be of uniform density, and to have the same total mass and the same moments of inertia as our system.

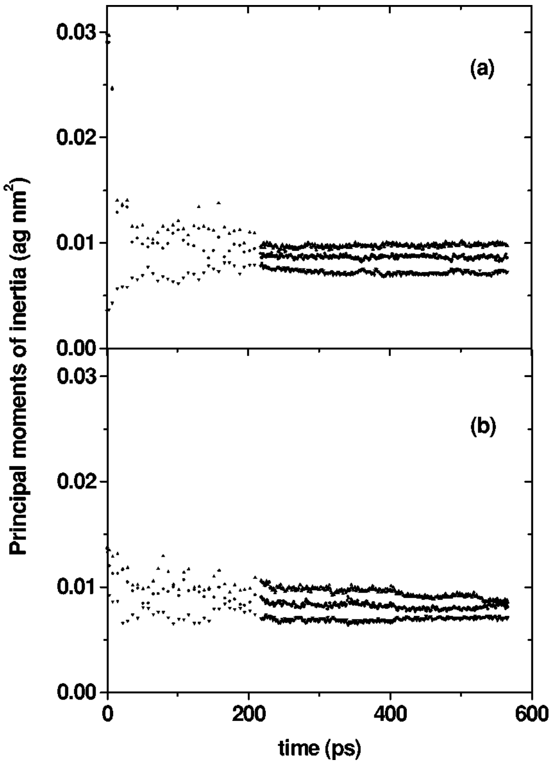

FIG. 6. The principal moments of inertia (in units of $10^{-40}\ \mathrm{kg\,m^2}$) as a function of time for 26 molecules at 150 K, starting from (a) array and (b) hedgehog configurations.

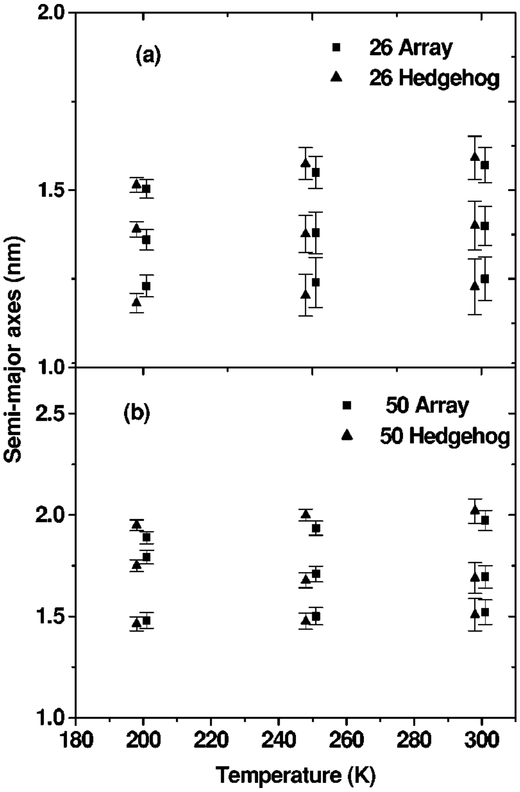

FIG. 7. The three semiaxes of the equivalent ellipsoid are shown as a function of temperature for (a) 26 molecules that had initially been in the array and hedgehog configurations, (b) 50 molecules initially in the array and hedgehog configurations. The points at each temperature are displaced laterally for the sake of clarity.

For an ellipsoid with semiaxes of length a, b, and c and total mass $M=N\Sigma_i m_i$, the moments of inertia are given by $I_{aa}=(M/5)(b^2+c^2)$ and its cyclic permutations. From these relations we find $a=\sqrt{5(I_{bb}+I_{cc}-I_{aa})/2M}$, and its cyclic permutations, as the lengths of the three semiaxes. Figures 7(a) and 7(b) show the lengths of the three semiaxes for the 26- and 50-molecule systems as a function of temperature for the two different initial configurations. In all cases the values of the three semiaxes are significantly different, which suggests that the shape is not spherical, or even spheroidal. This result is somewhat surprising. For a macroscopic nematic droplet we would expect that there would be an axis of symmetry, so that two of the three semiaxes would be approximately equal. The droplet would thus resemble either an oblate or prolate spheroid, depending on the effective anchoring at the vacuum interface. Our simulations indicate a less symmetric shape in equilibrium, even when the starting point of the simulation was highly symmetric, as in the case of the hedgehog initial conditions.

To check that this result was not due merely to random fluctuations, a similar simulation was run for a cluster of 50

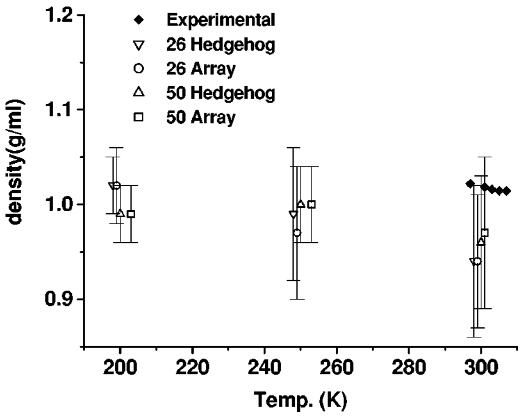

FIG. 8. Density for 26 and 50 molecules of 5CB initially in array and hedgehog configurations as a function of temperature. The simulation points at each temperature are displaced laterally for the sake of clarity. The experimental values were taken from Ref. [14].

argon atoms. The deviations from sphericity were then found to be much smaller, and to vary with time. For our system of 5CB molecules the plots given in Figs. 6(a) and 6(b) show that the lengths of the three semiaxes stay essentially constant in time, and do not cross each other.

This suggestion that microdroplets of 5CB may have a biaxial symmetry is supported by the results for the order-parameter tensor given in Fig. 3. There the two most negative eigenvalues are unequal, as is the case for biaxial order, particularly at the lowest temperatures. At the highest temperatures, however, this effect is barely significant statistically.

A check on the validity of our results may be made by comparing the density found for the equivalent ellipsoid with the experimental values for 5CB. Figure 8 shows the density of the equivalent ellipsoids for the droplets consisting of 26 and 50 molecules as a function of temperature for the two different initial configurations. Although our error bars are large, the densities we find are consistent with the experimental values [14] and show a coefficient of thermal expansion of appropriate size. The number of molecules again does not seem to influence the result to any great extent.

When we examine the combined results for the tensor order parameter, the geometric shape, and the density of the droplets we find a consistent, if unexpected, set of results. While there is statistically significant nematic ordering and a significant departure from a spherical shape, there is little correlation between the directions of these departures from isotropy. Table I shows the time-averaged angle that the eigenvector corresponding to the largest eigenvalue of the order-parameter tensor makes with the major-axis direction of the equivalent ellipsoid. All the angles shown are fairly close to the value of 57° that would be found if there were a complete absence of correlation.

TABLE I. Angle between the eigenvector corresponding to the largest eigenvalue of the order-parameter tensor and the major-axis direction of an equivalent ellipsoid.

Temperature (K)	26 hedgehog	26 array	50 hedgehog	50 array
300	70	65	60	62
250	55	53	57	60
200	50	49	56	60

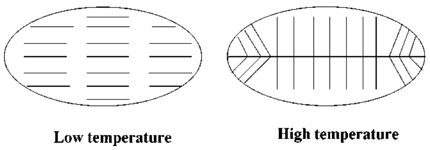

FIG. 9. Representation of the director at (a) low and (b) high temperatures.

Although these angles suggest that the correlations are weak, there is nevertheless a discernible trend in the temperature variation of this angle. As the temperature is raised, the angle between director and major axis increases. This tendency is illustrated in an exaggerated form in Fig. 9. At low temperatures the director tends to be aligned with the major axis, while at higher temperatures it tends to be more perpendicular.

This schematic picture suggests that the low-temperature form might be more crystalline, while the higher-temperature structure might have some of the characteristics of a micelle [15]. To decide whether this was the case we examined the locations of the polar CN groups during the course of the simulations. If there were a tendency to micelle formation, this would presumably be driven by the mutual attraction of the polar ends of the 5CB molecules. Our results are shown in Fig. 10(a) and Fig. 10(b) for 50-molecule systems at 250 K that had started, respectively, from the array and hedgehog configurations. There we see that the average distance of the CN group from the center of mass decreases with time as the

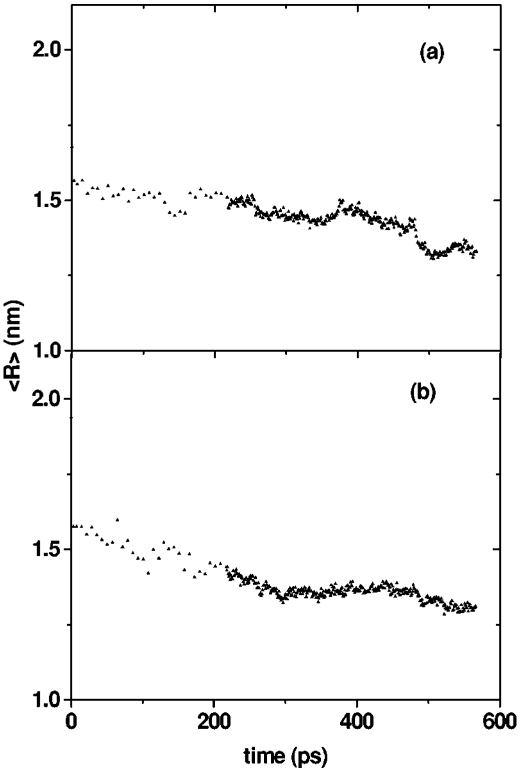

FIG. 10. The average distance of the CN group from the center of mass as a function of time for a droplet of 50 molecules initially in (a) array and (b) hedgehog configuration.

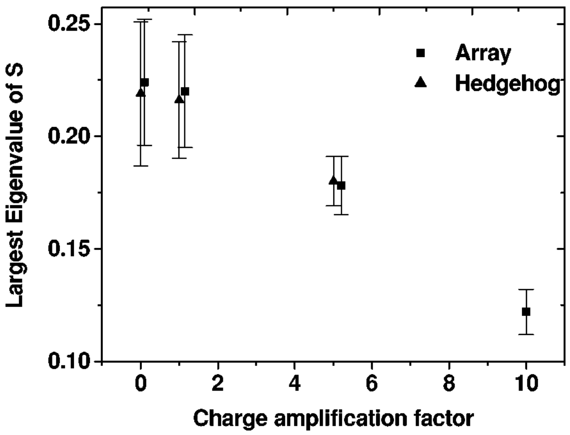

FIG. 11. The largest eigenvalue of the order-parameter tensor as a function of the ratio of partial charges placed on the CN groups to their usual value. The points at each charge amplification factor are displaced for the sake of clarity.

simulation runs. This indicates that there is indeed some tendency for the polar ends of the 5CB molecules to congregate at the center of these microdroplets in a manner reminiscent of micelle formation.

To check the robustness of this result we decided to check whether the orientation of the molecules at the end of the simulation depended on how the molecules were initially oriented. We reconsidered the array configuration shown in Fig. 1(b) for different possible orientations of the polar end groups. In one case all the CN groups were made to point towards each other and in the other case they were arranged to point outwards. We then ran simulations that started from these two initial configurations. We observed the same micelle structure at the end of each simulation, regardless of the starting configuration.

This tendency to micelle formation at higher temperatures leads us to ask what the driving force for this process might be. Is it the electrostatic interaction between the CN dipoles, or is it an entropic effect associated with the ability of the flexible alkane groups to move more freely at the droplet surface? To decide this question we modified our system in a way that no experimentalist can achieve — we varied the strength of the partial charges making up the CN dipole over a wide range, and repeated the simulations.

We first set all the partial charges to zero, and ran the 50-molecule system at 250 K. At the end of the simulation we again observed micelle formation and also found the order parameter for the array configuration to be 0.224 ± 0.028 and for the hedgehog configuration to be 0.219 ± 0.032 as shown in Fig. 11. These values are not significantly different from those previously obtained. We thus saw no observable effect of the partial charges on the resultant orientation of the molecules.

In an effort to determine the actual significance of the dipole interactions, we then set the partial charges of the atoms to be five times and ten times their normal values. In this case we observed a significant decrease in the order parameter. It was reduced to 0.180 ± 0.011 for the hedgehog configuration and 0.178 ± 0.013 for the array configuration when the partial charges were set to be five times their normal value. When the partial charges were set to be ten times their normal size, we found the order parameter to be 0.122 ± 0.01, close to the random assembly value [9], for the array configuration. Thus, in the normal simulation, where the partial charges have realistic values, the influence of the dipole moment seems to be negligible.

Our finding that the mutual electrostatic interaction of the CN dipoles has little effect on ordering runs counter to much of the previous thinking on this subject [16,17], which has included suggestions that an effective dimerization might occur. However, some recent Raman studies [18] have provided experimental evidence that dipole-induced molecular association may not occur to the extent previously believed. The results of our simulations should thus perhaps not have been totally unexpected, given that the proximity of surfaces may also be a factor in the weakening of molecular association [19].

IV. CONCLUSIONS

We have seen that it is possible to simulate at an atomistic level the molecular motions within very small droplets of 5CB, and to reach an equilibrium state that is independent of the initial configuration of the assembly. The scalar order parameter, calculated as the largest eigenvalue of the nematic-order-parameter tensor, was found to decrease with increasing temperature up to 300 K. Even at this temperature, it remained significantly larger than would be expected from a randomly oriented assembly of molecules.

The shapes of these microdroplets were somewhat nonspherical, and generally had a longest axis that was some 25% larger than the shortest axis. There was little angular correlation between the nematic director and the long-axis direction. The density of the equilibrium droplet was close to the experimentally known value.

The effect of the partial charges of the CN group in orienting the molecules was investigated. It was found that removing these charges had no effect on the order parameter. Only when the partial charges were increased to several times their normal value was the order parameter significantly reduced. This left unexplained the observed tendency to micelle formation in the 50-molecule droplets, where most of the CN groups were found in the interior of the droplet. One possible explanation could be that the flexible tails of the 5CB molecules tended to move to the surface of the droplet because this allowed an increase in entropy, as more phase space was then available for their motion.

ACKNOWLEDGMENTS

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