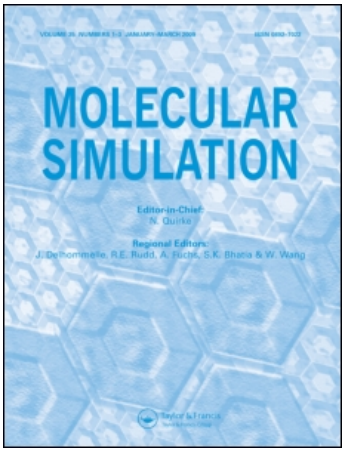

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Investigations of Nematic-Isotropic Transition by Means of Constant Pressure Molecular Dynamics Simulations

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INVESTIGATIONS OF NEMATIC-ISOTROPIC TRANSITION BY MEANS OF CONSTANT PRESSURE MOLECULAR DYNAMICS SIMULATIONS

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Constant pressure molecular dynamics simulations, which secure the system to be under hydrostatic pressure, are used to simulate the behavior of liquid crystals consisting of anisotropic molecules with both translational and orientational freedom. In order to investigate to what extent can the properties known to real liquid crystalline phases be explained by the anisotropy of the shape of the molecules alone, the molecular dynamic (MD) simulation uses purely repulsive short-range pair potentials representing soft spherocylinders. A clear change in the microscopic as well as the macroscopic physical properties are observed near the phase transition from nematic liquid crystal to isotropic liquid.

KEY WORDS: Constant pressure MD, liquid crystals, phase transition, anisotropic diffusion, nematic.

1 INTRODUCTION

Liquid crystal comprises mesomorphic phases where three dimensional positional order is lost although some of the orientational order remains. In such states the material flows and conforms to the shape of the container but still has anisotropic physical properties, such as optical anisotropy (birefringence), dielectric anisotropy and anisotropy in magnetic susceptibility. In liquid crystalline phases there exists a direction of preferred orientation of molecules on average, which is called the director, corresponding macroscopically to the optical axis. The phase transition from nematic liquid crystal to isotropic liquids is characterized by the loss of orientational order and alternation of self diffusion of molecules from anisotropic to isotropic.

It has been demonstrated by Frenkel and coworkers by their work on hard-core anisotropic models [1–6] that investigations by means of molecular simulation can play an important role in the studies of liquid crystals. Interests in the molecular models, consisting of purely repulsive potentials as a reference system to liquid crystals, have significantly increased since the simulations showed that not only the nematic phase but also the smectic phase (which were believed to need attractive force for existence) appear by the use of systems with hard spherocylinders [3–6].

Among various computational methods, the constant pressure molecular-dynamics (MD) simulations is especially a powerful tool. However, conventional constant pressure methods encounter difficulties when used for simulating anisotropic

molecules of system size, say, under a few hundred molecules. We have proposed constant pressure MD methods [9] which guarantee the system to be under hydrostatic pressure even for anisotropic molecules, thereby secure the true equilibrium state of the system. The above methods have been applied to systems of parallel spherocylinders, and have succeed in explaining, with the model of repulsive force alone, the transition from crystalline solids to smectic liquid crystals [9]. Scaling properties have also been obtained for this case [10].

The present paper investigates the nature of nematic-isotropic phase transition, extending the above studies to systems of spherocylinder with both translational and orientational freedom. The anisotropic molecules interacting via purely repulsive short-range pair potentials are used in order to investigate to what extent can the properties known to real liquid crystalline phases be explained by the anisotropy of the shape of the molecules alone.

2 MODEL AND METHODS

The anisotropic shape of the spherocylinder is described by the following pair potential representing the interaction, through the minimum distance r_{ij}, between molecule i and j having hard lines of length L in the core. The model is based on the following short-range repulsive pair potential for particle-particle interactions.

$$\phi_{ij} = \begin{cases} \varepsilon\left[\left(\dfrac{D}{r_{ij}}\right)^{12} - \left(\dfrac{D}{r_{ij}}\right)^{6} + \dfrac{1}{4}\right] & \text{if } |\mathbf{r}_{ij}| < r_0 \\ 0 & \text{otherwise} \end{cases}$$

where $r_0 = 2^{1/6} D$, D being the characteristic length representing the diameter of the spherocylinder. The units of length D and energy ε are used throughout this work. This pair potential ϕ_{ij} has a technical advantage over commonly used potentials since this pair potential smoothly decays to zero at $|\mathbf{r}_{ij}| = r_0$, requiring no correction term for the internal pressure calculation. In this model, the spherocylinder is described as a hard line of length L covered with a blanket of uniform thickness $D/2$ at the contour of energy $\varepsilon/4$. Since the effective core diameter changes in accord with the temperature of the system in this model, comparison with systems of hard-core spherocylinders must be done with care.

Conventional MD simulation methods can not be used to simulate the true equilibrium state for systems involving anisotropic diffusion for the following reasons. Constant volume or conventional constant pressure (Andersen's method [7]) methods yield anisotropic pressure where the diagonal elements of the shear tensor are not identical. This gives rise to tilted smectic and columnar phases which do not appear under hydrostatic pressure for systems having repulsive intermolecular potentials of moderate anisotropy, say length and width ratio of less than 5. The original Parrinello and Rahman method [8], which is most appropriate to study crystalline structure phase transitions, often causes the system to collapse in the direction perpendicular to the main direction of molecule diffusion. For instance, in

smectic phase the whole system tend to collapse into one layer. In the nematic phase the simulation box becomes elongated in the direction of the director, which is in accord with the main direction of molecule diffusion. This suggests that a longer time average of the internal pressure is required to modify the simulation box for a method capable of handling the liquid crystalline phases. It is interesting to note that the problems that arise when one uses the Parrinello and Rahman method for simulating liquid crystalline phases do not depend on the molecular model. To avoid the above difficulties and obtain a true equilibrium state under hydrostatic pressure for a system of appropriate size, we modified conventional constant pressure methods. The modified method have been proven to be effective in simulating liquid crystalline phases [9].

3 RESULTS

The simulation results for systems with molecular length $L = 3$ and molecular number $N = 360$ are presented in this paper. The transition from nematic liquid crystalline phase to isotropic liquids are described.

3.1 Nematic Liquid Crystalline Phase

First, the microscopic properties are examined to see if the system is in the nematic phase. The orientational order parameter $S_2 = \langle (3\cos^2\theta - 1)/2 \rangle$ is calculated from the angle θ of each molecule against the director. Figure 1 shows the time evolution of S_2 at $T^* = 0.74$ when the run is started from a state of complete orientational order. We use the reduced temperature $T^* = T/T_{N-I}$ where T_{N-I} refers to the

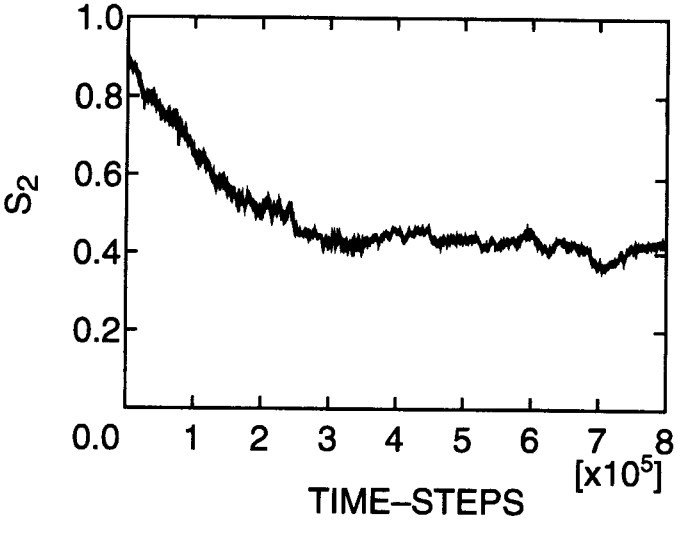

Figure 1 The evolution of the order parameter S_2 in nematic phase for a run when molecules are initially in complete order.

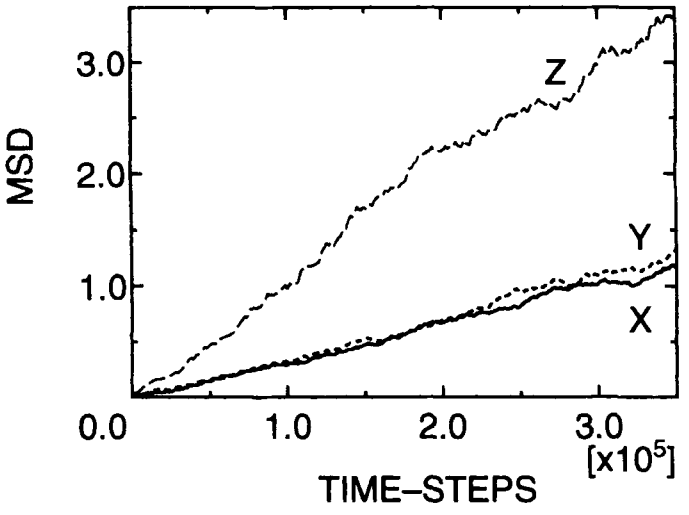

Figure 2 Mean square displacement in X, Y, Z directions in nematic phase for last 3.5×10^5 time steps of the run shown in Figure 1. The director is nearly parallel to Z direction.

nematic-isotropic transition temperature. After 3×10^5 time-steps, the value of S_2 becomes quite stable around $S \simeq 0.41$. Although it can be seen from Figure 1 that, in addition to small fluctuations of short characteristic time, there are fluctuations of long characteristic time (in the order of few 10^5 time steps). These fluctuations of long characteristic time do not appear in isotropic liquids and can be interpreted as being a feature of liquid crystalline phases.

To examine the magnitude of self-diffusion in varying directions, the mean-square-displacements (MSDs) of the last 3.5×10^5 time-steps of the same run as in Figure 1 are plotted in Figure 2. The MSD is defined as

$$\langle r^2(t) \rangle = \left\langle \frac{1}{N} \sum_{i=1}^{N} [\vec{r}_i(t + t_0) - \vec{r}(t_0)]^2 \right\rangle$$

where $\vec{r}_i$ is the position of the i-th particle. The director is approximately in the Z-direction in this run. As seen from Figure 2, the magnitude of diffusion along the director is two to three times larger than that in the direction perpendicular to the director (X and Y-directions), confirming that the system is in the nematic phase at $T^* = 0.74$.

3.2 Nematic-Isotropic Phase Transition

In this subsection, the macroscopic physical properties in the vicinity of the transition from nematic liquid crystalline phase to isotropic liquids are observed.

The temperature dependence of volume per molecule V/N near the nematic-isotropic transition is shown in Figure 3. The symbols $\times$ and $\circ$ represent, respectively, the values of time average of 1×10^5 and 2×10^5 time-steps at the end of the

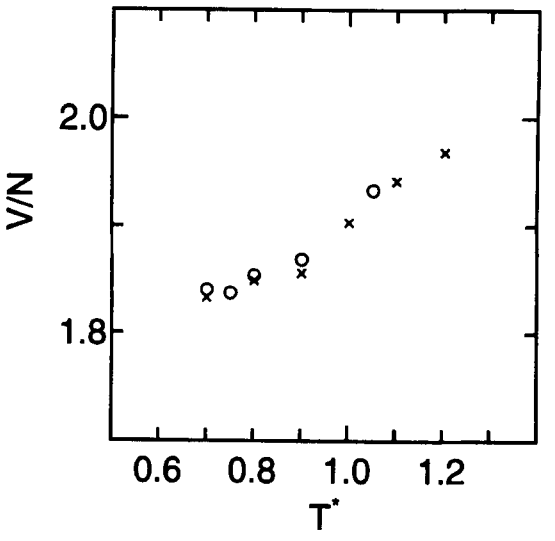

Figure 3 Volume per molecule vs. reduced temperature $T^* = T/T_{N-I}$ near nematic-isotropic phase transition. Symbols × and ○ represent, respectively, the values of time average of 1×10^5 and 2×10^5 time-steps at the end of the run.

run. The behavioral change in the volume at nematic-isotropic transition can be clearly observed.

Figure 4 shows entalpy per molecule $H/N = (U + PV)/N$ near the nematic-isotropic phase transition versus reduced temperature T^*, where U is the total potential energy, and P the pressure. The symbols × and ○ represent the same time averages as those in Figure 3. Evident on inspection of Figure 3 and 4 is that the transition from nematic liquid crystalline phase to isotropic liquids is a weak first order or a second order transition. However, simulation of longer times and of different system sizes is necessary to evaluate the precise nature of the transition.

Finally, we present the orientational order parameter S_2 versus reduced temperature T^* in Figure 5. It can be seen from Figure 5 that the orientational order persists at higher temperatures ($T^* > 1$), even after the macroscopic properties have shown a clear change. Further investigation is necessary to ascertain whether this is due to the effect of pre-transitional characteristics or relaxation time.

4 CONCLUDING REMARKS

We have demonstrated that not only the change in microscopic properties but also the change in macroscopic properties, such as volume or entalpy at the transition, can be simulated by our model and that the constant pressure method we have proposed is effective in simulating liquid crystalline phases with few hundred molecules. The simulation results of the orientational order parameter S_2 agree fairly well with experiments. The anisotropic self-diffusion of the nematic phase has been observed directly by our simulations.

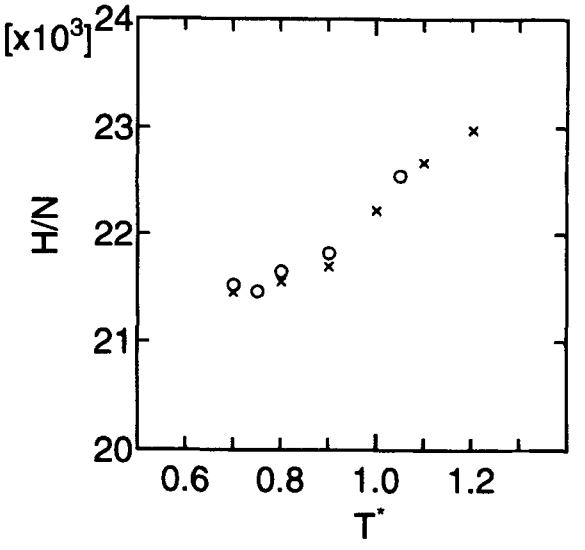

Figure 4 Entalpy per molecule $H/N = (U + PV)/N$ vs. reduced temperature $T^* = T/T_{N-I}$ near nematic-isotropic phase transition. Symbols × and ○ represent, respectively, the values of time average of 1×10^5 and 2×10^5 time-steps at the end of the run.

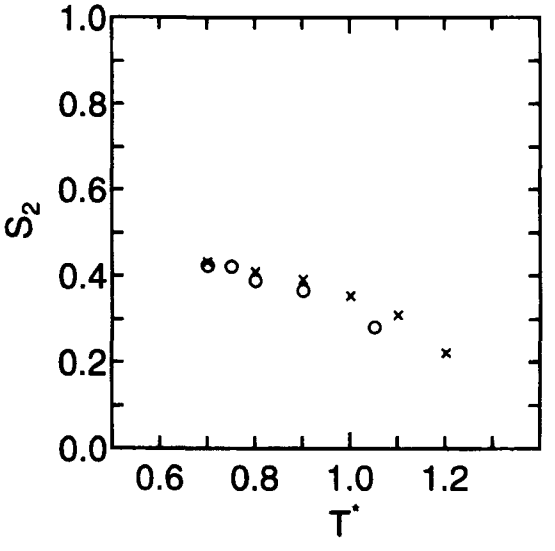

Figure 5 Orientational order parameter $S_2 = \langle (3\cos^2\theta - 1)/2 \rangle$ vs. reduced temperature $T^* = T/T_{N-I}$ near nematic-isotropic phase transition. Symbols × and ○ represent, respectively, the values of time average of 1×10^5 and 2×10^5 time-steps at the end of the run.

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