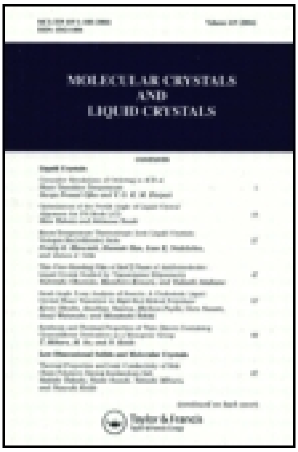

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Investigation of Liquid Crystalline Phases by Means of Constant-Pressure Molecular-Dynamics Simulation

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INVESTIGATION OF LIQUID CRYSTALLINE PHASES BY MEANS OF CONSTANT-PRESSURE MOLECULAR-DYNAMICS SIMULATION

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Abstract Constant pressure molecular-dynamics (MD) simulations of systems consisting of soft spherocylinders with both translational and orientational freedom are performed to study the behavior of liquid crystalline phases and its transitions. 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 MD simulation uses purely repulsive short-range pair potentials representing soft spherocylinders. Both the nematic and smectic phases are simulated and the properties of each phase are investigated.

INTRODUCTION

Interests in molecular models with purely repulsive potentials as a reference system to liquid crystals has significantly increased[1] after Frenkel and coworkers[2] has proved by computer simulation that not only the nematic phase but also the smectic phase, which were believed to need attractive forces for it's existence, appear by the use of models with repulsive potentials alone.

Constant pressure molecular-dynamics (MD) simulation is especially a powerful tool, among various computational methods, to investigate phase transitions. However, conventional constant pressure methods encounter difficulties when used for simulating anisotropic molecules of system size, say, under a few hundred molecules. For instance the original Parrinello and Rahman method[3], which is most appropriate to study crystalline-structure phase transition, change the shape and volume of the simulation box according to the instantaneous internal pressure, which often lead the system to collapse in one layer[4] in the smectic phase. This suggests that we need a longer time-average of the internal pressure to change the simulation box for such a case. Conventional Andersen's method[5] often leads to situations where the total pressure is constant but the diagonal elements of the stress tensor are not identical. In other words the system is under anisotropic pressure. Such a situation is more likely to occur when the orientational order parameter S gets higher (or the temperature gets lower), leading to tilted smectic and columnar phases which do not appear under hydrostatic pressure[6]. To avoid the above difficulties and obtain a true equilibrium state under hydrostatic pressure for a system of appropriate system size, we modified conventional constant pressure methods, which have proven to be effective in simulating liquid crystalline phases[4]. By using this modified constant pressure methods, it has been shown that a clear phase transition from crystalline solid to smectic liquid crystalline phase occurs in systems of parallel spherocylinders with repulsive force[7] alone. Scaling properties has also been obtained for this case[8].

This paper investigate the nature of the liquid crystalline phases, extending the above studies[7,8] to systems of spherocylinders with both translational and orientational freedom.

MODEL AND METHODS

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 following purely repulsive short-range pair potential was used. The formula represents soft spherocylinders.

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

where r_{ij} is the minimum distance between molecules i and j, and $r_0 = D2^{1/6}$. This potential has an advantage for constant pressure MD simulations compared to other continuous soft-core potentials, since it smoothly diminish at distance r_0, requiring no correction term for the internal pressure calculation. In this model, the spherocylinder can be described as a hardline of length L covered with a blanket of uniform thickness $D/2$ at the contour of energy $\varepsilon/4$, though it is more appropriate to introduce an effective core diameter d_Φ and calculate the effective anisotropy of the system using d_Φ. The effective core diameter d_Φ can be defined as the distance that the neighboring molecules feel the potential energy $\Phi(d_\Phi)$, which is equivalent to the kinetic energy on average. Since the effective anisotropy L/d_Φ will change with temperature, comparison with systems of hard-core spherocylinders must be done with care. In this study, the length is measured in unit D and the energy in ε.

The methods of constant pressure MD simulations, successfully applied to systems of parallel spherocylinders[4], are used in this work. These methods guarantee the system to be under hydrostatic pressure even for anisotropic molecules, thereby the true equilibrium state of the system is secured.

RESULTS

The simulation results for systems with molecular length $L = 2$ and molecule number $N = 168$ are presented in this paper. Comparison between the isotropic phase, the nematic phase and the smectic phase is done.

Isotropic Phase

An isotropic phase is observed for this system of soft spherocylinders at high enough temperatures. Figure 1 shows the time evolution of the orientational order parameter $S = \langle (3\cos^2\theta - 1)/2 \rangle$ for a run when molecules were initially in a complete order with length $L = 2$ at temperature $T^* = T/T_{N-I} = 5.56$.

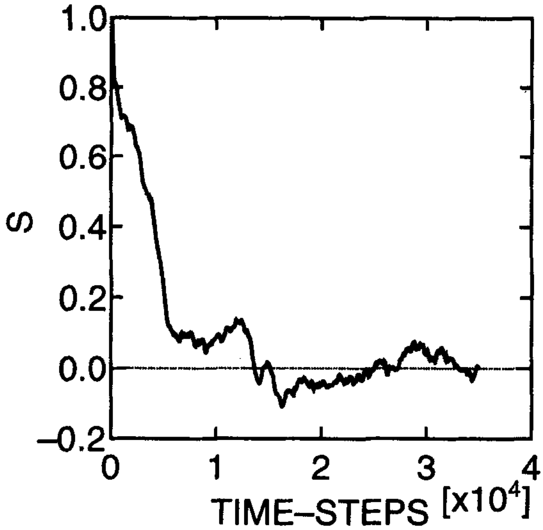

FIGURE 1 The evolution of the order parameter S in isotropic phase for a run when molecules are initially in complete order.

In this figure the order parameter S fluctuates around $S = 0$ after 1×10^4 time-steps, indicating the state is in the isotropic phase.

The mean-square-displacements (MSDs) is defined as

$$\langle r^2(t) \rangle = \langle \frac{1}{N} \sum_{i=1}^{N} [\vec{r_i}(t + t_o) - \vec{r_i}(t_o)]^2 \rangle$$

where $\vec{r_i}$ is the position of the i-th particle. From the slope of the MSD against time, we are able to obtain the diffusion constant of the molecules. The MSDs are observed in three directions, each coinciding with the edges of the simulation box. When the MSD is obtained for the same run as that of figure 1 after 1.5×10^4 time-steps, the molecules are seen to diffuse isotropically as shown in figure 2.

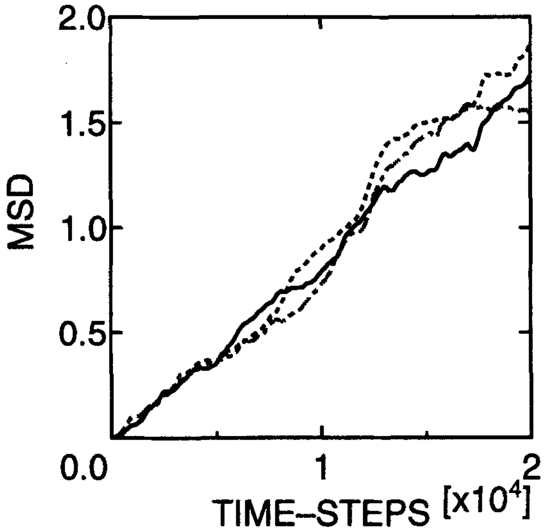

FIGURE 2 Mean-square-displacement in X (solid curve), Y (dashed curve), and Z directions (broken curve) in isotropic phase.

Nematic Phase

Lower temperature is required to simulate the the nematic phase. Below the nematic-isotropic transition temperature ($T^* = T/T_{N-I} = 0.92$) the order parameter S is plotted against time-steps in figure 3 for a run when the molecules are initially in a perfect orientational order. Notice that at early times (time-steps $< 1 \times 10^4$) the order parameter S appears to be stable for a short time period at a value around 0.74, then sharply decreases and eventually levels off at a time step of approximately 1×10^4. This suggests that there is a meta-stable state at the order parameter $S \simeq 0.7$. It can be said that if the requirement that the system be under hydrostatic pressure is not fulfilled, the system tends to be caught in this meta-stable state.

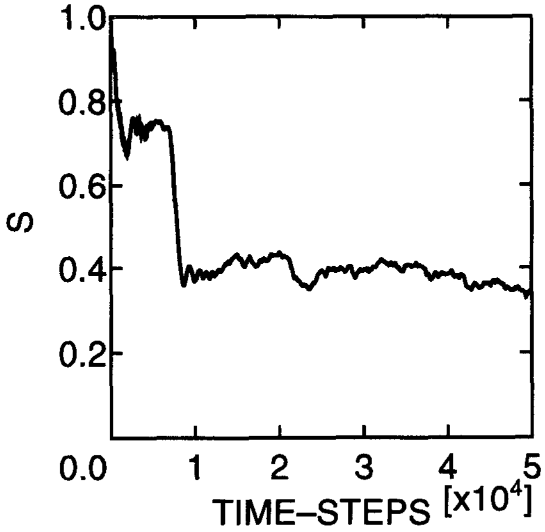

FIGURE 3 Order parameter S vs. time-steps when the system is at slightly below the NI-transition temperature.

The average value of S is 0.36 for the last 1×10^4 time-steps for a run consisting of 5×10^4 time-steps in total. This value seems reasonable compared to experimental values. To confirm the generality of the preceding results we should make simulations on systems with different anisotropies and system sizes.

The MSD for three directions are shown in figure 4 for the same run as that in figure 3. For this nematic phase, the average molecular orientation (the director) is nearly in accord with the Z-direction. After 1.5×10^4 time-steps, the MSD in each direction shows a steady increase. It can be seen from figure 4 that the diffusion along the director (Z-direction) is much larger than in other directions, confirming that the phase we observe is truly the nematic phase where diffusion along the director is greater than those in other directions.

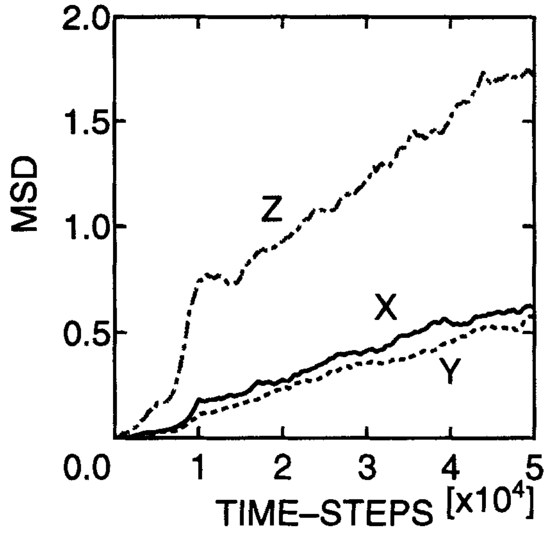

FIGURE 4 Mean-square-displacement in X, Y, and Z-direction at a temperature slightly below the NI-transition.

Smectic Phase

We have succeeded, as shown in figure 5, to simulate the smectic phase as well. For a run when molecules are initially in complete orientational order, the orientational order parameter S settles down to a value higher than that in the nematic phase.

The MSD for the smectic phase is shown in figure 6. The director of the system is also nearly in accord with the z-axis in this case too. It can be seen from figure 6 that the fluctuation along the director is quite large at the beginning of the run which is reasonable considering the fact that molecules are initially in complete orientational order. However, after around 6×10^4 time-steps, the MSD in z-direction becomes stable. The diffusion of the molecules in the xy-plane show a steady increase throughout the run, exhibiting the characteristic diffusion pattern in the smectic phase.

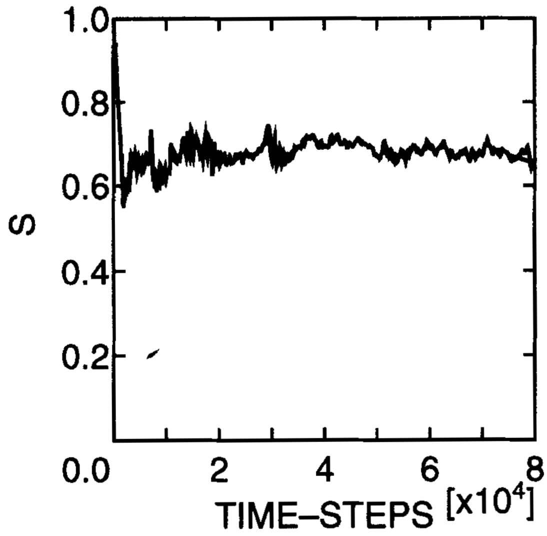

FIGURE 5 The orientational order parameter S in the smectic phase for a run when molecules are initially in complete orientational order.

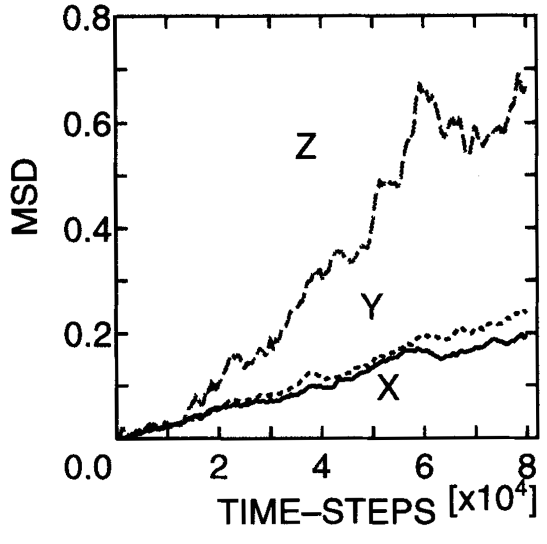

FIGURE 6 Mean-square-displacement in X, Y, and Z-direction at a temperature in the smectic region.

The pair distribution function in the direction of Z-axis, which is nearly in accord with the direction of the director, is shown in figure 7.

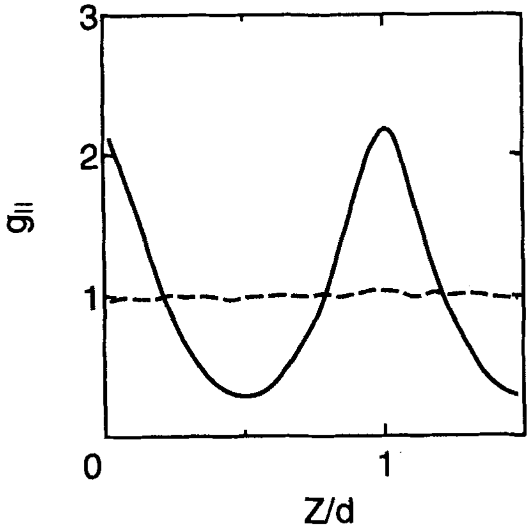

FIGURE 7 Pair distribution function in the direction of the Z-axis. The solid curve denotes the density wave in the smectic phase, and the broken line the nematic phase.

A clear density wave, a proof of the existence of smectic layers, can be observed in figure 7 although some diffusion can also be observed along the director as was observed in figure 6. Since we use periodic boundary conditions, there should be more than three layers in the simulation box for the smectic phase to avoid the situation that one layer is being surrounded by two identical layers. As shown in figure 7 there are three layers in our simulated smectic phase, indicating that the above requirement is fulfilled. For comparison, the pair distribution function in the same direction for the nematic phase treated in the previous subsection is also plotted in figure 7 with a broken curve, which exhibits no density fluctuation, contrasting to the distribution in the smectic phase.

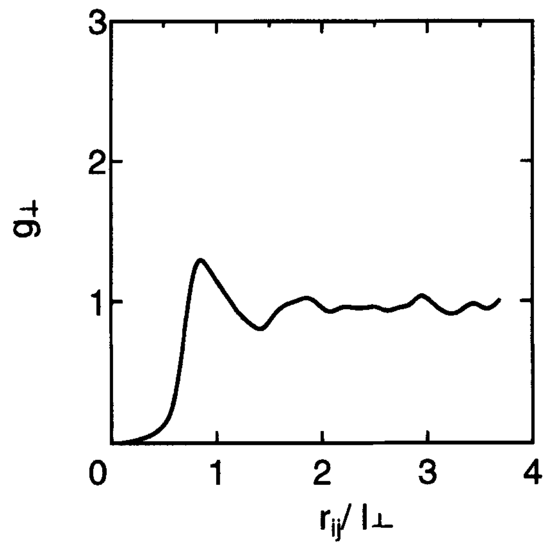

FIGURE 8 Pair distribution function inside the layers of smectic phase.

The pair distribution function inside the smectic layers are also observed. Figure 8 shows the pair-distribution function in each of the smectic layers in the direction of the xy-plane. The xy-plane is nearly perpendicular to the direction of the director. Figure 8 shows that the layers of the smectic phase are liquid like.

CONCLUDING REMARKS

The nematic and the smectic phases were analyzed through computer simulation by the method of constant-pressure MD simulations modified for systems with anisotropic diffusions. We have confirmed that not only the nematic phase but also the smectic phase appear for systems of soft spherocylinders with short-range repulsive pair-potential. The simulation results of the orientational order parameter S fairly well agree with experiments and also with results obtained from different theoretical approaches. The anisotropic diffusion of liquid crystalline states has directly been observed by our simulations.

The model simulation of the present research seems effective in describing liquid crystalline phases, however, since the system size of the simulations of this paper is rather small, further systematic investigation is necessary.

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