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MOLECULAR DYNAMICS SIMULATIONS OF LIQUID CRYSTAL PHASE TRANSITIONS

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Abstract Phase transitions in a sequence of crystal(C)-smecticA(SmA)-nematic(N)-isotropic(I) phases are investigated by constant pressure molecular-dynamics (MD) simulations, in which the hydrostatic pressure is preserved. The present MD simulation uses a simple model that represents soft spherocylinders with both translational and orientational freedoms. This model enables us to investigate to what extent the properties known to real liquid crystal phases can be explained by the anisotropy of the molecular shape alone. The phase transitions are manifested not only in the macroscopic properties, such as enthalpy, but also in the microscopic properties as well. Anisotropic diffusion of molecules in liquid crystal phases is also investigated.

INTRODUCTION

It has been proven by many authors that, in the case of simple liquids, a wide range of structural and thermodynamic properties is determined primarily by the short-range repulsive force of the intermolecular interaction[1]. Molecular simulations have been indispensable in establishing the theory of simple liquids in that the simulations have made it possible to study separately each of the effects of repulsive and attractive forces working between the molecules.

In the study of complex liquids, similar approaches that stress the importance of the local packing and steric effects have been pursued by many authors, the seminal work being that of Onsager[3] in the field of liquid crystals (LCs). Recently, many studies based on molecular simulations with hard core anisotropic models have been reported[4], however, more work remains to be done to clarify to what extent a model with only the repulsive force can describe complex liquids. Systematic investigation using constant pressure MD simulations has not been done yet since it is difficult to obtain the hydrostatic equilibrium state when one simulates anisotropic molecules confined in a rigid simulation box.

The present study is concerned with constant pressure MD simulations of soft spherocylinders. To cope with the difficulties mentioned above we use such methods that allow the simulation box to change its shape in accord with the internal stress. This has made it possible to simulate the true equilibrium state under hydrostatic pressure from crystals to isotropic liquid, via LC phases by a single model.

MODEL AND METHODS

The model consists of a hard line of length L which is embedded inside a soft purely repulsive potential. The hard line of length L corresponds to the long axis of the molecule. The interaction between particles occurs at the nearest points (the ends of the vector giving the minimum distance $\mathbf{r}_{ij}$) between two long axes. The following pair potential determines the strength of the force;

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

where $|\mathbf{r}_{ij}|$ is the minimum distance between the long axes of particles i and j, and $r_0 = 2^{1/6}D$. This model, in effect, represents soft spherocylinders.

In simulating phase transitions of anisotropic molecules, it is most important to allow the simulation box to change its shape in accord with the internal stress, because the shape of the space occupied by a molecule changes during LC phase transitions. In the crystal phase, we use the method of Parrinello and Rahman[5] (PR) with a simulation box of fixed normal angles. For the LC phases, we use such methods that secure the system to be under hydrostatic pressure with a few hundreds of molecules[6]. Some problems encountered in simulating LC phases by PR method are discussed elsewhere.[6,7]

RESULTS

In this paper, we report results of constant pressure MD simulations of particle number $N = 672$ with length $L = 4$ at pressure $P^* = 1.0 \times 10^4$.

Crystal-SmecticA-Nematic Isotropic Phase Transition

First, we take an overall look at temperature dependence of the enthalpy per particle, averaged over $3 - 5 \times 10^5$ time-steps (Fig. 1). Enthalpy per particle is defined as $H/N = (U + PV)/N$ where the internal energy is calculated by $U = \sum_{i>j} \Phi(r_{ij})$. A jump in the value of enthalpy is recognized at each phase transition, showing the existence of first-order phase transition.

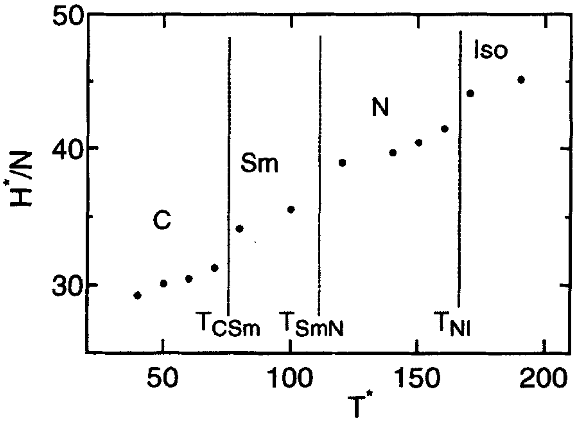

FIGURE 1 Enthalpy per molecule H^*/N versus temperature T^* which shows the phase transitions in the sequence of C-SmA-N-I phases.

Smectic Phase

A snapshot of the Sm phase is shown in Fig.2, which clearly reveals the smectic layers, although the structure is disturbed by the fluctuation of the particles.

Self-diffusion of LC molecules have been extensively studied in the past by various experimental methods.[8] In the nematic phase, the diffusion constant along the director $D_{\parallel}$ has been reported to be 1.2 – 4.0 times larger than the diffusion constant in direction perpendicular to the director $D_{\perp}$. Two types of anisotropic diffusions were reported in the smectic phase: (i) $D_{\parallel} > D_{\perp}$ [8,9] and (ii) $D_{\perp} \geq D_{\parallel}$ [8].

In MD simulations, diffusion is characterized by the values of mean-square-displacements (MSDs). The slope of MSD corresponds to the diffusion constant D. The MSD is defined as

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

where $\vec{r_i}(t)$ is the position of the i-th particle measured at time t. We observe the MSDs in three different directions, namely X, Y, Z. The director is parallel to the Z-direction.

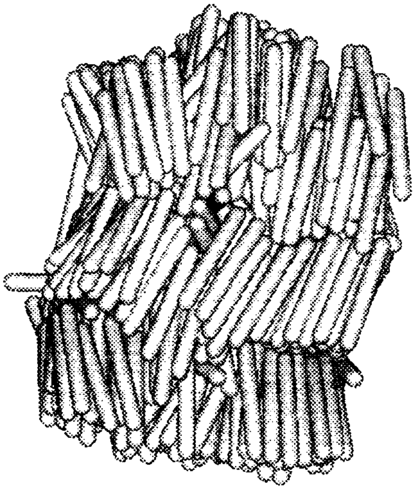

FIGURE 2 Snapshot of smectic phase at $T^* = 100$.

The MSDs in the smectic phase are shown in Fig.3. It can be seen from Fig.3 that the present model, with both translational and orientational freedoms, shows the anisotropic diffusion of type (i)$D_{\parallel} > D_{\perp}$. At lower temperatures (for instance at $T^* = 80$), the diffusion constants were nearly equal, $D_{\parallel} \simeq D_{\perp}$ (not shown). It is interesting to note that parallel soft spherocylinders with only translational freedom[6] have shown type (ii) diffusion,$D_{\perp} > D_{\parallel}$. This suggests that systems with a restrictive force for the rotational movement of molecules tend to show type (ii) diffusion.

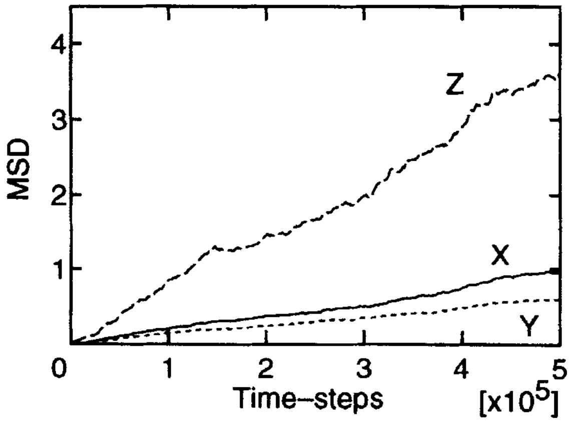

FIGURE 3 Mean-square-displacements in X, Y, and Z-directions of smectic phase at $T^* = 100$.

Nematic Phase

A snapshot and the MSDs of the N phase are shown in Figs.4 and 5, respectively.

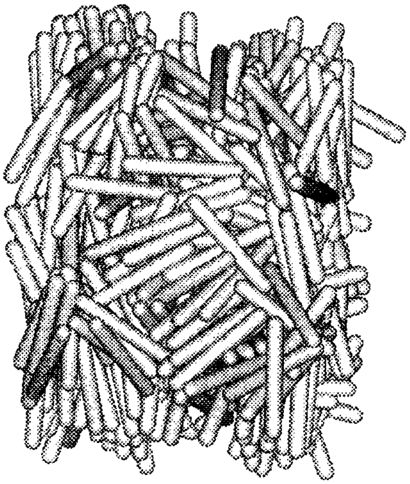

FIGURE 4 Snapshot of nematic phase at $T^* = 160$.

A comparison of Figs.3 and 5 indicates that the MSDs in the N phase and Sm phase are surprisingly similar, and the diffusion constants in the N phase are larger than those in the N phase. From Fig.5 we have the value of $D_{\parallel}/D_{\perp} = 3$, which is in agreement with experimental data[8].

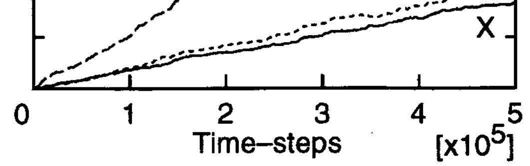

FIGURE 5 Mean-square-displacements in X, Y, and Z-directions of nematic phase at $T^* = 160$.

CONCLUDING REMARKS

We have performed constant pressure MD simulations under hydrostatic pressure to investigate to what extent a model that only account for the anisotropic shape of molecules (repulsion models) can be a reference system to real liquid crystals. The C-SmA-N-I phase transition was clearly recognized on both macroscopic and microscopic levels, the full account of which will be published elsewhere. A phase diagram showing the effects of anisotropy in the phase transitions will be reported in a future work.

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