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### SIMULATION STUDIES OF CRYSTAL-SMECTIC TRANSITION

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## Simulation Studies of Crystal-Smectic Transition

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To obtain the true thermodynamic equilibrium of systems of anisotropic molecules is difficult because of the complicated potential landscape. There is a high probability that simulated system may be caught in one of the many local minima. Especially, simulated systems of anisotropic molecules often yield anisotropic pressure under periodic boundary conditions. The situation is especially critical for high density phases such as crystal and smectic.

We discuss how to simulate the thermodynamic equilibrium under hydrostatic pressure, and investigate the properties of crystal-smectic transition.

**Keywords:** Molecular Dynamics Simulation; Crystal-Smectic phase transition

### INTRODUCTION

Molecular simulation is a powerful tool to investigate material properties. However, to obtain really useful results one must always be careful not to introduce artifacts by methodology commonly used in molecular simulations. In research of phase transitions, it is ex-

tremely important to search for the thermal equilibrium states, *i. e.* the global minima. On the contrary to the expectations, to obtain the desired thermal equilibrium state is not always so easy. Complex systems easily get trapped in local energy minima due to the complex energy landscape. Among many reasons for a system to get trapped in a local energy minima, the anisotropy of the pressure, exerted by the periodic boundary conditions or the simulation box, is one important factor in simulations of anisotropic molecules. Here, we investigate the crystal-smectic transition by paying attention that hydrostatic pressure is realized.

The present study is concerned with constant pressure MD simulations of freely rotating soft spherocylinders as a model of liquid crystals. This model enables us to investigate to what extent can the properties known to real LC phases be explained by the anisotropy of the molecular shape alone. 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 at high densities, such as crystal-smectic transition.

## MODEL AND METHODS

Soft spherocylinders are expressed in terms of a Kihara type potential[1], which interact through the minimum distance of the two bodies in interaction. The model consists of a hard line of length  $L$  as a core of the spherocylinder which is embedded inside a purely repulsive soft core. 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, which determine how the force exerted on the spherocylinder will be divided between rotational and

translational forces. The soft core is expressed by the following pair potential;

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

where  $|r_{ij}|$  is the minimum distance between the long axes of particles  $i$  and  $j$ , and  $r_0 = 2^{1/6}D$ . Reduced simulation units, where  $D = 1$ ,  $\epsilon = 1$ , and mass of particle  $m = 1$ , are used throughout this work.

The interactions among the spherocylinders we consider here are purely repulsive and short-range (cf. original Kihara potential includes attractive force) and the system is expected to share common characters with systems of hard spherocylinders. This expectation comes from the fact that systems of hard-core spheres share common properties with systems of soft-core spheres and can be scaled to each others[2]. In case where the rotation of the spherocylinders are hindered (complete orientational order), the scaling laws of soft-core spherocylinders including the  $L/D$  dependence of properties are discussed elsewhere[3].

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(PR)[4] with a simulation box of fixed normal angles[5]. In this method, the simulation box length in x, y, z-direction separately change in accord to the internal pressure. For simulating the smectic phase, PR method is too sensitive to the internal pressure change and fail. This is due to the fact that there exists a long time fluctuation of the pressure tensor in LC phases. So a longer time average of the pressure values must be used to change the simulation box length and shape. Several methods are proposed to overcome this problem[6]. Here we use a

method which temporary fix the length in one direction (z-direction in our case:  $L_z$ ), where the long time average of the pressure is taken to change the simulation box length in that direction. The other simulation box lengths  $L_x$  and  $L_y$  are freely changing their length according to temporary pressure change.

Two simulation methods mentioned above are implemented separately by two algorithms: (a) velocity Verlet algorithm with rotation treated by leap-frog algorithm for linear molecules and (b) Gear predictor-corrector algorithm (rotation treated as [7]).

## RESULTS

In this paper, we report results of constant pressure MD simulations of particle number  $N = 672, 2016$  with length  $L = 4$  at pressure  $P^* = 1.0 \times 10^4$ .

In Fig.1, we show volume per molecule versus temperature. Each symbol refers to different simulation method, algorithm or system size. In the crystal region, each run is independently started from complete orientation with stacked triangular lattice (ABC for  $N=672$ , ABAB for  $N=2016$ ). Each run are equilibrated for more than  $2.1 \times 10^6$  time steps, where  $dt=2.0 \times 10^{-6}$  or  $1.0 \times 10^{-6}$ . Near the phase transition, *i.e.*  $T^* \simeq 110$ , it takes a longer time until the systems seems to be in equilibrium, so many systems where ran up to  $3.1 \times 10^6$  time steps or even longer. We only use data where anisotropy in pressure (diagonal elements of stress tensor) are within 7%. Even though each data (except of  $T^* = 110$ ) in Fig.1 appeared to be in equilibrium and the physical properties seemed to be stable, they did not necessary reach thermal equilibrium and have been trapped in local minima. However, connecting the minima of  $V/N$  in each temperature give rise to quite a linear boarder, suggesting the thermal equilibrium line. When the system size is larger (symbols o

and  $\bullet$  are for  $N=2016$ ), many data (but not necessarily all) become closer to the lower boarder line. In principle, system size scaling to a infinite system size should be done for such minimum boarder to get a more precise evaluation of thermal equilibrium. We show tentative data for  $T^* = 110$ , since the system did not reach equilibrium within the time scale of calculations.

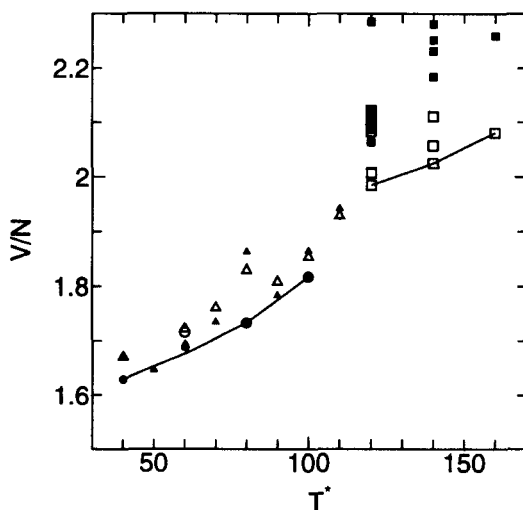


FIGURE 1 Volume per molecule  $V^*/N$  versus temperature  $T^*$  around the phase transition crystal-smectic for various methods and system size.

In Figs.2 through 5, we show properties around the crystal-smectic transition of the most reliable (energetically favorable with isotropic pressure) data.

In Figs.2 and 3, we plot the molecular length (occupied length per particle) in directions parallel and perpendicular to the director, respectively. Fig.2 shows that the layer thickness  $l_z$  is smaller in the smectic phase compared to that in the crystal phase, and show a jump near the phase transition. On the other hand, Fig.3 shows

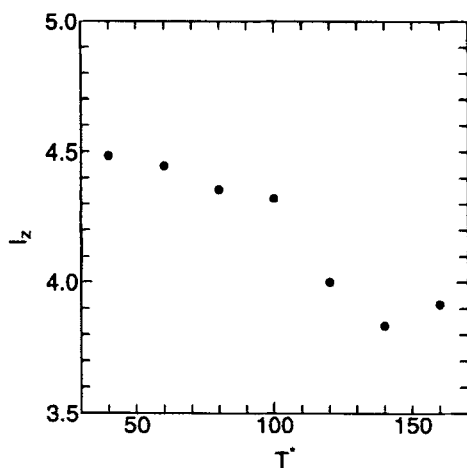


FIGURE 2 Layer thickness (length per molecule) in z-directions  $l_z$  which is parallel to the director on average.

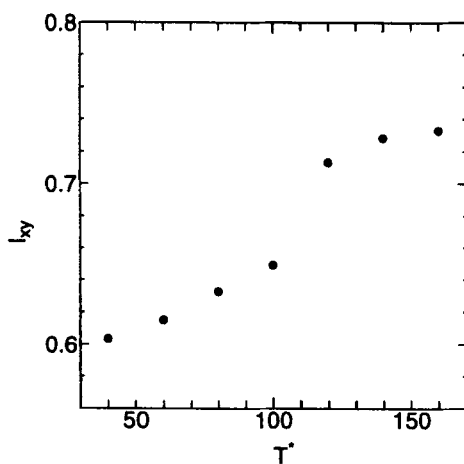


FIGURE 3 Length per molecule in xy-directions which is perpendicular to the director on average.



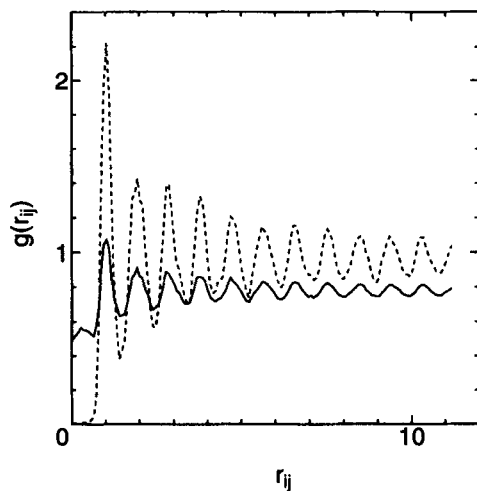


FIGURE 4 Orientational pair distribution function  $g_{\perp} = \langle P_2(\mathbf{l}(\mathbf{r}_1) \cdot \mathbf{l}(\mathbf{r}_2)) \rangle$  where  $\mathbf{l}(\mathbf{r})$  is orientation (unit vector) at  $\mathbf{r}$ , in crystal phase ( $T^* = 60$ ) for all particles (solid line), and inside the layer (dotted line).

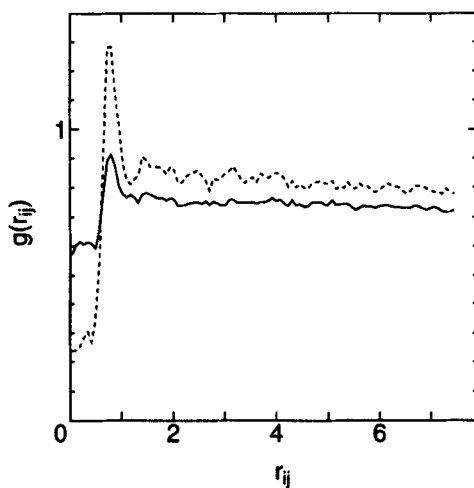


FIGURE 5  $g_{\perp}$  in smectic phase ( $T^* = 140$ )

that the molecular length in direction parallel to the layers increase as the temperature increase and show a jump near the phase transition. Figs.2 and 3 clearly indicate that anisotropic melting, where the layers expands in direction perpendicular to the director, occur for the crystal-smectic transition. Orientational pair distribution functions (Figs.4 and 5) show the crystalline nature and smectic nature of structures.

### CONCLUDING REMARKS

It has been shown that investigating thermal equilibrium at high densities of anisotropic molecules is a challenging task, since carefully conducted simulations can even be easily trapped in many local minima. The difficulties are enhanced by the anisotropy of the shape of the particles which easily lead to anisotropic pressure.

The necessity of the simulation box length to be adjustable to the internal stress is clearly demonstrated in the nature of anisotropic melting which occur at the crystal-smectic transition.

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