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CONSTANT PRESSURE MD SIMULATION METHOD

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By introducing an anisotropic factor in the cell dynamics of constant pressure molecular dynamics simulations, we dramatically reduce the artifacts related to cell shapes and overcome the difficulties of simulating anisotropic molecules under hydrostatic pressure. The method is especially effective for anisotropic liquids, such as smectic liquid crystals and membranes, however it can also be used for crystals and isotropic liquid as well. Crystal-smectic-nematic-isotropic phase transitions in systems of soft spherocylinders are observed.

Keywords: crystal-smectic phase transition; molecular dynamics simulation; smectic-nematic phase transition

INTRODUCTION

In contrast to crystals, smectic liquid crystals and membranes possess elasticity but only in the direction normal to the layers. The layer itself is liquid and only elastic under uniform compressive force. As liquids need a container to avoid spreading out, liquid crystals also need some support in the direction parallel to the layers to maintain the number of smectic layers. The layer thickness and compressibility depend on temperature, changing especially drastically near the phase transitions [1]. There is also a large difference in the time scales of fluctuations parallel and perpendicular to the layers in these systems. The above mentioned physical properties all contribute to the difficulty in simulating these anisotropic liquids. The temperature dependence of the layer thickness requires the simulation cell to change its shape not matching the periodicity of the cubic cell of Andersen's method [2]. When the periodicity of the smectic layers does not match the simulation cell, artifacts are introduced and as a result a uniform

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hydrostatic pressure is not achieved. The absence of elasticity in the direction parallel to the layers results in a large strain fluctuation in this direction, thus leading to the divergence of cell lengths in the Parrinello and Rahman (P & R) method developed for simulating crystals [3]. The large stain fluctuation itself is a natural phenomena; if the model truly reproduces liquid crystalline phases there should exist large differences in visco-elastic properties depending on the direction which lead to divergence of cell lengths in the P & R method [4]. Similar problems should even occur in the simulation of nematics, because of the large difference in visco-elastic properties depending on the direction whether it is parallel or perpendicular to the director. These problems readily appear in simple models where the internal degree of freedom is completely or partially frozen [5]. For atomistic models the appearance of these problems could be easily suppressed because many internal degrees of freedom exist which absorb the artificial effects caused by the simulation cell shape. There is also a possibility that the system is not simulated long enough for the problems to appear due to the time consuming calculation of atomic detailed models. In such circumstances, it is very difficult to be confident that simulations of realistic models are truly simulating the thermal equilibrium. In any case, we believe that the problems mentioned in this paragraph are common to all models of anisotropic molecules.

To do proper simulations of anisotropic liquid under hydrostatic pressure, the dynamics of the simulation cell must fulfill the following requirements which are contradictory to some extent; a) the simulation cell must be able to change shape and volume, b) the simulation cell must have some rigidity in shape to stop the anisotropic soft matter from spreading out. The latter requirement is necessary to avoid the system collapsing when the visco-elastic properties are strongly anisotropic. For instance, it is to avoid the smectic layers collapsing to one layer which is inconvenient under periodic boundary condition. Since the layer thickness depends on pressure and temperature, the requirement to change the cell shape remains even under constant volume. Methods to overcome these problems were suggested [6]; to keep certain simulation cell length constant in the P & R method for a sufficiently long time scale, long enough to meet the time scale of the stress fluctuations in those particular directions. Or to chose an appropriate cell shape instead of a cubic cell in Andersen's method. However, the suggested methods have serious drawbacks in that the appropriate cell lengths of shapes under hydrostatic pressure are not known a priori. Thus to obtain the true thermodynamic equilibrium, a series of simulations must be done. To use calculation sources effectively, an automatic algorithm which leads to the appropriate cell lengths and shape is urgently needed for the growing importance of anisotropic liquids, such as liquid crystals and membranes. We use the new method [7] to

overcome such difficulties and simulate the crystal-smectic-nematic-isotropic phase transitions.

SIMULATION METHOD

Instead of treating the edge lengths of the simulation cell separately as dynamical variables, here we chose two variables concerning the simulation cell, namely the anisotropic factor α and the isotropic volume factor Q. The volume V of the simulation cell is $V = \alpha Q$. For instance, if we consider simulating smectic liquid crystals it is natural to take $\alpha = L_z/L_{xy}$ and $Q = L_{xy}^3$, where L_z and L_{xy} are the cell lengths perpendicular and parallel to the smectic layers, respectively. The anisotropic factor α takes care of the layer compressibility (elasticity perpendicular to the layers) while the isotropic volume factor Q takes care of the bulk elasticity under isotropic compressive force. The kinetic energy of the cell is given by

$$K_{cell} = \frac{M}{2}\dot{V}^2 = \frac{M}{2}(\dot{\alpha}Q + \alpha\dot{Q})^2. \tag{1}$$

The coordinates $\mathbf{r}_i$ of the particles are related to the scaled coordinates $\mathbf{s}_i$ by $\mathbf{r}_i = \mathbf{H}\mathbf{s}_i = \{Q^{1/3}, Q^{1/3}, \alpha Q^{1/3}\}\mathbf{s}_i$. The Hamiltonian is

$$\mathcal{H} = \sum_{i=1}^{N} \frac{1}{2mQ^{2/3}}\left(\pi_{ix}^2 + \pi_{iy}^2 + \frac{\pi_{iz}^2}{\alpha^2}\right) + \sum_{j>i=1}^{N} \phi(\mathbf{H}\mathbf{s}_{ij}) + \frac{1}{4M}\left\{\left(\frac{\Pi}{\alpha}\right)^2 + \left(\frac{\Lambda}{Q}\right)^2\right\} + P_{ex}\alpha Q \tag{2}$$

Where $\Lambda = MQ(\alpha\dot{Q} + Q\dot{\alpha})$ and $\Pi = M\alpha(\alpha\dot{Q} + Q\dot{\alpha})$ are respectively the momentum conjugates to α and Q. The momentum conjugate to $\mathbf{s}_i$ is $\pi_i = m\{Q^{2/3}, Q^{2/3}, \alpha^2 Q^{2/3}\}\dot{\mathbf{s}}_i$. The final formula obtained by solving the Hamiltonian equations of motion are [7]:

$$\frac{d^2 s_{x,y}}{dt^2} = \sum_{j\neq i} \frac{\int_{ij}^{x,y}}{mQ^{1/3}} - \frac{2\dot{Q}}{3Q}\dot{s}_{x,y} \tag{3}$$

$$\frac{d^2 s_z}{dt^2} = \sum_{j\neq i} \frac{\int_{ij}^{z}}{m\alpha Q^{1/3}} - \frac{2\dot{Q}}{3Q}\dot{s}_z - 2\frac{\dot{\alpha}}{\alpha}\dot{s}_z \tag{4}$$

$$\frac{d^2\alpha}{dt^2} = \frac{\alpha}{2MV}(\mathcal{P}_z - P_{ex}) - \frac{\dot{\alpha}^2}{\alpha} \tag{5}$$

$$\frac{d^2Q}{dt^2} = \frac{Q}{2MV}(\mathcal{P} - P_{ex}) - \frac{\dot{Q}}{Q} \tag{6}$$

Where $\mathbf{f}_{ij} = -\partial\phi/\partial\mathbf{r}_{ij}$, $\mathcal{P}_z = \left(\Sigma_{i=1}^{N} m\dot{r}_{iz}^2 + \Sigma_{j>i=1}^{N} f_{ij}^z r_{ij}^z\right)/V$ and $\mathcal{P} = \{\Sigma_{i=1}^{N} m \cdot \left(\dot{r}_{ix}^2 + \dot{r}_{iy}^2 + \dot{r}_{iz}^2\right) + \Sigma_{j>i=1}^{N} \mathbf{f}_{ij} \cdot \mathbf{r}_{ij}\}/3V$. The equation of motion for the volume V

$$\frac{d^2V}{dt^2} = \frac{1}{M}(\mathcal{P} - P_{ex}) = \frac{1}{M}(\mathcal{P}_z - P_{ex}). \tag{7}$$

Thus, at equilibrium $\langle\ddot{V} = 0\rangle$, the virial theorem $\langle\mathcal{P} - P_{ex}\rangle = 0$ and hydrostatic pressure $\langle\mathcal{P}_{xy}\rangle = \langle\mathcal{P}_z\rangle = P_{ex}$ will be satisfied automatically (where $P_{xy} = (P_x + P_y)/2$). The new method introduces an anisotropic factor α which is intended to treat the large difference in visco-elastic properties in two directions: *i.e.* parallel and perpendicular to the smectic layers or membranes. In the case of nematics, α takes care of the differences in visco-elastic properties parallel and perpendicular to the orientational director.

When simulating anisotropic liquids under constant volume, an anisotropic factor α can be introduced similarly to the cell dynamics [7].

MODEL AND RESULTS

We report simulation results for systems of soft spherocylinders which are known to give the phase sequence of crystal-smectic LC-nematic LC-isotropic liquids. The model of soft spherocylinders is of the kihara type [8]. They interact through the vector of minimum distance $\mathbf{R}_{ij}$ between the hard lines representing the long axis core of the spherocylinders i and j [9]. The soft core is purely repulsive and expressed by the follsing pair potential energy between particles i and j;

$$\Phi_{ij} = \begin{cases} \epsilon\left[\left(\frac{D}{\mathbf{R}_{ij}}\right)^{12} - \left(\frac{D}{\mathbf{R}_{ij}}\right)^{6} + \frac{1}{4}\right] & \text{if } \left|\mathbf{R}_{ij}\right| < r_0 \\ 0 & \text{otherwise} \end{cases} \tag{8}$$

where $r_0 2^{1/6} D$. The force $\mathbf{f}_{ij} = -\partial\Phi_{ij}/\partial\mathbf{R}_{ij}$ acts at each end of $\mathbf{R}_{ij}$ which is divided in rotation and translation forces correctly reflecting the geometry of the particles. Thus, the kinetic energy is interchanged freely among translational and rotational degrees of freedom and express the correct dynamics of spherocylinders. Reduced simulation units, where $D = 1$, $\epsilon = 1$, and mass of particle $m = 1$, are used throughout this work. Two separate programs with different algorithms were implemented: (a) velocity

Verlet algorithm with special treatment of rotation for linear molecules [10] and (b) Gear predictor-corrector algorithm (rotation treated as [11]).

Here, we report results of constant pressure MD simulations of particle number $N = 2016$, with length $L^* = 3$ at pressure $P^* = 1.0 \times 10^4$. In the crystal region, each run is independently started from completely oriented particles with stacked triangular lattices (ABAB for N = 2016). Each run was equilibrated for 2.3×10^6 to 6.2×10^6 time steps and then averaged over 4×10^5 times steps to obtain physical properties, where the time step is $dt^* = 1.0 \times 10^{-6}$.

Figure 1 shows the preliminary temperature dependence of the volume per molecule. Note that Figure 1 includes some data which might not have reached final equilibrium values. The phases are determined not only from the macroscopic physical properties, but also the microscopic and dynamic properties, such as the mean square displacements. It can be discerned form Figure 1 that not only the transition between the crystal and smectic but also the smectic-nematic transition is clearly a first order transition. The smectic-nematic transition of soft spherocylinders were suggested to be first order in [9], however this was not determined precisely. The jump in V/N at the nematic-isotropic transition is small for these preliminary

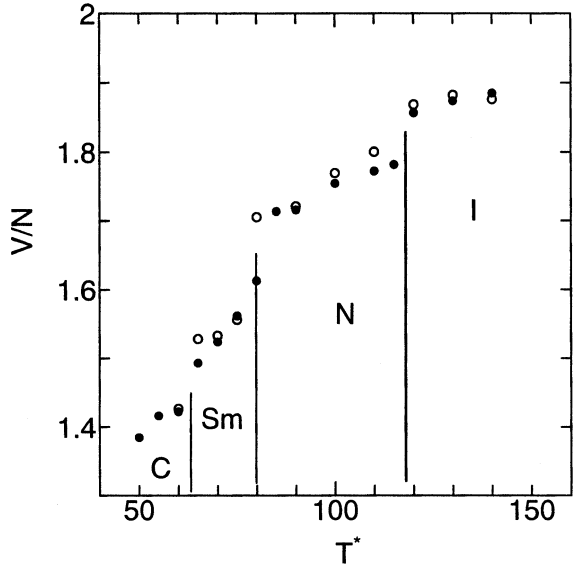

FIGURE 1 Volume per molecule V^*/N versus temperature T^* including preliminary data. The symbols ○ and ● denote, respectively, data obtained from algorithms (a) and (b). The regions of crystal, smectic, nematic and isotrophic liquid are shown by *C*, *Sm*, *N* and *I* respectively.

data, however we confirm from the mean square displacements that the diffusion in directions parallel and perpendicular to the director is nearly the same above $T^* = 120$, *i.e.* isotropic.

Figure 2 shows the temperature dependence of the orientational order parameter S_2 (○ and ●) and McMillan's order parameter $\sigma = \langle \cos(2\pi z_{ij}/d)(3\cos^2\theta_{ij} - 1)/2 \rangle$ (open and closed ◇), where z_{ij} is the distance in the direction normal to the layers [12]. In the smectic region σ remains, while in the nematic region $\sigma = 0$.

Figure 3 shows the pair distribution function parallel and perpendicular to the director near the crystal-smectic transition. The pair distribution functions in the parallel direction $g_{\parallel}$ show well confined layers for crystal ($T^* = 60$) while the smectic layers are more loose ($T^* = 65$). The pair distribution functions in the perpendicular direct ion $g_{\perp}$ are quantitatively different for the two curves. In the crystal region ($T^* = 60$), the modulation of $g_{\perp}$ continues for a long distance, while in the smectic region ($T^* = 65$), only the first and second peaks are clear.

Figure 4 shows the pair distribution function parallel and perpendicular to the director near the smectic-nematic transition. Note that the temperature difference for the two curves is quite small ($\Delta T^* = 5$). The density curve $g_{\parallel}$ almost disappears after the macroscopic physical quantities, such

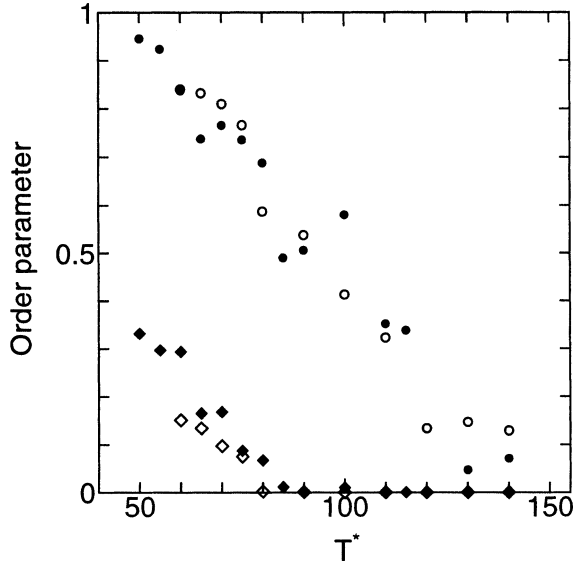

FIGURE 2 Orientational order parameter S_2 (circles) and order parameter σ (diamonds) versus temperature T^*. Open and solid symbols respectively denote data obtained from algorithms (a) and (b).

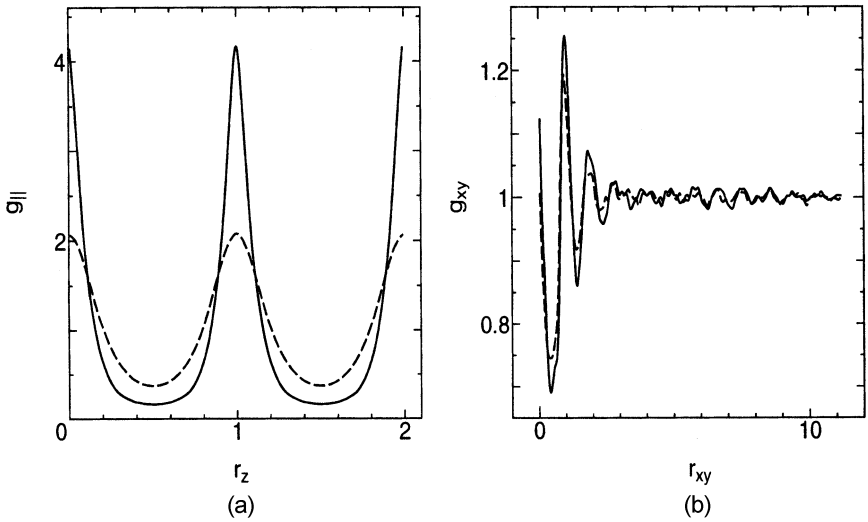

FIGURE 3 Pair distribution functions (a) parallel and (b) perpendicular to the average molecular orientation around the crystal-smectic transition. The solid curve denotes the density wave at $T^* = 60$ (Crys), and the broken curve at $T^* = 65$ (Sm).

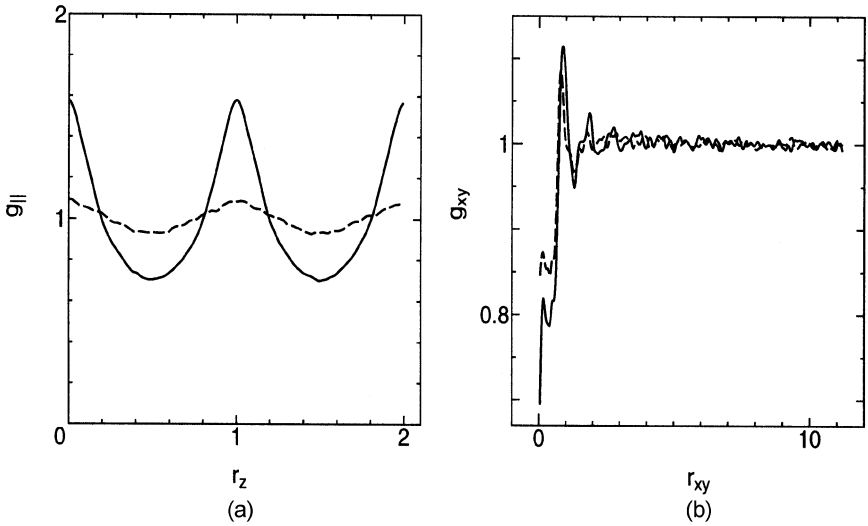

FIGURE 4 Pair distribution functions (a) parallel and (b) perpendicular to the average molecular orientation around the smectic-nematic transition. The solid curve denotes the density wave at $T^* = 80$ (Sm), and the broken curve at $T^* = 85$ (N).

as volume or enthalpy, show a jump. The pair distribution functions in the perpendicular direction $g_\perp$ are not so different for the two temperatures. The small peak before the first large peak is a consequence that the pair distribution function $g_\perp$ is a projection to the plane perpendicular to the director.

CONCLUDING REMARKS

By using a new method developed to simulate anisotropic liquids under constant pressure, we have investigated the crystal-smectic-nematic-isotrophic phase transitions for systems of soft spherocylinders of $L^* = 3$. Not only the crystal-smectic transition, but also the smectic-nematic transition is of first order. Investigation of the dependence of the phase diagram on the anisotrophy of the soft spherocylinders will be conducted in the near future.

REFERENCES

[1] Yamamoto, J. & Okano, K. (1991). *Jpn. J. Appl. Phys.*, *30*, 754.
[2] Anderson, H. C. (1980). *J. Chem. Phys.*, *72*, 2384.
[3] Parinello, M. & Rahman, A. (1980). *Phys. Rev. Lett.*, *45*, 1196.
[4] (a) Parinello, M. & Rahman, A. (1981). *J. Appl. Phys.*, *52*, 7182.
(b) (1982). *J. Chem. Phys.*, *76*, 2662.
[5] Aoki, K. M. (1993). PhD Dissertation, (Keio University).
[6] Aoki, K. M. & Yonezawa, F. (1992). *Phys. Rev. A*, *46*, 6541.
[7] Aoki, K. M., Yoneya, M., & Yokoyama, H. (2003). *J. Chem. Phys.*, *120*, 5876.
[8] Kihara, T. (1953). *Rev. Mod. Phys.*, *25*, 831.
[9] (a) Aoki, K. M. & Sakiyama, T. (1995). *Mol. Cryst. Liq. Cryst.*, *262*, 543.
(b) (1996). *Mol. Sim.*, *16*, 99.
(c) (1997). *Mol. Cryst. Liq. Cryst.*, *299*, 45.
(d) (2001). *Mol. Cryst. Liq. Cryst.*, *366*, 117.
[10] Allen M. P. & Tildesley, D. J. (1987). *Computer Simulation of Liquids*, Oxford Science Publications.
[11] Cheung, P. S. Y. & Powles, J. G. (1975). *Mol. Phys.*, *30*, 921.
[12] McMillan, W. L. (1972). *Phys. Rev. A*, *6*, 936.