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Constant pressure molecular dynamics simulations of the crystal–smectic transition in systems of soft parallel spherocylinders as a model for liquid crystals

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We present the results of constant pressure molecular dynamics simulation under hydrostatic pressure for soft parallel spherocylinders. A clear first order transition from crystal to smectic phase is observed. The anisotropy of the molecular volume plays an important role in this transition. We study the anisotropy of the diffusion process in the smectic phase by the mean-square displacement in each direction. Also the structures before and after the transition are analysed by means of the pair distribution functions.

1. Introduction

Molecular dynamics (MD) computer simulations are now an established method for analysing microscopic structures and have the advantage over theoretical approaches such as mean field approximations, that the MD techniques do not involve any uncontrolled approximations once the interactions among the molecules are given.

The early MD simulations of anisotropic particles of Robertus and Sando did not show any liquid crystal phase for hard spherocylinders [1]. In 1987, Stroobants, Lekkerkerker and Frenkel studied a system of parallel spherocylinders by Monte Carlo (MC) simulations and ascertained that the smectic phase, which was widely believed to be realizable only in the presence of an attractive force, can also be formed by hard core repulsion [2]. In 1990, Veerman and Frenkel extended this work to a system of hard spherocylinders with full orientational freedom and carried out constant volume MD simulations after preparing well equilibrated configurations by MC simulations and observed stable nematic and smectic phases [3]. This work shows that the introduction of orientational freedom increases the anisotropy necessary to exhibit the smectic phase when compared to the system with molecules constrained to be parallel to each other.

In order to investigate the crystal-smectic transition, we present the results of constant pressure MD simulation under hydrostatic pressure for soft parallel spherocylinders. We show that the anisotropy of the molecular volume plays an important role in this transition. To investigate the anisotropy of the diffusion processes in the smectic phase, we observe the mean square displacement in each direction. Structural analysis is performed in terms of the pair distribution functions, both parallel and perpendicular to the molecular axis. In both diffusion and structural analysis, a clear difference is observed between crystalline and smectic phases.

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2. Model and methods

Systems of soft-core parallel spherocylinders (cylinders with length L and diameter D, capped at each end with hemispheres of the same diameter) were adopted as our model to understand physical properties of liquid crystals which can be described by repulsive force alone. The long axes of the molecules are fixed to the z axis of the MD simulation box. We use a potential defined by

$$\phi(d_{ij}) = \varepsilon\left(\frac{D}{r_{ij}}\right)^n \quad \begin{cases} -L < z_{ij} < L\colon & d_{ij}^2 = x_{ij}^2 + y_{ij}^2, \\ \text{otherwise:} & d_{ij}^2 = x_{ij}^2 + y_{ij}^2 + (|z_{ij}| - L)^2, \end{cases} \tag{1}$$

where r_{ij} is the distance between ith and jth molecule, i.e. $r_{ij} = |\mathbf{r}_{ij}| = |\mathbf{r}_i - \mathbf{r}_j|$, $\mathbf{r}_i$ and $\mathbf{r}_j$ being respectively the positional vectors of the ith and jth molecule; x_{ij}, y_{ij} and z_{ij} are respectively the x, y and z components of $\mathbf{r}_{ij}$. The inverse power of the potential n is 14 in our model. We take the unit of energy as ε and the unit of length as D. The ratio L/D is fixed at unity for these simulations, so the anisotropy of the molecule $[L/D+1]$ is 2. Since the effective diameter of the molecule in soft-core potentials depends on temperature (or density) we must be careful that the effective anisotropy differs depending on the temperature, unlike the hard spherocylinders.

We perform constant pressure MD simulations in several ways. To simulate the actual environment under hydrostatic pressure, we apply the method of Andersen [4], as well as the method of Parrinello and Rahman [5], to a right parallelepiped simulation box. For the details of the simulation methods, the reader should refer to our former paper [6].

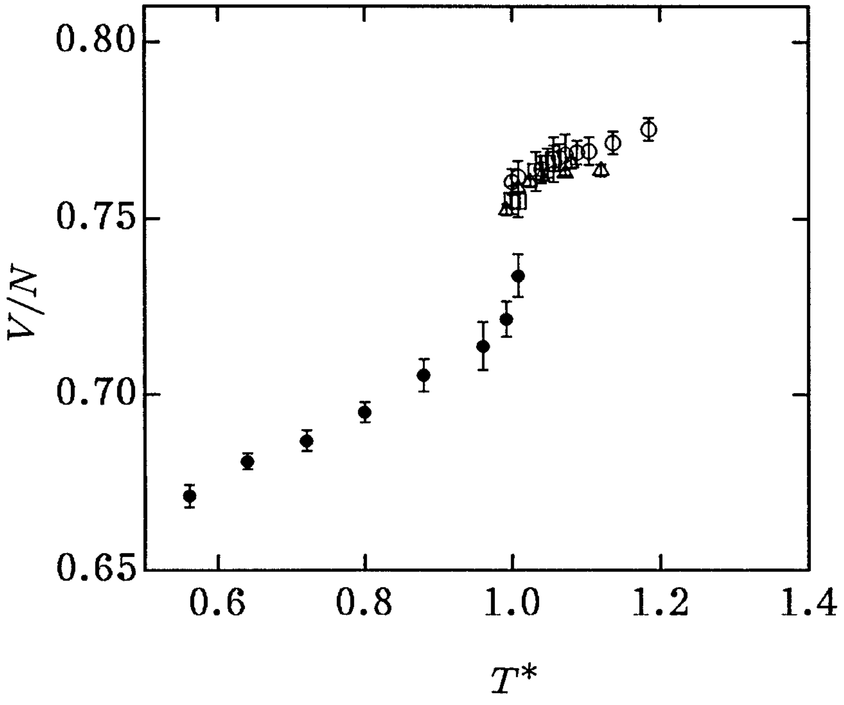

Figure 1. Specific volume V/N as a function of reduced temperature T^* for system size $N = 600$. Each symbol denotes different methods [6].

3. Results

In this article, we report the result for systems with $N=600$ molecules. All the properties we observe in this paper are the averages of the last 1000 time steps of each simulation run, which consists of more than 5000 time steps.

We first see the specific volume V/N drawn against the reduced temperature $T^*=T/T_m$, where T_m is the melting temperature (see figure 1). Each symbol specifies different methods [6]. We observe a clear first order transition.

It is interesting to see the anisotropy of the specific volume associated with each molecule. We define the specific length parallel $l_{\|}$ and perpendicular $l_{\perp}$ to the molecular axis as $l_{\|}=L_{\|}/(\text{number of layers})$ and $l_{\perp}=(L_{\perp}/n_{\perp})^{1/2}$, where $L_{\|}$ and $L_{\perp}$ are the edge length of the simulation box parallel and perpendicular to the molecular axis and $n_{\perp}=N/(\text{number of layers})$. The ratio $l_{\|}/l_{\perp}$ serves as a measure for the anisotropy of the space required for each molecule, say the molecular volume. From figure 2 we see that in the region we study, the anisotropy of the molecular volume $l_{\|}/l_{\perp}$ is larger than the anisotropy of the molecule $(L/D+1=2)$. In the crystal region, the value $l_{\|}/l_{\perp}$ decreases as the temperature approaches the melting temperature. After the jump at the melting temperature, it becomes quite constant in the smectic region. From this fact, we understand how fatal it is to fix the shape of the simulation box for simulating anisotropic molecules.

We check the diffusion process after the system melts by analysing the mean-square displacement in each direction. In figure 3, we show the mean-square displacement at $T^*=1{\cdot}12$ for the direction perpendicular (solid curve; x-direction and dashed curve: z direction) to the molecular axis. We can see from this figure that the molecules diffuse mainly along the direction perpendicular to the molecular axis (along the layers) which is the characteristic of the smectic liquid crystal phases.

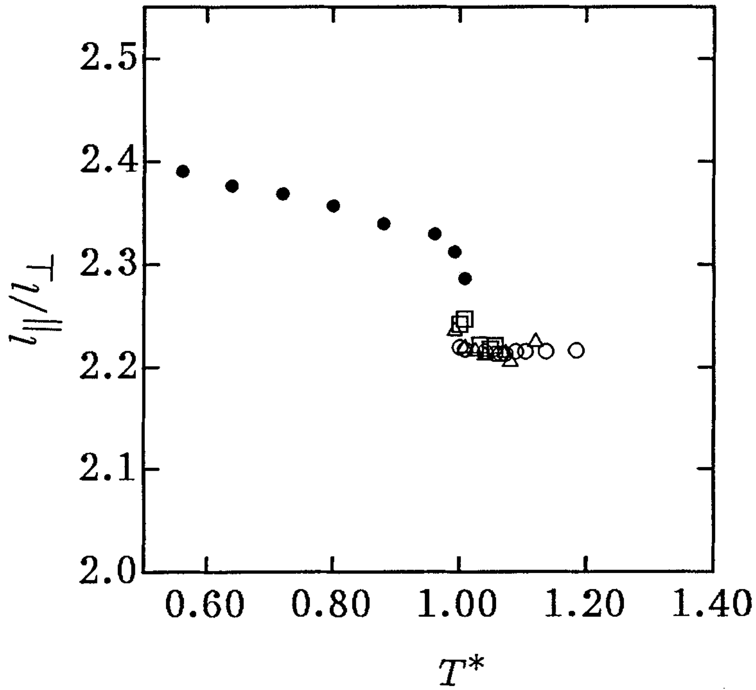

Figure 2. Anisotropy of the molecular volume $l_{\|}/l_{\perp}$ versus reduced temperature T^* for $N=600$.

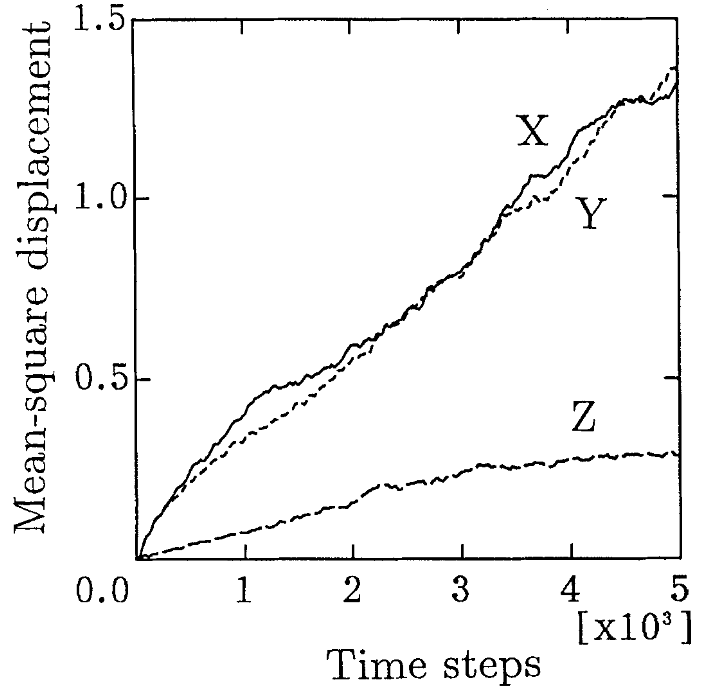

Figure 3. Mean-square displacement of a system of $N = 600$ soft, parallel spherocylinders at $T^* = 1{\cdot}12$. The solid curve (x direction) and the dashed curve (y direction) denote the diffusion along the layers. The broken curve (z direction) denotes the diffusion in the direction of the molecular axis.

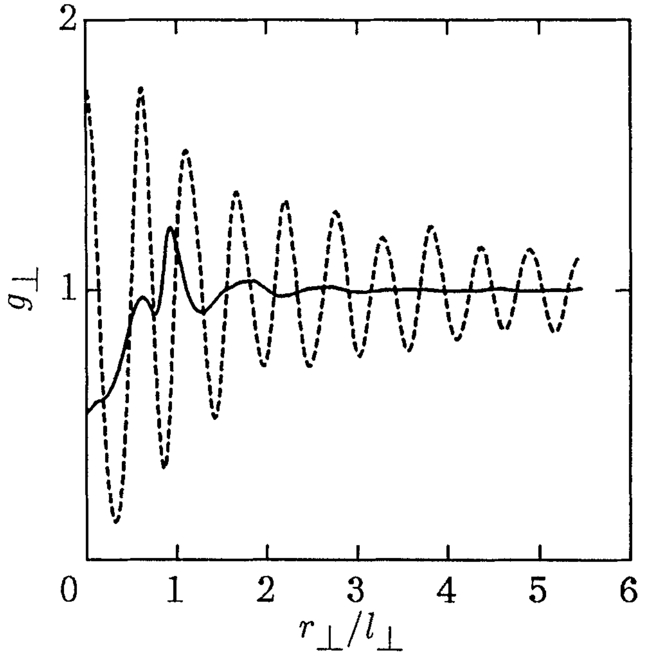

Figure 4. Total pair distribution function $g_\perp$ along the direction perpendicular to the molecular axis as a function of the distance $r_\perp/l_\perp$ at $T^* = 0{\cdot}64$ (dashed line) and $T^* = 1{\cdot}12$ (solid line).

In order to investigate the final configuration in each phase, crystalline and smectic, we calculate average pair distribution functions in directions parallel ($g_{\parallel}$) and perpendicular ($g_{\perp}$ and $g'_{\perp}$) to the molecular axis. We show in the following figures the data at $T^* = 0{\cdot}64$ (dashed line) and $T^* = 1{\cdot}12$ (solid line). We mainly discuss the structure of the liquid crystal phase here. For a precise study of the crystalline solid please to refer to our paper [6].

The total pair distribution function which is defined by the projected value of $\mathbf{r}_{ij}$ into the xy plane is shown in figure 4. The distance $r_{\perp}$ is measured in units of the specific length $l_{\perp}$. It must be noted that $l_{\perp}$ is 7 per cent larger at $T^* = 1{\cdot}12$ than the value $l_{\perp}$ at $T^* = 0{\cdot}64$. A strong correlation is observed in the crystal region (dashed line). In the smectic region, the dip at $r_{\perp}/l_{\perp} = 0$ and the small hump at $r_{\perp}/l_{\perp} = 0{\cdot}63$ in this figure indicates that the molecules are diffusing in a manner that retains some vestiges of the packed stacking of adjacent layers. As can be seen from figure 4, there exists no correlation between the molecular configuration of two distant layers.

For the purpose of studying the molecular structure within a layer, we define that two molecules are in the same layer when $-L/2 \leqslant dz_{ij} \leqslant +L/2$, and then we calculate the in-layer pair distribution function $g'_{\perp}$ as a function of $r_{\perp}/l_{\perp}$ for which the molecules only in the same layer are counted (see figure 5). Figure 5 shows that a clear crystalline structure (dashed line) of a two dimensional close packed lattice melts in layers with no clear positional correlation (solid line).

Figure 6 describes the pair distributions in the direction parallel to molecular axis $g_{\parallel}$ as a function of $r_{\parallel}/l_{\parallel}$ where $r_{\parallel}$ is the distance in the direction parallel to the molecules in units of the specific length $l_{\parallel}$ of the MD simulation box. From this figure we can see that the system has a periodic layer structure even after the melting temperature.

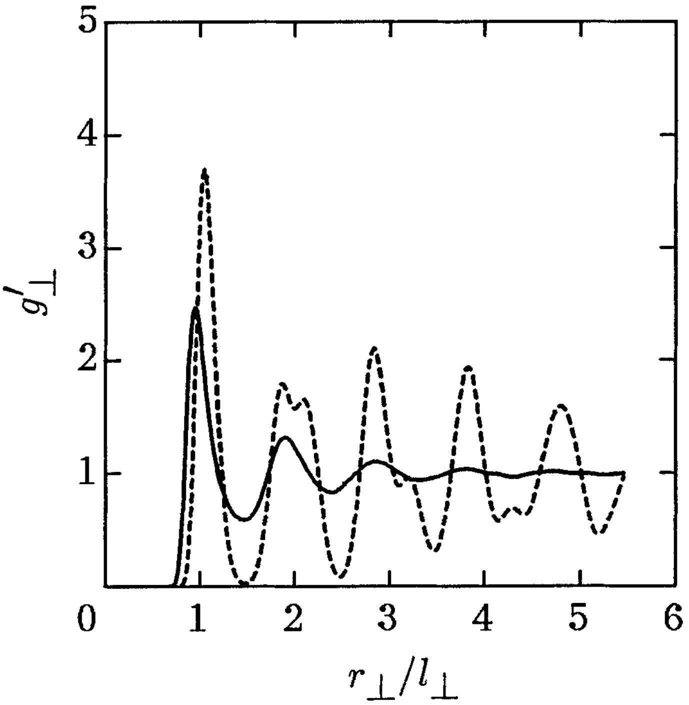

Figure 5. Pair distribution function $g'_{\perp}$ of molecules in the same layers versus $r_{\perp}/l_{\perp}$ at $T^* = 0{\cdot}64$ (dashed line) and $T^* = 1{\cdot}12$ (solid line).

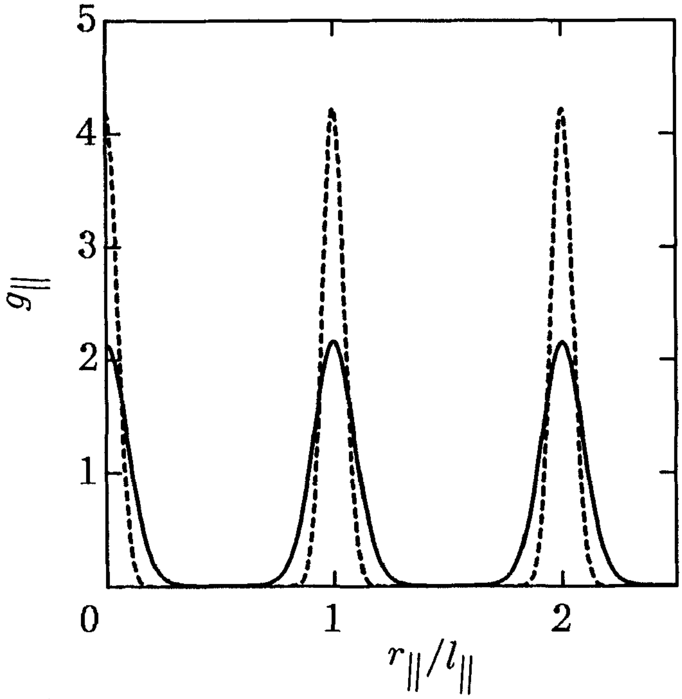

Figure 6. Pair distribution function $g_{\parallel}$ in the direction parallel to the molecular axis as a function of distance $r_{\parallel}/l_{\parallel}$ at $T^* = 0{\cdot}64$ (dashed line) and $T^* = 1{\cdot}12$ (solid line).

4. Concluding remarks

In order to reveal the nature of the crystalline solid phase and smectic liquid crystal phase formed by anisotropic molecules with repulsive interactions alone, constant pressure MD computer simulations under hydrostatic pressure in systems of soft, parallel spherocylinders has been performed. We have studied the properties around the crystal–smectic transition. It has been shown that the anisotropy of the molecular volume plays an important role in this transition. In the smectic phase, the mean-square displacement and the pair distribution functions show that the molecules in a layer diffuse in a manner that retains some vestiges of the packed stacking of adjacent layers.

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