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Effect of Addition of Hard Spheres to the Smectic-A Phase of Parallel Hard Spherocylinders

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Constant pressure Monte Carlo simulation is used to discuss the structure of binary mixtures of parallel hard spherocylinders and hard spheres. Results of the simulation indicate that the smectic layer periodicity is stretched when we add the spheres to the smectic-A phase of the spherocylinders.

Keywords: smectic-A phase; Monte Carlo simulation; microphase separation; spherocylinder

INTRODUCTION

Structures of mesomorphic phases are determined by interactions between molecules which compose the system. Two electrically neutral molecules separated far enough attract each other due to dispersion force. When the two molecules come close, they are repulsive due to overlap between the clouds of electrons around molecular cores.

Importance of repulsive force between molecules for the liquid crystalline structures has been notified at first by Onsager whose theory examined isotropic-nematic phase transition of the system of hard rod-like molecules[1]. His theory indicates that long rod-like hard core molecules can stabilize the nematic phase without attractive interaction.

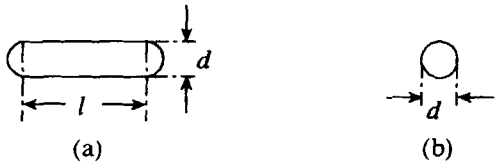

FIGURE 1 A spherocylinder (a) and a sphere (b).

The existence of smectic-A phase without attractive interaction has been also indicated by experiments[2], simulations[3-6] and theories[7-9].

Among the models of hard repulsive molecules, there are the systems of hard spherocylinders. One component system of them is known to show the nematic phase and smectic-A phase as liquid crystalline phases[3-6].

In this study we consider a binary mixture of parallel hard spherocylinders and hard spheres. We discuss the effect of addition of hard spherical molecules to the smectic-A phase of the hard spherocylinders.

MODEL AND SIMULATION

Model System

The binary system of the present study consists of parallel hard spherocylinders and hard spheres. The spherocylinder is a cylinder each end of which is capped with a hemisphere. In Fig. 1, we show a spherocylinder and a sphere. As described in Fig. 1, we denote length of the cylinder by l and diameter by d. For the present case, the sphere also has diameter d which is the same with the diameter of the cylinder. We assume for simplicity that the long axes of all the cylinders are aligned parallel to z-direction. This assumption neglects fluctuations of directions of the cylinders.

The shape of the cylinder is characterized by length to diameter ratio $q = l/d$. Because the pure system of the spherocylinders with $q = 5$ has been well studied by computer simulations[3,4], we also choose $q = 5$ for the present binary system.

Intermolecular force for the present model molecules is hard core

repulsion. Then the potential energy u between two molecules are expressed as

$$u = \begin{cases} \infty, & \text{if cores of the two molecules intersect,} \\ 0, & \text{otherwize.} \end{cases} \quad (1)$$

Simulation

We have performed constant pressure Monte Carlo(MC) simulation for the present system. Simulation procedure is the same with our previous work [10], which follows the simulation method used by Stroobants, Lekkerkerker and Frenkel to obtain equilibrium structures of the pure system of parallel spherocylinders[3]. We denote number of spherocylinders in the system by N_c and number of spheres by N_s.

The simulation starts with constructing an initial state. At first closed packed lattice of aligned N_c+N_s spherocylinders, which take ABC-stacking along the alignment direction, is expanded uniformly to the volume which is five times the volume of the closed packed volume. After this expansion, randomly chosen N_s spherocylinders are changed to spheres. Then we have a binary mixture of N_c spherocylinders and N_s spheres with which we start the MC simulation.

Unit MC step consists of $N_c + N_s$ trials of uniform random displacements of randomly chosen molecules and trials to change the system volume under constant pressure. The maximum displacements of molecular positions and the system volume are adjusted during the simulation as acceptance ratios of the trials are kept around 30 to 40 percent.

We denote the system size along x-, y-, and z-direction by L_x, L_y and L_z, respectively.

For the Metropolis trials of the present simulation, there are two types of volume changes. One is a change along z-direction to which we take the alignment axis of the cylinders. The other is a simultaneous change along x- and y- direction. For each type of change, we generate random uniform displacement ΔV of the system volume. The change along z-direction is done by change in L_z: $L_z \to L_z + \Delta L_z$, where ΔL_z is given by $\Delta L_z = \Delta V/(L_x L_y)$. The simultaneous change along x- and y-direction, $L_x \to L_x + \Delta L_x$ and $L_y \to L_y + \Delta L_y$, is given by $\Delta L_x = \alpha L_x$ and

$\Delta L_y = \alpha L_y$, where

$$\alpha = -1 + \sqrt{1 + \frac{\Delta V}{V}}. \tag{2}$$

With these procedures, the ratio L_x/L_y is kept unchanged, while L_z is changed independently.

When $\Delta V \geq 0$, the allowance of the change is determined due to transition probability $\exp[-p\Delta V/(k_B T)]$, where k_B is Boltzmann's constant, T temperature and p pressure. The change with $\Delta V < 0$ is not allowed when it makes pair molecules which intersect to each other and it is otherwise allowed.

Definitions of Pair Distribution Functions

For analyses, we have calculated following pair distribution functions. We denote the position of j-th spherocylinder and the position of the k-th sphere by (x_{cj}, y_{cj}, z_{cj}) and (x_{sk}, y_{sk}, z_{sk}), respectively. Longitudinal pair distribution functions for the present study are defined as

$$g_{\parallel}^{cc}(z) = \frac{V}{2N_c N_c L_x L_y} \sum_{j=1}^{N_c} \sum_{\substack{k=1 \\ j \neq k}}^{N_c} \delta(z - |z_{cj} - z_{ck}|), \tag{3}$$

$$g_{\parallel}^{cs}(z) = \frac{V}{2N_c N_s L_x L_y} \sum_{j=1}^{N_c} \sum_{k=1}^{N_s} \delta(z - |z_{cj} - z_{sk}|), \tag{4}$$

$$g_{\parallel}^{ss}(z) = \frac{V}{2N_s N_s L_x L_y} \sum_{j=1}^{N_s} \sum_{\substack{k=1 \\ j \neq k}}^{N_s} \delta(z - |z_{sj} - z_{sk}|), \tag{5}$$

where $\delta(z)$ is the Dirac δ function. Transverse distribution functions are defined as

$$g_{\perp}^{cc}(r) = \frac{V}{4N_c N_c \pi r h} \sum_{j=1}^{N_c} \sum_{\substack{k=1 \\ j \neq k}}^{N_c} \delta(r - \sqrt{(x_{cj} - x_{ck})^2 + (y_{cj} - y_{ck})^2}) \times H(h - |z_{cj} - z_{ck}|), \tag{6}$$

$$g_{\perp}^{cs}(r) = \frac{V}{4N_c N_s \pi r h} \sum_{j=1}^{N_c} \sum_{k=1}^{N_s} \delta(r - \sqrt{(x_{cj} - x_{sk})^2 + (y_{cj} - y_{sk})^2}) \times H(h - |z_{cj} - z_{sk}|), \tag{7}$$

$$g_{\perp}^{ss}(r) = \frac{V}{4N_sN_s\pi rh}\sum_{\substack{j=1\\ j\neq k}}^{N_s}\sum_{k=1}^{N_s}\delta(r-\sqrt{(x_{sj}-x_{sk})^2+(y_{sj}-y_{sk})^2}) \times H(h-|z_{sj}-z_{sk}|), \quad (8)$$

where $H(x)$ is the Heaviside function which has values $H(x) = 0$ for $x \leq 0$ and $H(x) = 1$ for $x > 0$, and h is a depth along z-direction, molecules within which depth are taken into account for the calculation of transverse distribution functions. In the present study, we take $h = l$.

Superscript 'cc' indicates spherocylinder-spherocylinder pair distribution, 'cs' spherocylinder-sphere and 'ss' sphere-sphere.

RESULTS

Equilibration of the System

The equilibrium structure of the present system depends on the length to diameter ratio q, pressure p and molar fraction of the spheres

$$X = \frac{N_s}{N_c + N_s}. \quad (9)$$

In the present study, we fix pressure p as

$$\frac{pd^3}{k_BT} = 0.6. \quad (10)$$

In this subsection we show results obtained from a simulation for the system of $N_c = 1152$ and $N_s = 288$, which give the molar fraction of the spheres $X = 0.2$.

We define packing fraction η of the system as

$$\eta = \frac{N_cv_c + N_sv_s}{V}, \quad (11)$$

where $v_c = (\pi d^2 l/4) + (\pi d^3/6)$ is volume of the cylinder, and $v_s = \pi d^3/6$ is volume of the sphere. The packing fraction η is a fraction of volume occupied by molecules to the system volume.

The packing fraction of the closed packed system η_c depends on the molar fraction X of the spheres. Hence we denote it by $\eta_c(X)$. The pure

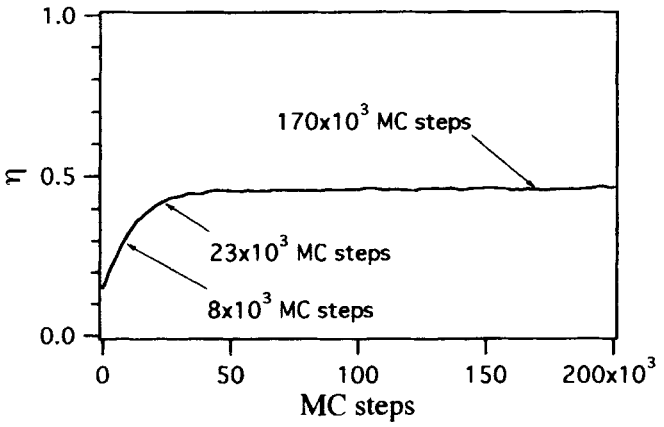

FIGURE 2 Equilibration of the packing fraction. The packing fractions at 8×10^3, 23×10^3 and 170×10^3 MC steps are indicated by arrows.

system of spheres has the closed packed value $\eta_c(1) = \pi\sqrt{2}/6 = 0.740$, while the pure system of the spherocylinders with length to diameter ratio q has the value

$$\eta_c(0) = \frac{1}{6} \cdot \frac{\pi(3q+2)}{q\sqrt{3}+\sqrt{2}}. \tag{12}$$

We have $\eta_c(0) = 0.884$ for $q = 5$. The $\eta_c(X)$ is given by

$$\eta_c(X) = \frac{(1-X)(2+q\sqrt{6})\eta_c(0) + 2X\eta_c(1)}{(1-X)(2+q\sqrt{6}) + 2X}. \tag{13}$$

For $q = 5$, we have $\eta_c(0.2) = 0.879$.

As described in the previous section, the initial system configuration has the volume which is about five times larger than the size of closed packed configuration of the spherocylinder system. At the pressure given by Eq. (10), the system size shrinks from the initial value to an equilibrium size as the MC steps proceed. Figure 2 shows a relaxation of the packing fraction under the simulation. We have calculated the spherocylinder-spherocylinder pair distribution functions $g_{||}^{cc}(z)$ from configurations at 8×10^3, 23×10^3 and 170×10^3 MC steps. The pair distributions at 8×10^3 and 23×10^3 MC steps represent ones in relaxation process under MC simulation. The pair distributions at 170×10^3 MC steps represent ones after equilibration.

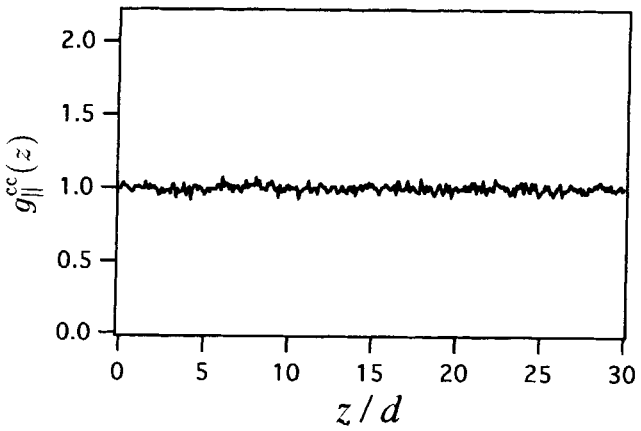

FIGURE 3 Pair distribution $g_{\|}^{cc}(z)$ at 8×10^3 MC steps.

The initial state for the simulation is made by uniform expansion of closed packed lattice. Initial molecular positions are hence placed at the expanded lattice site which has tree dimensional periodic structure. When we start the simulation, the periodic structure melts at first to form uniform nematic-like structure indicated by Figs. 3 and 4. Figures 3-6 show that smectic layer structure grows from the uniform structure as the system moves to equilibrium.

Equilibrium Structure

In Fig. 7, we show a snapshot of an equilibrium configuration of the system with $N_c = 1152$ and $N_s = 288$. Figure 7 indicates that the spheres favor to stay in the interstitial regions among layers of the cylinders. In other words, as was noted also in our previous work[10], the structure of the smectic-A phase of the present system appears as a microphase separation between cylinders and spheres. This type of alternating structure of spherocylinders and spheres are also indicated by pair distribution functions of Figs. 5 and 6. In these figures, the peaks of spherocylinder-spherocylinder pair distribution function and the peaks of spherocylinder-sphere pair distribution function appear alternately. Phase difference between them is almost 180 degrees.

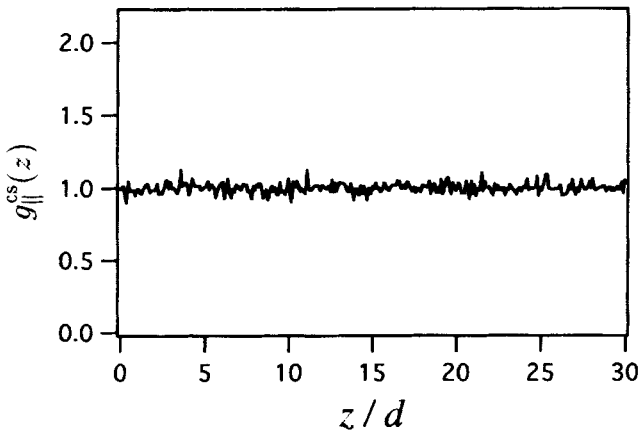

FIGURE 4 Pair distribution $g_{\|}^{cs}(z)$ at 8×10^3 MC steps.

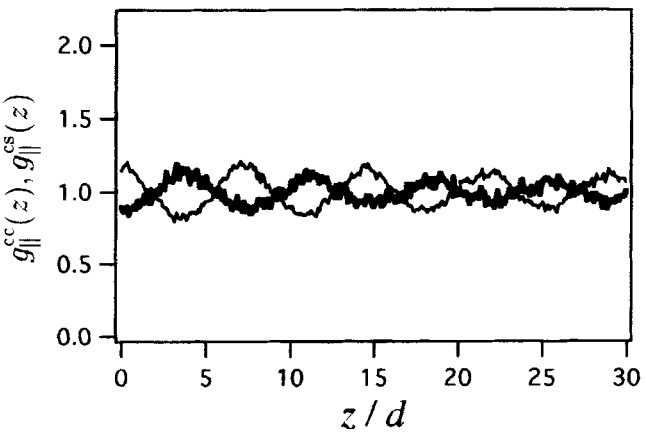

FIGURE 5 Pair distributions at 23×10^3 MC steps. Thin solid line: $g_{\|}^{cc}(z)$. Thick solid line: $g_{\|}^{cs}(z)$.

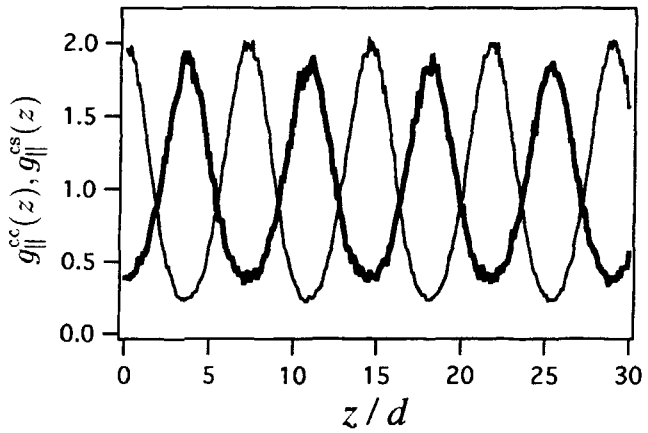

FIGURE 6 Pair distributions at 170×10^3 MC steps. Thin solid line: $g_{||}^{cc}(z)$. Thick solid line: $g_{||}^{cs}(z)$.

After the system goes to the equilibrium, we take statistical average of pair distribution functions from 200 configurations during 20×10^3 MC steps. Figure 8 shows averaged transverse pair distribution functions $< g_{\perp}^{cc}(r) >$ for $X = 0$ and $X = 0.2$. The system with $X = 0$ corresponds to one component system of spherocylinders. Averaged longitudinal pair distribution functions $< g_{||}^{cc}(z) >$ for $X = 0$, $X = 0.1$ and $X = 0.2$ are shown by Fig. 9. The transverse distributions show no long range order, while the longitudinal distributions indicate periodic structure.

Figures 8 and 9 show that addition of hard spheres to the smectic-A phase of spherocylinders affects the longitudinal distribution of cylinders, though it dose not give remarkable effect to the transverse distribution. Periodicity of the longitudinal distribution functions of Fig. 5, 6 expresses the layer periodicity of the smectic-A phase. Figure 9 indicates that the layer spacing increase, when we add spheres to the smectic-A phase of spherocylinders.

CONCLUDING REMARKS

We have performed MC simulations of the binary mixtures of parallel hard spherocylinders and hard spheres under constant pressure given by

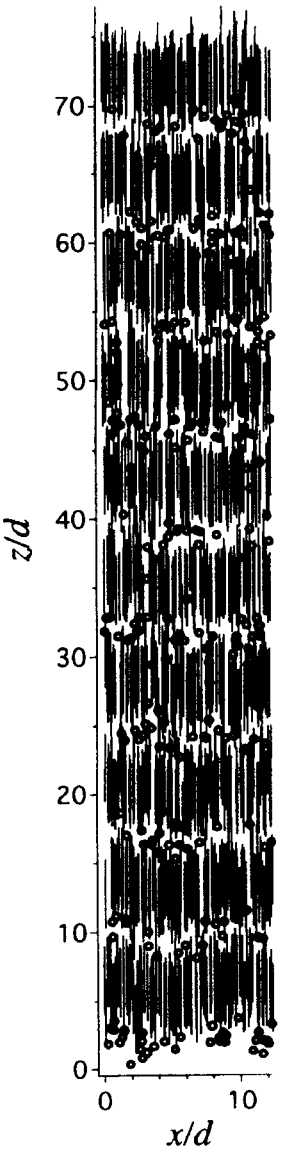

FIGURE 7 A snapshot taken from y-direction of the equilibrium structure of the system with $N_c = 1152$ and $N_s = 288$. Line segments indicate cores of spherocylinders and open circles positions of spheres.

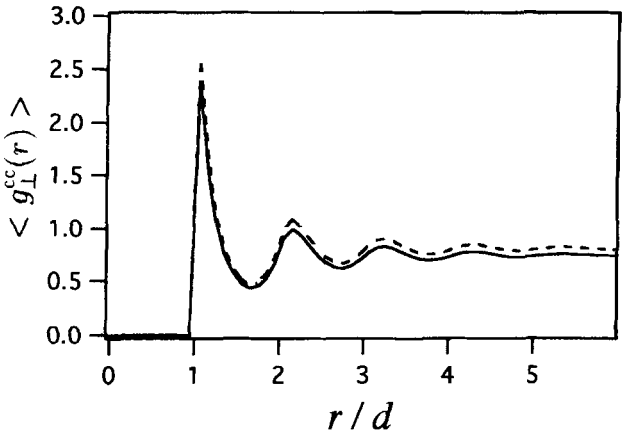

FIGURE 8 Averaged transverse pair distribution functions of $X = 0$ (solid line) and $X = 0.2$ (dashed line).

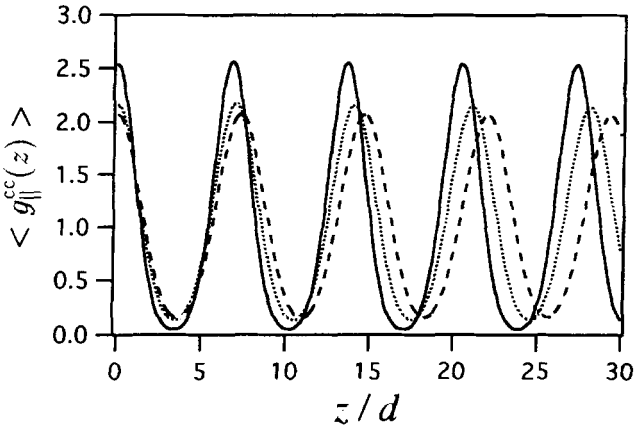

FIGURE 9 Averaged longitudinal pair distribution functions of $X = 0.0$ (solid line), $X = 0.1$ (dotted line) and $X = 0.2$ (dashed line).

Eq. (10). We show in Fig. 7 the snapshot of the equilibrium structure of the mixture. It shows smectic layers with alternating condensation of cylinders and spheres. In Fig. 9, we have compared distribution functions of several molar fraction X of spheres.

Experiments for semiflexible virus particles have argued effects of flexibility of molecules to the smectic phase[11]. They indicate that flexibility lowers the smectic periodicity.

Our present simulations indicate that one of effects of addition of hard spheres to the smectic-A phase of parallel hard spherocylinders is an extension of layer spacing. Intercalation of spherical molecules into interstitial regions of layers extends the layer spacing.

Intermolecular forces of actual molecules consist of repulsive part and attractive part, and shapes of actual molecules are more complicated. Flexibility of molecules also have to be considered. To relate the present results with actual phenomena, experiments should be made to examine changes in layer spacing of smectics by adding some other particles.

Acknowledgments

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