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Simulations on Phase Separations on Mixtures of Two Kinds of Liquid Crystal Molecules

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By use of molecular dynamical simulations, liquid crystal phase transitions and phase separations are investigated on the mixture of hard rod-like molecules and hard spherical molecules. Our model for the rod-like molecule is supposed to be a linear chain of 7 hard spheres connected with strong springs. We demonstrate that randomly added spherical molecules generally incline to diminish their orientational ordering. Specially in the smectic phase we have found that these mixing causes a phase separation, where the smectic rod-rich layers and sphere-rich layers are alternatively stacked in the low concentration of spheres. In the higher concentration they show 'domain phase', where the clusters of rod-like molecules are dispersed in the sea of spherical molecules, like a phase separation.

Keywords: liquid crystal; phase transition; phase separation; mixture; molecular dynamics

1 Introduction

Liquid crystals consisting of hard rod-like molecules are essentially lyotropic and generally known to show successively isotropic, nematic and smectic phases, with increase of packing ratio. Frenkel and Mulder's Monte Carlo simulations [1] on hard uniaxial ellipsoidal molecules indicated a nematic(N) phase, but did not exhibit a smectic(Sm) phase. Later Strootbants, Lekerkerker and Frenkel [2] demonstrated to appear Sm phase in the case of hard columnar molecules, capped with hard half-spheres on its both tops. Recently Williamson and Jackson [3] investigated on the I-N transition on the same model as ours, by the isobaric MC method.

A purpose of our simulations consists in how to change phase transitions among isotropic, nematic and smectic phases by binary mixtures of different shaped molecules.

We simply expect to decrease the orientational ordering with increase of the mixing ratio of hard spheres against hard rod-like molecules. Our simulations have generally confirmed these behaviors. Moreover we have found to emerge new phase separations caused by mixing. In the smectic region, we have found that sandwich-like structures composed of the smectic rod-rich layers and hard spheres layers are built up by adding hard spheres. By further adding spheres, another new 'Domain phase' appears, where domains or clusters of rod-like molecules are dispersed randomly in the sphere molecule-rich sea.

2 Our model and simulation method

Our rod-like molecule is composed by a linear chain of identical hard spheres, which are connected each other with strong springs. Let us take, hereafter, units of length by the radius of hard sphere. Molecular dynamical simulation methods have been applied these molecular system. In judgment for on-collision or out-of-collision, our model is more convenient than the columnar or spheroidal molecules. So it contributes to save computing times.

In this paper one rod-like molecule is fixed to be composed of seven hard spheres and their container size is $42 \times 42 \times 42$ with the periodic boundary condition. As the initial condition, the long axis of all rod-like molecules is fixed to parallel to z axis and the positions of center of molecules are randomly distributed on face-centered cubic lattice sites. Hard spheres are also randomly distributed on unoccupied sites. Initial velocities of molecules also selected randomly.

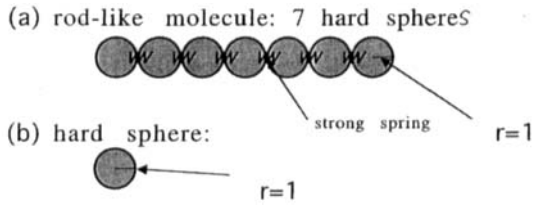

Figure 1: Our model of rod-like molecule and hard sphere

We have estimated two types of order parameters: one is the orientational order param-

eter and the other is the spatial order parameters or the pair-correlation in the z direction.

orientational order parameter

The orientational order parameter S is defined as

$$S = \left\langle \frac{3\cos^2\theta_i - 1}{2} \right\rangle,$$

where θ_i is the angle between the long axis of ith molecule and the director and $< \cdots >$ indicates the statistical average. In the isotropic phase, the long axes are randomly distributed and $S = 0$. The nematic and smectic phases proves to be $S \neq 0$.

In the simulation we could not easily know the direction of the director, therefore we have calculated a tensor orientational order parameter $Q_{\alpha,\beta}$ defined by

$$Q_{\alpha,\beta} = \frac{1}{N_m} \sum_{j=1}^{N_m} \left(\frac{3}{2} a_{j,\alpha} a_{j,\beta} - \frac{1}{2} \delta_{\alpha,\beta} \right),$$

where N_m is the number of rod molecules, $\alpha, \beta = x, y, z$ and $a_{j,\alpha}$ indicates α component of direction cosine of the long axis of the j-th rod-like molecules. The diagonalized Q tensor has three principle axes, its components are estimated as Q_1, Q_2, Q_3. If the uniaxial alignment appears, that is, any two components are identical, for example, $Q_1 = Q_2$, the uniaxial order parameter S is given by

$$S = \frac{2}{3}[Q_3 - \frac{1}{2}(Q_1 + Q_2)] = \frac{2}{3} Q_3,$$

because of the restriction of $Q_1 + Q_2 + Q_3 = 0$ by the definition of $Q_{\alpha,\beta}$.

spatial pair correlation

In the Sm phase the spatial density of center of rod-like molecules should be periodic. The following pair-correlation function $G_z(\mathbf{r})$ is important, as defined by

$$G_z(\mathbf{r}) = \frac{1}{N_m^2} \sum_{i}^{N_m} \sum_{j \neq i}^{N_m} \delta(\mathbf{r} - \mathbf{r}_{i,j}^z),$$

where $\mathbf{r}_{i,j}^z$ is the z component of the relative position vector of center of i, j-th molecules and here z direction is the perpendicular to the smectic layer. If the spatial distribution of rod-molecules contains periodicity, such as in Sm phase, the distance dependence of $G_z(\mathbf{r})$ will show periodic behavior.

3 Results of simulations

pure hard rod-like molecule

Studies on our model of pure hard rod-like molecules cover the packing ratio from 0 to 65%. The packing ratio p is defined by V_m/V_{max}, where V_{max} is the close-packing volume and V_m means the occupied volume of total molecules. Above $p = 65\%$ it can be rather hard to realize a random distribution of rod-like molecules on f.c.c. lattice. We have found in the pure case that the isotropic(I) phase appears below 43% of packing ratio, the nematic(N) phase does between 47% and 50% and the smectic(Sm) phase above around 55%.

mixtures of hard spheres and rod-like molecules

For the mixture the mixing ratio c is defined by V_s/V_m, where V_s is the total volume of hard spheres. In case hard spheres are randomly added into the isotropic phase, for examples $p = 43\%$, and c =10 and 60%, our simulations show homogeneous mixing of rods and spheres and their orientational order parameters S's are unchanged to be zero.

In the nematic phase, by adding spheres, as shown in Fig.2, the order parameter S generally decreases with increase of mixing ratio and finally goes to 0 for the isotropic phase.

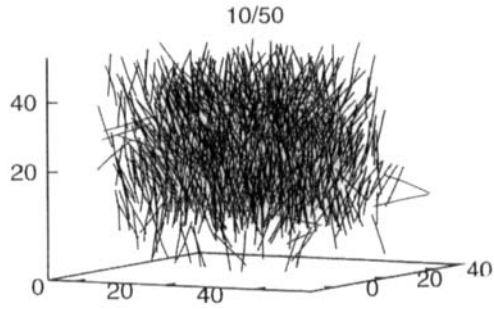

Figure 2: A snap shot of nematic phase at $p = 50\%$ and $c = 10\%$. Only rod-like molecules are displayed

In the smectic phase, however, we have no homogeneous mixing, and a phase separation

occurs. As shown in Fig.3, added spheres prefers to penetrate into between smectic layers. A sandwich-like structure of the smectic rod-like molecule-rich layer and sphere-rich layers in the low mixing ratio is built.

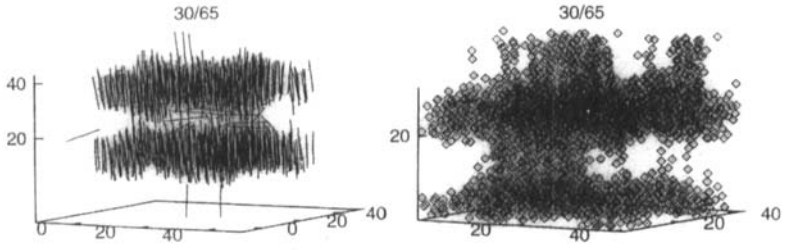

Figure 3: A snap shot of sandwich-like phase of the smectic rod-rich region and sphere-rich region : $p = 65\%$ and $c = 30\%$. (a)Only rod-like molecules are only displayed (b)Hard spheres only.

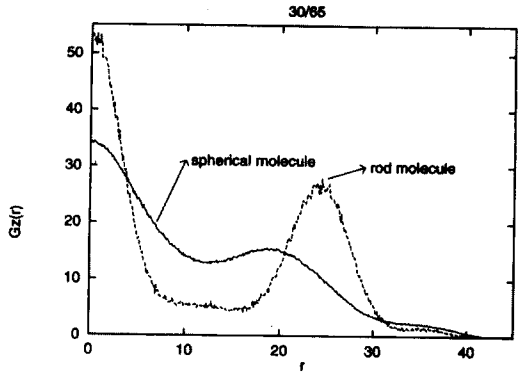

Figure 4: Pair-correlation function of the center of the rod-like molecules vs. the z component of mutual position vector for $p = 65\%$ and $c = 30\%$.

The figure 4 shows pair-correlation of the center of rod-like molecules as the function of relative position. The second peak of G_z vs. the z component of mutual separation indicates a layer structure .

With increase of mixing ratio, this sandwich-like structure becomes unstable, though the orientational order parameter S has not so small value. Therefore it exhibits a uniaxial symmetry.

Further adding spheres, we have found a new 'Domain' phase, as shown in Fig.5, where many clusters of rod-like molecules disperse in the sea of spheres. Within cluster the orientational order may not be zero, but as a whole they have no order. These behaviors are considered to be a typical phase separation between rod-rich and sphere-rich domain.

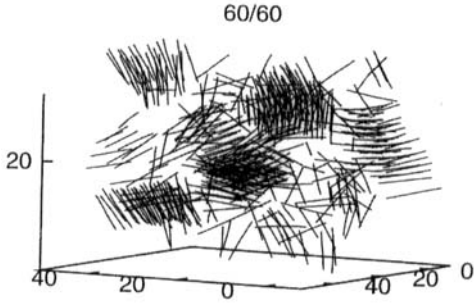

Figure 5: A snap shot of Domain phase. Only rod-like molecules are displayed for $p = 60\%$ and $c = 60\%$.

In the case of higher mixing ratio, clusters disappear and isotropic and homogeneous phase is recovered.

4 Conclusions

We have studied , by use of molecular dynamics, varieties of the phase changes in the liquid crystal of the mixture of hard rod-like molecules and hard spheres.

The obtained phase diagram is shown in Fig.6. Generally speaking, the orientational order diminishes with increase of ratio of sphere. Specially in the smectic phase the phase separation occurs between two kinds of molecules.

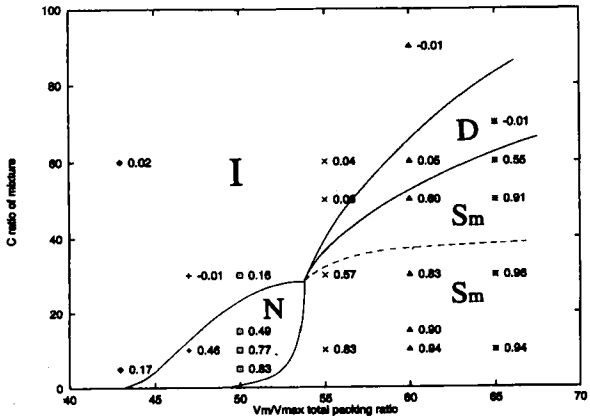

Figure 6: Phase diagram for mixed hard spheres and rod-like molecules. The attached figures on marks represent the orientational order parameter S and each phase boundary curves are not quantitatively determined, rather deduced by inspection based on snap shots of distribution of molecules and their order parameters. The upper and lower parts separated by broken curve in the Sm region indicate rather fluctuating and stable, respectively, in time-dependence of our simulation

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