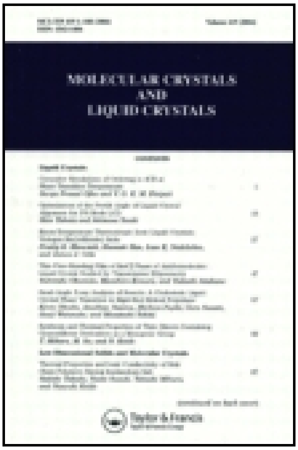

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Theory and Simulation of the Successive Phase Transitions of Chiral Smectics

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Theory and Simulation of the Successive Phase Transitions of Chiral Smectics

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We propose a molecular theoretical model free energy which enables us to discuss the successive phase transitions of chiral smectics. Monte Carlo simulation combined with the free energy is also performed in order to examine the structure described by our model.

Keywords: chiral smectic; phase transitions; Monte Carlo simulation

INTRODUCTION

Since the discovery of the successive ferroelectric-antiferroelectric phase transitions of chiral smectics(Sm)[1], they have attracted those who have investigated the structures of the subphases appearing in the transitions and who have investigated the mechanism of the transitions, and so on[2].

Recently, our theory[3, 4] and the theory by Yamashita[5] have indicated that the successive phase transitions between the Sm-C^*_A phase and the Sm-C^* phase originate from the head-tail asymmetry of molecular potential.

In the present paper, we introduce a free energy as a functional of the distribution of molecular directions. In the description of the free energy, not only the head-tail asymmetry but also the freedom of azimuthal angle of molecular tilt is taken into consideration. At the end of this paper we show results of Monte Carlo (MC) simulation to show the behavior of the present model.

MODEL AND FREE ENERGY

Free energy and model density structure

There is the general form of the free energy for molecular systems[6]. At the second virial approximation, which is equivalent to the mean field approximation, we have

$$F/k_{\mathrm{B}}T = N\Lambda(T) + \iint \mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{\Omega} P(\boldsymbol{r},\boldsymbol{\Omega}) \ln P(\boldsymbol{r},\boldsymbol{\Omega})$$
$$-\frac{1}{2}\iiiint \mathrm{d}\boldsymbol{r}'\mathrm{d}\boldsymbol{\Omega}'\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{\Omega} P(\boldsymbol{r}',\boldsymbol{\Omega}')P(\boldsymbol{r},\boldsymbol{\Omega})b(\boldsymbol{\Omega}',\boldsymbol{\Omega},\boldsymbol{r}'-\boldsymbol{r}) \,, \qquad (1)$$

where k_{B} is Boltzmann constant, $P(\boldsymbol{r},\boldsymbol{\Omega})$ density of molecules at position $\boldsymbol{r}$ with direction $\boldsymbol{\Omega}$, N the number of molecules in the system, $\Lambda(T)$ the contribution of kinetic energy, and $b(\boldsymbol{\Omega}',\boldsymbol{\Omega},\boldsymbol{r}'-\boldsymbol{r})$ is the Mayer function.

To describe the layer structure of the smectic, we assume

$$P(\boldsymbol{r},\boldsymbol{\Omega}) = \begin{cases} \frac{NL}{VW}v_j(\boldsymbol{\Omega}) & \text{for } z_j - (W/2) < z < z_j + (W/2), \\ 0 & \text{for } z_j + (W/2) \le z \le z_{j+1} - (W/2), \end{cases} \qquad (2)$$

where we take z-direction along the layer normal, V is the system volume, W the thickness of a smectic layer, L is the layer periodicity which is related to z_j, the z-component of the center of the j-th layer, by $z_{j+1} = z_j + L$, and $v_j(\boldsymbol{\Omega})$ is the distribution of the molecules with direction $\boldsymbol{\Omega}$ in the j-th layer. For the present study $\boldsymbol{\Omega}$ is a unit vector which points from the tail to the head of the molecule along the molecular long axis.

Eqs. (1) and (2) give

$$F/k_{\mathrm{B}}T = n\sum_{j=1}^{m}\int \mathrm{d}\boldsymbol{\Omega} v_j(\boldsymbol{\Omega}) \ln v_j(\boldsymbol{\Omega})$$
$$+ \frac{n}{2}\sum_{j=1}^{m}\iint \mathrm{d}\boldsymbol{\Omega}'\mathrm{d}\boldsymbol{\Omega}\Big\{v_j(\boldsymbol{\Omega}')v_j(\boldsymbol{\Omega})J(\boldsymbol{\Omega}',\boldsymbol{\Omega},\boldsymbol{e}_z,0)$$
$$+2v_{j+1}(\boldsymbol{\Omega}')v_j(\boldsymbol{\Omega})J(\boldsymbol{\Omega}',\boldsymbol{\Omega},\boldsymbol{e}_z,1)\Big\}. \qquad (3)$$

where n is the number of molecules per layer, $\boldsymbol{e}_z$ the layer normal which points to z-direction as a unit vector. In deriving Eq. (3), we have neglected terms which do not depend on $\{\psi_j(\boldsymbol{\Omega})\}$. The J in Eq. (3) is given as a integration of the Mayer function. The $J(\boldsymbol{\Omega}', \boldsymbol{\Omega}, \boldsymbol{e}_z, j-k)$ describe the energetic contribution between a molecule in the j-th layer with direction $\boldsymbol{\Omega}'$ and a molecule in the k-th layer with direction $\boldsymbol{\Omega}$. Then $J(\boldsymbol{\Omega}', \boldsymbol{\Omega}, \boldsymbol{e}_z, 1)$ describe the nearest neighbor interlayer interaction, and $J(\boldsymbol{\Omega}', \boldsymbol{\Omega}, \boldsymbol{e}_z, 0)$ the intralayer interaction. Because we assume that the molecular potential is short-range, only the cases $|j-k| = 1$ and $|j-k| = 0$ appear in the expression of Eq. (3).

The Mayer function can be split into

$$b(\boldsymbol{\Omega}', \boldsymbol{\Omega}, \boldsymbol{r}'-\boldsymbol{r}) = b_{\rm h}(\boldsymbol{\Omega}', \boldsymbol{\Omega}, \boldsymbol{r}'-\boldsymbol{r}) + b_{\rm a}(\boldsymbol{\Omega}', \boldsymbol{\Omega}, \boldsymbol{r}'-\boldsymbol{r}), \tag{4}$$

where $b_{\rm h}$ is the contribution of hard core interaction and $b_{\rm a}$ of attractive interaction[3]. Hence J is also split into hard core part $J_{\rm h}$ and attractive part $J_{\rm a}$ as

$$J(\boldsymbol{\Omega}', \boldsymbol{\Omega}, \boldsymbol{e}_z, j-k) = J_{\rm h}(\boldsymbol{\Omega}', \boldsymbol{\Omega}, \boldsymbol{e}_z, j-k) + J_{\rm a}(\boldsymbol{\Omega}', \boldsymbol{\Omega}, \boldsymbol{e}_z, j-k). \tag{5}$$

Expression of $J_{\rm h}$

In Figure 1 the $\boldsymbol{\Omega}$ is denoted by arrow fixed at the head of a rod-like molecule. As Figure 1 describes, molecular tilt is determined by tilt angle θ and azimuthal angle ϕ. Figure 1 also shows that the $\boldsymbol{\Omega}$ can flip-flop without changing the tilt of molecular long axis. We assume for the present study that the tilt angle θ is constant throughout the system.

Knowing the expression for the hard core part of the Mayer function:

$$b_{\rm h}(\boldsymbol{\Omega}', \boldsymbol{\Omega}, \boldsymbol{r}'-\boldsymbol{r}) = \begin{cases} -1 & \text{if the molecules intersect,} \\ 0 & \text{otherwise,} \end{cases} \tag{6}$$

we can have numerical estimation of $J_{\rm h}$ for given shape of molecules. Assuming that the molecular shape is the spherocylinder, we have confirmed numerically that when the tilt angle θ is small, the $J_{\rm h}$ is approximated as

$$J_{\rm h}(\boldsymbol{\Omega}', \boldsymbol{\Omega}, \boldsymbol{e}_z, 1) = K_{11}\sqrt{\frac{1-|\boldsymbol{\Omega}'\cdot\boldsymbol{\Omega}|}{2}} + K_{01}. \tag{7}$$

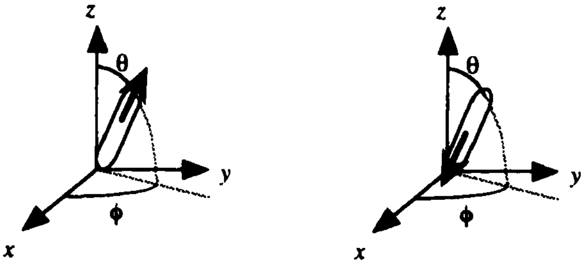

FIGURE 1 Two different molecular directions having the same tilt θ and azimuthal angle ϕ.

$$J_h(\boldsymbol{\Omega}', \boldsymbol{\Omega}, \boldsymbol{e}_z, 0) = K_{10}\sqrt{\frac{1 - |\boldsymbol{\Omega}' \cdot \boldsymbol{\Omega}|}{2}} + K_{00}. \tag{8}$$

When we take typical experimental values[3] $\theta \sim 15°$, $L \sim 34$Å and $N/V \sim 1.2 \times 10^3$Å with assumption $W \sim 0$ and assume that the diameter and the length of representing spherocylinders are, respectively, ~ 5Å and ~ 40Å, we have estimations

$$K_{00} = 3.3, \quad K_{10} = 31.47, \tag{9}$$

$$K_{01} = 3.3, \quad K_{11} = 3.8. \tag{10}$$

Expression of J_a

We assume

$$J_a(\boldsymbol{\Omega}', \boldsymbol{\Omega}, \boldsymbol{e}_z, 0) = 0, \tag{11}$$

for simplicity. Thus the intralayer attractive force is neglected from our formulation.

We know that J_a is a function of three vectors $\boldsymbol{\Omega}'$, $\boldsymbol{\Omega}$ and $\boldsymbol{e}_z$. There is an expression of a scalar in terms of complete orthogonal set of functions which are described by the combinations of three vectors[7]. We pick up from the expression the lowest order terms which are needed for the description of the successive transitions. Then we propose

$$\begin{aligned} J_a(\boldsymbol{\Omega}', \boldsymbol{\Omega}, \boldsymbol{e}_z, 1) &= \varepsilon_4 \{\boldsymbol{\Omega}' \cdot \boldsymbol{e}_z - \boldsymbol{\Omega} \cdot \boldsymbol{e}_z + 3(\boldsymbol{\Omega}' \cdot \boldsymbol{\Omega})[\boldsymbol{\Omega}' \cdot \boldsymbol{e}_z - \boldsymbol{\Omega} \cdot \boldsymbol{e}_z]\} \\ &+ \varepsilon_5 \left[3(\boldsymbol{\Omega}' \cdot \boldsymbol{\Omega})^2 - 1\right]. \end{aligned} \tag{12}$$

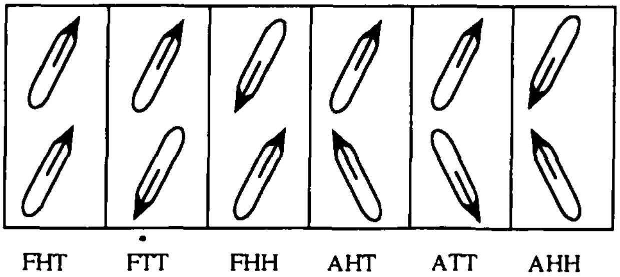

FIGURE 2 Six types of nearest neighbor interlayer pair molecules.

where ε_4 and ε_5 are the intensive parameters which control the phase transitions.

In our previous studies[3,4], we have assumed that molecular tilt direction is restricted onto yz-plane. In such case we have six types of neighboring interlayer pair molecules shown in Figure 2. The types of pair molecules in Figure 2 are denoted by three capital letters, FHT, FTT, FHH, and so on. The F stands for ferroelectric by which we mean the long axes of the pair molecules are parallel to each other, while the A stands for antiferroelectric by which we mean the long axes tilt in directions which are opposite to each other.

Let us denote energetic contribution J of such types of pairs as J(FHT), J(FTT), etc. We define a parameter ε as

$$\varepsilon = \frac{1}{4}\{[J(FHH) - J(FTT)] - [J(AHH) - J(ATT)]\} . \qquad (13)$$

The theory of Yamashita have indicated that the existence of the successive phase transitions stems from $\varepsilon \neq 0$[5]. The first term with ε_4 of the right hand side of Eq. (12) is the lowest order term which give non-zero ε in the complete set.

We define another parameter ν by

$$\begin{aligned} \nu &= \frac{1}{4}\Big\{[2J(AHT) + J(ATT) + J(AHH)] \\ &- [2J(FHT) + J(FTT) + J(FHH)]\Big\}. \end{aligned} \qquad (14)$$

which describe the energy difference between antiferroelectric ordering and ferroelectric ordering of neighboring layers. When $\nu > 0$ ferroelectric ordering of neighboring layers is more favorable than the antiferroelectric one, while when $\nu < 0$ antiferroelectric one is favorable. For the present case with constant θ, the ν and ε are related to ε_4 and ε_5 with equations

$$\nu = K_{11}\sin\theta + 3\varepsilon_5\left[\cos^2 2\theta - 1\right]. \tag{15}$$

$$\varepsilon = 3\varepsilon_4(1 - \cos 2\theta)\cos\theta. \tag{16}$$

RESULTS OF MC SIMULATION

Describing the density distribution of the j-th layer by Dirac δ function as

$$c_j(\boldsymbol{\Omega}) = \frac{1}{n}\sum_{k=1}^{n}\delta(\boldsymbol{\Omega} - \boldsymbol{\Omega}_{jk}). \tag{17}$$

we have performed the mean field MC simulation[8]. In Eq. (17) $\boldsymbol{\Omega}_{jk}$ is the direction of the k-th molecule in the j-th layer.

For the present simulation we have set the number of layers as $m = 12$ which induces periodic boundary condition, and we set the number of molecules per layer as $n = 100$. Metropolis trials are made to move the molecular coordinate $\boldsymbol{\Omega}_{jk}$ calculating the increase of the free energy of Eq. (3) with the expression of J_h and J_a given in the foregoing section. The trials are made under the assumption that the tilt angle θ is constant, but they include flip-flop of a molecule along its long axis.

Results of Figures 3 and 4 are obtained after each molecular coordinate is tried to move 2×10^4 times. Figure 3 shows obtained molecular number distribution in azimuthal angle ϕ of the forth and the fifth layer under the condition $\nu = -0.15$ and $\varepsilon = -0.5$.

From the simulation we can calculated $\mathbf{c}_j$, the C-director of the j-th layer. Defining the normalized C-director of the j-th layer by $\boldsymbol{u}_j = \mathbf{c}_j/|\mathbf{c}_j|$, we obtain q_T which is given by

$$q_T = \frac{1}{m}\sum_{j=1}^{m}\frac{1 + \boldsymbol{u}_{j+1}\cdot\boldsymbol{u}_j}{2}. \tag{18}$$

The q_T express the fraction of ferroelectric ordering of neighboring layers. We have $q_T = 0$ for the Sm-C^*_A phase, $q_T = 1$ for the Sm-C^* phase, and

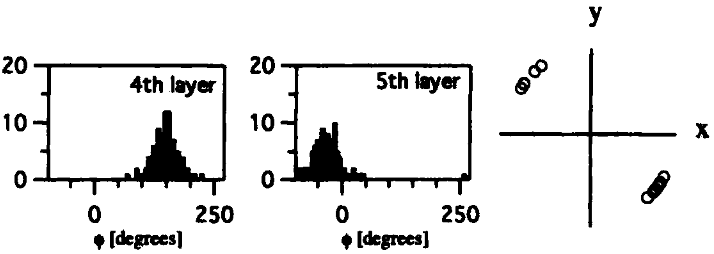

FIGURE 3 Two histograms in left hand side show molecular number distribution in azimuthal angle ϕ. Directions of the unit C-director of layers viewed from z-axis are shown by circles in the right hand side figure.

$0 < q_T < 1$ for the subphases. The plot in the right hand side of Figure 3 shows the distribution of u_j viewed from z-axis.

We have performed the MC simulation for various values of ν with $\varepsilon = -0.5$. The q_T is obtained from the final state of each simulation. Figure 4 summarize the results. The calculated q_T shows a type of staircase which is similar to the successive transitions. However the final state depends both on the initial condition of the system and random number sequence produced under simulation.

CONCLUDING REMARKS

We have given the approximated and assumed forms of J_h and J_a which determine the expression of the free energy.

The state obtained after the simulation depends on the initial conditions. This indicates the existence of metastable states for the present model system. We have not compared the free energy to determine which one is the most stable.

Our results show a similarity with experiments in that the average direction of molecular tilts are almost in one plane as Figure 3 shows.

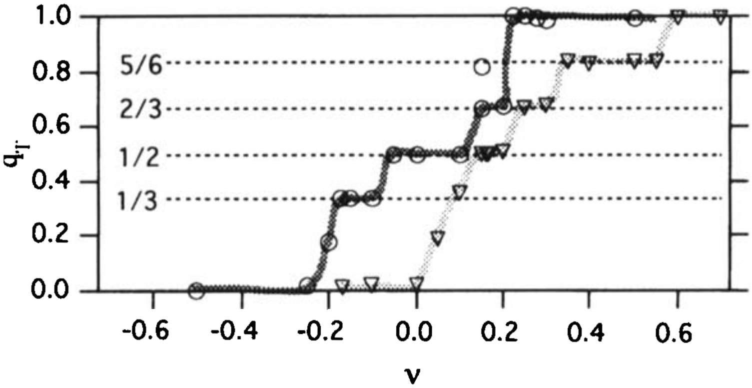

FIGURE 4 Dependence on ν of obtained q_T with $\varepsilon = -0.5$. The levels of rational 5/6, 2/3, 1/2 and 1/3 are indicated by dotted line. Circles: final values of simulations starting with the Sm-C^* state. Triangles: final values of simulations starting with the Sm-C_A^*. Thick lines help us to see the plots.

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