

PHASE TRANSITIONS IN CHIRAL SMECTIC LIQUID CRYSTALS

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Introduction

There are chiral smectic materials which show intermediate phases between ferroelectric Smectic(Sm)-C* and antiferroelectric Sm-C_A* phase. The appearing phases, which depend on materials, follow the order of phases: Sm-C* $\leftrightarrow$ AF $\leftrightarrow$ FI_H $\leftrightarrow$ Sm-C _{γ} * $\leftrightarrow$ FI_L $\leftrightarrow$ Sm-C_A*, from higher temperature to lower temperature[1,2].

The phases are composed of fluids of orientationally ordered rod-like molecules assembled into layers. The director, the average direction of molecular long axes, tilts from the layer normal. The tilt angle θ , which is an angle between the director and the layer normal, is uniform in the system, but the azimuthal angle of the tilt changes from layer to layer choosing one of two in the same tilting plane. In Fig. 1, taking the layer normal to z -direction, we set this plane to yz -plane, and we denote the two tilts by $\sigma = \pm 1$.

The σ changes from layer to layer periodically along z -direction with a wave number q a unit of which is $1/(\text{layer spacing})$. The phases are characterized by this q . The Sm-C* phase, AF phase, Sm-C _{γ} * phase and Sm-C_A* phase are phases of $q = 0$, $q = 1/4$, $q = 1/3$ and $q = 1/2$, respectively.

In the present study, we discuss these phase transitions using a simple molecular theoretical model.

Model and free energy

Liquid crystalline molecules mostly distinguish their heads and tails on their chemical structures. It is, hence, natural to consider that a molecular pair potential of such molecules has a head-tail asymmetry, that is, the potential of a pair molecules in head-to-head configuration is different from the potential of the pair in head-to-tail or in tail-to-tail configuration.

We consider that a molecular pair potential consists of hard core repulsive part and attractive part. And we assume that the attractive part has the head-tail asymmetry and favors a interlayer antiferroelectric order.

We consider that the long axis of a molecule can take one of two tilts ± 1 of σ . If we distinguish the head and tail of the molecule, the molecule take one of four directions shown in Fig. 2 where we indicate the molecular head by a solid circle and distinguish the four directions by integer α . Assuming that the layers are given by the square density wave of centers of

molecules, we have, at the second virial approximation, the free energy f of the present model:

$$f(\{\psi_\alpha^j\})/k_B T = \frac{1}{m} \sum_{j=1}^m \sum_{\alpha=1}^4 \left\{ \psi_\alpha^j \ln \psi_\alpha^j + \left(\nu - \frac{\epsilon_0}{T} \right) (\psi_\alpha^j \psi_{\alpha+1}^{j+1} + \psi_{\alpha+1}^j \psi_\alpha^{j+1}) \right. \\ \left. - \frac{\epsilon}{2T} (\psi_1^j \psi_2^{j+1} + \psi_4^j \psi_3^{j+1}) + \left(\xi - \frac{\zeta}{T} \right) \psi_\alpha^j \psi_{\alpha+1}^j \right\}, \quad (1)$$

where k_B is Boltzmann constant, T temperature, m the number of layers in the system, ϵ the parameter which indicate the strength of the head-tail asymmetry of attractive potential, ν , ϵ_0 , ξ , and ζ are contributions from interlayer excluded volume, interlayer attractive potential, intralayer excluded volume and intralayer attractive potential, respectively, ψ_α^j is the fraction of molecules having direction α in j -th layer which is normalized as $\sum_{\alpha=1}^4 \psi_\alpha^j = 1$, and obeys a periodic boundary condition: $\psi_\alpha^j = \psi_{\alpha+m}^{j+m} = \psi_{\alpha+4}^j$. For given conditions, the equilibrium structure is given by the $\{\psi_\alpha^j\}$ which minimizes f .

Resultant phases and conclusion

For the case $1 \ll \xi - \frac{\zeta}{T}$, the appearing phases are Sm-C*, AF, and Sm-C*_A phase from higher to lower temperature [3].

In the case $0 < \epsilon/T \ll 1$, a free energy derived from eq.(1) coincides with the free energy of ANNNI model at mean field approximation[4], then the appearing phases are basically Sm-C* phase, a phase of $q = 1/6$, AF phase, Sm-C*_ γ phase and Sm-C*_A phase.

When $\epsilon = 0$, there is no head-tail asymmetry, then only Sm-C* and Sm-C*_A phase appear without any intermediate phase. Thus our present study indicates that the head-tail asymmetry of a molecular potential is one of mechanisms which induce the successive phase transitions of chiral smectics.

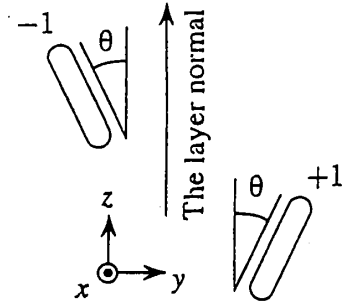


Figure 1

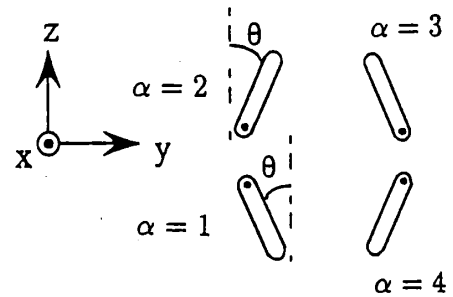


Figure 2

References

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