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Influence of Chiral Interactions on Smectic Phases in Free-Standing Films

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Free energy of thin smectic films in an antiferroelectric system is analyzed within the discrete phenomenological model. The effect of chirality within the region of uniplanar structures and on the SmC^*_α structure is studied. As a result the SmC^*_α regions with less tilted surface layers widen and uniplanar structures transform into wound structures having less tilted inner layers.

Keywords Antiferroelectric; chirality; smectic; thin film

1. Introduction

Antiferroelectric liquid crystals have been the hot research topic for several years, but one can still find a number of interesting experimental and theoretical questions. Sun *et al.'* discretization of the free energy description of antiferroelectric liquid crystal [1] had stimulated some authors [2,3] to introduce the discrete model of antiferroelectric liquid crystal. Since the discrete model allowed the explicit consideration of interactions between individual smectic layers [4], it is especially suitable for analyzing antiferroelectric liquid crystal in free standing films having small finite number of layers. The theoretical analysis by Rovšek *et al.* [5] showed the existence of the uniplanar (all tilts in one plane) phases for some sets of model coefficients neglecting chiral interactions. Some experimental results support this type of structures [6,7], while some elucidate the opposite [8,9]. As antiferroelectric liquid crystals studied experimentally are mostly chiral, we were interested to analyze the effects of chirality on the uniplanar structures and structures of thin antiferroelectric films below the SmA phase in general.

2. Theoretical Model

By assuming high smectic order, our analysis starts with the discrete Landau phenomenological model. This model expresses the free energy of an antiferroelectric

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smectic liquid crystal as follows [2]:

$$G = \sum_{i=1}^{N} \frac{1}{2} a_0 \vec{\xi}_i^{\,2} + \frac{1}{4} b_0 \vec{\xi}_i^{\,4} + \frac{1}{2} a_1 \left(\vec{\xi}_i \cdot \vec{\xi}_{i+1} \right) + \frac{1}{8} a_2 \left(\vec{\xi}_i \cdot \vec{\xi}_{i+2} \right) + \frac{1}{2} f \left(\vec{\xi}_i \times \vec{\xi}_{i+1} \right)_z \tag{1}$$

The order parameter $\vec{\xi}_i$, is a projection of the usual liquid crystal director $\hat{\boldsymbol{n}}$ on the xy plane, with components $\vec{\xi}_{i,x}$ and $\vec{\xi}_{i,y}$. The coefficient a_0 is temperature dependent as $a_0 = a(T - T_0)$, where $a > 0$ and T_0 is the transition temperature at which an isolated smectic layer becomes tilted. We consider b_0 as positive, which means that the transition to the tilted structure is continuous. The coefficient a_1 indicates the nearest layers interaction and can be positive or negative, thus favoring anticlinic or synclinic tilt configuration in neighboring layers. On the other hand, a_2 is positive to allow for SmC^*_α phases. Chiral interaction presented by f acts between neighboring layers and was previously neglected [5]. It could be positive or negative favoring left or right handed modulations. This discrete chiral parameter f is related to the Lifshitz coefficient Λ with relation [10]

$$\Lambda = fd \tag{2}$$

where d is the smectic layer thickness. The magnitude of f is assumed to be smaller than a_1. The free energy of the film is obtained as a sum of all terms over all layers.

To find the effects of chirality on a N-layered thin smectic film, one needs to construct the phase diagram of $\frac{a_0}{a_2}$ *versus* $\frac{a_1}{a_2}$ at different $\frac{f}{a_2}$ values with respect to the stable structures. The smectic free energy is first expanded with respect to $\vec{\xi}_{i,x}$ and $\vec{\xi}_{i,y}$ from $i = 1$to $i = N$. The Hessian matrix of the free energy is:

$$\begin{bmatrix}
\frac{\partial^2 G}{\partial \xi_{1,x}^2} & \cdots & \frac{\partial^2 G}{\partial \xi_{1,x} \partial \xi_{N,x}} & \frac{\partial^2 G}{\partial \xi_{1,x} \partial \xi_{1,y}} & \cdots & \frac{\partial^2 G}{\partial \xi_{1,x} \partial \xi_{N,y}} \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
\frac{\partial^2 G}{\partial \xi_{N,x} \partial \xi_{1,x}} & \cdots & \frac{\partial^2 G}{\partial \xi_{N,x}^2} & \frac{\partial^2 G}{\partial \xi_{N,x} \partial \xi_{1,y}} & \cdots & \frac{\partial^2 G}{\partial \xi_{N,x} \partial \xi_{N,y}} \\
\frac{\partial^2 G}{\partial \xi_{1,y} \partial \xi_{1,x}} & \cdots & \frac{\partial^2 G}{\partial \xi_{1,y} \partial \xi_{N,x}} & \frac{\partial^2 G}{\partial \xi_{1,y}^2} & \cdots & \frac{\partial^2 G}{\partial \xi_{1,y} \partial \xi_{N,y}} \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
\frac{\partial^2 G}{\partial \xi_{N,y} \partial \xi_{1,x}} & \cdots & \frac{\partial^2 G}{\partial \xi_{N,y} \partial \xi_{N,x}} & \frac{\partial^2 G}{\partial \xi_{N,y} \partial \xi_{1,y}} & \cdots & \frac{\partial^2 G}{\partial \xi_{N,y}^2}
\end{bmatrix}$$

The phase transition from the non-tilted film structure to the tilted film structure is found by the following procedure. Starting with $a_0 = 0$ (the temperature equal to the transition temperature), one increases its value in small ΔT steps. Only the diagonal terms of the Hessian matrix contain the term a_0, which depends on temperature. Eigenvalues and corresponding eigenvectors are related to the fluctuation modes. The critical fluctuation of SmA is reached when all of the 2 N eigenvalues become positive and the two smallest eigenvalues are zero at the same temperature. The transition temperature of the critical SmA is found for different $\frac{a_1}{a_2}$ values (see Fig. 1 and Fig. 2).

Chiral interactions increase the transition temperature to the SmA. This is clearly shown in Figures 1 and 2. Phases at temperatures above the dashed lines

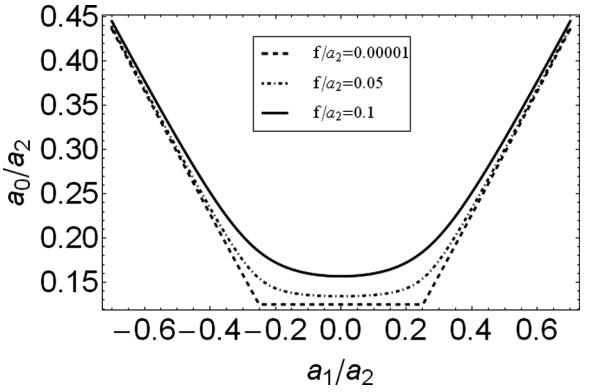

Figure 1. Critical SmA temperature of $\frac{a_0}{a_2}$ *versus* $\frac{a_1}{a_2}$ at various $\frac{f}{a_2}$ ratios for N = 3.

are SmA, while below are either uniplanar phases or wound $\mathrm{Sm}C^*_\alpha$ depending on $\frac{a_1}{a_2}$ values.

To obtain structures below the transition temperature, the procedure is the following. The small fraction of the critical fluctuation eigenvector, which is normalized to 1, is considered as a first approximation of the structure close to the transition temperature for a certain set of ratios $\frac{a_1}{a_2}$ and $\frac{f}{a_2}$. The search is simplified as one can choose the x- component or the y- component fluctuation eigenvectors only, which is allowed due to the rotational symmetry of the problem. For a solution to be stable, its free energy first derivatives with respect to $\xi_{i,\,x}$ and $\xi_{i,\,y}$ have to be zero. In this case, the non-trivial $\xi_{i,x}$ and $\xi_{i,y}$ solution is found by approximation using the eigenvectors fraction as the initial approximation. Using Newton's approximation, the real solution is found step by step. The first derivatives are expanded in terms of small corrections. The expanded derivatives are equated to the first derivatives using initial approximation. The small correction found is used to find the new initial approximation again. New initial approximation is checked with the first derivatives. If the desired degree of accuracy is not achieved, the cycle is repeated once more. At every step, the eigenvalues should not be negative for the solution to be stable.

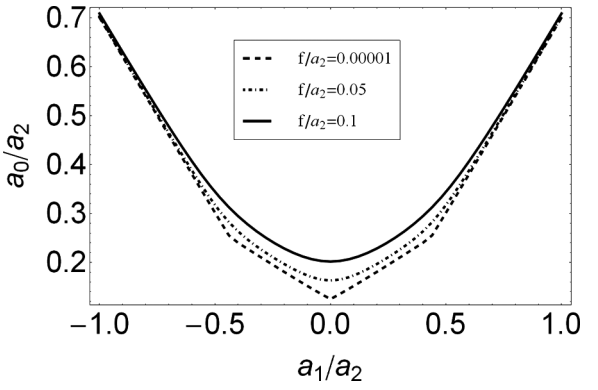

Figure 2. Critical SmA temperature of $\frac{a_0}{a_2}$ *versus* $\frac{a_1}{a_2}$ at various $\frac{f}{a_2}$ ratios for N = 4.

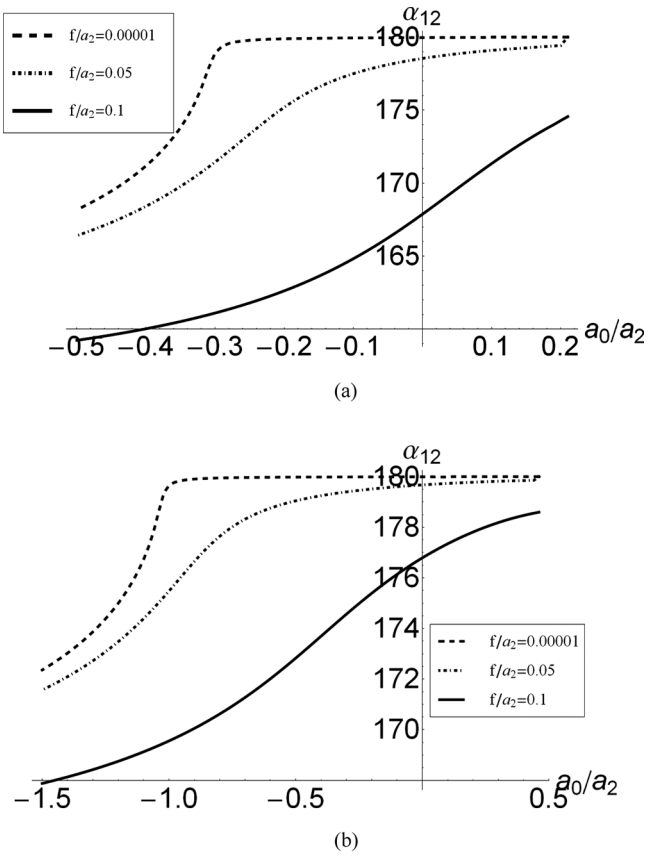

Figure 3. (a) Phase difference between tilt vectors 1 and 2 for $N = 4$, $\frac{a_1}{a_2} = 0.30$; (b) Phase difference between tilt vectors 1 and 2 for $N = 4$, $\frac{a_1}{a_2} = 0.70$.

Solutions showed that structures of achiral films immediately below the critical SmA are uniplanar except at few particular $\frac{a_1}{a_2}$ values. These uniplanar structures become unstable again when the second lowest eigenvalue reaches zero. The rotational symmetry is reflected in the existence of one zero eigenvalue representing the Goldstone mode. This condition usually serves as an additional verification of the solution. The uniplanar and non-planar SmC^*_α structures found by the method described above with the initial solution to be a fraction of the eigenvectors correspond to second minimum eigenvalue that are now zero-valued.

When chirality is considered, the second minimum eigenvalue does not reach zero and the structure continuously develops into the tilted structure (Fig. 3). Without the zero eigenvalue, which marks the transition temperature, as a criterion for transition one could use the structure. Figure 3a and 3b below shows the phase difference between two tilt vector of $N = 4$ system.

3. Results and Discussion

For $\frac{f}{a_2}$ which is much smaller than $\frac{a_1}{a_2}$, for example at $\frac{f}{a_2} = 0.00005$ which is $\frac{1}{1000}$ smaller, the boundary between the uniplanar and the SmC^*_α phase is still evident by the

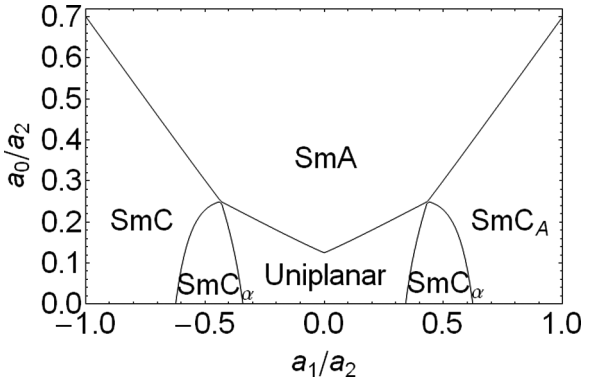

Figure 4. Phase diagram of $\frac{a_0}{a_2}$ *versus* $\frac{a_1}{a_2}$ at $\frac{f}{a_2} = 0$ for $N = 4$.

abrupt change of phase difference from 0 or π in the uniplanar phase. Then transition may be defined as the point where the second derivative (related to the curvature of the line giving the phase difference) of phase difference with respect to a_0 reaches the maximum. This definition is most applicable when chirality is small. However as $\frac{f}{a_2}$ increases, the abrupt change of the phase difference is diminished by continuous increment or decrement of angle within the uniplanar phase. This becomes obvious at $\frac{f}{a_2} = 0.005$. When $\frac{f}{a_2}$ is comparable to $\frac{a_1}{a_2}$ (say $\frac{1}{10}$ smaller), the phase difference is far from uniplanar immediately after critical SmA which makes the separation of the phase diagram to different structures more difficult or even impossible. One has to bear in mind, that all structures now have the same symmetry. Figure 4 is the phase diagram of the case $N = 4$, $\frac{f}{a_2} = 0$. In $\frac{f}{a_2} \neq 0$ case, the SmC^*_α regions in the phase diagram are expected to be wider, growing to the left, right and upward.

Figure 5 is the phase difference graph of $N = 3$ system. By looking at it, the SmC^*_α regions in Figure 6 should grow as well.

If one applies the criterion of maximal second derivative, one still sees two different regions. In the uniplanar region the structures are more similar to the uniplanar phases by the fact that inner layers are less tilted, while in the SmC^*_α phase the opposite is true. Figures 7(a–d) and 8(a–b) showed the structures at the same

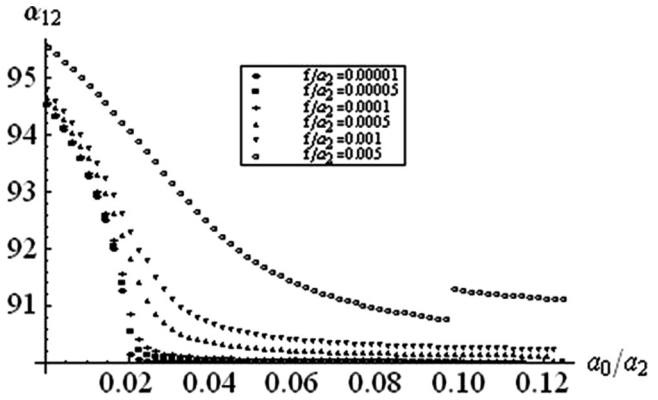

Figure 5. Phase difference between tilt vectors 1 and 2 for $N = 3$, $\frac{a_1}{a_2} = 0.10$.

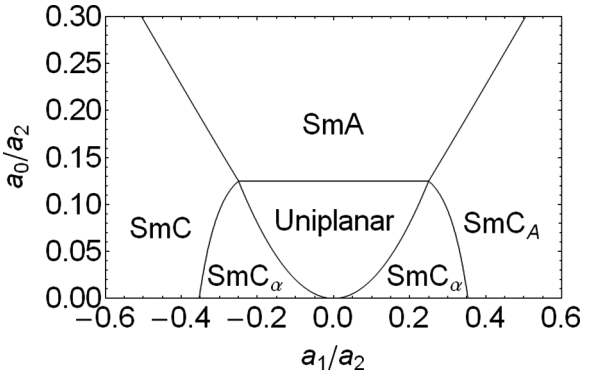

Figure 6. Phase diagram of $\frac{a_0}{a_2}$ *versus* $\frac{a_1}{a_2}$ at $\frac{f}{a_2} = 0$ for $N = 3$.

temperature for the cases with and without chiral interaction. For the case without chirality, the structures are still uniplanar while when $\frac{f}{a_2} = 0.005$ at the same temperature of $\frac{a_0}{a_2} = 0$, the structures are clearly not uniplanar.

For the structure that is already SmC^*_α at a certain temperature, imposing chirality does not significantly change the whole structure. We show the data for two film structures in the table below (Table 1); the first is formed of achiral and the second of chiral molecules.

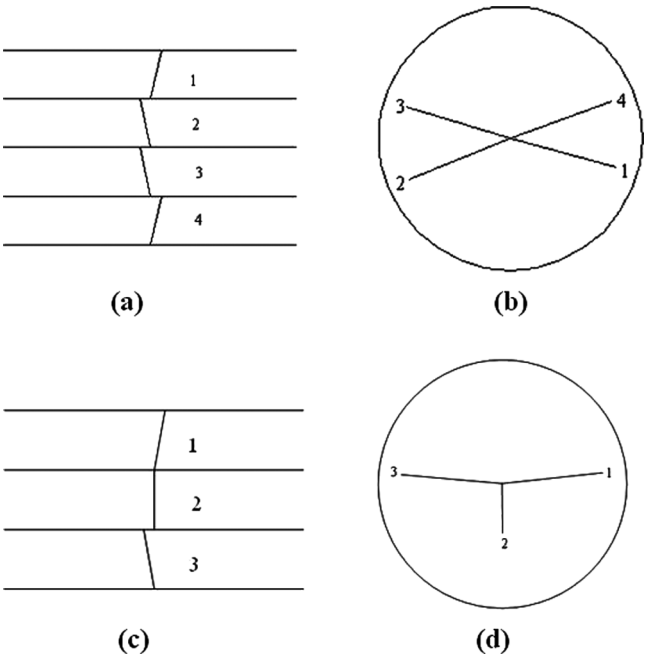

Figure 7. (a) Side view of the structure and (b) bird view of the structure at $N = 4$, $\frac{a_1}{a_2} = 0.02, \frac{a_0}{a_2} = 0, \frac{f}{a_2} = 0.005$ (with circle's radius = 2.5 degree). (c) Side view of the structure and (d) bird view of the structure at $N = 3$, $\frac{a_1}{a_2} = 0.10, \frac{a_0}{a_2} = 0, \frac{f}{a_2} = 0.005$ (with circle's radius = 2.5 degree).

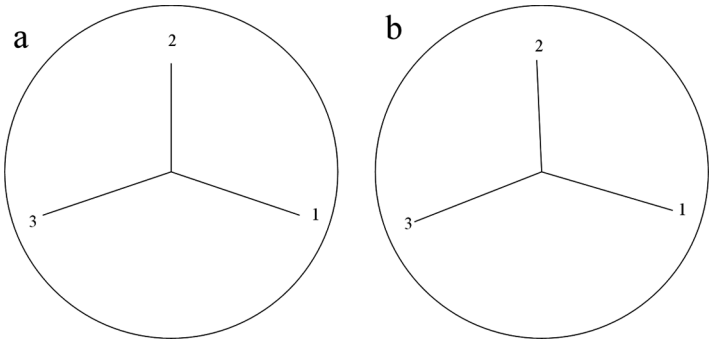

Figure 8. (a) Bird view of the structure at N = 3, $\frac{a_1}{a_2} = 0.20, \frac{a_0}{a_2} = 0$, $\frac{f}{a_2} = 0$ (with circle's radius = 2.5 degree) and (b) bird view of the structure at N = 3, $\frac{a_1}{a_2} = 0.20, \frac{a_0}{a_2} = 0$, $\frac{f}{a_2} = 0.005$ (with circle's radius = 2.5 degree).

Table 1. Data for structures at $\frac{a_1}{a_2} = 0.20$ for $\frac{f}{a_2} = 0$ and $\frac{f}{a_2} = 0.005$

Chirality	α_{12} (degree)	α_{13} (degree)	θ_1 (degree)	θ_2 (degree)
$\frac{f}{a_2} = 0$	108.7	142.7	2.0	1.6
$\frac{f}{a_2} = 0.005$	108.9	142.1	2.0	1.7

4. Conclusions

We have shown that the uniplanar structures of free standing antiferroelectric smectic films, which are stable below the SmA phase at various $\frac{a_1}{a_2}$ values are narrower, if chiral interactions are present. Chirality increases the transition temperature of uniplanar to SmC^*_α when its value is small, and the increase of chirality eliminates the uniplanar structure below the SmA. The structures that are uniplanar when chirality is not present, become non-uniplanar with the influence of chirality; while for structures that are already non-planar, imposing chirality does not further change the structures much.

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