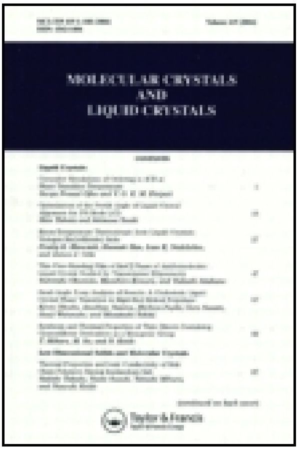

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Surface Transitions in Free Standing Films of Antiferroelectric Liquid Crystals Within the Discrete Phenomenological Model

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To cite this article: Barbara Rovšek, Mojca Čepič & Boštjan Žekš (1999): Surface Transitions in Free Standing Films of Antiferroelectric Liquid Crystals Within the Discrete Phenomenological Model, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 329:1, 365-373

To link to this article: http://dx.doi.org/10.1080/10587259908025958

Mol. Cryst. Liq. Cryst., 1999, Vol. 329, pp. 365-373
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Surface Transitions in Free Standing Films of Antiferroelectric Liquid Crystals Within the Discrete Phenomenological Model

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Within the discrete phenomenological model of antiferroelectric liquid crystals we study phase transitions in free standing films. Commonly observed rise as well as recently reported lowering of the temperature of the transition from the SmA to the tilted phase, compared to the bulk transition temperature, can be explained in view of the excess surface order in the first case or missing inter-layer interactions at the surfaces in the second case. We also expose the possibility of forming non-planar SmC_α phase in a narrow temperature region near the bulk SmA ↔ SmC transition temperature, although the particular compound exhibits only SmA and SmC (or SmC*, if chiral) phases in the bulk sample.

Keywords: antiferroelectric liquid crystals; free standing films; discrete model of antiferroelectric liquid crystals

INTRODUCTION

In free standing films of antiferroelectric liquid crystals phase transitions between different smectic phases follow different courses than in the bulk. They are strongly influenced by the finite number of the smectic layers present in the film as well as by higher smectic order at the free surfaces. It has been pointed out many times that the later leads to the separate surface transition, which occurs at some definite temperature above the bulk transition temperature and where only the few surface layers undergo the transition to the low temperature phase, while the interior of the film remains in the high temperature phase [1]. We explain the surface transition in view of the discrete phenomenological model of antiferroelectric liquid crystals [2,3]. We also show how the missing inter-layer interactions at the surfaces influence the phase transition temperature and the structures of the tilted phases in free standing films. Opposite to the effects of the higher smectic order at the surfaces, missing neighboring layers at the surfaces may lead to a decrease of the transition temperature (reported in [4]) and smaller magnitude of the tilt in the surface layers, compared to the interior of the film. It may and it was notified to occur in some real samples that both effects almost exactly cancel each other [5], leaving the transition temperature equal to the bulk transition temperature. All the three possibilities of changing the transition temperature, decreasing, increasing or staying the same, may be explained within the discrete model. The missing inter-layer interactions at the surfaces are basically built into the model, while the excess of the surface smectic order is considered by a choice of the model parameters.

Particularly we were interested to find an interpretation of experimental results, obtained by the ellipsometry measurements [6]. A compound MHPOOCBC, that measurements refer to, is reported to exhibit the straightforward bulk phase sequence *isotropic* $\overset{104^\circ C}{\longleftrightarrow}$ SmA $\overset{87^\circ C}{\longleftrightarrow}$ SmC. Yet the measurements done on the free standing films are leading up to the conclusion, that the phase transition between SmA and SmC phase in the film goes indirectly through an intermediate, possibly non-planar phase. However, we managed to chose the model parameters that qualitatively satisfy the known facts about the phase transitions and the structures formed by the definite liquid crystal compound, as in the bulk, as in the free standing films.

Discrete model

For a N-layers film of achiral liquid crystal compound, which may appear in SmA, SmC, SmC$_A$ and SmC$_\alpha$ phases, an expansion of the free energy in the discrete order parameter - tilt vector $\boldsymbol{\xi}_i$ - is [3]

$$\begin{aligned} G &= \sum_{i=1}^{N}\left[\frac{1}{2}a_0\boldsymbol{\xi}_i^2+\frac{1}{4}b_0\boldsymbol{\xi}_i^4+\frac{1}{4}a_1\left(\boldsymbol{\xi}_i\cdot\boldsymbol{\xi}_{i-1}+\boldsymbol{\xi}_i\cdot\boldsymbol{\xi}_{i+1}\right)\right. \\ &+ \frac{1}{16}a_2\left(\boldsymbol{\xi}_i\cdot\boldsymbol{\xi}_{i-2}+\boldsymbol{\xi}_i\cdot\boldsymbol{\xi}_{i+2}\right)+\frac{1}{4}a_1'\boldsymbol{\xi}_i^2\left(\boldsymbol{\xi}_i\cdot\boldsymbol{\xi}_{i-1}+\boldsymbol{\xi}_i\cdot\boldsymbol{\xi}_{i+1}\right) \\ &+ \left.\frac{1}{16}a_2'\boldsymbol{\xi}_i^2\left(\boldsymbol{\xi}_i\cdot\boldsymbol{\xi}_{i-2}+\boldsymbol{\xi}_i\cdot\boldsymbol{\xi}_{i+2}\right)\right]. \qquad (1) \end{aligned}$$

The sum (1) is formally correct if $\xi_{-1}=\xi_0=\xi_{N+1}=\xi_{N+2}=0$. The only temperature dependent parameter is $a_0=a(T-T_0)$, a is positive and T_0 would be a temperature of transition to a tilted phase if there wasn't any interaction between the neighboring layers. Parameter b_0 is positive as is usual when transitions are of the second order.

In order to phenomenologically describe the effects of the excess of the smectic order in the surface layers, compared to the rest of the film, we take different parameters $\tilde{a}_0$ and $\tilde{b}_0$ for the surface layers. To obtain surface transition, i.e. transition in the surface layers, at temperature higher than in the bulk, the temperature dependent parameter $\tilde{a}_0$ for the surface layer is less than a_0 for the interior layers and the transition temperature $\tilde{T}_0$ is larger than T_0. The difference $\Delta a_0=a_0-\tilde{a}_0$ is temperature independent. The parameter $\tilde{b}_0$ was taken smaller than b_0.

Terms with parameters a_1 and a_1' describe interactions between the nearest layers and terms with a_2 and a_2' represents the next-nearest layers interactions. In the systems which exhibit SmC$_\alpha$ phase, a_2 is positive and large enough, compared to the a_1.

Parameters

Qualitatively only the ratios of the model parameters matter, therefore we take all of them to be dimensionless. In the bulk sample of the compound MHPOOCBC the common ferroelectric SmC phase succeeds the SmA phase immediately, therefore the parameter a_1 has to be negative. If a_2 was also negative, we would not have any frustrating situation, the minimum of the free energy would always correspond to the SmC phase. But for the free standing films, we have experimental evidence of possible existence of the non-planar phase in narrow temperature interval around the SmA ↔ SmC bulk transition temperature. That led us to set the parameter a_2 positive, but smaller than a_1 in absolute value, because the non-planar phase may only form in the restricted geometry of the free standing film and not in the bulk. The surface transition in the film occurs at temperatures much higher than the bulk transition temperature, therefore the difference $\Delta a_0 = a_0 - \tilde{a}_0$ must be substantial.

TRANSITION SmA ⟷ TILTED PHASE

Minimization of the harmonical part of the free energy in fluctuations of the order parameter in the SmA phase gives a system of $2N$ coupled homogeneous linear equations, which are, introducing a general vector notation

$$\delta\boldsymbol{\xi} = \{\delta\boldsymbol{\xi}_x, \delta\boldsymbol{\xi}_y\} = \{\delta\xi_{1,x}, \delta\xi_{2,x}, ...\delta\xi_{N,x}, \delta\xi_{1,y}, \delta\xi_{2,y}, ...\delta\xi_{N,y}\}, \tag{2}$$

written as vector equation

$$A_o\, \delta\boldsymbol{\xi} = 0\,, \tag{3}$$

where $\delta\boldsymbol{\xi}$ is $2N$-dimensional vector, which describes the $x-$ and $y-$ components of the tilt fluctuations in N layers and A_0 is a matrix of coefficients, dependent on the model parameters. The first non-trivial solution of the eqn.(3) appears at the temperature of transition from the SmA to the tilted phase. It corresponds to the temperature, where the first order parameter fluctuation becomes unstable. In Fig.1 we have plotted SmA ⟷ *tilted phase* transition temperature in dependence of the excess surface order, i.e. Δa_0, for nine- and fifteen- layers films.

If temperature dependent parameter $\tilde{a}_0$ in the surface layers is the same as in the rest of the film, i.e. $\Delta a_0 = 0$, the transition temperature T_c^{film} in the film is lower than the transition temperature T_c^{bulk} in the bulk. Namely, the inter-layer interactions increase the transition temperature, $T_c^{bulk} > T_0$. If a part of the interactions are missing, as is the case at the surfaces of the free standing film, the transition temperature in the film

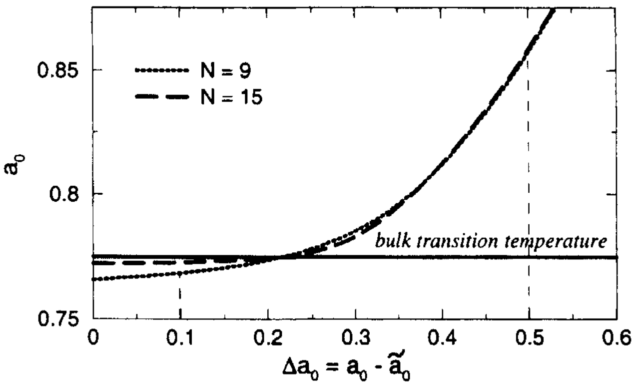

Figure 1: Temperatures a_0, where the first fluctuation becomes unstable, for $a_1 = -1$, $a_2 = 0.9$ and different values of Δa_0. SmA and tilted phases are stable above and below the curve, respectively.

would consequently appear lower than in the bulk. With increasing the number of layers the difference between the film and the bulk transition temperature diminishes and approaches zero. In the case of larger smectic order at the surfaces, Δa_0 is larger than zero and the transition temperature is increased. If the transition temperature in the film is larger than in the bulk, it corresponds to the surface transition temperature. For the chosen parameters a_1 and a_2 the transition temperature in the film equals the bulk transition temperature around $\Delta a_0 \approx 0.22$.

TILTED LOW TEMPERATURE PLANAR PHASES

The tilted structure just after the transition is always planar, characterized by the in-plane tilt of the director everywhere in the film. Structure of the planar phase at lower temperatures can be found by solving a set of nonlinear equations obtained by minimization of the complete expression for the free energy (1) in the order parameters ξ_i.

It is distinctive of the restricted geometry of the free standing film, that we may get more than one stable structures at the same temperature - one represents the real minimum of the free energy and others are metastable.

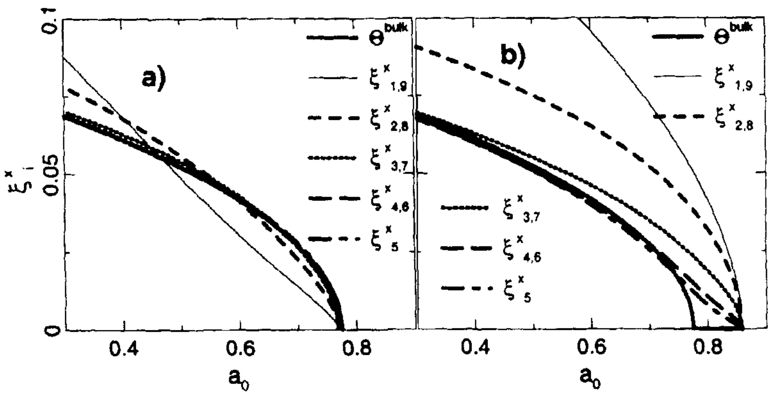

Figure 2: Temperature evolution of the planar structure in a nine-layers film, for a set of parameters $a_1 = -1$, $a_2 = 0.9$, $a_1' = a_2' = 0$, $b_0 = 100$, $\tilde{b}_0 = 20$, **a)** $\Delta a_0 = 0.1$ and **b)** $\Delta a_0 = 0.5$.

By changing the temperature the first order phase transitions between them are possible. On Figs.2a&b we show temperature evolution of the first symmetrical planar structures, corresponding to the cuts at two values of Δa_0 on the Fig.1. In the case where $\Delta a_0 = 0.1$, the effect of the larger surface order is weaker than the effect of the missing inter-layer interaction, therefore the transition temperature is lower than in the bulk and the tilt in the surface layers is smaller than in the rest of the film. In the second case, where $\Delta a_0 = 0.5$, the situation is opposite and we get a surface transition at higher temperature and larger tilt in the surface layers.

By properly choosing the model parameters we may get into regime, where the first symmetrical planar structure, which develops after the transition from the SmA phase, is not sinclinic. To our belief (as we shall point out later) this is the situation relevant to the experiments [6]. An example is shown in Fig.3. At the surface transition temperature ($a_0 \approx 0.31$, see Fig.3a) a continuous transition takes place from the SmA phase to the tilted planar, the first symmetrical phase. By lowering the temperature the structure develops from the one, where the tilt is considerable only in the surface layers, to the one, where the tilt is large through the whole film, but not sinclinic. As can be seen from the Fig.3a, the tilt in the middle layers is opposite to the tilt in the few surface layers. Looking at the Fig.3e, where a difference between the free energy of the first symmetrical and the free energy of the sinclinic ferroelectric phase is shown in dependence of temperature, we see the first symmetrical structure is stable to the temperature around $a_0 \approx 0.05$, where a first order phase transition to the sinclinic ferroelectric phase may occur. Ferroelectric planar phase (see Fig.3b) exists as metastable phase also at higher temperatures, and the first symmetrical phase remains metastable at lower temperatures.

NON-PLANAR PHASE

The stability of the planar structures against the out-of-plane fluctuations was analyzed in the same manner as the stability of the SmA phase. We discovered that the transition from the non-sinclinic, first symmetrical planar phase to the sinclinic ferroelectric phase may proceed continuously through the non-planar, twisted, we call it SmC$_\alpha$ phase. By a suitable choice of the model parameters we obtain optionally narrow temperature interval, where SmC$_\alpha$ exists. The existence of the SmC$_\alpha$ phase is a distinctive property of the limited ranging of the liquid crystal film. We stress again that for the same parameters SmC$_\alpha$ phase does not appear in bulk.

As suggested in [2,3], the structure of the SmC$_\alpha$ phase turns out characterized by a rotation of the layer-tilt vector, as we proceed from the i-th layer to the next, for a certain angle $\Delta\phi_i = \phi_{i+1} - \phi_i$, which, in general, may have any value between 0 and π. The resulting helicoidal modulation of the structure is a consequence of the competing nearest and next-nearest layers interactions alone disregarding a weak additional modulation due to the eventual chirality of the liquid crystal. In the bulk sample $\Delta\phi_i$ is the same everywhere as well as the magnitude of the tilt Θ_i, while in the finite size films there are discrepancies at the free surfaces, due to the fact that the surface layers have the neighboring layers, which they interact with, just on one side. As the temperature is varied, the structure of the SmC$_\alpha$ phase changes continuously. For a seven-layers film

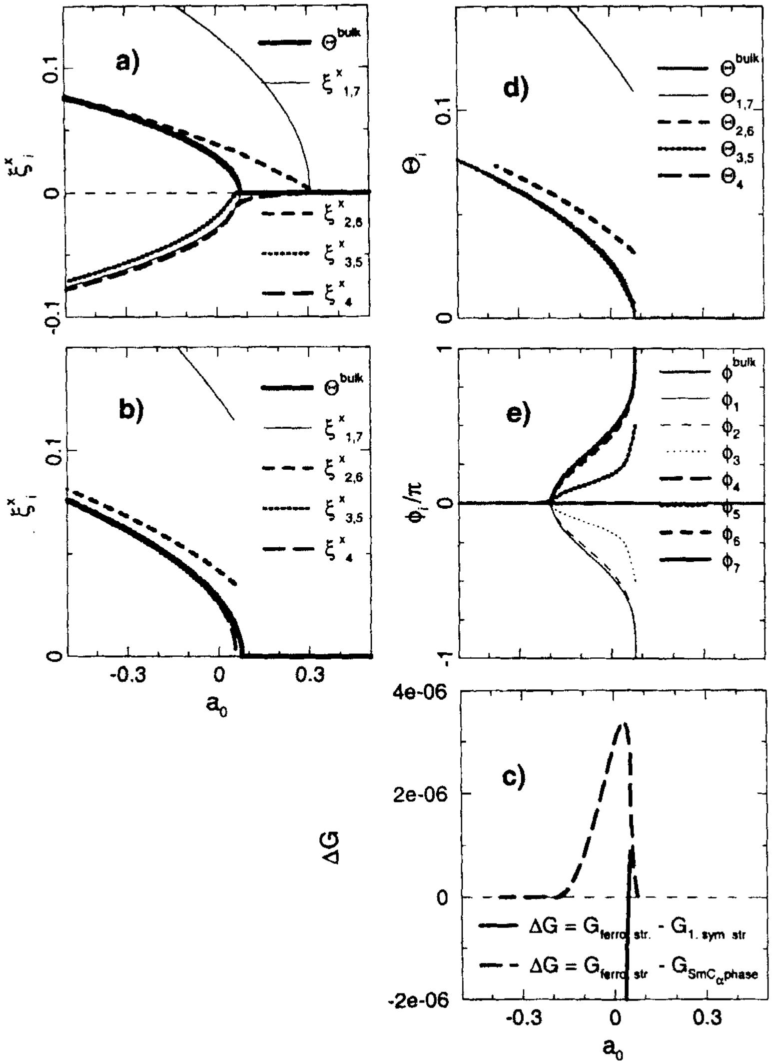

Figure 3: Different structures in a seven-layers film, **a)** the first symmetrical planar phase, **b)** the ferroelectric phase, **c)** the magnitude and **d)** the phase of the tilt in the SmC$_\alpha$ phase and **e)** the difference of the energies of various (meta)stable structures. Parameters are $\Delta a_0 = 0.3$, $a_1 = -0.1$, $a_2 = 0.09$, $a_1' = 0$, $a_2' = -1$, $b_0 = 100$ and $\tilde{b}_0 = 20$.

magnitudes and phase angles of the tilt in different layers are shown in Figs.3c&d in dependence of temperature. In absence of an external field the structure is invariant upon rotation around the normal to the smectic layers, therefore the phase angle ϕ_4 in the middle layer was arbitrarily chosen to be zero. SmC_α phase is a link between the two planar phases, the first symmetrical phase, which is stable at higher temperatures, and the ferroelectric phase, which is stable at lower temperatures. A comparison of the energies of different structures is shown on the Fig.3e. For the SmC_α phase a temperature dependence of an average tilt exhibits a continuous drop to zero at temperature close below the bulk transition temperature.

CONCLUSIONS

The results are in qualitative agreement with experiment [6]. We can explain unusual and unexpected change of the ellipsometric parameters Δ_+ and Δ_-, which become almost equal in a narrow temperature range near the bulk transition temperature, with the appearance of the non-planar phase. The difference $(\Delta_- - \Delta_+)$ is a direct measure of the average tilt angle in the film [6], which is zero in SmA and antiferroelectric phase and equals the tilt angle in ferroelectric phase. In the SmC_α it may be anything from zero to the maximum average tilt angle, which corresponds to the sinclinic ferroelectric phase. We believe that behavior of the ellipsometric parameters near the bulk transition temperature for a compound MHPOOCBC in free standing films may be ascribed to the existence of the intermediate non-planar phase between the SmA and sinclinic SmC phase, as we described.

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