

## Theoretical analysis of continuous pitch evolution and reversed phase sequence in antiferroelectric liquid crystals

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Recent studies reported continuous shortening of the pitch from more than four layers to less than four layers in the helicoidally modulated tilted Sm  $C_\alpha^*$  phase. In a different system, the reversed phase sequence was found: the ferroelectric tilted Sm  $C^*$  phase appeared below the four-layer Sm  $C_{F12}^*$  phase upon cooling. In this contribution we quantitatively explain the behavior within the discrete phenomenological model and we found that both behaviors are the consequence of the same reason: the quadrupolar interlayer interactions.

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Antiferroelectric liquid crystals are chiral smectics (Sm) in which a whole zoo of phases having very different structures within a relatively narrow temperature range exists. Usually the most general phase sequence upon lowering the temperature is Sm  $A$ -Sm  $C_\alpha^*$ -Sm  $C^*$ -Sm  $C_{F12}^*$ -Sm  $C_{F11}^*$ -Sm  $C_A^*$  [1]. Within this sequence the Sm  $A$  phase is a usual orthogonal smectic phase and the Sm  $C^*$  phase is a usual tilted chiral ferroelectric phase. The lowest-temperature smectic phase in the sequence is usually the antiferroelectric Sm  $C_A^*$  phase where molecules are tilted in opposite directions in neighboring layers. This phase has given materials the name antiferroelectric liquid crystals. In addition to three “simple” phases, three more phases were experimentally observed and their structures were unambiguously determined by resonant x-ray measurements [2]. The Sm  $C_\alpha^*$  phase which always appears strictly below the Sm  $A$  phase has a very short helical modulation extending over few layers only. The two intermediate phases, Sm  $C_{F12}^*$  and Sm  $C_{F11}^*$ , have structures that have periodicities of four and three layers, respectively, and two different phase angles between tilt directions in neighboring layers. They appear below the Sm  $C^*$  phase or the Sm  $C_\alpha^*$  phase if the Sm  $C^*$  phase is absent. Both phases appear always above the antiferroelectric Sm  $C_A^*$  phase.

Two theories describe the possible phase sequences and their dependence on the optical purity of the samples. The discrete phenomenological model [3,4] and the Hamaneh-Taylor model [5,6]. The discrete model separates intermolecular interactions into phenomenologically expressed interactions within the layer and between the neighboring layers. The model allows for the reproduction of phase structures and sequences although a single model coefficient is considered as temperature dependent. The reason for lock-in is the biquadratic coupling between neighboring layers originating from quadrupolar interactions and in the quadrupolar ordering [4,13]. The Hamaneh-Taylor model considers elastic layer fluctuations as a source for the lock-in to commensurate structures. Various phase sequences can be reproduced, but one has to consider the temperature dependence of two model coefficients: the favorable phase difference between tilts in neighboring layers and the interlayer coupling [5,6].

Two recent reports opened new questions. The continuous

evolution of the incommensurate nanoscale helical pitch (INHP) through four layers [7] and the partially reversed phase sequence Sm  $C_\alpha^*$ -Sm  $C_{F12}^*$ -Sm  $C^*$  with nonmonotonous development of the INHP in the Sm  $C_\alpha^*$  phase [8] were never detected before. The authors mentioned the qualitative explanation of the observations within the Hamaneh-Taylor model as the only possibility.

In this paper we show that both experimental results can be quantitatively reproduced within the discrete phenomenological model with proper choice of model coefficients and a single coefficient depending on temperature. Even more, we show that both very different phenomena, the continuous pitch evolution and the appearance of the Sm  $C^*$  phase below the Sm  $C_{F12}^*$  phase, can be explained by the competition of the electrostatic quadrupolar and van der Waals interactions phenomenologically described by the same term—the biquadratic coupling between neighboring layers. The basic discrete phenomenological free energy [3] where interlayer interactions are taken into account explicitly is given by

$$G = \sum_j \frac{1}{2} a_0 \vec{\xi}_j^2 + \frac{1}{4} b_0 \vec{\xi}_j^4 + \frac{1}{2} a_{10} (\vec{\xi}_j \cdot \vec{\xi}_{j+1}) + \frac{1}{2} a_{11} \vec{\xi}_j^2 (\vec{\xi}_j \cdot \vec{\xi}_{j+1}) + \frac{1}{8} a_2 (\vec{\xi}_j \cdot \vec{\xi}_{j+2}). \quad (1)$$

Here first two terms consider interlayer interactions and are usual terms describing the transition to the tilted phase. The transition to the tilted phase takes place at the temperature  $T_0$  in the presence of intralayer interactions only. The next two terms give achiral interactions of the  $j$ th layer with its nearest layers. The term with the coefficient  $a_{11}$  resumes that the increasing tilt order influences the interlayer interactions. The fourth term  $a_2$  gives interactions to next-nearest layers, which arise due to the flexoelectric interactions mainly [9–11]. The piezoelectrically induced polarization is of chiral origin and it strongly influences the achiral interlayer coupling  $a_1$  [9]. It is reasonable to expect that interlayer interactions decrease with the distance of interacting layers. However, if more competing interactions come into play the interactions between nearest layers may cancel out and the interactions to more distant layers may become important.

This scenario seems to be the most probable reason that so many phases appear within a narrow temperature range in antiferroelectric liquid crystals. The interactions between nearest layers consist of steric interactions, where the same tilt in neighboring layers is promoted due to the interlayer molecular diffusion. The molecular chirality results in effective polarization when molecules are tilted, and dipoles order antiparallely [12], i.e., antiparallel ordering of tilts in neighboring layers is favored. In addition, taking into account positional correlations of molecules in neighboring layers, the van der Waals attractive forces favor antiparallel tilt ordering as well. If the tilt affects these interactions, it may happen that one of the interactions prevail in one and the other in another temperature window resulting in the formation of different phases. With increasing tilt interactions change continuously and so one can expect that the phase properties like helical pitch change continuously as well. Chiral interactions, which are related to the long helical modulations in the  $\text{Sm } C^*$  and the  $\text{Sm } C_A^*$  phases, are the consequence of chiral interactions originating in the deviation of molecular structure from the mirror symmetrical. They are usually small and are not the reason for the short modulation in the  $\text{Sm } C_\alpha^*$  phase. Therefore, we neglect the influence of chiral interactions on the magnitude of the tilt and on the difference in tilt directions in neighboring layers in the continuation.

The tilt order parameter in the  $j$ th layer is

$$\vec{\xi}_j = \theta \{\cos(j\alpha + \varphi_0), \sin(j\alpha + \varphi_0)\}, \quad (2)$$

where  $\theta$  gives the magnitude of the tilt and the expression in the trigonometric braces gives the tilt direction with respect to the arbitrary chosen direction in the smectic plane. The difference between tilt directions in neighboring layers, i.e., the phase difference, is given by  $\alpha$  and  $\varphi_0$  is the direction of the tilt in the layer enumerated as zero. The  $\varphi_0$  can have any value due to the rotational symmetry of the bulk structure. The free-energy equation (1) becomes

$$G = \frac{1}{2}a_0\theta^2 + \frac{1}{4}b_0\theta^4 + \frac{1}{2}(a_{10} + a_{11}\theta^2)\theta^2 \cos \alpha + \frac{1}{8}a_2\theta^2 \cos 2\alpha. \quad (3)$$

The minimization of the free-energy equation (4) with respect to the phase difference  $\alpha$  gives three solutions

$$\alpha = \arccos\left(-\frac{a_{10} + a_{11}\theta^2}{a_2}\right), \quad \alpha = 0, \quad \text{or} \quad \alpha = \pi. \quad (4)$$

For a positive  $a_2$  the phase difference  $\alpha$  has a general value if  $|a_{10} + a_{11}\theta^2| < a_2$ . If  $|a_{10} + a_{11}\theta^2| > a_2$  tilts in neighboring layers are parallel ( $\alpha=0$ ) for negative numerator or antiparallel ( $\alpha=\pi$ ) for the positive one. If interlayer interactions can be considered as much weaker than intralayer interactions, one can neglect their influences on the magnitude of the tilt and the tilt can be expressed as

$$\theta^2 = -\frac{a(T - T_0)}{b_0}, \quad (5)$$

which allows for a direct comparison of theoretical and experimental values of INHP,

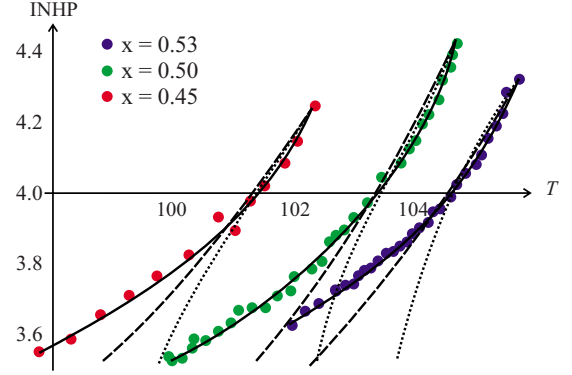


FIG. 1. (Color online) Continuous pitch evolution in three mixtures and the fitted curves. Dashed line: Eq. (6); solid line: Eq. (8); dotted line: Eq. (8) but with negative  $\tilde{b}_Q$ . Sets of measurements correspond to the following concentrations:  $x=0.45$  (left red dots),  $x=0.50$  (middle green dots), and  $x=0.53$  (right blue dots). Measurements were taken from Ref. [7].

$$\alpha = \arccos\left[-\left(\frac{a_{10}}{a_2} + \frac{a_{11}}{a_2} \frac{a}{b_0}(T - T_0)\right)\right] \\ = \arccos\{-[\tilde{a}_{10} + \tilde{a}_{11}(T - T_0)]\},$$

$$\text{INHP} = \frac{2\pi}{\alpha}. \quad (6)$$

The coefficients  $\tilde{a}_{10}$  and  $\tilde{a}_{11}$  are expressed in  $a_2$  and the effective influence of the tilt on the pitch is transformed to the dependence on the temperature by inserting Eq. (5) into Eq. (4). Let us first consider if the solution allows for the continuous change in the INHP over four layers without a usually observed lock-in. If the parameter  $\tilde{a}_{10}$  is negative, the initial pitch is larger than four layers. The positive parameter  $\tilde{a}_{11}$  leads to a continuous increase in the phase difference  $\alpha$  upon decreasing temperature. At the temperature where the numerator in Eq. (6) becomes zero the phase difference  $\alpha$  is  $90^\circ$  and the INHP is equal to four layers. With further decreasing temperature the phase difference  $\alpha$  continues to increase and the INHP continuously develops toward values smaller than 4.

To compare Eq. (6) with experimental results from [7] one has to find parameters that can reproduce the behavior. The value of  $\tilde{a}_{10}$  is extracted from the value of the INHP at the transition temperature when  $(T - T_0) = 0$  and the value of  $a_{11}$  is extracted from the temperature where the INHP is equal to 4. A comparison of experimental measurements and theoretical results (Fig. 1 dashed lines) shows that continuous pitch evolution is allowed by the basic free-energy equation (1) already; however, the description is not optimal. But it is known that quadrupolar interactions either of electrostatic [12] or geometric [14] origin are important [13]. Quadrupolar interlayer interactions are phenomenologically given by

$$\frac{1}{4}b_Q(\vec{\xi}_j \cdot \vec{\xi}_{j+1})^2. \quad (7)$$

Besides the dipole moment molecules forming chiral tilted smectic phases possess the electrostatic quadrupole moment.

TABLE I. Best-fit coefficients for the continuous evolution of pitch given in Fig. 1.

$x$	$\tilde{a}_{10}$	$\tilde{a}_{11}$	$\tilde{b}_Q$
0.53	-0.13	0.11	0.24
0.50	-0.15	0.11	0.15
0.45	-0.08	0.08	0.08

Electrostatic molecular quadrupoles give rise to interlayer interactions where perpendicular tilts are favorable [12] and they contribute to  $b_Q$  positively. If molecules have lathlike structure, the quadrupolar ordering occurs due to the hindered rotation around the long molecular axes when the molecules are tilted. As the result the interlayer molecular diffusion promoting the parallel tilt ordering increases with increasing quadrupolar order. But, van der Waals attractive interactions favor antiparallel ordering as parts of molecules in neighboring layers are effectively closer as well [13]. Both consequences can be phenomenologically given by the negative contribution to the coefficient  $b_Q < 0$ . The prevailing interactions give the coefficient  $b_Q$  the sign. The lock-in to commensurate structures appears for large enough negative values of quadrupolar coefficient only [4].

In order to answer the question if the INHP dependence on temperature can be better reproduced considering quadrupolar ordering and consequent coupling, we fitted INHP with the following expression:

$$\alpha = \arccos\left(-\frac{[\tilde{a}_{10} + \tilde{a}_{11}(T - T_0)]}{1 + \tilde{b}_Q(T - T_0)}\right),$$

$$\tilde{b}_Q = \frac{b_Q a}{a_2 b_0}. \quad (8)$$

The expression is the result of the free-energy equation (1) minimization if term (7) is added.  $\tilde{b}_Q$  was left as the free fitting parameter and the best fit is seen in Fig. 1 (solid line for values of coefficients given in Table I). Consistent with the theoretical prediction, the best fit was obtained for the positive value of coefficient  $\tilde{b}_Q$ , which does not allow for the locked periods of INHP. For comparison we plotted the curve obtained for the negative value of the coefficient  $\tilde{b}_Q$ . It is clearly seen that the observed behavior cannot be reproduced by the negative value of  $\tilde{b}_Q$  because the behavior is also qualitatively different.

Let us now turn to the second observation [8]. In the mixture of compounds called 9OHF, 10OHF, and 11OHF,  $\text{Sm } C_\alpha^*$  develops to  $\text{Sm } C_{FI2}^*$  with four-layer periodicity upon lowering the temperature. However, below the  $\text{Sm } C_{FI2}^*$  phase the simple  $\text{Sm } C^*$  phase becomes stable. The phase sequence is reversed with respect to usually observed phase sequences, where  $\text{Sm } C_A^*$  is always found below the  $\text{Sm } C_{FI2}^*$  phase. In addition, the authors measured the detailed temperature dependence of INHP in the (73% 10OHF/27% 11OHF)<sub>0.85</sub>C<sub>9,0.15</sub> mixture having the same phase sequence. The INHP depends nonmonotonously on temperature. The

INHP at first decreases upon the lowering temperature, then starts to increase again and eventually locks to the four-layer  $\text{Sm } C_{FI2}^*$  phase. Decreasing the temperature further, the four-layer phase develops discontinuously to the ferroelectric  $\text{Sm } C^*$  phase with a long pitch. Both phases above and below the four-layer phase have very similar character. The angle between tilt directions in neighboring layers is constant and smaller than  $90^\circ$ . They both have the same symmetry only the magnitude of the angle is different. In this sense the phase sequence can be considered as the re-entrance of the  $\text{Sm } C_\alpha^*$  phase. Similar behavior has been experimentally detected and theoretically explained before [13]. If the system has a significant quadrupolar ordering, two things happen: the bilinear interaction to the nearest layers become nonmonotonous and the biquadratic coupling with the negative sign of  $b_Q$  becomes important. Because the quadrupolar order increases as the fourth order of the tilt [14], one can expect that for high geometric quadrupolar order the diffusion is more favored than for the low order. The promoted diffusion for higher order can be described by the term

$$\frac{1}{2}a_{12}\xi_j^4(\xi_j \cdot \xi_{j+1}), \quad (9)$$

with negative coefficient  $a_{12}$ . The strong quadrupolar ordering results in the negative  $\tilde{b}_Q$  as well. If  $b_Q$  is negative the four-layer structure of  $\text{Sm } C_{FI2}^*$  with two different phase differences between neighboring layers minimizes the free energy in the temperature region where the INHP is close to four layers. The sum of both angles is close to  $\pi$ , but the magnitude of smaller (larger) angle is defined by chiral interactions.

In order to find if the described scenario can reproduce the observed phase sequence and the behavior of the INHP in dependence of the temperature, one has to compare the free energy of the helicoidal structure for the  $\text{Sm } C_\alpha^*$  and the  $\text{Sm } C^*$  phases with the free energy for the  $\text{Sm } C_{FI2}^*$  phase. As detailed measurements of the  $\text{Sm } C_{FI2}^*$  phase were not performed, there is no data on the distortion from the clock structure. Therefore, we can compare the free energies only semiquantitatively. If chiral interactions are negligible the four-layer  $\text{Sm } C_{FI2}^*$  structure is approximately described by the sequence of the interchanging phase differences:  $\alpha=0$  and  $\beta=\pi$ . The free energy of the  $j$ th layer for the  $\text{Sm } C_{FI2}^*$  phase (1) including Eqs. (7) and (9) is

$$G_j = \frac{1}{4}b_Q\theta^4 - \frac{1}{8}a_2. \quad (10)$$

The solution for the phase difference  $\alpha$  in the same temperature region of the  $\text{Sm } C_\alpha^*$  structure and the consequent INHP is

$$\alpha = \arccos\left(-\frac{[\tilde{a}_{10} + \tilde{a}_{11}(T - T_0) + \tilde{a}_{12}(T - T_0)^2]}{1 + \tilde{b}_Q(T - T_0)}\right), \quad (11)$$

where also  $\tilde{a}_{12}$  is the coefficient  $a_{12}$  expressed in the units of  $a_2$ . The free energy is obtained by inserting Eqs. (5) and (11) into Eq. (4). The detailed measurement of INHP was fitted with coefficients  $\tilde{a}_{11}$ ,  $\tilde{a}_{12}$ , and  $\tilde{b}_Q$  and the free energies were compared. It is clearly seen that the nonmonotonous behavior of INHP can be obtained with coefficients having pre-

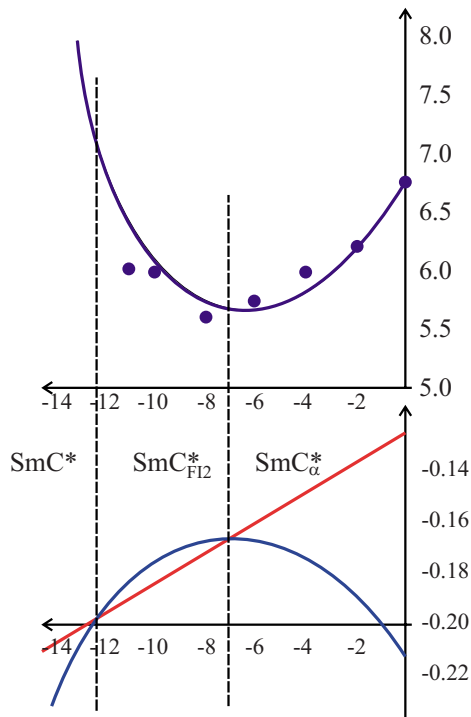


FIG. 2. (Color online) Fit of nonmonotonous INHP evolution in the  $\text{Sm } C_\alpha^*$  phase and corresponding free energies for the  $\text{Sm } C_\alpha^*$  (curved blue line) and the  $\text{Sm } C_{FI2}^*$  (straight red line) phases. The coefficients used for the fit are  $\tilde{a}_{10}=-0.6$ ,  $\tilde{a}_{11}=1.9$ ,  $\tilde{a}_{12}=-1.1$ , and  $\tilde{b}_Q=-0.4$ . Measurements were taken from Ref. [8].

dicted signs [Fig. 2 (above)]. In addition, the four-layer structure of  $\text{Sm } C_{FI2}^*$  becomes stable below the  $\text{Sm } C_\alpha^*$  phase in the region where the INHP starts to increase again, and finally it destabilizes again at temperatures where the INHP is already large typical for the  $\text{Sm } C^*$  phase. As the transition to or from the helicoidally modulated  $\text{Sm } C_\alpha^*$  and  $\text{Sm } C^*$  to  $\text{Sm } C_{FI2}^*$  is of first order, the actually observed transitions upon cooling are shifted to lower values. One could also expect a pronounced hysteresis for both transitions, which was not measured unfortunately.

To conclude, the discrete phenomenological model allows for the explanation of both observations [7,8]. Only one model coefficient has to be considered as temperature dependent. The model predicted the continuous development of  $\text{Sm } C_\alpha^*$  already in its initial form [3]. The addition of the biquadratic coupling with the positive sign of coefficient  $b_Q$  allows for the perfect fit of the observed behavior. The same model allows for the reproduction of nonmonotonous behavior of INHP including the lock-in to the four-layer  $\text{Sm } C_{FI2}^*$  and the unexpected appearance of the  $\text{Sm } C^*$  phase below the four-layer phase. Very different behaviors are the consequence of the competing electrostatic quadrupolar interactions and “geometric” quadrupolar interactions to the nearest layers. The prevailing interaction decides about the lock-in when the system approaches the period of four layers. Although the recent reports questioned the validity of the discrete phenomenological model, the reported observation actually supports its general validity.

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