Flexoelectricity and Piezoelectricity: The Reason for the Rich Variety of Phases in Antiferroelectric Smectic Liquid Crystals

Mojca Čepič[1,2] and Boštjan Žekš[1,3]
[1]J. Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia
[2]Faculty of Education, Kardeljeva ploščad 16, 1000 Ljubljana, Slovenia
[3]Institute of Biophysics, Medical Faculty, Lipičeva 2, 1000 Ljubljana, Slovenia

(Received 29 March 2001; published 31 July 2001)

The free energy of antiferroelectric smectic liquid crystals which takes into account polar order explicitly is presented. Steric, van der Waals, piezoelectric, and flexoelectric interactions to the nearest layers, and dipolar electrostatic interactions to the nearest and to the next-nearest layers, induce indirect tilt interactions with chiral and achiral properties, which extend to the third- and to the fourth-nearest layers. Although the strength of microscopic interactions changes monotonically with decreasing temperature, the effective interlayer interactions change nonmonotonically and give rise to a nonmonotonic change of the modulation period through various phases. Increased chirality changes the phase sequence.

DOI: 10.1103/PhysRevLett.87.085501 PACS numbers: 61.30.Cz

Chiral polar smectics are materials which form layered phases. In these phases the average direction of elongated molecules is tilted for an angle with respect to the layer normal. Smectic layers are spontaneously polarized in the plane of the layer and perpendicular to the direction of the tilt [1]. Among these polar smectics the most widely experimentally and theoretically studied materials are ferroelectric liquid crystals. Ten years ago in an attempt to synthesize ferroelectric liquid crystals with larger polarization, antiferroelectric liquid crystals were discovered [2]. Their synthesis stimulated extensive experimental research which resulted in the discovery of many new polar liquid crystalline phases. In all phases molecules are tilted with respect to the layer normal and tilt direction is modulated along the layer normal. The modulation period was shown to vary nonmonotonically with decreasing temperature [3] from a few layers in the Sm C_{α}^{*} phase, to a few hundred layers in the Sm C^{*} phase, where tilts in neighboring layers are almost parallel, i.e., synclinic, to approximately four layers in the Sm C_{FI2}^{*} phase, to approximately three layers in the Sm C_{FI1}^{*} phase, and to approximately two layers in the Sm C_{A}^{*} phase at low temperatures where tilts in neighboring layers are almost antiparallel, i.e., anticlinic.

Antiferroelectric liquid crystals can be theoretically described by continuous models [4–6] that predict only two of the experimentally observed phases, the ferroelectric Sm C^{*} phase and the antiferroelectric Sm C_{A}^{*} phase. Discrete models [7–9] take interlayer interactions between the tilt vectors explicitly into account. The model [7], later called the clock model [3], considers competing interactions between tilts in nearest layers and in next-nearest layers and predicts various structures where the direction of the tilt varies uniformly from layer to layer.

Within this model the observed nonmonotonic temperature dependence of the modulation period can be reproduced only with nonmonotonic temperature dependences of model parameters, which cannot be understood from microscopic interactions. Although the model can predict structures of the Sm C_{FI2}^{*} and of the Sm C_{FI1}^{*} for the specific set of clock model parameters, these phases cannot exist as stable phases in a broader temperature interval. For this some synclinic interactions would be needed between the third- and between the fourth-nearest layers [9].

In this Letter we present the model where the polarization of smectic layers is taken explicitly into account and is treated as a secondary order parameter to the tilt. In addition to the steric and van der Waals interactions to the nearest layers between the tilt vectors we consider also piezoelectric and flexoelectric couplings between the tilt and the polarization and electrostatic interactions between the polarizations of the nearest layers and polarizations with the next-nearest layers [10].

To describe the structure of phases, we introduce the tilt vector $\boldsymbol{\xi}_j$ which gives the magnitude and the direction of the tilt in the jth smectic layer and the polar order parameter $\boldsymbol{\eta}_j = \{\eta_{jx}, \eta_{jy}\}$, which gives the magnitude and the direction of the in plane transverse polar order in the jth layer. Polar order $\boldsymbol{\eta}$ is induced by the tilt and it is therefore improper order parameter. The spontaneous polarization in the jth layer is proportional to the polar order $\boldsymbol{\eta}$: $P_j = P_0\boldsymbol{\eta}_j$, where P_0 is a layer polarization for a completely polarly ordered layer [1]. Therefore polar order parameter $\boldsymbol{\eta}$ will here shortly be called *polarization*. We express the free energy of the smectic system with N layers in simplest invariant terms of both order parameters as

0031-9007/01/87(8)/085501(4)$15.00

$$G = a \sum_{j=1}^{N} \frac{1}{2}(T - T_0)\xi_j^2 + \frac{1}{4} b\xi_j^4 + \frac{1}{2} a_1(\boldsymbol{\xi}_j \cdot \boldsymbol{\xi}_{j+1}) + \frac{1}{2} f_1(\boldsymbol{\xi}_j \times \boldsymbol{\xi}_{j+1})_z + \frac{1}{2} b_0 \boldsymbol{\eta}_j^2 + \frac{1}{2} b_1(\boldsymbol{\eta}_j \cdot \boldsymbol{\eta}_{j+1}) + \frac{1}{8} b_2(\boldsymbol{\eta}_j \cdot \boldsymbol{\eta}_{j+2}) + c_p(\boldsymbol{\eta}_j \times \boldsymbol{\xi}_j)_z + \frac{1}{2} \mu(\boldsymbol{\xi}_{j+1} - \boldsymbol{\xi}_{j-1}) \cdot \boldsymbol{\eta}_j . \tag{1}$$

Here the first two terms give part of the free energy which depends on the magnitude of the tilt. Both terms describe the isolated layer where continuous transition from the nontilted to the tilted molecular arrangement takes place at T_0 due to intralayer van der Waals interactions. Factoring out the parameter a, we express all model parameters in the units of temperature. Parameter a_1 corresponds to steric and van der Waals interactions between nearest layers. Steric interactions favor synclinic molecular alignment in neighboring layers and give a negative contribution to a_1, while van der Waals interactions favor anticlinic ordering in neighboring layers and give a positive contribution to a_1. The parameter a_1 is of the order of a few degrees Kelvin [8,11]. We believe that steric and van der Waals interactions are negligible farther than to the nearest layers. The parameter f_1 gives the chiral part of van der Waals interactions between molecules [12] in neighboring layers and vanishes in racemic mixtures. We assume that f_1 is smaller than a_1 and it is a few tenths of a degree Kelvin. The parameter b_0 is positive, and both b_1 and b_2 favor antiparallel dipolar order and are therefore positive [10]. Electrostatic interactions between neighboring layers are present only when positional correlations between molecules exist [13]. Since positional correlations decrease exponentially we expect that $b_0 \gg b_1 \gg b_2$ and interactions with more distant layers are neglected. Transition temperatures from the Sm C^* phase to the Sm C_A^* phase are a few degrees lower in nonpolar racemic mixtures than in pure samples [2], which suggests that b_0 is also of the order of a few degrees Kelvin. Polarization is induced in chiral polar smectics by the tilt and the piezoelectric coupling is given by c_p. The parameter c_p has also a chiral character and vanishes in racemic mixtures. The magnitude of the layer polarization is only one-tenth of the polarization of a completely polarly ordered system [14]; i.e., the magnitude of $\boldsymbol{\eta}_j$ is of the order of 0.1, which means that also the value of c_p is of the order of a Kelvin. The last term corresponds to the flexoelectric effect, as it couples nonhomogeneous tilt and the polarization. The flexoelectric parameter μ is of the same order as c_p [15,16].

The part of the free energy Eq. (1), which includes polarization explicitly, can be written as

$$G_P = \boldsymbol{\eta} \cdot \underline{C} \cdot \boldsymbol{\xi} + \tfrac{1}{2}\boldsymbol{\eta} \cdot \underline{B} \cdot \boldsymbol{\eta} . \tag{2}$$

The tilt vector is a $2N$-dimensional vector of the form $\boldsymbol{\xi} = \{\xi_{1x}, \ldots, \xi_{jx}, \ldots, \xi_{Nx}, \xi_{1y}, \ldots, \xi_{Ny}\}$ and similar for the polarization $\boldsymbol{\eta}$. The five-diagonal $2N$-dimensional matrix $\underline{B}$ gives intralayer and interlayer electrostatic interactions with elements $B_{j,j} = b_0, B_{j,j\pm1} = \frac{1}{2}b_1$, and $B_{j,j\pm2} = \frac{1}{8}b_2$. The $2N$-dimensional matrix $\underline{C}$ gives the coupling between tilts and polarizations. The off diagonal elements $C_{j,j\pm1} = C_{j+N,j+N\pm1} = \frac{1}{2}\mu$ and $C_{j,j+N} = -C_{j+N,j} = c_p$. Minimization of Eq. (2) with respect to polarization $\boldsymbol{\eta}$ gives

$$\boldsymbol{\eta} = -\underline{B}^{-1} \cdot \underline{C}\boldsymbol{\xi} , \tag{3}$$

where $\underline{B}^{-1}$ is the inverse matrix of the five-diagonal matrix $\underline{B}$. As $b_0 \gg b_1 \gg b_2$ we keep in $\underline{B}^{-1}$ only the terms up to the second order in b_1/b_0 and up to the first order in b_2/b_0. The elements of $\underline{B}^{-1}$ are $B_{j,j}^{-1} = \frac{1}{b_0}[1 + \frac{1}{2}(\frac{b_1}{b_0})^2], B_{j,j\pm1}^{-1} = -\frac{1}{2b_0}(\frac{b_1}{b_0})$, and $B_{j,j\pm2}^{-1} = \frac{1}{8b_0}[2(\frac{b_1}{b_0})^2 - (\frac{b_2}{b_0})]$. Inserting the tilt dependent polarization Eq. (3) into Eq. (2) we obtain the polar part of free energy as

$$G_P = -\tfrac{1}{2}\boldsymbol{\xi}\underline{C}\,\underline{B}^{-1}\underline{C}\boldsymbol{\xi} , \tag{4}$$

and the free energy due to interlayer interactions is

$$G_{\text{int}} = \frac{1}{2} \sum_{j=1}^{N} \left(\sum_{k=1}^{4} \tilde{a}_k(\xi_j \cdot \xi_{j+k}) + \sum_{k=1}^{3} \tilde{f}_k(\xi_j \times \xi_{j+k}) \right). \tag{5}$$

Parameters $\tilde{a}_k$ and $\tilde{f}_k$, which appear after polarization elimination, give effective interactions between tilts. Although direct van der Waals and steric interactions are significant only to the nearest layers and electrostatic interactions are significant up to the next-nearest layers, effective interactions are significant up to the fourth-nearest layers.

$$\begin{aligned}
\tilde{a}_1 &= a_1 + \left(\frac{c_p^2}{b_0} + \frac{1}{4}\frac{\mu^2}{b_0}\right)\left(\frac{b_1}{b_0}\right), \\
\tilde{a}_2 &= \frac{1}{2}\frac{c_p^2}{b_0}\left[\frac{1}{2}\left(\frac{b_2}{b_0}\right) - \left(\frac{b_1}{b_0}\right)^2\right] \\
&\quad + \frac{1}{2}\frac{\mu^2}{b_0}\left[1 + \frac{1}{4}\left(\frac{b_2}{b_0}\right)\right], \\
\tilde{a}_3 &= -\frac{1}{4}\frac{\mu^2}{b_0}\left(\frac{b_1}{b_0}\right), \\
\tilde{a}_4 &= \frac{1}{8}\frac{\mu^2}{b_0}\left[\left(\frac{b_1}{b_0}\right)^2 - \frac{1}{2}\left(\frac{b_2}{b_0}\right)\right], \\
\tilde{f}_1 &= f_1 - \frac{2c_p\mu}{b_0}\left[1 + \frac{1}{4}\left(\frac{b_1}{b_0}\right)^2 + \frac{1}{8}\left(\frac{b_2}{b_0}\right)\right], \\
\tilde{f}_2 &= \frac{c_p\mu}{b_0}\left(\frac{b_1}{b_0}\right), \\
\tilde{f}_3 &= \frac{1}{2}\frac{c_p\mu}{b_0}\left[-\left(\frac{b_1}{b_0}\right)^2 + \frac{1}{2}\left(\frac{b_2}{b_0}\right)\right].
\end{aligned} \tag{6}$$

Achiral effective interactions between nearest layers $\tilde{a}_1$ consist of direct steric and van der Waals interactions (a_1), as well as of indirect interactions due to piezoelectrically and flexoelectrically induced polarization. Achiral interactions between next-nearest layers are only indirect and can be for systems with negligible flexoelectric interactions ($\mu \approx 0$) either competing [7] ($\tilde{a}_2 > 0$) or noncompeting with ($\tilde{a}_2 < 0$) [17]. The second case leads to the validity of the continuous bilayer models [4–6], although it seems that the present experimental knowledge supports this possibility by a single experimental evidence [17]. In systems with large flexoelectric interactions ($|c_p|\frac{b_1}{b_0} < |\mu|$, $\tilde{a}_2$ is always positive and competes with interactions between nearest layers $\tilde{a}_1$. Indirect effective interactions between third neighbors are given by $\tilde{a}_3$. The term is always negative and favors synclinic tilt directions in interacting layers. Therefore this term in systems with significant flexoelectric interactions tends to stabilize the structures with three layer periodicity. Indirect effective interactions between fourth-nearest layers $\tilde{a}_4$ can be either negative or positive.

The effective chiral coupling between neighboring layers $\tilde{f}_1$ has two contributions: the van der Waals originated (f_1) and the polarization part which appears due to the combination of piezoelectricty and flexoelectricity ($c_p \mu / b_0$). Even systems with negligible direct chiral interactions $f_1 \approx 0$ are helicoidally modulated. In all previous models, chiral interactions have always been treated as weak interactions which induce only slight perturbations in the structure, i.e., helicoidal modulations with very long periods. In antiferroelectric liquid crystals this is not always the case. The ratio $c_p \mu / b_0$ can have the value of a few degrees Kelvin and is comparable to other achiral interlayer interactions. The competition between the van der Waals part of chiral interactions (f_1) and indirect chiral interactions due to the piezoelectric and the flexoelectric effect ($c_p \mu / b_0$) can explain the helix unwinding without polarization reversal as observed in the antiferroelectric phase of various systems [2,17].

The simplest solution, which minimizes the free energy Eq. (4) for competing interlayer interactions ($\tilde{a}_2 > 0$) , is the clock model solution with the constant phase difference between neighboring layers over the whole sample [7]. The tilt in the jth layer is $\xi_j = \theta\{\cos(j\alpha), \sin(j\alpha)\}$, where θ is constant and the phase difference α is the difference in directions of the tilt vectors in neighboring layers. The phase difference α is obtained by the minimization of the free energy Eq. (4) with respect to α.

We have analyzed the temperature dependence of solutions for the following behavior of model parameters with decreasing temperature: a_1 increases monotonically from the negative value to the positive value, the piezoelectric parameter c_p monotonically increases, and the flexoelectric parameter μ monotonically decreases. Let us consider a microscopic mechanism of the described parameter dependence with decreasing temperature. The monotonic increase of direct interactions a_1 with decreasing temperature from a negative value, which is due to interpenetrating molecules through nearest layers, to a positive value in the region where van der Waals interactions favor anticlinic order is due to increasing smectic order [18]. The flexoelectric coupling (μ) decreases monotonically with decreasing temperature, since the smectic order and hindrance of the rotation becomes less affected by the molecules above and below the interacting layer. In contrast, with decreasing temperature piezoelectric coupling (c_p) monotonically increases since higher smectic order strengthens the rotation hindrance within the layer.

For positive $\tilde{a}_2$ we can introduce the measure of the competition—the *competition ratio* $4\tilde{a}_1/\tilde{a}_2$. In racemic mixtures in the temperature region where the competition ratio is smaller than -1, the synclinic nonmodulated Sm C^* phase is stable. In the temperature region where the competition ratio is larger than 1, the anticlinic nonmodulated Sm C_A^* phase exists. In the region in between, the phase angle α changes with decreasing temperature rapidly from 0° to 180°, i.e., the modulation period changes from infinity to two layers. In slightly chiral systems the Sm C_α^* phase appears above the ferroelectric Sm C^* phase. With an additional increase of the enantiomeric excess or increased chirality of the system (larger c_p), the ferroelectric Sm C^* phase disappears, leaving only a modulated phase with short pitch (Fig. 1).

Experimental observations have shown that in racemic mixtures only the synclinic Sm C^* phase and the anticlinic Sm C_A^* phase exist with the first order transition between them [2]. The narrow temperature range of the modulated phase (Fig. 1—solid line) can be experimentally seen as the first order transition. In chiral samples two additional phases, the Sm C_α^* phase and the Sm C_γ^* phase, appear. In chiral systems where piezoelectric coupling c_p is important, below the transitions temperature to the tilted phase, the modulation period is much shorter and increases with decreasing temperature. The temperature region where competition ratio is between -1 and $+1$ becomes wider and can be experimentally observed as a

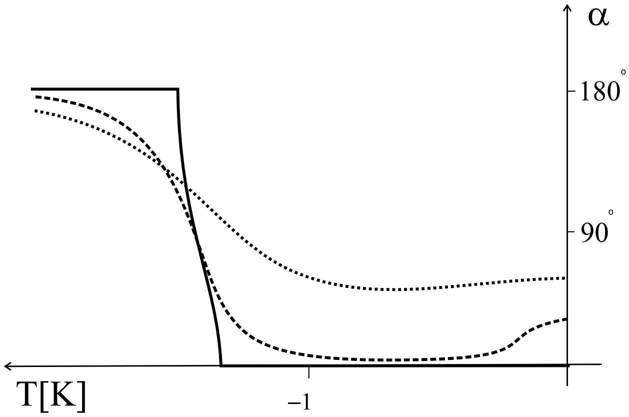

FIG. 1. Temperature dependence of the phase difference α. Model parameters change with temperature monotonically as $a_1 = (-4.1\ \mathrm{K} - 3.2T)$, $c_p = x(0.15\ \mathrm{K} - 0.16T)$, $\mu = (2.12\ \mathrm{K} + 1.32T)$. The other values were $f = 0$ K, $b_0 = 2$ K, $b_1 = 0.2$, $b_2 = 0.02$. The parameter x gives enantiomeric excess and has the following values: $x = 0$—solid line; $x = 0.2$—dashed line; and $x = 1$—dotted line.

distinguished Sm C_γ^* phase. Similar behavior is observed in chiral samples of MHPOBC [2] and 10OTBBB1M7 [3] (Fig. 1—dashed line). If piezoelectric c_p coupling is still stronger, the ferroelectric Sm C^* phase disappears, which was observed in some systems [19] (Fig. 1—dotted line).

The symmetry of structures with various α is the same, since the symmetry operation common to all structures consists from the translation for a layer thickness and the rotation for an angle α. If α changes discontinuously, the temperature range of different phases can be defined by differential scanning calorimetry or similar measurements. If transitions are continuous, the temperature ranges of various phases are defined by changes of the macroscopic properties and are to some extent arbitrary. The phase difference α can be used as a parameter which distinguishes between different phases. In the Sm C_α^* phase varies from $\alpha \approx 10°$ to $70°$, which means that the modulation period varies from 40 to 5 layers. In the Sm C^* phase is $\alpha \approx 0$, i.e., the infinite modulation period in racemic mixtures and a few hundred layers in pure samples. In the Sm C_{FI2}^* phase is $\alpha \approx 90°$ or 4 layers; in the Sm C_{FI1}^* phase is $\alpha \approx 120°$ or 3 layers. In the Sm C_A^* phase is $\alpha \approx 180°$. The modulation period is 2 layers and can also be analyzed within a bilayer model [4–6] where it is treated as a long double helix.

To conclude, we present the phenomenological model based on microscopic intralayer and interlayer interactions. Polarization is induced by the piezoelectric and the flexoelectric effect and is taken into account explicitly. Although tilts directly interact only with nearest layers and polarizations interact up to the next-nearest layers, indirect achiral interactions which tend to stabilize structures with three layer and four layer periodicities extend to the fourth-neighboring layers. Chiral piezoelectric couplings influence also the effective achiral interactions between nearest layers. Additionally, chiral interactions due to the flexoelectric effect are important to the third-nearest layers and can be strong. Direct interactions between nearest layers correspond to elastic terms in continuous models. As a consequence of the piezoelectric and the flexoelectric coupling, the corresponding Lifshitz parameter in continuous models is renormalized. In contrast, variation of polarization, which is considered as electrostatic interlayer coupling, has no corresponding terms in continuous models. The large variety of phases in antiferroelectric liquid crystals is a consequence of a delicate balance between various mechanisms. In chiral samples all interactions change with temperature monotonically. But the competition ratio varies nonmonotonically and therefore also phase difference α; i.e., the modulation period changes nonmonotonically and the ferroelectric Sm C^* phase with long modulation period can be stable between two phases (Sm C_α^* and Sm C_{FI2}^*) with much shorter modulation periods.

Within the phenomenological discrete model we studied only the simplest possible interlayer interactions that can describe nonmonotonic but continuous temperature dependence of the pitch. The experimentally observed discontinuous dependences could be a consequence of the influence of the pitch on the tilt [8] and/or higher order terms which tend to lock the pitch to three or four layers or like quadrupolar terms which could induce quadrupolar ordering and allow for distorted clock model solutions [20].

The authors are very grateful to Ewa Gorecka and Nataša Vaupotič for many stimulating discussions. The financial support of Ministry of Education, Science and Sport of Slovenia, Grant No. PO-518 is acknowledged.

[1] D. J. Photinos and E. T. Samulski, Science **270**, 783 (1995).
[2] A. D. L. Chandani, E. Gorecka, Y. Ouchi, H. Takezoe, and A. Fukuda, Jpn. J. Appl. Phys. **28**, 1265 (1989).
[3] P. Mach, R. Pindak, A.-M. Levelut, P. Barois, H. T. Nguyen, C. C. Huang, and L. Furenlid, Phys. Rev. Lett. **81**, 1015 (1998).
[4] H. Orihara and Y. Ishibashi, Jpn. J. Appl. Phys. **30**, L1819 (1990).
[5] B. Žekš and M. Čepič, Liq. Cryst. **14**, 445 (1993).
[6] V. L. Lorman, A. A. Bulbitch, and P. Toledano, Phys. Rev. E **49**, 1367 (1994).
[7] M. Čepič and B. Žekš, Mol. Cryst. Liq. Cryst. **263**, 61 (1995).
[8] M. Škarabot, M. Čepič, B. Žekš, R. Blinc, G. Heppke, A. V. Kityk, and I. Muševič, Phys. Rev. E **58**, 575 (1998).
[9] A. Roy and N. V. Madhusudana, Eur. Phys. J. E **1**, 319 (2000).
[10] M. Čepič and B. Žekš, Mol. Cryst. Liq. Cryst. **301**, 221 (1997).
[11] D. R. Link (private communication).
[12] A. B. Harris, Randall D. Kamien, and T. C. Lubensky, Phys. Rev. Lett. **78**, 1476 (1997).
[13] R. Bruinsma and J. Prost, J. Phys. II (France) **4**, 1209 (1994).
[14] I. Muševič, R. Blinc, and B. Žekš, *The Physics of Ferroelectric and Antiferroelectric Liquid Crystals* (World Scientific, Singapore, 2000).
[15] P. O. Andreeva, V. K. Dolganov, C. Gors, R. Fouret, and E. I. Kats, Phys. Rev. E **59**, 4143 (1999).
[16] D. R. Link, G. Natale, J. E. Maclennan, N. A. Clark, M. Walsh, S. S. Keast, and M. E. Neubert, Phys. Rev. Lett. **83**, 3665 (1999).
[17] I. Muševič, A. Rastegar, M. Čepič, B. Žekš, M. Čopič, D. Moro, and G. Heppke, Phys. Rev. Lett. **77**, 1769 (1996).
[18] D. Pociecha, E. Gorecka, M. Čepič, N. Vaupotič, B. Žekš, D. Kardas, and J. Mieczkowski, Phys. Rev. Lett. **86**, 3048 (2001).
[19] M. Čepič, G. Heppke, J. M. Hollidt, D. Loetsch, D. Moro, and B. Žekš, Mol. Cryst. Liq. Cryst. **263**, 207 (1995).
[20] P. M. Johnson, D. A. Olson, S. Pankratz, T. Nguyen, J. Goodby, M. Hird, and C. C. Huang, Phys. Rev. Lett. **84**, 4870 (2000).