

## Coupling of Polarization and Dislocation in Ferroelectric Smectic Liquid-Crystal Films

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The polarization vector in ferroelectric smectic- $C^*$  films preferably aligns along a dislocation line due to the Coulomb interaction between polarization charges. The electric field locally perpendicular to the dislocation line distorts it, and in the case of a dislocation loop an  $n$ -finger structure is formed, with  $n$  depending on the applied voltage. This phenomenon has been observed in an experiment in which the screening effect of ion impurities has been partially lifted in a low-frequency (3 Hz) electric field. A characteristic length scale related to this phenomenon is of the order of  $10^4$  Å. [S0031-9007(98)08017-X]

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In the ferroelectric smectic liquid crystal ( $S_C^*$ ) [1] (invented by Meyer and synthesized by French chemists) the polarization vector  $\mathbf{P}$  (per unit volume), perpendicular to the director and parallel to smectic layers, forms a helicoidal structure with a characteristic pitch (wavelength) of the order of micrometers. These smectics often contain ion impurities which screen the strong Coulomb interaction between polarization charges, given by

$$F_c = \frac{P^2}{2\epsilon} \int d^3r \int d^3r' \frac{\nabla \cdot \hat{\mathbf{p}}(\mathbf{r}) \nabla \cdot \hat{\mathbf{p}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (1)$$

where  $\hat{\mathbf{p}}$  is a unit vector along  $\mathbf{P}$  and  $\epsilon$  is an average of the permittivity coefficients. In a pure sample this interaction would dominate over standard elasticity [2] and we observe that in the presence of dislocations it would strongly favor an alignment of  $\mathbf{P}$  along a dislocation line. This is because of a sudden change in the position of the smectic layers in the region of the defect and the microscopic constraint that  $\mathbf{P}$  is parallel to the layer. In the infinite system with a straight dislocation line  $F_c$  diverges unless  $\mathbf{P}$  is parallel to the line. Only then  $\mathbf{P}$  is uniform and  $F_c = 0$ .

In this work, we present a theoretical study and give qualitative experimental verification of the polarization-dislocation coupling. The main problem in experiment is as follows: since  $S_C^*$  samples are contaminated by ions, the effect of  $F_c$  on the system is hardly observed [2,3]. Here we show that despite the ionic contamination it is possible to partially lift the screening of polarization charges induced by ions and observe the effect of polarization-dislocation coupling. This new phenomenon should be important from both the fundamental and the technological points of view, because  $S_C^*$  are used as fast (1000 times faster than nematic displays) electro-optical switches [4,5]. Their application is based on Clark and Lagerwall [4] observation that in thin samples (of micrometer size) the helix unwinds, and polarization

adopts the same direction in each layer. The dislocation-polarization coupling effect could be sufficiently strong to unwind the helix even in the bulk sample.

One can observe the polarization-dislocation coupling by placing the dislocation line perpendicularly to an electric field. Then the line should distort due to the polarization-electric-field interaction. In order to observe this effect we have prepared a freely suspended film of  $S_C^*$  liquid crystal by expanding its droplet on a frame with one movable edge [6], and placing the frame into a hot stage. The film is observed with a video camera via the reflected light microscopy [7]. In order to produce dislocation loops, a stainless steel needle of diameter 0.36 mm (initially coated with the liquid crystal and approached from below) is passed through the homogeneous film [8]. The needle is mounted on a hot stage in order to avoid the heat transfer between the needle and the film. The meniscus that forms around the needle consists of dislocation loops [8]. We apply a rectangular voltage to the needle, and a radial electric field is created around the needle. When the frequency of the applied field is large ( $>1$  kHz) nothing happens. The ions are immobile and the screening at large distances is achieved. When the frequency is lowered and reaches 10 Hz we start to observe a distortion of the meniscus. The dislocation loops forming the meniscus change their shape with the frequency of the applied field. A characteristic "flower pattern" appears with a certain number of petals (fingers). This number depends on the applied voltage as shown in Fig. 1. The dark part around the dark needle shows the meniscus consisting of dislocation loops. The change of shade in Fig. 1 is related to the change of the thickness of the sample. The observation was made without cross polarizers, and the change of thickness was clearly visible as a change of shade for monochromator light or the change of color for white light. We have used C7 material [4-(3-methyl-2-chloropentanoyloxy)-4'-heptyloxybiphenyl]

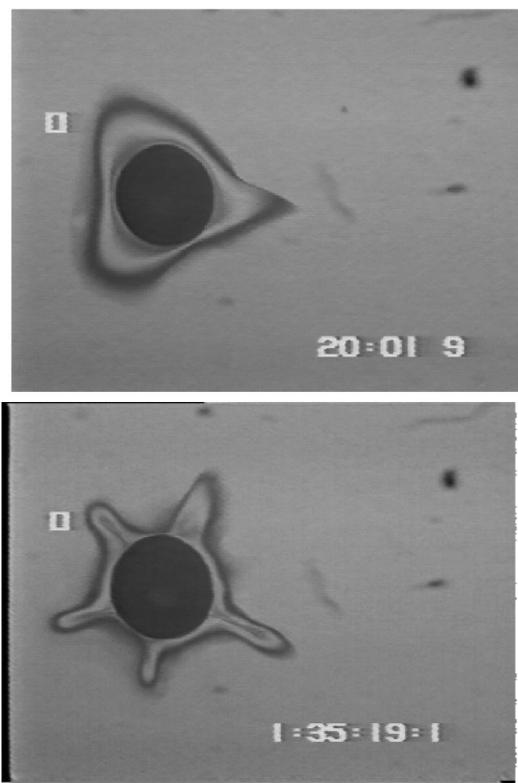


FIG. 1. Top view of the  $S_C^*$  film of C7 with a needle inserted (dark circular part) and a meniscus around it (dark part). Three fingers (at 20 V) and five fingers (at 60 V) are clearly visible. Observation was made in unpolarized light with the reflected light microscopy. The dark line around fingers corresponds to the change of the film thickness.

[9,10], which has the following sequence of phase transitions:  $S_G \rightarrow S_C^*$  (42.4 °C),  $S_C^* \rightarrow S_A$  (54 °C),  $S_A \rightarrow I$  (61.3 °C). The effect disappeared when the sample was heated above the  $S_C^*-S_A$  transition temperature. It also disappeared in  $S_C^*$  when the frequency of the ac electric field was high (>100 Hz) or, also, in the case of dc electric field. When the frequency was very low ( $\sim 0.1$  Hz) the fingers appeared for a short moment every few seconds (according to the frequency of the applied voltage). The effect clearly involves dislocations (change of thickness is visible), the polarization (no effect in  $S_A$ ), and a partial lifting of the ion screening (no effect for ac field at high frequency or for dc field).

A qualitative explanation of the phenomenon is as follows: when the voltage changes sign the ions move for a very short period of time, and the screening is partially lifted. A comparison with theoretical predictions shows that the screening is lifted at distances of the order of  $10^4 - 10^5$  Å. Then the Coulomb interaction between polarization charges orients  $\mathbf{P}$  along the dislocation loops. The radial electric field, perpendicular to the loops, distorts them in a characteristic way due to the polarization-electric field interaction. This explanation is supported by our theoretical calculations.

To study the problem theoretically we assume the presence of a circular dislocation line formed around a cylindrical electrode placed in the middle of the film. The electric field depends only on the distance from the electrode. We are interested in the effect of the electric field on the shape of the dislocation line. To solve this problem we assume that the interaction given by (1) leads to the boundary condition that  $\mathbf{P}$  on the dislocation line is oriented along this line. In order to simplify the problem further we neglect the standard in plane Frank elasticity and flexoelectric terms [2], and to get some insight into the problem we consider a free-energy functional in which only the interaction of the defect region with the electric field is considered. In the following we assume that the film is uniform in the  $z$  direction and consider a two dimensional problem of a dislocation line in an external electric field  $\mathbf{E}$ . The presence of the defect changes the distribution of dipole moments in its neighborhood, provided that the local orientation of the dislocation line is different from  $\mathbf{E}$ . The energetic effect of this line can be obtained by calculating first the free energy of the system in the presence of the line and then subtracting the free energy of the system without that line. The difference corresponds to the interaction of the dislocation line with  $\mathbf{E}$ . The free energy of this interaction can be approximated as follows:

$$F_e = - \oint (P_l |\mathbf{E} \cdot d\mathbf{l}| - P_l |\mathbf{E}| |d\mathbf{l}|), \quad (2)$$

where the integration is along a closed contour and  $P_l$  is the dipole moment per unit length. It follows from (2) that a piece of line parallel to  $\mathbf{E}$  does not contribute to  $F_e$ . The presence of  $|\mathbf{E} \cdot d\mathbf{l}|$  reflects the fact that the dipoles always choose the direction along the line corresponding to the lower energy. We assume that  $P_l = P_l D$ , where  $l_0$  is an average distance over which the polarization is parallel to the dislocation line and  $D$  is the thickness of the film.  $l_0$  is a fitting parameter, which roughly describes the range of influence of the long-range Coulomb interaction on the polarization distribution in the sample.

Deformation of the circular shape of the dislocation line also costs energy, and this cost is proportional to the line tension [2]  $\gamma = \sqrt{K_1 B} m^2 d^2 / 2\xi + e_c$ , where  $K_1$  and  $B$  are the elastic constants corresponding to the layer undulation and compression, respectively,  $d$  is the average layer thickness,  $md$  is the Burger's vector of the dislocation,  $\xi \sim md$  is a cutoff length, and  $e_c$  is the core energy of the dislocation. Here we set  $m = 1$  since in smectic films only elementary edge dislocations form [8].

The position of the deformed line in polar coordinates is given by  $(l_x, l_y) = R[1 + l_r(\varphi)](\cos \varphi, \sin \varphi)$ , where  $R$  is the radius of the unperturbed line, and  $l_r$  denotes the amplitude of the deformation. Assuming that  $\mathbf{E} = E_0 R \hat{\mathbf{r}}/r$  we obtain the following expression for the free

energy functional:  $F[l_r] = \gamma R \int_0^{2\pi} d\varphi f(l_r, \dot{l}_r)$ , where

$$f(l_r, \dot{l}_r) = \left[ \sqrt{(1 + l_r)^2 + \dot{l}_r^2} - 1 \right] - \frac{a}{1 + l_r} \times \left[ |\dot{l}_r| - \sqrt{(1 + l_r)^2 + \dot{l}_r^2} \right] \quad (3)$$

denotes the dimensionless free energy per unit angle,  $\dot{l}_r = dl_r/d\varphi$ , and  $a = P_1 E_0/\gamma$ .  $E_0$  can be expressed in terms of the difference of the electrostatic potential between the electrodes  $\Delta\Phi$  and the distance  $L$  between them, i.e.,  $E_0 = \Delta\Phi/[R \ln(1 + L/R)]$ . In the absence of any deformation ( $l_r = 0$ )  $F = 2\pi a$ . The above functional is not bound from below if we allow for deformations of either sign. However, in practice the dislocation line forms close to the inner electrode, which acts as a hard circular wall. Thus, we minimize  $F[l_r]$  under constraint  $l_r \geq 0$ .

Because of the presence of  $|\dot{l}_r|$  in (3)  $\dot{l}_r$  can be discontinuous at some points, which are disclination points, where a local polarization is not well defined (see cusps in Fig. 2). In fact, in three dimensions we have disclination lines oriented along the film normal. We expect that the energy of these disclinations is of the same order

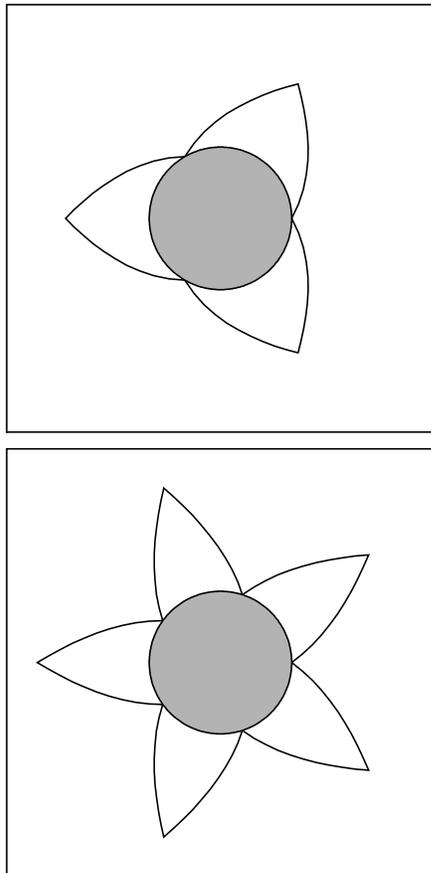


FIG. 2. Three and five fingers obtained from the theory for the parameters corresponding to the experimental situation shown in Fig. 1 (see also Fig. 3).

as in a nematic liquid crystal. The latter, calculated per unit length, is given by [2]  $\tau = \pi K m_1^2 \ln(\rho_{\max}/a_0) + e_c$ , where  $K$  is the average elastic constant,  $m_1$  is the strength of the disclination (integer or half integer),  $a_0$  is of molecular size,  $\rho_{\max}$  is of the order of the distance to other disclinations, and  $e_c$  is the core energy of the disclination; typically  $\ln(\rho_{\max}/a_0) \sim 10$ , hence  $\tau \sim 30K$  (we set  $m_1 = 1$ ). The energy of disclination lines, which is proportional to the film thickness, must be added to the free energy. Our strategy is as follows: first we minimize  $F[l_r]$  at fixed  $a$  and for a fixed number  $2n$  of disclinations located along the dislocation line. Then we take into account the free energy of disclinations, which is in the first approximation proportional to their number. The equilibrium number of disclinations corresponds to the minimum of the total free energy at a given value of  $a$ .

To proceed we consider structures of  $n$ -fold symmetry, i.e., we assume that  $l_r(2\pi/n \pm \varphi) = l_r(\varphi)$ . Then the free-energy functional can be expressed as follows:

$$F[l_r] = 2\gamma R n \int_0^{\pi/n} d\varphi f(l_r, \dot{l}_r), \quad (4)$$

where it is assumed that the sign of  $\dot{l}_r(\varphi)$  does not change for  $0 \leq \varphi \leq \pi/n$ . Minimization of  $F$  at  $n$  fixed leads to the Euler-Lagrange equation together with the two boundary conditions:  $\partial f/\partial \dot{l}_r(\pi/n) = 0$  and  $l_r(0) = 0$ . The latter boundary condition corresponds to the fact that  $F[l_r]$  is not bound from below, and only the presence of the inner electrode introduces a geometrical constraint  $l_r \geq 0$ . Thus, it is energetically favorable to have the inner part of a deformed dislocation line as close to the electrode as possible.

Since  $H = \dot{l}_r \partial f/\partial \dot{l}_r - f = \text{const}$  for  $l_r(\varphi)$  satisfying the Euler-Lagrange equation, we find that

$$\dot{l}_r = \frac{1}{|c|} (1 + l_r) \sqrt{(1 + a + l_r)^2 - c^2}, \quad (5)$$

where the integration constant  $c$ , obtained from the first boundary condition, satisfies  $c^2 = [1 + a + l_r(\pi/n)]^2 - a^2$ . The equilibrium  $l_r(\varphi)$  is given implicitly by

$$\int_0^{l_r(\varphi)} \frac{dl_r}{(1 + l_r) \sqrt{(1 + a + l_r)^2 - c^2}} = \frac{\varphi}{|c|}. \quad (6)$$

Using (6) for  $\varphi = \pi/n$  together with the expression for  $c$  we find, for given  $a$  and  $n$ , the amplitude  $l_r(\pi/n)$  and the free energy  $F(n, a)$  of the structure. The total free energy  $F_{\text{tot}}$  is obtained by adding to  $F$  the contribution from disclinations, i.e.,

$$\frac{F_{\text{tot}}(n, a)}{\gamma R} = \frac{F(n, a)}{\gamma R} + 2ne_d, \quad (7)$$

where  $e_d = \tau D/(\gamma R)$ . The equilibrium value of  $n$  corresponds to the minimum of  $F_{\text{tot}}$ , provided that this

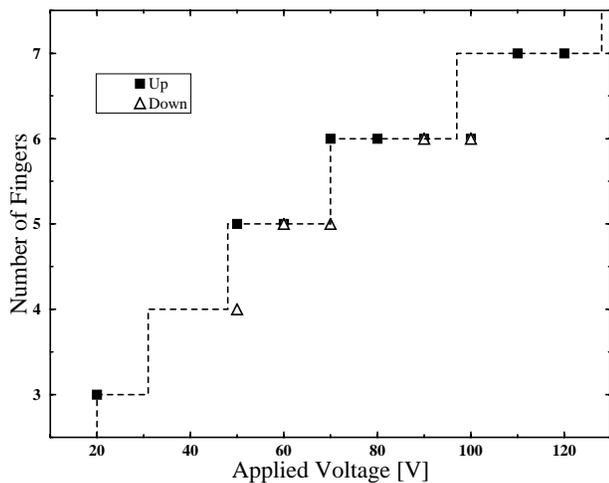


FIG. 3. Number of fingers vs voltage for C7 obtained from the experiment (squares and triangles) and theory (dashed line); “up” and “down” correspond to the direction of the voltage changes. The fitting parameters:  $e_d = 1.0$  and  $a/\Delta\Phi = 0.246 \text{ V}^{-1}$  ( $l_0 \approx 1.6 \times 10^4 \text{ \AA}$ ).

minimum is lower than  $F[l_r = 0] = 2\pi a$ , and we consider  $n \geq 2$ .

In order to estimate  $e_d$  we assume that  $K_1 = K$ , which gives  $e_d \sim 30\lambda D/dR$ . Since  $\lambda = \sqrt{K_1/B} \approx 300 \text{ \AA}$  is large compared to  $d \approx 30 \text{ \AA}$  in smectic C liquid crystals [11] it should also be large in  $S_C^*$ . For  $R = 0.36 \text{ mm}$  and  $D \approx 10^3 \text{ \AA}$  up to  $10^4 \text{ \AA}$  we find that  $e_d$  is between 0.1 and 1.

From the definition of the parameter  $a$  we have

$$a = \frac{Pl_0\Delta\Phi}{\gamma} \frac{D}{R \ln(1 + L/R)} \quad (8)$$

and we assume  $\gamma = 10^{-7} \text{ dyn}$ ,  $D = 10^3 \text{ \AA}$ ,  $R = 0.36 \text{ mm}$ ,  $L = 1 \text{ cm}$ ,  $P = 600 \text{ statcoulomb cm}^{-2}$  (for C7). For these values  $a \approx 1.65 \times 10^3 l_0 \Delta\Phi (\text{cm V})^{-1}$ , ( $300 \text{ V} = 1 \text{ statvolt}$ ). Since the Coulomb interactions given by (1) are of long range, we expect  $l_0$  to be large ( $\sim 10^4 \text{ \AA}$ ).

We observe the following behavior: for small voltage ( $V$ ) the dislocation line remains circular up to the threshold field at which the first transition to a symmetric structure occurs. Then the increase of  $V$  leads to a sequence of transitions, and at each transition  $n$  increases by one. This is shown in Fig. 3, where the experimental results are compared with the theory.

Our analysis of the phenomenon can only be qualitative, since we do not know how good the screening is and how the partial screening changes with time when ions [12] and dislocations move. The long range character of the Coulomb interactions has been only partially included

in the parameter  $l_0$  and in the condition that the polarization is always parallel to the dislocation line. Nevertheless, our results suggest that the Coulomb interaction between polarization charges prefers the polarization aligned parallel to the dislocation line. Our simplified theory also grasps the essence of the phenomenon.

For the technological applications it is important to understand the behavior of polarization when the electric field is switched between two states. The fast process of the polarization reorientation ( $\sim$ microseconds) in ferroelectric smectics is very well understood [13]. However, the processes that take place at low frequencies of the applied field are not [14]. Here we have shown that the combination of the defects and the low-frequency electric field in ferroelectric smectics leads to the deformation of the sample. In the presence of dislocations the interaction given by (1) may lead to the unwinding of the helix in a bulk sample, provided that the sample is sufficiently pure.

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- [1] R. B. Meyer, L. Liebert, L. Strzelecki, and P. Keller, *J. Phys. (Paris), Lett.* **36**, 69 (1975).
  - [2] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Oxford Science Publications, Oxford, England, 1993).
  - [3] C. Young, R. Pindak, N. A. Clark, and R. B. Meyer, *Phys. Rev. Lett.* **40**, 773 (1978).
  - [4] N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.* **36**, 899 (1980).
  - [5] M. A. Handschy, N. Clark, and S. T. Lagerwall, *Phys. Rev. Lett.* **51**, 471 (1983).
  - [6] P. Pierański *et al.*, *Physica (Amsterdam)* **194A**, 364 (1993).
  - [7] E. B. Sirota, P. S. Pershan, L. B. Sorensen, and J. Collett, *Phys. Rev. A* **36**, 2890 (1987).
  - [8] J.-C. Geminard, R. Hofyst, and P. Oswald, *Phys. Rev. Lett.* **78**, 1924 (1997).
  - [9] Ch. Bahr and D. Fliegner, *Phys. Rev. A* **46**, 7657 (1992).
  - [10] E. Hoffmann and H. Stegemeyer, *Ferroelectrics* **179**, 1 (1996).
  - [11] D. Johnson and A. Saupe, *Phys. Rev. A* **15**, 2079 (1977).
  - [12] Z. Zou, N. A. Clark, and M. A. Handschy, *Ferroelectrics* **121**, 147 (1991).
  - [13] D. C. Ulrich, M. J. Cherrill, and S. J. Elston, *Liq. Cryst.* **23**, 797 (1997).
  - [14] V. Novotna, M. Glogarova, A. M. Bubnov, and H. Sverenyak, *Liq. Cryst.* **23**, 511 (1997).