

Formation of a twisted synclinic structure by an antiferroelectric liquid crystal material with strong quadrupolar interlayer coupling

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(Received 29 November 2002; published 21 April 2003)

Following the work of Rudquist *et al.* [J. Mater. Chem. **9**, 1257 (1999)], the thresholdless mode exhibited by some devices filled with some antiferroelectric liquid crystal materials is widely accepted to be due to the formation of a twisted synclinic structure in the device. In this work, we consider under what circumstances this structure forms in preference to the expected anticlinic structure. We show that a strong polar interaction at the surfaces is a necessary but not sufficient condition, and that a strong quadrupolar component of the interlayer interaction is also required. Examination of the stability of the possible ground states reveals a simple explanation for the frequency and temperature dependent electro-optical properties that are observed experimentally, including priming.

DOI: 10.1103/PhysRevE.67.041712

PACS number(s): 61.30.Cz

Antiferroelectric liquid crystals (AFLCs) [1–3] are members of the general class of tilted smectic liquid crystals. In these materials, the molecules are arranged approximately into layers, and the average molecular direction (or director) within the layer is at a fixed cone angle θ to the layer normal. The relationship between the azimuthal angles in adjacent layers is different for the various tilted smectic phases. For example, the ferroelectric phase has the same azimuthal angle from layer to layer, and the antiferroelectric phase has alternating tilt directions. In both cases, the chirality of the molecules gives rise to a net polarization perpendicular to the molecular tilt plane in each layer, and a macroscopic helical structure along the layer normal.

In most cases, an antiferroelectric liquid crystal confined to a cell geometry, in which the layers are formed perpendicular to the surfaces, displays thresholded and hysteretic electro-optic characteristics, as shown in Fig. 1(a). However, in some cases, a thresholdless, V-shaped electro-optic characteristic is obtained, as shown in Fig. 1(b). Following the work of Rudquist and co-workers [4,5] published in 1999, it is now widely accepted that the cause of the V-shaped electro-optic characteristic is the formation of a twisted ferroelectric structure in the device. While it has been postulated that a strong polar interaction between the surfaces and the liquid crystal is required in order for this twisted ferroelectric structure to form, it has not been shown that this is sufficient to cause the material to change from being antiferroelectric as a bulk specimen to being ferroelectric in a device geometry.

Here we present a theoretical model which shows that the surface polar interaction is a necessary but not sufficient condition for the formation of a twisted ferroelectric structure. The liquid crystal is modeled according to a one-dimensional model across the thickness of the device, z . We consider only two smectic layers, since we assume that the device is thin enough to suppress the macroscopic helical structure of the material. Assume that the azimuthal angles of the director in the two layers are ϕ_o and ϕ_e , representing the odd and even layers, respectively. Let us now define the order parameters

$$\phi_a = \frac{\phi_e + \phi_o}{2} \quad \text{and} \quad \phi_b = \frac{\phi_e - \phi_o}{2}. \quad (1)$$

ϕ_a represents the local average azimuthal angle of the director. In a twisted device, ϕ_a will vary linearly between 0 and π from one surface to the other, whereas in a nontwisted device it will be constant. ϕ_b , however, is half the difference of the local azimuthal angles, and therefore represents the type of ordering present: for anticlinic ordering, $\phi_b = \pi/2$, and for synclinic ordering $\phi_b = 0$. The pair of smectic layers will be represented by the following expression for the free energy:

$$F = -EP_a \cos \phi_a \cos \phi_b + \frac{K}{2} \left(\frac{\partial \phi_a}{\partial z} \right)^2 + \frac{K}{2} \left(\frac{\partial \phi_b}{\partial z} \right)^2 + \Gamma \cos^2 \phi_b - \Delta \cos^2 2\phi_b. \quad (2)$$

The first term represents the interaction of the applied field E with the spontaneous polarizations P_s in the two layers [it is $-EP_s (\cos \phi_e + \cos \phi_o)/2$]. The second two terms are the elastic energy stored due to distortions to the liquid crystal structure across the device width, using an elastic constant K . The final two terms account for the antiferroelectric nature of the interaction between adjacent layers. The first of these is a dipolar interaction (of strength Γ) that favors anticlinic ordering compared with synclinic ordering. The term with coefficient Δ is a quadrupolar interaction that favors both states

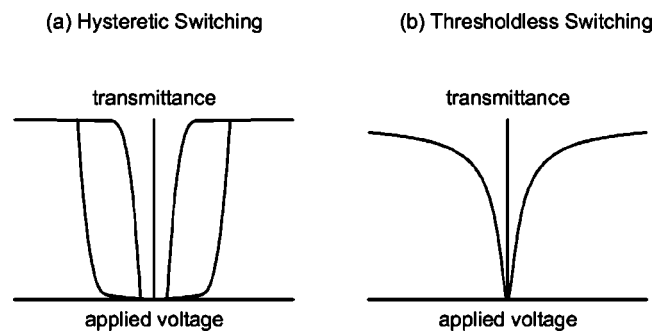


FIG. 1. Example of the possible electro-optic characteristics of an antiferroelectric liquid crystal. (a) shows typical hysteretic switching and (b) the thresholdless mode exhibited by some materials in a device geometry. The curves are generated using a model of uniform and domain switching in an AFLC device.

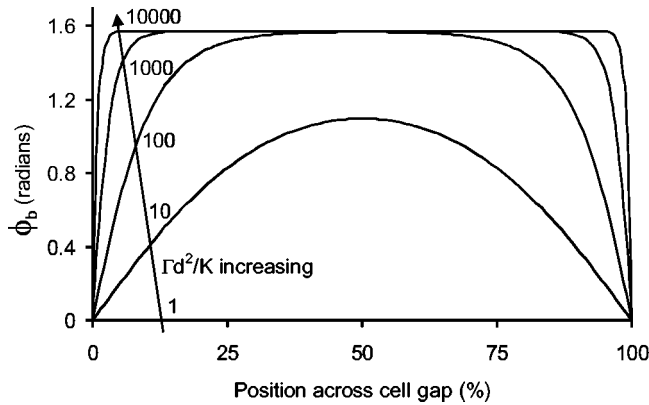


FIG. 2. Illustration of the stable ground state in a device with strong polar anchoring at the surfaces, and no quadrupolar interaction between layers. When the parameter $\Gamma d^2/K$ is greater than about 5, the system is antiferroelectric in the bulk of the device, whereas if $\Gamma d^2/K$ is smaller than this, the liquid crystal is ferroelectric throughout the device.

equally. It is the inclusion of the quadrupolar component of the interlayer interaction that sets our work apart from other models of thresholdless antiferroelectricity, including earlier work from Mottram and Elston [6]. As the following discussion shows, this quadrupolar term is the key to the formation of a twisted synclinic structure in a cell geometry.

The boundary conditions are those of a strong polar nature, i.e., so that the layer polarizations of both layers are pointing either into or out of both surfaces. The anchoring is considered to be infinitely strong so that the surface directors will not switch under applied field. Since the polarizations are pointing in the same direction in the two layers at either surface, $\phi_b = 0$ at the surfaces (i.e., the liquid crystal must be ferroelectric at the surface). In order for the polarizations to be oppositely directed at the two surfaces, if ϕ_a is defined to be 0 on one surface (say $z=0$), then it must be π on the other (at $z=d$, where d is the thickness of the device).

We first consider the ground state of the device, i.e., $E = 0$ in Eq. (2). In this case, the minimization of the free energy with respect to ϕ_a leads to

$$\frac{\partial^2 \phi_a}{\partial z^2} = 0 \rightarrow \phi_a = \frac{\pi z}{d}, \quad (3)$$

i.e., a linear variation in ϕ_a from 0 at one surface to π at the other. In order to find the solution for ϕ_b , the Euler-Lagrange equation is formed:

$$K \frac{\partial^2 \phi_b}{\partial z^2} + \Gamma \sin 2\phi_b - 2\Delta \sin 4\phi_b = 0. \quad (4)$$

The equilibrium director profile is found by solving the above Euler-Lagrange equation numerically, using a relaxation technique. The results are shown in Fig. 2 for a range of values of the dimensionless parameter $\Gamma d^2/K$, in the case where the quadrupolar coefficient Δ has been set to zero. In order for the twisted ferroelectric state to be formed in preference to the twisted antiferroelectric state, the value of the parameter $\Gamma d^2/K$ must be less than about 5. For a given material (i.e., a certain Γ and K), this condition requires a

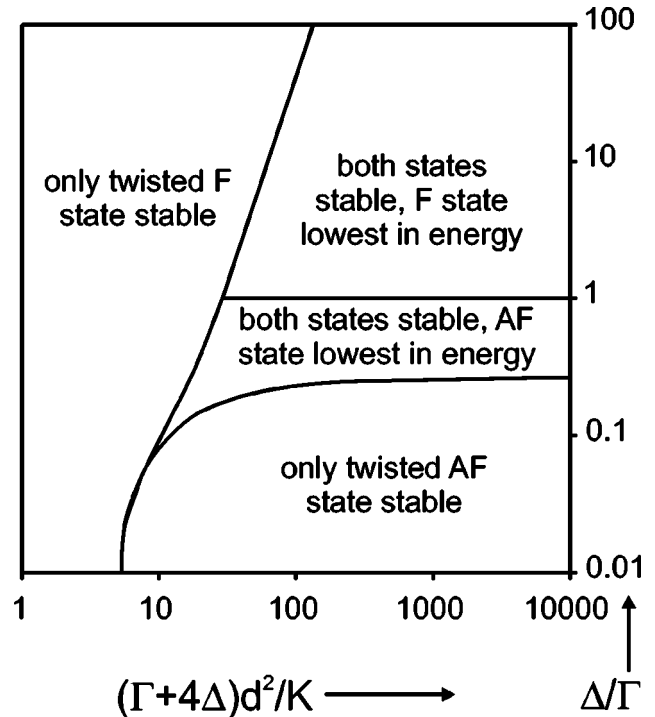


FIG. 3. Phase diagram showing the regions of stability of the twisted F and twisted AF states as a function of the material and device parameters. If there is very little quadrupolar ordering (small Δ/Γ), the system is monostable and a very thin device is required to form the twisted ferroelectric state. For higher ratios of Δ/Γ , there are regions of bistability, and for $\Delta > \Gamma$ the ferroelectric state is lowest in energy.

minimum device thickness. To obtain an order of magnitude for this thickness we use values for the parameters Γ and K that have been previously measured in AFLC mixture CS4001 [7], that is, $\Gamma \approx 4000 \text{ J/m}^3$ and $K \approx 10^{-11} \text{ N}$. A device made with this material would have to be thinner than about $0.1 \mu\text{m}$, which is unrealistic. However, when the quadrupolar ordering term is included, the maximum device thickness that will support a twisted ferroelectric structure becomes much larger, as illustrated in Fig. 3. This phase diagram shows the stability of the twisted ferroelectric (F) and twisted antiferroelectric (AF) states as a function of the dimensionless parameters $(\Gamma + 4\Delta)d^2/K$ and Δ/Γ . It can be seen that when the quadrupolar term is low, the critical value of $(\Gamma + 4\Delta)d^2/K$ is about 5, in agreement with the results for $\Delta = 0$ described above. However, as the amount of quadrupolar ordering is increased, the critical thickness becomes much larger. In fact, for $\Delta/\Gamma > 1$ the twisted ferroelectric state is preferred to the twisted antiferroelectric state, independently of the cell gap. It is therefore clear that provided a tilted smectic liquid crystal has an appropriate interlayer interaction, it is possible for a material that is antiferroelectric in the bulk to form a twisted ferroelectric structure when confined to a cell geometry with a strong surface polar interaction.

The region of the phase diagram in Fig. 3 in which both twisted AF and F states are stable, but the twisted AF state is lower in energy, is particularly interesting. Consider the application of a quasistatically increasing electric field to the

ground (twisted AF) state. Apart from any variations close to the surface to satisfy the surface boundary conditions, the liquid crystal will behave as a zero-dimensional AFLC [8]. The directors will rotate around the smectic cone until the plane of the directors is approximately parallel to the applied field. The driving mechanism for this change is that a small deviation of the directors from being completely coplanar results in a net polarization along the applied field. This also causes a small rotation of the optic axis away from the layer normal and hence some light leakage: the pretransitional effect. At a critical electric field, there is a field-induced transition to the ferroelectric state, which occurs by domain nucleation and growth. At all times, however, the surface directors remain unswitched due to the strong anchoring. A quasistatically varying electric field therefore results in hysteretic switching between the antiferroelectric and ferroelectric states, with an electro-optic characteristic that is very similar to that of an untwisted device (since the distortion at the surfaces contributes very little to the overall optical effect). This is shown in Fig. 1(a), where the results have been generated using a theoretical model that takes into account the domain growth and has been reported elsewhere [9].

As the frequency of the applied field is increased, the domain growth becomes slower than the changes in applied field, and hence once switched into the twisted F state, the device remains in that state. As Fig. 1(b) shows, the device therefore undergoes thresholdless F - F switching with a V-shaped electro-optic characteristic. This is possible because the device is bistable between the AF and F states, and although the AF state is lower in energy for a range of voltages centered on zero, this state will not be accessed if the voltage is changing too rapidly for domains that cause the transition from F to AF. It is therefore clear that for some AFLC materials (those whose parameters fall into this particular region of the phase diagram), the switching characteristics will be frequency dependent. This prediction is consistent with observations of “priming,” in which the liquid crystal switches initially from AF to F with a distinct voltage threshold, but thereafter undergoes V-shaped switching [4,5]. When the voltage is removed, a period of rest (which has been reported to be up to a few minutes) is required in order for the initial thresholded switching to be observed again (otherwise the device resumes V-shaped switching). Accord-

ing to our theory, this time period corresponds to the time taken for the device to switch at 0 V by domains from the twisted F state to the twisted AF state. This time period can be very long if the energies of the two states are very similar. In the case where the energies of the two states are not so similar, we would expect there to be a critical frequency of the applied field before V-shaped switching is observed. This is consistent with many observations of the frequency dependence of V-shaped switching [10,11].

Our theory is also consistent with the observed temperature dependence of AFLC switching, since the interlayer coupling coefficients Γ and Δ must depend on the temperature of the cell. It is clear that the coefficient Γ (which corresponds to the dipolar term) will change sign at the phase transition between the smectic- C_A^* state and the smectic- C^* phases. Since Δ will remain positive across the phase transition, the ratio of Δ/Γ will increase as the temperature is increased towards the phase transition between smectic- C_A^* and smectic- C^* . Therefore, even if at room temperature only the twisted AF state is stable, as the temperature is increased, the twisted F state will first become stable and then be energetically preferred. The electro-optic switching will therefore change from being hysteretic and thresholded to V-shaped and thresholdless, in agreement with experimental observations [10,11].

In this work, therefore, we have shown the importance of the quadrupolar component of the interlayer interaction in the formation of a twisted synclinic structure by a material that is antiferroelectric in its bulk form. We have also explained how the influence of the finite speed of domain nucleation and growth can affect the shape of the electro-optic characteristic observed: in particular, as the frequency is increased a change from hysteretic to thresholdless switching is observed. The priming effect is an extreme case in which the energies of the two states is very similar and so V-shaped switching occurs (once primed into the F state) for any reasonable frequency of applied field. We also show that the temperature dependence of the switching characteristics can be explained in terms of the temperature dependence of the interlayer coupling coefficients.

The authors would like to thank the Royal Society and the Leverhulme Trust for funding. L.P.J. would also like to thank Nigel Mottram for useful discussions.

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