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Fréedericksz transition in antiferroelectric liquid crystals and cooperative motion of smectic layers

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We study the theory of the Fréederiksz transition in antiferroelectric liquid crystals, and find the conditions under which an applied electric field can cause a homogeneously nucleated transition of the system from antiferroelectric to ferroelectric alignment. We demonstrate that taking into account the cooperative motion of smectic layers results in a significant reduction of the predicted critical electric field at which this transition occurs. [S1063-651X(98)06011-5]

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I. INTRODUCTION

In a recent paper [1], it was shown that the transition from antiferroelectric to ferroelectric alignment in an antiferroelectric liquid crystal (AFLC) can be homogeneously nucleated only under certain conditions. In particular, the critical electric field was found at which the antiferroelectric configuration loses its stability in an applied field. One of the major simplifications made in Ref. [1] was to neglect molecular rotations in those layers of the AFLC that contained molecules initially aligned in the direction of the applied electric field. In the present work we extend the calculation to include the *cooperative* motion of all the smectic layers as the transition occurs. It appears that the scenario of the transition from an antiferroelectric to a ferroelectric state in an AFLC changes drastically as soon as the cooperative motion of all the smectic layers is included. The critical field at which the homogeneous nucleation occurs is now determined mostly by the thickness of the AFLC cell, and not by the molecule-molecule interaction potential. As a result, this field may become much smaller in the model that takes cooperative motion of smectic layers into account than in the model of Ref. [1], which ignores this possibility.

Our starting point is an expression for the effective Hamiltonian of a cell containing an AFLC. Figure 1 shows our model. The N smectic layers lie in the x-z plane, and the director is characterized by the constant angle θ_0 that it everywhere makes with the y axis and by the variable azimuthal angle $\phi_l(x,z)$ that it makes relative to the x axis in the x-z plane and in layer l. The Hamiltonian is then taken to be

$$\mathcal{H}=D\sum_{l=1}^{N}\int dx\,dz\left\{\frac{k}{2}\left[\left(\frac{\partial\phi_l}{\partial x}\right)^2+\left(\frac{\partial\phi_l}{\partial z}\right)^2\right]+U\cos(\phi_l-\phi_{l-1})-P_0E\cos\phi_l-\frac{\varepsilon_0\Delta\epsilon\sin^2\theta_0}{2}E^2\sin^2\phi_l+W(z)\sin^2\phi_l\right\}. \tag{1}$$

In this expression, D is the layer thickness, k is an elastic constant, and $W(z)$ is a surface anchoring energy which we take to act only at the top and bottom surface of the cell, and thus to be of the form $w_0[\delta(z-d/2)+\delta(z+d/2)]$ with d the height of the cell. We assume planar anchoring, so that $w_0>0$. The elastic energy terms come from the variation of ϕ in the x-z plane. Because each layer is only one molecule thick, there is no variation of ϕ in the y direction within a layer. Instead there is the interlayer interaction, which is assumed to favor the herringbone structure first considered by Beresnev *et al.* [2] and confirmed experimentally by Galerne and Liebert [3], and by Bahr *et al.* [4]. Such a structure has an antiparallel orientation of adjacent dipoles, as described by the term with coefficient U. The small chiral deviation from a perfectly antiparallel orientation is neglected in this treatment. Finally, there are two terms containing the electric field E, which is assumed to be in the z direction. The first of these represents the effects of polarization, while the second arises as a consequence of the dielectric anisotropy, $\Delta\epsilon$. The quantity ε_0 is the vacuum permittivity. The large number of terms in this expression reflects the richness of phases and complicated dielectric behavior [5] of the AFLC.

II. AFLC IN AN ELECTRIC FIELD

For moderately thin cells, in which the tendency to form a helical structure can be ignored [1], the liquid crystal molecules in the absence of an applied electric field form an

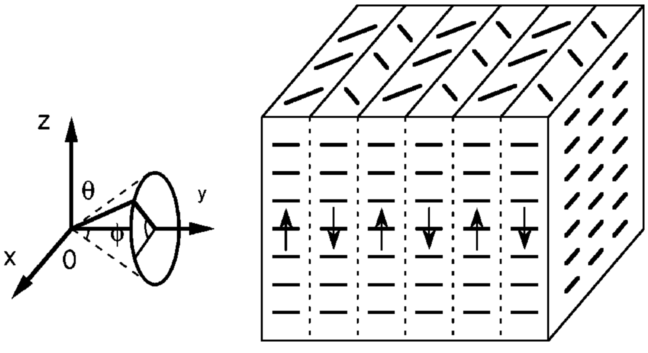

FIG. 1. Geometry of the model antiferroelectric liquid crystal.

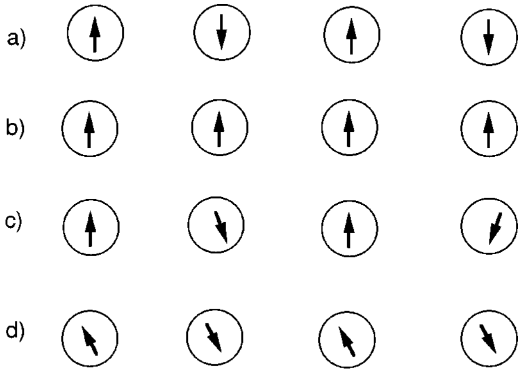

FIG. 2. Different configurations of the model AFLC: (a) Antiferroelectric state. (b) Ferroelectric state. (c) Intermediate state of the AFLC according to the ''uncoupled'' model. (d) Intermediate state of the AFLC according to the ''coupled'' model.

antiparallel sequence $\phi_{i+1}=\phi_i+\pi$. When an applied electric field reaches the value $E_{c2}=2U/P_0$, the ferroelectrically aligned state is reduced in energy below the antiferroelectric one.

We shall see from the calculation below that the transition from the antiferroelectric into the ferroelectric state will not instantaneously occur at an electric field exactly equal to E_{c2} unless nucleated at a defect or a boundary. The transition in a homogeneous system contained in a thin cell (i.e., one having a small d) may not occur until fields considerably in excess of E_{c2} are reached. In thick cells, on the other hand, the transition may begin at fields lower than E_{c2}, but not become complete until fields greater than E_{c2} are reached.

In the rest of this section the stability requirements for the antiferroelectric state subject to an electric field will be analyzed in two different model approaches. In the first calculation, which closely follows Ref. [1], molecular rotations in the odd layers of the AFLC, which contain molecules initially aligned in the direction of the electric field, will be neglected. Correspondingly, the motion of only the even layers will be considered. In the second model calculation the cooperative motion of all layers will be taken into account.

A. Uncoupled case

Let us now examine the stability of the antiferroelectric state when subject to an applied electric field. That is, we will calculate the conditions under which an applied electric field can cause a homogeneously nucleated transition of the system from the antiferroelectric alignment shown in Fig. 2(a) to the ferroelectric alignment shown in Fig. 2(b). For this analysis, which expands on the brief treatment already presented in Ref. [1], we take ϕ to be a function of z alone in the even-numbered smectic layers, and write $\phi_{2l}=\pi+(-1)^l\phi(z)$. For the odd layers, which contain molecules with dipole moments initially aligned *along* the applied electric field, we put $\phi_{2l+1}=0$. These assumptions are illustrated in Fig. 2(c).

When an electric field is applied of sufficient strength to make the antiferroelectric state unstable, $\phi(z)$ will begin to deviate from zero. We accordingly examine the energy of the system when $\phi\ll\pi$. To second order in $\phi(z)$, the energy per unit length of the smectic layer can be obtained as an expansion of Eq. (1):

$$\mathcal{E}=D\int dz\left\{\frac{k}{2}\phi_z^2+\left[U-\frac{1}{2}P_0E-\frac{1}{2}\varepsilon_0\Delta\epsilon E^2\sin^2\theta_0+W(z)\right]\phi^2(z)\right\},\qquad(2)$$

where $\phi_z\equiv\partial\phi/\partial z$.

In order to find the requirements for the Fréedericksz transition to occur, we must find the conditions under which there exists a nonzero $\phi(z)$ that minimizes Eq. (2) in the bulk of the sample and also makes the total energy $\mathcal{E}$ negative. Minimization of Eq. (2) in the interior of the sample, where $W(z)$ vanishes, gives a differential Euler-Lagrange equation for $\phi(z)$, whose solution is $\phi(z)=\phi_0\cos(qz)$ with

$$q(E)=\sqrt{\frac{-2U+P_0E+\varepsilon_0\Delta\epsilon E^2\sin^2\theta_0}{k}}.\qquad(3)$$

A nonzero $\phi(z)$ will occur only when the total energy is negative. Substituting $\phi(z)$ into Eq. (2) and applying the condition $\mathcal{E}<0$, we obtain

$$\tan\left(\frac{qd}{2}\right)>\frac{2w_0}{kq}.\qquad(4)$$

This condition enables us to extract the electric field E_{c3} at which the antiferroelectric configuration becomes unstable. This critical field is always larger than the field E_{c2} at which the ferroelectrically aligned state becomes energetically preferred, and may even become much larger than E_{c2} if the thickness of the AFLC cell becomes small. The phase diagram of the AFLC in this model is shown in Fig. 3 as the line labeled ''uncoupled case.''

Equation (4) bears some similarity to a closely related result of Handschy and Clark [6] [their Eq. (13)], who studied the threshold fields in ferroelectric liquid crystals. The difference between the two cases lies in the fact that our theory refers to discrete layers rather than a continuum and includes the effects of dielectric anisotropy, but does not include the sensitivity of the anchoring potential to the direction of the electric polarization.

In the limit of strong anchoring ($w_0\rightarrow\infty$) Eq. (4) reduces to the condition

$$q(E)d>\pi.\qquad(5)$$

For the case of positive dielectric anisotropy, $\Delta\epsilon>0$, condition (5) can always be achieved at sufficiently strong electric fields. The critical field for infinitely strong anchoring is

$$E_{c3}=\frac{P_0}{2\alpha}\left[\sqrt{1+\frac{4\alpha}{P_0^2}\left(2U+\frac{\pi^2k}{d^2}\right)}-1\right],\qquad(6)$$

where $\alpha=\varepsilon_0|\Delta\epsilon|\sin^2\theta_0$.

If, on the other hand, the dielectric anisotropy $\Delta\epsilon$ is negative, there is a maximum value that q can attain. As a result, there exists a critical cell thickness

$$d_c=\pi\sqrt{\frac{k}{P_0^2/4\alpha-2U}},\qquad(7)$$

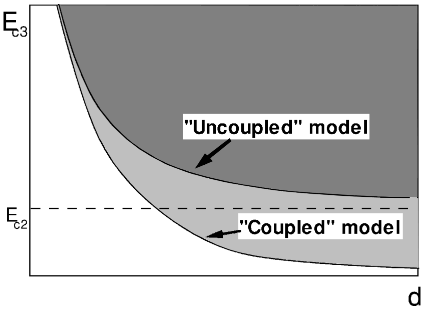

FIG. 3. The critical field E_{c3}, at which the system leaves an ideally aligned antiferroelectric state, is shown for ''coupled'' and for ''uncoupled'' models as a function of cell thickness d.

such that, for thicknesses $d<d_c$, there is no possible electric field that can destabilize the antiferroelectric configuration. For the cell with $d>d_c$, the critical field for the Fréedericksz transition at infinitely strong anchoring is

$$E_{c3}=\frac{P_0}{2\alpha}\left[1-\sqrt{1-\frac{4\alpha}{P_0^2}\left(2U+\frac{\pi^2k}{d^2}\right)}\right]. \tag{8}$$

B. Coupled case

Up to this point we have considered an idealized special case, in which a transition is initiated by a rotation of each layer in the sense shown in Fig. 2(c). All odd layers remain unchanged, while the orientation ϕ of the even layers alternates in direction. This arrangement was chosen as a reasonable approximation for a thin cell, in which anchoring forces dominate, and because of its mathematical convenience. In a thick cell, however, the scenario of the Fréedericksz transition may not be that simple, so we now consider a more probable path for this transition. Such a path is shown in Fig. 2(d). Now the odd layers are allowed to rotate as well as the even ones. The path of lowest energy is then for the even layers to all rotate in the same direction, while the odd layers also undergo a small rotation in this direction. This results in an effective *softening* of the system, which permits it to have a lower energy than in the previous, uncoupled, arrangement.

We now calculate the critical electric field E_{c3}, at which the system leaves the ideally aligned state shown in Fig. 2(a) to begin the transformation into the state shown in Fig. 2(d). We will show that taking into account the cooperative motion of even and odd smectic layers may result in a significant reduction of the critical field when the cell thickness is not very small. Furthermore, this field does not necessarily have to be larger than E_{c2}. As we will show, for an infinitely thick cell and in the absence of any tendency to form a helical structure, the AFLC leaves the ideally aligned antiferroelectric configuration even when a very weak electric field is applied.

For our analysis we take $\phi_{2l}=\phi(z)$ for the even layers, and $\phi_{2l+1}=\pi+\psi(z)$ for the odd layers, and assume both $\phi(z)$ and $\psi(z)$ to be much smaller than unity. Expansion of Eq. (1) to second order in ϕ and ψ gives, with omission of all angle-independent terms,

$$\mathcal{E}=D\int dz\left\{\frac{k}{2}(\phi_z^2+\psi_z^2)+U(\phi-\psi)^2-\frac{P_0E}{2}(\psi^2-\phi^2)-\left(\frac{1}{2}\varepsilon_0\Delta\epsilon E^2\sin^2\theta_0-W(z)\right)(\psi^2+\phi^2)\right\}. \tag{9}$$

Minimization of this free energy in the bulk of the layer now gives us a pair of coupled Euler-Lagrange equations, whose solutions yield

$$\phi(z)=\phi_0\cos(\tilde{q}z), \tag{10}$$

$$\psi(z)=\psi_0\cos(\tilde{q}z). \tag{11}$$

Here self-consistency dictates that

$$\frac{\psi_0}{\phi_0}=A(E)\equiv-\frac{P_0E}{2U}+\sqrt{\left(\frac{P_0E}{2U}\right)^2+1}$$

and

$$\tilde{q}(E)=\sqrt{\frac{-2U+\varepsilon_0\Delta\epsilon E^2\sin^2\theta_0+\sqrt{(P_0E)^2+4U^2}}{k}}. \tag{12}$$

As in the uncoupled case, nonzero ϕ and ψ occur only when the total energy [Eq. (9)] is negative. After substitution of Eqs. (10) and (11) into Eq. (9), we obtain the condition for this to be true:

$$\tilde{q}^2\left(1-\frac{\sin\tilde{q}d}{\tilde{q}d}\right)+\left[\frac{2U}{k}\frac{(1-A)^2}{(1+A^2)}-\frac{P_0E}{k}\left(\frac{1-A^2}{1+A^2}\right)-\frac{\varepsilon_0\Delta\epsilon E^2\sin^2\theta_0}{k}\right]\left(1+\frac{\sin\tilde{q}d}{\tilde{q}d}\right)+\frac{4w_0}{kd}(1+\cos\tilde{q}d)<0. \tag{13}$$

In the limit of strong anchoring ($w_0\rightarrow\infty$), Eq. (13) reduces to the condition

$$\tilde{q}(E)d>\pi. \tag{14}$$

In the limit of small cell thickness, and hence large electric fields, for which $E/E_{c2}\gg1$, both Eqs. (13) and (14) reduce to the corresponding equations describing the uncoupled case, Eqs. (4) and (5). For moderate cell thicknesses, however, Eq. (13) predicts a Fréedericksz transition to occur at much smaller electric fields than before. For such fields we can neglect the dielectric anisotropy, and find the following expression for the critical field in the case of infinitely strong anchoring:

$$E_{c3}=\frac{1}{P_0}\sqrt{[2U+k(\pi/d)^2]^2-4U^2}. \tag{15}$$

We note that the critical field E_{c3}, at which the system leaves an ideally aligned antiferroelectric state, may be much smaller than the field E_{c2}, at which the purely ferroelectric state shown in Fig. 2(b) becomes energetically preferred to the purely antiferroelectric one shown in Fig. 2(a). This is shown schematically in Fig. 3, which indicates the critical field for homogeneous nucleation in each model as a function of cell thickness. The thickness d_1 at which a field of strength E_{c2} sufficient to cause ferroelectric alignment can also cause homogeneous nucleation is given by $d_1 = 3.45\sqrt{k/U}$.

To place these results in context, we can substitute typical values for the parameters involved [7]. With $k = 10^{-11}$ N, $P_0 = 7.5\times10^{-4}$ C m^{-2}, $U = 3\times10^3$ J m^{-3}, $\Delta\epsilon \sin^2\theta_0 = -0.1$, and infinitely strong anchoring, we find the critical cell thickness d_c to be as small as 25 nm. At the more typical experimental cell thickness of 1 μm the electric field at which homogeneous nucleation is predicted to occur is 4.6×10^5 V m^{-1} in the coupled model, and more than an order of magnitude higher, $\sim 8\times10^6$ V m^{-1} in the uncoupled model. We should note, however, that the magnitude of the interlayer interaction U is known only from indirect estimates, and so these figures may be subject to considerable revision.

III. CONCLUSIONS

In summary, we have studied the Fréederiksz transition in antiferroelectric liquid crystals in a model containing only nearest-neighbor interactions between smectic layers of the AFLC. We find the conditions under which an applied electric field can cause a homogeneously nucleated transition of the system from the antiferroelectric to the ferroelectric alignment. We demonstrate that taking into account the cooperative motion of the AFLC layers results in a significant reduction in the critical electric field for the transition.

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