Devil's Staircase, Critical Thickness, and Propagating Fingers in Antiferroelectric Liquid Crystals

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From an expression for the energy of a cell containing an antiferroelectric smectic liquid crystal with only nearest-neighbor interactions between layers we conclude the following: (1) a critical cell thickness exists at which the commensurability of the system changes from unity to higher values; (2) for negative dielectric anisotropy there is another critical thickness below which a transition to ferroelectric alignment cannot be homogeneously nucleated at any field; and (3) the transition to and from ferroelectric alignment propagates as a stable solitary wave under certain conditions.

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As mesophases between liquids and crystals, liquid crystals combine some of the richness of phases shown by crystalline solids with the comparatively rapid responses to deforming forces shown by liquids. This makes them particularly suitable substances in which to study nonlinear behavior [1]. Of their many possible phases, antiferroelectric liquid crystals (AFLCs) are among the most intriguing. Experiments have indicated that antiferroelectric smectic liquid crystals in the phase known as SmC_A^* have a layered structure in which the herringbone formation of the director orientation in successive layers undergoes a gentle helical rotation [2]. This complex structure gives rise to a correspondingly intricate dielectric behavior [3–5]. The aim of the present work is to present a model for the energy of AFLCs, and to analyze some of the phenomena that it yields.

The experimental observations that a theory should be capable of describing include the "devil's-staircase" behavior of the commensurability of the helix describing the director orientation [3,6–11], the conditions of applied electric field and cell thickness under which homogeneous and heterogeneous nucleation of phase transitions occur [4], and the velocity with which the domain wall between phases advances for a given field and cell thickness [4]. A previous approach to explaining the commensurability is that of Yamashita and Miyazima [12], who proposed an Ising model with third-nearest-neighbor interactions; in contrast, our model requires only nearest-neighbor forces. Various models capable of supporting solitary-wave propagation in liquid crystals have also been previously suggested [1]. Ours differs from these in a number of respects, including the treatment of the surface anchoring potential.

In the model we propose, the N smectic layers lie in the x-z plane as indicated in Fig. 1. 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

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

Here D is the layer thickness, k is an elastic constant, I is the moment of inertia per unit volume for rotation about the y axis, and $W(z)$ is a surface anchoring energy which we shall 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 [2,13] having an antiparallel orientation of adjacent dipoles, as described by the term with coefficient U. Steric hindrance acts to introduce a small chiral deviation from a perfectly antiparallel orientation, and is represented by the term with the small coefficient b. Finally, the two terms

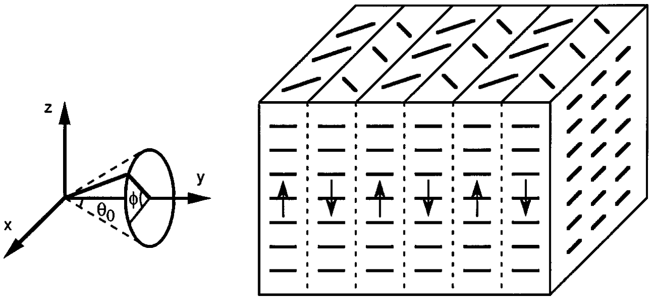

FIG. 1. Geometry of the model antiferroelectric liquid crystal.

containing the electric field E, which is assumed to be in the z direction, represent the effects of polarization and of the dielectric anisotropy, $\Delta\epsilon$, respectively, while ε_0 is the vacuum permittivity.

To the equations of motion obtained from the Hamiltonian (1) we add a dissipative term to account for the viscosity γ. The result is

$$I\frac{\partial^2\phi_l}{\partial t^2} + \gamma\frac{\partial\phi_l}{\partial t} = k\left(\frac{\partial^2\phi_l}{\partial x^2} + \frac{\partial^2\phi_l}{\partial z^2}\right) - P_0E\sin\phi_l\left(\frac{\varepsilon_0\Delta\epsilon\sin^2\theta_0}{2}E^2 - W(z)\right)\sin 2\phi_l + U[\sin(\phi_l - \phi_{l-1} - \alpha) - \sin(\phi_{l+1} - \phi_l - \alpha)]. \tag{2}$$

Here the antiferroelectric and chiral steric terms have been combined into a single set of terms by defining $\alpha \equiv \arctan(b/U)$ and approximating $\sqrt{U^2 + b^2}$ by U. The natural pitch of the helix formed by a sample with no boundaries and in zero field would then be $2\pi D/\alpha \simeq 2\pi DU/b$. This set of coupled nonlinear partial differential equations must now be examined in the hope of extracting some of the richness of the observed behavior of AFLCs.

We start by looking for stationary solutions of Eq. (2) in the case where $E = 0$ and where there is no variation of the ϕ_l in the x and z directions. Integration over x and z then give us the set of equations

$$2\Gamma\sin 2\phi_l = \sin(\phi_l - \phi_{l-1} - \alpha) - \sin(\phi_{l+1} - \phi_l - \alpha), \tag{3}$$

where $\Gamma \equiv w_0/Ud$. This set of coupled nonlinear difference equations has already been studied by Banerjea and Taylor [14], who found that the lowest-energy solutions were helices whose pitch formed an incomplete devil's staircase when plotted as a function of α for fixed Γ. By this we mean that the pitch of the helix is constant over certain ranges of α and changes either continuously or discontinuously between these ranges. When p is the smallest integer for which ϕ_{l+p} is identical to ϕ_l, modulo π, we say that the commensurability of this commensurate state is p. The phase diagram in α-Γ space is shown in Fig. 2, and shows the commensurabilities in a number of regions of this parameter space. Because Γ varies inversely as the cell thickness d, we see that the order of commensurability is 1 for thin cells and small α. As the cell thickness is increased, Γ falls until one crosses from the region where $p = 1$ to those where $p > 1$. The critical cell thickness above which this higher commensurability can occur is about $d_{c1} \sim 2w_0/b$. If we regard the Hamiltonian (1) as an effective free energy, then we can allow b and hence α to be a function of temperature. A change in temperature then represents a horizontal movement across Fig. 2 from commensurability 1 to higher commensurabilities. We stress that this devil's staircase of commensurate helices is quite different from the commensurate ferroelectric structures formed in Ising models with longer-range interactions [15]. In the Ising-model picture, all the ϕ are quantized at 0 or π, while in our solution the ϕ can take on any value. The Ising-model picture applies to very thin cells, and requires interactions to be of greater range than nearest neighbor. Our picture applies to cells of arbitrary thickness, and requires only nearest-neighbor forces.

Application of an electric field adds further complications. For this case we first consider thick cells, which will be in states of high commensurability, and look for static solutions at modest fields. We then drop the terms in W and in E^2 and are left with the equations

$$P_0E\sin\phi_l + U[\sin(\phi_{l+1} - \phi_l - \alpha) - \sin(\phi_l - \phi_{l-1} - \alpha)] = 0, \tag{4}$$

when ϕ is again assumed independent of x and z. The zero-field solution, $\phi_l = l(\pi + \alpha)$, is then modified by the electric field by an amount $\Delta\phi_l \simeq (-1)^l EP_0\sin(\alpha l)/4U$, and the energy is reduced to an amount $-U - E^2P_0^2/16U$ per unit volume. The ferroelectrically aligned state, in which all ϕ_l vanish, has an energy per unit volume of $U - P_0E$, and is thus preferred at a critical field $E_{c1} \simeq 2.3U/P_0$. For states of commensurability 1, in which all the ϕ_l are either 0 or π, the critical electric field at which the ferroelectrically

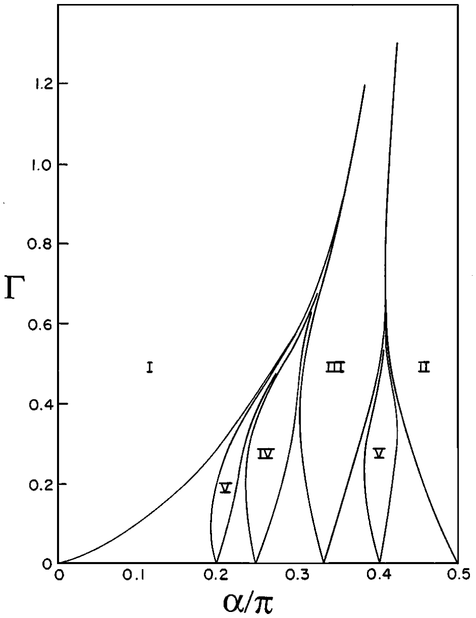

FIG. 2. In the devil's-staircase structure of an antiferroelectric liquid crystal, the lower orders of commensurability are shown as a function of anchoring strength Γ and helical twist α.

aligned state is reduced in energy below the antiferroelectric state is simply $E_{c2} = 2U/P_0$. The phase diagram in E-d space is then of the form shown schematically by the bold lines in Fig. 3.

In a perfect cell, however, the transition to the state of lower energy may not occur until a higher field is reached at which the ferroelectrically aligned stated is homogeneously nucleated. To determine whether this is the case we now examine the stability of the commensurability-1 states when subjected to an electric field. For this analysis we must restore the z dependence of ϕ, and so we put $\phi = 0$ in all odd layers and $\phi_l = \pi + (-1)^{l/2}\tilde{\phi}(z)$ in all even layers, realizing, however, that this symmetric solution will not always be realized [5]. The energy of an even layer can then be written to second order in $\tilde{\phi}$ as

$$\mathcal{E} = D\int dxdz\left\{\frac{k}{2}\left(\frac{\partial\tilde{\phi}}{\partial z}\right)^2 + \left[U - \frac{1}{2}P_0E - \frac{1}{2}\varepsilon_0\Delta\epsilon E^2\sin^2\theta_0 + W(z)\right]\tilde{\phi}^2\right\}. \quad (5)$$

While the first term is always positive, the second set of terms may become negative at sufficiently large electric field. Minimization of this expression in the bulk of the layer, where $w(z)$ vanishes, gives us a differential equation whose solution is $\tilde{\phi} = \tilde{\phi}_0\cos(qz)$, where $q = \sqrt{G/k}$ and

$$G \equiv -2U + P_0E + \varepsilon_0\Delta\epsilon E^2\sin^2\theta_0\,. \quad (6)$$

A nonzero $\tilde{\phi}$ will occur only when the total energy is negative. The condition for this is

$$\tan\left(\frac{qd}{2}\right) > \frac{2w_0}{kq}\,. \quad (7)$$

In the limit of strong anchoring ($w_0 \rightarrow \infty$) this reduces to the condition $qd > \pi$, and can always be achieved in a sufficiently thick sample or strong electric field if $\Delta\epsilon > 0$.

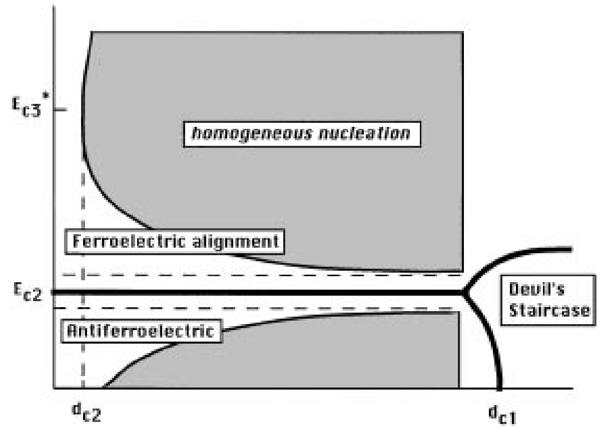

FIG. 3. This schematic phase diagram shows the ranges of electric field and cell thickness where the different phases are stable, and also the region of homgeneous nucleation where propagating solitary waves of polarization may be unstable. For clarity of illustration it is not drawn to scale; in actuality $d_{c1} \gg d_{c2}$ and $E_{c3}^* \gg E_{c2}$.

An interesting situation arises when the dielectric anisotropy is negative, as then there is a maximum value that G, and hence q, can attain. The upper shaded area in Fig. 3 represents schematically the field E_{c3} necessary to make the AFLC unstable in the limit of strong anchoring. For cells below the critical width marked as d_{c2}, there is no possible electric field that can destabilize the AFLC. For weaker anchoring the curve is displaced to the left, and the critical thickness is correspondingly reduced. The value E_{c3}^* of E_{c3} at which the cell of critical width becomes unstable is $P_0/2\varepsilon_0|\Delta\epsilon|\sin^2\theta_0$ regardless of the strength of the anchoring. If the electric field is reduced while the sample is in the ferroelectrically aligned state, there is a similar critical field for homogeneous nucleation into the AF state. This is shown for strong anchoring in the lower shaded area in Fig. 3, and is given by the inequality (7), but with $G = 2U - P_0E + \varepsilon_0\Delta\epsilon E^2\sin^2\theta_0$.

The critical field E_{c3} for homogeneous nucleation may be appreciably larger than the field E_{c2} at which the aligned state becomes energetically preferred. We then expect that nucleation will occur at isolated imperfections within a cell or at the cell boundary. When a region of ferroelectrically aligned material is formed, it will tend to spread by a process of domain-wall propagation along the layer in the x direction. In order to examine this process we restore the time dependence to the problem, and look at the dynamical process in which fingers of ferroelectrically aligned material propagate along the smectic layers into an AFLC sample. As before, we start with the commensurability-1 state where $\phi_l = 0$ for l odd, but now include the dependence of the ϕ_l for even l on x and t, while assuming that the z dependence can be neglected when $E < E_{c3}$. Equation (2) then takes the form

$$I\frac{\partial^2\phi_l}{\partial t^2} + \gamma\frac{\partial\phi_l}{\partial t} - k\frac{\partial^2\phi_l}{\partial x^2} = A\sin\phi + B\sin 2\phi\,, \quad (8)$$

with

$$A = 2U - P_0E; \quad B = \frac{\varepsilon_0\Delta\epsilon E^2\sin^2\theta_0}{2} - \frac{2w_0}{d}\,. \quad (9)$$

We seek traveling-wave solutions of this equation to describe the advance of ferroelectrically ordered fingers into the antiferroelectric layers when a sufficiently strong electric field is applied. Exact solutions to Eq. (8) may be found [16]. They are of the form

$$\phi(x,t) = 2\,\mathrm{arctan}e^{r(x-vt)}, \quad (10)$$

where $r = \sqrt{-2B/k + A^2I/k\gamma^2}$. For these to be valid, r must be real, which is always the case when the dielectric anisotropy $\Delta\epsilon$ is negative. When $A > 0$ they represent a rotation of ϕ from π to 0 as the finger advances; for negative A the velocity v is negative, and the ferroelectric finger recedes. These solutions have been shown [16] to be stable whenever $|A| < -2B$. The width of this window of stability of the solitary wave is closely related to the range of E for which homogeneous nucleation is possible. In fact, the condition $A < -2B$ for a stable solitary wave is simply an approximation to the converse of inequality (7). Were a more accurate treatment of the solitary-wave problem possible in which the z dependence of ϕ was included, it would presumably show that the waves were stable outside the regime of homogeneous nucleation.

The velocity of the solitary waves is

$$v = (E - E_{c2})\frac{P_0}{\gamma} \times \sqrt{\frac{k}{\varepsilon_0|\Delta\epsilon|E^2 \sin^2\theta_0 + 4w_0/d + (E - E_{c2})^2 P_0^2 I/\gamma^2}}\,, \tag{11}$$

and is proportional to $E - E_{c2}$ when this quantity is small. The term proportional to the moment of inertia density, I, is neglected in the overdamped limit where γ is large, as is the case in many materials. At very large fields the velocity saturates at a value

$$v_\infty = \frac{P_0}{\gamma}\sqrt{\frac{k}{-\varepsilon_0\Delta\epsilon \sin^2\theta_0}}\,. \tag{12}$$

In the homogeneous-nucleation regime, where these solitary waves are unstable, one cannot in general predict with any confidence what the velocity of the advancing or receding ferroelectrically aligned fingers will be. Although expression (10) is still a solution of the equation of motion (8), any propagating wave will then tend to change its shape and velocity in an unpredictable way. There is, however, one special case where a prediction can be made. When $E = 0$ and the cell is either very thick or very weakly anchored then the term in $\sin 2\phi$ vanishes and the equation of motion reduces to the damped sine-Gordon equation. If the inertia term I can be ignored then Aronson-Weinberger theory [17] allows one to state that the velocity of the stable solitary wave by which the ferroelectrically aligned state returns to the AF state is

$$v^* = \frac{2}{\gamma}\sqrt{2Uk}\,. \tag{13}$$

This is very different from the incorrect value, $v_i^* = \sqrt{k/I}$, that would be found as the $E = 0$ limit of Eq. (11). One need only look at the limit of large viscosity to verify that v^* will then vanish, as expected on physical grounds, while v_i^* is a constant independent of γ.

Finally, we put the preceding calculations in perspective by noting some numerical magnitudes for a typical LC material. We put $k = 10^{-11}$ N, $I = 10^{-16}$ kg/m, $w_0 = 10^{-4}$ J/m^2, $\gamma = 10^{-2}$ J s/m^3, $P_0 = 7.5 \times 10^{-4}$ C/m^2, $b = 1.5 \times 10^{-3}U$, and U, determined by the observed value [4] of E_{c2}, as 3×10^{-3} J/m^3. We then find E_{c2} to be 8 V/μm, E_{c3} the unrealizably high value of 400 V/μm, d_{c1} to be 20 μm, and d_{c2} to be the extremely low value of 25 nm.

In summary, we have seen that the commensurability of the layers in a SmC_A^* liquid crystal changes from unity at a critical cell thickness related to the planar anchoring strength of the cell surface. Application of an electric field to the commensurability-1 AF state can lead to homogenous nucleation of ferroelectrically aligned material only for cells of thickness greater than another critical value. The regime where homogeneous nucleation is forbidden corresponds to that in which the material may make transitions between the AF and ferroelectrically aligned states by propagation of stable solitary waves. These waves represent fingers of ferroelectrically aligned liquid crystal advancing into or receding from the AF material.

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