Field-Induced First-Order Orientation Transitions in Ferroelectric Liquid Crystals

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Two new effects specific to ferroelectric liquid crystals are described: (a) ferroelectric polar surface interactions and (2) spontaneous splay of the polarization. It is shown that a consequence of these effects is the possibility of first-order reorientation transitions induced by applied electric fields.

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It is characteristic of liquid crystals that their orientation distribution is easily manipulated with applied electric or magnetic fields. The study of these field effects has been one of the most fruitful approaches to the physics of liquid crystals. The Fréedericksz transition is widely used to study the distortion and surface elasticities of liquid crystals, and it typifies all previously studied field effects in that increasing applied field strength results in *continuous* changes in the orientation field of the liquid crystal. In this Letter we demonstrate applied-field–induced transitions in liquid crystals that are first order, that is the bulk and surface reorientations are *discontinuous* with increasing field strength. We show that this is a consequence of two new effects specific to ferroelectric liquid crystals: (1) ferroelectric polar surface interactions and (2) spontaneous splay of the polarization field. In thin samples, either of these two effects contribute to the stabilization of a state of nonuniform molecular orientation, characterized by splay of the polarization field, which undergoes a discontinuous transition to a state of uniform polarization field under the influence of an applied electric field.

Ferroelectric liquid crystals are characterized by a spontaneous electric polarization $\vec{P}$ in the plane of the smectic layers, perpendicular to the molecular director $\hat{n}$. Hence, $\vec{P} \propto \hat{n} \times \hat{z}$, where the z axis is normal to the layers, and $\hat{P} = \vec{P}/|\vec{P}|$. For a given smectic-$C$ tilt angle θ the polarization field, and hence the director field, is uniquely characterized by the azimuthal angle φ as shown in Fig. 1(a). The lowest-free-energy state of a bulk sample of ferroelectric liquid crystal exhibits a helicoidal structure, where $\hat{n}$ spirals about the z axis. However, the introduction of parallel bounding surfaces normal to the layers, that interact with the director, can suppress this helix. This is the basis of the surface-stabilized ferroelectric-liquid-crystal (SSFLC) geometry.[1,2] For example, if the director orientation parallel to the bounding plates is favored by a sufficiently strong nonpolar surface energy of the form $W_s = -\gamma_1(\hat{P} \cdot \hat{s})^2$ ($\hat{s}$ is the outward surface normal unit vector), the bounding plates will unwind the helix when their spacing is smaller than a few helix pitches, resulting in two stable states of uniform and opposite polarization, up and down, as shown in Fig. 1(b).

Our subsequent studies on a variety of ferroelectric liquid crystals and various boundary materials have shown that, in the absence of an electric field, other, nonuniform, states of the

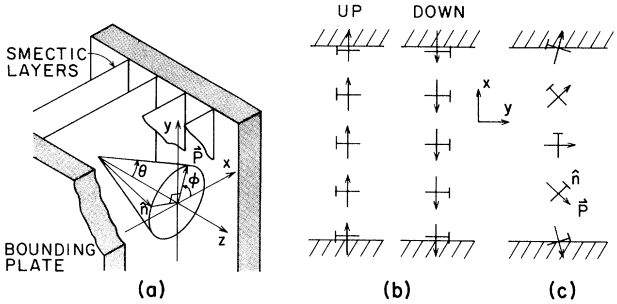

FIG. 1. (a) Geometry of the ferroelectric liquid crystal. The layers are parallel to the x-y plane. The director $\hat{n}$ is parallel to the average molecular long axis, and lies on a cone, making an angle θ with the z axis. The polarization $\vec{P}$ is in the plane of the layers, and perpendicular to $\hat{n}$, making an angle φ with the x axis. (b) The two stable states of the *nonpolar* SSFLC geometry, up and down, viewed in the plane of a smectic layer. The end of the director which projects out of the page is indicated by the crossbar. (c) The stable state of splayed polarization, at zero applied field. The polarization makes the angles φ_t and φ_b to the x axis at the top and bottom surfaces, respectively.

polarization field can be stable, in particular, the state shown in Fig. 1(c). Here, $\vec{P}$ makes the same angle to $\hat{s}$ at both top and bottom surfaces, so that $\varphi_t = \pi - \varphi_b$ (φ_t and φ_b are, respectively, the angles between $\vec{P}$ and the x axis at the top and bottom surfaces). As shown in the illustration, the projection of the director onto the x-y plane twists about the z axis as the sample is traversed from bottom to top. The rotation of polarized light by this twist is similar to that of a twisted nematic, and is the principal identifying feature of this state. Our samples are generally quite thin ($d \approx 1$ μm), and so the adiabatic limit of Mauguin is only approximately satisfied; in general, the exiting light is therefore elliptically polarized, and samples viewed between crossed polarizers typically show a characteristic powder blue color, with no orientation relative to the crossed polarizer and analyzer producing complete extinction.

We report two new effects unique to chiral tilted smectics that stabilize these states of nonuniform orientation.

(1) Ferroelectric polar surface interactions.—The symmetry of ferroelectric liquid crystals in general requires surface orientations that differ in the sign of $\vec{P}\cdot\hat{s}$ to have different energies, resulting in a term in the surface energy of the form $W_s = -\gamma_2(\hat{P}\cdot\hat{s})$. For example, this energy may arise from the electrostatic interaction of $\vec{P}$ with surface charges or dipoles, or from the same steric interactions that produce polarization in the bulk. While these interactions are isotropic, that is γ_2 does not depend on the orientation of the smectic layers in the x-y plane, the anisotropic treatment of the surfaces, for example, by oblique evaporation of SiO, will result in an additional term of the form $-\gamma_3(\hat{P}\cdot\hat{s})$, where γ_3 *does* depend on the layer orientation. However, our bounding surfaces are not significantly anisotropic, having no deliberately anisotropic treatment, and all smectic layer orientations in a fan texture behave identically.

(2) Spontaneous polarization splay.—As originally pointed out by Meyer *et al.*[3] the symmetry of tilted chiral smectics allows terms linear in director twist and bend to appear in the distortion-free energy density:

$$W_d = \tfrac{1}{2}K_1(\nabla\cdot\hat{n})^2 + \tfrac{1}{2}K_2(\hat{n}\cdot\nabla\times\hat{n} + q_{\parallel})^2 + \tfrac{1}{2}K_3(\hat{n}\times\nabla\times\hat{n} + \vec{q}_{\perp})^2,$$

which results in the nonzero $\partial\varphi/\partial z$ of the familiar helicoidal minimum-energy state. However, it has not been previously appreciated that the minimum-energy state of finite samples has nonzero $\partial\varphi/\partial x$, corresponding to local splay of the polarization field. Such a splayed state does not exist in a bulk sample without disclination walls, which are apparently energetically costly enough to allow only the disclination-free helicoidal state. In a thin sample, however, the disclinations are effectively located on the sample surfaces, and the favorable sign of polarization splay is obtained throughout the sample without the disclination energy cost, as shown in Fig. 1(c). In the one-constant approximation to the elastic distortion energy, the wave vector characteristic of the polarization twist (director helix) is $q_{\mathrm{twist}} = q_{\parallel} + |\vec{q}_{\perp}|\cot\theta$, and the wave vector characteristic of polarization splay is $q_{\mathrm{splay}} = q_{\parallel}\cot\theta + |\vec{q}_{\perp}|$. For typical ferroelectric liquid crystals, $\cot\theta$ is of the order unity, so that q_{twist} and q_{splay} are comparable in magnitude.

The application of a voltage V across the bounding plates separated by a distance d produces an electric field $E = V/d$ along the x axis. The interaction energy of the ferroelectric dipoles is $W_e = -\vec{P}\cdot\vec{E} = -PE\cos\varphi$. The bound charge arising from nonuniformities of $\vec{P}$ may be neglected, since for short-wavelength distortions the electrostatic energy of the bound charge is small compared to the elastic energy of the distortion, and for long-wavelength distortions the bound charge is screened by ionic impurities of the liquid crystal.[4] If we assume that the surface energy is of the form $W_s = -\gamma_1(\hat{P}\cdot\hat{s})^2 - \gamma_2(\hat{P}\cdot\hat{s})$, and that φ depends only on x, then the total scaled free energy of the ferroelectric liquid crystal of single elastic constant K has the form

$$Wd/K = \int_{-1/2}^{1/2}(\tfrac{1}{2}\varphi x^2 - \lambda_3{}^2\cos\varphi)dx - \lambda_1(\cos^2\varphi_t + \cos^2\varphi_b) - \lambda_2(\cos\varphi_t - \cos\varphi_b),$$

where $\lambda_1 = \gamma_1 d/K$, $\lambda_2 = (q_{\mathrm{splay}} + \gamma_2/K)d$, and $\lambda_3{}^2 = PED^2/K$. Note that both the ferroelectric polar surface interactions and the intrinsic splay of the polarization contribute to the energy in an equivalent way, their strengths adding to give λ_2. If φ_b is held fixed, minimizing this free energy gives the Euler-Lagrange equation, $\varphi_{xx} = \lambda_3\sin\varphi$, and boundary condition on the derivative of φ at the top surface, $\varphi_x(x = d/2) = -\lambda_1\sin 2\varphi_t - \lambda_2\sin\varphi_t$. In the absence of an applied field, the splayed state has the

lowest energy of any of the solutions of the above system of equations, if λ_2 is sufficiently large compared to λ_1. The total energy of this splayed state has been calculated numerically and is plotted for $\lambda_1 = 1$ and $\lambda_2 = 3$ as a function of φ_b for various field strengths, λ_3, in Fig. 2.

The minimum of W at $\varphi_b \neq 0$, in Fig. 2(a), indicates the stabilization of the splayed state. As the field strength is increased, an energy minimum develops for the uniform state [$\varphi_b = 0$, Fig. 2(b)]. As the field is further increased, the uniform state is increasingly favored, allowing the possibility of a transition to a field-induced state with a first-order change in surface orientation and energy [Fig. 2(c)]. Further increases in the field result in the disappearance of the energy minimum for the splayed state [Fig. 2(e)], finally resulting in stability only for the state with $\vec{P}$ uniformly along $\vec{E}$ [Fig. 2(f)].

This corresponds to our observations shown in Fig. 3. These are transmission polarizing photomicrographs of MORA-8,[5] constrained by parallel plates separated by 1 μm. The surface of the plates is cleaned indium-tin oxide, as in Refs. 1 and 2. In Fig. 3(a) the applied electric field is high enough to produce a state of uniform polarization, up, with the sample so oriented with respect to the crossed polarizer and analyzer as

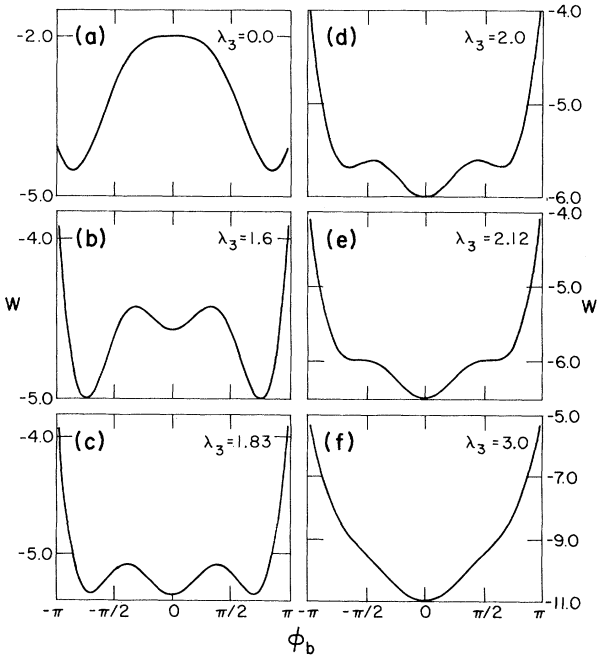

FIG. 2. The energy of the splayed state as a function of φ_b, for increasing electric field, with $\lambda_1 = 1$ and $\lambda_2 = 3$. At zero field (a) only the splayed state is stable. As the applied field is increased, an energy minimum at $\varphi_b = 0$ develops, stabilizing the up state in (b) at $\lambda_3 = 1.6$; the depth of the up-state minimum overtakes, in (c) at $\lambda_3 = 1.83$, and exceeds that of the splayed state, in (d) at $\lambda_3 = 2.0$. Eventually, the splayed state becomes marginally stable, in (e) at $\lambda_3 = 2.12$, leaving only the up state stable, in (f) at $\lambda_3 = 3.0$. (Note that the plots are not on the same scale.)

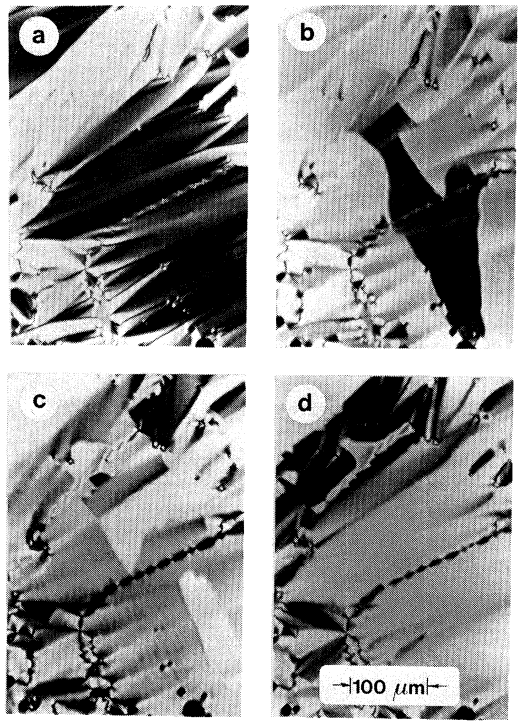

FIG. 3. Sequence of transmission photomicrographs of MORA-8 between crossed polarizers at various voltages V. The sample is confined between parallel transparent conductive plates spaced by 1 μm, at $T = 86.5\,^{\circ}$C, and exhibits the fan texture typical of the smectic-C phase with the layers perpendicular to the plates. At low fields, the brushes of the fans do not extinguish between the crossed polarizer and analyzer, and appear a powder blue color, while at high fields, the texture has the yellow birefringence color characteristic of its 1-μm thickness, with extinguishing brushes. In (a), $V = +4.7$ V, the sample is in the uniform up state, and oriented with respect to the crossed polarizer and analyzer so as to be largely extinguishing over the region shown. As V is decreased, domain walls appear, surrounding splayed regions which increase in area and coalesce, leaving isolated regions of the sample still up, as in (b) at $V = +2.2$ V. As V is further decreased, the up regions disappear, leaving the entire sample in the splayed state. For sufficiently negative voltages, a second set of domain walls appear, surrounding down regions, as in (c) at $V = -1.4$ V. In (d), $V = -3.9$ V, and the sample is entirely down, allowing the sample to be largely transmitting.

to give extinction over most of the field of view. In Fig. 3(b), the field is reduced to allow a domain-wall–mediated first-order transition to the splayed state. The domain wall is still visible in the figure, surrounding a region still up. Reversal of the field eliminates the up region, and by the motion of a second domain wall another first-order transition to a state of uniform polarization down is initiated, as shown in Fig. 3(c). Further increase of the reversed field results in a sample uniformly down, as in Fig. 3(d). The sample orientation with respect to the polarizer and analyzer has been unchanged throughout, so that the sample is now largely transmitting. This dependence of transmission on applied field suggests applications to electro-optic devices with highly nonlinear responses including sharp thresholds and hysteresis.

We have made similar observations on the smectic-*C* phase of DOBAMBC,[6] which under some circumstances exhibits a stable splayed state in the absence of applied electric field. However, in the lower-temperature smectic-*I* phase, which has larger elastic constants, only the uniform (up, down) states are stable. A possible explanation of this observation is that the surface interactions are predominantly responsible for stabilizing the splayed state in the *C* phase, and that the enhanced Frank elasticity of the *I* phase reduces λ_2 below that necessary to stabilize the splayed state.

In earlier theoretical considerations of the response of nematic liquid crystals with finite surface anchoring strength to applied fields by Nehring, Kmetz, and Schaffer[7] and Rapini and Papoular,[8] it was shown that Fréedericksz transitions involving continuous change of surface orientation should be possible. Their effective surface interactions are equivalent to ours with $\gamma_1 = 0$, once the transformation from dielectric to ferroelectric coupling is made. The first-order transition observed here results only when $\gamma_1 \neq 0$, and would appear in the nematic case with appropriate higher-order surface interaction energies.

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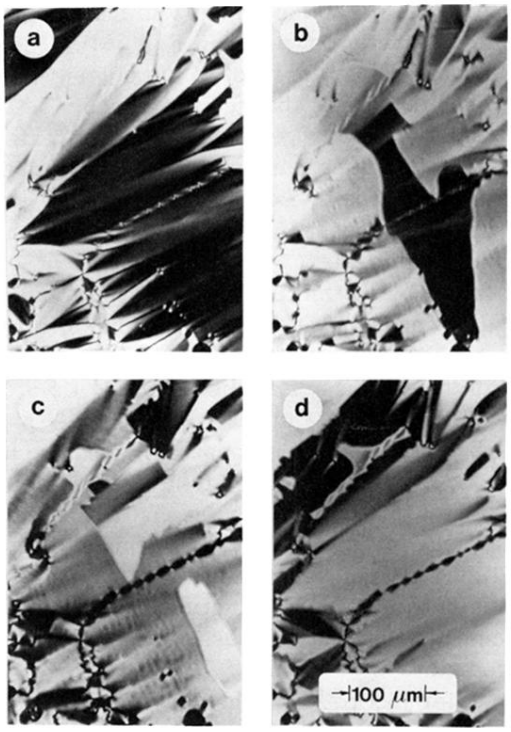

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