

FREEDERICKSZ TRANSITION IN AN ANTICLINIC LIQUID CRYSTAL

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Abstract

It is shown experimentally that a very-long-pitch, surface-stabilized, anticlinic liquid crystal undergoes a two-step electric-field-induced transition to the synclinic phase. The liquid crystal remains undistorted below a threshold field E_{th} . For $E > E_{th}$ a Fredericksz transition occurs, wherein molecules in adjacent smectic layers undergo unequal azimuthal rotations about the layer normal. At higher fields a transition to the synclinic phase occurs *via* solitary waves.

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Anticlinic liquid crystals offer a wide array of scientifically fascinating and technologically useful phenomena [1, 2]. In the anticlinic phase, also known as the smectic C_A^* phase, the director \hat{n} tilts by polar angle θ with respect to the smectic layer normal (Fig. 1). Additionally, the azimuthal orientation of the director changes by $\Delta\phi \approx \pi$ from one layer to the next. For the typical chiral anticlinic material, $\Delta\phi$ differs from π by typically one or two percent; on the other hand, for a pitch-compensated mixture where the helical pitch is infinite, $\Delta\phi$ is identically equal to π . Thus, for typical chiral anticlinic materials, the director is arranged in a double helix — one helix for the odd-numbered layers and another for the even-numbered layers — whose identical pitches are typically several hundreds of smectic layers. In each layer there is a polarization \vec{P} that lies perpendicular to the tilt plane of the molecules, where the azimuthal orientation of \vec{P} also changes by approximately $\Delta\phi \approx \pi$ from one layer to the next (Fig. 1). If the helical pitch is not infinite, then the polarizations are not quite antiparallel and a nonzero average polarization exists locally. Thus, when subjected to a weak electric field, the helices distort [3], giving rise to a small change in the transmitted light intensity when the cell is placed between a pair of crossed polarizers. At a much stronger field there is a sudden transition from the distorted anticlinic phase to the synclinic phase (the smectic C^* phase, Fig. 1), such that the azimuthal orientation of the director is spatially uniform and all layer polarizations \vec{P} are parallel to the applied field. Associated with this field-induced transition, which occurs by finger-like solitary waves [4], is a large change in the transmitted light intensity.

For very-long-pitch, surface-stabilized, anticlinic liquid crystals, the behavior at small electric fields is expected to be considerably different. For these materials it is possible to achieve a helix-free, near-perfect bookshelf alignment (see Fig. 1), so that $\Delta\phi = \pi$ and the tilt plane of the molecules lies parallel to the plane of the cell throughout. Under these circumstances Qian and Taylor have predicted that, instead of a continuous variation of the director orientation with field

beginning at $E = 0$, a sharp Freedericksz transition occurs [5]. For $E < E_{th}$, where E_{th} is the Freedericksz threshold field, the splay elasticity and the anticlinic interactions dominate the free energy, and the director profile is undisturbed. For $E > E_{th}$, the electric field is sufficient to overcome both the elasticity and the anticlinic interactions: Molecules in adjacent layers undergo *unequal* azimuthal rotations, resulting in a locally-averaged nonzero polarization that couples to the electric field. At a much higher field $E_{s.w.}$ the distorted anticlinic order switches rapidly to synclinic order by means of solitary waves, analogous to the solitary wave behavior observed in short-helical-pitch materials [4]. The purpose of this paper is to demonstrate experimentally the low-field Freedericksz switching mechanism in an anticlinic liquid crystal. We find that the threshold field E_{th} is proportional to d^{-1} , where d is the cell thickness, and is of the same order as that predicted by theory.

Let us first consider a simple model. For the geometry in Fig. 2, the bulk free energy F for a pair of adjacent layers may be written:

$$F = \int d^3r \left\{ PE[\cos(\beta + \alpha) - \cos(\beta - \alpha)] + \frac{1}{2} K \left\{ \left[\frac{\partial(\beta - \alpha)}{\partial z} \right]^2 + \left[\frac{\partial(\beta + \alpha)}{\partial z} \right]^2 \right\} + 2U(1 - \cos 2\alpha) - \frac{\Delta\epsilon \sin^2 \theta}{8\pi} E^2 [\cos^2(\beta - \alpha) + \cos^2(\beta + \alpha)] \right\} \quad (1)$$

where azimuthal rotation angles α and β are functions of z , the axis perpendicular to the cell walls.

Here β corresponds to the azimuthal rotation of the symmetry axis for a pair of molecules in adjacent layers, and α corresponds to half the deviation from perfect anticlinic order, *i.e.*, $\alpha = \frac{1}{2}(\pi - \Delta\phi)$. Additionally, U is the interaction coefficient associated with deviations from anticlinic order [4], *i.e.*, deviations from $\alpha = 0$; $K = K_{11} \sin^2 \theta$, where K_{11} is the splay elastic constant; and $\Delta\epsilon$ is the dielectric anisotropy. Finally, we assume strong anchoring, which requires that β and α vanish at the two surfaces. We then expand F in powers of β and α to quadratic order, substitute the Fourier

components $\beta = \sum_q \beta_q e^{iqz}$ and $\alpha = \sum_q \alpha_q e^{iqz}$ into F , where $q = \frac{\pi}{d} j$ and j is an integer, and minimize

F with respect to variations in β_q and α_q for all q . It turns out that the dielectric term is about two orders of magnitude smaller than the polarization term, and can be neglected. For very small electric fields F is minimized for $\beta_q = \alpha_q = 0$, for all q . Above a threshold field $E_{th} =$

$\frac{1}{P} \sqrt{Kq^2 (4U + Kq^2)}$, however, the free energy is minimized for a nonzero rotation β_q . The field E_{th}

has its lowest value when $j = 1$, *i.e.*, when $q = \pi/d$; this corresponds to the Freedericksz transition.

Moreover, for $q = \pi/d$, $Kq^2 \ll 4U$, and E_{th} can be approximated as $E_{th} = \frac{2\pi}{d} \sqrt{\frac{UK}{P^2}}$. Retention of

higher-order terms in F allows one to calculate that just above the threshold $\beta_{q=\pi/d} \approx 2 \sqrt{\frac{E - E_{th}}{E_{th}}}$,

and $\beta_q \gg \alpha_q$. These rotations give rise not only to a change in the optical retardation, but to a tilt of the optic axis as well. From the expression for E_{th} we find that the threshold *voltage* is independent

of d and is given by $V_{th} = 2\pi \sqrt{\frac{UK}{P^2}}$.

Two cells were prepared by cleaning two pairs of indium-tin-oxide coated glass slides, spin-coating the slides with polyimide RN1266 (Nissan Chemicals), and baking. The coated slides were then rubbed with a cotton cloth using a dedicated rubbing machine and placed together, separated by Mylar spacers. The cells were then cemented. The measured thicknesses of the two cells were (7 ± 1) and (11 ± 1) μm . The cells were filled in the isotropic phase with a binary mixture of (R)-TFMHPOBC [4-(1-trifluoromethylhexyloxy-carbonyl) phenyl 4'-octyloxybiphenyl 4-carboxylate] [Ref. 6] and (R)-MHPOBC [4-(1-methylheptyloxy-carbonyl)phenyl 4'-octyloxybiphenyl-4-carboxylate] [Ref. 1]. The polarizations of these materials add constructively, but their helices wind in opposite directions [7]. We found that a 70:30 wt.% mixture of (R)-TFMHPOBC and (R)-

MHPOBC provides an extremely long pitch (well over $10\ \mu\text{m}$) that easily could be surface-stabilized in the bookshelf geometry. Each cell was then slowly cooled through the isotropic - smectic A phase transition at $138\ ^\circ\text{C}$, through the smectic A – smectic C_A^* transition at $120\ ^\circ\text{C}$, and stabilized at $113\ ^\circ\text{C}$ in the anticlinic Smectic C_A^* phase. A focused beam from a 5 mW He-Ne laser passed consecutively through a light chopper, a polarizer, a Babinet-Soleil compensator, the cell, an analyzer, and into a detector. The detector output was fed into a lock-in amplifier that was referenced to the chopping frequency of $\omega = 2004\ \text{s}^{-1}$ ($f = 319\ \text{Hz}$), allowing us to measure the d.c. intensity in an illuminated room. The polarizer and analyzer were oriented at 45° with respect to the liquid crystal's optic axis at $E = 0$, which is perpendicular to the smectic layers. The compensator was adjusted in the absence of an applied field so that the total optical phase retardation δ of the compensator + liquid crystal was $\delta = 0$, corresponding to a near zero intensity at the detector.

A d.c. electric field may be used to induce a Fredericksz transition. However, because the electrical resistance of the thin polyimide layers was at least an order of magnitude larger than that of the liquid crystal — and both were larger than $1\ \text{M}\Omega$ — the voltage drop across the polyimide layer would have been much larger than that across the liquid crystal. This is an undesirable situation, as it is difficult to determine accurately the applied field across the liquid crystal. On the other hand, for a sufficiently high frequency a.c. field, the free charges in the cell are unable to follow the field. In this case the electric fields across the thin polyimide layers and the much thicker liquid crystal region would be determined by their dielectric constants (which are similar) and their thicknesses, and therefore the field across the liquid crystal could be taken as $E \approx V/d$. We thus chose to perform an a.c. experiment. One must meet three conditions for the driving frequency ω . First, ω needs to be larger than approximately $30\ \text{s}^{-1}$ in order to avoid effects due to motion of the free charges. Second, ω needs to be considerably larger than the Fredericksz

transition relaxation rate Γ_F so that β_q would not vary with the a.c. field. Fortunately, Γ_F is typically of order a few tenths s^{-1} near E_{th} , and vanishes at E_{th} , so that this condition is automatically met by meeting the first condition. Finally ω needs to be somewhat smaller than the q-independent relaxation rate Γ_{OM} of the optic mode, *i.e.*, the natural relaxation rate for fluctuations involving α . Using an in-plane electric field to drive the optic mode [8], we have found that Γ_{OM} is approximately $5000 s^{-1}$ for this mixture at $T = 113^\circ C$. Therefore, in order to meet all three criteria, $30 < \omega < 5000 s^{-1}$. We have chosen $\omega = 710 s^{-1}$ (corresponding to $f = 113$ Hz) at which to perform the experiment.

The rms amplitude of the a.c. voltage was ramped from 0 to 0.08 statvolts at a rate of 2.7×10^{-5} statvolts s^{-1} , and the detector intensity was computer-recorded. Figure 3a shows a trace of the intensity I vs. voltage for the $d = 7 \mu m$ cell, and Fig. 3b for the $d = 11 \mu m$ cell. We note that, for our optical geometry, just above the Freedericksz transition $I \propto \delta^2 \propto \beta_q^4$, and according to Ref. 5, $\beta_q \propto (V - V_{th})^{1/2}$. Thus, in Fig. 4a we show $I^{1/2}$ vs. V in the vicinity of the threshold voltage V_{th} for the $d = 7 \mu m$ cell, and in Fig. 4b we show $I^{1/2}$ vs. V for the $d = 11 \mu m$ cell. The linear behavior for $V > V_{th}$ allows us to extract the threshold voltage $V_{th} = (0.0038 \pm 0.0004)$ statvolts for the $d = 7 \mu m$ cell, and $V_{th} = (0.0037 \pm 0.0004)$ statvolts for the $d = 11 \mu m$ cell. The fact that the threshold voltages are the same is a clear indication of Freedericksz behavior which, for moderately strong anchoring, predicts a thickness-independent threshold voltage. As an aside, we note that the experiment was also conducted at a higher frequency of $\omega = 2000 s^{-1}$, with virtually identical results. Additionally, when the voltage was slowly swept downward, hysteresis was minimal.

Above the threshold voltage the intensity continues to increase, but at a slower rate, as both β_q and α_q increase. Qian and Taylor predicted [5] that at a large field a sharp transition to synclonic order would occur, where $\beta_q = \alpha_q = \frac{1}{2} \pi$. Although they did not theoretically examine the dynamics

of this transition, observations using a polarizing microscope at a visually-accessible driving frequency of $\omega \approx 70 \text{ s}^{-1}$ reveal synclincic fingers, approximately $10 \mu\text{m}$ in width, propagating along the smectic layers into the anticlinic region. These fingers advance and retreat at frequency ω , with β_q remaining fixed and α_q changing sign at each field reversal. At our experimental frequency $\omega = 710 \text{ s}^{-1}$ the finger reversal could not be detected by eye, although the intensity at the detector exhibited a sharp increase with voltage (Fig. 3). We found that for the $d = 7 \mu\text{m}$ cell a threshold *field* $E_{s.w.} = (77 \pm 7) \text{ statvolt cm}^{-1}$ for the onset of solitary waves, which was similar to $E_{s.w.} = (75 \pm 10) \text{ statvolts cm}^{-1}$ for the $d = 11 \mu\text{m}$ cell, consistent with a field-dependent, rather than voltage-dependent, solitary wave threshold [4]. The uncertainty in $E_{s.w.}$ is due primarily to the uncertainty in cell thickness d rather than to an uncertainty in determining the voltage.

Although the experimental results confirm the existence of a Fredericksz transition, discrepancies exist between our results and the model. First, the model predicts that $V_{th} = 2\pi\sqrt{\frac{UK}{P^2}}$. For our material at $T = 113 \text{ }^\circ\text{C}$ we previously measured [9] $P = 300 \text{ esu cm}^{-2}$, $U = 2 \times 10^4 \text{ erg cm}^{-3}$, and $\theta = 22.5^\circ$. If we assume that $K_{11} = 1.5 \times 10^{-6} \text{ dyn}$, corresponding to $K = 2.2 \times 10^{-7} \text{ dyn}$, we would expect $V_{th} \approx 0.0015 \text{ statvolts}$. The experimental values of V_{th} are larger, by a factor of two to three, than that predicted by the simple theory. One possible explanation could be that our assumed value for K_{11} is small, and that due to interlayer correlations in the anticlinic phase K_{11} is somewhat larger than our estimate. Unfortunately we are unaware of extant data for elastic constants in the anticlinic phase. Another problem may lie with the simplicity of the model, which assumes two-layer periodicity and does not account for next nearest neighbor interactions [10]. A more robust theoretical treatment is beyond the scope of this paper, however.

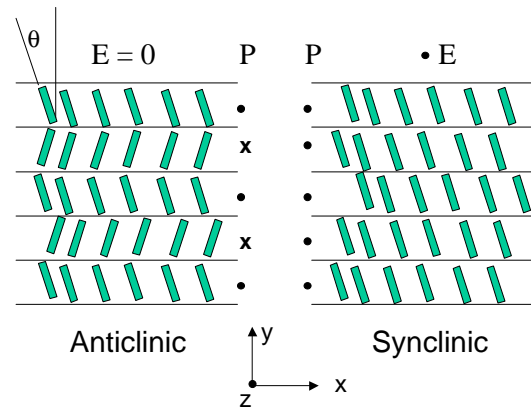
To summarize, we demonstrate that a Fredericksz transition occurs at low voltages in a very long pitch, surface-stabilized anticlinic liquid crystal if the voltage is increased sufficiently

slowly with time. Therefore, the switching mechanism from the anticlinic to synclinic orientation is a two-step process involving a Freedericksz transition followed by solitary waves.

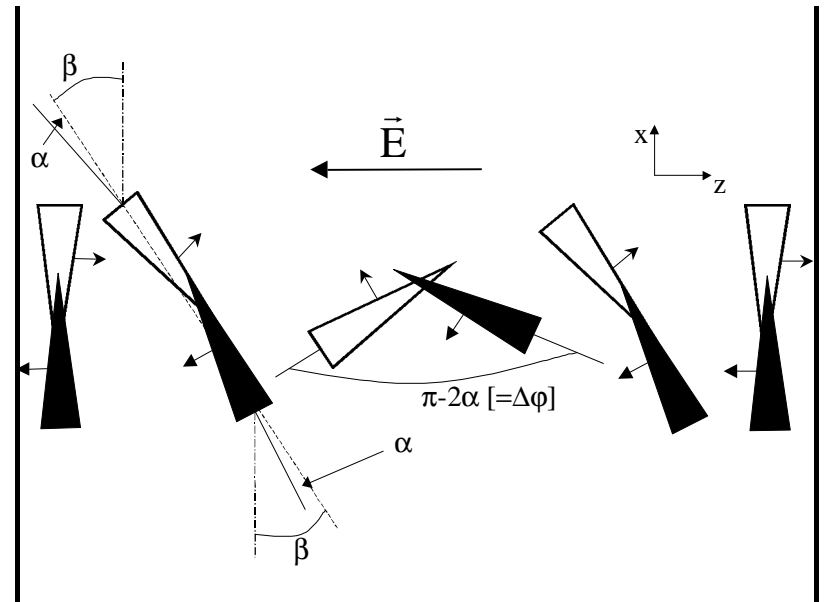
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Figures

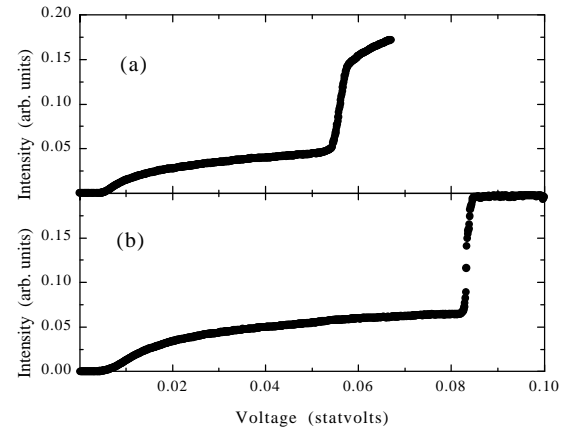
1. Schematic representation of anticlinic (Smectic C_A^*) phase (left) for an infinitely long helical pitch at electric field $E = 0$. θ corresponds to the polar tilt angle of the molecules and P corresponds to the layer polarization. For sufficiently large electric field E , a transition to the synclinic (Smectic C^*) phase (right) occurs.



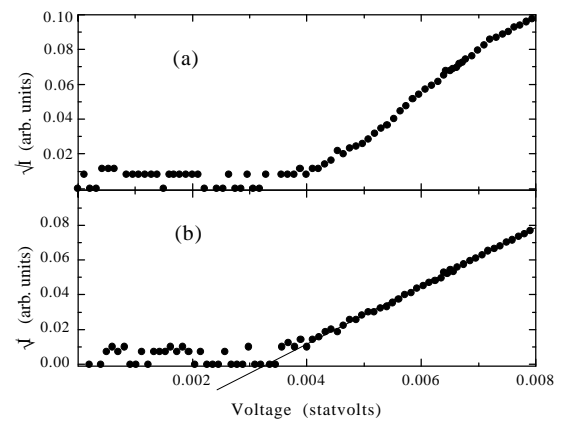
2. Schematic representation of molecular orientations in two successive smectic layers (black above white) for $E > E_{th}$. Molecules are assumed to remain anchored at the walls. Angle β corresponds to the average azimuthal rotation of a pair of molecules in adjacent layers; α corresponds to the deviation from this average, *i.e.*, the deviation from perfect anticlinic order. Arrows correspond to the layer polarization, which is locally perpendicular to the molecular tilt plane.



3. Intensity vs. voltage for a) the $d = 7 \mu\text{m}$ cell and b) the $d = 11 \mu\text{m}$ cell. Note both the Fredericksz transition and the onset of solitary waves.



4. $I^{1/2}$ vs. V in the vicinity of the Fredericksz transition for a) the $d = 7 \mu\text{m}$ cell and b) the $d = 11 \mu\text{m}$ cell. Note that for $V < V_{\text{th}}$ fluctuations in $I^{1/2}$ are artificially accentuated because of the digital signal.



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