

## Surface-Induced Polarization at a Chiral-Nematic-Substrate Interface

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A novel linear electro-optic effect is observed in a surface-stabilized chiral nematic cell above the Fréedericksz transition threshold field. The slow dynamic response indicates that this effect arises from the interfacial region which elastically couples to the bulk, rather than directly from the bulk. Moreover, evidence suggests that the primary effect is a spontaneous electric polarization very near the interface. Other possible contributions to this effect are discussed.

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The relationship between symmetry and spontaneous polarizations in liquid crystals has long been the subject of intense study. In 1969 Meyer showed [1] that in the presence of a bend or splay distortion the nematic symmetry is reduced to  $C_2$ , giving rise to a spontaneous electron polarization  $\mathbf{P}$  along the twofold axis. Several years later Meyer *et al.* proposed and demonstrated the existence of "ferroelectricity" in liquid crystals [2], an effect which exists in the absence of elastic deformations. In simple mean-field theory, the polarization scales as the polar tilt angle  $\theta$ . (Although deviations from this linear relationship have been observed [3], they turn out to be of only minor importance in the work described herein.) Finally, in addition to its presence in bulk tilted phases, ferroelectricity exists at a symmetry-breaking interface in samples composed of *nonchiral* molecules. The surface destroys inversion symmetry, allowing for the existence of a spontaneous polarization normal to the interface [4,5]. In this paper we report on experiments in a system which has macroscopic, as opposed to local,  $C_2$  symmetry. We argue that this allows for the observation of a *chiral* polarization which is concentrated at the *surfaces* of the cell.

Inversion symmetry is broken at a liquid-crystal-substrate interface. If, in addition, the molecular director is tilted by an angle  $\theta$  with respect to the surface normal (which can be accomplished with an external magnetic field), then a chiral nematic would exhibit  $C_2$  symmetry at the interface. This symmetry group is identical to that of the chiral smectic- $C^*$  phase. In consequence, we would expect a spontaneous two-dimensional electric polarization which resides very close to the surface and is oriented perpendicular to the director and in the plane of the interface. In order to probe this polarization, an in-plane ac electric field of magnitude  $|\mathbf{E}|$  and frequency  $\nu$  is applied perpendicular to the dipole, thereby inducing a small periodic azimuthal rotation  $\phi$  of the interfacial molecules. This surface-driven motion then propagates elastically into the sample's interior by a combination of bend and twist elasticity. Finally, the overall azimuthal motion of the bulk sample can be detected by observing the depolarized component of transmitted light in the classical electroclinic geometry [6]. The expected optical signal would thus be proportional to  $|\mathbf{E}|$ , a behavior which is ob-

served experimentally.

An indium-tin-oxide- (ITO-) coated glass slide, approximately  $20 \Omega/\square$ , was chemically etched to leave two parallel conducting strips 7 mm apart to facilitate application of an electric field in the plane of the glass. The ITO slide, as well as an ordinary glass microscope slide, was treated with the surfactant hexadecyltrimethyl ammonium bromide for homeotropic alignment. They were then placed together, separated by Mylar spacers of nominal thickness  $25 \mu\text{m}$ , and epoxied to form the sample cell. Two such cells were made, one containing the chiral mixture SCE12 (British Drug House), and the other cell its racemic version SCE12R. Both materials were kindly supplied by EM Industries and used without further purification. The chiral cell was placed in a magnet with transverse optical access so as to induce a bend-type Fréedericksz reorientation of the director. In addition, the magnetic field  $\mathbf{H}$  made a small angle (approximately  $3^\circ$ ) with the plane of the sample so as to facilitate a monodomain texture above the Fréedericksz threshold  $H_{\text{th}}$  (Fig. 1). Note that, owing to a finite anchoring strength coefficient  $W$ , a nonzero molecular tilt angle  $\theta$  is

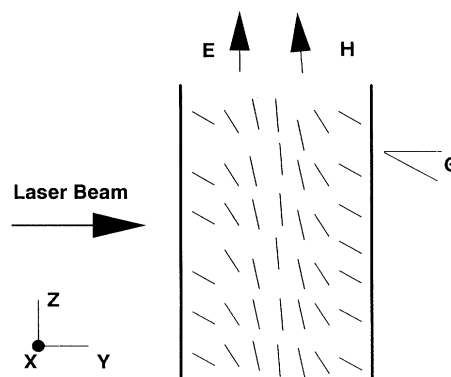


FIG. 1. Schematic representation of experimental geometry for  $H$  well above  $H_{\text{th}}$ . At the surface, molecules tilt by an angle  $\theta$  with respect to their homeotropic alignment ( $H < H_{\text{th}}$ ). On application of an electric field the molecules rotate in and out of the  $y$ - $z$  plane by an angle  $\phi$ . (Note that the magnetic field is not quite parallel to the  $z$  axis in order to facilitate a monodomain sample.)

obtained at the surfaces when  $H > H_{th}$  [7], giving rise to the  $C_2$  symmetry at the interfaces. A voltage was also applied between the ITO electrodes along the  $z$  axis, creating an electric field  $E$  nearly parallel to the magnetic field. To probe the sample, light from a 5-mW He-Ne laser, focused to a spot size of less than  $50 \mu\text{m}$  midway between the electrodes, was incident on the sample along the  $y$  axis, as shown. Note that over the spot size the electric field is, for all intents and purposes, uniform [8]. The beam was polarized at an angle of  $22.5^\circ$  with respect to the  $z$  axis, and a crossed analyzer was placed after the sample and before the photodiode detector. The intensity at the detector was monitored with a lock-in amplifier referenced to the ac voltage applied to the electrodes. In this geometry we note that, for a spatially uniform azimuthal rotation  $\phi$  [ $=\phi_0 \sin(\omega t)$ ],  $\delta I/I_0 = 4\phi$ , where  $\delta I$  is the intensity of the ac signal and  $I_0$  the intensity of the depolarized dc component [6].

The experiment was performed well above  $H_{th}$  at a magnetic field  $H = 13.4 \text{ kG}$  and at a temperature  $T = 88.8^\circ\text{C}$ , which is  $4.9^\circ\text{C}$  above the nematic-smectic- $A$  transition temperature. Figure 2 shows the magnitude of the depolarized ac optical signal  $\delta I$  at the detector as a function of applied ac voltage at frequency  $\nu = 20 \text{ Hz}$ . The observed linear relationship, moreover, was seen over the range  $5 \text{ Hz} \leq \nu \leq 100 \text{ Hz}$ . As an aside we note that the ac signals at  $\nu = 20 \text{ Hz}$  were approximately 3 to 4 orders of magnitude smaller than the depolarized dc components. In addition, we observed a frequency dependence to  $\delta I$  at fixed temperature and magnetic field. Figure 3 shows the relative magnitude of  $\delta I$  as a function of angular frequency  $\omega$  ( $=2\pi\nu$ ) for three different magnetic fields, where the data for each value of magnetic field were normalized to 1 at the lowest experimental frequency,  $\nu = 5 \text{ Hz}$ . If we assume that for small  $\omega$  the magnitude of  $\delta I \propto (1 + \omega^2\tau^2)^{-1/2}$ , and that the  $\omega \rightarrow 0$  behavior

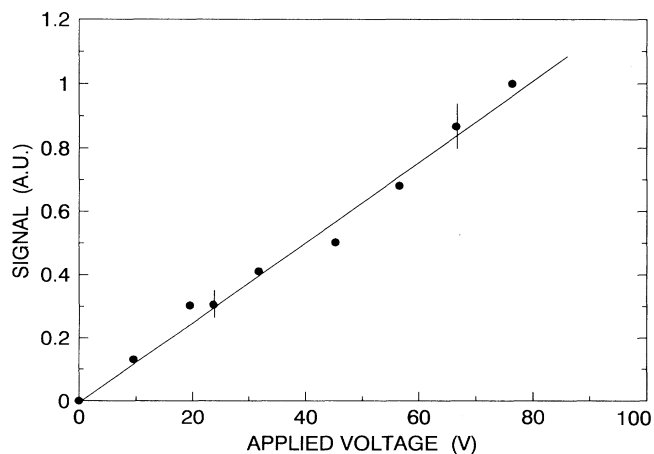


FIG. 2. Magnitude of the ac signal vs rms applied voltage at  $H = 13.4 \text{ kG}$  and at  $\nu = 20 \text{ Hz}$  ( $\omega = 125.7 \text{ s}^{-1}$ ). Typical error bar is shown.

is well approximated at the slowest experimental frequency, then at  $H = 17.3 \text{ kG}$  the response time  $\tau$  is approximately 3 times faster than at  $H = 10.6 \text{ kG}$ . Quantitative comparisons must be made with caution because the relative uncertainty in our measurements is large, especially when the signals are small, and this form for  $\delta I$  is not expected to hold for large  $\omega$ . Nevertheless, it is clear that the characteristic time  $\tau$  increases when  $H$  is small.

To explain these results we consider a surface polarization induced by the  $C_2$  symmetry, which occurs when  $\theta \neq 0$  at the interface. In the presence of strong surface anchoring, even for  $H > H_{th}$ , the director at the two glass surfaces would lie parallel to the  $y$  axis. Numerous studies, however, have shown [9-11] that the surface anchoring in nematics is not completely rigid, and that an interfacial term  $\frac{1}{2}W\theta^2$  must be included in the free energy.  $W$  is the (finite) anchoring strength coefficient, and is characteristic of the liquid crystal, the surface preparation, and the temperature. Experimentally,  $W$  is generally found to be of the order of  $10^{-3}$  to  $10^{-1} \text{ erg/cm}^2$  [9-11]. From the development in Ref. [7] one can easily show that, well above  $H_{th}$ ,  $(K\Delta\chi H^2)^{1/2} \cos\theta = W\theta$ . This relationship assumes that the director at the center of the sample is oriented nearly parallel to  $H$ , which is indeed the case for  $H > 2H_{th}$ . Moreover, we have assumed that the bend and splay elastic constants,  $K_{11}$  and  $K_{33}$ , are equal to each other and to  $K$ . Taking  $K \sim 10^{-6} \text{ dyn}$ ,  $\Delta\chi \sim 10^{-7} \text{ cgs}$ ,  $H \sim 10^4 \text{ G}$ , and using a typical upper limit for  $W$ , e.g.,  $W = 5 \times 10^{-2} \text{ erg/cm}^2$  [9-11], we find a tilt angle  $\theta$  between  $4^\circ$  and  $6^\circ$  at the surface for the magnetic fields used in the experiment. Since  $W$  is, in fact, likely to be smaller,  $\theta$  is apt to be even larger than  $6^\circ$ . These tilts are macroscopic and, if they were associated with a

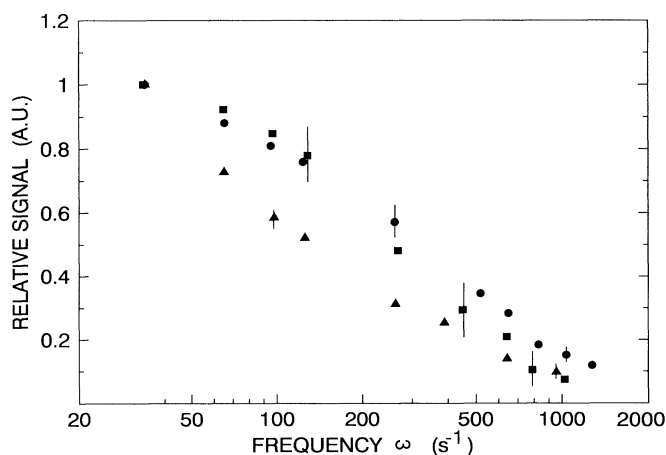


FIG. 3. Relative magnitude of the ac signal (normalized to 1 at  $\nu = 5 \text{ Hz}$ ) vs frequency  $\omega$  of driving voltage at  $H = 10.6 \text{ kG}$  ( $\blacktriangle$ ),  $H = 13.4 \text{ kG}$  ( $\bullet$ ), and  $H = 17.3 \text{ kG}$  ( $\blacksquare$ ). Data are scaled to unity at  $\omega = 31.4 \text{ s}^{-1}$  ( $\nu = 5 \text{ Hz}$ ) for each magnetic field. Note that error bars depend on both  $\omega$  and  $H$ , and that the smaller signals at higher magnetic fields result in a larger relative error.

smectic- $C^*$  phase, they would give rise to a significant electric polarization along the  $x$  axis.

Owing to the nonzero surface tilt  $\theta$ , the  $C_\infty$  symmetry operation at the interface is destroyed, leaving only a twofold rotation axis parallel to the interface and perpendicular to the tilt plane. Thus, at the surface, a spontaneous polarization  $P_x$  will exist parallel to this  $C_2$  axis. The ac electric field  $E_z$  causes a torque  $\mathbf{P} \times \mathbf{E}$  along the  $y$  axis, thereby inducing an azimuthal rotation  $\phi$  of the interfacial molecules in and out of the  $y$ - $z$  plane (see Fig. 1). In effect, the *projection* of the interfacial molecules in the  $x$ - $z$  plane oscillates about the  $z$  axis at frequency  $\nu$  by a small angle  $\phi$  ( $\propto E$ ). Owing to the bend and twist elasticity of the nematic, the molecules in the interior are azimuthally driven by the interfacial layer. As noted above, since this is precisely the geometry employed in typical electroclinic experiments [6], we would expect that, for a spatially uniform rotation  $\phi_0 \sin(\omega t)$ , an ac intensity component  $\delta I = 4\phi_0 I_0$  at angular frequency  $\omega$  would be observed. The director, however, is *not* spatially uniform, since there is also a magnetic torque on the sample which tends to align the molecules along the magnetic field. Any deviations from this alignment will decay exponentially over a magnetic coherence length  $\xi_H$ . Here  $\xi_H \sim (K/\Delta\chi H^2)^{1/2}$ , where  $K$  is an elastic constant and  $\Delta\chi$  the magnetic susceptibility anisotropy. The length scale  $\xi_H$  is typically of the order of a few microns at  $H = 10$  kG. (This relationship is only approximate since the director orientation is a function of position, and thus  $H$ .) Thus, only regions of thickness of order  $\xi_H$  near the two walls would, in principle, oscillate elastically at frequency  $\nu$ , and the interior would remain parallel to  $\mathbf{H}$ . This gives rise to a difficult optical problem, as the optical dielectric tensor varies on length scales comparable to the wavelength of light. While this makes detailed calculations of  $\delta I$  difficult, it remains true that  $\delta I \propto \phi$ , and thus  $\propto E$ .

The dynamic data in Fig. 3 can now be used to examine our hypothesis, which predicts an elastic response over a distance  $\xi_H$  near the two surfaces. For a process in which the tilt  $\phi$  propagates elastically from the surface over a distance  $\xi_H$ , the characteristic relaxation time  $\tau = \eta/Kq^2$ , where the viscosity  $\eta$  is of the order of  $10^{-2}$  to  $10^{-1}$  P [12,13]. We first note that  $\tau \propto q^{-2} \sim \xi_H^2$ . Thus  $\tau$  should be proportional to  $H^{-2}$ , which is consistent with the results in Fig. 3 over a wide frequency range. (The rapid decrease in signal with increasing  $\omega$  and especially with large  $H$ , which results in large relative error bars, is the likely cause of deviations from  $H^{-2}$  in the high- $\omega$  and high- $H$  regimes.) Additionally, we can examine the magnitude of  $\tau$  in light of our model. Taking  $K$  to be  $10^{-6}$  dyn and, for the magnetic fields used in the experiment,  $q$  to be several  $\mu\text{m}^{-1}$ , we find from this model that  $\tau$  is of order several milliseconds, again consistent with the results of Fig. 3.

Since the proposed origin of the effect requires the absence of a mirror plane of symmetry, we also investigated

the cell containing the racemic mixture. The ac response appeared to be simply noise, with an upper limit about 2 orders of magnitude smaller than the response of the chiral material. It is clear then that this electro-optic effect depends upon the presence of chirality, as predicted by the  $C_2$  symmetry.

We now turn to other possible explanations for the observed linear electro-optic effect. This experimental geometry is sensitive to chiral couplings of the molecular tilt to electric fields. One such possible effect is the nematic electroclinic effect (NECE) [14,15], which might be expected to contribute to the observed behavior as the director is neither parallel nor perpendicular to the electric field over large regions of the sample. However, measurements of the time response of the nematic electroclinic effect [16] show the NECE to be much more rapid ( $\tau_{\text{NECE}} < 10^{-6}$  s) than the effect reported herein, and with a response time independent of the magnetic field. We thus dismiss this possibility.

Ordinary flexoelectricity [1] can also be eliminated on several grounds. If this mechanism were responsible for the observed effect, the signal should be the same for both the enantiomer and racemic mixture; as noted above, however, the effect vanishes in the racemate. Moreover, one of our measurements was performed at  $H = 10.6$  kG, where the dc intensity at the detector is a local maximum; the ac intensity arising from any flexoelectric effect in this geometry would therefore be weak and proportional to  $E^2$ . Finally, in this geometry symmetry implies that the optical effects at the two surfaces would cancel.

It is important to note, however, that in a chiral system it is expected that there are additional polarizations proportional to the product of two first derivatives of the director [17]. (Terms proportional to second derivatives of the director can be shown to be equivalent to products of two first derivatives.) While there are a number of such terms, only one is expected to contribute in the geometry of our experiment, viz.,  $\mathbf{P} = \lambda(\mathbf{V} \cdot \mathbf{n})\mathbf{n} \times [\mathbf{n} \times (\mathbf{V} \times \mathbf{n})]$ , which is proportional to a product of bend and splay. It is easy to show [17] that the ratio of the contribution of this term to that of the polarization at the surface is  $R \sim \lambda W/tK'P_{\theta=1}$ , where  $K'$  is some combination of elastic constants,  $P_{\theta=1}$  is the polarization in the surface region divided by the tilt angle at the surface, and  $t$  is the width of the surface layer. Experiments on thin films in which the scaled polarization is seen to be essentially independent of the thickness [13] suggest that the polarization per angle of the surface layer should approximate the polarization of a bulk smectic  $C$ . Theoretical estimates of  $\lambda$  [17] suggest that  $\lambda \sim 0.1P_{\theta=1}l^2$ , where  $l$  is a typical molecular length ( $\sim 20$  Å, of the order of  $t/3$  or  $t/4$  deep into the nematic phase). Finally, as can be seen from the experimental measurements given above,  $R < Wl/K$  is small, of the order of  $10^{-2}$  to  $10^{-4}$ . (Simple dimensional analysis would suggest that it is of order unity; its smallness is not understood theoretically.) We thus conclude

that the contribution of these second-order chiral flexoelectric terms are likely to be small relative to the contributions of the polarization at the surface.

A last possibility is order electricity [18], which comes about from gradients in the nematic or smectic order parameter near the surfaces. As was the case with ordinary flexoelectricity, *nonchiral* contributions to these polarizations would be antiparallel at the two surfaces, and would thus cancel. Moreover, light-scattering results from free-standing ferroelectric films indicate that the polarization, scaled by the film thickness and polar tilt angle, is independent of film thickness [13]. If *chiral* contributions to order electricity were important, the polarization would certainly have been dependent on film thickness. Since the scaled polarization was essentially independent of film thickness, we discount this effect as well.

In summary, we have shown that when a chiral molecule in a bulk nematic phase tilts with respect to a symmetry-breaking interface, a transverse polarization obtains. This polarization can be manipulated with an external field, such that the interfacial molecules couple elastically with the interior of the sample.

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