

Surface-anisotropy-induced linear electro-optic effect in a nematic liquid crystal

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A liquid-crystal cell treated for homeotropic alignment with different surfactants at the two surfaces was subjected to an electric field E in the plane of the cell. The differential optical retardation $\delta\alpha$ was found to be linear in field over a frequency range $10 < \omega < 100\,000\text{ s}^{-1}$, where $d(\delta\alpha)/dE \propto \omega^{-1}$. A model is proposed that explains this result and facilitates the determination of the anchoring strength coefficient W .

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Surfaces play an important—even dominant—role in both fundamental and applied liquid-crystal physics. They affect the bulk orientation, elastic behavior, the presence of disclinations, and the purity of the sample. In recent years, interest has turned to effects based on the inherent symmetry at the interface, especially as the interface may give rise to new and potentially useful phenomena not found in the bulk. For example, the absence of inversion symmetry leads to a spontaneous polarization normal to the surface [1,2], which may result in surface-specific phenomena such as a field-induced orientational instability [3]. The further reduction of symmetry associated with chiral liquid crystalline molecules may give rise to a component of polarization *parallel* to the interface: When the molecules tilt with respect to the layer, a component of \vec{P} may exist normal to the molecular axis and parallel to the surface [4,5]. Unless the experimental geometry is judiciously selected, however, these symmetry-based phenomena are often not seen in bulk measurements due to cancellation of the experimentally observable quantity at the two surfaces of the cell. To circumvent this problem Lee and Patel suggested that a macroscopic effect obtains when the two surfaces are treated *anisotropically* [6]. Using a planar cell with different treatments at the two surfaces, they observed an electro-optical effect which depends on the polarity of the applied field E in the high-field limit, well above the Fréedericksz threshold. Their data were consistent with a pair of anisotropic flexoelectric polarizations due to the anisotropy in the anchoring strength coefficients at the two surfaces. Numerical simulations have since been carried out by Lee *et al.* [7]. More recently, Lavrentovich realized that a net polarization \vec{P} obtains, even in the absence of flexoelectricity, from an anisotropic surface treatment [8]. Using such a cell in the homeotropic geometry, he demonstrated a unipolar electro-optic effect: On applying a field normal to the cell, he showed that the bulk director orientation is stable when $\vec{E} \parallel \vec{P}$, but is destabilized (with a concomitant loss in optical transmission) when \vec{E} is antiparallel to \vec{P} [9]. This effect has important technological implications, as Lavrento-

vich has coined the term “optical diode” for this geometry.

In this paper we report on an experiment which demonstrates a linear electro-optic effect for a liquid-crystal cell with two dissimilar surfaces. The two surfaces were treated for homeotropic alignment with different surface agents, and an ac electric field was applied *parallel* to the surfaces. Owing to a combination of anisotropic polarizations and surface anchorings, the optical signature from the two surfaces did not cancel, resulting in a net differential optical retardation $\delta\alpha$ linear in \vec{E} . Measurements were performed as a function of frequency, where we observed that $\delta\alpha \propto \omega^{-1}$ over most of the frequency range. A model is presented which predicts that in the limit of high frequencies, $\delta\alpha \propto (1/\omega) \sum_{i=1}^2 P_i$, where P_i is the polarization at the i th surface. In the limit of low frequencies the model predicts $\delta\alpha \propto (1/\sqrt{\omega}) \sum_{i=1}^2 P_i/W_i$, where W_i is the anchoring strength coefficient of surface i .

An indium-tin-oxide (ITO) coated glass slide was chemically etched to leave two parallel conducting strips in order to facilitate application of an electric field in the plane of the glass; the strips were separated by a distance $l = 1\text{ mm}$. For a cell of thickness $t \ll l$, one can show [10] that for semi-infinite electrodes, the electric field in the center is $E = 2V/\pi l$, where V is the potential difference between the two electrodes. (This field is slightly reduced if the electrodes are wide but finite in extent). The ITO slide, with the exposed glass strip of width $l = 1\text{ mm}$, was treated with the surfactant hexadecyltrimethyl ammonium bromide (HTAB), approximately 0.5% by weight in ethanol. Several drops were placed on the substrate, allowed to dry, and the excess gently removed with a Kimwipe. For the other substrate, an ordinary microscopic slide was similarly treated with a 0.7% by weight in hexane solution of silicon elastomer (SE), $(\text{CH}_3)_3\text{SiO}[(\text{CH}_3)_2\text{SiO}]_n\text{Si}(\text{CH}_3)_3$, $n \approx 25\,000$. A cell was constructed by using a pair of Mylar spacers of nominal thickness $t = 12.5\ \mu\text{m}$, and was filled in the isotropic phase with the liquid crystal pentylcyanobiphenyl (5CB), obtained from Merck and used as received. Owing to the polar nature of the HTAB, the cyano group of the liquid crystal is expected to point toward that surface; on the other hand, the silicon elastomer is relatively nonpolar, and thus we might expect the 5CB tail to point toward

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the SE surface [8]. In consequence, the dipole moments at opposite surfaces are likely to be parallel to each other, resulting in a net polarization in the cell pointing in the direction of the HTAB surface. It should be noted that the observed electro-optic effect is not predicated on the two polarizations being parallel; all that is required is that the polarizations not be both equal and antiparallel.

The cell was filled in the isotropic phase and cooled into the nematic phase in an oven which was temperature controlled to approximately 10 mK. The temperature was stabilized at 30.3 °C, approximately 4.0 °C below the nematic-isotropic transition temperature T_{NI} . Light from a He-Ne laser passed through a focusing lens and a polarizer oriented in the yz plane at 45° with respect to the z axis (Fig. 1). After passing through the sample (tilted by 45° with respect to the z axis in the xz plane), the beam passed through a Babinet-Soleil compensator, an analyzer, a second lens to reexpand the beam, and into a photodiode detector. The detector output, proportional to the total light intensity I , was fed into a lock-in amplifier referenced to the driving voltage $V(\omega)$; its output was proportional to the amplitude of the component of intensity I_{ac} at frequency ω . The field $E(\omega)$, which was applied to the sample as shown in Fig. 1, induced a tilt of the molecules, thereby causing a change $\delta\alpha$ in the optical retardation, and thus an ac intensity $I_{ac} \propto \delta\alpha$. The compensator was adjusted to maximize the signal at frequency ω from the lock-in amplifier, corresponding to a maximum in $dI_{ac}/d(\delta\alpha)$. (This compensator setting likewise corresponds to a dc optical intensity equal to one-half of its maximum value, i.e., the total retardation $\alpha_{tot} [\equiv \alpha_{sample} + \alpha_{compensator}] = (2n + 1)\pi/2$, where n is an integer). By adjusting the compensator, and thus α_{tot} , in this manner, results among samples could be quantitatively compared, independent of precise sample thickness, and thus independent of α_{sample} .

Owing to the longitudinal polarizations at each of the two surfaces, the surface layers experience a torque, causing them to rotate in the xz plane. If the polarizations were equal and opposite, molecules at one surface would rotate by an angle $\theta_1 [\propto E]$ so as to increase the local birefringence, and at the other surface by $\theta_2 [= -\theta_1]$ to decrease the birefringence. Thus, the net change in optical retardation $\delta\alpha$ would be zero. If, on the other hand, the polarizations were different at the two surfaces, then $\theta_1 \neq -\theta_2$, and a nonzero $\delta\alpha$ would obtain. The amplitude of the ac field was varied stepwise from zero to 65 V rms, and the lock-in signal was recorded. A typical trace of I_{ac} vs E is shown in Fig. 2. Since the signal I_{ac} was found to be linear in voltage for several representative frequencies over the range $10 < \omega < 100\,000 \text{ s}^{-1}$, the response $dI_{ac}/dE(\omega)$ from two such asymmetrically treated cells (shown in Fig. 3) was taken to be the quantity $I_{ac}/E(\omega)$ at 65 V. A third cell was similarly prepared, although the surfactant HTAB was used at *both* surfaces. Results from this "symmetric" cell are also shown in Fig. 3.

Several features are readily apparent in Fig. 3. First, $dI_{ac}/dE(\omega) [\propto d(\delta\alpha)/dE(\omega)]$ decreases with increasing frequency. We propose that this is due to the fact that the field couples to the liquid crystal primarily at the sur-

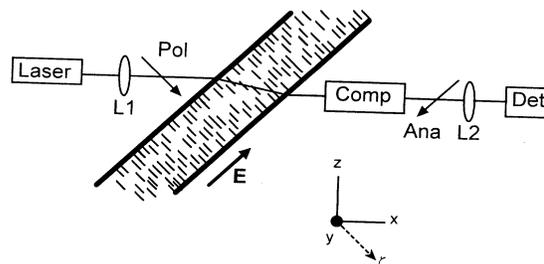


FIG. 1. Schematic representation of experimental geometry. $L1$ corresponds to the focusing lens, Pol to the polarizer, Comp to the Babinet-Soleil compensator, Ana to the analyzer, $L2$ to the expanding lens, and Det to the detector.

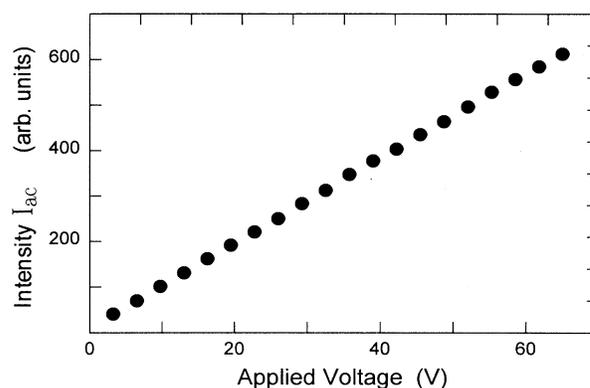


FIG. 2. Typical response of sample. This sample corresponds to a 12.5- μm -thick asymmetric cell at $\omega = 125 \text{ s}^{-1}$.

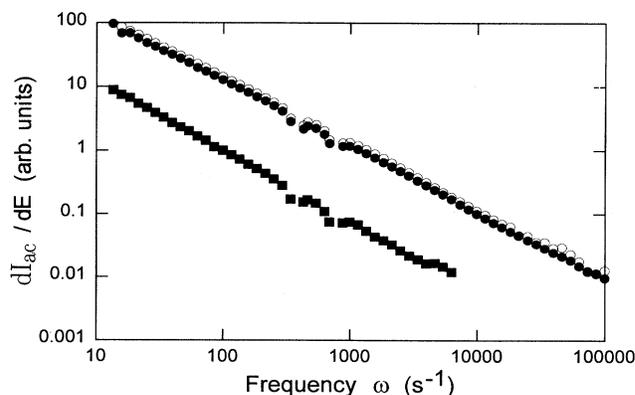


FIG. 3. dI_{ac}/dE vs ω for two $t = 12.5\text{-}\mu\text{m}$ -thick asymmetric samples (open and closed circles) and for a "symmetric" sample (squares).

faces, and that the resulting torque is transmitted elastically via a bend distortion into the viscous bulk. It can be shown [5] that the optical response of the cell is therefore proportional to the integral of the local molecular tilt $\theta(\xi)$ through the cell, where the vector ξ is normal to the surface of the cell, i.e., $\hat{\xi} \equiv 1/\sqrt{2}(\hat{x} - \hat{z})$ (Fig. 1). Thus, at higher driving frequencies the elastic response becomes "sluggish," resulting in a smaller tilt angle in the interior, and a concomitant decrease in overall optical response. This will be dealt with in more detail below. The second feature to note is that although the "symmetric" cell was expected to have a null response, the shape of the curve is similar to that of the asymmetric cell, albeit much smaller in magnitude. When applying the surfactant HTAB it was unlikely that the two surfaces were treated exactly alike; additionally, the two substrates were not identical. We would thus expect a small symmetry to obtain, giving rise to a net polarization. The fact that the optical signature of the "symmetric" cell is much smaller than the intentionally treated asymmetric cell is evidence for a net polarization.

One can quantitatively understand the observed behavior by assuming an elastic response in the bulk to a $\vec{P} \times \vec{E}$ torque at the surfaces. First, we note that the dispersion relationship for a bend mode is $\omega = K_{33}q^2/\eta$, where K_{33} is the bend elastic constant, q the wave vector of the distortion, and η the viscosity. For a sample of thickness $t \approx 12.5 \mu\text{m}$, we can take $q \approx \pi/t$. If we take for 5CB $K_{33} = 5 \times 10^{-7}$ dyn and $\eta = 0.1$ P [11], we find a characteristic frequency $\omega_c \sim 30 \text{ s}^{-1}$. If driven below this frequency, the elastic response from the two surfaces will penetrate deeply into the bulk and interact; if driven above ω_c , the elastic response will penetrate less deeply into the bulk, and the two surfaces can be treated independently. This effect becomes more apparent for thinner samples. Figure 4 shows an asymmetric cell of thickness $t \approx 4 \mu\text{m}$, such that ω_c is of order 300 s^{-1} . Above this frequency, the two surfaces clearly respond independently, and indeed the response of the cell is quantitatively similar to that in Fig. 3. Below ω_c the sample responds collectively, and shows little frequency dependence. The independent response of the surfaces at high frequencies greatly simplifies the problem, and will be the approach taken in the analysis below.

Having experimentally demonstrated the polarization effect and having determined its frequency response, we now turn to modeling the behavior. Consider the behavior near one surface i . For small deviations θ_i from homeotropic orientation, the free energy in the bulk is given by

$$F = \frac{1}{2}K_{33} \left(\frac{d\theta_i}{d\xi} \right)^2 - \frac{1}{2}\Delta\chi E^2 \theta_i^2, \quad (1)$$

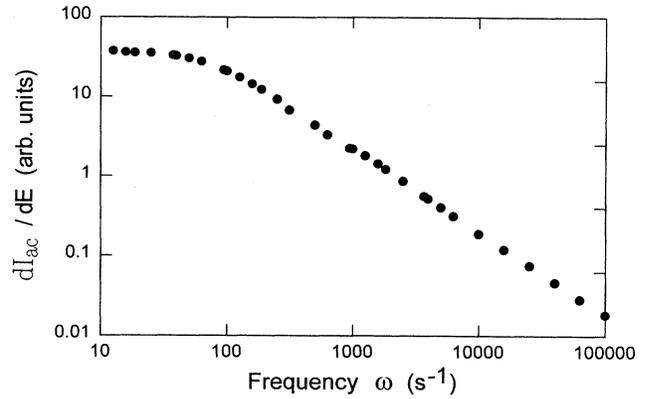


FIG. 4. dI_{ac}/dE vs ω for a $t \sim 4\text{-}\mu\text{m}$ -thick asymmetric sample.

where $\Delta\chi$ is the electric susceptibility anisotropy. As the applied field is small, and the optical response is measured at the driving frequency, we shall neglect the electric-field term. This physically corresponds to the boundary condition $\theta_i \rightarrow 0$ deep into the bulk. Applying the Euler-Lagrange equation, neglecting the E^2 term, and introducing the viscosity η , we obtain the diffusion equation $\eta \partial \theta_i / \partial t = K_{33} \partial^2 \theta_i / \partial \xi^2$ for the director orientation. If we take $\theta_i(\xi, t) = \theta_{i,0}(\xi) e^{i\omega t}$ relative to the surface at $\xi = 0$, we find for the above boundary condition that $\theta_i(\xi, t) = A \exp[-\sqrt{i\omega\eta/K_{33}}\xi] e^{i\omega t}$, where A is a constant. At the surface the torque balance equation is

$$-K_{33} \left[\frac{\partial \theta}{\partial \xi} \right]_{s_i} + W_i \theta_{s_i} = P_i E, \quad (2)$$

where the subscript s_i refers to values at the surface i . Taking $E = E_0 e^{i\omega t}$ and substituting the form for $\theta_i(\xi, t)$ at the surface ($\xi = 0$), we obtain

$$\theta_i(\xi, t) = \frac{P_i E_0}{W_i + \sqrt{iK_{33}\omega\eta}} \exp \left[-\sqrt{\frac{i\omega\eta}{K_{33}}} \xi \right] e^{i\omega t}. \quad (3)$$

The optical response I_{ac} is proportional to $|\sum_{i=1}^2 \text{Re}(\int \theta_i d\xi)| \equiv |\sum_{i=1}^2 \text{Re}(\Gamma_i)|$ summed over the two surfaces, where

$$\text{Re}(\Gamma_i) = \frac{P_i E_0}{W_i^2 \left[\frac{\omega\eta}{2K_{33}} \right] + \left[W_i \sqrt{\frac{\omega\eta}{2K_{33}}} + \omega\eta \right]^2} \left[W_i \sqrt{\frac{\omega\eta}{2K_{33}}} \cos\omega t + \left[W_i \sqrt{\frac{\omega\eta}{2K_{33}}} + \omega\eta \right] \sin\omega t \right]. \quad (4)$$

If the polarizations are equal and opposite and $W_1 = W_2$, $|\sum_{i=1}^2 \text{Re}(\Gamma_i)| = 0$; otherwise, a nonzero response obtains. In the low-frequency limit, but for $\omega > \omega_c$, $|\sum_{i=1}^2 \text{Re}(\Gamma_i)| \rightarrow \sum_{i=1}^2 (P_i E_0 / W_i) \sqrt{K_{33} / \omega \eta}$; in the limit of high frequencies it goes to $\sum_{i=1}^2 P_i E_0 / \omega \eta$. It is this latter behavior which was observed over most of the experimental frequency range. The characteristic crossover frequency ω_0 between the low- and high-frequency behavior is obtained from Eq. (4) and is given by

$$W_i \sqrt{\frac{\omega_0 \eta}{2K_{33}}} = \omega_0 \eta. \quad (5)$$

This crossover is exceptionally slow, requiring four or more decades of frequency to go from one asymptotic behavior to the other. Moreover, if the anchoring strengths W_i differ at the two surfaces, the crossover would be washed out even more. From the results in Fig. 3, we see that the response scales as ω^{-1} over nearly the entire frequency range, as predicted in the high-frequency

region of the model. From Eq. (5) this places an upper limit on a characteristic anchoring strength coefficient W in the range of a few times 10^{-3} erg cm $^{-2}$, a figure which is small, although not inconsistent with results obtained from more traditional techniques [12]. We note that the model breaks down on approaching ω_c , as the two surfaces can no longer be treated independently.

To summarize, we have demonstrated a scientifically important and potentially useful electro-optic effect in liquid crystals based on symmetry considerations. The accompanying model argues for a small anchoring strength coefficient. Further work is necessary to clearly probe the crossover region, as well as the low-frequency response of the system.

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