

## Quasidivergent nematic surface electroclinic effect

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A polyimide coated substrate is treated so that vertical liquid crystal alignment ( $\theta=0$ ) obtains over the temperature range  $T_{NA} < T < T_a$ , where  $T_{NA}$  is the nematic-smectic-A transition temperature. When the cell is filled with a chiral liquid crystal whose helical pitch is unwound (surface stabilized), application of an in-plane electric field for  $T_{NA} < T < T_a$  induces a nonzero polar tilt  $\theta \propto E$  of the liquid crystal director at the surface, where the tilted orientation propagates elastically into the bulk. On heating toward  $T_a$ , this surface electroclinic response becomes large, corresponding to the onset of a surface tilt transition at  $T_a$  from  $\theta=0$  to nonzero  $\theta$ .

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In 1978, Garoff and Meyer demonstrated the “electroclinic effect” (ECE) for a bulk chiral smectic-A phase [1,2]. Owing to its  $C_2$  symmetry, an applied electric field  $E$  parallel to the smectic layers induces a polar tilt angle  $\theta \propto E$  in a plane perpendicular to the electric field. They found that the proportionality coefficient diverges on cooling toward the smectic-C phase, as the tilt susceptibility goes to infinity on approaching the transition temperature  $T_{AC}$ . Some years later we observed an analogous effect, viz., the reduced symmetry of a vertically aligned chiral nematic phase at a translational symmetry-breaking interface admits an electroclinic effect *at the interface* [3]. As with the smectic-A ECE,  $\theta$  is proportional to  $E$  for this nematic surface ECE, although unlike the former case, the director  $\hat{n}$  in the bulk interior responds elastically to the tilted surface region rather than directly to the applied electric field. At the time of that work no temperature dependence was observed, as the tilt susceptibility of the nematic at the interface showed no critical behavior. Several years ago, however, we demonstrated that a substrate coated with the Nissan Chemical Industries polyamic acid SE-1211, overbaked, and rubbed can induce a large polar pretilt angle from the vertical direction in a nematic liquid crystal [4]. This was found to be a result of the competition between two easy axes for orientation, one approximately parallel to the substrate and one approximately perpendicular [5,6]. If a smectic-A phase exists at a temperature below the nematic phase, a tilt transition [5] may be observed at a temperature  $T_a$  on cooling toward the nematic-smectic-A transition temperature  $T_{NA}$  [ $< T_a$ ]. This arises because of surface-induced smectic order in the nematic phase, which contributes an additional force promoting vertical alignment of the director on approaching  $T_{NA}$ . More formally, to order  $\theta^2$  the surface tilt free energy in the absence of an electric field may be written  $F_{\text{surf}} = \frac{1}{2}(A - B + D\xi)\theta^2$  [7], where  $A$  and  $B$  are the anchoring coefficients for the vertical and planar easy axes, respectively,  $D$  is the inverse molecular tilt susceptibility for the surface-induced smectic layers, and  $\xi$  is the smectic correlation length [8]. For sufficiently high baking temperature and strong rubbing,  $A - B < 0$  in the nematic phase, but  $F_{\text{surf}}$  may become positive on cooling because both  $D$  and  $\xi$  di-

verge on approaching  $T_{NA}$ . Thus, the tilt transition from tilted (at  $T > T_a$ ) to vertical alignment (at  $T < T_a$ ) on cooling is due to a tradeoff among the highly temperature-dependent surface-induced smectic layers and the two relatively temperature-insensitive nematic easy axes, and occurs when  $d^2F_{\text{surf}}/d\theta^2 = 0$ . Below  $T_a$  the quantity  $d^2F_{\text{surf}}/d\theta^2$  corresponds to the effective quadratic anchoring strength coefficient  $W_2^{\text{eff}}$ . Thus  $W_2^{\text{eff}}$  is positive below  $T_a$  and, on heating, goes to zero continuously at  $T_a$  [5]. Recently we examined the Freedericksz transition for a *nonchiral* liquid crystal in the region  $T_{NA} < T < T_a$ , finding that the Freedericksz threshold voltage is approximately equal to its value for rigid anchoring well below  $T_a$ —this is due to surface-induced smectic layering and the resulting small tilt susceptibility (and correspondingly large  $W_2^{\text{eff}}$ ). But on heating the Freedericksz threshold voltage decreases, and becomes vanishingly small at  $T_a$  [9] as  $W_2^{\text{eff}}$  goes to zero. The quadratic anchoring strength coefficient  $W_2^{\text{eff}}$ , as well as the first anharmonic term  $W_4^{\text{eff}}$  in the expansion of  $F_{\text{surf}}$  in powers of  $\theta^2$ , were measured as functions of temperature. In this paper we examine the surface ECE for a *chiral* nematic in the temperature region  $T_{NA} < T < T_a$ . Our central result is that the surface electroclinic effect, i.e., the constant of proportionality between  $\theta$  and  $E$ , becomes large on heating toward  $T_a$  as the effective quadratic anchoring strength coefficient  $W_2^{\text{eff}}$  goes to zero.

An indium-tin-oxide (ITO) coated glass slide was chemically etched to leave two parallel electrodes spaced a distance  $\ell = 1.0$  mm apart. This slide, as well as a second glass microscope slide, were cleaned consecutively in detergent, water, acetone, and ethanol, and then spin-coated with the polyamic acid SE-1211 (Nissan Chemical Industries, Ltd.). The ITO-coated slide was baked at 200 °C for 1 h and rubbed gently with a velvet cloth, and the other slide was baked at 180 °C for 1 h and was not rubbed. The higher baking temperature for the first slide causes cleavage of a large fraction of the side chains, as well as additional imidization of the backbone [4]. In conjunction with the rubbing, its effect is to enhance the propensity for nonzero polar tilt as compared to the alignment layer baked at lower temperature. The two slides were placed together, separated by mylar spacers, and cemented. Using an interferometry technique, the thickness of the cell was found to be  $(9.0 \pm 0.3)$   $\mu\text{m}$ . The cell was placed into an oven that was

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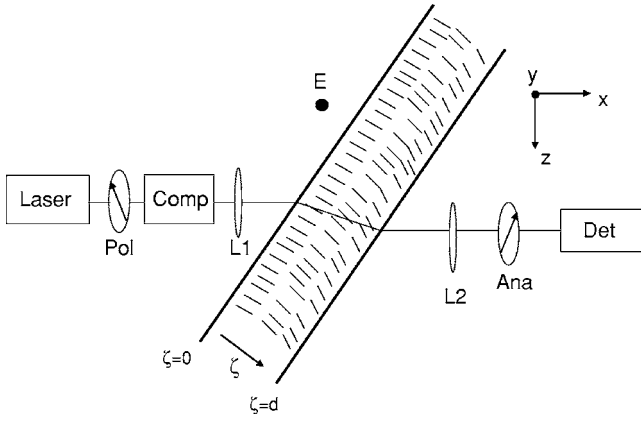


FIG. 1. Schematic view of optical arrangement. Pol is a polarizer, Comp is a Babinet-Soleil compensator, L1 is a focusing lens, L2 is a recollimating lens, Ana is an analyzer, and Det is a detector.

temperature controlled to approximately 10 mK and filled with a 1:1 mixture of the Merck liquid crystal mixtures SCE12 (chiral) and SCE12R (racemic) in the isotropic phase. The purpose of diluting the chiral liquid crystal mixture with its racemate was to reduce its tendency to undergo a twist deformation in the nematic phase, and thereby increase the temperature below which the mixture retains surface-stabilized vertical alignment. The liquid crystal was cooled into the nematic phase, and a transition from tilted to vertical alignment was observed a little above  $T_a=93.5^\circ\text{C}$  by optical microscopy. On further cooling we observed a transition into the smectic-A phase at  $T_{NA}=76.5^\circ\text{C}$ . The oven and sample then were placed in an optical apparatus (Fig. 1) in which light from a 5 mW He-Ne laser passed through a polarizer oriented at  $45^\circ$  with respect to the y axis in the yz plane; a Babinet-Soleil compensator with its fast axis along y; a lens L1 that focuses the beam to a spot size of  $70\ \mu\text{m}$  at the sample; the sample, which is rotated by  $45^\circ$  about the y axis and where the applied electric field is parallel to the y axis; a lens L2 that recollimates the beam; an analyzer; and into a photodiode detector. The detector's output was fed directly into both a lock-in amplifier (for higher frequency measurements) and the computer's analog-to-digital converter (for lower frequency measurements). The lock-in amplifier was referenced to the driving frequency  $f$  of the applied electric field. By adjusting the Babinet-Soleil compensator so that the average dc intensity at the detector is half its maximum value, a small electric field-induced tilt of the molecular director in the xz plane resulted in a linear amplitude change  $\delta I$  in the detector's output. Since the birefringence of the liquid crystal, and thus the optical retardation through the cell, changes little over the small temperature range in which the experiment is performed, it was not necessary to readjust the compensator at each temperature setting.

The temperature was stabilized a few degrees below  $T_a$ , and a voltage  $V=41.3\ \text{V}$ , corresponding to a field  $E=0.88\ \text{statvolts cm}^{-1}$ , was applied to the sample at 13 different frequencies  $0.3 \leq f \leq 70\ \text{Hz}$ . (Note that for this geometry,  $E=2V/\pi\ell$  at the center of the gap [3]). At each frequency 200 data points were collected over 20 s by the computer, at which time the frequency was stepped up to its

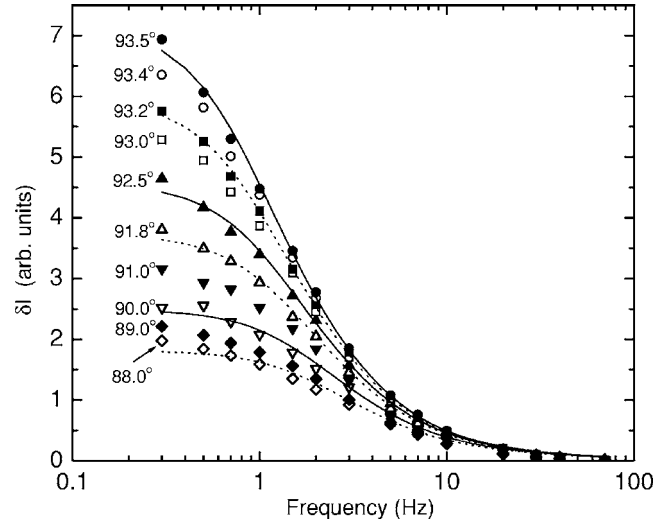


FIG. 2. Optical response  $\delta I$  versus frequency  $f$  for different temperatures. The highest temperature data are fitted to a three parameter form. The coefficient  $C_1$  and viscosity  $\eta_b$  are used for subsequent one parameter fits (for  $W_2^{\text{eff}}$ ) at lower temperatures. Several representative fits are shown. Error bars due to experimental noise is approximately  $\pm 5\%$  for all data points.

next value. The first  $\sim 50$  data points at each frequency were discarded, and the value of  $\delta I(f)$  was taken to be the average over the last  $\sim 150$  points. For  $f \leq 2\ \text{Hz}$  the total intensity trace (dc and ac) was recorded by the computer, and the rms value of  $\delta I$  was extracted. For  $f \geq 1\ \text{Hz}$  the rms value of  $\delta I$  was extracted by the lock-in amplifier. We ascertained that: (i)  $\delta I$  was proportional to the applied voltage, as expected, and (ii) the signals obtained by both the lock-in amplifier and the computer were consistent at the two frequencies (1 and 2 Hz) at which both instruments were able to operate simultaneously. Figure 2 shows the intensity  $\delta I$  versus frequency for all temperatures measured, where the low frequency results were obtained by computer and the high frequency results from the lock-in amplifier.

The cell then was removed, heated above the nematic-isotropic phase transition temperature  $T_{NI}=118^\circ\text{C}$ , and the liquid crystal was blown out with compressed air. The cell then was filled with racemic SCE12R, blown out, and then filled again with racemic SCE12R. Measurements were performed on the racemic sample, and in this case the corresponding values of  $\delta I$  were at least a factor of 25 smaller than the results for the SCE12/SCE12R mixture, indicating that the observed effect was indeed due to the chirality of the liquid crystal and the resulting symmetry at the surface.

In order to understand the results, we note that the applied electric field couples primarily to the two interfacial regions, which in turn couple elastically to the bulk. The bulk elastic free energy density is given by  $F_{el}=\frac{1}{2}K_{33}(d\theta/d\zeta)^2$ , where  $K_{33}$  is the bend elastic constant and  $\zeta$  is the coordinate perpendicular to the substrate (Fig. 1). Applying the Euler-Lagrange equation and introducing the bend viscosity  $\eta_b$ , we obtain the diffusion equation  $\eta_b d\theta/dt=K_{33}d^2\theta/d\zeta^2$  for the director orientation in the bulk. When driven at frequency  $\omega[=2\pi f]$ , we find  $\theta=\text{Re}[\theta_0\exp(i\omega t)]$ , where  $\theta_0$  is given by

$$\theta_0 = [R_1 \exp(-\sqrt{i\omega\eta_b/K_{33}\zeta}) + R_2 \exp(\sqrt{i\omega\eta_b/K_{33}\zeta})] e^{i\omega t}.$$

Here  $R_1$  and  $R_2$  are coefficients to be determined by the boundary conditions. Turning to the substrates, we treat the unrubbed substrate at  $\zeta=0$  as having an infinite quadratic anchoring strength coefficient, and thus  $\theta_{\zeta=0}=0$  at the substrate. We will discuss the consequences of this approximation below. For the substrate baked at higher temperature and rubbed, there is a surface electroclinic torque equal to  $CE$ , where  $E = \text{Re}[E_0 \exp(i\omega t)]$ , that tends to increase  $\theta$ . Here  $C$  is a constant related to polarization terms in the free energy [1,2] and is relatively independent of temperature over the temperature range examined in this experiment. Competing with the electroclinic torque are two restoring terms: a temperature-dependent effective anchoring term  $W_2^{\text{eff}}\theta_{\zeta=d}$  and an elastic torque  $K_{33}(d\theta/d\zeta)_{\zeta=d}$  due to the bulk. Torque balance at  $\zeta=d$  gives

$$K_{33}(d\theta/d\zeta)_{\zeta=d} + W_2^{\text{eff}}\theta_{\zeta=d} = CE.$$

The second boundary condition, viz.,  $\theta_{\zeta=0}=0$  follows from the infinite anchoring strength condition at  $\zeta=0$ . Thus, we obtain

$$\frac{\theta_0}{C} = \frac{E_0 \sinh(\sqrt{i\omega\eta_b/K_{33}\zeta})}{\sqrt{i\omega\eta_b K_{33}} \cosh(\sqrt{i\omega\eta_b/K_{33}d}) + W_2^{\text{eff}} \sinh(\sqrt{i\omega\eta_b/K_{33}d})}. \quad (1)$$

Finally,  $\delta I$  is proportional to the retardation between the two optical eigenmodes which, in fact, traverse slightly different paths inside the liquid crystal [3]. The retardation, in turn, is proportional to the integral of  $\text{Re}(\theta)$  across the cell. Whence,

$$\delta I = C_1 \sqrt{\left[ \int_0^d \text{Re}(\theta_0/C) d\zeta \right]^2 + \left[ \int_0^d \text{Im}(\theta_0/C) d\zeta \right]^2}, \quad (2)$$

where  $C_1$  is a proportionality constant, approximately independent of temperature.

The results shown in Fig. 2 were fitted to Eq. (2) using Eq. (1) for  $\theta_0/C$ . First, we performed a three parameter fit ( $C_1$ ,  $\eta_b$ , and  $W_2^{\text{eff}}$ ) for the highest temperature data (close to  $T_a$ ), where we took  $K_{33} = 1.0 \times 10^{-6}$  dyn. This value for  $K_{33}$  was obtained by an extrapolation of the data in Ref. [9] and, keeping in mind that the experimental temperature range was well above  $T_{NA}$ , this value of  $K_{33}$  was used for fits at all temperatures and is accurate to within 3.5%. The reason for choosing the highest temperature for the first fit is that  $W_2^{\text{eff}}$  at  $\zeta=d$  is very small, certainly much smaller than the effective anchoring strength coefficient at  $\zeta=0$ ; thus the infinite anchoring approximation at  $\zeta=0$  should be extremely good. The quality of the fit is excellent, and is shown in Fig. 2. Then, using the fitted values for  $C_1$  and  $\eta_b = (0.6 \pm 0.1) \text{P}$ , one parameter fits for  $W_2^{\text{eff}}$  were performed at all other temperatures; several representative fits are shown by the solid and dotted curves. The fits closer to  $T_a$  were excellent, but became worse at lower temperatures. Fitted values for  $W_2^{\text{eff}}$  are shown in Fig. 3.

Several points need to be considered. First, the poor fitting quality at lower temperatures is due primarily to the

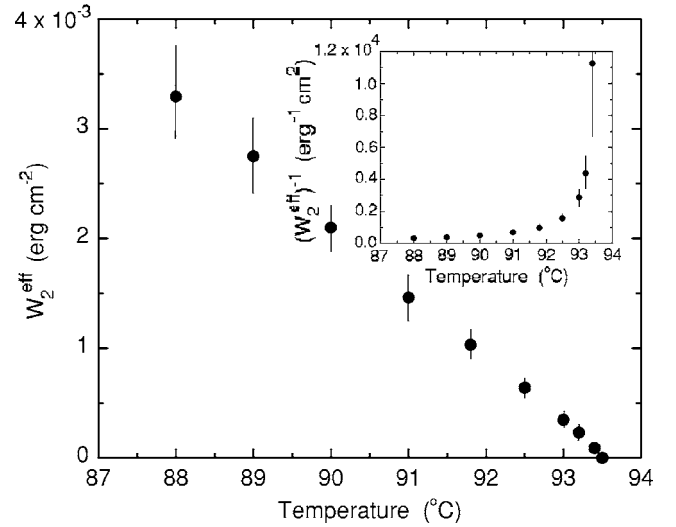


FIG. 3. Fitted values of the effective anchoring strength coefficient  $W_2^{\text{eff}}$  versus temperature.  $W_2^{\text{eff}}$  vanishes at temperature  $T_a$ . Inset shows  $1/W_2^{\text{eff}}$ .

assumed infinitely strong anchoring boundary condition at the unrubbed substrate. This is an excellent approximation close to  $T_a$ , where  $W_2^{\text{eff}}$  is small and therefore dominates the response of the bulk. At lower temperatures, however,  $W_2^{\text{eff}}$  becomes larger, and eventually becomes comparable to the actually finite anchoring strength at  $\zeta=0$ . In this region we no longer can take  $\theta_{\zeta=0}=0$  as the boundary condition. An alternative approach would have been to prepare both substrates identically, i.e., a high temperature baking followed by rubbing. In principle a cell arranged with antiparallel rubbing at opposite substrates would have symmetric boundary conditions with anchoring strength  $W_2^{\text{eff}}$  at both substrates. However, we have found experimentally that achieving identical rubbing conditions at both substrates is extremely difficult. In practice the anchoring strengths would differ at the two substrates, giving rise to different values of  $T_a$ . This would obviate any apparent advantage to this approach. In the end we believe that (relatively) rigid anchoring at one substrate facilitates a more reliable quantitative analysis of the data.

Second, let us consider the behavior of  $W_2^{\text{eff}}$  versus temperature. As noted above,  $W_2^{\text{eff}} = A - B + D\xi$ . Since  $A$  and  $B$  are relatively temperature insensitive, the temperature dependence of  $W_2^{\text{eff}}$  derives mostly from the variation of the quantity  $D\xi$  with temperature. Although this quantity diverges toward  $T_{NA}$  with a critical exponent  $3\nu$  [9], in the temperature range of this experiment  $D\xi$  is expected to vary approximately linearly with temperature; this is the behavior observed in Fig. 3, where  $W_2^{\text{eff}}$  decreases approximately linearly with temperature before vanishing at  $T_a$ . The small curvature is due to the progressively worse fits at lower temperatures as discussed in the preceding paragraph, and to small deviations from linearity in the quantity  $D\xi$ . Had we been able to use a pair of *identically* rubbed substrates arranged in an antiparallel configuration,  $\theta$  at both substrates would have diverged at  $T_a$  in the limit that  $f \rightarrow 0$ , i.e., a true divergent electroclinic response. In this case the director would have been spatially homogeneous in the limit of zero frequency, and thus there

would have been no elastic restoring torque. From a practical standpoint, however, it is not possible to prepare identical substrates, as noted above. We note that in our chosen setup  $\delta I$  does not diverge, even at zero frequency, owing to the presence of the bulk elastic torque. (A near-divergent response would have been possible for a very thick cell because of a reduction in elastic torque, although the characteristic frequency  $\propto 1/d^2$  and would have been extremely small).

It is important to ask whether some other effect could have given rise to the observed behavior. Dielectric couplings proportional to  $E^2$  [8] would cause a tilt  $\theta$ , although the optical responses would be at frequency  $2f$ , not at  $f$ . The same would be true for anisotropic order electricity [10] or surface vertical polarization (“optical diode”) [11] effects in which the director would tilt out of the  $xz$  plane and be relatively insensitive to chirality. An electric field also may induce a flexoelectric response [12] to the homeotropically oriented liquid crystal, again resulting in a signal at frequency  $2f$  rather than  $f$ . One also may imagine that once a surface electroclinic effect occurs, the resulting orientational distribution would give rise to a flexoelectric polarization in the  $xz$  plane. Such a polarization, when subjected to an electric field along the  $y$  axis, would cause a small azimuthal rotation  $\varphi$  (i.e., a twist) [13] proportional to  $E^2$  in the director

profile. But since  $\delta I \propto \varphi^2$  and, moreover, we observe that  $\delta I \propto E$ , this contribution to the signal is deemed negligible. Electric field induced biaxiality [14] also would have a  $2f$  response. In fact, we examined the  $2f$  response, and found it to be a factor  $<0.005$  of the response at  $f$ . One possible artifact at frequency  $f$  could be the nematic electroclinic effect in bulk [15], although the response time is much faster (of order 100 ns) and amplitude much smaller than that observed in this experiment. We conclude that our data reflect a chiral-based surface electroclinic effect.

In summary, we have observed a nematic surface electroclinic effect whose response becomes large with increasing temperature above the nematic-smectic-A transition temperature. The response is maximum at a temperature  $T_a$ , where the effective quadratic anchoring strength coefficient  $W_2^{\text{eff}}$  vanishes, and would diverge if the elastic restoring torque were absent.

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