Electro-optic response of surface-induced nematic order above the nematic-isotropic phase transition temperature

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The optical retardation of a liquid crystal above the nematic-isotropic phase transition temperature T_{NI} and subjected to planar alignment conditions at the substrate was investigated in the presence of an electric field applied normal to the substrates. The response was found to exhibit ''S''-shaped behavior with electric field, and was larger near T_{NI} than well above T_{NI}. The results were examined in the context of a model that permits both biaxiality and a field-induced tilt of the molecular director. The results suggest that the primary effect of the electric field is to induce biaxiality, and in consequence suppress the order induced by the surface. No clear indication of a Freedericksz-like transition, either experimental or theoretical, was observed. [S1063-651X(99)05811-0]

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The subject of wetting at the nematic-isotropic (NI) phase transition was investigated some 20 years ago [1], and since then has received considerable attention both experimentally and theoretically [2–6]. Above the NI transition temperature T_{NI}, an appropriately prepared surface can induce nematic ordering in the otherwise isotropic bulk phase, with the orientational order decreasing as one moves away from the surface. The precise behavior of the order parameter is dependent on the interaction energy between the liquid crystal and the alignment layer, and depends strongly on temperature, especially in the vicinity of T_{NI}. If the interaction between the liquid crystal and the surface is sufficiently strong, the uniaxial order parameter $S(z)$ integrated along the surface normal diverges logarithmically on approaching the first-order phase-transition temperature [1]; this would correspond to complete wetting by the nematic phase. If the surface-induced order (''paranematic order'') is not sufficiently large, only partial wetting occurs. These behaviors may be seen experimentally using optical ellipsometry techniques [1,3–5].

In this paper we report on an experiment that probes the influence of an applied electric field on the surface-induced nematic order above T_{NI}. Although previous work is relatively sparse, there nevertheless have been a few experimental results that have examined this issue. For example, Blinov, Kabayenkov, and Sonin used the saturation of the director response to an applied field to determine the surface anchoring energy in the nematic and isotropic phases [7]. Not surprisingly, they found a much smaller value of anchoring energy in the isotropic phase than in the nematic phase. Seo *et al.* examined the response of the planar-aligned director (i.e., aligned parallel to the substrate) to an electric field applied perpendicularly to the substrate [8]; the dielectric anisotropy $\Delta\varepsilon$ of their liquid crystal was $\Delta\varepsilon > 0$. Although they interpreted their electro-optic response as a Freedericksz transition, their optical phase retardation seems to be much too large to be associated with surface-induced nematic order. It may have been that their signal was due in part to heating effects from the applied ac field, although this is only conjecture on our part.

We recently have revisited this problem using a pulsed field technique, a method that obviates any heating problem when the duty cycle is small. Our central results are that the change of the phase retardation $\alpha[\equiv\int k\Delta n\,dz]$ has an ''S''-shaped behavior with applied field, and that there is no apparent Freedericksz transition. Here k is the wave vector of the light and Δn is the optical birefringence. These results, which appear to be at odds with those of Seo *et al.*, are analyzed in terms of both a possible Freedericksz transition and electric field-induced biaxiality of the order parameter.

Indium-tin-oxide coated glass slides were spin-coated with the polyimide CU-2012 (Du Pont) for 30 s at a rate of 3000 rpm; this polyimide is known to induce only a very tiny pretilt angle in the liquid crystal [9]. The slides were pre-baked for 30 min at 80 °C, and then baked for 1 h at 150 °C. The polyimide surfaces were then rubbed using an Optron rubbing machine to induce planar alignment of the liquid crystal. Two rubbed glass slides were separated by 6 μm Mylar spacers and cemented together. The cell was filled at a temperature above $T_{NI}=42.0$ °C with the liquid crystal heptylcyanobiphenyl (7CB), obtained from Merck. When cooled into the nematic phase, the cell showed clean planar alignment. The NI coexistence region was found to be approximately 20 mK, and the temperature differential across a 1 mm diameter spot on the cell was also about 20 mK. Thus, the laser beam sampled both bulk nematic and paranematic phases simultaneously over a ~40 mK region near T_{NI}. This places a lower limit on the experimentally accessible temperature region near the bulk phase transition temperature.

As the experiment was performed in the vicinity of T_{NI}, it was essential that we avoid field-induced temperature changes in the liquid crystal. Thus, we chose to use a pulsed field with alternating positive and negative pulses [10]. The temporal width of the pulse was 1 ms and the interval between pulses was 1s. This very long duty cycle was sufficient to avoid field-induced heating of the liquid crystal. Moreover, alternation of the pulse polarity prevented ion wall buildup in the cell. The cell was inserted into an oven that was temperature controlled to 2 mK, and temperature changes were made by ramping the temperature at a rate of 30 mK min^{-1}.
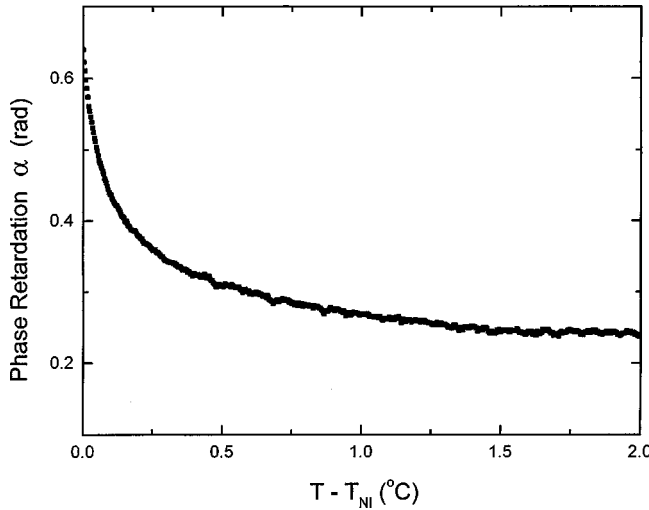
FIG. 1. Phase retardation α of the cell vs $T - T_{NI}$.

To determine the optical phase retardation that arises from the nematic layer, we used a Pockels cell modulated at approximately 100 kHz in conjunction with a phase sensitive detection scheme. Details are described elsewhere [11]. The Pockels cell was enclosed in its own temperature-controlled oven in order to minimize the drift of the offset signal with time. The liquid crystal was subjected to the applied voltage, and the time-dependent output from the lock-in amplifier (proportional to the optical retardation) was input to a digital storage oscilloscope. For each value of pulse height, i.e., electric field, the oscilloscope collected data for 500 pulses, resulting in a crisp, average optical profile of the optical retardation vs time. Pulse heights ranged from zero to 1200 statvolt cm^{-1}. Data were first collected at the highest temperature, and data from about a dozen values of pulse amplitudes were recorded. The temperature was then lowered, and data were again taken at a dozen different values of electric field. This sequence continued until the transition temperature was reached.

Figure 1 shows an example of the phase retardation α vs temperature for zero electric field. The existence and temperature variation of α come about from the surface-induced order of the liquid crystal, such that α increases as the transition temperature is approached from above [1]. For this case it appears that wetting is only partial at the transition [12]. The data in Fig. 1 serve as the baseline for the field-dependent measurements, i.e., on application of an electric field the phase retardation decreases from that shown in Fig. 1, and at a given temperature it is the change of α vs field E that is important in the analysis.

Figure 2 shows the raw data of the electric-field response averaged by the digital storage oscilloscope. Two different representative temperatures are shown (a) $T = T_{NI} + 1.8\,^\circ$C and (b) $T = T_{NI} + 0.24\,^\circ$C. Over the range of our experimental parameters we have verified that the main response to the electric field (after an initial relaxation time that is short compared to the pulse duration) depends only on the amplitude of the pulse. We note, however, that there is often a secondary response following the main response to the pulse, as seen in Fig. 2(b). The amplitude, duration, and shape of this secondary response depend in complicated ways on the amplitude and duration of the applied electric field. This sug-
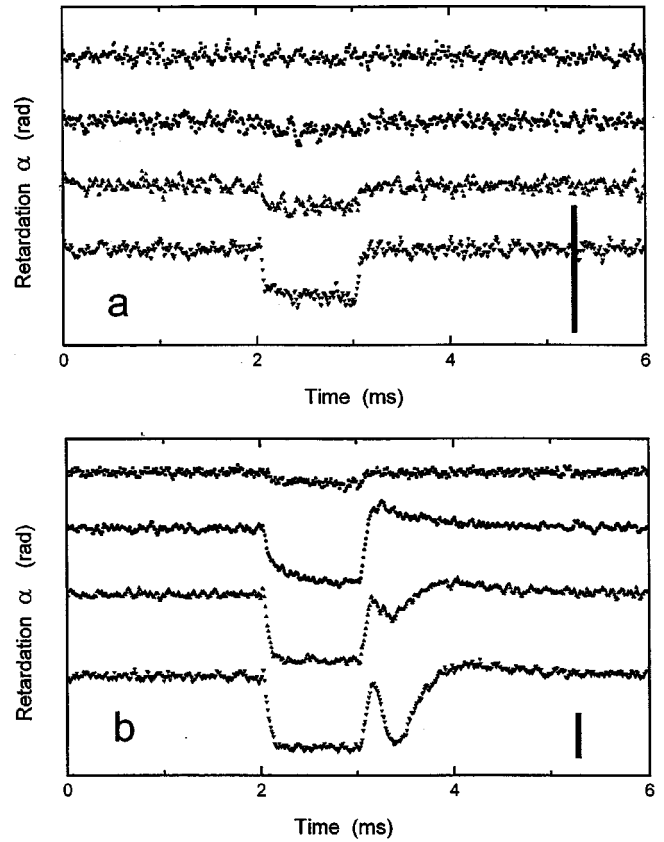

FIG. 2. Response of the cell to the electric field vs time. Data from two representative temperatures are shown. (a) $T = T_{NI} + 1.8\,^\circ$C, and (b) $T = T_{NI} + 0.24\,^\circ$C. In each panel, from top to bottom the applied field $E = 270$, 600, 930, and 1200 statv cm^{-1}. The vertical bar in each panel corresponds to a retardation of 0.01 rad for data in that panel.

gests that this response involves some non-Ohmic discharge of the cell or some other nonlinear response of the cell to the applied field. We will not discuss this response further in this paper, but rather concentrate only on the primary (rectangular) response to the applied pulse.

Figure 3 shows the *change* of phase retardation $\Delta\alpha$ vs applied electric field at five different temperatures ΔT [$= T - T_{NI}$] relative to the bulk phase transition temperature T_{NI}. $\Delta\alpha$ is defined as the difference between the baseline retardation (Fig. 2) in zero field and the depth of the trough in the presence of a field. Notice that the response $\Delta\alpha$ vs E is relatively small for weak fields, then shows a sharp rise at medium-level fields, and again flattens out at larger fields—this is the S shape referred to above. At lower temperatures, closer to T_{NI} the steep slope regime occurs at a lower field than it does at higher temperatures. Additionally, no discontinuity is observed in the slope, i.e., $\Delta\alpha$ is nonzero for all nonzero E. This result is inconsistent with the entire change in retardation being due to a Freedericksz transition, unless the threshold field E_{th} were identically zero. However, superficially it may be consistent with a slow change in the birefringence followed by a Freedericksz transition starting at the knee in the retardation curve. However, we find that the location of this knee corresponds to a bulk effect: The field-induced isotropic (paranematic)-to-nematic transition is close to this field [13]. Another feature of the data is that the flat-
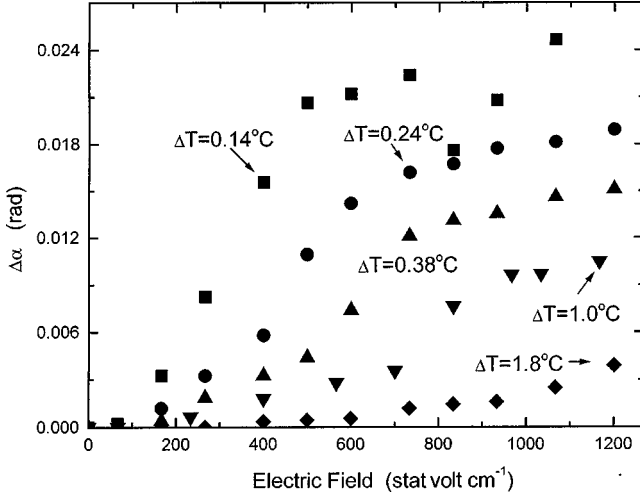
FIG. 3. Phase retardation change $\Delta\alpha$ vs applied electric field at five different temperatures $\Delta T = 0.14$ (■), 0.24 (●), 0.38 (▲), 1.0 (▼), and 1.8 °C (◆), where $\Delta T = T - T_{NI}$.

tening at high fields occurs at larger values of $\Delta\alpha$ for lower temperatures than it does at higher temperatures. This is not unexpected, as both the surface-induced order and the susceptibility are larger at lower temperatures. However, we are not certain that the high-field response is actually saturating, it may continue to increase with decreasing slope as E continues to grow.

Given these results, we now examine a model for the observed behavior. Prior to doing so we estimate the expected Freedericksz threshold field strength E_{th}. Unlike a typical bulk nematic, this system has an order parameter that changes rapidly in space. In particular, the bulk region in the center of the cell has at most a tiny order parameter that does not contribute to the threshold. Thus, we can assume that the length scale of the ordered region is of order a nematic coherence length $(L/3a)^{1/2}$, where a is the coefficient of the quadratic term and L is an elastic constant associated with spatial variations of the order parameter in the Landau-DeGennes free energy [14]. Using this value for the thickness d in the Freedericksz threshold field equation $E_{th} = \pi(K/\Delta\varepsilon)^{1/2}/d$, where K is an elastic constant and $\Delta\varepsilon$ is the dielectric anisotropy, we find $E_{th} \sim 1000$ statvolt cm^{-1} for typical values of these parameters. As this is within the range of our experiment, we allow in our theoretical model for such a transition.

First, we assume that the direction normal to the alignment surface corresponds to the z axis and the rubbing direction to the x axis. We begin with the usual Landau-DeGennes [14] free energy, including the electric field and surface terms:

$$F = \int dz \left[\frac{1}{2} L (\partial \overset{\leftrightarrow}{Q})^2 + \frac{1}{2} a(T-T^*) \overset{\leftrightarrow}{Q}^2 - \frac{1}{3} \overset{\leftrightarrow}{Q}^3 + \frac{1}{4} \overset{\leftrightarrow}{Q}^4 \right.$$

$$\left. - \frac{1}{8\pi} \Delta\varepsilon_o \mathbf{E} \cdot \overset{\leftrightarrow}{Q} \cdot \mathbf{E} \right] + \overset{\leftrightarrow}{W} \cdot \overset{\leftrightarrow}{Q}(z=0).$$

Here a, b, and c are the Landau-DeGennes coefficients for the free energy associated with the tensor order parameter $\overset{\leftrightarrow}{Q}$, $\Delta\varepsilon_o$ is the dielectric anisotropy for complete alignment,

T is the temperature, T^* is the supercooling limit of the isotropic phase, and $\overset{\leftrightarrow}{W}$ is the surface interaction parameter tensor.

In principle, it would be possible to minimize this free energy for a general tensor order parameter $\overset{\leftrightarrow}{Q}$. However, simple arguments suggested that there would be a Freedericksz transition. In order to account theoretically for this possibility we must consider a tensor order parameter with three independent components and solve three coupled, nonlinear differential equations. To make the calculation tractable, we divided the order parameter into two components: One is the surface-induced order parameter ($\overset{\leftrightarrow}{Q}_s$) and the other is the electric-field-induced order parameter ($\overset{\leftrightarrow}{Q}_E$). We assume that $\overset{\leftrightarrow}{Q}_E$ and $\overset{\leftrightarrow}{Q}_s$ are both uniaxial, any biaxiality comes from combining these two tensors, and the principle eigenvector of $\overset{\leftrightarrow}{Q}_E$ is parallel to the field (that is to the surface normal). To allow for the possibility of a Freedericksz transition, we assume that the director for $\overset{\leftrightarrow}{Q}_s$ can rotate in the plane containing the rubbing direction and the electric field. With these assumptions we can define the order parameter tensors by

$$\overset{\leftrightarrow}{Q} = \overset{\leftrightarrow}{Q}_E + \overset{\leftrightarrow}{Q}_s,$$

$$\overset{\leftrightarrow}{Q}_E = S_E \begin{pmatrix} -1/2 & 0 & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$\overset{\leftrightarrow}{Q}_s = S_s \overset{\leftrightarrow}{R} \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & -1/2 \end{pmatrix} \overset{\leftrightarrow}{R}^T, \quad (1)$$

where

$$\overset{\leftrightarrow}{R} = \begin{pmatrix} \cos\theta & 0 & \sin\theta \\ 0 & 1 & 0 \\ -\sin\theta & 0 & \cos\theta \end{pmatrix}$$

and

$$\overset{\leftrightarrow}{W} = w \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & -1/2 \end{pmatrix}.$$

Here θ corresponds to the rotation angle of the director in the x-z plane, $\overset{\leftrightarrow}{R}$ is a rotation tensor, S_E and S_s are scalar order parameters, and w is the strength of surface interaction.

The free energy may then be written as $F = F_E + F_s + F_{Es}$, where F_{Es} is a cross term that couples the surface-induced and field-induced order parameters, such that

$$F_E = \int dz \left[\frac{1}{2} L (\partial \overset{\leftrightarrow}{Q}_E)^2 + \frac{1}{2} a(T-T^*) \overset{\leftrightarrow}{Q}_E^2 - \frac{1}{3} b \overset{\leftrightarrow}{Q}_E^3 + \frac{1}{4} c \overset{\leftrightarrow}{Q}_E^4 \right.$$

$$\left. - \frac{1}{8\pi} \Delta\varepsilon_o \mathbf{E} \cdot \overset{\leftrightarrow}{Q}_E \cdot \mathbf{E} \right] + \overset{\leftrightarrow}{W} \cdot \overset{\leftrightarrow}{Q}_E,$$

$$F_s = \int dz \left[\frac{1}{2} L(\partial \vec{Q}_s)^2 + \frac{1}{2} a(T-T^*) \vec{Q}_s^2 - \frac{1}{3} b \vec{Q}_s^3 + \frac{1}{4} c \vec{Q}_s^4 \right]$$
$$+ \vec{W} \cdot \vec{Q}_s,$$

$$F_{Es} = \int dz \left[L(\partial \vec{Q}_E)(\partial \vec{Q}_s) + Q_s \left(a(T-T^*) \vec{Q}_E - b \vec{Q}_E^2 + c \vec{Q}_E^3 \right. \right.$$
$$\left. - \frac{1}{8\pi} \Delta \varepsilon_o E^2 \right) + \left(-b \vec{Q}_s^2 \vec{Q}_E + \frac{3}{2} c \vec{Q}_s^2 \vec{Q}_E^2 + c \vec{Q}_s^3 \vec{Q}_E \right) \bigg].$$

Additionally we assume that the surface-induced order parameter is small and does not affect the solution for $\vec{Q}_E$. On substituting the form for $\vec{Q}_E$ in Eq. (1) into F_E, we find

$$F_E = \int \left[\frac{1}{6} L \left(\frac{dS_E}{dz} \right)^2 + G_E(S_E) \right] + \frac{1}{4} w S_{Eo},$$

where

$$G_E(S_E) = \frac{1}{2} a(T-T^*) S_E^2 - \frac{1}{3} b S_E^3 + \frac{1}{4} c S_E^4 - \frac{1}{8\pi} \Delta \varepsilon_o E^2 S_E.$$

On minimizing F_E we obtain the differential equation and boundary condition:

$$\left(\frac{dS_E}{dz} \right) = \sqrt{\frac{6}{L}} [G_E(S_E) - G_E(S_{Eb})]^{1/2} \qquad (2)$$

and

$$[G_E(S_{Eo}) - G_E(S_{Eb})]^{1/2} = \frac{w}{8} \sqrt{\frac{6}{L}}.$$

S_{Eb} is the electric-field-induced bulk order parameter along the electric-field direction and S_{Eo} is the order parameter at the surface along the same direction. Moreover, in Eq. (2) we note that

$$G_E(S_E) - G_E(S_{Eb}) = (S_{Eb} - S_E) \left\{ -\frac{1}{2} a(T-T^*)(S_E + S_{Eb}) \right.$$
$$+ \frac{1}{3} b(S_E^2 + S_E S_{Eb} + S_{Eb}^2)$$
$$- \frac{1}{4} c(S_E^2 + S_{Eb}^2)(S_E + S_{Eb})$$
$$\left. + \frac{1}{8\pi} \Delta \varepsilon_o E^2 \right\}.$$

Near the boundary, the leading factor $S_{Eb} - S_E$ varies rapidly in space, although the remaining factor does not. In consequence we can take $S_E \approx S_{Eo}$ and the factor in braces {} may be defined as f_o, from which we obtain an approximate solution $S_E(z)$:

$$S_E(z) = S_{Eb} - \left((S_{Eb} - S_{Eo})^{1/2} - \frac{1}{2} \sqrt{\frac{6f_o}{L}} z \right)^2, \quad 0 < z < z_1,$$

$$S_E(z) = S_{Eb}, \quad z > z_1,$$

where

$$z_1 = 2 \sqrt{\frac{L}{6f_o}} (S_{Eb} - S_{Eo})^{1/2}.$$

We now calculate the behavior of the surface-induced order parameter by minimizing $F_s + F_{Es}$:

$$F_s + F_{Es} = F_{surf} + F_{bulk} + F_{coupling},$$

$$F_{surf} = w S_s \left(\frac{1}{2} \sin^2 \theta - \frac{1}{3} \right),$$

$$F_{bulk} = \int dz \left[\frac{L}{6} \left(\frac{dS_s}{dz} \right)^2 + \frac{1}{2} L S_s^2 \left(\frac{d\theta}{dz} \right)^2 + G(S_s) \right],$$

$$F_{coupling} = \int dz \left[-\frac{1}{2} b S_s^2 S_E (3 \sin^2 \theta - 1) \right.$$
$$\left. + \frac{3}{4} c S_s^2 S_E^2 (\sin^2 \theta + 1) + \frac{1}{2} c S_s^3 S_E (3 \sin^2 \theta - 1) \right],$$

where

$$G(S_s) = \frac{1}{2} a(T-T^*) S_s^2 - \frac{1}{3} b S_s^3 + \frac{1}{4} c S_s^4.$$

Using this free energy we obtain a pair of second-order differential equations from which we can extract $S_s(z)$ and $\theta(z)$. Note that the electric field appears indirectly as a consequence of the coupling between $\vec{Q}_E$ and $\vec{Q}_s$. On making the substitution $z' = (3a/L)^{1/2} z$, the differential equations for the bulk become dimensionless:

$$a(T-T^*) \frac{d^2 S_s}{dz'^2} = 3a(T-T^*) S_s \left(\frac{d\theta}{dz'} \right)^2 + \left(\frac{dG(S_s)}{dS_s} \right)$$
$$- b(3 \sin^2 \theta - 1) S_s S_E$$
$$+ \frac{3}{2} c(3 \sin^2 \theta - 1) S_s^2 S_E$$
$$+ \frac{3}{2} c(\sin^2 \theta + 1) S_s S,$$

$$a(T-T^*) S_s \frac{d^2 \theta}{dz'^2} + 2a(T-T^*) \frac{dS_s}{dz'} \frac{d\theta}{dz'}$$
$$= \left(-\frac{b}{2} S_s S_E + \frac{c}{2} S_s^2 S_E + \frac{c}{4} S_s S_E^2 \right) \sin(2\theta).$$

The boundary conditions are given by

$$\left. \frac{d\theta}{dz'} \right|_{z'=0} = \frac{w}{2\sqrt{3a(T-T^*)L}} \frac{1}{S_{so}} \sin(2\theta(0)),$$

$$\left. \frac{dS_s}{dz'} \right|_{z'=0} = \frac{3w}{2\sqrt{3a(T-T^*)L}} \left(\sin^2 \theta(0) - \frac{2}{3} \right),$$

where S_{so} is the scalar order parameter S_s at the interface. With these equations we may obtain $S_s(z)$ and $\theta(z)$ for a given electric field and temperature.

In our experiment the change of optical phase $\Delta \alpha$ is

$$\Delta\alpha = \frac{2\pi}{\lambda}\Delta n_o \left(\int_0^\infty S_s(z, E=0)dz \right.$$

$$\left. - \int_0^\infty S_s(z, E)\cos^2\theta(z)dz \right),$$

where Δn_o is refractive index anisotropy assuming fully saturated orientational order and λ is the wavelength of light. We have approximated the anisotropy of refractive index as being proportional to the order parameter.

Because we know neither the actual surface order parameter nor the interaction energy, we attempted to achieve a match between the measured signal $\Delta\alpha$ and the calculated result by choosing a reasonable surface order parameter S_{so} at a given temperature. With that value of S_{so} we were able to determine the interaction energy coefficient w that induces this value S_{so} by matching the calculated result with the boundary conditions—the surface-induced order parameter asymptotically goes to zero in the bulk—at that temperature when there is no electric field. With this now temperature-independent parameter w in hand, we then calculated S_{so} and $\Delta\alpha$ as *functions of temperature*. For these calculations we used the following material parameters: $\Delta\varepsilon_o = 17.5$; $L = 2.05 \times 10^{-6}$ dyn; $\Delta n_o = 0.4$; $a = 2.1 \times 10^6$ erg cm^{-3} K; $b = 3.3 \times 10^7$ erg cm^{-3}; $c = 8.1 \times 10^7$ erg cm^{-3}; $T_{NI} = 42.0$ °C; and $T^* = 40.6$ °C [15]. As $\Delta\varepsilon_o$ and L are the dielectric anisotropy and elastic constant for fully saturated order, we could calculate these quantities as functions of the order parameter [16,17] by assuming that the dielectric anisotropy is proportional to the order parameter and elastic constant is proportional to the square of order parameter. From the dependence of these quantities on the order parameter, we could then retrieve $\Delta\varepsilon_o$ and L at $S=1$, as required. Note that for L we chose to use the average of the splay and bend elastic constants K_{11} and K_{33}.

For these calculations we began with an interaction energy coefficient $w=0.63$ erg cm^{-2} and the surface order parameter $S_{so}=0.28$ at $T-T_{NI}=0.38$ °C. This value for w would correspond to an anchoring energy coefficient ~ 0.1 erg cm^{-2}, a value a bit larger than typical experimental results [7,18]. Although Blinov *et al.* noted that the anchoring energy should be reduced to about one-tenth its nematic phase value in the isotropic phase, there is no reason in our model for this to occur, and our value for w is quite reasonable.

In Fig. 4 we plot the behavior of the surface-induced scalar order parameter at the surface (S_{so}), the field-induced scalar order parameter in the bulk (S_{Eb}), and the field-induced scalar order parameter at the surface (S_{Eo}) calculated as a function of the electric field assuming that the tilt angle θ is always zero. Note that S_{Eo} has a negative value for small electric fields and becomes positive at high fields. This is because of the coupling between the interaction tensor of the surface and the field-induced order parameters, thus resulting in a small amount of biaxiality at the surface. On the other hand, S_{Eb} is a bulk response to the electric field, and is not significantly affected by the order S_{so} at the surface.

We also assessed the possibility of a Freedericksz transition by calculating the behavior when there is a small pretilt. One of two possibilities was expected: (i) at some field there
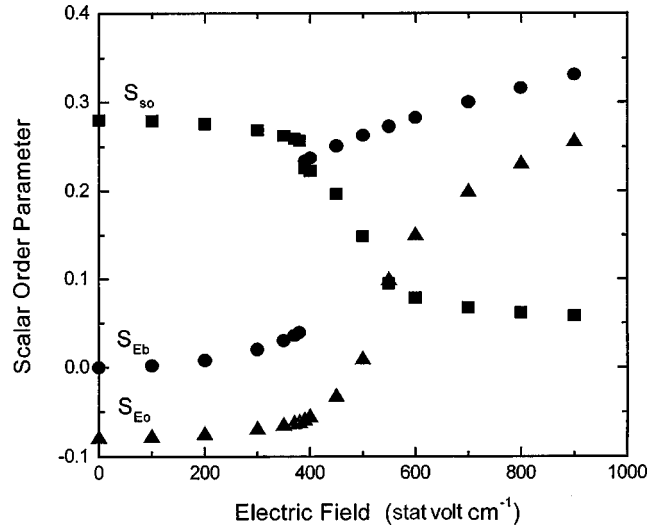

FIG. 4. Calculated order parameters vs electric field. S_{so} (■) is the surface-induced surface order parameter along the rubbing direction, S_{Eb} (●) is the field-induced order parameter in the bulk, and S_{Eo} (▲) is the field-induced order parameter at the surface along the electric-field direction. Values are obtained using $T = T_{NI} + 0.38$ °C, $w=0.63$ erg cm^{-2}, $E=0$, and $S_{so}=0.28$.

is a state that involves a 90° rotation of the order parameter, which at some other field has a lower free energy than the state with no rotation, and (ii) at some field there is a state that has a small rotation. The first of these cases would result in a first-order Freedericksz transition, the second would be a second-order Freedericksz transition. We found that there is usually a nearly equal free-energy state that has a 90° rotation of the director (so that the surface induced order parameter is, far from the surface, parallel to the electric field direction rather than along the rubbing direction). However, it is very difficult to satisfy the boundary conditions precisely with this solution, or at least there are always small numerical errors. Additionally, this 90° rotation of the director occurs when the surface-induced order is very small. This is why the free energy is always very close to the free energy of the undistorted state. Hence, we believe that this state is an artifact of our calculation method, rather than an actual new state: It would be extraordinary if there were two actual states that had such similar free energies over a range of conditions. The predicted birefringence of this state is, in any case, very similar to the predicted birefringence of the $\theta = 0$ state, so that distinguishing them experimentally would be difficult. Thus, we believe that there is no Freedericksz transition.

Let us return to the case of zero pretilt angle. In Fig. 5 we show the calculated retardation $\Delta\alpha$ as a function of electric field for three different temperatures. Semiquantitatively these results are similar to the experimental results in Fig. 2, viz, a nonzero retardation change even at small electric fields, a rapid increase of $\Delta\alpha$ with field in the neighborhood of several hundred statvolt cm^{-1}, and a leveling out at higher fields. Moreover, the maximum response at temperatures closer to T_{NI} is larger for both the experiment and model calculation, and the curves tend to be less sharp at higher temperatures. Despite these clear areas of agreement, differences between experiment and the model may be found in the details. For example, the experimental result displays a
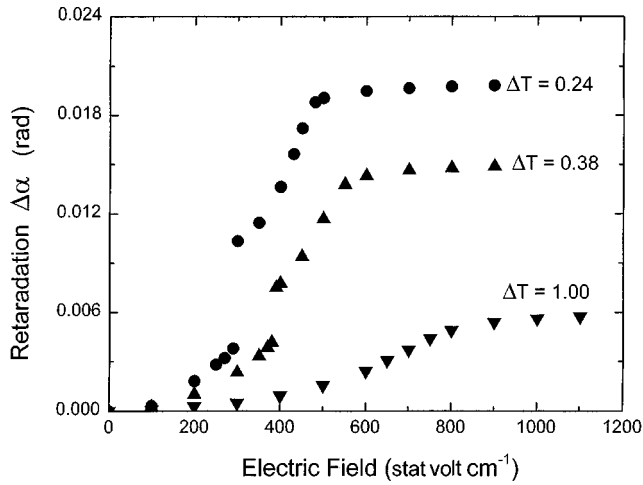
FIG. 5. Calculated phase retardation change $\Delta\alpha$ vs electric field at three different temperatures $\Delta T = 0.24$ (●), 0.38 (▲), and 1.0 °C (▼). $\Delta\alpha$ is calculated using the parameters in Fig. 4.

more gradual increase of $\Delta\alpha$ with E than does the model calculation, and the magnitudes of the experimental retardation are less strongly temperature dependent than the model calculations. For example, although values of $\Delta\alpha$ at $\Delta T = 0.38$ °C are similar for both experiment and model, the model calculations at $\Delta T = 0.24$ and 1.00 °C are larger and smaller, respectively, than corresponding experimental values.

In order to understand this behavior, we need to consider several sources of error and uncertainty. We note from Ref. [13] that the uncertainty in $T_{NI} - T^*$ is about 0.3 °C. If we were to change $T_{NI} - T^*$ by only 0.2 °C, we would find markedly better or worse fits to the experimental results, depending upon the particular temperature being fitted. Similarly, the uncertainty in our choice for L would have a like effect. We also need to consider the effects of a *distribution* of surface interaction energies. Because of the nature of the rubbing process, it is entirely possible that over very small length scales of order a nematic correlation length the interaction coefficient w may vary by as much as 40% [12]: A spatial distribution of w will affect S_{so} directly, and through the higher-order terms in the free energy, will affect S_E as well. The overall result would be to introduce some rounding of the experimental data, as observed. We also need to consider the possibility of a small pretilt angle. For this case there would be a small nonzero torque on the director, which also would tend to introduce rounding into the experimental results. We believe that this effect is at most a small contribution to the measured signal. Finally, we are able to show on symmetry grounds that neither order electricity [19,20] nor flexoelectricity [21] affect our system.

An additional issue involves the form we have chosen for the surface interaction term. In our model we assume that the interaction between the liquid crystal and the alignment layer is proportional to the surface order parameter, and thus the anchoring energy is proportional to the order parameter. Experimental results, however, indicate that the anchoring energy may be proportional to the *square* of the bulk order parameter [18,22]. It has been suggested that the surface interaction should also include a term proportional to the square of the order parameter [6,23]. Using this additional

term in the free energy, Moses and Shen were able to explain their observed dewetting phenomena at the NI phase transition. In this light, let us apply this additional surface term $\vec{\vec{W}}_2 \cdot \vec{\vec{Q}}^2$. Note that the two surface terms have the same symmetry, but different coefficients. Since this procedure introduces another parameter, we adjust the magnitudes of the two surface terms so that the difference of coefficients for the $\sin^2\theta$ term is comparable to a reasonable anchoring energy. Even with this additional $\vec{\vec{W}}_2 \cdot \vec{\vec{Q}}^2$ term, we still find no rotational response of the director to the electric field, although the agreement between the model and the experimental results is improved. Thus, the addition of a surface term proportional to the square of the order parameter improves the fit, but does not substantially change the physics of the problem.

If we examine the equations governing the system, there is no direct interaction between the surface induced director ($\vec{\vec{Q}}_s$) and the electric field, but rather an indirect interaction through the field-induced director ($\vec{\vec{Q}}_E$). Although both $\vec{\vec{Q}}_s$ and $\vec{\vec{Q}}_E$ are uniaxial, their interaction results in an overall biaxial order parameter. With increasing electric field, both the magnitude and spatial range of $\vec{\vec{Q}}_s$ decrease as the magnitude of $\vec{\vec{Q}}_E$ increases. In consequence the measured signal is closely related to the (indirect) response of $\vec{\vec{Q}}_E$. In the region of small electric field, the response of the director is Kerr-like, as $\Delta\alpha$ changes linearly with E^2 [15]. Close to the bulk transition temperature T_{NI}, S_E exhibits a discontinuity at a particular value of electric field, i.e., a field-induced transition from a paranematic to a nematic phase [13]. At higher temperatures this discontinuity is smaller, until the system eventually reaches a critical point at field E_c and temperature T_c beyond which the profile of $\Delta\alpha$ vs E is continuous. If we calculate the critical point for 7CB, we find $E_c \sim 530$ statvolt cm^{-1} and $T_c = T_{NI} + 0.7$ °C. This is not inconsistent with the model results in Fig. 4. Unfortunately, small temperature gradients in the experimental apparatus as well as a distribution in the surface interaction potential (and thus in S_{so}) make this discontinuity difficult to observe experimentally.

To summarize, we have used a pulsed-field technique to examine the optical response of a planar-aligned liquid crystal above the nematic-isotropic phase-transition temperature. We found that the optical phase retardation exhibits an S-shaped dependence on electric field. A model based upon field-induced biaxiality and the possibility of director rotation was presented, and is in reasonable agreement with the experimental results. For the fields used in the experiment, the model predicts that the primary response is a variation of the magnitude of the order parameter, with no rotation of the director.

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