Symmetry-Breaking Effect of Interfacial Interactions on Electro-optical Properties of Liquid Crystals

Sin-Doo Lee and J. S. Patel
Bellcore, 331 Newman Springs Road, Red Bank, New Jersey 07701

(Received 8 January 1990)

We show for the first time that the asymmetry comparable to the weak anchorage in anisotropic interfacial interactions between two surface layers of liquid crystals can produce a novel electro-optic effect. The effect depends on the polarity of an external electric field E, but the corresponding phase shift has E^2 dependence. In a simple geometry with homogeneous boundary conditions, we demonstrate that this polar effect is directly proportional to the difference in the anchoring strengths, and estimate the difference between two aligning polymer layers.

PACS numbers: 61.30.Gd, 78.20.Jq

Surface effects are of great importance in the field of liquid crystal (LC) for basic understanding of physical phenomena as well as for device applications. The properties of LCs are strongly influenced by the surface boundary conditions. For instance, the broken symmetry and specific interactions at an interface lead, under various circumstances, to novel orientational phenomena[1,2] in the layer adjacent to the interface which may not be observable in the bulk. It is known that a properly treated solid substrate can preferentially orient the constituent molecules of LCs in a certain direction, as a result of anisotropic interfacial interactions between the molecules and the substrate.[3] To study such a surface-anchoring effect the Fredericks transition,[4] which depends strongly on the boundary conditions, can be utilized. Considerable interest has been focused on the interfacial properties of the nematic phase[5] which is characterized by only the presence of orientational order. Because of the inversion symmetry of this system, most external-field effects are quadratic in nature, as, for example, in the coupling of the dielectric anisotropy with an external electric field. However, a coupling of the induced polarization associated with the orientational distortions can produce a linear effect which is known as the flexoelectric effect.[6] It has been reported that in the weak-anchoring regime this flexoelectric effect can be easily realized in certain geometries such as homeotropically[7] and hybrid[8] aligned samples, while homogeneously aligned samples exhibit only surface domains.[9]

In this Letter we predict that a strong polar effect can exist when the symmetry of the anisotropic interfacial interactions, externally imposed, between two surface layers is broken. This prediction has been confirmed experimentally by introducing the asymmetry in the interfacial interactions in the form of either different surface tilts or different anchorages. The induced polar effect is independent of the magnitude of the individual anchoring strengths but depends on the difference between them. For symmetrical interfaces, in the presence of an external electric field above the Fredericks threshold, two flexoelectrically induced polarizations in the upper and lower regions of the sample exactly cancel, while for asymmetrical interfaces, a net polarization exists and couples with the electric field to produce the polar effect. This leads to the conclusion that asymmetry in the interfacial interactions is an essential factor for the existence of the polar effect.

Consider the free energy of a nematic sample of the thickness d, aligned homogeneously along the y axis, in the presence of an electric field $\mathbf{E}$ in the z direction. Assume that the dielectric anisotropy ϵ_a is positive and the distortions, mostly splay, occur along the z direction. Denoting partial derivatives by subscripts, the free-energy density f per unit area can be written as

$$f=\int_0^d dz\left[\tfrac{1}{2}K\theta_z^2-(e_1+e_3)E\sin\theta\cos\theta\,\theta_z-(1/8\pi)\epsilon_a E^2\sin^2\theta\right]+f_{\rm sur}\,, \qquad (1)$$

where e_1 and e_3 represent the flexoelectric coefficients associated with splay (K_1) and bend (K_3) distortions, respectively, and $f_{\rm sur}$ denotes the surface-anchoring energy. Here we assumed $K_1=K_3\equiv K$ for the elastic constants, and ignored the space-charge effects. Minimizing the free energy, Eq. (1), the Euler-Lagrange equation leads to

$$\xi^2\theta_{zz}+\sin\theta\cos\theta=0 \quad (0<z<d)\,, \qquad (2)$$

where the dielectric coherence length ξ is given by $(4\pi K/\epsilon_a E^2)^{1/2}$. The boundary condition represents the torque balance at each surface,

$$\partial f/\partial\theta_z \pm \partial f_{\rm sur}/\partial\theta=0 \text{ at } z=0 \text{ and } d\,, \qquad (3)$$

respectively. Macroscopically, the effect of the surface torque can be described in terms of an anisotropic interfacial energy which depends on both the surface tilt and the anchoring strength. For simplicity, we choose the interfacial energy $f_{\rm sur}$ in a form[10] of $W(\hat{\mathbf{s}}\cdot\mathbf{n})^2=W\sin^2\theta$ with the surface normal $\hat{\mathbf{s}}$ and the director $\mathbf{n}$, ignoring terms of surface polarization $(\propto\sin\theta)$ on homogeneous surfaces.[11] Then, the two boundary conditions can be rewritten as

$$K\theta_z|_{1,2}-(e_1+e_3)E\sin\theta_{1,2}\cos\theta_{1,2} \pm W_{1,2}\sin\theta_{1,2}\cos\theta_{1,2}=0\,. \qquad (4)$$

As a consequence, integration of the Euler-Lagrange equation yields $z=\xi\int^{\theta}(C-\sin^2\alpha)^{-1/2}d\alpha$, where C is a field-dependent integration constant which can be determined from the boundary conditions [Eq. (4)]. In general, numerical calculations are required to solve the equation for $z(\theta)$ exactly, but it is interesting to see the qualitative features of the infinitely anchored case $(W_{1,2}\rightarrow\infty)$. Near the Fredericks threshold E_c, the maximum distortion angle $\theta_m\propto(E/E_c-1)^{1/2}$ which is a characteristic of the second-order transition, and $\theta(z)\approx\theta_m\sin(\pi z/d)$. The optical path difference $\delta\approx n_e d v(E/E_c-1)$, where $v=[(n_e/n_o)^2-1]\ll 1$, with n_e and n_o the extraordinary and ordinary refractive indices, respectively. For sufficiently high fields, a complete distortion of the sample is obtained, and the maximum distortion angle θ_m becomes $\pi/2$.

In examining the existence of the polar effect, we consider the director distortions to be due mainly to a linear coupling of the flexoelectric polarization with the field in the high-field limit. Suppose that the sample consists of two surface layers where the angle $\theta(z)$ varies continuously from $\theta_m\approx\pi/2$ to θ_1 and θ_2, respectively. For surface tilts up to the quadratic order, the first integral of Eq. (2), which satisfies that $\theta\approx\pi/2$ and $\theta_z\approx 0$ near the middle of the sample, and Eq. (4) yield the following field dependences of θ_1 and θ_2:

$$\theta_{1,2}(E)\approx[(\xi/\eta\pm\xi/b_{1,2})^2+1]^{-1/2}\,, \qquad (5)$$

where the flexoelectric coherence length $\eta=K/(e_1+e_3)E$, and the extrapolation length $b_{1,2}=K/W_{1,2}$. It should be noted that the flexoelectric coupling tends to amplify the surface tilt on one surface and to reduce that on the other. As $b_{1,2}\rightarrow 0$, then $\theta_1\approx\theta_2\rightarrow 0$, which is the case of the infinite anchoring.

In order to see the consequences of this flexoelectric effect in the simplest form, we assume a constant curvature of the director distortions $(\theta_{zz}\approx 0)$, and obtain

$$\theta_z\approx\pm\theta_{1,2}/t_{1,2} \text{ near } z=0 \text{ and } d\,, \qquad (6)$$

respectively, where $1/t_{1,2}=1/\eta\pm 1/b_{1,2}$. The constant-curvature equation [Eq. (6)] will correctly describe the director distortions to the leading order in θ_1 and θ_2. We now calculate the optical path difference δ due to the deformations under consideration:

$$\delta=n_e\left[d-\int_0^2[1+v\sin^2\theta(z)]^{-1/2}dz\right]$$
$$\approx(n_e v/4)(d+t_1+t_2)\,. \qquad (7)$$

The resulting polarity-dependent path difference $\Delta\delta$ is then given by

$$\Delta\delta=[\delta(+E)-\delta(-E)]/2$$
$$\approx(n_e v/4)\eta^2[b_2/(b_2^2-\eta^2)-b_1/(b_1^2-\eta^2)]\,. \qquad (8)$$

If the two interfaces are identical, i.e., $b_1=b_2$, then $\Delta\delta=0$, independent of the polarity of the field E. This implies that a disparity in the interfacial interactions $W_{1,2}$ is necessary to realize the existence of the polar effect. In the relatively low-field regime $(b_{1,2}\ll\eta)$, $\Delta\delta\approx(n_e v/4)[(b_1-b_2)+(b_1^3-b_2^3)/\eta^2]$ which has E^2 dependence. But, in the high-field regime $(b_{1,2}\gg\eta)$, $\Delta\delta\approx(n_e v/4)(1/b_2-1/b_1)\eta^2$ which is inversely proportional to E^2. Notice that the path difference $\Delta\delta$ is directly proportional to the difference in the anchoring strengths.

In the light of the above idea, we made measurements on a commercial material E7 (from EM Chemicals) which has the nematic phase at room temperature. All measurements were performed at room temperature. Two different interfaces were produced by two different aligning polymers deposited onto conductive indium-tin-oxide–coated glass substrates, respectively. The two polymers were poly(1,4-butylene terephthalate) (PBT) containing aromatic rings which resemble the cores of the liquid-crystal molecules, and nylon 6,6 (NYL) which resembles the tails of the liquid-crystal molecules. Details of the alignment procedure have been described previously.[12] The molecules were strongly anchored on the buffed polymer layers, and the alignment was exceptionally good. To investigate the existence of the polar effect in our samples, we monitored the transmitted intensity of a monochromatic light through the 3-μm-thick sample cell between crossed polarizers in the presence of an ac electric field. The ac signal of the transmitted intensity ΔI, in phase to the applied electric field, was monitored using a lock-in amplifier, and the dc signal I was monitored with a photodiode in conjunction with a digitizing

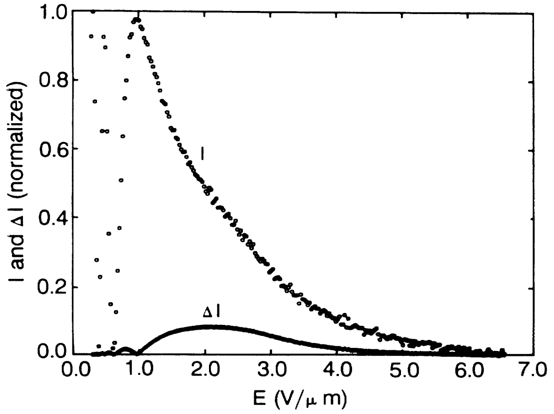

FIG. 1. The dc and ac transmitted intensities I and ΔI as a function of the applied field E of a square wave at 155 Hz. The sample cell was made with two different aligning polymer layers (PBT and NYL).

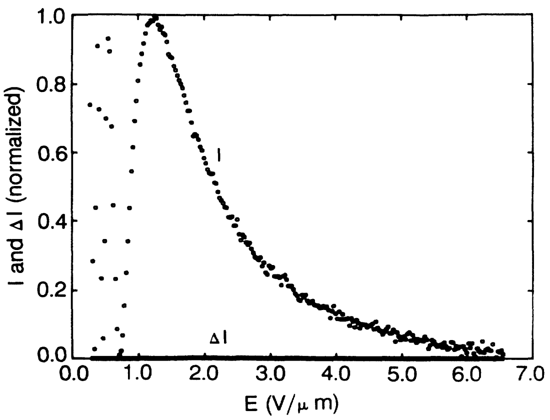

FIG. 2. The dc and ac transmitted intensities I and ΔI as a function of the applied field E of a square wave at 155 Hz. The sample was made with both PBT polymer layers.

oscilloscope. In terms of the corresponding path differences $\Delta\delta$ and δ_o the total transmitted intensity is proportional to $\sin^2[\pi(\delta_o \pm \Delta\delta)/\lambda]$, where λ is the wavelength of the light in vacuum.

Figure 1 shows results demonstrating the polar effect. The sample cell was made with two different polymer layers (PBT and NYL) and exhibited a strong polar effect. For comparison, the results from a sample with two PBT layers are shown in Fig. 2, where no polar effect is seen as expected. Figure 3 shows the phase shift $\Phi = 2\pi\Delta\delta/\lambda$ of the ac transmitted intensity at various frequencies in the high-field regime. The phase shift was fitted by a form $\Phi_b + a/E^2$, where Φ_b represents a background phase shift ($\Phi_b \approx 0$) and a denotes a constant which depends on such material parameters as n_e, n_o, $e_1 + e_3$, K, and the interfacial energy difference (ΔW). As shown in Fig. 3, all of the phase-shift data decay as E^{-2}, and fall remarkable well into a common curve. It might be noted that the observed phase shift becomes smaller at higher frequencies. In fact, the thickness ξ of the surface layers increases with decreasing the field strength E. Since the elastic distortion of a surface layer will relax like $(\gamma/K)\xi^2$ (with γ the relevant viscosity), we do not expect a full-amplitude response at frequencies f above $f_c \approx K/\gamma\xi^2 \approx \epsilon_a E^2/\gamma$. Thus, the observed $1/f$ divergence of the maximum response should terminate at $f \approx K/\gamma d^2$, which is the frequency corresponding to the relaxation of a surface layer of thickness equal to the sample thickness d.

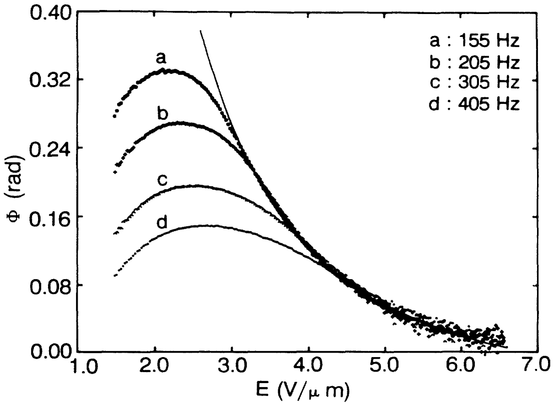

FIG. 3. The optical phase shift Φ of the ac transmitted intensity due to the polar effect as a function of the applied field E at various frequencies. The solid line was fitted by a form $\Phi_b + a/E^2$.

On the basis of the results above and the literature values of $K = 1.85 \times 10^{-7}$ dyn, $n_e = 1.724$, and $n_o = 1.513$ for the E7 material,[13] we can estimate the difference ΔW in the anchoring strengths. With the fitted value of $a = 3.3 \times 10^3$ cgs units, $\lambda = 0.514$ μm, and the typical value for $e_1 + e_3 \approx 1.0 \times 10^{-4}$ cgs units,[14] the difference ΔW is found to be 1.0×10^{-2} erg/cm^2 which is comparable to the strength for weak anchoring. It should be emphasized that the surface-energy *difference* plays an essential role in realizing the polar effect. Moreover, other surface-induced phenomena, such as surface electroclinic[15] and surface-stabilized ferroelectric[16] effects near the smectic-A-smectic-C^* transition, might be enhanced by exploiting the relative strengths of anisotropic interfacial interactions. A detailed account of our results together with the effect of a dc-bias field will be presented elsewhere.

In conclusion, we have shown for the first time that a strong polar effect exists in a homogeneously anchored nematic liquid crystal, resulting from the asymmetry in the anisotropic interfacial interactions between two surface layers irrespective of the individual anchoring strengths. The basic idea behind this phenomenon would be quite general and scientifically important in other condensed-matter systems. We see that a simple means of externally breaking the symmetry in a LC system is to introduce the *difference* in the anchoring strengths, which leads to a novel surface effect. Our prediction for this effect is based on a linear coupling of net flexoelectric polarization in the two surface layers with an electric field, and it has been confirmed in a commercial E7 material. Further studies on other materials will provide useful information for understanding fundamental aspects of surface phenomena associated with specific interactions at an interface.

We are indebted to D. W. Berreman and Professor R. B. Meyer for stimulating discussions, and J. Prost for pointing out the magnitude of the flexoelectric coefficient.

---

[1] W. Chen, M. B. Feller, and Y. R. Shen, Phys. Rev. Lett. **63**, 2665 (1989); W. Chen, L. J. Martinez-Miranda, H. Hsiung, and Y. R. Shen, Phys. Rev. Lett. **62**, 1860 (1989).

[2] P. Guyot-Sionnest, H. Hsiung, and Y. R. Shen, Phys. Rev.

Lett. **57**, 2963 (1986).

[3] For a comprehensive discussion, see J. Cognard, *Alignment of Nematic Liquid Crystals and Their Mixtures* (Gordon and Breach, London, 1982).

[4] See, for example, P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974).

[5] T. J. Sluckin and A. Poniewierski, in *Fluid Interfacial Phenomena,* edited by C. A. Croxon (Wiley, New York, 1986), Chap. 5, and references therein.

[6] R. B. Meyer, Phys. Rev. Lett. **22**, 918 (1969).

[7] W. Helfrich, Appl. Phys. Lett. **24**, 451 (1974).

[8] N. V. Madhusudana and G. Durand, J. Phys. (Paris), Lett. **46**, L195 (1985).

[9] H. P. Hinov, Mol. Cryst. Liq. Cryst. **89**, 227 (1982).

[10] A. Rapini and M. Papoular, J. Phys. (Paris), Colloq. **30**, C4-54 (1969).

[11] A. Derzhanski, A. G. Petrov, and M. D. Mitov, J. Phys. (Paris) **39**, 273 (1978).

[12] J. S. Patel, T. M. Leslie, and J. W. Goodby, Ferroelectrics **59**, 129 (1984); J. M. Geary, J. W. Goodby, A. R. Kmetz, and J. S. Patel, J. Appl. Phys. **62**, 4100 (1987).

[13] D. W. Berreman, in *The Physics and Chemistry of Liquid Crystal Devices,* edited by G. J. Sprokel (Plenum, New York, 1980), Chap. 1.

[14] J. Prost and P. S. Pershan, J. Appl. Phys. **47**, 2298 (1976).

[15] S. Garoff and R. B. Meyer, Phys. Rev. Lett. **38**, 848 (1977); J. Xue and N. A. Clark, Phys. Rev. Lett. **64**, 307 (1990).

[16] M. A. Handschy, N. A. Clark, and S. T. Lagerwall, Phys. Rev. Lett. **51**, 471 (1983).