Electric-field-induced twist and bend Freedericksz transitions in nematic liquid crystals

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(Received 21 July 1988)

By considering the Frank free energy, we show that the electric-field-induced twist and bend Freedericksz transitions can be first order. This agrees with the prediction of Arakelyan, Karayan, and Chilingaryan [Sov. Phys.–Dokl. **29**, 202 (1984)] from Landau theory for the bend geometry. We have carried out dielectric measurements on the liquid-crystal 5CB (4-cyano-4'-*n*-pentylbiphenyl) that provide the first experimental evidence that these transitions are first order. The effects of a competing magnetic field on the threshold voltage and on the width of the transition region are compared with theory. In the presence of a competing magnetic field, the bend transition in 5CB is to a modulated rather than a uniform phase.

INTRODUCTION

A liquid-crystal sample uniformly aligned between two parallel plane boundaries can undergo a transition to an elastically deformed state under the influence of external electric or magnetic fields. This transition, first observed by Freedericksz and Zolina[1] has been the subject of considerable study.

Two different sample geometries may be distinguished. If the direction of molecular alignment at the boundaries is constrained to be perpendicular to the boundary planes, the initial deformation caused by the applied field is a bend. If the alignment is parallel, the initial deformation can be either a splay or a twist, depending on whether the field is applied normal or parallel to the boundaries. In the case of a single static field applied either parallel or perpendicular to the boundaries, theory predicts all magnetic-field-induced transitions[2] and the electric-field-induced splay transition[3] to be second order. The electric-field-induced bend and twist transitions require an unusual experimental geometry associated with applying an electric field parallel to the boundary planes, and have not received much attention. Using a Landau approach, Arakelyan, Karayan, and Chilingaryan[4] have shown that the electric-field-induced bend transition is expected to be first order; their results do not appear to be widely known.

Other situations are known for which the Freedericksz transition is first order. For static fields, first-order transitions have been predicted to occur in systems with large conductivity anisotropy[5] and in systems where feedback is present.[6] Transitions may be first order if the alignment at the boundary surfaces is tilted.[7,8] Several authors[9–11] have suggested that the optical-field-induced Freedericksz transition could be first order in systems with specific material properties or if an additional external field is present.[12,13] These latter predictions have been confirmed experimentally.[14]

We have investigated the electric-field-induced twist and bend transitions in the presence of an external magnetic field by considering exact solutions which minimize the free energy. In addition, we have used a simple Landau expansion to predict qualitatively the behavior of the system, and to obtain simple analytic expressions relating the characteristics of the transition to material properties.

We have carried out dielectric measurements on samples of 5CB (4-cyano-4'-*n*-pentylbiphenyl) in the bend and twist geometry. We have studied the effects of an additional competing field and we compare the results of these measurements with theory. We have also observed the novel phenomenon that when the bend transition is induced by an electric field in the presence of a competing magnetic field, the transition is to a phase with a periodic modulation.

THEORY

We first consider the case of the bend transition. The sample geometry is shown in Fig. 1. Initial alignment is perpendicular to the glass plates. One field is applied parallel to the plates, in the $\hat{\mathbf{x}}$ direction, and the competing one along $\hat{\mathbf{z}}$, the direction of initial alignment. In a sample where the dielectric and magnetic susceptibility anisotropies are both positive, the field parallel to the plates induces the transition.

The direction of average orientation of the symmetry axes of the molecules in a liquid crystal is described by the director field $\hat{\mathbf{n}}$. The free-energy density is given by[2]

$$f=\tfrac{1}{2}[K_1(\nabla\cdot\hat{\mathbf{n}})^2+K_2(\hat{\mathbf{n}}\cdot\nabla\times\hat{\mathbf{n}})^2+K_3(\hat{\mathbf{n}}\times\nabla\times\hat{\mathbf{n}})^2-\mathbf{D}\cdot\mathbf{E}-\mathbf{B}\cdot\mathbf{H}] \ , \tag{1}$$

where $\mathbf{K}_1$, $\mathbf{K}_2$, and $\mathbf{K}_3$ are the splay, twist, and bend elastic constants, $\mathbf{E}$ and $\mathbf{D}$ are the electric field and displacement, and $\mathbf{H}$ and $\mathbf{B}$ are the magnetic field and induction. If the distortion is in the plane defined by the magnetic and electric fields, the director field may be written

$$\hat{\mathbf{n}}=(\sin\theta,0,\cos\theta) \ , \tag{2}$$

where $\theta=\theta(z)$ is the angle between the director and the direction of alignment at the boundaries. The cell area in the x-y plane is A, and the thickness (along $\hat{z}$) is l. At the center of the cell ($z=l/2$) the deformation angle is a

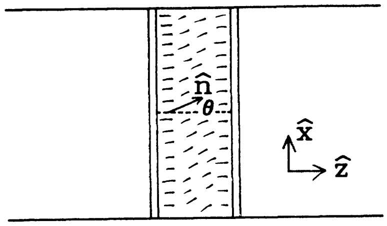

FIG. 1. Cell geometry for the bend transition. The glass walls are treated to give homeotropic alignment (along $\hat{\mathbf{z}}$) of the director. For the electric-field-induced case, magnetic field $\mathbf{B}$ is applied along $\hat{\mathbf{z}}$, voltage V is applied across the electrodes which are parallel to $\hat{\mathbf{z}}$.

maximum ($\theta = \theta_m$) and here

$$\theta' = \frac{\partial \theta}{\partial z} = 0 \ . \tag{3}$$

The Frank free energy due to elastic deformation is, in units of $AK_3/2l$,

$$F_F = l \int_0^l \left[1 - \kappa \sin^2\theta \right] \theta'^2 \, dz \ , \tag{4}$$

where $\kappa = 1 - K_1/K_3$.

If the magnetic field is along $\hat{\mathbf{x}}$ and the electric field is along $\hat{\mathbf{z}}$ then, following Ref. 3, the electric and magnetic contributions to the free energy for the magnetic-field-induced bend deformation are

$$F_{em} = -\frac{\epsilon_0 \epsilon_\parallel V^2}{K_3 \int_0^1 \frac{d(z/l)}{1 - u \sin^2\theta}} - \frac{\mu_0 \chi_a l^2}{K_3} H^2 \int_0^1 \sin^2\theta \, d(z/l) \ , \tag{5}$$

while if the applied electric field is along $\hat{\mathbf{x}}$ and the magnetic field is along $\hat{\mathbf{z}}$ then the free energy for the electric-field-induced bend deformation is[4]

$$F_{em} = -\frac{\epsilon_0 \epsilon_\perp V^2}{K_3} \left[\frac{l}{d} \right]^2 \int_0^1 \frac{d(z/l)}{1 - u \sin^2\theta} - \frac{\mu_0 \chi_a l^2}{K_3} H^2 \int_0^1 \cos^2\theta \, d(z/l) \ , \tag{6}$$

where V is the voltage applied to the cell, $u = 1 - \epsilon_\perp/\epsilon_\parallel$, $\epsilon_\perp$ and $\epsilon_\parallel$ are the principal values of the dielectric tensor, χ_a is the anisotropy of the diamagnetic susceptibility, and d is the width of the cell. We note that in the expression for the electric field contribution to the free energy in Eq. (6), higher-order terms in l/d have been omitted.

The free-energy expressions of Eqs. (4) and (6) also describe the electric-field-induced twist deformation, where the initial alignment is along $\hat{\mathbf{x}}$, if we set $\kappa = 0$ and replace K_3 by K_2.

First, we investigate the qualitative behavior of the system by assuming a solution of the form

$$\theta = \theta_m \sin \left[\frac{\pi z}{l} \right] \tag{7}$$

and expanding the free energy in terms of the order parameter θ_m. This gives

$$F = a\theta_m^2 + \frac{b}{2}\theta_m^4 + \frac{c}{3}\theta_m^6 \ , \tag{8}$$

where the coefficients for the magnetic- and electric-field-induced bend and electric-field-induced twist deformations are given explicitly in Table I. The transition is first order for $b < 0$. Using the material parameters for 5CB,[15] we find that b is positive and the transition is second order if it is induced by a magnetic field. When the transition is induced by an electric field, b is negative and the transition is first order for both twist and bend deformations. The tricritical point at $b = 0$ might be accessible in materials with smaller dielectric anisotropy. For 5CB, the value of the order parameter at the transition, given by

$$\theta_m = \left[-\frac{3b}{4c} \right]^{1/2} \tag{9}$$

is large, suggesting that the transition is strongly first order and that the Landau theory may not provide a good description.

We therefore pursue an exact solution for the electric-field-induced twist and bend deformations by solving the Euler-Lagrange equation that results from minimizing the free energy given by Eqs. (4) and (6). At the center of the cell, this gives

TABLE I. Coefficients of the Landau expansion of the free energies for various geometries.

Configuration	a	b	c
Magnetic-field-induced bend $e = \epsilon_0 \epsilon_\parallel u V^2/K_3$ $h = \chi_a B^2 l^2/(\mu_0 K_3)$	$1-(h-e)/\pi^2$	$\frac{1}{2}[-\kappa+(h-e+eu)/\pi^2]$	$\frac{1}{8}[\kappa+(-\frac{2}{3}h+\frac{3}{4}eu^2 - eu+\frac{1}{6}e)/\pi^2]$
Electric-field-induced bend $e = \epsilon_0 \epsilon_\perp u V^2 (l/d)^2/K_3$ $h = \chi_a B^2 l^2/(\mu_0 K_3)$	$1-(e-h)/\pi^2$	$\frac{1}{2}[-\kappa-(h-e+3eu)/\pi^2]$	$\frac{1}{8}[\kappa+(\frac{2}{3}h-15eu^2 +10eu-\frac{2}{3}e)/\pi^2]$
Electric-field-induced twist $e = \epsilon_0 \epsilon_\perp u V^2 (l/d)^2/K_2$ $h = \chi_a B^2 l^2/(\mu_0 K_2)$	$1-(e-h)/\pi^2$	$-\frac{1}{2}(h-e+3eu)/\pi^2]$	$\frac{1}{8}(\frac{2}{3}h-15eu^2 +10eu-\frac{2}{3}e)/\pi^2]$

$$\frac{l}{2}=\int_0^{\theta_m}\left[\frac{(1-\kappa\sin^2\theta)(1-u\sin^2\theta)(1-u\sin^2\theta_m)}{[e-h(1-u\sin^2\theta)(1-u\sin^2\theta_m)](\sin^2\theta_m-\sin^2\theta)}\right]^{1/2}d\theta\ , \tag{10}$$

which can be solved for θ_m at a given voltage and magnetic field. Here

$$e=\frac{\epsilon_0\epsilon_\perp u l^2V^2}{K_i d^2}\quad\text{and}\quad h=\frac{\chi_a l^2\mathbf{B}^2}{\mu_0 K_i}\ , \tag{11}$$

where $i=2$ and $\kappa=0$ for twist, and $i=3$ and $\kappa=1-K_1/K_3$ for bend deformations. The free energy is then given by

$$F(\theta_m)=2\int_0^{\theta_m}d\theta\left[(1-\kappa\sin^2\theta)\theta'-\frac{[e+h\cos^2\theta(1-u\sin^2\theta)]}{(1-u\sin^2\theta)\theta'}\right] \tag{12}$$

and the capacitance is

$$C(\theta_m)=2C_0\int_0^{\theta_m}\frac{d\theta}{(1-u\sin^2)\theta'}\ , \tag{13}$$

where C_0 is the cell capacitance when $\theta_m=0$ and

$$\theta'=\left[\frac{[e-h(1-u\sin^2\theta)(1-u\sin^2\theta_m)](\sin^2\theta_m-\sin^2\theta)}{(1-\kappa\sin^2\theta)(1-u\sin^2\theta)(1-u\sin^2\theta_m)}\right]^{1/2}\ . \tag{14}$$

The integrals in Eqs. (10), (12), and (13) are badly behaved in the limit as $\theta_m\to\pi/2$; we have therefore expressed them in terms of elliptic integrals as outlined in Ref. 16. Since the transition is first order, Eq. (10) is satisfied by two values of θ_m for voltages in the range $V_{\min}<V<V_{\max}$. We used an iterative numerical method to solve Eq. (10) for e, given θ_m and h, and then calculated the corresponding free energy and capacitance. For the bend transition, the capacitance, order parameter θ_m, and free energy as functions of $1/e$ are shown in Fig. 2, while the e-h phase diagram is shown in Fig. 3. The results for the twist transition are similar, although for 5CB this transition is less strongly first order. In both cases, agreement between exact results and the predictions of the Landau expansion are surprisingly close.

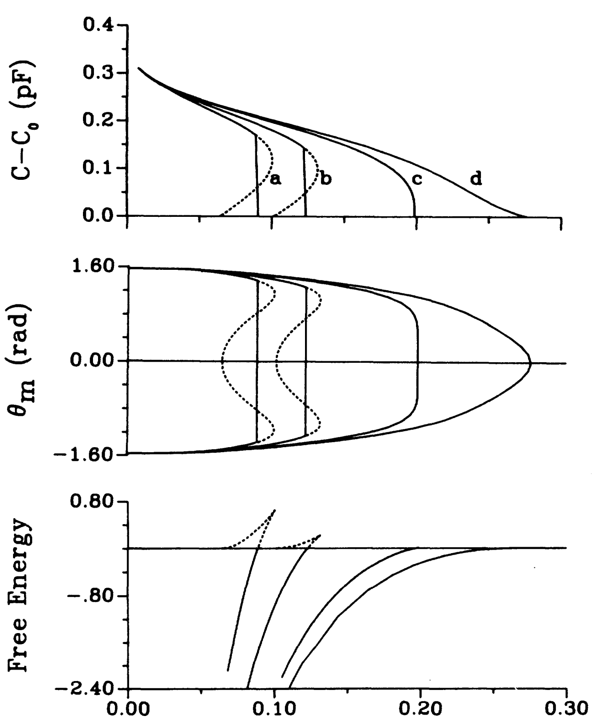

FIG. 2. Capacitance, order parameter, and dimensionless free energy for the electric-field-induced bend transition as a function of $1/e$ for (a) $h=5.66$, (b) $h=0.0$, (c) $h=-4.83$, and (d) $h=-6.24$; $e=\epsilon_0\epsilon_\perp uV^2(l/d)^2/K_3$; $h=\chi_a\mathbf{B}^2l^2/(\mu_0K_3)$.

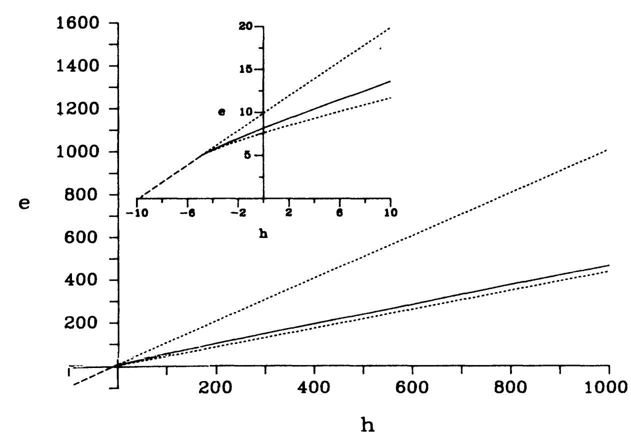

FIG. 3. Phase diagram for the electric-field-induced bend transition, calculated from theory for $u=0.56$, $\kappa=0.14$. Negative values of h correspond to negative diamagnetic anisotropy. The solid line indicates first-order transitions, the dashed line indicates second-order transitions, and the dotted lines indicate the limits of the spinodal region. The inset shows detail near the tricritical point which occurs at $h=-4.83$ and $e=5.04$.

EXPERIMENT

Two types of cells using different methods of surface treatment were constructed. In order to apply an electric field parallel to the boundary planes, the first type consists of two slender, rectangular pieces of glass (30.0 mm×3.3 mm×1.0 mm) separated by 0.5 mm and sandwiched between two stainless-steel electrodes (30.0 mm×12.5 mm×0.5 mm) so that the electrodes are separated by 3.3 mm. In order to enable the application of an electric field perpendicular to the boundary planes, the second type consists of two pieces of indium tin oxide (ITO) coated glass separated by two 0.5 mm teflon spacers 3.5 mm apart. To induce alignment perpendicular to the glass plates, the glass was treated with a silane compound [Dow-Corning X1-6136 3-(trimethoxysilyl) propyldimethyloctadecyl ammonium chloride]. To induce director alignment parallel to the glass, the plates were coated with a solution of poly(vinyl formal) and chloroform and were buffed when dry.[17] The liquid crystal used in the experiments was 5CB synthesized by G. S. Bates at the Department of Chemistry, University of British Columbia. The cells were placed in a thermostatted housing with temperature control of ±1 mK mounted between the poles of an electromagnet.

The capacitance was measured with a GenRad 1615-A capacitance bridge using an HP 3312 function generator amplified by a Kepco BOP 72-5 operational amplifier as an external generator. A lock-in amplifier (EG&G 5102) was used to detect the null. Measurements were made at 2 kHz, with sample voltages ranging from 0–60 V rms applied via the ratio transformer of the bridge. In the case of the electric field induced bend transition, the sample approached equilibrium slowly at voltages near the critical voltage. Here data points were taken once an hour, 0.25 V apart. Samples undergoing magnetic-field-induced bend approached equilibrium much faster. Here, and in the electric-field-induced twist, measurements were made every 10 min.

Our results for the magnetic-field-induced bend show no evidence of hysteresis, within experimental error, in agreement with the predicted second-order nature of the transition.

Figure 4 shows experimental results for the electric-field-induced bend transition in the presence of a competing 0.12-T magnetic field. These are typical results for this geometry, showing clear evidence of hysteresis. We estimate $V_{\rm min}$ and $V_{\rm max}$ from the voltages where the derivative of the capacitance with respect to voltage is a

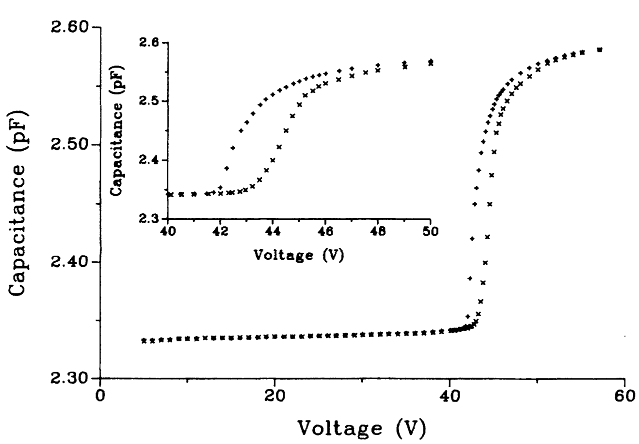

FIG. 4. Experimental results for electric-field-induced bend transition showing hysteresis for $B=0.12$ T and $T=33.4\,^{\circ}$C. The inset shows detail of the hysteresis.

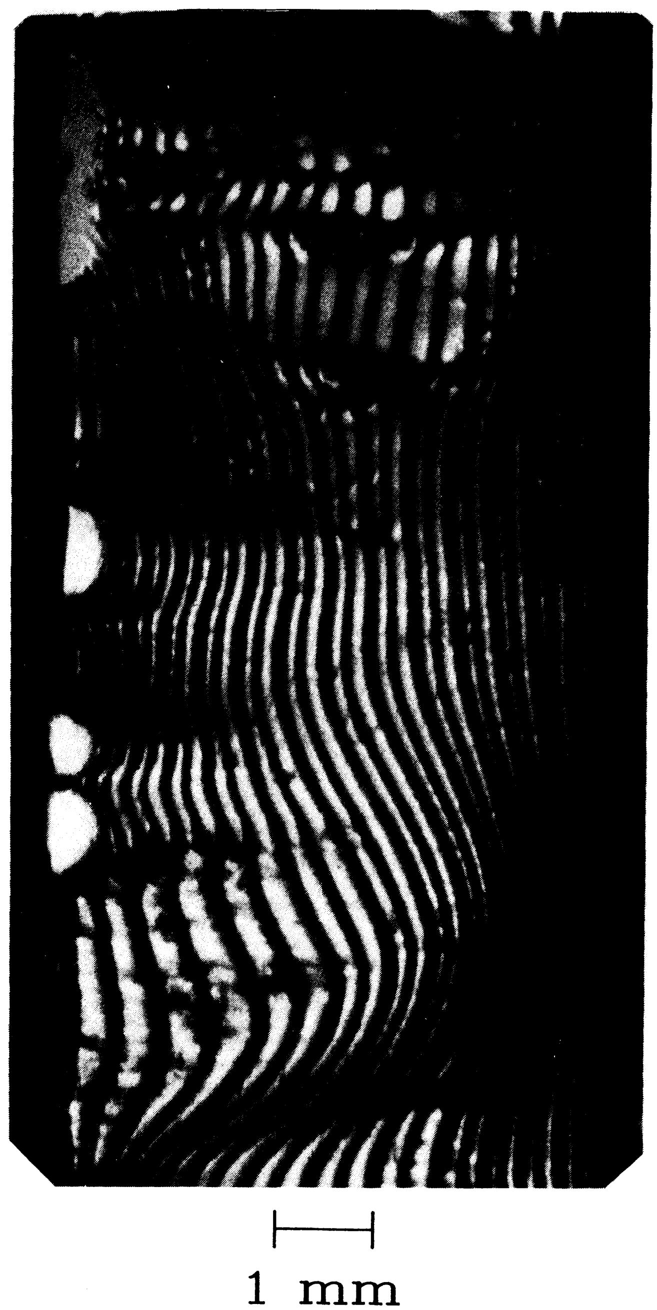

FIG. 5. Periodic modulations observed at the electric-field-induced bend transition viewed along the direction of the magnetic field. The stripes are parallel to the electrodes and perpendicular to the magnetic field.

TABLE II. Comparison of theoretical and experimental data for electric-field-induced bend and twist Freedericksz transitions.

Transition	Temperature (°C)	B (T)	Theory V_{th}	Theory ΔV	Experiment V_{th}	Experiment ΔV
Bend	33.4	0	6.14 V	0.50 V	5.1 V	0.5 V
		0.12	46.9	19	43.5	1.8
Twist	22.5	0	6.62	1.39	7.8	0.5
		0.12	57.1	38.5	50	0.5

maximum, and we estimate the threshold voltage V_{th} by the average of these. Table II shows the experimental values of the threshold voltage V_{th} and the transition width ΔV together with theoretical values calculated using the material parameters of 5CB from sources quoted in Ref. 15. There is good agreement between measured and predicted values in all cases except that the experimentally observed width of the transition at nonzero magnetic field is significantly less than predicted by theory. We have no ready explanation for this discrepancy. It is worth noting that the theoretical results are sensitively dependent on the form of the electric field contribution to the free energy (for example, if the z dependence of the potential is ignored, the transition is predicted to be second order). In our system, $l/d=0.15$, and higher-order terms in Eq. (6) may play a significant role.

We have observed the unexpected result that in the case of the electric-field-induced bend transition when the competing magnetic field is nonzero, the transition is not to a uniform but rather to a modulated phase. Figure 5 shows this modulated phase, viewed along the magnetic field direction ($\hat{\mathbf{z}}$) with a single polarizer parallel to the direction of the electric field ($\hat{\mathbf{x}}$). The wave vector of the stripes is primarily in the direction of the electric field, and we have observed wavelengths ranging from 0.2 l to 1.1 l in a variety of cells under different conditions. For voltages slightly above the threshold ($\sim 3-5\%$) the stripes form slowly (~ 10 min) and persist indefinitely. If the voltage is increased, the stripes disappear. In some respects, this pattern resembles that of Williams domains;[2] however, we have found no evidence of electrohydrodynamic instabilities. We shall present detailed results of our studies of this phenomenon elsewhere.

Capacitance measurements of the electric field induced twist transition resemble the results for the bend transition shown in Fig. 4. Again, hysteresis is clearly evident, indicating that the transition is first order. Measured and calculated values of the threshold voltage and the width of the transition are shown in Table II. As in the bend case, we find that the theory overestimates the width of the transition. In this geometry, there is no evidence of a modulated phase.

We have also measured the intensity of light transmitted by the sample between crossed polarizers.[18] This provided another method of monitoring the transitions. The threshold voltages were found to be in good agreement with the phase diagram shown in Fig. 2; details of these measurements will be published elsewhere.

CONCLUSIONS

We have studied the electric-field-induced bend and twist Freedericksz transitions in the nematic liquid crystal 5CB. We carried out exact calculations and Landau expansions of the free energy; both methods predict these transitions to be first order. We have carried out dielectric measurements which show clear evidence of hysteresis. Furthermore, the threshold voltages and the width of the transitions in the absence of a competing magnetic field are in good agreement with theory. In the case of the bend geometry, the transition is to a modulated phase; no such modulations are observed in the twist geometry.

Note added in proof. Additional measurements of the electric-field-induced twist transition for 5CB indicate that the width of the hysteresis in the dielectric response of the cell decreases as the sweep rate of the applied voltage is decreased. The hysteresis width nontheless remains finite at the longest equilibriation times (4 h) allowed by the stability of our system. Regarding the stability of the modulated phase, recent calculations show that, for certain values of physical parameters, the free energy is reduced by a static modulation of the director in the x-z plane.[19]

ACKNOWLEDGMENTS

Financial support from the Liquid Crystal Institute and the Natural Sciences and Engineering Research Council of Canada, and useful conversations with D. W. Allender, B. Bergersen, D. A. Dunmur, Michael A. Lee, H. L. Ong, and R. G. Petschek are gratefully acknowledged.

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[1] V. Freedericksz and V. Zolina, Trans. Faraday Soc. **29**, 919 (1933).

[2] P. G. de Gennes, *The Physics of Liquid Crystals* (Oxford University Press, Oxford, 1974).

[3] H. J. Deuling, Mol. Cryst. Liq. Cryst. **19**, 123 (1972).

[4] S. M. Arakelyan, A. S. Karayan, and Yu. S. Chilingaryan,

Dokl. Akad. Nauk. SSSR **275**, 52 (1984) [Sov. Phys.–Dokl. **29**, 202 (1984)].

[5]H. J. Deuling and W. Helfrich, Appl. Phys. Lett. **25**, 129 (1974).

[6]Peng-ye Wang, Hong-jun Zhang, and Jian-hua Dai, Opt. Lett. **12**, 654 (1987).

[7]T. Motooka and A. Fukuhara, J. Appl. Phys. **50**, 3322 (1979).

[8]L. G. Fel and G. E. Lasene, Kristallografiya **31**, 726 (1984) [Sov. Phys.—Crystallogr. **31**, 428 (1986)].

[9]B. Ya. Zel'dovich, N. V. Tabiryan, and Yu. S. Chilingaryan, Zh. Eksp. Teor. Fiz. **81**, 72 (1981) [Sov. Phys.—JETP **54**, 32 (1981)].

[10]S. D. Durbin, S. M. Arakelian, and Y. R. Shen, Phys. Rev. Lett. **47**, 1411 (1981).

[11]H. P. Ong, Phys. Rev. A **28**, 2393 (1983).

[12]S. R. Nersisyan and N. V. Tabiryan, Mol. Cryst. Liq. Cryst. **116**, 111 (1984).

[13]H. L. Ong, Phys. Rev. A **31**, 3450 (1985).

[14]A. J. Karn, S. M. Arakelian, Y. R. Shen, and H. L. Ong, Phys. Rev. Lett. **57**, 448 (1986).

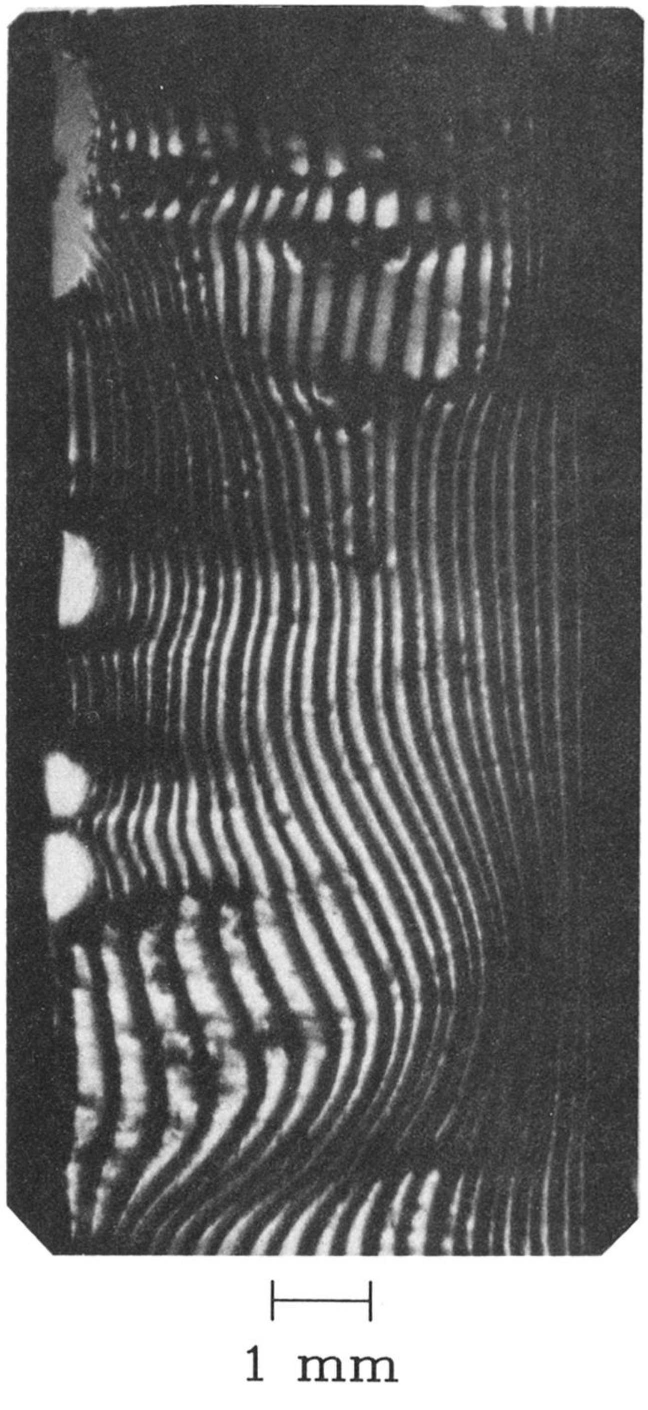
[15]For 5 CB at 32 °C, $K_1/K_3=0.14$ [J. D. Bunning, T. E. Faber, and P. L. Sherrel, J. Phys. (Paris) **42**, 1175 (1981), $\epsilon_{\parallel}=18.8$, $\epsilon_{\perp}=8.2$ (D. A. Dunmur), and $\chi_a=1.01\times10^{-6}$ (mks) [B. J. Frisken, J. F. Carolan, P. Palffy-Muhoray, J. A. A. J. Perenboom, Mol. Cryst. Liq. Cryst. Lett. **3**, 57 (1986)].

[16]Stephen W. Morris, P. Palffy-Muhoray, and D. A. Balzarini, Mol. Cryst. Liq. Cryst. **193**, 263 (1986).

[17]J. T. Gleeson, M. Sc. thesis, University of British Columbia, 1988.

[18]B. J. Frisken and P. Palffy-Muhoray, Liq. Cryst. (to be published).

[19]D. W. Allender, B. J. Frisken, and P. Palffy-Muhoray, Liq. Cryst. (to be published).



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