Temperature- and electric-field-induced inverse Freedericksz transition in a nematogen with weak surface anchoring

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We report electric field dependence of the anchoring transition in a mesogen on cooling in a cell with perfluoropolymer treated surfaces. Below a crossover voltage V_{co} the transition is *discontinuous* between planar and homeotropic alignments, and as the temperature is lowered, the transition temperature *decreases quadratically* with the *field*. Above V_{co} the transition is *continuous* between planar and tilted alignments, the transition temperature decreasing essentially *linearly* with the *rms field*. We develop a simple model to account for these results and argue that the higher field regime corresponds to a temperature driven *inverse Freedericksz transition* in which the director orientation starts tilting at the weakly anchored surfaces while the tilt angle remains zero at the midplane of the cell.

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I. INTRODUCTION

Nematic liquid crystals have an orientational order which is *apolar* in nature [1] and described by a dimensionless unit vector $\mathbf{n}(\mathbf{r})$ called the director. Spatial gradients in $\mathbf{n}(\mathbf{r})$ cost a very small curvature elastic energy, making the nematic a prime example of a soft material. The apolar director couples to an external electric field through the dielectric anisotropy $\Delta\epsilon=\epsilon_{\parallel}-\epsilon_{\perp}$ of the material, the subscripts indicating directions with reference to $\mathbf{n}$. A classic experiment on liquid crystals concerns the Freedericksz transition, in which a material with positive $\Delta\epsilon$ is taken between two indium tin oxide (ITO) coated conducting glass plates, whose surfaces have been treated to get a *strong planar anchoring* of the director, and separated by a gap d along the z direction. The Rapini-Papoular [2] form of the anchoring energy per unit surface area is given by

$$F_s = \frac{1}{2}A \sin^2 \psi_s, \tag{1}$$

where ψ_s is the tilt angle of $\mathbf{n}$ with respect to the surface and the positive coefficient A is the anchoring strength. The anchoring energy is "strong" if the extrapolation length $\lambda=K_{11}/A$ is of molecular dimensions, K_{11} being the splay elastic constant [1]. If an electric field E is applied between the ITO plates, the dielectric energy is lowered by a tilting of the director. As $\psi_s=0$, the tilt angle can be expected to acquire a maximum value ψ_M at the center of the cell with $z=d/2$, and the resulting curvature distortion of $\mathbf{n}(\mathbf{z})$ costs an elastic energy. Indeed the distortion occurs only beyond a threshold voltage, around which the bulk free-energy density is given by

$$g_2(z) = \frac{1}{2}K_{11}\left(\frac{d\psi(z)}{dz}\right)^2 - \frac{\epsilon_0}{2}\Delta\epsilon E^2 \sin^2 \psi(z). \tag{2}$$

The corresponding Euler-Lagrange (EL) equation can be solved in the usual manner [3] by noting that $d\psi(z)/dz=0$ at the center of the sample $(z=d/2)$. The threshold voltage is given by [3] $U_{th}=\pi\sqrt{\frac{K_{11}}{\epsilon_0\Delta\epsilon}}$, beyond which the cell taken between appropriately placed crossed polarizers exhibits an electro-optic effect. Analogous electro-optic effects in various geometries are exploited in the ubiquitous liquid-crystal displays [4].

If the anchoring is not strong in the sense mentioned above, the threshold voltage is reduced [5] and the nonuniform $\psi(z)$ profile at any finite value of the electric field can be calculated by solving the EL equation and explicitly taking into account the surface torque balance conditions at both $z=0$ and d. Usually the anchoring strength A decreases with temperature T in the nematic range, and $A(T)$ depends on both the surface treatment and the chemical composition of the nematic [6,7]. Some surface treatments give rise to a nonzero pretilt angle ψ_t, in which case there is no true threshold. ψ_t can also vary with temperature, and in general the right-hand side of Eq. (1) should be replaced by $A(T)\sin^2[\psi_s-\psi_t(T)]/2$.

We recently reported that the mesogen 4-butyl-4-heptyl-bicyclohexyl-4-carbonitrile (CCN-47), taken on glass plates treated with poly[perfluoro(4-vinyloxy-1-butene)] also known as CYTOP, undergoes an abrupt *anchoring transition* (ATr) from planar $(\psi_t=0)$ to homeotropic $(\psi_t=\pi/2$ rad) alignment as the temperature is lowered to 48 °C [8] in the nematic range. In the present paper we study this transition under varying electric fields to find that the character of ATr remains abrupt below a crossover voltage of $\sim 0.5V$, while above that voltage ATr changes to a temperature driven continuous transition. We develop a simple model to account for

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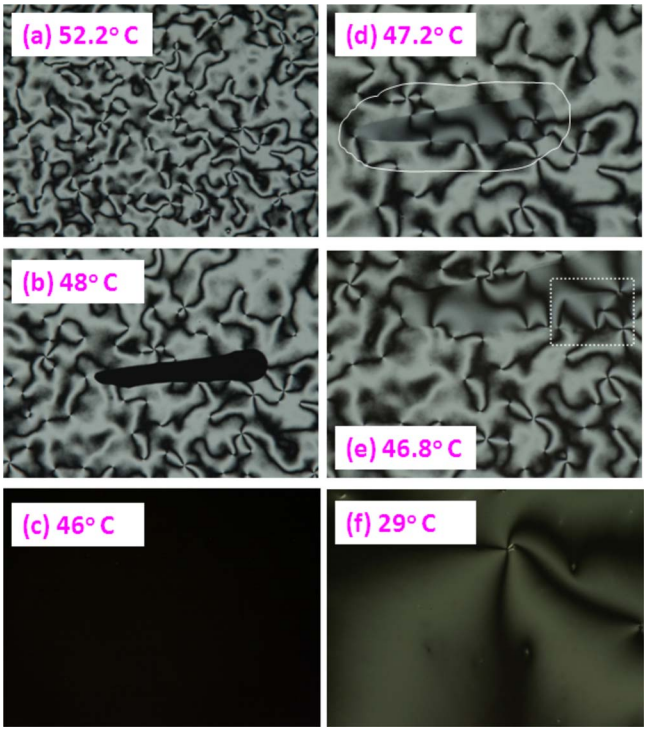

FIG. 1. (Color online) Photomicrographs of the textures around the anchoring transition temperature in CCN-47 between crossed polarizers at (a) 52.2, (b) 48, and (c) 46 °C, all under zero field. Textures in the same region under an electric field 0.29 V/μm, as photographed at (d) 47.2, (e) 46.8, and (f) 29 °C. White dotted lines in Fig. 1(d) enclose a domain with tilted director. Cell thickness 5.2 μm.

these results and argue that the higher voltage regime corresponds to an inverse Freedericksz transition.

II. EXPERIMENT

CYTOP is spin coated on ITO-coated glass plates which are used to construct the liquid-crystal cells. Typical thickness of the cells used in the experiment is ~5.2 μm. CCN-47 is filled in the cell in the isotropic phase by capillary action. CCN-47 exhibits the following sequence of phase transitions: Cr 25.6 °C Sm- *A* 28.2 °C *N* 57.3 °C I, and has a large negative dielectric anisotropy ($\Delta\epsilon$=−5.7 at 30 °C). The textures are observed using a polarizing optical microscope (Olympus BX-51). The temperature of the sample is controlled by a Mettler hotstage to an accuracy of 0.1 °C. A signal generator is used to apply sinusoidal voltages at a frequency of 3.11 KHz.

III. RESULTS AND DISCUSSION

We first show the textures observed under a polarizing microscope in the absence of an electric field. The compound exhibits a planar texture as it is cooled below the isotropic to nematic transition temperature. At 52.2 °C mostly half-strength disclinations are observed [Fig. 1(a)]. The physical inferences from the occurrence of the two-brush defects are twofold. First the director is apolar, i.e., **n** and **−n** are physically equivalent, and second the director is in the plane parallel to the plates, forming line defects [9]. As the temperature is lowered dark domains are nucleated at about 48 °C in a few locations of the sample and spread with time [Fig. 1(b)] even if the temperature is held fixed. In the dark domains the director is normal to the substrate, i.e., the alignment is homeotropic. Thus at the ATr the director rotates by 90°, from planar to homeotropic, discontinuously. On further cooling to about 46 °C, the entire texture turns completely dark [Fig. 1(c)]. A careful observation of the sample shows that the medium is uniaxial. The details of the discontinuous anchoring transition in the absence of a field have already been reported [8]. Further studies on the sample are carried out by applying different electric fields and observing the evolution of the textures. Initially the sample is heated to the isotropic phase and slowly cooled (at 0.2 °C/min) in the presence of the desired ac field (at 3.11 KHz). Interestingly, after the transition from isotropic to nematic phase, the appearance of the texture is essentially the same as in the zero-field case. The half-strength and one-strength defects appear at the same locations in the sample as in the field free run. For low fields (≤0.1 V/μm) homeotropic domains also nucleated at the *same locations* as in the zero-field case but at field-dependent *lower* temperatures [Fig. 1(d)]. The growth of any given domain is also similar to that in the field free sample. The ATr occurs with the formation of dark domains (i.e., discontinuously) up to the field of ~0.1 V/μm when the ATr temperature is 47.2 °C. Beyond this field the ATr occurs with the appearance of regions with *reduced birefringence*, instead of dark domains, but located at the same places. Textures exhibited by the sample which undergoes a continuous ATr under the field are also shown in Figs. 1(d)–1(f). As shown in Fig. 1(d), a domain with lower birefringence appears as the temperature is reduced under an electric field of 0.29 V/μm. This domain grows in size on further cooling [Fig. 1(e)]. Curiously, most of the defects are expelled from the growing domains such that their nuclei collect at the interface between the domains and the surrounding sample which continues to have a planar alignment. On very rare occasions, a half-strength defect is trapped inside the domain, and a relatively thin wall connects such a defect to the edge of the domain. These observations indicate that the director inside the domain is titled with respect to the plane of the sample [Fig. 1(e)]. The tilted director field inside the domain can merge with the planar director field outside the domains only if the 1/2 strength defects lie on the boundaries of the domains. If the defect is inside the domain, a wall across which the tilt angle changes sign has to lie between the defect and the boundary of the domain [Figs. 1(e) and 2(c)]. On further cooling the texture finally becomes very dark but for a few one-strength defects [Fig. 1(f)] suggesting that the director is now almost vertical with respect to the substrates.

Further careful observations across the periphery of the tilted domain in Fig. 1(e) show that the contrast of the texture changes gradually, indicating that the tilt angle of the director changes continuously from planar to tilted across the periphery. The side and the top views of the director orientation across the periphery are shown schematically in Figs. 2(a) and 2(b), respectively. The reason for choosing the spe-

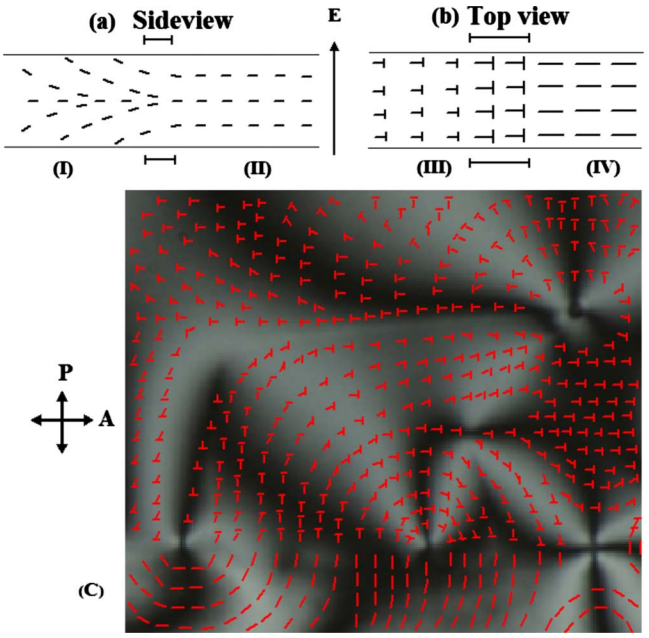

FIG. 2. (Color online) Schematic drawings of (a) the side view and (b) the top view (say in the upper half of the cell) of the director orientation across boundary between the untilted and tilted regions. In (b) the length of the line is a measure of the projection of the director in the plane of the plate. Regions in (I) and (III) represent tilted and (II) and (IV) represent planar director orientations. (c) Part of the texture taken from Fig. 1(e) including a half-defect connected by a inversion wall and the superimposed director orientations across the boundary between the regions with tilted and planar alignments of the director.

cific director profile shown in Fig. 2(a) will be clear later. The detailed director orientation is superimposed on the texture in Fig. 2(c) which includes a boundary between tilted and non tilted domains and a half-defect connected with an inversion line inside the tilted domain as well.

The variation in anchoring transition temperature, i.e., the temperature at which the nucleation of the domain starts at some particular location, is measured as a function of the applied field from the microscope observation and is shown in Fig. 3. The anchoring transition temperature decreases with increasing electric field with a change in slope at ~ 0.1 V/μm, corresponding to the crossover from discontinuous to continuous ATr. It may be mentioned that this is not a thermodynamic phase transition as the phase remains nematic before and after the transition; instead it is an anchoring transition bringing about a change in the director orientation. The lowering of the anchoring transition temperature on the application of the field is a result of the competition between the surface anchoring and dielectric response to the electric field. At a temperature lower than 48 °C, the surface interaction favors a homeotropic alignment, whereas the electric field favors a planar alignment as the dielectric anisotropy of the material is negative, whose magnitude increases with decreasing temperature. We develop a theoretical model to account for the above observations by assuming that, in the absence of an electric field, the anchoring energy per unit area can be expressed in the form

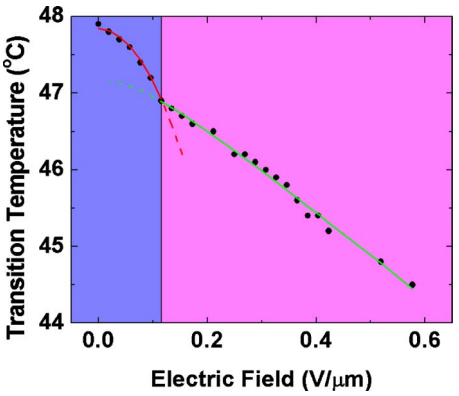

FIG. 3. (Color online) Variation in anchoring transition temperature with applied electric field. Continuous lines are best fit to the theoretical Eqs. (5) and (13) with fit parameter $u=1.6\times10^{-6}$ J/m^2 K. The type 2 and type 1 transitions, shown by the dashed lines are superceded by transitions of the other type occurring at higher temperatures.

$$F_s = \frac{u}{2}(T - T_A)\sin^2\psi_s, \tag{3}$$

where $T_A=48$ °C and u is positive. This means that the anchoring strength favoring planar alignment above T_A weakens rapidly as that temperature is approached from above, and changes sign at T_A to favor homeotropic anchoring whose strength rapidly increases as the temperature is lowered. A possible origin of the abrupt anchoring transition is the build up of smectic-A type short-range order near the CYTOP coated surfaces at temperatures lower than T_A, which favors the homeotropic alignment. An external electric field favors the tilt angle ψ to be zero both in the bulk and the surfaces, as the dielectric anisotropy $\Delta\epsilon$ is negative. When the sample is cooled under the action of an electric field, four possible director profiles are possible below T_A, which arise from the mutually antagonistic preferred orientations arising from the surface anchoring and dielectric energy density. This can in turn give rise to three different types of anchoring transitions. In type 1 transition, the director can have a *uniform* tilt angle $\psi(z)=\psi_s$ independent of the position z even below the transition temperature. The curvature elastic energy is zero, and the total energy per unit area of the cell of thickness d is given by

$$F_1(T) = -\frac{\epsilon_0}{2}(\epsilon_\parallel \sin^2\psi + \epsilon_\perp \cos^2\psi)E^2 d + u(T - T_A)\sin^2\psi,$$

$$F_1(T) = \left[u(T - T_A) - \frac{\epsilon_0}{2}\Delta\epsilon E^2 d\right]\sin^2\psi - \frac{\epsilon_0}{2}\epsilon_\perp E^2 d. \tag{4}$$

As $\Delta\epsilon$ is negative, the term in the square brackets of Eq. (4) changes sign at the anchoring transition temperature,

$$T_{1at} = T_A - \frac{\epsilon_0}{2}|\Delta\epsilon|\frac{E^2 d}{u}. \tag{5}$$

At temperatures *above* T_{1at} the term in the square brackets of Eq. (4) will have a *positive* sign, and the energy $F_1(T)$ is

(a) **(b)**

FIG. 4. Schematic diagram illustrating the director orientations near the two surfaces and the midplane of the cell below the anchoring transition of type 2 corresponding to (a) the even and (b) the odd solutions of $\psi(z)$.

minimized by $\psi=0$, i.e., by a uniform *planar* alignment of the director throughout the cell. Below T_{1at} the term becomes *negative*, and the total energy is minimized by $\psi=\frac{\pi}{2}$, i.e., the director adopts a uniform *homeotropic* alignment throughout the cell. The anchoring transition is very similar to that in the field-free sample, and ignoring the temperature dependence of $\Delta\epsilon$, the transition point T_{1at} decreases *quadratically* with the applied field E, from T_A when $E=0$. The fitted line as shown in Fig. 3 takes into account the temperature dependence of $\Delta\epsilon$.

As the applied field E is increased, the dielectric energy density, which depends quadratically on the field, favors the director tilt angle $\psi(z)$ to be zero in the bulk. As we will show below, this changes the nature of the anchoring transition when the sample is cooled under relatively large values of the applied electric field E. The tilt angle $\psi(\frac{d}{2})$ in the central plane of the cell with $z=\frac{d}{2}$ can be expected to be smaller than that at the surfaces, ψ_s at $z=0$ or d. This means that the director profile has a curvature deformation, and the elastic energy of the medium has to be taken into account. In the present paper our main interest is in the analysis of the anchoring transition, just beyond which the director field has only a splay deformation. The bulk free-energy density of the medium is again given by Eq. (2) but with a *negative* $\Delta\epsilon$. As we are interested only in locating the transition at which the tilt angle $\psi(z)$ just starts deviating from 0, we linearize the Euler-Lagrange Eq [5], which reads as

$$\frac{d^2\psi}{dz^2} - \frac{\epsilon_0|\Delta\epsilon|E^2}{k_{11}}\psi = 0. \tag{6}$$

As the sample is cooled under an electric field E in a temperature range favoring homeotropic anchoring at the surfaces located at $z=0$ and d, we can expect that $\psi(0)$ and $\psi(d)$ start deviating from 0 at the transition. There are two possible solutions: (a) both $\psi(0)$ and $\psi(d)$ are assumed to have the same sign, and we look for a solution characterized by $\psi(z)=\psi(d-z)$ [Fig. 4(a)]

$$\psi(z) = \alpha\cosh[\beta(d/2 - z)], \tag{7}$$

where α is a measure of the amplitude of $\psi(z)$ and $\beta^2=(\epsilon_0|\Delta\epsilon|E^2/K_{11})$. The surface torque balance equation at $z=0$ reads as

$$\frac{dF_s}{d\psi(0)} = K_{11}\left(\frac{d\psi(z)}{dz}\right)_{z=0}. \tag{8}$$

A similar equation holds at the surface with $z=d$. Again linearizing the above equation and using the solution for $\psi(z)$, we get

$$u(T - T_A)\cosh(\beta d/2) + K_{11}\beta\sinh(\beta d/2) = 0. \tag{9}$$

The continuous anchoring transition temperature in this regime 2a is given by

$$T_{2eat} = T_A - \frac{1}{u}\sqrt{\epsilon_0|\Delta\epsilon|K_{11}E^2}\tanh\left(\frac{d}{2}\sqrt{\frac{\epsilon_0|\Delta\epsilon|E^2}{K_{11}}}\right), \tag{10}$$

where the subscript e signifies that $\psi(z)$ is an even function. As $\tanh(x)\approx 1$ for all $x\geq 2.5$, in this regime the anchoring transition temperature essentially decreases linearly with increase in rms value of E, reflecting the experimentally observed trend. However, as $\tanh(x)\approx x$ for very small values of x (say ≤ 0.25), the above equation actually reduces to Eq. (5) derived for the discontinuous anchoring transition between the planar and homeotropic states, while the derivation of the last equation above is valid only for a continuous transition, in which $\psi(z)$ just starts acquiring a nonzero value. This is an unsatisfactory feature of the even solution assumed for $\psi(z)$. Thus, even though at first sight Eq. (10) seems to mathematically describe both the experimentally found distinct regimes as far as the dependences on the electric field are concerned, it is really valid only in the regime 2 in which the transition is continuous. Indeed by equating the anchoring transition temperatures derived for the two regimes we get the condition for the crossover as

$$\tanh\left(\frac{d}{2}\sqrt{\frac{\epsilon_0|\Delta\epsilon|E^2}{K_{11}}}\right) = \left(\frac{d}{2}\sqrt{\frac{\epsilon_0|\Delta\epsilon|E^2}{K_{11}}}\right), \tag{11}$$

which is valid only for $E=0$. Thus the above solution does *not* describe the experimentally found nonzero value of the crossover field satisfactorily. Hence we look for another possible solution to the linearized Euler-Langrange equation [Eq. (6)].

(b) We now assume that $\psi(0)$ and $\psi(d)$ have opposite signs, and more generally, $\psi(z)=-\psi(d-z)$. This implies that the tilt angle of the director at the mid plane of the cell $\psi(d/2)=0$ even in the distorted state, which is favored by the dielectric interaction of the medium with the external field [Fig. 4(b)]. The solution is

$$\psi(z) = \alpha\sinh[\beta(d/2 - z)]. \tag{12}$$

Proceeding as before, the continuous anchoring transition temperature corresponding to the above odd solution is given by

$$T_{2oat} = T_A - \frac{1}{u}(\sqrt{\epsilon_0|\Delta\epsilon|K_{11}E^2})\coth\left(\frac{d}{2}\sqrt{\frac{\epsilon_0|\Delta\epsilon|E^2}{K_{11}}}\right). \tag{13}$$

As $\coth(x)$ also tends to the constant value 1 for large x, the essentially linear dependence of the anchoring transition temperature T_{2oat} on the rms electric field E is recovered in

the regime 2b. The condition for the crossover between the two regimes is again found by equating T_{1at} to T_{2oat} and reads as

$$\coth\left(\frac{d}{2}\sqrt{\frac{\epsilon_0|\Delta\epsilon|E^2}{K_{11}}}\right)=\left(\frac{d}{2}\sqrt{\frac{\epsilon_0|\Delta\epsilon|E^2}{K_{11}}}\right). \tag{14}$$

This is satisfied for $(d/2)\sqrt{\epsilon_0|\Delta\epsilon|E^2/K_{11}}\approx 1.199\,68$. The crossover voltage is thus given by

$$V_{co}=E_{co}d\approx 2.4\sqrt{\frac{K_{11}}{\epsilon_0|\Delta\epsilon|}}. \tag{15}$$

The above equation shows that (i) the crossover occurs at a well-defined applied *voltage* V_{co}, which is independent of the sample thickness, and (ii) more remarkably, the crossover voltage does *not* depend on the anchoring coefficient u. It only depends on the material parameters K_{11} and $\Delta\epsilon$. The temperature dependence of the dielectric anisotropy of CCN-47 has been measured [10]. Only the bend elastic constant K_{33} of CCN-47 has been measured, and we will discuss he method of estimating K_{11} later. Using the data near the relevant temperature, the calculated value of V_{co} is $\simeq 0.5$ V, which agrees extremely well with the measured value. Thus the odd solution for $\psi(z)$ gives the correct description of the director distortion below the anchoring transition in the regime 2. We fit the experimental data in the two regimes using Eqs. (5) and (13), respectively. As K_{11} has not been measured for CCN-47, we estimate it using the mean field result, viz., $K_{11}(T)=K_0S^2$, where S is the orientational order parameter whose temperature dependence has been measured [10]. The estimated value of $K_0\simeq 7.2\times 10^{-12}$ N. The agreement between the theoretical expressions Eqs. (5) and (13) and the experimental data is highly satisfactory (Fig. 3). The overall agreement of the experimental and calculated electric field variations in the anchoring transition temperatures in both regimes shows that the assumption made in Eq. (3) about the temperature variation of the anchoring energy A is appropriate for the ATr in the system studied. The calculations corresponding to the type 2b regime can be extrapolated all the way down to $E=0$ (Fig. 3). Indeed as $\coth(x)=1/x$ for very small values of x, for low values of E, Eq. (13) leads to a field-independent anchoring transition temperature

$$T_{2oat}(E\to 0)=T_A-\frac{2K_{11}}{ud}. \tag{16}$$

This *hypothetical continuous anchoring transition* would have taken place when the temperature is just low enough for the gain in anchoring energy by a tilting of the director at the two surfaces to exceed the positive energy cost of the resulting elastic distortion of the director field. Of course this hypothetical transition is cut off at a higher temperature by the discontinuous transition of type 1. There is some similarity between this phenomenon and the nematic to isotropic (NI) transition. In the latter case, as was pointed out by de Gennes [1], the thermodynamically first-order NI transition occurs at a temperature slightly higher than that of a hypothetical second-order transition. The analogy is not perfect, however, as the two types of anchoring transitions discussed by us lead to two very different director distributions in the cell. It may be noted that the anchoring transition of type 2b occurs as the sample is cooled under an electric field $|E|$, with the tilt angle at the center of the sample ψ_m remaining at a value $=0$ and the tilt angles at the two surfaces ψ_s exhibiting a transition to a nonzero value. The transition occurs as the surfaces favor homeotropic alignment ($\psi_s=\frac{\pi}{2}$) with a *very weak* anchoring energy. In contrast, as described earlier, the familiar Freedericksz transition in the above geometry occurs if a sample with *positive dielectric anisotropy* and a *strong planar anchoring* is subjected to an appropriate electric field across the cell. This transition is characterized by $\psi_s=0$ and $\psi(d/2)$ acquiring a nonzero value. We can thus describe the type 2 anchoring transition in our system as an inverse Freedericksz transition. Further, in the usual Freedericksz transition, the tilt angle at the mid plane $\psi(d/2)$ takes a maximum value, decreasing to 0 at both surfaces if the anchoring is strong, or to some finite nonzero value smaller than $\psi(d/2)$ if the anchoring is weak. This necessarily requires the solution $\psi(z)$ be an even function [5]. On the other hand, in the inverse Freedericksz transition investigated by us, the odd solution is relevant.

IV. CONCLUSIONS

In conclusion, we have shown that the discontinuous anchoring transition of CCN-47 observed on CYTOP becomes continuous beyond a crossover voltage. The quadratic and linear variations of the anchoring transition temperature in the low voltage discontinuous and high voltage continuous regimes with an applied field have been accounted for by a simple physical model. The latter can be described as an inverse Freedericksz transition. The observations also show that disclinations tend to get expelled from regions in which this transition takes place. A half-strength defect trapped inside the tilted region is connected with a tilt-inversion wall. The effect of an electric field on the homeotropic state (i.e., below T_A) and the detailed analysis of the evolution of the defects and the director profile will be published elsewhere.

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