

In-plane anchoring energy in ferroelectric liquid crystals: Evidence for its existence and measurement

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(Received 16 December 1994)

Direct evidence for the existence of an in-plane term in the anchoring energy of a ferroelectric liquid crystal (FLC) cell is provided. This energy term arises from the anisotropy of the interaction of the FLC with the rubbed surface. A method for the measurement of the in-plane anchoring energy based on the offset of the electro-optic hysteresis curve is proposed. Investigations of different surface conditions in the cells reveals that the in-plane energy depends on the manner in which the alignment layer is prepared. The dependence of the optical bistability properties on this energy term is also discussed.

PACS number(s): 68.45.Ws, 68.35.Md, 77.84.Nh, 42.70.Df

The interaction between liquid crystal molecules and the boundary solid surfaces plays an important role in the electro-optic and the dielectric properties of liquid crystal devices (LCD's). In surface stabilized ferroelectric liquid crystal (SSFLC) [1] cells this interaction suppresses the FLC helical structure and this is the source of the bistability properties. The anchoring properties of ferroelectric liquid crystals (FLC's) are not yet completely understood. Usually, the interaction between the FLC and a solid surface is considered to be of the form proposed by Handschy *et al.* [2] where the surface anchoring energy density W'_s is

$$W'_s = -\gamma_p \cos \varphi - \gamma_d \cos^2 \varphi, \quad (1)$$

where γ_p and γ_d are the polar and dispersion parts of the surface interactions, respectively, and φ is the azimuthal angle (the angle between the spontaneous polarization P_s and the X axis) (Fig. 1). The dispersion part of the surface interaction γ_d will always be positive for conventional alignment layers which induce homogeneous (planar) alignment. In this paper we consider only alignment agents which cause homogeneous alignment.

In a recent publication Schiller [3] from elegant symmetry considerations has shown that for different types of surface treatment there should exist additional terms in the anchoring energy for the smectic-C liquid crystals. Thus for rubbed low-pretile surfaces (C_2 symmetry) an additional term arises from the orientation of the molecular director relative to the rubbing direction. This energy is responsible for the orientation of the molecules along the rubbing direction in the Y - Z plane, the plane of the glass plate, and is called the in-plane anchoring energy. The purpose of this paper is to demonstrate that this orientation energy term, already shown to be important for nematic liquid crystals, should also be included in the surface anchoring energy W'_s for FLC's.

The in-plane anchoring energy of nematic liquid crystals (known as azimuthal anchoring energy in nematics) has been somewhat investigated before [4–6]. However, the nature of

these forces is not yet clear. Berreman [4] suggested that the aligning forces occur due to elastic distortions on the treated glass surface. Later papers [6] have shown that the orientational energy arises not only from surface elastic deformations but mostly from intermolecular interactions between the molecules and the alignment layer.

The main purpose of this paper is to demonstrate the existence of an in-plane energy term (W_0) in FLC cells, without clarification of its exact nature at this stage of the work. The function $W_0(\alpha)$ is assumed to exist in the interval $[-\theta, +\theta]$ (θ is the molecular tilt angle) and thus it can be expanded to the power series of α :

$$W_0(\alpha) = \sum_{i=0}^{\infty} a_i \alpha^i, \quad (2)$$

where α is the angle between the projection of the molecular director on the electrode and the rubbing direction. To a first approximation ($\alpha \leq \theta < 1$) we can use the first and the quadratic terms of the power series. We shall therefore use the following general form for the description of the orientation energy for a rubbed polymer surface:

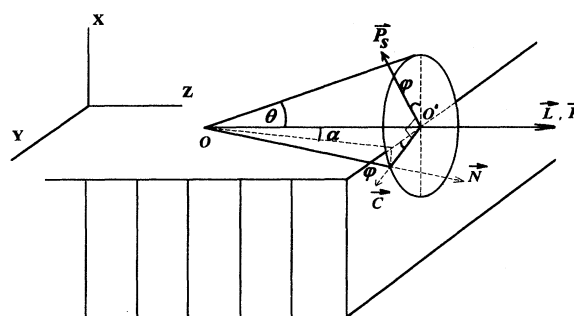


FIG. 1. Smectic layer structure and coordinate system for a bookshelf cell. (X, Y, Z), coordinate system; $\vec{N}$, molecular director; $\vec{L}$, smectic layer normal; $\vec{C}$, C director (projection of $\vec{N}$ on smectic layer plane); $\vec{P}_s$, spontaneous polarization vector; θ , molecular tilt angle; φ , azimuthal angle; α , angle between the projection of molecular director on the electrode and the rubbing direction $\vec{R}$.

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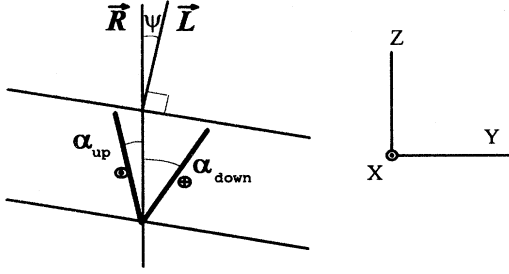


FIG. 2. Asymmetric director positions in the quasiooriented cell. α_{up} and α_{down} denote the director positions relative to the rubbing direction for opposite electric fields. ψ is the angle between the projection of the smectic layer normal on the electrode (Y-Z plane) and the rubbing direction.

$$W_0 \approx a_0 + a_1 \alpha + \gamma_0 \alpha^2, \quad (3)$$

where $\gamma_0 \equiv a_2$ and denotes the nonpolar in-plane contribution to the surface anchoring energy.

For simplicity we consider that the FLC cell possesses the bookshelf structure (Fig. 1). Such a structure is easily achieved by the application of a high electric field ($>10^7$ V/m) in cells containing FLC mixtures of sufficiently high spontaneous polarization (2×10^{-4} C/m²). It has been shown [7] that such field-induced bookshelf cells possess the striped structure where the smectic layers are not perpendicular to the rubbing direction, but the layer normal ($\vec{L}$) lies at an angle ψ to the rubbing direction ($\vec{R}$) (Fig. 2). In the bookshelf geometry the angle α is related to the angles θ , φ , and ψ by the following relation:

$$\alpha = \sin^{-1}(\sin \theta \cos \varphi) + \psi \approx \theta \cos \varphi + \psi \quad (\theta \ll 1), \quad (4)$$

where θ is the molecular tilt angle as indicated in Fig. 1. Thus the excess orientation energy W_0 takes the form

$$W_0 \approx a_0 + a_1 \psi + a_1 \theta \cos \varphi + \gamma_0 \theta^2 \cos^2 \varphi + 2 \gamma_0 \theta \psi \cos \varphi + \gamma_0 \psi^2. \quad (5)$$

On combining Eqs. (1) and (5), we are led to the following expression for the total surface density of the anchoring energy with *one* rubbed surface:

$$W_s = W'_s + W_0 \approx a_0 + a_1 \psi + (\gamma_0 \theta^2 - \gamma_d) \cos^2 \varphi (2 \gamma_0 \theta \psi + a_1 \theta - \gamma_p) \cos \varphi + \gamma_0 \psi^2. \quad (6)$$

In deriving Eq. (6), we have assumed that changes in α are caused primarily by those in φ arising from the rotation of the molecular director around a cone of angle 2θ . Since the experimental electro-optic measurements are made for $E < 1$ V/ μ m, the dilation of the layers can be reasonably neglected.

Schiller [3] derived a formula for the surface free energy of a rubbed surface with low-pretit angle (in our notations) as follows:

$$W_s = (\beta_3 - \beta_2) \theta^2 \cos^2 \varphi - 2 \theta (\Gamma_2 \psi + \Gamma_{12}) \cos \varphi + \alpha_2 \psi^2 + 2 \beta_2 \theta^2 + \alpha_3 \delta^2 + 2 \alpha_{12} \psi + 2 \Gamma_3 \delta \theta \sin \varphi, \quad (6a)$$

where δ is the smectic layers tilt angle, θ is the molecular tilt angle, α , β , and Γ are the tensor coefficients as defined in Ref. [3]. Let us note that Eqs. (6) and 6(a) are of the same

form for the case of the bookshelf structure ($\delta=0$), but the coefficients in Eq. (6) possess a physical meaning as discussed before.

Because a cell has two surfaces, the terms containing the angles φ and ψ should be transformed to the values $\varphi + \pi$ and $-\psi$ correspondingly. For example, the term $\gamma_p \cos \varphi$ will have the value $-\gamma_p \cos(\varphi + \pi)$ at one surface and $-\gamma_p \cos \varphi$ at the other. Therefore we may neglect this term and the terms $a_1 \theta \cos \varphi$ and $a_1 \psi$ in what follows. However, the $\cos^2 \varphi$, $\gamma_0 \psi^2$, and $\theta \psi \cos \varphi$ terms for the two surfaces will be of the same sign and hence we shall introduce a factor 2 in these terms.

Furthermore, the results of a study of the director switching process in a thin bookshelf FLC cell under low fields ($E < 5 \times 10^6$ V/m) have demonstrated that after the field is reversed there first arise domains of opposite signs ($\varphi \approx 0$ or $\varphi \approx \pi$); these domains then grow in size and finally a completely uniform state is achieved. For this case, $\partial \varphi / \partial x = 0$ for all domains with the exception of the domain walls. In view of φ being independent of x for all the domains and by neglecting the elastic energy of the domain walls, the total surface energy density of the FLC cell which consists of two similar surfaces can be written in the following form:

$$F(\varphi) = P_s V \cos \varphi + 2(\gamma_0 \theta^2 - \gamma_d) \cos^2 \varphi + 4 \gamma_0 \theta \psi \cos \varphi + 2 \gamma_0 \psi^2 + 2 a_0, \quad (7)$$

where $V = Ed$ and P_s is the spontaneous polarization. An analytical investigation of the function $F(\varphi)$ within the range $0 \leq \varphi \leq \pi$ shows that for low applied voltage [lower than critical values defined later in Eq. (9)] this function possesses three critical points: $\varphi_1 = 0$, $\varphi_2 = \pi$, and φ_3 where

$$\varphi_3 = \cos^{-1} \left[\frac{P_s V + 4 \gamma_0 \theta \psi}{4(\gamma_d - \gamma_0 \theta^2)} \right], \quad (8)$$

and under sufficiently strong planar conditions ($\gamma_d > \gamma_0 \theta^2$) the potential $F(\varphi)$ possesses a double-well structure with two minima at the angles $\varphi_1 = 0$ and $\varphi_2 = \pi$, separated by one maximum at φ_3 . Whether the director state is φ_1 or φ_2 depends on the previous switched state. This explains the bistability properties. For homeotropic conditions (γ_d is negative) the potential $F(\varphi)$ possesses only one minimum at φ_3 and bistability is not observed. In further discussions we will only consider alignment layers which induce strong planar anchoring because of their practical importance. The application of an applied field will shift the position of the maximum φ_3 to zero or π according to Eq. (8).

When V has the critical value

$$V_c^+ = \frac{+4(\gamma_d - \gamma_0 \theta^2 + \gamma_0 \theta \psi)}{P_s} \quad (9)$$

or

$$V_c^- = \frac{-4(\gamma_d - \gamma_0 \theta^2 - \gamma_0 \theta \psi)}{P_s}$$

for positive and negative threshold voltages the double-well structure disappears and only one minimum occurs. This minimum will be at either $\varphi = 0$ or $\varphi = \pi$ depending on the polarity of the applied field. The double-well structure is responsible for the hysteresis properties of FLC cells. Note that for nonzero ψ the threshold voltages V_c^+ and V_c^- differ

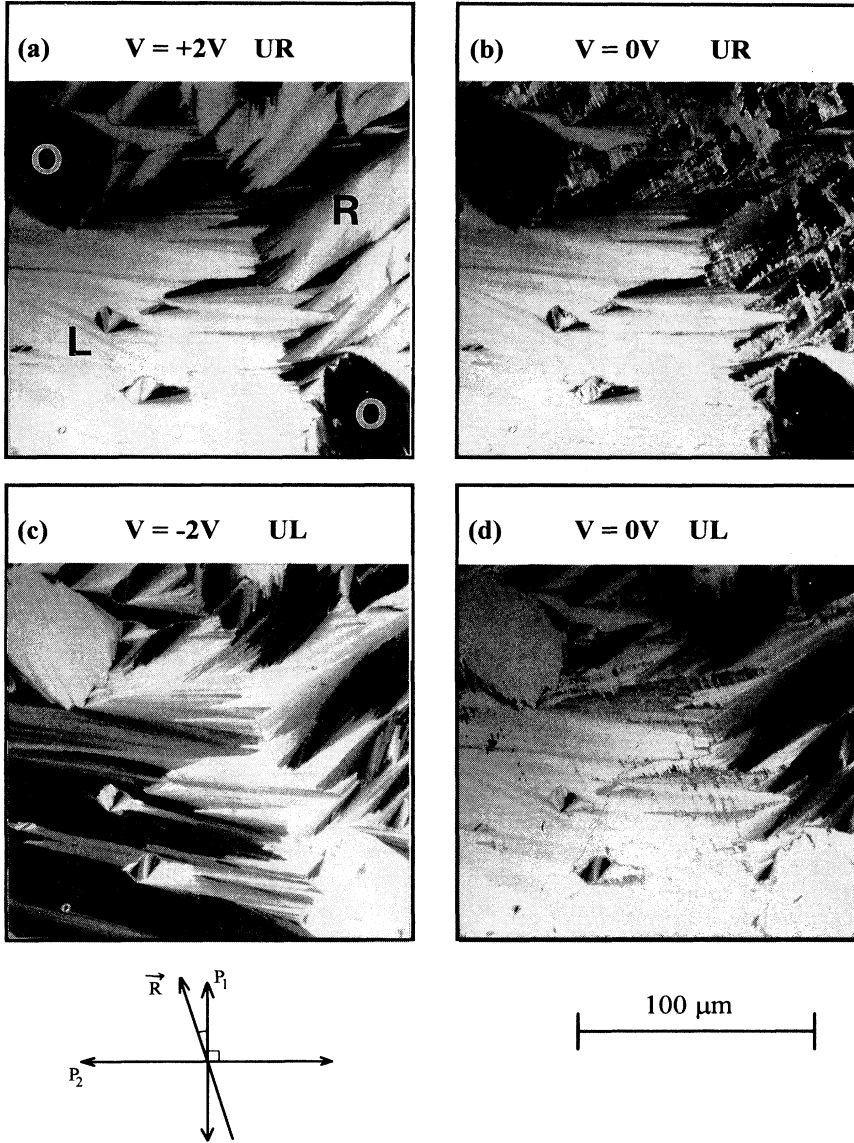


FIG. 3. Sequence of microphotographs of a quasioriented FLC cell between crossed polarizers. (a) $V = +2$ V, switched uniform right (UR) state to (b) short circuited ($V = 0$) state to (c) $V = -2$ V, switched uniform left (UL) state to (d) short circuited ($V = 0$) state. The areas with the layer normal parallel to the rubbing direction (denoted by O) are bistable in all cases. The areas turned right of the rubbing direction (denoted by R) are stable in UL state, areas turned left of rubbing direction (denoted by L) are stable in UR state. P_1 and P_2 are the axes of the cross polarizers and $\vec{R}$ is the rubbing direction.

and the hysteresis curve is nonsymmetric with respect to zero voltage. The corresponding coercive voltages are no longer equal in magnitude and the offset of the hysteresis (ΔV) defined as the horizontal displacement of the center of the hysteresis loop:

$$\Delta V = \frac{(V_c^+ + V_c^-)}{2} = \frac{4\gamma_0 \theta \psi}{P_s} \quad (10)$$

is linearly dependent on ψ . This property forms the basis of the method for measuring the in-plane energy term γ_0 . It should be noted from Eq. (10) that ΔV is proportional to the orientational energy term γ_0 and the angle ψ . If the hysteresis shift ΔV is of the same order of magnitude as its width—then this will lead to a degradation of the optical bistability of the cell and ultimately to monostability.

To measure this in-plane orientational term γ_0 we prepared so-called “quasioriented” cells where layer normals in different areas of the cell (domains) are at different angles

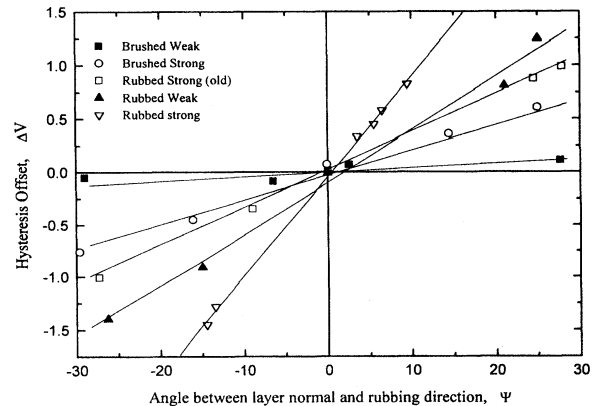


FIG. 4. Dependence of the hysteresis shift (in volts) on the angle (ψ in degrees) for different treatments of PVA alignment layer.

TABLE I. The in-plane anchoring energy (γ_0) for different treatment techniques of various alignment layers.

Curve No.	Fig. No.	Alignment layer	Treatment technique	In-plane energy (γ_0) (10^{-3} (J/m ²))
1	4	PVA ^a	weak brushing	0.04
2	4	PVA	strong brushing	0.24
3	4	PVA	strong rubbing (old)	0.35
4	4	PVA	weak rubbing	0.54
5	4	PVA	strong rubbing	0.94
1	5	PVA	strong rubbing	0.94
2	5	ZLI-2650	strong rubbing	0.36
3	5	Nylon 6/6	strong rubbing	0.55
4	5	PMA ^b	strong rubbing	0.20

^aPVA, abbreviation for polyvinyl alcohol.

^bPMA, abbreviation for pyromelestic acid.

(ψ) to the rubbing direction. Cells were prepared using the FLC mixture SCE13 (Merck, $P_s \approx 2.7 \times 10^{-4}$ C/m²). Sample cells consisted of indium tin oxide (ITO) coated glass plates with various alignment layers and separated by spacers. The cells were filled in the isotropic phase. Cells of 2–4 μ m thicknesses were allowed to cool slowly to the cholesteric phase (chiral nematic N^*) and then quickly to the Sm-A and Sm-C* phases. This procedure ensured quasioriented cells. Prior to measurements, in order to produce the bookshelf geometry we applied low frequency (1–20 Hz) high electric fields ($> 10^7$ V/m) to the cells. For a sequence of microphotographs see Fig. 3.

The microscope diaphragm was used to enable us to concentrate on small quasioriented areas. The FLC cell to be measured was placed between the crossed polarizers at an angle θ with the polarizer axis to achieve maximum optical contrast. We used a triangular alternating voltage of 3 V p.p. of very low frequency (0.01 Hz) so as to guarantee almost static conditions and to avoid ionic polarization phenomena [8]. Switching between the uniform states was achieved through the domain reversal process and at any one instant there existed only uniform domains in the cell. Thus we believe that the conditions for Eqs. (7)–(10) were satisfied.

Using the technique described above, we investigated the dependence of the alignment properties in terms of the in-plane anchoring energy for different treatment conditions. Figure 4 shows the dependence of the hysteresis shift (ΔV) on the angle between the layer normal and the rubbing direction for polyvinyl alcohol (PVA) alignment layers treated for different strengths of rubbing. The values of the orienta-

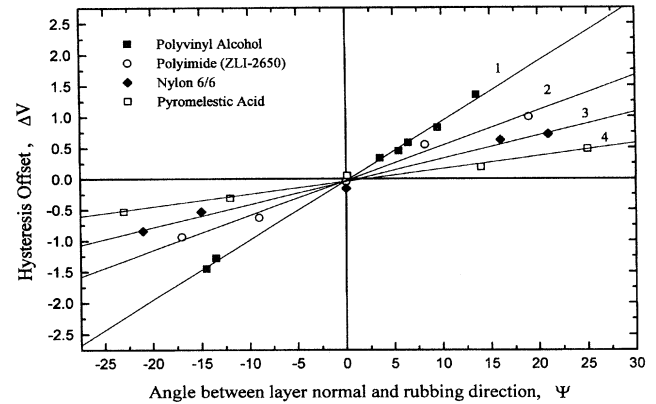


FIG. 5. Dependence of the hysteresis shift (in volts) on the angle (ψ in degrees) for different alignment layers strongly rubbed on a velvet track.

tional in-plane anchoring energy density term γ_0 [calculated using Eq. (10)] for different treatment techniques are given in Table I. It can be seen from the curves in Fig. 4 that increasing the rubbing strength increases γ_0 . It should be noted that there is a linear dependence of the hysteresis shift [in accordance with Eq. (10)] on the angle ψ between the smectic layer normal and the rubbing direction (Fig. 2).

We also provide investigations of the anchoring properties of different alignment polymers, namely, PVA, nylon 6/6, polyimide (ZLI-2650), and pyromelestic acid rubbed strongly on a velvet track. The thicknesses of the alignment layers in each case were approximately equal to 150 Å. Results of these measurements are shown in Fig. 5 and Table I. From the results presented in Table I it can be seen that the value of the in-plane anchoring energy depends strongly on both the type of polymer used for alignment and the rubbing technique.

In conclusion, we have shown that the in-plane anchoring energy should also be taken into account for describing the interaction between FLC's and solid surfaces. This energy effects the bistability properties of FLC cells in two ways. Firstly, it decreases the width of the hysteresis loop and secondly it shifts the center of the hysteresis curve given by Eq. (10) causing the hysteresis loop to become nonsymmetric and eventually leads to monostability in the cell.

We would like to thank Professor B. K. P. Scaife and Dr. Yu. P. Kalmykov for useful suggestions and helpful criticisms. This work was partly funded by the E. U. Science Twinning Grant No. SC*0291.

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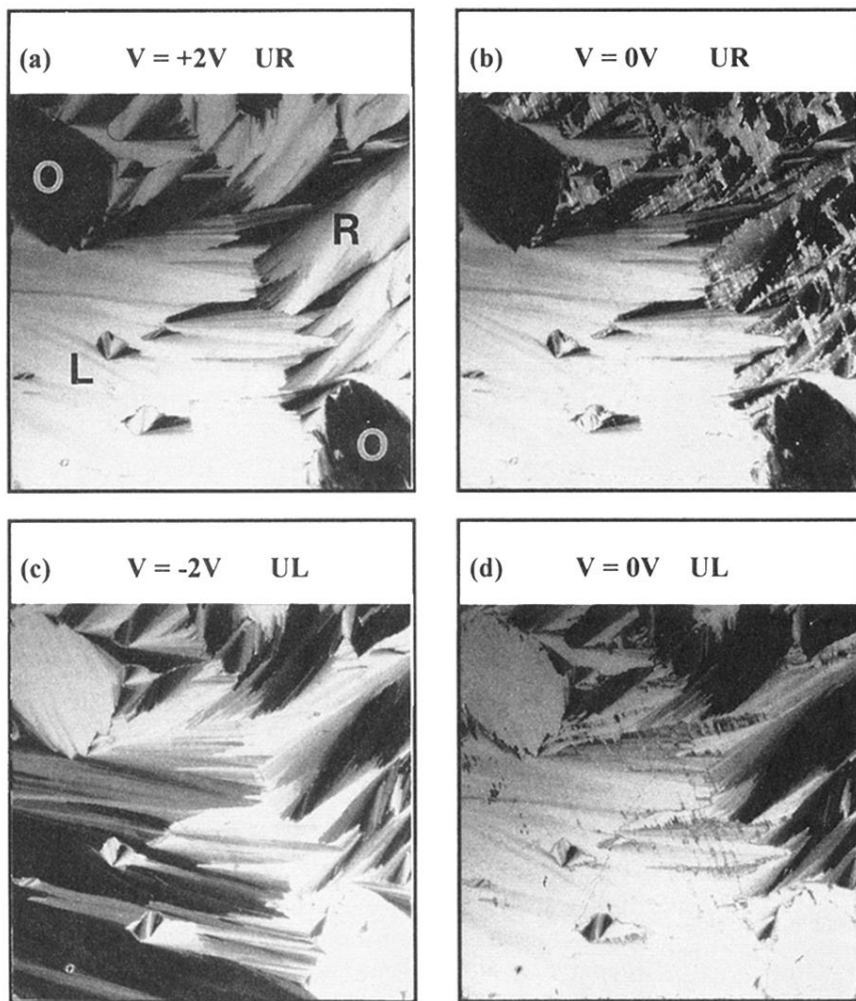


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