

Orientational plasticity at a smectic-liquid-crystal-anisotropic-solid interface

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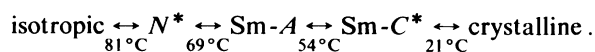
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We demonstrate a plastically deformable coupling of liquid-crystal molecules to a rubbed polymer surface, showing that the large electric-field-induced torques available in ferroelectric liquid crystals can overwhelm the intrinsic surface anisotropy to produce new stable surface orientations.

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Although rubbed-polymer films are widely used to preferentially orient molecules in liquid crystals (LCs), very little is known of the origin and basic physics of the LC-polymer interaction [1-3]. Several experiments suggest that short-range (molecular level) interactions are responsible for the surface orientation, with the LC molecules anisotropically adsorbed on polymer crystallites oriented by the rubbing [4,5]. Rubbed-polymer surfaces have been thought to be orientationally *elastic*, externally applied torques reversibly reorienting the director from the surface-energy minimum established by the anisotropic adsorption. In this paper we show, using the depolarized total internal reflection (TIR) technique [6], that a rubbed-polymer surface can orient the interfacial director \mathbf{n} of a chiral smectic liquid crystal to be parallel to the surface and along the rubbing direction even though this orientation is off of the bulk smectic- C^* (Sm- C^*) tilt cone. Application of an electric field irreversibly pulls \mathbf{n} at the surface back onto the tilt cone, reorienting it away from the rubbing direction and permanently altering the orientation characteristics of the surface.

The detailed TIR experimental arrangement has been published elsewhere [6]. The experiment was carried out in surface-stabilized ferroelectric-liquid-crystal (SSFLC) [7] geometry with the FLC being sandwiched between a glass plate and the flat surface of a high-index glass hemisphere ($n_g = 1.9082$ at 6328 \AA). Both the inner surface of the glass plate and the flat surface of the hemisphere were coated first with a thin layer of indium tin oxide (ITO) ($\sim 120 \text{ \AA}$) and then with a thin layer of nylon 6/6 (400 \AA) spin coated out of formic acid. The nylon layer was buffed with a buffing wheel afterwards and the sample cell was assembled with the buffing direction on the two coated surfaces parallel to each other, using polystyrene microspheres as the spacers. The cell was filled with FLC by capillarity in the isotropic phase in a vacuum chamber. The sample thickness is about $3 \mu\text{m}$. The liquid crystal used in the experiment is the Chisso mixture 1014 (Chisso Petrochemical Corporation), with the nominal phase sequence:



The existence of a nematic (N) phase enabled us to get

very good alignment with the buffed nylon coating. The observed Sm- C^* to Sm- A phase transition temperature in our sample is 56.2°C .

In the experiment a He-Ne laser beam polarized in the plane of incidence (p -wave) illuminates the planar FLC-hemisphere interface at a fixed angle of 80° , giving the evanescent wave a penetration depth of $\sim 900 \text{ \AA}$ (1000 \AA) for the ordinary (extraordinary) polarization into the nylon-FLC interface. Hereafter we will denote depolarization ratio R as the ratio of the detected s -wave signal to the incident p -wave intensity. This depolarization ratio, $R(\beta)$, measured as a function of β , the angle between the rubbing direction and the plane of incidence as depicted in Fig. 1(a), gives information about the orientation of LC molecular director \mathbf{n} near the nylon-FLC interface. We will identify the orientation of \mathbf{n} near the interface with two angles: Ω , the angle between \mathbf{n} and the interface plane; and η , the angle between the projection of \mathbf{n} onto the interface plane and the rubbing direction. Both of them can be extracted from $R(\beta)$ by fitting the experimental data using our theoretical model.

The numerical calculation of $R(\beta)$ was carried out using Berreman's method [8]. The rubbed polymer and the FLC were modeled as layers of uniaxial materials characterized by their thickness, refractive indices, and the optical axis orientations. The rubbed-nylon layer was 400 \AA thick and birefringent, $\Delta n_{\text{nylon}} = 0.002$ [4], with its optical axis along the rubbing, and an ordinary index of refraction of $n_{\text{nylon}} = 1.5$. The birefringence (nematic ordering) of FLC, Δn_{LC} , was varied with its ordinary refractive index fixed at $n_o = 1.49$. At each temperature, the experimental data were fitted by varying Δn_{LC} , and the angles η and Ω of the LC.

Figure 2 illustrates the anchoring effect of the rubbed polymer on interfacial FLC molecules, orienting them along the rubbing direction in a virgin sample, which was never previously exposed to external electric field. The plots show the measurements of $R(\beta)$ at four different temperatures, one in Sm- A phase, and three in Sm- C^* phase: one at room temperature and two others at higher temperatures (one from heating and the other from cooling as indicated by the arrows in the figure). As can be easily seen in the figure, there is no shift in β of $R(\beta)$ as

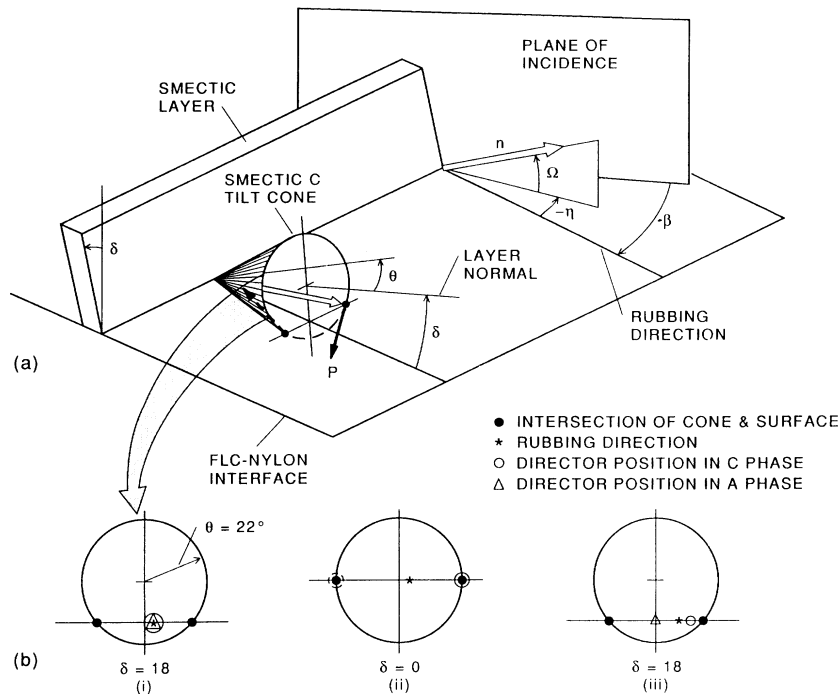


FIG. 1. (a) The FLC-rubbed-nylon interface geometry. (b) Schematics of orientational evolution of director \mathbf{n} at FLC-rubbed-polymer interface: (i) the virgin chevron cell; (ii) bookshelf cell with field applied; (iii) chevron cell after temperature cycling the sample of (ii).

the temperature is lowered from the Sm-A phase to Sm-C* phase, showing that the director distribution near the surface does not change. Additionally, the four minima in $R(\beta)$ have the same height, indicating that $\Omega \approx 0^\circ$ [6]. The fit to the model gave $\eta = 0^\circ \pm 0.5^\circ$ and $\Omega = 0^\circ \pm 2^\circ$,

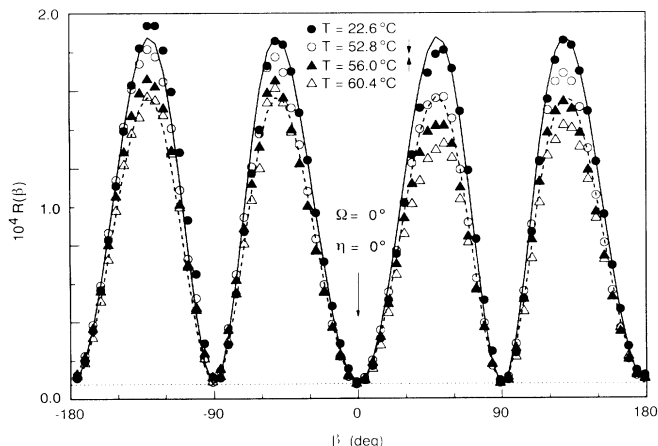


FIG. 2. Depolarization ratio $R(\beta)$ vs β , at four different temperatures for the virgin sample with no field applied. The solid and dashed curves are the best fits for experiment results at $T = 22.6^\circ\text{C}$ (Sm-C*) and $T = 60.4^\circ\text{C}$ (Sm-A), respectively, which were given by changing only the birefringence of the FLC slab. The difference in the width of the minima of $R(\beta)$ was used to determine whether \mathbf{n} is parallel or perpendicular to the plane of incidence (see Ref. [9]). The dotted line indicates the normalized signal level of the dark current of the photodiode.

which was then set to be 0° in the numerical model. These results show that with no electric field applied an interfacial layer of FLC molecules with a thickness up to the evanescent wave penetration depth (about 500 \AA into the FLC) was anchored to the surface along the rubbing direction by the rubbed-nylon film even when the bulk FLC was cooled well into the Sm-C* phase. The bulk smectic layers in this cell had the chevron structure [10], with a smectic bulk director cone angle $\theta = 22^\circ$ and a layer tilt angle of $\delta = 18^\circ$ [11]. Since $\theta > \delta$ the smectic tilt cone should intersect the surface. Figure 1 illustrates this intersection, and \circ and Δ in Fig. 1(b)(i) denote the orientation of \mathbf{n} according to the data of Fig. 2 in the Sm-C* and Sm-A phases, respectively. The surface thus either pulled \mathbf{n} off of the bulk tilt cone and \mathbf{n} did not relax back to the cone in the 500-\AA -thick interfacial layer being probed, or changed the layer tilt angle δ in the immediate vicinity of the interface, making the tilt cone tangent to it. For a smectic phase we expect the surface orientation to penetrate a distance $\xi = (K/D)^{1/2}$ into the bulk, where K is a Frank constant and D is the smectic orientational elastic constant [12]. For typical bulk values of $K = 10^{-6} \text{ erg/cm}$ and $D = 10^8 \text{ erg/cm}^3$, $\xi \sim 10 \text{ \AA}$ which is much less than the probed surface layer thickness, providing direct evidence against the first possibility. The latter case would require edge dislocations to join the surface and bulk region with a change of δ and is similar to the surface-induced layer twist found by Patel, Lee, and Goodby [13]. As the temperature was lowered, the amplitude of $R(\beta)$ increased because Δn_{LC} increased.

When we applied a voltage V_a across the cell, significant shifts in the depolarization curve appeared and

bistable interfacial states were established. The applied field altered the layer structure, permanently uprighting the layers into the bookshelf structure ($\delta=0^\circ$). Figure 3(a) shows $R(\beta)$ at three different applied voltages V_a at room temperature: $V_a=0$ V of the virgin sample, and $V_a=+50$ V (-50 V) reduced from $V_a=+90$ V (-90 V) for the up (down) polarization state. The electric field forced the \mathbf{n} to deviate away from the rubbing direction by $\eta=22^\circ \pm 0.5^\circ$ ($\eta=-18^\circ \pm 0.5^\circ$) in the up (down) state, with 22° being the bulk Sm-C* tilt cone angle, and kept \mathbf{n} parallel to the interface ($\Omega=0^\circ \pm 2^\circ$) in both states. The nice fit to the R curve and the orientation of these two states show a high degree of smectic LC ordering at the interface, induced by the electric field. The asymmetry about rubbing direction of the director field orientation in these two extreme polarization states may reflect the polar surface interaction [6,14]. Figure 3(b) gives the dependence on V_a of $R(\beta=-18^\circ)$, which is R at the cell orientation for which the director \mathbf{n} is in the plane of incidence when the interface is in the down polarization state. The

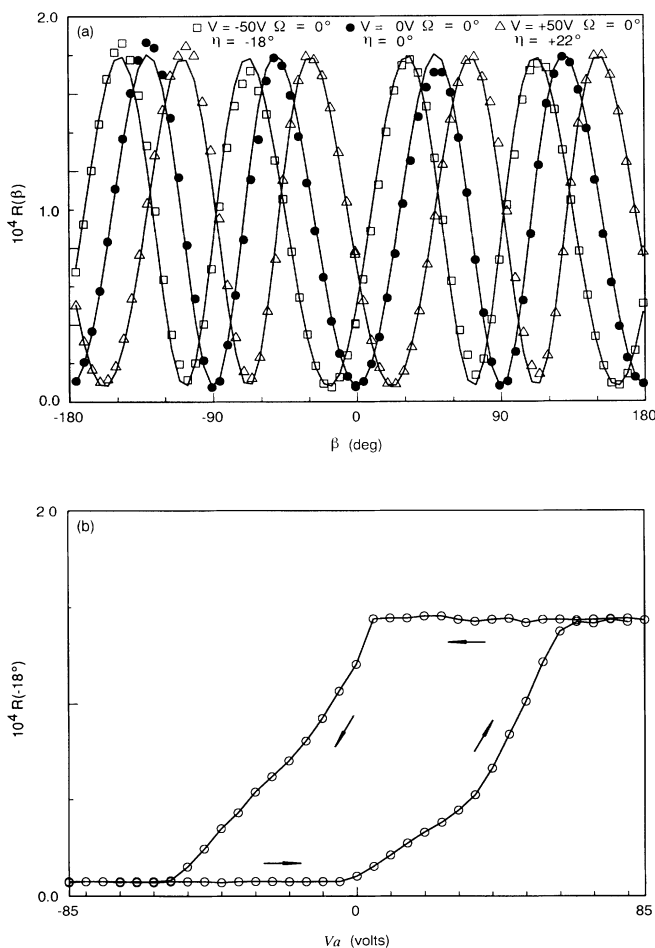


FIG. 3. External electric-field-induced bistability at room temperature: (a) Depolarization ratio $R(\beta)$ for interfacial FLC state in the nonfield virgin sample and the two field induced bistable interfacial states. The solid curves are best fits. (b) Hysteresis curve of $R(\beta=-18^\circ)$ as applied voltage V_a varies between -85 to $+85$ V.

curve shows a strong hysteresis which indicates the up and down polarization states are bistable at $V_a=0$ V, having the director \mathbf{n} oriented to positions where the tilt cone intersects the surface, and the transition between them is first order. This bistable behavior is very similar to that at the clean ITO coated glass surface [6], where there is no preferred orientation intrinsic to the surface.

In order to make a direct comparison with the initial chevron layer structure, we temperature cycled the field altered cell up to the S_A phase and back down to room temperature to regenerate the chevron structure, and then probed the surface orientation of \mathbf{n} with zero applied field at various temperatures. The results are shown in Fig. 4. As was the case for the bistable states in the bookshelf structure generated by high field, \mathbf{n} was found to be close to the intersection of the cone, which was tilted with the bulk tilt angle δ , with the surface plane in Sm-C* phase, and rotating to the layer normal direction as the temperature was increased again into the smectic-A phase. Thus the interfacial \mathbf{n} orientation is now mostly determined by the elastic torque imposed by the bulk smectic layering and θ , in contrast to the situation before the external field was ever applied. For this cell the temperature cycling slightly reoriented the Sm-A layer normal direction [14]. Figure 1(b) depicts the evolution of the LC director orientation at the interface. The amplitude of R curves in Fig. 4 are lower than those of Fig. 2, indicating a decrease of Δn_{LC} at the interface during the cycling.

The data of Fig. 2 show the initial $\Omega=0^\circ$, $\eta=0^\circ$ surface orientation well down in the Sm-C* phase. This director orientation was achieved in spite of the fact that it was not compatible with the constraint given by the bulk cone orientation and cone angle, being $\sim 5^\circ$ off of the cone and $\sim 13^\circ$ away from the position where the bulk cone intersects the surface. The application of the field and the resulting field-induced rotation of the LC director away from the $\Omega=0^\circ$, $\eta=0^\circ$ position, permanently alters the interface structure so that upon further switching or

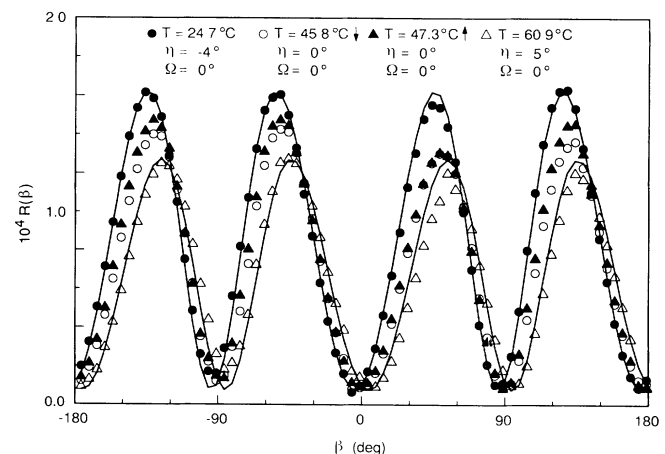


FIG. 4. Temperature dependence of $R(\beta)$ with no field applied for the chevron cell generated by temperature cycling the sample of Fig. 3. Two solid curves are the best theoretical fits for experimental data at $T=24.7^\circ\text{C}$ (Sm-C*) and $T=60.9^\circ\text{C}$ (Sm-A), respectively.

temperature change the director remains close to the position where the bulk tilt cone intersects the surface. This situation is related to the surface memory effect observed by Clark [15], who found that the exposure of an initially isotropic (random planar) polymer-coated glass surface to orientationally ordered LC phases rendered the glass surface anisotropic, the gliding anchoring effect reported by Oliveira, Neto, and Durand [16], and the bistable switching between orientationally degenerate surface states found in FLC [6] and nematic [17] cells. However the present results differ fundamentally from the aforementioned phenomena in that in the present case the interface

is initially strongly anisotropic and this anisotropy is overwritten by the subsequent LC reorientations.

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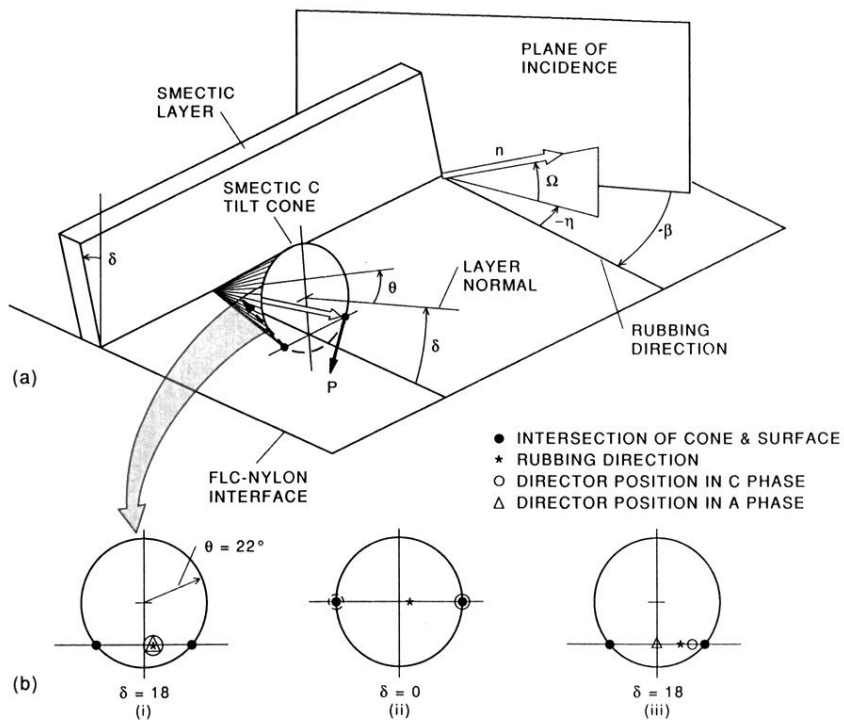


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