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Dynamics of Polarization Reversal in the Surface Layer of Ferroelectric Liquid Crystals

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Using a triangular wave method, we have studied the polarization reversal dynamics in the surface layer of a ferroelectric liquid crystal in a surface-stabilized geometry. It is found that there exist two distinct current peaks associated with two types of molecular reorientation processes in the polarization reversal. A simple model for the two processes occurred in the bulk and the surface layer is developed to describe the physical origin of the second peak under an external electric field. The non-polar and polar surface anchoring energies are estimated as 6.0×10^{-1} erg/cm^2 and 3.7×10^{-2} erg/cm^2, respectively.

I. INTRODUCTION

Ferroelectric liquid crystals (FLCs) exhibit a variety of structures depending on the anisotropic interactions at FLC/solid interfaces, the aligning procedure, and external fields. Particularly, knowledge of the interfacial interactions is of great importance for understanding the nature of the molecular reorientation and the polarization reversal occurred in the surface layer of FLCs. For instance, the molecular orientation of a surface-stabilized ferroelectric liquid crystal (SSFLC), characterized by two energetically degenerate states, is governed by the interfacial interactions that tend to unwind the intrinsic helix of FLCs [1]. In the presence of an external electric field E, one of the two states of SSFLC is preferred, depending on the polarity of E, by means of a ferroelectric coupling with E. The molecular switching of FLCs has been extensively studied by polarization reversal [2], stroboscopic micrography [3,4] and electro-optic measurements [5]. Among them, the polarization reversal revealed two current peaks in the SSFLC geometry [6]. Although the physical origin of the second peak is somewhat related to the chevron structures and/or the interfaces of FLCs [7–9], a complete picture remains to be explored.

In the present work, we describe how the interfacial interactions influence the dynamics of the polarization reversal and the associated molecular reorientation processes of FLCs. The experimental results together with numerical simulations in a simple model clearly indicate that the second current peak in the polarization reversal comes from the surface layer of FLCs. The effect of the chevron structures on the polarization reversal is also discussed.

II. EXPERIMENTAL

The FLC material used in this study was SCE 12 of British Drug House. The phase transition sequence is as follows : isotropic → (118.0° C) → cholesteric →(78.8° C) → smectic A → (64.0° C) → smectic C* → (−20.0° C) → crystalline. The sample cell was made up of conductive indium-tin-oxide coated glasses which were treated with poly(1,4-butylene terephthalate) (PBT) containing aromatic rings which resemble the cores of the liquid crystal (LC) molecules. The thickness of the polymer layer was about 300 Å, and both glass surfaces of the cell were unidirectionally rubbed so as to give a planar orientation. The cell gap was maintained by glass spacers of 3 μm thick, and the effective electrode area was 0.64 cm^2. The FLC was filled in the isotropic state, and cooled into the mesophase. Electric contacts were made directly to the internal surfaces of the glasses to apply an external electric field.

The sample cell was mounted in a home-made microfurnace for temperature control and the temperature fluctuations were approximately 0.02 °C. For uniform alignment of both the FLC molecules and smectic layers, the sample cell was cooled down at a rate of 0.1 °C/min into the ferroelectric, smectic C* phase. In addition, the square wave voltage of 100 Hz was applied to the cell in the vicinity of the smectic A - smectic C* (Sm A - Sm C*) phase transition temperature [10]. No apparent chevron structures were observed in the electrode area of the cell. For measuring the spontaneous polarization of the FLC sample, we employed a triangular wave method to monitor the shape and the time evolution of the polarization current peaks as a function of the applied voltage.

III. THE POLARIZATION REVERSAL IN THE SURFACE LAYER

We first describe the polarization current peaks in

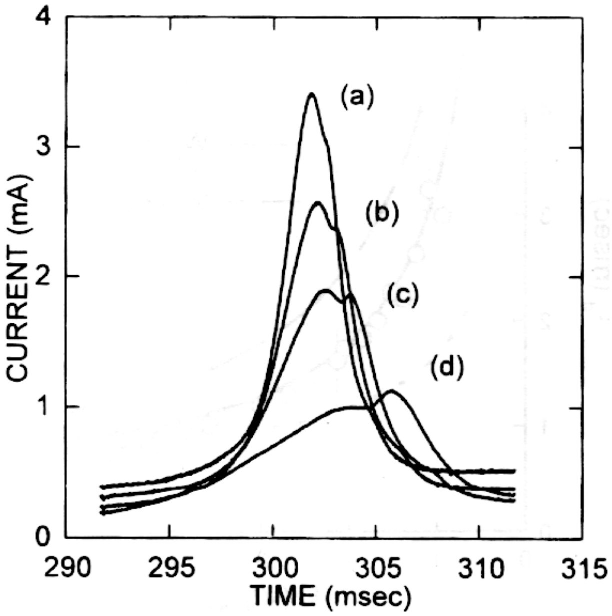

Fig. 1. The polarization reversal currents at various electric fields of 12 Hz; (a) 4.2 V/μm, (b) 3 V/μm, (c) 2.1 V/μm and (d) 1.1 V/μm. The measurements were made at $(T_c - T) = 29$ °C where T_c denotes the critical temperature for the Sm A - Sm C* transition.

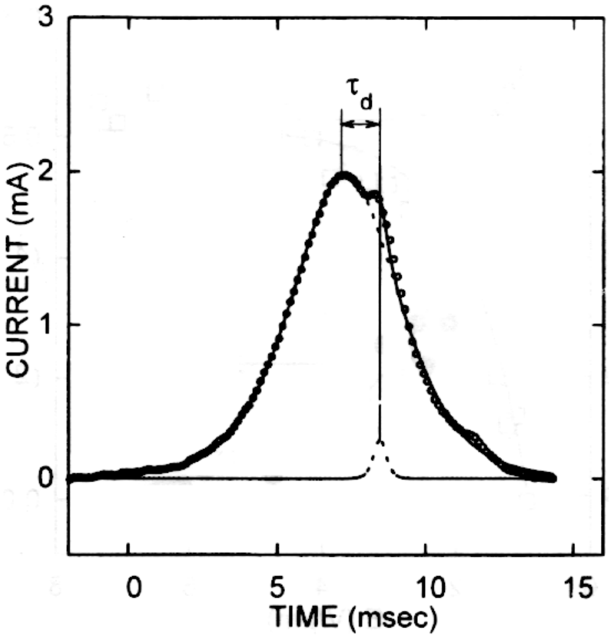

Fig. 2. Deconvolution of the polarization current, measured with 3.0 V/μm, into two distinct peaks. The circles represent the experimental data and two dotted lines correspond to the two peaks obtained by deconvolution, respectively. The solid line is the sum of the two dotted lines.

terms of the molecular reorientation processes. Fig. 1 shows typical polarization reversal currents at several electric fields at 12 Hz. The measurements were made at $(T_c - T) = 29.0$ °C where T_c denotes the critical temperature for the Sm A - Sm C* transition. As shown in Fig. 1, two distinct current peaks were clearly observed. The shape of the second peak depends on the magnitude of the external electric field E, and the delay in time between the first peak and the second varies with E. This may be attributed to either the molecular reorientation in the surface layer or the deformation of possible chevron kinks present in the cell. In our case, the molecular switching at the chevron interface is not energetically favorable since it requires relatively high electric field (of the order of 10 V/μm) [9]. Therefore, the second peak comes essentially from the surface switching. Basically, the relative magnitude of the polarization of the second peak to that of the first gives the thickness of the surface layer as a function of the electric field. In addition, the delay in time between the two peaks is related to the dynamical behavior of the surface layer during the polarization reversal.

Based on the above argument, the polarization reversal current can be deconvoluted into two parts, one of which is associated with the polarization in the bulk and the other in the surface layer. The convolution was performed using the polarization current form [11] of $E_o \sin\omega t/\cosh^2(PE_o\cos\omega t/\eta\omega)$ with $E_o \sin\omega t$ the applied electric field and η the relevant viscosity. Fig. 2 shows an example of two deconvoluted currents at $E =$ 3.0 V/μm, together with the total current. Here, τ_d represents the delay in time between the two peaks.

We now describe the dynamics of the polarization reversal in the surface layer and determine the thickness of the surface layer within a simple model. Fig. 3 shows the total polarization (P_T) and the polarization in the surface or boundary layer (P_b) resulting from the second peak as a function of the electric field E. As expected, the surface polarization (P_b) decreases with increasing the electric field E, meaning that the effective thickness of the surface layer l decreases as E increases. Above a certain threshold ($E_{th} = 6$ V/μm), only a single current peak was observed and the total polarization P_T was then saturated. In this region, the surface layer is negligibly thin and no molecules are allowed for reorientation. Assuming that $l \sim d(P_b/P_T)$ with d the cell thickness, l is estimated as about 200 Å at 4 V/μm, which is consistent with a typical surface coherence length [12].

Let us now introduce the concept of the relevant coherence length and discuss the dynamics of the surface polarization. In the presence of an electric field $\vec{E}$ along the $\hat{z}$ axis, consider the smectic layers aligned along the $\hat{y}$ axis and perpendicular to the cell surface. In the one elastic constant approximation, the free energy density f per unit area is written as [13]

$$f = \int_0^d dz \left[\frac{K}{2}{\phi_z}^2 - PE\cos\phi + Kq_s\sin\phi\phi_z\right] + f_s, \quad (1)$$

where K is the elastic constant, ϕ the azimuthal angle between the $\hat{z}$ axis and the direction of the polarization P, q_s the wavevector characteristic to the spontaneous

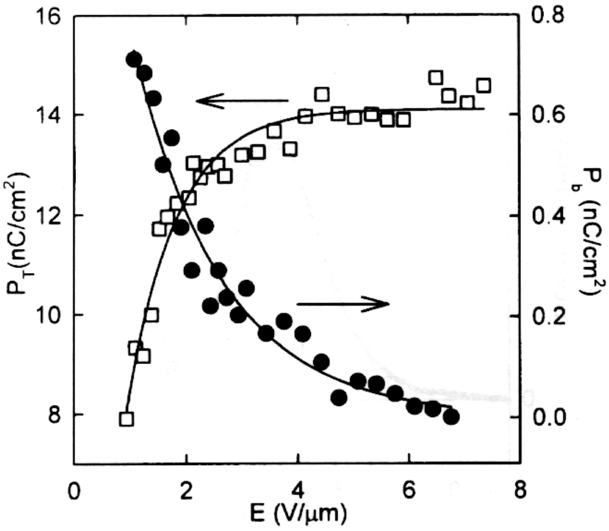

Fig. 3. The electric field dependence of the spontaneous polarization. The squares and circles represent total polarization (P_T) and the polarization (P_S) in the surface layer, respectively.

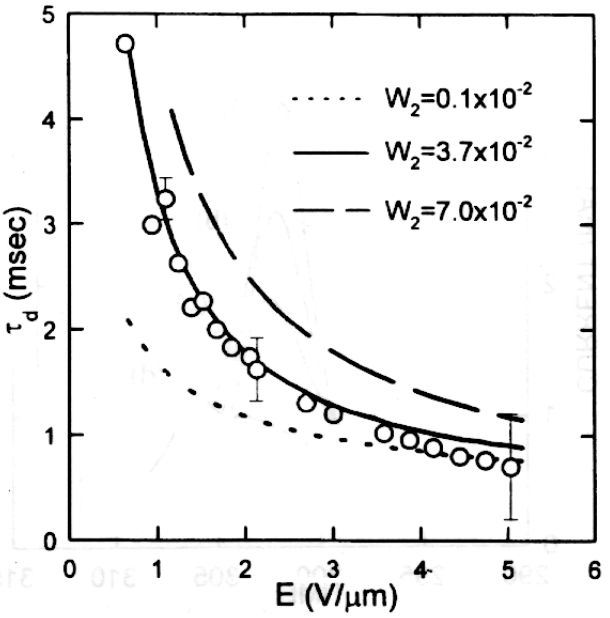

Fig. 4. The delay in time, τ_d, between two current peaks, as a function of E. The circles represents the experimental data and the solid line is the least-square fit to the numerical simulations. From the best fit with $K = 6.0 \times 10^{-7}$ dyne, $P = 14$ nC/cm^2, $\theta = 22.5°$ and $\gamma_s = 0.1$ poise, $W_1 = 6.0 \times 10^{-1}$ erg/cm^2 and $W_2 = 3.7 \times 10^{-2}$ erg/cm^2 were obtained. The dotted and dashed lines correspond to $W_2 = 1.0 \times 10^{-2}$ erg/cm^2 and $W_2 = 7.0 \times 10^{-2}$ erg/cm^2, respectively.

splay of the polarization and f_s the surface anchoring energy.

Macroscopically, the surface anchoring energy f_s is given by a combination of the nonpolar and polar parts as follows [14].

$$f_s = -W_1 \sin^2\theta \cos^2(\phi_s - \phi_0) - (\hat{s}\cdot\hat{z}) W_2 \cos(\phi_s - \phi_0)\ , \tag{2}$$

where the layer tilt is ignored. Here, $\hat{s}$ is the surface normal, θ the tilt angle in the Sm C* phase, ϕ_s the azimuthal angle and ϕ_0 the easy angle at the surface.

For the electric field E below a certain strength, i.e., less than a surface field (E_s), the molecules at the surface will not experience reorientation. In this case, the coherence length in the bulk will be scaled as $\xi = \sqrt{K/P(E - E_s)}$ while the effective length λ in the surface layer will be $(\xi - b)$ where the extrapolation length b is defined as $b = K/(W_1 \sin^2\theta + W_2)$ [13]. With the measured values of $\theta = 22.5°$ and $P = 14$ nC/cm^2, the values of $E_s = (6.2 \pm 0.6) \times 10^{-1}$ V/μm, $K = (6.4 \pm 1.4) \times 10^{-7}$ dyne, $W = (6.7 \pm 2.7) \times 10^{-1}$ erg/cm^2 and $b = (9.6 \pm 1.3) \times 10^2$ Å were determined from the least-square fit of $l \sim d(P_b/P_T)$ to a form of λ. Above a certain threshold E_{th}, the surface layer disappears ($\lambda \to 0$). E_{th} is estimated as $(W^2/KP + E_s) \approx 5.7$ V/μm, which is shown in Fig. 3.

We now discuss the delay in time, τ_d, observed in the polarization reversal in a dynamic model based on Eq. (1). Fig. 4 shows τ_d, between the first and second current peaks as a function of the electric field E. In describing the field dependence of τ_d, we start with the dynamic equation in the surface layer from the torque balance. Most of the molecules in the bulk are expected to contribute to the first peak in the polarization reversal as discussed above. Moreover, in the presence of an electric field, the molecules at the unfavorable surface will be reoriented along the field direction while those at the favorable surface will keep the initial orientation. This reorientation process in the surface layer will produce the second peak in the polarization reversal. The above assertion is not physically unreasonable since the chevron switching, if any, will occur only at relatively high fields [10]. Thus, in our dynamic model, any change in the smectic layers such as the chevron deformation and layer tilting is ignored. Now, we assume that the molecules are relaxed from the bulk to the favorable surface within the effective coherence length l. In this surface layer, ϕ will continuously vary as $(\phi_0 - \phi_s)z/l + \phi_s$, with ϕ_0 the azimuthal angle and ϕ_s the easy angle at the surface, respectively. At the favorable surface, the torque balance is then given by [15]

$$\begin{aligned} \gamma_s l \frac{\partial \phi_s}{\partial t} &= 2PEl \frac{(\cos\phi_0 - \cos\phi_s)}{\phi_0 - \phi_s} \\ &+ \frac{K}{l}(\phi_0 - \phi_s)[1 + \sin(\phi_s - \phi_0)] \\ &- W_1 \sin^2\theta \sin(\phi_s - \phi_0)\cos(\phi_s - \phi_0) \\ &+ W_2 \sin(\phi_s - \phi_0), \end{aligned} \tag{3}$$

where the viscous surface torque $\gamma_s l(\partial\phi_s/\partial t)$ is considered as the volume integral over l of the volume torque density. The dynamics of the molecular reorientation in the surface layer l is readily determined from Eq. (3).

Let us define the time during molecular switching from ϕ_s to ϕ_0 as the characteristic (or delay) time τ_d. For numerical simulations, we used $K = 6.0 \times 10^{-7}$ dyne, $P = 14$ nC/cm^2, $\theta = 22.5°$ and $\gamma_s = 0.1$ poise in Eq. (3). Together with experimental data of τ_d, the numerical results were shown in Fig. 4 as a function of E for several different anchoring energies. From the best fit of τ_d, the non-polar and polar parts of the surface anchoring energy are determined as $W_1 = 6.0 \times 10^{-1}$ erg/cm^2 and $W_2 = 3.7 \times 10^{-2}$ erg/cm^2, respectively. As suggested previously [7], the characteristic time increases with increasing W_1 for fixed W_2. This implies that the second peak disappears quickly with increasing temperature. One important point is that most of SSFLCs exhibit chevron structures associated with tilted layer formation, which can be transformed into quasi-bookshelf structures after the electric field treatment [10]. In fact, the molecular switching at the chevron interfaces will occur only at relatively high fields.

IV. CONCLUDING REMARKS

We have presented experimental results for the polarization reversal and characteristic time associated with molecular reorientation in the surface layer of FLCs. It was found that there exist two current peaks in the polarization reversal related to the two kinds of molecular reorientation processes. In our simple model, a rather complete picture of the reorientation process from the bulk to the surface region was obtained. The time characteristic to the molecular switching and the thickness of the surface layer decrease with increasing the electric field. The polar part of the surface anchoring energy was found to play a critical role on the polarization reversal in the surface layer.

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