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# Molecular reorientation dynamics due to direct current voltage-induced ion redistribution in undoped nematic planar cell

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We discuss the influence of mobile ions in liquid crystalline materials on the dc voltage-induced molecular reorientation dynamics. We investigate the conventional case of an undoped planar nematic sample aligned by thin polymeric films deposited on the electrodes. A simple model for the ion drift towards the electrodes has been developed in the limit of negligible diffusion current in order to obtain the time dependence of the internal electric field and, subsequently, the dynamics of the director distribution. This model describes the buildup of two electric charge double layers near each electrode reducing the effective voltage drop across the nematic sample. We report the measurement of the dynamics of the phase retardation in a conventional 5CB planar cell when a stepwise dc voltage above the Freedericksz threshold is applied to the electrodes. We demonstrate that our model reproduces the experimentally determined curve, thereby providing reliable values for the physical parameters used in the fitting procedure. © 2004 American Institute of Physics. [DOI: 10.1063/1.1756693]

## I. INTRODUCTION

In recent years, several studies on the transport mechanisms of ionic impurities in nematic liquid crystal (NLC) cells have been published.<sup>1–5</sup> To elucidate the processes involved, the investigations have mainly focused on the diffusion process, charge injection and generation of ions due to the external field. The interest in this field is mainly due to the application of NLC in liquid crystal displays in which ion transport and accumulation influence the display performance and lead to defects such as image retention and flicker.<sup>4,5</sup>

Recent experimental investigations on surface induced photorefractive phenomena in NLC cells<sup>6–8</sup> have shown that the foregoing phenomena are of great importance for understanding effects, such as photoinduced charge injection and recombination or ion desorption, that are not directly related to the display technology. Steady state phase retardation measurements as a function of the applied dc voltage in polyvinyl alcohol (PVA)-aligned E7 cells have confirmed the creation of electric charge double layers at each aligning surface due to dc field induced separation of ions in the NLC bulk.<sup>9</sup> The accumulation of charge at the surfaces results in a screening effect of the applied external voltage, reducing the effective voltage for molecular reorientation in the NLC sample. Moreover, surface ions may modify the anchoring strength and preferred direction on the aligning layers,<sup>8</sup> as suggested by the latest theoretical studies on selective ion adsorption and external electric field effect on NLC containing impurities.<sup>10,11</sup> Nevertheless, according to the analysis

reported in Ref. 9, the possible modification of anchoring conditions on the PVA substrates does not seem to play a significant role in the explored range of applied voltages. The experimental investigation presented herein demonstrates the possibility to optically modulate the surface density of accumulated ions, showing interesting prospects for application in photonics [i.e., optically addressed-spatial light modulator (SLM)]<sup>6,9</sup> and so stimulating further studies on the ion transport and accumulation processes, especially regarding the mechanism of director reorientation. Different measurement techniques have been reported, which mainly characterize the electrical properties of liquid crystal (LC) cells and show a complex phenomenology.<sup>1–5</sup>

We report a simple model describing the transient behavior of the ion distribution in a NLC cell under the influence of an externally applied dc field, in the limit of negligible diffusion current. The goal of the model is to explain the transient molecular reorientation occurring after the application of a stepwise dc voltage above the Freedericksz threshold in a planar aligned 5CB cell containing ions. In order to verify the effectiveness of the model, we present a typical optical retardation measurement on a conventional planar cell, filled with the well known liquid crystalline material (5CB), whose physical parameters are firmly established.

We show that the model reproduces the dynamics of the optical retardation process and yields realistic values for the physical parameters of the system, even though anchoring modifications were not considered. Information on the ion density and the ionic mobility in the NLC have been determined through fitting the temporal evolution of the optical retardation. Although the model is simple, the obtained values are in good agreement with the reference values, under-

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lining that it is suitable to describe the observed phenomenon.

## II. MODEL

We consider a nematic layer of thickness  $d$ , bounded by two parallel electrodes covered with an insulating film of thickness  $L$  to avoid charge injection.

At thermodynamic equilibrium, commercial LCs contain a density of ions  $n_0$  due to dissociated impurities. When an external electric field is applied to the sample the ions move towards the electrode of opposite sign. If the external field is strong enough, all of the ions are pushed close to the electrodes, and the LC bulk remains free of ions. This conclusion holds true if the thermodynamic equilibrium is not perturbed by the electric field, as we assume in our analysis. If the field is suddenly removed and adsorption phenomena are absent, the ions redistribute homogeneously throughout the sample. In this sense, field-induced ion separation is a reversible effect.

In the following we limit our discussion to the movement of ions under the influence of an external applied field and obtain an expression for the relaxation time and the voltage drop across the NLC layer. Finally, the dielectric molecular reorientation in the NLC due to the effective field is considered.

### A. Movement of the ions under the influence of an external electric field

In the absence of an external field the ions are homogeneously distributed throughout the LC, with a bulk density  $n_0$ . When a dc voltage is applied between the electrodes, the ions move towards the electrode of opposite sign. We assume that the diffusion current is negligible compared to the conduction current. This means that, in the presence of an external field, the bulk density of ions  $n$  is less than the initial one,  $n_0$ , but is still uniform within the NLC layer. In the following calculations,  $V$  is the applied voltage,  $q\sigma$  is the surface charge density of the ions collected in front of the electrode, and  $q\Sigma$  is the external charge density deposited by the power supply to set up  $V$ . We assume that the mobility of the positive and negative ions are the same, although this simplifying hypothesis can be easily removed for further developments of the model.

The electric field in the surface layers of thickness  $L$  is

$$E_S = \frac{\Sigma}{\epsilon_S} q \tag{1}$$

and in the bulk it is

$$E_B = \frac{\Sigma - \sigma}{\epsilon_B} q, \tag{2}$$

where  $\epsilon_S$  and  $\epsilon_B$  are the dielectric constants of the surface film and the NLC layer, respectively. Since the applied voltage is  $V$ , we have  $V = 2E_S L + E_B d$ , by using Eqs. (1) and (2) this can be rewritten as

$$V = \left( 2 \frac{L}{\epsilon_S} + \frac{d}{\epsilon_B} \right) q \Sigma - \frac{d}{\epsilon_B} q \sigma. \tag{3}$$

Equation (3) connects the applied voltage  $V$  and the surface density of charges provided by the power supply to the electrode. From Eq. (3) we get

$$q \Sigma = \gamma \frac{\epsilon_B}{d} \left( V + q \frac{\sigma}{\epsilon_B} d \right), \tag{4}$$

where

$$\frac{1}{\gamma} = 1 + 2 \frac{L}{d} \frac{\epsilon_B}{\epsilon_S} \tag{5}$$

is a parameter that depends on the properties of the insulating film and of the NLC. Using Eqs. (1), (2), and (4) we obtain expressions for the surface and bulk electric fields

$$E_S = \gamma \frac{\epsilon_B}{\epsilon_S} \left( \frac{V}{d} + q \frac{\sigma}{\epsilon_B} \right), \tag{6}$$

and

$$E_B = \gamma \left( \frac{V}{d} - 2q \frac{\sigma}{\epsilon_S} \frac{L}{d} \right). \tag{7}$$

The voltage drop across the NLC  $V_B = E_B d$  is then

$$V_B = \gamma \left( V - 2 \frac{\sigma}{\epsilon_S} q L \right), \tag{8}$$

which is responsible for the change in birefringence of the NLC layer.

We can now evaluate the time evolution of  $\sigma = \sigma(t)$  when an external voltage is applied at  $t=0$ . Due to ion accumulation, the actual bulk density of ions within the NLC layer is given by

$$n = n_0 - \frac{\sigma}{d}. \tag{9}$$

The conduction current density is given by  $j = nqv$ , where  $v = \mu E_B$  is the drift velocity, and  $\mu$  the mobility. Taking Eq. (9) into account, in a time  $dt$  an amount of charge  $dQ$ , given by

$$dQ = jA dt = \left( n_0 - \frac{\sigma}{d} \right) q \mu E_B A dt \tag{10}$$

is collected just in front of the electrode because of conduction. The definition of the surface ion density allows us to write

$$dQ = q d\sigma A. \tag{11}$$

From Eqs. (10) and (11), taking Eq. (7) into account, we obtain

$$d\sigma = \sigma_M \left( 1 - \frac{\sigma}{\sigma_M} \right) \left( 1 - \frac{\sigma}{S} \right) \frac{dt}{\tau_i}, \tag{12}$$

where  $\sigma_M = n_0 d$  is the maximum surface ion density that it is possible to collect in front of the electrode,  $S = \epsilon_S V / (2qL)$  is a surface ion density that depends on the physical properties of the surface layer and on the applied voltage, and  $\tau_i^{-1} = \gamma \mu V / d^2$  is the field-driven ion transport time. Using Eq. (12) we get

$$\sigma(t) = \sigma_M S \frac{1 - \exp\{[1 - (\sigma_M/S)](t/\tau_i)\}}{\sigma_M - S \exp\{[1 - (\sigma_M/S)](t/\tau_i)\}}, \quad (13)$$

giving the time evolution of  $\sigma = \sigma(t)$  that we were looking for.

We notice that the condition  $\sigma_M > S$  implies

$$V < V_c = 2L \frac{n_0 q d}{\epsilon_S}. \quad (14)$$

In terms of  $V_c$ , Eq. (13) can be rewritten as

$$\sigma(t) = \sigma_M \frac{1 - \exp(t/\tau_R)}{(V_c/V) - \exp(t/\tau_R)}, \quad (15)$$

where

$$\frac{1}{\tau_R} = \left(1 - \frac{\sigma_M}{S}\right) \frac{1}{\tau_i} = \gamma \mu \frac{V - V_c}{d^2}. \quad (16)$$

From Eq. (15) it follows that the effective ion transport relaxation time is  $\tau_R$ , and Eq. (16) shows that as  $V \rightarrow V_c$ ,  $\tau_R$  diverges.

From Eq. (15) we have

$$\begin{aligned} \sigma(f) &= \lim_{t \rightarrow \infty} \sigma(t) = S, \quad \text{for } V < V_c \\ \sigma(f) &= \lim_{t \rightarrow \infty} \sigma(t) = \sigma_M, \quad \text{for } V > V_c. \end{aligned} \quad (17)$$

According to Eq. (8), the voltage drop across the NLC layer  $V_B = V_B(t)$  is

$$V_B(t) = \gamma V \frac{[(V_c/V) - 1] \exp(t/\tau_R)}{(V_c/V) - \exp(t/\tau_R)}. \quad (18)$$

It follows that  $V_B$  tends to

$$\begin{aligned} V_B(f) &= \lim_{t \rightarrow \infty} V_B(t) = 0, \quad \text{if } V < V_c \\ V_B(f) &= \lim_{t \rightarrow \infty} V_B(t) = \gamma(V - V_c), \quad \text{if } V > V_c \end{aligned} \quad (19)$$

in the infinite time limit. The function  $V_B = V_B(t)$  is always a decreasing function of  $t$ , but for  $V < V_c$  it tends to zero, whereas for  $V > V_c$  it tends to a finite value.

During the ion collection in front of the electrode,  $\sigma(t)$  is given by Eq. (13). Since the surface charge on the electrodes,  $\Sigma(t)$ , depends on  $\sigma(t)$  via Eq. (4), it follows that there is a net current  $i = dQ_{\text{ext}}/dt$  in the circuit, where  $Q_{\text{ext}} = q\Sigma A$  is the total charge provided by the external power supply. Taking Eqs. (4) and (15) into account we get

$$i(t) = \gamma q A \frac{\sigma_M}{\tau_i} \left( \frac{\sigma_M - S}{\sigma_M - S \exp(t/\tau_R)} \right)^2 \exp(t/\tau_R). \quad (20)$$

From Eq. (20) it follows that for  $t \rightarrow \infty$ ,  $i \rightarrow 0$  for all applied voltages, as expected.

## B. Orientational response of the nematic layer to the effective field

We consider a planar aligned cell of NLC with a positive dielectric anisotropy ( $\epsilon_a = \epsilon_{\parallel} - \epsilon_{\perp} > 0$ ). The bounding surfaces of the NLC layer are at  $z = \pm d/2$ . If the sample is

submitted to an effective electric field  $\mathbf{E} = E(t)\mathbf{k}$ , the electric torque destabilizes the initial planar orientation and a distortion of the director occurs if the Freedericksz threshold is exceeded. Our aim is to analyze the dynamics of the field-induced director reorientation.

In the single-constant approximation, the free energy density is

$$f = \frac{1}{2} K \left( \frac{d\theta}{dz} \right)^2 - \frac{1}{2} \epsilon_a E^2(t) \sin^2 \theta, \quad (21)$$

where  $\theta$  is the angle between the nematic director  $\mathbf{n}$  and the  $x$  axis and  $K$  is the elastic constant. We assume strong anchoring to the surfaces. This means that  $\theta(\pm d/2) = 0$  for all external fields.

The reorientation dynamics within the NLC layer are described by  $\theta(z, t)$ , which is governed by the equation

$$K \frac{\partial^2 \theta}{\partial z^2} + \frac{1}{2} \epsilon_a E^2(t) \sin(2\theta) - \eta \frac{\partial \theta}{\partial t} = 0, \quad (22)$$

where  $\eta$  is the rotational viscosity coefficient of the LC. It is more convenient to write Eq. (22) in the form

$$\frac{\partial^2 \theta}{\partial u^2} + \frac{1}{2} h^2(t) \sin(2\theta) - \tau \frac{\partial \theta}{\partial t} = 0, \quad (23)$$

where  $u = \pi(z/d)$  is a reduced spatial coordinate ( $-\pi/2 \leq u \leq \pi/2$ ),  $h(t) = E(t)/E_{\text{th}}$  is the electric field expressed in units of the threshold field [ $E_{\text{th}} = (\pi/d)\sqrt{K/\epsilon_a}$ ], and  $\tau = (\eta/K)(d/\pi)^2$  is the characteristic elastic relaxation time for the NLC cell.

In the limit of small  $\theta$ , i.e., for  $E \approx E_{\text{th}}$ , to first order in  $\theta$ , Eq. (22) can be written as

$$\frac{\partial^2 \theta}{\partial u^2} + h^2(t) \theta - \tau \frac{\partial \theta}{\partial t} = 0. \quad (24)$$

Since we are considering the case of strong anchoring,  $\theta$  can be expanded in a Fourier series as follows:

$$\theta(u, t) = \sum_n C_n(t) \cos[(2n+1)u]. \quad (25)$$

Close to the Freedericksz threshold we assume that a good approximation for  $\theta$  is

$$\theta(u, t) = \theta_M(t) \cos u. \quad (26)$$

In this case Eq. (24) becomes

$$\frac{d\theta_M(t)}{dt} + \frac{1 - h^2(t)}{\tau} \theta_M(t) = 0. \quad (27)$$

From Eq. (27) we get

$$\theta_M(t) = \theta_M(0) \exp\left[ \int_0^t \frac{h^2(t') - 1}{\tau} dt' \right], \quad (28)$$

where  $\theta_M(0)$  is the initial small fluctuation responsible for the instability.

In Sect. II A, the dynamics of the voltage drop across the bulk was calculated neglecting the diffusion current. In this framework, the NLC bulk always remains electrically neu-

tral; the electric field is position independent; and its time dependence is related to the evolution of the surface density of the ions  $\sigma(t)$ . In our analysis, we have also assumed that the material is isotropic. However, since we are interested in the influence of the electric field on the optical response of the NLC, it is necessary to discuss the role of the dielectric anisotropy on the electric field itself. Strictly speaking, if the diffusion current is neglected, the bulk electric field is determined by solving the Maxwell equation  $\text{div } \mathbf{D}=0$ , with the boundary conditions  $D_z = \pm q\sigma$ , at  $z = \mp d/2$ .  $\mathbf{D}$  is the electric displacement, and  $D_z$  is its component normal to the bounding surfaces. Taking into account that NLCs are linear media, the constitutive equation connecting  $\mathbf{D}$  to the electric field  $\mathbf{E}$  is  $D_i = \epsilon_{ij}E_j$ , where  $\epsilon_{ij} = \epsilon_a n_i n_j + \epsilon_{\perp} \delta_{ij}$ , in which  $n_i$  are the Cartesian components of  $\mathbf{n}$ . In the one-dimensional problem under consideration, since  $\text{rot } \mathbf{E}=0$ , only  $E_z = E \neq 0$ , and the electric field is obtained by the differential equation

$$\frac{d}{dz} \{ [\epsilon_{\perp} + \epsilon_a \sin^2(\theta)] E(z,t) \} = 0, \quad (29)$$

with the boundary conditions

$$[\epsilon_{\perp} + \epsilon_a \sin^2(\theta)] E(z,t) = \pm q\sigma, \quad \text{for } z = \mp d/2, \quad (30)$$

which has to be solved together with Eq. (22). However, since we are limiting our investigation to small values of  $\theta$ , the dielectric anisotropy gives a contribution to the electric field that is second order in  $\theta$ , as follows from Eq. (30). This contribution to the field can be neglected in our linearized analysis because in Eq. (24) it gives rise to a term that is third order in  $\theta$ .

### III. EXPERIMENTAL RESULTS AND DISCUSSION

An experimental investigation was carried out on a 30- $\mu\text{m}$ -thick cell filled with the commercial LC 4-pentyl-4'-cyanobiphenyl, 5CB (K15, from Merck). The cell was built using two flat glass substrates (PD5005, from Donnelly Corporation) coated with a 20-nm-thick transparent and conductive indium-tin-oxide (ITO) layer. A thin PVA film ( $L \approx 10 \text{ nm}$ ) was deposited onto the ITO-coated glasses through spin coating a PVA (87%–89% hydrolyzed, MW 31 000–50 000, from Aldrich) aqueous solution and then baking the glass slides at 120 °C for 1 h. After slowly cooling to room temperature, the PVA films were rubbed with a velvet cloth in order to obtain uniform planar NLC alignment. The cell was assembled by putting Mylar spacers between two parallel-oriented glass substrates and gluing them together with epoxy resin from the outside. After measuring the thickness of the empty cell ( $d \approx 30.1 \mu\text{m}$ ) by an interferometric method, the cell was filled with the LC in the nematic phase at room temperature.

The measurements were performed at a temperature of about 25 °C. Because of the positive dielectric anisotropy of our NLC,  $\epsilon_a \equiv \epsilon_{\parallel} - \epsilon_{\perp} \approx 13 \times \epsilon_0$ , an electric field normal to the glass walls tends to orient the nematic director and hence the optical axis along the field direction, i.e., homeotropically, thus reducing the cell's average birefringence. The change in the effective birefringence can be detected with a

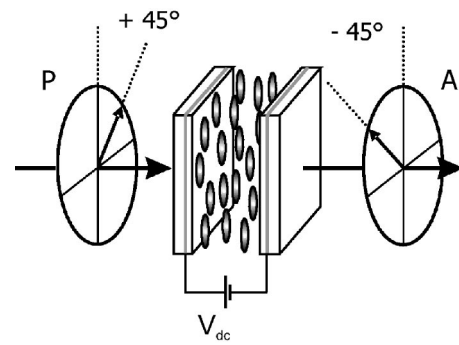


FIG. 1. Experimental setup for optical phase retardation measurement. The planar cell is placed between crossed polarizers ( $P$  and  $A$ ), with its optical axis oriented at  $45^\circ$  with respect to both the polarizer ( $P$ ) and the analyzer ( $A$ ) axes. A low power He–Ne laser beam ( $\lambda=632.8 \text{ nm}$ ) is used to probe the NLC cell birefringence, while a stepwise dc voltage is applied.

linearly polarized He–Ne probe beam by measuring the intensity transmitted through a crossed analyzer. The experimental setup is sketched in Fig. 1. The NLC cell is oriented with its optical axis at  $45^\circ$  with respect to the probe beam polarization. A relative phase retardation  $\Delta\phi$  occurs due to the different propagation velocity of the ordinary and extraordinary waves in the NLC film

$$\Delta\phi = 2\pi d\Delta n/\lambda, \quad (31)$$

where  $\Delta n$  is the effective NLC cell birefringence and  $\lambda$  is the probe beam wavelength ( $\lambda=632.8 \text{ nm}$ ). The intensity  $I_{\perp}$  traversing the polarizer–cell–analyzer system depends on  $\Delta\phi$

$$I_{\perp} \propto I_0 \sin^2\left(\frac{\Delta\phi}{2}\right), \quad (32)$$

where  $I_0$  is the probe beam intensity after the polarizer. The time evolution of the optical phase retardation  $\Delta\phi(t)$  has been calculated by measuring the transmitted intensity  $I_{\perp}(t)$ .<sup>12</sup>

In Fig. 2 we report the experimental phase retardation versus time (open circles) when a stepwise voltage is applied to the cell's electrodes. The voltage ( $V_{\text{dc}}=1.3 \text{ V}$ ) was chosen so as to be above the Freedericksz threshold ( $V_{\text{th}}$

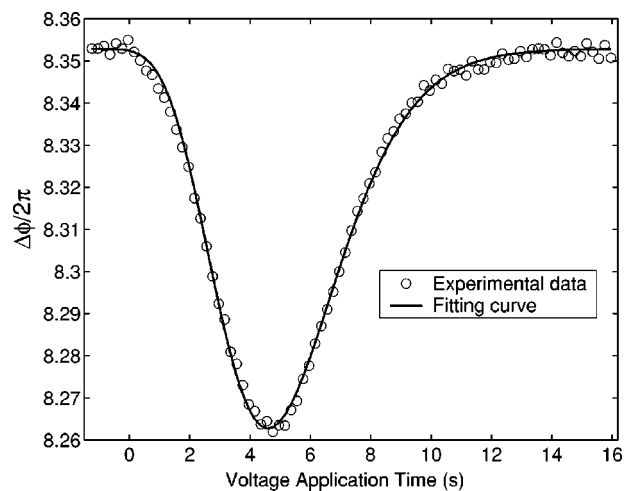


FIG. 2. Experimental (open circles) and calculated (solid line) optical phase retardation, in units of  $2\pi$ , vs the dc voltage application time.



$\approx 0.8$  V) but yet small enough to avoid saturation of the director reorientation in the middle of the cell and charge generation due to molecular dissociation.<sup>2</sup> Both of these events are, in fact, neglected in the model discussed above.

After application of the voltage, an initial decrease of the optical phase retardation occurs due to the nematic director reorientation towards the homeotropic configuration. It reaches a minimum, corresponding to the maximum director distortion, and then relaxes back to the initial value when the undistorted configuration is approached again. The elastic distortion relaxation is ascribed to the decrease of the effective voltage drop across the NLC bulk ( $V_B$ ) to below the Freedericksz threshold ( $V_{th}$ ).

In order to check the validity of the model in describing the director distortion dynamics, we calculated the phase retardation taking into account the time dependence of the effective voltage drop across the nematic layer, as reported in Eq. (18). Starting from Eq. (28), which represents the evolution of the director angle in the middle of the cell, the phase shift can be evaluated by

$$\begin{aligned}\Delta\phi(t) &= \frac{2\pi}{\lambda} \int_{-d/2}^{d/2} [n_e(z,t) - n_0] dz \\ &= -\frac{2d\pi n_0}{\lambda} + \frac{2d}{\lambda} \int_{-\pi/2}^{\pi/2} n_e(u,t) du,\end{aligned}\quad (33)$$

and

$$n_e(u,t) = \frac{n_e n_0}{\sqrt{n_e^2 \sin^2 \theta(u,t) + n_0^2 \cos^2 \theta(u,t)}}, \quad (34)$$

where  $\theta(u,t)$  describes the evolution of the distortion profile as reported in Eq. (26), and  $h(t) = V_B(t)/V_{th}$  in Eq. (28). By means of Eq. (33) we fitted the experimental phase retardation dynamics choosing appropriate fitting parameters: the ion mobility  $\mu$ ; the maximum voltage drop at the two double layers  $V_c$ , which accounts for the bulk density of ions  $n_0$  through Eq. (14); and the initial fluctuation angle  $\theta_M(0)$  at the cell's central point. Characteristic values of  $\mu$  in NLCs are on the order of  $10^{-10} - 10^{-9} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$ ,<sup>1,13,14</sup> while the ion concentration  $n_0$ , and then  $V_c$ , may strongly depend on the purity of the LC: typical values of  $n_0$  range from  $10^{19} \text{ m}^{-3}$  to more than  $10^{22} \text{ m}^{-3}$ .<sup>3</sup> The observed distortion relaxation towards the initial planar configuration (see Fig. 2) suggests that  $V_c$  is high enough to drive the effective voltage  $V_B$  below the Freedericksz threshold, i.e.,  $V_c \geq V - V_{th} \approx 0.5$  V, for  $\gamma \approx 1$  in Eq. (19). Because of the good planar alignment, with a pretilt angle at the aligning surfaces on the order of  $10^{-2}$  rad, the fluctuation angle  $\theta_M(0)$  is expected to be small. Representative values of the physical parameters involved in the model and used in the fitting procedure are given in Table I.

The solid line in Fig. 2 represents the best fit of the experimental phase retardation data and has been obtained for the following values of the fitting parameters:

$$\begin{aligned}\mu &\approx 2.21 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}, \\ V_c &\approx 0.85 \text{ V},\end{aligned}\quad (35)$$

TABLE I. Representative values of the significant parameters involved in the fitting procedure.

Parameter	Symbol	Representative value
Cell thickness	$d$	30.1 $\mu\text{m}$
Surface layers thickness	$L$	$10 \times 10^{-3} \mu\text{m}$
Applied voltage	$V$	1.3 V
Probe wavelength	$\lambda$	$632.8 \times 10^{-3} \mu\text{m}$
Ordinary refractive index <sup>a</sup>	$n_o$	1.5309
Extraordinary refractive index <sup>a</sup>	$n_e$	1.7063
PVA dielectric constant	$\epsilon_S$	$2 \times \epsilon_0$
Ordinary dielectric constant <sup>a</sup>	$\epsilon_B = \epsilon_{\perp}$	$6.7 \times \epsilon_0$
Dielectric anisotropy <sup>a</sup>	$\epsilon_a = \epsilon_{\parallel} - \epsilon_{\perp}$	$13 \times \epsilon_0$
Elastic constant <sup>a</sup>	$K$	$6.4 \times 10^{-12} \text{ N}$
Rotational viscosity <sup>a</sup>	$\eta$	$8.1 \times 10^{-2} \text{ Pa s}$
Mobility <sup>b</sup>	$\mu$	$10^{-10} - 10^{-9} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$
Ion density <sup>c</sup>	$n_0$	$10^{19} - 10^{22} \text{ m}^{-3}$

<sup>a</sup>5CB at 25 °C (Ref. 14).

<sup>b</sup>Typical values for NLC (Ref. 13).

<sup>c</sup>Typical values for 5CB (Ref. 3).

$$\theta_M(0) \approx 0.96 \times 10^{-2} \text{ rad.}$$

The fitting procedure has been carried out through a constrained nonlinear minimization of the sum of the quadratic differences between the experimental and theoretical phase retardation values versus time. By choosing different initial estimates within the variability range of the three fitting parameters and accounting for the values of the other 5CB parameters (see Table I), the fits uniquely converge towards the values reported in (35). A quantitative estimation of the goodness-of-fit can be provided by the chi-square test. The reduced chi square  $\chi^2_{\nu} = \chi^2/\nu$  value for the best fit has been calculated to be  $\chi^2_{\nu} \approx 0.22$ , where  $\nu = n - m = 84$  is number of data points used in the fit ( $n = 87$ ) minus the number of fitting parameters ( $m = 3$ ). According to the estimated  $\chi^2_{\nu}$  value and the degrees of freedom, the probability of exceeding  $\chi^2$  is higher than 0.99. Even though many approximations were made to simplify the proposed model, it provides realistic estimates of the three fitting parameters, yielding a good fit for the phase retardation dynamics. The ion mobility  $\mu$  remains within the typical range for NLCs reported in Table I, and the fluctuation angle in the middle of the cell  $\theta_M(0)$  is of the same order as the pretilt angle. The maximum bulk voltage reduction value  $V_c$  is comparable with the result of Ref. 9, according to which the voltage drop at the two double layers matches the applied voltage for applied voltages up to nearly 1 V. This allows the estimation of the bulk ion density in the NLC cell to be  $n_0 \sim 10^{20} \text{ m}^{-3}$  through Eq. (14), which is also consistent with the typical values for 5CB cells (see Table I). The value of  $V_c$  indicates that the ion density is not sufficient to completely shield the applied voltage ( $V = 1.3$  V),<sup>9</sup> but it is high enough to drive the effective voltage below the Freedericksz threshold, so that the field-induced distortion relaxes completely. From the estimated values of  $\mu$  and  $V_c$  and by means of Eq. (16), we can calculate the effective ion transport relaxation time to be  $\tau_R \approx 9.1$  s in our cell's configuration, which controls the time evolution of the surface charge density and of the effective bulk voltage, through Eqs. (15) and (18), respectively. The value of  $\tau_R$  is of the same order of magnitude as the field-

driven ion transport time reported in Ref. 1, provided that the cell thickness  $d$  and the screening effect due to the ions are taken into account.

#### IV. CONCLUSION

We have discussed a simple model describing the transport and accumulation of ions and the dielectric reorientation response in a NLC cell due to a stepwise dc field. The model has been developed in the limit of strong anchoring, negligible ion diffusion current, and small reorientation angle. It provides a satisfactory agreement with the experimental phase retardation dynamics and yields realistic values for the physical parameters. The analysis confirms that the main effect of ion accumulation at the surfaces on the molecular reorientation is the reduction of the effective bulk voltage, whereas the anchoring energy modification can be disregarded. We can describe all of the reorientation dynamics by a single effective relaxation time ( $\tau_R$ ) for the electric processes, and we obtain estimates for the ion bulk density and mobility within the nematic layer by means of an optical measurement technique.

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