

Influence of the ions on the dynamical response of a nematic cell submitted to a dc voltageM. Scalerandi,¹ P. Pagliusi,² G. Cipparrone,² and G. Barbero¹¹*Dipartimento di Fisica del Politecnico di Torino, and INFM, UdR di Torino Politecnico, Corso Duca degli Abruzzi 24, I-10129 Torino, Italy*²*LiCryL-INFM, Dipartimento di Fisica, Università della Calabria, Rende (CS) I-87036, Italy*

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The influence of the ions present in a liquid crystal on the dynamical response of a nematic slab submitted to a dc voltage is studied. The evolution of the system toward the equilibrium state is investigated by solving the continuity equation for the electric charge, taking into account the current of drift and of diffusion. Our analysis shows that the formation of the double layers close to the electrodes strongly modifies the distribution of the electric field across the sample. We evaluate the surface polarization due to the ions movements and the contribution to the anisotropic part of the surface energy having a dielectric origin. We show also that, even if the optical response of the liquid crystal is a slow phenomenon, the distribution of the ionic charge is rather fast. Consequently, the presence of the ions cannot be neglected in the determination of the flexoelectric coefficients when the nematic sample is submitted to a square wave having a period of the order of 1 s.

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I. INTRODUCTION

Nematic liquid crystals are organic liquids formed by anisometric molecules. From the optical point of view they behave as uniaxial media, whose optical axis coincides with the statistical average of the molecular directions \mathbf{n} called director. The orientation of \mathbf{n} is imposed by the confining surfaces and modified by means of external fields. For practical applications in the display technology, the orientation of \mathbf{n} is modified with a dc electric field. Then, since nematic liquid crystals, as other organic liquids, usually contain ions, it is important to know how the presence of the ions modifies the physical properties of nematic samples submitted to dc electric fields.

A systematic analysis of the influence of the ions on the surface anchoring energy of nematic liquid crystals [1] has been presented by several groups [2–8], in the framework of the Poisson-Boltzmann theory [9]. Recently we have investigated the influence of the ions on the surface energy of a nematic sample submitted to a dc bias voltage, and shown that this influence can be rather large for commercial liquid crystals [10,11]. The effect of the ions on the flexoelectric effect has been discussed by Ponti *et al.* [12]. The authors of Ref. [12] show that the impurities dissolved in the nematic liquid crystal play a fundamental role in determining the behavior of the sample in the low voltage regime, where the flexoelectric effect is relevant. Similar conclusions have been derived by Derfel *et al.* [13,14].

All the papers quoted above refer to the static influence of the ions on the physical properties of nematic samples. In other words, no time dependence of the optical effects connected with the ions is considered. Only in the seminal paper by Thurston *et al.* [15], the time dependence of the switching time of a nematic sample due to the ions was partially analyzed. More recently, transient currents in nematic samples have been investigated by Sugimura *et al.* [16], and by Naito *et al.* [17], and explained by means of a simple model based on the time variation of the applied voltage and the internal electric field induced by the adsorbed ions. However, a full analysis of the problem was not presented.

The aim of our paper is to consider the dynamical behavior of a nematic cell submitted to a steplike voltage. This kind of analysis is fundamental for practical applications of ferroelectric liquid crystals, as discussed by Pauwels *et al.* [18–20] and by Zhang and D’Have [21].

Our paper is organized as follows. In Sec. II we present the equations of the model by considering the particular case in which there is chemical adsorption at the surfaces limiting the nematic liquid crystal. In Sec. III we determine the distribution of the ions, of the electric field and of the electric potential in the sample at different times, by solving numerically the continuity equations for the positive and negative ions and the Maxwell equation for the electric field. In the same section we evaluate also the contribution of dielectric origin to the anisotropic part of the anchoring energy connected with the dielectric anisotropy and with the flexoelectric effect, and the surface polarization having an ionic origin. In Sec. IV the deformation of the nematic director across the sample is determined by solving the equilibrium equation, where the mechanical, electrical, and viscous torques are taken into account. In the same section we compare our predictions concerning the optical transmission with the experimental data. In Sec. V the main results of our paper are discussed.

II. BASIC EQUATIONS FOR THE ELECTRICAL VARIABLES

Let us consider a nematic sample in the shape of a slab of thickness d . The z axis of the Cartesian reference frame is normal to the bounding surfaces at $z = \pm d/2$. In our analysis we suppose that the electrodes are covered by a layer of thickness λ of dielectric material avoiding transfer of charge from the nematic sample to the circuit, see Fig. 1. Consequently, the electrodes can be considered as blocking. An external power supply is connected to the sample to fix the electric potential of the electrodes at $z = \mp(d/2 + \lambda)$ at $\mp V_0/2$. The external charge densities sent by the power sup-

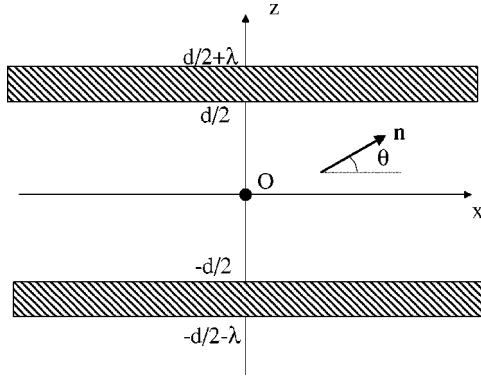


FIG. 1. Nematic sample considered in the analysis. λ is the thickness of the dielectric material, of dielectric constant ϵ_S , deposited on the electrodes to avoid charge injection. The dielectric constant of the liquid crystal is ϵ_\perp . The electrodes are considered as blocking. The electric potentials of the electrodes at $z = \pm(d/2 + \lambda)$ are $\pm V_0/2$. \mathbf{n} is the nematic director, coinciding with the optical axis of the nematic liquid crystal, and θ the tilt angle formed by \mathbf{n} with the x axis. In the absence of the external field the nematic orientation is homogeneous across the sample at an angle θ_0 , due to the surface treatments. The surface anchoring energy is assumed strong.

ply to the electrodes to fix this difference of potential will be indicated by $\pm q\Sigma$, where q is the unit charge and Σ the surface density of charged particles.

We assume that all physical quantities entering in the problem depend only on the z coordinate. We also assume that in thermodynamical equilibrium, in the absence of an external electric field, the liquid crystal contains a density $n_{0+}(z,0) = n_{0-}(z,0) = n_0$ of ions, uniformly distributed. We do not consider the recombination of the ions [15], even if this phenomenon can be easily taken into account [18]. However, according to the investigations performed by Murakami and Naito on the low frequency dielectric properties of nematic samples, this assumption seems supported experimentally [22]. In fact, the experimental data reported in Ref. [22] show that the concentration of ions is practically temperature independent, in the limit of low applied voltage. This behavior is not consistent with a chemical reaction of association dissociation.

The presence of the ions modifies deeply the electrical properties of the liquid crystal when an external electric field is applied to the sample, because the electric potential is no longer a harmonic function. Furthermore, also the concept of electrical conductivity has no longer a clear meaning since the ionic charge distribution depends on the applied voltage. In fact, in presence of an external electric field, the ions move under the effect of the electric force until an equilibrium distribution is reached. In this situation the bulk density of positive ions $n_+(z,t)$ differs from the bulk density of negative ions $n_-(z,t)$. Some of the ions can also be chemically adsorbed by the dielectric layers deposited on the electrodes. In this case the conservation of the number of the ions imposes that

$$\sigma_{1+}(t) + \sigma_{2+}(t) + \int_{-d/2}^{d/2} n_+(z,t) dz = n_0 d + \sigma_{1+}(0) + \sigma_{2+}(0),$$

$$\sigma_{1-}(t) + \sigma_{2-}(t) + \int_{-d/2}^{d/2} n_-(z,t) dz = n_0 d + \sigma_{1-}(0) + \sigma_{2-}(0), \quad (1)$$

where $\sigma_{1\pm}$ and $\sigma_{2\pm}$ are the surface densities of positive and negative ions adsorbed at the surfaces at $z = \mp d/2$, respectively.

The current densities of positive and negative charges are

$$J_+ = -\mu_+ q \left\{ n_+ \frac{\partial V}{\partial z} + \frac{k_B T}{q} \frac{\partial n_+}{\partial z} \right\},$$

$$J_- = -\mu_- q \left\{ n_- \frac{\partial V}{\partial z} - \frac{k_B T}{q} \frac{\partial n_-}{\partial z} \right\}, \quad (2)$$

where $J_\pm = J_\pm(z,t)$, $n_\pm = n_\pm(z,t)$, and $V = V(z,t)$. In Eqs. (2) the first terms represent the current densities due to the drift connected with the electric field, whereas the remaining terms are the diffusion current densities. The parameters μ_\pm are the mobilities of the positive and negative ions, and $D_\pm = (k_B T/q)\mu_\pm$ the diffusion coefficients of the two type of ions [15]. The charge conservation equations are

$$\frac{\partial n_+}{\partial t} - \mu_+ \frac{\partial}{\partial z} \left\{ n_+ \frac{\partial V}{\partial z} + \frac{k_B T}{q} \frac{\partial n_+}{\partial z} \right\} = 0,$$

$$\frac{\partial n_-}{\partial t} + \mu_- \frac{\partial}{\partial z} \left\{ n_- \frac{\partial V}{\partial z} - \frac{k_B T}{q} \frac{\partial n_-}{\partial z} \right\} = 0. \quad (3)$$

From Eqs. (3), it follows the conservation of the net charge $\rho = q(n_+ - n_-)$ and net current density $J = J_+ + J_-$, expressed by the equation

$$q \frac{\partial n(z,t)}{\partial t} - \frac{\partial J(z,t)}{\partial z} = 0, \quad (4)$$

where $n(z,t) = n_+(z,t) - n_-(z,t)$ [15].

Equations (3) have to be solved with the Maxwell equation $\text{div } \mathbf{D}(z,t) = \rho(z,t)$, where $\mathbf{D}(z,t)$ is the dielectric displacement and $\rho(z,t)$ the net electric charge density at the point z and time t . In the two dielectric layers, of thickness λ and dielectric constant ϵ_S , deposited over the electrodes to avoid charge injection, the net charge is zero. Consequently $D_S(z,t) = D_S(t) = -q\Sigma(t)$, where $-(d/2 + \lambda) \leq z \leq -d/2$ and $d/2 \leq z \leq d/2 + \lambda$. The electric field in the surface layer is then $E_S(t) = D_S(t)/\epsilon_S = -q\Sigma(t)/\epsilon_S$. In the liquid crystal, where the ions are present, the electric field satisfies the Poisson's equation

$$\frac{d\{\epsilon_{zz} E_B(z,t)\}}{dz} = q n(z,t). \quad (5)$$

In Eq. (5) $qn(z,t)$ is the net bulk electric charge due to the ions, ϵ_{zz} is the z, z component of the dielectric tensor of the nematic liquid crystal, and $E_B(z,t)$ is the z component of the electric field, which is the only one different from zero in the case under consideration.

The dielectric tensor of a nematic liquid crystal can be decomposed as $\varepsilon_{ij} = \varepsilon_a n_i n_j + \varepsilon_\perp \delta_{ij}$, where n_i and n_j , $i, j = x, y, z$, are the Cartesian components of the director \mathbf{n} and $\varepsilon_a = \varepsilon_\parallel - \varepsilon_\perp$, being ε_\parallel and ε_\perp the dielectric constants along \mathbf{n} and perpendicular to \mathbf{n} , respectively. In the simple case where the nematic distortion is contained in a plane, coinciding with the (x, z) plane, the director is fully described by the tilt angle θ formed by \mathbf{n} with the x axis. In this case, to which we limit our investigation, $\varepsilon_{zz} = \varepsilon_\parallel \sin^2 \theta + \varepsilon_\perp \cos^2 \theta = \varepsilon_\perp + \varepsilon_a \sin^2 \theta$. In a first approximation, for simplicity, we assume that the nematic liquid crystal can be considered as an isotropic liquid. This is equivalent to consider small deformations (*small* θ), or nematic media having small dielectric anisotropy. In this framework the electrical equations can be solved independently from the mechanical equation describing the nematic deformation induced by the field. The extension of the calculation to the general dielectric anisotropy can be, however, easily done.

By means of this simplifying hypotheses $\varepsilon_{zz} = \varepsilon_\perp$, and from Eq. (5) we get that the electric field in the liquid crystal is given by

$$E_B(z, t) = \frac{q}{\varepsilon_\perp} \int_{-d/2}^z n(z', t) dz' + \mathcal{L}(t). \quad (6)$$

The function $\mathcal{L}(t)$ is fixed by the boundary condition on the electric displacements at the interface in $z = -d/2$: $D_B(-d/2, t) - D_S(t) = q\sigma_1(t)$, where $q\sigma_1(t) = q[\sigma_{1+}(t) - \sigma_{1-}(t)]$ is the total charge density adsorbed at the surface at $z = -d/2$. Consequently, $\mathcal{L}(t) = -q[\Sigma(t) - \sigma_1(t)]/\varepsilon_\perp$. The value of Σ is determined by imposing that the difference of potential on the sample is V_0 . By means of the condition

$$V_0 = - \int_{(-d/2+\lambda)}^{d/2+\lambda} E(z, t) dz = - 2E_S(t)\lambda - \int_{-d/2}^{d/2} E_B(z, t) dz, \quad (7)$$

we obtain

$$\Sigma(t) = \gamma \left\{ \varepsilon_\perp \frac{V_0}{qd} + \sigma_1(t) + \frac{1}{d} \int_{-d/2}^{d/2} \left(\int_{-d/2}^z n(z', t) dz' \right) dz \right\}, \quad (8)$$

where $\gamma^{-1} = 1 + 2(\lambda \varepsilon_\perp / d \varepsilon_S)$ is a physical parameter which depends on the dielectric properties of the surface layers. By substituting $\Sigma(t)$ given by Eq. (8) into Eq. (6) we get

$$E_B(z, t) = \frac{q}{\varepsilon_\perp} \left\{ \int_{-d/2}^z n(z', t) dz' - \frac{\gamma}{d} \int_{-d/2}^{d/2} \left(\int_{-d/2}^{z'} n(z'', t) dz'' \right) dz' \right\} - \gamma \frac{V_0}{d} - \frac{\gamma - 1}{\varepsilon_\perp} \sigma_1 q. \quad (9)$$

Equation (9) gives the electric field $E_B(z, t)$ in terms of the distribution of the ions and of the applied voltage V_0 .

To determine the evolution of the distribution of the ions with time when the external voltage V_0 is applied we have to solve Eqs. (3), where $-\partial V / \partial z = E_B$ is given by Eq. (9). The

boundary conditions for Eqs. (3) are $n_\pm(z, 0) = n_\pm(z, 0) = n_0$, i.e., before the application of the external field the distribution of the ions is homogeneous across the sample. The other boundary conditions depend on the adsorption on the limiting surfaces. If the ions cannot leave the liquid crystal, and hence there are not surface adsorbed charges, $\sigma_1 = \sigma_2 = 0$, and the current densities have to vanish for $z = \pm d/2$. In this special case, the relevant boundary conditions for Eqs. (3) are

$$J_+ = -\mu_+ q \left\{ n_+ \frac{\partial V}{\partial z} + \frac{k_B T}{q} \frac{\partial n_+}{\partial z} \right\} = 0 \text{ for } z = \pm d/2, \\ J_- = -\mu_- q \left\{ n_- \frac{\partial V}{\partial z} - \frac{k_B T}{q} \frac{\partial n_-}{\partial z} \right\} = 0 \text{ for } z = \pm d/2. \quad (10)$$

In the opposite case, where there is adsorption of ions from the limiting surfaces, it is necessary to formulate the exchange of ions at the surfaces. Following Pauwels *et al.* [18] we assume that

$$J_\pm = \pm q \frac{d\sigma_{1\pm}}{dt} = \pm q \left(k_{\pm} n_\pm - \frac{1}{\tau_{\pm}} \sigma_{1\pm} \right) \text{ for } z = -d/2, \\ J_\pm = \pm q \frac{d\sigma_{2\pm}}{dt} = \pm q \left(k_{\pm} n_\pm - \frac{1}{\tau_{\pm}} \sigma_{2\pm} \right) \text{ for } z = d/2, \quad (11)$$

where k_{\pm} and τ_{\pm} are phenomenological parameters describing the adsorption phenomenon of positive and negative ions, whose physical meaning is evident. From Eqs. (11) it follows that in the steady state, where $d\sigma_{\pm}/dt = 0$, for $t \rightarrow \infty$, the surface densities of adsorbed ions are

$$\sigma_{1\pm}(t \rightarrow \infty) = \tau_{\pm} k_{\pm} n_\pm(-d/2, t \rightarrow \infty),$$

$$\sigma_{2\pm}(t \rightarrow \infty) = \tau_{\pm} k_{\pm} n_\pm(d/2, t \rightarrow \infty). \quad (12)$$

In our analysis we suppose that there is adsorption at the limiting surfaces, and hence the boundary conditions for Eqs. (3) are Eqs. (11).

In conclusion we observe that it is possible to rewrite Eqs. (3) in a form giving information on the time evolution of the ions distribution in the bulk. By introducing the reduced quantities $u_\pm = n_\pm / n_0$, $\zeta = z/d$, $v = V/V_0$, $\tau_{d\pm} = d^2 / (\mu_\pm V_0)$, and $r = k_B T / (qV_0)$, we get

$$\frac{\partial u_+}{\partial t} - \frac{1}{\tau_{d+}} \frac{\partial}{\partial \zeta} \left\{ u_+ \frac{\partial v}{\partial \zeta} + r \frac{\partial u_+}{\partial \zeta} \right\} = 0, \\ \frac{\partial u_-}{\partial t} - \frac{1}{\tau_{d-}} \frac{\partial}{\partial \zeta} \left\{ u_- \frac{\partial v}{\partial \zeta} - r \frac{\partial u_-}{\partial \zeta} \right\} = 0. \quad (13)$$

It follows that the characteristic times connected with the evolution of n_\pm are of the order of $\tau_{d\pm} = d^2 / (\mu_\pm V_0)$. Furthermore, from Eqs. (11), the characteristic times connected with the evolution of $\sigma_{1\pm}$ and $\sigma_{2\pm}$ depend on τ_{\pm} and $\tau_{d\pm}$.

TABLE I. Values of the physical parameters used in the simulations in SI units ($q=1.6\times 10^{-19}$ C and $\epsilon_0=8.85\times 10^{-12}$ F/m).

| Variable | Symbol | Value | References |
|---|--------------------|-------------------------------|------------|
| Initial ions density | n_0 | 5×10^{19} | [15] |
| Ions mobility | μ | 0.8, 2.1, 10×10^{-11} | [21,31] |
| Specimen length | d | 30×10^{-6} | |
| Dielectric layer thickness | λ | 0.02×10^{-6} | |
| External potential | V_0 | 1, 1.1, 1.2, 1.3 | |
| Temperature | T | 290° K | |
| Dielectric constant of the layer | ϵ_S | $2\epsilon_0$ | |
| Dielectric constant of the liquid crystal | ϵ_{\perp} | $6.7\epsilon_0$ | [28] |
| Dielectric anisotropy | ϵ_a | $13\epsilon_0$ | [28] |
| Absorption coefficient | k_t | 10^{-6} | [18] |
| Desorption coefficient | τ_t | 0.01 | [18] |
| Initial orientation of the director | θ_0 | 0.05 rad | |
| Frank's elastic constant | K | 6.4×10^{-12} | [28] |
| Rotational viscosity | η | 0.094 | [28] |
| Ordinary refraction index | n_{ord} | 1.53 | [28] |
| Extraordinary refraction index | n_{ext} | 1.71 | [28] |
| Total flexoelectric coefficient | e | 5×10^{-11} | [10] |

III. NUMERICAL SOLUTION OF THE ELECTRICAL EQUATIONS

A. Implementation

To solve numerically Eqs. 3, we have discretized both time and space and applied a usual finite difference forward scheme to define the derivatives [23]. Convergence of the numerical solution has been carefully verified by choosing fine discretization grids and testing the independence of the solution from the choice of the discretization time and space steps [24,25]. We observe that, as expected, convergence is extremely sensitive to the choice of the latter [26]. Finally, the boundary conditions [Eq. (10)] have been discretized through the usual formalism for adsorption [27].

We suppose that the ions dissolved in the nematic sample are identical in all the aspects. From this hypothesis it follows that $\mu_+=\mu_-=\mu$, $k_{t+}=k_{t-}=k_t$, and $\tau_{t+}=\tau_{t-}=\tau_t$. In this framework $\tau_{d+}=\tau_{d-}=\tau_d=d^2/(\mu V_0)$, and the characteristic time connected with the evolution of the adsorbed charge is the largest between τ_d and τ_t . The steady-state values of the net surface adsorbed charge are $\sigma_{1,2}(t\rightarrow\infty)=\tau_t k_t n(\mp d/2, t\rightarrow\infty)$.

For the numerical calculations the values of the physical parameters used are reported in Table I. Also, we simulate a steplike applied voltage. The order of magnitude of the contact resistance is $R\sim 6$ k Ω [29]. The effective capacitance of the sample is $C=\gamma\epsilon_{\perp}(S/d)$, where γ takes into account of the two layers deposited over the electrodes and $S\sim 2$ cm² is the surface of the limiting surface. Using the values of Table I, we get $C\sim 0.4$ nF. The time constant of the electric circuit is then $\tau=RC\sim 2.4$ μ s. Since τ is negligibly small with respect to τ_d and τ_t we can suppose that the applied voltage passes immediately from 0 to V_0 .

In our analysis, where the applied voltage is steplike, the adsorption phenomenon does not play an important role. In

fact, the bulk distribution of the electric field is, practically, independent of the chemical adsorption of the ions from the limiting surfaces. Only the value of the surface electric field depends on it, but its influence on the nematic orientation is negligible.

B. Results

In Fig. 2 we show the time dependence of the positive [Fig. 2(a)], σ_{1+} , and negative [Fig. 2(b)], σ_{1-} , adsorbed densities of ions, and the net surface charge density [Fig. 2(c)], $\sigma_1=\sigma_{1+}-\sigma_{1-}$, at the surface at $z=-d/2$, for three representative values of the ionic mobility [30,31]. σ_{1+} is a monotonic increasing function, whereas σ_{1-} is a monotonic decreasing function of t . Since the electrode at $z=-(d/2+\lambda)$ is at $-V_0/2$, $\sigma_{1+}\gg\sigma_{1-}$ and hence $\sigma_1\sim\sigma_{1+}$.

In Fig. 3 the behavior of the ions density is analyzed. In the upper row, the profile of $n(-d/2, t)=n_+(-d/2, t)-n_-(-d/2, t)$ is shown for several times, for the three representative values of μ reported in Table I. As expected, the charge distribution is localized close to the limiting surface, in a region whose thickness is slightly smaller than Debye's screening length $L_D=\sqrt{\epsilon_{\perp}k_B T/(2q^2 n_0)}\sim 0.3$ μ m, Ref. [10]. Note also that the distribution at $t=12.5$ s and $t=17.5$ s almost coincide (more for the largest mobility value). In the second row of Fig. 3, the time dependence of $n(-d/2, t)$, for the same values of μ , are reported. With the values of the physical parameters reported in Table I, $n_+(-d/2, t)$ is a monotonic increasing function, whereas $n_-(-d/2, t)$ a monotonic decreasing function of t (not reported) [32]. In the bottom row of Fig. 3, we show the time dependence of $n(0, t)$. As expected, both $n_+(0, t)$ and $n_-(0, t)$ decrease uniformly with t (not reported), whereas $n(0, t)$ remains zero, indicating that the center of the sample remains locally neutral.

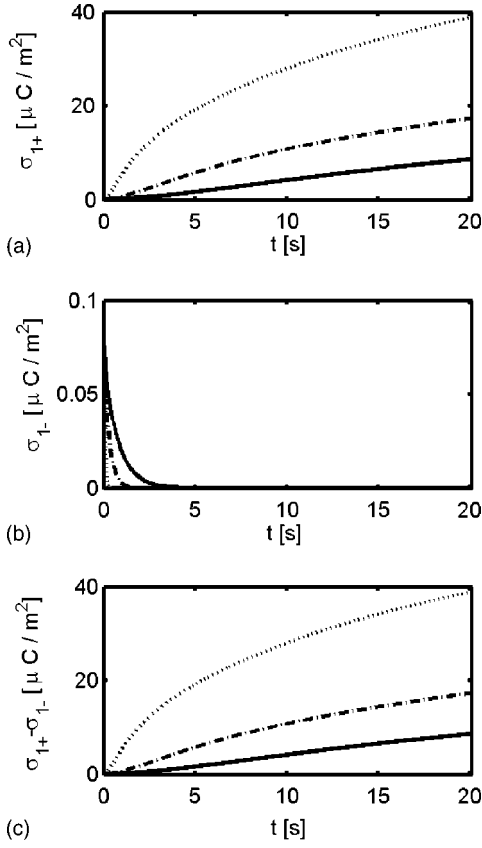


FIG. 2. Surface densities of adsorbed positive (a) and negative (b) ions. The net surface charge density adsorbed on the dielectric layer deposited on the electrodes is $q(\sigma_{1+} - \sigma_{1-})$ (c). The applied voltage is $V_0 = 1.3$ V. Solid, $\mu = 0.8 \times 10^{-11} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$; dash dot, $\mu = 2.1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$; dot $\mu = 10 \times 10^{-11} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$.

In Fig. 4(a) the charge density $q\Sigma$ sent by the power supply on the electrodes to maintain the difference of potential at the value V_0 is reported vs time, for $\mu = 2.1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$ and several voltages. In our case $q\Sigma$ is connected only with the ions moving inside the liquid crystal, because we have assumed that the nematic can be considered isotropic from the dielectric point of view. In the more general case, where also the dielectric anisotropy is taken into account, the external charge is due also to time variation of the z , z -dielectric constant connected with the time dependence of the tilt angle $\theta(t)$. The electric current density flowing in the circuit is given by $J_{\text{ext}}(t) = q d\Sigma(t)/dt$. By taking into account Eq. (8) we get

$$J_{\text{ext}}(t) = q \frac{d\Sigma}{dt} = q \gamma \left\{ \frac{d\sigma_1}{dt} + \frac{1}{d} \int_{-d/2}^{d/2} \left(\int_{-d/2}^z \frac{\partial n(z', t)}{\partial t} dz' \right) dz \right\}. \quad (14)$$

By using Eq. (4), $J_{\text{ext}}(t)$ can be rewritten in the form

$$J_{\text{ext}}(t) = \gamma \left\{ q \frac{d\sigma_1}{dt} - J(-d/2) + \frac{1}{d} \int_{-d/2}^{d/2} J(z, t) dz \right\}, \quad (15)$$

that, making use of Eq. (11), is equivalent to

$$J_{\text{ext}}(t) = \frac{\gamma}{d} \int_{-d/2}^{d/2} J(z, t) dz. \quad (16)$$

By means of Eq. (2), we get for $J_{\text{ext}}(t)$ the final expression

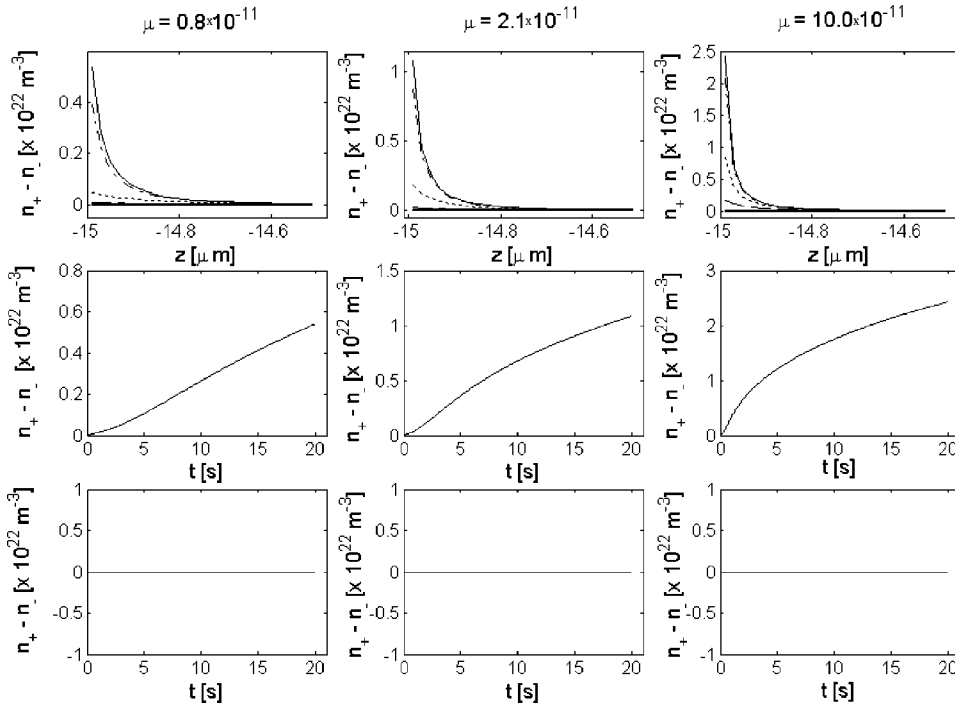


FIG. 3. Net density of ions $n(z, t) = n_+(z, t) - n_-(z, t)$ in the nematic sample, for $\mu = 0.8 \times 10^{-11} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$, first column, $\mu = 2.1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$, second column; $\mu = 10 \times 10^{-11} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$, third column. First row: profiles at several times after the application of the external voltage, solid thick, $t = 0.0$ s; dash, $t = 0.5$ s; dot, $t = 2.5$ s; dash dot, $t = 17.5$ s; solid thin, $t = 17.5$ s. Second row: Net density of ions just in front to the limiting surface $n(-d/2, t)$. Third row: Net density of ions in the middle of the sample $n(0, t)$.

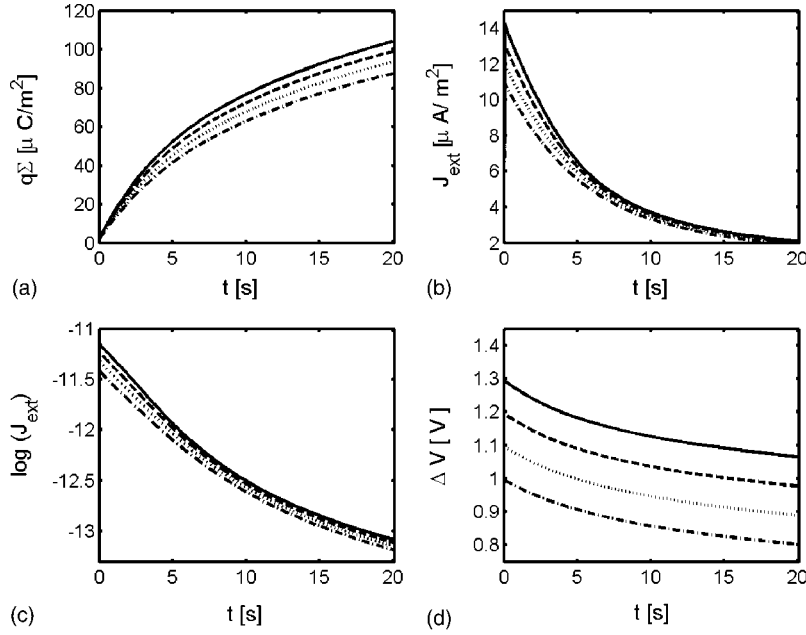


FIG. 4. Electric charge $q\Sigma(t)$ vs t sent by the power supply on the electrodes to maintain the difference of potential on the sample at $V_0(a)$. Electric density current $J_{\text{ext}}(t)$ flowing in the circuit vs $t(b)$, and $\ln J_{\text{ext}}$ vs $t(c)$. The time dependence of $J_{\text{ext}}(t)$ is not simply exponential. Actual difference of potential on the nematic sample vs $t(d)$. The value to which tends $V_B(t)$ is well below V_0 , for the screening effect due to the presence of the ions. The ionic mobility is $\mu=2.1 \times 10^{-11} \text{ m}^2\text{s}^{-1}\text{V}^{-1}$. Solid, $V_0=1.3 \text{ V}$; dash, $V_0=1.2 \text{ V}$; dot, $V_0=1.1 \text{ V}$; dash dot $V_0=1.0 \text{ V}$.

$$J_{\text{ext}}(t) = -q \mu \frac{\gamma}{d} \int_{-d/2}^{d/2} \left\{ [n_+(z,t) + n_-(z,t)] \frac{\partial V}{\partial z} + \frac{k_B T}{q} \left[\frac{\partial n_+(z,t)}{\partial z} - \frac{\partial n_-(z,t)}{\partial z} \right] \right\} dz, \quad (17)$$

in our case where $\mu_+ = \mu_- = \mu$. In Fig. 4(b) we show $J_{\text{ext}}(t)$ vs t . As it is clear from Fig. 4(c), the time dependence of $J_{\text{ext}}(t)$ is not simply exponential. This result can be easily understood because the transit time of the ions in the nematic cell depends on the ions already present close to the limiting surfaces. In other words, the transit time depends on the effective profile of the electrical potential, that, in turns, depends on the distribution of ions. This feedback is responsible for the deviation of $J_{\text{ext}}(t)$ from a simple exponential law. It is also to be noted that the current decays very slowly with time, due to the rather large value of the characteristic time τ_d for the given value of mobility and specimen length. In Fig. 4(d) the actual difference of potential across the nematic sample, given by

$$V_B(t) = V(d/2, t) - V(-d/2, t) = - \int_{-d/2}^{d/2} E_B(z, t) dz, \quad (18)$$

is reported. As it is evident from this figure, the actual V_B tends to a saturation value, which is well below V_0 . This reduction is due to the back electric field connected with the separation of ions induced by the external electric field due to the power supply.

The profiles of the electric field $E_B(z, t)$ and of the electrical potential $V(z, t)$ in the nematic sample for several times are shown in Figs. 5(a) and 5(b), respectively, for $\mu=2.1 \times 10^{-11} \text{ m}^2\text{s}^{-1}\text{V}^{-1}$. The electric field is more and more localized close to the nematic surface with increasing time, while, at long times, the bulk of the liquid crystal is almost equipotential (zero electric field). The time dependence of the electric field at the surface $E_B(-d/2, t)$ and in the middle

of the sample $E_B(0, t)$ are shown in Figs. 5(c) and 5(d) for the representative values of μ reported in Table I. As it is evident from Fig. 5(c) the surface electric field is, for the chosen values of μ , k_t , and τ_t , a monotonic increasing function of t . On the contrary, the electric field in the bulk decreases monotonically from the initial value to an equilibrium value equal to the external field diminished of the back electric field created by the separation of ions induced by the external field itself [32].

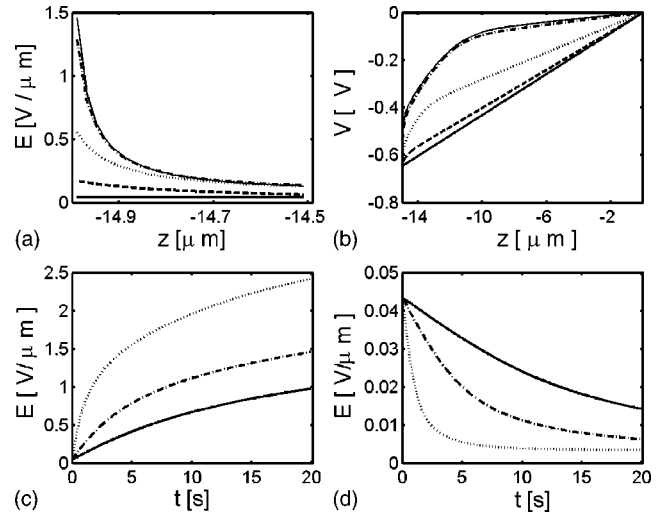


FIG. 5. Profile of the electric field $E_B(z, t)$ close to the limiting surface (a), and of the electrical potential $V(z, t)$ across the sample (b), for different times t after the application of the external voltage $V_0=1.3 \text{ V}$. In (a) and (b) the ionic mobility is $\mu=2.1 \times 10^{-11} \text{ m}^2\text{s}^{-1}\text{V}^{-1}$, solid thick, $t=0.0 \text{ s}$; dash, $t=0.5 \text{ s}$; dot, $t=2.5 \text{ s}$; dash dot $t=7.5 \text{ s}$; solid thin, $t=17.5 \text{ s}$. Time dependence of the surface electric field $E_B(-d/2, t)$ (c), and of the electric field in the middle of the sample $E_B(0, t)$ (d). In (c) and (d) solid, $\mu=0.8 \times 10^{-11} \text{ m}^2\text{s}^{-1}\text{V}^{-1}$; dash dot, $\mu=2.1 \times 10^{-11} \text{ m}^2\text{s}^{-1}\text{V}^{-1}$; dot, $\mu=10 \times 10^{-11} \text{ m}^2\text{s}^{-1}\text{V}^{-1}$.

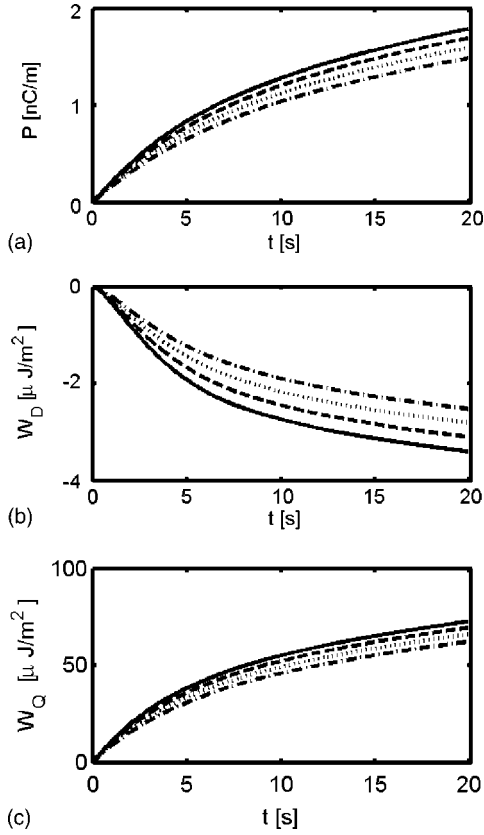


FIG. 6. Surface polarization \mathcal{P} due to the ions separation connected with the external field vs t (a). Surface anchoring energy $W_D(t)$ connected with the dielectric anisotropy of the nematic liquid crystal due to the surface field of ionic origin vs t (b), and surface anchoring energy of flexoelectric origin $W_Q(t)$ vs t (c). Solid, $V_0 = 1.3$ V; dash, $V_0 = 1.2$ V; dot, $V_0 = 1.1$ V; dash dot, $V_0 = 1.0$ V. The ionic mobility is $\mu = 2.1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$.

By means of the profile $n(z, t) = n_+(z, t) - n_-(z, t)$ it is possible to evaluate the contribution of the ions to the surface polarization. It is given by

$$\mathcal{P}(t) = \int_{-d/2}^0 q z n(z, t) dz + q \sigma_1(t) \frac{d}{2}, \quad (19)$$

where the latter contribution is connected with the charge adsorbed on the limiting surface. The time dependence of $\mathcal{P}(t)$ is shown in Fig. 6(a). The order of magnitude of \mathcal{P} is the same as the one determined by Mazzulla *et al.* [33], and due, according to the authors of [33], to molecular properties of the liquid crystal. On the contrary in our analysis, it is simply due to the ions dissolved in the liquid crystal [34,35]. As follows from Fig. 5(a) the electric field across the sample is not homogeneous. Its spatial variation is localized in a surface layer close to the limiting surfaces. In this case, as discussed elsewhere [10], the electrostatic energy connected with the interaction of the electric field localized in the surface layer with the nematic liquid crystal can be considered as a surface energy. Following the analysis reported in Ref. [10] the contribution connected with the dielectric anisotropy is

$$W_D(t) = -\frac{1}{2} \epsilon_a \int_{-d/2}^0 [E_B^2(z, t) - E_B^2(0, t)] dz, \quad (20)$$

whereas the contribution associated to the flexoelectric polarization is

$$W_Q(t) = -e[E_B(-d/2, t) - E_B(0, t)], \quad (21)$$

where $e = e_{11} + e_{33}$ is the total flexoelectric coefficient [10]. The anchoring energy strengths $W_D(t)$ and $W_Q(t)$ vs t are shown in Figs. 6(b) and 6(c), respectively.

IV. DEFORMATION INDUCED BY THE EXTERNAL FIELD ON THE NEMATIC SAMPLE

A. Equations

The nematic sample is a slab of thickness d . In the absence of the external field the nematic director \mathbf{n} is oriented, by means of the surface treatment, at an angle θ_0 very small with respect to the x axis, homogeneous across the sample. The parameter θ_0 could be measured by means of the birefringence of the sample in the absence of the external field. However, in our case it will be considered as a free parameter, and determined by the fit of the curve of the birefringence vs time, for different values of the applied voltage. We consider the case of $\epsilon_a = \epsilon_{\parallel} - \epsilon_{\perp} > 0$. If the sample is submitted to an electric field $\mathbf{E} = E(t)\mathbf{k}$, where \mathbf{k} is the unit vector parallel to the z axis, the electric torque can destabilize the initial orientation. We are in the situation to observe a kind of Fredericksz transition [36]. In this section we investigate the dynamics of the orientation induced by the external field in the case of strong anchoring on the surfaces. In this framework $\theta(\pm d/2) = \theta_0$ for any external field.

The dynamical evolution of the system is governed, in the one constant approximation, by the equation [15]

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

where K is the Frank's elastic constant, and η the rotational viscosity coefficient of the liquid crystal. We note that in the strong anchoring hypothesis the flexoelectric effect does not enter in the dynamical equilibrium equation. In the following we write Eq. (22) in the form

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

where $\zeta = z/d$, $h(\zeta, t) = E(\zeta, t)/E_{\text{th}}$ is the electric field expressed in units of the threshold field [$E_{\text{th}} = (\pi/d)\sqrt{K/\epsilon_a}$], and $\tau_v = (\eta/K)d^2$ the viscous relaxation time of the sample under consideration. In the limit of small θ , i.e., for E of the order of the critical field E_{th} , Eq. (22) at the first order in θ can be written as

$$\frac{\partial^2 \theta}{\partial \zeta^2} + \pi^2 h^2(\zeta, t) \theta - \tau_v \frac{\partial \theta}{\partial t} = 0. \quad (24)$$

From Eq. (24) it follows that the time evolution of the tilt angle is the largest between the characteristic times τ_d and τ_v .

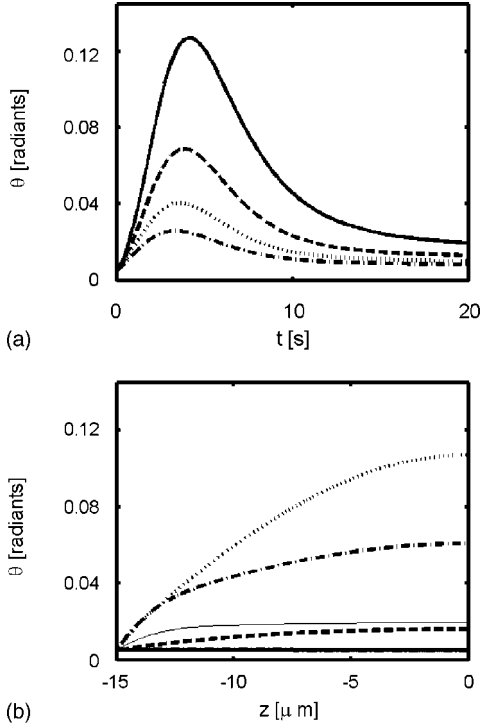


FIG. 7. Tilt angle in the middle of the sample $\theta(0,t)$ vs t , solid, $V_0=1.3$ V; dash, $V_0=1.2$ V; dot, $V_0=1.1$ V; dash dot, $V_0=1.0$ V (a). Tilt angle profiles $\theta(z,t)$ for several t , after the application of the external voltage $V_0=1.3$ V, solid thick, $t=0.0$ s; dash, $t=0.5$ s; dot, $t=2.5$ s, dash dot, $t=7.5$ s; solid thin, $t=17.5$ s (b). The ionic mobility is $\mu=2.1 \times 10^{-11} \text{ m}^2\text{s}^{-1}\text{V}^{-1}$.

B. Results

Equation (22) has been again solved numerically with a forward finite difference scheme, taking care of stability conditions for the choice of the ratio between space and time steps [23]. Furthermore, provided the space discretization to be very fine, different implementations for the strong anchoring boundary conditions have been proven to be equivalent (with differences of the results of the order of a few per thousands). Hence, convergence of the numerical solutions have been ensured.

In Fig. 7(a) we show the tilt angle in the middle of the sample vs t . In Fig. 7(b) the profiles of the tilt angle at different times are presented. As it follows from this figure, the time dependence of the tilt angle, in a given point, is a nonmonotonic function of t . At low times the bulk deformation is determined by the appearance of the electric field, while, as soon as the field in the bulk decays to low values [see Fig. 5(a)] the tilt angle is dragged by the one close to the limiting surface, where the electric field is stronger than the one in the bulk.

Since nematic media are uniaxial liquid crystals, whose optical axis coincides with the director \mathbf{n} , it follows that to a nematic distortion corresponds a change in the birefringence for transmitted light. For this reason we calculate the phase retardation taking into account the temporal dependence of the effective difference of potential across the nematic layer. By indicating with n_{ext} and n_{ord} the extraordinary and ordi-

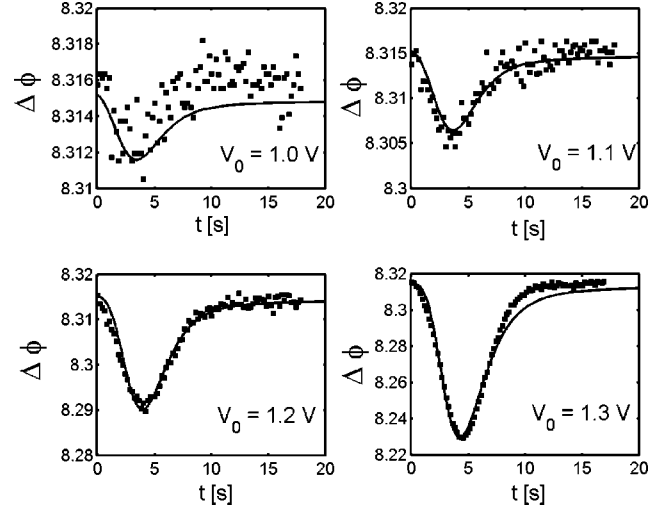


FIG. 8. Phase shift $\Delta\phi(t)$ vs t theoretically evaluated by using $\mu=2.1 \times 10^{-11} \text{ m}^2\text{s}^{-1}\text{V}^{-1}$ and the physical parameter values reported in Table I for different applied voltages. The dots represent the corresponding experimental data.

nary index of refraction of the nematic liquid crystal, the phase shift between the two components of a linearly polarized beam impinging perpendicularly on the sample is given by

$$\begin{aligned} \Delta\phi(t) &= \frac{2\pi}{\lambda} \int_{-d/2}^{d/2} [n_{\text{eff}}(z,t) - n_{\text{ord}}] dz \\ &= -\frac{2d\pi n_{\text{ord}}}{\lambda} + \frac{2d}{\lambda} \int_{-1/2}^{1/2} n_{\text{eff}}(\zeta,t) d\zeta, \end{aligned} \quad (25)$$

where

$$n_{\text{eff}}(\zeta,t) = \frac{n_{\text{ext}} n_{\text{ord}}}{\sqrt{n_{\text{ext}}^2 \sin^2 \theta(\zeta,t) + n_{\text{ord}}^2 \cos^2 \theta(\zeta,t)}}. \quad (26)$$

In order to test the validity of the model presented above, we have experimentally investigated the phase retardation of a nematic cell submitted to an external voltage. The measurements were carried out on a $30 \mu\text{m}$ thick slab filled with commercial 4-pentyl-4'-cyanobiphenil, 5CB by Merck. Thin films of poly vinyl alcohol (PVA), with $\lambda \sim 20$ nm were layered on the ITO electrodes, and rubbed in order to obtain a good homogeneous quasiplanar orientation. The cell was assembled putting Mylar spacers, and filled at room temperature with the liquid crystal in the nematic phase. The measurements of $\Delta\phi$ were performed in the standard manner, for different applied voltages [37]. The results are reported in Fig. 8. In our framework, where the mobility of positive and negative ions are assumed the same, a good agreement between the theoretical prediction and the experimental data is obtained for an average mobility $\mu=2.1 \times 10^{-11} \text{ m}^2\text{s}^{-1}\text{V}^{-1}$. This value of $\mu \sim (\mu_- + \mu_+)/2$ is comparable with the one reported by Ref. [18], which is rather small with respect to the one reported by Ref. [15]. We note that only for $V=1$ V the experimental data are systematically higher than the theoretical predictions. However, in this case small un-

certainties on the ordinary index of refraction n_{ord} , of the order of 0.1%, gives rise to a shift of the theoretical curve of the same order of the observed discrepancies.

The agreement is reasonably good, taking into account the simplifying hypotheses performed in our analysis. In particular, we have assumed that in the liquid crystal there is only one kind of positive and negative ions, with the same mobility, that probably it is not realistic. Furthermore, as discussed by Sawada *et al.* [30,31], different kinds of ions, with different mobility, can be present simultaneously in the nematic cell. Some of these ions can also be originated by the film deposited on the electrode to align the liquid crystal [19,22]. Consequently the model has to be extended to consider a population of different type of ions. The work is in progress.

V. CONCLUSION

We have analyzed the influence of the ions on the dynamical response of a nematic sample submitted to an external steplike voltage. We have presented the basic equations of the hydrodynamic model for the case in which there is chemical adsorption at the surfaces limiting nematic sample. We have determined the distribution of the electrical field

and potential, and of the ions by solving numerically the continuity equations for the positive and negative ions and the Maxwell equation for the electric field. The characteristic times of drift, trapping and reorientation have been determined. We have investigated also the contribution of dielectric origin to the anisotropic part of the anchoring energy connected with the dielectric anisotropy and with the flexoelectric effect, and the surface polarization having an ionic origin, and analyzed their time dependence. Finally, we have evaluated the deformation of the nematic director across the sample by solving the equilibrium equation, and the optical transmission of the nematic cell. The comparison of our predictions with the experimental data is reasonably good in the low voltage region, where the developed linear theory works well. The main conclusion of our investigation is that the ions play an important role on the reorientation induced by a steplike voltage on a nematic cell.

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 - [32] With the representative values of the ionic mobility chosen in our numerical calculations the drift time falls in the range $9 \text{ s} \leq \tau_d \leq 112 \text{ s}$, whereas the trapping time is $\tau_t = 0.01 \text{ s}$. In this case $\tau_d \gg \tau_t$. Consequently, the ions pushed by the electric force close to the border of the sample are rapidly adsorbed, and the phenomenon of accumulation of ions close to the lim-

iting surfaces is absent. Of course, in the opposite case where $\tau_t \gg \tau_d$, there is accumulations of ions just in front of the surface. These ions are, subsequently, adsorbed by the surface with the characteristic time τ_t . In this situation, $n_+(-d/2, t)$ presents a maximum for a time of the order of τ_d . After that it relaxes to the equilibrium value on a time of the order of τ_t . A similar behavior is expected for the surface electric field. The numerical calculations confirm these trends for $n_+(-d/2, t)$ and $E_B(-d/2, t)$.

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