Relaxation time for the ionic current in a nematic cell under a large electric field

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We evaluate the ionic relaxation time of a nematic cell subjected to a potential difference, V_0, very large with respect to $V_T=K_BT/q=0.025$ V, where K_BT is the thermal energy, and q the electrical charge of the ions, assumed monovalent. The analysis is performed by assuming that the mobilities of the positive and negative ions are the same, and that the ions can be considered pointlike. We show that, for $V_0 \gg V_T$, the relaxation time tends to the time of flight of the ions. In our analysis the ionic charges are assumed to form two surface layers responsible for a partial screening of the external field. In this framework, the evolution of the surface-charge density is determined by a simple differential equation related to the conservation of the ions number. According to our calculations, the relaxation time of the surface density of ionic origin, and of the electrical potential close to the electrodes, depends on the applied voltage, in agreement with the experimental observations.

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I. INTRODUCTION

Nematic liquid crystals used in displays usually contain ions, which are responsible for their rather large ionic conductivity [1,2]. When an external field is applied to a liquid crystal cell, the ionic impurities move close to the electrode of opposite sign, causing a reduction of the effective electric field in the bulk [3,4]. The time evolutions of the ions densities present in a nematic liquid crystal cell subjected to an external electrical voltage V_0 are determined by solving the equations of continuity for the positive and negative ions, and the equation of Poisson for the electrical potential [5]. Recently, the problem of the diffuse-charge dynamics in electrochemical system has been reconsidered by Bazant *et al.* [6], by assuming that the positive and negative ions are pointlike, and they have the same mobility in the liquid in which they are dispersed. In this framework they show that, for small applied voltages ($V_0 \ll V_T=K_BT/q=0.025$ V, where K_BT is the thermal energy and q the electrical charge of the ion, assumed monovalent), the evolution of the bulk density of ions and of the potential is simply exponential, and they deduce the relaxation time. On the contrary, for large applied voltages ($V_0 \gg V_T$), the time evolution of the bulk density of ions is more complicated. By analyzing numerically the problem with the same simplifying hypotheses of pointlike ions with the same mobility, we have shown [7] that the time evolution of the electric voltage can still be well approximated by a simple exponential, whose relaxation time depends on the applied voltage. By using simple arguments we proposed a formula for the relaxation time containing two free parameters, able to fit in a reasonable manner the numerical results. In this framework, a possible approach to obtain an approximated formula for the relaxation time could be based on the analogy of the present problem with the one named Maxwell-Wagner relaxation [8]. By assuming that the ions collected close to the electrodes can be assimilated to a dielectric medium, with dielectric constant equal to that of the bulk, it is possible to write an expression for the relaxation time similar to Eq. (16) of Ref. [4], where $L=d(V_T/V_0)$ [3]. However, following this approach, some questions remain unanswered: (i) is the diffusion of the ions taken into account? (ii) is it necessary to take into account both types of ions in the electrical current? (iii) what is the screening effect of these boundary ionic layers on the bulk electric field acting on the ions responsible for the migration of the ions close to the electrodes? Another way to face the problem is to assume that the ions collected close to the electrodes give rise to a charge surface-density, whose time evolution is controlled by the electric field in the bulk [3,9]. Even in this case it is not clear how to write the total current responsible for the collection of ions close to the electrodes, and if the effective electric field in the bulk takes into account, correctly, the ions already pushed towards the electrodes. The aim of the present paper is to analyze the dynamics of the ions present in the dielectric liquid when the cell is subjected to a large external electrical voltage, and to deduce a formula for the relaxation time of the current flowing in the circuit containing the sample. As in Refs. [6,7] we assume that the ions are pointlike, and that the positive and negative ions have the same mobility. Since we are considering ions dissolved in a nematic liquid crystal, where the hydration phenomenon is absent, the assumption that the ions have the same mobility can be considered reasonable, and the result of our calculations can be considered as a first approximation of the problem under investigation.

II. THEORY

We assume that the sample is in the shape of a slab of thickness d, and that N is the bulk density of positive and negative ions, in thermodynamical equilibrium (i.e., for $d \to \infty$ and in the absence of the external electric field). The Cartesian reference frame has the z axis normal to the bounding surfaces, coinciding with that of the electrodes. In this framework all physical quantities entering in the problem depend only on the coordinate z and time t. In the presence

of an external electric field, we indicate by n_p and n_m the bulk densities of positive and negative ions, respectively, by V the electrical potential, by V_0 the difference of potential applied to the cell by means of an external power supply, and assume that $V(d/2,t)=-V(-d/2,t)=V_0/2$. Due to the symmetry of the problem it follows that $V(z,t)=-V(-z,t)$. The basic equations of the problem are

$$\frac{\partial n_p}{\partial t} = D\frac{\partial}{\partial z}\left(\frac{\partial n_p}{\partial z} + \frac{q}{K_B T} n_p \frac{\partial V}{\partial z}\right), \tag{1}$$

$$\frac{\partial n_m}{\partial t} = D\frac{\partial}{\partial z}\left(\frac{\partial n_m}{\partial z} - \frac{q}{K_B T} n_m \frac{\partial V}{\partial z}\right), \tag{2}$$

$$\frac{\partial^2 V}{\partial z^2} = -\frac{q}{\varepsilon}(n_p - n_m), \tag{3}$$

where D is the diffusion coefficient of the ions. As stated before, we have assumed that $D_p=D_m=D$, consistently with the hypothesis that the ions are identical in all the aspects except for the sign of the electrical charge, and that the equation of Einstein-Smolucowsky between the mobility, μ, and the diffusion coefficient, D, holds $[\mu/D=q/(K_B T)]$. Equations (1) and (2) are strongly nonlinear due to the presence of $n_p(\partial V/\partial z)$, and analogous for n_m, in the equation of continuity. Consequently, an analytical solution is possible only in the case in which $\delta n_p=n_p-N \ll N$. As discussed in Ref. [6] this implies that $V_0 \ll V_T=K_B T/q$. Here, on the contrary, we are interested in the evolution of the ionic charge in the nematic cell when $V_0 \gg V_T$. In this case, practically all the ions are pushed close to the electrodes [10]. This means that the bulk density of positive ions is very large close to the negative electrode, and vice versa for the negative ions, but in the bulk it is negligibly small [11]. In the presence of the external voltage V_0, we indicate by n_b the bulk density of positive ions, equal to that of negative ions. The densities of the positive and negative ions close to the electrode of opposite sign are indicated by $n_p(z)$ and $n_m(z)$, respectively. The thickness of the surface layer in which are confined the ionic charges is indicated by ℓ, where $\ell \sim d(V_T/V_0)$ [3]. Since $n_p(z) \gg n_b$, as well as $n_m(z) \gg n_b$, we can introduce the concept of surface density of ions according to the relations

$$\sigma_p = \int_{-d/2}^{-d/2+\ell} n_p(z)dz = \langle n_p \rangle \ell, \tag{4}$$

$$\sigma_m = \int_{d/2-\ell}^{d/2} n_m(z)dz = \langle n_m \rangle \ell, \tag{5}$$

where, due to the symmetry of the problem, $\langle n_p \rangle = \langle n_m \rangle = n_s$. It follows that $\sigma_p=\sigma_m=\sigma=n_s \ell$, and $n_s \gg n_b$ [10]. In the following we consider just the positive charges localized in the surface layer $(-d/2,-d/2+\ell)$. However, due to the symmetry of the problem, similar results are valid also for the negative charges localized in $(d/2-\ell,d/2)$. From Eq. (1), integrating from $-d/2$ to $-d/2+\ell$, and taking into account Eq. (4) we get

$$\frac{d\sigma_p}{dt} = D\left(\frac{\partial n_p}{\partial z} + \frac{q}{K_B T} n_p \frac{\partial V}{\partial z}\right)_{-d/2}^{-d/2+\ell}. \tag{6}$$

From the discussion made above we have that

$$\left(\frac{\partial n_p}{\partial z}\right)_{-d/2+\ell} = 0 \quad \text{and} \quad n_p(-d/2+\ell) = n_b. \tag{7}$$

Furthermore, since the electrodes are assumed to be blocking, the current density of positive ions must vanish on the electrode. This implies that

$$-D\left(\frac{\partial n_p}{\partial z} + \frac{q}{K_B T} n_p \frac{\partial V}{\partial z}\right)_{-d/2} = 0. \tag{8}$$

Equation (8) simply states that the ions cannot leave the sample. If the adsorption-desorption phenomenon is present [5], close to the limiting surfaces the ions are subjected also to a localized potential responsible for the adsorption, whose penetration range is mesoscopic [12]. In this case, as discussed in Ref. [13], it is possible to write a kinetic equation describing the accumulation of particles in the mesoscopic layer close to the electrodes. However, Eq. (8) remains valid. In our case, the evolutions of the bulk densities of ions and of the electrical potential depend on the densities of ions localized close to the limiting surfaces. In this sense, it does not matter if they are close to the electrodes or adsorbed by them. It follows that Eq. (6) can be rewritten as

$$\frac{d\sigma_p}{dt} = \frac{qD}{K_B T} n_b \left(\frac{\partial V}{\partial z}\right)_b, \tag{9}$$

in which the subscript b states for bulk. The number of ions of a given sign, per unit area, is

$$\int_{-d/2}^{d/2} n_p(z)dz = Nd, \tag{10}$$

where N is the bulk density of ions in thermodynamical equilibrium introduced above. Consequently, the bulk density of ions, n_b, when on the boundary-surface layer is present the surface density of ions σ_p, is given by

$$n_b = N - \sigma_p/d. \tag{11}$$

By taking into account these results, and the symmetry of the problem, from Eq. (9) we obtain the differential equation [4]

$$\frac{d\sigma}{dt} = \mu\left(N - \frac{\sigma}{d}\right)\left(\frac{\partial V}{\partial z}\right)_b, \tag{12}$$

where $\mu=qD/(K_B T)$. We stress that Eq. (12) was obtained from the equation of continuity of the positive ions, and it takes into account the diffusion current. To proceed further it is necessary to evaluate the electric field in the bulk, $(\partial V/\partial z)_b$, when the ionic charges have formed the boundary-surface layers, whose surface densities are $\pm\sigma$.

III. BULK ELECTRIC FIELD

In order to evaluate the bulk electric field we take into account that in the sample there are two boundary-surface

layers, whose bulk electrical charge densities are $\rho_p = n_s q = \rho$, for $-d/2 \leqslant z \leqslant -d/2+\ell$, and $\rho_m = -n_s q = -\rho$, for $d/2-\ell \leqslant z \leqslant d/2$. It follows that the Poisson's equations of the problem under consideration are

$$\frac{d^2V_1}{dz^2} = -\frac{\rho}{\varepsilon}, \tag{13}$$

$$\frac{d^2V_b}{dz^2} = 0, \tag{14}$$

$$\frac{d^2V_2}{dz^2} = \frac{\rho}{\varepsilon}, \tag{15}$$

where $V_1(z) = V(-d/2 \leqslant z \leqslant -d/2+\ell)$, $V_b(z) = V(-d/2+\ell \leqslant z \leqslant d/2-\ell)$, and $V_2(z) = V(d/2-\ell \leqslant z \leqslant d/2)$ [14]. From Eqs. (13)–(15), taking into account that $V(z) = -V(-z)$, we get

$$V_1(z) = -(\rho/2\varepsilon)z^2 + \alpha_s z - \beta_s, \tag{16}$$

$$V_b(z) = \alpha_b z, \tag{17}$$

$$V_2(z) = (\rho/2\varepsilon)z^2 + \alpha_s z + \beta_s, \tag{18}$$

where α_s, α_b, and β_s are integration constants to be determined by imposing the boundary conditions $V_1(-d/2) = -V_0/2$, $V_1(-d/2+\ell) = V_b(-d/2+\ell)$, and $dV_1/dz = dV_b/dz$, for $z = -d/2+\ell$, connected with the continuity of the electrical potential and of the electrical displacement. Simple calculations give

$$\alpha_b = \frac{V_0}{d} - \frac{\rho}{\varepsilon}\frac{\ell^2}{d}, \tag{19}$$

$$\alpha_s = \frac{V_0}{d} - \frac{\rho}{\varepsilon}\frac{(d^2/2) + \ell^2 - \ell d}{d}, \tag{20}$$

$$\beta_s = \frac{\rho}{2\varepsilon}\left(\frac{d}{2} - \ell\right)^2. \tag{21}$$

It follows that the electric field in the bulk is

$$|E_b| = \frac{dV_b}{dz} = \frac{V_0}{d} - q\frac{\sigma\ell}{\varepsilon d}, \tag{22}$$

whereas the one at the surface is

$$|E_s| = |E_b| + q\frac{\sigma}{\varepsilon}, \tag{23}$$

in agreement with Eq. (3).

IV. TIME EVOLUTION OF THE SURFACE DENSITY

The differential equation (12), taking into account Eq. (22), can be rewritten as

$$\frac{d\sigma}{dt} = g(r-\sigma)(s-\sigma), \tag{24}$$

where $g = \mu q\ell/(\varepsilon d^2)$, $r = Nd$, and $s = \varepsilon V_0/(q\ell)$. The solution of Eq. (24), such that $\sigma(0) = 0$, is

$$\sigma(t) = rs\frac{1-\exp(-t/\tau)}{s - r\exp(-t/\tau)}, \tag{25}$$

where the relaxation time τ is defined by

$$\frac{1}{\tau} = (s-r)g = \frac{\mu}{d^2}\left(V_0 - \frac{Nqd\ell}{\varepsilon}\right). \tag{26}$$

For practical applications it is better to rewrite Eq. (26) in terms of the Debye length of the liquid containing ions, in thermodynamical equilibrium, defined by $\lambda_0^2 = \varepsilon K_B T/(2Nq^2)$ [12], taking into account that $\ell = dV_T/V_0$ [3]. Simple calculations give

$$\frac{1}{\tau} = \frac{1}{\tau_0}\left[1 - \frac{1}{2}\left(\frac{dV_T}{\lambda_0 V_0}\right)^2\right], \tag{27}$$

where $\tau_0 = d^2/(\mu V_0)$ is the flight time of the ion in the electric field V_0/d. An expression similar to Eq. (27) was proposed in Ref. [7] by using simple considerations. We note that Eq. (27) implies, in particular, that $V_0 \gg (d/\lambda_0)V_T$. Since Eq. (27) is valid in the limit of $V_0 \gg V_T$, it follows that the relaxation time for the surface-charge density is of the order of τ_0. The current in the external circuit is given by $j = d(\varepsilon E_s)/dt$, that taking into account Eq. (22) and Eq. (23) can be written as

$$j = q\left(1 - \frac{V_T}{V_0}\right)\frac{d\sigma}{dt}. \tag{28}$$

From Eq. (28) it follows that the relaxation time of the current in the external circuit is also τ given by Eq. (27). From Eq. (28) it follows that the initial current in the circuit is given by

$$j(0) = \mu q N\frac{V_0}{d}\left(1 - \frac{V_T}{V_0}\right). \tag{29}$$

In Eq. (27) the parameters characterizing the liquid are the Debye length in thermodynamical equilibrium, λ_0, and the mobility of the ions, μ. It follows that measurements of the relaxation time of the current as a function of the external applied voltage, for $V_0 \gg V_T$, allow the determination of these parameters by means of a best-fit procedure. In Ref. [7] the expression for the relaxation time proposed is of the type

$$\tau = A\tau_0\left[1 - B\left(\frac{dV_T}{\lambda_0 V_0}\right)^2\right]^{-1}, \tag{30}$$

where A and B were two numerical constants that could not be determined by means of simple considerations. In Ref. [7], comparing the exact numerical calculations with the predictions of Eq. (30), the best fit is obtained for $A = 1$ and $B = 1/2$, in agreement with Eq. (27) reported above.

V. CONCLUSIONS

We have considered the relaxation of the ions and of the electrical potential in a cell of dielectric liquid containing ions subjected to a large difference of electrical potential $V_0 \gg V_T$. Our analysis has been performed by assuming that the mobilities of the positive and negative ions are the same,

and that the ions can be considered pointlike, as in the usual Poisson-Boltzmann approximation [12]. We have assumed that, for $V_0 \gg V_T$, the ionic charges are responsible for two surface densities of electrical charge. In this framework we have determined the time evolution of the ionic charges collected on the electrodes. Moreover, the bulk and surface electric field were calculated. By assuming that the electrodes are perfectly blocking, we have determined the electrical current in the circuit containing the cell, and shown that its relaxation time coincides with the one of the surface density of charge. The physical parameters characterizing the system under analysis are the Debye length and the mobility of the ions. Hence the model proposed here can be used to determine these parameters, when the relaxation time of the current in the external circuit is measured as a function of the applied voltage to the sample. As stated above, the ions are assumed pointlike and this assumption implies that their density must be very small with respect to $n_M = 1/(2R_0)^3$, where R_0 is of the order of the geometrical dimension of the ion. As discussed in Ref. [3], in the static case, close to the electrode, the bulk density of ions is of the order of $N(V_0/V_T)$. It follows that our analysis works well for $N(V_0/V_T) \ll 1/(2R_0)^3$, i.e., for $V_0 \ll V_T/[N(2R_0)^3]$. This condition is always verified for usual values of R_0 ($\sim$1 nm) and of N ($<10^{20}$ m^{-3}).

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