Adsorption phenomenon and external field effect on an isotropic liquid containing impurities

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The steady-state distribution of ionic charges in a liquid, in the presence of surface adsorption, is determined. The effect of an electric field applied by means of blocking electrodes is considered. The analysis shows that the surface adsorption of ions dissolved in the liquid is responsible for an asymmetry in the electric-field distribution. In the model, the liquid is assumed to be dielectric but to contain impurities. These impurities, by means of a chemical reaction, can bring about ions. The theory takes into account the activation energy for the ionization chemical reaction and the adsorption energy of the ions at the surface.

I. INTRODUCTION

The influence of adsorbed ions on the molecular orientation of a nematic liquid crystal (NLC) with ionic conductivity (i.e., a weak electrolyte) has been investigated in recent years in connection with both surface and bulk phenomena. The ionic adsorption can be the main mechanism to explain the thickness dependence [1] of the anisotropic part of the anchoring energy connected to the NLC-substrate interface [2–8]. It is also responsible for the presence of a surface electric field, which can induce destabilization in the NLC orientation [5,9], or for the observed surface polarization in a hybrid NLC cell [10]. The phenomenon of ionic adsorption has been recently invoked to explain the asymmetric electro-optical response in a LC cell, for which experimental evidence of a polarity-sensitive response has been reported [11].

As is well known, the adsorption of ionic impurities produces a counterion cloud forming a diffuse electric double layer in the liquid [12], which gives rise to an internal field. The asymmetry in the electric-field distribution that results when an external field is combined with the internal field, due to the surface adsorption, has been used as the mechanism to explain the dc switching of a liquid-crystal display [13]. The problem has been solved in the situation of a static equilibrium field distribution under constant voltage across the cell, whose thickness is d, for which the ratio λ_D/d is not small, where λ_D is the Debye screening length [14].

In the theoretical analysis presented in [14], it is assumed that there are equal amounts of positive and negative ionic charges per unit area in the liquid, but that some of these charges are stuck at the walls by electrochemical forces. The immobilized ions at the surfaces are assumed to be of negative sign and represented by a surface charge density. It is supposed to be independent of the electrical potential difference applied by an external power supply to the cell [14]. However, as is well known, the adsorption phenomenon of ions from a solid surface depends on the actual electrical potential, due to the electric charges of the external origin and to the adsorbed charges. Hence, the hypothesis that the surface density of adsorbed charges can be used as a control parameter to describe the charge and field distribution when intrinsic and voltage-induced charge layers are combined is questionable.

In this paper, we present a more general model to determine the equilibrium distributions of charges and fields in an isotropic liquid containing ions, submitted to an external field, removing this simplifying hypothesis. The liquid is assumed to be dielectric, but containing impurities able to give rise to ions by means of a chemical dissociation reaction. The activation energy of this chemical reaction enters in the model. We suppose that the electrodes are perfectly blocking, and the surfaces are assumed to adsorb positive ions with a given adsorption energy. The model is built in the framework of the Poisson-Boltzmann theory [6]. The basic assumptions of this theory are that (i) the ions can be considered as dimensionless point charges; (ii) the surface charge is assumed to be uniformly smeared over the surface; and (iii) the electrolyte solution is described as a continuum with uniform dielectric constant. In the absence of an external field, it is possible to determine, by means of the proposed model, the chemical potential and the electric potential profile in the sample. For this situation, one observes that, once an adsorption energy is fixed, in the limit of small thickness the surface charge of adsorbed particles presents a linear behavior with the thickness d. For very large values of d, the surface density of charges tends to a saturation value [6]. In the absence of an external field, the electric potential due to the adsorption phenomenon is symmetric only if the adsorption energies on the two surfaces have the same value, as expected. When an external field is applied, the potential at one of the surfaces increases, whereas the other one decreases. This is the reason why the final distribution of the field becomes asymmetric. This asymmetry is also present in the surface charge density at both surfaces. We show that the density at the surface of a high potential decreases rapidly with increasing external voltage difference due to an external power supply. On the contrary, the surface density of charge at the surface of a low potential tends to a saturation that depends on the bulk density of ions.

In Sec. II, the model is presented and the basic equations are discussed. There it is shown that, according to the value of the external difference of the potential applied to the sample by an external power supply, two regimes are possible. The border between the two regimes is fixed by the surface density of ions, originated from the chemical dissociation of the impurities present in the liquid. In the low-

voltage region, discussed in Sec. II A, the electric field in the sample changes sign. On the contrary, in the high-voltage region, considered in Sec. II B, the electric field is everywhere oriented in the same direction. In Sec. III, the charge and the field distributions, obtained by numerical calculation, are analyzed. An approximate analytical expression for the critical voltage separating the two regimes is also obtained. In Sec. IV, a possible generalization of our model is sketched. The main results of the paper are discussed in Sec. V.

II. THE MODEL

Let us consider a cell in the shape of a slab of thickness d, filled with a liquid characterized by a dielectric constant ϵ, but containing impurities that, by means of a chemical reaction, are the source of the ions. The activation energy of this reaction will be indicated by $E_{activation}$. The liquid is globally neutral and we consider first the general case in which the sufaces are not identical, i.e., the adsorption energy is different on each surface.

We use a Cartesian reference frame whose z axis is normal to the limiting walls, located at $z = \pm d/2$. We assume that all the physical quantities entering in the model are only z-dependent. The distribution of charges produced by the ionic adsorption gives rise to a liquid that is locally charged but globally neutral. For simplicity, we assume that only positive ions are adsorbed, and in Sec. IV a possible extension of the model is discussed for the case in which both positive and negative ions are adsorbed. We denote by n_0 the bulk density of impurities (in an infinite sample), which will be the source of the ions due to the chemical reaction mentioned above (internal charges). The equilibrium distribution of the bulk density of nondissociated impurities (i.e., those that remain neutral) is given by $n_b = n_0 e^{\mu}$, where μ is the chemical potential in $k_B T$ units. In the same manner, the bulk densities of positive and negative ions are given by

$$n_{\pm}(z) = n_0 e^{\mu - \Delta \mp \psi(z)}, \tag{1}$$

where $\Delta = E_{activation}/k_B T$ is the activation energy and $\psi(z) = qV(z)/k_B T$ is the electrostatic energy of the charge q in $k_B T$ units. In our analysis, we assume that the liquid is locally neutral in an infinite sample, in the absence of the adsorption phenomenon. This condition fixes the zero of the potential. In the Maxwell-Boltzmann distribution of ionic charges in the sample, when the adsorption phenomenon is present and the sample is submitted to an external field, the potential is measured with respect to this ground state. The activation energy $E_{activation}$ can be identified with the electrostatics interaction energy between the positive and negative ions resulting from the dissociation of the particle. The surface densities of (internal) adsorbed charges are given by

$$\sigma_i = N_i e^{\mu - A_i - \psi_i} \quad \text{for} \quad i = 1,2, \tag{2}$$

where $\psi_1 = \psi(z = -d/2)$ and $\psi_2 = \psi(z = d/2)$ are the values of the surface potentials, and A_1 and A_2 are the adsorption energies of the surfaces, measured in $k_B T$ units. Furthermore, N_i is the surface density of sites where the ions can be ad-

sorbed. The adsorption energy can be identified with the electrostatics interaction energy of an adsorbed ion with its image in the substrate (physical adsorption) [18].

Let us now establish the fundamental equations governing our model. We consider that only the internal charges can move to the surface. The external charges supplied to the system remain in the surface and are separated from the liquid by the blocking electrodes. In this manner, the surface densities of charges will have both the internal and the external contribution, which, as we shall show later, gives rise to an asymmetry in the surface density of charges. The first requirement to be satisfied by the system is the conservation of the number of particles, per unit surface, namely

$$\frac{N_+ + N_-}{2} + N_B + \frac{\sigma_1 + \sigma_2}{2} = n_0 d, \tag{3}$$

where

$$N_{\pm} = \int_{-d/2}^{d/2} n_{\pm}(z) dz \quad \text{and} \quad N_B = \int_{-d/2}^{d/2} n_b(z) dz = n_b d. \tag{4}$$

Using the definitions of $n_{\pm}(z)$ and σ_i given above, it is possible to rewrite Eq. (3) in the form

$$e^{\mu} \left\{ n_0 e^{-\Delta} \int_{-d/2}^{d/2} \cosh \psi(z) dz + n_0 d + \frac{N_1 e^{-A_1 - \psi_1} + N_2 e^{-A_2 - \psi_2}}{2} \right\} = n_0 d. \tag{5}$$

In this case, the chemical potential is given by

$$e^{-\mu} = 1 + \frac{1}{2 n_0 d} (N_1 e^{-A_1 - \psi_1} + N_2 e^{-A_2 - \psi_2}) + \frac{e^{-\Delta}}{d} \int_{-d/2}^{d/2} \cosh \psi(z) dz. \tag{6}$$

This equation connects the chemical potential μ with the surface potentials ψ_1 and ψ_2.

We are interested in the final equilibrium distribution of charges and field when the applied voltage is held constant, i.e., no transients are considered. In the framework of the Poisson-Boltzmann theory, in the steady state the charge distribution and the electrical potential are related by Poisson's equation,

$$\frac{d^2 V}{dz^2} = -\frac{q}{\epsilon} [n_+(z) - n_-(z)], \tag{7}$$

which can be easily written as

$$\frac{d^2 \psi}{dz^2} = \frac{1}{L^2} e^{\mu - \Delta} \sinh \psi, \tag{8}$$

where $L = (\epsilon k_B T / 2 n_0 q^2)^{1/2}$ is an intrinsic length of the problem. This length is connected to the Debye screening length

λ_D through the relation [6] $\lambda_D = Le^{\Delta/2}$. A first integration of Eq. (8) can be easily performed giving

$$\frac{1}{2}\left(\frac{d\psi}{dz}\right)^2 = \frac{e^{\mu-\Delta}}{L^2}[\cosh\psi(z)+c], \qquad (9)$$

where c is an integration constant to be determined by the boundary conditions. The electric field is $E(z) = -dV/dz = -(k_BT/q)d\psi/dz$. In the absence of an external field, its surface values are $E(\pm d/2) = \mp q\sigma_{1,2}/\epsilon$, and outside the slab the field is zero because the system is globally neutral. Notice that if the adsorption energies (A_1 and A_2) are different, or if the densities of sites on the surfaces (N_1 and N_2) are different, the electrical potential is not symmetric with respect to $z=0$ also in the absence of external applied voltage. When an external field is applied, the above conditions become

$$E(\mp d/2) = -\frac{k_BT}{q}\left(\frac{d\psi}{dz}\right)_{\mp d/2} = \pm q\frac{\sigma_{1,2}\mp\Sigma}{\epsilon}, \qquad (10)$$

where Σ is the surface density of external charges. Equations (10) are written by assuming that the surface at $z=-d/2$ is connected with the negative pole of the external power supply. The requirement that the system is globally neutral can be expressed as

$$\sigma_1 + \sigma_2 + \int_{-d/2}^{d/2} n_+(z)dz = \int_{-d/2}^{d/2} n_-(z)dz, \qquad (11)$$

which, with the help of Eq. (1), can be written in the form

$$\sigma_1 + \sigma_2 = 2n_0 e^{\mu-\Delta}\int_{-d/2}^{d/2}\sinh\psi(z)dz. \qquad (12)$$

A simple calculation shows that Eq. (12) is an identity if Eqs. (10) are taken into account. This means that it is equivalent to Eq. (10) [15]. In order to solve the problem under consideration, we consider the two separated cases in which $\sigma_1 - \Sigma > 0$ and $\sigma_2 - \Sigma < 0$, defining, respectively, the regimes of low and high external voltage.

A. Low-voltage region

We limit first our analysis to the case of low external voltage, where $\sigma_1 - \Sigma \geq 0$. Since in our hypotheses $E(z=-d/2) > 0$ and $E(z=d/2) < 0$, the electrical potential has a minimum at some point z^* in the sample, where the electric field vanishes [16]. It follows that $(d\psi/dz)_{z=z^*} = 0$, and in Eq. (9) the integration constant c can be written in terms of $\psi^* = \psi(z^*)$ as $c = -\cosh\psi^*$. From Eq. (9), we obtain

$$\frac{d\psi}{dz} = \mp\frac{\sqrt{2}}{L}e^{(\mu-\Delta)/2}\sqrt{\cosh\psi - \cosh\psi^*}, \qquad (13)$$

where "$-$" refers to the region $-d/2 \leq z \leq z^*$, and "$+$" refers to the region $z^* \leq z \leq d/2$. Equations (13) can be integrated to give

$$\int_{\psi^*}^{\psi_2}\frac{d\psi}{\sqrt{\cosh\psi - \cosh\psi^*}} - \int_{\psi_1}^{\psi^*}\frac{d\psi}{\sqrt{\cosh\psi - \cosh\psi^*}}$$

$$= \sqrt{2}\frac{d}{L}e^{(\mu-\Delta)/2}. \qquad (14)$$

Furthermore, by using Eqs. (10) and (13) we have

$$\frac{\sqrt{2}k_BT}{q^2L}e^{(\mu-\Delta)/2}\sqrt{\cosh\psi_{1,2} - \cosh\psi^*} = \frac{\sigma_{1,2}\mp\Sigma}{\epsilon}. \qquad (15)$$

The fundamental equations of our model are Eqs. (6), (14), and (15). We have to solve this system of four equations to obtain μ, ψ_1, ψ_2, and ψ^*. Once this system of equations is solved, it is straightforward to obtain the surface charge densities σ_i by means of Eqs. (2). As it follows from these equations, the surface charge densities depend on the external charges at the surface through the chemical potential and the electric potentials at the surfaces.

B. High-voltage region

The border separating the two regimes is defined by $\sigma_1(\Sigma_c) - \Sigma_c = 0$, where Σ_c is the critical surface density of external charges. For $\Sigma = \Sigma_c$, $\psi^*(\Sigma_c) = \psi_1(\Sigma_c)$, as it follows from Eqs. (15). In the high-voltage regime, the adsorbed charge, at $z=-d/2$, is then smaller than the one sent by the power supply on the electrode. From Eqs. (10), we now have that $E(-d/2) < 0$ and $E(d/2) < 0$. The electrical potential is a monotonic function of z and, consequently, the electric field never vanishes for $-d/2 \leq z \leq d/2$ [16]. In this case, from Eq. (9) we obtain

$$\int_{\psi_1}^{\psi_2}\frac{d\psi}{\sqrt{\cosh\psi + c}} = \sqrt{2}\frac{d}{L}e^{(\mu-\Delta)/2}, \qquad (16)$$

connecting c to ψ_1 and ψ_2. By using Eqs. (9) and (10), we deduce that the boundary conditions read

$$\frac{k_BT}{q}\frac{\sqrt{2}}{L}e^{(\mu-\Delta)/2}\sqrt{\cosh\psi_{1,2} + c} = q\frac{\Sigma\mp\sigma_{1,2}}{\epsilon}. \qquad (17)$$

In this regime, the fundamental equations are Eqs. (6), (16), and (17). These equations give μ, ψ_1, ψ_2, and c in terms of Σ and d.

III. THE CHARGE AND FIELD DISTRIBUTIONS

In this section, we shall consider the particular situation in which the adsorption energy is the same at both surfaces, and the system is submitted to an external field. The purpose is to obtain the charge and field distributions in the presence of an applied voltage, taking into account the phenomenon of ionic adsorption. The problem is analyzed in the framework of the model presented in the preceding section. The solution of the system of four nonlinear equations (6), (14), and (15) in the low-voltage regime and Eqs. (6), (16), and (17) in the high-voltage regime is searched numerically. To do this, we start with an estimation of the parameters entering in the model,
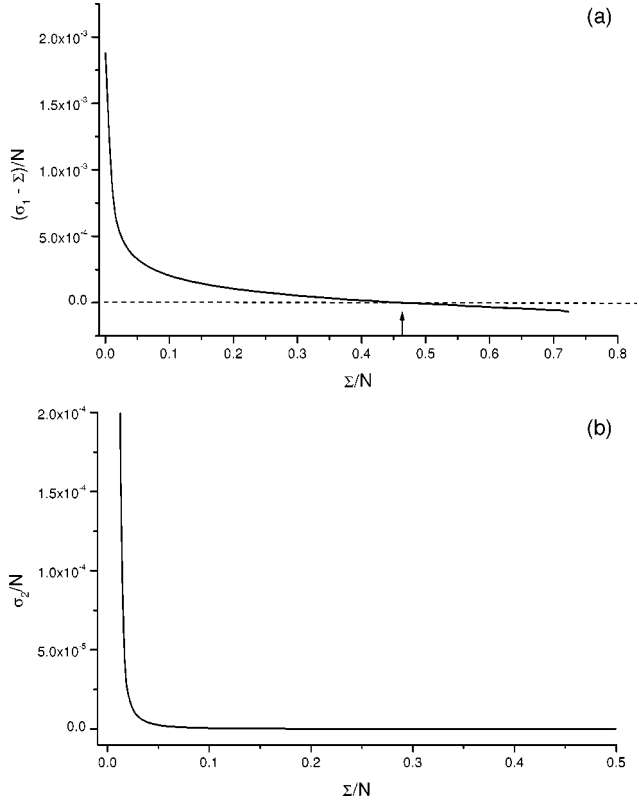
FIG. 1. The behavior of the surface charge densities $\sigma_{1,2}$ as a function of the external charge density Σ. In (a), $(\sigma_1 - \Sigma)/N$ vs Σ/N is reported in the two regimes of low and high applied voltage. The border between the two regimes is $\Sigma_c/N \approx 0.46$, where this difference changes its sign. In (b), σ_2/N vs Σ/N is shown. The curves have been depicted for $\Delta = 8.0$ and $A = -0.1$.

FIG. 2. (a) Surface electrical potentials ψ_1 and ψ_2 and the minimum value of $\psi(z)$, ψ^* vs the external charge density Σ/N; (b) the voltage difference across the sample $\psi_2 - \psi_1$ vs Σ/N.

as was done in [6]. We assume $\Delta = 8.0$, $N_1 = N_2 = N$, and $A_1 = A_2 = -0.1$. We work at a fixed thickness $d/2L = 200$, which implies that $\lambda_D \approx 0.6$ μm and $d \approx 4$ μm. Using these estimations, we can determine the electrical potential and the field profiles in the regimes of low ($\sigma_1 > \Sigma$) and high ($\sigma_1 < \Sigma$) external potential, at a fixed $n_0 d/N = 0.85$.

In Fig. 1(a), we report the difference $\sigma_1 - \Sigma$ versus Σ, where Σ represents the external charge density sent by the power supply on the limiting surfaces. This quantity decreases rapidly with Σ, and vanishes for $\Sigma = \Sigma_c$. For $\Sigma > \Sigma_c$, $\sigma_1 - \Sigma < 0$. Notice that for $\Sigma = 0$, σ_1 coincides with the adsorbed charges density in the absence of an external field. It depends on A, Δ, and d. For very large Σ, $\sigma_1 \rightarrow n_0 d$. In this limit, all positive ions are adsorbed on the surface at $z = -d/2$, connected with the negative electrode of the power supply. Figure 1(b) shows the surface density of adsorbed charges versus Σ at the surface at a high potential. This quantity is a decreasing function of Σ. The trends of σ_i versus Σ can be easily understood taking into account that σ_i are given by Eq. (2), in which the surface electrical potentials ψ_i are introduced.

The dependences of ψ_i versus Σ are reported in Fig. 2(a). The potential ψ_1 is a monotonic decreasing function of Σ, whereas ψ_2 is a monotonic increasing function of Σ. Notice that for $\Sigma \rightarrow \Sigma_c$, ψ_1 vanishes. For $\Sigma > \Sigma_c$, ψ_1 is negative. In
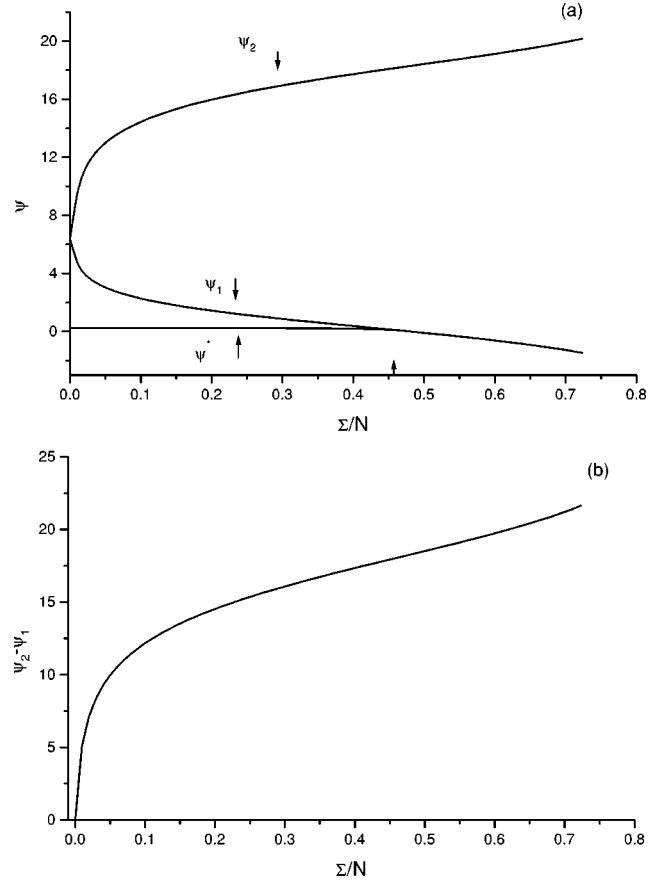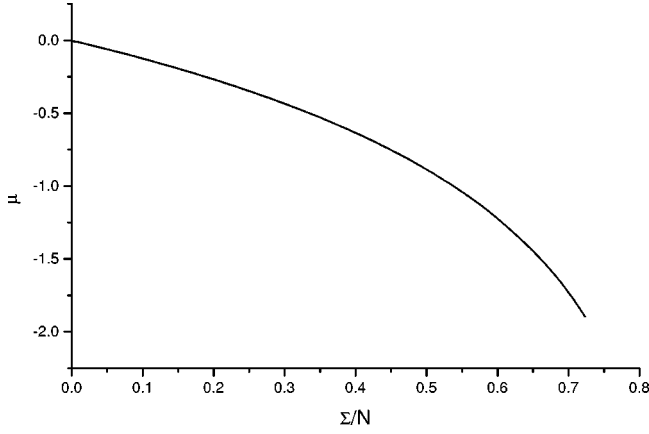
Fig. 2(a), the minimum value of ψ, $\psi^* = \psi(z^*)$, versus Σ is also reported. It presents a maximum for $\Sigma/N \approx 0.25$ and it decreases abruptly to zero for $\Sigma \rightarrow \Sigma_c$. Our analysis shows that $\psi^* \rightarrow \psi_1$ for $\Sigma \rightarrow \Sigma_c$. However, $\psi_1 \rightarrow 0$ in a monotonic manner, whereas ψ^* for $\Sigma \leqslant \Sigma_c$ increases up to a maximum value, and then it decreases to zero. In Fig. 2(b), the actual voltage difference across the sample $\psi_2 - \psi_1$ versus Σ is shown. As expected, for Σ very large it tends to be proportional to Σ.

The chemical potential μ versus Σ is displayed in Fig. 3. As is evident from this figure, in the absence of an external field (i.e., for $\Sigma = 0$), $\mu(\Sigma = 0)$ is rather small in absolute value and depends on A, Δ, and d. μ changes very much with Σ and tends to $-\infty$ for $\Sigma \rightarrow \infty$. In fact, in this limit all the positive ions are adsorbed at the surface at a lower potential, and an exchange of particles between the surface and the bulk becomes impossible.

The electrical potential profiles for various Σ are shown in Fig. 4. The dashed curve corresponds to the case in which the electrical potential is due only to the adsorption phenomenon ($\Sigma = 0$). In the symmetric case under consideration ($A_1 = A_2, N_1 = N_2$), $\psi(z)$ is an even function of z, with respect to the middle of the sample (at $z = 0$). The other curves correspond to $\Sigma/N \approx 0.4$ (low-voltage regime) and $\Sigma/N \approx 0.7$ (high-voltage regime). For the case we are illustrating here, the border between the two regimes is $\Sigma_c/N \approx 0.46$.

FIG. 3. Chemical potential μ vs Σ/N.

FIG. 4. Electrical potential $\psi(z)$ vs $2z/d$. Dashed curve corresponds to $\Sigma/N=0.0$ (no external potential), dotted curve to $\Sigma/N \approx 0.41$, and solid curve to $\Sigma/N \approx 0.72$.

Finally, in Fig. 5 the electric-field profiles for various Σ are reported. Notice that, as pointed out before, for $\Sigma < \Sigma_c$ the electric field changes sign across the sample, whereas for $\Sigma > \Sigma_c$ it has the same direction everywhere.

As stated above, Σ_c is the border separating the two regimes. It is possible to obtain Σ_c by operating on the fundamental equations of the model. Let us consider these equations in the high-voltage regime. We can rewrite Eq. (6) and Eq. (16), respectively, in the form

$$e^{-\mu} = 1 + \frac{1}{2n_0 d}[N_1 e^{-A_1 - \psi_1} + N_2 e^{-A_2 - \psi_2}]$$

$$+ \frac{L}{\sqrt{2}d} e^{-(\mu+\Delta)/2} J[\psi_1, \psi_2; c] \qquad (18)$$

and

$$I[\psi_1, \psi_2; c] = \frac{\sqrt{2}d}{L} e^{(\mu-\Delta)/2}, \qquad (19)$$

where

$$J[\psi_1, \psi_2; c] = \int_{\psi_1}^{\psi_2} \frac{\cosh \psi}{\sqrt{\cosh \psi + c}} d\psi$$

and

$$I[\psi_1, \psi_2; c] = \int_{\psi_1}^{\psi_2} \frac{d\psi}{\sqrt{\cosh \psi + c}}. \qquad (20)$$

In this manner, by using Eq. (20) it is possible to rewrite Eq. (18) as

$$e^{-\mu} = 1 + \frac{1}{2n_0 d}[N_1 e^{-A_1 - \psi_1} + N_2 e^{-A_2 - \psi_2}]$$

$$+ e^{-\Delta} \frac{J[\psi_1, \psi_2; c]}{I[\psi_1, \psi_2; c]}. \qquad (21)$$

From the definitions of the surface charge densities [Eq. (2)] we have $\sigma_1(\Sigma) = e^{\mu - A_1 - \psi_1}$, i.e.,
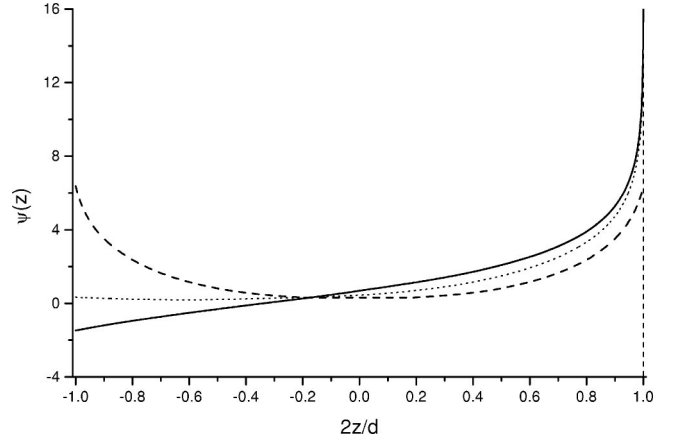
$$\sigma_1(\Sigma) = \frac{N_1 e^{-A_1 - \psi_1}}{1 + [N_1 e^{-A_1 - \psi_1} + N_2 e^{-A_2 - \psi_2}]/2n_0 d + e^{-\Delta} J[\psi_1, \psi_2; c]/I[\psi_1, \psi_2; c]}. \qquad (22)$$

For $\Sigma \to \Sigma_c^+$, $c \to -1$, $\psi_1 \to 0$, and $\psi_2 \to \psi_{2c} \gg 1$, as can be deduced from the numerical calculations reported above. Consequently,

$$\sigma_1(\Sigma_c) = \Sigma_c = \frac{N_1 e^{-A_1}}{1 + N_1 e^{-A_1}/2n_0 d + R}, \qquad (23)$$

where

$$R = e^{-\Delta} \frac{J[0, \psi_{2c}; -1]}{I[0, \psi_{2c}; -1]}. \qquad (24)$$

Numerical calculations show that

$$R \approx \frac{N_1 e^{-A_1}}{2n_0 d}. \qquad (25)$$

Therefore, Σ_c is found to be

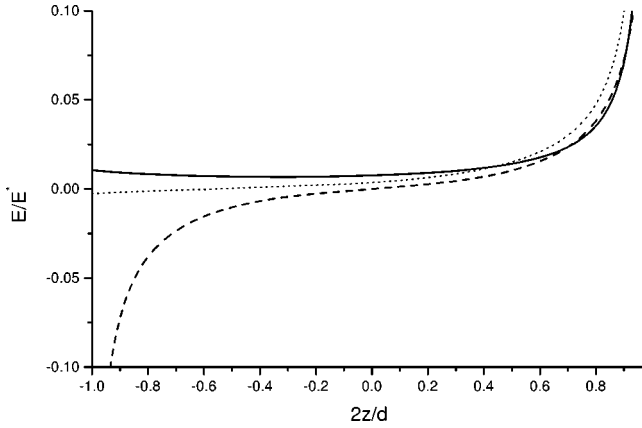$$\Sigma_c \approx \frac{N_1 e^{-A_1}}{1 + N_1 e^{-A_1}/n_0 d}. \qquad (26)$$

FIG. 5. Reduced electric field E/E^*, where $E^* = \sqrt{2}k_B T/qL$ vs $2z/d$ in correspondence with the values of Σ/N considered in Fig. 4.

Notice that for $N_1 \to 0$ or $A_1 \to \infty$, $\Sigma_c \to 0$, as expected. In the opposite limit of $N_1 \to \infty$ or $A_1 \to -\infty$, $\Sigma_c \to n_0 d$, which corresponds to the case in which all the positive ions are adsorbed on the surface at $z = -d/2$. This behavior is illustrated in Fig. 6, where Σ_c is depicted versus the adsorption energy A_1 as it comes from the numerical calculations. Notice that the curve is quite well represented by Eq. (26) given above.

We have presented most of the results of the numerical calculations for an adsorption energy that is relatively low, just to emphasize the crucial role played by this quantity in a real sample. However, if we consider higher values for the adsorption energy, the magnitude of the quantities reported above are shifted, as expected, but the global behavior of the system remains the same.

IV. EXTENSIONS OF THE MODEL

Before we proceed, it is convenient to establish some particular cases that can be analyzed in the framework of the proposed model. The first one is the situation in which the adsorption energies are different on the surfaces $A_1 \neq A_2$
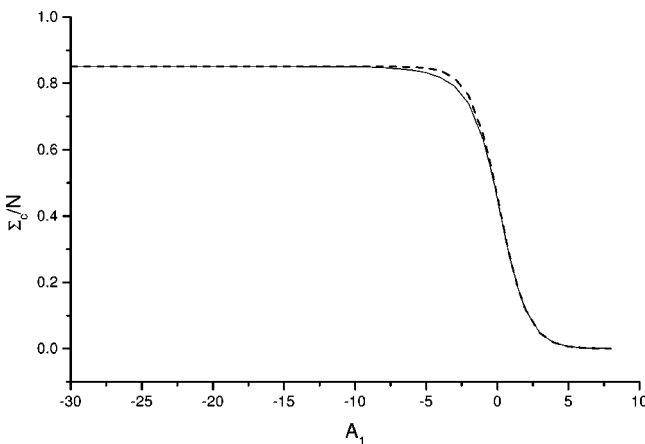

FIG. 6. Critical external density of charge Σ_c vs adsorption energy A_1. The solid line corresponds to the numerical calculations; the dashed line is the approximated relation represented by Eq. (26).

(asymmetric case) but the external voltage is absent. The fundamental equations of the model are easily obtained from the ones presented before by taking the limit $\Sigma \to 0$. A practical situation in which this model has revealed its usefulness is the asymmetric electro-optical response in a nematic-liquid-crystal cell [11,17]. Another limiting case to be considered refers to the situation in which the adsorption phenomenon is absent, but the sample is submitted to an external voltage. In this case, we have $A_1 = A_2 \to \infty$. Consequently, $\sigma_i \to 0$, as given by Eq. (2). In this case, as it follows from Eqs. (17), $\psi_1 = -\psi_2 = \Psi$. Again, the fundamental equations of the model, now reduced to three coupled equations, can be easily obtained from the previous ones. They will connect μ, Ψ, and c with Σ and d.

In the preceding analysis, we have considered a selective ion adsorption phenomenon in which only the positive ions are supposed to be adsorbed on the surface. This implies considering that the adsorption energy for the negative ones is taken as infinite. Let us now consider the case in which both positive and negative ions can be adsorbed by the surfaces. We suppose, for simplicity, that the surfaces are identical, and A_+ and A_- are the adsorption energies for both species of ions. The surface density of adsorbed ions of a given sign is given by [see Eq. (2)]

$$\sigma_{i,\pm} = N_\pm e^{\mu - A_\pm \mp \psi_i}, \qquad (27)$$

where $i = 1,2$ refers to the surfaces and $N_\pm$ are the surface densities of sites for $+$ and $-$ ions. We assume, furthermore, that $N_+ = N_- = N$. The actual surface density of adsorbed ions is given by

$$N_i = N e^\mu (e^{-A_+ - \psi_i} + e^{-A_- + \psi_i}), \qquad (28)$$

whereas the actual surface charge density is

$$Q_i = q(\sigma_{i,+} - \sigma_{i,-}) = q\sigma_i. \qquad (29)$$

The equation representing the conservation of the number of particles [see Eq. (3)] is slightly modified, giving for the chemical potential

$$e^{-\mu} = 1 + \frac{N}{2n_0 d}[e^{-A_+}(e^{-\psi_1} + e^{-\psi_2}) + e^{-A_-}(e^{\psi_1} + e^{\psi_2})]$$

$$+ \frac{e^{-\Delta}}{d}\int_{-d/2}^{d/2} \cosh\psi(z)dz. \qquad (30)$$

The basic equations of the model are then Eqs. (30), (14), and (15) for the low-voltage regime and Eqs. (30), (16), and (17) for the high-voltage regime, if we consider in these equations $\sigma_{1,2}$ as defined in Eq. (29).

V. CONCLUSIONS

We have analyzed the electric potential profile in a cell containing an isotropic liquid in thermodynamical equilibrium. The liquid is supposed to contain impurities that can give rise to ions for chemical decomposition. The dissociation energy Δ controls the chemical reaction of ionization. By assuming a selective ionic adsorption from the surface, we have evaluated the surface densities of charges when the

sample is submitted to an external field. Our analysis has shown that there are two regimes of the actual electrical potential in the cell, with respect to the external applied potential.

In the low regime, the potential profile presents a minimum inside the cell. Increasing the external potential, this minimum moves towards the potential of one of the surfaces. For a critical value of the external applied voltage, the minimum value of the actual profiles coincides with the potential of one of the surfaces. In this situation, the actual potential profile has a minimum just at the surface. This corresponds to the case in which the adsorbed charge density is equal to the external charge density sent by the external power supply on the electrodes. For external applied voltages larger than this critical value, the actual potential profile is a monotonic function inside the cell.

In the low-voltage regime, we have shown that the surface density of adsorbed charges at the high potential surface tends rapidly to zero when the external charge density increases. The opposite behavior is observed for the surface density of adsorbed charges at the lowest potential. We have also evaluated the chemical potential of the system versus the density of external charges sent on the surface by the power supply. Our analysis generalizes the one presented by Thurston [14] and Thurston *et al.* [13] to interpret the dc switching effect observed in liquid-crystal displays based on bistable boundary-layer configuration, taking into account that the actual densities of adsorbed charges depend on the actual potential.

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[15] To verify that Eq. (12) is an identity, if Eqs. (10) hold, it is possible to do as follows. From Eq. (8) we have $\sinh \psi = L^2 \exp(-\mu+\Delta)d^2\psi/dz^2$. By substituting this result into Eq. (12), we obtain $\sigma_1+\sigma_2 = 2n_0L^2[(d\psi/dz)_{-d/2}-(d\psi/dz)_{d/2}]$, which is an identity, taking into account the definition of L and the boundary conditions (10).

[16] A simple inspection shows that $\psi(z)$ can have only one extremum in $-d/2 \leq z \leq d/2$. In fact, from Eq. (9), $d\psi/dz=0$ implies $\cosh \psi + c = 0$, which has only one solution. In the low voltage regime, since $d\psi/dz < 0$ for $z=-d/2$ and $d\psi/dz > 0$ for $z=d/2$, this point corresponds to a minimum. On the contrary, in the high voltage region, where $d\psi/dz < 0$ for $z = \pm d/2$, the $\psi(z)$ profile has to be monotonic. In fact, if not, $\psi(z)$ has to present at least two extrema, which is impossible for Eq. (9).

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