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A Model for Selective Ion Adsorption Including van der Waals Interaction

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A model for the selective adsorption phenomenon in an isotropic liquid accounting for a van der Waals interaction between the ions and the surface is presented, in the framework of the Poisson–Boltzmann theory. The fundamental equations governing the electric field distribution are exactly solved for low and high potential regimes.

1. Introduction

Adsorption phenomena in nematic liquid crystals (NLC) cells have been investigated mainly in connection with their effects on the surface energy. This happens because the interaction of an NLC with a solid substrate can be accounted for by a surface energy. In most cases, the mechanism that controls the surface orientation of the nematic results from short-range forces, so that the resulting anchoring energy strength, W , is expected to be a quasilocal property of the NLC–solid interface. Although being of great interest, the real knowledge of the interactions that determine the alignment of molecules in the surface is not well understood. A consistent argument compatible with the experimental data invokes the ionic adsorption by the surfaces limiting the sample.¹ The mechanism works as follows: The bulk NLC is neutral, but contains positive and negative ions; the surface adsorbs positive ions, which, upon accumulation, produce a surface electric field. This surface field can modify the surface energy, W , renormalizing it² or explaining its dependence on the applied voltage.^{3,4} The final electric field distribution across the sample is usually determined in the framework of the Poisson–Boltzmann theory, by considering the presence of an adsorption energy localized at the surfaces.

The aim of this work is to present a theory for the selective adsorption phenomenon in an isotropic liquid—having in mind further application to NLC systems—by taking into account a van der Waals interaction between the ions and the surface. The new ingredient of the model is just this delocalized surface interaction. In the framework of Poisson–Boltzmann theory, we establish the fundamental equations governing the adsorption phenomena and solve them in the limits of low and high potentials for a simplified form of the interaction energy between the molecules in the fluid and the substrate. In these limits, all the solutions can be exactly obtained. Therefore, we determine the electric field distribution inside the sample and the behavior of the chemical potential as a function of the thickness of the sample d , for representative values of the material parameters. The results are compared with the ones obtained in the framework of the model (hereafter referred to as the localized model), in which a localized adsorption energy on the surfaces is considered, and indicate that the use of a localized energy is essentially enough to achieve a good description of the key mechanisms governing the selective adsorption of ions in these

samples. In the present analysis, we will assume that the system is diluted, i.e., the bulk fraction of potentially adsorbed particles is small. For this reason, the model is developed in the framework of the Poisson–Boltzmann theory, which, in recent years, has been the object of analytical models and numerical simulations in several other contexts.^{5–7} For the case in which the bulk density of potentially adsorbed particles is high, other models for adsorption of ions in NLC cells can be considered, as, for instance, the one using a free-energy formalism to generalize the Maxwell–Boltzmann distribution⁸ or the one using Fermi–Dirac distribution.⁹ Recent modifications of the Poisson–Boltzmann approach can be found in refs 10–12.

Our work is organized as follows. In Section 2, the fundamental equations governing the behavior of the chemical potential, the surface potential, and the minimum of the potential inside the sample are presented, by incorporating the van der Waals interaction energy. In Section 3, a simplified expression for the potential representing the van der Waals interaction is introduced. Subsequently, the fundamental equations of the model are solved in closed form in the limit of small electric potential. In Section 4, we present a detailed analysis for the case in which the surfaces are identical, in the limits of low and high potentials. In Section 5, some potential profiles are presented to illustrate the behavior predicted by the model and to compare this behavior with the potential profiles obtained in the framework of the localized model. Finally, some concluding remarks are presented in Section 6.

2. Poisson–Boltzmann Theory with van der Waals Interaction

We consider a sample in the shape of a slab of thickness d , as shown in Figure 1, in which the presence of impurities, after dissociation, gives rise to the ions in the sample. In equilibrium, at a temperature T , the distributions of positive and negative ions are given by

$$n_{\pm}(z) = n_0 e^{(\mu - \Delta \mp qV - u_{\pm})/k_B T} \quad (1)$$

where μ is the chemical potential, $V(z)$ is the electrostatic potential, q is the charge of the ion, $u_{\pm}(z)$ are the van der Waals energies, and k_B is the Boltzmann constant. We assume that $u_{\pm} = u(z)$, i.e., the same interaction energy exists for both kinds of ions. We denote by n_0 the bulk density of impurities for an infinite sample, whose activation energy is Δ . For convenience,

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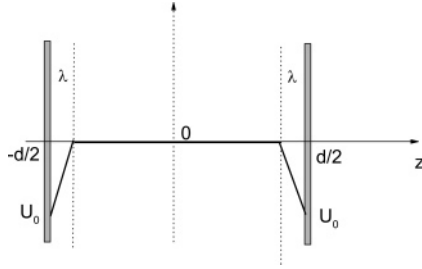


Figure 1. Nematic sample limited by two flat surfaces located in $z = \pm d/2$. The profile of a simplified short-range interaction is also shown as an example of an interaction energy delocalized over a distance λ .

the electrical potential may be written in a nondimensional form as $\psi(z) = qV/k_B T$, and all the energies are measured in units of $k_B T$, i.e., $\mu/k_B T \rightarrow \mu$, $\Delta/k_B T \rightarrow \Delta$, and $u(z)/k_B T \rightarrow U(z)$. The electrical displacement is given by $\nabla \cdot \mathbf{D} = \rho/\epsilon_0$, where ρ is the bulk density of the charges in the cell. This quantity is given by

$$\begin{aligned} \rho(z) &= q(n_+ - n_-) \\ &= -2qn_0 e^{\mu - \Delta} e^{-U(z)} \sinh \psi(z) \end{aligned} \quad (2)$$

For the system we are considering, all the physical quantities depend only on the coordinate z . Thus, from the electrical displacement, by means of the relation $\mathbf{D} = \epsilon \mathbf{E} = -\epsilon \nabla V$, the electrical potential can be obtained by solving the equation $\nabla^2 V = d^2 V/dz^2 = -\rho/(\epsilon \epsilon_0)$, which, using the above results, can be put in the form

$$\frac{d^2 \psi}{dz^2} = \frac{e^{\mu - \Delta}}{L^2} e^{-U(z)} \sinh \psi(z), \text{ with } L^2 = \frac{\epsilon k_B T}{2n_0 q^2} \quad (3)$$

in which the dielectric coefficient is measured in units of ϵ_0 . The differential eq 3 must be resolved in such a way that the value of the potential is minimum at a point of coordinate z^* inside the sample, i.e., $(d\psi/dz)_{z=z^*} = 0$. This condition establishes a first relation connecting the quantities $\psi^* = \psi(z = z^*)$, μ , $\psi_1 = \psi(z = -d/2)$, and $\psi_2 = \psi(z = d/2)$, the latter quantities being the values of the potential at the surfaces. On the surfaces, the solution obeys the following conditions:

$$E(z = \mp d/2) = -\frac{k_B T}{q} \left(\frac{d\psi}{dz} \right)_{z=\mp d/2} = \pm \frac{q\sigma_{1,2}}{\epsilon_0} \quad (4)$$

where σ_1 is the density of the particles in the surface placed at $z = -d/2$ and σ_2 refers to the density at the position $z = d/2$. Furthermore, $\sigma_i = N_i e^{\mu - \psi_i}$, for $i = 1$ or 2 , where N_i is the number of sites per unit surface on each surface. These equations provide two more relations involving ψ_1 , ψ_2 , ψ^* , and μ . To obtain the fourth and last relation involving these quantities, the conservation of the number of particles has to be imposed, namely,

$$\frac{N_+ + N_-}{2} + N_B + \frac{\sigma_1 + \sigma_2}{2} = n_0 d \quad (5)$$

where $N_{\pm} = \int_{-d/2}^{d/2} n_{\pm}(z) dz$ and $N_B = \int_{-d/2}^{d/2} n_0 e^{\mu} dz$. Combining the above expressions and conditions, it is possible to write

$$\begin{aligned} e^{-\mu} &= 1 + \frac{1}{2n_0 d} (N_1 e^{-\psi_1} + N_2 e^{-\psi_2}) + \\ &\quad e^{-\Delta} \frac{1}{d} \int_{-d/2}^{d/2} e^{-U(z)} \cosh \psi(z) dz \end{aligned} \quad (6)$$

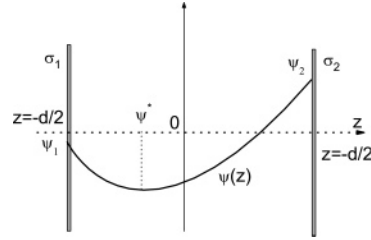


Figure 2. The cell in the shape of a slab of thickness d with two different flat surfaces placed at $z = \pm d/2$.

In Figure 2 the expected profile of the electric potential is shown to be asymmetric with respect to the middle of the sample. The electric potentials ψ_1 , ψ_2 , and ψ^* are indicated on the figure, together with the surface density of adsorbed charges σ_1 and σ_2 . The complete problem is governed by these four relations connecting μ , ψ_1 , ψ_2 , and ψ^* . The requirement that the system is globally neutral is fulfilled by the condition

$$\sigma_1 + \sigma_2 + \int_{-d/2}^{d/2} n_+(z) dz = \int_{-d/2}^{d/2} n_-(z) dz \quad (7)$$

which is now expressed by the identity

$$\sigma_1 + \sigma_2 = 2n_0 e^{\mu - \Delta} \int_{-d/2}^{d/2} e^{-U(z)} \sinh \psi(z) dz \quad (8)$$

This model for the adsorption of ions is a modification of the localized model proposed by Barbero et al.,¹³ and generalized by Evangelista and Barbero,¹⁴ in order to consider a delocalized interaction between the ions and the surface, instead of a localized adsorption energy.

3. Simplified Interaction

Let us consider a simplified and piecewise continuous potential, strongly localized in the neighborhoods of the surfaces, as representing the van der Waals interactions between the ions and the surfaces, in the form depicted in Figure 1:

$$U(z) = \begin{cases} \alpha z + \beta, & -\frac{d}{2} \leq z < \lambda - \frac{d}{2} \text{ (I)} \\ 0, & \lambda - \frac{d}{2} < z < \frac{d}{2} - \lambda \text{ (II)} \\ \alpha' z + \beta, & \frac{d}{2} - \lambda < z \leq \frac{d}{2} \text{ (III)} \end{cases} \quad (9)$$

where $U_0 < 0$, $\alpha = -\alpha' = -U_0/\lambda$, and $\beta = U_0(1 - d/(2\lambda))$. The Poisson equation (eq 3) can be put in the form

$$\frac{d^2 \psi}{dz^2} = \frac{e^{\mu - \Delta}}{L^2} \begin{cases} e^{-(\alpha z + \beta)} \sinh \psi \text{ (I)} \\ \sinh \psi \text{ (II)} \\ e^{-(\alpha' z + \beta)} \sinh \psi \text{ (III)} \end{cases} \quad (10)$$

The set of equations in eq 10 will be solved in the limits of low and high potentials. From now on, we will consider the linearized version of the equations, i.e., we assume that $\sinh \psi \approx \psi$. An approach of this type implies that $V/V_T \leq 0.4$ if $V_T = k_B T/q \approx 25$ mV (i.e., at room temperature). This means that our analysis can be valid when the electric potential effectively present in the sample is such that $V \leq 10$ mV. The equations to be solved in the regions I and III, in the above approximation and after performing a suitable change of the variable, will have the form

$$x \frac{d^2\psi}{dx^2} + \frac{d\psi}{dx} - B\psi = 0 \quad (11)$$

where $x = e^{\alpha z}$ (Region I) and $x = e^{\alpha' z}$ (Region III), while, for both regions, $B = (\lambda/U_0 L)^2 e^{\mu-\Delta-U_0/2} [1-d/(2\lambda)]$. The general solution of eq 11 is

$$\psi(x) = c_1 I_0[X(z)] + 2c_2 K_0[X(z)] \quad (12)$$

where $I_0(x)$ and $K_0(x)$ are, respectively, the modified Bessel functions of first and second kind¹⁵ and

$$X(z) = 2\sqrt{Bx} = \begin{cases} X_s e^{U_0/2\lambda(z+(d/2))} \text{ (I)} \\ X_s e^{-U_0/2\lambda(z-(d/2))} \text{ (III)} \end{cases} \quad (13)$$

where $X_s = X(z = -d/2) = X(z = d/2) = -2(\lambda/U_0 L) e^{(\mu-\Delta-U_0)/2}$. In view of the condition requiring that the potential is minimum inside the sample, the electrical potential has to be a decreasing function of z in region I and an increasing function of z in region III. This behavior is accounted for only by $I_0(X)$. For this reason, we choose $c_2 = 0$, and the solution of the Poisson equation in regions I and III will have the simple forms

$$\psi_I(z) = \frac{\psi_1}{I_0(X_s)} I_0[X(z)] \text{ and } \psi_{III}(z) = \frac{\psi_2}{I_0(X_s)} I_0[X(z)] \quad (14)$$

respectively. In region II, the general solution is

$$\psi_{II}(z) = a_1 e^{\gamma z} + a_2 e^{-\gamma z} \quad (15)$$

where $\gamma = e^{(\mu-\Delta)/2}/L$. The integration constants a_1 and a_2 can be determined by imposing the continuity of the potential at $z = z_1 = -d/2 + \lambda$ and $z = z_2 = -z_1$, i.e., by requiring that $\psi_I(z_1) = \psi_{II}(z_1)$ and $\psi_{II}(z_2) = \psi_{III}(z_2)$. After some simple calculations, one obtains

$$a_1 = \frac{I_0(X_1)}{4I_0(X_s)} \left[\frac{\psi_1 - \psi_2}{\sinh \gamma z_1} + \frac{\psi_1 + \psi_2}{\cosh \gamma z_1} \right]$$

$$a_2 = \frac{I_0(X_1)}{4I_0(X_s)} \left[-\frac{\psi_1 - \psi_2}{\sinh \gamma z_1} + \frac{\psi_1 + \psi_2}{\cosh \gamma z_1} \right] \quad (16)$$

where $X_1 = X_s e^{U_0/2}$. Now, we use the requirement that the potential has a minimum at a particular point $z = z^*$ inside the sample, i.e., $(d\psi/dz)_{z=z^*} = 0$, to obtain

$$\psi^* = \psi(z^*) = a_1 e^{\gamma z^*} + a_2 e^{-\gamma z^*} \quad (17)$$

where

$$z^* = \frac{1}{\gamma} \operatorname{arctanh} \left[\frac{\psi_1 - \psi_2}{\psi_1 + \psi_2} \coth \gamma \left(\lambda - \frac{d}{2} \right) \right] \quad (18)$$

The boundary conditions (eq 4) may be rewritten as

$$-\frac{k_B T}{q} \left(\frac{d\psi}{dz} \right)_{z=-d/2} = \frac{q}{\epsilon} N_1 e^{\mu-\psi_1}$$

$$-\frac{k_B T}{q} \left(\frac{d\psi}{dz} \right)_{z=d/2} = -\frac{q}{\epsilon} N_2 e^{\mu-\psi_2} \quad (19)$$

giving two equations connecting ψ_1 , ψ_2 , and μ , in the form

$$e^{\mu-\psi_1} = \frac{2n_0 L}{N_1} e^{(\mu-\Delta-U_0)/2} \frac{\psi_1 I_1(X_s)}{I_0(X_s)}$$

$$e^{\mu-\psi_2} = \frac{2n_0 L}{N_2} e^{(\mu-\Delta-U_0)/2} \frac{\psi_2 I_1(X_s)}{I_0(X_s)} \quad (20)$$

where $I_1(X) = dI_0(X)/dX$ is the first-order modified Bessel function of first kind.¹⁵ Notice that eqs 20 imply the simple relation $\psi_2 - \psi_1 = \ln(N_2/N_1) + \ln(\psi_1/\psi_2)$. When the surfaces are identical, $N_2 = N_1$, and, consequently, $\psi_2 = \psi_1$. The third relation is furnished by eq 6, which, in the low potential limit, may be put in the form

$$e^{-\mu} = 1 + \frac{1}{n_0 d} (N_1 e^{-\psi_1} + N_2 e^{-\psi_2}) + e^{-\Delta} \left[1 - \frac{2\lambda}{U_0 d} (-1 + U_0 + e^{-U_0}) \right] \quad (21)$$

The set of equations to be solved now is formed by eqs 20 and 21, which furnish ψ_1 , ψ_2 , and μ . Once these equations are solved, one can immediately determine ψ^* by means of eq 17.

Some representative results are shown in Figures 3 and 4. In Figure 3, the behavior of the surface potentials is shown as a function of the strength of the van der Waals interaction. The difference of potential in the cell, $\psi_2 - \psi_1$, presents a maximum and tends to zero for $|U_0| \gg 1$. This behavior was used to explain the non-monotonic trend presented by the anchoring energy as a function of the applied voltage in a typical NLC cell.^{3,4} In Figure 4, the behavior of the chemical potential is shown as a function of the same quantity. Likewise, other quantities accounting for the electric field distribution inside the sample can be obtained by using the fundamental equations of the model. In the next section, we consider in detail the distributions of electric and chemical potential for a sample limited by identical surfaces.

4. Identical Surfaces

4.1. Low Potential Limit. To proceed with a more detailed comparison between the present model and the one that considers a localized adsorption energy, we particularize the analysis to the case in which the system is formed by two

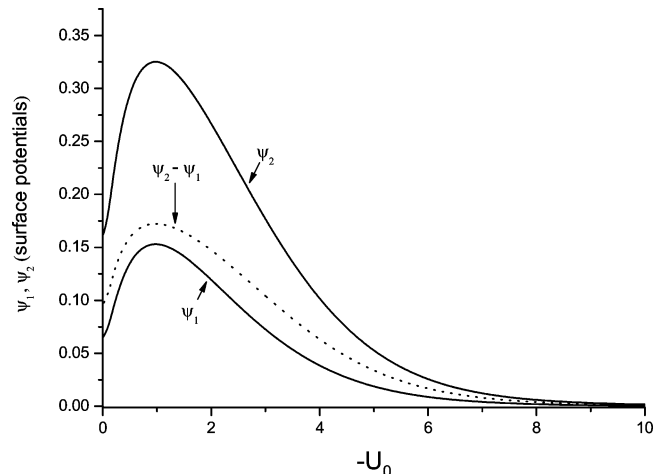


Figure 3. Surface potentials ψ_1 and ψ_2 (solid lines) and the difference of potential in the cell $\psi_2 - \psi_1$ vs $-U_0$. The curves were depicted for $b_1 = N_1/2n_0L = 0.01$, $b_2 = N_2/2n_0L = 0.03$, $d/2L = 200$, $\Delta = 4.0$, and $c = L/\lambda = 1.0$.

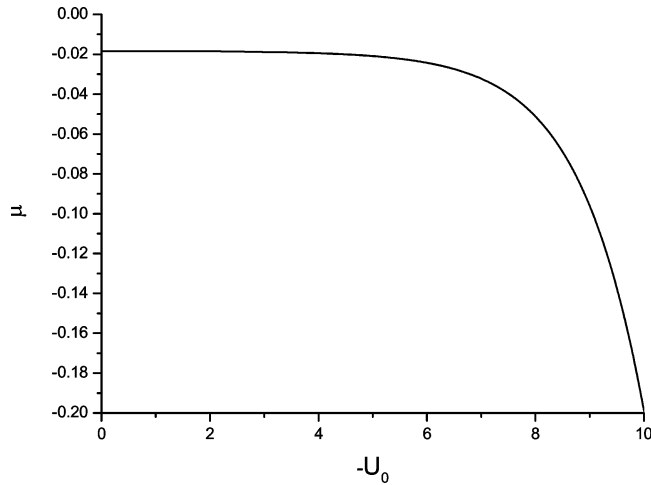


Figure 4. Chemical potential μ vs $-U_0$. The parameters are the same as those in Figure 3.

identical surfaces, such that $N_2 = N_1 = N$. In this case, the surface potentials become $\psi_1 = \psi_2 = \psi_s$, and the electrical potential has to be minimum at the middle of the sample, i.e., $(d\psi/dz)_{z=0} = 0$ and $\psi^* = \psi(z=0) = \psi_0$. From eqs 16 and 17, with $z^* = 0$, one easily obtains

$$\psi_0 = \psi_s \frac{I_0(X_1)}{I_0(X_s)} \operatorname{sech} \left[\frac{U_0}{2} X_1 \left(1 - \frac{d}{2\lambda} \right) \right] \quad (22)$$

which represents now one relation connecting ψ_0 , ψ_s , and μ . A second relation involving these quantities can be obtained by recognizing that the boundary conditions in eq 20 reduce to

$$e^{\mu-\psi_s} = \frac{2n_0L}{N} e^{(\mu-\Delta-U_0)/2} \frac{\psi_s I_1(X_s)}{I_0(X_s)} \quad (23)$$

The last relation is provided by eq 21, which, for identical surfaces, is simply written as

$$e^{-\mu} = 1 + \frac{N}{n_0 d} e^{-\psi_s} + e^{-\Delta} \left[1 - \frac{2\lambda}{U_0 d} (-1 + U_0 + e^{-U_0}) \right] \quad (24)$$

These equations have to be compared with the ones emerging from the model that considers an adsorption energy localized on the surface. By performing the limiting operations on the fundamental equations of the localized model (as discussed in refs 13 and 14), one obtains the following set of equations:

$$\psi_s = \psi_0 \cosh \left[\frac{d}{2L} e^{(\mu-\Delta)/2} \right] \quad (25)$$

$$e^{(\mu-\psi_s)} = \frac{2n_0L\psi_0}{N} e^{(\mu-\Delta)/2} \sinh \left[\frac{d}{2L} e^{(\mu-\Delta)/2} \right] \quad (26)$$

and, for the chemical potential,

$$e^{-\mu} = 1 + \frac{N}{n_0 d} e^{-A-\psi_s} + e^{-\Delta} \quad (27)$$

where A is the adsorption energy in units of $k_B T$. A direct comparison between eqs 27 and 21 shows that, while in the localized model the adsorption energy works as renormalizing the surface potential, in the present approach, the strength of the van der Waals interaction acts as a bulk contribution connected with the activation energy, Δ .

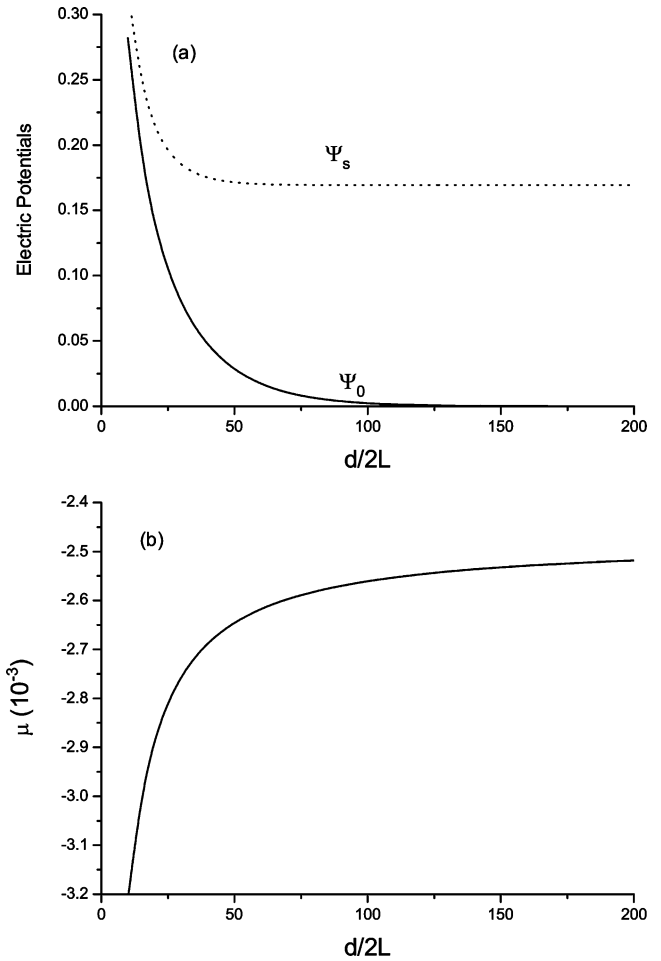


Figure 5. (a) Electric potentials at the surface, ψ_s (dotted line), and at the middle of the sample, ψ_0 (solid line), vs the reduced thickness of the sample, $d/2L$. (b) The same for the chemical potential μ . The curves were drawn for $A = -0.01$, $\Delta = 6.0$, and $b = N/2n_0L = 0.01$.

4.2. High Potential Limit. Let us rewrite the Poisson–Boltzmann equation (eq 3) in the form

$$\frac{d^2\psi}{dz^2} = \frac{e^{\mu-\Delta}}{2L^2} (e^{|U(z)|+\psi(z)} - e^{|U(z)|-\psi(z)}) \quad (28)$$

In the limit of high potential, $\psi(z) \gg 1$, it is possible to assume that $e^{|U(z)|+\psi(z)} \gg e^{|U(z)|-\psi(z)}$ and then neglect the last term in eq 28. By promoting the change of the variable $\phi(z) = \psi(z) + |U(z)|$, we may rewrite eq 28 as

$$\frac{d^2\phi}{dz^2} = \frac{e^{\mu-\Delta}}{2L^2} e^{\phi(z)} \quad (29)$$

because, from eq 9 one deduces that $d^2|U(z)|/dz^2 = 0$. Equation 29 can be integrated to give

$$\frac{d\phi}{dz} = \frac{e^{(\mu-\Delta)/2}}{L} \sqrt{e^{\phi} + k} \quad (30)$$

where the integration constant k may be determined by requiring that $(d\phi/dz)_{z=0} = 0$. This condition yields $k = -e^{\phi_0}$, where $\phi_0 = \psi_0$ since, from eq 9, $U(0) = 0$. After some simple calculations, one obtains for the electrical potential

$$\psi = -|U| + \psi_0 + \ln \left\{ 1 + \tan^2 \left[\frac{z}{2L} e^{(\mu-\Delta+\psi_0)/2} \right] \right\} \quad (31)$$

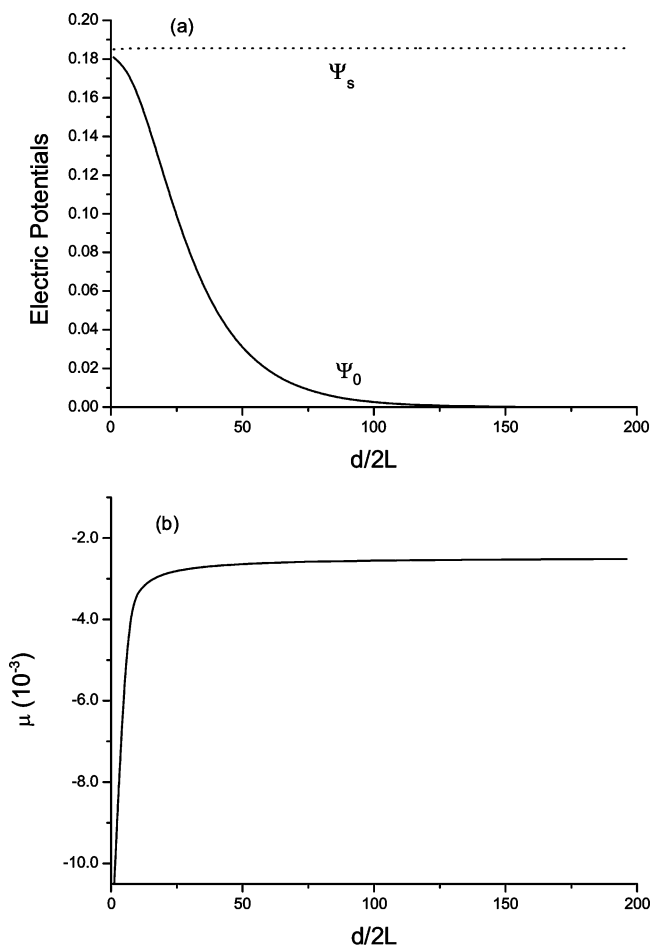


Figure 6. (a) Electric potentials at the surface, ψ_s (dotted line), and in the middle of the sample, ψ_0 (solid line), vs the reduced thickness of the sample, $d/2L$. (b) The same for the chemical potential μ . The curves were drawn for $U_0 = -0.01$, $\Delta = 6.0$, $b = N/2n_0L = 0.01$, and $c = L/\lambda = 1.0$.

Notice that, when $U(z) = 0$, this result is reduced to the one obtained in ref 16 where, instead of a delocalized interaction, here represented by $U(z)$, a localized adsorption energy (represented by A) is considered. From eq 31, by using again the boundary conditions, one may easily obtain

$$e^{\mu - \psi_s - U_0} = \frac{4\epsilon k_B T}{q^2 N d} t \tan t \quad (32)$$

where we have introduced the quantity

$$t = \arctan \sqrt{e^{U_0 + \psi_s - \psi_0} - 1} = \frac{d}{4L} e^{(\mu - \Delta + \psi_0)/2}$$

Finally, the equation governing the chemical potential, eq 6, may be rewritten as

$$e^{-\mu} = 1 + \frac{N}{n_0 d} e^{-\psi_s} + \frac{e^{-\Delta}}{d} \int_{-d/2}^{d/2} \frac{(e^{|U|+\psi} + e^{|U|-\psi})}{2} dz \quad (33)$$

which, in the limit of high potential, becomes

$$e^{-\mu} = 1 + \frac{N}{n_0 d} e^{-\psi_s} + \frac{e^{\psi_0 - \Delta}}{2t} \tan t = 1 + \frac{N}{n_0 d} e^{-\psi_s} (1 + e^{-U_0}) \quad (34)$$

if eq 33 is used. As expected, these equations are very similar to the ones obtained in ref 16, where the localized model was

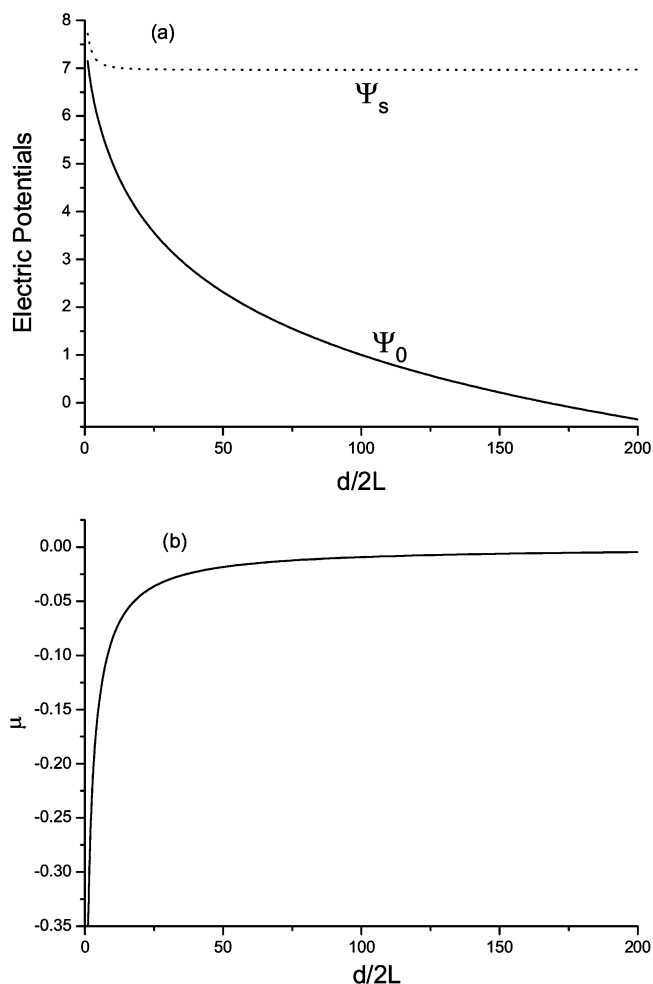


Figure 7. (a) Electric potentials at the surface, ψ_s (dotted line), and in the middle of the sample, ψ_0 (solid line), vs the reduced thickness of the sample, $d/2L$. (b) The same for the chemical potential μ . The curves were drawn for $U_0 = -0.5$, $\Delta = 8.0$, and $b = N/2n_0L = 300$.

considered in the limit of high potential. In the present approach, however, the van der Waals energy plays the role of the adsorption energy. This similarity, which is not a strict equality, indicates that the two approaches have an evident equivalence in this limit. Simple numerical calculations permit us to illustrate this similarity by showing the behavior of the main quantities as calculated in both approaches for a small set of values of the representative parameters.

5. Potential Profiles in the Sample

In Figure 5, some results for the case of a localized adsorption energy in the limit of small potentials are shown. In Figure 5a, the surface potential decreases with increasing thickness until it reaches a saturation value for large thickness; the potential in the center of the sample, ψ_0 , decreases when the thickness of the sample increases and tends to zero. The curves were depicted for the case $N \ll 2n_0L$, i.e., the number of adsorbing sites at the surface is very small when compared with the number of impurities found in a layer of thickness L in front of the surface. The thickness L is connected with Debye's screening length, λ_D , by means of the relation $L = \lambda_D e^{-\Delta/2}$.¹³ For a commercial liquid crystal such that $\lambda_D \approx 0.5 \mu\text{m}$, one has $L \approx 0.025 \mu\text{m}$. In this case, $d/2L = 200$ corresponds to a sample whose thickness is $d \approx 10 \mu\text{m}$, which is in the range of a typical NLC sample.¹⁷ Notice, moreover, that the limit $\psi \leq 0.4$ is always satisfied. In Figure 5b, the behavior of the chemical

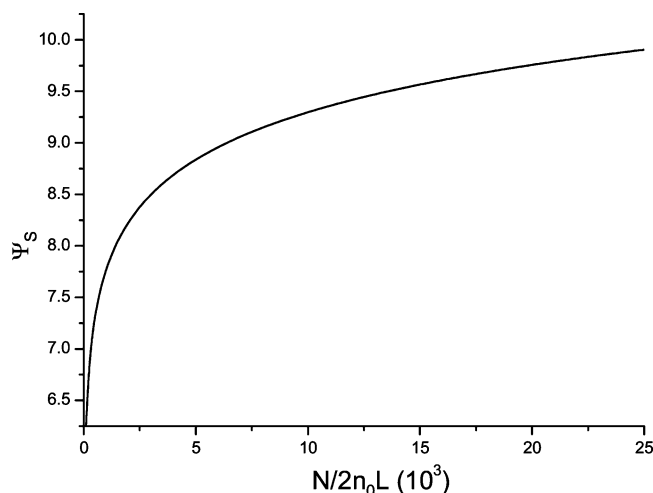


Figure 8. Electric potentials at the surface, ψ_s vs the parameter $b = N/2n_0L$ for $U_0 = -0.5$ and $d/2L = 100$.

potential is shown and presents the expected behavior, tending to zero for large values of the thickness of the sample. In Figure 6, the same quantities, but now calculated according to the lines discussed in Section 4.1, are shown. The behavior is essentially the same, except that the surface potential (Figure 6a) is practically constant because the strength of the van der Waals potential U_0 is very small. The chemical potential (Figure 6b) presents the same behavior and is of the same order of magnitude as the one shown in Figure 5b. Notice that, in the present calculations, another parameter has been considered: $c = L/\lambda = 1.0$. The inverse of this parameter is a measure of the penetration of the van der Waals interaction in the sample.

In Figure 7, the profiles of the potentials in the high potential limit are shown. To keep the approximation $\psi \gg 1$ valid, values of the parameters different from the preceding cases (shown in Figures 5 and 6) have been used. As a consequence, the general trend of the potentials are the same as the ones obtained in the low potential limit, but the order of magnitude is different.

One also observes that the behavior of the potential is not sensible to the value of λ , i.e., it is independent of the parameter $c = L/\lambda$, and the results are strongly co-incident with the ones of the localized model.

Finally, in Figure 8, the behavior of the surface potential ψ_s is shown as a function of the parameter $b = N/2n_0L$. Since $d/2L$ is fixed, the curve gives essentially the behavior of ψ_s as a function of the number of sites per unit surface at the surface, N . As the number of sites increases, the surface potential also increases because more and more ions can be adsorbed at the surface. However, the saturation behavior of the curve is also expected, because the maximum number of ions per unit surface that can be adsorbed is given by $n_0d/2$, which corresponds to the initial surface density of positive ions.

6. Conclusions

We have considered the influence of the energy of van der Waals on the phenomenon of selective adsorption of ions in

NLC systems. First, we have modified a previous model, which assumes that the adsorption energy is a localized quantity, for the selective ion adsorption in order to take into account a delocalized physical interaction between the particles in the fluid (ions in the NLC medium) and the substrate. Upon establishing the general expressions of the modified model, valid for an arbitrary form of the potential, to perform a comparison between the predictions of these two models, an approximate expression for the van der Waals interaction was considered. As a further simplification, necessary to perform all the calculations analytically, we have considered the limiting cases of low and high potential. The calculations have shown that the predictions of the localized model are essentially the same as the ones arising from the more realistic model in which the interaction of the ions with the surface is delocalized over a typical distance λ , expected to be much less than the thickness of the sample. These conclusions are valid for a simplified potential like the one we have proposed in eq 9. For more general potentials, the complete electrostatic problem, whose fundamental equations were established in Section 2, has to be faced by means of numerical methods, but no significant changes are expected in view of the preliminary results we have presented.

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References and Notes

- (1) Alexe-Ionescu, A. L.; Barbero, G.; Petrov, A. G. *Phys. Rev. E* **1993**, 48, R1631.
- (2) Barbero, G.; Evangelista, L. R. *Adsorption Phenomena and Anchoring Energy in Nematic Liquid Crystals*; Taylor & Francis: London, 2006.
- (3) Zola, R. S.; Evangelista, L. R.; Barbero, G. *J. Chem. Phys. B* **2006**, 110, 11047.
- (4) Zola, R. S.; Evangelista, L. R.; Barbero, G. *J. Chem. Phys. B* **2006**, 110, 10186.
- (5) Bhuiyan, L. B.; Bratko, D.; Outhwaite, C. W. *J. Phys. Chem.* **1991**, 95, 336.
- (6) Attard, P. *J. Phys. Chem.* **1995**, 99, 14174.
- (7) Bostrom, M.; Tavares, F. W.; Bratko, D.; Ninham, B. W. *J. Phys. Chem. B* **2005**, 109, 24489.
- (8) Gosselin, P.; Mohrbach, M. *Phys. Rev. E* **2005**, 71, 021502.
- (9) Barbero, G.; Batalioto, F.; Evangelista, L. R. *Phys. Lett. A* **2001**, 283, 257.
- (10) Kornyshev, A. A. *J. Phys. Chem. B* **2007**, 111, 5545.
- (11) Kilic, M. S.; Bazant, M. Z.; Ajdari, A. *Phys. Rev. E* **2007**, 75, 021502.
- (12) Kilic, M. S.; Bazant, M. Z.; Ajdari, A. *Phys. Rev. E* **2007**, 75, 021503.
- (13) Barbero, G.; Zvezdin, A. K.; Evangelista, L. R. *Phys. Rev. E* **1999**, 59, 1846.
- (14) Evangelista, L. R.; Barbero, G. *Phys. Rev. E* **2001**, 64, 021101.
- (15) Butkov, E. *Mathematical Physics*; Addison-Wesley Publishing Co.: Reading, MA, 1973.
- (16) Pereira, H. A.; Batalioto, F.; Evangelista, L. R. *Phys. Rev. E* **2003**, 68, R040701.
- (17) Alexe-Ionescu, A. L.; Ionescu, A. T.; Barna, E. S.; Scaramuzza, N.; Strangi, G. *J. Phys. Chem. B* **2003**, 107, 5487.