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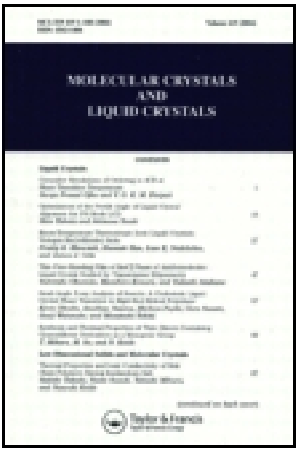

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# Role of Van der Waals Interaction on Selective Ion Adsorption in Liquid Crystals

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# Role of Van der Waals Interaction on Selective Ion Adsorption in Liquid Crystals

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*The fundamental equations of a Poisson-Boltzmann model to investigate the effects of a de-localized surface interaction energy on the ionic adsorption in a finite-length electrolytic cell are solved. Two distinct, physically plausible, forms of the interaction energy, having different decaying spatial behavior are explicitly analyzed. The surface and chemical potentials are evaluated in terms of the strengths of these van der Waals-like interactions characterizing the adsorption energy. A quantity playing the role of an integral double-layer capacitance of the cell is introduced and its behavior is investigated as a function of the parameters of the adsorption potentials.*

**Keywords** Physisorption; electrolytes; anchoring

**PACS** 68.43.-h; 82.45.Gj; 61.30.Hn

## 1. Introduction

Adsorption phenomena in condensed matter samples have been investigated by several groups by focusing a broad variety of physical and chemical contexts [1, 2, 3, 4]. For practical applications, as well as for fundamental purposes, the selective adsorption of charged particles has been considered to address the significant effects on the molecular orientation in nematic liquid crystals (NLC) [5, 6, 7]. In fact, the adsorption of ionic impurities is responsible for a counterion cloud forming a diffuse electric double layer in the liquid [8] which, in turn, is responsible for an internal electric field. The asymmetry in the electric field distribution resulting when an external electric field is combined with this internal field, due to the surface adsorption, is an important mechanism to explain the electrical response of NLC samples [6]. In some preceding models for the adsorption phenomena in the context of liquid-crystalline materials, the inter-atomic forces acting between the ions in the fluid and the substrate have been accounted for by assuming a localized adsorption energy [9, 10]. This adsorption energy, in a first approximation, was

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identified with the electrostatic energy of an adsorbed ion with its image on the substrate, i.e., a physisorption process.

In a recent approach, a modification of this model was proposed. The localized interaction energy between the ion and the substrate was replaced by an approximate expression for describing a de-localized van der Waals interaction [11]. The results of this simplified analysis showed that, for strongly localized interactions energy, the predictions of both kind of models were essentially the same, as expected. However, in order to keep the calculations as simple as possible, i.e., to obtain analytical results, the approach developed in Ref. [11] was carried out by using a very simplified expression for the adsorption potential. For this reason, the aim of this paper is to re-analyse the problem by considering, in more detail, the role of a van der Waals-like de-localized interaction energy on the distribution of charges and fields in a typical electrolytic cell, having in mind an NLC system. The analysis is done by choosing two distinct, physically plausible, de-localized interactions to represent the adsorption energy characterizing the process. In this framework, the surface potentials as well as the chemical potential of the adsorbate are determined in a self-consistent manner. In all the cases, these quantities are analysed as functions of the strength of the interaction between the ions and the substrate which, in this model, is the analogous to a localized adsorption energy. In addition, using dimensional arguments, we introduce a quantity playing the role of an integral double-layer capacitance. It is defined in absence of external field, but invoking the selective adsorption phenomenon as the main mechanism responsible for the accumulation of charges on the substrates and for the production of the electric field.

## 2. Fundamental Equations

As pointed out before, the model for the adsorption of ions used in this work is a modification of the localized model proposed by Barbero et al. [9], and generalized by Evangelista and Barbero [10]. This model was employed in a previous analysis by Igarashi et al. [11] in order to study the effects of a de-localized interaction between the ions and the surface, using a simplified inter-particle interaction, by means of analytical methods. For the sake of clarity, here we briefly discuss the main assumptions of the model and recall the fundamental equations characterizing its predictions, by following closely the presentation done in Ref. [11].

The model is built for a cell in the shape of a slab of thickness $d$, filled with an isotropic liquid characterized by a dielectric constant $\varepsilon$ (measured in $\varepsilon_0$ units), but containing impurities that, by means of a chemical reaction involving an activation energy, $E_{activation}$, can be the source of the ions. The Cartesian reference frame used in the analysis has the $z$-axis perpendicular to the bounding surfaces of the cell, located at $z = \pm d/2$. Due to the adsorption phenomenon in the sample one expects a distribution of charges giving rise to a locally electrically charged liquid, while remaining globally neutral. In equilibrium, at a temperature $T$, the distributions of positive and negative ions are given in the framework of classical statistics by [9, 12]

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

where $\mu$ is the chemical potential, in $k_B T$ units, and $\psi(z) = qV(z)/k_B T$ is the electrostatic energy of the charge $q$, in $k_B T$ units, in which $k_B$ is the Boltzmann constant. The de-localized surface interaction, $U_{\pm}(z) = U(z) = u(z)/k_B T$, is assumed to be the same for both positive and negative ions, where $u(z)$ is the intermolecular interaction. We indicate by $n_0$ the bulk density of impurities for an infinite sample, whose activation energy is also measured in $k_BT$ units as $\Delta = E_{activation}/k_BT$.

The net charge density of the system is given by

$$\rho(z) = q\,[n_+(z) - n_-(z)] = -2q\;n_0\;e^{\mu-\Delta-U(z)}\sinh\psi(z). \tag{2}$$

The charge distribution and the electrical potential are connected by Poisson's equation $d^2V/dz^2 = -\rho/\varepsilon$, which can be put in the form

$$\frac{d^2\psi}{dz^2} = \frac{e^{\mu-\Delta}}{L^2}e^{-U(z)}\sinh\psi(z),\;\text{ with }\; L^2 = \frac{\varepsilon k_BT}{2n_0q^2}, \tag{3}$$

in which the thickness $L$ is connected with Debye's screening length, $\lambda_D$, by means of the relation $L = \lambda_D e^{-\Delta/2}$ [9]. This non-linear Poisson-Boltzmann (PB) equation has to be solved with the following boundary conditions on the electric field:

$$E(z = \mp d/2) = -\frac{k_BT}{q}\left(\frac{d\psi}{dz}\right)_{z=-d/2} = \pm\frac{q\;\sigma_{1,2}}{\varepsilon}, \tag{4}$$

in which $\sigma_i = N_i\,e^{\mu-\psi_i}$, for $i = 1$ or 2, are the surface densities of adsorbed charges, where $N_i$ is the number of sites per unit surface, on each surface, and $\psi_1 = \psi(z = -d/2)$ and $\psi_2 = \psi(z = +d/2)$ are the values of the surface potentials. Furthermore, the differential Eq. (3) must be solved in such way that the value of the potential is minimum at a point of coordinate $z^*$ inside the sample, i.e., $(d\psi/dz)_{z=z^*} = 0$.

The conservation of the number of particles is expressed by the constraint:

$$\frac{N_+ + N_-}{2} + N_B + \frac{\sigma_1 + \sigma_2}{2} = n_0 d, \tag{5}$$

where $N_\pm = \int_{-d/2}^{d/2} n_\pm(z)dz$, and $N_B = \int_{-d/2}^{d/2} n_0 e^{\mu}dz$ represents the number of non-dissociated particles in the bulk. By taking into account the above expressions and conditions, one can write

$$e^{-\mu} = 1 + \frac{1}{2n_0d}(N_1e^{-\psi_1} + N_2e^{-\psi_2}) + e^{-\Delta}\frac{1}{d}\int_{-d/2}^{d/2} e^{-U(z)}\cosh\psi(z)dz. \tag{6}$$

The four fundamental equations governing the electrical behaviour in the sample are, therefore, (3), (4), and (6), because they permit to determine $\psi^*$, $\psi_1$, $\psi_2$, and $\mu$. Once they are solved, it is possible to obtain the electrical potential (field) and charge distributions across the sample.

## 3. Electric Potential Profiles

The set of fundamental equations above stated has been numerically solved for two different, representative, de-localized adsorption energies $U(z)$, namely:

$$U_a(z) = U_0\frac{\cosh(Z\frac{d}{2\lambda_s})}{\cosh(\frac{d}{2\lambda_s})}, \tag{7}$$

and

$$U_b(z) = \frac{B}{[Z - (1 + 2\lambda_s/d)]^3} - \frac{B}{[Z + (1 + 2\lambda_s/d)]^3}, \tag{8}$$

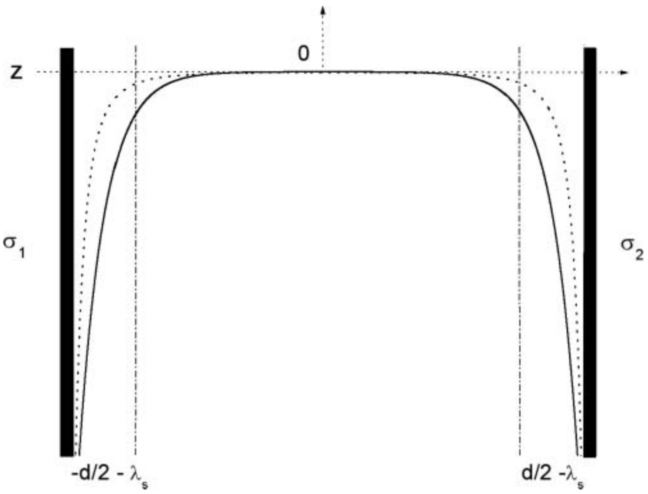

**Figure 1.** The adsorption potentials: $U_a(z)$ (solid), $U_b(z)$ (dotted).

where

$$B = -\frac{(2\lambda_s/d)^3\,[(2\lambda_s/d)+2]^3}{2\left[(2\lambda_s/d)^3+3(2\lambda_s/d)^2+6(2\lambda_s/d)+4\right]}\,U_0.$$

In the above expressions, $U_0$ is the strength of the van der Waals potential, $-1 \leq Z = 2z/d \leq 1$ is the reduced coordinate, and $U_\alpha(Z = \pm 1) = U_0 < 0$, where $\alpha = a, b$. In addition, $\lambda_s$ is a typical length over which the interaction energy decays. The two chosen potentials are such that they reach a maximum value in the middle of the sample and are strongly attractive near the surfaces, as shown in Fig. 1.

The numerical calculations have been performed for $d/2\lambda_s = 200$, as shown in Fig. 2, where the profiles of the potentials at the surfaces of the sample are shown as functions of the strength of the van der Waals interactions, for $U_\alpha(z)$.

The equations are solved firstly by considering that the two surfaces are different. In particular, we have analysed the cases for which $b_1 = N_1/2n_0L = 0.01$ and $b_2 = N_2/2n_0L = 0.03$. These quantities give the ratio between the number of sites potentially adsorbing per unit area on each surface, $N_i$, and the number of particles per unit area located on a bulk layer of thickness $L$, just in front of it. By choosing $b_2 = 3b_1 \ll 1$, we are assuming that the surfaces are different and that the number of adsorbing sites per unit area is small when compared with the number of potentially adsorbed particles. As expected, the surface potentials are decreasing with the increasing of the absolute value of the strength of the interaction. This behaviour can be understood better if we look for the trends of the adsorption potentials depicted in Fig. 1. One observes that near the surface, for instance, in the surface layer represented by $-d/2 \leq z \leq -d/2 + \lambda_s$, the potential $U_b(z)$ undergoes a variation that is more intense than the variation of $U_a(z)$ over the same distance. Indeed, the interaction $U_a(z)$, de-localized over a length of the order of $\lambda_s$, is nevertheless less localized than $U_b(z)$. Anyway, both $U_a(z)$ and $U_b(z)$ vary strongly but increase until reaching a maximum value at $Z = 0$. This means that the majority of the charged particles is attracted to the surface of the sample. Thus, the surface potentials of Fig. 2a decrease faster when compared with the same behaviour produced in the case represented by $U_b(Z)$

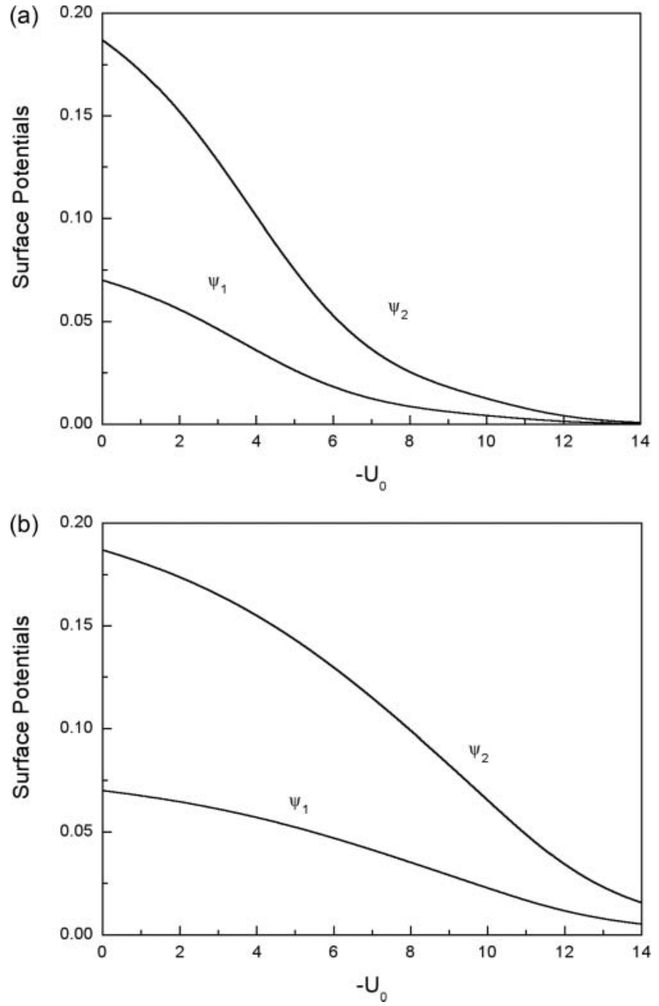

**Figure 2.** Electric potentials at the surfaces, $\psi_1$ and $\psi_2$, vs. $-U_0$ for two de-localized interactions: (a) $U_a(z)$ and (b) $U_b(z)$. The curves have been drawn for $\Delta = 4, d/2L = 200$, $L/\lambda_s = 1.0$, $b_1 = N_1/2n_0L = 0.01$ and $b_2 = N_2/2n_0L = 0.03$.

(Fig. 2b) because it is expected that the concentration of charges near the surfaces is more pronounced in the latter case. The order of magnitude of the potentials are the same as the ones found in Ref. [11], but the trends are different for low values of $|U_0|$. This is due to the strong approximations (as, for instance, the linearization of the PB equation and the simplified form used for the adsorption potential) made in Ref. [11]. Thus, a direct comparison between the two approaches may be meaningless, because here the non-linear PB equation is numerically solved for two continuous van der Waals interactions, i.e., no approximations are made, and the results are expected to be close to the exact ones.

The chemical potential $\mu$ versus $-U_0$ is displayed in Fig. 3. The solid curve corresponds to the case in which the adsorption energy is $U_a(z)$ whereas the dotted one corresponds to $U_b(z)$. The values of $\mu$ are very similar and decay monotonically for both the cases as the value of $|U_0|$ increases.

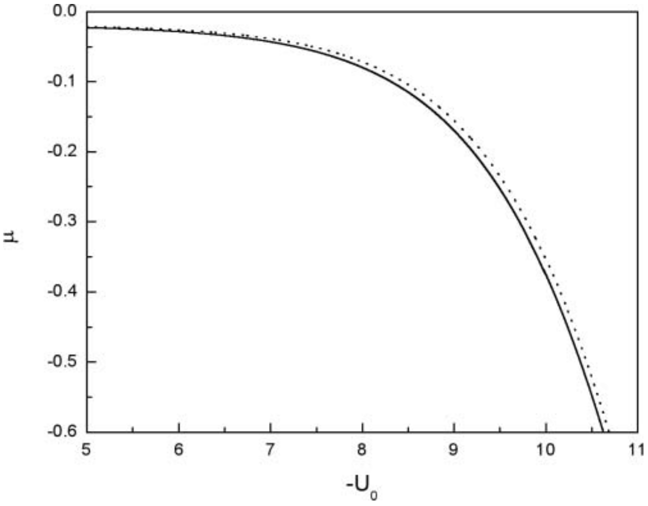

**Figure 3.** The chemical potential $\mu$ vs. $-U_0$, for different adsorption potentials: $U_a(z)$ (solid) and $U_b(z)$ (dotted). The parameters are the same as those in Fig. 2.

Let us now particularize the analysis for the case in which the system is limited by two identical surfaces, such that $N_1 = N_2 = N$. In this case, the surface potentials become $\psi_1 = \psi_2 = \psi_s$, and hence the electric potential has to be symmetric with respect to the middle of the sample, i.e., $(d\psi/dz)_{z=0} = 0$ and $\psi(z = 0) = \psi_0 = \psi^*$. Thus, only three of the fundamental equations have to be solved to obtain the field profile of the system. By numerically solving the system of fundamental equations, it is possible to calculate $\psi_s$, $\psi_0$, and $\mu$. In addition, from Eq. (4), it is also possible to obtain the interfacial surface-charge

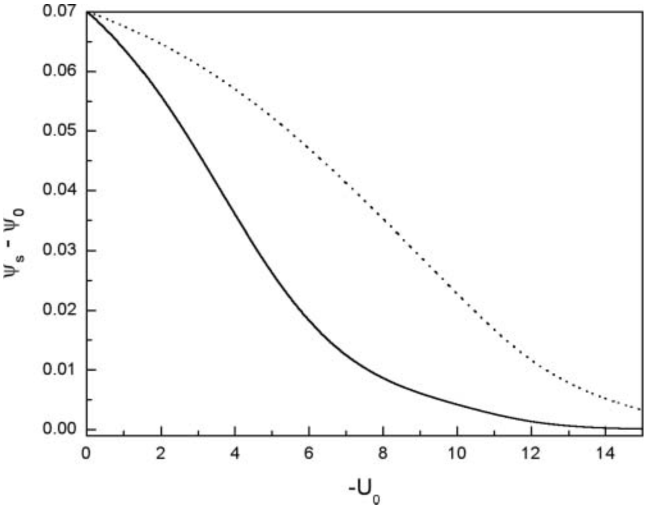

**Figure 4.** Difference of potential $\psi_s - \psi_0$ vs. $-U_0$, for the van der Waals interactions: $U_a(z)$ (solid) and $U_b(z)$ (dotted). The curves have been drawn for $\Delta = 4$, $d/2L = 200$, $L/\lambda_s = 1.0$ and $b = N/2n_0L = 0.01$.

density produced by the adsorption phenomenon as

$$\sigma = \varepsilon E(z = -d/2) = -\varepsilon \frac{k_B T}{q} \left( \frac{d\psi}{dz} \right)_{z=-d/2} .$$

In view of these results, one is tempted to introduce a quantity that is analogous to the integral double-layer capacitance, but here defined in absence of external field, as was done in Ref. [13]. On dimensional grounds, one could define the quantity:

$$C = \frac{\sigma}{v_{\mathrm{D}}} = C_0 L \frac{1}{v_D} \left( \frac{d\psi}{dz} \right)_{z=-d/2} , \tag{9}$$

where $C_0 = \varepsilon/L$ and $v_{\mathrm{D}} = \psi_S - \psi_0$ is the overall potential drop, between the bulk of the electrolyte and the electrode surface, here playing a role similar to the potential drop

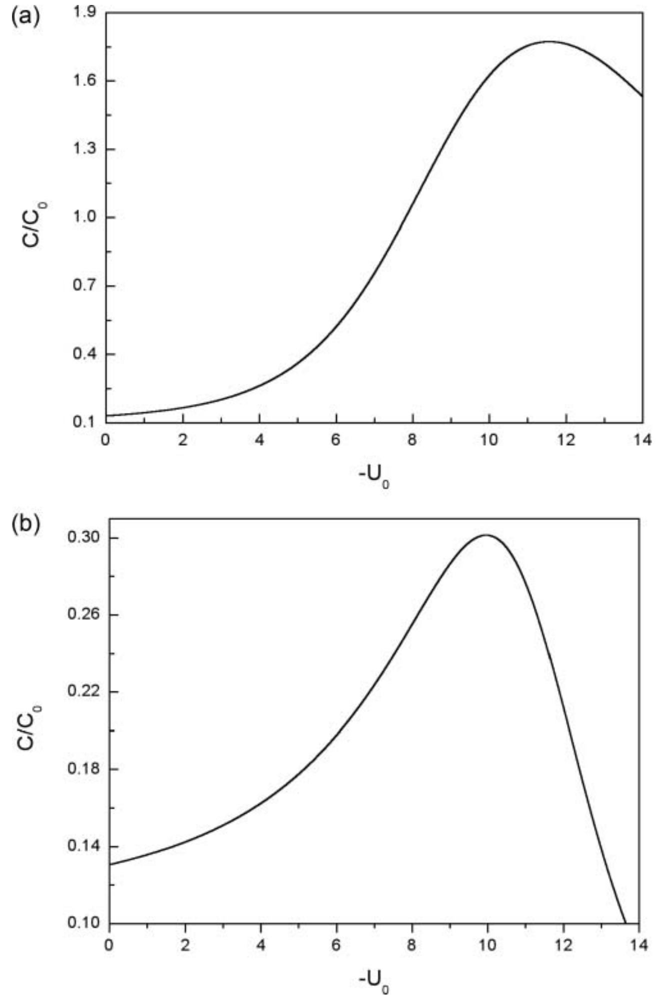

**Figure 5.** Integral double-layer capacitance vs. $-U_0$, for the van der Waals interactions: (a) $U_a(z)$ and (b) $U_b(z)$. The curves have been drawn for $\Delta = 4, d/2L = 200, L/\lambda_s = 1.0$ and $b = N/2n_0L = 0.01$.

produced by an external power supply. This quantity is represented essentially by $\psi_s$, because $\psi_s \gg \psi_0$, and is strongly decreasing for increasing values of $|U_0|$, as shown in Fig. 4.

We notice however that while $v_D$ decreases in both cases (as shown in Fig. 4), its behavior is non-monotonic and more intense for $U_a(z)$. This feature has noteworthy consequences on the trends of the capacitance curves.

Indeed, the values of the capacitance obtained for the two adsorption potentials strongly differ as can be seen by comparing the curves shown in Fig. 5a for $U_a(z)$ and in Fig. 5b for $U_b(z)$. For low values of $|U_0|$, $C$ has the same order of magnitude for the two potentials. As the potential drop, $v_D$, decreases, $C$ starts to assume very different values for $U_a(z)$ and $U_b(z)$. In the present approach, the surface density of charge may be well approximated by $\sigma \propto e^{\mu-\psi_s}$. Thus, the trend of the capacitance is first governed by $C = \sigma/v_D \propto e^{-\psi_s}/\psi_s$ because the values of the chemical potentials for both forms of $U(z)$ are very similar but it is strongly decreasing for high values of $|U_0|$ (see Fig. 3). In fact, as $|U_0|$ increases, the chemical potential is such that $|\mu| \gg \psi_s$ and becomes the dominant quantity in the behavior of the capacitance, i.e., $C \propto e^{\mu-\psi_s}/\psi_s$. This competition between the values of $\psi_s$ and $\mu$, as the absolute values of $U_0$ varies, is the main responsible for the non-monotonic behaviour observed in the capacitance.

A final remark is in order here. We notice that even if this quantity $C$ is not precisely the double-layer capacitance defined in the presence of the external field, it is surprising to verify that it exhibits the essential non-monotonic features (e.g., maximum and minimum points) characteristics of the double-layer capacitance of electrolytic cells and ionic liquids [14, 15, 16, 17, 18], when investigated as a function of the external voltage. Moreover, the trends exhibited in Fig. 5 have some resemblance with the ones shown in Ref. [13] for the same quantity.

## 4. Concluding Remarks

A Poisson-Boltzmann model for the selective ion adsorption, in a typical electrolytic sample, in the shape of a slab of thickness $d$, was discussed for some simple illustrative situations in the absence of external fields. The main feature of the model is the incorporation of an adsorption energy represented by some kind of van der Waals-like interaction, i.e., some de-localized interaction energy between the mobile charge in the fluid and the substrate. To shed some light on the role of the de-localized adsorption potential, on the behaviour of representative quantities, like surface and chemical potentials, the fundamental equations of the model have been solved in two cases. The analysis reveals that, when the interaction energy is strongly localized, the predictions of the localized models previously proposed are recovered. However, the model introduced above, and illustrated for some simple situations, is able to easily incorporate the action of external voltage. This will permit one to analyse the combined effects of adsorption and external fields on the electrical response of an NLC cell in a broad conceptual framework.

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