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Ionic adsorption and equilibrium distribution of charges in a nematic cell

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We consider the steady-state distribution of ionic charges in a nematic sample of slab shape, whose limiting surfaces are supposed to adsorb positive ions. Our analysis allows the calculation of the electrical potential at the surfaces and in the bulk, and of the chemical potential versus the thickness of the sample *d*. The surface density of ions and the intensity of the electric field in the double layer are evaluated in terms of *d*. In the limit of small *d* we show that the surface density of adsorbed ions is proportional to the thickness, whereas in the opposite limit of large *d* it is nearly independent of it. We analyze also the influence of the surface charges on the effective anchoring energy of nematic liquid crystals, as well as the thickness dependence of this parameter. Our analysis generalizes similar calculations previously published. [S1063-651X(99)08902-3]

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The influence of adsorbed ions and the resulting surface electric field on the anchoring properties of nematic liquid crystals (NLC) with ionic conductivity has been analyzed by different groups [1–6]. Recently the ionic adsorption has been invoked to explain the thickness dependence [7] of the anisotropic part of the anchoring energy characterizing the NLC-substrate interface [8–10]. To obtain the thickness dependence of the anchoring energy it is necessary (1) to assume a selective ionic adsorption from the surfaces, due to some electrochemical forces at the walls; (2) to evaluate the surface density of the adsorbed charges versus the thickness of the sample; (3) to analyze the effect of the resulting electric field in the surface double layer on the NLC. In Ref. [8] a simple model was proposed to evaluate the surface density of adsorbed charges, by extending the classical Langmuir problem of adsorption [11].

The aim of this paper is to present a general theory for the adsorption phenomenon in liquids, removing all the simplifying hypotheses used in Ref. [8]. We deduce, in addition to the surface density of adsorbed charges, the chemical potential and the electrical potential at the surface and in the middle of the sample. The limiting cases of small and large thickness are considered separately. Our results show that in the limit of small thickness, the surface charge density is nearly proportional to the thickness. On the contrary, in the limit of large thickness, the surface charge density saturates to a value independent of the thickness. These results confirm the result obtained in the framework of the simple model presented in Ref. [8] in these two limiting cases. The possible applications of our study to the surface properties of the NLC are also discussed.

Let us consider a sample of slab shape of a liquid. Let d be the thickness of the slab and ϵ the dielectric constant of the liquid. The liquid is globally neutral. The chemical reaction $X\rightarrow B^{+}+C^{-}$, where X is a molecule of the liquid and B^{+} and C^{-} the ions resulting from its dissociation, has an activation energy $E_{\mathrm{activation}}$. We assume that the limiting surfaces are identical and adsorb selectively positive ions [12]. The surface adsorbed charges and the diffuse layer of oppositely charged mobile ions that they attract constitute the Debye double layer [13]. Since we do not consider external electric field, there is a similar double layer at each wall. We use a Cartesian reference frame having the z axis normal to the bounding walls, located at $z=\pm d/2$. All physical quantities are assumed to be only z dependent, which is consistent with the slab shape of the sample under consideration. Let us adopt the following notation for the relevant quantities entering in the model: (i) n_0 is the bulk density of particles (in an infinite sample); (ii) N is the surface density of site for the adsorbed charges; (iii) $\Delta=E_{\mathrm{activation}}/k_BT$ is the activation energy (in k_BT units); (iv) $A=E_{\mathrm{adsorption}}/k_BT$ is the adsorption energy (in k_BT units); (v) μ is the chemical potential (in k_BT units); (vi) q is the electric charge of the positive ions B^{+}.

Due to the adsorption phenomenon in the sample there is a distribution of charges giving rise to a locally electrically charged liquid, which is globally neutral. In this situation the electrical potential $V(z)$ is not constant across the cell. Since the surfaces are assumed to be identical, the electric potential is symmetric with respect to the middle of the sample, $V(z)=V(-z)$, and hence the electric field $E=-dV/dz$ vanishes at $z=0$. We indicate by $\psi(z)=qV(z)/k_BT$ the electrostatic energy of the charge q in k_BT units. According to the statistical mechanics the bulk densities of positive and negative ions are given by $n_{\pm}(z)=n_0e^{\mu-\Delta\mp\psi(z)}$. In a similar manner, the bulk density of neutral molecules is $n_b=n_0e^{\mu}$, whereas the surface density of adsorbed charge is $n_s=Ne^{\mu-A-\psi_s}$, where ψ_s is the value of the surface potential, i.e., $\psi_s=\psi(\pm d/2)$ [13,14]. The conservation of the number of particles, per unit surface, is expressed by

$$\frac{N_{+}+N_{-}}{2}+N_B+\frac{2n_s}{2}=n_0d, \tag{1}$$

where

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

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By taking into account the definitions of $n_\pm(z)$ and of n_b, we can rewrite Eq. (1) in the form

$$e^{\mu}\left\{n_0e^{-\Delta}\int_{-d/2}^{d/2}\cosh\psi(z)dz+n_0d+Ne^{-A-\psi_s}\right\}=n_0d, \tag{3}$$

from which we obtain

$$e^{-\mu}=1+\frac{N}{n_0d}e^{-A-\psi_s}+e^{-\Delta}\frac{1}{d}\int_{-d/2}^{d/2}\cosh\psi(z)dz. \tag{4}$$

Equation (4) connects the chemical potential μ with the electrical potential $\psi(z)$. In the steady state the charge distribution and the electrical potential are connected by Poisson's equation, namely,

$$\frac{d^2V}{dz^2}=-\frac{1}{\epsilon}q[n_+(z)-n_-(z)]. \tag{5}$$

By using the definition of $\psi(z)$ and the expressions for $n_\pm(z)$, Eq. (5) becomes

$$\frac{d^2\psi}{dz^2}=\frac{1}{L^2}e^{\mu-\Delta}\sinh\psi, \tag{6}$$

where $L=(2\epsilon k_BT/n_0q^2)^{1/2}$ is an intrinsic length of the problem. It is reminiscent of the Debye screening length λ_D. The main difference is that in λ_D the bulk density of ions n_i appears, instead of n_0 [13]. As will be shown later, for $d\to\infty$ the chemical potential tends to zero. Consequently $n_i\approx n_0e^{-\Delta}$ and hence $\lambda_D\approx Le^{\Delta/2}$. From Eq. (6), taking into account that the electrical potential is an even function of z, we obtain

$$\frac{1}{2}\left(\frac{d\psi}{dz}\right)^2=\frac{e^{\mu-\Delta}}{L^2}[\cosh\psi(z)-\cosh\psi_0], \tag{7}$$

where $\psi_0=\psi(0)$. From Eq. (7) it follows that $\psi(z)$ is given by

$$\int_{\psi_0}^{\psi(z)}\frac{d\psi}{\sqrt{\cosh\psi-\cosh\psi_0}}=\frac{\sqrt{2}}{L}e^{(\mu-\Delta)/2}z. \tag{8}$$

From Eq. (7) we derive, furthermore,

$$\int_{\psi_0}^{\psi_s}\frac{d\psi}{\sqrt{\cosh\psi-\cosh\psi_0}}=\frac{\sqrt{2}d}{2L}e^{(\mu-\Delta)/2}, \tag{9}$$

which connects ψ_s and ψ_0 to the chemical potential μ. Since the system is globally neutral we have that

$$2n_s+\int_{-d/2}^{d/2}n_+(z)dz=\int_{-d/2}^{d/2}n_-(z)dz. \tag{10}$$

The electrical field $E(z)=-dV/dz$ is identically zero for $z>d/2$ and for $z<-d/2$. It has a discontinuity for $z=\pm d/2$. In particular, $E(-d/2)=n_sq/\epsilon$. Since $E(x)=-dV/dz=-(k_BT/q)d\psi/dx$, by means of Eq. (7) we have for the surface field

$$E(-d/2)=\sqrt{2}\frac{k_BT}{qL}e^{(\mu-\Delta)/2}\sqrt{\cosh\psi_s-\cosh\psi_0}. \tag{11}$$

By taking into account the expressions giving $E(-d/2)$ and n_s we obtain

$$\sqrt{2}\frac{k_BT}{qL}e^{(\mu-\Delta)/2}\sqrt{\cosh\psi_s-\cosh\psi_0}=\frac{qN}{\epsilon}e^{\mu-A-\psi_s}, \tag{12}$$

from which it follows that

$$e^{\mu}=2\left(\frac{\epsilon k_BT}{NLq^2}\right)^2e^{-\Delta+2(A+\psi_s)}(\cosh\psi_s-\cosh\psi_0). \tag{13}$$

The fundamental equations of our model are Eqs. (4), (9), and (13). They connect ψ_0, ψ_s, and μ. When these equations are solved n_s can be calculated, and hence also the surface charge density $\sigma=qn_s$, which is due to the adsorption phenomenon.

Let us assume, as usual, $\Delta\gg1$, i.e., $E_{\text{activation}}\gg k_BT$. We consider first the limit of small thickness $(d\to0)$. This implies, as will be verified *a posteriori*, $\psi_s\gg1$, $\psi_0\gg1$, and $\psi_s-\psi_0$ is small. In this special case from the general formulas (4), (9), and (13) we obtain

$$\psi_s-\psi_0\approx(d/2L)^2e^{\mu-\Delta+\psi_0}, \tag{14}$$

and

$$\psi_s\approx\frac{\Delta-A}{2}+\frac{1}{2}\ln\left(\frac{N}{n_0d}\right)+\frac{1}{2}\ln2+O(d^2). \tag{15}$$

Equations (14) and (15) show that in the considered limit of large Δ and small d, both ψ_s and ψ_0 are large quantities, such that $\psi_s-\psi_0=O(d^2)$, as previously assumed. We have, furthermore, for the chemical potential μ,

$$\mu=\frac{A+\Delta}{2}-\frac{1}{2}\ln\left(\frac{N}{n_0d}\right). \tag{16}$$

Equations (14)–(16) solve the adsorption problem in the limit of small thickness. By substituting these equations in $\sigma=qn_s$ we obtain for the surface charge density the expression

$$\sigma=\frac{(Nn_0d/2)^{1/2}e^{-(\Delta+A)/2}}{1+(2N/n_0d)^{1/2}e^{-(\Delta+A)/2}}, \tag{17}$$

that, in the limit of $|-(\Delta+A)/2|\gg1$, tends to

$$\sigma=q\frac{n_0d}{2}. \tag{18}$$

Let us consider now the limit $d\to\infty$. In this limit ψ_0 and ψ_s are expected to tend to a constant value. Consequently from the general equations (4), (9), and (13) we have that $\lim_{d\to\infty}\psi_0=0$. In this framework, by assuming again $\psi_s\gg1$, from Eq. (12) we get

$$\psi_s=\frac{2}{3}\ln\left(\sqrt{2}\frac{N}{n_0L}\right)+\frac{\Delta}{3}-\frac{2}{3}A. \tag{19}$$

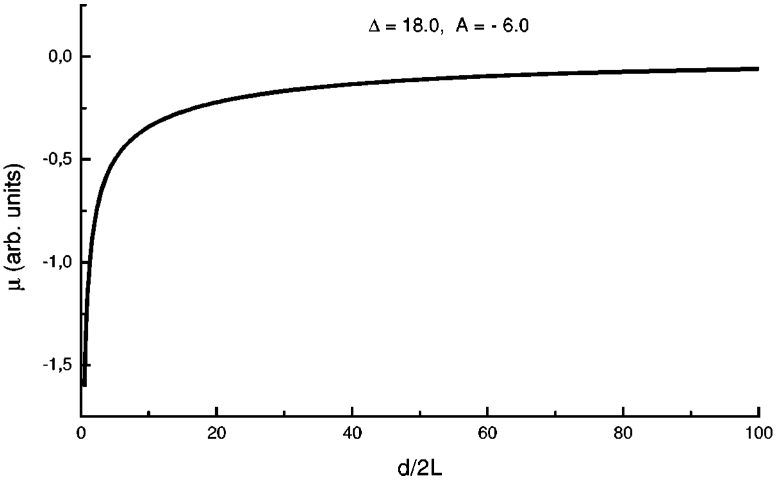

FIG. 1. Chemical potential μ vs the thickness of the sample d.

By substituting Eq. (19) into $\sigma=qn_s$ we obtain

$$\sigma=Nq\left(\frac{n_0L}{N}\right)^{2/3}e^{-(\Delta+A)/3}, \tag{20}$$

which is thickness independent. Equations (18) and (20) show that in the limit of small d the surface charge density σ is proportional to d, whereas in the opposite case of large d it tends to a constant value.

Let us consider now the general solution of the adsorption problem for arbitrary thickness of the sample. The general solution has to be searched by numerically solving the set of three coupled nonlinear equations (4), (9), and (13) for a significant set of parameters Δ, A, N, and n_0. The adsorption energy $E_{\text{adsorption}}$, in a first approximation, can be identified with the electrostatics energy of an adsorbed ion with its image in the substrate. It is given by [15]

$$E_{\text{adsorption}}=\frac{q^2}{2r_+}\,\frac{\epsilon_1-\epsilon_2}{\epsilon_1(\epsilon_1+\epsilon_2)}, \tag{21}$$

where r_+ is the radius of the adsorbed positive ion, and ϵ_1 and ϵ_2 are the dielectric constants of the liquid and of the substrate, respectively. Note that the adsorption phenomenon takes place, for electrostatics reasons, only if $\epsilon_2>\epsilon_1$, as we will assume. In a similar manner, the activation energy $E_{\text{activation}}$ can be identified with the electrostatics interaction energy between the ions B^+ and C^- resulting from the dissociation of the molecule X. It is $E_{\text{activation}}=(1/\epsilon_1)[q^2/(r_+ + r_-)]$, where r_- is the radius of the negative ion. We assume $q=2e$, where e is the modulus of the electronic charge, $r_+=10$ Å, $r_-=30$ Å, $\epsilon_1\approx 4$, which is typical for organic liquid, and $\epsilon_2\approx$ 6, which refers to a glass. A representative estimation for the parameters entering in the model can be obtained by considering a typical nematic liquid crystal medium sample of slab shape limited by two glasses. The typical dimension of a molecule is $R\simeq 40$ Å and $n_0\approx 1/(4/3)\pi R^3$. Furthermore $N\approx 1/\pi R^2$. From the definition of L written above one obtains $L\simeq 30$ Å. In this framework $A=E_{\text{adsorption}}/k_BT\approx -6$ and $\Delta=E_{\text{activation}}/k_BT\approx 18$. Note that if $\epsilon_2\rightarrow\infty$, i.e., if the substrate is a metal, the adsorption energy tends to $A=-28.8$. By means of these values Debye's screening length λ_D is found to be of the order of the micron, which is consistent with the value reported in Ref. [16]. More precise estimations can be performed, but the general results do not change in a significant manner. Figure 1 shows the chemical potential μ vs the thickness of the sample d. In the limit of small d, μ presents a logarithmic divergence, in agreement with Eq. (16). In the opposite limit of large d, μ tends to zero, as expected. The electrical potential at the surface, ψ_s, and in the middle of

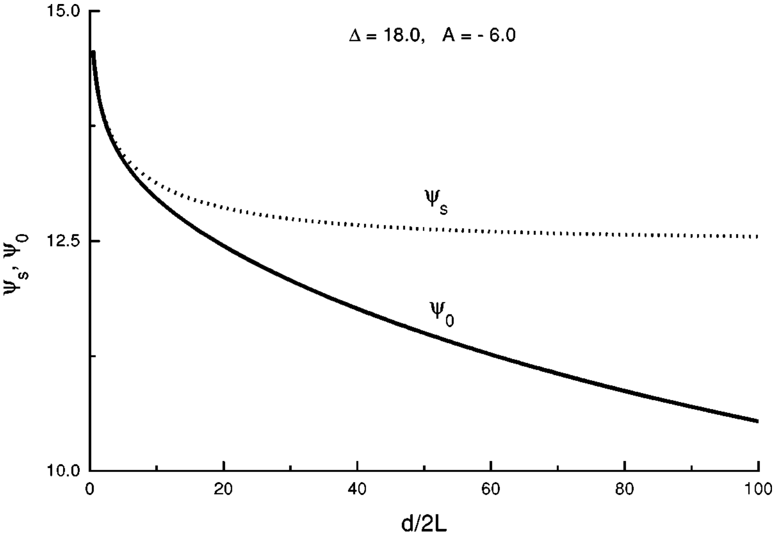

FIG. 2. Electrical potential at the surface, ψ_s, and in the middle of the sample, ψ_0, vs the thickness of the sample d.

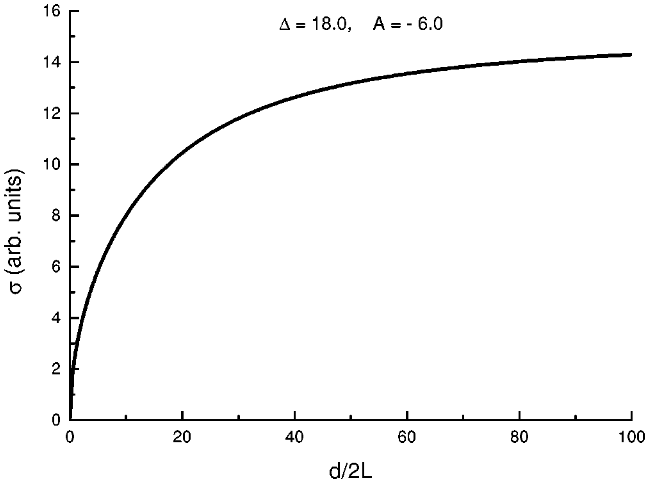

FIG. 3. Surface density of adsorbed positive ions, σ, vs the thickness of the sample d.

the sample, ψ_0, vs d are shown in Fig. 2. For small d, ψ_s, and ψ_0 are large, but $\psi_s-\psi_0\rightarrow 0$ as $d\rightarrow 0$. For large d, $\psi_0\rightarrow 0$ and ψ_s tends to a constant value. Figure 3 shows the trend of the surface charge density σ vs the thickness d. The global behavior is the expected one from the limiting cases discussed above. There is a linear behavior for small d and a clear saturation for large d. The general trend of $\sigma=\sigma(d)$ is reminiscent of Langmuir's isotherm [11]. However, we note that in the Langmuir problem of adsorption, the mutual interaction among the particles is neglected. On the contrary, in our model this interaction is explicitly taken into account by means of the electrical potential entering in the definition of $n_\pm$ and n_s.

An application of the above model can be immediately done for a liquid crystalline medium in the nematic phase. The surface energy of a NLC originates from two fundamental interactions: the first one is the NLC-NLC interaction whereas the second one is the NLC-substrate interaction. This surface energy is delocalized over a few molecular lengths near the limiting surface [17]. Moreover, when the solid substrate is in contact with the NLC the selective ion adsorption takes place. It is experimentally found [7] that the surface energy, in some situations, strongly depends on the thickness of the sample. For this reason the anchoring energy has to be considered as a nonlocal property. The model we have presented above can be used to justify, from a fundamental point of view, the thickness dependence of the anchoring energy. In a first approximation the electrostatic contribution to the effective surface energy can be evaluated as follows. The ionic adsorption phenomenon gives rise to an electric field, localized over the Debye screening length, near the surfaces. The dielectric energy density due to the interaction of the electric field with the NLC is, beside a constant term independent of the nematic orientation, $(1/8\pi)\epsilon_a(\vec{n}\times\vec{E})^2$, where ϵ_a is the dielectric anisotropy of the NLC and $\vec{n}$ is the nematic director [18]. The electric field is localized in a surface layer of thickness λ_D and parallel to the z axis. Consequently, the surplus of surface energy of electrostatics origin is of the order of $W_{\text{ion}}\approx(1/16\pi)\epsilon_a E(0)^2\lambda_D\cos^2\theta(0)$, where $\theta=\cos^{-1}(\vec{n}\cdot\vec{k})$ is the angle formed by $\vec{n}$ with the z axis, and $\theta(0)$ its value at the surface. By using the values reported above for the physical parameters of the liquid, we can evaluate the maximum electrostatics contribution to the anchoring strength. It is $W_\infty=W_{\text{ion}}(d\rightarrow\infty)$. In this limit, as it follows from Eq. (20), $\sigma\approx q/60\pi R^2$. This means that the average distance between neighbors at the surface, at the saturation, is of the order of $8R$. The connected electric field is $E=4\pi\sigma$, and for large thickness, $W_\infty\approx 10^{-2}$–10^{-1} erg/cm^2, which is of the correct order of magnitude to explain the observed thickness dependence of the anchoring energy [7].

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