PHYSICAL REVIEW E, VOLUME 65, 031701

Ions and nematic surface energy: Beyond the exponential approximation for the electric field of ionic origin

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(Received 07 September 2001; published 7 February 2002)

We present a general model to describe the influence of the ionic adsorption on the anisotropic part of the surface energy of a nematic liquid crystal in contact with a substrate. We show that in the limit of small adsorption energy, the exponential approximation for the electric field of ionic origin works well. In this limit, the dielectric and flexoelectric contributions to the surface energy are quadratic and linear on the density of adsorbed ions, respectively. In the opposite limit of large adsorption energy, the exponential approximation for the electric field does not work, and the two contributions to the surface energy are both found to depend linearly on the surface density of adsorbed charges. Approximated formulas reported in literature are derived from our general equations as particular cases, and their limits discussed. An expression for the surface polarization in nematic liquid crystal due to the ionic adsorption is also deduced. Our analysis is performed in the framework of the Poisson-Boltzmann theory, where dimensionless ions are treated within a mean field approach. Possible extensions of our model are indicated.

DOI: 10.1103/PhysRevE.65.031701 PACS number(s): 61.30.Gd, 66.10.−x, 41.20.−q, 82.45.−h

I. INTRODUCTION

In the continuum theory, a nematic liquid crystal is described by means of bulk and surface energies. The bulk energy F depends on the elastic distortion of the nematic liquid crystal and on the presence of external fields interacting with its anisotropic properties. The surface energy f_S takes into account the surplus of energy due to the presence of the limiting surface. It is due to the direct interaction between the liquid crystal and the substrate, and the reduced symmetry of the liquid crystal close to the substrate [1]. Long ago, it has been suggested that the selective ionic adsorption phenomenon can contribute to f_S [2]. In Ref. [3], using the exponential approximation for the electric field created by the ionic adsorption, the ionic contribution to the nematic surface energy connected with the dielectric anisotropy of the liquid crystal has been evaluated. In the same approximation, the model has been extended to take into account the flexoelectric contribution to the surface energy [4]. The model developed in Refs. [3,4] has been used to interprete the experimental data obtained by several groups [5–9] devoted to investigate the surface properties of nematic liquid crystals. The agreement between experimental data and the predictions of the model was rather good.

Recently, in a different context, Kuhnau *et al.* [10] and Nazarenko *et al.* [11,12] have shown that the exponential approximation for the electric field due to the the adsorption phenomenon is valid only in the case of weak adsorption energy.

In this paper, we will discuss the ionic contribution to the surface energy in the general case, obtaining explicit formulas valid for the weak and strong adsorption energies. Our analysis is performed in the framework of the Poisson-Boltzmann theory, where the ions are assumed to be dimensionless, and the problem is faced by employing a mean field approach. An extension of our model is possible following the procedure suggested by Kralj-Iglic and Iglic [13] and Bohinc *et al.* [14] for what concerns the influence of the ion size on the problem.

Our paper is organized as follows. In Sec. II, the well known equations of the Poisson-Boltzmann theory are recalled [15,16], and the boundary condition for the electric potential discussed. The ionic contributions to the nematic surface energy connected with the dielectric anisotropy and with the flexoelectric properties of the liquid crystal are also derived in Sec. II. The limits of small and large adsorption energies are considered in Sec. III. The charge distribution and the meaning of surface layer are analyzed in Sec. IV. In the same section, a discussion on the surface polarization for an isotropic liquid and for a nematic liquid crystal is reported. The main results of the paper are discussed in Sec. V.

II. THEORETICAL MODEL

Let us consider a neutral liquid containing n_0 ions per unit volume in the thermodynamical limit (infinite sample). In this situation, it is locally and globally neutral. When the liquid is limited by two surfaces of infinite area at a distance d apart, due to the selective ions adsorption phenomenon, the liquid will be locally charged. If d is very large with respect to the Debye's screening length λ_0, in the middle of the sample, the liquid will be, practically, locally neutral [14]. We will limit our analysis to this case, which represents a good approximation for ordinary samples ($d \sim 10$ μm), made with commercial nematic liquid crystals (typically $\lambda_0 \sim 0.5$ μm [17]). This case is known as the half-space approximation ($d/\lambda_0 \gg 1$), where it is possible to consider only one surface, placed at $z=0$, with surface charge density $\sigma = n_{ad}q$. n_{ad} represents the surface density of adsorbed ions of charge q. We indicate by $V(z)$ the electrical potential, with respect to the reference state where the liquid is locally neutral (at $z \to \infty$), and by $V_T = k_B T/q$ the thermal electrical potential ($V_T \sim 25$ mV at room temperature for monovalent

1063-651X/2002/65(3)/031701(5)/$20.00

ions). The quantity $\psi(z)=qV(z)/k_BT=V(z)/V_T$, which is the electrostatic energy of the ion in k_BT units or the electrical potential measured in V_T units, will be called reduced potential. We assume that only positive ions are adsorbed. According to Maxwell statistics, the densities of positive and negative ions are $n_\pm(z)=n_0\exp[\mp\psi(z)]$. It follows that the net charge density is $\rho(z)=q[n_+(z)-n_-(z)]=-2qn_0\sinh[\psi(z)]$, and Poisson's equation div$\mathbf{E}=\rho/\epsilon$ reads

$$\psi''(z)=\lambda_0^{-2}\sinh[\psi(z)], \tag{1}$$

where a prime means a derivative with respect to z, and $\lambda_0^2=\epsilon k_BT/(2n_0q^2)$ is the Debye's screening length. The surface electric field (at $z=0$) is $E_S=E(0)=\sigma/\epsilon=n_{ad}q/\epsilon$, from which we obtain

$$\psi'(0)=-1/L, \tag{2}$$

where $L=\epsilon k_BT/(\sigma q)=\epsilon k_BT/(n_{ad}q^2)$, is a new length connected with the adsorption phenomenon, first introduced in Ref. [10]. Note that $L\propto n_{ad}^{-1}$. Hence, it diverges for $n_{ad}\to 0$ (weak adsorption), and tends to zero for $n_{ad}\to\infty$ (strong adsorption).

From Eq. (1), we obtain

$$(1/2)\psi'^2(z)=\lambda_0^{-2}\cosh[\psi(z)]+K, \tag{3}$$

where K is an integration constant. Since in our case $\lim_{z\to\infty}\psi(z)=0$ and $\lim_{z\to\infty}\psi'(z)=0$, from Eq. (3) it follows that $K=-\lambda_0^{-2}$, and hence

$$\psi'(z)=-(2/\lambda_0)\sinh[\psi(z)/2]. \tag{4}$$

From Eq. (4), we obtain

$$\psi(z)=2\ln\left\{\frac{1+\gamma\exp(-z/\lambda_0)}{1-\gamma\exp(-z/\lambda_0)}\right\}, \tag{5}$$

where $\gamma=\tanh(\psi_S/4)$, and

$$E(z)=2(V_T/\lambda_0)\sinh[\psi(z)/2], \tag{6}$$

for the reduced potential and the electric field. From Eq. (6), we get, in particular,

$$E_S=E(0)=2(V_T/\lambda_0)\sinh(\psi_S/2), \tag{7}$$

connecting the surface field with the surface potential. From boundary condition (2) and Eq. (7), we deduce

$$\sinh(\psi_s/2)=\Lambda, \quad \text{where} \quad \Lambda=\lambda_0/2L. \tag{8}$$

The quantity $\Lambda=\lambda_0/2L$ is a measure of the importance of the adsorption phenomenon on the electric potential distribution across the sample. The cases of weak and strong adsorption correspond to small and large Λ, respectively. By means of Eq. (8), the parameter γ defined above is

$$\gamma=\tanh(\psi_S/4)=\sqrt{\frac{\sqrt{1+\Lambda^2}-1}{\sqrt{1+\Lambda^2}+1}}. \tag{9}$$

From Eq. (8), we deduce

$$\psi_S=2\ln(\Lambda+\sqrt{1+\Lambda^2}). \tag{10}$$

Equation (10) shows that in our half-space approximation the reduced surface potential depends only on $\Lambda=\lambda_0/2L$, the ratio between the two intrinsic lengths of the problem. For $\Lambda\sim 10$ [11] one obtains $\psi_S\sim 6$. Note that, if $\Lambda\ll 1$ then $\psi_S\ll 1$, whereas if $\Lambda\gg 1$ implies $\psi_S\gg 1$. It is possible to write the inequalities $\Lambda\ll 1$ and $\Lambda\gg 1$, corresponding to the cases of weak and strong adsorption, respectively, as $n_{ad}\ll 4n_0\lambda_0$, and $n_{ad}\gg 4n_0\lambda_0$, if the definitions of Λ, λ_0, and L are used. From the inequalities written above, it follows that there is a weak adsorption when the number of adsorbed ions is small with respect to $n_0\lambda_0$, i.e., with respect to the surface density of ions contained in a layer whose thickness coincides with λ_0, in thermodynamical equilibrium.

By substituting $\psi(z)$ given by Eq. (5) into the expressions for $n_\pm(z)$ the bulk densities of positive and negative ions are found to be

$$n_\pm(z)=n_0\left\{\frac{1\mp\gamma\exp(-z/\lambda_0)}{1\pm\gamma\exp(-z/\lambda_0)}\right\}^2. \tag{11}$$

Up to now the liquid was assumed isotropic. However, if the liquid is a nematic medium, in a first approximation it is possible to evaluate the ionic distribution as reported above (for a general discussion on this point see Ref. [18]). After that, we can evaluate the coupling between the electric field of ionic origin, $E(z)$, with the anisotropic properties of the nematic liquid crystals [2–4]. The coupling of $E(z)$ with the dielectric anisotropy and with the flexoelectric properties of the liquid crystal gives rise to a surplus of anchoring energy strength, of the kind

$$f_D=\int_0^\infty -\frac{1}{2}\epsilon_aE^2(z)dz, \tag{12}$$

and

$$f_Q=\int_0^\infty eE'(z)dz, \tag{13}$$

where $\epsilon_a=\epsilon_\parallel-\epsilon_\perp$, is the dielectric anisotropy ($\parallel$ and $\perp$ refer to the nematic director $\mathbf{n}$, [19]), and $e=e_{11}+e_{33}$ is the total flexoelectric coefficient, as discussed in Ref. [4]. Equations (12), (13) hold in the hypothesis of constant nematic orientation over the spatial region where the electric potential is changing, as we assume in our analysis. Using Eq. (6), f_D and f_Q given by Eqs. (12), (13) become $f_D=-4(\epsilon_aV_T^2/\lambda_0)\sinh^2(\psi_S/4)$, and $f_Q=-2(eV_T/\lambda_0)\sinh(\psi_S/2)$. The electrostatic contribution of ionic origin to the anchoring energy strength, $f=f_D+f_Q$, is then

$$f=-2(V_T/\lambda_0)[2\epsilon_aV_T\sinh^2(\psi_S/4)+e\sinh(\psi_S/2)]. \tag{14}$$

Equation (14) generalizes the formula reported in Ref. [4], for the same phenomenon, valid only in the case small adsorption. Using Eq. (8), it is possible to rewrite f_D and f_Q in terms of $\Lambda=\lambda_0/2L$. Simple calculations give $f_D=-2(\epsilon_a V_T^2/\lambda_0)(\sqrt{1+\Lambda^2}-1)$, and $f_Q=-2(eV_T/\lambda_0)\Lambda$. The total contribution to the anchoring energy strength is then

$$f=-2(V_T/\lambda_0)[\epsilon_a V_T(\sqrt{1+\Lambda^2}-1)+e\Lambda]. \tag{15}$$

From Eq. (15), it follows that for $\Lambda\rightarrow 0$ (weak adsorption),

$$f=-2(V_T/\lambda_0)[(1/2)\epsilon_a V_T\Lambda^2+e\Lambda]+O(\Lambda^3). \tag{16}$$

In the opposite limit, where $\Lambda\rightarrow\infty$ (strong adsorption), Eq. (15) gives

$$f=-2(V_T/\lambda_0)(\epsilon_a V_T+e)\Lambda. \tag{17}$$

These cases will be reconsidered in the next section, to compare the results of our analysis with the ones reported by other groups.

Before concluding this section, we analyze when the adsorption phenomenon can play an important role on the renormalization of the anchoring energy strength. To this end, we rewrite Eq. (15) as

$$f=-f_0[\sqrt{1+\Lambda^2}-1+(e/\epsilon_a V_T)\Lambda], \tag{18}$$

where $f_0=2\epsilon_a V_T^2/\lambda_0$. By assuming $\epsilon_a\sim 10\epsilon_0$ and $e\sim 5\times 10^{-11}$ C/m, typical for a nematic liquid crystal such as 5CB [20] and 0.1 $\mu\text{m}\leqslant\lambda_0\leqslant 0.5$ μm [17], we obtain 2×10^{-7} $\text{J/m}^2\leqslant f_0\leqslant 10^{-6}$ J/m^2. In this case, $f\sim 10^{-6}$ J/m^2 if $0.2\leqslant\Lambda\leqslant 1$, whereas $f\sim 10^{-4}$ J/m^2 for $10\leqslant\Lambda\leqslant 50$. Hence, we can conclude that in the limit of weak adsorption f can be important only if the interface nematic liquid crystal/solid substrate is characterized by weak anchoring energy. In the case, where the bare anchoring energy strength of the interface is rather strong ($\sim 10^{-4}$ J/m^2), $10\leqslant\Lambda\leqslant 50$ and $L=\lambda_0/2\Lambda$ is in the nm scale. The estimation reported above shows that the Debye's screening length plays an important role in surface effects of liquid crystals. Consequently, in all experimental investigations devoted to the characterization of surface energy or flexoelectric coefficients, this parameter has to be measured carefully. Without information on this quantity, all discussions on the origin of the surface energy strength or on the surface polarization based on experimental investigation, could be meaningless.

III. LIMIT OF WEAK AND STRONG ADSORPTION

Let us analyze first the case of weak adsorption, already considered in Ref. [4] in another framework. In this limit $\psi_S\ll 1$ and hence $\gamma=\tanh(\psi_S/4)\sim\psi_S/4$. From Eq. (5), we obtain $\psi(z)=\psi_S\exp(-z/\lambda_0)$, and $E(z)=E_S\exp(-z/\lambda_0)$, where $E_S=V_T(\psi_S/\lambda_0)=V_T/L$, as it follows from Eqs. (7), (8). The bulk densities of ions are then $n_\pm(z)=n_0[1\mp\psi_S\exp(-z/\lambda_0)]$. In particular, $n_\pm(0)=n_0(1\mp\psi_S)$. As expected, if $\psi_S\ll 1$, the electrical equilibrium is only slightly perturbed. The electrostatic contribution to the anchoring energy strength are, in this limit, $f_D=-(1/4)\epsilon_a\lambda_0 E_S^2$, and $f_Q=-eE_S$, as it follows from the expressions reported above for f_D and f_Q in terms of ψ_S and from Eq. (7). Hence,

$$f=-\frac{1}{4}\epsilon_a\lambda_0 E_S^2-eE_S, \tag{19}$$

as reported in Ref. [4]. In this approximation $f_D\propto E_S^2$ and $f_Q\propto E_S$.

Let us consider now the case of strong adsorption. In this framework, $\psi_S\gg 1$ and $\gamma=\tanh\psi_S\sim 1-2\exp(-\psi_S/2)$. Hence

$$\psi(z)=2\ln\left\{\frac{1+[1-2\exp(-\psi_S/2)]\exp(-z/\lambda_0)}{1-[1-2\exp(-\psi_S/2)]\exp(-z/\lambda_0)}\right\}, \tag{20}$$

and the electric field is still given by Eq. (6). For $z/\lambda_0\ll 1$, $\psi(z)\gg 1$. Consequently, $\sinh(\psi/2)\sim(1/2)\exp(\psi/2)$, that by using Eq. (20) in the limit $\psi_S\gg 1$ is equivalent to

$$\sinh\left(\frac{\psi}{2}\right)=\frac{\exp(\psi_S/2)}{2+(z/\lambda_0)\exp(\psi_S/2)}. \tag{21}$$

In the considered limit of $\psi_S\gg 1$ from Eq. (6) we have $\exp(\psi_S/2)=(\lambda_0/V_T)E_S$. By substituting this expression into Eq. (21) and the result in Eq. (6), one obtains

$$E(z)=\frac{E_S}{1+(z/2L)}. \tag{22}$$

In this limit ($\psi_S\gg 1$, $z/\lambda_0\ll 1$), $n_\pm(z)$ are given by

$$n_\pm(z)=n_0\left\{\frac{1\mp[1-2\exp(-\psi_S/2)](1-z/\lambda_0)}{1\pm[1-2\exp(-\psi_S/2)](1-z/\lambda_0)}\right\}^2. \tag{23}$$

In particular, $n_+(0)=n_0\exp(-\psi_S)\sim 0$, and $n_-(0)=n_0\exp(\psi_S)$.

Equation (22) has been deduced in Ref. [10] and presented as a general result, valid for all z. On the contrary, it is valid only for $z/\lambda_0\ll 1$. For large z/λ_0 from Eq. (5), we obtain, for all ψ_S, $\psi(z)=4\gamma\exp(-z/\lambda_0)$, showing that the reduced potential, and hence the electric field, is always exponentially decreasing, and Eq. (22) does not work. In this case, we have, furthermore, $n_\pm(z)=n_0\{1\mp 2[1-2\exp(-\psi_S/2)]\exp(-z/\lambda_0)\}^2$, showing again that for $z\rightarrow\infty$, $n_\pm(z)\rightarrow n_0$, as expected.

In the limit under consideration ($\psi_S\gg 1$) from the expression of f_D and f_Q in terms of ψ_S, we derive $f_D=-\epsilon_a V_T E_S$, and $f_Q=-eE_S$. These expressions show that, in this limit, f_D and f_Q are both linear in E_S. The total electrostatic contribution to the surface energy strength ($f=f_D+f_Q$) is then

$$f=-(\epsilon_a V_T+e)E_S. \tag{24}$$

Equation (24) was not reported before in literature. From Eq. (24) it follows that in the limit of large adsorption the electrostatic contribution can stabilize or destabilize the planar orientation according to the sign of $(\epsilon_a V_T+e)$, independently of the number of adsorbed ions. The importance of the flexoelectric term was already recognized in Ref. [4] using the exponential approximation for the electric field.

IV. CHARGE DISTRIBUTION AND THICKNESS OF THE SURFACE LAYER

The net charge density is $\rho(z)=-2n_0q\sinh\psi(z)$, as discussed above. Using Eq. (4) it is easy to show that

$$\mathcal{Q}(\infty)=\int_0^\infty \rho(z)\,dz=-\sigma, \tag{25}$$

as expected, since the system is globally neutral. The electric charge, per unit surface, contained in a surface layer of thickness b is, in analogy with Eq. (25),

$$\mathcal{Q}(b)=\int_0^b \rho(z)\,dz. \tag{26}$$

By rewriting Eq. (26) in the form

$$\mathcal{Q}(b)=\mathcal{Q}(\infty)-\int_b^\infty \rho(z)\,dz, \tag{27}$$

and using Eq. (4) and Eq. (5) we obtain

$$R=1-\frac{\mathcal{Q}(b)}{\mathcal{Q}(\infty)}=\frac{2}{\Lambda}\,\frac{\gamma\exp(-b/\lambda_0)}{1-\gamma^2\exp(-2b/\lambda_0)}, \tag{28}$$

where we have used Eq. (25) and the definitions of λ_0, L, and Λ. The meaning of R is evident from the definition. If $R\to 0$, the layer of thickness b contains practically all the counterions. In the opposite case of $R\to 1$, the counterions present in the surface layer are a negligible fraction of the total number .

In general, fixing R, from Eq. (28) it is possible to obtain the corresponding thickness of the surface layer b, as discussed in Ref. [14]. Straightforward calculations give

$$b=\lambda_0\ln\left\{\frac{R\Lambda}{\sqrt{1+(R\Lambda)^2}-1}\sqrt{\frac{\sqrt{1+\Lambda^2}-1}{\sqrt{1+\Lambda^2}+1}}\right\}. \tag{29}$$

From Eq. (29), we obtain that for $\Lambda\to 0$, $b\to-\lambda_0\ln R$, i.e., $b\sim\lambda_0$, and for $\Lambda\to\infty$, $b\to(\lambda_0/R)\Lambda^{-1}$, as expected. For $R=0.1$ and $\Lambda\sim 10$, $b\sim\lambda_0$. In this case (9/10) of the ionic charge is contained in a surface layer of thickness λ_0 [11].

Using the simple results reported above, we can now obtain the total dipole moment and the bulk polarization of the sample under consideration. If the sample is symmetric, i.e., it has the same adsorption energy on the two surfaces, the net dipole moment vanishes, for symmetry reasons. The dipole moment, per unit surface, of half sample is given by

$$p=\int_0^\infty z\rho(z)\,dz, \tag{30}$$

and the corresponding bulk polarization is $P(z)=z\rho(z)$. The quantity p defined in Eq. (30) is also known as "surface polarization," as we will call from now on. Taking into account that $\rho(z)=\epsilon\,\mathrm{div}\mathbf{E}$, and using $\psi(z)$ instead of $\mathbf{E}$, one obtains $P(z)=-\epsilon V_T z\psi''(z)$. In our half-space approximation, $\psi(z)$ is given by Eq. (5), and $P(z)$ can be written in the form

$$P(z)=-8n_0qz\gamma\exp(-z/\lambda_0)\frac{1+\gamma\exp(-2z/\lambda_0)}{[1-\gamma\exp(-2z/\lambda_0)]^2}. \tag{31}$$

If $\psi_S\ll 1$, Eq. (31) becomes

$$P(z)=-2n_0qz\psi_S\exp(-z/\lambda_0), \tag{32}$$

where $\psi_S\sim\lambda_0/L=2\Lambda$, as it follows from Eq. (8). In the opposite limit of $\psi_S\gg 1$, Eq. (31) gives

$$P(z)=-8n_0qz\exp(-z/\lambda_0)\frac{1+\exp(-2z/\lambda_0)}{[1-\exp(-2z/\lambda_0)]^2}. \tag{33}$$

Equations (32), (33) show that $P(z)$ is localized over a few L or λ_0, according to the considered limit.

Using Eq. (30), it is possible to evaluate the surface polarization. Simple calculations give $p=-\epsilon V_T\psi_S=-\epsilon V_S$. By assuming $\epsilon\sim 10\epsilon_0$ and $\psi_S\sim 4$, which implies $\Lambda\sim 5$, we obtain $p\sim 10^{-11}$ C/m. If this formula is applied to a nematic liquid crystal, ϵ has to be substituted with an average value that in a first approximation is $\langle\epsilon\rangle=(2\epsilon_\perp+\epsilon_\parallel)/3$.

Finally, we evaluate the polarization induced by the electric field of ionic origin on a nematic liquid crystal. The macroscopic polarizability tensor of a nematic medium is $\chi_{ij}=\chi_a n_i n_j+\chi_\perp\delta_{ij}$, where $\mathbf{n}$ is the nematic director of Cartesian components n_k, $\chi_a=\chi_\parallel-\chi_\perp$ and where $\chi_\parallel$ and $\chi_\perp$ are the polarizability along and perpendicular to $\mathbf{n}$ [19]. If the nematic liquid crystal is submitted to an electric field the induced polarization is $P_i=\epsilon_0\chi_{ij}E_j=\epsilon_0[\chi_a n_i(\mathbf{n}\cdot\mathbf{E})+\chi_\perp E_i]$. Since $\mathbf{E}(z)$, which is parallel to the z axis, is different from zero, practically, only in a surface layer of thickness ranging between λ_0 and a few L, we conclude that $P_i(z)$ is localized near the adsorbing substrate. The surface polarization in the nematic liquid, of ionic origin, is obtained by integrating $P_i(z)$ from $z=0$ to $z\to\infty$. Simple calculations give $p_i=\epsilon_0(\chi_a n_i n_z+\delta_{iz})V_S$. Let us assume that the substrate isotropic and the easy axis parallel to the z axis (homeotropic orientation). In this case, the nematic liquid crystal possess cylindrical symmetry around the z axis, and the average surface polarization is

$$\langle p_z\rangle=\epsilon_0(\chi_a n_z^2+\chi_\perp)V_S. \tag{34}$$

The net surface polarization p_S is obtained by adding to $\langle p_z\rangle$ the quantity p evaluated above, and it is found to be given by

$$p_S=\{(\epsilon_a-\epsilon_0)n_z^2-[(\epsilon_a/3)+\epsilon_0]\}V_S. \tag{35}$$

As expected, p_S depends on n_z^2. Its amplitude, by assuming $\epsilon_a\sim 10\epsilon_0$ is of the order of 10^{-11} C/m for $\psi_S\sim 4$, i.e., $\Lambda\sim 5$. This value is of the same order [21,22], or larger [23] than the values reported in literature for the nematic surface polarization. From this result, we conclude that, probably, the observed surface polarization in nematic liquid crystals has an ionic origin. This possibility was already mentioned in the past [21–23], but no estimations were reported. It is different from the one discussed by Petrov and Derzhanski [24], which is linear in n_z, whose origin is connected with the different chemical affinities of the two extremities of the nematic molecules with the substrate.

V. CONCLUSIONS

We have analyzed the influence of the ionic adsorption on the anisotropic part of the surface energy of a nematic liquid crystal in contact with a solid substrate. It has been shown that the exponential approximation for the electric field of ionic origin works well only in the limit of weak adsorption. In this case, the dielectric contribution to the anchoring strength is quadratic, whereas the flexoelectric contribution is linear, in the surface electric field. In the opposite limit of strong adsorption, both contributions are linear in the surface field. We have also shown that the surface polarization, experimentally observed in nematic samples, can have an ionic origin. Our paper generalizes the results reported in Ref. [4] to the case of strong ionic adsorption, shows the limits of the analysis performed in Ref. [10], and completes the theory developed in Ref. [11,12].

In our analysis, we have focused our attention to the electric field distribution and the energy contributions of electrostatic origin to the anchoring energy strength. In this study, we have assumed the adsorbed charge density as a given quantity. As it is well known, it depends on the actual surface potential, but this aspect of the problem is well known [11].

ACKNOWLEDGMENTS

We thank A. G. Petrov and L. R. Evangelista for useful discussions.

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