

## Contribution of the ionic adsorption phenomenon to the effective anchoring energy of a nematic liquid-crystal sample

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The effective anchoring energy resulting from the ionic adsorption phenomenon in a nematic liquid-crystal sample in the shape of a slab of thickness  $d$  is investigated. The electric field distribution is determined in the framework of a general nonlinear Poisson-Boltzmann approach. The analysis is particularized for the case in which  $d \gg \lambda_D$ , where  $\lambda_D$  is the Debye screening length. In this limit, the spatially dependent electric field distribution across the sample as well as the contribution, of dielectric and flexoelectric origins, to the effective anchoring energy is obtained in an exact manner.

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The ions that can be found in the bulk of a nematic liquid-crystal (NLC) sample can be adsorbed at the bounding solid surfaces [1–11]. For practical applications, as well as for fundamental purposes, it is important to investigate the influence of these ions on the molecular orientation of a NLC. Since NLC's are conductive and contain impurities, due to some electrochemical forces the surface limiting the sample can selectively adsorb one type of ions (for instance, the positive ones), giving rise to a counterion cloud forming a diffuse double layer in the NLC medium. Consequently, a spatially dependent electric field distribution across the sample arises. This electric field is very strong near the surface and decays fast as we move away from it [1]. The presence of the electric field, with a strong gradient near the surfaces, is responsible for detectable effects on the molecular orientation which are not very usual [7,8].

In this work, the effect of the surface electric field, produced by selective ionic adsorption, on the effective anchoring energy of a NLC sample is analyzed for a cell in the shape of a slab of thickness  $d$ . The electric field distribution is investigated in the framework of a nonlinear Poisson-Boltzmann approach [12–14]. From this general distribution we obtain an approximated expression (which, actually, becomes exact for thick samples) for the electric field profile across the sample, justifiable for  $d \gg \lambda_D$ , where  $\lambda_D$  is the Debye screening length [1]. In this framework it is possible to obtain also analytical expressions for the contribution of dielectric and flexoelectric origin to the effective anchoring energy of the sample [15,16]. This contribution “renormalizes” the anchoring energy and is shown to have an order of magnitude that can also be compared with the “bare” (i.e., the usual) anchoring energy [17] depending on the value of the adsorption energy. The same problem has been recently investigated by other groups. In particular, an approach dealing with a non-Debye charge screening in NLC has been presented in Refs. [9–11]. These works indicate that the surface field can be screened within a very dense charged sub-surface layer of thickness  $\lambda_s$ , considered in Ref. [9]. The immediate consequence of the non-Debye screening is that the flexoelectric contribution to the anchoring energy can be the dominant one. This length is present in our analysis too, by means of the boundary conditions on the electric field used to solve the electrostatic problem.

We shall obtain the electric field distribution—whose origin is due to the selective ion adsorption by the surface—of a sample of thickness  $d$ , limited by two adsorbing surfaces located at  $x = \pm d/2$ , filled out with a liquid of dielectric permittivity  $\epsilon$  [12,13]. The neutral liquid is supposed to contain impurities that suffer dissociation, thus producing positive and negative ions in the bulk. In the presence of these ions, the surfaces selectively adsorb positive charges. These charges give rise to a surface electric field that, in turn, connects with the dielectric and flexoelectric properties of the medium. By assuming the surfaces as identical, the electric potential generated in the sample is symmetrical with respect to the center of the sample, i.e.,  $V(x) = V(-x)$ , where it is minimum [18]. A requirement to be satisfied by this model is that the number of particles in the whole sample (bulk plus surface) is a conserved quantity, namely  $(N_+ + N_-)/2 + N_b + n_s = n_0 d$ , where  $n_0$  is the bulk density of particles defined in relation to an infinite sample,  $N_{\pm} = \int_{-d/2}^{d/2} n_{\pm}(x) dx$  and  $N_b = \int_{-d/2}^{d/2} n_b dx = n_b d$ , are, respectively, the number of charged particles of both signs ( $\pm$ ) and the number of non-dissociated impurities in the bulk, per unit surface. In the bulk, in equilibrium at an absolute temperature  $T$ , the densities of positive and negative charges are given in terms of the Boltzmann distribution as  $n_{\pm}(x) = n_0 e^{\mu - \Delta \mp \psi(x)}$ , where  $\Delta$  is the activation energy (in  $K_B T$  units) and  $n_b = n_0 e^{\mu}$ . Furthermore,  $n_s$  is the surface density of adsorbed particles, given by [1,19]

$$n_s = N e^{\mu - A - \psi_s}, \quad (1)$$

where  $N$  is the number of sites per unit surface at each surface. In Eq. (1) we have introduced three important quantities: the electrostatic energy  $\psi(x) = qV(x)/K_B T$  whose value at the surfaces is given by  $\psi_s$ , the chemical potential  $\mu$ , and the adsorption energy  $A$ . For simplicity, all these quantities are measured in  $K_B T$  units. The adsorption energy, in a first approximation, can be identified with the electrostatics energy of an adsorbed ion with its image in the substrate (physical adsorption) [20]. The value of  $A$  ranges from a few units, which corresponds to the region of physical adsorption, to a few ten of units, which corresponds to a region of chemisorption [21].

By using the above definitions, it is possible to rewrite the equation for the conservation of the number of particles as a relation connecting the chemical ( $\mu$ ) to the surface electric potential ( $\psi_s$ ), in the form

$$e^{-\mu} = 1 + \frac{N}{n_0 d} e^{-A - \psi_s} + e^{-\Delta} \frac{1}{d} \int_{-d/2}^{d/2} \cosh \psi(x) dx. \quad (2)$$

On the other hand, 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  $d^2 V/dx^2 = -(q/\epsilon)[n_+(x) - n_-(x)]$ , where  $q$  is the electric charge of the positive ions and  $\epsilon$  is the dielectric permittivity of the liquid. This equation can be put in the form

$$\frac{d^2 \psi}{dx^2} = \frac{1}{L^2} e^{\mu - \Delta} \sinh \psi, \quad (3)$$

where  $L = (\epsilon K_B T / 2 n_0 q^2)^{1/2}$  is an intrinsic length of the problem. It is connected with the Debye screening length  $\lambda_D$  by means of the relation  $L = \lambda_D e^{-\Delta/2}$  [12]. Taking into account that the electric potential is an even function of  $x$  it is possible to integrate Eq. (3) to obtain

$$\left( \frac{d\psi}{dx} \right)^2 = \frac{2e^{\mu - \Delta}}{L^2} [\cosh \psi(x) - \cosh \psi_0], \quad (4)$$

where  $\psi_0 = \psi(x=0)$ . A further integration yields

$$\int_{\psi_s}^{\psi_0} \frac{d\psi}{\sqrt{\cosh \psi - \cosh \psi_0}} = \frac{d}{\sqrt{2} L} e^{(\mu - \Delta)/2}, \quad (5)$$

which establishes a relation between the chemical potential  $\mu$  and the electric potentials  $\psi_0$  and  $\psi_s$ . The electrical field  $E(x) = -dV/dx$  is identically zero for  $|x| > d/2$ . It presents discontinuities at  $x = \pm d/2$ . Since  $E(x) = -(K_B T/q)d\psi/dx$  and  $E(-d/2) = qn_s/\epsilon$ , it is possible, by means of Eqs. (1) and (4), to obtain the following expression for the chemical potential

$$e^{\mu} = 2 \left( \frac{\epsilon K_B T}{NLq^2} \right) e^{-\Delta + 2(A + \psi_s)} (\cosh \psi_s - \cosh \psi_0). \quad (6)$$

Notice that from the condition  $E(-d/2) = qn_s/\epsilon$ , rewritten in terms of  $\psi$ , and using Eq. (1) we have

$$\left( \frac{d\psi}{dx} \right)_{x=-d/2} = - \frac{Nq^2}{\epsilon K_B T} e^{\mu - A - \psi_s}. \quad (7)$$

The quantity  $\lambda_s = (\epsilon K_B T / Nq^2) e^{-\mu + A}$  has the dimension of a length, and coincides with the length introduced in Refs. [9,11]. The fundamental equations of the model are Eqs. (2), (5), and (6). This set of equations has to be solved to obtain the electric field distribution across the sample [13]. Numerical calculations have shown that the curves for several different values of  $A$  can be well represented by a function of the form

$$E(X) = \alpha \tan \left[ \frac{\beta \pi X}{2} \right], \quad (8)$$

for  $-1 \leq X (= 2x/d) \leq 1$ , where  $\alpha$  and  $\beta$  are, in principle, depending on the adsorption energy characterizing the surfaces, and on the thickness of the sample (see below). Therefore, for the cases we are dealing with here, solution (8) can be considered as the exact one, as we shall demonstrate.

In the limit  $d \gg \lambda_D$  the Poisson-Boltzmann equation (3) can be approximated by

$$\frac{d^2 \psi}{dx^2} = \frac{1}{L^2} e^{\mu - \Delta} \sinh \psi \approx \frac{1}{2L^2} e^{\mu - \Delta} e^{\psi}, \quad (9)$$

which is equivalent to considering that  $\psi = qV/(K_B T) \gg 1$ . This means that the number of positive charges remaining in the bulk (not adsorbed) is very small, as can be seen from the definition of  $n_{\pm}(x)$  introduced before. Equation (9) can be integrated to give

$$\frac{d\psi}{dx} = \mp \frac{1}{L} e^{(\mu - \Delta)/2} \sqrt{e^{\psi} - e^{\psi_0}}, \quad (10)$$

where “−” refers to the interval  $-d/2 \leq x < 0$  and “+” to  $0 < x \leq d/2$ . The electric potential can be obtained from Eq. (10) by further integration, giving

$$t[\psi, \psi_0] = - \frac{1}{2L} e^{(\mu - \Delta + \psi_0)/2} \left( x + \frac{d}{2} \right) + t[\psi_s, \psi_0], \quad (11)$$

where  $t[a, b] = \tan^{-1}[\sqrt{e^{a-b} - 1}]$ . From Eq. (11) one obtains (at  $x=0$ )

$$t[\psi_s, \psi_0] = \frac{d}{4L} e^{(\mu - \Delta + \psi_0)/2}. \quad (12)$$

By using Eq. (12) into Eq. (11), one explicitly obtains the electric potential as

$$\psi(x) = \psi_0 + \ln \left\{ 1 + \tan^2 \left[ \frac{x}{2L} e^{(\mu - \Delta + \psi_0)/2} \right] \right\}. \quad (13)$$

In this manner one can also determine the electric field distribution

$$E(x) = - \frac{4K_B T}{qd} t[\psi_s, \psi_0] \tan \left[ \frac{2x}{d} t[\psi_s, \psi_0] \right], \quad (14)$$

where Eq. (12) has been used. Comparison of Eq. (14) with Eq. (8) yields

$$\alpha = - \frac{4K_B T}{qd} t[\psi_s, \psi_0] \quad \text{and} \quad \beta = \frac{2}{\pi} t[\psi_s, \psi_0]. \quad (15)$$

To complete the solution of the entire electrostatics problem, in the approximation in which  $d \gg \lambda_D$ , we have to take into account that  $E(-d/2) = qn_s/\epsilon$ . By using Eqs. (1) and (14) we obtain another relation connecting  $\mu$ ,  $\psi_0$ , and  $\psi_s$  in the form

$$e^{\mu-A-\psi_s} = \frac{4\epsilon K_B T}{q^2 N d} t[\psi_s, \psi_0] \tan t[\psi_s, \psi_0]. \quad (16)$$

Finally, the last expression is obtained from Eq. (2) which reduces to

$$e^{-\mu} = 1 + \frac{N}{n_0 d} e^{-A-\psi_s} + e^{\psi_0-\Delta} \frac{\tan t[\psi_s, \psi_0]}{2 t[\psi_s, \psi_0]}. \quad (17)$$

The set formed by Eqs. (12), (16), and (17) permits to determine  $\mu$ ,  $\psi_0$  and  $\psi_s$  as functions of the adsorption energy  $A$  and of the thickness of the sample  $d$ , in equilibrium at a temperature  $T$ . The sensibility of  $\psi_s$  with respect to changes in  $d$  is not significant, for a fixed value of the adsorption energy, in the limit in which  $d/2L \gg 1$ , because, in this case, the surface density of adsorbed charges, given by Eq. (1), reaches a saturation, i.e., tends to a value independent of  $d$  [12]. On the contrary,  $\psi_0$  changes in a substantial manner. The system, in any case, remains neutral, but an overwhelming adsorption of positive charges takes place. The situation is such that now  $\psi_s$  changes in a substantial manner with  $A$  for a fixed thickness, whereas  $\psi_0$  is less sensible to the changes in  $A$ . Notice that when  $d$  is large  $\mu \rightarrow 0^-$ . In fact, by using Eqs. (12) and (16) it is possible to rewrite Eq. (17) in the form  $e^{-\mu} = 1 + (2N/n_0 d) e^{-A-\psi_s}$ , which shows that when  $d \rightarrow \infty$ ,  $\mu \rightarrow 0^-$ .

Let us now analyze the influence of the ionic adsorption on the anchoring energy of the sample. It is well known that the presence of ionic charges in the medium gives rise to a surplus of surface energy characterizing the NLC-substrate interface. This surface energy has a dielectric as well as a flexoelectric contribution coming from the coupling of the spatially dependent electric field with the dielectric and the flexoelectric properties of the medium. These contributions have been calculated for a NLC sample in the shape of a slab of thickness  $d$ , as the one being considered here [8,15]. The relevant contribution to the anchoring strength of dielectric origin is given by [15]

$$W_D = -\frac{1}{2} \epsilon_a \int_{-d/2}^0 [E(x)^2 - E_B^2] dx, \quad (18)$$

where  $E_B = E(x=0)$  is the value of the electric field in the bulk. The flexoelectric contribution to the anchoring strength is shown to be given by [15]

$$W_Q = \pm e(E_S - E_B), \quad (19)$$

where  $E_S$  is the value of the field at the surface and  $\pm$  refer to  $x = \pm d/2$ . Equations (18) and (19) represent only the contribution of dielectric origin to the anchoring energy. There is also a localized surface energy which does not depend on the presence of ions in the sample. It is an intrinsic characteristic of the interface. Therefore, the dielectric contribution renormalizes this "bare" anchoring energy  $W_0$ , giving rise to an effective anchoring energy that can be written as  $W_{\text{eff}} = W_0 + W_D + W_Q$ . By using Eqs. (14)–(16), with the definitions of

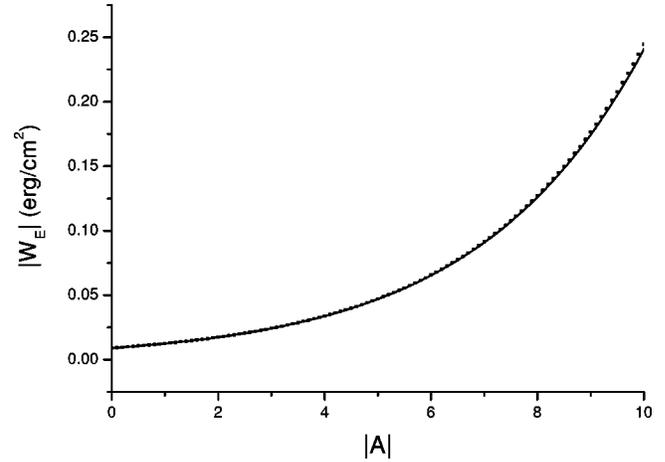


FIG. 1. Anchoring energy of dielectric origin,  $|W_E|$ , vs the adsorption energy (absolute value) for a sample of thickness  $d = 8 \mu\text{m}$  (solid line) and  $d = 15 \mu\text{m}$  (dotted line). The material parameters are (in SI units)  $K = 4 \times 10^{-11}$ ,  $e = 10^{-11}$ , and  $\epsilon_a = 1 \epsilon_0$ .

$L$  and  $\lambda_s$ , in Eqs. (18) and (19), we obtain, respectively, for the dielectric and flexoelectric contributions to the anchoring strengths the expressions

$$W_D = \frac{1}{2} \epsilon_a \left( \frac{K_B T}{q} \right)^2 \left[ \left( \frac{n_0 d}{N \lambda_s} \right) e^{A-\Delta+\psi_0} - \frac{2e^{-\psi_s}}{\lambda_s} \right],$$

$$W_Q = -\frac{e}{\lambda_s} \left( \frac{K_B T}{q} \right) e^{-\psi_s}. \quad (20)$$

Equations (20) show that the effective anchoring energy of a sample can be thickness dependent as is found in many experimental results [22]. Moreover, these equations show also that the anchoring energy is renormalized by the contribution coming from the electrical properties whose origin is connected with the presence of ions in the sample. This dependence is here represented also by the adsorption energy. However, in recent papers [14,15] it has been demonstrated that this contribution exists even in the absence of the ad-

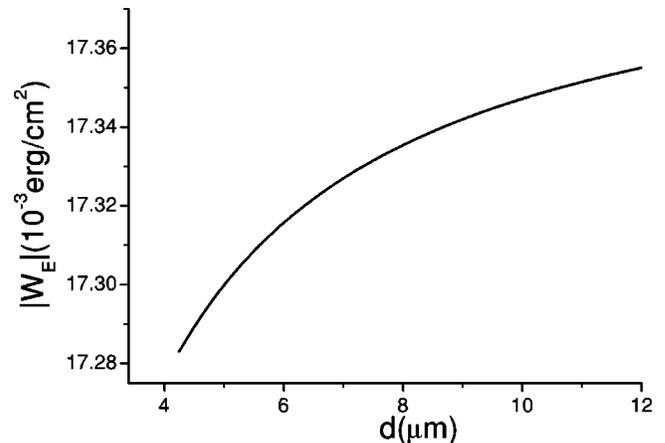


FIG. 2. Anchoring energy of dielectric origin,  $W_E$ , vs the thickness of the sample for  $A = -2.0$ . The parameters are the same as in Fig. 1.

sorption energy. Furthermore, in Ref. [16], by means of numerical calculations, it has been shown that, due to its order of magnitude, the anchoring energy whose origin lies in the ionic adsorption phenomenon cannot be, in general, neglected.

In Fig. 1 the dependence of  $W_E = W_D + W_Q$  on the adsorption energy  $A$  is shown for two typical NLC samples. Changing the thickness of the sample the trend of  $W_E$  does not change in a significant manner. However, the absolute value of the anchoring strength changes in a substantial manner with  $A$ . By changing  $A$  of one order of magnitude implies to change the anchoring strength by the same amount. Moreover, the order of magnitude of  $|W_E|$  indicates that this contribution cannot be neglected because it can be of the same order of the bare anchoring strength [16].

In Fig. 2 is the dependence of  $W_E$  on the thickness of the sample that is exhibited. In the limit we are considering, this dependence is not very strong, because the dominant contribution comes from  $\psi_s$ , which is not changing too much with

$d$ . For this particular example, by changing  $d$  of one order of magnitude, the change in  $|W_E|$  is very small  $\Delta|W_E|/|W_E| \approx 0.5\%$ .

In this work the effect of the surface electric field produced by selective ionic adsorption on the effective anchoring energy of a nematic liquid sample of slab shape was analyzed. The electric field distribution was determined in the framework of a nonlinear Poisson-Boltzmann approach. In this model, the electric field is thickness dependent, but it depends also on the adsorption energy characterizing the surfaces. We have established the exact field distribution in the limit of large thickness, i.e., when  $d \gg \lambda_D$ . In this limit we have also established a closed analytical model for the contribution to the anchoring energy resulting from the ionic adsorption phenomenon.

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- [1] J. Israelachvili, *Intermolecular and Surface Forces* (Academic Press, London, 1985).
- [2] G. Barbero and G. Durand, *Liq. Cryst.* **2**, 401 (1987).
- [3] G. Barbero and G. Durand, *J. Phys. (France)* **51**, 281 (1990).
- [4] B. Valenti, M. Grillo, G. Barbero, and P. Taverna Valabrega, *Europhys. Lett.* **12**, 407 (1990).
- [5] A.L. Alexe-Ionescu, G. Barbero, and A.G. Petrov, *Phys. Rev. E* **48**, R1631 (1993).
- [6] V.G. Nazarenko and O.D. Lavrentovich, *Phys. Rev. E* **49**, R990 (1994).
- [7] G. Barbero, L.R. Evangelista, and N.V. Madhusudana, *Eur. Phys. J. B* **1**, 327 (1998).
- [8] H.A. Pereira and L.R. Evangelista, *Eur. Phys. J. E* **3**, 123 (2000).
- [9] U. Kuhnau, A.G. Petrov, G. Klose, and H. Schmiedel, *Phys. Rev. E* **59**, 578 (1999).
- [10] V.G. Nazarenko, V.M. Pergamenschik, O.V. Koval'chuk, A.B. Nych, and B.I. Lev, *Phys. Rev. E* **60**, 5580 (1999).
- [11] V.G. Nazarenko, V.M. Pergamenschik, O.V. Koval'chuk, and B.I. Lev, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **352**, 1 (2000).
- [12] G. Barbero, A.K. Zvezdin, and L.R. Evangelista, *Phys. Rev. E* **59**, 1846 (1999).
- [13] L.R. Evangelista and G. Barbero, *Phys. Rev. E* **64**, 021101 (2001).
- [14] D. Olivero and G. Barbero, *Phys. Rev. E* **65**, 031701 (2002).
- [15] D. Olivero, L.R. Evangelista, and G. Barbero, *Phys. Rev. E* **65**, 031721 (2002).
- [16] H.A. Pereira, L.R. Evangelista, D. Olivero, and G. Barbero, *Braz. J. Phys.* **32**, 2B, 584 (2002).
- [17] A. Rapini and M. Papoular, *J. Phys. (Paris), Colloq.* **30**, C4-54 (1969).
- [18] This particular case is presented here only for simplicity. The general model for different surfaces, taking into account also the possibility of adsorption of positive and negative ions, is detailed in Ref. [13].
- [19] C. Garrod, *Statistical Mechanics and Thermodynamics* (Oxford University Press, Oxford, 1995), Chap. 7.
- [20] L.D. Landau and E.I. Lifchitz, *Electrodynamique des Milieux Continus* (MIR, Moscow, 1956).
- [21] A.W. Adamson, *Physical Chemistry of Surfaces* (Wiley, New York, 1997).
- [22] L.M. Blinov, A.Y. Kabayenkov, and A.A. Sonin, *Liq. Cryst.* **5**, 645 (1989).