Influence of the bias-voltage on the anchoring energy for nematic liquid crystals

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The influence of the bias-voltage on the anisotropic part of the nematic surface energy is analyzed. The experimental data show a strong dependence of the anchoring strength on the bias-voltage when the electrodes of the nematic cell are covered with WO_3. The observed dependence can be interpreted taking into account the ions dissolved in the liquid crystal. We propose a model in which the effect of the bias-voltage is to collect the ions near the electrodes, in a surface layer whose thickness is of the order of the Debye's screening length. The surplus of electric field due to this ions confinement gives rise to an electrostatic contribution to the total energy that can be considered as a surface energy. The proposed model is in good agreement with the experimental data. The model is used to interpret the observed independence of the anchoring strength on the bias-voltage when the (indium-tin-oxide) electrode is covered with a film of polyimide, or it is without any covering. The influence of a charge emission from the electrodes under the bias voltage on the anchoring energy is also analyzed. Possible applications of the observed phenomenon are discussed.

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I. INTRODUCTION

In the framework of the continuum theory, the surface properties of nematic liquid crystals (NLC) are described by a surface energy γ. It takes origin from the reduced symmetry close to the surface, and from the direct interaction between the NLC and the substrate [1]. It is a property of the interface NLC substrate, independent of the thickness of the sample and of the external fields applied to the NLC. It is usually written in the form $\gamma = \gamma_0 + f_s$, where γ_0 is the isotropic surface tension and f_s its anisotropic part. f_s, which is a scalar quantity, is a local property of the interface [2]. It depends on the nematic orientation **n** and on the geometrical normal to the interface in the considered point **k**. In general $f_s = f_s(\mathbf{n} \cdot \mathbf{k})$. The surface orientation for which f_s is minimum is known as easy axis, and indicated by $\mathbf{n}_e$. The curvature around this minimum is called anchoring energy, and indicated by w. Very often f_s is approximated by $f_s = -(1/2)w(\mathbf{n} \cdot \mathbf{n}_e)^2$, proposed by Rapini and Papoular [3].

Long ago it has been observed a thickness dependence of w [4], and interpreted in terms of selective ions adsorption [5]. The influence of the ionic adsorption on the anchoring energy has been invoked also to explain anchoring transitions [6–8] and other surface effects [9–12] in NLC.

The aim of this paper is to propose a theoretical interpretation of the dependence of w on a bias-voltage applied to the NLC sample, ΔV, observed when the electrodes of the nematic cell are covered with WO_3. The experimental data were originally reported by some of the present authors in Ref. [13]. This effect can be rather important for applications, because it gives the possibility to modify the anchoring energy by means of an external field. We will show that the observed phenomenon can be interpreted by taking into account the electrostatic energy connected with the ionic distribution induced by the applied bias-voltage.

Our paper is organized as follows. In Sec. II the experimental technique used to determine the anchoring energy is described. In Sec. III a discussion on the saturation field is reported, and possible interpretations of the phenomenon are analyzed. In Sec. IV a simple model taking into account the ionic distribution induced by the bias presented. The comparison of the experimental data with our model is reported in Sec. V. In the same section we discuss the role of a film of polyimide on the electrodes on the phenomenon, and the case in which the indium-tin oxide (ITO) electrodes are without any covering. The influence of cold emission from the WO_3, induced by the bias voltage, on the anchoring energy is investigated in Sec. VI. Finally, in Sec. VII the main results of our paper are critically analyzed. In Appendix A the general solution of the Poisson-Boltzmann equation for a liquid containing ions, in presence of a bias voltage, is presented, and in Appendix B the case of unipolar emission from the electrodes is considered.

II. EXPERIMENTAL ANALYSIS

The NLC cell consists of two glass-ITO plates covered with a layer of WO_3 deposited by radio-frequency sputtering [14]. The sample plates are fixed at a distance of about 10 μm apart by using Mylar spacers. On the two ITO surfaces two ohmic contacts (with indium-tin alloy) are soldered. The cell was filled with a NLC called BL001 (produced by Merck) with initial planar alignment and oriented in such a way to have maximum transmitted light on a microscope stage between crossed polarizers.

The NLC used in our experimental analysis has $\varepsilon_a = \varepsilon_\parallel - \varepsilon_\perp > 0$, and it is initially in planar orientation, with $\mathbf{n}_e$ parallel to the surfaces of the sample. When an electric field, normal to the surfaces, is applied to the sample, and its amplitude is increased one observes the cascade of orientation transitions: planar→ distorted→ homeotropic, where distorted means that **n** is not constant across the sample, and homeotropic that **n** is perpendicular to the surfaces of the sample. The order transition planar→distorted is the usual

Freedericksz transition, and it takes place at a threshold field E_{th}. The second transition distorted→homeotropic is called saturation transition, and takes place at a saturation field E_{sat} [15].

Upon application of both a dc or ac electric field to the LC samples, the molecules undergo a reorientation which is responsible of the modification of the effective birefringence. The effective birefringence changes can be found out by monitoring the ellipticity e of the transmitted light, which varies between $e=0$ (linear polarization) and $e=1$ (circular polarization).

In our experiments, described in details in Ref. [13], owing to the induced reorientation of the NLC samples the ellipticity of the state of polarization of the transmitted light decreases linearly (high-field regime). The ellipticity starts to decrease from an initial value, which depends on both the cell thickness and the material birefringence, until it drops to zero when all the molecules are aligned homeotropically at the saturation voltage V_{sat}.

To evaluate the saturation voltage V_{sat}, we measured the ellipticity e of the transmitted light as long as the amplitude of the applied alternating voltage is increased. The saturation voltages V_{sat} have been determined by extrapolation for the linear state of polarization of the transmitted light ($e=0$).

To investigate the influence of the ionic charge on the anchoring energy, the experiment has been repeated with a dc voltage bias ΔV (up to 7 V), superimposed to the ac voltage. ΔV was kept fixed during the sweeping of the alternating electric field giving rise to a controlled charge-separation process during the induced molecular reorientation of the NLC sample. The results show a nonmonotonic behavior of the saturation voltage versus the superimposed bias-voltage [13].

In order to confirm this effect we carried out the same investigations on usual symmetric cells ($d \sim 10 \ \mu$m) with the same glass-ITO plates covered with polyimide deposited by spin coating. The polyimide alignment layers have been hardly rubbed to align planarly the NLC slab, filled with the same nematic BL001 by Merck. In this case the saturation voltage is found to be a monotonic increasing function of the bias voltage. The same result has been found when the ITO electrodes are without any covering.

III. SATURATION FIELD

Let us consider a NLC slab of thickness d, planarly oriented in the absence of a distorting field. When an ac electric field **E** is applied along the normal to the surfaces the total energy, per unit surface, of the sample is

$$F = \int_{-d/2}^{d/2} \left(\frac{1}{2} k \phi'^2 - \frac{1}{2} \varepsilon_a E^2 \cos^2 \phi \right) dz + \frac{1}{2} w_1 \cos^2 \phi_1$$

$$+ \frac{1}{2} w_2 \cos^2 \phi_2, \tag{1}$$

where the z axis is normal to the bounding surfaces, at $z = \pm d/2$, ϕ is the angle formed by the NLC director **n** with the z axis, $\phi' = d\phi/dz$, and $\phi_1 = \phi(-d/2)$, $\phi_2 = \phi(d/2)$ are

the surface tilt angles. Equation (1) is valid in the one-constant approximation. Since we are interested in the saturation field, where $\phi \to 0$, $k \sim k_{33}$ [16].

The tilt angle profile is the one minimizing F given by Eq. (1). It is determined by solving the differential equation

$$2\xi^2 \phi'' - \sin(2\phi) = 0, \tag{2}$$

where $\xi = (1/E)\sqrt{k/\varepsilon_a}$ is the electric coherence length, with the boundary conditions

$$2L_1 \phi_1' + \sin(2\phi_1) = 0,$$

$$2L_2 \phi_2' - \sin(2\phi_2) = 0, \tag{3}$$

where $L_i = k/w_i$ are the extrapolation lengths, at $z = \mp d/2$, respectively. For large fields the NLC is close to the homeotropic orientation, where **n** is nearly parallel to z axis. To determine the saturation field corresponding to the stable NLC orientation $\phi(z) = 0$, for $-d/2 \leq z \leq d/2$, we have to consider the solution of Eqs. (2) and (3) in the limit $\phi \to 0$. A standard analysis shows that the homeotropic orientation is stable for $\xi \leq \xi_{sat}$ given by

$$\tanh\left(\frac{d}{\xi_{sat}}\right) = \frac{\xi_{sat}(L_1 + L_2)}{\xi_{sat}^2 + L_1 L_2}. \tag{4}$$

Equation (4) defines the saturation field $E_{sat} = (1/\xi_{sat})\sqrt{k/\varepsilon_a}$. It was deduced long ago by Nehring *et al.* [15] in the symmetric case ($w_1 = w_2$), and generalized by Barberi *et al.* [17] to the nonsymmetric case. If the applied field is larger than the saturation field, for the NLC is more convenient, from the energy point of view, to break the surface alignment, imposed by the treatment, than to support a large distortion localized near the surfaces. If the saturation field is very large with respect to the usual critical field for the Freedericksz transition $d/\xi_{sat} \gg 1$, and consequently $\tanh(d/2\xi_{sat}) \sim 1$ [18]. In this case Eq. (4) becomes

$$\left(\frac{1}{\xi_{sat}} - \frac{1}{L_1}\right)\left(\frac{1}{\xi_{sat}} - \frac{1}{L_2}\right) = 0, \tag{5}$$

whose solutions are $\xi_{sat1} = L_1$ or $\xi_{sat2} = L_2$. It follows that in the limit of relatively strong anchoring energy the saturation field is given by

$$E_{sat} = \frac{1}{\xi_{sat,m}} \sqrt{\frac{k}{\varepsilon_a}} = \frac{1}{L_m} \sqrt{\frac{k}{\varepsilon_a}}, \tag{6}$$

where $\xi_{sat,m}$ is the minimum saturation electric coherence length, and L_m is the minimum extrapolation length between L_1 and L_2.

Equation (6) has been deduced by assuming that the anisotropic part of the surface energy has the form proposed by Rapini and Papoular [3], with easy axis parallel to the substrate. In this case $\phi = 0$ is a maximum and $\phi = \pi/2$ is a minimum of f_s. A simple extension of the calculations presented above shows that the saturation field E_{sat} is given by Eq. (6) even in the more general case, where the Rapini-

Papoular approximation for f_s does not work, but f_s has a maximum for $\phi = 0$. In this situation in Eq. (6) $w = -(d^2 f_s/d\phi^2)_0$, represents the curvature of f_s around its maximum.

Equation (6) shows that the saturation field is fixed by the strongest anchoring energy. Consequently, the experimental data relevant to the reduction of the anchoring energy induced by the bias-voltage cannot be interpreted as a reduction of the anchoring energy only on one surface. Hence a mechanism connected with a unipolar emission stimulated by the bias-voltage, a kind of ''cold emission'' of the WO$_3$, is unable to explain the observed phenomenon. It is, on the contrary, connected with a reduction of the anchoring energy on both surfaces. This point is discussed more in details in Sec. VI.

With our experimental technique we measure the saturation voltage $V_{sat} = E_{sat}d$. With this parameter it is possible to evaluate the strongest anchoring energy w_{max} between the two orienting surfaces by means of Eq. (6). It is given by

$$w_{max} = \frac{\sqrt{k\varepsilon_a}}{d} V_{sat}. \qquad (7)$$

In the following section we discuss the influence of the ions contained in the NLC on the anchoring energy characterizing the interface WO$_3$-NLC.

IV. INFLUENCE OF THE IONS ON THE ANCHORING ENERGY

Let us consider a NLC containing, in thermodynamics equilibrium, n_0 ions per unit volume, of charge q, in the absence of applied voltage. In this situation the NLC is globally and locally neutral. When a slab of NLC of thickness d is submitted to and external voltage, there is a migration of positive ions toward the negative surface and of negative ions toward to the positive surface. In this case the sample is still globally neutral, but locally charged. In our analysis we assume that the adsorption energies for positive and negative ions are the same, and hence there is not selective ion adsorption. We suppose also that the conductivity of the electrode covered with WO$_3$ or polyimide is low enough, in such a manner that it can be considered as a blocking electrode. In this situation, the ionic charges moving toward the surface of opposite sign, give rise to an electrical cloud formed of counterions localized in a surface layer whose thickness is of the order of the Debye's screening length λ, defined by

$$\lambda^2 = \frac{\varepsilon k_B T}{2n_0 q^2}, \qquad (8)$$

where $k_B T$ is the Boltzmann factor and ε is the dielectric constant of the liquid [19]. Since the measurements are performed near to the saturation regime, where the NLC is aligned along the z axis, $\varepsilon \sim \varepsilon_\parallel$. The rigorous analysis of the nematic cell submitted to an external field is presented in Appendix A. In the following we present a naive approach to

the problem, which takes into account the main points of the correct model, and allows an easy understanding of the physics of the phenomenon.

In a very simple analysis we assume that the NLC sample submitted to the dc voltage ΔV can be approximated as two charged surfaces, at $z = \mp d/2$, with a charge densities $\mp\Sigma$, due to the external power supply, and two inner surfaces with charge densities $\pm\sigma$ due to the counterions at $z = \mp(d/2 - \lambda)$ [20]. The electrical potentials of the two surfaces are $\mp\Delta V/2$. In this approximation we have two surface layers of thickness λ, where the electric field is $E_S = \Sigma/\varepsilon$, and a bulk region, in which the electric field is $E_B = (\Sigma - \sigma)/\varepsilon$. In the surface layers there is an excess of electric field given by $\delta E_0 = E_S - E_B = \sigma/\varepsilon$. The quantities Σ, σ, and ΔV are connected by the relation $2E_S\lambda + E_B(d - 2\lambda) = \Delta V$, which can be rewritten in the form

$$(\Sigma - \sigma)d + 2\sigma\lambda = \varepsilon\Delta V. \qquad (9)$$

For low ΔV, the NLC behaves as a conductor. In other words, there is a migration of ions until the bulk field $E_B = 0$. In this range of ΔV the counterions charge density is $\sigma = \Sigma = \varepsilon \Delta V/(2\lambda)$, and the excess of surface electric field is found to be

$$\delta E_{0,low} = \frac{\Delta V}{2\lambda}. \qquad (10)$$

In the opposite limit of large ΔV, all bulk ions are pushed near to the surfaces. The maximum value of the ionic charge density of a given sign is $\sigma_{max} = n_0 q d$. Consequently, in this limit the excess of surface field is

$$\delta E_{0,high} = \frac{n_0 q d}{\varepsilon}. \qquad (11)$$

The critical voltage ΔV_c separating the two regimes is obtained by putting into Eq. (9) $\Sigma = \sigma_{max}$. It is given by $\Delta V_c = 2(n_0 q d/\varepsilon)\lambda$, that taking into account Eq. (8) can be rewritten as

$$\Delta V_c = \frac{k_B T}{q} \frac{d}{\lambda}. \qquad (12)$$

For $\Delta V < \Delta V_c$, δE_0 is given by Eq. (10), whereas for $\Delta V > \Delta V_c$, δE_0 is given by Eq. (11). For all values of ΔV, δE_0 can be approximated by

$$\delta E_0 = \frac{n_0 q d}{\varepsilon} \tanh\left(\frac{\Delta V}{\Delta V_c}\right). \qquad (13)$$

Expression (13) for δE_0 is useful to fit the experimental data. However, the agreement between the model and the experimental data does not depend critically on the form of this expression. In other words a good agreement is obtained also by assuming that for δE_0 the expressions (10) and (11) for $\Delta V \lesssim \Delta V_c$ and for $\Delta V \gtrsim \Delta V_c$, respectively.

Equation (13) holds in the hypothesis that the NLC sample can be approximated as a three-layers system. In the more realistic approximation, where the ionic charge bulk

density is exponentially decreasing with the distance from the surface, the excess of surface field can be supposed of the kind

$$\delta E(z) = \delta E_0 e^{-z/\lambda}, \qquad (14)$$

if a semi-infinite sample is considered [21], or

$$\delta E(z) = \delta E_0 \frac{\cosh(z/\lambda)}{\cosh(d/2\lambda)}, \qquad (15)$$

if the sample has thickness d, as assumed in our analysis. As discussed in Ref. [21] to the excess of surface field it is possible to associate an extra surface energy of electrostatic origin given by $f = f_{el} + f_q$, where, in the exponential approximation,

$$f_{el} = -\frac{1}{4}\varepsilon_a (\delta E_0)^2 \lambda (\cos^2\phi_1 + \cos^2\phi_2), \qquad (16)$$

taking origin from the dielectric anisotropy of the NLC $\varepsilon_a = \varepsilon_\parallel - \varepsilon_\perp$, and

$$f_q = -(e_{11} + e_{33})\delta E_0 (\cos^2\phi_1 - \cos^2\phi_2), \qquad (17)$$

due to the quadrupolar properties of the NLC. In Eq. (17) $e_{11} + e_{33}$ is the total flexoelectric coefficient [22]. By assuming that the anisotropic part of the surface energy is simply given by the Rapini-Papoular form $f_s = (1/2)w\cos^2\phi$, as assumed above, the total anchoring energy is

$$f_{eff} = f_s + f_{el} + f_q = \frac{1}{2}w_{eff,1}\cos^2\phi_1 + \frac{1}{2}w_{eff,2}\cos^2\phi_2, \qquad (18)$$

where the effective anchoring energy strengths $w_{eff,i}$ are given by

$$w_{eff,1} = w_1 - \frac{1}{2}\varepsilon_a(\delta E_0)^2 \lambda - 2(e_{11} + e_{33})\delta E_0,$$

$$w_{eff,2} = w_2 - \frac{1}{2}\varepsilon_a(\delta E_0)^2 \lambda + 2(e_{11} + e_{33})\delta E_0, \qquad (19)$$

in which w_i are the bare anchoring energy strengths, at zero bias-voltage. In our experimental arrangement the two limiting surfaces are the same. Consequently we assume $w_1 = w_2 = w$. For the discussion reported at the end of Sec. III with our experimental technique we measure the strongest anchoring energy. Since $\varepsilon_a > 0$, if $e_{11} + e_{33} < 0$ we measure $w_{eff,1}$, whereas if $e_{11} + e_{33} > 0$, we measure $w_{eff,2}$.

V. COMPARISON WITH THE EXPERIMENTAL DATA

In this section we compare our theoretical predictions with the experimental data. We discuss also the role of a polymer deposited on the electrodes on the observed phenomenon, and the case in which the ITO electrodes are without any covering.

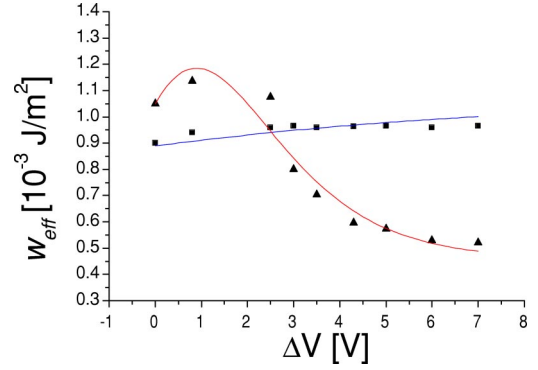In Fig. 1 we show the experimental data relevant to the

FIG. 1. Experimental results relevant to the anchoring energy strength w_{eff} vs the bias-voltage ΔV when the ITO electrodes of the nematic cell are covered with WO_3 (triangles), and polyimide (squares). Continuous curves are the best fits according to the proposed model. The best fits are obtained by fixing the physical parameters of the NLC, since in our investigations it was the same for the two sets of data.

ITO-electrodes covered with WO_3 and the best fit obtained by Eq. (19) rewritten as

$$w_{eff} = w_0 - P_1 \tanh^2(P_2 \Delta V) + P_3 \tanh(P_2 \Delta V), \qquad (20)$$

where

$$P_1 = \frac{1}{2}\varepsilon_a \left(\frac{n_0 q d}{\varepsilon}\right)^2 \lambda, \quad P_2 = \frac{1}{\Delta V_c} = \frac{q}{k_B T}\frac{\lambda}{d},$$

$$P_3 = 2\frac{|e_{11} + e_{33}|}{\varepsilon}n_0 q d, \qquad (21)$$

obtained by assuming for $\delta E_0 = \delta E_0(\Delta V)$ expression (13), and $w_0 = w(\Delta V = 0) = 1.05 \times 10^{-3}$ J/m², as experimentally detected. The parameters of the best fit are

$$P_1 = 1.49 \times 10^{-3} \text{ J/m}^2, \quad P_2 = 0.34 V^{-1},$$

$$\text{and} \quad P_3 = 0.91 \times 10^{-3} \text{ J/m}^2. \qquad (22)$$

Assuming $\varepsilon_a = 14 \times \varepsilon_0$, $\varepsilon = \varepsilon_\parallel = 19 \times \varepsilon_0$, $\lambda \sim 0.1$ μm [23], $|e_{11} + e_{33}| = 2.7 \times 10^{-11}$ C/m [24], and $d \sim 11$ μm, we obtain for the parameters P_1, P_2, and P_3 the values reported above. We note that the value of $\Delta V_c = 1/P_2 \sim 3V$ is comparable with the one deduced by Pagliusi and Cipparrone by means of a direct measurement of the this quantity [25].

Until now the analysis has been performed by assuming that the NLC is not ferroelectric. This means that, although the electric dipole of the molecule forming the mesophase is different from zero, in the absence of an external electric field there is not electric polarization. This result is connected with the equivalence, in the bulk, of **n** with −**n**. As it is known, at an interface the equivalence between **n** and −**n** does not exist any longer, due to the different chemical affinity of the two extremities of the molecules forming the nematic phase with the substrate. In this case close to the homeotropic orientation a surface electric polarization can exist even in the absence of an external field [26]. In our

analysis we have neglected the electrostatic energy connected with this possible surface polarization. However, as discussed in Ref. [20], the connected electrostatic energy is of the order of 10^{-6} J/m^2, i.e., negligible with respect to the other contributions listed above.

When a film of polyimide is deposited over the ITO electrodes the effect of reduction of the surface energy with the bias-voltage disappears. This can be easily explained in the following manner. Let us assume that a film, of thickness d_p and dielectric constant ε_p, is deposited over the ITO electrodes. In this case an analysis of the same kind reported above shows that in the limit of low ΔV the excess of surface electric field is given by

$$\delta E_{0,\text{low}} = \frac{\Delta V}{2\lambda} \frac{\varepsilon_p \lambda}{\varepsilon_p \lambda + \varepsilon d_p}, \qquad (23)$$

whereas in the opposite limit of large ΔV it is

$$\delta E_{0,\text{high}} = \frac{n_0 q d}{\varepsilon}, \qquad (24)$$

as in the absence of the film. Now the critical voltage separating the two regimes is

$$\Delta V_c = 2\frac{n_0 q d}{\varepsilon} \lambda \left(1 + \frac{\varepsilon d_p}{\varepsilon_p \lambda}\right). \qquad (25)$$

Since $\varepsilon \sim 20 \times \varepsilon_0$, $\varepsilon_p \sim 4 \times \varepsilon_0$, for $d_p \sim \lambda$, ΔV_c is of the order of a few tens of volts, i.e., out of the region explored by us. In Fig. 1 we show also the best fit for the data relevant to the ITO-electrodes covered with polyimide. The best fit is obtained by considering w_0 and P_2 as free parameters, because the substrate is changed whereas the liquid crystal is the same as before. The values for best fit are

$$w_0 = 8.7 \times 10^{-4} \text{ J/m}^2 \quad \text{and} \quad P_2 = 0.025 \text{ V}^{-1}. \qquad (26)$$

To the value of P_2 reported above corresponds a $\Delta V_c = 40$ V. From this quantity the thickness of the film is found to be of the order of a few hundreds of nanometer.

We have also performed the same kind of investigations on a NLC cell whose ITO electrodes are without any covering. For this system the anchoring energy has been found independent of the bias voltage. According to our interpretation, in this case the electrodes are no longer blocking, and there is an electric current across the NLC sample [27]. Consequently, when the ions present in the NLC reach the electrodes are neutralized by the injected charges, and the effect of the double layer is strongly reduced, because the screening length is in the molecular scale. Immediate consequence of this non-Debye screening is that the dielectric coupling contribution to the anchoring becomes negligible, and only the flexoelectric one survives, as it follows from Eq. (19). This aspect of the problem is discussed, in a different context, in Refs. [7,8]. Consequently the phenomenon described above gives rise to an effective anchoring energy which is practically independent on the bias voltage, in agreement with our experimental data.

VI. INFLUENCE OF THE ELECTRODES ON THE EFFECTIVE ANCHORING ENERGY

In the model proposed above, the reduction of the effective surface energy is a bulk effect, because the ions are present in the liquid crystal itself. They are not created by the bias, since in our analysis we have assumed that n_0 is independent of ΔV. According to our point of view, the bias-voltage produces a charge separation responsible for the creation of two double layers close to the electrodes.

At first sight, a charge emission from the electrodes under the bias voltage, a kind of cold emission [27], could give the same $w_{\text{eff}} = w_{\text{eff}}(\Delta V)$. However, a deeper analysis shows that this model predicts a behavior of $w_{\text{eff}} = w_{\text{eff}}(\Delta V)$ completely different from the one observed by us with our technique. A simple manner to arrive at this conclusion is the following.

We assume that the WO$_3$ electrodes contains $N_+ = N_- = N$ ions, in the absence of the bias. The negative ions are supposed fixed, whereas the positive charges can move. We indicate with A the extraction energy, in $k_B T$. Let us consider now a sample in the shape of a slab, formed by an insulating liquid limited by two electrodes of WO$_3$. When a bias voltage is applied to the sample, there is an emission of positive charges from the positive electrode. These charges move to the negative electrode, forming a double layer near to it. The thickness of this double layer is of the order of $\ell \sim \sqrt{bd}$, where

$$b = \frac{\varepsilon k_B T}{2 N q^2} \qquad (27)$$

is a new intrinsic length connected with the emission phenomenon, discussed in details in Appendix B. Using for N the value determined in Ref. [28], and assuming $\varepsilon \sim 19\varepsilon_0$, and $d \sim 10$ μm, we have $\ell \sim 0.1$ μm, comparable with the Debye's length used in our numerical estimation. This means that, according to this model, there is one charged layer localized near to the negative electrode. For this double layer we can repeat the discussion reported above on the influence of the localized electrostatic energy on the effective surface energy w_{eff}, whereas the surface energy of the other surface does not change with the bias. In this framework two are the possibilities.

(1). The electrostatics contribution to the surface energy reduces the bare w: $w > w_{\text{eff}}$. In this case, since the anchoring energy is evaluated by measuring the saturation voltage, we are sensible only to the strongest anchoring energy, and hence to w. Consequently, the detectable anchoring energy should be independent of ΔV.

(2). The electrostatics contribution to the surface energy increases the bare w: $w < w_{\text{eff}}$. Repeating step by step previous discussion, we arrive at the conclusion that the detectable anchoring energy should be an increasing function of ΔV.

According to our experimental results, the effective anchoring energy is a nonmonotonic function of ΔV, tending to a saturation voltage smaller than the bare one. From this result we conclude that the mechanism responsible for the observed $w_{\text{eff}} = w_{\text{eff}}(\Delta V)$ is the one connected to the pres-

ence of the ions in the liquid crystal. Probably the electrodes contribute also to the effective anchoring energy, but with our experimental technique we cannot analyze it.

VII. CONCLUSIONS

We have analyzed, experimentally and theoretically, the influence of the bias-voltage ΔV on the anisotropic part of the anchoring energy of a nematic liquid crystal in contact with a substrate, w_{eff}. Experimentally we have observed a rather strong dependence of w_{eff} on ΔV, if ITO electrodes of the nematic cell are covered with WO_3. In this case the dependence of w_{eff} on ΔV is nonmonotonic, and w_{eff} tends to a constant value for large ΔV. On the contrary, w_{eff} is practically independent of ΔV if the ITO electrodes are covered with a film of polyimide, or are without any covering. To interpret the experimental data we have developed a simple model in which the ions dissolved in the liquid crystal are the source of the phenomenon. According to our model, in the absence of the bias-voltage the liquid crystal is globally and locally neutral. When a bias-voltage is applied, the liquid crystal remains globally neutral, but locally charged, due to the charge separation induced by the bias-voltage. In particular, there are two surface layers, whose thickness are of the order of the Debye's screening length, charged near to the electrodes. These charged surface layers are responsible for an excess of electric field localized near the electrodes. The electrostatic energies of the liquid crystal connected to these excesses of electric field can be considered as surface contributions to the energy of the liquid crystal, because Debye's screening length is very small with respect to the thickness of the sample. According to our model, the dependence of the anchoring energy on the bias-voltage is due to the dependence of the electrostatic energy connected with the ions on the bias-voltage. This dependence takes origin from the circumstance that increasing the bias-voltage the ions are pushed close to the electrodes, up to the liquid crystal is without ions in the bulk. The electrostatic interactions between the liquid crystal and the electric field due to the ions distributions are of two kinds. One is connected with the anisotropic part of the dielectric constant, the other one with the quadrupolar properties of the NLC. The first contribution is quadratic, whereas the second one is linear with respect to the excess of electric field of ionic origin.

The observed phenomenon is, in some manner, similar to the dependence of w on the thickness of the sample d, observed long ago by Blinov *et al.* [4]. However, in that case the $w = w(d)$ dependence is connected with a selective ion adsorption [5], whereas in the present case it is connected with the formation of ionic surface clouds induced by the bias-voltage.

In our analysis we have neglected the selective ion adsorption, by assuming that the adsorption energies are the same for the positive and negative ions. But, as it is easy to understand, the effect described by us exists also in the case in which the selective ions adsorption is present. We have assumed that the density of ions in the liquid crystal, n_0, is independent on the bias-voltage, which seems reasonable in the range of bias-voltage considered in our analysis.

We have also studied the effect of a film deposited on the ITO electrodes of the nematic cell on the phenomenon. Our analysis shows that a dependence of w_{eff} on ΔV is expected for bias-voltage larger than the one used in the experimental investigation. The shift toward larger bias-voltage is connected with a reduction of the surface electric field when a film is present. It is simply due to a kind of screening effect.

The same type of investigations performed on a NLC cell whose ITO electrodes are not covered show that the anchoring energy is bias independent. This experimental result has been interpreted taking into account that when the electrodes are not blocking, the surface double layer is strongly reduced, and so the surface electric field responsible for the variation of the anchoring energy with the bias.

Finally we have shown that our experimental data cannot be interpreted by means of a model based on the unipolar injection of charge by one of the electrodes covered with WO_3.

The phenomenon described in our paper looks rather interesting from the application point of view because it gives an indication to reduce the anisotropic part of the anchoring energy.

APPENDIX A

In this appendix we present the rigorous solution of the Poisson-Boltzmann equation of a liquid containing ions, submitted to an external electric field. We will show that, according to the bias-voltage, the liquid behaves as a conductor or as a perfect insulating material. We will give also the critical bias-voltage separating the two regimes.

We assume that there is not selective ion adsorption and that the electrodes are perfectly blocking. In the absence of external electric field the liquid is globally and locally neutral, i.e., $n_+(z) = n_-(z) = n_0$. If ΔV is the difference of potential across the sample due to the external power supply we have, according to Poisson-Boltzmann theory

$$n_{\pm}(z) = n \exp[\mp \psi(z)], \tag{A1}$$

where $\psi(z) = qV(z)/k_BT$ is the electric potential in k_BT/q units and n is the density of ions where $\psi = 0$. Equation (A1) has been obtained by assuming $V(\pm d/2) = \pm \Delta V/2$, i.e., $V(z) = -V(-z)$. In Eq. (A1) $n = n_{\pm}(0)$ has to be determined by imposing the conservation of the number of ions. From Eq. (A1) the bulk density of electric charge is $\rho(z) = q[n_+(z) - n_-(z)] = -2nq \sinh \psi(z)$. A simple calculation shows that

$$\int_{-d/2}^{d/2} \rho(z)dz = -2nq \int_{-d/2}^{d/2} \sinh \psi(z)dz = 0, \tag{A2}$$

as required. The conservation of the number of ions implies that

$$n_0 d = \int_{-d/2}^{d/2} n_+(z)\,dz. \tag{A3}$$

The distribution of $\psi(z)$ across the sample is obtained by solving the Poisson equation $V''(z) = -(\rho/\varepsilon)$, which can be written as

$$\Lambda^2 \psi''(z) = \sinh \psi(z), \tag{A4}$$

with the boundary conditions

$$\psi(\pm d/2) = \pm u = \pm \frac{1}{2} \frac{q\Delta V}{k_B T}. \tag{A5}$$

In Eq. (A4), Λ is the effective Debye screening length of the liquid when the bias-voltage is ΔV. It is given by $\Lambda^2 = \varepsilon k_B T/2q^2 n = (n_0/n)\lambda^2$, where $\lambda^2 = \varepsilon k_B T/(2q^2 n_0)$ is the usual Debye's screening length introduced in the text, see Eq. (8). In the present problem Λ depends on the applied voltage.

From Eq. (A4) we easily obtain

$$\Lambda \psi'(z) = \sqrt{2(\cosh \psi + m)}, \tag{A6}$$

where m is an integration constant. By means of Eq. (A6) we can rewrite Eqs. (A3) and (A5) in the form

$$J(m,u) = \sqrt{2}(d/\Lambda) \quad \text{and} \quad I(m,u) = \sqrt{2}(d\Lambda/\lambda^2), \tag{A7}$$

respectively, where

$$J(m,u) = \int_{-u}^{u} \frac{e^{-\psi}}{\sqrt{\cosh \psi + m}}\,d\psi$$

and

$$I(m,u) = \int_{-u}^{u} \frac{1}{\sqrt{\cosh \psi + m}}\,d\psi. \tag{A8}$$

We obtain

$$I(m,u)J(m,u) = 2(d/\lambda)^2, \tag{A9}$$

which determines $m = m(u)$. When this quantity is known, the effective Debye's screening length is $\Lambda = \sqrt{2}[d/J(m,u)]$.

The above equations indicate that for small bias-voltage the ionic charges screen completely the field due to the external power supply. This is the region of low ΔV considered in the text. The liquid behaves as a conductor: the ions moves until the electric field inside it vanishes. In this case

the electric field is localized close to the bounding surfaces over a thickness of the order of $\lambda = \Lambda(0)$. In the opposite limit of large bias voltage ($u \gg 1$), the ionic charge is localized in a surface layer whose thickness is of the order of $d/(2u)$. A perturbative analysis of Eq. (A4) allows to show [29] that the border between the two regimes is at $u_c \sim d/(2\lambda)$, i.e., at $\Delta V_c \sim (k_B T/q)(d/\lambda)$, as determined in the text in a rough manner [see Eq. (12)].

APPENDIX B

Let us assume that the electrodes contain $N_+ = N_- = N$ ions per unit surface. The negative ions are fixed, and the positive ones are free to move. The extraction energy, in $k_B T$ is A. As in Appendix A, we put $\psi = qV/k_B T$. In the mean field approximation the partition function is

$$Z = e^{A - \psi(-d/2)} + e^{A - \psi(d/2)} + \frac{1}{d} \int_{-d/2}^{d/2} e^{-\psi(z)}\,dz. \tag{B1}$$

The surface and bulk densities of positive ions are then

$$N(-d/2) = 2N \frac{e^{A - \psi(-d/2)}}{Z},$$

$$N(d/2) = 2N \frac{e^{A - \psi(d/2)}}{Z}, \tag{B2}$$

and

$$n(z) = \frac{2N}{dZ} e^{-\psi(z)}. \tag{B3}$$

Poisson's equation reads in the present case

$$\frac{d^2\psi}{dz^2} = -2 \frac{Nq^2}{\varepsilon k_B T} \frac{1}{dZ} e^{-\psi(z)}. \tag{B4}$$

The quantity $b = \varepsilon k_B T/(2Nq^2)$ is an intrinsic length similar to the one introduced in Ref. [7]. By defining $\ell = \sqrt{bd}$ we can rewrite Eq. (B4) in the form

$$\frac{d^2\psi}{dz^2} = -\frac{1}{\ell^2 Z} e^{-\psi(z)}. \tag{B5}$$

This equation shows that in the present case the potential changes over ℓ. From now on the problem is standard, and can be easily solved taking into account the boundary conditions on the potential. This analysis is not important in the present context because, as it has been discussed in the text, the mechanism connected with the electrodes is unable to explain the experimental observations.

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quently the electric coherence length can be written as $\xi=(d/\pi)(E_{th}/E)$, and hence $d/\xi=\pi(E/E_{th})$. For the NLC used in our investigations $k_{11}\sim 11\times 10^{-12}$ N, $k_{33}\sim 17\times 10^{-12}$ N, $\varepsilon_a\sim 14\times\varepsilon_0$. Consequently the threshold voltage $V_{th}=E_{th}d\sim 1.16$ V. Since the saturation voltages are of the order of 150 V, the quantity d/ξ is of the order of 300, and the approximation $\tanh(d/\xi)=1$ works very well.

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