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Non-Debye screening of a surface charge and a bulk-ion-controlled anchoring transition in a nematic liquid crystal

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We study the anchoring mechanism due to substrate-adsorbed ions by examining a related anchoring transition. An analytical solution to the Poisson equation shows that, as their number suffices for a non-negligible anchoring contribution, the surface field is screened over some characteristic microscopic distance. It is shown both theoretically and experimentally that the critical temperature of the transition can be controlled by bulk ion density through its relation to the density of adsorbed ions. [S1063-651X(99)17710-9]

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I. INTRODUCTION

Anisotropic surface tension, called anchoring in the physics of liquid crystals, is a major mechanism for aligning the nematic director. It is characterized by its easy axis, showing the director alignment when any bulk forces are absent, and its strength, showing the energy needed to be spent to cause the director to deviate from this direction. Anchoring is an integral effect due to many forces acting at the nematic interface as a result of the translational symmetry breaking of the infinite medium (see, e.g., reviews [1,2], and references in [3]) that makes identification of a specific mechanism behind the observed phenomenon very difficult. The total balance of these forces manifests itself most distinguishably in anchoring transitions when the easy direction begins to change at some critical temperature T_c. Particularly important for studying anchoring are such transitions where a few dominating forces can be isolated from all other possible forces and thus studied more comprehensively. Recently such a transition was observed in Ref. [3] for a nematic liquid crystal composed of centrosymmetric molecules of p',p-di-n-heptylazobenzene (DHAB) with zero dipole moment on a substrate coated with dimethyldichlorosilane. To provide the coating, the glass plates were dipped in a 10% hexane solution of dimethyldichlorosilane and then washed in distilled water (see [3] for details).

The behavior of the easy direction was found to depend on washing time. In the entire temperature range of a nematic phase ($305.9\ \mathrm{K} < T < 320.4\ \mathrm{K} = T_{NI}$), it was homeotropic for unwashed substrates and tilted for long washed ones; while for some intermediate time, as T increased the homeotropic to tilted anchoring transition occurred at $T_c \simeq 310$ K. Since a correlation was found between the washing time and the presence of ions on the substrates (the longer the washing the less ions accumulated on the substrate), the observed behavior of the easy axis was attributed to ions adsorbed by the substrate [3]. The anchoring strength was estimated to be $(5\text{–}8)\times 10^{-4}\ \mathrm{erg\,cm^{-2}}$.

The anchoring energy f as a function of a small angle θ between the surface normal and the director can be written as

$$f = \frac{1}{2}(\beta_1 S + \beta_2 S^2 + W_i)\theta^2 + O(\theta^4), \tag{1}$$

where β_1 and β_2 are some T-independent coefficients, S is the T-dependent scalar order parameter, and W_i is a T-dependent contribution of ions present in the system. Equation (1) shows that positive terms favor homeotropic state $\theta = 0$, whereas negative terms favor a tilt $\theta \neq 0$.

The form of W_i was proposed in Refs. [4,5]. The idea is that surface-adsorbed ions with surface density n_{ad} produce the electric field $E_S = 4\pi\sigma/\varepsilon$, where $\sigma = n_{ad}q$ is the surface charge density, q is the ion charge, and ε is the dielectric permittivity of the nematic liquid crystal. This field is screened by bulk ions over the distance from the surface given by the Debye length $\lambda_D = \sqrt{\varepsilon kT/8\pi n q^2}$, where n is the bulk ion density and k is the Boltzmann constant. The energy density of the dielectric interaction of the field with the nematic is then $[\varepsilon_a E_S^2/(2\times 8\pi)]\lambda_D\theta^2$ and thus

$$W_{i,D} = \frac{2\pi\varepsilon_a\sigma^2}{\varepsilon^2}\lambda_D, \tag{2}$$

where the subscript D indicates the ion-related anchoring term obtained under the assumption of exponential Debye screening of the surface field [4,5]. Since for the DHAB nematic liquid crystal, $\varepsilon_a > 0$ and $W_{i,D} > 0$, the correlation between washing time and the easy direction observed in [3] can naturally be explained as follows: surface ions are washed off the surface so that, the longer the washing time, the less σ, the smaller $W_{i,D}$, and thus the weaker the homeotropic state. Clear evidence that the transition is ion driven provides an opportunity for experimental and theoretical investigation into the role that different parameters of a bulk nematic phase can play in the ion-induced surface anchoring.

It is known that the exponential Debye screening takes place only in a quasineutral plasma where the uncompensated charge density is very small compared to the density of positive and negative ions, i.e., $|n_+ - n_-| \ll n_+ \simeq n_-$ [6]. In this case, the total numbers N_+ and N_- of positive and negative ions in a liquid crystal cell are much larger than the total number of ions $|N_+ - N_-|$ with uncompensated charge. However, analysis shows that it is a standard situation when $|N_+ - N_-|$, equal to the number of surface-adsorbed ions by

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*Electronic address: vnazaren@iop.kiev.ua virtue of the total neutrality of the surface-nematic system, is at least of the same order as the number of bulk ions N_+ or N_-. In this case, the quasineutrality is violated, and formula (2) should be reexamined.

In this paper we derive a formula for the ion-induced anchoring term W_i, which is valid if the quasineutrality is violated, and report an experimental study of its relation to the density n of the bulk ions. This relation appears in W_i via the dependence of n_{ad} on n [7]. It is found that if n_{ad} is sufficient to produce a non-negligible anchoring contribution W_i, the surface field is screened over some microscopic distance λ_S from the surface, which naturally arises in the problem along with the standard Debye length λ_D. The existence of this length was recently shown in [8]. A strong correlation between critical temperature T_c of the anchoring transition and n is demonstrated experimentally. The ion-induced anchoring term W_i is an exponentially decreasing function of T and thus can play the role of a principal driving force for the observed anchoring transition.

II. NON-DEBYE SCREENING OF A SURFACE ELECTRIC FIELD AND THE ION-INDUCED ANCHORING TERM

Consider a nematic layer normal to the z axis and sandwiched between two identical plane substrates located at $z = \pm d/2$. Let the density of positive and negative bulk ions be $n_+(z)$ and $n_-(z)$, respectively. Since the energy of the electric field is proportional to the distance over which it penetrates in the cell, this distance can be expected to be much smaller than d (this was recently suggested by a numerical result in [9]). Hence at the cell center, $z=0$, the uncompensated charge should be very small, i.e., $n_+(0) \cong n_-(0) = n$, which will be justified *a posteriori* with great accuracy. Then the Poisson equation for the reduced potential $U = q\varphi/kT$ takes the form

$$U'' = \lambda_D^{-2} \sinh U. \tag{3}$$

Since $U(z) = U(-z)$, the boundary conditions to this equation are

$$U'(d/2) = \lambda_S^{-1}, \tag{4}$$

$$U'(0) = 0, \tag{5}$$

where $\lambda_S = \varepsilon kT/4\pi\sigma q$ is a quantity of the dimension of length in addition to the standard Debye length, λ_D. This length, found in [8] from the asymptotic behavior of the electric field in the proximity of surface, is inversely proportional to the number of adsorbed ions n_{ad} and, for $n_{ad} \sim 10^{10}$–10^{11} cm^{-2}, is of order $\lambda_S = 5\times(10^{-6}$–$10^{-7})$ cm. At the same time, for the standard bulk ion density $n \sim 10^{13}$ cm^{-3}, $\lambda_D \sim 3\times 10^{-5}$ cm, which is one or two orders of magnitude larger. Further, integrating Eq. (3) yields

$$U' = \lambda_D^{-1} \sinh \frac{U}{2} = \frac{2\lambda_D^{-1} \exp\left(\dfrac{z+C}{\lambda_D}\right)}{1-\exp\left(\dfrac{z+C}{\lambda_D}\right)}, \tag{6}$$

where C is an arbitrary constant. Combined with Eq. (4) this gives

$$\frac{2 \exp\left(\dfrac{d/2+C}{\lambda_D}\right)}{1-\exp\left(2\dfrac{d/2+C}{\lambda_D}\right)} = \frac{\lambda_D}{\lambda_S} \gg 1. \tag{7}$$

This equation indicates that the denominator is very small and hence $(d/2+C)/\lambda_D \ll 1$. Then expanding the exponents, one has $C = -\lambda_S - d/2$. As a result, boundary condition (5) is satisfied with great accuracy if the cell size is much larger than the Debye length: $U'(0) \simeq 2\lambda_D^{-1}\exp(-d/2\lambda_D) \cong 0$.

For certainty, assume $\sigma>0, q>0$, which corresponds to the experiment described below. Then from Eq. (6), the spatial behavior of the density of negative ions obtains in the form

$$n_- = n \exp U = n\left[\frac{1+\exp\left(-\dfrac{\lambda_S+\Delta z}{\lambda_D}\right)}{1-\exp\left(-\dfrac{\lambda_S+\Delta z}{\lambda_D}\right)}\right]^2, \tag{8}$$

where $\Delta z = d/2 - z$ is the distance from the surface $z = d/2$. The density of the positive bulk ions is $n_+ = n\exp(-U)$. There are three areas where $\exp U$ has a distinguishably different behavior, which can be written as

$$\exp U = \begin{cases} \dfrac{\lambda_D^2}{(\lambda_S+\Delta z)^2}, & 0<\Delta z \ll \lambda_D, \\ 1+\exp\left(-\dfrac{\Delta z}{\lambda_D}\right), & \Delta z \sim \lambda_D, \\ 1, & \Delta z \gg \lambda_D. \end{cases} \tag{9}$$

The first area with the power low screening extends over several λ_S from the surface and, as can be obtained by integration of Eq. (8), contains the uncompensated charge $-\sigma[\Delta z/(\Delta z+\lambda_S)]$. For instance, the subsurface layer of thickness $10\lambda_S$ contains 0.91 of the total bulk charge $-\sigma$ of half of the cell. Here $n_-(z) \gg n_+(z)$, $n_-(0) = \lambda_D^2/\lambda_S^2 \gg n$, $n_+(0) = (\lambda_S^2/\lambda_D{}^2)n \ll n$, which means that the negative ions are attracted to the surface so strongly that thermal energy kT is unable to make this dense layer diffuse. Farther from the surface where the quasineutrality condition $|n_+ - n_-| < n$ is marginally met, there occurs a crossover to the Debye exponential screening, kT is of order or larger than $q\varphi$, and the charged layer is diffusive. Finally, for $\Delta z \gg \lambda_D$ the surface field is completely screened and $n_+(z) \cong n_-(z) = n$. Obviously, the dense layer disappears and the diffusive one begins right at the surface when $\lambda_S \sim \lambda_D$, i.e., for $\sigma \sim \sqrt{\varepsilon nkT/2\pi}$, which gives $n_{ad} \sim 10^9$ cm^{-2}.

To calculate the surface-field–nematic interaction energy $\varepsilon_a \theta^2/8\pi\int_0^{d/2} E^2 dz$ for small angles θ, it is sufficient to note that E^2 behaves as $\exp(U)$, and hence the principal contribution to this integral comes from the dense layer. Then one obtains the ion-induced anchoring term in the form

$$W_i = \frac{\varepsilon_a}{\varepsilon} n_{ad} kT. \tag{10}$$

This term is of order 10^{-4}–10^{-3} erg cm^{-2} for $n_{ad} \sim 10^{11}$–10^{12} cm^{-2}, which agrees with the experimental estimates given below. It is important to note that at the edge of the crossover to the pure Debye regime, when $n_{ad} \sim 10^9$ cm^{-2} and $\lambda_S \sim \lambda_D$, both formulas (2) and (10) predict anchoring of the same negligible order 10^{-6} erg cm^{-2}. We see that adsorbed ions can produce substantial anchoring effects when the screening occurs in the dense layer, whereas the contribution from the diffusive layer can be neglected. As the dense layer is of a molecular scale, applicability of the macroscopic ε_a is questionable and it should be replaced by some effective microscopic quantity $\varepsilon_{a,ef}$ related to an individual polarizability of liquid crystal molecules. Thus the ratio $\varepsilon_a/\varepsilon$ is to be thought of as some effective coefficient of order unity that, nonetheless, is proportional to S similar to ε_a.

III. BULK ION DENSITY AND THE ANCHORING TERM W_i

The term W_i cannot be studied directly, but n_{ad} entering W_i depends on the distribution of positive ions $n \exp(-U)$ [7] and thus on their bulk density n, which can be estimated from experimental data on the conductivity. Let us find n_{ad} as a function of n. According to Stern theory [10], if N_{ad} is the number of sites on the substrate, n_{ad} obeys the relation

$$n_{ad} = \frac{N_{ad} \exp\left(\dfrac{\mu + A}{kT} - U(d/2)\right)}{1 + \exp\left(\dfrac{\mu + A}{kT} - U(d/2)\right)}, \tag{11}$$

where $\mu = \ln[n(2\pi\hbar/kTM)^{3/2}]$ is the chemical potential of bulk (positive) ions with mass M, $\hbar$ is the Planck constant, and $A > 0$ is the energy gained by an absorbed ion. It follows from the first line in Eq. (9) that $\exp[-U(d/2)] = \lambda_S{}^2/\lambda_D^2 = \varepsilon kTn/2\pi q^2 n_{ad}^2$. Substituting this into Eq. (11) and solving the obtained cubic equation with respect to n_{ad} yields

$$n_{ad} = \left(\frac{n^2 N_{ad} p}{3}\right)^{1/2} \left[\left(1 + \sqrt{1 + \frac{27 N_{ad}}{4pn^2}}\right)^{1/3} + \left(1 - \sqrt{1 + \frac{27 N_{ad}}{4pn^2}}\right)^{1/3}\right], \tag{12}$$

$$p = \left(\frac{2\pi\hbar^3}{kTM^3}\right)^{1/2} \frac{\varepsilon}{q^2} \exp\left(\frac{A}{kT}\right). \tag{13}$$

In particular, if $n_{ad} \ll N_{ad}$ the derived $n_{ad} \propto N_{ad}^{1/3} n^{2/3}$, as in Ref. [7], where only the adsorption regime far from the saturation [i.e., when the Fermi-like distribution (11) can be replaced by the Boltzmann one] was considered.

The dependence of n_{ad} on n is even stronger than on N_{ad}, which should manifest itself in anchoring phenomena. Indeed, formula (12) implies that an increase of n results in an increase of W_i and hence in the shifting upward of the critical temperature T_c of the anchoring transition described in the Introduction. In addition, n_{ad} is a decreasing function of T, which contributes to the mechanism of the homeotropic to tilted anchoring transition. Moreover, since the exponential T dependence of n_{ad} is much stronger than that of S (see [11]), the T dependence of W_i can be expected to be dominant for this transition. If the shift $\Delta T_c = T_c(n) - T_c(n_0)$ when the bulk density changes from n_0 to n is small, it can be found from the above formulas.

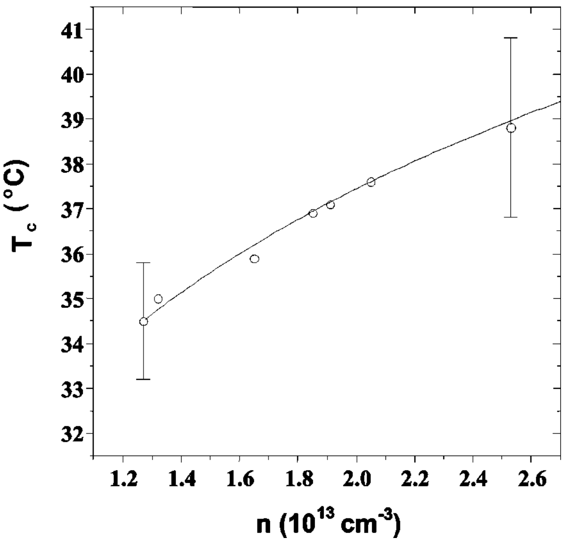

FIG. 1. Critical temperature of the anchoring transition versus effective bulk ion density for seven cells (circles) and the fit (solid line).

The critical condition for the anchoring transition is the vanishing of the expression in brackets in Eq. (1). Neglecting all the T dependences but the exponential one in Eq. (13) and noting that then n_{ad} depends just on $n^2 \exp(A/kT)$, this critical condition reduces to the requirement that $n^2 \exp(A/kT_c) = \text{const}$ along the transition line. This immediately gives

$$\Delta T_c = \frac{2kT_c^2(n_0)}{A} \ln \frac{n}{n_0}. \tag{14}$$

To detect experimentally the tendency predicted by formula (14), several cells were prepared using the method developed in [3]. We used glass plates covered by a S_nO_2 transparent conductive layer. The orienting coating is a result of chemical reaction between the molecules $(CH_3)_2S_iCl_2$ and the glass surface containing S_i-OH groups; this reaction releases hydrogen chloride, which crucially influences the commonly used ITO coating. The cells had the same washing time and differed only by the amount of ionic impurities in the liquid crystal. These impurities were the molecules of thetrabutyl ammoniumbromide added to the DHAB liquid crystal. Dissociating, these molecules give foreign ions. The thickness of all cells controlled by glass microspheres was 20 μm. The concentration of ions n was estimated from measurements of the cell conductivity and effective mobility of all present charges by the method described in [12].

Thus prepared cells exhibited a homeotropic to tilted anchoring transition when the temperature increased. The obtained dependence T_c versus bulk ion density n is shown in Fig. 1 by circles for seven cells. The solid line is the best theoretical fit to this curve using Eq. (14) obtained for $A = 96kT \approx 2$ eV. We took $M = 80$ amu, which corresponds to a plausible dissociation of the impurity whose mass is 252 into the positive ion Br^+ with mass 80 and negative ion with mass 172.

To determine the sign of the adsorbed ions and estimate their density, we performed the following experiment. An asymmetric cell was made, using two different substrates. The first one was covered with dimethyldichlorosilane without additional washing, which corresponds to a large adsorbed charge. The second one was covered with an ordinary polyimide layer that was found to give a planar orientation of DHAB. This planar anchoring was separately measured by the Fréedricksz technique in a 10 kHz ac electric field to be $(2\text{–}10)\times 10^{-4}$ erg cm^{-2}. This value was of the same order as the homeotropic anchoring on the first surface but did not exhibit any significant temperature effect. This implies that n_{ad} on this substrate at worst is of the same order as that on the surface producing the anchoring transition, which enables one to estimate the order of n_{ad}. After assembling and filling, the cell was short-cut via a multimeter. Detecting the direction and the value of current induced by temperature change, we found that it is positive ions that are trapped by the surface in question. Their density estimated by the total charge passed is $n_{ad} = (0.5\text{–}5)\times 10^{11}$ cm^{-2}.

The usual value of the adsorption energy is varied around 1 eV. Calculation with Eqs. (12) and (13) shows that for $A = 96kT$ the adsorption is saturated and $n_{ad} \cong N_{ad}$. This, of course, contradicts the fact that n_{ad} is sensitive to the bulk density n. However, the accuracy in measuring n from which A was deduced is low, whereas n_{ad} is very sensitive to A. For instance, twice smaller $A = 45kT$, which corresponds to an inaccuracy of 50% in A, results in a well undersaturated adsorption regime [the exponent in Eq. (11) is about 0.1]. For $N_{ad} = 10^{13}$ cm^{-2} and $A = 45kT$, one obtains $n_{ad} = (3\text{–}7)\times 10^{-11}$ cm^{-2}, which produces the anchoring term $W_i = (3\text{–}9)\times 10^{-3}$ erg cm^{-2}, as desired. At the same time, the accuracy in estimating A cannot be expected to be higher than 50%. Indeed, the estimates of n from the conductivity data essentially depend on the estimate of the mobility. In our case, both the ''own'' cell ions, brought by the substrate and always present in the liquid crystal, and the ''foreign'' ions, produced by the added impurities, contribute to the mobility. However, the mobility employed in the calculation was effective rather than the differential one. If the differential mobility of the ''foreign'' ions is higher than that of the ''own'' ions, the actual n is lower, which implies a lower value of A. Another factor of reducing A can be a T dependence (decreasing) of the non-ion terms in Eq. (1), which were set constant in our model for simplicity.

IV. CONCLUSION

Solving the Poisson equation, we have predicted the existence of a thin very dense ion layer close to a substrate that adsorbs ions. The thickness of this layer is given by the fundamental length λ_S that naturally arises in the problem of surface charge screening along with the well-known Debye length λ_D. This λ_S is essential for the anchoring related effects, since adsorbed ions can affect anchoring for such n_{ad} that the Debye screening is already not important. The ion-induced anchoring is given by formula (10), and the number of adsorbed ions is given by formulas (12),(13), which generalize the result obtained in [7]. Experimental results on the dependence of the critical temperature T_c of the homeotropic to tilted anchoring transition are in qualitative agreement with our theoretical prediction. They show that T_c can be controlled by the density of ions in the bulk. This throws light on the mechanism of this anchoring transition, which most likely is driven by the exponential T dependence of the ion-induced term.

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