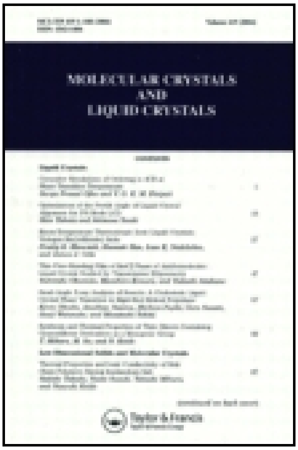

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Non-Debye Charge Screening and Adsorbed-Ion-Induced Anchoring Transition in a Nematic Liquid Crystal

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Anchoring transition mechanism due to substrate-adsorbed ions is studied. It is shown that the surface field is screened by a very dense charged subsurface layer whose thickness λ_S is much smaller than the Debye length λ_D. It is shown both theoretically and experimentally that critical temperature of the transition can be controlled by bulk ion density through its relation to the density of adsorbed ions.

Keywords: ions; adsorption; screening; anchoring

INTRODUCTION

Anchoring is an integral effect due to many forces acting at the nematic interface as a result of translational symmetry breaking of the infinite medium (see, e.g., reviews [1], [2], and Refs. in [3]). 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 are such transitions where a few dominating forces can be isolated and thus studied more comprehensively. Recently such a transition was observed in Ref. [3] for a nematic composed of centrosymmetric molecules of p',p-di-n-heptylazobenzene (DHAB) with zero dipole moment on a substrate coated with dimethyldichlorosilane. To provide

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the coating, the glass plates were dipped in a 10% hexane solution of dimethyldichlorosilane and then washed in a distilled water (see [3] for details).

The easy direction was found to depend on washing time. In the temperature range of a nematic phase ($305.9\text{K} < T < 320.4\text{K} = T_{\text{NI}}$), 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 $T_c \cong 310\text{K}$. Since a correlation was found between the washing time and presence of ions on the substrates (the longer washing the less ions are accumulated on the substrate), the observed behavior of the easy axis was attributed to ions adsorbed by the substrate [3].

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

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

where β_1 and β_2 are some T-independent coefficients, $S(T)$ is the scalar order parameter, and W_i is the contribution of ions present in the system. Eq. (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 Ref. [4]. The idea is that 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 $\varepsilon = \varepsilon_{\parallel} - \varepsilon_a \sin^2\theta$ is the standard permittivity of the nematic. This field is screened by bulk ions over 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 anchoring contribution is then

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

where the subscript D indicates the anchoring term obtained under the assumption of exponential Debye screening [4]. Since for DHAB nematic $\varepsilon > 0$ and $W_{i,D} > 0$, Eq.(2) explains the effect observed in [3] 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. A clear evidence that the transition is ion-driven provides an opportunity for experimental and theoretical investigation of 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 is very small compared to the total charge density of positive and negative ions, i.e., $|n_+ - n_-| << n_+ \approx n_-$. 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 $|N_+ - N_-|$ is equal to the number of surface-adsorbed ions by virtue of 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 quasi-neutrality is violated, and formula (2) should be reexamined.

Here we derive a formula for the ion-induced anchoring term W_i, valid if the quasineutrality is violated, and report an experimental study of its dependence on the conductivity of the nematic sample which is connected to the density n of the bulk ions [5]. It is found that if n_{ad} is sufficient to produce a nonnegligible 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. An existence of this length was recently shown in [6]. 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 a decreasing function of T and thus can play the role of a principal driving force for the observed anchoring transition.

DENSE SURFACE LAYER 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 tends to be much smaller than d. Hence at the cell center $z = 0$, the uncompensated charge should be very small, i.e., $n_+(0) \cong n_-(0) = n$. 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 condition to this equation is $U'(d/2) = \lambda_S^{-1}$, where

$$\lambda_S = \frac{\varepsilon kT}{4\pi\sigma q} \tag{3a}$$

is the length additional to the standard Debye length λ_D. This length, found in [6] from the asymptotic behavior of the electric field in the proximity of surface, is inverse proportional to n_{ad} and, for $n_{ad} \approx 10^{10} - 10^{11}\ cm^{-2}$, is of order $\lambda_S = 5 \times (10^{-6} - 10^{-7})cm$. At the same time, for the standard bulk ion density $n \approx 10^{13} cm^{-3}$, $\lambda_D \approx 3 \times 10^{-5} cm$, which is one or two orders of magnitude larger.

For certainty, assume $\sigma > 0$, $q > 0$, which corresponds to the experiment described below. Then the joint solution of Eq. (3) and the boundary condition gives spatial behavior of the density of negative ions in the form

$$n_- = n \exp U = n \left[\frac{1 + \exp\left(-\frac{\lambda_S + \Delta z}{\lambda_D} \right)}{1 - \exp\left(-\frac{\lambda_S + \Delta z}{\lambda_D} \right)} \right]^2, \tag{4}$$

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

$$n \exp U = n \begin{cases} \dfrac{\lambda_D^2}{(\lambda_S + \Delta z)^2}, & 0 < \Delta z << \lambda_D, \\ 1 + \exp\left(-\dfrac{\Delta z}{\lambda_D} \right), & \Delta z \sim \lambda_D, \\ 1, & \Delta z >> \lambda_D. \end{cases} \tag{5}$$

The first area with the power low screening extends over several λ_S from the surface and contains the uncompensated charge

$-\sigma[\Delta z/(\Delta z+\lambda_D)]$. Here $n_-(z) >> n_+(z)$, $n_- = \frac{\lambda_D^2}{\lambda_S^2} n >> n$, $n_+(0) = \frac{\lambda_S^2}{\lambda_D^2} n << n$, which means that the negative ions are attracted to the surface so strongly that the thermal energy kT is unable to make this dense layer diffuse. Farther from the surface, where the quasi-neutrality condition $|n_+ - n_-| < n$, equivalent to $\Delta z > \lambda_D$, is met, a crossover occurs to the Debye exponential screening, kT is of order or larger than $q\varphi$, and the charged layer is diffusive. Finally, for $\Delta z >> \lambda_D$ 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 $\lambda_S \approx \lambda_D$, i.e., for $\sigma \approx \sqrt{\frac{\varepsilon nkT}{2\pi}}$, which gives $n_{ad} \approx 10^9\ cm^{-2}$.

To calculate the surface field-nematic interaction energy $\frac{\varepsilon_a \theta^2}{8\pi}\int_0^{d/2} E^2 dz$ 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

$$W_i = \frac{\varepsilon_a}{\varepsilon} n_{ad} kT. \tag{6}$$

This term is of order $10^{-3} - 10^{-4} erg \cdot cm^{-2}$ for $n_{ad} \approx 10^{11} - 10^{12} cm^{-2}$ 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 $n_{ad} \approx 10^9\ cm^{-2}$ and $\lambda_S \approx \lambda_D$, both formulae (1) and (6) predict anchoring of the same negligible order $10^{-6}\ erg \cdot cm^{-2}$. We see that if adsorbed ions can produce substantial anchoring effects then the screening occurs in the dense layer, whereas the contribution from the diffusive layer can be neglected.

BULK ION DENSITY AND THE ANCHORING TRANSITION

The term W_i cannot be studied directly, but n_{ad} entering W_i depends on the distribution of positive ions $n\exp(-U)$ [5] and thus on their bulk density n, which can be estimated from experimental data on the conductivity. According to Stern theory [7], if N_{ad} is the number of sites on the substrate, n_{ad} obeys the relation

$$n_{ad} = \frac{N_{ad} \exp\left(\frac{\mu + A}{kT} - U(d/2)\right)}{1 + \exp\left(\frac{\mu + A}{kT} - U(d/2)\right)}, \tag{7}$$

where $\mu \propto \ln n$ is the chemical potential of the bulk (positive) ions, $A > 0$ is the energy gained by an absorbed ion, and $\exp[-U(d/2)] = \frac{\lambda_S^2}{\lambda_D^2} \propto n_{ad}^2 n$, Eq.(5). Then Eq.(7) is a cubic equation with respect to n_{ad}. Its solution [5] shows that an increase of n results in an increase of W_t and hence in the shifting upward of the critical temperature T_c of the anchoring transition [3] described in Introduction. Since n_{ad} is a decreasing function of T and its exponential T-dependence is much stronger than that of S, W_t can be dominant for this transition. If the shift $\Delta T_c = T_c(n) - T_c(n_0)$ is small, it can be found from the above formulas.

The critical condition for the anchoring transition is vanishing of the expression in the bracket in (1). Neglecting all the T-dependencies but the exponential one in (7) and noting that then n_{ad} depends just on $n^2 \exp\left(\frac{A}{kT}\right)$, this critical condition reduces to the requirement that $n^2 \exp\left(\frac{A}{kT_c}\right) = const$ along the transition line. This immediately gives

$$\Delta T_c = \frac{2kT_c^2(n_0)}{A} \ln\left(\frac{n}{n_0}\right). \tag{8}$$

To detect experimentally the tendency (8), several cells were prepared using the method developed in [3]. We used glass plates covered with S_nO_2 transparent conductive layer. The cells had the same washing time and differed only by the amount of ionic impurities - molecules of thetrabutyl ammoniumbromide - added to the liquid crystal. Dissociating, these molecules give additional ions. The thickness of all cells was 20 μm. The concentration of ions n was estimated from measurements of the cell conductivity and effective mobility of all prese

nt charges by method [8].

Thus prepared cells exhibited a homeotropic to tilted anchoring transition when T increased. The obtained dependence $T_c(n)$ is shown in Fig.1 by circles for seven cells. The solid line is the theoretical fit to this curve using (8). This fit is good for $A = 96kT \approx 2\,eV$.

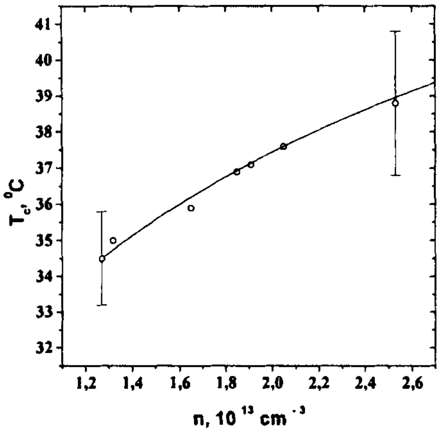

FIGURE 1. Critical temperature T_c of the anchoring transition versus effective bulk ion density n for seven cells (circles) and the fit with formula (8) (solid line).

To find the sign of adsorbed ions and estimate the surface-adsorbed charge 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 polyamide layer which was found to give a planar orientation of DHAB which corresponds to a small adsorbed charge. After assembling and filling, the cell was short-cut via multimeter. Detecting the direction and the value of current with the change of the temperature, we found that it is positive ions that are trapped by the surface in question and estimated their surface density as $n_{ad} \approx 5\times10^{11}cm^{-2}$. Then $W_t \approx 10^{-3}erg\cdot cm^{-2}$ is in accordance with the findings of Ref. [3].

CONCLUSION

We have predicted existence of a thin very dense ion layer close to a substrate with adsorbed ions. The thickness of this layer is given by the fundamental length λ_S which is found to naturally arise 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. The ion-induced anchoring is given by formula (6). Experimental dependence of the critical temperature T_c of the homeotropic to tilted anchoring transition on n is in a qualitative agreement with our theoretical prediction. It is shown that T_c can be controlled by the bulk ion density. This throws the light on the mechanism of the anchoring transition which most likely is driven by the T-dependence of the ion-induced term.

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