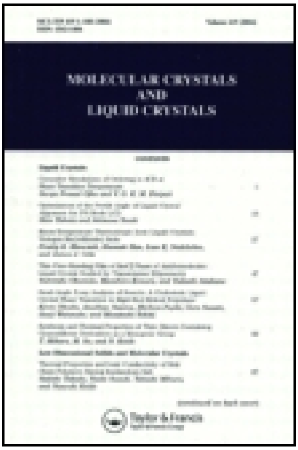

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Polar Surface Interactions Vs. Long Range Interactions in the Problem of Nematic Anchoring

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Polar Surface Interactions Vs. Long Range Interactions in the Problem of Nematic Anchoring

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A complete theory of surface nematic anchoring was developed earlier, including steric, dielectric, flexoelectric, and notably, surface polarization coupling mechanisms. In the last three cases surface electric field due to the adsorption of surface charges on the substrates is of ultimate importance. The extent of penetration of surface electric field inside a nematic is shorter than believed, due to the important surface screening. This leads to a substantial dehancement of dielectric coupling.

Surface polarization, due to the biphilic character of the short-range interaction of asymmetric nematic mesogens with the substrates, can be parallel or antiparallel to the surface electric field. This amounts to a stabilization or a destabilization of the anchoring. Based on the general theory the nonmonotonic behavior of anchoring energy of 5CB on LB films of DPPC with variable surface density is rationalized.

Keywords: surface polarization; surface field; LB films; DPPC; 5CB

INTRODUCTION

The role of surface polarization of nematic layers was first recognized long time ago in connection to some electrostructural transitions, notably flexoelectric ones[1-5]. Its origin was related to the biphilic asymmetry of nematic molecules (of dipolar type) and to the biphilic field of a surface, hydrophilic or hydrophobic one[3, 6, 7]. By orienting biphilic dipoles of nematogens, this short-range biphilic surface field simultaneously orients the electric dipoles of the molecules, and creates in this way an electrically polarized monolayer of nematic molecules. Furthermore, the diffusion of oriented molecules from the surface towards the bulk leads to a penetration of the orienting action over some additional molecular lengths[3,5]. As a result, surface polarization of homeotropic layers of strongly polar nematics like cyanobiphenyls can be estimated as about $1 \cdot 10^{-10}$ C/m. An electrooptic effect, essentially due to surface polarization, was reported[8].

Recently, surface polarization was also included in a general theoretical framework comprising various aspects of nematic anchoring on LB films, as a manifestation of the biphilic aspect of anchoring[9]. Its effect on some surface instabilities was briefly discussed.

The present work is motivated by some recent experiments providing first quantitative measurements of the strength of anchoring (using magnetic Fréedericksz transition) of a cyanobiphenyl nematic, 5CB, on a LB film of DPPC, as a function of LB film packing density[10]. These experiments demonstrate a non-monotonic behavior of the anchoring energy and can only be rationalized if a destabilizing action of the surface polarization is properly taken into account.

THEORY

Along with the surface polarization, an important factor is the surface electric field. It may arise as a result of the selective adsorption of one type of ions over the substrates confining LC layer[11, 12], or may be due to the charges carried by the polar group of surfactants deposited over the substrates[13,14, 10].

In this work we underline the importance of the screening of the surface field by the *own* counterions of the surface charges, which by far exceeds the effect of bulk screening. The screening by the ions present in the bulk of a weak electrolyte (i.e., the liquid crystal) is well known and sufficiently well described by the Debye-Hückel theory[21]. The limit of vanishing bulk ion concentration n_∞ (far from the walls) is less familiar (cf. also[20] in this respect).

We take the limit $n_\infty \to 0$, i.e. $\psi_0 \to \infty$ of the Gouy-Chapman solution of the non-linear Poisson-Boltzmann equation (Eq.(12.39) in[21]) and of the Grahame equation (Eq.(12.30) in[21]). In this way we obtain the distance dependence of the surface field with no bulk screening in the following, *not very common*, form:

$$E(z) = \frac{\sigma}{\varepsilon\,\varepsilon_o}\frac{1}{1+\left(z/\lambda_S\right)} = \frac{E_o}{1+\left(z/\lambda_S\right)}, \qquad \lambda_S = \frac{2\varepsilon\varepsilon_o k_B T}{q_e\sigma} \tag{1}$$

where z is a coordinate, normal to the substrate plane, σ is the surface charge density, ε is an appropriate dielectric constant of the liquid crystal (e.g.,$\varepsilon_{//}$ for a homeotropically oriented LC), ε_o is the absolute dielectric permittivity of free space, and λ_S is a characteristic length of surface screening, where q_e is the proton charge and $k_B T$ is the thermal energy. If we assume even a very low surface charge density of one elementary charge per 500 nm^2, we see that in pure materials surface screening is much more important than the bulk one, even at such very low surface charge values: under the same conditions λ_S = 14 nm, while the bulk Debye screening length is λ_D = 580 nm [11]!

Now, with a surface field in the form of Eq.(1) we can get from[9] for the surface energy function the following expression:

$$F_{surf} = \frac{1}{2}\left(\frac{1}{2}\lambda_S\Delta\varepsilon\varepsilon_o E_o^2 + eE_o + W_o\right)\sin^2\theta_s - P_S E_o\cos\theta_s, \tag{2}$$

where $\Delta\varepsilon$ is dielectric anisotropy of the liquid crystal, $e\ (=e_{1z}+e_{3x})$ is its total flexoelectric coefficient, P_S is the surface polarization and θ_s is the angle between the surface director and the substrate normal (z-direction). The importance of surface electric field coupling to dielectric anisotropy of LC was experimentally demonstrated by Blinov et al.[13, 14] and by Nazarenko and Lavrentovich[15]. However, we noted above that $\lambda_S \ll \lambda_D$, even for low surface charge density. Therefore, the numerical value of the dielectric term needs to be reconsidered.

The magnetic deformation of a LC layer (of thickness d) was described by minimization of the free elastic energy functional containing surface terms. The surface energy was assumed to have the *non*-Rapini-Papoular form of Eq.(2) (cf. Ref.16) with W_S from the brackets of Eq. (2). Elastic and magnetic energy densities have their familiar form (with two elastic constants).

Integration of the corresponding Euler-Lagrange equations for the function $\theta(z)$ under the constraint of the (symmetric) boundary conditions leads to:

$$\frac{1}{\kappa}\frac{H}{H_S} = \frac{2}{\pi}\int_0^{\psi(\theta_s)}\sqrt{\frac{\cos^2\psi + \eta\sin^2\theta_s\cos^2\theta}{\cos^2\psi - \sin^2\theta_s\cos^2\theta}}\,d\theta\,, \tag{3}$$

where

$$\psi(\theta_s) = \arctan\left[\frac{H_S}{H}\frac{\cos\theta_s + \dfrac{P_S E_0}{W_S}}{\sqrt{1 + \eta\sin^2\theta_s}}\right], \tag{4}$$

and

$$\eta = \frac{K_{11} - K_{33}}{K_{33}},\ \kappa = \frac{\pi K_{33}}{W_S d},\ H_F = \frac{\pi}{d}\sqrt{\frac{K_{33}}{\mu_0 \chi_a}},\ H_S = \frac{H_F}{\kappa} = \frac{W_S}{\sqrt{\mu_0 \chi_a K_{33}}},$$

where K_{33} is the bend elastic constant, K_{11} is the splay elastic constant, χ_a is the diamagnetic anisotropy and μ_0 is the absolute magnetic permittivity of free space.

For any given values of anchoring strength W_S and surface polarization energy $P_S E_0$, Eq. (3) provides a relationship between θ_s and the ratio of the applied magnetic field H to the ideal Fréedericksz threshold H_F, which is the threshold field for infinitely strong anchoring and vanishing surface polarization energy. Eq. (3) was solved numerically[22] with χ_a taken from[18].

Surface angles as a function of field for a number of $\tilde{p}$ values ($\tilde{p} = P_S E_0 / W_S$), positive, resp. negative ones were also calculated[22]. With a stabilizing, i.e. $\tilde{p} > 0$ term, the double threshold character of the $\theta_S(H/H_S)$ curve for $\tilde{p} = 0$ is completely changed, and the approach to saturation becomes asymptotic, with horizontal tangent. Actually, saturation field now tends to infinity, however small $\tilde{p}$ is. Moreover, surface angles for the same field are decreasing with increasing $\tilde{p}$. On the contrary, these are increasing for a destabilizing, $\tilde{p} < 0$ term. At a certain value of θ_s (decreasing with increasing absolute value of $\tilde{p}$) the orientation changes with a jump to the saturated value $\theta_s = 90°$. At this point a change of the order of the transition from 2nd to 1st one takes place. The threshold field is a decreasing function of $|\tilde{p}|$ until at $\tilde{p} = -1$ the transition does not require an external field any more and we arrive at the surface instability of Ref. 9.

We wish to stress that under usual conditions the deviations from the Rapini-Papoular form of surface energy close to the threshold may be insignificant, and experiments limited to relatively low deformation angles would then provide an effective value of the anchoring energy, containing also surface polarization term which may feature a minimum under destabilizing conditions. Indeed, in the small angle limit Eq. (2) simplifies to:

$$F_{surf} = \frac{1}{2}\left(\frac{1}{2}\lambda_S \Delta\varepsilon\varepsilon_0 E_0^2 + eE_0 + P_S E_0 + W_0\right)\theta_s^2 = \frac{1}{2}W_S^{eff}\theta_s^2 \tag{5}$$

EXPERIMENTAL

Precise numerical values of the anchoring energy are of considerable interest both for surface liquid crystal physics and for technical applications. However, in dependence of various experimental methods for measurement and surface preparation techniques anchoring energy values may vary by orders of magnitude[17]. In addition, these values for strong anchoring case depend critically on LC cell parameters, in contrast to the case of weak anchoring. For example, a small variation in parameters like cell thickness or bulk elastic constants results in a dramatic change in the value of anchoring energy extracted from the same experimental data set. Therefore, we prepared an extended set of 15 LC cells differing in thickness and surface density of orienting LB films from DPPC (from 1.05 to 1.40 mol/nm^2). The dependence of anchoring energy on surface density and temperature was found by taking into account *all* samples of this set. The experimental procedure and some of our experimental results (for room temperature) were reported earlier[10].

We fitted the optical retardation curves of the Fréedericksz transition, minimizing the difference between experiment and theory (based on Eqs. 3 and 4, where explicit P_S term is neglected for simplifying the fit, since applied magnetic fields are close to the threshold) of a number of LC cells by variation of K_{33} and K_{11} for *all* the cells and by separate variation of d (within its error limits from crystal rotation method) and W_S^{eff} for every *single* cell (Table 1).

In order to discuss the density dependence of W_S^{eff} in terms of the coupling model of surface polarization to surface electric field, we need to explicitly relate these two surface properties to the monolayer lipid density n_{LB}. Most simple is then to assume that each lipid molecule carries a charge $\beta\, q_e$, where β (<<1) is the partial charge per lipid head. Additionally, we can take into account the possible desorption of a small proportion of lipids, $(1-\alpha)$, from the surface after filling the cell with 5CB, so that the actual number of lipids left is $\alpha\, n_{LB}$. In such a case surface electric field (close to the homeotropic-planar threshold) will be:

$$E_o = \frac{\alpha\,\beta\,q_e}{\varepsilon_{//}\varepsilon_o} n_{LB}\,. \tag{6}$$

The area dependence of surface polarization we shall model, following the "hole concept" [23-25] with the following Ansatz:

$$P_S = P_{S0}\left(1 - \alpha\, n_{LB}/n_{LB}^{\max}\right). \tag{7}$$

where $n_{LB}^{\max}$ is the maximum lipid density at close packing (in our case $n_{LB}^{\max} = 2.22 \cdot 10^{18}\ \mathrm{m}^{-2}$, corresponding to a minimum area of 0.45 nm^2 from the DPPC isotherm). In this way surface polarization is linearly related to the total hole area, available for 5CB molecules to penetrate. With Eqs. (6) and (7) in mind, Eq. (5) then takes the form:

$$W_S = W_o + (\Delta\varepsilon\varepsilon_o k_B T/q_e + e + P_{S0})An_{LB} - P_{S0}\alpha\, An_{LB}^2/n_{LB}^{\max} \quad (8)$$

where $A = \alpha\beta q_e/\varepsilon_{//}\varepsilon_o$. Eq. (8) represents a parabola with a minimum at

$$n_{LB}^{\min} = \frac{n_{LB}^{\max}}{2\alpha}\left(1 + \frac{e + (k_B T/q_e)\Delta\varepsilon\ \varepsilon_o}{P_{S0}}\right), \quad (9)$$

providing that $\mathrm{sign}(P_{S0}\beta) = -1$, i.e. that the surface field and the polarization are oppositely directed with respect to one another. With a cyanogroup of 5CB molecule facing the surface, polarization will be oriented like surface normal, i.e. in positive direction; this means that $\beta < 0$, i.e. the surface charge must bear a negative sign.

P_{S0} could be estimated from the longitudinal dipolar moment of 5CB, $16.3 \cdot 10^{-30}\ \mathrm{C.m}$ [26] or $21.6 \cdot 10^{-30}\ \mathrm{C.m}$[27] and the cross section area of an erected 5CB molecule, 0.4 nm^2 (the collapse area of a pure 5CB monolayer on water/air interface[28]) as $4 \cdot 10^{-11}\ \mathrm{C.m}$. To account for the larger than a monolayer thickness of surface polarized layer due to a diffusion of the oriented molecules inside the bulk within about three molecular lengths[3, 5], we can triple this value and arrive at $P_{S0} \approx 1 \cdot 10^{-10}\mathrm{C.m}$. If we then neglect the smaller second term in the brackets of Eq. (9) we can calculate the desorption coefficient from the position of the minimum. Finally, from the parabola's curvature, the partial charge per head β can be calculated.

The results from a second order polynomial regression of W_S^{eff} data are given in the Table 1. Bulk elastic constants show a decrease with temperature that is familiar for a NLC (let us note, that our K_{ii} values are slightly higher than the literature ones, but in general higher values are more reliable than lower ones). In contrast, surface parameters (apart form the absolute values of W_S) are rather constant in this temperature interval, demonstrating the dominance of surface forces over the bulk ones. Indeed, for example desorption coefficients show that only 5% of the deposited molecules are actually desorbed in the bulk of the liquid crystal. Moreover, the temperature-independent position $n_{LB}^{\min}$ of the W_S minimum justifies the estimation

TABLE 1. Bulk elastic constants of 5CB and surface anchoring parameters of 5CB on an LB film of DPPC. $W_S^{\min}$ and $n_{LB}^{\min}$ are fitted parameters of anchoring energy minimum, α is desorption coefficient and β is partial charge per lipid head.

T, °C	K_{33}, pN	K_{11}, pN	$W_S^{\min}$, μJ/m^2	$n_{LB}^{\min}$, nm^{-2}	α	β
23	10.1	8.1	44	1.18	0.94	−0.082
25	9.3	7.8	37	1.17	0.95	−0.058
27	8.3	7.2	32	1.17	0.95	−0.078
29	7.4	6.6	26	1.17	0.95	−0.032
31	5.8	6.2	22	1.16	0.96	−0.036
33	4.8	4.6	20	1.17	0.95	−0.032

$P_{S0} \approx 1\cdot 10^{-10}$C.m, permitting to neglect the second term in the brackets of Eq. (9); with a lower P_{S0} the temperature dependencies of e and $\Delta\varepsilon$ would have shown up.

The values for the partial charge of DPPC could be favorably compared to some recent findings[29, 30], indicating that the PC head group, although zwitterionic, is weakly negatively charged.

CONCLUSIONS

We have shown that taking into account surface polarization and its coupling to surface electric field leads to a non-standard surface energy term, which, under destabilizing geometry can modify in a non-trivial way the magneto-structural transition in homeotropic NLC layers.

We presented here first quantitative measurements of anchoring energy of a nematic liquid crystal on a LB film in dependence of film packing density, demonstrating a non-monotonic behavior of anchoring and a minimum of anchoring energy. The appearance of such a minimum was rationalized as mainly due to an electric coupling between surface field and surface polarization of the nematic, both being dependent on LB film surface density. Partial desorption of LB film molecules into NLC was also accounted for.

Relative temperature stability of anchoring parameters, established by our experiments, may be of substantial practical interest. Very few examples about practical application of surface polarization in nematic displays are known until now[19]. Our results may initiate further activity in this area, leading to new concepts of surface-driven displays.

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