Surface polarization and effective anchoring energy in liquid crystals

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The influence of the surface polarization (SP) on the effective anchoring energy for both homeotropic and planar alignments of polar liquid crystals at a solid substrate is discussed from the energy point of view. It is shown that in a certain range of surface charge density the destabilizing SP mechanism may lead to destruction of the homeotropic or planar alignment of liquid crystalline molecules, such as 4-n-pentyl-4'-cyanobiphenyl.

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Textures of nematic liquid crystals (NLCs) are produced by orienting a drop of bulk material between two surfacetreated plates, which usually define a fixed orientation for the boundary molecules. When examining NLCs in the bulk, their properties are characterized by the average molecular orientation $\hat{\mathbf{n}} = \langle \hat{\mathbf{a}} \rangle$, called the director, and the fluctuation of the molecular orientation $\hat{\mathbf{a}}$ with respect to $\hat{\mathbf{n}}$ is expressed by the order parameter (OP) $\overline{P}_2 = \frac{3}{2}(\langle \hat{\mathbf{n}} \cdot \hat{\mathbf{a}} \rangle^2 - \frac{1}{3})$, where $\langle \cdots \rangle$ denotes the statistical average. The states of the director $\hat{\mathbf{n}}$ and $-\hat{\mathbf{n}}$ are indistinguishable, and the ordering is defined by a traceless OP tensor having a quadrupolar structure [1]

$$Q_{ij} = \frac{3}{2} \overline{P}_2 \left(\hat{\mathbf{n}} \hat{\mathbf{n}} - \frac{1}{3} I \right), \tag{1}$$

where $\hat{\mathbf{n}}\hat{\mathbf{n}}$ is a dyad and *I* is a unit tensor. In the vicinity of a solid substrate there is a well defined direction called the easy axis $\hat{\mathbf{n}}_0$, which minimizes the anisotropic part of the surface energy of the two media in contact [2]. For a small deviation of the surface director $\hat{\mathbf{n}}_s$ from $\hat{\mathbf{n}}_0$, the surface energy may be written in the form [3]

$$f_0 = -\frac{1}{2} w_0 (\hat{\mathbf{n}}_s \cdot \hat{\mathbf{n}}_0)^2 = -\frac{1}{2} w_0 \cos^2(\theta_s - \theta_0), \qquad (2)$$

where w_0 is the anchoring strength and θ_s and θ_0 are the polar angles of $\hat{\mathbf{n}}_s$ and $\hat{\mathbf{n}}_0$, respectively. In the past few years, for both fundamental and display application reasons, there has been increasing interest in studying the anchoring properties on different solid substrates [2]. Polymers such as polyamide are found to produce the planar orientation (nematic director parallel to the surface) [4], whereas amphiphilic molecules such as lecithin [5] or silane [6] yield the homeotropic orientation (nematic director perpendicular to the surface). More recently, a nonmonotonic behavior has been observed for the anchoring energy of a monolayer deposited with the Langmuir-Bladgett (LB) technique while varying its surface charge density [7]. In spite of the interest in getting precise numerical values of anchoring energy, measurements of this quantity may vary by orders of magnitude depending on the boundary substrates, essentially indium tin oxide (ITO) glass plates coated with organic materials. The surface energy f_0 must depend both on the properties of the equilibrium bulk nematic system [8] and on the way the surface interacts with the bulk. This energy is delocalized over a thin bulk layer of thickness λ_s (of the order of 10 nm [9]) close to a substrate. When the solid substrate is in contact with the nematic, selective ion adsorption takes place. For instance, the positive ions are attracted by the substrate, whereas the negative ones are repelled. In this case, the surface electric field E_0 , originating from surface charge density σ , will penetrate the bulk on the order of the Debye screening length λ_D [10], due to ions present in the bulk of the liquid crystal (a weak electrolyte). The distance dependence of the surface electric field with bulk screening is given by [10]

$$\mathbf{E}(z) = E_0 \exp\left(-\frac{z}{\lambda_D}\right) \hat{\mathbf{k}},\tag{3}$$

where $E_0 = \sigma/\epsilon_0 \overline{\epsilon}$ is the surface electric field of the charged plane, ϵ_0 is the absolute dielectric permittivity of free space, $\overline{\epsilon} = (\epsilon_{\parallel} + 2\epsilon_{\perp})/3$ is the average dielectric permittivity, ϵ_{\parallel} and ϵ_{\perp} are the dielectric constants parallel and perpendicular to the director $\hat{\mathbf{n}}$, respectively, and $\hat{\mathbf{k}}$ is a unit vector directed away from and perpendicular to the substrate. The electric field given by Eq. (3) has, therefore, an orienting effect on the NLC, and the related dielectric energy per unit area has been shown to be [11]

$$f_{el} = \int_0^\infty F_{el}(z) dz = -\frac{1}{4} \epsilon_0 \epsilon_a E_0^2 \lambda_D \cos^2\theta, \qquad (4)$$

where $F_{el}(z)$, the dielectric energy density, is simply given by

$$F_{el}(z) = -\frac{1}{2} \epsilon_0 \epsilon_a (\mathbf{E} \cdot \hat{\mathbf{n}})^2, \qquad (5)$$

 $\theta = \cos^{-1}(\hat{\mathbf{n}} \cdot \hat{\mathbf{k}})$ is the angle between the surface director and the substrate normal, and $\epsilon_a = \epsilon_{\parallel} - \epsilon_{\perp}$ is the dielectric anisotropy of the NLC. Moreover, when the mirror symmetry is broken at the substrate, a surface polarization \mathbf{P}_s may arise perpendicular to the surface. The microscopic reason for this polarization might be preferential asymmetric attachment of

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dipolar molecules to the surface, ion adsorption, or spatial dependence of the nematic OP $\overline{P}_2(z)$ (the so-called ordoelectric polarization [12])

$$\mathbf{P}_{s} = r_{1} [\mathbf{\hat{n}} \cdot \boldsymbol{\nabla} \bar{P}_{2}(z)] \mathbf{\hat{n}} + r_{2} \boldsymbol{\nabla} \bar{P}_{2}(z), \qquad (6)$$

where r_1 and r_2 are ordoelectric coefficients. In the quadrupolar approximation, the surface (ordoelectric) polarization takes the form [13,14]

$$\mathbf{P}_{s} = \frac{3}{2} e^{*} \boldsymbol{\nabla} \bar{P}_{2}(z) \cdot \left(\hat{\mathbf{n}} \hat{\mathbf{n}} - \frac{1}{3} I \right), \tag{7}$$

where e^* is the quadrupolar coefficient of the nematic. Surface polarization arises in a thin surface layer λ_s for any (planar, homeotropic, or oblique) alignment of a liquid crystal [15]. Despite the fact that the concept of surface polarization has been discussed for many years, quantitative data on the surface polarization remain scarce. Experiments on optical second-harmonic generation from a solid-LC interface [16,17] can probe the surface polarization, whose sign and magnitude are, nevertheless, controversial. Although the difference in direction of the \mathbf{P}_s vector for homeotropic and planar alignments follows, of course, from the dipolar nature of the surface layers [15], it can also be explained in the framework of the ordoelectric polarization model [Eq. (7)]. By putting the director normal to the substrate and on the xzplane to give $\hat{\mathbf{n}} = (\sin \theta, 0, \cos \theta)$, and by integrating over the z component of the \mathbf{P}_s vector $P_s \hat{\mathbf{k}}$, one has

$$\langle P_s^z \rangle = \int_0^\infty \frac{3}{2} e^* \frac{d\bar{P}_2(z)}{dz} \left(\cos^2 \theta - \frac{1}{3} \right) dz$$
$$= \frac{3}{2} e^* \left(\cos^2 \theta - \frac{1}{3} \right) \Delta \bar{P}_2, \tag{8}$$

where $\Delta \bar{P}_2 = \bar{P}_{2,b} - \bar{P}_2(0)$, and $\bar{P}_{2,b}$ and $\bar{P}_2(0)$ are the bulk and surface OPs, respectively. For the homeotropic alignment (θ =0), $\langle P_s^z \rangle_h = e^* \Delta \bar{P}_2$, whereas for the planar one ($\theta = \pi/2$), $\langle P_s^z \rangle_p = -\frac{1}{2}e^* \Delta \bar{P}_2$. Since the quadrupolar coefficient e^* and the flexoelectric coefficients e_1 and e_3 related to the splay and bend distortions of the NLC [18] are connected by the simple relationship [19]

$$e^* = \frac{e_1 + e_3}{3\bar{P}_2(z)},\tag{9}$$

the following expressions for the *z* components of the \mathbf{P}_s vector are obtained: $\langle P_s^z \rangle_h = e_+ \Delta \overline{P}_2 / 3 \overline{P}_2(z)$ and $\langle P_s^z \rangle_p = -e_+ \Delta \overline{P}_2 / 6 \overline{P}_2(z)$. Here $e_+ = e_1 + e_3$. Hence, in the case of $e_+ < 0$ and homeotropic alignment, \mathbf{P}_s is parallel to $\hat{\mathbf{k}}$ when $\overline{P}_2(0) > \overline{P}_{2,b}$ (i.e., strong anchoring with $\Delta \overline{P}_2 < 0$), while \mathbf{P}_s is antiparallel to $\hat{\mathbf{k}}$ when $\overline{P}_2(0) < \overline{P}_{2,b}$ ($\Delta \overline{P}_2 > 0$). The latter case is seen in 4-*n*-pentyl-4'-cyanobiphenyl (5CB) [15], corresponding to the orientation of 5CB molecules with their hydrophobic tails attached to the substrate. The orientation of the surface polarization vector \mathbf{P}_s for a planar alignment is

the reverse of that for a homeotropic one: when $e_+<0$ and $\Delta \bar{P}_2 < 0$, one has \mathbf{P}_s antiparallel to $\hat{\mathbf{k}}$, whereas for $\Delta \bar{P}_2 > 0$ one has \mathbf{P}_s parallel to $\hat{\mathbf{k}}$. In the case of an oblique alignment $(0 < \theta_{tilt} < \pi/2)$, the orientation of the surface polarization vector \mathbf{P}_s may switch direction at the critical value $\theta_{tilt} = \cos^{-1}(1/\sqrt{3})$ depending on other factors in Eq. (8).

Now the surface polarization takes the form

$$\mathbf{P}_{s} = A \,\hat{\mathbf{k}}_{1} \cdot \left(\,\hat{\mathbf{n}}\hat{\mathbf{n}} - \frac{1}{3}I \right) = A \,\xi \left[\frac{1}{2} \sin(2\,\theta) \,\hat{\mathbf{i}} + \left(\,\cos^{2}\theta - \frac{1}{3} \right) \hat{\mathbf{k}} \right], \tag{10}$$

where $A = [e_+(z)/2][d \ln \overline{P}_2(z)/dz]$, $\hat{\mathbf{k}}_1$ is a unit vector that defines the direction of the surface polarization, and $\hat{\mathbf{i}}$ is a unit vector perpendicular to $\hat{\mathbf{k}}$. The coefficient $\xi = 1$ when $\hat{\mathbf{k}}_1$ is parallel to $\hat{\mathbf{k}}$ and $\xi = -1$ when $\hat{\mathbf{k}}_1$ is antiparallel to $\hat{\mathbf{k}}$. In the simplest case of the electric field $\mathbf{E}(z) = E(z)\hat{\mathbf{k}}$, the surface polarization energy per unit area can be obtained by integrating the linear term

$$F_{surf}(z) = -\mathbf{P}_s \cdot \mathbf{E}(z) \tag{11}$$

to give

$$f_{surf} = \int_0^\infty F_{surf}(z) dz = -\frac{e_+}{2} E_0 J(\lambda_D) \xi \cos^2 \theta + \text{const},$$
(12)

where

$$J(\lambda_D) = \int_0^\infty \frac{d\ln \bar{P}_2(z)}{dz} \exp\left(-\frac{z}{\lambda_D}\right) dz$$
$$= -\ln \bar{P}_2(0) + \frac{1}{\lambda_D} \int_0^\infty \ln \bar{P}_2(z) \exp\left(-\frac{z}{\lambda_D}\right) dz.$$

In Eq. (12), the flexoelectric coefficient $e_+(z)$ in the vicinity of the surface has been assumed to change weakly in comparison with the spatial variations of the OP $\overline{P}_2(z)$, and the constant term is not important in our analysis, since it is independent of the nematic orientation. The total energy per unit area, playing the role of the effective anchoring energy, is given by

$$f_{eff} = f_0 + f_{el} + f_{surf}. \tag{13}$$

The effective anchoring energy strength w_{eff} can be expressed as

$$f_{eff} = -\frac{1}{2} w_{eff} \cos^2 \theta, \qquad (14)$$

where

$$w_{eff} = w_0 + \frac{1}{2} \epsilon_0 \epsilon_a E_0^2 \lambda_D + e_+ J(\lambda_D) E_0 \xi.$$
(15)

Because $E_0 = \sigma / \epsilon_0 \overline{\epsilon}$, w_{eff} may increase or decrease according to the increasing or decreasing adsorbed charge density σ

on the surface. Such surface properties of LCs in relation to the spatial dependence of the equilibrium OP $\overline{P}_2(z)$ in the vicinity of the surface can be calculated, for example, in the framework of the integral equation approach [9], taking into account translational and orientational correlations as well as their coupling. If one further supposes

$$\overline{P}_2(z) = \overline{P}_2(0) \left(\frac{\Delta \overline{P}_2}{\overline{P}_2(0)} \frac{z}{\lambda_s} + 1 \right), \tag{16}$$

then $J(\lambda_D)$ takes the simple form $J(\lambda_D) = (\lambda_D / \lambda_s) [\Delta \bar{P}_2 / \bar{P}_2(0)]$, and the effective anchoring energy strength is given by

$$w_{eff} = \alpha_1 \sigma^2 + \alpha_2 \sigma + w_0, \qquad (17)$$

where $\alpha_1 = \frac{1}{2} \epsilon_a \lambda_D / \epsilon_0 \overline{\epsilon}^2$, $\alpha_2 = (\xi e_+ / \epsilon_0 \overline{\epsilon}) (\lambda_D / \lambda_s) [\Delta \overline{P}_2 / \overline{P}_2(0)]$. It is noted that Eq. (16) produces the limiting OP $\overline{P}_{2,b}$ at $z \ge \lambda_s$ and the linear σ term in Eq. (17) has been predicted, but for an entirely different mechanism, i.e., electric energy arising in the bulk NLC due to the electric quadrupole density [11] in a nonuniform electric field.

Now, in the case of $\alpha_1 > 0$ ($\epsilon_{\parallel} > \epsilon_{\perp}$) and $\alpha_2 < 0$ (the sign of α_2 is determined by three independent factors e_+ , ξ , and $\Delta \bar{P}_2$), or $\alpha_1 < 0$ and $\alpha_2 > 0$, one can formally calculate the magnitude of the critical surface charge density σ that leads to $w_{eff}(\sigma) = 0$, i.e.,

$$\sigma_{1,2} = -X \pm (X^2 - d)^{1/2}, \tag{18}$$

where $X = (\xi e_+ / \lambda_s) [\Delta \overline{P}_2 / \overline{P}_2(0)](\overline{\epsilon} / \epsilon_a)$ and $d = 2\epsilon_0 \overline{\epsilon}^2 w_0 / \epsilon_a \lambda_D$. Thus, the equation $w_{eff}(\sigma) = 0$ has real roots at $d \leq X^2$. It is important to stress that the inclusion of the surface polarization mechanism may lead to the disruption of the homeotropic alignment of, for example, cyanobiphenyls in a region bounded by the critical negative charge densities $\sigma_{1,2}$. In the case of a positive charge density on the surface, one deals with enhancing the effective anchoring. It should also be noted that the quadratic σ dependence in $w_{eff}(\sigma)$ was observed in Ref. [7], where the homeotropically oriented 5CB on a glass substrate covered by dipalmitoyl phosphatidylcholine was investigated.

Homeotropic alignment. In order to discuss the homeotropic alignment of 5CB on an ITO-coated glass plate, one needs the data for e_+ , ϵ_{\parallel} , ϵ_{\perp} , $\overline{P}_2(0)$, and the bulk OP $\overline{P}_{2,b}$. In the following, we use the calculated $e_+ = -33.5 \text{ pCm}^{-1}$ at T=300 K based on the statistical-mechanical approach [9,20,21] for a system composed of dipolar Gay-Berne particles [22], the calculated $\epsilon_{\parallel}=18$, $\epsilon_{\perp}=8$, $\overline{\epsilon}=11.3$, and $\epsilon_a=10$, as well as $\overline{P}_{2,b}=0.501$ from molecular dynamics simulation of 5CB [23] at the same temperature using the conventional potential energy function composed of intra- and intermolecular contributions. We note that the above e_+ is lower than the reported experimental data [15] ($e_+=-8.5-13 \text{ pCm}^{-1}$ at T=298 K) and the above bulk OP is in good agreement with NMR data ($\overline{P}_{2,b}=0.51$) [24]. Our previous calculations of the equilib



FIG. 1. The surface charge density σ dependence of $w_{eff}(\sigma)$, calculated using Eq. (17): (a) for homeotropic alignment at different values of w_0 (J/m²): 10⁻⁴ (solid squares), 10⁻⁵ (solid circles), 10⁻⁶ (solid triangles); (b) for planar alignment at the $w_0 = 10^{-3}$ (J/m²) (solid diamonds). The arrow shows the critical value of the $\sigma = 1.58 \times 10^{-3}$ C/m², which leads to destabilization of the planar alignment.

rium OP at a solid-nematic interface [9] show that the length of the spatial variation of $\overline{P}_2(z) \ \lambda_s \approx 10$ nm in agreement with the experimental data [15]. Thus, in the case of homeotropic alignment of 5CB on the ITO-coated glass plate, the surface polarization \mathbf{P}_s is directed from the substrate to the liquid crystal along the vector $\hat{\mathbf{k}}$ for $\overline{P}_2(0) > \overline{P}_{2,b}$, or directed from the liquid crystal to the substrate, antiparallel to \mathbf{k} , for $\overline{P}_2(0) < \overline{P}_{2,b}$. Taking into account that the equilibrium bulk ion concentration $n_{eq} \approx 5 \times 10^{20} \text{ m}^{-3}$ [10], one can calculate the bulk Debye screening length $\lambda_D = (\epsilon_0 \epsilon k_B T/2e^2 n_{eq})^{1/2}$ [25], where e is the proton charge, k_B is the Boltzmann constant, and $\epsilon = \epsilon_0 (\epsilon_{\parallel} \cos^2 \theta + \epsilon_{\parallel} \sin^2 \theta)$. The magnitude of the Debye length depends solely on the properties of the LC and not on any property of the surface. In the case of homeotropic alignment of 5CB at 300 K, one has $\lambda_D \approx 580 \text{ nm} [25]$. Moreover, when $\overline{P}_2(0) > \overline{P}_{2,b}$, a quite realistic situation for the case of strong anchoring, i.e., $\overline{P}_2(0) \approx 1$ at the surface, one has $\Delta \bar{P}_2 = -0.5$. This means that $\xi = 1$, and the surface polarization vector \mathbf{P}_s is directed from the substrate into the liquid crystal. Figure 1(a) shows the dependence of $w_{eff}(\sigma)$ on the surface charge density σ for a number of w_0 values: 10^{-4} , 10^{-5} , and 10^{-6} J/m². In the case of $\bar{P}_{2,b} > \bar{P}_2(0)$ $(\Delta \bar{P}_2 > 0, \xi = -1)$ and positive σ , one also deals with an enhancement of the effective strength of the anchoring energy $w_{eff}(\sigma)$. The upper bounds for the homeotropic alignment of 5CB molecules at an ITO surface, at which two real roots $\sigma_{1,2}$ of $w_{eff}(\sigma) = 0$ exist, are $w_0 \le 7.25 \times 10^{-4}$ J/m² (for $\xi = 1$, $\bar{P}_2(0) \approx 1$, $\Delta \bar{P}_2 = -0.5$) and $\leq 1.8 \times 10^{-4} \text{ J/m}^2 \text{ (for } \xi = -1, \bar{P}_2(0) = 0.4, \Delta \bar{P}_2 = 0.1 \text{)}.$ Such values of w_0 are in agreement with the experimental

data for homeotropically aligned LCs obtained using different experimental techniques, viz., $w_0 \in [10^{-8}, 10^{-3}] \text{ J/m}^2$ [8]. The σ value for two equal roots, which leads to vanishing $w_{eff}(\sigma)$, is $\sigma = -1.8 \times 10^{-3} \text{ C/m}^2$ (for strong anchoring and $w_0 = 7.25 \times 10^{-4} \text{ J/m}^2$), and for weak anchoring σ $= -0.94 \times 10^{-3} \text{ C/m}^2$ (with $w_0 = 1.8 \times 10^{-4} \text{ J/m}^2$). It should be pointed out that $\sigma = qn_{surf}$, where $q = -1.602 \times 10^{-19}$ C and n_{surf} is the surface charge density. n_{surf} can be estimated from the critical value of the negative charge density $\sigma = -1.8 \times 10^{-3} \text{ C/m}^2$ as $n_{surf} = 1.12 \times 10^{16} \text{ m}^{-2}$, which agrees with experimental values $\approx 10^{15} - 10^{16} \text{ m}^{-2}$ [10]. It is also clear that in the event of unequal real roots the surface polarization can destabilize the homeotropic alignment in the σ interval bounded by the two roots.

Planar alignment. In the case of planar alignment of 5CB on a polyamide-coated surface, $\xi = -1$ and $\Delta \overline{P}_2 < 0$ [15]. At the same bulk ion concentration $n_{eq} \approx 5 \times 10^{20}$ m⁻³ and T = 300 K, one obtains $\lambda_D = 850$ nm. Hence, the anchoring strength $w_0 \le 1.06 \times 10^{-3}$ J/m² allows two real roots for the equation $w_{eff}(\sigma) = 0$. The experimental data for planar alignment of LCs using different techniques [8] show $w_0 \approx 10^{-3}$ J/m². The limiting case in which surface polarization can destabilize the planar alignment is for the surface

charge density $\sigma = 1.9 \times 10^{-3}$ C/m² ($w_0 = 1.06 \times 10^{-3}$ J/m²). Figure 1(b) shows the surface charge density dependence of $w_{eff}(\sigma)$ for $w_0 = 10^{-3}$ J/m². The corresponding critical value for the surface charge density at which the planar anchoring is destabilized is $\sigma \approx 1.58 \times 10^{-3}$ C/m², which leads to $n_{surf} \approx 9.8 \times 10^{15}$ m⁻².

In conclusion, it has been shown that the interaction between the surface polarization (in the quadrupole approximation) and the surface electric field, caused by the charge separation taking place between the boundary surface and the NLC, has an important influence on the effective anchoring energy strength w_{eff} . Thus, w_{eff} may be sensitive to the condition of the boundary substrates, which can govern the charge separation. The dependence of $w_{eff}(\sigma)$ on σ up to a quadratic term has indeed been observed experimentally using the LB technique [7]. Finally, given that e_+ is negative, the critical surface charge density is negative and positive for homeotropic and planar alignment, respectively, regardless of whether the anchoring condition at the surface is strong or weak. In the present study, flexoelectricity is not considered as it is important only in the bulk NLC [15].

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