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Disorientation-induced disordering at a nematic-liquid-crystal–solid interface

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To explain the observed deviation from the Rapini-Papoular surface energy of nematic liquid crystals, we propose a model of the form $\mathrm{Tr}[(Q_{ij}-Q_{0ij})^2]$ (Q_{ij} is the quadrupolar order parameter of the nematic liquid crystal and Q_{0ij} a quadrupolar surface field). For a broken anchoring, this model predicts a surface order decrease $\Delta S \approx \frac{3}{2}(\xi/d)S_B$, where ξ and d are the coherence and surface extrapolation lengths of the nematic liquid crystal and S_B is the bulk order parameter. A quantitative check is presented on planar anchoring of various strengths and temperatures.

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Nematic liquid crystals can be oriented by solid boundaries. This orientation is phenomenologically described by a surface energy W, which depends in principle on the surface order parameter S of the nematic liquid crystal and on the relative orientation of its surface director $\mathbf{n}$ compared to the surface easy axis $\mathbf{n}_0$ $[\angle(\mathbf{n},\mathbf{n}_0)=\alpha]$ [1]. For the simplest case of planar amorphous solids, $\mathbf{n}_0$ is usually along the normal to the solid surface ("homeotropic" orientation), or perpendicular to it ("planar"). In both cases, W is usually written in the Rapini-Papoular (RP) form [1]:

$$W=-\tfrac{1}{2}(K/d)(\mathbf{n}\cdot\mathbf{n}_0)^2\,, \tag{1}$$

where K is the usual curvature elastic constant of the nematic liquid crystal and d an extrapolation length. In the presence of a surface disorientation α, W generates a stabilizing surface torque $\approx \sin(2\alpha)$. Experimentally the RP form (1) is found surprisingly to be good [2], at least for weak anchorings, where $d > \xi$ [ξ is the coherence length of the nematic-isotropic (N-I) ordering]. Even in cases where a departure from RP was observed [3], a correct reanalysis led to its validity [4]. For stronger anchoring, a departure from RP was reported [5,6]. The stabilizing surface torque contains new terms $\approx \sin(4\alpha)$. This correction is stronger close to the N-I transition in the form of an apparent decrease of anchoring strength for large surface distortions ($\mathbf{n}\perp\mathbf{n}_0$) [6–8]. All these analyses were performed in the approximation that S remains constant. In this Rapid Communication we show that in the anchoring of nematic liquid crystals, the departure from the RP form can be simply explained by a decrease of the surface order parameter S, induced by the surface disorientation from the easy axis $\mathbf{n}_0$.

In the RP form, S is considered constant and equal to the bulk value S_B, and the prefactor K depending on S, is in the form $K=\frac{9}{2}L_1S_B^2$ [9]. The problem is to find a generalization of the RP form, which takes into account both S and $\mathbf{n}$ variations. To discuss wetting problems, a linear S term was included in W long ago [10]. A more elaborate angular dependence of W was recently proposed [11], but with no explicit $S(\alpha)$ dependence. We imagine a simple model where the nematic density does not vary at the surface, and where the nematic ordering remains uniaxial, i.e., W depends only on the traceless quadrupolar order parameter $Q_{ij}=\frac{3}{2}S(n_in_j-I_{ij}/3)$. The surface is supposed to orient the nematic liquid crystal through a localized quadrupolar surface field $Q_{0ij}=\frac{3}{2}\;S_0(n_{0i}n_{0j}-I_{ij}/3)$. The obvious generalization of the RP form is now

$$W=\tfrac{1}{2}A\,\mathrm{Tr}[(Q_{ij}-Q_{0ij})^2]\,. \tag{2}$$

S_0 is the preferred surface ordering for $\mathbf{n}=\mathbf{n}_0$, calculable in principle by a microscopic model. We write W as

$$W=\tfrac{1}{2}A\tfrac{3}{2}\{S^2+S_0^2-SS_0[3(\mathbf{n}\cdot\mathbf{n}_0)^2-1]\}\,, \tag{3}$$

i.e., W looks like RP if S is constant. Equation (3) tells us the preferred surface ordering $S'(\alpha)$. Writing $\partial W/\partial S=0$, we obtain

$$S'(\alpha)=(S_0/2)(3\cos^2\alpha-1)\,. \tag{4}$$

For $\alpha=0$, $S'=S_0$ as expected. For large surface disorientation ($\alpha=\pi/2$), the preferred surface ordering is $S'=-S_0/2$. This is easily understandable: If we force $\mathbf{n}\perp\mathbf{n}_0$, the nematic molecules tend to take a negative "diskotic" ordering since at least half of them are well aligned along Q_{0ij}. Equation (3) contains indeed a term linear in S, as in [10] and is a simplified version for W of the Ref. [11] expression.

For a realistic prediction on the surface-order–orientation coupling, we must introduce the effect of the bulk nematic liquid crystal. For a given surface orientation, S results from a balance between W which tends to fix $S=S'(\alpha)$, and the bulk nematic liquid crystal which tends to keep $S=S_B$. A surface torque equation must also be written to determine $\mathbf{n}$. We write the two surface equations which determine $\mathbf{n},S$ in a simple case. $\mathbf{n}_0$ is assumed to be planar. $\mathbf{n}$ is oriented toward the normal $\mathbf{z}$ by an external field $\mathbf{E}\parallel\mathbf{z}$, through the dielectric anisotropy $\epsilon_a>0$ of the nematic liquid crystal. We call $(\mathbf{n},\mathbf{z})=\theta$. As usual, we introduce the electric coherence length ξ_E defined by $(\varepsilon_a/4\pi)E^2=K\xi_E^{-2}$. The surface torque equation now becomes

$$\frac{\partial W}{\partial\theta}=K\frac{d\theta}{dZ}\bigg|_{z=0}=-(K/\xi_E)\sin\theta\,. \tag{5}$$

The surface order equation, in the isotropic approximation, is [10]

$$\frac{\partial W}{\partial S} = \tfrac{3}{2} L_1 \frac{dS}{dz}\bigg|_{z=0} = -\tfrac{3}{2} L_1 (S - S_B)/\xi\,, \tag{6}$$

valid when S is close to S_B.

In the absence of angular distortion ($\theta = \pi/2$), (6) and (3) allow one to calculate the surface order $S(\pi/2)$, as

$$S(\pi/2) = [S_B + (A\xi/L_1)S_0]/[1 + A\xi/L_1]\,. \tag{7}$$

$S(\pi/2) = S_B$ (the RP model) if $S_0 = S_B$. For small angular disorientation $\alpha = \pi/2 - \theta$, we can fit W with the RP expression (1) in the form $W = \frac{1}{2}(K/d)(\pi/2-\theta)^2$, by choosing $A = (L_1/d)[S_B^2/S(\pi/2)S_0]$. For an arbitrary θ, we obtain from (6) the surface order value:

$$S(\theta) = S_B\{1 - (\xi/d)[S_B - S'(\theta)]/S_0\}\,. \tag{8}$$

The normalized decrease in surface order $\Delta s(\theta) = [S(\pi/2) - S(\theta)]/S_B$ is maximum for $\theta = 0$ with the value

$$\Delta s = \tfrac{3}{2}(\xi/d)\,. \tag{9}$$

Δs is independent of S_0. It occurs even when $S_0 = S_B$; i.e., the constant S hypothesis is incompatible with our model. The point is that Δs can be measured even when one does not know S_0. The disorientation-induced $\Delta s(\theta)$ is linear in ξ/d, i.e., visible only for disoriented strong anchorings. It is intrinsically different from the curvature-induced surface melting [12], which is quadratic in ξ/d, maximum at maximum torque (i.e., when $\theta \approx \pi/4$), and zero for $\theta = 0$. From (3) and (8) we obtain the torque equation:

$$\frac{\partial W}{\partial \theta} = -(K/d)[(1 - \Delta s/2)\sin(2\theta)/2 - (\Delta s/2)\sin(4\theta)/4]\,. \tag{10}$$

The disorientation-induced decrease of the surface order leads to a relative decrease in the surface torque $\approx (\xi/d)\sin 4\theta$. From (10) and (5) we obtain the electrical saturation length ξ_{ES} for the complete surface disorientation $\theta = 0$ in the form

$$\xi_{\mathrm{ES}} \approx d[1 + \Delta s(1 + \tfrac{1}{2} + \tfrac{2}{3}\epsilon_a/\epsilon_\parallel)]\,. \tag{11}$$

For $\Delta s = 0$, we do obtain the RP result: $\xi_{\mathrm{ES}} = d$. For $\Delta s \neq 0$, (11) predicts $\xi_{\mathrm{ES}} > d$, i.e., a complete surface "breaking" for a smaller electrical field. The first term in Δs comes from (10), the second one from the S dependence of ξ_E. The last term in Δs comes from the change in the applied surface electric field $E(\Delta s)$, through the dielectric condition (D_z = const, **D** electric displacement). For small θ, a simple calculation gives

$$\Delta E/E(0) = [E(\Delta s) - E(0)]/E(0) = \tfrac{2}{3}(\epsilon_a/\epsilon_\parallel)\Delta s\,,$$

where $\epsilon_\parallel$ is the dielectric constant for $\mathbf{E} \parallel \mathbf{n}$.

Our model explains well the observed $\sin(4\theta)$ dependence of the anchoring torque from Refs. [5,6]. In these first observations, however, the anchoring strength and temperature dependence of the effect were not measured. To check our predicted ξ/d dependence, we resume the experimental determination of the surface torque for various nematic planar anchorings under the action of a disorienting electric field.

The planar surface to study is associated with a homeotropic plate to result in a "hybrid" nematic cell. The cell boundaries consist of two indium tin oxide- (ITO) coated glass plates which act as transparent electrodes: the upper plate is silane dimethyloctadecyl-3-(trimethoxysilyl) propylammonium chloride (DMOAP) coated [13] to obtain strong homeotropic anchoring. The lower planar plate is obliquely SiO evaporated or by rubbing of polivinyl alcohol (PVA). The two plates are sandwiched with 3-5-μm-thick Mylar spacers. The empty cell thickness h is adjusted by screw tightening and is measured in the range (2.7–3.5) ± 0.1 μm with an optical interference setup. The cell is filled with the nematic compound 4-pentyl 4'-cyanobiphenyl (5CB), which presents a positive dielectric anisotropy $\epsilon_a \approx 10$ [14], and placed in an electric oven, with temperature control better than 0.025 °C. The antagonistic boundary conditions force a splay-bend texture in the volume, the profile of which can be exactly calculated from the known corresponding curvature constants K_1 and K_3 [15]. We apply an ac pulsed electrical field E, perpendicular to the electrodes, with $\xi_E < h$. The field tends to align the molecules along **z**, normal to the plates. It decreases the hybrid cell birefringence down to zero when $\xi_E = \xi_{\mathrm{ES}}$, i.e., when the planar anchoring is forced to become homeotropic. A measurement of ΔL, the cell difference optical thickness for ordinary and extraordinary rays, allows the calculation [16] of the surface angle $\theta(\xi_E)$ at the planar plate, and of the volume integrated surface torque $\Gamma(\xi_E)$; we obtain $\Gamma(\theta)$ $(0 \le \theta \le \pi/2)$ as in Ref. [6]. In these calculations we take into account not only the nonuniformity of the field but also the elastic constant renormalization from the flexoelectric effect [17], because, for strong anchoring, $\xi_E \approx d$ can be smaller than the Debye screening length. The electrical field E is pulsed, with pulse duration $\Delta\tau \approx 1$ ms and pulse interval $\tau \approx 1$ s, to minimize heating effects. The ac frequency is chosen ≈ 100 kHz, lower than the dielectric relaxation, but high enough to prevent a linear flexoelectric response. We can measure ΔL down to ± 5 Å.

We present $\Delta L(\xi_E)$ in Fig. 1(a) and $\Gamma(\theta)$ in Fig. 1(b) for the SiO-coated planar anchoring, at $\Delta T = T_{N\text{-}I} - T = 0.025$ °C. In Fig. 1(a), the dashed curve represents the RP extrapolation fitted on low-field (large ξ_E) measurements. It is not a straight line, because of the aforementioned corrections. We find $d = 1200$ Å. One sees clearly a deviation for high field, as already reported [5,6]. ΔL goes down to zero for $\xi_{\mathrm{ES}} > d$. Actually, we find $\xi_{\mathrm{ES}} = 2400$ Å by extrapolating the experimental points to $\Delta L = 0$. From ξ_{ES}, d, and (11), we estimate the maximum decrease of normalized order parameter $\Delta s = 0.55$. This means that the surface order parameter S decreases by a factor of 2 when the surface orientation is broken. Using (9), we now calculate $\xi = 440$ Å. At the transition, the coherence length is known to be between 85 and 120 Å [18]. Our measured ξ is about 4 times larger than the bulk one. This could be related to the poor validity of linear expansions (9) and (11) when $\Delta s = 0.55$. In Fig. 1(b), the dashed curve is the RP [$\sin(2\theta)$] prediction, fitted again from the low-field data. The solid line is the least-squares fit of $\Gamma(\theta)$ in Eq. (10). One sees clearly an important contribution of $\sin(4\theta)$. The fit gives $\Delta s = 0.65$.

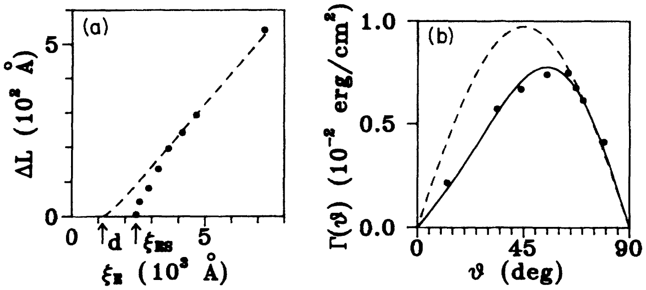

FIG. 1. (a) The cell difference optical thickness for ordinary and extraordinary rays (ΔL) vs the electrical coherence length (ξ_E) for planar SiO anchoring at $\Delta T=0.025\,^\circ\mathrm{C}$. The dashed curve represents the RP extrapolation fitted on low-field (large ξ_E) measurements. d and ξ_{ES} are determined by the extrapolation to $\Delta L=0$ of the RP curve and the interpolation of experimental points, respectively. We find $d=1200$ Å and $\xi_{\mathrm{ES}}=2400$ Å. (b) The surface torque $\Gamma(\theta)$ vs the surface polar angle θ reconstructed from $\Delta L(\xi_E)$ data of (a). The dashed curve represents the RP torque fitted on angle $\theta\approx\pi/2$ measurements. The solid line represents the fit on all points via Eq. (10) with $d=1200$ Å. We find $\Delta s=0.65$.

In fact, as explained for the birefringence data, the field, ξ_E and then Γ and θ must be corrected. As the $\Gamma(\theta)$ data are reconstructed from $\Delta L(\xi_E)$, we should make the same corrections on Δs as we have made for ξ_{ES}. The correction factor corresponds to the three contributions in Δs in (11), whose sum is ≈ 1.8. This results in $\Delta s\approx 0.65/1.8\approx 0.35$. The discrepancy ($\Delta s=0.35$ vs $\Delta s=0.55$) could be due to the fact that the expansion (11) is valid for $\theta\approx 0$, whereas the fit in Fig. 1(b) takes into account the whole range of θ angles $[0, \pi/2]$. A more exact calculation will be given elsewhere [16].

The temperature dependence of the effect on Δs is shown in Table I. For SiO, for instance, we measure d and ξ_{ES} for five different temperatures. We calculate Δs from (11), ξ from (9), and ξ_{th} by the expression $\xi_{\mathrm{th}}=\xi_0[(T^{**}-T_{N\text{-}I})/(T^{**}-T)]^{1/2}$, where $\xi_0=85$–120 Å [18] and $T^{**}-T_{N\text{-}I}=0.16$ [10]. Qualitatively, we can observe that Δs is larger for temperatures $T\approx T_{N\text{-}I}$ where even the values of ξ are different from those expected of $\xi=\xi_{\mathrm{th}}$; again this discrepancy is likely due to the poor validity of our model for $\Delta s\approx 1$. In contrast, for temperatures where $\Delta s\ll 1$; i.e., in the limit of validity of linear expansions (9) and (11), the predictions of our model are in good agreement with the experimental data. A more detailed report on the temperature dependence will be given elsewhere [16].

TABLE II. Anchoring extrapolation length (d), electrical saturation length (ξ_{ES}), the maximum decrease of normalized surface order parameter (Δs), and the coherence length (ξ) for three planar anchorings measured at the same temperature $\Delta T=0.1\,^\circ\mathrm{C}$. The values of Δs and ξ are obtained by the measured value of d and ξ_{ES} via Eqs. (11) and (9).

Substrates	d (Å)	ξ_{ES} (Å)	Δs	ξ (Å)
PVA1	600	1400	0.73	290
SiO	900	1300	0.24	145
PVA2	1500	1650	0.055	55

Finally in Table II, we compare the anchoring strengths and the decrease of order parameter of three planar anchorings using the same liquid crystal 5CB at the same temperature $\Delta T=0.1\,^\circ\mathrm{C}$. In addition to the already studied SiO-coated plate, we measure the behavior of two PVA-coated plates rubbed with different velvets. We can observe that Δs is larger when d is smaller, i.e., for stronger anchoring. This trend agrees with our model.

To conclude, the surface anchoring torque of nematic liquid crystals on solid amorphous surfaces was reported to deviate from the simple harmonic angular law, the so-called RP approximation. In this paper, we have presented a model and have performed experiments to explain this deviation. The easy surface orientation is defined by the direction of a quadrupolar surface field. A disorientation from this surface field direction results in a disordering of the nematic liquid crystal at the surface, from the competition between the surface field and the nematic ordering mean field. The maximum decrease of surface order is proportional to $(\xi/d)\,S_B$, i.e., the ratio of the coherence length of the N-I transition to the surface extrapolation length times the bulk order parameter. Our experiments on various planar anchorings of different strengths at different temperatures, are in good agreement with our model within its validity limit, i.e., $\xi/d\ll 1$. Formally, our model of anchoring energy appears to be a particular case of previously proposed expressions; however, it also considers the disorientation-ordering coupling. Any other model of surface anchoring energy has to take into account this coupling. It could be improved by weighing the biaxial character of the distorted surface ordering, and a

TABLE I. Temperature dependence of the anchoring extrapolation length (d), electrical saturation length (ξ_{ES}), the maximum decrease of normalized surface order parameter (Δs), and the coherence lengths (ξ and ξ_{th}) for planar SiO anchoring. Δs and ξ are calculated from d and ξ_{ES} via Eqs. (11) and (9). ξ_{th} is obtained by $\xi_{\mathrm{th}}=\xi_0[(T^{**}-T_{N\text{-}I})/(T^{**}-T)]^{1/2}$, with $\xi_0=85$–120 Å [18] and $T^{**}-T_{N\text{-}I}=0.16$ [10].

ΔT (°C)	d (Å)	ξ_{ES} (Å)	Δs	ξ (Å)	ξ_{th} (Å)
0.025	1200	2400	0.55	440	105 ± 20
0.1	900	1300	0.24	145	80 ± 10
0.28	700	900	0.16	75	60 ± 10
0.4	720	870	0.11	55	50 ± 10
0.5	580	700	0.11	45	45 ± 5

possible change of surface density. It would be interesting to measure directly the drop of order at the surface and, also, to use the proposed surface energy to discuss surface wetting problems. Note finally that analogous deviations from a simple harmonic angular torque dependence have been reported on other anisotropic ordered systems, as high-T_c superconductors in magnetic field [19]. It would be interesting to investigate that part of the deviation which could be related to an angular change of the superconductor order parameter.

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