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Splay-bend curvature and temperature-induced surface transitions in nematic liquid crystals

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We present an elastic model to explain the temperature-induced surface transitions observed on the spontaneous orientation of nematic liquid crystals on solid surfaces. The destabilizing effect is due to the mixed splay-bend curvature elasticity K_{13}. The transition is temperature driven by the change in the nematic-liquid-crystal order parameter S. The transition is continuous. A large angular variation localized close to the boundary is predicted. Analyzing experimental data, we estimate $|K_{13}|\cong 10^{-7}$ cgs units.

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I. INTRODUCTION

Nematic liquid crystals (NLC's) present a quadrupolar ordering **Q** around a mean direction **n**, the "director," characterized by a scalar amplitude S (the scalar order parameter). A solid surface Σ is able to orient **Q**, i.e., **n**, in a well-defined direction. An amorphous flat surface of normal **k**, for instance, can give rise to "planar" ($\mathbf{n}\perp\mathbf{k}$) or "homeotropic" ($\mathbf{n}\|\mathbf{k}$) anchoring. In a naive description, the angular anchoring originates from a direct interaction between the NLC and the substrate. For a solid surface, one would then expect this orientation to be temperature independent. In fact, for some situations, one does observe a temperature-induced surface transition (TST), where the anchoring orientation goes, more or less rapidly, from homeotropic to planar (or vice versa), when cooling the material down its NLC phase [1–8]. One can describe phenomenologically this TST with Landau-like models based on the symmetry, similar to the ones used for the bulk [9–18], with microscopic models based on the Onsager theory [19–23] or similar to Ising model [24]. Other models, more or less microscopic, have also been proposed [25–32].

To explain these TST's, one must consider mechanisms which are *intrinsic* to the NLC, since only the NLC, and not the surface, changes its symmetry at the TST. One such possibility comes from the well-known mixed splay-bend or saddle-splay curvature distortions. They are associated with the so-called K_{13} and K_{24} elastic constants, and give pure divergence terms in the elastic bulk free-energy density [33]. These terms can be integrated out as surface contributions.

The saddle-splay term K_{24} is well known to be equivalent to a quadratic term in first-order **n** derivatives [33] and does not lead to any spectacular surface effect. The splay-bend term K_{13}, on the contrary, implies a second-order derivative of **n** and has led to controversies [34,35]. Its brute-force introduction [35] induces a discontinuity in the surface angles since, in the absence of saturation, an isolated second derivative of **n** in the bulk leads, after an approximate minimization, to an infinite surface curvature [36]. This absurd result has been corrected by the introduction of a volume saturation elastic term proportional to the square of the second derivative of the angular distortion [37], according to the usual recipe used in crystal elasticity [38].

More recently, the elastic constant K_{13} has been shown [39] to depend *linearly* on the scalar order parameter S, contrary to the other usual curvature constants, proportional to S^2 [9]. Using the temperature dependence of S, and a continuum theory model including mixed splay-bend and second-order elastic constants, we show in this paper that TST's in NLC's can be the result of the intrinsic surface destabilizing effect of the K_{13} elastic constant. Our paper is organized as follows: In Sec. II, we review the previous model for TST. In Sec. III, we develop our intrinsic model. We discuss the validity of the model in Sec. IV, before concluding in Sec. V.

II. REVIEW OF PREVIOUS MODELS FOR TST

TST's in NLC's have been observed long ago by Bouchiat and Langevin-Cruchon [1]. More recently the same phenomenon has been observed by different groups [2–8] in NLC samples with different surface treatments. TST's can be easily described by means of phenomenological expressions for the surface energy density f_s. As is well known, f_s is partially due to the NLC-substrate interaction and partially to the NLC-NLC interaction near the boundary, where the bulk symmetry of the NLC is broken. The simplest way to obtain f_s is to expand it in terms of the tensorial order parameter **Q** characterizing the NLC's at the surface [9] and of the symmetry elements characterizing the surface. In the case in which the limiting surface may be considered isotropic and flat, its element of symmetry is the geometrical normal **k**. A simple calculation gives now for f_s the expression

$$f_s=\beta_{11}k_iQ_{ij}k_j+\beta_{20}Q_{ij}Q_{ji}+\beta_{21}k_iQ_{ij}Q_{jl}k_l+\beta_{22}(k_iQ_{ij}k_j)^2\ , \tag{1}$$

proposed long ago [10–12].

The first "idea" is to give to a term such as β_{20} a linear dependence in temperature such as $(T-T_s)$, where T_s is the surface transition temperature [40,41]. A slightly more physical description is to keep all coefficients temperature independent. The temperature enters in f_s by means of the surface tensor order parameter. The various terms appearing in (1) are due to the direct interaction between the NLC and the substrate (the first one) and to the NLC-NLC interaction (the second one). The other terms are due to both interactions, and they can be interpreted in different manners. This depends on the subjective judgment of the individual researcher because it is very difficult to build an accurate microscopic theory of the surface interaction.

Equation (1) states that the surface tries to impose a scalar order parameter S_0 [9] and average orientation $\mathbf{n}_0$, in the absence of bulk constraints. By means of S_0 and $\mathbf{n}_0$ it is possible to build the easy surface order parameter, defined by

$$Q_{ij}^0=\tfrac{3}{2}S^0[n_i^0n_j^0-\tfrac{1}{3}\delta_{ij}] \ . \tag{2}$$

Q_{ij}^0 is obtained by minimizing (1) with respect to S and n_i. By taking into account (2), expression (1) can be rewritten in the form [13]

$$f_s=-\tfrac{1}{2}w(Q_{ij}-Q_{ij}^0)^2 \ , \tag{3}$$

which is a generalization of the well-known Rapini-Papoular form for the surface energy density [14]. By using (1) it is easy to interpret the TST in NLC's. In [11,12] the surface scalar order parameter is supposed equal to the bulk one and the NLC orientation uniform across the NLC interface. With this hypothesis the NLC orientation is obtained by minimizing (1) with respect to n_i.

In the event in which $\mathbf{n}$ is everywhere parallel to a plane, it is possible to use as variable the tilt angle ϕ made by $\mathbf{n}$ with $\mathbf{k}$ instead of $\mathbf{n}$. In this case from (1), by setting

$$\frac{\partial f_s}{\partial\phi}=0 \ , \quad \frac{\partial^2 f_s}{\partial\phi^2}>0 \ , \tag{4}$$

one obtains

$$\phi=\phi(S,\beta_{ij}) \ , \tag{5}$$

where S is equal to the bulk value S_b, whose temperature dependence is known. According to the values of the phenomenological parameters β_{ij}, a TST can appear or not. It is important to emphasize that in (5) β_{20} is absent, because the term $\beta_{20}Q_{ij}Q_{ji}$ is ϕ independent, and hence it disappears during the process of minimization of f_s [Eqs. (4)]. This implies that the NLC-NLC interaction characterized by β_{20} does not play an important role in the TST, since S is supposed constant across the interface.

More recently it has been pointed out that the hypothesis S(surface)$=S$(bulk) is not very realistic because S is expected to vary near the surface over a layer whose thickness is of the order of the NLC coherence length ξ [15]. By taking into account this spatial dependence of S it is possible to show that a source of the TST is the difference S(bulk)$-S$(surface). In this frame the β_{20} coefficient plays an important role because it is responsible of the tilted orientation [15].

The phenomenological model we have described above [Eq. (1)] is based on the hypothesis that Q_{ij} characterizes completely the NLC. This is true for the bulk, but, as pointed out by Parson [16], near a surface a polar order can be present. This implies that near a limiting surface the NLC has to be described by Q_{ij} and a polar vector of components P_i. A phenomenological theory of this kind has been recently proposed by McMullen and Moore [17,18]. They show that interfacial polar ordering at the isotropic-NLC interfaces may affect the tilt angle of a bulk NLC. Their theory invokes the up-down asymmetry of the molecules to account for the tilted orientation of NLC at the interface.

The phenomenological theory of McMullen and Moore [17,18] has been proposed for the NLC-isotropic interface, but it can be extended to NLC-solid substrates. In fact, let us suppose that the polar order is described by

$$P_i=\mu_{ij}n_j \ , \tag{6}$$

where $\mathbf{P}/P$ is the nematic polar order parameter, whose value is zero in the bulk, as the tensor $\boldsymbol{\mu}$ itself. Now the surface energy $f_s^{(P)}$ is, instead of (1), given by

$$f_s^{(P)}=\alpha_{11}P_i+\alpha_{22}(k_iP_i)^2+f_s \ , \tag{7}$$

where f_s is given by (1). Since in the bulk $\boldsymbol{\mu}\equiv 0$, it is now necessary to solve the complete problem. This requires that one has to solve the two Euler-Lagrange equations, i.e., two coupled second-order differential equations. Except in certain special limits, an analytical solution is very difficult [17,18]. Furthermore the phenomenological model proposed by McMullen introduces new phenomenological parameters, with a difficult mathematical background.

More recently, a new version of the Onsager theory has been extended to investigate the behavior of the NLC in contact with a solid substrate [19]. The NLC is supposed to be formed of hard rigid rods having perfect uniform alignment and uniform spatial density. In this frame it is shown [19] that, in the absence of any particle-wall interactions besides excluded-volume forces, the NLC orientation is parallel to the wall. This is due to the entropy associated with the larger volume available to the particles in their parallel orientation. In the event in which an adsorption energy favors normal alignment, a TST from parallel to perpendicular orientation is possible. Other models more or less microscopic have been proposed, in which the number of simplifying assumptions is usually large [20–24].

In this paper we want to analyze the TST in NLC's by using a simple model based on the continuum theory. This method has already been used in another context. Kanel *et al.* [25] have discussed the contribution of local smectic order to the free energy of the nematic at the wall. Mada and co-workers [26,27] introduced the concept of a surface elastic constant. Although their theoretical analysis is not correct, the idea was interesting from a physical point of view. An "ordoelectric" model has also been proposed to describe the TST of an NLC-isotropic or NLC-air interface [28,29]. Our point of view is, however, different from the one proposed in [25,26].

We suppose that the anchoring energy connected with the surface orientation due to the direct NLC-substrate interaction is of the order of the anisotropy of the NLC interfacial tension, i.e., very large, in the range of a few erg/cm^2. We suppose furthermore that near the interface a rapid variation of angle forces us to introduce into the elastic theory terms proportional to the square of the second derivative of the tilt angle. The rapid variation of the tilt angle close to the surface is produced by the introduction of the splay-bend elasticity K_{13}. We find a critical condition for an homeotropic toward planar (or planar toward homeotropic) transition, which depends on the temperature through the different S dependences of K_{13} and of the usual elastic constants. We assume that the NLC scalar order parameter S is position independent. This point of view was partially proposed a few years ago, but never analyzed in detail [30–32].

III. THE SURFACE SPONTANEOUS CURVATURE MODEL OF THE TST

Let us consider a semi-infinite NLC sample. The **z** axis of the Cartesian reference frame is normal to the boundary wall and $z>0$ corresponds to the NLC half space. Let us suppose, furthermore, that the NLC director **n** is always parallel to the $(\mathbf{x},z)$ plane and $\phi=\cos^{-1}(\mathbf{n}\cdot\mathbf{k})$, where **k** is the unit vector parallel to the z axis. ϕ is the so-called tilt angle, and in the following it will be considered only z dependent: $\phi=\phi(z)$. The anchoring energy due to the NLC-substrate and NLC-NLC interaction will be written in the Rapini-Papoular form [14], characterized by an easy direction parallel to **k**. This means that the wall tends to give homeotropic orientation. In this frame the total energy of the NLC sample under consideration is given by

$$F=\tfrac{1}{2}\left\{\int_0^\infty\left[K\left[\frac{d\phi}{dz}\right]^2+K^*\left[\frac{d^2\phi}{dz^2}\right]^2\right]dz+w\sin^2\phi_0+K_{13}\sin(2\phi_0)\left[\frac{d\phi}{dz}\right]_0\right\}. \quad (8)$$

In (8), K is the usual curvature elastic constant introduced by Frank [43], K^* is the elastic constant connected with the second-order derivative [31], w is the anchoring strength, and K_{13} is the splay-bend elastic constant [33]. In the bulk free-energy density, the covariant form of this term is $K_{13}\mathrm{div}[\mathbf{n}(\mathrm{div}\mathbf{n})]$. Using a Gaussian theorem, it can be rewritten as the surface contribution in Eq. (8). Its peculiarity is its dependence on $(d\phi/dz)_0$ at the surface. As discussed elsewhere [30–32], in order to have a well-defined variational problem when the K_{13} term is considered, it is necessary to take into account the K^* term too. In (8) $\phi_0=\phi(0)$ is the surface tilt angle.

By minimizing (8) one obtains the bulk Euler-Lagrange equation

$$K^*\left[\frac{d^4\phi}{dz}\right]-K\left[\frac{d^2\phi}{dz^2}\right]=0 \quad \forall z\in[0,\infty] \quad (9)$$

whose solution is

$$\phi(z)=\phi_b+(\phi_s-\phi_b)\exp[-(z/b)]\ , \quad (10)$$

in which

$$b^2=K^*/K \quad (11)$$

is a mesoscopic length, as discussed in [32,39]. This length plays an important role whenever the elastic energy density is written in terms of first- and second-order derivatives. As shown in [39], b is expected to be, in a first approximation, temperature independent. In (10), $\phi_b=\lim_{z\to\infty}\phi(z)$ and $\phi_s=\phi(0)=\phi_0$. The solution (10) shows that, in the case where ϕ_b and ϕ_s are different from zero, a sharp variation of $\phi(z)$ occurs over b near the orienting wall [30,32]. The integration constants ϕ_b and ϕ_s can be determined by taking into account the boundary conditions following from the minimization of F. For our aim, it is simpler to substitute (10) into (8). In this manner F will be an ordinary function of ϕ_b and ϕ_s. By taking into account that F has to be minimum for the actual NLC profile, the integration constants will be determined by setting

$$\frac{\partial F}{\partial\phi_b}=\frac{\partial F}{\partial\phi_s}=0\ . \quad (12)$$

The solution of system (12) is stable, i.e., corresponds to a minimum of F, if

$$\frac{\partial^2F}{\partial\phi_b^2}>0\ ,$$
$$H=\left[\frac{\partial^2F}{\partial\phi_b^2}\right]\left[\frac{\partial^2F}{\partial\phi_s^2}\right]-\left[\frac{\partial^2F}{\phi_b\partial\phi_s}\right]^2>0\ . \quad (13)$$

As is well known, the two manners to determine the integration constants are equivalent, but the second one is simpler, and furthermore it gives the possibility to analyze, in a straightforward way, the stability of the NLC distortion. By substituting (10) into (8) one obtains for the total energy the expression

$$F(\phi_b,\phi_s)=(K/2b)(\phi_s-\phi_b)^2+(w/2)\sin^2\phi_s-(K_{13}/2b)(\phi_s-\phi_b)\sin(2\phi_s)\ . \quad (14)$$

The first term in (14) is the elastic contribution, in the Frank approximation, due to the sharp variation of ϕ_b, as previously emphasized. Instead of $F(\phi_b,\phi_s)$ it is more convenient to consider the adimensional energy $g(\phi_b,\phi_s)$ defined by

$$g(\phi_b,\phi_s)=(2b/K)F(\phi_b,\phi_s)=(\phi_s-\phi_b)^2+(b/L)\sin^2\phi_s+R(\phi_s-\phi_b)\sin(2\phi_s)\ , \quad (15)$$

where

$$L=K/w \quad (16)$$

is the usual extrapolation length due to the elastic (K) and surface (w) properties of the elastic medium, and

$$R=-K_{13}/K \quad (17)$$

gives an idea of the importance of the K_{13} elastic constant with respect to the usual Frank elastic constant.

From (15) we can immediately predict an orientational instability. Expanding to second order in tilt angles, we find

$$g_2=[1+2R+(b/L)]\phi_s^2-2(1+R)\phi_s\phi_b+\phi_b^2+\cdots \ . \tag{18}$$

Since at least the curvature of g_2 along ϕ_b is independent of the parameters, one expects g_2 to become unstable by going from a paraboloid to a saddle point, through a cylinder. g_2 becomes a pure square $[(1+R)\phi_s-\phi_b]^2$ for $b/L=R^2$. This is the threshold condition.

At the point of instability, one eigenvector, stable, of $g_2(\phi_s,\phi_b)$ is orientated along the cylinder cross section $\phi_b=(1+R)\phi_s$. The other, unstable, order parameter is the direction of the cylinder axis: $\psi=\phi_s+\phi_b(1+R)$.

Taking $\phi_b=(1+R)\phi_s$ to minimize the stable order parameter, g_2 reduces to

$$g_2=[(b/L)-R^2]\phi_s^2=[b/L-R^2]\psi^2/[1+(1+R)^2]^2 \ .$$

g_2 changes its sign across the threshold as expected.

To obtain the tilt amplitude above threshold, it would be necessary to expand g to fourth order. This is not necessary since a direct calculation is possible. From (15), we find

$$\begin{aligned}\frac{\partial g}{\partial\phi_b}&=-2(\phi_s-\phi_b)+R\sin(2\phi_s)] \ ,\\ \frac{\partial g}{\partial\phi_s}&=2(\phi_s-\phi_b)[1+R\cos(2\phi_s)]\\ &\quad+[R+(b/L)]\sin(2\phi_s) \ ,\end{aligned} \tag{19}$$

and

$$\begin{aligned}\frac{\partial^2 g}{\partial\phi_b^2}&=2 \ ,\\ \frac{\partial^2 g}{\partial\phi_s^2}&=2\{I+[(b/L)+2R]\cos(2\phi_s)\\ &\qquad-R(\phi_s-\phi_b)\sin(2\phi_s)\} \ .\\ \frac{\partial^2 g}{\partial\phi_b\partial\phi_s}&=-2[1+R\cos(2\phi_s)] \ .\end{aligned} \tag{20}$$

The function H, introduced in (13), is then given by

$$\begin{aligned}H=4[&(b/L)\cos(2\phi_s)-R(\phi_s-\phi_b)\sin(2\phi_s)\\ &-R^2\cos^2(2\phi_s)] \ .\end{aligned} \tag{21}$$

By setting $\partial g/\partial\phi_b=\partial g/\partial\phi_s=0$, one obtains the system of equations

$$\begin{aligned}&2(\phi_s-\phi_b)+R\sin(2\phi_s)=0 \ ,\\ &2(\phi_s-\phi_b)[1+R\cos(2\phi_s)]+[R+(b/L)\sin(2\phi_s)=0\end{aligned} \tag{22}$$

from which simple calculations show that the surface tilt angle ϕ_s is given by the transcendental equation

$$[(b/LR^2)-\cos(2\phi_s)]\sin(2\phi_s)=0 \tag{23}$$

and the bulk tilt angle ϕ_b by

$$\phi_b=\phi_s+(R/2)\sin(2\phi_s) \ . \tag{24}$$

Equation (23) has the solutions

$$\phi_s=\begin{cases}0 \ , & \text{giving } \phi_b=0 \text{ (homeotropic alignment)}\\ \pi/2 \ , & \text{giving } \phi_b=\pi/2 \text{ (planar alignment)} \ ,\end{cases} \tag{25a}$$

$$\cos(2\phi_s)=b/LR^2 \quad \text{(tilted alignment) , giving} \tag{25b}$$

$$\phi_b=\tfrac{1}{2}[\cos^{-1}(b/LR^2)+R\sqrt{1-(b/LR^2)^2}] \ . \tag{25c}$$

Of course, the solution (25c) exists only if $b/LR^2<1$. By taking into account that $\partial^2 g/\partial\phi_b^2=2>0$ to analyze the stability of the three phases, it is enough to analyze the sign of H. Simple calculations give

$$H(0,0)=4R^2[(b/LR^2)-1] \ , \tag{26a}$$

$$H(\pi/2,\pi/2)=-4R^2[(b/LR^2)+1] \ , \tag{26b}$$

$$H(\phi_b,\phi_s)=2R^2[1-(b/LR^2)^2] \ . \tag{26c}$$

Equations (26) show that the planar alignment is never stable if $w>0$, as assumed. The homeotropic alignment is stable for

$$b/LR^2>1 \ , \quad \text{giving } bwK/K_{13}^2>1 \ . \tag{27}$$

On the contrary, the tilted alignment is stable for

$$b/LR^2<1 \ , \quad \text{giving } bwK/K_{13}^2<1 \ . \tag{28}$$

It is important to stress that the temperature dependences of w, K, and K_{13} are not the same. Consequently the threshold condition

$$bwK/K_{13}^2=1 \tag{29}$$

defines a critical temperature T_s at which a surface transition takes place. By taking into account that near T_c (the clearing temperature), one can write

$$\begin{aligned}&w=\alpha S+\beta S^2 \text{ (Ref. [11]) ,}\\ &K=\gamma S^2 \text{ (Ref. [9]) ,}\\ &K_{13}=\mu S \text{ (Ref. [39]) ,}\end{aligned} \tag{30}$$

where α,β,γ,μ are temperature independent, Eq. (29) gives, at the first order in S,

$$S_s=\mu^2/(\gamma b\alpha) \ . \tag{31}$$

For $S>S_s$ (which implies $T<T_s$), (27) holds and the sample is in homeotropic alignment. On the contrary, for $S<S_s$ (i.e., $T>T_s$), (28) holds and the NLC is in tilted alignment. For $T>T_s$, where ϕ_s is small, one obtains

$$\phi_s=\{\tfrac{1}{2}[1-(b/LR^2)]\}^{1/2} \tag{32}$$

for the surface tilt angle and

$$\phi_b=(1+R)\{\tfrac{1}{2}[1-(b/LR^2)]\}^{1/2} \tag{33}$$

for the bulk tilt angle. Equations (32) and (33), taking into account (29) and (30) and the definition of S_s, give

$$\phi_s=A(S_s-S)^{1/2} \tag{34}$$

and

$$\phi_b = B(S_s - S)^{1/2} , \quad (35)$$

where A and B, for $T \sim T_s$, can be considered temperature independent. By assuming for $S(T)$ the second-order transition law

$$S(T) = \Delta[1-(T/T_c)]^{1/2} , \quad (36)$$

where Δ is a constant, Eqs. (34) and (35) can be rewritten as

$$\phi_s(T) = A'(S_s)[(T-T_s)/(T_c-T_s)]^{1/2} \quad (37)$$

and

$$\phi_b(T) = B'(S_s)[(T-T_s)/(T_c-T_s)]^{1/2} , \quad (38)$$

in agreement with the experimental trend of ϕ_b versus T observed by Chiarelli, Faetti, and Fronzoni [4]. The continuity of ϕ_s and ϕ_b from zero, above threshold, shows that the TST is a continuous transition. Their $(\Delta T)^{1/2}$ dependence is the same as the one deduced from the simplest Landau-like models based on a phenomenological expansion of f_s [41]. A very recent paper describing a continuous anchoring transition in liquid crystals confirms on a larger temperature scale the $(\Delta T)^{1/2}$ dependence of the tilt angle [42].

IV. DISCUSSION

Let us first generalize our predictions. Obviously, one could have chosen a *planar* stable low-temperature anchoring. The K_{13} destabilizing effect allows us to predict in the same way a *planar* toward *homeotropic* transition. The only requirement to observe a surface instability is to start from a symmetric situation. An initial tilted orientation would just present a continuous temperature variation without threshold, as recently discussed [39]. The surface destabilizing effect of the mixed splay-bend elasticity is evident from its linear dependence in surface curvature: this curvature can choose the right sign to minimize the free energy, whatever may be the sign of K_{13} and the symmetrical initial geometry. A more serious question bears on the existence of K_{13} itself. This term was discarded by Frank [43]. One knows from Nehring and Saupe [33] that K_{13} is related to the angular dependence of the nematic-nematic interactions. Everyone now agrees that this interaction is indeed anisotropic and that K_{13} should exist. Only one K_{13} measurement has been performed until now [44], but its reliability can be questioned since the data analysis is based on an approximated model [35]. Anyway, the estimated value of K_{13} from Ref. [44] is $K_{13}=10^{-6}$ cgs units. Assuming the validity of our model, we can try to estimate K_{13} from the threshold condition [Eq. (31)]. The transition temperature T_s is close to T_c, the nematic-isotropic temperature transition. S_s can then be estimated as $S_s \sim 0.4$. Taking a strong anchoring $\alpha \simeq 1$ cgs units, $\gamma \simeq 1$ cgs units, and $b \simeq 25$ Å, we find $\mu \simeq 3\times10^{-7}$ cgs units, i.e., $|K_{13}| = \mu S \sim 10^{-7}$ cgs units, a bit smaller than the usual curvature constants. We cannot say anything on the K_{13} sign, which does not intervene in the problem, as previously explained.

One specific prediction of the model is the large variation of the tilt angle close to the surface, after the onset of the TST. It is interesting to compare this prediction to the experimental observations. Surface tilt angle measurements have been made, close to the transition, using a volume birefringence measurement or a total reflection technique. These two methods give in general different results [41]. This is unexplained in all previous simple models. It can easily be understood with the present K_{13} induced TST model. Depending on the sign of K_{13}, ϕ_s is smaller or larger than ϕ_b.

A last simplification of our model is the lack of a flexoelectric term in the energy. The surface localized curvature induces a flexoelectric polarization even in absence of an external field, with an electrostatic self energy. The flexoelectric charges cannot be assumed screened by ions, since the localization size $b \simeq \xi$ is expected smaller than the Debye screening length, of the order of 1000 Å for the usual NLC conductivity. This self-energy is well known [29] to renormalize the NLC elastic constants, at least for small distortions. This can affect the amplitude above threshold, but not the threshold itself. A complete quantitative model should take flexoelectricity into account, in addition to the initial anisotropy of the usual bend and splay curvature elastic constants.

Note, finally, that, from symmetry considerations, one does not expect any flexoelectric polarization from the second-order $\mathbf{n}$ derivatives. We could write the polarization $\mathbf{P}$ as

$$P_i = \lambda_{ijkl} n_{j,kl} .$$

$\mathbf{P}$ should be invariant for the inversion operation $\mathbf{n} \rightarrow -\mathbf{n}$. λ must be zero, since the undistorted NLC is not polar.

V. CONCLUSION

We have proposed a mechanism to explain the observed temperature surface transitions of nematic liquid crystals anchored on solid boundaries. We describe the stable low-temperature orientation by a strong nematic-substrate anchoring potential around, for example, the *homeotropic* orientation. We introduce the splay-bend K_{13} curvature elasticity, which tends to create a strong spontaneous distortion at the boundaries. This self-curvature tendency is localized near the surface, by an elastic saturation term proportional to the square of the second derivative of the tilt angle. Heating the nematic, the surface transition appears because the destabilizing effect from K_{13}, proportional to S, becomes larger than the stabilizing effects from the bulk usual curvature elasticity and surface anchoring, proportional to S^2. The transition toward *planar* anchoring is predicted to be continuous, with the square of the tilt angle proportional to the temperature difference from the surface transition temperature, justifying previous phenomenological models. The weak resulting anchoring energy, which goes to zero at the transition, appears as the difference between two larger quantities: the strong direct nematic-substrate interaction, and the destabilizing nematic-nematic interaction. One can make symmetrical predictions for a *planar* toward *homeotropic* transition, under heating.

This temperature-induced surface transition model has been developed in the frame of continuum theory. The intrinsic length connected with second-order elasticity is expected to range between the usual coherence length ξ of the nematic-isotropic transition and a molecular size. We are obviously at the limit of validity of continuum theory. However, since our predictions agree with and explain previously understood experimental observations, we believe that the model is at least qualitatively correct. If one believes our model, the temperature-induced surface transitions would probably be the strongest evidence of the existence of the mixed splay-bend elasticity K_{13} in nematic liquid crystals. Future experiments should help us to choose between the present model for the temperature-driven surface transitions and previous ones.

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[1] M. A. Bouchiat and D. Langevin-Cruchon, Phys. Lett. **34A**, 331 (1971).

[2] S. Faetti and L. Fronzoni, Solid State Commun. **25**, 1087 (1978).

[3] P. Chiarelli, S. Faetti, and L. Fronzoni, J. Phys. (Paris) **44**, 1061 (1983).

[4] P. Chiarelli, S. Faetti, and L. Fronzoni, Phys. Lett. **101A**, 31 (1984).

[5] G. A. DiLisi, C. Rosenblatt, A. C. Griffin, and Uma Hari, Liq. Cryst. **7**, 359 (1990).

[6] L. Flatischler, L. Komitov, S. T. Lagerwall, B. Stebler, and A. Strigazzi, Mol. Cryst. Liq. Cryst. **189**, 119 (1991).

[7] L. Komitov, S. T. Lagerwall, A. Sparavigna, B. Stebler, and A. Strigazzi, Mol. Cryst. Liq. Cryst. **223**, 197 (1992).

[8] G. Barbero, T. Beica, A. L. Alexe-Ionescu, and R. Moldovan, Liq. Cryst. **14**, 1125 (1993).

[9] P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974).

[10] J. W. Goossens, Mol. Cryst. Liq. Cryst. **124**, 305 (1985).

[11] T. J. Sluckin and A. Poniewiersi, in *Fluid and Interfacial Phenomena,* edited by C. A. Croxton (Wiley, Chichester, 1984).

[12] G. Barbero, Z. Gabbasova, and M. A. Osipov, J. Phys. II (France) **1**, 691 (1991).

[13] M. Nobili and G. Durand, Phys. Rev. A **46**, 6174 (1992).

[14] A. Rapini and M. Papoular, J. Phys. (Paris) Colloq. **30**, C4-54 (1969).

[15] A. L. Alexe-Ionescu, R. Barberi, G. Barbero, T. Beica, and R. Moldovan, Z. Naturforsch. A **47**, 1235 (1992).

[16] J. D. Parson, Phys. Rev. Lett. **41**, 877 (1978).

[17] W. E. McMullen, Phys. Rev. A **40**, 2649 (1989).

[18] W. E. McMullen and B. G. Moore, Mol. Cryst. Liq. Cryst. **198**, 107 (1991).

[19] M. F. Sharlow and W. M. Gelbart, Liq. Cryst. **11**, 25 (1992).

[20] R. Holyst and A. Poniewierski, Phys. Rev. A **38**, 1527 (1988).

[21] A. Poniewiersi and R. Holyst, Phys. Rev. A **38**, 3721 (1988).

[22] R. Holyst and A. Poniewiersi, Mol. Cryst. Liq. Cryst. **192**, 65 (1990).

[23] W. E. McMullen, Phys. Rev. A **38**, 6384 (1988).

[24] C. Buzano, Mol. Cryst. Liq. Cryst. **199**, 419 (1991).

[25] H. V. Kanel, J. D. Litster, J. Mengalis, and H. I. Smith, Phys. Rev. A **24**, 2713 (1981).

[26] H. Mada, Mol. Cryst. Liq. Cryst. **51**, 43 (1979); **53**, 127 (1979).

[27] A. Toda, H. Mada, and S. Kobayashi, Jpn. J. Appl. Phys. **17**, 261 (1978).

[28] G. Barbero, I. Dozov, J. Palierne, and G. Durand, Phys. Rev. Lett. **56**, 2056 (1986).

[29] G. Barbero and G. Durand, J. Phys. (Paris) **47**, 2129 (1986).

[30] G. Barbero, Z. Gabbasova, and Yu. A. Kosevich, J. Phys. II (France) **1**, 1505 (1991).

[31] G. Barbero and A. Stringazzi, Liq. Cryst. **5**, 693 (1989).

[32] G. Barbero, N. V. Madhusudana, and C. Oldano, J. Phys. (Paris) **50**, 2263 (1989).

[33] J. Nehring and A. Saupe, J. Chem. Phys. **54**, 337 (1971).

[34] G. Barbero, Mol. Cryst. Liq. Cryst. **195**, 199 (1991).

[35] H. P. Hinov, Mol. Cryst. Liq. Cryst. **148**, 197 (1987).

[36] C. Oldano and G. Barbero, J. Phys. Lett. (Paris) **46**, 451 (1985).

[37] G. Barbero, A. Sparavigna, and A. Strigazzi, Nuovo Cimento D **12**, 1259 (1990).

[38] For a recent review see A. L. Alexe-Ionescu, Mod. Phys. Lett. B **7**, 307 (1993).

[39] A. L. Alexe-Ionescu, G. Barbero, and G. Durand, J. Phys. II (France) **3**, 1247 (1993); P. I. C. Teixera, V. M. Pergamenshchik, and T. J. Sluckin, Phys. Rev. E (to be published).

[40] H. Mada and S. Kobayashi, *Liquid Crystals,* edited by S. Chandrasekar (Cambridge University Press, Cambridge, 1992).

[41] S. Faetti, in *Physics of Liquid Crystalline Materials,* edited by I. C. Khoo and F. Simoni (Gordon and Breach, New York, 1991).

[42] S. Patel and H. Yokayama, Nature **362**, 525 (1993).

[43] F. C. Frank, Disc. Faraday Soc. **25**, 19 (1958).

[44] N. V. Madhusudana and R. Pratiba, Mol. Cryst. Liq. Cryst. **179**, 207 (1990).