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van der Waals–induced distortions in nematic liquid crystals close to a surface

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By a discrete-layer model, we investigate theoretically the alignment of a nematic liquid crystal close to a flat amorphous substrate. We show that the presence of van der Waals interactions induces a strong distortion localized in a few molecular lengths. We compare these predictions with that of a continuum model recently developed by some of us. In the continuum model, we derive approximate analytical expressions for the distortion profile, showing that, asymptotically, the distortion decays as the inverse of the distance from the substrate. The amplitude of the distortion according to the two models is different, but the main qualitative features remain unchanged. We show that the main distorting mechanism can be attributed to an effective surface field. The existence of a subsurface distortion is compatible with some recent measurements of the alignment of the first molecular layer, performed with optical second-harmonic generation techniques. [S1063-651X(96)01305-8]

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I. INTRODUCTION

Long-range bulk distortions in nematic liquid crystals (NLC's) are well described by the continuum theory proposed long ago by Frank [1]. According to this theory the bulk elastic energy density F of a distorted NLC is a quadratic form of the deformation tensor $n_{i,j}=\partial n_i/\partial x_j$, where $\boldsymbol{n}$ is the NLC director. This means that

$$F=F_0+K_{ij}n_{i,j}+\frac{1}{2}K_{ijkl}n_{i,j}n_{k,l}, \tag{1.1}$$

where $F_0=F(n_{i,j}=0)$ is the energy density of the undeformed state and K_{ij} and K_{ijkl} are the elements of the elastic tensors. The elastic tensors can be decomposed in terms of the elements of symmetry of the NLC phase and of the unit tensor δ_{ij}. In the bulk $K_{ij}=0$, F_0 is constant and $f=F-F_0$ may be written in the form

$$f=\frac{1}{2}[k_{11}(\nabla\cdot\boldsymbol{n})^2+k_{22}(\boldsymbol{n}\cdot\nabla\times\boldsymbol{n})^2+k_{33}(\boldsymbol{n}\times\nabla\times\boldsymbol{n})^2]$$
$$-(k_{22}+k_{24})\nabla\cdot(\boldsymbol{n}\nabla\cdot\boldsymbol{n}+\boldsymbol{n}\times\nabla\times\boldsymbol{n}). \tag{1.2}$$

In this framework the equilibrium director field, in the absence of external fields, is found by minimizing the total energy of the NLC sample defined by

$$G=\int\int\int_\tau f\,d\tau+\int\int_\Sigma f_S\,d\Sigma, \tag{1.3}$$

where τ is the volume of the sample and Σ its surface. The surface energy density f_S takes origin from the direct NLC-substrate interaction and from the NLC-NLC interaction and is generally assumed to be of the kind $f_S=f_S(n_i)$, i.e., only depending on the surface director.

In this approximation the elastic constants entering in Eq. (1.2) are supposed position independent up to the bounding surface. A variation of these constants is expected in a boundary layer having a thickness of the order of the range of the intermolecular forces. Such position dependences of the elastic constants are taken into account in f_S, which gives the surplus of the elastic energy density localized near the boundary surface and characterizing the NLC-substrate interactions.

To connect the elastic constants with the intermolecular interaction energy g responsible for the NLC phase, it is necessary to use a molecular model. In the mean field approximation we obtain [2]

$$F=F_0+K_{ij}n_{i,j}+K_{ijk}n_{i,jk}+\frac{1}{2}K_{ijkl}n_{i,j}n_{k,l}, \tag{1.4}$$

where F_0, K_{ij}, K_{ijk}, and K_{ijkl} depend on the form of the intermolecular interaction energy. In the bulk $K_{ij}=0$ and $K_{ijk}n_{i,jk}$ can be written as the sum of a "surfacelike" term $k_{13}\nabla\cdot(\boldsymbol{n}\nabla\cdot\boldsymbol{n})$ and of terms that simply renormalize the Frank bulk elastic constants k_{11}, k_{22}, and k_{33}. The bulk k_{13}-dependent term can be integrated, giving a surface contribution to the elastic energy that depends on the surface gradient of $\boldsymbol{n}$.

Long ago it had been shown that the variational problem that defines the director field is not a standard problem when the k_{13} term is present [3]. In fact, the presence of a surface term depending on the normal derivative of $\boldsymbol{n}$ introduces a surface "discontinuity" of $\boldsymbol{n}$, which has been interpreted as a strong distortion of the director field within the boundary layer [3]. Recently, it has been shown that near the boundary the quantities K_{ij} are different from zero and renormalize the

k_{13} term, introducing an effective splay-bend elastic constant [4]. More precisely, it has been shown that nonzero energy terms depending on k_{13} and K_{ij} are related to the presence of distorting intermolecular interactions [2] and that the distorting effects of such terms partially compensate each other [4].

A well posed variational problem giving a well defined subsurface distortion is obtained by taking into account also terms proportional to the square of the second-order derivatives of $\boldsymbol{n}$, connected to a new elastic constant k^* in the limit of small deformations [5]. In the framework of this extended elastic theory, the usual elastic constants are assumed to be position independent and their position dependence near the boundaries is at least partially taken into account by the new terms. As in all the extended elastic theories, it appears an intrinsic mesoscopic length, defined by $b=\sqrt{k^*/k}$, over which deviations from the standard predictions take place. Here k is an average bulk Frank elastic constant, of the order of k_{11}, k_{22}, k_{33}. The length b is of the order of the interaction range of the intermolecular forces responsible for the NLC phase [6]. Following this approach, an elastic model [7] has been proposed to interpret the temperature surface transitions in NLC in terms of the different temperature dependences of k_{13} and k [8,9].

Since the surface distortion of the average molecular orientation takes place over the mesoscopic length b, an elastic description in the surface layer can be questioned. Hence the extended elastic theory has to be considered as a rough approximation of the true description.

The existence of a possible strong subsurface distortion has been criticized by some authors. In particular Pergamenshick and co-workers [10–12] and Hinov [13–15] suggest that the subsurface discontinuity is an artifact of the theory. They also suggest a method to solve the variational problem without the introduction of new terms, which gives smooth profiles up to the surface [10–15]. However, several authors have pointed out the inconsistencies of this theory [16–20]: for example, the conservation of the angular momentum does not seem to be satisfied [17].

Other models have been proposed to describe the elastic properties of the surface layer, by introducing position-dependent surface elastic constants, obtained by taking into account of the reduced symmetry of the NLC close to the surface [21–23]. These approaches have the drawback that the number of surface elastic constants is relatively large and their position dependences give rise to cumbersome Euler-Lagrange equations.

In this paper we propose a molecular approach to analyze the possibility of a subsurface distortion. The director profile is obtained by minimizing the total molecular interaction energy. We consider a two-body interaction energy g given by a superposition of a short-range Maier-Saupe-like interaction [24] and of the long-range-induced dipole-induced dipole Nehring-Saupe contribution [25]. The Maier-Saupe-like term stabilizes a uniform orientation and can be approximated by an effective elastic constant. This amounts to assuming that the stabilizing terms are mainly due to steric contact interactions. The Nehring-Saupe term, as we will show, is responsible for the subsurface deformation. These potentials are known to be not too realistic: for instance, they lead to values of elastic constants that are not very close to the experimental data [9]. However, they are good model potentials, as they greatly simplify the calculations, retaining the essential kind of functional dependence of more realistic, but much more complex, interaction laws, as the Gay-Berne potential [26]. In Sec. II we consider a discrete-layer model, in which a smecticlike order is supposed. In Sec. III we compare this model with a continuum approach, recently developed by some of us, in which the molecular density is supposed to be uniform [27]. Even though the amplitude of the subsurface distortion is found to be much smaller in the discrete-layer model, its qualitative characteristics remain almost unchanged. In the limit of surface distortions with a small amplitude, by a suitable approximation, we derive an analytical expression for the distortion profile in the continuum model. This approximation shows that the main contribution to the surface distortion comes from an anisotropic energy density confined close to the surface. This anisotropic energy depends only on the profile and not on its derivatives. The amplitude of the subsurface deformation versus the surface tilt angle shows a behavior similar to that obtained in the framework of the extended elastic theory proposed in [5]. In Sec. IV the limits of the model and its possible extensions are discussed. In Sec. V we draw the main conclusions of our models.

II. DISCRETE MODEL

Let us consider a NLC slab having a finite size in the z direction. We consider only planar distortions, with the nematic director $\boldsymbol{n}$ in the (y,z) plane forming the tilt angle $\varphi=\varphi(z)$ with the z axis. The scalar order parameter is assumed to be equal to one; the major molecular axis coincides with the NLC director. We make a discrete model along z by supposing that the NLC consists of equally spaced planes orthogonal to the z direction, with a constant surface density in each plane. This last approximation amounts to supposing a smecticlike ordering: it might be most appropriate to describe Langmuir-Blodgett multilayers.

Our approximations are rather crude; in particular, in a more realistic situation, contributions to the free-energy coming from gradients of the scalar order parameter and of the molecular density should appear. In Sec. IV we will discuss in more detail these approximations and we will outline some possible extensions of this model.

According to our hypotheses, the molecular density per unit volume is

$$\rho(\boldsymbol{r})=\rho\sum_{n=0}^{N}\delta(\zeta-n), \tag{2.1}$$

where $N+1$ is the number of planes, ρ is a constant molecular density, and $\zeta=z/r_0$ is a normalized coordinate along the surface normal. Here r_0 is the thickness of each smectic plane; therefore it is of the order of the molecular dimensions.

Let the interaction energy between two molecules at $\boldsymbol{R}$ and $\boldsymbol{R}'$ contains a Nehring-Saupe-induced dipole-induced dipole contribution [25]

$$g_{\mathrm{NS}}(\boldsymbol{R},\boldsymbol{R}')=-\frac{C}{r^6}[\boldsymbol{n}\cdot\boldsymbol{n}'-3(\boldsymbol{n}\cdot\boldsymbol{u})(\boldsymbol{n}'\cdot\boldsymbol{u})]^2, \tag{2.2}$$

where $\boldsymbol{n}=\boldsymbol{n}(\boldsymbol{R})$, $\boldsymbol{n}'=\boldsymbol{n}(\boldsymbol{R}'=\boldsymbol{R}+\boldsymbol{r})$, $\boldsymbol{u}=\boldsymbol{r}/r$, and C is a positive constant. Thanks to Eq. (2.1), the corresponding energy per unit surface can be written as

$$\begin{aligned}\mathscr{F}_{\mathrm{NS}}&=\frac{1}{2}\int g_{\mathrm{NS}}(\mathbf{r},\mathbf{r}')\rho(\mathbf{r})\rho(\mathbf{r}')d\mathbf{r}'dz\\&=\mathscr{F}_0\sum_{m,n=0}^{N} f(\varphi_m,\varphi_n,m,n),\end{aligned}\tag{2.3}$$

with $\mathscr{F}_0=\pi C\rho^2/(64r_0^2)$ and $\varphi_m=\varphi(\zeta=m)$. The function $f(\varphi_m,\varphi_n,m,n)$ for $m\neq n$ can be readily evaluated by substituting the interaction energy (2.2) in (2.3). One thus obtains, up to a term independent of the angle,

$$f(\varphi_m,\varphi_n,m,n)=-3\frac{(\cos^2\varphi_m+\cos^2\varphi_n+3\cos^2\varphi_m\cos^2\varphi_n)}{(m-n)^4}.\tag{2.4}$$

For $m=n$ the interaction energy (2.2) would give a divergent contribution; a suitable cutoff should be introduced. Alternatively, one can observe that, for any nematic interaction, the interaction energy of each molecule must be independent of the director orientation in a unlimited homogeneously aligned sample. This means that

$$\sum_{n=-\infty}^{\infty} f(\varphi_m,\varphi_m,m,n)=\text{const.}\tag{2.5}$$

By exploiting this general property and setting the arbitrary constant value of the energy to zero, we arrive at

$$\begin{aligned}f(\varphi_m,\varphi_m,m,m)&=-\sum_{\substack{n=-\infty\\ n\neq m}}^{\infty} f(\varphi_m,\varphi_m,m,n)\\&=-\frac{\pi^4}{15}(2\cos^2\varphi_m+3\cos^4\varphi_m).\end{aligned}\tag{2.6}$$

We suppose that all the other molecular interactions favor a uniform nematic order such as, e.g., the Maier-Saupe interaction [24], and that they can essentially be accounted for by a usual elastic contribution [27]. Its discrete implementation can be written as

$$\mathscr{F}_{\mathrm{el}}=\mathscr{F}_0\kappa\sum_{m=0}^{N-1}(\varphi_{m+1}-\varphi_m)^2,\tag{2.7}$$

κ being a normalized elastic constant.

To determine the director profile, we minimize the sum of the two energies (2.3) and (2.7) by considering the angles φ_m of each layer as minimization parameters. A strong symmetric anchoring is imposed: $\varphi(0)=\varphi(N)=\varphi_s$. In this situation the profile is symmetric with respect to the center of the sample: $\varphi_m=\varphi_{N-m}$. Good results are obtained for $\varphi_s\lesssim 75°$, whereas for $\varphi_s>75°$ the convergence is slower due to the low sensitivity of the energy on the profile. Figure 1 shows the director profile obtained for 42 layers, for different surface angles φ_s in the absence of the elastic contribution ($\kappa=0$). As one immediately notes, the Nehring-Saupe interaction induces a distortion of the director profile confined in a few layers close to the surface, tending to align the director parallel to the surface. The largest distortion is among the first two layers. The first half of the director profile can be fitted very well with the function

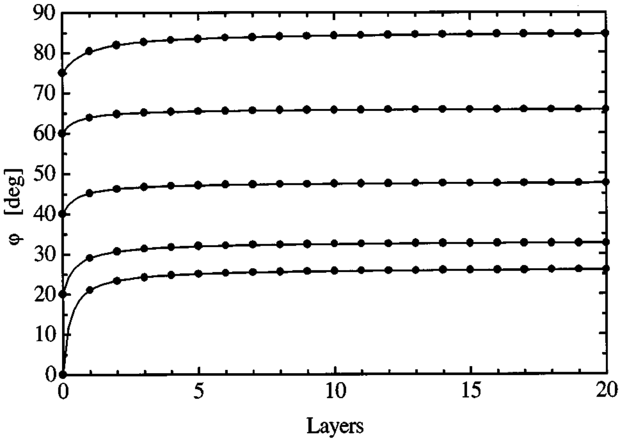

FIG. 1. Discrete director profile φ_m (circles) and fit (solid line) according to Eq. (2.8), for different surface angles, in a symmetric sample with 42 layers. The normalized elastic constant κ is zero. Only half of the profiles are shown.

$$\varphi(z)=\varphi_b-(\varphi_b-\varphi_s)\frac{\lambda}{\zeta+\lambda},\tag{2.8}$$

where φ_b is the saturation bulk angle and λ plays the role of a normalized penetration length. The fit is shown by the solid lines in Fig. 1. The functional dependence (2.8) is always a very good approximation of the true profile for $\varphi_s<75°$ and allows a faster determination of the director profile by minimizing the total energy only with respect to the two parameters φ_b and λ. For $\kappa=0$ the maximum subsurface distortion $\Delta\varphi=\varphi_b-\varphi_s$, as a function of the surface angle φ_s, is reached for the homeotropic anchoring $\varphi_s=0$.

The introduction of the elastic term decreases the amplitude of the distortion and shifts the maximum subsurface distortion $\Delta\varphi$, as a function of the surface angle φ_s, from $\varphi_s=0$ to $\varphi_s\approx 35°$. This is shown in Fig. 2. In Fig. 3 we

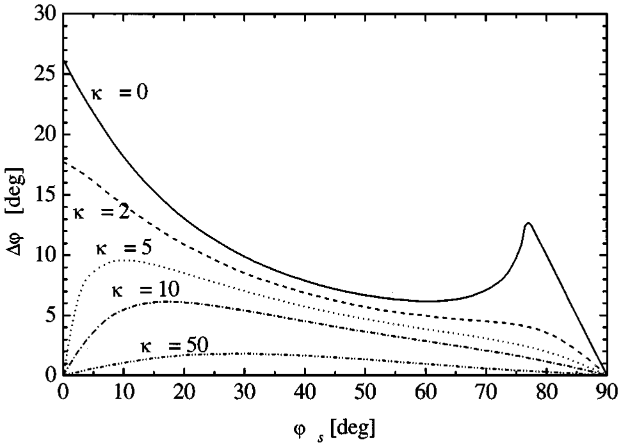

FIG. 2. Distortion angle $\Delta\varphi=\varphi_b-\varphi_s$ as a function of the surface anchoring angle φ_s for different values of the normalized elastic constant κ.

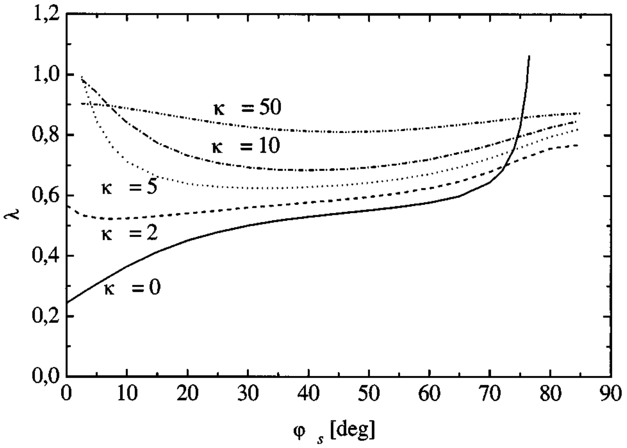

FIG. 3. Normalized penetration length λ corresponding to the distortion angles shown in Fig. 2.

report the values of the normalized penetration length λ corresponding to the curves shown in Fig. 2. As the elastic contribution increases, λ correspondingly increases: as expected, the distortion tends to be less abrupt. We note that for $\kappa=0$, φ_b reaches 90° for $\varphi_s \geqslant 78°$: this explains the linear behavior of $\Delta\varphi$ in this region (see Fig. 2). The corresponding values of λ cannot be properly determined, as the profile cannot be well approximated with the expression (2.8). Considering the bulk angle φ_b as an order parameter and the normalized elastic constant κ as a control parameter, for $\varphi_s=0$ we find a second-order transition at $\kappa=\kappa_c \cong 3.41$ as shown in Fig. 4: for $\kappa > \kappa_c$ the uniform homeotropic alignment is stable.

III. CONTINUUM MODEL

In Ref. [27], a continuum model of the molecular orientation close to an interface has been developed and numerically analyzed by using a trial function: a subsurface deformation arising from van der Waals interactions has been clearly demonstrated. In this section we want to compare the results obtained in Ref. [27] with those previously discussed. This comparison is particularly interesting since the continuum and the discrete-layer model somewhat represent two extreme idealized situations: the first model assumes that close to the surface the nematic order is unchanged, while the latter supposes that a smecticlike ordering is induced.

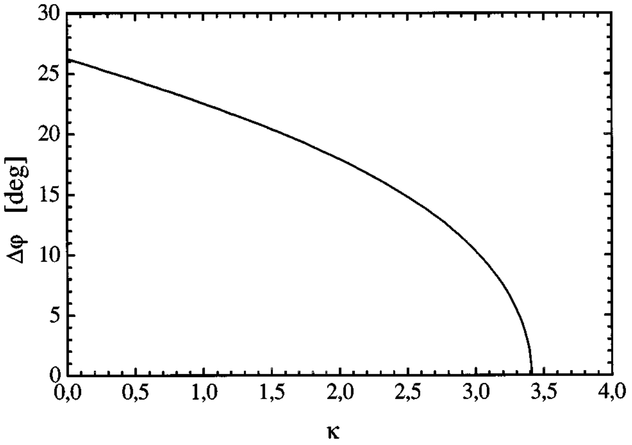

FIG. 4. Distortion angle $\Delta\varphi$ as a function of the normalized elastic constant κ for the anchoring angle $\varphi_s=0$ (homeotropic anchoring). A second-order transition takes places at $\kappa=\kappa_c \cong 3.41$.

In the numerical approach used in Ref. [27] an exponential trial function for the director profile had been assumed for the sake of simplicity. Here, in the limit of small distortions, we derive approximated analytical expressions for the distortion profile that shed some light on the origin of the distorting mechanism.

From now on we will consider a semi-infinite NLC sample since, as it has been shown in Sec. II, the NLC orientation changes only over a few molecular layers near the surfaces. Let us focus our attention on the case of surface distortions with a small amplitude $\Delta\varphi \ll 1$, corresponding to a small van der Waals contribution. In the continuum model the energy per unit surface is given by [27]

$$\mathscr{F}=\mathscr{F}_0\left[(1-\nu)\int_0^{+\infty}d\zeta\int_{-\zeta}^{+\infty}f(\zeta,\zeta')d\zeta' + \nu\int_0^{+\infty}\varphi'^2(\zeta)d\zeta\right], \tag{3.1}$$

where, as in Sec. II, $\mathscr{F}_0=\pi\rho^2 C/(64\,r_0^2)$, $\zeta=z/r_0$ is the normalized distance of one molecule from the surface, $\zeta'=z'/r_0$ is the normalized distance between two molecules along the z axis, and [22]

$$\begin{aligned} f(\zeta,\zeta') &= -3[\cos^2\varphi(\zeta)+\cos^2\varphi(\zeta+\zeta') \\ &\quad +3\cos^2\varphi(\zeta)\cos^2\varphi(\zeta+\zeta')]\zeta'^{-4} \quad \text{for } |\zeta'|>1, \\ f(\zeta,\zeta') &= (63\,\zeta'^4-88\,\zeta'^2+22)[\cos^2\varphi(\zeta)+\cos^2\varphi(\zeta+\zeta')] \\ &\quad +(-171\,\zeta'^4+200\,\zeta'^2-38)\cos^2\varphi(\zeta) \\ &\quad \times\cos^2\varphi(\zeta+\zeta')+(36\,\zeta'^4-40\,\zeta'^2+4)\sin[2\varphi(\zeta)] \\ &\quad \times\sin[2\varphi(\zeta+\zeta')] \quad \text{for } |\zeta'|<1. \end{aligned} \tag{3.2}$$

The first term in Eq. (3.1), proportional to $(1-\nu)$, comes from the Nehring-Saupe interaction, the second one, proportional to ν, from the Maier-Saupe interaction. The parameter ν is related to the normalized elastic constant κ introduced in Sec. II as $\nu=\kappa/(1+\kappa)$.

The Nehring-Saupe contribution is difficult to treat owing to its highly nonlocal character. The energy of a given distorted profile depends on the values of φ at pairs of distant points ζ and $\zeta+\zeta'$: a power series expansion in ζ', which would eliminate this nonlocal character by introducing the derivatives of the profile at a generic point ζ, is not possible because it does not converge. This is related to the long-range character of van der Waals interactions. However, if the distortion $\Delta\varphi$ is small, we may hope that a good approximation can be obtained by setting $\varphi(\zeta+\zeta')=\varphi(\zeta)$ in Eq. (3.2). This amounts to neglecting the rotation of the molecules in a few interaction radii r_0. Within this approximation, Eq. (3.1) becomes

$$\mathscr{F}=\mathscr{F}_0\left\{\int_0^1[(1-\nu)(54\zeta^5-112\zeta^3+60\zeta)\cos^2\varphi(\zeta)+(-63\zeta^5+120\zeta^3-54\zeta)\cos^4\varphi(\zeta)+\nu\varphi'^2(\zeta)]d\zeta+\int_1^{+\infty}\left[(1-\nu)\frac{\cos^2\varphi(\zeta)[2+3\cos^2\varphi(\zeta)]}{\zeta^3}+\nu\varphi'^2(\zeta)\right]d\zeta\right\}. \tag{3.3}$$

Now the functional (3.3) has a standard form and its minimum is given by the solution of the associated Euler-Lagrange equation. Following the starting hypothesis that the distortion is small and in the strong anchoring situation $\varphi(0)=\varphi_s$, we set $\varphi(\zeta)=\varphi_s+\epsilon(\zeta)$, where $|\epsilon(\zeta)|\ll 1$, and we linearize the Euler-Lagrange equation with respect to the distortion $\epsilon(\zeta)$. At lowest order, for $0<1-\nu\ll 1$, we get

$$\epsilon''(\zeta)=(1-\nu)[-27\zeta^5+56\zeta^3-30\zeta+(63\zeta^5-120\zeta^3+54\zeta)\cos^2\varphi_s]\sin(2\varphi_s) \quad \text{for } \zeta<1, \tag{3.4a}$$

$$\epsilon''(\zeta)=-(1-\nu)(1+3\cos^2\varphi_s)\sin(2\varphi_s)\zeta^{-3} \quad \text{for } \zeta>1. \tag{3.4b}$$

Equations (3.4) have to be solved with the boundary conditions $\epsilon(0)=0$ and $\epsilon'(+\infty)=0$ and with the continuity of $\epsilon(1)$ and $\epsilon'(1)$. This gives the profile

$$\epsilon(\zeta)=(1-\nu)\left[-\frac{9}{14}\zeta^7+\frac{14}{5}\zeta^5-5\zeta^3+6\zeta+\left(\frac{3}{2}\zeta^7-6\zeta^5+9\zeta^3-6\zeta\right)\cos^2\varphi_s\right]\sin(2\varphi_s) \quad \text{for } \zeta<1, \tag{3.5a}$$

$$\epsilon(\zeta)=(1-\nu)\left[\frac{128}{35}-\frac{1}{2\zeta}(1+3\cos^2\varphi_s)\right]\sin(2\varphi_s) \quad \text{for } \zeta>1. \tag{3.5b}$$

The asymptotic shape of the profile given by this approximation is in agreement with the profiles numerically found in the discrete-layer approximation. The corresponding subsurface deformation $\Delta\varphi=\varphi(+\infty)-\varphi_s=\epsilon(+\infty)$ is

$$\Delta\varphi=\frac{128}{35}(1-\nu)\sin(2\varphi_s). \tag{3.6}$$

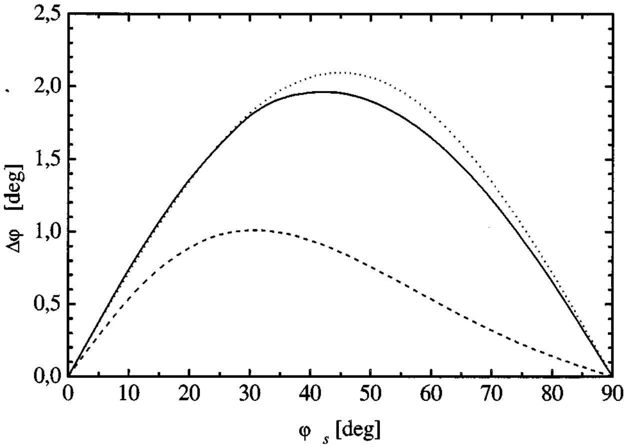

FIG. 5. Subsurface deformation $\Delta\varphi$ as a function of the anchoring tilt angle φ_s in the continuum model for $\nu=0.99$. The solid line is the numerical value obtained with an exponential trial function. The dotted line is the approximation given by Eq. (3.6). The dashed line is the numerical prediction according to the discrete-layer model for the normalized elastic constant $\kappa=99$, corresponding to the value of $\nu=0.99$.

As shown in Fig. 5, for $\nu\cong 1$ the approximate expression (3.6) reproduces quite well the numerical results obtained with an exponential trial function [27]. In the same figure we show also the subsurface deformation numerically computed according to the previously described discrete-layer model, for the same parameters. It is immediately apparent that the subsurface distortion obtained with the continuum model is nearly twice as large as that predicted by the discrete-layer model. This is not surprising, as in the discrete-layer model the molecules are more "rigid," due to the smecticlike ordering. However, the distortion is similar in both models and reminds the behavior predicted by the extended elastic theory of Refs. [5,7]. The approximation $\varphi(\zeta+\zeta')=\varphi(\zeta)$ that we used to derive the profile (3.6) can also be employed in the discrete-layer model. Again, good results are obtained in the limit of surface distortions with small amplitude. In this case, however, no analytical solutions can be derived.

This analysis has shown that the main contribution to the subsurface deformation comes from the "homogeneous" (i.e., independent of $n_{i,j}$) part of the energy density. This anisotropic contribution is similar to the van der Waals interaction with a crystalline substrate considered in [28]. The approximated analytical expressions, obtained by considering only this anisotropic homogeneous contribution, show that the distortion asymptotically decays as $1/z$. We can define a typical distortion length δ as an average of the distance of the distortion profile weighed by the amplitude of the distortion

$$\delta=\frac{1}{\Delta\varphi}\int_0^{\Delta\varphi}z\,d\varphi=\frac{1}{\Delta\varphi}\int_0^{+\infty}z\frac{d\varphi}{dz}dz. \tag{3.7}$$

δ is connected to the optical path difference between the ordinary and the extraordinary ray propagating in the anisotropic medium. For the profile in Eq. (3.6) the distortion length δ is logarithmically divergent. However, since it is known that van der Waals interactions decay faster for distances greater than $d_c\sim 1000$ Å, due to retardation effects [28], we expect that δ should be of the order of $r_0\ln(d_c/r_0)\sim 100$ Å. This distortion length, therefore, hardly seems accessible by means of optical phase shift measurements.

IV. EXTENSION OF THE MODEL

In the previous sections we have analyzed in detail the existence of a subsurface distortion by considering the effective g as due to a superposition of short-range Maier-Saupe and long-range Nehring-Saupe interactions. As discussed elsewhere, the subsurface distortion originates from the functional dependence of g on the relative orientation of $\boldsymbol{n}$ with respect to $\boldsymbol{r}$. For an arbitrary interaction law g, the total energy per unit surface of the NLC semi-infinite slab is still given by Eq. (3.1), where $f(\zeta,\zeta')=f[\varphi(\zeta),\varphi(\zeta+\zeta');\zeta']$ depends on the interaction law. As before, $f(\zeta,\zeta')$ takes into account the contribution to the interaction energy between the NLC molecules, which depends also on $\boldsymbol{n}\cdot\boldsymbol{u}$ and $\boldsymbol{n}'\cdot\boldsymbol{u}$. On the contrary, the elastic term proportional to φ'^2 takes origin from the $\boldsymbol{n}\cdot\boldsymbol{n}'$ dependence of the NLC interaction energy, which favors $\boldsymbol{n}\|\boldsymbol{n}'$ everywhere. Again in the hypothesis of small distortions over r_0, it is possible to assume $\varphi(\zeta)=\varphi(\zeta+\zeta')$. In this manner, from Eq. (3.1) and in the limit of small distortions, one obtains

$$\mathscr{F}=\mathscr{F}_0\int_0^{+\infty}[\nu\varphi'^2+(1-\nu)h(\varphi,\zeta)]d\zeta, \tag{4.1}$$

where

$$h(\varphi,\zeta)=\int_{-\zeta}^{+\infty}f[\varphi(\zeta),\varphi(\zeta);\zeta']d\zeta'. \tag{4.2}$$

The tilt angle profile $\varphi(\zeta)$ is a solution of the differential equation

$$\varphi''-\frac{1-\nu}{2\nu}\frac{dh(\varphi,\zeta)}{d\varphi}=0, \tag{4.3}$$

satisfying the boundary condition $\varphi(0)=\varphi_s$, connected to the strong anchoring hypothesis. Operating as in Sec. III, we find that $\epsilon(\zeta)=\varphi(\zeta)-\varphi_s$ is given by

$$\epsilon''-\frac{1-\nu}{2\nu}\left[\frac{dh(\varphi,\zeta)}{d\varphi}\right]_{\varphi=\varphi_s}=0, \tag{4.4}$$

satisfying the boundary conditions $\epsilon(0)=0$ and $\epsilon'(\zeta\rightarrow\infty)=0$. It is possible to obtain an order of magnitude of $\Delta\varphi=\epsilon(\infty)$ by supposing that φ' is different from zero only in a surface layer of mesoscopic thickness $r_0 l$. In a first approximation $\varphi(\zeta)=\varphi_s+(\Delta\varphi/l)\zeta$. In the limit $1-\nu\ll 1$, $|\Delta\varphi|\ll 1$ and is expected to be proportional to $1-\nu$. By supposing $\varphi'=\Delta\varphi/l$ for $0\leqslant\zeta\leqslant l$, Eq. (4.1) gives

$$\mathscr{F}=\mathscr{F}_0\int_0^{l}\left\{\nu\left(\frac{\Delta\varphi}{l}\right)^2+(1-\nu)\left[h(\varphi_s,\zeta)+\left(\frac{dh}{d\varphi}\right)_{\varphi_s}\frac{\Delta\varphi}{l}\zeta\right]\right\}d\zeta. \tag{4.5}$$

The value of $\Delta\varphi$ minimizing $\mathscr{F}$ is

$$\Delta\varphi=-\frac{1-\nu}{2\nu}\int_0^{l}\zeta\left(\frac{dh}{d\varphi}\right)_{\varphi_s}d\zeta. \tag{4.6}$$

Equation (4.6) generalizes the result obtained in Sec. III, according to which the anisotropic part of the energy density introduces a subsurface deformation localized over a mesoscopic length $r_0 l$.

Up to now in our discussion we have supposed a perfect nematic order, corresponding to a scalar order parameter $S=1$. To generalize our model in order to take into account the temperature, it is necessary to solve a difficult problem of statistical mechanics. However, at least from a phenomenological point of view, it is possible to draw a few consequences from the above reported discussion. To this purpose, let us recall that the Frank elastic constants are expected to be proportional to S^2 [8,9]. Hence, in Eq. (4.5) the elastic term $\nu(\Delta\varphi/l)^2$ has to be replaced by $\nu S^2(\Delta\varphi/l)^2$. For what concerns the temperature dependence of h, let us suppose a flat and isotropic substrate with a normal unit vector $\boldsymbol{k}$ parallel to the z axis. In general, in the uniform orientation approximation $\boldsymbol{n}=\boldsymbol{n}'$, one obtains the function $h(\boldsymbol{n},\zeta)$ appearing in Eq. (4.1) by integrating $g(\boldsymbol{n},\boldsymbol{n}';\boldsymbol{r})$ in the half space $\zeta'\geqslant-\zeta$. To take into account the temperature, instead of using $\boldsymbol{n}$ to characterize the NLC phase, it is necessary to use the tensor order parameter $\boldsymbol{Q}$ of elements $Q_{ij}=S(n_i n_j-1/3\delta_{ij})$. By expanding $h(\boldsymbol{Q},\zeta)$ in a power series of the tensor order parameter one obtains, at second order in S,

$$h(\boldsymbol{Q},\zeta)=h_1(\zeta)k_iQ_{ij}k_j+h_2(\zeta)(k_iQ_{ij}k_j)^2+h_3(\zeta)k_iQ_{ij}Q_{jl}k_l+h_4(\zeta)Q_{ij}Q_{ji}, \tag{4.7}$$

where

$$\lim_{\zeta\rightarrow\infty}h_i(\zeta)=0 \quad \text{for } i=1,2,3,$$

since F_0 in the bulk has to be $\boldsymbol{n}$ independent. From Eq. (4.7) simple calculations give

$$h(\varphi,\zeta)=m_0(\zeta)+m_2(\zeta)\cos^2\varphi+m_4(\zeta)\cos^4\varphi, \tag{4.8}$$

where

$$m_0(\zeta)=-\frac{h_1(\zeta)}{3}S+\frac{h_2(\zeta)+h_3(\zeta)+6h_4(\zeta)}{9}S^2,$$

$$m_2(\zeta)=h_1(\zeta)S+\frac{h_3(\zeta)-2h_2(\zeta)}{3}S^2, \tag{4.9}$$

$$m_4(\zeta)=h_2(\zeta)S^2.$$

For $S\neq 1$ Eq. (4.6) becomes then

$$\Delta\varphi=-\frac{1-\nu}{2\nu}\sin(2\varphi_s)\frac{A_{21}+(A_{22}+2A_{42}\cos^2\varphi_s)S}{S}, \tag{4.10}$$

where

$$A_{21}=\int_0^{l}\zeta h_1(\zeta)d\zeta, A_{22}=\int_0^{l}\zeta\frac{h_3(\zeta)-2h_2(\zeta)}{3}d\zeta,$$

$$A_{42}=\int_0^{l}\zeta h_2(\zeta)d\zeta.$$

Equation (4.10) shows that even in the case of strong anchoring, in which φ_s is fixed by the surface treatment, $\Delta\varphi$ is temperature dependent. Hence the above described model could explain the temperature surface transitions in NLC's. This model is, in some respects, similar to the elastic model presented a few years ago [7]. In that case, instead of Eq. (4.10) one has $\Delta\varphi=(k_{13}/2k)\sin(2\varphi_s)$, where $k_{13}=\alpha S+\beta S^2$ and $k=k_0S^2$ [8,9]. Note that k_{13} and F_0 are both connected to the dependence of g on $\boldsymbol{n}\cdot\boldsymbol{u}$. Hence the temperature surface transition gives information about this functional dependence.

V. CONCLUSION

In this paper we have shown that, in general, close to an amorphous surface a nematic liquid crystal undergoes a distortion localized over a few molecular lengths. This distortion is connected to the dependence of the molecular interaction energy from the orientation of the molecules with respect to their relative position. This dependence gives rise to a homogeneous anisotropic energy density confined in a surface layer of the order of the molecular length. It is also responsible for elastic terms associated with surface contributions depending on the nematic director gradients. These terms are the source of the subsurface deformation. The usual elastic approach poses several self-consistency problems: from a mathematical viewpoint the variational problem is ill posed [3]; from a physical point of view, the use of an elastic theory over microscopic lengths is somehow questionable. To overcome all these difficulties, in this paper we have tackled the analysis by means of a molecular model. We have supposed a perfect nematic order and a flat amorphous substrate inducing a strong anchoring. By using a hybrid discrete model, in which the molecules have a smectic-like order in planes parallel to the bounding surfaces, we have numerically determined the tilt angle profile inside a finite sample. Our results show that, for any tilted anchoring, a subsurface distortion exists. The largest distortion is localized over the first molecular layers, but it has an asymptotic long tail decaying as the inverse of the distance from the surface. This tail is responsible for a logarithmic divergence of the distortion length. Retardation effects should actually bound the distortion length to a value of the order of 100 Å, which is hardly accessible by means of optical measurements. The amplitude of the distortion depends on the anchoring tilt angle: it is always zero for a planar anchoring, while for the homeotropic one it can be zero or not according to the relative weight of the destabilizing contribution with respect to the stabilizing one. The same kind of analysis has been performed using a continuum model, in which the molecules are supposed to be uniformly distributed in a liquid-like manner. In this framework, we have obtained an analytical expression for the tilt angle profile in the limit of surface distortions with small amplitude. The comparison with the numerical results indicates that the main distorting mechanism is the uniform anisotropic part of the free energy density. One could therefore attribute the distortion to an effective surface field actually induced by the reduced symmetry close to the boundary. From this point of view, the situation resembles the distortion induced by a crystalline substrate on a nematic presenting no intrinsic distortion mechanisms, as analyzed in [28]. Hence one can conclude that a phenomenological elastic theory for planar distortions could be formulated in terms only of the usual Frank elastic constants [1] by introducing an effective surface energy including the intrinsic destabilizing contribution.

The continuum model gives a distortion amplitude higher than the discrete-layer model. However, the qualitative conclusions remain the same. This shows that the details of the surface ordering, i.e., the possible existence of a smectic ordering close to the surface [26], although changing the quantitative results, do not suppress the subsurface distortion.

Furthermore, we have generalized the continuum model to include different kinds of interaction energies and to take into account a nematic scalar order parameter lower than one. Simple expressions able to describe temperature-induced surface transitions [29,30] have been obtained.

A direct determination of the behavior of the molecular orientation close to a surface is still lacking. Partial experimental indications of the possibility of a subsurface deformation have been recently reported [31,32]: by means of an optical second-harmonic technique it has been shown that the orientation of the first molecular surface layer differs from the bulk molecular orientation of a macroscopically homogeneous sample. In [32] the difference between the surface and the bulk tilt angles has been attributed to the biaxial distribution of the molecules close to the surface, giving a distortion confined in a surface layer whose thickness is of the order of the nematic-isotropic coherence length ξ. Here we have shown that even if the surface orientation is not incompatible with the bulk uniaxial ordering, a surface deformation is still to be expected, on a thickness comparable with ξ. Also its value is of the same order of magnitude as the experimentally observed data [32].

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