Surface fields and the splay-bend elastic constant

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We show that a surface field localized near the bounding surface over a mesoscopic length gives rise to a subsurface discontinuity. Our result is compared with a recent elastic theory in which the subsurface distortion is due to the splay-bend elastic constant. By means of our model, the interpretation of continuous surface variations of the average nematic orientation is given and compared with the elastic model. [S1063-651X(96)51205-5]

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I. INTRODUCTION

The orienting effects of external fields on nematic liquid crystals have been extensively analyzed in the past, mainly due to their possible applications [1]. From a fundamental point of view, the interaction between an external field and nematics has been used to measure the elastic, dielectric, or diamagnetic properties of these materials [2,3]. Usually the magnetic field is considered position independent across the sample. This is a consequence of the small value of the diamagnetic anisotropy of these media [4]. On the contrary, when considering the interaction between an external electric field and a nematic, due to the large dielectric anisotropy of the nematic materials [5], the electric field could not be supposed as position independent. However, for small deviations from the undeformed state, the field could still be considered constant, as discussed in [6]. There is another class of effects which involves external electric fields that are strongly position dependent. For instance, when a nematic is in contact with an anisotropic material, the van der Waals interaction connected with the fluctuating electric field decreases as z^{-3}, where z is the distance between a considered point from the interface [7]. Another interesting problem is related to selective ion adsorption [8]. In this case, near the surface limiting the sample over a surface layer whose thickness is of the order of the Debye screening length, there exists an exponentially decreasing electric field [8]. The interaction between the surface field and the nematic could give rise to an apparent dependence of the anchoring energy strength with the thickness of the sample [9].

Recently the influence of a surface field on the nematic orientation supposing weak anchoring has been theoretically analyzed [10]. It has only been considered as having homeotropic or planar easy axes. According to this hypothesis only second order transitions in the nematic average orientation are expected. It has also been shown that due to the presence of the surface field, temperature induced surface transitions could be observed.

In this paper, we extend the theoretical analysis presented in [10], considering tilted easy axes. In this framework we shall show that continuous changes in the surface orientation induced by temperature could be expected [11–14]. Furthermore, we shall show that a surface field gives rise to a subsurface deformation of the average nematic orientation. This reminds us, in some aspects, of the subsurface deformation due to the splay-bend elastic constant in a nematic sample characterized by surface tilted alignment [15,16]. Therefore, we conclude that the detectable splay-bend elastic constant [17] also has a contribution connected with the substrate.

II. THEORY

Let us consider a nematic sample of very large thickness d, about several microns, which is to be considered semi-infinite. A Cartesian reference frame having the z axis normal to the limiting surface is used. The nematic occupies the $z>0$ half-space. On the surface at $z=0$ the easy axis characterizing the nematic-solid substrate interaction is supposed at an angle Φ with respect to the z axis. The surface anchoring energy is assumed to be weak. In the following, we shall consider a planar and one-dimensional problem in which $\vec{n}=\vec{n}(z)=\sin\phi(z)\vec{i}+\cos\phi(z)\vec{k}$, where $\phi(z)$ is the tilt angle formed by the nematic director $\vec{n}$ with the z axis. The surface field is supposed to be localized in the surface layer $0\leqslant z\leqslant\lambda$ where λ is a mesoscopic length. In our analysis we suppose that λ is larger than the coherence length of the nematic-isotropic phase transition ξ. In the opposite case a continuum description does not work any longer, and other effects, like the spatial variation of the scalar order parameter should be considered [18]. In the case of the van der Waals interaction, $\lambda\sim10^3$ Å [19]. On the contrary, if the selective ion adsorption is important, λ coincides with the Debye screening length.

The surface field $\vec{E}(z)$ is supposed to be oriented along the z axis, and the relevant bulk free energy density is given by

$$f=-\frac{1}{2}\varepsilon_0\varepsilon_a E^2(z)\cos^2\phi+e\left(\cos^2\phi-\frac{1}{3}\right)\frac{dE}{dz}+\frac{e}{2}E(z)\sin(2\phi)\frac{d\phi}{dz}. \tag{1}$$

The first term is the anisotropic part of the dielectric energy (ε_0 is equal to the vacuum dielectric permittivity, $\varepsilon_a = \varepsilon_\parallel - \varepsilon_\perp$ is equal to dielectric anisotropy). The second term is the dielectric energy due to the quadrupolar properties of the nematic ($e = e_{11} + e_{33}$ is equal to the flexoelectric coefficient) [9]. The latter term takes into account the dielectric energy of flexoelectric origin. The total energy, per unit surface of the nematic sample, is given by

$$F = \int_0^\infty \left\{ \frac{1}{2} k \left(\frac{d\phi}{dz} \right)^2 + \frac{1}{2} \left(\varepsilon_0 \varepsilon_a E^2(z) - 2e \frac{dE}{dz} \right) \sin^2 \phi + \frac{e}{2} E(z) \sin(2\phi) \frac{d\phi}{dz} \right\} dz + \frac{1}{2} w \sin^2(\phi_s - \Phi), \qquad (2)$$

where $\phi_s = \phi(0)$ is the actual surface tilt angle. In Eq. (2) the first term in the integral is the elastic energy density in the one constant approximation. The latter term is the anisotropic part of the surface anchoring energy in the Rapini-Papoular approximation [8]. The terms representing the interaction between the nematic and the surface field have been written to neglect terms that are ϕ independent. Note that for fluctuating surface fields, such as the van der Waals ones, the linear terms in the fields and in its derivative are, in time average, zero. In this case, ε_a is the value of the dielectric anisotropy at high frequency.

Let us consider the case where the surface field induces a small surface distortion of the $\phi(z)$ profile. Since $E(z)$ is localized in a surface layer of thickness λ, we may assume, in a first approximation [20],

$$\phi(z) = \phi_s + \Delta\phi(z/\lambda) \quad \text{for} \quad 0 \leqslant z \leqslant \lambda$$

$$\phi(z) = \phi_b \quad \text{for} \quad \lambda \leqslant z < \infty. \qquad (3)$$

This means that the $\phi(z)$ distortion is assumed to be localized in the same surface layer where $E(z) \neq 0$. When substituting Eq. (3) into Eq. (2) one obtains

$$F = \frac{1}{2} \left[k \left(1 + 2\frac{e}{k} \cos(2\phi_s) \langle zE \rangle \right) \left(\frac{\Delta\phi}{\lambda} \right)^2 + \left(\varepsilon_0 \varepsilon_a \langle zE^2 \rangle - 2e \left\langle z \frac{dE}{dz} \right\rangle + e \langle E \rangle \right) \sin(2\phi_s) \frac{\Delta\phi}{\lambda} + \left(\varepsilon_0 \varepsilon_a \langle E^2 \rangle - 2e \left\langle \frac{dE}{dz} \right\rangle \right) \sin^2 \phi_s \right] \lambda + \frac{w}{2} \sin^2(\phi_s - \Phi), \qquad (4)$$

where $\langle X \rangle = (1/\lambda) \int_0^\lambda X(z) dz$ is the mean value of X in the surface layer. The actual $\Delta\phi$ is the one minimizing F given by Eq. (4). Simple calculations give

$$\Delta\phi = -\frac{\lambda}{2k} \frac{\varepsilon_0 \varepsilon_a \langle zE^2 \rangle + 3e \langle E \rangle}{1 + 2(e/k)\cos(2\phi_s) \langle zE \rangle} \sin(2\phi_s), \qquad (5)$$

because $\langle z dE/dz \rangle = -\langle E \rangle$. In the case of the fluctuating fields Eq. (5) reduces to

$$\Delta\phi = -\frac{\lambda}{2k} \varepsilon_0 \varepsilon_a \langle zE^2 \rangle. \qquad (6)$$

It is also possible to deduce Eqs. (5) and (6) by means of a perturbative method, starting directly from the Euler-Lagrange equation associated with functional (2). By minimizing F, given by (4), with respect to ϕ_s it is possible to obtain the actual surface tilt angle ϕ_s. However, this analysis is not important in the present context. In the case where $E(z) = E_0 \exp - (z/\lambda)$, simple calculations give $\langle zE^2 \rangle \sim E_0^2 \lambda/4$, $\langle E \rangle \sim E_0$, and $\langle zE \rangle \sim E_0 \lambda$. Hence, we could conclude that for static fields, for small λ, the quadrupolar and flexoelectric contributions in Eq. (1) are more important than the dielectric energy associated to ε_a. In this case Eq. (5) becomes

$$\Delta\phi = -\frac{3}{2} \frac{\lambda e E_0}{k} \sin(2\phi_s), \qquad (7)$$

where $E_0 = E(0)$ is the amplitude of the surface field. The subsurface discontinuity $\Delta\phi$ given by Eq. (5) [or by Eqs. (6) or (7) in the particular cases of fluctuating or static fields, respectively] takes place over the surface layer λ. If we compare Eq. (5) with the subsurface discontinuity connected with the k_{13} splay-bend elastic constant which is

$$\Delta\phi_{\text{splay-bend}} = -\frac{k_{13}}{2k} \sin(2\phi_s), \qquad (8)$$

we derive that a surface field is equivalent to an effective splay-bend elastic constant given by

$$k_{13} = \lambda \frac{\varepsilon_0 \varepsilon_a \langle zE^2 \rangle + 3e \langle E \rangle}{1 + 2(e/k)\cos(2\phi_s) \langle zE \rangle}, \qquad (9)$$

in general, either $k_{13} = \lambda \varepsilon_0 \varepsilon_a \langle zE^2 \rangle$ for fluctuating fields or $k_{13} = 3\lambda e E_0$ for the static surface fields. From the results reported above we predict continuous surface transitions of the tilt angle induced by the temperature . In fact, as it follows from Eq. (5), $\Delta\phi$ depends on $(\varepsilon_0 \varepsilon_a \langle zE^2 \rangle + 3e \langle E \rangle)/[k + 2e\cos(2\phi_s) \langle zE \rangle]$. Since $\varepsilon_a \propto S$ and $e \propto S$, where S is the scalar order parameter [21], whereas $k \propto S^2$, one deduces that $\Delta\phi$ is expected to be temperature dependent. This conclusion is valid even in the case in which the anchoring is strong and, hence, ϕ_s is temperature independent.

III. CONCLUSIONS

We have shown that a surface field introduces a subsurface deformation delocalized over a surface thickness in which the surface field exists. The analytical expression for this subsurface ''discontinuity'' reminds us of the one introduced by the splay-bend elastic constant. Therefore we can conclude that the detectable splay-bend elastic constant has an intrinsic and an extrinsic contribution. The extrinsic contribution to k_{13} is proportional to the penetration length of the surface field λ. Hence, in principle, it is possible to obtain information on the intrinsic part of k_{13} changing λ. This can be done, for instance, by doping the nematic liquid crystal in order to change the Debye screening length. Considering the temperature dependence of the energy connected with the interaction between the surface field and the nematic, and of the Frank elastic constant, we predict continuous surface transitions of the nematic tilt angle induced by the temperature.

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