Theory of surfacelike elastic contributions in nematic liquid crystals

Sandro Faetti
Dipartimento di Fisica dell'Università di Pisa and Consorzio Interuniversitario di Fisica della Materia, Piazza Torricelli 2, 56100 Pisa, Italy
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In a recent paper we carried out a systematic expansion of the free-energy density of nematic liquid crystals (NLC's) in the director derivatives for planar director distortions and small director angles. At any order of expansion, the director distortion is the superposition of a standard long-range bulk director distortion and a very-short-range subsurface distortion. The bulk macroscopic distortion is found to be the same as that which is obtained using the Frank elastic form of the free-energy density and an effective anchoring energy function f_s which implicitly contains the surfacelike elastic constant K_{13} and all higher-order elastic constants. In this paper we generalize this theoretical result and extend it to the case of large director angles using the Gibbs theory of interfacial phenomena. Furthermore we extend the theoretical analysis to the more general case of nonplanar director distortions. An alternative theoretical expression of the first-order free-energy density that does not present mathematical problems, and allows us to study any kind of director distortion in NLC's, is proposed. In the nonplanar case, both of the surfacelike elastic constants K_{13} and K_{24} are shown to make explicit contributions to the first-order free-energy density. Recent theoretical and experimental results concerning the elastic behavior of a NLC sample enclosed in a cylindrical cavity are reanalyzed in terms of the present theoretical procedure. Rough estimates of the surfacelike elastic constants K_{13} and K_{24} are obtained from the analysis of the experimental results. A surface orientational transition, which makes it possible to measure the K_{13} surfacelike elastic constant, is predicted to occur at a critical value of the radius R of the cylindrical cavity.

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I. INTRODUCTION

According to Nehring and Saupe, the free energy of nematic liquid crystals (NLC's) is [1]

$$F_1=\int f_s\,dS+\int \{f_F+f_{\rm ext}+K_{13}\nabla\cdot[\mathbf{n}(\nabla\cdot\mathbf{n})]\}\,dV$$
$$-\int (K_{22}+K_{24})\nabla\cdot[\mathbf{n}(\nabla\cdot\mathbf{n})+\mathbf{n}\times\nabla\times\mathbf{n}]\,dV$$
$$=\int (f_F+f_{\rm ext})\,dV+\int (f_s+f_{13}+f_{24})\,dS\ , \quad (1)$$

where dV and dS are volume and surface elements, $f_{\rm ext}$ is the free-energy density due to external fields (magnetic or electric), f_F is the standard Frank elastic free-energy density, f_{13} and f_{24} are two surface elastic contributions, and f_s is the anchoring energy at the interfaces. The explicit form of the elastic contributions is

$$f_F=\tfrac{1}{2}[K_{11}(\nabla\cdot\mathbf{n})^2+K_{22}(\mathbf{n}\cdot\nabla\times\mathbf{n})^2+K_{33}(\mathbf{n}\times\nabla\times\mathbf{n})^2]\ , \quad (2)$$

$$f_{13}=K_{13}(\mathbf{k}\cdot\mathbf{n})(\nabla\cdot\mathbf{n})\ , \quad (3)$$

and

$$f_{24}=-(K_{22}+K_{24})\mathbf{k}\cdot[\mathbf{n}(\nabla\cdot\mathbf{n})+\mathbf{n}\times\nabla\times\mathbf{n}]\ , \quad (4)$$

where K_{11}, K_{22}, K_{33}, K_{13}, and K_{24} are elastic constants, $\mathbf{n}$ is the director, and $\mathbf{k}$ is the unit vector orthogonal to the interface. In Eq. (1) the bulk integral over the two divergence terms has been transformed into the integral over the surface, exploiting the Gaussian theorem. We wish to emphasize here that this procedure is correct if there are no discontinuities in the director field within the integration volume. In the following we will call the free energy of Eq. (1) the *Nehring-Saupe first-order elastic free energy*. The anchoring energy f_s is a phenomenological parameter which is assumed to be a function of the director azimuthal and polar angles at the interfaces and is minimized for one or more easy director orientations (*easy axes*).

Let us consider a NLC sandwiched between two parallel plates that induce an easy director alignment in the x-z plane where z is the coordinate of the axis perpendicular to both the plates. We consider planar distortions where the director remains everywhere in the plane x-z and makes an angle $\theta(z)$ with axis z. In this case, the elastic contribution f_{24} in Eq. (1) vanishes and the free-energy density only depends on the bulk and surface values of θ and θ' (θ' is the first derivative of θ). The equilibrium director angle $\theta(z)$ is obtained by minimizing the total free energy of Eq. (1) with respect to any arbitrary variation of $\delta\theta$. By using the standard Euler-Lagrange variational procedure one finds the bulk director angle must satisfy a *second-order differential equation.* It is well know that the general solution $\theta(z)$ of a second-order differential equation depends on *two* arbitrary integrations constants α_1 and α_2 that, in principle, can be determined by substituting the general solution into *two* boundary conditions. However, due to the presence of K_{13}, the surface free-energy density depends on surface angle θ_s but also on derivative θ'_s of the surface angle at the two interfaces of the NLC. Therefore, according to Oldano and Barbero [2–5], the minimization of the surface free energy with respect to the *independent* director variations $\delta\theta_s$ and $\delta\theta'_s$ gives *two* boundary conditions for each plate. Therefore there are four boundary conditions, while the bulk solution only depends on two arbitrary constants. It is evident that, in these conditions, there are no values of the *two* arbitrary constants that can solve simultaneously the *four* boundary conditions and thus the mathematical problem is ill posed. According to Oldano and Barbero [2–5], the equilibrium director field must exhibit a discontinuity at the interfaces ($\theta'_s=\pm\infty$). This unusual behavior is due to the fact that the free energy per unit surface area due to K_{13} is $f_{13}=\pm K_{13}\sin(2\theta_s)\theta'_s$, where signs + and − stand for the upper and the lower interface, respectively. This surface free energy is not minimized for any finite value of θ'_s and thus it favors an infinite value of the normal derivative θ'_s of the director angle at the interface. Therefore, a discontinuity of the director field is expected to occur at both the interfaces of the NLC layer. Obviously this discontinuity is an artifact of the first-order elastic theory of Eq. (1) due to the disregard of higher-order elastic contributions. These higher-order contributions are expected to limit the values of subsurface derivatives and the actual director field is expected to be a continuous function which shows a sharp variation on a few molecular lengths close to the interfaces (see, for instance, Fig. 2). From the macroscopic point of view this sharp director variation is fully equivalent to the discontinuity of the director field which is predicted by the first-order elastic theory [2–5].

The theoretical arguments above show that the problem of finding the correct director field in a NLC is not mathematically well posed if the K_{13} elastic constant is different from zero and the first-order elastic free energy in Eq. (1) is used. Obviously no mathematical problem occurs if $K_{13}=0$. In a recent paper [6], Somoza and Tarazona questioned the effective presence of the surface-like elastic contribution in the free energy of NLC's. In particular, starting from the general expression of the free energy of a NLC, they showed that second derivatives in the expansion of the free-energy density can vanish if we make a suitable change of integration variables. Their theoretical approach has been reanalyzed by Teixeira, Pergamenshchik, and Sluckin [7], who showed that the proposed change of integration variables makes the free-energy density a nonlocal function and thus it cannot represent a physical density. Therefore, according to Teixeira, Pergamenshchik, and Sluckin, no ambiguity in the definition of surface elastic constants exists. Furthermore, microscopic calculations of elastic constants [1,7,8] show that K_{13} and K_{24} are different from zero and are expected to be of the same order of magnitude as the other Frank elastic constants.

To bypass the mathematical problems related to the surfacelike elastic constant K_{13}, three different theoretical approaches are currently used in the literature.

(i) Some authors [9–11] have considered the discontinuous behavior of the director field at the interfaces as an artifact of the elastic first-order theory. Therefore they conjecture that higher-order elastic terms make the occurrence of strong director derivatives in the subsurface layer impossible. According to this conjecture, the solution $\theta(z)$ of the first-order elastic theory must also be a continuous function at the interfaces [limit for $z\rightarrow 0$ of $\theta(z)=\theta(0)$]. This means that the surface director angle $\theta_s=\theta(0)$ and the surface derivative $\theta'_s=\theta'(0)$ are no longer independent parameters but must satisfy the bulk Euler-Lagrange equation. The solution $\theta(z)$ of the Euler-Lagrange equation is univocally defined once the surface values θ_s of the director angles at the two interfaces are given. Therefore, with this assumption, the variations $\delta\theta_s$ of the surface director angles at the interfaces of the NLC and $\delta\theta'_s$ are not independent parameters and thus the minimization procedure of the surface free energy can be shown to provide only *one boundary condition* for each plate and the mathematical problem becomes well posed [9]. The occurrence of spontaneous macroscopic distortions is predicted in some cases using this theoretical approach [12–14]. An experimental value of K_{13} has been measured by analyzing the experimental data in terms of this theoretical approach [14].

(ii) A completely different approach has been proposed by Barbero, Sparavigna, and Strigazzi. They developed a new expansion procedure of the elastic free-energy density in terms of the director derivatives of any order [15]. Using this expansion procedure, they were able to obtain a general expression of the free-energy density at the fourth order in the director derivatives (*second-order elastic theory*). The new expression of the free-energy density is found to be bounded from below and a minimum of the free-energy functional is attained. The bulk Euler-Lagrange equation is, now, a fourth-order differential equation whose general solution depends on four arbitrary coefficients while the minimization of the surface free energy provides two boundary conditions for each plate. This means that there are four arbitrary constants and four boundary conditions and thus the mathematical problem is well posed. Unfortunately the second-order elastic free energy contains 35 new elastic contributions and thus its use for general cases is impractical. However, in the simplest case of small director angles ($\theta\ll 1$), only one new second-order elastic constant K^* plays an important role. In this simplest case, the director angle $\theta(z)$ is found to be the superposition of the macroscopic bulk contribution $\theta_b(z)$, which is coincident with that predicted by the first-order theory, and a short-range contribution, which is appreciably different from zero only within two very thin interfacial layers close to the interfaces. The thickness δ of the interfacial layers is of the order of a few molecular lengths [16–18].

The main drawback to this second-order elastic theory is that the director derivatives in the interfacial layer assume very high values and thus, in principle, all elastic terms of an order higher than fourth order are expected to make important contributions and should not be disregarded. Furthermore mathematical difficulties make the analysis of director distortions with no small angles practically impossible.

(iii) Most authors bypass the mathematical problems related to the K_{13} elastic constant by simply disregarding this contribution in the free energy. In this case the surface free energy becomes the Frank elastic form which depends on the director angle alone and does not depend on the normal surface derivative of the director angle. Therefore the boundary conditions are reduced to two alone and no mathematical problem arises in this case. However, so far, there is no physical justification for this procedure.

In recent papers [8,19], we analyzed certain consequences of the theoretical procedures (i) and (ii). By using the theoretical test of surface torques [19], we showed that the theoretical predictions of procedure (i) are in contrast with the general principles of mechanics (GPM). Therefore we infer that procedure (i) is not correct and *a director discontinuity must always occur close to the interfaces,* in agreement with the theoretical analysis in [2–5,16,17].

The theoretical test of surface elastic torques has also been used to assess the internal consistency of procedure (ii). This procedure is found to be consistent with the GPM, although this result does not necessarily mean that the second-order theory describes the actual behavior of a NLC correctly. To understand the influence of higher-order elastic contributions which have been disregarded in second-order elastic approach (ii), we have used the same expansion procedure as in [15] to obtain the expression of the elastic free-energy density at any order N in the director derivatives [19]. We have considered the special case of *planar director distortions and very small director angles.* At a given order $N=2n$ in the director derivatives (with n an integer number), the bulk Euler-Lagrange equation is a linear differential equation of order N with N boundary conditions. Therefore there is always a definite solution to the mathematical problem for any value of N.

At any expansion order N, the director distortion is found to be the superposition of a short-range distortion which occurs within a very thin interfacial layer of thickness δ close to the interfaces and a long-range bulk macroscopic distortion. From the macroscopic point of view the short-range subsurface distortion behaves as an apparent discontinuity of the director field in close agreement with the predictions of Refs. [2–5]. Therefore this theoretical result still confirms that conjecture (i) cannot account for the actual behavior of the director field close to the interfaces, in agreement with the result of the surface torque test. The actual shape of the short-range director distortion is found to depend greatly on N and is given by the superposition of $(N-2)$ exponential functions with complex arguments. The interfacial distortion can be characterized either by real exponential functions or by damped oscillatory functions [in the case of second-order theory ($N=4$), only a real exponential decay was predicted]. For N which tends to infinity, the number of these interfacial functions tends to infinity and thus the interfacial behavior is very complicated. However, at any order N, the macroscopic distortion can be shown to be *virtually the same* as that obtained using the Frank elastic free-energy density f_F and a renormalized anchoring energy f_{sN}, in a *qualitative* agreement with the theoretical predictions of the second-order elastic theory. For $N\rightarrow\infty$, the effective anchoring energy tends to a limit value f_s, which depends on *all higher-order elastic constants* which are infinite in number.

The theoretical analysis above shows that second-order elastic theory (ii), although it qualitatively accounts for the main interfacial effects (strong subsurface director distortions and existence of an effective anchoring function), cannot give an accurate quantitative description of the actual director field in a NLC. Indeed any higher-order elastic contribution greatly affects the subsurface director field and the limit value f_s of the anchoring energy f_{sN} for $N\rightarrow\infty$ can greatly differ from the second-order value f_{s4}. Therefore the macroscopic bulk director distortion predicted by higher-order elastic theories is different from that predicted by the second-order theory due to the different values of the anchoring energies. Our theoretical results have important consequences as far as the experimental measurement of the surfacelike elastic constant K_{13} is concerned. According to higher-order theories, the elastic constant only affects the subsurface director distortion and the anchoring energy. Both the subsurface distortion and the anchoring energy depend on the K_{13} elastic constants together with all other surfacelike and bulk higher-order elastic constants. Therefore, *K_{13} is not a measurable parameter if planar director distortions are studied.* In particular, the proposed measurement methods of the elastic constant K_{13} [20], which are based on the theoretical results of the second-order elastic theory, cannot give correct values of K_{13}.

The main surprising consequence of the theoretical results above is a strong support for naive procedure (iii), which is currently used in the literature to investigate *planar director distortions.* From the macroscopic point of view, the only distortion which has a macroscopic relevance is the long-range bulk director distortion characterized by the bulk director angle $\theta_b(z)$ (see the discussion in Sec. II). According to the predictions of higher-order elastic theories in the limit $N\rightarrow\infty$ and of small director angles, this macroscopic distortion can be always obtained using the Frank elastic free-energy density and a surface anchoring energy f_s, which implicitly contains any effect due to surfacelike and bulk higher-order elastic constants.

The theoretical results above were obtained by assuming that the first-order and higher-order elastic constants have constant values everywhere in the NLC sample. In real NLC samples this assumption does not hold good close to the interfaces where elastic anomalies are expected to occur [17,21–23]. The important contribution of elastic subsurface effects to the anchoring of NLCs has been already emphasized by Yokoyama, Kobayashi, and Kamei in a very interesting paper [21], by Faetti *et al.* [22,23], and by Barbero, Gabbasova, and Kosevich [17]. In particular, according to Yokoyama, Kobayashi, and Kamei [21], any elastic anomaly which occurs in a thin subsurface layer can be considered as a new source of director anchoring. The different kinds of elastic anomalies that can occur close to interfaces and affect the surface anchoring are the following.

(a) Due to the breaking of the translation symmetry, the elastic constants close to the interface are expected to become functions of the distance z from the interface and of the director angle. Furthermore new elastic contributions [for instance, $K_1(\nabla\cdot\mathbf{n})$], which are forbidden by symmetry in the bulk, can play an important role close to the interfaces [17,24].

(b) The scalar order parameter S close to the interface can greatly differ from the bulk value [25] and thus the Frank elastic constants which are approximately proportional to S^2 are expected to be greatly affected by the interfacial nematic order [21,22].

(c) Finally, the surfacelike and the higher-order elastic constants can make important subsurface elastic distortions [17,19]. All these different kinds of elastic anomalies are expected to make an important contribution to the subsurface interfacial free-energy density and to the anchoring energy of a NLC.

The theoretical results in [19] have been obtained by considering a *planar director distortion* and by making the simplifying assumption of *very small director angles.* Furthermore any elastic anomaly such as those in points (a) and (b) was disregarded in our analysis. However, according to the theoretical discussion in Sec. II, our main theoretical result concerning the existence of an effective anchoring function, which fully accounts for anomalous subsurface elastic effects, remains correct for any value of the director angles. Therefore, *planar director distortions can always be correctly studied using procedure (iii).* In Sec. II we will justify this point of view in terms of the Gibbs approach to interfacial phenomena. In Sec. III we extend our analysis to the more general case of nonplanar director distortions and we propose a new theoretical expression for the first-order elastic free energy. There are no mathematical problems involved in this new expression and it allows us to obtain the equilibrium bulk director distortions for any general case. The expression of the elastic free energy proposed here depends explicitly on the bulk Frank elastic constants and on the two surfacelike elastic constants K_{13} and K_{24} (in the general case of nonplanar director distortions). Therefore both the surfacelike elastic constants K_{13} and K_{24} can be measured, in principle, by investigating suitable nonplanar distortions. Section IV is devoted to analysis of certain nonplanar director distortions that occur in NLC samples enclosed in cylindrical cavities. Recent experimental results obtained in this confined geometry are reanalyzed in terms of our model and a rough estimate of both the surface elastic constants K_{13} and K_{24} is given. Section V contains our conclusions.

II. THE GIBBS THEORY OF INTERFACES AND THE ANCHORING ENERGY

In the preceding section we showed that simple theoretical reasoning predicts that the main effect of the surfacelike elastic constant K_{13} is the occurrence of a sharp director distortion close to the interfaces of NLCs [2–5]. This theoretical reasoning is entirely confirmed by the elastic surface torques test [19] and by the analysis of higher-order elastic contributions within the limit of small director angles [16–19]. Analogous subsurface distortions are also predicted to occur if elastic anomalies (a) and (b) are taken into account [17,21–23]. In this section we will show that, according to the Gibbs theory of interfacial phenomena, any director distortion which occurs in a thin layer of a thickness comparable with that which characterizes the surface interactions must be considered as a new source of director anchoring and must be enclosed in the phenomenological expression of the anchoring energy. In this way we are able to generalize the theoretical results of higher-order theories obtained for small director angles, disregarding subsurface elastic anomalies (a) and (b).

Let us consider the interface between a semi-infinite NLC ($z>0$) and an other semi-infinite medium ($z<0$) as shown schematically in Fig. 1. At a great distance from the interface the system has a translational symmetry and thus the local physical parameters of the NLC (mass density ρ, scalar order parameters S, director $\mathbf{n}$, free energy density, and so on) do not depend on position $\mathbf{r}$ in space. Furthermore no easy direction exists for the director in the bulk in the absence of external orienting fields. Near the interface, however, the translational symmetry is broken and the local parameters depend on distance z from the interface and one (or more) easy directions exist for the director at the interface. Figure 1 schematically shows a possible z dependence of the free-energy density near the interface $z=0$. We note that the actual free energy density (full line) is different from that expected in the absence of surface effects (horizontal dashed lines). According to Gibbs's thermodynamic approach, we can express the free energy per unit surface area (total area below the full line) as the sum of a bulk contribution (free energy corresponding to the area below the dashed line) and an interfacial contribution $\gamma_{\rm NM}$, which is called the *excess of surface free energy per unit area* (shaded area in Fig. 1) and is given by

$$\gamma_{\rm NM}=\int_0^{\infty}[F_{\rm N}(z)-F_{\rm Nb}]\,dz+\int_{-\infty}^{0}[F_{\rm M}(z)-F_{\rm Mb}]\,dz\ , \tag{5}$$

where $F_{\rm N}(z)$ is the free energy density in the NLC at distance z from the interface and $F_{\rm Nb}$ is its asymptotic value in the bulk ($z\rightarrow\infty$); $F_{\rm M}(z)$ is the free-energy density in the second medium (substrate) and $F_{\rm Mb}$ is its asymptotic

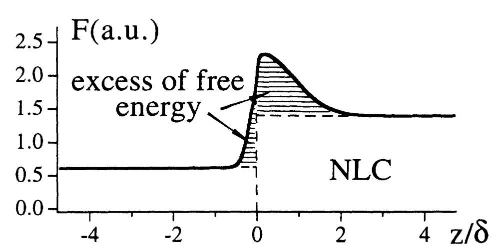

FIG. 1. A possible dependence of free energy density F on reduced distance z/δ from the interface between a NLC ($z>0$) and another medium ($z<0$). δ is the characteristic interfacial length. The unit on the vertical axis is dimensionless. The full line denotes the actual z dependence of the free-energy density. The horizontal broken lines in the $z<0$ and $z>0$ regions denote the extrapolation of the bulk free energy in the medium and in the NLC, respectively. The shaded regions denote the surface excess of free energy.

value in the bulk ($z \rightarrow -\infty$). Note that $F_N(z)$ in Eq. (5) accounts for any interfacial interaction. In particular $F_N(z)$ can be written as the sum of an internal contribution $F_{int}(z)$ due to nematic-nematic interactions and an external contribution $F_{ext}(z)$ due to the interactions between NLC molecules and the substrate.

At equilibrium and in the absence of external torques, profiles $\rho(z)$, $S(z)$, and $\mathbf{n}(z)$ in the interfacial layer are those that minimize the surface excess of free energy γ_{NM} in Eq. (5). Far from the interface these functions approach the bulk equilibrium uniform values, while large spatial variations are expected to occur within a very thin interfacial layer with a thickness δ of the order of the range of intermolecular interactions ($\delta \cong 50$ Å for van der Waals forces [30,31]). This thickness is usually much smaller than the characteristic length ξ associated with bulk distortions ($\xi \cong 1-100$ μm). In particular, the director orientation in the interfacial layer is characterized by the polar and azimuthal angles $\theta(z)$ and $\varphi(z)$ that rapidly approach two constant values θ_0 and φ_0 just above the interfacial layer ($z \gg \delta$). The two angles θ_0 and φ_0 minimize the excess of surface free energy and represent the *macroscopic easy director angles* at the interface. Note that the macroscopic easy angles can greatly differ from the actual director angles at $z=0$.

If an external magnetic field is applied on the NLC, a macroscopic director distortion occurs in the bulk of the NLC, as shown schematically in Fig. 2. The characteristic thickness ξ of this distortion is much greater than the thickness δ of the interfacial layer. For $z \gg \xi$ the director is uniformly aligned along the magnetic field while the values of director angles θ and φ just above the interfacial layer are given by two new values θ_s and φ_s. Note that, due to the great separation of the scale lengths ξ and δ, the director angles θ_s and φ_s are virtually coincident with

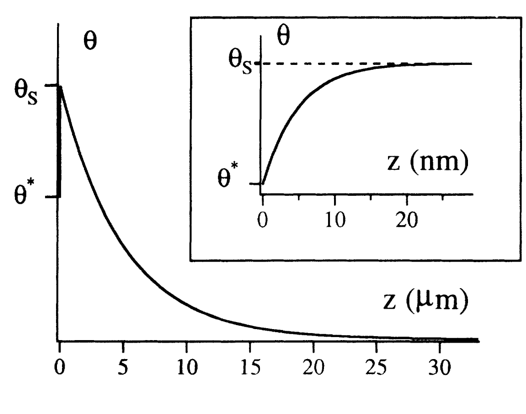

FIG. 2. Typical behavior of the polar angle of the director versus distance z from the interface. The characteristic length of the bulk distortion is $\xi=5$ μm and the characteristic thickness of the interfacial layer is $\delta=5$ nm. θ^* denotes the actual surface polar angle while θ_s denotes the macroscopic surface angle that corresponds to the limit of the bulk director angle for $z \rightarrow 0$. A detail of the subsurface interfacial distortion is shown in the inset. Note the very different scales in the main figure and in the inset. The dashed line (in the inset) denotes the extrapolation of the bulk director field at interface $z=0$.

the limit angles for $z \rightarrow 0$ of the bulk macroscopic distortion (see the inset in Fig. 2). Therefore, *from the macroscopic point of view, θ_s and φ_s correspond to the "surface director angles," although the actual surface angles $\theta^*=\theta(0)$ and $\varphi^*=\varphi(0)$ can differ greatly from θ_s and φ_s.* The actual shape of the subsurface director distortion will depend on the nature of the interactions between the NLC molecules and the substrate, on the intermolecular interactions between the NLC molecules in the subsurface layer, and on the values of the director angles θ_s and φ_s outside this layer. The interactions between NLC molecules are strictly related to the elastic contributions to the free-energy density and thus the director distortion in the subsurface layer will depend directly on the elastic behavior in the NLC interfacial layer. For given values of the macroscopic surface angles θ_s and φ_s just above the interfacial layer, a well defined director field will minimize the surface excess of free energy in Eq. (5). The director angles in this subsurface layer will be represented by two functions $\theta=\theta(z,\theta_s,\varphi_s)$ and $\varphi=\varphi(z,\theta_s,\varphi_s)$ that satisfy the boundary conditions $\theta=\theta_s$ and $\varphi=\varphi_s$ for $z/\delta \rightarrow \infty$ and minimize the surface excess of free energy in Eq. (5). We wish to emphasize here that this theoretical result holds good because the characteristic scale length of the macroscopic bulk distortion is much greater than the interfacial thickness. In this assumption, the director field in the interfacial layer is not affected by details of the bulk director field but only depends on the two angles θ_s and φ_s. Then, for a given NLC sample, the free-energy density in the interfacial layer will be a function $F(z,\theta_s,\varphi_s)$, which depends solely on z and on the two macroscopic surface angles θ_s and φ_s. This means that, according to Rapini and Popoular, the excess of surface free energy per unit surface area in Eq. (5) is a function of these two macroscopic surface angles only:

$$\gamma_{NM}(\theta_S,\varphi_S)=\gamma_{NM}(\theta_0,\varphi_0)+f_s(\theta_S,\varphi_S) , \quad (6)$$

where $\gamma_{NM}(\theta_0,\varphi_0)$ is the equilibrium value of $\gamma_{NM}(\theta_S,\varphi_S)$ in the absence of external fields and corresponds to the work which must be done to increase by a unit the area of the interface at constant temperature, volume, and composition. $f_s(\theta_S,\varphi_S)$ is the anchoring function in Eq. (1) that corresponds to the work which is needed to rotate the director (above the surface layer) from the equilibrium axis to that characterized by the two angles θ_S and φ_S. Note that the only important assumption which has been used to obtain Eq. (6) is the great separation of scale lengths ξ and δ, while no assumption was made as far as the values of θ_S and φ_S are concerned. Therefore any strong subsurface director distortion which occurs in a thin interfacial layer, such as that due to K_{13} and to others subsurface elastic anomalies, can be entirely accounted for by defining a suitable phenomenological anchoring function. This analysis is in complete agreement with the main predictions of the higher-order elastic theories [19] and allows us to extend them to the case where the director angles are not small and the subsurface distortion is also produced by the elastic anomalies (a) and (b).

Some authors [26,27] have proposed that the surface excess of free energy can be written as a function which depends on the macroscopic "surface" director angles and also on the normal director derivatives of these angles. These derivative-dependent contributions are introduced to account phenomenologically for the variations of the macroscopic director angles in the interfacial layer $[\Delta\theta \approx (\partial\theta/\partial z)\delta$ and $\Delta\varphi \approx (\partial\varphi/\partial z)\delta]$. If these derivative-dependent contributions are included in the expression of the anchoring energy, we have the same kind of mathematical problems which characterize the K_{13} elastic constant [2–5]. On the basis of the aforegoing discussion, the assumption of a surface free energy which explicitly depends on the normal director derivatives is not compatible with the Gibbs approach. Indeed, the Gibbs approach is based on the assumption of a nearly vanishing value of the interfacial thickness δ. This means that the macroscopic director field is virtually uniform across the subsurface layer and the values of the director angles θ_s and φ_s above the interfacial layer are practically coincident with the limit angles of the bulk macroscopic distortion for $z \rightarrow 0$ (see the inset in Fig. 2). Then, any variation $\Delta\theta \approx (\partial\theta/\partial z)\delta$ and $\Delta\varphi \approx (\partial\varphi/\partial z)\delta$ of the *macroscopic* director angles across the interfacial layer must be disregarded in this macroscopic approach $[\Delta\theta \approx (\partial\theta/\partial z)\delta \rightarrow 0$ and $\Delta\varphi \approx (\partial\varphi/\partial z)\delta \rightarrow 0$ for $\delta \rightarrow 0]$. If this variation is not negligible, one cannot substitute the actual values of the director angles above the interfacial layer with their limit values for $z \rightarrow 0$ and the shape of the director distortion in the interfacial layer becomes sensitive to details of the bulk distortion. In this case, *bulk and surface contributions cannot be separated in two independent contributions* and a much more complicated approach should be used to describe the actual behavior of the system.

In order to shed further light on this very important point, we can consider, for instance, the theoretical predictions of higher-order elastic theories. In particular we consider the simplest case $N=4$ (second-order theory) for a NLC layer subjected to a magnetic field [18]. According to the second-order theory, the director field is found to be the superposition of a short-range interfacial distortion of characteristic thickness L_{int} and a long-range macroscopic distortion of characteristic thickness L_{mac}. The theoretical expressions of these characteristic lengths are [18]

$$L_{\text{int}} = \frac{1}{\left[\dfrac{1+\left[1-\dfrac{4\delta^2}{\xi^2}\right]^{1/2}}{2\delta^2}\right]^{1/2}} \approx \frac{\delta}{\left[1+\dfrac{\delta^2}{\xi^2}\right]^{1/2}}, \tag{7}$$

$$L_{\text{mac}} = \frac{1}{\left[1-\dfrac{\left[1-\dfrac{4\delta^2}{x_2}\right]^{1/2}}{2\delta^2}\right]^{1/2}} \approx \frac{\xi}{\left[1+\dfrac{\delta^2}{\xi^2}\right]^{1/2}}, \tag{8}$$

where δ is a characteristic length of the order of a few molecular lengths while ξ is the ordinary magnetic coherence length $\xi=(K/\chi_a)^{1/2}/H$. In the limit case $\delta \rightarrow 0$, the interfacial distortion becomes completely insensitive to the presence of the magnetic field [$\delta/\xi \rightarrow 0$ in Eq. (7)] and the bulk characteristic length L_{mac} is reduced to the standard magnetic coherence length ξ, as predicted by the first-order Frank elastic free energy. Therefore, in this case ($\delta/\xi \rightarrow 0$), bulk and interfacial phenomena are completely decoupled and the macroscopic effect of the interfacial distortion can be shown to be fully equivalent to a renormalization of the anchoring energy [18,19]. On the contrary, if thickness δ is not completely negligible with respect to magnetic coherence length ξ, the total free energy of the system cannot be separated into two *independent* surface and bulk contributions and thus the Gibbs approach cannot be used. In particular, in this case, the bulk distortion is no longer represented by the Frank form with the standard characteristic length ξ, but it is directly influenced by the presence of the subsurface distortion [see Eq. (8)]. The same kind of conclusions are obtained by using elastic theories of a higher order ($N>4$). Therefore, if there is no complete separation of characteristic scale lengths, the effect of the finite value of the interfacial length δ cannot be accounted for by only including surface director derivatives along the axis orthogonal to the interface in the interfacial anchoring energy. Indeed, due to the interplay of interfacial and bulk effects, both the short-range distortion and the macroscopic distortion are modified if δ/ξ is not negligible [see Eqs. (7) and (8)].

According to the analysis above, we then expect the effects due to a non-negligible value of the ratio δ/ξ between the interfacial and bulk characteristic thicknesses not to be accounted for by introducing phenomenologically director derivatives in the expression of the anchoring energy. In this case (δ non-negligible with respect to ξ) the correct director field can only be obtained by a direct minimization of the *exact* free energy of the system:

$$F=\int f(\mathbf{r})\,dV, \tag{9}$$

where $f(\mathbf{r})$ is the exact free energy density at point **r**, which is a *nonlocal functional* that depends on the direction orientation in all the other points of the NLC (see, for instance, Refs. [24,28–32]). We wish to emphasize here that, even with the choice of very simple intermolecular potentials, the problem of finding the correct director field which minimizes Eq. (9) is a very complex problem which can be solved only by using complex numerical minimization procedures [30,31]. In conclusion, the Gibbs macroscopic theory of interfacial phenomena requires the two length scales ξ and δ to be well separated ($\delta/\xi \rightarrow 0$) and thus any explicit contribution of macroscopic surface derivatives cannot be present in the expression of the surface free energy. This is, in our opinion, the main physical reason for the occurrence of mathematical problems when surface derivatives are introduced in the phenomenological expression of the surface anchoring energy.

Our considerations above show that, within the Gibbs theoretical approach, any elastic subsurface anomaly which favors a short-range subsurface distortion can greatly affect the excess of surface free energy. Obviously any macroscopic approach (higher-order elastic theories too) is unable to predict the correct subsurface director distortion and thus the correct anchoring energy because all physical parameters (order parameter, density, elastic constants) are expected to depend in a very complex way on the distance from the interface and elastic contributions of any order play an important role. Therefore, within a macroscopic approach, the anchoring energy must be considered as a *phenomenological macroscopic parameter,* which, in principle, can only be obtained by microscopic calculations [28–32] or by experimental measurements.

III. A GENERAL THEORETICAL APPROACH TO STUDYING NONPLANAR DIRECTOR DISTORTIONS

In Sec. II we showed that the main physical effects of a subsurface director distortion which occurs within a scale length of the same order of magnitude as the interfacial layer can be entirely accounted for by defining a suitable anchoring energy function. Therefore these theoretical results confirm and generalize the predictions of higher-order elastic models as far as the K_{13} elastic constant and small amplitude planar director distortions are concerned. In particular, *for planar director distortions, the correct macroscopic bulk distortion can be obtained by minimizing the Frank elastic free energy and a standard phenomenological anchoring energy,* which implicitly accounts for any subsurface elastic anomaly [procedure (iii)].

In this section we discuss the more general case where the director distortion depends on two or three different spatial coordinates and the interfaces may be curved. To understand the physical behavior of the system in this general case we shall make use of an important theoretical result which has recently been obtained by Pergamenshchik [9]. He shows that, in the general case of three-dimensional director distortions and curved interfaces, the surface elastic free-energy density f_{13} and f_{24} in Eqs. (3) and (4) can be separated into two different contributions. The first contribution, which only contains the K_{13} elastic constant, depends on the normal director derivative along the local axis orthogonal to the interface, while the second contribution, which contains both K_{13} and K_{24}, only depends on tangential director derivatives. Furthermore, only the first term (normal derivatives) gives rise to mathematical inconsistencies while the second term does not produce any mathematical problems [9,15]. According to our theoretical analysis, the first contribution cannot be explicitly introduced into the elastic expression of the first-order free-energy density since it produces a strong variation of the director field in a thin interfacial layer and thus only affects the interfacial behavior. As shown above, the macroscopic effect of this contribution is expected to be a mere renormalization of the anchoring energy function f_s. On the contrary, the tangential contribution f_{tang} is a macroscopic contribution which must be retained in the general expression of the first-order elastic free energy. Therefore we propose here that the correct macroscopic behavior of the director field in the general case of three or two-dimensional director distortions and curved interfaces must be obtained using the following expression for the free energy:

$$F_1 = F_F + F_{\text{ext}} + F_s = \int (f_F + f_{\text{ext}})\, dV + \int (f_{\text{tang}} + f_s)\, dS \,, \qquad (10)$$

where f_F is the Frank elastic energy density of Eq. (2), f_s is the phenomenological anchoring energy which depends only on the macroscopic surface director angles and implicitly also contains the effects of elastic subsurface anomalies, and f_{tang} is the tangential contribution due to the surface-like elastic constants K_{13} and K_{24}. In the most general case of nonplanar interfaces f_{tang} is [9]

$$f_{\text{tang}} = -(K_{22}+K_{24})J + \frac{K_{13}-K_{22}-K_{24}}{\sqrt{g}} \times \left\{ n_3^2 \partial_3 \sqrt{g_3} + \sum_{s=1}^{2} n_3 \partial_s \left[n_s \left[\frac{g}{g_{ss}} \right]^{1/2} \right] \right\} , \qquad (11)$$

where g_{ij} is the metric tensor of an orthogonal curviline coordinate system (x_1, x_2, x_3) in which the interface coincides with the coordinate surface $x_3 = \text{const}$, ∂_i denotes the derivative with respect to the coordinate x_i at the interface, $g_3 = g_{11} g_{22}$, and $g = g_{11} g_{22} g_{33}$. J is defined as

$$J = \frac{1}{\sqrt{g}} [n_1^2 \sqrt{g_{22}} \partial_3 \sqrt{g_{11}} + n_2^2 \sqrt{g_{11}} \partial_3 \sqrt{g_{22}} - (n_2 \sqrt{g_{11}} \partial_2 + n_1 \sqrt{g_{22}} \partial_1)(\sqrt{g_{33}} n_3)] \,. \qquad (12)$$

The tangential elastic free energy f_{tang} in Eq. (11) can be also written in terms of director $\mathbf{n}$ and unit vector $\mathbf{k}$ orthogonal to the interface, in the vectorial form

$$f_{\text{tang}} = K_{13}(\mathbf{n}\cdot\mathbf{k})[\nabla\cdot\mathbf{n} - (\mathbf{k}\cdot\nabla)(\mathbf{n}\cdot\mathbf{k})] - (K_{22}+K_{24})\mathbf{k}\cdot[\mathbf{n}(\nabla\cdot\mathbf{n}) + \mathbf{n}\times\nabla\times\mathbf{n}] \,. \qquad (12')$$

The director field which minimizes the functional of Eq. (10) is obtained by using the standard variational procedure. According to [9] and [15], *a surface free energy which contains only tangential director derivatives does not give any mathematical inconsistency.* In particular, the variation δf_{tang} is found to be only dependent on the variation δn_k of the surface director field and does not depend on the director derivative variations $\delta \partial_i n_k$.

The bulk Euler-Lagrange equation for the director field is

$$\frac{\partial f_{\text{tot}}}{\partial n_k} - \frac{1}{\sqrt{g}} \partial_m \left[\sqrt{g} \frac{\partial f_{\text{tot}}}{\partial(\partial_m n_k)} \right] + \lambda_v n_k = 0 \,, \qquad (13)$$

where $\lambda_v = \lambda_v(\mathbf{r})$ is the volume Lagrange factor and $f_{\text{tot}} = f_F + f_{\text{ext}}$ is the total bulk free-energy density which is given by the sum of the Frank free-energy density in Eq. (2) and the free-energy density f_{ext} due to external fields. The boundary conditions for the director at the interfaces in the case of *smooth interfaces* are (for details of the calculations see the Appendix to Ref. [9])

$$\frac{\partial f_{\rm tot}}{\partial(\partial_3 n_k)}+\frac{\partial f_s}{\partial n_k}+\frac{\partial f_{\rm tang}}{\partial n_k}-\frac{1}{\sqrt{g_3}}\partial_s\left[\sqrt{g_3}\frac{\partial f_{\rm tang}}{\partial(\partial_s n_k)}\right]+\lambda_s n_k=0\ , \quad (14)$$

where λ_s is the surface Lagrange factor. A more general expression for not smooth interfaces is given in the Appendix to Ref. [9].

We emphasize here that, for planar interfaces and for director distortions where the director only depends on x_3, $f_{\rm tang}=0$ and the elastic free energy is reduced to the Frank form. In the opposite case both the surfacelike elastic constants give an important explicit contribution to the macroscopic free-energy density. Therefore it should be possible to obtain both these constants in experiments where nonplanar director distortions are investigated. We note that in recent years a number of authors have investigated the physical consequences of the elastic constant K_{24} [33–45] and estimates of the value of K_{24} have been made [37,38,42,43]. Due to the mathematical difficulties connected with the problem of K_{13}, so far, authors have disregarded this contribution retaining the K_{24} contribution only. This procedure is obviously unsatisfactory and can lead to incorrect theoretical predictions while the theoretical approach which we propose in this section allows us to account for any macroscopic effect of both the surfacelike elastic constants.

IV. NONPLANAR PROBLEMS

In this section we shall consider certain kinds of nonplanar director distortions which occur when a NLC is enclosed in a cylindrical cavity [37–50] of radius R and we shall analyze them using the theoretical approach proposed in Sec. III. This geometry has been extensively investigated in the literature without accounting for surfacelike contributions [46–50] and by including the K_{24} elastic contribution but disregarding K_{13} [42–46]. Experimental values of K_{24} obtained by making experiments on these systems have been reported in Refs. [42,43]. The bulk Euler-Lagrange equation for the director field does not depend on surface elastic constants and thus the general solutions for the bulk director field which have been published by Allender and co-workers [42,43] are still correct in our case. Therefore, in this section we will make a systematic use of the theoretical results which have already been reported in Refs. [42] and [43] by showing how these theoretical results are modified if one accounts for the effects of the surfacelike elastic constant K_{13}. To avoid any confusion, it is important to emphasize that the authors of Ref. [43] used a different notation for the surfacelike elastic contribution f_{24} in Eq. (4) in the present paper. In particular the elastic constant $K_{22}+K_{24}$ which appears in Eq. (4) was replaced by $K_{24}/2$ in Refs. [42] and [43].

The main conclusions of the following theoretical analysis are the following.

(a) The surfacelike elastic constant K_{13} appreciably modifies the quantitative predictions of the theory. In particular the experimental values of K_{24} which have been obtained by disregarding K_{13} must be revised.

(b) The presence of the K_{13} elastic constant gives rise to new phenomena and thus the qualitative behavior of the system is also affected by this elastic constant. In particular, for positive values of K_{13}, a new orientational transition is predicted to occur when the critical radius of the cylindrical cavity becomes lower than a critical value $R_c=2K_{13}/W_0$, where W_0 is the anchoring energy coefficient [51] [see Eq. (15)]. The experimental investigation of this transition makes it possible to obtain the surface elastic constant K_{13} directly and provides a unambiguous test for the validity of the elastic theory proposed here.

A. The planar-radial configuration

Let us consider a NLC confined in a cylindrical cavity of radius R and length $l_0 \gg R$. The easy director alignment at the cylindrical interface is assumed to be homeotropic. In these conditions, the equilibrium configuration of the director field is not uniform due to the competition between bulk and surface contributions in the free energy. According to Allender and co-workers [42,43], four different stable (or metastable) director fields can be predicted, as shown schematically in Figs. 3–6. These configurations are denoted as the planar-radial (PR), planar-polar (PP), escaped-radial (ER), and escaped-radial-with-point-defects (ERPD) configurations. The first three kinds of distortions can be demonstrated to correspond to a relative minimum of the free energy while the fourth configuration corresponds to a metastable state. According to Ref. [43] we assume the anchoring energy given by the Rapini-Popoular expression [51]:

$$f_s(\psi_s)=\frac{W_0\sin^2\psi_s}{2}\ , \qquad (15)$$

where W_0 is the anchoring energy coefficient and ψ_s is the surface angle between the local director and the radial axis at the cylindrical interface. According to our theoretical analysis of Secs. II and III, the anchoring energy coefficient also accounts implicitly for any elastic subsurface anomaly and, in particular, for the contribution of the surfacelike elastic terms that depend on normal director derivatives. Here we use a cylindrical reference system with the z axis coincident with the cylinder axis. The three curviline coordinates x_1, x_2, and x_3 introduced in Sec. III will correspond here to θ, z, and r, respectively. Therefore $g_{11}=r^2$, $g_{22}=1$, $g_{33}=1$, $(g_3)^{1/2}=r$, and $(g)^{1/2}=r$ in Eqs. (11)–(14).

The PR configuration is shown schematically in Fig. 3. The director is radial everywhere and a line singularity exists along the cylinder axis. This singularity is usually treated as a cylindrical defect of radius ρ of the order of a typical molecular length which is excluded from the integration volume. In this geometry the surfacelike elastic constants K_{13} and K_{24} and the anchoring energy coefficient W_0 do not contribute to the total free energy because the surface contribution $\int f_{\rm tang}\,dS$ at the inner surface $r=\rho$ cancels with that at $r=R$. Therefore, the free energy per unit cylinder length is [43]

PR

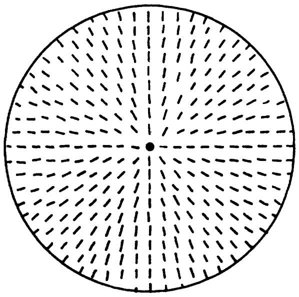

FIG. 3. Top view of the cylinder showing the director field in the planar-radial (PR) configuration. The full circle at the center denotes the disclination line.

$$F_{PR}=\pi K_{11}\ln\left[\frac{R}{\rho}\right]+F(\text{core}) , \tag{16}$$

where F(core) denotes the free energy of the isotropic core of the axial disclination line. A more accurate expression of the free energy for this case has been obtained by accounting for variations of the local scalar order parameter close to the defect [52,53].

The PR configuration has no practical interest since one can easily show that the PP configuration corresponds to a lower free energy except in the case of very small cylinder radii and thus this latter configuration is energetically favored, in agreement with experimental observations [42].

B. The planar-polar configuration

The PP configuration is shown schematically in Fig. 4. To investigate the PP and the other director fields, we will make use of the approximation $K_{11}=K_{33}=K$, which allows us to greatly reduce mathematical difficulties without substantially modifying the main features. For typical NLCs far from a nematic-smectic transition, the values of these two elastic constants are close to each other (the relative difference between K_{11} and K_{33} is usually lower than 30%). Therefore, the use of the average value $K=(K_{11}+K_{33})/2$ is expected not to greatly change the theoretical results. The director field in the PP configuration is

PP

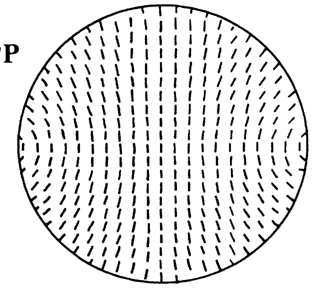

FIG. 4. Top view of the cylinder showing the director field in the planar-polar (PP) configuration for a finite positive value of the effective anchoring energy coefficient. A rather different shape of the director field is obtained for a negative effective anchoring energy (see Ref. [46]).

$$\mathbf{n}=\cos\psi\hat{\mathbf{r}}+\sin\psi\hat{\boldsymbol{\theta}} , \tag{17}$$

where $\psi=\psi(r,\theta)$ is the local angle between the director and the radial direction which depends on r and θ alone. The surface elastic free energy per unit surface area f_{tang} in Eq. (11) is

$$f_{\text{tang}}=-\frac{K_{22}+K_{24}}{R}\left[1+\frac{\partial\psi_s}{\partial\theta}\right]+\frac{K_{13}}{R}\cos^2\psi_s+\frac{K_{13}}{R}\frac{\partial f(\psi_s)}{\partial\theta} , \tag{18}$$

where $f(\psi_s)=(\sin 2\psi_s)/4+\psi_s/2$. The total free energy per unit length due to the surface contributions is obtained by integrating the surface free energies f_{tang} and f_s over the θ angle. We obtain

$$F_{\text{surf}}=\int_0^{2\pi}R(f_{\text{tang}}+f_s)\,d\theta =\pi K_{13}+\int_0^{2\pi}\left[\frac{W_0R}{2}-K_{13}\right]\sin^2\psi_s\,d\theta . \tag{19}$$

To obtain Eq. (19) we exploited the condition $\psi_s(2\pi)-\psi_s(0)=-2\pi$, which is satisfied because no disclination is present at the cylinder axis. Note that K_{24} does not enter in the total free energy of the PP configuration since $\nabla\cdot[\mathbf{n}(\nabla\cdot\mathbf{n})+\mathbf{n}\times\nabla\times\mathbf{n}]=0$ in this case. Apart from the inessential constant contribution πK_{13}, the K_{13} elastic constant makes a surface contribution which is of the same kind as that due to anchoring [see Eq. (19)]. In particular it simulates an apparent anchoring energy coefficient:

$$W_0^*=W_0\left[1-\frac{2K_{13}}{RW_0}\right] . \tag{20}$$

Therefore the main effect of the K_{13} elastic constant in the PP configuration is an "apparent" change of the anchoring energy coefficient. However, we must emphasize that this latter effect, although qualitatively similar to that discussed in Sec. II due to director derivatives along the axis orthogonal to the interface, is very different from the previous one. Indeed, the presence of normal director derivatives produces a strong subsurface director distortion which only modifies the interfacial layer of thickness $\delta\ll R$. Therefore, according to our analysis in Sec. II, this effect must be considered as a true source of surface anchoring energy which is undistinguishable from other anchoring contributions. In particular, the resulting anchoring coefficient is completely independent of geometrical parameters such as, for instance, the curvature radius of the interface. On the contrary, the surface free-energy contribution $K_{13}\sin^2\psi_s$, which appears in Eq. (19), comes from the integral of the bulk elastic free energy in the whole cylindrical volume and thus it is a bulk effect. In particular, the elastic contribution to the anchoring energy in Eq. (20) depends explicitly of curvature radius R and thus it is not an intrinsic surface parameter.

According to Eq. (20), the main effect of K_{13} in this geometry is an increase in the effective anchoring coefficient if $K_{13}<0$ and a decrease if $K_{13}>0$. In particular, for $K_{13}>0$, an orientational transition is expected to occur if radius R of the cylinder approaches the critical value:

$$R_c=\frac{2K_{13}}{W_0} . \tag{21}$$

For $R>R_c$ the easy surface director orientation is $\psi_s=0$, which corresponds to the homeotropic alignment, while the planar alignment $\psi_s=\pi/2$ is favored for $R<R_c$.

The bulk Euler-Lagrange equation for the director field and the boundary condition at the interface $r=R$ can be obtained by minimizing the total free energy in Eq. (10) with respect to any variation $\delta\psi$ of the director angle. The Euler-Lagrange equation for the director angle is

$$\frac{1}{r^2}\frac{\partial^2\psi}{\partial\theta^2}+\frac{1}{r}\frac{\partial\psi}{\partial r}+\frac{\partial^2\psi}{\partial r^2}=0 , \tag{22}$$

with the boundary condition

$$\frac{W_0^*}{2}\sin 2\psi_s+K\frac{\partial\psi}{\partial r}=0 , \tag{23}$$

where the derivative [in Eq. (23)] is calculated at interface $r=R$. Equation (24) is reduced to that used in Ref. [43] if the apparent anchoring coefficient is replaced by anchoring coefficient W_0. The general solution of Eq. (22) that satisfies the boundary condition (23) is

$$\psi=\frac{\pi}{2}-\tan^{-1}\left[\tan(\theta)\left[\frac{R^2+\gamma r^2}{R^2-\gamma r^2}\right]\right] , \tag{24}$$

where

$$\gamma=\mathrm{sgn}(\beta)(\beta^2+1)^{1/2}-\beta , \quad \beta=\frac{2K}{W_0^*R} , \tag{25}$$

where $\mathrm{sgn}(\beta)=+1$ for $\beta>0$ and $\mathrm{sgn}(\beta)=-1$ for $\beta<0$. Coefficient γ becomes negative if $\beta<0$. In this case ($\gamma<0$) one can easily show that the director field in Eq. (24) coincides with the planar-bipolar structure described in Ref. [45]. The free energy per unit length of cylinder is

$$F_{\mathrm{PP}}=\pi K\left[-\ln(2\beta\gamma)+\frac{1-\gamma}{\beta}\right]+\pi K_{13} . \tag{26}$$

Equation (26) is reduced to the form given in Ref. [44] for $K_{13}=0$. Note that the director field in Eq. (24) and the free energy per unit length F_{PP} do not depend on K_{24}. Therefore, by studying the director bulk distortion in this case one can measure the other surfacelike elastic constant K_{13}. In particular, if $K_{13}>0$, a very simple and accurate experimental method should consist in measuring the critical radius R_c for the homeotropic-planar transition. At $R=R_c$, the effective anchoring energy vanishes and the director alignment is everywhere uniform in the bulk.

It is important to emphasize here that the experimental analysis of the dependence of the apparent anchoring coefficient W_0^* on cylinder radius R may provide a direct test for the validity of our theory. Indeed, the standard approach utilized in Refs. [42,43] predicts no dependence of this parameter on R [see Eq. (20) with $K_{13}=0$] while our theory predicts the dependence given in Eq. (20).

C. The escaped-radial configuration

The ER configuration is shown schematically in Fig. 5. This configuration has been investigated in Refs. [47–50] without accounting for the surfacelike elastic constants and in Ref. [43] by accounting for K_{24} but disregarding K_{13}. The director field in this case is

$$\mathbf{n}=\cos\Omega\hat{\mathbf{z}}+\sin\Omega\hat{\mathbf{r}} , \tag{27}$$

where $\Omega=\Omega(r)$ is the angle between the director and the cylinder axis that is assumed to depend only on the radial coordinate r. As in the previous case we use the approximation $K_{11}=K_{33}=K$. An analytical solution for the bulk director field in the case $K_{11}\neq K_{33}$ is given in [43]. The surface free energy per unit length due to f_{tang} and f_s is

$$F_{\mathrm{surf}}=\int_0^{2\pi}(f_{\mathrm{tang}}+f_s)R\,d\theta$$
$$=\int_0^{2\pi}\frac{W_0'}{2}(\cos^2\Omega_s)R\,d\theta+\pi K_s , \tag{28}$$

with $\Omega_s=\Omega(r=R)$ and where we have defined the apparent anchoring energy coefficient

$$W_0'=W_0\left[1-\frac{K_s}{RW_0}\right] \tag{29}$$

and the effective surface elastic constant

$$K_s=2(K_{13}-K_{22}-K_{24}) . \tag{30}$$

Apart from the constant contribution πK_s, which is inessential for the determination of the equilibrium director field, in this case too the main effect of the surfacelike elastic constants is an apparent variation of the anchoring coefficient. If $K_s>0$, an orientational transition from planar ($\Omega_s=0$) to homeotropic easy orientation ($\Omega_s=\pi/2$) is expected to occur when the cylinder radius exceeds the critical value

$$R_c'=\frac{K_s}{W_0} . \tag{31}$$

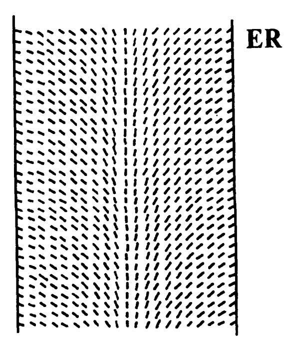

FIG. 5. Lateral view of the cylinder showing the director field in the escaped-radial (ER) configuration.

However, as will be shown below, this transition does not occur because it is preceded by another transition at a greater value of the cylinder radius. The Euler-Lagrange equation for the director field is

$$-\frac{\sin 2\Omega}{2r}+\frac{d\Omega}{dr}+r\frac{d^2\Omega}{dr^2}=0 , \qquad (32)$$

with the boundary condition

$$\frac{d\Omega}{dr}=\frac{\sin(2\Omega_s)[W_0R-K_s-K]}{2KR} , \qquad (33)$$

where the derivative is calculated at $r=R$. Equation (33) with K_s given in Eq. (30) is reduced to that already given in [43] if we put $K_{13}=0$ and if we substitute $2(K_{22}+K_{24})$ with K_{24} in Eq. (30). The general solution of Eq. (32) that satisfies the boundary condition (33) is

$$\Omega=2\tan^{-1}\left[\frac{r\tan(\Omega_s/2)}{R}\right] , \qquad (34)$$

where

$$\Omega_s=\cos^{-1}\left[\frac{1}{\sigma}\right] , \qquad (35)$$

with

$$\sigma=\frac{RW_0}{K}-\frac{K_s}{K}-1=\frac{RW_0'}{K}-1 . \qquad (36)$$

Solution (34) holds for $\sigma>1$. If $\sigma<1$, the general solution is a uniform alignment along the z axis ($\Omega=0$ everywhere). It is important to note that the uniform alignment is reached at a greater critical radius than that in Eq. (31). Therefore the transition from homeotropic to planar easy alignment predicted in Eq. (31) cannot be observed.

The total free energy per unit length in the two cases $\sigma>1$ and $\sigma<1$ is

$$F_{\mathrm{ER}}=\pi K\left[3+\frac{K_s}{K}-\frac{1}{\sigma}\right] \quad \text{for } \sigma>1 \qquad (37)$$

and

$$F_{\mathrm{ER}}=\pi W_0 R \quad \text{for } \sigma<1 . \qquad (38)$$

In this geometry, the only effect of K_{13} is a variation of the effective surface elastic constant K_s. Therefore K_{13} does not modify the qualitative behavior of the system but only the quantitative behavior. This means that the experimental investigation of the ER structure alone is not a good test for the validity of our theory.

D. The escaped-radial-with-point-defects configuration

The ERPD configuration is shown schematically in Fig. 6. This configuration is characterized by a director angle Ω which depends on both the radial coordinate r and the z coordinate. Two point defects occur at $z=0$ (radial defect) and $z=L$ (hyperbolic defect), as shown in Fig. 6. According to Ref. [43], an analytical solution cannot be found for the ERPD configuration. A detailed numerical analysis of this configuration has been given in Ref. [50] together with a discussion of its stability. A different kind of ERPD structure is predicted to occur for weak director anchoring [50]. In principle, the ERPD configuration would relax to the energetically favored ER configuration, but the boundary conditions at the ends of the cylinder repel point defects and thus the ERPD cannot relax. Therefore the ERPD configuration appears to be a metastable state which is usually observed for high values of cylinder radius R while at lower values of R the ERPD configuration is replaced by the PP. Crawford, Allender, and Doane [43] showed that, in the case where $\sigma>1$ and the distance L between point defects is lower than $2R$, a suitable trial solution which satisfies the boundary conditions is

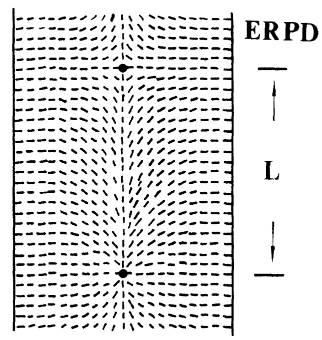

FIG. 6. Lateral view of the cylinder showing the escaped-radial-with-point-defects (ERPD) configuration. A radial point defect occurs close to the bottom of the figure, while a hyperbolic defect occurs close to the top of the figure at the distance L from the radial defect.

$$\Omega=\tan^{-1}\left[\frac{\sigma r}{z\left[1-\frac{z}{L}\right]\left[\sigma-\frac{(\sigma-1)r}{R}\right]}\right] \qquad (39)$$

for $r\le R$ and $0\le z\le L$. In the region $r\le R$ and $-L\le z\le 0$ angle Ω at point z is the supplement of that given by Eq. (39) at $-z\{\Omega(-z)=\pi-\Omega(z)\}$. This approximate solution agrees satisfactorily with the numerical solutions of the Euler-Lagrange equation [50].

Although $F_{\mathrm{ERPD}}>F_{\mathrm{ER}}$, the point defects are unable to relax by going to the ends of the cylinder and an array of more or less equally spaced defects occurs along the z axis of the cylinder. The value of L/R is expected to be sample dependent and has been found to be $L/R\approx1.5-2$ in the case of the NLC 4'-pentyl-4-cyanobiphenyl (5CB) enclosed in nucleopore membranes [43]. The only configurations which have been observed in the experiments are the PP configuration for small cylinder radii and weak anchoring and the ERPD configuration for higher radii or strong anchoring.

E. Analysis of experimental results

From the theoretical discussion above it is clear that both the surfacelike elastic constants K_{13} and K_{24} can be obtained, in principle, by investigating the behavior of NLCs enclosed in a cylindrical cavity. In particular, from measurements in the PP geometry, the anchoring energy coefficient and the surfacelike elastic constant K_{13} can be determined while the value of the effective surface elastic constant K_s in Eq. (31) and thus K_{24} can be obtained from measurements in the ERPD geometry. The effect of surfacelike elastic constants on the macroscopic behavior of the NLC is expected to become important when the cylinder radius is comparable with the extrapolation length $b = K/W_0$, which is usually much smaller than 1 μm. For this reason measurements with nucleopore membranes with cylindrical cavities of radii smaller than 1 μm seem to be very promising [41–45]. In Refs. [42] and [43] the experimental behavior of the NLC 5CB enclosed in nucleopore membranes was investigated by using NMR. Cavities with radii ranging from 0.05 to 0.5 μm were investigated and the NMR method was shown to be very sensitive to details of the director field. From independent measurements the authors obtained both the anchoring coefficient and the K_{24} surfacelike elastic constant by disregarding the K_{13} elastic constant in their analysis. Both untreated nucleopore membranes (strong anchoring) and membranes treated by applying a lecithin surfactant (weak anchoring) were investigated. In this latter case a transition from the PP to the ERPD structure was found for $R = 0.5$ μm. This latter case seems to be the more interesting since both the surfacelike elastic constants can be measured, in principle, by making measurements in the PP and ERPD configurations, respectively. The PP structure was observed at the radii $R = 0.3$ and 0.4 μm while the ERPD structure was obtained at $R = 0.5$ μm. In principle both the anchoring coefficient W_0 and the K_{13} elastic constant can be obtained from the experimental results concerning the PP configuration by substituting the experimental values $\beta(R = 0.3)$ and $\beta(R = 0.4)$ in Eqs. (25) and (20). Once these two parameters are obtained, the latter unknown elastic constant K_{24} can be obtained from the measurement of the parameter σ [see Eqs. (36) and (29)] at $R = 0.5$ μm in the ERPD configuration. Unfortunately the variation of the R radius in the two measurements concerning the PP configuration is rather small (25%) and thus both the anchoring coefficient and the K_{13} elastic constant can be found with a very large uncertainty due to the experimental uncertainty on the β coefficient. This uncertainty also produces much uncertainty concerning the value of K_{24}. A greater precision should be obtained by repeating the same kind of measurements using a wide range of cylinder radii. This should not be a practical problem since nucleopore membranes are produced with radii ranging from 0.006 to 6 μm.

Here we briefly reanalyze the main experimental results of Refs. [42] and [43] in order to obtain a first rough estimate of the two surfacelike elastic constants K_{13} and K_{24}. We start our analysis by using the experimental results obtained with untreated nucleopore membranes at three different radii 0.05, 0.1, and 0.2 μm. In this case, the ERPD configuration is always observed and the K_s surface constant can be obtained by exploiting the experimental values of σ obtained at different cylinder radii. By using the experimental values $\sigma(R = 0.05\ \mu\text{m}) = 2.0 \pm 0.2$, $\sigma(R = 0.1\ \mu\text{m}) = 4.0 \pm 0.2$, and $\sigma(R = 0.2\ \mu\text{m}) = 8.0 \pm 0.4$ we obtain $K_s/K = -1.0 \pm 0.6$. By exploiting the experimental value $2K_{22}/K = 0.85 \pm 0.10$ at room temperature [54] $[K = (K_{11} + K_{33})/2]$ and substituting it in Eq. (30) we find

$$(K_{24} - K_{13})/K = 0.08 \pm 0.40 . \tag{40}$$

To obtain the two surfacelike elastic constants separately, we make use of the experimental results in Refs. [42] and [43] that were obtained using lecithin treated nucleopore membranes. At $R = 0.5$ μm the ERPD structure was observed and the parameter $\sigma = 3.1 \pm 0.2$ was measured [59]. Substituting this value in Eq. (37) together with the previous experimental value $K_s/K = -1.0 \pm 0.6$, we find $W_0/K = 6.2 \pm 1.6\ \mu\text{m}^{-1}$. At the cylinder radii $R = 0.3$ and 0.4 μm the authors observed a PP structure and measured $\beta(R = 0.3\ \mu\text{m}) = 1.1 \pm 0.1$ and $\beta(R = 0.4\ \mu\text{m}) = 0.83 \pm 0.08$. Since W_0/K is known, and K_{13} elastic constant can be obtained by substituting the experimental values of β and W_0/K in Eqs. (25) and (20). From the two measurements at $R = 0.3$ and 0.4 μm we find $K_{13}/K = 0.02 \pm 0.35$ and 0.04 ± 0.40, respectively. The average value of these two independent measurements is

$$K_{13}/K = 0.03 \pm 0.30 . \tag{41}$$

Substitution of Eq. (41) into Eq. (40) gives

$$K_{24}/K = 0.11 \pm 0.70 . \tag{42}$$

In order to avoid any confusion we still wish to emphasize that the definition of the K_{24} elastic constant in Eq. (4) is different from that utilized in Refs. [42] and [43].

We see that the uncertainty on the experimental values in Eqs. (41) and (42) is rather large. We think that much more accurate values should be obtained making new measurements on the same system for a more extended range of cylinder radii. In particular we expect to obtain very accurate values of K_{13} if the surface transition in Eq. (21) is observed.

V. CONCLUSIONS

In this paper, by using the general Gibbs theory of interfacial phenomena, we have generalized the theoretical predictions of higher-order elastic theories for planar director distortions and small director angles. In particular we show that the main effect of surface derivatives along the axis orthogonal to the interface is a mere anchoring effect which can be entirely accounted for by defining a phenomenological anchoring energy f_s, which depends solely on the director surface angles. This anchoring energy implicitly accounts for any elastic interfacial anomaly and depends, in principle, on all higher-order elastic constants. Our theoretical approach allows us to generalize our theoretical results to include the more general case of nonplanar director distortions. In this case the surface free energy can be separated into two different contributions. The first contribution depends on the normal derivatives of the director at the interfaces and thus it can be entirely accounted for in the phenomenological expression of the surface anchoring.

The second contribution depends on tangential director derivatives alone and thus it does not produce any mathematical problems [9,15]. Therefore we propose here a general expression for the first-order elastic free energy. This expression is the sum of the standard bulk Frank from f_F, of a surface elastic contribution f_{tang}, which depends on the two surfacelike elastic constants and on the tangential director derivatives and, finally, a phenomenological anchoring energy f_s, which depends solely on the surface director angles. This expression for free energy does not present any mathematical problems.

On the basis of the present theoretical approach, we find that both the surfacelike elastic constants K_{13} and K_{24} make important contributions to the director field in nonplanar cases. In particular, in the case of a NLC enclosed in a cylindrical cavity, we predict the existence of a new orientational transition when the cylinder radius approaches a critical value R_c. This transition can only occur if the contribution of K_{13} is taken into account and thus an experimental observation of this transition might provide a strong support to our theoretical approach and might make possible to obtain an accurate experimental value for K_{13}.

The comparison of our theoretical results with the experimental observations in NLCs enclosed in nucleopore membranes allows us to find a rough estimate of the surfacelike elastic constants K_{13} and K_{24}.

Before concluding this paper, we note that the assumption of isotropic elastic constants $K_{11}=K_{33}$ should be removed if accurate values of the two surfacelike elastic constants are required. In this case, numerical solutions for the bulk director field must be utilized. Furthermore we wish to emphasize that the surfacelike elastic constants enter in the boundary conditions (14) together with the phenomenological expression $f_s(\theta_s,\varphi_s)$ of the surface anchoring energy. The explicit functional dependence of the anchoring energy on the macroscopic surface angles θ_s and φ_s is not known. For an isotropic substrate the more general expression of f_s, in the absence of polar surface effects is [23,25]

$$f_s(\theta_s)=\sum_{n=0}^{\infty} f_{2n}\cos^{2n}\theta_s \; , \tag{43}$$

where all the coefficients f_{2n} can, in principle, be different from zero. Equation (43) is reduced to the Rapini form in Eq. (15) if $f_{2n}=0$ for $n>1$. At the present time there is no physical justification for the use of Eq. (15), while many experimental results have been obtained in planar geometries showing that the actual behavior of the anchoring function is more complex than that given by Eq. (15). In particular, experimental results indicate that at least the contribution $f_4\cos^4\theta_s$ in Eq. (43) plays an important role [55–58]. Furthermore a simple microscopic model based on van der Waals interactions between molecules predicts a nonvanishing value of the f_4 coefficient [24]. Therefore the use of the Rapini form to obtain the experimental values of the surfacelike elastic constants may be a further source of experimental uncertainty, especially if the characteristic length R of the bulk director distortion is close to or smaller than the extrapolation length $b=K/W_0$. In this latter case the theoretical predictions of the Rapini expression can greatly differ from the actual surface behavior of the director field. Therefore, in our opinion, accurate experimental measurements of the surface elastic constants can only be obtained by making measurements in the $b \ll R$ case or by using an expression of the surface anchoring potential which contains at least the first two contributions $n=1$ and 2 in Eq. (43). In this latter case a numerical integration of the Euler-Lagrange equations for the director field is needed.

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