Resummation of higher-order terms in the free-energy density of nematic liquid crystals

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The presence of the surfacelike elastic constant K_{13} in the expression of the elastic free-energy density F_2 for a nematic liquid crystal (NLC) makes the free-energy functional unbounded from below. A discontinuity of the director field has been predicted to occur at the interfaces of the NLC. In recent years two very different theoretical approaches have been proposed to bypass mathematical difficulties related to the K_{13} problem. Hinov and Pergamenshchik [Mol. Cryst. Liq. Cryst. **148**, 197 (1987); **178**, 53 (1990), and references therein; Phys. Rev. E **48**, 1254 (1993)] consider the surface director discontinuity is an artifact of theory and make the assumption that the director field must be sought in the class of continuous functions. With this assumption a well defined solution for the equilibrium director field can be found and new phenomena are predicted to occur. Barbero and co-workers [Nuovo Cimento D **12**, 1259 (1990); Liq. Cryst. **5**, 693 (1989)] expanded the free-energy functional F up to the fourth order in the director derivatives (*second-order elastic theory*) and showed that the minimization problem now becomes mathematically well posed. A strong subsurface director distortion on a length scale of the order of the molecular length is predicted to occur by using this approach. The macroscopic consequence of the strong subsurface distortion is an apparent renormalization of the anchoring energy as far as the long-range bulk distortion is concerned. In the first part of this paper we propose a simple and rigorous test based on the general principles of mechanics to establish the internal consistency of these very different theoretical approaches. The second-order elastic theory is found to satisfy this test, while the Hinov-Pergamenshchik model is found to be in contrast with it. In the second part of this paper we make a systematic expansion of the free energy at any order in the director derivatives and we analyze the physical effects of the higher-order contributions that were disregarded by the second-order theory. At any expansion order a strong subsurface director distortion is predicted to occur and its macroscopic effect is shown to be equivalent to an apparent renormalization of the anchoring energy. Therefore, the main qualitative predictions of the second-order elastic theory remain satisfied at any expansion order, although the quantitative behavior of the system is found to be greatly affected by higher-order contributions.

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I. INTRODUCTION

The macroscopic behavior of nematic liquid crystals (NLC's) is described by the director **n** which denotes the average molecular orientation. The space variation of the director can be obtained by minimizing the Frank elastic free energy [1]. Nehring and Saupe [2], in 1971, showed that a new term must be added to the free energy. This new contribution, which is proportional to the surfacelike elastic constant K_{13}, explicitly contains second order derivatives of the director and, thus, behaves as a surface free-energy contribution. Oldano and Barbero [3], in 1985, showed that this new surface contribution makes the free energy unbounded from below, so that no minimum of the free energy can be found. In these conditions, a discontinuity of the director field is predicted to exist at the interfaces [4–6]. This mathematical discontinuity is due to an oversimplification of the surface problem and it tends to simulate an actual strong director distortion which occurs in a very thin subsurface layer of molecular characteristic length. In this greatly distorted subsurface layer, the director derivatives assume very high values and thus one expects higher-order elastic contributions in the expansion of the free energy to play a considerable role. On the basis of this idea, Barbero and co-workers [7,8] generalized the Frank theory of elasticity by making a power expansion of the free elastic energy density of a NLC up to the fourth order in the director derivatives. In the following we will refer to this elastic theory as the "second-order elastic theory." The second-order free energy is shown to be bounded from below and to possess a minimum. The equilibrium director field is now represented by a continuous function but there is a sharp variation close to the interfaces within a thickness of the order of the molecular length. From the macroscopic point of view this short-range subsurface distortion is equivalent to a discontinuity of the director field in agreement with the theoretical predictions of the first-order elastic theory [4–6]. The macroscopic effect of the subsurface distortion has been demonstrated to be equivalent to an apparent reduction of the surface anchoring energy coefficient W [8,9].

A very different solution to the problem of the surfacelike elastic constant K_{13} was proposed some years ago by Hinov [10,11], who made the *a priori* assumption that discontinuities of the director field at the interfaces are unphysical and the director field that minimizes the free energy must be sought in the class of continuous solutions of the bulk Euler-Lagrange equations everywhere (also at the interfaces). More recently, Pergamenshchik [12] reached the same conclusion on the basis of different physical arguments. The main idea of Pergamenshchik is that the presence of a strong subsurface distortion is an artifact of theory because the theory consists of a power expansion of the free energy that is stopped at a finite order. According to the Pergamenshchik conjecture, the truncation procedure at a finite order automatically produces surface elastic contributions and a solution for the director field which is characterized by surface discontinuities, while a complete resummation over all the higher-order terms should bound the free energy from below in such a way that director distortions with a very short characteristic length are no longer possible. Therefore he suggests that the true director field can be obtained by using the Nehring and Saupe first-order elastic theory (with $K_{13}\neq 0$) on the condition that the director distortion must be sought in the class of continuous functions that are solutions of the bulk Euler-Lagrange equations. With this assumption, the mathematical problem is shown to be well posed and qualitatively new phenomena are predicted to occur [13,14]. In the following we will refer to this theoretical procedure as the "modified first-order elastic theory."

Both these theoretical models made special assumptions or approximations whose actual validity should be verified. In particular, the modified first-order theory makes the assumption that the director field does not exhibit any discontinuity. On the other hand, the second-order theory consists in a power expansion of the free-energy density up to the fourth order in the director derivatives. In principle, a truncated power expansion is justified only if the length scale of the director distortion is much higher than the molecular scale length. This is certainly not the case as far as the strong subsurface distortion is concerned and thus the role that elastic contributions of order higher than the second order may play is not clear.

In this paper we want to analyze in detail the validity of these assumptions. In particular, we want to answer the following questions.

(1) Are the two theoretical approaches consistent with the principles of mechanics?

(2) What is the influence of higher-order elastic contributions that are not taken into account by the second-order elastic theory? Can these contributions modify the main predictions of the second-order elastic theory?

In Sec. II we answer question 1 by proposing a simple and rigorous theoretical test to assess the internal physical consistency of these elastic theories. This test is based on two general laws of mechanics: the principle of virtual work and the equilibrium laws for a mechanical system. The modified first-order theory is found not to satisfy this test, while the second-order theory is found to satisfy it. Therefore the modified first-order theory is inconsistent with the principles of mechanics. We remind that this theory is based only on the assumption that no director discontinuity is present at the interfaces. Therefore the direct consequence of our theoretical analysis is that, within a first-order elastic theory, a discontinuity of the director-field must always occur at the interfaces if the surfacelike elastic constant K_{13} is different from 0.

Although the second-order elastic theory is found to be consistent with the principles of mechanics, it cannot be considered to be a definitive solution for the K_{13} problem, since the role that elastic contributions of order higher than the second order may play is not clear. A complete analysis of the elastic problem would require a resummation over all higher-order contributions of the elastic free energy for any kind of director distortion. This is an impossible task in practice due to the very great number and the complex form of the new higher-order contribution that must be taken into consideration. However, in order to obtain some understanding of the effects of higher-order surface and bulk contributions, we can restrict our attention to the very special case of *planar director distortions* and *very small director angles.* In this way we can greatly reduce the number of significant new elastic contributions and infer certain important general trends of solutions for the director field by exploiting the great scale separation between the macroscopic characteristic length scale related to the first-order elastic contributions and length scale which characterizes the higher-order contributions. In Sec. III we summarize briefly the main aspects of the expansion procedure used by Barbero, Sparavigna, and Strigazzi [7] to obtain the second-order elastic free energy and we discuss the main consequences of this approach. In Sec. IV we make a systematic expansion of the free-energy density at any order in the director derivatives by using the same theoretical approach as [7] and we analyze the shape of the equilibrium director distortions. At any expansion order n, a strong subsurface director distortion is predicted to occur. The amplitude and the spatial shape of the strong subsurface distortions are found to depend greatly on all new higher-order elastic contributions. At any expansion order n, the macroscopic distortion is found to be fully equivalent to that which is predicted by using the Frank elastic form for the free energy (with $K_{13}=0$) with a renormalized value of the anchoring energy coefficient and of the easy axis angle. Therefore we infer that a complete resummation over all higher-order contributions does not qualitatively modify the main conclusions of the second-order elastic theory as far as the macroscopic distortion is concerned. However, we must emphasize that the discontinuity $\Delta\theta$ of the director angle at the surface and the renormalized value of the effective anchoring coefficient are functions of the surfacelike elastic constant K_{13} and of all higher-order surface and bulk elastic constants. Therefore the theoretical predictions of the second-order elastic theory are not quantitatively correct.

II. THE ELASTIC TORQUE TEST

Consider a NLC layer of thickness d, sandwiched between two parallel plates as shown schematically in Fig. 1. We suppose that the easy director alignment at both the bounding plates lies in the vertical x-z plane of an orthogonal right-handed Cartesian system and makes the angle β_0 with respect to the normal z to the plates. For the sake of simplicity, we assume the same anchoring energy at both the plates. A magnetic field $\mathbf{H}$ is applied along an axis which makes the angle α with the normal to the plates.

The surface torque per unit surface area that must be

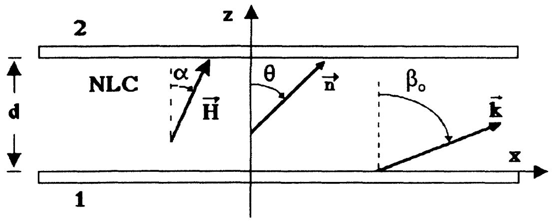

FIG. 1. Schematic view of a nematic LC layer sandwiched between two parallel plates. d is the thickness of the layer, $\theta=\theta(z)$ is the angle between the director **n** and the normal z to the plates, α is the angle which the magnetic field **H** makes with the z axis, and β_0 is the easy angle at both the surfaces.

applied on the solid bounding plates to maintain mechanical equilibrium when the magnetic field is applied can be calculated using two different theoretical procedures. The first method consist in making a virtual rotation $\Delta\eta$ of both the plates around the y axis (see Fig. 1). According to the principle of virtual work, the total mechanical work which must be spent by the operator to make this rotation is equal to the variation of the free energy of the system. Therefore the total torque per unit surface area which must be applied to the system of two plates to maintain mechanical equilibrium can be written in the general form

$$\tau=\tau_1+\tau_2=\frac{dF}{d\eta}\hat{\mathbf{y}} , \tag{1}$$

where F is the free energy per unit surface area, $\tau=\tau\hat{\mathbf{y}}$ is the total mechanical torque per unit surface area, τ_1 and τ_2 are the mechanical surface torques acting on plates 1 and 2, and $\hat{\mathbf{y}}$ is the versor of the axis orthogonal to the x-z plane. The second theoretical procedure for calculating the total surface mechanical torque consists in applying the general laws for the equilibrium of a mechanical system. At equilibrium the total external torque, which is given by the sum of surface torques acting on the plates and the bulk magnetic torque exerted by the magnetic field, must be zero. All other torques such as the elastic torques and the surface anchoring torques are internal to the system and cannot influence the balance of external torques. Therefore the total torque per unit surface area which must be exerted on the plates to maintain mechanical equilibrium is

$$\tau=-\int_0^d \chi_a(\mathbf{n}\cdot\mathbf{H})(\mathbf{n}\times\mathbf{H})dz , \tag{2}$$

where χ_a is the anisotropy of the diamagnetic susceptibility of the NLC. Equations (1) and (2) are direct consequences of the general principles of mechanics and thus any theory of elastic properties must satisfy both these equations. The proposed surface torque test consists, then, in verifying the identity

$$\frac{dF}{d\eta}\hat{\mathbf{y}}=-\int_0^d \chi_a(\mathbf{n}\cdot\mathbf{H})(\mathbf{n}\times\mathbf{H})dz . \tag{3}$$

In order to reduce the mathematical difficulties and to make the theoretical analysis clearer, we make the following simplifying assumptions.

(i) The bulk elastic constants K_{11} and K_{33} have the same value K ($K_{11}=K_{33}=K$).

(ii) The magnetic coherence length $\xi=(K/\chi_a)^{1/2}/H$ is much smaller than the thickness d of the nematic layer, where H is the intensity of the magnetic field. This condition can be satisfied, for instance, using a NLC layer of thickness $d=200$ μm and a magnetic field $H=10$ kG ($\xi\approx 2$ μm).

It is important to emphasize here that conditions (i) and (ii) are not necessary to our analysis and the same main conclusions are obtained without making these simplifying assumptions. In this case, however, the theoretical calculations become more complicated and numerical integration of the Euler-Lagrange equations for the equilibrium director field is needed.

The anchoring energy of the director at the two interfaces of the NLC layer is represented by the anchoring energy function $W(\theta_s)$ which is assumed to be the same at both interfaces. This function represents the work which must be spent to rotate the director from the easy angle β_0 that minimizes the surface free energy to the actual surface angle θ_s. In the literature, authors often assume the Rapiniand Popoular form [15],

$$W(\theta_s)=\frac{W}{2}\sin^2(\theta_s-\beta_0) , \tag{4}$$

where W is the anchoring energy coefficient. This expression is not the most general form for the surface potential; in particular, the symmetry of the interface makes other more complex contributions possible [16] which have been effectively observed in experiments [17–20]. Therefore, to avoid any model-dependent theoretical result, we do not make any assumption as to the actual form of the surface potential.

A. The first-order elastic torque

According to the foregoing assumptions, the Nehring-Saupe first-order elastic free energy per unit surface area is

$$F_2=\tfrac{1}{2}\int_0^d [K\theta'^2-\chi_a H^2\cos^2(\theta-\alpha)]dz+W(\theta_1)$$
$$+W(\theta_2)-\frac{K_{13}}{2}(\theta_2'\sin 2\theta_2-\theta_1'\sin 2\theta_1) , \tag{5}$$

where K_{13} is the surfacelike elastic constant and $\theta=\theta(z)$ is the angle between the director and the axis z orthogonal to the plates. The primes denote differentiation with respect to z and the subscripts 1 and 2 correspond to quantities measured at the surfaces $z=0$ and $z=d$, respectively. Equation (5) has been obtained by assuming a planar distortion of the director field. The Euler-Lagrange equation for the bulk director distortion is

$$\theta''-\frac{\sin 2(\theta-\alpha)}{2\xi^2}=0 . \tag{6}$$

The director distortions close to the two interfaces are identical and thus we can restrict our attention to the region $0\le z\le d/2$, where the first integral of Eq. (6) becomes

$$\theta' = -\frac{\sin(\theta-\alpha)}{\xi}, \tag{7}$$

where we have considered the case $\beta_0 > 0$ and $\beta_0 < \alpha < \pi/2+\beta_0$. Equation (7) has been obtained by using the "semi-infinite sample approximation" which consists in assuming $\theta(d/2)=\alpha$. Indeed, for $\xi \ll d$, the director distortion remains almost entirely confined within two thin subsurface layers of characteristic thickness of a few coherence lengths ξ, while the director orientation is virtually parallel to the magnetic field at the center of the nematic layer. As shown in Appendix A, this approximation is very accurate if $d/\xi \gg 1$. The free energy per unit surface area is obtained by substituting Eq. (7) in Eq. (5) and by accounting for the symmetry of the director field with respect to the center $z=d/2$ of the nematic layer [$\theta_1=\theta_2, \theta(z)=\theta(d-z)$]. After some straightforward calculation we find

$$F_2 = 2K\left[g_0 - \frac{1}{\xi}\cos(\theta_1-\alpha) + \frac{W(\theta_1)}{K} - \frac{R}{2\xi}\sin 2\theta_1 \sin(\theta_1-\alpha)\right], \tag{8}$$

where $g_0 = -1/\xi(d/2\xi - 1)$ is an isotropic contribution and $R = K_{13}/K$ is the surfacelike adimensional coefficient. The surface director angle θ_1 is obtained by minimization of F_2 and thus must satisfy

$$\frac{\partial F_2}{\partial\theta_1} = \frac{1}{\xi}\sin(\theta_1-\alpha)\frac{\partial W(\theta_1)}{K\partial\theta_1} - \frac{R}{\xi}\cos(2\theta_1)\sin(\theta_1-\alpha) - \frac{R}{2\xi}\sin(2\theta_1)\cos(\theta_1-\alpha) = 0 . \tag{9}$$

The solution of Eq. (9) can be found in a close analytical form only if we make special assumptions on the anchoring energy function $W(\theta_1)$. However, as far as our theoretical discussion is concerned, the actual value of the surface director angle is not an important parameter and thus we do not make any specific assumption on $W(\theta_1)$.

At equilibrium the y component of the total surface torque per unit surface area is given by Eq. (1), which becomes

$$\tau = -\left[\frac{\partial F_2}{\partial\alpha} + \frac{\partial F_2}{\partial\theta_1}\frac{\partial\theta_1}{\partial\alpha}\right] = -\frac{\partial F_2}{\partial\alpha}, \tag{10}$$

where we have exploited the equilibrium condition $\partial F_2/\partial\theta_1 = 0$ in Eq. (9) and the fact that a simultaneous rotation $\Delta\eta$ of both the plates is fully equivalent to a rotation $-\Delta\alpha$ of the magnetic field (see Fig. 1). Substituting F_2 given by Eq. (8) in Eq. (10), we find

$$\tau = \frac{2K}{\xi}\left[\sin(\theta_1-\alpha) - \frac{R}{2}\sin 2\theta_1 \cos(\theta_1-\alpha)\right]. \tag{11}$$

Now we calculate the surface torque by using Eq. (2) with $\mathbf{n}=(\sin\theta, 0, \cos\theta)$ and $\mathbf{H}=H(\sin\alpha, 0, \cos\alpha)$. Exploiting the symmetry of the director field with respect to $z=d/2$, we find

$$\tau = 2\int_0^{d/2} \chi a H^2 \sin(\theta-\alpha)\cos(\theta-\alpha)dz = \frac{2K}{\xi}\sin(\theta_1-\alpha), \tag{12}$$

where we have exploited Eq. (7) and the boundary values $\theta(0)=\theta_1$ and $\theta(d/2)=\alpha$. Note that a very unusual behavior is predicted by Eq. (11) if the magnetic field is applied parallel to the director at the surface ($\alpha=\theta_1$). In this case the surface torque in Eq. (12) correctly vanishes, as expected by simple physical arguments, while that in Eq. (11) becomes $\tau=(KR/\xi)\sin(2\theta_1)$. For $R\neq 0$, Eq. (12) differs substantially from Eq. (11) if $\theta_1 \neq 0$ or $\theta_1 \neq \pi/2$. Therefore the modified first order elastic theory is found to be inconsistent with the principles of mechanics. Note that this inconsistency also remains for small values of angles θ_1 and α.

We discuss now briefly the accuracy of the theoretical results in Eqs. (11) and (12). To obtain Eqs. (11) and (12) we have made two approximations: the isotropic elastic constants approximation ($K_{ii}=K$) and the semi-infinite sample approximation. The calculations above can be repeated for $K_{11} \neq K_{33}$ using the semi-infinite sample approximation. In this case, Eq. (11) becomes

$$\tau = \tau_0 = \frac{K_{33}}{\xi_3}\left\{\sin(\theta_1-\alpha)\sqrt{1+\eta\sin^2(\theta_1)} + \frac{1+\eta}{\sqrt{-\eta}}\sin(\alpha)\left[\operatorname{arcsinh}\left[\frac{\sqrt{-\eta}\cos(\alpha)}{\sqrt{1+\eta}}\right] - \operatorname{arcsinh}\left[\frac{\sqrt{-\eta}\cos(\theta_1)}{\sqrt{1+\eta}}\right]\right] + \frac{\cos(\alpha)}{\sqrt{-\eta}}\{\arcsin[\sqrt{-\eta}\sin(\theta_1)] - \arcsin[\sqrt{-\eta}\sin(\alpha)]\}\right\} - \frac{K_{13}\sin(2\theta_1)\cos(\theta_1-\alpha)}{\xi_3\sqrt{1+\eta\sin^2(\theta_1)}}, \tag{11'}$$

while Eq. (12) becomes

$$\tau = \tau_0 + \frac{K_{13}\sin(2\theta_1)\cos(\theta_1-\alpha)}{\xi_3\sqrt{1+\eta\sin^2(\theta_1)}}, \tag{12'}$$

where $\eta=(K_{11}-K_{33})/K_{33}$ is the relative anisotropy of the elastic constants and $\xi_3=(K_{33}/\chi_a)^{1/2}/H$ is the bend magnetic coherence length. To obtain Eqs. (11′) and (12′) we have assumed $-1<\eta<0$. Analogous expressions for the elastic torques can be obtained if $\eta>0$. We easily verify that Eqs. (11′) and (12′) coincide with Eqs. (11) and (12) in the limit $\eta\to 0$. Note that the same kind of inconsistency already found for Eqs. (11) and (12) is still present in Eqs. (11′) and (12′). Therefore this inconsistency is not due to the use of the isotropic constants approximation.

The second approximation we have used to obtain Eqs. (11) and (12) is the semi-infinite layer approximation, which allows us to obtain theoretical results in a closed analytical form. In order to check the accuracy of our approximate solutions, we have performed a high precision numerical integration of the exact Euler-Lagrange equation (6) to obtain the director field and we have found Eqs. (11) and (12) represent very accurate approximations to the "exact" results (see Appendix A). For instance, we find that the above relative difference between exact and approximate torques is much smaller than 10^{-6} for $d/\xi=30$ and goes to zero as well as $\exp(-d/2\xi)$ for increasing values of the ratio d/ξ. Therefore our theoretical results in Eqs. (11) and (12) can be considered as virtually exact theoretical results for large values of d/ξ. Finally we emphasize that Eqs. (11) and (12) are obtained without making use of any specific expression of the surface anchoring potential.

From the discussion above we infer that the inconsistency between Eqs. (11) and (12) [or between Eqs. (11′) and (12′)] cannot be interpreted as due to approximations but represents a basic inconsistency of the modified first-order theory. We recall that the modified first-order theory is based only on the assumption that the director field is continuous everywhere in the NLC layer. Therefore our theoretical test shows this assumption to be incorrect and thus we can infer that a subsurface director discontinuity at the interfaces must always occur if $K_{13}\neq 0$ [4–6].

B. The second-order elastic torque

We now calculate the surface torque by using the second-order elastic theory. A general analysis of this problem by means of the second-order theory is practically impossible since the expression of the second-order free energy density contains 35 new elastic constants that make the mathematical problem practically impossible to solve [7]. For this reason we restrict our attention here to the special case of small values of the angle θ,β_0 and $\alpha(\theta\ll 1,\beta_0\ll 1$, and $\alpha\ll 1)$ where only one second-order bulk elastic constant K^* plays an important role [7,8,21]. Under these assumptions, the surface anchoring potential becomes

$$W(\theta_s)=\frac{W}{2}(\theta_s-\beta_0)^2=\frac{K}{2L_{\rm ext}}(\theta_s-\beta_0)^2\ , \tag{13}$$

where W is the anchoring energy coefficient and $L_{\rm ext}=K/W$ is the extrapolation length [16]. The second-order free energy per unit surface area is [7]

$$F=F_2+F_4=\tfrac{1}{2}K\left\{\int_0^d\left[\delta^2(\theta'')^2+(\theta')^2-\frac{1}{\xi^2}\left[1-\frac{(\theta-\alpha)^2}{2}\right]\right]dz\right\}+\frac{K}{2}\left[\frac{(\theta_1-\beta_0)^2}{L_{\rm ext}}+\frac{(\theta_2-\beta_0)^2}{L_{\rm ext}}-2R(\theta_2\theta_2'-\theta_1\theta_1')\right]\ , \tag{14}$$

where F_2 and F_4 are the first-order and second-order free energies per unit surface area, respectively, and $\delta=(K^*/K)^{1/2}$ is a characteristic length of the order of typical molecular dimensions (≈ 20 Å), where K^* is the second-order elastic constant. Minimization of Eq. (12) with respect to small variations of $\theta(z)$ gives the following Euler-Lagrange equations for the director field in the bulk:

$$\delta^2\theta^{\rm IV}-\theta''+\frac{\theta-\alpha}{\xi^2}=0\ , \tag{15}$$

where the superscript IV denotes the fourth derivative with respect to z. The general solution of Eq. (15) in the semispace $0<z<d/2$ [disregarding very small contributions proportional to $\exp(-\lambda_1 d/2)$ and to $\exp(\lambda_2 d/2)$], is given by

$$\theta(z)=Ae^{-\lambda_1 z}+Be^{-\lambda_2 z}+\alpha\ , \tag{16}$$

where

$$\lambda_1=\left[\frac{1-(1-4\delta^2/\xi^2)^{1/2}}{2\delta^2}\right]^{1/2}\approx\frac{1}{\xi}$$
$$\lambda_2=\left[\frac{1+(1-4\delta^2/\xi^2)^{1/2}}{2\delta^2}\right]^{1/2}\approx\frac{1}{\delta} \tag{17}$$

with $\lambda_2\gg\lambda_1$. The A and B coefficients must solve the two boundary conditions [8]

$$\delta^2\theta_1'''-(1-R)\theta_1'+\frac{(\theta_1-\beta_0)}{L_{\rm ext}}=0 \tag{18}$$

and

$$\delta^2\theta_1'''-R\theta_1=0\ . \tag{19}$$

The total free energy per unit surface area can be obtained by substituting the director angle $\theta(z)$ given by Eq. (16) in Eq. (14) and by exploiting the symmetry of the director field with respect to the center $z=d/2$ of the nematic layer. After some straightforward calculations [disregarding very small contributions proportional to $\exp(-\lambda_1 d/2)$ and to $\exp(\lambda_2 d/2)$], we find

$$F=F_2+F_4=K\left[\lambda_1A^2+\lambda_2B^2+2\varphi AB+\frac{1}{L_{\rm ext}}(A+B+\alpha-\beta_0)^2-2R(A+B+\alpha)(\lambda_1A+\lambda_2B)-\frac{d}{2\xi^2}\right]\ , \tag{20}$$

where coefficient φ, exploiting the secular equation for λ_1 and λ_2 $(\delta^2\lambda^4-\lambda^2+1/\xi^2=0)$, can be written in the form

$$\varphi=-\delta^2(\lambda_1^3+\lambda_2^3)+(\lambda_1+\lambda_2)+\delta^2\lambda_1\lambda_2(\lambda_1+\lambda_2)\ . \tag{21}$$

At equilibrium the total external torque per unit surface area is

$$\tau=-\left[\frac{\partial F}{\partial\alpha}+\frac{\partial F}{\partial A}\frac{\partial A}{\partial\alpha}+\frac{\partial F}{\partial B}\frac{\partial B}{\partial\alpha}\right]=-\frac{\partial F}{\partial\alpha}, \quad (22)$$

where we have exploited the equilibrium conditions $\partial F/\partial A=\partial F/\partial B=0$. We can easily show, after straightforward but tedious calculations, that these equilibrium conditions are totally equivalent to the boundary conditions (18) and (19). By substituting (20) in (22), we obtain

$$\tau=2K\left[R(\lambda_1 A+\lambda_2 B)-\frac{1}{L_{\rm ext}}(A+B+\alpha-\beta_0)\right]. \quad (23)$$

The parameter $(A+B+\alpha-\beta_0)/L_{\rm ext}$ can be obtained from Eqs. (18) and (19) in terms of R, A, B, λ_1, and λ_2. Substituting this parameter in Eq. (23) and exploiting the equalities $-\delta^2\lambda_1^4+\lambda_1^2=1/\xi^2$ and $-\delta^2\lambda_2^4+\lambda_2^2=1/\xi^2$, we obtain, finally,

$$\tau=\frac{2K}{\xi^2}\left[\frac{A}{\lambda_1}+\frac{B}{\lambda_2}\right]. \quad (24)$$

Note that, since $\lambda_1\approx 1/\xi \ll \lambda_2\approx 1/\delta$, τ is virtually coincident with the surface torque $\tau=2KA/\xi$ predicted by the standard Frank elastic theory (with $K_{13}=0$). By using the alternative equation [Eq. (2)] for calculating surface torque, we find

$$\tau=2\int_0^{d/2}\chi_a H^2(\theta-\alpha)dz=\frac{2K}{\xi^2}\left[\frac{A}{\lambda_1}+\frac{B}{\lambda_2}\right], \quad (25)$$

where we have disregarded contributions proportional to $\exp(-\lambda_1 d/2)$ and to $\exp(\lambda_2 d/2)$. Equation (25) is coincident with Eq. (24). Therefore the second-order elastic theory is consistent with the principles of mechanics.

We wish to emphasize that this theoretical test does not demonstrate that the second-order elastic model is correct but only that its predictions are compatible with the general laws of mechanics. In particular, as discussed in the Introduction of this paper, we can expect that higher-order elastic contributions can play an important role in the subsurface distorted layer. In the further sections we will investigate this point in detail by making a systematic expansion of the elastic free-energy density at any order n.

III. FIRST- AND SECOND-ORDER ELASTIC THEORIES

To make the following theoretical analysis clearer, in this section we summarize briefly the main aspects of the procedure developed by Barbero, Sparavigna, and Strigazzi [7] for obtaining higher-order elastic contributions and we discuss the main predictions of the first-order and second-order elastic theories in the case of a tilted nematic layer. A NLC system in a similar geometry has already been investigated in Ref. [22] for strong anchoring boundary conditions.

A. Expansion of the free-energy density

The local free-energy density can be expressed as a function of the deformation sources $n_{i,j}$, $n_{i,jk}$, and $n_{i,jkl}$ as $F=F(n_{i,j};n_{i,jk};n_{i,jkl},\dots)$. The virtual variation of the free-energy density is written in the general form

$$dF=\lambda_{i,j}\delta n_{i,j}+\mu_{ikj}\delta n_{i,jk}+\beta_{ijkl}\delta n_{i,jkl}+\cdots, \quad (26)$$

where $n_{i,j}$ denote the first derivatives of the i component of the director with respect to $x_j, n_{i,jk}$ the second derivatives with respect to x_j and x_k, and so on. λ_{ij}, μ_{ijk}, and β_{ijkl} are tensor fields which can be expressed as suitable power expansions of $n_{i,j}$, $n_{i,jk}$, and $n_{i,jkl}$. According to the point of view put forward in Ref. [7] at the lowest order (first-order theory) the only deformation source which must be retained is $n_{i,j}$, at the second order (second-order theory) both $n_{i,j}$ and $n_{i,jk}$ must be retained, and so on. The main advantage of this expansion procedure is that the free-energy density is bounded from below at any order n of expansion and thus the mathematical problem is well posed at any order. In particular, the first-order free-energy density F is reduced to the standard Frank elastic expression which does not contain the surfacelike elastic contribution K_{13}. Indeed, this contribution depends on the second derivatives $n_{i,jk}$ and thus within the present theoretical formalism, it must be considered as a second-order contribution. More details on this and other important aspects of the expansion procedure can be found in [7]. At the second order both the deformation sources n_{ij} and $n_{i,jk}$ must be introduced, and the second-order surfacelike elastic constant K_{13} appears together with other second-order elastic contributions that depend on square powers of $n_{i,jk}$ and make the second-order free-energy functional bounded from below. The same kind of phenomenology occurs at any order n of expansion. By exploiting the symmetry properties of NLC's, Barbero, Sparavigna, and Strigazzi were able to find a general expression of the second-order free-energy density where a great number (35) of new second-order elastic constants occur, which make it practically impossible to find the general expression of the bulk director distortions. The problem can be greatly simplified if the amplitude of the elastic distortion is very small, such as, for instance, close to a distortion threshold, and the director lies everywhere in the same plane (planar distortions). In this case, all terms of the kind $n_{i,j}n_{k,l}n_{m,pq}$ and $n_{i,j}n_{k,l}n_{m,p}n_{q,r}$ can be disregarded with respect to $n_{i,jk}n_{l,mp}$ and thus one can easily show that the second-order new elastic constants are reduced to only two, the surfacelike elastic constant K_{13} and the bulk elastic constant K^* [7–9].

We consider the same geometry of Fig. 1 with the director which lies everywhere in the x-z plane (planar deformation) and can be written in the form $\mathbf{n}=(\sin\theta,0,\cos\theta)$ with $\theta=\theta(z)$. Furthermore, we make the simplifying assumption of small angles θ_1, β_0, and α. Under these conditions the anchoring energy is given by Eq. (13) and linear differential equations for the director angle $\theta(z)$ are obtained at any order n of expansion. These equations admit exact analytical solutions. However, in the following sections, we will use the semi-infinite layer approximation ($d/\xi \gg 1$) in order to simplify the theoretical expressions and to make clearer the theoretical analysis. This means that small contributions of the kind $\exp(-d/2\xi)$ are disregarded in our theoretical analysis. We emphasize, however, that our theoretical conclusions are not affected by this simplification, which only simplifies the form of the analytical expressions.

B. Predictions of the first-order elastic theory

Under previous assumptions, the first-order elastic free energy per unit surface area of Ref. [7] coincides with the Frank elastic free energy:

$$F_2=\frac{1}{2}\int_0^d\left[K\theta'^2-\chi_a H^2\left[1-\frac{(\theta-\alpha)^2}{2}\right]\right]dz+\frac{1}{2}W(\theta_1-\beta_0)^2+\frac{1}{2}W(\theta_2-\beta_0)^2 . \quad (27)$$

The Euler-Lagrange equation for the director field is

$$\theta''-\frac{(\theta-\alpha)}{\xi^2}=0 , \quad (28)$$

while the boundary condition at the lower interface $z=0$ is

$$\theta_1'+\frac{1}{L_{\rm ext}}(\theta_1-\beta_0)=0 . \quad (29)$$

The solution of Eqs. (28) and (29) in the region $0\le z\le d/2$ is

$$\theta(z)=\alpha+\frac{\beta_0-\alpha}{1+L_{\rm ext}/\xi}\exp\left[-\frac{z}{\xi}\right] . \quad (30)$$

This means that the surface director angle is

$$\theta_1=\alpha+\frac{\beta_0-\alpha}{1+L_{\rm ext}/\xi} . \quad (31)$$

C. Predictions of the second-order elastic theory

At the second order, the deformation sources are θ' and θ'' and, for $\theta\ll 1$, the bulk elastic free-energy density becomes [7,9]

$$F=\frac{1}{2}K(\theta')^2+\frac{1}{2}K^*(\theta'')^2+K_{13}(\theta\theta')' . \quad (32)$$

The Euler-Lagrange equation for the director angle is

$$\delta^2\theta^{\rm IV}-\theta''+\frac{\theta-\alpha}{\xi^2}=0 , \quad (33)$$

while the boundary conditions at the lower plate ($z=0$) are given by Eqs. (18) and (19). The solution of Eq. (33) in the semispace $0<z<d/2$ is given by

$$\theta(z)=Ae^{-\lambda_1 z}+Be^{-\lambda_2 z}+\alpha , \quad (34)$$

where $\lambda_1\approx 1/\xi$ and $\lambda_2\approx 1/\delta\gg\lambda_1$ are given in Eqs. (17). Coefficient A in Eq. (34) is the amplitude of the standard macroscopic slow solution [see Eq. (30)], while coefficient B is the amplitude of the short-range distortion due to the second-order elastic contributions. Coefficients A and B can be obtained by substituting Eq. (34) in the boundary conditions (18) and (19), which become

$$\left[a+\frac{1-R}{\xi}+\frac{1}{L_{\rm ext}}\right]A+cB=\frac{\beta_0-\alpha}{L_{\rm ext}} \quad (35)$$

and

$$[b+R]A+dB=-R\alpha , \quad (36)$$

where

$$a=-\frac{\delta^2}{\xi^3}\ll\frac{1}{\xi} , \quad b=-\frac{\delta^2}{\xi^2}\ll 1 , \quad (37)$$

$$c=\left[-\delta^2\lambda_2^3+(1-R)\lambda_2+\frac{1}{L_{\rm ext}}\right]\approx\left[-\frac{R}{\delta}+\frac{1}{L_{\rm ext}}\right] , \quad (38)$$

and

$$d=-(\delta^2\lambda_2^2-R)\approx-(1-R) . \quad (39)$$

Note that, due to the large separation of scale lengths ($\xi\gg\delta$), the coefficients a and b can be set to zero in Eqs. (35) and (36). Therefore Eqs. (35) and (36) become

$$\left[+\frac{1-R}{\xi}+\frac{1}{L_{\rm ext}}\right]A+cB=\frac{\beta_0-\alpha}{L_{\rm ext}} , \quad (40)$$

$$RA+dB=-R\alpha . \quad (41)$$

The solution of Eqs. (40) and (41) is

$$A=\frac{\beta_0^*-\alpha}{1+L_{\rm eff}/\xi} \quad (42)$$

and

$$B=\frac{R[(L_{\rm eff}\alpha/\xi)+\beta_0^*]}{(1-R)(1+L_{\rm eff}/\xi)} , \quad (43)$$

where we have defined the "effective extrapolation length" $L_{\rm eff}$ and the "effective easy angle" β_0^* by

$$\frac{1}{L_{\rm eff}}=\frac{1}{1-R}\left[\frac{1}{L_{\rm ext}}-\frac{c}{d}R\right] \quad (44)$$

and

$$\beta_0^*=\frac{\beta_0 L_{\rm eff}}{(1-R)L_{\rm ext}} . \quad (45)$$

By substituting in Eq. (44) the values of c and d given by Eqs. (38) and (39), we find

$$\frac{1}{L_{\rm eff}}=\frac{1}{(1-R)^2}\left[\frac{1}{L_{\rm ext}}-\frac{R^2}{\delta}\right] . \quad (44')$$

We must emphasize that the short-range director distortion of amplitude B, predicted by Eq. (34), occurs on the molecular scale length δ ($\delta\approx 20$Å) which is hardly accessible to standard experimental methods. In particular, standard optical methods are not very sensitive to director distortions which occur on a much smaller length scale than the optical wavelength λ($\lambda\approx 5000$Å$\gg\delta$). Therefore, from the macroscopic point of view, the bulk director distortion is indistinguishable from the long-range distortion $\theta(z)=A\exp(-z/\xi)+\alpha$, which is just the same kind as that predicted by the first-order theory [see Eq. (30)]. In particular, the macroscopic surface director angle, which is defined as the limit for $z \to 0$ of the macroscopic bulk director distortion, is then given by

$$\theta_1 = A + \alpha = \alpha + \frac{\beta_0^* - \alpha}{1 + L_{\rm eff}/\xi} . \quad (46)$$

By comparing Eq. (46) with Eq. (31), obtained in the case of the first-order elastic theory, we infer that the first-order elastic theory correctly describes the macroscopic behavior of the NLC layer if the easy director angle β_0 is substituted by the effective easy angle β_0^* and the extrapolation length $L_{\rm ext}$ is replaced by the effective extrapolation length $L_{\rm eff}$. Therefore the only macroscopic effect of the second-order surfacelike and bulk elastic constants is an apparent variation of the easy tilt angle and of the anchoring energy coefficient. Note that this interpretation of the theoretical results is also in agreement with the Gibbs thermodynamic approach, according to which the free energy per unit surface area can be expressed as the sum of a bulk contribution and a surface contribution that accounts for the modified molecular interactions close to the interface [16,23]. According to this point of view, the greatly distorted interfacial layer behaves effectively as a new source of excess free energy, which renormalizes the ordinary surface tension of the NLC interface. Note that B_0^* corresponds effectively to the experimental value of the surface easy director orientation, which is measured by means of standard optical or dielectric methods [16–18], since these methods are practically insensitive to distortions with a much smaller characteristic length that the optical wavelength.

The above discussion suggests that, as far as planar director distortions are concerned, one can correctly investigate the macroscopic director distortions in a NLC by using the Frank first-order elastic theory (with $K_{13} - 0$) and be defining an effective anchoring energy $W_{\rm eff}$ which implicitly accounts for surfacelike and second-order elastic contributions. This is very close to the point of view put forward in Ref. [21].

IV. PREDICTIONS OF HIGHER-ORDER ELASTIC THEORIES

A. Third-order elastic theory

The theoretical procedure described above gives a very interesting interpretation of the anchoring in NLC's and provides strong support for the current theoretical and experimental procedure of disregarding the surfacelike elastic constant K_{13} in the expression for the free-energy density. However, the theoretical results above have been obtained by disregarding elastic contributions of order higher than the second order. In this section we shall analyze the case where the third-order deformation source $n_{i,jkl}$ is taken into account. By using the same theoretical procedure as in Ref. [7], we can show (see Appendix B) that the only important new contributions which are allowed by the symmetry properties of NLC's and which are of the second order in the amplitudes of the distortion sources are two elastic contributions proportional to $\theta'\theta'''$ and $(\theta''')^2$. The first elastic term can be decomposed into the surfacelike contribution $(\theta'\theta'')'$ and the bulk contribution $(\theta'')^2$ which only renormalizes the second-order elastic constant K^* in Eq. (32). The Euler-Lagrange equation for the third order distortion is then

$$-\delta_2^4\theta^{\rm VI} + \delta_1^2\theta^{\rm IV} - \theta'' + \frac{\theta - \alpha}{\xi^2} = 0 , \quad (47)$$

where δ_1 and δ_2 are two characteristic lengths of the order of molecular dimensions. Note that δ_1 does not coincide with δ given by the second-order theory, since third-order terms renormalize this coefficient. The third-order boundary conditions which must be satisfied at the lower surface $z = 0$ are

$$-\delta_2^4\theta_1^V + \delta_1^2\theta_1''' - (1-R)\theta_1' + \frac{1}{L_{\rm ext}}(\theta_1 - \beta_0) = 0 , \quad (48)$$

$$-\delta_2^4\theta_1^{\rm IV} + (\delta_1^2 + h^2)\theta_1'' - R\theta_1 = 0 , \quad (49)$$

$$-\delta_2^4\theta_1''' + h^2\theta_1' = 0 , \quad (50)$$

where h is a new third-order parameter of the order of a typical molecular dimension. Note that the free-energy functional is also bounded from below. Indeed, the bulk Euler-Lagrange equation is of the sixth order and the general solution depends on six arbitrary coefficients that can be obtained by solving the six boundary equations (three at the lower interface and three at the upper interface). Therefore in this case, too, the problem of finding the director field is mathematically well posed. This important point is always satisfied at any order if the expansion procedure in Ref. [7] is used. Depending on the values of δ_1 and δ_2 there are two different possible cases.

(a) $\Delta = \delta_1^4 - 4\delta_2^4 > 0$. In this case, the general solution of Eq. (47) in the region $0 < z < d/2$ for $\xi \ll d/2$ and $\delta_1, \delta_2 \ll \xi$ is

$$\theta(z) = \alpha + A \exp\left[-\frac{z}{\xi}\right] + B \exp(-\lambda_1 z) + C \exp(-\lambda_2 z) , \quad (51)$$

where λ_1 and λ_2 are of the order of the inverse of a molecular characteristic length and are given by

$$\lambda_{1,2} = \sqrt{(\delta_2^2 \pm \sqrt{\Delta})/2\delta_1^4} . \quad (52)$$

(b) $\Delta = \delta_1^4 - 4\delta_2^4 < 0$. In this case the general solution for $\xi \ll d/2$ and $\delta_1, \delta_2 \ll \xi$ is

$$\theta(z) = \alpha + A \exp\left[-\frac{z}{\xi}\right] + B \exp(-kz)\cos(\omega z) + C \exp(-kz)\sin(\omega z) , \quad (53)$$

where

$$k = {\rm Re}\left[\sqrt{(\delta_2^2 + \sqrt{\Delta})/2\delta_1^4}\right] , \quad \omega = {\rm Im}\left[\sqrt{(\delta_2^2 + \sqrt{\Delta})/2\delta_1^4}\right] , \quad (54)$$

and where $Re(Z)$ and ${\rm Im}(Z)$ denote the real and the imaginary part of the complex number Z, respectively.

The unknown coefficients A, B, and C can be obtained by substituting Eq. (51) [or Eq. (53)] in the boundary conditions (48)–(50). In both cases we find a linear system of the kind

$$\left[a_{11}+\frac{1-R}{\xi}+\frac{1}{L_{\text{ext}}}\right]A+a_{12}B+a_{13}C=\frac{\beta_0-\alpha}{L_{\text{ext}}}\ , \tag{55}$$

$$[a_{21}+R]A+a_{22}B+a_{23}C=-R\alpha\ , \tag{56}$$

$$a_{31}A+a_{32}B+a_{33}C=0\ , \tag{57}$$

where the a_{ij} coefficients depend on ξ and on higher-order constants δ_1, δ_2, and h. We can easily show (see Appendix C) that, due to the large separation of length scales between the short-range and long-range distortions, a_{11}, a_{21}, and a_{31} are negligible, and thus the linear system becomes

$$\left[\frac{1-R}{\xi}+\frac{1}{L_{\text{ext}}}\right]A+a_{12}B+a_{13}C=\frac{\beta_0-\alpha}{L_{\text{ext}}}\ , \tag{58}$$

$$RA+a_{22}B+a_{23}C=-R\alpha\ , \tag{59}$$

$$a_{32}B+a_{33}C=0\ . \tag{60}$$

From Eq. (60) we obtain directly $C=-(a_{32}B)/a_{33}$, which can be substituted in Eqs. (58) and (59) to give

$$\left[\frac{1-R}{\xi}\frac{1}{L_{\text{ext}}}\right]A+cB=\frac{\beta_0-\alpha}{L_{\text{ext}}}\ , \tag{61}$$

$$RA+dB=-R\alpha\ , \tag{62}$$

where

$$c=a_{12}-\frac{a_{13}a_{32}}{a_{33}}\ \text{and}\ d=a_{22}-\frac{a_{23}a_{32}}{a_{33}}\ . \tag{63}$$

Equations (61) and (62) are formally identical to Eqs. (40) and (41). Therefore their solution is still given by Eqs. (42)–(45); this means that in this case also, the macroscopic behavior of the system is fully equivalent to that predicted by the linear elastic theory if the extrapolation length L_{ext} and the easy director angle β_0 are substituted by the effective values given by Eqs. (44) and (45) with c and d given by Eqs. (63). Note that the values of c and d predicted by the third order theory can differ greatly from those which were predicted by the second-order theory since they also depend on the two new third-order elastic constants (see Appendix C). Therefore the second-order expression for L_{eff} [Eq. (44′)] is no longer valid.

B. Higher-order elastic theories

Analogous results can be obtained if we consider the fourth-order distortion source θ^{IV}. In this case, the bulk director distortion is the superposition of the usual long-range distortion of amplitude A with characteristic length ξ and three short-range distortions of amplitudes B, C, and D which must satisfy four boundary conditions at the lower interface. The coefficients A, B, and C, and D are obtained by solving a linear system of four equations of the kind

$$\left[a_{11}+\frac{1-R}{\xi}+\frac{1}{L_{\text{ext}}}\right]A+a_{12}B+a_{13}C+a_{14}D=\frac{\beta_0-\alpha}{L_{\text{ext}}}\ , \tag{64}$$

$$[a_{21}+R]A+a_{22}B+a_{23}C+a_{24}D=-R\alpha\ , \tag{65}$$

$$a_{31}A+a_{32}B+a_{33}C+a_{34}D=0\ , \tag{66}$$

$$a_{41}A+a_{42}B+a_{43}C+a_{44}D=-a_{41}\alpha\ . \tag{67}$$

We can show that the coefficients a_{11}, a_{21}, and a_{31} which multiply the A amplitude and come from the higher-order elastic constants are completely negligible, and thus they can be set to zero. By solving the two equations (66) and (67) with $a_{31}=0$ we find $C=\alpha_1(A+\alpha)+\alpha_2 B$ and $D=\alpha_3(A+\alpha)+\alpha_4 B$, where α_1, α_2, α_3, and α_4 are suitable functions of the coefficients $a_{3,i}$ and $a_{4,i}$ with $i=1,\ldots,4$. By substituting these expressions in the two equations (64) and (65), the linear system of equations (64)–(67) is reduced to the linear system of two equations in the unknown coefficients A and B

$$\left[\beta_1+\frac{1-R}{\xi}+\frac{1}{L_{\text{ext}}}\right]A+cB=\frac{\beta_0-\alpha}{L_{\text{ext}}}-\beta_1\alpha\ , \tag{68}$$

$$(\beta_2+R)A+dB=-R\alpha-\beta_2\alpha\ , \tag{69}$$

where β_1, β_2, c, and d are coefficients that depend on all elastic constants. The dimension of β_1 and c is the inverse of a length, while β_2 and d are adimensional coefficients. A very important peculiar characteristic of this system is that the two coefficients β_1 and β_2 which multiply A on the left-hand side of Eqs. (68) and (69) are equal and opposite to the new coefficients which multiply α on the right-hand side of Eqs. (68) and (69). We can easily show that, due to this special feature of the linear system, the general solution for the amplitude A of the macroscopic director distortion has the same general form as in Eq. (42) with β_0^* still given by Eq. (45), but with a renormalized expression for the effective extrapolation length, which becomes

$$\frac{1}{L_{\text{eff}}}=\frac{1}{1-R}\left[\frac{1}{L_{\text{ext}}}-\left[R\frac{c}{d}+\beta_2\frac{c}{d}-\beta_1\right]\right]\ . \tag{70}$$

Therefore amplitude A of the macroscopic bulk distortion is still well represented by the first order elastic theory with suitably renormalized values of the extrapolation length and of the easy tilt angle. It is important to emphasize, however, that both these renormalized parameters are dependent, in principle, on all elastic constants. As far as the amplitudes B, C, and D of the short-range distortions are concerned, we note that their theoretical expressions are very complex and depend explicitly on the "macroscopic" parameters L_{eff} and β_0^* but also on all higher-order elastic constants.

It can be shown that, due to the large separation of scale lengths, the same kind of behavior occurs at any order. In particular, at any expansion order n, we always obtain a system of two linear equations with the general structure of Eqs. (68) nd (69) with different expressions for the coefficients c, β_1, β_2, and d. If we use c_n, β_{1n}, β_{2n}, and d_n to denote the values of the coefficients c, β_1, β_2, and d which are found at the nth order, we can expect these successions to be convergent to well defined values c, β_1, β_2, and d for $n \to \infty$. If this is the case, we can conclude that the macroscopic behavior of the system is fully equivalent to that of a nematic layer with the easy angle β_0^* and the extrapolation length L_{eff} given by Eqs. (45) and (70), respectively.

V. THEORETICAL DISCUSSION AND CONCLUSIONS

This paper is devoted to the analysis of two elastic models which have recently been proposed in the literature to bypass the mathematical problems related to the K_{13} surfacelike elastic constant: the modified first-order theory and the second-order theory. In the first part of this paper we show that the modified first-order theory is inconsistent with mechanics. The second part of this paper is devoted to analyzing the effects due to higher-order elastic constants that are disregarded by the second-order elastic theory.

It is important to emphasize that our theoretical results are a direct consequence of the special expansion procedure proposed in Ref. [7], where the order of the free-energy expansion is related to the order of the deformation source. According to this procedure, the K_{13} surfacelike contribution must be considered as a second-order contribution since it comes from the second-order deformation source θ'', although it is formally of the same order of magnitude as $(\theta')^2$. Therefore, the first-order elastic free energy does not contain K_{13}, while this contribution is present in the second-order elastic energy together with a new stabilizing contribution $(\theta'')^2$. In both these cases, the free-energy functional is bounded from below. Note that, if the standard method of grouping the elastic contributions depending on their order of magnitude were used instead of the previously mentioned method, the K_{13} contribution should be added to the first order Frank elastic free energy since it is apparently of the same order of magnitude. In this case, the Nehring-Saupe expression for the free energy is obtained [2] and the free-energy functional becomes unbounded from below. The same behavior occurs at any expansion order. For instance, the third-order surfacelike elastic contribution $(\theta'\theta'')'$ which comes from the deformation source θ''' is of the same order as $(\theta'')^2$, and thus it should be added to the second-order expression of the free-energy, rendering the free energy functional unbounded from below. On the contrary, the expansion procedure described by Barbero, Sparavigna, and Strigazzi [7] produces a bounded free energy functional at any order of expansion.

Our main theoretical results are restricted to the special case of *planar director distortions* and can be summarized in the following main points.

(i) As far as macroscopic distortion is concerned, at any expansion order we find that the bulk director field is exactly the same as that obtained by using the Frank elastic free-energy density (with $K_{13}=0$) with a suitable effective anchoring energy coefficient and easy angle. In a subsequent paper [23] we will show that this conclusion is in complete agreement with the Gibbs theory of interfaces. These theoretical results are in a qualitative agreement with the predictions of the second-order theory. However, we wish to emphasize that the effective easy angle and the effective extrapolation length depend on all the elastic constants. Therefore the second-order expression for the effective extrapolation length [Eq. (44′)] is not accurate from the quantitative point of view.

(ii) At any expansion order, a strong subsurface distortion is found to occur close to the interface of a NLC with a tilted director orientation. Therefore the "macroscopic" surface director easy angle β_0^* can greatly differ from the actual surface easy angle β_0 if $\beta_0 \neq 0$ [see Eq. (45)]. Note that a strong subsurface distortion of this kind has been detected by using the very sensitive optical method of second harmonic generation [24]. This point, too, is in qualitative agreement with the predictions of the second-order elastic theory. However, the actual quantitative value of the surface director discontinuity $\Delta\theta=\beta_0-\beta_0^*$ can greatly differ from that predicted by the second-order theory. Indeed, $\Delta\theta$ is expected to be a very complex combination of all surface and bulk elastic coefficients. In particular, K_{13} does not play any special role with respect to all other higher order elastic constants since its contribution to the effective easy angle and to the effective anchoring energy coefficient is of the same order of magnitude as those of the other higher-order contributions. Therefore, in our opinion, the K_{13} elastic constant cannot be measured by making experiments with planar distorted NLC layers. We here emphasize that our theoretical results concern only the special case of planar director distortions. In the more general case of nonplanar distortions, we can show that the surfacelike elastic constant K_{13} produces new important macroscopic effects that make possible a direct experimental measurement of this constant [23].

(iii) The above theory has been developed by making the implicit assumption that the elastic constants do not depend on the distance z from the interface. This assumption is certainly correct if the distance z from the interface is much greater than the interaction range of intermolecular forces, but it is no longer correct in the opposite case. Therefore, close to the surface, all the elastic constants are expected to depend greatly on the distance z. Furthermore, the presence of the interface breaks the translation symmetry of the system, and thus new elastic constants, which were forbidden by the symmetry properties of NLC's can play an important role as far as interfacial behavior is concerned [21]. Some of these new contributions can favor the occurrence of a director distortion close to the interface and can greatly affect the actual form of the subsurface director distortion and of the anchoring energy coefficient. Some of these effects have been recently analyzed in Ref. [21] by using a first-order elastic expression and have been shown to be equivalent to a new anchoring source. Finally, the elastic constants also depend on the local value of the scalar order parameter S which is known to be very sensitive to the presence of the interface [25–28]. A spatial variation of S produces a spatial variation of the elastic constant and thus it makes a new important contribution to the anchoring energy as shown in Refs. [27] and [28].

(iv) The theoretical analysis in this paper was restricted to the very special case of small director angles. However, in our opinion, the main conclusions of this approach are still valid even in the more general case of arbitrary amplitudes of the distortions. In particular, we can expect the strong subsurface distortion to still be equivalent to a new anchoring contribution, since this result is a direct consequence of the large separation of lengths scales more than of the special form of the free-energy density [23]. However, if the condition $\Delta\theta \ll 1$ is not satisfied, many more elastic terms must be retained. These elastic terms are complex functions of $\sin\theta$ and $\cos\theta$ (see, for instance, Ref. [7]) and thus one can expect the elastic contribution to the anchoring energy functional to show a complex dependence on θ. This means that strong deviations of the anchoring energy function from the Rapini form $W(\theta)=W\sin^2\theta$ can be expected, in agreement with the experimental results 17–19. On the contrary, as far as azimuthal anchoring is concerned, surfacelike elastic constants do not make any contribution to the azimuthal anchoring function. Indeed, the azimuthal anchoring energy potential has recently been found to be in very close agreement with the simple Rapini expression [29,30].

From the macroscopic point of view, our theoretical analysis shows that the influence of the higher order elastic constants on the bulk director orientation in planar NLC layers can be entirely accounted for by defining a suitable phenomenological anchoring energy coefficient according to the "standard" theoretical approach. Therefore our theoretical analysis lends strong support to the usual theoretical and experimental procedure of using the Frank elastic free energy in place of the Nehring-Saupe free energy for studying the macroscopic behavior of planar NLC's.

According to higher order theories, the anchoring energy coefficient implicitly account for any subsurface anomaly. However, it is almost impossible to calculate this anchoring energy using an elastic theory since an infinite number of elastic constants plays an important role in the interfacial layer. In our opinion, the use of microscopic theoretical models of NLC interactions [30–36] could be more suitable in order to establish the relative influence of strong subsurface distortions on the anchoring properties of NLC's.

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APPENDIX A: THE SEMI-INFINITE SAMPLE APPROXIMATION

In this Appendix, we briefly analyze the accuracy of the semi-infinite sample approximation which has been extensively used in this paper to obtain simple analytical solutions. The exact director field in the NLC layer should be obtained by solving the exact Euler-Lagrange equation (6). Due to the symmetry of the NLC layer with respect to the center $z=d/2$ of the layer, we can solve Eq. (6) in the region $0\le z\le d/2$ with the boundary conditions $\theta(0)=\theta_1$ and $\theta'(d/2)=0$. The exact first integral of Eq. (6) in the region $0\le z\le d/2$ is

$$\varphi'=-\left[\frac{\sin^2(\varphi)}{\xi^2}-\frac{\sin^2(\varphi_0)}{\xi^2}\right]^{1/2}, \tag{A1}$$

where we have exploited the conditions $\theta'(d/2)=0$ and where $\varphi(z)=\theta(z)-\alpha$ and $\varphi_0=\theta(d/2)-\alpha$. Integration of Eq. (A1) gives

$$\int_{\varphi_1}^{\varphi(z)}\frac{d\varphi}{\sqrt{\sin^2(\varphi)-\sin^2(\varphi_0)}}=-\frac{z}{\xi}, \tag{A2}$$

where $\varphi_1=\theta_1-\alpha$. φ_0 can be obtained as a function of φ_1 by solving

$$\int_{\varphi_1}^{\varphi_0}\frac{d\varphi}{\sqrt{\sin^2(\varphi)-\sin^2(\varphi_0)}}=-\frac{d}{2\xi}. \tag{A3}$$

Equations (A2) and (A3) cannot be solved analytically. However, if $d\gg\xi$, the director field is nearly parallel to the magnetic field at the center $z=d/2$ of the NLC layer. Therefore a very accurate approximate expression for $\varphi(z)$ can be obtained by setting $\varphi_0=0$ in Eq. (A2). With this assumption, the solution of Eq. (A2) is

$$\tan\left[\frac{\varphi}{2}\right]=\tan\left[\frac{\varphi_1}{2}\right]\exp\left[-\frac{z}{\xi}\right]. \tag{A4}$$

Equation (A4) is known in the literature as the *semi infinite sample approximation.* In order to estimate the order of magnitude of the difference $\Delta\varphi$ between the exact solution of Eq. (A2) and the approximate value in Eq. (A4), we consider the special case where $\theta\ll 1$ and $\alpha\ll 1$. In this case Eq. (6) is reduced to Eq. (28), whose exact solution (symmetric with respect to $z=d/s$) is

$$\varphi(z)=A\{\exp(-z/\xi)+\exp[(z-d)/\xi]\}, \tag{A5}$$

where $A=\varphi_1/[1+exp(-d/\xi)]$. For $\varphi_1\ll 1$ and $\varphi\ll 1$, the semi-infinite sample solution in the region $0\le z\le d/2$ [see Eq. (A4)] becomes $\varphi(z)=\varphi_1\exp(-z/\xi)$. Therefore the difference $\Delta\varphi$ between the exact and the approximate solution is $\Delta\varphi\approx\varphi_1\exp[(z-d)/\xi]$. $\Delta\varphi$ reaches its maximum value $\Delta\varphi_{max}=\varphi_1\exp(-d/2\xi)$ at the center $z=d/2$ of the NLC layer. By analogy with this simple case, in the more general case $\theta_1\approx 1$ and $\alpha\approx 1$, one can expect $\Delta\varphi_{max}$ to be

$$\Delta\varphi_{max}\le 2\tan(\varphi_1/2)\exp(-d/2\xi). \tag{A6}$$

In order to confirm the validity of Eq. (A6) we have performed a numerical integration of the exact Euler-Lagrange equation (6) by using a high precision numerical algorithm. Our numerical results and in good agreement with Eq. (A6). Therefore the semi-infinite sample approximation in Eq. (A4) is a very accurate approximation if $d\gg\xi$. Let us consider, for instance, a 5CB NLC layer of thickness $d=100$ μm in the presence of a 10 kG magnetic field. The magnetic coherence length is $\xi\approx 2$ μm and thus $\Delta\varphi_{max}/\varphi_1\approx 10^{-11}$.

APPENDIX B: HIGHER-ORDER EXPANSION

Third-order expression of the free-energy density

At the third order, the free-energy density must be expressed in terms of the deformation sources $n_{i,j}, n_{i,jk}, n_{i,jkl}$: $F=F(n_{i,j};n_{i,jk};n_{i,jkl})$. The virtual variation of the free-energy density can be written in the general form

$$dF=\lambda_{ij}\delta n_{i,j}+\mu_{ijk}\delta n_{i,jk}+\beta_{ijkl}\delta n_{i,jkl} \ , \tag{B1}$$

where $n_{i,j}$ denotes the first derivatives of the i component of the director with respect to x_j, $n_{i,jk}$ the second derivatives with respect to x_j and x_k, and so on. λ_{ij}, μ_{ijk}, and β_{ijkl} are tensor fields that can be expressed as suitable power expansions of $n_{i,j}$, $n_{i,jk}$, and $n_{i,jkl}$ up to the fifth, the fourth, and the third order, respectively. Here we restrict our attention to the special case of small amplitudes of the director distortions ($\theta \ll 1, \theta' \ll 1, \theta'' \ll 1, \theta''' \ll 1$). This means that only the contributions which are linear in the deformation sources must be retained in the expressions for λ_{ij}, μ_{ijk}, and β_{ijkl}. Furthermore, most of these contributions were already found in writing the second order expression [7]. Therefore the new contributions which must be considered are

$$\lambda_{ij}=a_{ijklmp}n_{k,lmp} \ , \tag{B2}$$

$$\mu_{ijk}=b_{ijklmpq}n_{l,mpq} \ , \tag{B3}$$

$$\beta_{ijkl}=c_{ijkl}+c_{ijklmp}n_{m,p}+c_{ijklmpq}n_{m,pq} + c_{ijklmpqr}n_{m,pqr} \ . \tag{B4}$$

The tensor fields a_{ijklmp}, $b_{ijklmpq}$, c_{ijkl}, c_{ijklmp}, $c_{ijklmpq}$, and $c_{ijklmpqr}$ can be expressed as a complete expansion on the basis $(n_i,\delta_{ij},\varepsilon_{ijk})$ where δ_{ij} is the Kronecker symmetric tensor and ε_{ijk} is the Levi-Civitá antisymmetric pseudotensor. This expansion procedure is known as the Rivlin rule [37]. Furthermore, the free-energy density must satisfy the symmetry properties of NLC's: invariance for any up-down or right-left transform. This symmetry property greatly limits the number of possible elastic contributions. Finally the differential dF must be exact, and thus the tensor fields in Eqs. (B2)–(B4) must satisfy the Maxwell thermodynamic relations. This means that the following equalities must be satisfied

$$a_{ijklmp}=c_{klmpij} \ ; \ \ b_{ijklmpq}=c_{mpqijkl} \ . \tag{B5}$$

By integrating Eq. (B1) and exploiting Eqs. (B5), we find that the new third order contribution to the free-energy density is

$$F_{\mathrm{III}}=a_{ijklmp}n_{k,lmp}n_{i,j}+b_{ijklmpq}n_{l,mpq}n_{i,jk} + c_{ijkl}n_{i,jkl}+\tfrac{1}{2}c_{ijklmpq}n_{m,pqr}n_{i,jkl} \ . \tag{B6}$$

A further great simplification is obtained if we consider planar deformations with the director field given by $\mathbf{n}=(\sin\theta,0,\cos\theta)$ and $\theta=\theta(z)\ll 1$. In these conditions, only director derivatives with respect to z (coordinate $i=3$) do not vanish. For $\theta \ll 1$, by disregarding contributions higher than the first order in the small amplitudes θ, θ', θ'', and θ''', we easily find

$$\mathbf{n}\approx(\theta,0,1) \ ; n_{i,3}\approx(\theta',0,0) \ ;$$
$$n_{i,33}\approx(\theta'',0,0) \ ; \ \ n_{i,333}\approx(\theta''',0,0) \ . \tag{B7}$$

This means that, in the general expansion of the tensor fields a_{ijklmp}, $b_{ijklmpq}$, c_{ijkl}, and $c_{ijklmpqr}$ on the basis $(n_i,\delta_{ij},\varepsilon_{ijk})$, the products of the kind $n_m n_{i,j}$, $n_m n_{i,jk}$, and $n_m n_{i,jkl}$ are negligible or zero if $m,j,k,l\neq 3$ and $i\neq 1$. By exploiting all these simplifying conditions together with the invariance for any up-down or right-left transform, we easily find that the first term on the right-hand side of Eq. (B6) gives a contribution of the kind $K_1^*\theta'\theta'''$, and the last term in Eq. (B6) gives $K_2^*(\theta''')^2/2$. The other two terms vanish due to the symmetry properties of the NLC. Note that the contribution $K_1^*\theta'\theta'''$ can be rewritten as the sum of the bulk and surface contributions $K_1^*(\theta'')^2$ and $K_1^*(\theta'\theta'')'$. The bulk contribution is of the same kind as the higher order elastic term in the expression for the second order elastic free-energy density, and thus it only renormalizes the elastic constant K^*.

Fourth- and higher-order expansion contributions.

By using the same general procedure we find that the new fourth-order terms in the expression of the free-energy density that are of second order in the deformation sources θ, θ', θ'', θ''', and θ^{IV} are $(\theta^{\mathrm{IV}})^2$; $\theta''\theta^{\mathrm{IV}},\theta\theta^{\mathrm{IV}}$. These expressions are suitable for a simple generalization to any expansion order. The possible new contributions which are allowed at the nth order of expansion can be expressed as the product of θ^n and θ^{n-2k} where $0\leq k \leq n/2$ and where n and $n-2k$ denote the order of the derivative.

APPENDIX C: THIRD-ORDER COEFFICIENTS

In this section we show that the third-order coefficients a_{11}, a_{21}, and a_{31} of Eqs. (55), (56), and (57) are negligible. Let us consider, for instance, case (a) of Sec. IV A, where the bulk solution for $\theta(z)$ is given by Eq. (51). By substituting Eq. (51) in the boundary conditions (48)–(50), we find the following values for coefficients a_{ij} ($i=1,\ldots,3$, $j=1,\ldots,3$) of system (55)–(57).

$$a_{11}=\frac{\delta_2^4}{\xi^5}-\frac{\delta_1^2}{\xi^3}\ll\frac{1}{\xi} \ ,$$
$$a_{1i}=\delta_2^4\lambda_i^5-\delta_1^2\lambda_i^3+(1-R)\lambda_i+\frac{1}{L_{\mathrm{ext}}} \quad \text{with } i=2,3 \ , \tag{C1}$$

$$a_{21}=-\frac{\delta_2^4}{\xi^4}+\frac{\delta_1^2+h^2}{\xi}\ll 1 \ ,$$
$$a_{2i}=-\delta_2^4\lambda_i^4+(\delta_1^2+h^2)\lambda_i^2-R \quad \text{with } i=2,3 \ , \tag{C2}$$

$$a_{31}=-\frac{\delta_2^4}{\xi^3}+\frac{h^2}{\xi}\ll\delta_2 \ ,$$
$$a_{3i}=-\delta_2^4\lambda_i^3+h^2\lambda_i \quad \text{with} i=2,3 \ . \tag{C3}$$

By exploiting the condition $\delta_1, \delta_2, h \ll \xi$, we find that a_{11} can be completely disregarded with respect to the contribution $s=(1-R)/\xi+1/L_{\mathrm{ext}}$ in Eq. (55), while a_{12} and a_{13} are of the same order of magnitude as s. Furthermore, $a_{21} \ll 1$, while a_{22} and a_{23} are of the order of unity. Finally $a_{31} \ll \delta_2$, while a_{32} and a_{33} are of the order of a characteristic molecular length. Similar considerations hold as far as case (b) in Sec. IV A is concerned.

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