

Splay-bend surface elastic constant of nematic liquid crystals: A solution of the Somoza-Tarazona paradox

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The Nehring-Saupe [J. Chem. Phys. **54**, 337 (1971); **56**, 5527 (1972)] elastic free energy of nematic liquid crystals (NLCs) contains the splay-bend elastic constant K_{13} , which affects only the elastic surface free energy. Several years ago, Somoza and Tarazona [Mol. Phys. **72**, 991 (1991)] showed that the value of K_{13} depends on the nonlocal to local mapping that is used to define the local elastic free energy. Then they concluded that the splay-bend constant is not a well-defined physical parameter. In the present paper we show that the Somoza-Tarazona result comes from an inconsistent treatment of the boundary effects. If all the boundary effects are correctly taken into account in an elastic approach, the elastic surface free energy contains an effective elastic constant K_{13}^{eff} that is mapping independent. K_{13}^{eff} is the sum of three different constants: the classical Nehring-Saupe bulk constant K_{13} and two specific interfacial constants K_1 and K_h . While each surface constant (K_{13} , K_1 , and K_h) depends on the kind of nonlocal to local mapping, the resulting surface constant $K_{13}^{\text{eff}} = K_{13} + K_1 + K_h$ is mapping independent. Using a simple molecular model of the intermolecular interactions, we obtain explicit expressions of K_{13}^{eff} in terms of the characteristic parameters of the intermolecular energy. In the final part of this paper we discuss the meaning and the physical consequences of the elastic surface free energy F_s . We show that F_s is a semimacroscopic parameter that provides an approximate elastic description of the interfacial layer. Furthermore, we point out that the elastic surface free energy should not be confused with the thermodynamic surface free energy that appears in a consistent continuum theory of NLCs. [S1063-651X(98)07606-5]

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I. INTRODUCTION

The macroscopic properties of nematic liquid crystals (NLCs) are described in terms of a unit vector field $\mathbf{n}(\mathbf{r})$, which is called the *director* and represents the local average molecular orientation of the long molecular axes [1]. In many important cases, $\mathbf{n}(\mathbf{r})$ is a smoothly and slowly varying function of \mathbf{r} with a characteristic macroscopic length L_{mac} , which is much greater than the typical range R_{int} of the interactions between the NLC molecules ($R_{\text{int}} \approx 100 \text{ \AA}$). In such a case, the total free energy is reduced to the elastic form

$$F = \int (f_e + f_{\text{ext}}) dV + \int f_s dS, \quad (1)$$

where dV and dS are bulk and surface infinitesimal elements and f_e is the Oseen-Frank elastic free-energy density [2,3]

$$f_e = f_0 + \frac{K_{11}}{2} (\nabla \cdot \mathbf{n})^2 + \frac{K_{22}}{2} (\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + \frac{K_{33}}{2} (\mathbf{n} \times \nabla \times \mathbf{n})^2 - (K_{22} + K_{24}) \nabla \cdot (\mathbf{n} \nabla \cdot \mathbf{n} + \mathbf{n} \times \nabla \times \mathbf{n}) + K_{13} \nabla \cdot (\mathbf{n} \nabla \cdot \mathbf{n}). \quad (2)$$

f_0 is a unessential constant contribution, K_{11} , K_{22} , and K_{33} are the splay, twist, and bend elastic constants, and K_{24} and K_{13} are the saddle-splay and splay-bend surface-like elastic constants. f_{ext} is the interaction free-energy density with external fields (magnetic or electric) and f_s is the excess of surface free-energy density. In the classical approach [1], f_s

is assumed to be a function of the orientation of the director at the surface, which is called the *anchoring energy*. Using the Gauss theorem, the last two terms in Eq. (2) can be transformed into the surface integral

$$F_s = \int dS [- (K_{22} + K_{24}) \mathbf{k} \cdot (\mathbf{n} \nabla \cdot \mathbf{n} + \mathbf{n} \times \nabla \times \mathbf{n}) + K_{13} \mathbf{k} \cdot (\mathbf{n} \nabla \cdot \mathbf{n})], \quad (3)$$

where \mathbf{k} denotes the outgoing surface normal. The K_{13} constant was introduced by Oseen, then eliminated by Frank, and finally reintroduced by Nehring and Saupe in 1972 on the basis of phenomenological and molecular arguments [4,5]. In principle, the equilibrium director field can be obtained minimizing the free energy in Eq. (1) with the standard variational method. This procedure leads to some Euler-Lagrange equations for the bulk director field and some boundary conditions. Oldano and Barbero [6,7] showed that the presence of the \mathbf{K}_{13} term in Eq. (2) leads to a paradoxical result: The free energy is unbounded from below and the variational approach leads to a ill-posed mathematical problem. Different solutions to this problem have been proposed in the literature [8–15]. Of course, no problem arises if $K_{13} = 0$. For this reason, some authors calculated directly the K_{13} elastic constant using specific microscopic molecular models [4,5,16,17]. The molecules were assumed to interact via a two-body energy $U(\hat{\mathbf{e}}, \hat{\mathbf{e}}', \mathbf{u})$, where $\hat{\mathbf{e}}$ and $\hat{\mathbf{e}}'$ denote the long molecular axes at the points \mathbf{r} and \mathbf{r}' in the NLC sample and $\mathbf{u} = \mathbf{r} - \mathbf{r}'$ is the intermolecular vector. In the simplest approach [5,16], which we will call the Nehring-Saupe molecular approach, one assumes perfect nematic order (order pa-

parameter $S=1$ [1]) and a uniform single-particle density. Then the free energy due to the interactions between nematic molecules becomes

$$F = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' g(\mathbf{n}, \mathbf{n}', \mathbf{u}) = \int d\mathbf{r} f(\mathbf{r}), \quad (4)$$

where the integrals are extended to the whole volume of the NLC

$$g(\mathbf{n}, \mathbf{n}', \mathbf{u}) = \rho^2 U(\mathbf{n}, \mathbf{n}', \mathbf{u}) \quad (5)$$

and

$$f(\mathbf{r}) = \frac{1}{2} \int d\mathbf{r}' g(\mathbf{n}, \mathbf{n}', \mathbf{u}). \quad (6)$$

ρ is the single-particle density and $f(\mathbf{r})$ is the free-energy density at the point \mathbf{r} in the NLC. \mathbf{n} and \mathbf{n}' are the director orientations at the points \mathbf{r} and \mathbf{r}' , i.e.,

$$\mathbf{n} = \mathbf{n}(\mathbf{r}), \quad \mathbf{n}' = \mathbf{n}(\mathbf{r}'). \quad (7)$$

$g(\mathbf{n}, \mathbf{n}', \mathbf{u})$ vanishes for $u \gg R_{\text{int}}$, where R_{int} is the characteristic interaction length of a few molecular lengths. For a director field that varies over a macroscopic characteristic length $L_{\text{mac}} \gg R_{\text{int}}$, $f(\mathbf{r})$ is well approximated [at the order $(R_{\text{int}}/L_{\text{mac}})^2$] by the elastic free-energy density

$$f_e(\mathbf{r}) = \frac{1}{2} \int d\mathbf{r}' g(\mathbf{n}, \mathbf{n}, \mathbf{u}) + \frac{1}{2} \int d\mathbf{r}' \left. \frac{\partial g(\mathbf{n}, \mathbf{n}', \mathbf{u})}{\partial n'_i} \right|_{\mathbf{n}'=\mathbf{n}} \delta n_i + \frac{1}{4} \int d\mathbf{r}' \left. \frac{\partial^2 g(\mathbf{n}, \mathbf{n}', \mathbf{u})}{\partial n'_i \partial n'_k} \right|_{\mathbf{n}'=\mathbf{n}} \delta n_i \delta n_k, \quad (8)$$

with

$$\delta n_i = n'_i - n_i \approx -\frac{\partial n_i}{\partial r_j} u_j + \frac{1}{2} \frac{\partial^2 n_i}{\partial r_j \partial r_s} u_j u_s. \quad (9)$$

Here n_i , u_i , and r_i are the i th components of vectors \mathbf{n} , \mathbf{u} , and \mathbf{r} , the symbol $\left. \frac{\partial}{\partial n'_i} \right|_{\mathbf{n}'=\mathbf{n}}$ denotes the derivative calculated at $\mathbf{n}' = \mathbf{n}$, and the repeated indices stand for a sum. Substitution of δn_i into Eq. (8) leads to an expression of the free-energy density in terms of the first and second director derivatives. If point \mathbf{r} is at a distance $d \gg R_{\text{int}}$ from the surface of the NLC, many terms in Eq. (8) become negligible and the bulk free-energy density in Eq. (2) is recovered [5,16] with the elastic constants that are given in terms of the intermolecular energy. For the typical interactions characterizing NLCs, the constant K_{13} is found to be different from zero [5,16]. The same conclusion has been reached using a more general theoretical approach based on the density-functional theory [17].

In the analysis above, the local free-energy density was obtained using the integration variables \mathbf{r} and \mathbf{r}' in Eq. (4). However, according to the general analysis in [18], this is not the unique way to obtain a local free-energy density from a nonlocal energy functional. In particular, Somoza and Tarazona [19] replaced variables \mathbf{r} and \mathbf{r}' with $\mathbf{R} = (\mathbf{r} + \mathbf{r}')/2$ and $\mathbf{u} = \mathbf{r} - \mathbf{r}'$ and obtained $F = \int d\mathbf{R} f(\mathbf{R})$. By expanding $f(\mathbf{R})$ in a power series of the director derivatives

calculated at point \mathbf{R} , they obtained a different expression of the bulk elastic free-energy density. The bulk elastic constants K_{11} , K_{22} , and K_{33} remain unchanged, but K_{13} becomes zero. Then they argued that the splay-bend constant K_{13} cannot be a well-defined physical parameter. The Somoza-Tarazona argument originated some debate in the literature [17,20].

In a recent paper [21], Faetti and Riccardi showed that the procedure used to obtain the surface elastic free energy F_s does not take correctly into account the boundary effects. Indeed, F_s in Eq. (3) was obtained by integration of the divergence terms in the bulk free-energy density f_e of Eq. (2). However, f_e differs greatly from the ‘‘true’’ elastic free-energy density $f_e(\mathbf{r})$ in a thin interfacial layer of thickness $\delta \approx R_{\text{int}}$. In particular, by substituting δn_i of Eq. (9) into the second integral in Eq. (8), one obtains some elastic terms that are proportional to the first director derivatives $\partial n_i / \partial x_j$ [22–24]. These elastic terms vanish out of the interfacial layer, but assume enormous values (with respect to the bulk terms) in the interfacial layer. The integral of this excess of interfacial elastic free energy over the interfacial layer leads to contributions to the surface elastic free energy that renormalize the surface elastic constants in Eq. (3). In particular, K_{13} in Eq. (3) is replaced by $K_{13}^* = K_1 + K_{13}$, where K_1 denotes a surface constant coming from the integral of the interfacial elastic linear terms (a different symbol was used in [21] to denote K_1). For any two-body energy law $g(\mathbf{n}, \mathbf{n}', \mathbf{u})$ that satisfies the invariance $\mathbf{n} \rightarrow -\mathbf{n}$ and $\mathbf{n}' \rightarrow -\mathbf{n}'$, K_1 satisfies the general equality $K_1 = -K_{13}$ and thus $K_{13}^* = 0$ [21]. Yokoyama (see Appendix C in [20]) reached the same conclusion using a more general theoretical argument that exploited only the symmetry property

$$\left. \frac{\partial g(\mathbf{n}, \mathbf{n}', \mathbf{u})}{\partial n_i} \right|_{\mathbf{n}=\mathbf{n}'} = \left. \frac{\partial g(\mathbf{n}, \mathbf{n}', \mathbf{u})}{\partial n'_i} \right|_{\mathbf{n}'=\mathbf{n}}. \quad (10)$$

Using Eq. (10), he showed that the second integral in Eq. (8) vanishes at first order in δn_i . Then he concluded that the bulk K_{13} elastic constant must be zero.

All the analysis above concerned only the linear elastic terms coming from the second integral in Eq. (8). It has been shown recently [25,26] that also the first integral in Eq. (8) (the *homogeneous* free-energy term) leads naturally to a surface free energy that is formally equivalent to the K_{13} surface free energy and contains a different *homogeneous* surface constant K_h . Then, if this interfacial contribution is taken into account, the surface free energy is characterized by the effective surface constant $K_{13}^{\text{eff}} = K_{13} + K_1 + K_h = K_h$.

In the present paper we use the Nehring-Saupe molecular model to calculate the effective surface constant K_{13}^{eff} . Exploiting only the symmetry properties of the function $g(\mathbf{n}, \mathbf{n}', \mathbf{u})$, we show that the value of the constant K_{13}^{eff} is independent of the kind of nonlocal to local mapping. This result gives a satisfactory solution to the Somoza-Tarazona paradox and shows that there is no ambiguity in the definition of the surface elastic constants if the boundary effects are entirely taken into account. Furthermore, we calculate the effective surface constant K_{13}^{eff} in terms of the characteristic parameters of the intermolecular two-body energy. In order to avoid the very involved calculations that characterize a

three-dimensional geometry (see, for instance, Refs. [21, 24]), we consider the case of a semi-infinite nematic liquid crystal with a surface at $z=0$ and a planar director field $\mathbf{n} = [\sin \theta(z), 0, \cos \theta(z)]$. We recover the known expressions of the bulk and interfacial elastic constants K_{13} and K_1 and we calculate the surface constant K_h . We find $K_h = K_h^e + K_h^i$, where K_h^e is an external contribution due to the interactions between the NLC molecules and the surrounding media, while K_h^i is an internal contribution due to the interactions between nematic molecules. In Sec. II, by exploiting only the symmetry properties of the interaction law, we find the general result $K_h^i = K_{13}$ [here K_{13} denotes the surfacelike constant that is obtained using the standard integration variables \mathbf{r} and \mathbf{r}' as in Eq. (4)]. Then, with this standard mapping, the effective splay-bend elastic constant is always given by $K_{13}^{\text{eff}} = K_h^e + K_{13}$. In Sec. III we consider a nonlocal to local mapping that depends on a free parameter a and we calculate the corresponding expression for the effective surface constant $K_{13}^{\text{eff}}(a)$. By exploiting only the symmetry properties of the interaction law, we find $K_{13}^{\text{eff}}(a) = K_{13}^{\text{eff}}$, while the single contributions $K_{13}(a)$, $K_1(a)$, and $K_h(a)$ are a dependent. This means that each contribution does not have a well-defined physical meaning, but the resulting splay-bend constant K_{13}^{eff} is a well-defined physical parameter. The invariance of K_{13}^{eff} is found only if *all* the three different contributions $K_{13}(a)$, $K_1(a)$, and $K_h(a)$ are taken into account. In particular, the homogeneous contribution $K_h(a)$, which was disregarded in [20,21], plays here a fundamental role.

In Sec. IV we discuss the physical meaning of the surface elastic term and we show that this term represents the source of a director distortion in a very thin interfacial layer. We show that the elastic surface free energy F_s is a useful semi-macroscopic parameter that makes it possible to obtain a rough but qualitatively correct description of the distorted interfacial layer. However, we emphasize that F_s should not be confused with the thermodynamic surface free energy $\mathcal{F}_s^{\text{th}}$ that appears the continuum theory of NLCs [1]. In particular, we show that the presence of a normal-derivative surface term in the elastic surface free energy does not imply that a similar term has to be present also in the thermodynamic surface free energy. On the contrary, there are some indirect arguments that suggest that the thermodynamic surface free energy does not depend on the normal derivative of the director field [13–15].

II. CASE 1: VARIABLES z AND z'

A. The molecular free energy of nematic liquid crystals and its elastic approximation

Consider a semi-infinite NLC sample that lies in the lower semispace ($z < 0$) in contact with a different medium in the upper semispace ($z > 0$). Here we use the simplifying assumptions of perfect nematic order ($S=1$) and uniform single-particle density ρ in the NLC, which have been extensively used in the literature [4,5,16,23,24]. We consider a planar director field with \mathbf{n} given by

$$\mathbf{n} = (\sin \theta(z), 0, \cos \theta(z)). \quad (11)$$

Let $g(\theta_1, \theta_2, \mathbf{u})$ be the interaction law, where $\theta_1 = \theta(z)$, θ_2

$= \theta(z')$, and $\mathbf{u} = \mathbf{r} - \mathbf{r}'$. Since the director field depends only on z , the free-energy density $f(\theta; z)$ is a functional that depends on z and on the function $\theta = \theta(z)$. $f(\theta; z)$ is given by

$$\begin{aligned} f(\theta; z) &= f_{\text{ext}}(\theta, z) + \int_{-\infty}^0 G(\theta_1, \theta_2, s) dz' \\ &= f_{\text{ext}}(\theta, z) + \int_z^{\infty} G(\theta_1, \theta_2, s) ds, \end{aligned} \quad (12)$$

where

$$s = z - z', \quad \theta_1 = \theta(z), \quad \theta_2 = \theta(z'), \quad (13)$$

and

$$G(\theta_1, \theta_2, s) = \frac{1}{2} \int_{-\infty}^{+\infty} dx' \int_{-\infty}^{+\infty} dy' g(\theta_1, \theta_2, \mathbf{u}). \quad (14)$$

$f_{\text{ext}}(\theta, z)$ is the free-energy density due to interactions with the bounding media, which goes rapidly to zero below a thin interfacial layer. In order to simplify the notations, it is convenient to define

$$\begin{aligned} G_i(\theta, s) &= \left. \frac{\partial G(\theta_1, \theta_2, s)}{\partial \theta_i} \right|_{\substack{\theta_1 = \theta \\ \theta_2 = \theta}}, \\ G_{ij}(\theta, s) &= \left. \frac{\partial G(\theta_1, \theta_2, s)}{\partial \theta_i \partial \theta_j} \right|_{\substack{\theta_1 = \theta \\ \theta_2 = \theta}}, \end{aligned} \quad (15)$$

with $i=1,2$ and $j=1,2$. The function $G(\theta_1, \theta_2, s)$ satisfies the following important properties, which will be essential for our further analysis.

(i) $G(\theta_1, \theta_2, s)$ and its θ_1 and θ_2 derivatives are even function of s .

(ii) $G(\theta_1, \theta_2, s)$ and its θ_1 and θ_2 derivatives are functions of s that go to zero for $s \rightarrow \infty$ with an infinitesimal order higher than $(\sigma/s)^3$, where σ is an average molecular length. Then $G(\theta_1, \theta_2, s)$ and its θ_1 and θ_2 derivatives become negligible if σ is greater than a microscopic interaction radius R_{int} of a few tenths of a molecular length.

(iii) From the general symmetry condition in Eq. (10) we find that the θ_1 and θ_2 derivatives of $G(\theta_1, \theta_2, s)$ must satisfy the equalities

$$G_1(\theta, s) = G_2(\theta, s), \quad G_{11}(\theta, s) = G_{22}(\theta, s). \quad (16)$$

As shown in Appendix A, properties (i) and (iii) are the direct consequence of the inversion symmetry of the interaction energy in the real and the director isotopic space [20]. According to the analysis given in Ref. [24], condition (ii) is necessary to build a local elastic free-energy density. Then quadrupole-quadrupole interactions that are characterized by $G(\theta_1, \theta_2, s) \approx 1/s^3$ cannot be described by an elastic local free-energy density. For a discussion of this important aspect of the elastic theory that is related to the intrinsically nonlocal character of the quadrupole-quadrupole interactions we refer the reader to [24]. The free-energy density per unit surface area is

$$F = \int_{-\infty}^0 f(\theta; z) dz = \int_{-\infty}^0 f_{\text{ext}}(\theta, z) dz + \int_{-\infty}^0 dz \int_z^{\infty} G(\theta_1, \theta_2, s) ds. \quad (17)$$

The basic assumption of the elastic theory is that the director field is a slowly and smoothly varying function of z . This means that the characteristic macroscopic length L_{mac} of the director distortion is much greater than the interaction length R_{int} ($R_{\text{int}} d\theta/dz \approx R_{\text{int}}/L_{\text{mac}} \ll 1$). In such a case, $\delta\theta = \theta_2 - \theta_1$ is a small quantity (of order $R_{\text{int}}/L_{\text{mac}}$) within the interaction region. Then the molecular free energy F in Eq. (17) can be replaced by the elastic expansion

$$F_e = \int_{-\infty}^0 dz \left[f_{\text{ext}}(\theta, z) + \int_z^{\infty} G(\theta, \theta, s) ds \right] + \int_{-\infty}^0 dz \int_z^{\infty} G_2(\theta, s) \delta\theta ds + \int_{-\infty}^0 dz \int_z^{\infty} G_{22}(\theta, s) \frac{\delta\theta^2}{2} ds, \quad (18)$$

with

$$\delta\theta \approx -\dot{\theta}s + \frac{\ddot{\theta}}{2}s^2, \quad (19)$$

where $\dot{\theta} = d\theta/dz$, $\ddot{\theta} = d^2\theta/dz^2$, and $\theta = \theta_1 = \theta(z)$. Substituting $\delta\theta$ into Eq. (18) and disregarding the contributions of infinitesimal order higher than $(R_{\text{int}}/L_{\text{mac}})^2$, we obtain

$$F_e = \int_{-\infty}^0 dz \{ [f_{\text{ext}}(\theta, z) + f_h^i(\theta, z)] + [f_1(\theta, \dot{\theta}, z) + f_{13}(\theta, \ddot{\theta}, z)] + f_2(\theta, \dot{\theta}^2, z) \} = \int_{-\infty}^0 f_{\text{ext}}(\theta, z) dz + \int_{-\infty}^0 f(\theta, \dot{\theta}, \ddot{\theta}, z) dz, \quad (20)$$

where

$$f_h^i(\theta, z) = \int_z^{\infty} G(\theta, \theta, s) ds, \quad (21)$$

$$f_1(\theta, \dot{\theta}, z) = \left(- \int_z^{\infty} G_2(\theta, s) s ds \right) \dot{\theta}, \quad (22)$$

$$f_{13}(\theta, \ddot{\theta}, z) = \left(\int_z^{\infty} G_2(\theta, s) \frac{s^2}{2} ds \right) \ddot{\theta}, \quad (23)$$

$$f_2(\theta, \dot{\theta}^2, z) = \left(\int_z^{\infty} G_{22}(\theta, s) \frac{s^2}{2} ds \right) \dot{\theta}^2. \quad (24)$$

The function $f(\theta, \dot{\theta}, \ddot{\theta}, z)$, which is implicitly defined in Eq. (20), is the local elastic free-energy density due to the intermolecular interactions in the NLC, while $f_{\text{ext}}(\theta, z)$ is the local free-energy density due to the interactions with the substrate. It is easy to show that $F = F_e + O((R_{\text{int}}/L_{\text{mac}})^3)$,

where $O((R_{\text{int}}/L_{\text{mac}})^3)$, represents infinitesimal contributions of third order in the small expansion parameter $R_{\text{int}}/L_{\text{mac}}$. Far from the interface ($z \rightarrow -\infty$), $f_h^i(\theta, z) \rightarrow f_0 = \text{const}$, $f_1(\theta, \dot{\theta}, z) \rightarrow 0$, and $f(\theta, \dot{\theta}, \ddot{\theta}, z)$ is reduced to the classical bulk Oseen-Frank elastic free-energy density $f_e = f(\theta, \dot{\theta}, \ddot{\theta}, -\infty)$ in Eq. (2), which does not depend explicitly on z . On the contrary, in a very thin interfacial layer of thickness $\delta \approx R_{\text{int}}$, $f_1(\theta, \dot{\theta}, z)$ is different from zero and $f_h^i(\theta, z)$ is not constant. Then $f(\theta, \dot{\theta}, \ddot{\theta}, z)$ differs greatly from the bulk expression $f_e(\theta, \dot{\theta}, \ddot{\theta})$ in this interfacial layer.

B. The bulk and interfacial contributions to the surface free energy

In order to separate the classical bulk contribution from the purely interfacial one, we rewrite the free energy for unit surface in the equivalent form

$$F_e = \int_{-\infty}^0 f(\theta, \dot{\theta}, \ddot{\theta}, -\infty) dz + \int_{-\infty}^0 \Delta f(\theta, \dot{\theta}, \ddot{\theta}, z) dz, \quad (25)$$

where $f(\theta, \dot{\theta}, \ddot{\theta}, -\infty)$ is the Oseen-Frank bulk free energy, while $\Delta f(\theta, \dot{\theta}, \ddot{\theta}, z) = f(\theta, \dot{\theta}, \ddot{\theta}, z) + f_{\text{ext}}(\theta, z) - f(\theta, \dot{\theta}, \ddot{\theta}, -\infty)$ represents the *excess of interfacial free-energy density*. The function $\Delta f(\theta, \dot{\theta}, \ddot{\theta}, z)$ vanishes below the interfacial layer of thickness $\delta \approx R_{\text{int}}$. The functions $f(\theta, \dot{\theta}, \ddot{\theta}, -\infty)$ and $\Delta f(\theta, \dot{\theta}, \ddot{\theta}, z)$ are given by

$$f(\theta, \dot{\theta}, \ddot{\theta}, -\infty) = f_0 + f_{13}(\theta, \ddot{\theta}, -\infty) + f_2(\theta, \dot{\theta}^2, -\infty) \quad (26)$$

and

$$\Delta f(\theta, \dot{\theta}, \ddot{\theta}, z) = f_{\text{ext}}(\theta, z) + \Delta f_h^i(\theta, z) + \Delta f_1(\theta, \dot{\theta}, z) + \Delta f_{13}(\theta, \ddot{\theta}, z) + \Delta f_2(\theta, \dot{\theta}^2, z), \quad (27)$$

where

$$f_0 = f_h^i(\theta, -\infty), \quad (28)$$

$$\Delta f_h^i(\theta, z) = f_h^i(\theta, z) - f_0, \quad (29)$$

$$\Delta f_1(\theta, \dot{\theta}, z) = f_1(\theta, \dot{\theta}, z) - f_1(\theta, \dot{\theta}, -\infty) = f_1(\theta, \dot{\theta}, z), \quad (30)$$

$$\Delta f_{13}(\theta, \ddot{\theta}, z) = f_{13}(\theta, \ddot{\theta}, z) - f_{13}(\theta, \ddot{\theta}, -\infty), \quad (31)$$

$$\Delta f_2(\theta, \dot{\theta}^2, z) = f_2(\theta, \dot{\theta}^2, z) - f_2(\theta, \dot{\theta}^2, -\infty). \quad (32)$$

In writing Eqs. (28) and (30) we have used the properties $f_h^i(\theta, -\infty) = f_0 = \text{const}$ and $f_1(\theta, \dot{\theta}, -\infty) = 0$ that are immediately recovered using the definitions in Eqs. (21) and (22) and the symmetry property $G(\theta_1, \theta_2, s) = G(\theta_1, \theta_2, -s)$. The z integrals of Δf_{13} and Δf_2 can be disregarded because they are of order $(R_{\text{int}}/L_{\text{mac}})^3$. Then the free energy for the unit surface area in Eq. (25) is reduced to

$$\begin{aligned}
F_e = & \int_{-\infty}^0 [f_0 + f_{13}(\theta, \ddot{\theta}, -\infty) + f_2(\theta, \dot{\theta}^2, -\infty)] dz \\
& + \int_{-\infty}^0 [f_{\text{ext}}(\theta, z) + \Delta f_h^i(\theta, z)] dz + \int_{-\infty}^0 f_1(\theta, \dot{\theta}, z) dz.
\end{aligned} \tag{33}$$

The integrand of the first integral is the classical Oseen-Frank free-energy density f_e . The function $f_{\text{ext}}(\theta, z) + \Delta f_h^i(\theta, z)$ depends only on z and the local orientation of the director and vanishes far from the interface. $f_{\text{ext}}(\theta, z)$ is the external free-energy contribution due to the interactions with the substrate, while $\Delta f_h^i(\theta, z)$ is the internal contribution due to the intermolecular interactions in the NLC. According to Eqs. (29) and (21), $\Delta f_h^i(\theta, z)$ represents the local free-energy density of NLC molecules when they are oriented at the same angle θ . For this reason, we will call this term the *internal homogeneous term*. The function $f_1(\theta, \dot{\theta}, z)$ is an elastic free-energy contribution that vanishes far from the interface but becomes enormous (with respect to the classical Frank-Oseen terms) in a very thin interfacial layer. The z integral of this latter term over the interfacial layer of thickness $\delta \approx R_{\text{int}}$ leads to a surface free-energy density $F_1(\theta_s, \dot{\theta}_s)$ of the same order of magnitude as the classical K_{13} surface energy. We will call $f_1(\theta, \dot{\theta}, z)$ the *elastic interfacial term*.

In the standard elastic theory [4,5,16,17] only the first integral in Eq. (33) is taken into account. In a recent paper, Faetti and Riccardi [21] calculated explicitly the third elastic contribution in Eq. (33) and showed that it leads to a surface elastic term that is exactly equal and opposite to the classical K_{13} term. They concluded that the total surface elastic term is zero. This conclusion was recovered by Yokoyama (see Appendix C in [20]) using a more general theoretical approach. He showed that the second integral in Eq. (18), which is linear in $\delta\theta$ and is responsible for the f_1 and f_{13} terms, vanishes at the first infinitesimal order in $\delta\theta$. However, Skacej *et al.* [25] and Alexe-Ionescu and Barbero [26] have recently shown that also the homogeneous term in the second integral in Eq. (33) leads to a surface term $F_h(\theta_s, \dot{\theta}_s)$ that is not of elastic origin but is formally equivalent to the K_{13} surface free energy. In this section, by using only the symmetry properties of $G(\theta_1, \theta_2, s)$, we will obtain simple expressions for all the surface terms.

We start our analysis from the classical Oseen-Frank free energy in the first integral in Eq. (33). Using the definitions in Eqs. (23) and (24) and adding and subtracting the same term $G_{12}(\theta, s)(s^2/2)\dot{\theta}^2$, we obtain

$$\begin{aligned}
& f_{13}(\theta, \ddot{\theta}, -\infty) + f_2(\theta, \dot{\theta}^2, -\infty) \\
& = \int_{-\infty}^{\infty} \{G_2(\theta, s)\ddot{\theta} + [G_{22}(\theta, s) + G_{12}(\theta, s)]\dot{\theta}^2\} \frac{s^2}{2} ds \\
& - \int_{-\infty}^{\infty} G_{12}(\theta, s) \frac{s^2}{2} \dot{\theta}^2 ds.
\end{aligned} \tag{34}$$

Using the definition of the function $G_2(\theta, s)$ given in Eq. (15), we find that the first integral in Eq. (34) is the z derivative of the function

$$F_{13}(\theta, \dot{\theta}) = \int_{-\infty}^{\infty} G_2(\theta, s) \frac{s^2}{2} \dot{\theta} ds. \tag{35}$$

Then the z integration of the first integral in Eq. (34) leads to the surface elastic free-energy density

$$\begin{aligned}
F_{13}(\theta_s, \dot{\theta}_s) & = \int_{-\infty}^{+\infty} \frac{z^2}{2} G_2(\theta_s, z) \dot{\theta}_s dz \\
& = \int_{-\infty}^0 z^2 G_2(\theta_s, z) \dot{\theta}_s dz,
\end{aligned} \tag{36}$$

where $\theta_s = \theta(0)$ and $\dot{\theta}_s = |d\theta/dz|_{z=0}$ and $F_{13}(\theta_s, \dot{\theta}_s)$ is the classical K_{13} surface free energy. In Eq. (36) we have renamed the s variable z . To obtain the last integral in Eq. (36) we have used the symmetry property $G_2(\theta_s, z) = G_2(\theta_s, -z)$. It can be also shown (see Appendix B) that the function $F_{13}(\theta_s, \dot{\theta}_s)$ has the well-known form [4,5]

$$F_{13}(\theta_s, \dot{\theta}_s) = \frac{K_{13}}{2} [\sin(2\theta_s) \dot{\theta}_s], \tag{37}$$

where K_{13} is the splay-bend elastic constant. Furthermore, it can be shown (see Appendix B) that the last integral in Eq. (34) gives the well-known Oseen-Frank quadratic free-energy density

$$\left[\frac{K_{11}}{2} \sin^2 \theta + \frac{K_{33}}{2} \cos^2 \theta \right] (\dot{\theta})^2, \tag{38}$$

where K_{11} and K_{33} are the splay and bend elastic constants, respectively. A very general expression for a two-body interaction law is [16,24]

$$g(\mathbf{n}, \mathbf{n}', \mathbf{u}) = - \sum_{i,j,k} J_{i,j,k}(u) \left(\mathbf{n} \cdot \frac{\mathbf{u}}{u} \right)^i \left(\mathbf{n}' \cdot \frac{\mathbf{u}}{u} \right)^j (\mathbf{n} \cdot \mathbf{n}')^k. \tag{39}$$

By substituting $g(\mathbf{n}, \mathbf{n}', \mathbf{u})$ into Eq. (14) and using the definition of $G_2(\theta, s)$ given in Eq. (15), K_{13} in Eqs. (36) and (37) becomes (see Appendix B)

$$K_{13} = - \frac{1}{2} \sum_{ijk} I(i, j, k) \frac{j}{(i+j+1)(i+j+3)}, \tag{40}$$

where

$$I(i, j, k) = 4\pi \int_0^{\infty} J_{ijk}(u) u^4 du. \tag{41}$$

The expression of K_{13} in Eq. (40) has already been obtained by Barbero and Barberi [16] in the three-dimensional case.

C. The interfacial contributions to the surface free energy

The integrands in the two last integrals in Eq. (33) vanish rapidly below a thin interfacial layer. Then we can replace θ and $\dot{\theta}$ with the local expansions $\theta = \theta(z) = \theta_s + \dot{\theta}_s z + \dots$ and $\dot{\theta} = \dot{\theta}(z) = \dot{\theta}_s + \dots$. By disregarding infinitesimal contributions of order $(R_{\text{int}}/L_{\text{mac}})^3$, the two last integrals in Eq. (33) lead to the surface excess of free energy

$$\begin{aligned}
F_{\text{surf}} &= \int_{-\infty}^0 f_{\text{ext}}(\theta_s, z) dz + \int_{-\infty}^0 \Delta f_h^i(\theta_s, z) dz \\
&+ \int_{-\infty}^0 \left| \frac{\partial f_{\text{ext}}(\theta, z)}{\partial \theta} \right|_{\theta=\theta_s} \dot{\theta}_s z dz \\
&+ \int_{-\infty}^0 \left| \frac{\partial f_h^i(\theta, z)}{\partial \theta} \right|_{\theta=\theta_s} \dot{\theta}_s z dz + \int_{-\infty}^0 f_1(\theta_s, \dot{\theta}_s, z) dz \\
&= F_s^e(\theta_s) + F_s^i(\theta_s) + F_h^e(\theta_s, \dot{\theta}_s) + F_h^i(\theta_s, \dot{\theta}_s) \\
&+ F_1(\theta_s, \dot{\theta}_s), \tag{42}
\end{aligned}$$

where the functions $F_s^e(\theta_s)$, $F_s^i(\theta_s)$, $F_h^e(\theta_s, \dot{\theta}_s)$, $F_h^i(\theta_s, \dot{\theta}_s)$, and $F_1(\theta_s, \dot{\theta}_s)$ represent the first, second, third, fourth, and fifth integrals, respectively. In writing the integrand of the fourth integral we have used the property $\partial \Delta f_h^i(\theta, z) / \partial \theta = \partial f_h^i(\theta, z) / \partial \theta$, which comes from Eq. (29). The first two integrals are the external and internal anchoring energies $F_s^e(\theta_s)$ and $F_s^i(\theta_s)$ that depend only on the surface director angle. The explicit dependence of the internal term $F_s^i(\theta_s)$ on the characteristic parameters of the intermolecular energy in Eq. (39) has been calculated in [21]. The other integrals are surface free energies that depend on θ_s and are proportional to the surface derivative $\dot{\theta}_s$. We will show that these integrals have the same form as the classical K_{13} surface term in Eq. (37) and thus they renormalize the K_{13} elastic constant. The third integral (F_h^e) and the fourth integral (F_h^i) come from the external and internal homogeneous interfacial terms. The fifth integral (F_1) is the purely elastic interfacial contribution, which had been already considered in [21]. For an isotropic substrate that interacts with the NLC via nonpolar interactions, $f_{\text{ext}}(\theta, z)$ is a function of $(\mathbf{n} \cdot \mathbf{k})^2 = \cos^2 \theta$. Then, in such a case, $\partial f_{\text{ext}}(\theta, z) / \partial \theta = L(\cos^2 \theta) \sin 2\theta / 2$ and $F_h^e(\theta_s, \dot{\theta}_s)$ becomes

$$F_h^e(\theta_s, \dot{\theta}_s) = K_h^e(\cos^2 \theta_s) \sin 2\theta_s / 2. \tag{43}$$

In the general case, $K_h^e(\cos^2 \theta_s)$ is a function of $\cos^2 \theta_s$, but it is reduced to a simple constant for van der Waals interactions [27]. Note that the homogeneous external contribution has the same functional form as the classical K_{13} term in Eq. (37).

Due to the definitions of $f_h^i(\theta, z)$ and $f_1(\theta, \dot{\theta}, z)$ in Eqs. (21) and (22), the last two integrals in Eq. (42) require a double integration on variables z and s . However, both of them can be transformed into integrals in only one variable using the integration by parts and the general property (ii) of the function G . In particular, integration by parts with respect to the function $y = z^2$ in the fourth integral in Eq. (42) leads to

$$\begin{aligned}
F_h^i(\theta_s, \dot{\theta}_s) &= \left[\frac{z^2}{2} \left| \frac{\partial f_h^i(\theta, z)}{\partial \theta} \right|_{\theta=\theta_s} \dot{\theta}_s \right]_{-\infty}^0 \\
&- \int_{-\infty}^0 \frac{z^2}{2} \frac{d}{dz} \left| \frac{\partial f_h^i(\theta, z)}{\partial \theta} \right|_{\theta=\theta_s} \dot{\theta}_s dz. \tag{44}
\end{aligned}$$

The first term in Eq. (44) vanishes due to property (ii). Furthermore, from Eq. (21) we get

$$\frac{d}{dz} \left| \frac{\partial f_h^i(\theta, z)}{\partial \theta} \right|_{\theta=\theta_s} = -G_1(\theta_s, s) - G_2(\theta_s, s) = -2G_2(\theta_s, s). \tag{45}$$

The last equality in Eq. (45) derives directly from the symmetry property $G_1(\theta_s, s) = G_2(\theta_s, s)$. Then $F_h^i(\theta_s, \dot{\theta}_s)$ in Eq. (44) is reduced to

$$F_h^i(\theta_s, \dot{\theta}_s) = \int_{-\infty}^0 z^2 G_2(\theta_s, z) \dot{\theta}_s dz = F_{13}(\theta_s, \dot{\theta}_s). \tag{46}$$

By operating at the same way on the last integral in Eq. (42) we get easily

$$F_1(\theta_s, \dot{\theta}_s) = - \int_{-\infty}^0 z^2 G_2(\theta_s, z) \dot{\theta}_s dz = -F_{13}(\theta_s, \dot{\theta}_s), \tag{47}$$

which coincides with the theoretical result already found in [21]. In conclusion, the total surface term that is linear in $\dot{\theta}_s$ ($F_h^e(\theta_s, \dot{\theta}_s) + F_h^i(\theta_s, \dot{\theta}_s) + F_1(\theta_s, \dot{\theta}_s) + F_{13}(\theta_s, \dot{\theta}_s)$) is reduced to

$$F_s(\theta_s, \dot{\theta}_s) = F_h^e(\theta_s, \dot{\theta}_s) + F_{13}(\theta_s, \dot{\theta}_s). \tag{48}$$

Then the splay-bend elastic constant K_{13} has to be replaced by the effective constant

$$K_{13}^{\text{eff}} = K_h^e(\cos^2 \theta_s) + K_{13}. \tag{49}$$

In the special case of the interface between a NLC and its vapor phase, $F_h^e(\theta_s, \dot{\theta}_s) = 0$ and the elastic surface free energy $F_s(\theta_s, \dot{\theta}_s)$ is reduced to the classical $F_{13}(\theta_s, \dot{\theta}_s)$ term in Eq. (37) with K_{13} given in Eq. (40).

In the next section we will give a solution to the Somoza-Tarazona paradox. In agreement with Somoza and Tarazona [19], we will show that the classical surfacelike free energy $F_{13}(\theta_s, \dot{\theta}_s)$ depends explicitly on the nonlocal to local mapping used to define the local free-energy density. Then this surface free energy does not have a well-defined physical meaning. However, we will also show that the total surface free energy $F_h^e(\theta_s, \dot{\theta}_s) + F_h^i(\theta_s, \dot{\theta}_s) + F_1(\theta_s, \dot{\theta}_s) + F_{13}(\theta_s, \dot{\theta}_s)$ is mapping independent. This means that such a surface free energy has an unambiguous physical meaning. Therefore, no paradox arises if all the boundary effects are correctly taken into account.

III. CASE 2: VARIABLES Z AND s

A. The local free-energy density

According to Sec. II, the total free energy of the NLC is

$$F = \int_{-\infty}^0 dz \left[f_{\text{ext}}(\theta, z) + \int_{-\infty}^0 G(\theta_1, \theta_2, z - z') dz' \right], \tag{50}$$

where $\theta_1 = \theta(z)$ and $\theta_2 = \theta(z')$. Then the functional

$$f(\theta; z) = f_{\text{ext}}(\theta, z) + \int_{-\infty}^0 G(\theta_1, \theta_2, z - z') dz' \tag{51}$$

can be interpreted as the local free-energy density at the point z . However, it is known [18] that this is not the only way to define a free-energy density starting from a nonlocal free-energy functional. In particular, one can use the variables

$$Z = az + (1-a)z', \quad s = z - z', \quad (52)$$

with $0 \leq a \leq 1$. These variables satisfy the following properties: (a) $Z = z$ if $z' = z$, (b) the Jacobian of the transform is $|J| = 1$, and (c) Z is always internal to the $z-z'$ interval. By substituting Z and s in the double integral in Eq. (50), F becomes

$$F = \int_{-\infty}^0 f_{\text{ext}}(\theta, z) dz + \int_{-\infty}^0 dZ \int_{Z/a}^{-Z/(1-a)} G(\theta_1, \theta_2, s) ds, \quad (53)$$

where now θ_1 and θ_2 are defined as $\theta_1 = \theta(Z + [1-a]s)$ and $\theta_2 = \theta(Z - as)$. Note that the integration extremes for the Z variable in Eq. (53) are the same as for the z variable. This important property is a consequence of property (c) and remains satisfied also for a NLC layer with two surfaces at $z = -d$ and 0. It is convenient to rename Z as z in Eq. (53) so that

$$F = \int_{-\infty}^0 dz \left[f_{\text{ext}}(\theta, z) + \int_{z/a}^{-z/(1-a)} G(\theta_1, \theta_2, s) ds \right], \quad (54)$$

where

$$\theta = \theta(z), \quad \theta_1 = \theta(z + [1-a]s), \quad \theta_2 = \theta(z - as). \quad (55)$$

Then the functional

$$f^a(\theta; z) = f_{\text{ext}}(\theta, z) + \int_{z/a}^{-z/(1-a)} G(\theta_1, \theta_2, s) ds \quad (56)$$

can be interpreted as a different expression of the free-energy density at the point z in the NLC. For $a = 1$, $Z = z$ in Eq. (52) and $f^a(\theta; z)$ is reduced to the standard free-energy density $f(\theta; z)$ in Eq. (51).

B. The elastic free energy

In order to obtain the elastic free energy, one has to expand function $G(\theta_1, \theta_2, s)$ in Eq. (54) with respect to the reference state $\theta = \theta(z)$. Then θ_1 and θ_2 must be replaced by $\theta_1 = \theta + \delta\theta_1$ and $\theta_2 = \theta + \delta\theta_2$. At second order in $\delta\theta_1$ and $\delta\theta_2$, we get

$$\begin{aligned} F_e^a &= \int_{-\infty}^0 dz \left[f_{\text{ext}}(\theta, z) + \int_{z/a}^{-z/(1-a)} ds G(\theta, \theta, s) \right] \\ &+ \int_{-\infty}^0 dz \left[\int_{z/a}^{-z/(1-a)} ds G_2(\theta, s) (\delta\theta_1 + \delta\theta_2) \right] \\ &+ \int_{-\infty}^0 \frac{dz}{2} \int_{z/a}^{-z/(1-a)} ds [G_{22}(\theta, s) (\delta\theta_1^2 + \delta\theta_2^2) \\ &+ 2G_{12}(\theta, s) \delta\theta_1 \delta\theta_2], \end{aligned} \quad (57)$$

where $G_i(\theta, s)$ and $G_{ij}(\theta, s)$ are the derivatives defined in Eq. (15) and we have exploited the equalities $G_1(\theta, s) = G_2(\theta, s)$ and $G_{11}(\theta, s) = G_{22}(\theta, s)$. The elastic free energy at the infinitesimal order $(R_{\text{int}}/L_{\text{mac}})^2$ is obtained by substituting in Eq. (57)

$$\delta\theta_1 = (1-a)s\dot{\theta} + \frac{(1-a)^2 s^2}{2} \ddot{\theta} \quad (58)$$

and

$$\delta\theta_2 = -as\dot{\theta} + \frac{a^2 s^2}{2} \ddot{\theta}. \quad (59)$$

$\delta\theta_1$ and $\delta\theta_2$ have been obtained using Eq. (55). By following the same procedure as in Sec. II, we can separate the bulk and interfacial energy contributions. By disregarding the interfacial terms of order $(R_{\text{int}}/L_{\text{mac}})^3$ and exploiting the equalities $G_1(\theta, s) = G_2(\theta, s)$ and $G_{11}(\theta, s) = G_{22}(\theta, s)$, we get

$$\begin{aligned} F_e^a &= \int_{-\infty}^0 [f_0 + f_{13}^a(\theta, \ddot{\theta}, -\infty) + f_2^a(\theta, \dot{\theta}^2, -\infty)] dz \\ &+ \int_{-\infty}^0 [f_{\text{ext}}(\theta, z) + \Delta f_h^{ia}(\theta, z)] dz + \int_{-\infty}^0 f_1^a(\theta, \dot{\theta}, z) dz, \end{aligned} \quad (60)$$

where

$$f_{13}^a(\theta, \ddot{\theta}, -\infty) = [(1-a)^2 + a^2] \int_{-\infty}^{+\infty} ds G_2(\theta, s) \frac{s^2}{2} \ddot{\theta}, \quad (61)$$

$$\begin{aligned} f_2^a(\theta, \dot{\theta}^2, -\infty) &= \int_{-\infty}^{+\infty} ds \{ G_{22}(\theta, s) [(1-a)^2 + a^2] \\ &- 2a(1-a)G_{12}(\theta, s) \} \frac{s^2}{2} \dot{\theta}^2, \end{aligned} \quad (62)$$

$$\Delta f_h^{ia}(\theta, z) = \int_{z/a}^{-z/(1-a)} ds G(\theta, \theta, s) - f_0, \quad (63)$$

$$f_1^a(\theta, \dot{\theta}, z) = (1-2a) \int_{z/a}^{-z/(1-a)} ds G_2(\theta, s) s \dot{\theta}. \quad (64)$$

f_0 in Eq. (63) is the constant contribution in the bulk free-energy density, which is defined as $f_0 = \int_{-\infty}^{+\infty} ds G(\theta, \theta, s)$. By adding and subtracting the same term $G_{12}(\theta, s) s^2 \dot{\theta}^2 / 2$ in the integrand in Eq. (62), $f_2^a(\theta, \dot{\theta}^2, -\infty)$ can be written in the more convenient form

$$\begin{aligned} f_2^a(\theta, \dot{\theta}^2, -\infty) &= [(1-a)^2 + a^2] \int_{-\infty}^{+\infty} ds \{ G_{22}(\theta, s) \\ &+ G_{12}(\theta, s) \} \frac{s^2}{2} \dot{\theta}^2 \\ &- \int_{-\infty}^{+\infty} ds G_{12}(\theta, s) \frac{s^2}{2} \dot{\theta}^2. \end{aligned} \quad (65)$$

Then the bulk elastic free-energy density $f_{\text{bulk}} = f_{13}^a(\theta, \ddot{\theta}, -\infty) + f_2^a(\theta, \dot{\theta}^2, -\infty)$ becomes

$$f_{13}^a(\theta, \ddot{\theta}, -\infty) + f_2^a(\theta, \dot{\theta}^2, -\infty) = \frac{dF_{13}^a(\theta, \dot{\theta})}{dz} - \int_{-\infty}^{+\infty} ds G_{12}(\theta, s) \frac{s^2}{2} \dot{\theta}^2, \quad (66)$$

where

$$F_{13}^a(\theta, \dot{\theta}) = [(1-a)^2 + a^2] \int_{-\infty}^{+\infty} ds G_2(\theta, s) \frac{s^2}{2} \dot{\theta}. \quad (67)$$

The first derivative term in Eq. (66) corresponds to the surface K_{13} term, while the second term is the bulk contribution that depends on the bulk elastic constants K_{11} and K_{33} . Note that this latter term is identical to that already found in Eq. (34) of Sec. II B. Then, in agreement with the Somoza-Tarazona results, the bulk elastic constants are not affected by the variable's transform. On the contrary, by comparing Eq. (67) with Eq. (36) of Sec. II B, we find

$$F_{13}^a(\theta_s, \dot{\theta}_s) = [(1-a)^2 + a^2] F_{13}(\theta_s, \dot{\theta}_s). \quad (68)$$

This means that the splay-bend constant K_{13} is mapping dependent, in agreement with the Somoza-Tarazona conclusions. Using the same approach as in Sec. II C, the last two interfacial contributions in Eq. (60) can be written in terms of the surface angle θ_s and its surface derivative. Then the sum of the last two integrals in Eq. (60) is reduced to the sum of the five surface free energies per unit surface area

$$F_s^{ea}(\theta_s) = \int_{-\infty}^0 dz f_{\text{ext}}(\theta_s, z), \quad (69)$$

$$F_s^{ia}(\theta_s) = \int_{-\infty}^0 dz \Delta f_h^{ia}(\theta_s, z), \quad (70)$$

$$F_h^{ea}(\theta_s, \dot{\theta}_s) = \int_{-\infty}^0 dz z \left| \frac{\partial f_{\text{ext}}(\theta, z)}{\partial \theta} \right|_{\theta=\theta_s} \dot{\theta}_s, \quad (71)$$

$$F_h^{ia}(\theta_s, \dot{\theta}_s) = \int_{-\infty}^0 dz z \left| \frac{\partial \Delta f_h^{ia}(\theta, z)}{\partial \theta} \right|_{\theta=\theta_s} \dot{\theta}_s, \quad (72)$$

and

$$F_1^a(\theta_s, \dot{\theta}_s) = \int_{-\infty}^0 dz f_1^a(\theta_s, \dot{\theta}_s, z). \quad (73)$$

The external surface free energies $F_s^{ea}(\theta_s)$ and $F_h^{ea}(\theta_s, \dot{\theta}_s)$ are equal to surface energies $F_s^e(\theta_s)$ and $F_h^e(\theta_s, \dot{\theta}_s)$ defined implicitly in Eq. (42). Furthermore, it is also easy to show that the internal surface free energy $F_s^{ia}(\theta_s)$ is equal to $F_s^i(\theta_s)$ defined in Eq. (42) (see Appendix C). Then we infer that these two contributions are mapping independent. The surface terms $F_h^{ia}(\theta_s, \dot{\theta}_s)$ and $F_1^a(\theta_s, \dot{\theta}_s)$ can be reduced to simple z integrals substituting in Eqs. (72) and (73) the ex-

PLICIT expressions of $\Delta f_h^{ia}(\theta, z)$ and $f_1^a(\theta_s, \dot{\theta}_s, z)$ given in Eqs. (63) and (64) and using integration by parts to eliminate the s variable (see Appendix C). In such a way, we obtain explicit expressions of the surface free energies in terms of the z integral $F_{13}(\theta_s, \dot{\theta}_s)$ defined in Eq. (36). After straightforward calculations, we obtain

$$F_s^{ea}(\theta_s) = F_s^e(\theta_s), \quad (74)$$

$$F_s^{ia}(\theta_s) = F_s^i(\theta_s), \quad (75)$$

$$F_h^{ea}(\theta_s, \dot{\theta}_s) = F_h^e(\theta_s, \dot{\theta}_s), \quad (76)$$

$$F_h^{ia}(\theta_s, \dot{\theta}_s) = [a^2 + (1-a)^2] F_h^i(\theta_s, \dot{\theta}_s) = [a^2 + (1-a)^2] F_{13}(\theta_s, \dot{\theta}_s), \quad (77)$$

$$F_1^a(\theta_s, \dot{\theta}_s) = (1-2a)^2 F_1(\theta_s, \dot{\theta}_s) = -(1-2a)^2 F_{13}(\theta_s, \dot{\theta}_s). \quad (78)$$

It is evident from Eqs. (77), (78), and (68) that each surface-derivative term due to the internal intermolecular interactions is affected by the change of variables. However, the total surface free energy, which is given by the sum of the five terms in Eqs. (74)–(78) and the one in Eq. (68), is mapping independent and is given by

$$F_s = F_s^e(\theta_s) + F_s^i(\theta_s) + F_h^e(\theta_s, \dot{\theta}_s) + F_{13}(\theta_s, \dot{\theta}_s), \quad (79)$$

where $F_s^e(\theta_s)$, $F_s^i(\theta_s)$, $F_h^e(\theta_s, \dot{\theta}_s)$, and $F_{13}(\theta_s, \dot{\theta}_s)$ are the surface functions defined in Sec. II. This theoretical result gives a satisfactory solution to the Somoza-Tarazona paradox. In conclusion, the separation of the surface elastic terms into a bulk (F_{13}) and two interfacial (F_h and F_1) contributions does not have a well-defined physical meaning because one contribution that is interpreted as a bulk contribution with a given nonlocal to local mapping becomes an interfacial contribution if a different mapping is used. The only well-defined physical parameter is the total surface free energy that is mapping independent. Our theoretical results also show that the homogeneous surface contribution $F_h(\theta_s, \dot{\theta}_s)$ introduced in Refs. [25,26] plays a very important role. Indeed, if this interfacial term is disregarded, the mapping independence of the surface free energy is no longer recovered.

In conclusion, the surface elastic free energy is always given by F_s in Eq. (79). Explicit expressions for $F_s^i(\theta_s)$ in terms of the characteristic parameters of the generic interaction law of Eq. (39) can be found in [24], while the expression of $F_{13}(\theta_s, \dot{\theta}_s)$ is given in Eqs. (37) and (40) of Sec. II. The other two parameters can be easily obtained if the specific form of the interaction energy $f_{\text{ext}}(\theta, z)$ is given.

IV. THE PHYSICAL MEANING OF THE ELASTIC SURFACE FREE ENERGY

In Sec. IV A we discuss the physical meaning and the consequences of the elastic surface free energy that has been obtained in Sec. II and III. We show that the surface elastic constant K_{13}^{eff} represents the source for sharp director distortions that occur in a very thin interfacial layer. The elastic surface free energy makes it possible to build approximate

elastic models for the interfacial director field. In Sec. IV B we emphasize that the elastic surface free energy should not be confused with the thermodynamic surface free energy that appears in a consistent continuum theory of NLCs. The presence of a normal-derivative term on the elastic surface free energy does not imply that a similar term has to be present in the thermodynamic surface free energy. On the contrary, we show that there are some indirect arguments that suggest strongly the absence of a normal-derivative term in the thermodynamic surface free energy. Then the theoretical results that have been obtained in the present paper do not conflict with the expression of the thermodynamic surface free energy that was proposed in Refs. [14,15] and with Yokoyama's recent results [20].

A. The equilibrium director field

Here we will call the free energy per unit surface area F in Eq. (17) the *molecular free energy*, while its elastic approximation will be called the *elastic free energy*. In this subsection we will discuss the physical meaning and the consequences of the K_{13} surface term. For simplicity, we consider the special case of a NLC layer of thickness d sandwiched between two identical solid plates that interact with the NLC via short-range interactions. Then the external free-energy density due to the interactions with the solid plates is

$$f_{\text{ext}}(\theta, z) = W(\theta) \delta(z + d/2) + W(\theta) \delta(z - d/2), \quad (80)$$

where $\delta(z)$ is the Dirac function. In this case, the effective constant K_{13}^{eff} in Eq. (49) is reduced to K_{13} because $K_h^e(\cos^2\theta_s) = 0$. The equilibrium director angle $\theta_{\text{eq}}(z)$ should be obtained by minimizing the Nehring-Saupe molecular free energy F in Eq. (17). This leads to an integral equation that requires a numerical treatment [26]. In order to obtain an approximate solution for the same problem, one could minimize the elastic free energy per unit surface area F_e obtained in Sec. II. In the present case, F_e becomes

$$\begin{aligned} F_e = & \int_{-d/2}^{+d/2} \left[\frac{K_{11}}{2} \sin^2\theta + \frac{K_{33}}{2} \cos^2\theta \right] (\dot{\theta})^2 dz + F_s^i(\theta_1) \\ & + F_s^i(\theta_2) + W(\theta_1) + W(\theta_2) + \frac{K_{13}}{2} [\sin(2\theta_2) \dot{\theta}_2] \\ & - \frac{K_{13}}{2} [\sin(2\theta_1) \dot{\theta}_1], \end{aligned} \quad (81)$$

where $\theta_1 = \theta(-d/2)$ and $\theta_2 = \theta(d/2)$ are the angles at the surfaces $z = -d/2$ and $d/2$ and we have disregarded the unessential constant contribution f_0 . The variational approach leads to a second-order differential equation for $\theta(z)$ and *four* boundary conditions [6,7]. Since the general solution of a second-order differential equation depends only on two arbitrary constants B and C , it cannot satisfy simultaneously four boundary conditions. Then the variational problem is ill posed. It has been shown [6,7] that this paradoxical result is due to the splay-bend elastic constant in Eq. (81) that makes the elastic free energy unbounded from below. In particular, the free energy approaches $-\infty$ if the z derivative of $\theta(z)$ at the interfaces approaches $\pm\infty$, depending on the sign of K_{13} . This means that a director angle $\theta(z)$ that has a discon-

tinuity at the interfaces is energetically favored. Oldano and Barbero argued that the surface discontinuity mimics a sharp variation that occurs in a very thin interfacial layer of thickness comparable to the molecular length. Note that the molecular free energy F is bounded from below. This means that the higher-order contributions that have been disregarded in the elastic expansion bound the free energy from below. Following this idea, Barbero, Sparavigna, and Strigazzi [8,9] developed a *second-order elastic theory* where contributions up to order $(R_{\text{int}}/L_{\text{mac}})^4$ were retained in the expansion of the bulk elastic free-energy density. The second-order elastic free energy contains many different second-order elastic terms. However, for small director angles ($\theta \ll 1$), only the second-order elastic term $K_2 \dot{\theta}^2/2$ is not negligible. The constant K_2 is a second-order elastic constant of the order of $K_{33} R_{\text{int}}^2$. The second-order elastic term bounds the free energy from below and the variational approach leads to a *fourth-order* Euler-Lagrange equation with *four* boundary conditions. Then the mathematical problem is well posed. The equilibrium solution has the general form [9,13]

$$\theta_{\text{eq}}(z) = \Delta\theta(z) + \theta_{\text{mac}}(z), \quad (82)$$

where $\theta_{\text{mac}}(z)$ is a slowly and smoothly varying function and $\Delta\theta(z)$ is a function that vanishes exponentially out of two thin interfacial layers of thickness $\delta_2 = (K_2/K_{33})^{1/2} \approx R_{\text{int}}$. The surface discontinuity that is predicted by the first-order elastic theory is immediately recovered for $K_2 \rightarrow 0$ because $\delta_2 = (K_2/K_{33})^{1/2} \rightarrow 0$. The amplitude of the surface discontinuity is given by $\Delta\theta(0) = K_{13}\theta(0)/K_{33}$ [9,13]. In the second-order theory, the elastic contributions of order higher than $(R_{\text{int}}/L_{\text{mac}})^4$ were disregarded. However, it is evident that, for $L_{\text{mac}} \approx \delta_2 \approx R_{\text{int}}$ the elastic terms of order $(R_{\text{int}}/L_{\text{mac}})^m$, with $m > 4$, are not negligible. Pergamenschik proposed [12] that the higher-order terms remove entirely the interfacial distortion. In order to investigate the role of the higher-order terms, Faetti [13] developed an N th-order elastic theory where contributions up to order $(R_{\text{int}}/L_{\text{mac}})^{2N}$ were retained. For any finite value of N , the equilibrium director angle always has the general form in Eq. (82) with a sharp interfacial distortion $\Delta\theta(z)$. Therefore, he concluded that the higher-order terms do not remove the interfacial distortion, although the amplitude and the analytical expression of the interfacial function $\Delta\theta(z)$ are appreciably affected by the higher-order terms. Then the second-order theory gives a correct qualitative view of the interfacial field, but is unable to reproduce the details.

We remark that the existence of the sharp interfacial distortion $\delta\theta(z)$ is not an artifact of the higher-order elastic theories but corresponds to an actual feature of the intermolecular interactions. This has been shown recently in some papers where the molecular free energy F in Eq. (17) was minimized using numerical procedures [25,28–30]. It was shown that the director field exhibits a sharp interfacial distortion in qualitative agreement with the predictions of the second-order theory.

The second-order and higher-order elastic theories are not the only possible ways to obtain a mathematically well-posed problem and an approximate solution for the interfacial distortion. In particular, one can follow an alternative

approximate approach using the semielastic free energy that is given in Eq. (33) of Sec. II [30]. Disregarding the unessential constant contribution f_0 , the semielastic free energy in Eq. (33) is written

$$F_{se} = W(\theta_1) + W(\theta_2) + \int_{-d/2}^{d/2} \Delta f_h^i(\theta, z) dz + \int_{-d/2}^{d/2} [f_{13}(\theta, \ddot{\theta}, -\infty) + f_1(\theta, \dot{\theta}, z) + f_2(\theta, \dot{\theta}^2, -\infty)] dz, \quad (83)$$

where $\Delta f_h^i(\theta, z)$ is the interfacial homogeneous free energy defined in Eq. (29), while the second integral contains the bulk and interfacial elastic terms. Note that F_{se} is different from the elastic free energy F_e in Eq. (81) because the interfacial contributions $\Delta f_h^i(\theta, z)$ and $f_1(\theta, \dot{\theta}, z)$ have not yet been expanded with respect to $\theta(0) = \theta_s$. According to Sec. II, the two linear surface derivative contributions coming from the bulk elastic free-energy density $f_{13}(\theta, \ddot{\theta}, -\infty) + f_2(\theta, \dot{\theta}^2, -\infty)$ and from the expansion of $f_1(\theta, \dot{\theta}, z)$ are equal and opposite. Then the second integral in Eq. (83) is reduced to the classical bulk Oseen-Frank elastic free energy and the semielastic free energy F_{se} becomes

$$F_{se} = W(\theta_1) + W(\theta_2) + \int_{-d/2}^{d/2} \Delta f_h^i(\theta, z) dz + \int_{-d/2}^{d/2} \left[\frac{K_{11}}{2} \sin^2 \theta + \frac{K_{33}}{2} \cos^2 \theta \right] (\dot{\theta})^2 dz. \quad (84)$$

We recall that the elastic free energy F_e in Eq. (81) was obtained from Eq. (84) by making a linear expansion of $\Delta f_h^i(\theta, z)$ in terms of $\Delta \theta = \theta(z) - \theta_s = \dot{\theta}_s z + \dots$, where θ_s is the surface director angle. Then the semielastic free energy F_{se} contains implicitly all the higher-order surface terms coming from the expansion of $\Delta f_h^i(\theta, z)$ that were disregarded in F_e . On the other hand, the second integral in Eq. (84) disregards entirely the higher-order surface and bulk elastic terms. In this sense, the semielastic free energy in Eq. (84) can be considered as complementary to the higher-order elastic free energies. Both these free energies take partially into account different higher-order terms (the homogeneous higher-order terms and the elastic ones, respectively). The semielastic free energy is bounded from below and the standard variational approach leads to the bulk Euler-Lagrange equation

$$\frac{\partial \Delta f_h^i(\theta, z)}{\partial \theta} - (K_{11} \sin^2 \theta + K_{33} \cos^2 \theta) \ddot{\theta} - (K_{11} - K_{33}) \frac{\sin 2\theta}{2} \dot{\theta}^2 = 0, \quad (85)$$

with the *two* boundary conditions

$$(K_{11} \sin^2 \theta_1 + K_{33} \cos^2 \theta_1) \dot{\theta}_1 + \frac{\partial W(\theta_1)}{\partial \theta_1} = 0, \quad (86)$$

$$-(K_{11} \sin^2 \theta_2 + K_{33} \cos^2 \theta_2) \dot{\theta}_2 + \frac{\partial W(\theta_2)}{\partial \theta_2} = 0. \quad (87)$$

Now the variational problem is well posed because the second-order differential equation (85) has only two boundary conditions. Dubois-Violette and de Gennes [27] studied the same kind of problem in the special case of a semi-infinite NLC sample lying in the semispace $z > 0$ with $\Delta f_h^i(\theta, z) = B(\sin^2 \theta)/z^3$. They obtained an analytical expression for the equilibrium director angle and showed that a sharp distortion occurs in a very thin interfacial layer. More recently Rajteri *et al.* [30] considered the Nehring-Saupe interaction energy and showed that the function $\theta(z)$ that minimizes F_{se} is in satisfactory *quantitative* agreement with the solution that is obtained by numerical minimization of the molecular free energy F .

In conclusion, the K_{13} term that appears in the Nehring-Saupe surface free energy has a well-defined physical meaning: It represents a physical source of interfacial distortions. A zero value of K_{13} means that the molecular interactions do not favor the occurrence of these distortions. This occurs, for instance, if the interaction law does not depend on the orientation of the intermolecular vector \mathbf{u} [$i=0$ and $j=0$ in Eqs. (39) and (40)]. The mathematical problems generated by the presence of the K_{13} term in the first-order elastic free energy can be removed by introducing higher-order contributions using either the second-order elastic free energy or the semielastic free energy. Both these approaches provide an approximate but qualitatively correct description of some features of the interfacial layer. However, the second-order approach is restricted to director distortions of very small amplitude ($\theta \ll 1$), while the semielastic model is not affected by this restriction. Furthermore, according to Ref. [30], the semielastic approach leads to better quantitative agreement (within 10%) with the results obtained from the numerical minimization of the molecular free energy.

B. The elastic surface free energy and the thermodynamic surface free energy

In Sec. II we obtained the surface elastic free energy density F_s of a NLC by making the expansion of a simple molecular free-energy functional. Below we will call this surface free energy the *elastic surface free-energy density*. According to Sec. IV A, the elastic surface free energy gives important information about some specific features of the interfacial field. We emphasize, however, that F_s is a physical parameter completely different from the *thermodynamic surface free-energy density* F_s^{th} that appears in the classical continuum theory of NLCs [31]. To clarify the fundamental difference between the elastic surface free energy and the thermodynamic one, we discuss a simple example. Consider the case of a nematic layer of thickness d sandwiched between two *identical* solid plates at $z = -d/2$ and $d/2$, respectively. The two solid plates favor a director alignment along the z axis (homeotropic anchoring). A uniform magnetic field \mathbf{H} is applied at an angle β with the z axis. In order to simplify the theoretical expressions, we make the following assumptions: (a) the β angle is very small ($\beta \ll 1$) and (b) the bulk director field is a planar field $\mathbf{n} = (\sin \theta, 0, \cos \theta)$. From condition (a) we deduce that $\theta(z) \ll 1$ everywhere.

Then all the contributions to the bulk free energy that are of order higher than θ^2 and β^2 can be disregarded. In particular, $K_{11} \sin^2 \theta + K_{33} \cos^2 \theta \approx K_{33}$. In the continuum theory, the NLC sample has to be considered as bulklike up to the interfaces. Then the bulk free energy per unit surface area is

$$\mathcal{F}_{\text{bulk}} = \int_{-d/2}^{+d/2} \left\{ \frac{K_{33}}{2} (\dot{\theta})^2 - \frac{\chi_a H^2}{2} [1 - (\theta - \beta)^2] \right\} dz, \quad (88)$$

where the second term represents the magnetic free-energy density for $\theta - \beta \ll 1$ and $\chi_a > 0$ is the anisotropy of the diamagnetic susceptibility [1]. The variational approach leads to the Euler-Lagrange bulk equation

$$\ddot{\theta} = \frac{\theta - \beta}{\xi^2}, \quad (89)$$

where $\xi = (K_{33}/\chi_a)^{1/2}/H$ is the magnetic coherence length [1]. Since the NLC layer is sandwiched between two identical plates, the physical solutions of Eq. (89) have to be even or odd functions of z . The low-energy solution is the even solution

$$\theta(z) = \beta + A \cosh(z/\xi), \quad (90)$$

where A is a free integration constant. It is convenient to rewrite $\theta(z)$ in Eq. (90) in the equivalent form

$$\theta(z) = \beta + (\theta_{\text{surf}} - \beta) \frac{\cosh\left(\frac{z}{\xi}\right)}{\cosh\left(\frac{d}{2\xi}\right)}, \quad (90')$$

where we have defined the constant $\theta_{\text{surf}} = A \cosh(d/2\xi) + \beta$. θ_{surf} is a free parameter that corresponds to the value of $\theta(z)$ in Eq. (90) at the two surfaces $z = -d/2$ and $d/2$ [$\theta_{\text{surf}} = \theta(-d/2) = \theta(d/2)$]. Of course, the free-energy density in Eq. (88) cannot describe the interfacial behavior. First of all, the interfacial local free-energy density is no longer given by the simple bulk Oseen-Frank form because the local elastic constants become z dependent and different interfacial energy contributions appear (see the Introduction). Furthermore, also other interfacial phenomena that were not taken into account by the Nehring-Saupe molecular model used in Sec. II play an important role in the interfacial layer. For instance, a local biaxiality [32], a smectic ordering [33], and spatial variations of the order parameter [33] can occur very close to the interfaces and the definition itself of a local director field in the interfacial layer becomes questionable. This means that the equilibrium molecular configuration M_{eq} that minimizes the exact total free energy of the NLC will be very complex in the interfacial layers. However, far from the interfaces, the local free-energy density is well represented by the Oseen-Frank bulk free energy. Then, far from the interfaces, the equilibrium molecular configuration M_{eq} will be reduced to the equilibrium uniaxial configuration described by $\theta(z)$ in Eq. (90'), with a well-defined value $\bar{\theta}_{\text{surf}}$ of the free parameter θ_{surf} . This means that the bulk director field that is given by the continuum theory with $\theta_{\text{surf}} = \bar{\theta}_{\text{surf}}$ represents the exact bulk equilibrium configuration. Note

that θ_{surf} is different from the surface angle θ_s considered in Secs. II and III because it does not represent the actual average orientation of the long molecular axes at the surface, but corresponds only to the extrapolation of the bulk director field on the surface. This surface angle is called the *extrapolated surface director angle*. The only aim of the continuum theory is to find the extrapolated surface angle $\bar{\theta}_{\text{surf}}$ that corresponds to the extrapolation of the exact equilibrium bulk director field. The study of the interfacial molecular configuration can only be the object of more or less approximate models of the interfacial layer, for instance, the N th-order elastic theories and the semielastic approach. By substituting $\theta(z)$ of Eq. (90') into Eq. (88), we obtain the bulk free energy

$$\mathcal{F}_{\text{bulk}} = F_0 + \frac{K_{33}(\theta_{\text{surf}} - \beta)^2}{2\xi} \frac{\sinh\left(\frac{d}{\xi}\right)}{\cosh^2\left(\frac{d}{2\xi}\right)}, \quad (91)$$

where F_0 is an inessential contribution that is independent of θ_{surf} . The bulk free energy does not take into account the excess of free energy that is stored in the interfacial layers where the molecular configuration and the local free-energy density are very different from the bulk energy. Then the exact total free energy \mathcal{F}_{tot} is different from $\mathcal{F}_{\text{bulk}}$. This leads naturally to the definition of the thermodynamic surface free-energy density

$$\mathcal{F}_s^{\text{th}} = \frac{\mathcal{F}_{\text{tot}} - \mathcal{F}_{\text{bulk}}}{2}. \quad (92)$$

The coefficient 2 in Eq. (92) is due to the presence of two identical interfaces and the choice of the even solution of Eq. (89). Since \mathcal{F}_{tot} represents the exact total free energy that corresponds to the exact molecular configuration, $\mathcal{F}_s^{\text{th}}$ is a macroscopic physical parameter that takes into account implicitly any free-energy contribution that has been disregarded in the bulk free energy $\mathcal{F}_{\text{bulk}}$. Yokoyama showed [31] that $\mathcal{F}_s^{\text{th}}$ is completely determined once the bulk director field in Eq. (90') is given. Then $\mathcal{F}_s^{\text{th}}$ can depend only on the macroscopic parameters that characterize the bulk director field. For a proof of this important but not obvious property of the thermodynamic surface free energy we refer the reader to the sound Yokoyama paper [31]. In the present case of the NLC subjected to the tilted magnetic field, the surface free energy can depend only on the macroscopic parameters θ_{surf} , β , and ξ that enter the bulk director field in Eq. (90'). Note that, in principle, the thermodynamic surface free energy can depend also on the parameters β and ξ that characterize the external field. For fixed values of β and H , $\mathcal{F}_s^{\text{th}}$ is a function $\mathcal{F}_s^{\text{th}}(\theta_{\text{surf}})$ of the extrapolated surface director angle θ_{surf} . This property makes the thermodynamic surface free energy $\mathcal{F}_s^{\text{th}}$ a physical parameter that is completely different from the elastic surface free energy F_s that depends on the actual surface angle θ_s (see Sec. II). If the explicit dependence of $\mathcal{F}_s^{\text{th}}(\theta_{\text{surf}})$ on θ_{surf} is known, the equilibrium value $\bar{\theta}_{\text{surf}}$ can be obtained by solving the equilibrium equation $\partial(2\mathcal{F}_s^{\text{th}} + \mathcal{F}_{\text{bulk}})/\partial\theta_{\text{surf}} = 0$. This procedure leads always to a well-posed mathematical

problem. Therefore, according to Yokoyama [31], no paradox arises within a consistent continuum theory of NLCs.

The discussion above shows that the exact bulk equilibrium director field can be easily found if the function $\mathcal{F}_s^{\text{th}}(\theta_{\text{surf}})$ is known. The knowledge of the explicit dependence of $\mathcal{F}_s^{\text{th}}$ on the extrapolated surface director field represents a fundamental but still open problem for the continuum theory. In particular, it has not yet been clearly established if a normal-derivative term can enter the thermodynamic surface free energy. Note that such a derivative term has to be intended as the extrapolated surface derivative of the bulk director angle in Eq. (90'), that is, $\pm(\theta_{\text{surf}} - \beta)\tanh(d/2\xi)$. Then $\mathcal{F}_s^{\text{th}}$ is yet a function of θ_{surf} and the surface free energy does not lead to any variational problem [10–12]. In a recent paper, using the density-functional theory, Yokoyama showed that some surface contributions proportional to the normal derivative of the extrapolated director field could be present in the thermodynamic surface free energy [20]. However, several years ago Faetti [13] showed that a normal-derivative term leads to a nonconservation of the angular momentum for a planar director field. More recently Stallinga and Vertogen [15] generalized this theoretical result to more general three-dimensional problems. Then they argued that the thermodynamic surface free energy cannot depend on the normal-director derivative.

Below we will use the example of the NLC layer lying in a tilted magnetic field with $\beta \ll 1$ and $\theta \ll 1$ to show that the absence of the normal-director derivative in the thermodynamic surface free energy is consistent with the predictions of the higher-order theories. This simple example will allow us to point out clearly the basic differences and the relation between the elastic surface free energy F_s and the thermodynamic surface free energy $\mathcal{F}_s^{\text{th}}$. The N th-order elastic free energy is given by the sum of the first-order elastic free energy obtained in Sec. II, the magnetic free energy, and an N th-order term F_N that contains the elastic contributions of order higher than $(R_{\text{int}}/L_{\text{mac}})^2$ and lower than $(R_{\text{int}}/L_{\text{mac}})^{2N+1}$. Due to the condition $\theta \ll 1$, we can disregard contributions of order higher than θ^2 and the effective surface elastic parameter $K_{13}^{\text{eff}}(\cos \theta_s)$ in Eq. (49) is reduced to a constant $K_{13}^{\text{eff}} = K_h^e(1) + K_{13}$. Furthermore, in the present case (homeotropic anchoring), the surface free energy $F_s(\theta_s) = F_s^i(\theta_s) + F_s^e(\theta_s)$ is reduced to $W_s + W_0\theta_s^2/2$, where W_0 is the anchoring energy coefficient and W_s is an inessential constant that will be disregarded. The N th-order free energy per unit surface area for an *even* function $\theta(z)$ is

$$\mathcal{F}_{\text{tot}}^N = \left\{ W_0\theta_s^2 + 2K_{13}^{\text{eff}}\theta_s\dot{\theta}_s + \int_{-d/2}^{+d/2} \frac{K_{33}}{2} (\dot{\theta})^2 - \frac{\chi_a H^2}{2} [1 - (\theta - \beta)^2] dz \right\} + F_N, \quad (93)$$

with

$$F_N = \int_{-d/2}^{+d/2} f_N(\theta; \theta_{,1}; \theta_{,2}; \dots; \theta_{,N}) dz, \quad (94)$$

where symbols $\theta_{,j}$ with $j = 1, \dots, N$ denote the N th derivative of the function $\theta(z)$. The function $f_N(\theta; \theta_{,1}; \theta_{,2}; \dots; \theta_{,N})$ in

Eq. (94) is a quadratic function of $\theta, \theta_{,1}, \theta_{,2}, \dots$, and $\theta_{,N}$. The explicit expression of the higher-order function f_N can be found in Appendix B of Ref. [13]. Minimization of the functional $\mathcal{F}_{\text{tot}}^N$ using the variational method leads to a linear differential equation for $\theta(z)$ of order $2N$. The even function that solves the bulk Euler-Lagrange equation has the general form [13]

$$\theta_N(z) = \Delta\theta_N(z) + \theta_{\text{mac}}^N(z), \quad (95)$$

with

$$\theta_{\text{mac}}^N(z) = \beta + A_N \cosh(z/\xi) \quad (96)$$

and

$$\Delta\theta_N(z) = \sum_{j=2}^N B_j h_j(z). \quad (97)$$

A_N and B_2, B_3, \dots, B_N are N arbitrary constants, while $h_j(z) = \cosh(z/\delta_j)$ with $\delta_j \approx R_{\text{int}}$. The function $\Delta\theta_N(z)$ goes rapidly to zero out of two very thin interfacial layers and thus $\theta_{\text{mac}}^N(z)$ has to be identified with the macroscopic bulk director field that appears in the continuum theory [see Eq. (90)]. Setting $A_N = (\theta_{\text{surf}} - \beta)/\cosh(d/2\xi)$ in Eq. (96), one recovers the bulk solution given in Eq. (90'). Substitution of the function $\theta_N(z)$ into Eq. (93) leads to $\mathcal{F}_{\text{tot}}^N = F(\theta_{\text{surf}}, B_2, \dots, B_N)$, which is a quadratic function of $\theta_{\text{surf}}, B_2, \dots, B_N$. The unknown coefficients $\theta_{\text{surf}}, B_2, \dots, B_N$ that minimize $F(\theta_{\text{surf}}, B_2, \dots, B_N)$ can be obtained by solving the system of N linear equations $\partial F/\partial \theta_{\text{surf}} = 0, \partial F/\partial B_2 = 0, \dots, \partial F/\partial B_N = 0$. It can be shown, after a tedious but straightforward analysis, that these equations are equivalent to the linear boundary conditions that were obtained in Ref. [13] using the standard variational method. For a given value of the surface extrapolated angle θ_{surf} , the set of $N-1$ linear equations $\partial F/\partial B_2 = 0, \dots, \partial F/\partial B_N = 0$ leads to well-defined values $B_2(\theta_{\text{surf}}), \dots, B_N(\theta_{\text{surf}})$ of the unknown interfacial parameters B_2, B_3, \dots, B_N in terms of θ_{surf} . This means that, in agreement with Yokoyama's general analysis, for a given bulk director field having the general form in Eq. (90'), the interfacial field is univocally determined. Then it is natural to assign to this bulk director field the total free energy $\mathcal{F}_{\text{tot}}^N(\theta_{\text{surf}}) = F(\theta_{\text{surf}}, B_2(\theta_{\text{surf}}), \dots, B_N(\theta_{\text{surf}}))$. The thermodynamic surface free-energy density that corresponds to the N th-order elastic model is

$$\mathcal{F}_s^{\text{Nth}}(\theta_{\text{surf}}) = \frac{\mathcal{F}_{\text{tot}}^N(\theta_{\text{surf}}) - \mathcal{F}_{\text{bulk}}(\theta_{\text{surf}})}{2}, \quad (98)$$

where $\mathcal{F}_{\text{bulk}}(\theta_{\text{surf}})$ is the bulk free energy in Eq. (91). Note that the thermodynamic surface free energy depends on θ_{surf} , in agreement with Yokoyama's general analysis [31]. The equilibrium extrapolated angle $\bar{\theta}_{\text{surf}}$ is obtained by solving the boundary condition

$$2 \frac{\partial \mathcal{F}_s^{\text{Nth}}(\theta_{\text{surf}})}{\partial \theta_{\text{surf}}} + \frac{\partial \mathcal{F}_{\text{bulk}}(\theta_{\text{surf}})}{\partial \theta_{\text{surf}}} = 0. \quad (99)$$

The total free energy $\mathcal{F}_{\text{tot}}^N(\theta_{\text{surf}})$ in Eq. (98) has been obtained by substituting in Eq. (93) the director angle $\theta_N(z)$, which is

given in Eqs. (95)–(97) with $B_2 = B_2(\theta_{\text{surf}}), \dots, B_N = B_N(\theta_{\text{surf}})$. Since $\theta_N(z)$ depends on the magnetic coherence length ξ and the angle β , the thermodynamic surface free energy could also depend on these parameters. To obtain the explicit form of $\mathcal{F}_s^{\text{Nth}}(\theta_{\text{surf}})$ we can exploit the theoretical results already found in [13]. Indeed, according to our analysis, the surface angle θ_{surf} that solves Eq. (99) is the solution of the system of linear equations $\partial F / \partial \theta_{\text{surf}} = 0$, $\partial F / \partial B_2 = 0, \dots, \partial F / \partial B_N = 0$. On the other hand, these equations are fully equivalent to the boundary conditions that were obtained in Ref. [13] using the standard variational method. Then the solution of Eq. (99) has to correspond to the solution that was obtained in Ref. [13]. In that paper it was shown that θ_{surf} has to satisfy the simple equation

$$\frac{\partial [W_N \theta_{\text{surf}}^2]}{\partial \theta_{\text{surf}}} + \frac{\partial \mathcal{F}_{\text{bulk}}(\theta_{\text{surf}})}{\partial \theta_{\text{surf}}} = 0, \quad (100)$$

where W_N is a constant coefficient that is independent of β and ξ . By comparing Eqs. (100) and (99) we infer that the bulk equilibrium director angle $\theta_{\text{mac}}^N(z)$ that minimizes the complex N th-order functional can be always obtained using the standard continuum theory with the thermodynamic surface free energy $W_N \theta_{\text{surf}}^2 / 2$. Therefore, as far as the bulk director field is concerned, the continuum free energy with $\mathcal{F}_s^{\text{Nth}}(\theta_{\text{surf}}) = W_N \theta_{\text{surf}}^2 / 2$ and $\mathcal{F}_{\text{bulk}}$ given in Eq. (88) is completely equivalent to the much more complex N th-order free energy. This result holds at any order N and thus we can expect that it remains satisfied also for $N \rightarrow \infty$.

Although the simple example above and other indirect arguments [14,15] suggest strongly that no normal-derivative term can enter the thermodynamic surface free energy, there is no definitive proof for this ansatz. Therefore, the knowledge of the general expression of the thermodynamic surface free energy remains an open problem that needs further theoretical and experimental investigations. On the contrary, according to the analysis in Sec. II and III, the presence of a normal-derivative term in the elastic surface free energy is obvious. Within an approximate elastic model of the interfacial layer, this surface term has a well-defined physical meaning: It represents the source for sharp interfacial distortions.

V. CONCLUDING REMARKS

In this paper we showed that the Somoza-Tarazona paradox is due to an incomplete analysis of the boundary effects. If all the boundary effects are taken into account, the normal-derivative term in the elastic surface free energy is independent of the nonlocal to local mapping. Simple relations that must be satisfied by the surface normal-derivative term have been obtained using the Nehring-Saupe molecular approach and exploiting the symmetry properties of the intermolecular energy. The surface-derivative term contains an effective constant K_{13}^{eff} that depends on the properties of the NLC and on the nature of the substrate. Therefore, except for the very special case of a free surface ($K_h^e = 0$), the surface elastic constant is a true surface parameter that can depend on the surface director angle as well as on the anchoring energy.

It is important to compare our theoretical results with those obtained by other authors on the same subject, in par-

ticular, by Somoza and Tarazona [19] and by Yokoyama [20]. Somoza and Tarazona showed that the surface elastic constant K_{13} that is obtained from the integration of the bulk free-energy density depends on the nonlocal to local mapping. They concluded that such an elastic constant is not a well-defined physical parameter. This conclusion is in a complete agreement with the result of our calculation of the bulk surfacelike elastic constant that is found to depend explicitly on the mapping parameter a [see Eq. (67)]. Therefore, we agree with Somoza and Tarazona that the classical bulk Nehring-Saupe constant is not a well-defined physical parameter. However, our theoretical results demonstrate also that the total surface elastic constant is independent of mapping and thus is a well-defined physical parameter.

As far as Yokoyama's paper [20] is concerned, we recall briefly the main results of that paper. Yokoyama used the functional-density theory and showed that the linear elastic terms [the second integral in Eq. (8) of the present paper] vanish at first order in $\delta \mathbf{n}$. In Appendix C of his paper he showed that this theoretical result comes directly from the symmetry properties of the interaction law. Then he concluded that the bulk surfacelike elastic constant is zero. The vanishing of the linear elastic term is in complete agreement with the analysis made by us in Sec. II and in Ref. [21]. Indeed, at first order in θ_s , the elastic linear integral in Eq. (8) is reduced to $F_1(\theta_s, \theta_s) + F_{13}(\theta_s, \theta_s)$, which is zero. However, we emphasize here that Eq. (8) is obtained using the standard mapping and thus the vanishing of the linear term in the elastic integral in Eq. (8) is a direct consequence of this special choice. As a matter of fact, if a different mapping is used, the linear elastic contribution is reduced to $F_1^a(\theta_s, \theta_s) + F_{13}^a(\theta_s, \theta_s)$, which is a function of the mapping parameter a and is different from zero in the general case ($a \neq 0, a \neq 1$). According to our analysis, the separation of the surface elastic energy into bulk and interfacial contributions depends strongly on the mapping that is used and thus it is somewhat arbitrary to decide what is really a bulk contribution and what is an interfacial contribution. Then we do not agree with Yokoyama's conclusion that the bulk constant K_{13} must always be zero. In his paper Yokoyama analyzed also the specific interfacial contributions due to the homogeneous term in the interfacial layer. He showed that the interfacial interactions lead to some surface contributions that are linear in the z derivative of the surface angle. In the special cases of homeotropic ($\theta_s = 0$) and planar anchoring ($\theta_s = \pi/2$), Yokoyama's surface terms have the same functional form as those obtained in the present paper. However, we emphasize here that a direct comparison between our surface terms and Yokoyama's is not possible because they are related to intrinsically different physical parameters: the actual director orientation at the surface in our paper and the "extrapolated" surface director angle in Yokoyama's paper. Although the elastic surface free energy represents a useful parameter to build approximate models of the interfacial field (the N th-order elastic theories), it cannot appear in a consistent continuum theory of NLCs. The thermodynamic surface free energy that appears in the continuum theory is a different macroscopic parameter that depends on the extrapolated surface director field. The explicit dependence of the thermodynamic surface free energy on the extrapolated sur-

face director field is still the subject of some debate in the literature. In particular, it is not completely clear if a normal-derivative term can appear in such a surface free energy, although there are some indirect arguments that suggest the absence of such a term.

The Nehring-Saupe molecular model used in Secs. II and III to obtain the elastic free energy makes use of strong simplifying assumptions: perfect nematic order ($S=1$) and a uniform single-particle density in the NLC. Then the expressions of the elastic constants that have been obtained in the present paper could be modified appreciably by using more accurate molecular approaches such as the density-functional theory [17,20]. However, the mapping independence of the K_{13}^{eff} constant has been obtained by exploiting only the symmetry properties of the molecular interactions. Thus we think that this theoretical result has a more general validity.

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APPENDIX A

In this appendix we show that properties (i) and (iii) of Sec. II A are a direct consequence of the inversion symmetry in the real and the director isotopic space (see Appendix C in [20]). This symmetry leads to the equality

$$g(\mathbf{n}, \mathbf{n}', \mathbf{u}) = g(\mathbf{n}', \mathbf{n}, -\mathbf{u}), \quad (\text{A1})$$

where $\mathbf{u} = \mathbf{r} - \mathbf{r}'$. It is convenient to use for $g(\mathbf{n}, \mathbf{n}', \mathbf{u})$ the explicit form given in Eq. (39):

$$g(\mathbf{n}, \mathbf{n}', \mathbf{u}) = - \sum_{i,j,k} J_{i,j,k}(u) \left(\mathbf{n} \cdot \frac{\mathbf{u}}{u} \right)^i \left(\mathbf{n}' \cdot \frac{\mathbf{u}}{u} \right)^j (\mathbf{n} \cdot \mathbf{n}')^k. \quad (\text{A2})$$

Due to the symmetry property in Eq. (A1), we infer that $i+j$ is an even integer and $J_{i,j,k}(u)$ is symmetric with respect to i and j . This means that $g(\mathbf{n}, \mathbf{n}', \mathbf{u}) = g(\mathbf{n}, \mathbf{n}', -\mathbf{u})$ and thus from Eq. (A1) we find

$$g(\mathbf{n}, \mathbf{n}', \boldsymbol{\mu}) = g(\mathbf{n}', \mathbf{n}, \mathbf{u}). \quad (\text{A3})$$

By setting $\mathbf{n}' = \mathbf{n} + \delta\mathbf{n}$ in Eq. (A3) we get $g(\mathbf{n}, \mathbf{n} + \delta\mathbf{n}, \mathbf{u}) = g(\mathbf{n} + \delta\mathbf{n}, \mathbf{n}, \mathbf{u})$ and thus

$$g(\mathbf{n}, \mathbf{n} + \delta\mathbf{n}, \mathbf{u}) - g(\mathbf{n}, \mathbf{n}, \mathbf{u}) = g(\mathbf{n} + \delta\mathbf{n}, \mathbf{n}, \mathbf{u}) - g(\mathbf{n}, \mathbf{n}, \mathbf{u}). \quad (\text{A4})$$

From the equality of the differentials in Eq. (A4), the equality of their Taylor expansions follows directly and thus

$$\left. \frac{\partial^k g(\mathbf{n}, \mathbf{n}', \mathbf{u})}{\partial n_j'^k} \right|_{\mathbf{n}' = \mathbf{n}} = \left. \frac{\partial^k g(\mathbf{n}, \mathbf{n}', \mathbf{u})}{\partial n_j^k} \right|_{\mathbf{n} = \mathbf{n}'}, \quad (\text{A5})$$

where k is an arbitrary integer. From Eq. (A5) property (iii) of the function $G(\theta_1, \theta_2, s)$ follows directly. From the equality $g(\mathbf{n}, \mathbf{n}', \mathbf{u}) = g(\mathbf{n}, \mathbf{n}', -\mathbf{u})$ we get $g(\theta_1, \theta_2, \mathbf{u}) = g(\theta_1, \theta_2, -\mathbf{u})$. Then

$$\begin{aligned} G(\theta_1, \theta_2, s) &= \frac{1}{2} \int_{-\infty}^{+\infty} du_x \int_{-\infty}^{+\infty} du_y g(\theta_1, \theta_2, u_x, u_y, s) \\ &= \frac{1}{2} \int_{-\infty}^{+\infty} du_x \int_{-\infty}^{+\infty} du_y g(\theta_1, \theta_2, -u_x, -u_y, -s) \\ &= G(\theta_1, \theta_2, -s). \end{aligned} \quad (\text{A6})$$

The last equality has been obtained by making the substitutions $-u_x \rightarrow u_x$ and $-u_y \rightarrow u_y$ in the second integral in Eq. (A6). Equation (A6) leads immediately to property (i) of the function $G(\theta_1, \theta_2, s)$ and its θ_1 and θ_2 derivatives.

APPENDIX B

Here we calculate explicitly the elastic constant K_{13} in terms of the characteristic parameters of the interaction law $g(\mathbf{n}, \mathbf{n}', \mathbf{u})$ given in Eq. (39). For the planar director field $\mathbf{n} = (\sin \theta, 0, \cos \theta)$, the function $g(\mathbf{n}, \mathbf{n}', \mathbf{u})$ becomes $g(\theta_1, \theta_2, u_x, u_y, u_z)$, where θ_1 and θ_2 are the angles that correspond to \mathbf{n} and \mathbf{n}' , while u_x , u_y , and u_z are the x , y , and z components of the vector \mathbf{u} . The function $F_{13}(\theta_s, \dot{\theta}_s)$ in Eq. (36) becomes

$$F_{13}(\theta_s, \dot{\theta}_s) = \frac{1}{2} \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} du_x \int_{-\infty}^{\infty} du_y z^2 g_2(\theta_s, u_x, u_y, z) \dot{\theta}_s, \quad (\text{B1})$$

where

$$g_2(\theta_s, u_x, u_y, z) = \left. \frac{\partial}{\partial \theta_2} g(\theta_1, \theta_2, u_x, u_y, z) \right|_{\theta_1 = \theta_2 = \theta_s}. \quad (\text{B2})$$

Using the explicit expression of $g(\mathbf{n}, \mathbf{n}', \mathbf{u})$ given in Eq. (39), the function $g_2(\theta_s, u_x, u_y, z)$ becomes

$$\begin{aligned} g_2(\theta_s, u_x, u_y, z) &= -\frac{1}{2} \left\{ \sum_{i,j,k} J_{ijk}(u) j [\mathbf{n}_s \cdot \hat{\mathbf{u}}]^{i+j-1} \left. \frac{\partial [\mathbf{n}' \cdot \hat{\mathbf{u}}]}{\partial \theta_2} \right|_{\mathbf{n}' = \mathbf{n} = \mathbf{n}_s} \right. \\ &\quad \left. + \sum_{i,j,k} J_{ijk}(u) k [\mathbf{n}_s \cdot \hat{\mathbf{u}}]^{i+j} \left. \frac{\partial [\mathbf{n} \cdot \mathbf{n}']}{\partial \theta_2} \right|_{\mathbf{n}' = \mathbf{n} = \mathbf{n}_s} \right\}, \end{aligned} \quad (\text{B3})$$

where $\hat{\mathbf{u}} = \mathbf{u}/u$ and \mathbf{n}_s denotes the director at the surface. Now we note that $\partial[\mathbf{n} \cdot \mathbf{n}']/\partial \theta_2 = \partial[\cos(\theta_1 - \theta_2)]/\partial \theta_2 = 0$ for $\theta_1 = \theta_2 = \theta_s$ and $\partial n_x'/\partial \theta_2 = \cos \theta_2 = n_z'$ and $\partial n_z'/\partial \theta_2 = -\sin \theta_2 = -n_x'$. Then

$$\left. \frac{\partial [\mathbf{n}' \cdot \hat{\mathbf{u}}]}{\partial \theta_2} \right|_{\mathbf{n}' = \mathbf{n} = \mathbf{n}_s} = \frac{n_{sz} u_x - z n_{sx}}{u}, \quad (\text{B4})$$

where $u = \sqrt{u_x^2 + u_y^2 + z^2}$. Then $F_{13}(\theta_s, \dot{\theta}_s)$ is reduced to

$$F_{13}(\theta_s, \dot{\theta}_s) = -\frac{1}{4} \int_{-\infty}^{\infty} du_x \int_{-\infty}^{\infty} du_y \int_{-\infty}^{\infty} dz \sum_{i,j,k} J_{ijk}(u) z^2 \times \frac{j[\mathbf{n}_s \cdot \mathbf{u}]^{i+j-1}}{u^{i+j}} (n_{sz}u_x - n_{sx}z). \quad (\text{B5})$$

To solve the integrals in Eq. (B5) it is convenient to pass to the coordinates u'_x , u'_y , and z' with the z' axis that is parallel to \mathbf{n}_s and to use polar coordinates ξ , ϕ , and r , where ξ denotes the polar angle with respect to the z' axis and ϕ denotes the azimuthal angle. With this choice, $F_{13}(\theta_s, \dot{\theta}_s)$ becomes

$$F_{13}(\theta_s, \dot{\theta}_s) = I_1 + I_2 + I_3, \quad (\text{B6})$$

where

$$I_1 = -\frac{1}{4} \int_0^{\infty} dr \int_{4\pi} d\Omega r^4 \cos^2 \theta_s \sum_{i,j,k} j J_{ijk}(r) \times (\cos \xi)^{i+j+1} \sin \xi \cos \phi, \quad (\text{B7})$$

$$I_2 = -\frac{1}{4} \int_0^{\infty} dr \int_{4\pi} d\Omega r^4 \sin^2 \theta_s \sum_{i,j,k} j J_{ijk}(r) \times (\cos \xi)^{i+j-1} \sin^3 \xi \cos^3 \phi, \quad (\text{B8})$$

and

$$I_3 = -\frac{1}{4} \int_0^{\infty} dr \int_{4\pi} d\Omega r^4 \sin 2\theta_s \sum_{i,j,k} j J_{ijk}(r) \times (\cos \xi)^{i+j} \sin^2 \xi \cos^2 \phi. \quad (\text{B9})$$

$d\Omega$ is the infinitesimal solid angle. By performing the integrals in Eqs. (B7)–(B9), we find $I_1 = I_2 = 0$, while exploiting the property that $i + j$ is an even number, it is easy to show that I_3 is given by expressions (37) and (40). Using the same procedure, it is easy to show that the integral in Eq. (34) leads to Eq. (38) with K_{11} and K_{33} expressed in terms of the characteristic parameters of the interaction energy.

APPENDIX C

Here we show that Eqs. (75), (77), and (78) come directly from Eqs. (70), (72), and (73), respectively. We first consider the function

$$F_s^i(\theta_s) = \int_{-\infty}^{\infty} dz \left[\int_{-\infty}^{\infty} G(\theta, \theta, z - z') dz' - f_0 \right]. \quad (\text{C1})$$

By making the change of variables $Z = az + (1 - a)z'$ and $s = z - z'$, we get

$$F_s^i(\theta_s) = \int_{-\infty}^{\infty} dZ \left[\int_{z/a}^{-z/(1-a)} G(\theta, \theta, s) ds - f_0 \right], \quad (\text{C2})$$

which is equal to the function $F_s^{ia}(\theta_s)$ in Eq. (70). Then $F_s^{ia}(\theta_s) = F_s^i(\theta_s)$, in agreement with Eq. (75). Now we consider the function

$$F_h^{ia}(\theta_s, \dot{\theta}_s) = \int_{-\infty}^0 dz z \left. \frac{\partial \Delta f_h^{ia}(\theta, z)}{\partial \theta} \right|_{\theta=\theta_s} \dot{\theta}_s, \quad (\text{C3})$$

which was defined in Eq. (72). Equation (C3) can be integrated by parts with respect to the part function z^2 . We get

$$F_h^{ia}(\theta_s, \dot{\theta}_s) = \left. \frac{z^2}{2} \frac{\partial \Delta f_h^{ia}(\theta, z)}{\partial \theta} \right|_{\theta=\theta_s} \dot{\theta}_s \Big|_{z=-\infty}^{z=0} - \int_{-\infty}^0 dz \times \frac{z^2}{2} \frac{d}{dz} \left\{ \left. \frac{\partial \Delta f_h^{ia}(\theta, z)}{\partial \theta} \right|_{\theta=\theta_s} \dot{\theta}_s \right\}. \quad (\text{C4})$$

The first term on the right-hand side vanishes due to the property $G(\theta_1, \theta_2, \infty) = 0$. Substituting in the second term the explicit expression of $\Delta f_h^{ia}(\theta, z)$ as given in Eq. (63), we find

$$F_h^{ia}(\theta_s, \dot{\theta}_s) = - \int_{-\infty}^0 dz z^2 \frac{d}{dz} \left\{ \int_{z/a}^{-z/(1-a)} ds G_2(\theta_s, s) \dot{\theta}_s \right\}, \quad (\text{C5})$$

where we have used the property $G_1(\theta_s, s) + G_2(\theta_s, s) = 2G_2(\theta_s, s)$. Now we use the identity

$$\frac{d}{dz} \left\{ \int_{z/a}^{-z/(1-a)} ds G_2(\theta_s, s) \dot{\theta}_s \right\} = - \frac{G_2(\theta_s, z/a) \dot{\theta}_s}{a} - \frac{G_2(\theta_s, z/(1-a)) \dot{\theta}_s}{1-a}. \quad (\text{C6})$$

To write the second term on the right-hand side in Eq. (C6) we have used the property $G_2(\theta_s, s) = G_2(\theta_s, -s)$. Substituting Eq. (C6) into Eq. (C5), we get

$$F_h^{ia}(\theta_s, \dot{\theta}_s) = \int_{-\infty}^0 dz z^2 \frac{G_2(\theta_s, z/a) \dot{\theta}_s}{a} + \int_{-\infty}^0 dz z^2 \frac{G_2(\theta_s, z/(1-a)) \dot{\theta}_s}{1-a}. \quad (\text{C7})$$

By making the variable changes $z \rightarrow z/a$ and $z \rightarrow z/(1-a)$ in the two integrals we find

$$F_h^{ia}(\theta_s, \dot{\theta}_s) = [a^2 + (1-a)^2] \int_{-\infty}^0 dz z^2 G_2(\theta_s, z) \dot{\theta}_s, \quad (\text{C8})$$

which is the equality in Eq. (77). Finally, operating in the same way on the function $F_1^a(\theta_s, \dot{\theta}_s)$ defined in Eq. (73), we obtain the equality in Eq. (78).

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