Full energy expression of a uniaxial nematic phase with spatially dependent density and order parameters: From microscopic to macroscopic theory

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We present a microscopic derivation of the full macroscopic energy expression of a spatially bounded uniaxial nematic phase. The surface is described by spatial variations of the density and scalar order parameters of all even orders. The method developed in the paper allowed us to unambiguously separate the surface elastic K_{24} and K_{13} terms and isotropic and anisotropic surface tension (anchoring). The full energy expression incorporating variations of the director, scalar order parameters, and density is obtained. The macroscopic coefficients are derived in terms of the isotropic and anisotropic fractions of the microscopic intermolecular interaction. An important physical consequence of the obtained formulas, in particular, is that the observed considerable difference $K_{33}-K_{11}$ between the bend and splay elastic constants unambiguously indicates that (i) the intermolecular interaction has a large anisotropic fraction, and thus, the effective constant K_{13} and intrinsic anchoring are considerable; (ii) at least some scalar order parameters of order four and higher are essentially nonzero. Relation of the developed theory with the Nehring-Saupe theory and Landau–de Gennes approach is considered.

I. INTRODUCTION

In spite of a considerable success in understanding complicated surface phenomena in a nematic liquid crystal (LC) (see reviews [1–5]), the studies of the recent decade have also revealed fundamental difficulties related to their incorporation and interpretation. Developing a consistent theory of surface phenomena requires the most general microscopic consideration of a uniaxial nematic phase. In particular, the theory has a connection to the Landau–de Gennes theory. Indeed, as the surface is represented by some surface layer where both the molecular density and scalar order parameters undergo spatial variations, a consistent approach has to incorporate not only director, but also the density and scalar order parameters [6]. Below we describe the current state of the problem concerning surface effects and other general problems of the theory of a nematic LC.

The two basic approaches in the physics of a nematic LC are the Nehring-Saupe theory and the Landau–de Gennes theory. In the Nehring-Saupe theory [7], the nematic phase is described by the director $\mathbf{n(x)}$ alone. The director deformations associated with director derivatives ∂n are assumed to be weak, $l_M \partial n \ll 1$, where l_M is the molecular length. The interaction between two points $\mathbf{x}$ and $\mathbf{x}'$ with the director $\mathbf{n}$ and $\mathbf{n}'$ is described by a function $G(\mathbf{n},\mathbf{n}')$ represented in the form $G(\mathbf{n},\mathbf{n}') = \Delta G(\mathbf{n},\mathbf{n}') + G(\mathbf{n},\mathbf{n})$, where

$$\Delta G(\mathbf{n},\mathbf{n}') = G(\mathbf{n},\mathbf{n}') - G(\mathbf{n},\mathbf{n}). \quad (1)$$

The surface is, however, missing in this approach since it essentially presupposes that the local symmetry in the vicinity of any spatial point inside the nematic body is the *symmetry of infinite nematic medium*. By virtue of this symmetry, on spatial integration the term $G(\mathbf{n},\mathbf{n})$ gives no director-dependent term, while $\Delta G(\mathbf{n},\mathbf{n}')$ results in elastic terms quadratic in $l_m \partial n$.

However, the surface elastic terms are sensitive to variation of the density and scalar order parameter [11] in the surface layer and thus cannot be considered in the scope of the Nehring-Saupe approach. In a spatially restricted body, both $\Delta G(\mathbf{n},\mathbf{n}')$ and $G(\mathbf{n},\mathbf{n})$ result in additional director-dependent energy terms. The kernel $\Delta G(\mathbf{n},\mathbf{n}')$ was shown to produce an elastic term F_1 linear in ∂n whose density vanishes in the bulk [8–10]. This term depends on the structure of a surface layer [11]. Moreover, the full expression for surface elastic terms linear in ∂n cannot be found by considering the kernel $\Delta G(\mathbf{n},\mathbf{n}')$ alone as the "nondeformational," the so-called homogeneous kernel $G(\mathbf{n},\mathbf{n})$ also contributes to it [12,13]. However, the total elastic contribution of $G(\mathbf{n},\mathbf{n})$ is not derived.

In spite of its simple form, the homogeneous kernel produces serious theoretical problems. It is known to contribute to the surface elastic terms, isotropic (**n**-independent) surface tension, anchoring (anisotropic, **n**-dependent surface tension), and the bulk **n**-independent term. However, so far these contributions have not been unambiguously separated from one another even in the simplified case when spatial inhomogeneity of the surface layer is disregarded. As a result, there are no full expressions for the surface elastic terms, no explicit local formulas (i.e., in form of an integral converging in the surface layer) for the anchoring and surface tension. This problem is solved in the present paper.

In a nematic phase, the effective pairwise potential $G(\mathbf{n},\mathbf{n}')$ depends on the modulus r of the separation vector $\mathbf{r} = \mathbf{x}' - \mathbf{x}$ and three **n**-dependent scalars: $(\mathbf{n \cdot n}')$, $(\mathbf{n \cdot r})$, and $(\mathbf{n}' \cdot \mathbf{r})$. Then, in general, one has

$$G(\mathbf{n},\mathbf{n}') = G_i[(\mathbf{n \cdot n}'),r] + \epsilon G_a[(\mathbf{n \cdot n}'),(\mathbf{n \cdot r}),(\mathbf{n}' \cdot \mathbf{r}),r], \quad (2)$$

where G_i is the isotropic fraction (does not depend on **r**) and

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G_a is the anisotropic fraction of the interaction potential; ϵ is a dimensionless coefficient showing relative magnitudes of the two fractions. This separation is essential as G_i and G_a lead to qualitatively different effects. In particular, G_a alone gives rise to the K_{13} term and intrinsic anchoring (i.e., anchoring induced by the interaction between nematogen molecules). Thus, if $\epsilon = 0$, then no problems associated with the spatial boundedness arise.

The standard idea is that ϵ is of the order of 1: examples are the induced-dipole induced-dipole, and Gay-Berne potential. In this and in a wider physical context, it would be highly desirable to get an independent indication as to how large an anisotropic fraction of the intermolecular potential can be. The hope to get such information has driven us to incorporating the scalar order parameters of all orders. This proved to be fruitful: the reliably observed difference $K_{33} - K_{11}$ between the bend and splay elastic constants is found to be proportional to ϵ and occurs only for nonzero scalar order parameters of orders higher than two. Since $K_{33} - K_{11}$ is considerable in known nematic LCs, this shows that the anisotropic interaction in nematogens is appreciable, and the problem of surface-induced elastic terms and intrinsic anchoring is indeed physically meaningful and practically important.

The phenomenological Landau–de Gennes theory considers smooth variations of **n** and the single scalar order parameter s_2. In this paper we develop a microscopic theory that along with smooth director variations incorporates both smooth and jumplike variations of the density and scalar order parameters of all even orders. As a result, we obtain microscopic formulas for all constants entering the macroscopic theory. In particular, the results throw the light on the origin of prediction of the Landau–de Gennes approach that the difference $K_{33} - K_{11}$ does not appear in the order s_2^2 (for the most recent publications, see Refs. [14,15]). It is also shown why the term linear in s_2, which can be, in principle, introduced in the Landau–de Gennes theory [14], does not actually appear.

In this paper we will be following the approach of Ref. [11] which considers a spatially restricted body and can be generalized as to incorporate all the order parameters and density. Another advantage of this approach is that, based on exploiting the inherent structure and symmetry of the theory, it drastically simplifies finding general relations between different quantities making specific calculations of no need at all. So are the results of this paper: they are obtained as general relations using known results of the Nehring-Saupe theory and the simple form [11] of the so-called K_{13} cancellation. Separating different energy terms from each other is achieved by means of Δ method which is developed in this paper and, similar to the approach of Ref. [11], does not involve specific calculations.

The paper is organized as following. In Sec. II, the general form of the effective pairwise potential is obtained from the microscopic energy expression and some formulas of the Nehring-Saupe theory employed later on are given. In Sec. III, the Δ method is introduced which allows for separating the elastic, anchoring, and other energy contributions of the pairwise potential of Sec. II, and general expressions for

these terms are derived. Section IV presents the total expressions for different energy terms. Section V is devoted to establishing a relation between the difference $K_{33} - K_{11}$, the form of the intermolecular potential, and the scalar order parameters. Section VI gives a brief resume of the obtained results.

II. GENERAL FORMULAS

A. The energy of pairwise interaction in a uniaxial nematic body

Here we incorporate spatial variations of the density ρ and scalar order parameters s_l in the macroscopic approach neglecting biaxiality. For brevity, we denote the function of a primed argument by the function with prime. Then the energy of a pairwise interaction of particles with orientational coordinates $\boldsymbol{\omega}$ and spatial coordinates **x** has the form

$$E = \frac{1}{2} \int d\mathbf{x}\, d\mathbf{x}' \int d\boldsymbol{\omega}\, d\boldsymbol{\omega}'\, gwg', \qquad (3)$$

where $g = g(\mathbf{x}, \boldsymbol{\omega})$ is the one-particle distribution function; $w = U g_2$, where $U = U[\boldsymbol{\omega} \cdot \boldsymbol{\omega}', (\mathbf{r} \cdot \boldsymbol{\omega})(\mathbf{r} \cdot \boldsymbol{\omega}'), r]$ is the microscopic pairwise interaction potential, and g_2 is the pair correlation function that can explicitly depend on **x** and **x**′ through the functions ρ, ρ', η and η', i.e., $g_2 = g_2[\boldsymbol{\omega}\boldsymbol{\omega}', (\mathbf{r} \cdot \boldsymbol{\omega})(\mathbf{r} \cdot \boldsymbol{\omega}'), r, \mathbf{x}, \mathbf{x}']$. Both U and g_2 are invariant under simultaneous permutations of $\boldsymbol{\omega}$ and $\boldsymbol{\omega}'$, and **x** and **x**′.

In a uniaxial phase $g = g(\mathbf{n} \cdot \boldsymbol{\omega}, \mathbf{x})$ that can be expanded in the even order Legendre polynomials P_l,

$$g(\mathbf{n} \cdot \boldsymbol{\omega}, \mathbf{x}) = \frac{\rho(\mathbf{x})}{4\pi}[1 + (2l+1)s_l(\mathbf{x})P_l(\mathbf{n} \cdot \boldsymbol{\omega})], \qquad (4)$$

where the summation over repeated indices is implied. The function $s_l(\mathbf{x})$ is considered as the l-order scalar order parameter, $l = 2, 4, \ldots$. Since $P_l(\mathbf{n} \cdot \boldsymbol{\omega})$ contains the $(\mathbf{n} \cdot \boldsymbol{\omega})$-independent constant $P_l(0)$, it is convenient to introduce the $(\mathbf{n} \cdot \boldsymbol{\omega})$-dependent part $\tilde{P}_l(\mathbf{n} \cdot \boldsymbol{\omega})$ of $P_l(\mathbf{n} \cdot \boldsymbol{\omega})$ and the l-dependent constant p_l,

$$\tilde{P}_l(\mathbf{n} \cdot \boldsymbol{\omega}) = (2l+1)[P_l(\mathbf{n} \cdot \boldsymbol{\omega}) - P_l(0)], \qquad (5)$$

$$p_l = \frac{1}{4\pi} \int d\boldsymbol{\omega}\, \tilde{P}_l(\mathbf{n} \cdot \boldsymbol{\omega}) = -(2l+1)P_l(0). \qquad (6)$$

Then, substituting Eq. (4) into Eq. (3), one has

$$E = I + F_\Delta + F_{0,1} + F_{0,2}, \qquad (7)$$

where

$$I = \frac{1}{2} \int d\mathbf{x}\, d\mathbf{x}'\, \rho\rho'(1 - 2p_l s_l + p_l p_{l'} s_l s'_{l'})\langle w \rangle, \qquad (8)$$

$$F_\Delta = \frac{1}{2} \int d\mathbf{x}\, d\mathbf{x}'\, \rho\rho'\, s_l s'_{l'} \Delta G_{ll'}, \qquad (9)$$

$$F_{0,1} = \frac{1}{2} \int d\mathbf{x}\, d\mathbf{x}'\, \rho\rho'\, s_l s'_{l'}[G_{ll'}(\mathbf{n}, \mathbf{n}) - 2p_{l'}G_l], \qquad (10)$$

$$F_{0,2} = \int d\mathbf{x}\, d\mathbf{x}'\, \rho\rho' s_l G_l. \tag{11}$$

Here $\langle \cdots \rangle = 1/(4\pi)^2 \int d\boldsymbol{\omega} d\boldsymbol{\omega}' \ldots$, and the kernels have the form

$$G_{ll'}(\mathbf{n},\mathbf{n}') = \langle \widetilde{P}_l(\mathbf{n}\cdot\boldsymbol{\omega}) w \widetilde{P}_{l'}(\mathbf{n}'\cdot\boldsymbol{\omega}') \rangle, \tag{12}$$

$$\Delta G_{ll'}(\mathbf{n},\mathbf{n}') = G_{ll'}(\mathbf{n},\mathbf{n}') - G_{ll'}(\mathbf{n},\mathbf{n}), \tag{13}$$

$$G_l(\mathbf{n},r) = \langle \widetilde{P}_l(\mathbf{n}\cdot\boldsymbol{\omega}) w \rangle. \tag{14}$$

The explicit symmetric dependence on $\mathbf{x}$ and $\mathbf{x}'$ is not indicated here for simplicity. The kernel G_l appeared first in Ref. [11]. Separating isotropic part w_i and anisotropic part w_a of the effective interaction w and the kernels (12) and (14), one has

$$w = w_i(\boldsymbol{\omega}\cdot\boldsymbol{\omega}',r) + \epsilon w_a[(\boldsymbol{\omega}\cdot\boldsymbol{\omega}'),(\mathbf{r}\cdot\boldsymbol{\omega})(\mathbf{r}\cdot\boldsymbol{\omega}'),r],$$

$$G_{ll'}(\mathbf{n},\mathbf{n}',r) = G_{ll',i}(\{w_i\}|(\mathbf{n}\cdot\mathbf{n}'),r)$$
$$+ \epsilon G_{ll',a}(\{w_a\}|(\mathbf{n}\cdot\mathbf{n}'),(\mathbf{n}\cdot\mathbf{r}),(\mathbf{n}'\cdot\mathbf{r}),r),$$
$$\tag{15}$$

$$G_l(\mathbf{n},r) = G_{l,i}(\{w_i\}|r) + \epsilon G_{l,a}(\{w_a\}|(\mathbf{n}\cdot\mathbf{r}),r),$$

where the curly brackets imply a functional dependence on the argument. Note, that in Eq. (3) the integration domains over both $\mathbf{x}$ and $\mathbf{x}'$ are not indicated which implies the *unrestricted space* R^3. The actual restriction of the integration to the body volume V and the presence of a surface and defects are related to the spatial behavior of ρ and s_l. The density ρ does not vanish only inside the body, for $\mathbf{x} \in V$, so that the integration is cut for $\mathbf{x} \notin V$ or, equivalently, for $\mathbf{x} \in R^3 \backslash V$ (the total three-dimensional space minus the volume). The surface S can be naturally associated with the layer where the density varies from its bulk value to zero. The order parameters s_l vanish outside a nematic phase thus indicating both the surface and the space occupied by a nematic phase.

Our task is to calculate elastic, anchoring, and all other contributions to the total energy E from the integrals (8)–(11). Before performing this, we will briefly give the main results of the elastic theory of an unrestricted nematic body in the form instructive to our following consideration.

B. Main results of the elasticity theory for an unrestricted nematic body (Nehring-Saupe theory)

The Nehring-Saupe theory is essentially the theory of an unrestricted body. It considers the energy of pairwise interaction in the form

$$E_{NS} = \frac{1}{2}\int_V d\mathbf{x} \int d\mathbf{x}'[\Delta G(\mathbf{n},\mathbf{n}') + G(\mathbf{n},\mathbf{n})],$$

where ΔG is defined in Eq. (1). The integration domain over $\mathbf{x}'$ is the *unrestricted space R^3 rather than the volume V*. This implies that the symmetry in the vicinity of each point $\mathbf{x}$ is the symmetry of infinite medium, and thus the boundary is

missing. For this reason, the only director-dependent contribution to E_{NS} comes from the kernel ΔG. Indeed, the integral $\int d\mathbf{x}' G(\mathbf{n},\mathbf{n}) = \int d\mathbf{r}\, G(\mathbf{n},\mathbf{n})$ is an $\mathbf{n}$-independent constant as the scalar $(\mathbf{nn}) = 1$ is the only one composed of $\mathbf{n}$.

In order to obtain the elastic free energy (FE) in a local form the pairwise potential is expanded in a power series of the components $\Delta n_i(\mathbf{x},\mathbf{x}') = n_i' - n_i$ of the director rotation vector up to the second order; the difference Δn_i is in turn expanded in a power series of the vector $\Delta \mathbf{x} \equiv \mathbf{r}$: $\Delta n_i(\mathbf{x}',\mathbf{x}) \simeq r_j \partial_j n_i + \frac{1}{2} r_j r_k \partial_{jk}^2 n_i'$. The result is the Nehring-Saupe elastic FE density f_{NS} in the form

$$f_{NS} = \frac{1}{2}\int d\mathbf{r}\, \Delta G(\mathbf{n},\mathbf{n}') \tag{16}$$

$$= \frac{1}{2}(K_{11}f_{11} + K_{22}f_{22} + K_{33}f_{33}) - K_{24}f_{24} + K_{13}f_{13}$$

with the standard infinite medium quadratic FE terms $f_{\alpha\beta}$ given by the formulas [7]

$$f_{11} = (\boldsymbol{\nabla}\cdot\mathbf{n})^2, \quad f_{22} = (\mathbf{n}\cdot\boldsymbol{\nabla}\times\mathbf{n})^2,$$

$$f_{33} = (\mathbf{n}\times\boldsymbol{\nabla}\times\mathbf{n})^2, \tag{17}$$

$$f_{24} = \boldsymbol{\nabla}\cdot\mathbf{f}_{24}, \quad f_{13} = \boldsymbol{\nabla}\cdot\mathbf{f}_{13},$$

where, for the later convenience, we introduced the vectors

$$\mathbf{f}_{24} = \mathbf{n}(\boldsymbol{\nabla}\cdot\mathbf{n}) - (\mathbf{n}\cdot\boldsymbol{\nabla})\mathbf{n}, \tag{18}$$

$$\mathbf{f}_{13} = \mathbf{n}(\boldsymbol{\nabla}\cdot\mathbf{n}).$$

The five elastic constants $K_{\alpha\beta}$ can be expressed in terms of the four integrals $K_{\alpha\alpha}^{(0)}$, $\alpha = 1, 2, 3$, and K_{13} [7],

$$K_{11} = K_{11}^{(0)} - 2K_{13}, \quad K_{33} = K_{33}^{(0)} + 2K_{13}, \tag{19}$$

$$K_{22} = K_{22}^{(0)},$$

$$K_{24} = (K_{11}^{(0)} + K_{22})/4. \tag{20}$$

We will only need the formula for K_{13}, i.e.,

$$K_{13} = \frac{\epsilon}{2}\int d\mathbf{r}\, r_1 r_3 (\partial G_a/\partial n_1')_{\mathbf{n}'=\mathbf{n}=(0,0,1)}. \tag{21}$$

It is important that the source of K_{13} is solely the anisotropic fraction of G [as $(\partial G_i/\partial n_1')_{\mathbf{n}'=\mathbf{n}} \propto n_1 = 0$], while $K_{\alpha\alpha}^{(0)}$ comes from both fractions [7].

We will also need some properties of the term in the expansion of ΔG which is linear in Δn_i. First, it was shown in Ref. [11] that the kernel ΔG and the antisymmetric part of its anisotropic fraction $\Delta G_{a,-} = \frac{1}{2}\epsilon[\Delta G_a(\mathbf{n},\mathbf{n}') - \Delta G_a(\mathbf{n}',\mathbf{n})]$ produce the same contribution to this linear term. Second, the part of this term

$$F_1 = \frac{1}{2}\int d\mathbf{r}\, \frac{\partial \Delta G}{\partial n_i'} r_j \partial_j n_i, \tag{22}$$

linear in the director derivatives, identically vanishes as the integral is over R^3. We will show that in the presence of a surface both integrals $\int d\mathbf{r}\, G(\mathbf{n},\mathbf{n})$ and F_1 produce elastic terms linear in the director derivatives, and the first one, in addition, results in a standard surface tension and anchoring.

III. SEPARATING DIFFERENT ENERGY TERMS IN INTEGRALS (8)–(11): THE Δ METHOD

A. The Δ method

The difference ΔG in the Nehring-Saupe calculations is related to the director rotation between two spatial points separated by $\Delta\mathbf{x}\equiv\mathbf{r}$ and thus is associated with the director derivatives and elasticity. In a homogeneous body, there are no other nonzero variations, but in a body with a surface and defects, the differences $\Delta\rho=\rho(\mathbf{x}')-\rho(\mathbf{x})$, $\Delta s_l=s_l(\mathbf{x}')-s_l(\mathbf{x})$, and $\Delta\eta_l=\eta_l(\mathbf{x}')-\eta_l(\mathbf{x})$, where $\eta_l=\rho s_l$, indicate location thereof. For instance, $\Delta\rho$ in the integrand indicates that this integral gives rise to a surface term as the integrand is nonzero just in the surface layer; $\Delta\rho\Delta G$ and $\Delta\eta\Delta G$ indicate a surface elastic term; $\Delta\rho\Delta\eta$ and $\Delta\rho^2$ indicate a surface tension including anchoring; no Δ indicates a nonelastic bulk term. This method will enable us to unambiguously separate all possible energy terms and solve the problems described in the Introduction.

Obviously, Δ's can enter the integrands of Eqs. (28)–(11) via the identities $\rho'\rho=\rho^2+\Delta\rho\rho$, $\eta_{l'}'\eta_l=\eta_{l'}\eta_l+\Delta\eta_{l'}\eta_l$, and $\eta_l'\rho=\eta_l\rho+\Delta\eta_l\rho$. A more elaborated procedure is, however, required to properly incorporate $G_{ll'}$ and G_l. The matter is that along with the term independent of $\Delta\mathbf{n}$, the function $G(\mathbf{n},\mathbf{n})$ contains elastic terms linear and quadratic in the separation vector $\Delta\mathbf{x}\partial\mathbf{n}$. As each Δ is connected to some degree of smallness, expressions containing $G(\mathbf{n},\mathbf{n})$ should be somehow reduced to the form quadratic in the operator Δ. This program can be realized by using the formulas

$$\int d\mathbf{x}\, d\mathbf{x}'\, \eta_l \Delta\eta_{l'}[G_{ll'}(\mathbf{n},\mathbf{n})-2p_{l'}G_l] \qquad (23)$$

$$=-\frac{1}{2}\int d\mathbf{x}\, d\mathbf{x}'[2\eta_l\Delta\eta_{l'}(\Delta G_{ll'}-p_{l'}\Delta G_l)$$
$$+\Delta\eta_l\Delta\eta_{l'}(G_{ll'}(\mathbf{n},\mathbf{n})-2p_{l'}G_l)],$$

$$\int d\mathbf{x}\, d\mathbf{x}'\, \Delta\rho\,\eta_l G_l=-\frac{1}{2}\int d\mathbf{x}\, d\mathbf{x}'(\eta_l\Delta\rho\Delta G_l+\Delta\rho\Delta\eta_l G_l). \qquad (24)$$

Let us derive the second one. Introducing $G_l'-G_l$, which coincides with the definition (1) of ΔG by virtue of Eq. (14), and substituting $G_l=G_l'-\Delta G$, one has

$$\int d\mathbf{x}\, d\mathbf{x}'\, \Delta\rho\,\eta_l G_l=-\int d\mathbf{x}\, d\mathbf{x}'\, \Delta\rho\,\eta_l \Delta G_l$$

$$+\int d\mathbf{x}'\, d\mathbf{x}(-\Delta\rho)\,\eta_l' G$$

$$=-\int d\mathbf{x}\, d\mathbf{x}'(\eta_l\Delta\rho\Delta G_l$$

$$+\Delta\rho\,\eta_l G_l+\Delta\rho\Delta\,\eta_l G_l),$$

where we permuted all primed and unprimed quantities, employed the identity $\eta_l'=\Delta\eta_l+\eta_l$, and changed the integration order. Equation (24) follows directly from the last formula. Derivation of Eq. (23) is similar, with the difference that the quantity $G_{ll'}(\mathbf{n}',\mathbf{n}')-G_{ll'}(\mathbf{n},\mathbf{n})$ in the sum over l and l' is equivalent to twice $\Delta G_{ll'}$ defined in Eq. (1). Equations (24) and (23) have the desired form as both right-hand sides are quadratic in Δ.

For an example, let us give the form of the function $\Delta\rho(\mathbf{x},\mathbf{x}')$ in quite a general case when the density at the surface S has first a jump from zero to ρ_S, and then slowly goes from ρ_S to the bulk value ρ_b, i.e., $\rho(\mathbf{x})=\rho_S+\widetilde{\rho}(\mathbf{x})$ where $\widetilde{\rho}(\mathbf{x})\to\rho_b-\rho_S$ in the bulk, and $|l_M\partial\widetilde{\rho}|\ll1$. The antisymmetric function $\Delta\rho(\mathbf{x},\mathbf{x}')$ has the form

$$\Delta\rho(\mathbf{x},\mathbf{x}')=\begin{cases} \rho(\mathbf{x}')=\rho_S+\widetilde{\rho}(\mathbf{x}'), & \mathbf{x}'\in V, \mathbf{x}\notin V; \\ -\rho(\mathbf{x})=-\rho_S-\widetilde{\rho}(\mathbf{x}), & \mathbf{x}\in V, \mathbf{x}'\notin V; \\ \Delta\widetilde{\rho}(\mathbf{x}',\mathbf{x})=\widetilde{\rho}(\mathbf{x}')-\widetilde{\rho}(\mathbf{x}), & \mathbf{x}\in V, \mathbf{x}'\in V; \\ 0, & \mathbf{x}\notin V, \mathbf{x}'\notin V. \end{cases} \qquad (25)$$

In the surface layer, the order parameter s_l and, thus, the product η_l are assumed to behave similarly: in the body $s_l(\mathbf{x})=s_{l,S}+\widetilde{s}_l(\mathbf{x})$, $\eta_l(\mathbf{x})=\eta_{l,S}+\widetilde{\eta}_l(\mathbf{x})$, where $\eta_{l,S}=\rho_S s_{l,S}$, $\widetilde{\eta}_l=\widetilde{s}_l\rho_S+\widetilde{\rho}s_{l,S}+\widetilde{s}_l\widetilde{\rho}$, and $\widetilde{s}_l$ is a slow function equal to $s_{l,b}-s_{l.S}$ in the bulk far from the surface. The antisymmetric functions $\Delta s_l(\mathbf{x},\mathbf{x}')$ and $\Delta\eta_l(\mathbf{x},\mathbf{x}')$ have the form similar to $\Delta\rho(\mathbf{x},\mathbf{x}')$.

As $\Delta\rho(\mathbf{x},\mathbf{x}')$, Eq. (25), is nonzero when one of the points $\mathbf{x}'$ and $\mathbf{x}$ is outside the body, the director must be formally defined outside the volume V. We will see that the physical results are independent of the specific form of the director extension outside the phase boundary.

B. Separating anchoring, surface tension, and surface elastic terms in the Δ method

Above we assumed that integrals over $\Delta\eta_l\Delta\rho$ and $\Delta\eta_l\Delta\eta_{l'}$, Eqs. (23) and (24), produce an anchoring and surface tension and do not produce elastic terms. Actually, however, separation of these three different surface terms is an unsolved problem. Here we show how the Δ method solves this problem.

To deal with surface integrals related to a surface jump $\rho_{l,S}$ and/or $s_{l,S}$ it is convenient to use a local Cartesian reference frame O_ν, $(x_1 x_2, z)$, connected to a point $\mathbf{x}$ on a surface element dS and the local outer surface normal ν. In

O_ν, the z axis is normal to dS, directed inward the body, and has the onset at $\mathbf{x}$; the x_1 axis is tangential to dS and lies in the plane made by the normal ν and surface director $\mathbf{n}_S(\mathbf{x})$ while the x_2 axis is normal to this plane: $\mathbf{x} = (x_1 x_2, z = 0)$, $\nu = (0,0,-1)$, and $\mathbf{n}_S(\mathbf{x}) = (n_1, 0, n_3)$. Clearly, $z > 0$ in the body and $z < 0$ outside.

Let us calculate a surface tension and anchoring associated to the functions $\Delta \eta \Delta \rho$ defined in Sec. III A (the subscripts l and l' may be dropped for simplicity; the case of $\Delta \eta_l \Delta \eta_{l'}$ is similar. One has

$$G(\mathbf{n}(z)) \simeq G_S + z\,\delta G_S, \qquad (26)$$

where $G_S = G(\mathbf{n}_S)$, $\delta G_S = (\partial G / \partial n_i)_{\mathbf{n}=\mathbf{n}_S}(\partial_3 n_i)_{z=0}$, and the dependence on z, r_1, r_2 is omitted for brevity. Besides a surface tension, on the z integration Eq. (26) can also give nonzero terms with the normal-to-surface director derivatives [12,13]. The advantage of our Δ method is that they are already separated from the anchoring terms: we will now show that the integral contribution of $z\,\delta G_S$ is zero.

Consider the integral under question in Eq. (24) and divide the integration domain as follows [see Eq. (25)]:

$$I_S = \int d\mathbf{x} \int d\mathbf{x}'\, \Delta\eta\Delta\rho\, G$$

$$= \int_V d\mathbf{x} \int_V d\mathbf{x}'\, \Delta\widetilde{\eta}\Delta\widetilde{\rho}\, G_S + \eta_S\rho_S \int_V d\mathbf{x} \int_{R_3\backslash V} d\mathbf{x}'\, G$$

$$+ \eta_S\rho_S \int_{R_3\backslash V} d\mathbf{x} \int_V d\mathbf{x}'\, G. \qquad (27)$$

In the first integral we neglected $z\,\delta G_S \sim \Delta\widetilde{\eta}\Delta\widetilde{\rho}\Delta n$; in the remaining two integrals, the smooth functions with a tilde are neglected compared to the surface jump $\eta_S\rho_S$ which dominates when $\mathbf{x}'$ or $\mathbf{x}$ is outside the body, Eq. (25). It is not difficult to show that the contributions of the derivative dependent term $z\,\delta G_S$ to the last two integrals cancel each other. To this end, we first note that only those terms in δG_S, which are even in r_3, do not vanish after integration over the surface layer. Indeed, in the reference frame O_ν both G_S and δG_S are the sums of terms $r_3^{even\ power} \times r_1^{even\ power}$ and $r_3^{odd\ power} \times r_1^{odd\ power}$. The later terms vanish after integration over the spatially unrestricted tangential component r_1. Hence one can consider G_S and δG_S to be functions of $r_3^2 = (z'-z)^2$, n_3^2, and $n_1^2 = 1 - n_3^2$. Then, under the variable change $z' = -z'$, $z = -z$, the second integral over $z\,\delta G_S$ immediately reduces to minus third one. Thus, the elastic term $z\,\delta G_S$ does give a zero contribution to integral (27) which justifies the Δ method: those integrals, whose integrands contain $\Delta\eta_l\Delta\rho$ and $\Delta\eta_l\Delta\eta_{l'}$, up to negligible terms give rise to the anchoring and surface tension alone. Below we derive general formulas for these nondeformational terms for a given kernel G.

In the context of the above consideration, integral (27) reduces to

$$I_S = \int_V d\mathbf{x} \int_{V_r} d\mathbf{r}'\, \Delta\widetilde{\eta}\Delta\widetilde{\rho}\, G_S + 2\,\eta_S\rho_S \int_V d\mathbf{x} \int_{R_3\backslash V} d\mathbf{x}'\, G_S. \qquad (28)$$

The first integral, which obviously represents the surface tension $\widetilde{\Sigma}$ and anchoring $\widetilde{A}$ of a pure diffusive surface, can be further simplified. By virtue of the definition of $\widetilde{\rho}(z)$ and $\widetilde{\eta}(z)$, Eq. (25), its integrand vanishes on S and remains very small at distances $\sim l_M$ from S. Then the principal contribution to the integral over $\Delta\widetilde{\eta}\Delta\widetilde{\rho}$ comes from the part of the surface layer not very close to S so that the r-integration domain can be extended to R_3, and this integral reduces to the form

$$\int_V d\mathbf{x}\, \partial_i \eta \partial_j \rho \int d\mathbf{r}\, r_i r_j G_S. \qquad (29)$$

The tensor structure of the $\mathbf{r}$ integral allows one to write

$$\int d\mathbf{r}\, r_i r_j G_S = d_1 \delta_{ij} + d_2 n_{i,S} n_{j,S}. \qquad (30)$$

Since the constants d_1 and d_2 are director independent, we choose the reference frame where $\mathbf{n} = (0,0,1)$. Then for $i = j = 1$ one obtains

$$d_1 = \frac{1}{2} \int d\mathbf{r}\, r_1^2 G|_{\mathbf{n}_S=(0,0,1)}. \qquad (31)$$

d_2 can be calculated by setting $i = 1$, $j = 3$, and differentiating both sides of Eq. (30) with respect to n_1,

$$d_2 = \begin{cases} K_{13}^l, & G = G_l, \\ K_{13}^{ll'} + K_{13}^{l'l}, & G = G_{ll'}, \end{cases} \qquad (32)$$

where $K_{13}^{ll'}$ and K_{13}^l are the Nehring-Saupe constant (21) for kernels G_l and $G_{ll'}$, respectively.

From Eq. (29) we see that for a pure diffusive surface, d_1 determines the isotropic tension $\widetilde{\Sigma}_G$ while d_2 determines the anchoring $\widetilde{A}_G$,

$$\widetilde{\Sigma}_G = -d_1\{G\} \int d\mathbf{x}(\nabla\rho)\cdot(\nabla\eta), \qquad (33)$$

$$\widetilde{A}_G = -d_2\{\epsilon G_a\} \int d\mathbf{x}(\mathbf{n}_S\cdot\nabla\rho)(\mathbf{n}_S\cdot\nabla\eta), \qquad (34)$$

where the functional dependence of d_1 and d_2 on kernel G is indicated. In these equations $\nabla\rho = \nabla\widetilde{\rho}$ and $\nabla\eta = \nabla\widetilde{\eta}$ since the jumps are separated and do not contribute to differentiation. Note that whereas the constant d_1, Eq. (31), comes from both isotropic and anisotropic fractions of G, the constant d_2, Eq. (32), coincides with the constant K_{13} whose source is the anisotropic fraction alone: $d_2 \propto \epsilon$.

The second term in Eq. (28) represents the anchoring A_J and surface tension Σ_J at sharp surfaces with a nonzero jump $(\rho s_l)_S$. An isotropic kernel $G_i(\mathbf{n}\cdot\mathbf{n})$ does not depend on the

director as $(\mathbf{n}\cdot\mathbf{n})=1$. In contrast, the integral over an aniso-tropic kernel $G_a(\mathbf{n},\mathbf{n})$ is a function of $(\boldsymbol{\nu}\cdot\mathbf{n}_S)^2$ which reduces to n_3^2 in $O_{\boldsymbol{\nu}}$. However, as in the case of a diffusive surface, the kernel $G_{a,S}$ also produces some director-independent term contributing to the isotropic tension. Namely, those terms in $G_{a,S}$ that do not contain n_3^2, cannot contribute to anchoring. These n_3-independent terms can be obtained from $G_{a,S}$, in which $n_1^2=1-n_3^2$ and $n_2=0$, by setting $n_3=0$. Therefore, the surface tension results from $G_{a,S}(n_3=0)$ $=G_{a,S}[\mathbf{n}_S=(1,0,0)]$ while the anchoring results from the rest of $G_{a,S}$, i.e., from $G_{a,S}-G_{a,S}(n_3=0)$. Using this recipe and z integrating by parts the second term in Eq. (27), one obtains the surface tension Σ_G and anchoring A_G induced by a surface jump of ρ_S and η_S,

$$\Sigma_{G,J}=-\rho_S\eta_S\int dS\int_0^\infty dz\, z$$
$$\times\int_{-\infty}^\infty dr_1\, dr_2[G_{i,S}+\epsilon G_{a,S}(n_3=0)]_{r_3=-z},$$
(35)

$$A_{G,J}=-\rho_S\eta_S\epsilon\int dS\int_0^\infty dz\, z$$
$$\times\int_{-\infty}^\infty dr_1\, dr_2[G_{a,S}-G_{a,S}(n_3=0)]_{r_3=-z},$$

where $n_1^2=1-n_3^2$ and $n_2=0$. Note that these integrals con-verge in the surface layer.

C. Calculation of integrals (8)–(11)

The first term I, Eq. (8), in the total energy (7) results in the director-independent bulk term and surface tension, and its calculation is trivial. Further, integral (9) reduces to the form

$$F_\Delta=\frac{1}{2}\int d\mathbf{x}\, d\mathbf{x}'(\eta_l\eta_{l'}\Delta G_{ll'}+\eta_l\Delta\eta_{l'}\Delta G_{ll',-}).\quad(36)$$

The internal integral in the first term in Eq. (36) is exactly the Nehring-Saupe density $f_{NS}^{ll'}$ (16) for the kernel $\Delta G_{ll'}$. In the second term, $\Delta G_{ll'}$ is replaced by its antisymmetric part $\Delta G_{ll',-}$ which is equivalent to neglecting contribution of the order $r^2(\partial n)^2\sim\Delta x^2\Delta n^2$, Sec. II B. This term reduces to the form (22) and can be calculated following the method of Ref. [11]. Finally, the sum of the two terms in Eq. (36) takes the form

$$F_\Delta=\int d\mathbf{x}\,\eta_l\eta_{l'}\left[\frac{1}{2}K_{\alpha\alpha}^{ll'}f_{\alpha\alpha}-\frac{1}{4}(K_{22}^{ll'}+K_{11}^{ll'})f_{24}\right],\quad(37)$$

where $K_{\alpha\alpha}^{ll'}$ are the standard splay, twist, and bend constants for the kernel $\Delta G_{ll'}$. The effect of spatial boundedness on the elastic density resulting from $\Delta G_{ll'}$ is that the constant $K_{24}=\frac{1}{4}(K_{22}+K_{11}^{(0)})$, Eq. (20), changes for $\frac{1}{4}(K_{22}+K_{11})$,

while the density f_{13} is absent [9–11]. The total coefficients K_{13} and K_{24} in a restricted nematic body have other sources and will be found below.

Applying the Δ method, the integral (10) can be reduced to the sum

$$F_{0,1}=\frac{1}{2}\int d\mathbf{x}\, d\mathbf{x}'(\eta_l\eta_{l'}+\eta_l\Delta\eta_{l'})[G_{ll'}(\mathbf{n},\mathbf{n})-2p_{l'}G_l].$$
(38)

The integral over $\eta_l\eta_{l'}$ is $\mathbf{n}$ independent and proportional to V, Sec. II B, and can be simplified by using formula

$$\int d\mathbf{r}\, G_l=p_l\int d\mathbf{r}\langle w\rangle.\quad(39)$$

The $\eta_l\Delta\eta_{l'}$ term is similar to Eq. (9) considered above and can be calculated in the same way. This gives

$$(K_{13}^{ll'}-p_{l'}K_{13}^l)\int d\mathbf{x}\,\eta_l\eta_{l'}(f_{13}-\tfrac{1}{2}f_{24})+\Sigma_1+A_1,\quad(40)$$

where the isotropic tension Σ_1 and anchoring A_1 can be found from general formulas (35) by replacing $\Delta\eta_l\Delta\rho$ with $\Delta\eta_l\Delta\eta_{l'}$ and G with $(G_{ll'}-2p_{l'}G_l)$.

Integral (11) can be written as

$$F_{0,2}=\int d\mathbf{x}\int d\mathbf{r}\left[\rho\eta G_l-\frac{1}{2}(\Delta\eta_l\Delta\rho G_l+\eta_l\Delta\rho\Delta G_l)\right].$$
(41)

Calculating the first term in $F_{0,2}$ reduces to using formula (39). The second term can be obtained from general formulas (35) by setting $G=G_l$. The third term in $F_{0,2}$ looks similar to that with $\eta_l\Delta\eta_{l'}\Delta G_l$ considered above, however, it can-not be treated in the same way. The matter is that $\eta_l'\rho$, which now replaces $\eta_l'\eta$ in the integrand thereof, is not symmetric (identity (15) of Ref. [11] breaks). For this reason we per-formed a direct calculation of $F_{el,2}$ assuming that s_l, ρ, and η_l have finite sharp jumps at the boundary and smooth com-ponents. The smooth components are assumed to change very little over the microscopic scale, so that the differences $\Delta\tilde\rho$ and $\Delta\tilde\eta$ can be approximated by the first differentials. As a result, the third term in Eq. (41) is found to be

$$K_{13}^l\int d\mathbf{x}[\eta\rho(f_{13}-\tfrac{1}{2}f_{24})+\rho^2(\boldsymbol{\nabla}s_l)\cdot(\mathbf{f}_{13}-\tfrac{1}{2}\mathbf{f}_{24})].\quad(42)$$

IV. THE FULL ENERGY EXPRESSION

Now we can write down the full energy expression col-lecting the results of the preceding section. The total energy E is a sum of the director-independent bulk term E_0, elastic term F_{el} containing the director derivatives, isotropic tension Σ, and anchoring A,

$$E=E_0+F_{el}+\Sigma+A.\quad(43)$$

In this section we consider each term individually.

A. Director-independent bulk term E_0

The director-independent bulk term E_0 has the form

$$E_0 = \frac{1}{2} \int d\mathbf{x}\, \rho^2 (a_0 + a_2^{ll'} s_l s_{l'}),$$

$$a_0 = \int d\mathbf{r} \langle w \rangle, \tag{44}$$

$$a_2^{ll'} = \int d\mathbf{r} [G_{ll'}(\mathbf{n},\mathbf{n}) - p_{l'} p_l \langle w \rangle].$$

Note that the bulk terms linear in s, though allowed by the symmetry and present in Eq. (8), canceled out in the total energy as it should be for having the correct nematic-isotropic phase transition, and the kernel G_l (14) is essential for this cancellation. By magnitude order, $a_0 \sim a_2 \sim K l_M^{-2}$. The bulk nematic phase is possible when the second term in Eq. (44) is negative, which imposes certain restrictions on possible nematogenic potentials w thus providing the selection procedure. As for the s independent term in Eq. (44), it can be used for finding the equilibrium distribution of the density, but this complicated problem lies beyond the task of our paper (e.g., see Ref. [16]). In our formulas the density $\rho(\mathbf{x})$ is to be considered as a known function, and the term $a_0 \rho^2$ gives rise to an unimportant constant.

B. Bulk and surface elastic terms

The elastic free energy is the sum of the terms $\widetilde{F}_{el}$ that would be present for no surface jumps, and the jump-induced terms $F_{el,J}$, i.e.,

$$F_{el} = \widetilde{F}_{el} + F_{el,J}. \tag{45}$$

This sum can be obtained by summing all the elastic terms obtained above and by part integrating those containing the densities $\mathbf{f}_{13}$ and $\mathbf{f}_{24}$. The nonjump term has the form

$$\widetilde{F}_{el} = \int d\mathbf{x} \left\{ \frac{1}{2} \eta_l \eta_{l'} (K_{11}^{ll'} f_{11} + K_{22}^{ll'} f_{22} + K_{33}^{ll'} f_{33}) \right.$$

$$+ \left[\kappa_{24}^{ll'} \nabla(\eta_l \eta_{l'}) + \frac{1}{2} K_{13}^l s_l \nabla \rho^2 \right] \cdot \mathbf{f}_{24}$$

$$\left. - [\kappa_{13}^{ll'} \nabla(\eta_l \eta_{l'}) + K_{13}^l s_l \nabla \rho^2] \cdot \mathbf{f}_{13} \right\}, \tag{46}$$

where

$$\kappa_{24}^{ll'} = \frac{1}{4} (K_{11}^{ll'} + K_{22}^{ll'} + 2\kappa_{13}^{ll'}), \tag{47}$$

$$\kappa_{13}^{ll'} = K_{13}^{ll'} - p_{l'} K_{13}^l,$$

It consists of the bulk splay, twist, and bend terms quadratic in the density and order parameters, and the terms nonvanishing in diffusive surface layers which, for obvious reason, can be referred to as the K_{24} and K_{13} terms [see Eqs.

(17) and (18)]. In contrast to the Landau–de Gennes FE, the constants $K_{\alpha\alpha}\{G_{ll'}\}$ are determined by the Nehring-Saupe formulas which do not imply $K_{11} = K_{33}$. Note, that the terms linear in the smooth component $\tilde{s}_l$ appear only where the density is not constant, i.e., at a diffusive surface.

The jump-induced term has the form

$$F_{el,J} = \int dS [-(\kappa_{24}^{ll'} \eta_l \eta_{l'} + \tfrac{1}{2} K_{13}^l \eta_l \rho)(\boldsymbol{\nu} \cdot \mathbf{f}_{24})$$

$$+ (\kappa_{13}^{ll'} \eta_l \eta_{l'} + K_{13}^l \eta_l \rho)(\boldsymbol{\nu} \cdot \mathbf{f}_{13})], \tag{48}$$

where $\boldsymbol{\nu}$ is the outer normal to S. The surface integral contains $\eta_S = \rho_S \eta_S$ and does not vanish only if both the order parameter and density have a finite jump.

Usual situation is that the size of a nematic body is much larger than the thickness l_S of the surface layer. Then, if structure of a surface layer is of no interest, one can describe the observable director far from the surface using the effective FE functional

$$\bar{F}\{\mathbf{n}\} = \bar{F}_{el} + \bar{A} \tag{49}$$

with effective constants that absorb the information of the surface layer. The effective surface elastic constants entering $\bar{F}_{el}$ can be obtained by integrating the exact surface energy densities in Eq. (45) across the surface layer (from $z = 0$ to $z = l_S$) assuming that the director changes negligibly within it; as V is much larger than the volume of the surface layer, the effective bulk elastic constants merely take their bulk values. As a result, the effective bulk elastic energy of a spatially restricted body is obtained in the form

$$\bar{F}_{el} = \frac{1}{2} \int_V d\mathbf{x} (\bar{K}_{11} f_{11} + \bar{K}_{22} f_{22} + \bar{K}_{33} f_{33})$$

$$+ \int dS\, \boldsymbol{\nu} \cdot (-\bar{K}_{24} \mathbf{f}_{24} + K_{13} \mathbf{f}_{13}), \tag{50}$$

where the effective elastic constants are given by the following expressions:

$$\bar{K}_{\alpha\alpha} = \eta_{lb} \eta_{l'b} K_{\alpha\alpha}^{ll'}, \quad \alpha = 1,2,3,$$

$$\bar{K}_{24} = \frac{1}{4} (\bar{K}_{11} + \bar{K}_{22} + 2\bar{K}_{13}), \tag{51}$$

$$\bar{K}_{13} = \eta_{lb} \eta_{l'b} (K_{13}^{ll'} - p_{l'} K_{13}^l) + \eta_{lS} \rho_S K_{13}^l + K_{13}^l \int_0^{l_S} dz\, s_l \partial_z \rho^2.$$

Formulas (50) and (51) give the large scale elastic energy of a spatially restricted body. The difference with the Nehring-Saupe functional F_{NS} appears in the values of K_{13} and K_{24}, in the surface tension and anchoring terms, and in the effective status of $\bar{F}_{el}$. The constants $\bar{K}_{\alpha\alpha}$ do not depend on the surface structure, whereas $\bar{K}_{24}$ and $\bar{K}_{13}$ do. For an ideal surface without any smooth component where the bulk and surface values of ρ and s coincide, and for a pure diffu-

sive surface where $s_S = \rho_S = 0$, the constant $\bar{K}_{13}$ is, respectively, given by the following expressions:

$$\bar{K}_{13,J} = \eta_{l,b} \eta_{l',b} (K_{13}^{ll'} - p_{l'} K_{13}^{l}) + s_{l,b} \rho_b^2 K_{13}^{l},$$

$$ \tag{52}$$

$$\bar{\bar{K}}_{13} = \eta_{l,b} \eta_{l',b} (K_{13}^{ll'} - p_{l'} K_{13}^{l}) + K_{13}^{l} \int_0^{l_S} dz \, s_l \partial_z \rho^2.$$

The last integral can be estimated as $K_{13}^{l} s_{lb} \langle \rho^2 \rangle_S$ where $\langle \rho^2 \rangle_S \sim 0.5 \rho_b^2$ is some mean value in the surface layer. The similar contribution due to the kernel $G_l(\mathbf{n} \cdot \mathbf{r})$ was obtained in Ref. [11]. We see, however, that in line with the numerical analysis [13], the full expression for the elastic constant K_{13} does not reduce to this term alone and contains more contributions from the apparently "nonelastic" homogeneous kernels. For instance, the kernel G_l gives rise to the two other contributions to K_{13} (51), one of which is quadratic in the order parameters.

The contribution $\eta_{lb} \eta_{l'b} K_{13}^{ll'}$ in $\bar{K}_{13}$ (52) is produced by the homogeneous kernel $G_{ll'}(\mathbf{n}, \mathbf{n})$. It coincides with the naive infinite medium Nehring-Saupe constant (21) that disappears in the elastic energy (37) of a spatially restricted body if just the pure "elastic" kernels $\Delta G_{ll'}$ and ΔG_l are considered. Therefore, the homogeneous kernel $G_{ll'}(\mathbf{n}, \mathbf{n})$ restores the infinite medium contribution to the K_{13} term.

C. Surface tension and anchoring

The general formulas for the isotropic surface tension and anchoring were obtained in Sec. III B. The total energy of the isotropic surface tension is the sum of the no-jump term $\tilde{\Sigma}$ and jump-induced term Σ_J, i.e., $\Sigma = \tilde{\Sigma} + \Sigma_J$. The diffusive part $\tilde{\Sigma}$ has the form

$$\tilde{\Sigma} = \frac{1}{2} \int d\mathbf{x} [b_0 (\nabla \rho)^2 + b_1^l (\nabla \eta_l) \cdot (\nabla \rho)$$

$$+ b_2^{ll'} (\nabla \eta_l) \cdot (\nabla \eta_{l'})], \tag{53}$$

where

$$b_0 = -\frac{1}{2} \int d\mathbf{r} \, r_1^2 \langle w \rangle,$$

$$b_1^l = -\int d\mathbf{r} \, r_1^2 [G_l(\mathbf{n}) - p_l \langle w \rangle]_{\mathbf{n}=(0,0,1)}, \tag{54}$$

$$b_2^{ll'} = -\frac{1}{2} \int d\mathbf{r} \, r_1^2 [G_{ll'}(\mathbf{n}, \mathbf{n}) - 2p_{l'} G_l(\mathbf{n})$$

$$+ p_l p_{l'} \langle w \rangle]_{\mathbf{n}=(0,0,1)}.$$

All b's $\sim K$. The energy (53) can be represented in the conventional form $\tilde{\Sigma} = \int dS \tilde{\sigma}$ with the surface density $\tilde{\sigma}$ defined by the expression in the square bracket in Eq. (53) (in the reference frame O_ν, ∇ is replaced by ∂_z).

Similarly, the energy of anchoring is the sum of the non-jump and jump-induced terms, i.e., $A = \tilde{A} + A_J$. The nonjump diffusive term has the form

$$\tilde{A} = -\int d\mathbf{x} [K_{13}^{l} (\mathbf{n}_S \cdot \nabla \rho)(\mathbf{n}_S \cdot \nabla \eta_l) + \kappa_{13}^{ll'} (\mathbf{n}_S \cdot \nabla \eta_l)$$

$$\times (\mathbf{n}_S \cdot \nabla \eta_{l'})]. \tag{55}$$

Its conventional form is found to be

$$\tilde{A} = \frac{1}{2} \int dS W (\mathbf{n} \cdot \boldsymbol{\nu})^2, \tag{56}$$

$$W = -2 \int_0^{l_S} dz [K_{13}^{l} (\partial_z \rho)(\partial_z \eta_l) + \kappa_{13}^{ll'} (\partial_z \eta_l)(\partial_z \eta_{l'})]. \tag{57}$$

A remarkable property of anchoring potential (56) for a pure diffusive surface is that it has exactly the Rapini-Popoular form and its strength W is proportional to the constants K_{13}^{l} and $\kappa_{13}^{ll'}$ given in Eq. (47). Thus, for a diffusive surface the fact that the constant K_{13} and intrinsic anchoring are obtained due to the same anisotropic interaction is expressed explicitly.

The jump-induced surface nonelastic energy is also a sum of the surface tension $\Sigma_J = \int dS \sigma_J$ and anchoring $A_J = \int dS f_{A,J} (\mathbf{n} \cdot \boldsymbol{\nu})$. In the reference frame O_ν, the density σ_J is found to be

$$\sigma_J = -\frac{1}{2} \rho_S^2 \int_0^{l_S} z \, dz \int_{-\infty}^{\infty} dr_1 \, dr_2 \, G_{\Sigma,J}(r_3 = -z),$$

$$G_{\Sigma,J} = \langle w \rangle - 2 s_l [p_l \langle w \rangle - G_l(\mathbf{n})]_{n_3=0} \tag{58}$$

$$+ s_l s_{l'} [p_l p_{l'} \langle w \rangle + G_{ll'}(\mathbf{n}, \mathbf{n}) - 2 p_{l'} G_l(\mathbf{n})]_{n_3=0}.$$

$f_{A,J}$ has the form

$$f_{A,J}((\mathbf{n}_S \cdot \boldsymbol{\nu})^2) = -\frac{1}{2} \rho_S^2 \epsilon \int_0^{l_S} z \, dz$$

$$\times \int_{-\infty}^{\infty} dr_1 \, dr_2 [G_{A,J} - G_{A,J}(n_3 = 0)]_{r_3=-z}, \tag{59}$$

$$G_{A,J}(\mathbf{n}) = \{2 s_{l'} G_{l,a} + s_l s_{l'} [G_{ll',a}(\mathbf{n}, \mathbf{n}) - 2 p_{l'} G_{l,a}]\}_S.$$

In contrast to the universal $(\mathbf{n}_S \cdot \boldsymbol{\nu})^2$ form of the anchoring potential for a diffusive surface, the power of $(\mathbf{n}_S \cdot \boldsymbol{\nu})^2$ in the jump-induced anchoring potential $f_{A,J}$, Eq. (59), depends on the power of n_z in the anisotropic part of the kernels $G_{ll'}$ and G_l.

Equations (53) and (57) show that the surface tension and anchoring for a diffusive surface are of the order $\tilde{\sigma} \sim W \sim K_{13}/l_S$. At the same time, the jump-induced quantities $\sigma_J \sim f_{A,J} \sim K_{13}/l_M$, which is larger by the factor l_S/l_M. We see that the anchoring and surface tension depend on the

structure of the surface layer and, roughly speaking, are inversely proportional to the thickness l_S thereof. Thus, the anchoring is weaker at a diffusive surface and is strongest at a pure ideal surface with a large jump of the density and order parameters. At the same time, the effective constant $\bar{K}_{13}$, Eq. (52), averaged across this layer is practically the same for any surface (the reason is that the K_{13} density depends on the first derivative of ρ or η whereas the density of anchoring and surface tension depends on the square of such derivatives, see also Ref. [17]). The above consideration, in particular, implies that the effects related to the K_{24} and K_{13} terms should be expected in samples with diffusive surfaces. Indeed, the size of such samples is determined by the anchoring extrapolation length [18] that takes macroscopic values only if the anchoring is weak.

V. MICROSCOPIC ORIGIN OF THE DIFFERENCE $K_{33} - K_{11}$ AND THE SURFACE PHENOMENA

The Landau–de Gennes theory predicts that, in the order s_2^2, the constants K_{11} and K_{33} are equal which is not in line both with the numerous experiments and Nehring-Saupe theory. In literature on the Landau–de Gennes theory, and the most recent related papers [14,15] are not an exclusion, the observed difference $K_{33} - K_{11}$ is attributed to the orders s_2^3 and higher which is not confirmed by the experimental findings. Our theory enables one to clarify this question. Moreover, we will see that addressing this problem gives us an important (and somewhat unexpected) connection between $K_{33} - K_{11}$, the amplitude ϵ of the anisotropic fraction in the intermolecular potential, and values of the higher-order scalar order parameters.

We prove the following two assertions. The first one is

$$K_{33}^{22} = K_{11}^{22}, \qquad (60)$$

which means that, for an arbitrary intermolecular potential w, restriction of the distribution function to the simplest scalar order parameter s_2 alone results in the equality $K_{11} = K_{33}$. Indeed, as far as the constants K_{11} and K_{33} are concerned, the restriction to $l = l' = 2$ implies dealing with the kernel $G_{22}(\mathbf{n}, \mathbf{n}') = \langle \tilde{P}_2 w \tilde{P}_2' \rangle$ where $\tilde{P}_2 = \frac{15}{2}(\mathbf{n} \cdot \boldsymbol{\omega})^2$, $\tilde{P}_2' = \frac{15}{2}(\mathbf{n}' \cdot \boldsymbol{\omega})^2$ [G_l does not contribute to $K_{\alpha\alpha}$, see Eq. (37)]. The kernel G_{22}, being quadratic in n_i and n_i', is a sum of the following invariants: n-independent constant (function on r), $(\mathbf{n} \cdot \mathbf{n}')^2$, $(\mathbf{n} \cdot \mathbf{n}')(\mathbf{n} \cdot \mathbf{u})(\mathbf{n}' \cdot \mathbf{u})$, $(\mathbf{n} \cdot \mathbf{u})^2 + (\mathbf{n}' \cdot \mathbf{u})^2$, and $(\mathbf{n} \cdot \mathbf{u})^2(\mathbf{n}' \cdot \mathbf{u})^2$. All these invariants result in $K_{33} = K_{11}$ which proves the first assertion (calculation of the constants is trivial if one uses the well-known formulas expressing the elastic constants in terms of the powers of the elementary invariants $(\mathbf{n} \cdot \mathbf{n}')$, $(\mathbf{n} \cdot \mathbf{u})$, and $(\mathbf{n}' \cdot \mathbf{u})$, see Ref. [19]).

The second assertion is that a pure isotropic interaction $w[(\boldsymbol{\omega} \cdot \boldsymbol{\omega}')^{2k}]$, $k = 1, 2, \ldots$, cannot give a nonzero $K_{33} - K_{11}$. Indeed, for any l and l', the kernel $G_{ll'}$ is a sum of even powers of $(\mathbf{n} \cdot \mathbf{n}')$. But the term $(\mathbf{n} \cdot \mathbf{n}')^{2k}$ results in $K_{33} = K_{11}$ for any k, which proves the second assertion.

It follows from the two facts proved above that, as far as the interaction form is concerned, a nonzero $K_{33} - K_{11}$ is obtained solely due to an anisotropic interaction that is a

source of the constant K_{13} and intrinsic anchoring; and, as far as the orientational one-particle distribution function is concerned, a nonzero $K_{33} - K_{11}$ is obtained due to the scalar order parameters of the orders higher than 2. This conclusion can be expressed by the following formula:

$$K_{33} - K_{11} = \epsilon(\Delta_{24}s_2s_4 + \Delta_{44}s_4^2 + \cdots), \qquad (61)$$

where $\Delta_{24} = K_{33}\{G_{a,24}\} - K_{11}\{G_{a,24}\}$, and so on. This result implies that the K_{24} term is also due to a nonzero ϵ. Indeed, it is known that the total elastic coefficient of the k_{24} terma is $K_{11} - 2K_{24}$ [12,18]. Then Eqs. (51) and (61) show that anisotropic potential is a source of *all* the sign-indefinite FE terms: for $\epsilon = 0$, one has $K_{13} = K_{11} - 2K_{24} = \Lambda = 0$.

It is known that the Landau–de Gennes theory assumes the order parameter to be of the form $Q_{ij} = s_2(n_i n_j - \frac{1}{3}\delta_{ij})$, directly related to the Legendre polynomial P_2 [21]. As this corresponds to incorporating a single-order parameter s_2, the formula (61) shows that prediction of a nonzero difference $K_{33} - K_{11}$ should not be expected of this approach. Contrary to that, to be consistent, the Landau–de Gennes theory *must* predict equal constants K_{33} and K_{11} as it indeed does in the order s_2^2. This demonstrates a high self-consistency of this theory in the order s_2^2: being pure phenomenological and not resorting to microscopic formulas, it predicts $K_{11} = K_{33}$ in accordance with the result of the microscopic theory. To make the picture complete, we note that terms cubic in s_2 do not change the elastic energy. Indeed, the energy, Eq. (3), is quadratic in the one-particle distribution function, and thus terms s_2^3 come from the entropy functional which is **n**-independent.

Now we can answer the question formulated in the Introduction as to how large the anisotropic interaction in a real system of nematogenic molecules is and, consequently, how important the elastic K_{13} term and intrinsic anchoring are. The clear message that reliably observed considerable values of the difference $K_{33} - K_{11}$ convey us is that the anisotropic fraction of the intermolecular potential is of the same magnitude as the isotropic one, and hence the K_{13} elasticity and intrinsic anchoring are an important integral part of the physics of LCs.

VI. CONCLUSION

A nematic body is not entirely spatially homogeneous: its density and order parameters undergo spatial variations in comparatively small areas of the space. This paper presents the full energy of such a uniaxial nematic body expressed in terms of the macroscopic order parameters and derived from the general microscopic formulas. The theory assumes both smooth and jumplike spatial inhomogeneities.

No usual assumption was made as to which kernels in the pairwise potential give rise to elastic terms and which do not. Instead we developed the Δ method that allows for an unambiguous separation of different macroscopic energy contributions, relating them with the spatial variations of the order parameters. As a result, full expressions for all the elastic terms, including the K_{13} and K_{24} terms, were derived.

The result simplifies calculation of the anchoring potential, reducing it to the procedure similar to the calculation of the elastic constants.

Incorporating all the scalar order parameters allowed for finding an important relation between the higher-order scalar parameters and the observed difference $K_{33} - K_{11}$. It indicates that at least some s_l with $l \geq 4$ and the anisotropic part of the intermolecular interaction must be considerable in a nematic phase. This allowed us to conclude that the elastic K_{13} term and intrinsic anchoring are an important integral part of the energy of a nematic phase. The effective constants $\bar{K}_{13}$ and $\bar{K}_{24}$ differ from the Nehring-Saupe values for any surface structure. In contrast to these constants, the strength of anchoring considerably depends on a surface layer: for a thick diffusive surface layer it can be much smaller than at sharp surfaces. This gives a clue for understanding why an intrinsic anchoring can be weak even if the anisotropic part of the intermolecular potential is considerable.

Finally, we believe that the approach developed in this paper can be generalized for derivation of the energy of a biaxial phase in a system of uniaxial molecules from the microscopic formulas. This task is under way.

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