

# Density-functional theory of surfacelike elasticity of nematic liquid crystals

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Based on the density-functional theory, we show that the splay-bend surfacelike bulk elastic constant  $K_{13}$  is an artifact of the phenomenological as well as the gradient expansion construction of the curvature elastic free energy of nematic liquid crystals, while the saddle-splay constant  $K_{24}$  is real and approximately obeys an extended Nehring-Saupe relation  $K_{24} \cong (K_{11} - K_{22})/2$ , with  $K_{11}$  and  $K_{22}$  being the splay and twist Frank constants, respectively. The result  $K_{13} = 0$  automatically resolves the Oldano-Barbero pathology, which inevitably accompanies a nonzero  $K_{13}$ , and gives a concrete rationale for the conventional approaches in the continuum theory disregarding the surfacelike elasticity. The source of an apparently nonzero  $K_{13}$  in previous microscopic theories is discussed in detail and is demonstrated to be a result of an inconsistent use of a nonlocal-to-local mapping of the elastic free-energy functional at the boundary. The absence of  $K_{13}$  can be regarded as a type of Cauchy relation in the nematic continuum theory in the sense that it is not directly rooted in any of the macroscopic symmetries existing in the nematic phase, but is a general consequence of the particular algebraic form of the nonlocal free-energy term from which  $K_{13}$  derives; its linearity in the distortion amplitude and the symmetry of the relevant direct correlation function with respect to the permutation of a molecular pair leads always to the vanishing  $K_{13}$ . In this respect,  $K_{13} = 0$  applies not only to nematic liquid crystals but also to a more general class of phases such as cholesteric liquid crystals, whose structure can be viewed as a weak modulation of a translationally invariant phase. We finally consider the elastic description of nematic liquid crystals in the presence of real interfaces. The present formulation allows a straightforward decomposition of the elastic excess free energy into the bulk contribution and the interfacial excess in the Gibbs sense. The bulk part yields the bulk Oseen-Frank elastic free-energy density along with the  $K_{24}$  term evaluated at the Gibbs dividing surface as an unambiguous local quantity. The interfacial excess, when gradient expanded, reduces to the surface free-energy density comprised of the anchoring energy, surface-excess Oseen-Frank elastic energy,  $K_{24}$ -like term, and elastic free-energy contributions reflecting the broken symmetry at the interface. The  $K_{24}$ -like term is formally similar to the bulk  $K_{24}$  term, but is no longer an intrinsic property of bulk nematic liquid crystal, as it depends also on the nature of the medium with which the nematic liquid crystal is in contact. [S1063-651X(97)02103-X]

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## I. INTRODUCTION

Nematic liquid crystals are an anisotropic fluid in which the molecular positions are randomly distributed, while their orientations are ordered along a certain direction specified by a unit vector  $\mathbf{n}$ , the director, taken along the symmetry axis [1]. In nematic liquid crystals, the uniform orientation of the director corresponds to the state of lowest free energy in the absence of orientational external fields and boundary constraints. Spatial variations in  $\mathbf{n}$  result in an increase in free energy, which is known to be well described by the phenomenological Oseen-Frank elastic free energy [2,3]

$$\begin{aligned} \delta F &= \int d\mathbf{R} f_{\text{elastic}}(\mathbf{R}) \\ &= \int d\mathbf{R} [f_b(\mathbf{n}, \partial\mathbf{n}) + f_{24}(\mathbf{n}, \partial\mathbf{n}) + f_{13}(\mathbf{n}, \partial\mathbf{n}, \partial^2\mathbf{n})], \end{aligned} \quad (1)$$

where

$$f_b = \frac{1}{2}K_{11}(\nabla \cdot \mathbf{n})^2 + \frac{1}{2}K_{22}(\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + \frac{1}{2}K_{33}(\mathbf{n} \times \nabla \times \mathbf{n})^2, \quad (2)$$

$$f_{24} = -\frac{1}{2}(K_{22} + K_{24})\nabla \cdot (\mathbf{n}\nabla \cdot \mathbf{n} + \mathbf{n} \times \nabla \times \mathbf{n}), \quad (3)$$

$$f_{13} = K_{13}\nabla \cdot (\mathbf{n}\nabla \cdot \mathbf{n}). \quad (4)$$

Ordinarily,  $f_{24}$  and  $f_{13}$  in Eq. (1) are neglected since they are convertible by Gauss's theorem to a surface integral over the boundary and thus do not affect the bulk equilibrium condition [1]. These terms were first introduced by Oseen [2] in his phenomenological theory of curvature elasticity, yet later  $f_{13}$  was omitted by Frank [3] from his expression for its second-order nature. This term was, however, reintroduced by Nehring and Saupe [4], who further gave a microscopic relation among the elastic constants,

$$K_{24} = (K_{11} - K_{22})/2. \quad (5)$$

The presence of these surfacelike bulk elastic terms has remained a matter of continued debate on their physical origins and mathematical consequences [5-43]. For example, it was Oldano and Barbero who pointed out that a naive inclusion of the  $K_{13}$  term in the minimization of the elastic free energy leads to a pathological result for equilibrium director distributions that involve a divergence of  $\nabla \cdot \mathbf{n}$  at the boundary [10-12]. This happens simply because the variational problem is made overly specified by the  $K_{13}$  term having the normal derivative of the director as an independent boundary variable along with the boundary director itself [16,40,44].

As a consequence, in order to make the variational problem well posed even in the presence of nonzero  $K_{13}$ , one has either to introduce an auxiliary boundary condition on  $\nabla \cdot \mathbf{n}$  to reduce the number of degrees of freedom at the boundary or to allow a higher-order bulk elastic energy to accommodate the increased number of boundary conditions by the  $K_{13}$  term. Despite several attempts following these two approaches of resolution, there is as yet no established way of handling this difficulty in a physically reasonable manner. The  $K_{24}$  term, in contrast, does not cause such a mathematically delicate problem since it involves only the tangential derivatives of director at the boundary so that the boundary director serves as the complete boundary condition for this surface term as well. The  $K_{24}$  term, however, automatically vanishes for one-dimensional deformations that are the case in most, if not all, practically important experimental configurations.

Under these circumstances, the nature of the surfacelike bulk elasticity had remained solely a matter of conceptual interest, until several recent attempts were made to measure  $K_{24}$  and/or  $K_{13}$  by direct experiments [22,34]. In particular, the observations of surface-induced three-dimensional modulations in an initially one-dimensionally deformed nematic layer offered dramatic evidence that the surface free energy depending on the tangential derivatives of the director such as the  $K_{24}$  term could play a physically perceivable role [23–25,27–29,33,35,36]. We should note, however, that all these experiments aimed at measuring  $K_{24}$  and/or  $K_{13}$  involve real interfaces where the nematic phase is interrupted by distinct solid or fluid media. Hence, even if these experimental results require the presence of surfacelike elastic terms for correct explanations, it is by no means a proof that the values assigned there to  $K_{24}$  and/or  $K_{13}$  should be unique, independent of the nature of the interface, as tacitly assumed in the literature.

The density-functional theory offers a general and rigorous basis for analyzing nonuniform systems, especially elastic properties of condensed media [45]. Poniewierski and Stecki [9] pioneered this approach in the liquid-crystal field by formulating rigorous statistical-mechanical expressions for the Oseen-Frank elastic constants of nematic liquids in terms of the Ornstein-Zernike direct correlation function. Though not emphasized in their paper, their analyses also addressed the surfacelike elasticity, giving  $K_{13}$  and  $K_{24}$  an explicit microscopic formula. The density-functional route to the liquid-crystal curvature elasticity has since then been exploited by a number of authors [14,21,26,46–49], who cultivated a simpler way to reach essentially the same formulas as those originally derived by Poniewierski and Stecki along the cluster expansion approach [9].

As postulated by Nehring and Saupe, the density-functional theory yields a nonlocal expression for the elastic free energy  $\delta F$  in the generic form

$$\delta F = \int d\mathbf{r} d\mathbf{r}' G(\mathbf{r}, \mathbf{r}'), \quad (6)$$

with  $\mathbf{r}$  and  $\mathbf{r}'$  being the molecular positions, as a manifestation of the finite range of the intermolecular interaction potential. The elastic free-energy density  $f_{\text{elastic}}(\mathbf{R})$  must be a local function defined at a single point  $\mathbf{R}$  in such a way as to satisfy

$$\int d\mathbf{r} d\mathbf{r}' G(\mathbf{r}, \mathbf{r}') = \int d\mathbf{R} f_{\text{elastic}}(\mathbf{R}). \quad (7)$$

Since there is no *a priori* reason to select a particular way of irreversible mapping  $(\mathbf{r}, \mathbf{r}') \rightarrow \mathbf{R}$  out of infinitely many different possible choices (detailed the discussion in Sec. IV), the resultant  $f_{\text{elastic}}(\mathbf{R})$  cannot necessarily be unique as a function of the director and its gradients evaluated at  $\mathbf{R}$  even in the weak deformation limit.

This is in fact a subtle problem always associated with defining a local quantity from an essentially nonlocal property such as energy, entropy, and free energy and is well known in statistical mechanics of ordinary liquids [50]. The relevance of this difficulty to the surfacelike bulk elasticity of nematic liquid crystals was initially commented on by Yokoyama [16] and later more specifically led Somoza and Tarazona [21] to argue that  $K_{13}$  cannot be a well-defined physical parameter, given its apparent dependence on the choice of the nonlocal-to-local mapping. Teixeira, Pergamenschchik, and Sluckin [26], nevertheless, rejected their reasoning for the physical ambiguity of  $K_{13}$ , by pointing out the inconsistency of Somoza and Tarazona's choice of the free-energy density for undeformed states. Then, they derived microscopic formulas for  $K_{13}$  and  $K_{24}$  in line with those by Poniewierski and Stecki [9]. Drawing on the existence of such a microscopic formula as a rationale for the physical reality of  $K_{13}$ , Pergamenschchik [27] and Faetti [31] considered, in a rather qualitative manner, the origin of the Oldano-Barbero pathology as resulting from the termination of the free-energy expansion at a finite order of gradients. These two authors, however, reach mutually contradicting conclusions about the microscopic structures that the presence of  $K_{13}$  would bring about in the immediate vicinity of an interface. With this as yet volatile status in mind, we may conclude that even after over 60 years in existence, the surfacelike bulk elasticity is still far from being mature, making a sharp contrast with the otherwise firmly established context of continuum theory of nematic liquid crystals.

The purpose of this paper is to sort out the confusion about the current status of the surfacelike bulk elasticity by analyzing in detail the physical origin of  $K_{13}$  and  $K_{24}$  on a general basis of the density-functional formalism. On a natural assumption that the director is uniformly oriented in the undistorted ground state of a bulk nematic liquid crystal, we show by expanding the free energy about the ground state that the splay-bend constant satisfies  $K_{13}=0$ . This result automatically resolves the Oldano-Barbero pathology and offers a rationale for conventional treatments of the director configuration problems with the negligence of  $K_{13}$ . Our argument rests on the following observation about the peculiar asymptotic behavior of  $f_{13}$  in the small and long-wavelength limit of director distortion, compared with the rest of the elastic contributions. Indeed, in terms of the characteristic amplitude  $\epsilon$  and wavelength  $\xi$  of distortion, as shown in Fig. 1, it follows from Eqs. (2)–(4) that the leading term in  $f_{13}$  is of order  $\epsilon \xi^{-2}$  because of its involvement of the second-order derivatives of the director, whereas  $f_b$  and  $f_{24}$  are of order  $\epsilon^2 \xi^{-2}$ . Hence, unless  $K_{13}=0$ , in the weak distortion limit ( $\epsilon \rightarrow 0$ ), the  $f_{13}$  contribution tends to dominate. Due to its linear dependence on  $\epsilon$ , the dominance of  $f_{13}$  inevitably destabilizes the uniform ground state, though this effect is lo-

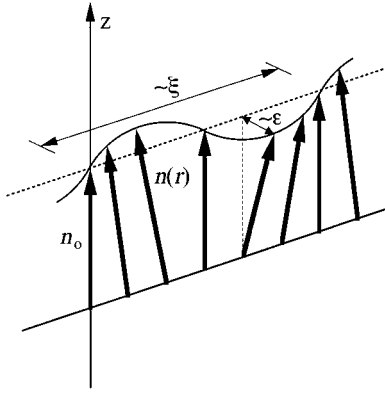


FIG. 1. Schematic illustration of an orientational deformation in nematic liquid crystals. The director is initially uniformly aligned in a homogeneous magnetic field  $\mathbf{H}_0$  along the  $z$  axis. By applying an orthogonal field  $\mathbf{H}_\perp$ , a weak director distortion with the characteristic amplitude  $\epsilon$  and wavelength  $\xi$  is induced. The long-wavelength limit is understood to be taken with the magnetic fields becoming infinitely small, i.e.,  $H_\perp \sim H_0 \sim O(\xi^{-2})$ .

calized to a boundary. This is actually an alternative way of pointing out the origin of the Oldano-Barbero pathology and presents a contradiction to our ansatz of the uniform ground state. Conversely, therefore, the presumption of the uniformity of the ground state results in the absence of  $K_{13}$  as an elastic constant of the bulk origin. On the other hand, the other surfacelike elastic constant  $K_{24}$ , making a contribution of order  $\epsilon^2 \xi^{-2}$ , is shown to be real and to approximately satisfy an extended Nehring-Saupe relation  $K_{24} \geq (K_{11} - K_{22})/2$  after incorporation of the density corrections in orientationally distorted states [21].

The seeming discrepancy of the present result  $K_{13}=0$  with the previous microscopic theories giving an apparently nonzero  $K_{13}$  [9,14,26] is then analyzed by making a more general gradient expansion of the intrinsic free energy in such a way as to potentially allow an appearance of a term linear in  $\epsilon$ . The  $K_{13}$  term comes formally from the ground-state part of the free-energy functional rather than from the elastic excess free energy. We show that the aforementioned freedom in choosing the integration variable makes it impossible to uniquely define  $K_{13}$ , even as a coefficient of the gradient expansion of the intrinsic free energy. This is in fact a manifestation of the physical irrelevance of  $K_{13}$ . We show here that  $K_{13}=0$  should result even in the gradient expansion of the ground-state free energy. Our argument rests on the general algebraic property of the part of the nonlocal free-energy functional  $G_{13}(\mathbf{r}, \mathbf{r}')$  responsible for the  $K_{13}$  term,

$$G_{13}(\mathbf{r}, \mathbf{r}') = -G_{13}(\mathbf{r}', \mathbf{r}) + O(\epsilon^2 \xi^{-2}). \quad (8)$$

So the double integral on  $G_{13}(\mathbf{r}, \mathbf{r}')$  is internally canceled to vanish to the order of  $O(\epsilon \xi^{-2})$  within the range of intermolecular interaction, thereby leaving  $K_{13}=0$ . It is further shown that the emergence of an apparently nonzero yet ambiguous  $K_{13}$  in previous theories is an artifact of the gradient expansion resulting from the inconsistent treatment of the nonlocal-to-local mapping at a boundary.

On the basis of the present formalism, we shall finally derive a microscopic expression for the interfacial elastic free energy for an obliquely aligning interface. Including the

tangential as well as the normal gradients of the director, the interfacial elastic free-energy density is shown to consist of the anchoring energy and a contribution formally identical to  $f_{24}$  together with other terms connected with the surface-specific symmetry at the interface having no counterparts in the bulk phase.

## II. FUNDAMENTALS OF DENSITY-FUNCTIONAL THEORY

According to the density-functional theory [45], the equilibrium density profile of a nonuniform anisotropic liquid can be determined as the one that minimizes the grand thermodynamic potential  $\Omega$  regarded as a functional of the single-particle density function  $\rho(\mathbf{r}, \boldsymbol{\omega})$  at the point  $\mathbf{r}$  and the orientation  $\boldsymbol{\omega}$ . For the sake of brevity of presentation, we restrict our attention here to an axially symmetrical rigid molecule whose orientation can be specified by a single unit vector  $\boldsymbol{\omega}$ .

The grand thermodynamic potential functional has the general form

$$\begin{aligned} \Omega[\rho] = & F_{\text{id}}[\rho] - \Phi[\rho] - \mu \int d\mathbf{r} d\boldsymbol{\omega} \rho(\mathbf{r}, \boldsymbol{\omega}) \\ & + \int d\mathbf{r} d\boldsymbol{\omega} \rho(\mathbf{r}, \boldsymbol{\omega}) V_{\text{ext}}(\mathbf{r}, \boldsymbol{\omega}), \end{aligned} \quad (9)$$

where  $V_{\text{ext}}(\mathbf{r}, \boldsymbol{\omega})$  is the single-particle external potential like the one that acts on a liquid-crystal molecule from a solid substrate and  $F_{\text{id}}[\rho]$  is the Helmholtz free energy of an ideal (noninteracting) gas given by

$$F_{\text{id}}[\rho] = k_B T \int d\mathbf{r} d\boldsymbol{\omega} \rho(\mathbf{r}, \boldsymbol{\omega}) \{ \ln[\lambda^3 \rho(\mathbf{r}, \boldsymbol{\omega})] - 1 \}, \quad (10)$$

with  $\lambda$  being the thermal wavelength. Finally,  $\Phi[\rho]$  is the excess part of the free-energy functional arising from the interparticle interactions. The aforementioned minimum property of the grand thermodynamic potential follows from the variational inequality

$$\Omega[\rho_{\text{eq}}] \leq \Omega[\rho], \quad (11)$$

which is valid under a fixed temperature and chemical potential, with  $\rho_{\text{eq}}$  being the equilibrium density function. The equality holds if and only if  $\rho(\mathbf{r}, \boldsymbol{\omega}) = \rho_{\text{eq}}(\mathbf{r}, \boldsymbol{\omega})$ .

Once  $\Phi[\rho]$  is given, the equilibrium density is found from the variational equation

$$\frac{\delta \Omega}{\delta \rho} = 0, \quad (12)$$

which, on account of Eqs. (9) and (10), specifically leads to

$$\ln[\lambda^3 \rho(\mathbf{r}, \boldsymbol{\omega})] = \frac{1}{k_B T} [\mu - V_{\text{ext}}(\mathbf{r}, \boldsymbol{\omega})] + c(\rho; \mathbf{r}, \boldsymbol{\omega}), \quad (13)$$

where

$$c(\rho; \mathbf{r}, \boldsymbol{\omega}) = \frac{1}{k_B T} \frac{\delta \Phi[\rho]}{\delta \rho(\mathbf{r}, \boldsymbol{\omega})} \quad (14)$$

denotes the first member of the hierarchy of direct correlation functions. We introduce here a parametrized density function, depending on a single parameter  $\alpha$  via

$$\rho_\alpha(\mathbf{r}, \boldsymbol{\omega}) = \rho_{\text{ref}}(\mathbf{r}, \boldsymbol{\omega}) + \alpha[\rho(\mathbf{r}, \boldsymbol{\omega}) - \rho_{\text{ref}}(\mathbf{r}, \boldsymbol{\omega})], \quad (15)$$

where  $\rho_{\text{ref}}(\mathbf{r}, \boldsymbol{\omega})$  stands for the density function in an arbitrarily chosen reference fluid. By definition,  $\rho_0(\mathbf{r}, \boldsymbol{\omega}) = \rho_{\text{ref}}(\mathbf{r}, \boldsymbol{\omega})$  and  $\rho_1(\mathbf{r}, \boldsymbol{\omega}) = \rho(\mathbf{r}, \boldsymbol{\omega})$ . Then, by integrating Eq. (14) from  $\alpha=0$  to 1, we readily obtain

$$\begin{aligned} & \Phi[\rho] - \Phi[\rho_{\text{ref}}] \\ &= \int_0^1 \frac{\partial \Phi[\rho_\alpha]}{\partial \alpha} d\alpha \\ &= k_B T \int_0^1 d\alpha \int d\mathbf{r} d\boldsymbol{\omega} [\rho(\mathbf{r}, \boldsymbol{\omega}) - \rho_{\text{ref}}(\mathbf{r}, \boldsymbol{\omega})] \\ & \quad \times c(\rho_\alpha; \mathbf{r}, \boldsymbol{\omega}) \end{aligned} \quad (16)$$

$$\begin{aligned} &= k_B T \int d\mathbf{r} d\boldsymbol{\omega} [\rho(\mathbf{r}, \boldsymbol{\omega}) - \rho_{\text{ref}}(\mathbf{r}, \boldsymbol{\omega})] \\ & \quad \times c(\rho_{\text{ref}}; \mathbf{r}, \boldsymbol{\omega}) - k_B T \int_0^1 (\alpha - 1) d\alpha \\ & \quad \times \int d\mathbf{r}' d\boldsymbol{\omega}' [\rho(\mathbf{r}, \boldsymbol{\omega}) - \rho_{\text{ref}}(\mathbf{r}, \boldsymbol{\omega})] \\ & \quad \times [\rho(\mathbf{r}', \boldsymbol{\omega}') - \rho_{\text{ref}}(\mathbf{r}', \boldsymbol{\omega}')] \\ & \quad \times c(\rho_\alpha; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}'). \end{aligned} \quad (17)$$

The third line follows by integrating the second by parts with respect to  $\alpha$  with the use of the definition of the Ornstein-Zernike direct correlation function

$$c(\rho; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') = \frac{1}{k_B T} \frac{\delta^2 \Phi[\rho]}{\delta \rho(\mathbf{r}, \boldsymbol{\omega}) \delta \rho(\mathbf{r}', \boldsymbol{\omega}')} \quad (18)$$

$$= c(\rho; \mathbf{r}', \boldsymbol{\omega}', \mathbf{r}, \boldsymbol{\omega}). \quad (19)$$

Successive application of integration by parts yields a formal series expansion of the free-energy functional in powers of  $\delta\rho \equiv \rho(\mathbf{r}, \boldsymbol{\omega}) - \rho_{\text{ref}}(\mathbf{r}, \boldsymbol{\omega})$ .

Rearranging Eq. (16), we get

$$\begin{aligned} \Phi[\rho] &= k_B T \int_0^1 d\alpha \int d\mathbf{r} d\boldsymbol{\omega} \{ [\rho(\mathbf{r}, \boldsymbol{\omega}) - \rho_{\text{ref}}(\mathbf{r}, \boldsymbol{\omega})] \\ & \quad \times c(\rho_\alpha; \mathbf{r}, \boldsymbol{\omega}) + \rho_{\text{ref}}(\mathbf{r}, \boldsymbol{\omega}) c(\alpha \rho_{\text{ref}}; \mathbf{r}, \boldsymbol{\omega}) \}. \end{aligned} \quad (20)$$

This formula, in combination with Eqs. (9) and (10), shows that, for a uniform fluid with the density  $\rho(\boldsymbol{\omega})$ , the free-energy density can be unambiguously defined by

$$\begin{aligned} f_u[\rho] &= k_B T \int_0^1 d\alpha \int d\boldsymbol{\omega} \rho(\boldsymbol{\omega}) \{ \ln[\lambda^3 \rho(\boldsymbol{\omega})] - 1 - \mu/k_B T \} \\ & \quad - k_B T \int_0^1 d\alpha \int d\boldsymbol{\omega} \{ [\rho(\boldsymbol{\omega}) - \rho_{\text{ref}}(\boldsymbol{\omega})] c(\rho_\alpha; \mathbf{r}, \boldsymbol{\omega}) \\ & \quad + \rho_{\text{ref}}(\boldsymbol{\omega}) c(\alpha \rho_{\text{ref}}; \mathbf{r}, \boldsymbol{\omega}) \}, \end{aligned} \quad (21)$$

where the reference fluid has also been regarded as being uniform.

### III. ABSENCE OF $K_{13}$ IN THE CURVATURE ELASTICITY OF NEMATIC LIQUID CRYSTALS

#### A. Symmetry in undistorted nematic liquid crystals

The point group of an undistorted nematic phase is  $D_{\infty h}$ , characterized by the presence of an axis of indefinite rotation about the director  $\mathbf{n}$  and a twofold axis and a mirror plane perpendicular to  $\mathbf{n}$ . This is an expression of the uniaxial and nonpolar nature of the nematic phase. Hence any ensemble-averaged functions of the molecular position  $\mathbf{r}$  and orientation  $\boldsymbol{\omega}$  pertaining to the undistorted nematic phase should remain invariant under the following transformations:  $(\mathbf{r}, \boldsymbol{\omega}) \rightarrow (\mathbf{T}[\mathbf{r}], \mathbf{T}[\boldsymbol{\omega}])$ , where  $\mathbf{T}[\ ]$  denotes the rotation operator about the director (taken along the  $z$  direction) by an arbitrary angle;  $(r_x, r_y, r_z) \rightarrow (r_x, -r_y, -r_z)$ ;  $(\omega_x, \omega_y, \omega_z) \rightarrow (\omega_x, -\omega_y, -\omega_z)$ ; and  $(\mathbf{r}, \boldsymbol{\omega}) \rightarrow (-\mathbf{r}, -\boldsymbol{\omega})$ . Being liquidlike in the molecular positions, furthermore, the undistorted nematic liquid crystal must also be invariant under arbitrary translations.

Any single-point function that is compatible with these symmetry transformations must be a function of  $(\mathbf{n} \cdot \boldsymbol{\omega})^2$  alone. In particular, therefore, the equilibrium density function must be of the form

$$\bar{\rho}(\mathbf{r}, \boldsymbol{\omega}) = \rho_0(\mathbf{n} \cdot \boldsymbol{\omega}), \quad (22)$$

with  $\rho_0(q) = \rho_0(-q)$ , which should also satisfy the equilibrium condition Eq. (13),

$$\ln[\lambda^3 \rho_0(\mathbf{n} \cdot \boldsymbol{\omega})] = \mu/k_B T + c(\bar{\rho}; \mathbf{r}, \boldsymbol{\omega}). \quad (23)$$

Similarly, the Ornstein-Zernike direct correlation function should depend only on the relative separation vector  $\mathbf{u} = \mathbf{r}' - \mathbf{r}$  due to the translational symmetry and satisfy the inversion relations

$$\begin{aligned} c(\bar{\rho}; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') &= c(\bar{\rho}; \mathbf{r}', -\boldsymbol{\omega}, \mathbf{r}, -\boldsymbol{\omega}') \\ &= c(\bar{\rho}; \mathbf{r}, -\boldsymbol{\omega}', \mathbf{r}', -\boldsymbol{\omega}). \end{aligned} \quad (24)$$

In addition to the real-space symmetries as above, the nematic phase has also a rotational symmetry in the isotopic space spanned by the director [51]. This symmetry is known as the Nambu-Goldstone degeneracy, which states that the free energy of a uniform nematic liquid crystal is invariant under any degree of homogeneous rotation of the director. By differentiating Eq. (23) by  $\mathbf{n}$ , we obtain an expression of the rotational degeneracy as

$$\left[ \int d\mathbf{r} d\boldsymbol{\omega} C_2(\bar{\rho}; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') \rho'_0(\mathbf{n} \cdot \boldsymbol{\omega}) \boldsymbol{\omega} \right] \cdot \delta \mathbf{n} = O(|\delta \mathbf{n}|^2), \quad (25)$$

which is valid for arbitrary  $\mathbf{n}$ . Here  $\rho'_0(t) = d\rho_0(t)/dt$  and

$$C_2(\bar{\rho}; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') \equiv \frac{\delta(\mathbf{r} - \mathbf{r}') \delta(\boldsymbol{\omega} - \boldsymbol{\omega}')}{\rho_0(\mathbf{n} \cdot \boldsymbol{\omega})} - c(\bar{\rho}; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}'). \quad (26)$$

We arrive at an alternative expression of the degeneracy by differentiating Eq. (21) after substituting  $\rho(\boldsymbol{\omega}) = \rho_0(\mathbf{n} \cdot \boldsymbol{\omega})$ :

$$\begin{aligned}
& \int_0^1 \alpha \, d\alpha \int d\mathbf{r}' \, d\boldsymbol{\omega} \, d\boldsymbol{\omega}' [c(\bar{\rho}_\alpha; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') \\
& - c(\bar{\rho}_\alpha; \mathbf{r}, \boldsymbol{\omega}', \mathbf{r}', \boldsymbol{\omega})][\rho_0(\mathbf{n} \cdot \boldsymbol{\omega}') - \rho_{\text{ref}}(\boldsymbol{\omega}')] \rho_0' \\
& \times (\mathbf{n} \cdot \boldsymbol{\omega}) \boldsymbol{\omega} \cdot \delta \mathbf{n} = O(|\delta \mathbf{n}|^2). \tag{27}
\end{aligned}$$

This becomes a trivial identity if  $c(\bar{\rho}_\alpha; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}')$  satisfies the inversion relation Eq. (24) all along the path of the integral with respect to  $\alpha$ .

### B. Density-functional expression of the elastic excess free energy

When the uniform nematic liquid crystal is subjected to an inhomogeneous external potential  $V_d(\mathbf{r}, \boldsymbol{\omega})$ , the nematic liquid crystal undergoes an orientational deformation from  $\mathbf{n}_0$  to  $\mathbf{n}(\mathbf{r}) = \mathbf{n}_0 + \delta \mathbf{n}(\mathbf{r})$ . The elastic excess free energy  $\delta F[\mathbf{n}]$  is then stored in the medium as an equivalent of the reversible work done by the external potential, as it has been turned on from  $V_{\text{ext}}(\mathbf{r}, \boldsymbol{\omega}) = 0$  to  $V_{\text{ext}}(\mathbf{r}, \boldsymbol{\omega}) = V_d(\mathbf{r}, \boldsymbol{\omega})$ . In terms of the density function  $\rho_d(\mathbf{r}, \boldsymbol{\omega})$  that is in equilibrium under the action of  $V_d(\mathbf{r}, \boldsymbol{\omega})$ , the elastic excess free energy is thus given by

$$\begin{aligned}
\delta F[\mathbf{n}] &= \Omega[\rho_d] - \Omega[\bar{\rho}] - \int d\mathbf{r} \, d\boldsymbol{\omega} \, \rho_d(\mathbf{r}, \boldsymbol{\omega}) V_d(\mathbf{r}, \boldsymbol{\omega}) \\
&= F_{\text{id}}[\rho_d] - F_{\text{id}}[\bar{\rho}] - \Phi[\rho_d] + \Phi[\bar{\rho}] \\
&\quad - \mu \int d\mathbf{r} \, d\boldsymbol{\omega} [\rho_d(\mathbf{r}, \boldsymbol{\omega}) - \bar{\rho}(\boldsymbol{\omega})], \tag{28}
\end{aligned}$$

where  $\bar{\rho}(\boldsymbol{\omega})$  denotes the density function in the uniform nematic liquid crystal.

Here, however, it must be noted that since the director embodies only contracted information of the full density function, the correspondence from a given  $\mathbf{n}(\mathbf{r})$  to the equilibrium density function  $\rho_d(\mathbf{r}, \boldsymbol{\omega})$ , or equivalently to  $V_d(\mathbf{r}, \boldsymbol{\omega})$ , is not unique. As a result, the elastic excess free energy as given above cannot be regarded in general as a unique functional of the director field, but must be understood to depend on the choice of the external potential as well. It is only if we restrict our attention to the asymptotic behavior of the nematic liquid crystal in the limit of small and long-wavelength deformations that a unique definition of the functional  $\delta F[\mathbf{n}]$  follows generally from the Nambu-Goldstone degeneracy. To be specific, let us imagine that the nematic director is at first uniformly aligned in a homogeneous magnetic field  $\mathbf{H}_0$  applied along the  $z$  axis (see Fig. 1) and then a small perturbing magnetic field  $\mathbf{H}_\perp(\mathbf{r})$  is turned on perpendicular to  $\mathbf{H}_0$  so as to induce a weak distortion in the director field. If we denote as shown in Fig. 1, the characteristic amplitude and wavelength of the distortion by  $\epsilon \ll 1$  and  $\xi$ , respectively, we have for sufficiently large  $\xi$

$$H_\perp/H_0 \sim O(\epsilon) \quad \text{and hence} \quad \nabla H_\perp/H_0 \sim O(\epsilon \xi^{-1}). \tag{29}$$

An immediate consequence of the Nambu-Goldstone degeneracy is that in a uniform system ( $\xi \rightarrow \infty$ ), the transverse susceptibility of the director, defined by  $(\partial \mathbf{n} / \partial H_\perp)_{H_\perp=0}$ , diverges to infinity like  $1/H_0$  as  $H_0 \rightarrow 0$  [51]. This means that as  $\xi \rightarrow \infty$ , the nematic liquid crystal becomes indefinitely soft

with respect to director rotation. According to the Oseen-Frank free energy, indeed, the curvature elastic stiffness for a distortion mode of wavelength  $\xi$  scales as  $\xi^{-2}$ , so that for a given  $\epsilon$ , we can assume, by virtue of the asymptotic softness, that the external field also vanishes as  $H_0 \sim H_\perp \sim O(\xi^{-1})$  while satisfying Eq. (29). Consequently, the corresponding external potential proportional to  $H^2$  behaves asymptotically as

$$V_d(\mathbf{r}, \boldsymbol{\omega}) \sim O(\xi^{-2}). \tag{30}$$

With this condition imposed on the external potential, only the distortion mode associated with the director that becomes infinitely susceptible as  $\xi \rightarrow \infty$  can contribute a free-energy density of the correct order of  $\xi^{-2}$ . The rest of the modes of density deviations, having a finite susceptibility even in the uniform state, can only yield a free-energy contribution of the order of  $\xi^{-4}$ , which indicates that the role of these modes is negligible in the long-wavelength limit. In this asymptotic sense,  $\delta F[\mathbf{n}]$  becomes a unique functional of the director field.

Under the assumption of small and long-wavelength deformations, we expand Eq. (28) in powers of

$$\delta \rho(\mathbf{r}, \boldsymbol{\omega}) = \rho_d(\mathbf{r}, \boldsymbol{\omega}) - \bar{\rho}(\boldsymbol{\omega}) \tag{31}$$

by substituting  $\rho_{\text{ref}}(\mathbf{r}, \boldsymbol{\omega}) = \bar{\rho}(\boldsymbol{\omega})$  in Eq. (17). After truncating the expansion at the order of  $\epsilon^2$  with the assumption of  $\delta \rho(\mathbf{r}, \boldsymbol{\omega}) = O(\epsilon)$ , we obtain

$$\begin{aligned}
\delta F[\mathbf{n}] &= \frac{1}{2} k_B T \int d\mathbf{r} \, d\boldsymbol{\omega} \, d\mathbf{r}' \, d\boldsymbol{\omega}' C_2(\bar{\rho}; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') \\
&\quad \times \delta \rho(\mathbf{r}, \boldsymbol{\omega}) \delta \rho(\mathbf{r}', \boldsymbol{\omega}'). \tag{32}
\end{aligned}$$

The term linear in  $\delta \rho$  automatically cancels out because of the equilibrium condition for  $\bar{\rho}(\mathbf{r}, \boldsymbol{\omega})$ , Eq. (13).

### C. Density function in a deformed nematic liquid crystal

For evaluation of the elastic excess free energy for a given director field, we need to know the equilibrium density function for the distorted nematic liquid crystal under the influence of the asymptotically weakening external potential. A conventional approach is to extend the density function for the undistorted nematic Eq. (22) into a weakly deformed state via

$$\rho_d(\mathbf{r}, \boldsymbol{\omega}) = \rho_0(\mathbf{n}(\mathbf{r}) \cdot \boldsymbol{\omega}) \tag{33}$$

by postulating that the local structure of a distorted nematic liquid crystal is indistinguishable from that of the undistorted state with the same director, as long as the deformation is of a sufficiently long wavelength. This quasihomogeneous approximation has indeed been employed by all the previous authors except Somoza and Tarazona [21] to work out the microscopic expressions of curvature elastic constants.

One should note, however, that the above approximate form automatically inherits the symmetry property of the uniform nematic liquid crystal for inversion of molecular orientation, i.e.,  $\boldsymbol{\omega} \rightarrow -\boldsymbol{\omega}$ , though it is no longer a general requisite in deformed states. In reality, Eq. (33) must be regarded as the leading term in the expansion of the true den-

sity function in terms of the spatial gradient of director. To the required order of  $\xi^{-1}$ , therefore, we must in general retain the contribution that is first order in the gradient of the director. This correction in density function beyond the quasihomogeneous approximation must be determined by the requirement that the external potential conjugate to  $\rho_d(\mathbf{r}, \boldsymbol{\omega})$  should behave as  $\xi^{-2}$  in the long-wavelength limit for the given director field  $\mathbf{n}(\mathbf{r})$ . As shown in Appendix A, in terms of the density-density correlation function  $C_2^{-1}(\bar{\rho}; \mathbf{u}, \boldsymbol{\omega}, \boldsymbol{\omega}')$  for the uniform nematic liquid crystal, the density correction can be rigorously written as

$$\begin{aligned} \Delta\rho(\mathbf{r}, \boldsymbol{\omega}) = & - \int d\mathbf{u} d\mathbf{u}' d\boldsymbol{\omega} d\boldsymbol{\omega}'' C_2^{-1}(\bar{\rho}; \mathbf{u}', \boldsymbol{\omega}, \boldsymbol{\omega}'') \\ & \times C_2(\bar{\rho}; \mathbf{u}, \boldsymbol{\omega}'', \boldsymbol{\omega}') \rho'_0(\mathbf{n}_0 \cdot \boldsymbol{\omega}') \boldsymbol{\omega}' \cdot [\mathbf{u} \cdot \nabla \mathbf{n}(\mathbf{r})], \end{aligned} \quad (34)$$

which is antisymmetrical for  $\boldsymbol{\omega} \rightarrow -\boldsymbol{\omega}$ . This formula clearly indicates the importance of short-range orientational correlations for the emergence of density correction. Moreover, the antisymmetry demands that, in order for  $\Delta\rho(\mathbf{r}, \boldsymbol{\omega})$  to survive, the molecule must be asymmetrical along at least one of its principal axes. This is the case for most real molecules, but is not so in most of the model molecules such as simple rods and disks.

#### D. Microscopic expressions for Oseen-Frank elastic constants

We shall first ignore the density correction and prove the absence of  $K_{13}$ . This result remains valid even after the inclusion of the density correction since its effect is solely to negatively renormalize the bulk elastic constants  $K_{11}$ ,  $K_{22}$ ,  $K_{33}$ , and  $K_{24}$  as shown in Appendix A. For a systematic evaluation of the elastic excess free energy, we make an extensive use of the identity

$$\begin{aligned} \delta\rho(\mathbf{r}, \boldsymbol{\omega}) \delta\rho(\mathbf{r}', \boldsymbol{\omega}') &= \frac{1}{2} [\delta\rho(\mathbf{r}, \boldsymbol{\omega}) \delta\rho(\mathbf{r}, \boldsymbol{\omega}') + \delta\rho(\mathbf{r}', \boldsymbol{\omega}) \delta\rho(\mathbf{r}', \boldsymbol{\omega}')] \\ &+ \frac{1}{2} [\delta\rho(\mathbf{r}, \boldsymbol{\omega}) \delta\rho(\mathbf{r}', \boldsymbol{\omega}') - \delta\rho(\mathbf{r}, \boldsymbol{\omega}') \delta\rho(\mathbf{r}', \boldsymbol{\omega})] \\ &+ \frac{1}{2} [\delta\rho(\mathbf{r}, \boldsymbol{\omega}) - \delta\rho(\mathbf{r}', \boldsymbol{\omega})] [\delta\rho(\mathbf{r}', \boldsymbol{\omega}') - \delta\rho(\mathbf{r}, \boldsymbol{\omega}')]. \end{aligned} \quad (35)$$

Each of the three terms on the right-hand side has a unique physical significance associated with the symmetry of the system and hence this formula allows a clear identification of bulk and interfacial contributions, as will be exploited in a later section. In fact, we show here that the first two terms vanish for symmetry reasons in the quasihomogeneous approximation, so they could make contributions only at a real physical boundary where the bulk symmetry may be broken. The last term is a volume contribution from which the Oseen-Frank elastic free energy comes.

Substitution of the above identity into Eq. (32) together with

$$\begin{aligned} \delta\rho(\mathbf{r}, \boldsymbol{\omega}) &= \delta\rho_0(\mathbf{r}, \boldsymbol{\omega}) = \rho_0(\mathbf{n} \cdot \boldsymbol{\omega}) - \rho_0(\mathbf{n}_0 \cdot \boldsymbol{\omega}) \\ &= \rho'_0(\mathbf{n}_0 \cdot \boldsymbol{\omega}) \boldsymbol{\omega} \cdot \delta\mathbf{n} + O(\epsilon^2) \end{aligned} \quad (36)$$

yields three independent contributions coming from each term of the identity. The first two contributions reflect primarily the breakdown of the Nambu-Goldstone degeneracy and of the inversion symmetry, respectively. Hence, on account of Eqs. (24) and (25), these two contributions are shown to vanish in the bulk nematic liquid crystal. For example, the second contribution  $\delta F_2[\mathbf{n}]$  can be transformed to

$$\begin{aligned} \delta F_2[\mathbf{n}] = & -\frac{1}{4} k_B T \int d\mathbf{r} d\boldsymbol{\omega} d\mathbf{r}' d\boldsymbol{\omega}' \delta\rho_0(\mathbf{r}, \boldsymbol{\omega}) \delta\rho_0(\mathbf{r}', \boldsymbol{\omega}') \\ & \times [c(\bar{\rho}; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') - c(\bar{\rho}; \mathbf{r}, -\boldsymbol{\omega}', \mathbf{r}', -\boldsymbol{\omega})] \end{aligned} \quad (37)$$

with the use of  $\delta\rho_0(\mathbf{r}, \boldsymbol{\omega}) = \delta\rho_0(\mathbf{r}, -\boldsymbol{\omega})$ . Using the inversion relation Eq. (24), we obtain  $\delta F_2[\mathbf{n}] = 0$ .

Consequently, we are finally left with only the third contribution, apparently related to the density gradients. Then, substituting Eq. (36), we obtain

$$\begin{aligned} \delta F[\mathbf{n}] = & \frac{1}{4} k_B T \int d\mathbf{r} d\boldsymbol{\omega} d\mathbf{r}' d\boldsymbol{\omega}' c(\bar{\rho}; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') \\ & \times \boldsymbol{\omega} \cdot [\delta\mathbf{n}(\mathbf{r}') - \delta\mathbf{n}(\mathbf{r})] \boldsymbol{\omega}' \cdot [\delta\mathbf{n}(\mathbf{r}') - \delta\mathbf{n}(\mathbf{r})]. \end{aligned} \quad (38)$$

Using  $\delta\mathbf{n}(\mathbf{r}') - \delta\mathbf{n}(\mathbf{r}) = \mathbf{u} \cdot \nabla \mathbf{n} + O(\epsilon \xi^{-2})$ , we can derive the elastic free-energy density, due originally to Poniewierski and Stecki [9], as

$$\delta F[\mathbf{n}] = \int d\mathbf{R} f_{\text{elastic}}(\mathbf{R}), \quad (39)$$

with

$$f_{\text{elastic}}(\mathbf{R}) = \frac{1}{2} M_{ijkl} \left( \frac{\partial n_k}{\partial R_i} \right) \left( \frac{\partial n_l}{\partial R_j} \right), \quad (40)$$

where the elastic constant tensor  $\mathbf{M}$  is specifically given by

$$\begin{aligned} M_{ijkl} = & \frac{1}{2} k_B T \int d\mathbf{u} d\boldsymbol{\omega} d\boldsymbol{\omega}' c(\bar{\rho}; \mathbf{u}, \boldsymbol{\omega}, \boldsymbol{\omega}') \rho'_0(\mathbf{n}_0 \cdot \boldsymbol{\omega}) \\ & \times \rho'_0(\mathbf{n}_0 \cdot \boldsymbol{\omega}') u_i u_j \omega_k \omega'_l. \end{aligned} \quad (41)$$

Here  $c(\bar{\rho}; \mathbf{u}, \boldsymbol{\omega}, \boldsymbol{\omega}') \equiv c(\bar{\rho}; \mathbf{0}, \boldsymbol{\omega}, \mathbf{r} - \mathbf{r}, \boldsymbol{\omega}')$  and the summation convention over repeated indices has been employed. Note that  $f_{\text{elastic}}(\mathbf{R})$  is positive and is also robust to changes in the nonlocal-to-local mapping in the sense that

$$f_{\text{elastic}}(\mathbf{R}) = f_{\text{elastic}}(\mathbf{R}') + O(\epsilon^2 \xi^{-3}), \quad (42)$$

which validates the meaning of  $f_{\text{elastic}}(\mathbf{R})$  as the elastic free-energy density.

It is evident from Eq. (40) that the tensor  $\mathbf{M}$  has a trivial symmetry for permutation of its indices as  $M_{ijkl} = M_{jikl}$ ; moreover, the specific form of  $\mathbf{M}$  given in Eq. (41) yields a more stringent Cauchy relation [52], which reads

$$M_{ijkl} = M_{jikl} = M_{ijlk} = M_{jilk}. \quad (43)$$

This relation originates from the particular microscopic structure we have adopted here for the nematic liquid crystal and goes beyond the requirements on tensor components set by the macroscopic symmetry of the nematic phase. Indeed, it is readily shown that the uniaxial symmetry about  $\mathbf{n}_0$  alone leaves us four independent tensor components  $M_{xxxx}$ ,

$M_{xxyy}$ ,  $M_{zzxx}$ , and  $M_{xyxy}$  (with the  $z$  axis taken along  $\mathbf{n}_0$ ), which could make nonzero contributions to the curvature elastic free energy and satisfy

$$M_{xxxx} = M_{yyyy}, \quad (44a)$$

$$M_{xxyy} = M_{yyxx}, \quad (44b)$$

$$M_{zzxx} = M_{zzyy}, \quad (44c)$$

$$M_{xyxy} + M_{xyyx} = M_{xxxx} - M_{xyyy}. \quad (44d)$$

With the use of these relations in Eq. (40), the free-energy density is rewritten into the Oseen-Frank form as

$$\begin{aligned} f_{\text{elastic}}(\mathbf{R}) &= \frac{1}{2} M_{xxxx} (\nabla \cdot \mathbf{n})^2 + \frac{1}{2} M_{xxyy} (\mathbf{n} \cdot \nabla \times \mathbf{n})^2 \\ &+ \frac{1}{2} M_{zzxx} (\mathbf{n} \times \nabla \times \mathbf{n})^2 \\ &- \frac{1}{2} (M_{xxyy} + M_{xyyx}) \nabla \cdot (\mathbf{n} \nabla \cdot \mathbf{n} + \mathbf{n} \times \nabla \times \mathbf{n}). \end{aligned} \quad (45)$$

No  $K_{13}$  term appears here as a direct consequence of the fact that second-order derivatives of the director are unable to make a contribution of the order of  $\xi^{-2}$  in Eq. (38). Comparing the above expression with the original Oseen-Frank free-energy density, we can make a tentative identification of the elastic constants as

$$K_{11} = M_{xxxx}, \quad (46a)$$

$$K_{22} = M_{xxyy}, \quad (46b)$$

$$K_{33} = M_{zzxx}, \quad (46c)$$

$$K_{24} = M_{xyyx}, \quad (46d)$$

$$K_{13} = 0. \quad (46e)$$

By applying the Cauchy relation to Eq. (44d), we get an additional relation

$$2M_{xyyx} = M_{xxxx} - M_{xxyy}, \quad (47)$$

which further reduces the number of independent components to 3. Furthermore, according to Eqs. (46a)–(46d), this equation is translated to

$$K_{24} = (K_{11} - K_{22})/2, \quad (48)$$

which may be most appropriately referred to as the Nehring-Saupe-Cauchy relation for its microscopic origin.

As mentioned at the beginning of this section, the result  $K_{13}=0$  is not affected even if the density correction is taken into account. According to Eq. (A13) in Appendix A, the decrease in the elastic free energy brought about by the density correction can be written in the local-density form

$$\Delta F_c[\mathbf{n}] = \int d\mathbf{R} f_c(\mathbf{R}), \quad (49)$$

with

$$\begin{aligned} f_c(\mathbf{R}) &= -\frac{1}{2} k_B T \int d\mathbf{u} d\boldsymbol{\omega} d\boldsymbol{\omega}' C_2(\bar{\rho}; \mathbf{u}, \boldsymbol{\omega}, \boldsymbol{\omega}') \\ &\times \Delta\rho(\mathbf{R}, \boldsymbol{\omega}) \Delta\rho(\mathbf{R}, \boldsymbol{\omega}'), \end{aligned} \quad (50)$$

where use has been made of the relation  $\Delta\rho(\mathbf{R}, \boldsymbol{\omega}) = \Delta\rho(\mathbf{R}', \boldsymbol{\omega}) + O(\epsilon\xi^{-2})$ , which implies the robustness of  $f_c(\mathbf{R})$  to changes in the nonlocal-to-local mapping. Since the density correction is linear to the first derivative of the director, it may be evident that no contribution of the type of  $K_{13}$  term is generated in the above equation. It is also notable that the correction in the elastic free energy is always negative, reflecting the favorable structural relaxations brought about by the density correction.

Substitution of the specific expression of the density correction Eq. (34) into Eq. (50) yields

$$f_c(\mathbf{R}) = -\frac{1}{2} \Delta M_{ijkl} \left( \frac{\partial n_k}{\partial R_i} \right) \left( \frac{\partial n_l}{\partial R_j} \right), \quad (51)$$

where

$$\begin{aligned} \Delta M_{ijkl} &= k_B T \int d\mathbf{u} d\mathbf{u}' d\mathbf{u}'' d\boldsymbol{\omega} d\boldsymbol{\omega}' d\boldsymbol{\omega}'' d\boldsymbol{\omega}''' \\ &\times C_2^{-1}(\bar{\rho}; \mathbf{u}'', \boldsymbol{\omega}'', \boldsymbol{\omega}''') c(\bar{\rho}; \mathbf{u}, \boldsymbol{\omega}', \boldsymbol{\omega}) \\ &\times c(\bar{\rho}; \mathbf{u}', \boldsymbol{\omega}', \boldsymbol{\omega}') \rho'_0(\mathbf{n}_0 \cdot \boldsymbol{\omega}) \rho'_0(\mathbf{n}_0 \cdot \boldsymbol{\omega}') u_i u'_j \omega_k \omega'_l. \end{aligned} \quad (52)$$

The indices in the above definition exactly correspond to those of the elastic constant tensor. With the addition of these corrections, the previous results are modified to

$$K_{11} = M_{xxxx} - \Delta M_{xxxx}, \quad (46a')$$

$$K_{22} = M_{xxyy} - \Delta M_{xxyy}, \quad (46b')$$

$$K_{33} = M_{zzxx} - \Delta M_{zzxx}, \quad (46c')$$

$$K_{24} = M_{xyyx} - \Delta M_{xyyx}, \quad (46d')$$

$$K_{13} = 0. \quad (46e')$$

As already mentioned, we still have  $K_{13}=0$ . This result automatically resolves the Oldano-Barbero pathology and offers a rationale for the tacit assumption made in almost all continuum theoretic treatments of director configurations [1]. This is also consistent with recent experimental estimates of  $K_{13}$  [41].

As shown in detail in Appendix A, there appears another Cauchy's relation connecting between the correction tensor components as

$$\Delta M_{xxyy} = \Delta M_{xyyx}, \quad (53)$$

which indicates that the corrections to  $K_{22}$  and  $K_{24}$  are identical. Due to the distinctness of this relation with the previous one in Eq. (43), the Nehring-Saupe-Cauchy relation must give up its general validity in the presence of density corrections. Under a plausible approximation ignoring the short-range intermolecular orientational correlation within a plane normal to the director, we can show that

$$\Delta M_{xxyy} = \Delta M_{xyyx} = 0. \quad (54)$$

Hence, in this situation, the correction applies only to  $K_{11}$  and  $K_{33}$  [21]. In view of the negative sign of the corrections, this result leads to the extended Nehring-Saupe relation

$$K_{24} \geq (K_{11} - K_{22})/2. \quad (55)$$

The absence of  $K_{13}$  is formally an immediate consequence of the uniformity of the nematic ground state. This condition demands that the excess free energy associated with a director distortion should always be quadratic in the distortion amplitude for stability reasons. However, since the  $K_{13}$  term is linear in the amplitude as already emphasized, there is no way for the  $K_{13}$  term to appear from such a quadratic free-energy expression. In this sense, the uniformity of the nematic ground state is a sufficient condition for the absence of  $K_{13}$ , but it may not be a necessary condition for it since the uniformity rules out not only  $K_{13}$ , but also any other spontaneously modulated structures such as the cholesteric twist. We shall look into this point in more detail in the next section.

#### IV. ORIGIN OF $K_{13}$ IN PREVIOUS THEORIES

The present result indicating  $K_{13}=0$  is apparently in sharp contradiction with the previous density-functional theories due to Poniewierski and Stecki [9], Lipkin, Rice, and Mohanty [14], and Teixeira, Pergamenschik, and Sluckin [26], all of which predict an apparently nonzero  $K_{13}$ . It should, therefore, be in order here to expound in detail the origin of this discrepancy and how it can be resolved.

Their common approach is to perform the functional Taylor expansion of the intrinsic free energy about some reference density function, which is assumed homogeneous yet is *not* the equilibrium density function in the undistorted ground state as we adopted in the preceding section. Poniewierski and Stecki took the vacuum as the reference, and Lipkin, Rice, and Mohanty and Teixeira, Pergamenschik, and Sluckin employed the isotropic liquid phase. A unified treatment of these two approaches is possible by starting with Eq. (20),

$$\begin{aligned} \Phi[\rho] = & k_B T \int_0^1 d\alpha \int d\mathbf{r} d\boldsymbol{\omega} [\rho(\mathbf{r}, \boldsymbol{\omega}) - \rho_{\text{ref}}(\boldsymbol{\omega})] c(\rho_\alpha; \mathbf{r}, \boldsymbol{\omega}) \\ & + \rho_{\text{ref}}(\boldsymbol{\omega}) c(\alpha \rho_{\text{ref}}; \mathbf{r}, \boldsymbol{\omega}), \end{aligned} \quad (56)$$

in which the position dependence of the reference density function has been dropped for the assumption of its homogeneity.

Our goal is to expand the intrinsic free-energy functional in powers of the density gradients in the Poniewierski-Stecki form

$$\begin{aligned} \Phi[\rho] = & \int d\mathbf{R} \left[ \int d\boldsymbol{\omega} \bar{\phi}(\rho(\mathbf{R}, \boldsymbol{\omega})) \right. \\ & + \int d\boldsymbol{\omega} a_i(\mathbf{R}, \boldsymbol{\omega}) \partial_i \rho(\mathbf{R}, \boldsymbol{\omega}) \\ & \left. + \int d\boldsymbol{\omega} \partial_i [b_{ij}(\mathbf{R}, \boldsymbol{\omega}) \partial_j \rho(\mathbf{R}, \boldsymbol{\omega})] \right] \end{aligned}$$

$$\begin{aligned} & + \frac{1}{2} \int d\boldsymbol{\omega} d\boldsymbol{\omega}' m_{ij}(\mathbf{R}, \boldsymbol{\omega}, \boldsymbol{\omega}') \\ & \times \partial_i \rho(\mathbf{R}, \boldsymbol{\omega}) \partial_j \rho(\mathbf{R}, \boldsymbol{\omega}') + \dots \end{aligned}, \quad (57)$$

where the coefficients of expansion  $a_i$ ,  $b_{ij}$ , and  $m_{ij}$  are functions of the local density. The first term in the large square brackets  $\int d\boldsymbol{\omega} \bar{\phi}(\rho(\mathbf{R}, \boldsymbol{\omega}))$  has the meaning of the intrinsic free-energy density in a hypothetical homogeneous fluid with its density everywhere equal to  $\rho(\mathbf{R}, \boldsymbol{\omega})$  for a fixed  $\mathbf{R}$ .

In order to systematically carry out the expansion about the local density, we introduce a new parametric density function defined by

$$\begin{aligned} \rho_{\alpha; \mathbf{r}; \alpha'}(\mathbf{r}', \boldsymbol{\omega}') & \equiv \rho_\alpha(\mathbf{r}, \boldsymbol{\omega}') + \alpha' [\rho_\alpha(\mathbf{r}', \boldsymbol{\omega}') - \rho_\alpha(\mathbf{r}, \boldsymbol{\omega}')] \\ & = \rho_\alpha(\mathbf{r}, \boldsymbol{\omega}') + \alpha' \alpha [\rho(\mathbf{r}', \boldsymbol{\omega}') - \rho(\mathbf{r}, \boldsymbol{\omega}')]. \end{aligned} \quad (58)$$

Taking similar steps as from Eqs. (16) and (17) with respect to  $\alpha'$ , we obtain

$$\begin{aligned} & c(\rho_\alpha; \mathbf{r}, \boldsymbol{\omega}) - c(\rho_{\alpha; \mathbf{r}}; \mathbf{r}, \boldsymbol{\omega}) \\ & = \alpha \int_0^1 d\alpha' \int d\mathbf{r}' d\boldsymbol{\omega}' \\ & \quad \times [\rho(\mathbf{r}', \boldsymbol{\omega}') - \rho(\mathbf{r}, \boldsymbol{\omega}')] c(\rho_{\alpha; \mathbf{r}; \alpha'}; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') \quad (59) \\ & = \alpha \int d\mathbf{r}' d\boldsymbol{\omega}' [\rho(\mathbf{r}', \boldsymbol{\omega}') - \rho(\mathbf{r}, \boldsymbol{\omega}')] c(\rho_{\alpha; \mathbf{r}}; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') \\ & \quad + \frac{1}{2} \alpha^2 \int d\mathbf{r}' d\boldsymbol{\omega}' d\mathbf{r}'' d\boldsymbol{\omega}'' \\ & \quad \times c(\rho_{\alpha; \mathbf{r}}; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}', \mathbf{r}'', \boldsymbol{\omega}'') [\rho(\mathbf{r}', \boldsymbol{\omega}') - \rho(\mathbf{r}, \boldsymbol{\omega}')] \\ & \quad \times [\rho(\mathbf{r}'', \boldsymbol{\omega}'') - \rho(\mathbf{r}, \boldsymbol{\omega}'')] + O(\xi^{-3}). \end{aligned} \quad (60)$$

Here  $\rho_{\alpha; \mathbf{r}}(\boldsymbol{\omega})$  denotes a homogeneous density function that is taken everywhere equal to  $\rho_\alpha(\mathbf{r}, \boldsymbol{\omega})$  for a fixed  $\mathbf{r}$ . Substitution of Eq. (60) into Eq. (56), with the use of Eq. (20), yields, up to the order of  $O(\xi^{-2})$ ,

$$\begin{aligned} \Phi[\rho] = & k_B T \int_0^1 d\alpha \int d\mathbf{r} d\boldsymbol{\omega} [\delta\rho(\mathbf{r}, \boldsymbol{\omega}) c(\rho_{\alpha; \mathbf{r}}; \mathbf{r}, \boldsymbol{\omega}) \\ & + \rho_{\text{ref}}(\boldsymbol{\omega}) c(\alpha \rho_{\text{ref}}; \mathbf{r}, \boldsymbol{\omega})] \\ & + k_B T \int_0^1 \alpha d\alpha \int d\mathbf{r} d\boldsymbol{\omega} d\mathbf{r}' d\boldsymbol{\omega}' \delta\rho(\mathbf{r}, \boldsymbol{\omega}) \\ & \quad \times [\rho(\mathbf{r}', \boldsymbol{\omega}') - \rho(\mathbf{r}, \boldsymbol{\omega}')] c(\rho_{\alpha; \mathbf{r}}; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') \\ & \quad + \frac{1}{2} k_B T \int_0^1 \alpha^2 d\alpha \int d\mathbf{r} d\boldsymbol{\omega} d\mathbf{r}' d\boldsymbol{\omega}' d\mathbf{r}'' d\boldsymbol{\omega}'' \\ & \quad \times c(\rho_{\alpha; \mathbf{r}}; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}', \mathbf{r}'', \boldsymbol{\omega}'') \delta\rho(\mathbf{r}, \boldsymbol{\omega}) [\rho(\mathbf{r}', \boldsymbol{\omega}') \\ & \quad - \rho(\mathbf{r}, \boldsymbol{\omega}')] [\rho(\mathbf{r}'', \boldsymbol{\omega}'') - \rho(\mathbf{r}, \boldsymbol{\omega}')], \end{aligned} \quad (61)$$

where  $\delta\rho(\mathbf{r}, \boldsymbol{\omega}) = \rho(\mathbf{r}, \boldsymbol{\omega}) - \rho_{\text{ref}}(\boldsymbol{\omega})$ . It may be worth emphasizing at this stage that the above expression is more general than the quadratic expansion of the free energy derived in



Sec. III, Eq. (32), in that no assumption has been made here regarding the nature of the ground state and there is no restriction on the distortion amplitude except that the wavelength be sufficiently large. Put differently, the functional Eq. (61) is applicable even for determining the ground-state structure, be it homogeneous or inhomogeneous, while Eq. (32) is not. Note that the formulas by Poniewierski and Stecki [9] and those by Lipkin, Rice, and Mohanty [14] and Teixeira, Pergamenschik, and Sluckin [26] follow by adopting in the above the quasihomogeneous density function  $\rho(\mathbf{r}, \boldsymbol{\omega}) = \rho_0(\mathbf{n}(\mathbf{r}) \cdot \boldsymbol{\omega})$ , along with  $\rho_{\text{ref}}(\boldsymbol{\omega}) = 0$  or  $\rho_{\text{iso}}(\boldsymbol{\omega})$  (the density function in the isotropic phase), respectively.

The gradient expansion is formally obtained by performing the Taylor expansion of the density function in Eq. (61) around a reference point  $\mathbf{R}$ . The first term is essentially local and thus we can unambiguously identify the integrand with  $\bar{\phi}(\rho(\mathbf{R}, \boldsymbol{\omega}))$  in Eq. (57) by substituting  $\mathbf{R}$  for  $\mathbf{r}$ . Here the Nambu-Goldstone degeneracy demands that, within the quasihomogeneous regime,  $\int d\boldsymbol{\omega} \bar{\phi}(\rho(\mathbf{R}, \boldsymbol{\omega}))$  should be a constant independent of  $\mathbf{R}$ , which is equal to the intrinsic free-energy density in the undistorted nematic liquid crystal. Therefore, as long as we can assume  $\rho(\mathbf{r}, \boldsymbol{\omega}) = \rho_0(\mathbf{n} \cdot \boldsymbol{\omega})$ , as done by Poniewierski and Stecki [9] and other authors [14,26] this term gives only a constant bias independent of the director field and hence can be safely neglected. Beyond the quasihomogeneous approximation, however, this is no longer true. Thus the density correction discussed in Sec. III is to make an excess contribution to the free-energy density, which the curvature elasticity should correctly take into account. We shall discuss this subject in Appendix B since the density correction does not have any effect on the  $K_{13}$  surfacelike elasticity.

The second integral is of central importance for the present purpose since it is this term from which the  $K_{13}$  term derives. The integral reflects the nonlocal pair interaction between  $\mathbf{r}$  and  $\mathbf{r}'$ ; as already stressed, the way to relate  $\mathbf{r}$  and  $\mathbf{r}'$  to the reference point  $\mathbf{R}$  always involves a certain degree of arbitrariness. To illustrate the influence of this arbitrariness on the gradient expansion, we restrict our attention to a subclass of nonlocal-to-local mapping schemes  $(\mathbf{r}, \mathbf{r}') \rightarrow (\mathbf{R}, \mathbf{u})$  that satisfy the set of plausible conditions

$$\frac{\partial(\mathbf{r}, \mathbf{r}')}{\partial(\mathbf{R}, \mathbf{u})} = 1, \quad (62)$$

$$\mathbf{R}(\mathbf{r}, \mathbf{r}) = \mathbf{r}, \quad (63)$$

$$\mathbf{R}(\mathbf{r} + \mathbf{a}, \mathbf{r}' + \mathbf{a}) = \mathbf{R}(\mathbf{r}, \mathbf{r}') + \mathbf{a}, \quad (64)$$

where the first condition is the requirement of nondilatationality and the last demands the translational covariance of  $\mathbf{R}$  for an arbitrary vector  $\mathbf{a}$ . The most general form of  $\mathbf{R}$  that meets these conditions is readily verified to be

$$\mathbf{R} = \frac{\mathbf{r} + \mathbf{r}'}{2} - \gamma(u^2)\mathbf{u}, \quad (65)$$

where  $\mathbf{u} = \mathbf{r}' - \mathbf{r}$  and  $\gamma(u^2)$  is an arbitrary regular function that solely takes care of the nonuniqueness of the nonlocal-to-local mapping in the present context. Poniewierski and Stecki; Teixeira, Pergamenschik, and Sluckin; and Lipkin, Rice, and Mohanty tacitly adopted  $\gamma = \frac{1}{2}$ , while Somoza and

Tarazona's choice, though criticized by Teixeira, Pergamenschik, and Sluckin, was  $\gamma = 0$  [21], which led them to argue that  $K_{13}$  is not a well-defined parameter. Since no *a priori*, if not aesthetic, reason exists to adopt a particular value for  $\gamma$ , it necessarily leads to a fundamental criterion that any physically meaningful local parameters such as elastic constants must be invariant under notional changes in  $\gamma(u^2)$ .

Taylor expansion of the density function about  $\mathbf{R}$  up to the order of  $\xi^{-2}$  gives

$$\begin{aligned} \rho(\mathbf{r}, \boldsymbol{\omega}) &= \rho(\mathbf{R}, \boldsymbol{\omega}) + (\gamma - \frac{1}{2})(\mathbf{u} \cdot \nabla)\rho(\mathbf{R}, \boldsymbol{\omega}) \\ &\quad + \frac{1}{2}(\gamma - \frac{1}{2})^2(\mathbf{u} \cdot \nabla)^2\rho(\mathbf{R}, \boldsymbol{\omega}) \end{aligned} \quad (66)$$

and a similar equation for  $\rho(\mathbf{r}', \boldsymbol{\omega})$ , which is found by replacing  $\gamma$  by  $\gamma + 1$  in Eq. (66). We note here the relation

$$\begin{aligned} &\int d\mathbf{u} d\mathbf{u}' [c(\rho_{\alpha; \mathbf{R}}; \mathbf{u}, \mathbf{u}', \boldsymbol{\omega}, \boldsymbol{\omega}', \boldsymbol{\omega}'') \\ &\quad + c(\rho_{\alpha; \mathbf{R}}; \mathbf{u}, \mathbf{u}', \boldsymbol{\omega}, \boldsymbol{\omega}'', \boldsymbol{\omega}')] u_i u_j \\ &= \int d\mathbf{u} d\mathbf{u}' [2c(\rho_{\alpha; \mathbf{R}}; \mathbf{u}, \mathbf{u}', \boldsymbol{\omega}, \boldsymbol{\omega}', \boldsymbol{\omega}'') \\ &\quad - c(\rho_{\alpha; \mathbf{R}}; \mathbf{u}, \mathbf{u}', \boldsymbol{\omega}', \boldsymbol{\omega}'', \boldsymbol{\omega})] u_i u_j, \end{aligned}$$

where

$$c(\rho_{\alpha; \mathbf{R}}; \mathbf{u}, \mathbf{u}', \boldsymbol{\omega}, \boldsymbol{\omega}', \boldsymbol{\omega}'') \equiv c(\rho_{\alpha; \mathbf{R}}; \mathbf{0}, \boldsymbol{\omega}, \mathbf{u}, \boldsymbol{\omega}', \mathbf{u}', \boldsymbol{\omega}''),$$

with  $\mathbf{u} = \mathbf{r}' - \mathbf{r}$  and  $\mathbf{u}' = \mathbf{r}'' - \mathbf{r}$ .

Then, substituting the above Taylor expansion into Eq. (61), we find

$$\begin{aligned} \Phi[\rho] &= \int d\mathbf{R} \int d\boldsymbol{\omega} \bar{\phi}(\rho(\mathbf{R}, \boldsymbol{\omega})) + k_B T \int d\mathbf{R} \int_0^1 \alpha d\alpha \\ &\quad \times \int d\mathbf{u} d\boldsymbol{\omega} d\boldsymbol{\omega}' c(\rho_{\alpha; \mathbf{R}}; \mathbf{u}, \boldsymbol{\omega}, \boldsymbol{\omega}') \\ &\quad \times \delta\rho(\mathbf{R}, \boldsymbol{\omega}) \mathbf{u} \cdot \nabla \rho(\mathbf{R}, \boldsymbol{\omega}') + k_B T \int d\mathbf{R} \int_0^1 \alpha d\alpha \\ &\quad \times \int d\mathbf{u} d\boldsymbol{\omega} d\boldsymbol{\omega}' \nabla \cdot [\gamma(u^2) c(\rho_{\alpha; \mathbf{R}}; \mathbf{u}, \boldsymbol{\omega}, \boldsymbol{\omega}') \\ &\quad \times \delta\rho(\mathbf{R}, \boldsymbol{\omega}) \mathbf{u} (\mathbf{u} \cdot \nabla) \rho(\mathbf{R}, \boldsymbol{\omega}')] \\ &\quad - \frac{1}{4} k_B T \int d\mathbf{R} \int d\mathbf{u} d\boldsymbol{\omega} d\boldsymbol{\omega}' c(\rho_{\mathbf{R}}; \mathbf{u}, \boldsymbol{\omega}, \boldsymbol{\omega}') \\ &\quad \times \mathbf{u} \cdot \nabla \rho(\mathbf{R}, \boldsymbol{\omega}) \mathbf{u} \cdot \nabla \rho(\mathbf{R}, \boldsymbol{\omega}') + \frac{1}{4} k_B T \int d\mathbf{R} \int_0^1 \alpha^2 d\alpha \\ &\quad \times \int d\mathbf{u} d\mathbf{u}' d\boldsymbol{\omega} d\boldsymbol{\omega}' d\boldsymbol{\omega}'' [c(\rho_{\alpha; \mathbf{R}}; \mathbf{u}, \mathbf{u}', \boldsymbol{\omega}, \boldsymbol{\omega}', \boldsymbol{\omega}'') \\ &\quad - c(\rho_{\alpha; \mathbf{R}}; \mathbf{u}, \mathbf{u}', \boldsymbol{\omega}, \boldsymbol{\omega}'', \boldsymbol{\omega}')] \\ &\quad \times \delta\rho(\mathbf{R}, \boldsymbol{\omega}) \mathbf{u} \cdot \nabla \rho(\mathbf{R}, \boldsymbol{\omega}') \mathbf{u}' \cdot \nabla \rho(\mathbf{R}, \boldsymbol{\omega}''). \end{aligned} \quad (67)$$

The second and third terms come from the second integral in Eq. (61), which is linear in the spatial difference in the density function. The third integral is a pure surface contribution, from which the  $K_{13}$  term apparently derives, as will be detailed below. A striking feature of this formula is that all the terms, except this surface contribution, is free from  $\gamma$ . In particular, if we employ the quasihomogeneous density function, it is immediately clear that the last integral disappears due to the inversion symmetry and the penultimate one generates exactly the same expressions for  $K_{11}$ ,  $K_{22}$ ,  $K_{33}$ , and  $K_{24}$  derived in Sec. III, Eqs. (41) and (46a)–(46d), before the density correction had been invoked. Furthermore, it can also be revealed that the only effect of density correction is to renormalize  $K_{11}$ ,  $K_{22}$ ,  $K_{33}$ , and  $K_{24}$  in the same manner as in Eqs. (46a')–(46d'); the detailed derivations are left to Appendix B for the ultimate irrelevance of this effect to the  $K_{13}$  issue.

To arrive at the expression for  $K_{13}$  formulated in the previous theories [9,14,26], we only need to substitute the quasihomogeneous density in the third integral of the above gradient expansion. The resultant elastic excess free energy  $\delta\Omega_{\text{surf}}[\mathbf{n}]$  can be written as

$$\delta\Omega_{\text{surf}}[\mathbf{n}] = \int d\mathbf{R} f_{\text{surf}}(\mathbf{R}) = \frac{1}{2} \int d\mathbf{R} \frac{\partial}{\partial R_i} \left( B_{ijk} \frac{\partial n_k}{\partial R_j} \right), \quad (68)$$

where

$$B_{ijk} = -2k_B T \int_0^1 \alpha d\alpha \int d\mathbf{u} d\boldsymbol{\omega} d\boldsymbol{\omega}' \gamma(u^2) c(\bar{\rho}_\alpha; \mathbf{u}, \boldsymbol{\omega}, \boldsymbol{\omega}') \\ \times [\rho_0(\mathbf{n}_0 \cdot \boldsymbol{\omega}) - \rho_{\text{ref}}(\boldsymbol{\omega})] \rho_0'(\mathbf{n}_0 \cdot \boldsymbol{\omega}') u_i u_j \omega'_k. \quad (69)$$

By the uniaxial symmetry about  $\mathbf{n}_0$  (taken along the  $z$  axis) and the symmetry about the permutation of the first two indices, we have

$$B_{zxx} = B_{zyy} = B_{xzx} = B_{yzy}, \\ B_{zxy} = B_{zyx} = B_{xzy} = B_{yzx} = 0. \quad (70)$$

With the aid of this relation, Eq. (68) is reduced to

$$f_{\text{surf}}(\mathbf{R}) = B_{xzx} \nabla \cdot (\mathbf{n} \nabla \cdot \mathbf{n}) - \frac{1}{2} B_{xzx} \nabla \cdot (\mathbf{n} \nabla \cdot \mathbf{n} + \mathbf{n} \times \nabla \times \mathbf{n}), \quad (71)$$

which allows an identification

$$K_{13} = B_{xzx}. \quad (72)$$

With  $\gamma(u^2) = \frac{1}{2}$  and  $\rho_{\text{ref}}(\boldsymbol{\omega}) = 0$ , Eq. (69) offers an integral representation of  $K_{13}$ , completely equivalent to the Poniewierski-Stecki formula [Eq. (3.3) in Ref. [9]]. On the other hand, the formulas due to Lipkin, Rice, and Mohanty [Eq. (4.10) in Ref. [14]] and Teixeira, Pergamenschchik, and Sluckin [Eq. (26b) in Ref. [26]] can be reproduced by setting  $\gamma(u^2) = \frac{1}{2}$  and  $\rho_{\text{ref}}(\boldsymbol{\omega}) = \rho_{\text{iso}}$  and replacing  $c(\bar{\rho}_\alpha; \mathbf{u}, \boldsymbol{\omega}, \boldsymbol{\omega}')$  by  $c(\rho_{\text{ref}}; \mathbf{u}, \boldsymbol{\omega}, \boldsymbol{\omega}')$ ; the result is approximate and is slightly different from Poniewierski and Stecki's result due to the negligence of higher-order direct correlation functions. The additional  $K_{24}$ -like term, along with the  $K_{13}$ , is to renormalize the  $K_{24}$  in Eq. (46d') to give

$$K_{24} = M_{xyyx} - \Delta M_{xyyx} + B_{xzx}. \quad (73)$$

Hence, unless  $B_{xzx} = 0$ , the Nehring-Saupe-Cauchy relation can no longer hold even in the quasihomogeneous regime. This result also agrees perfectly with the Poniewierski-Stecki formula; however, the expression derived by Teixeira, Pergamenschchik, and Sluckin is apparently lacking in this term, thereby inconsistently leaving the Nehring-Saupe-Cauchy relation intact. We shall leave it to Appendix B to show that the present results for  $K_{13}$  are unaffected even when the density correction is taken into account.

The above derivation clearly demonstrates that  $K_{13}$  as well as  $K_{24}$  has a twofold ambiguity in a general gradient expansion: First, they are linearly dependent on the arbitrary parameter  $\gamma(u^2)$ , so they can be assigned whatever value one wishes; second, the choice of the reference density also affects  $K_{13}$  and  $K_{24}$ . The first is in effect a restatement of the conjecture by Yokoyama [16] and by Somoza and Tarazona [21] that  $K_{13}$  does not possess a unique definition because of the ambiguity in the nonlocal-to-local mapping. The ambiguity is a clear indication that the surfacelike bulk elastic constants cannot be a well-defined material parameter, unless an independent condition is given whereby  $\gamma$  is uniquely fixed. This is, in fact, what Teixeira, Pergamenschchik, and Sluckin [26] claimed, in an objection to Somoza and Tarazona's argument; they argued that the only one natural choice of  $\gamma$  should be  $\frac{1}{2}$ , corresponding to  $\mathbf{R} = \mathbf{r}$ , for reasons of consistency in the choice of undistorted local reference state. In what follows, however, we shall demonstrate that the emergence of a surface term itself is an artifact of the gradient expansion that appears when a gradient expansion is formally applied to an essentially null functional. This eliminates the discrepancy in question in favor of our results derived in Sec. III; for a more detailed examination of the argument of Teixeira, Pergamenschchik, and Sluckin see Appendix C.

To look more closely into the nature of the surfacelike bulk elastic term, we introduce the symmetrical and the antisymmetrical components of the direct correlation function by

$$c^s(\rho; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') = \frac{1}{2} [c(\rho; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') + c(\rho; \mathbf{r}, \boldsymbol{\omega}', \mathbf{r}', \boldsymbol{\omega})], \\ c^a(\rho; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') = \frac{1}{2} [c(\rho; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') - c(\rho; \mathbf{r}, \boldsymbol{\omega}', \mathbf{r}', \boldsymbol{\omega})].$$

Using these definitions in Eq. (67), we can rewrite the second and third integrals in a more comprehensible form as

$$\Phi[\rho] = \cdots + k_B T \int d\mathbf{R} \int_0^1 \alpha d\alpha \\ \times \int d\mathbf{u} d\boldsymbol{\omega} d\boldsymbol{\omega}' c^a(\rho_{\alpha; \mathbf{R}}; \mathbf{u}, \boldsymbol{\omega}, \boldsymbol{\omega}') \delta\rho(\mathbf{R}, \boldsymbol{\omega}) \\ \times \mathbf{u} \cdot \nabla \rho(\mathbf{R}, \boldsymbol{\omega}') + k_B T \int d\mathbf{R} \int_0^1 \alpha d\alpha \\ \times \int d\mathbf{u} d\boldsymbol{\omega} d\boldsymbol{\omega}' \nabla \cdot [\gamma(u^2) c^s(\rho_{\alpha; \mathbf{R}}; \mathbf{u}, \boldsymbol{\omega}, \boldsymbol{\omega}') \\ \times \delta\rho(\mathbf{R}, \boldsymbol{\omega}) \mathbf{u} \cdot \nabla] \rho(\mathbf{R}, \boldsymbol{\omega}') + \cdots. \quad (74)$$

This equation clearly reveals the distinct symmetry origins of these two terms, though both come from a single linear term

in the original nonlocal expression. For the quasihomogeneous density function, the former integral involving the antisymmetrical component is readily confirmed to yield a contribution linear to  $\mathbf{n} \cdot (\nabla \times \mathbf{n})$ , thereby indicating its role in spontaneous twisting in a cholesteric phase containing chiral molecules. The intimate connection between the absence of the antisymmetric component and the Nambu-Goldstone degeneracy may be evident in Eq. (27).

The latter integral, on the other hand, is the source of  $K_{13}$ , which could also have an effect to induce a spontaneous modulation due to its linear nature as emphasized in the previous sections. Here, returning to the original free-energy expression Eq. (61), we define a free-energy kernel function by

$$G(\mathbf{r}, \mathbf{r}') \equiv \int d\boldsymbol{\omega} d\boldsymbol{\omega}' \delta\rho(\mathbf{r}, \boldsymbol{\omega}) [\rho(\mathbf{r}', \boldsymbol{\omega}') - \rho(\mathbf{r}, \boldsymbol{\omega}')] \times c^s(\rho_{\alpha; \mathbf{r}}; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}'), \quad (75)$$

which, on gradient expansion, yields the  $K_{13}$  term. Making use of the permutation symmetry of the direct correlation function appearing in the above, we can prove the approximate antisymmetrical relation

$$G(\mathbf{r}, \mathbf{r}') = -G(\mathbf{r}', \mathbf{r}) + O(|\rho(\mathbf{r}) - \rho(\mathbf{r}')|^2). \quad (76)$$

The second term on the right-hand side represents a term quadratic in the density difference, from which no surface terms (involving  $\gamma$ ) can be generated. Consequently, substituting this relation into Eq. (61), we reach our central result

$$\int d\mathbf{r} d\mathbf{r}' G(\mathbf{r}, \mathbf{r}') = \int d\mathbf{r} d\mathbf{r}' d\boldsymbol{\omega} d\boldsymbol{\omega}' \delta\rho(\mathbf{r}, \boldsymbol{\omega}) [\rho(\mathbf{r}', \boldsymbol{\omega}') - \rho(\mathbf{r}, \boldsymbol{\omega}')] c^s(\rho_{\alpha; \mathbf{r}}; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') = O(\epsilon^2 \xi^{-2}) \quad (77)$$

and hence

$$K_{13} = 0. \quad (78)$$

It must be clearly noted that, in the above derivation of  $K_{13}=0$ , we have not assumed the permutation symmetry of the direct correlation function. Rather, we showed that  $K_{13}$  comes only from the permutation symmetrical part of the direct correlation function, and when it is combined with the linearity of the term in the density difference, the free-energy contribution with the relevant order to  $K_{13}$  vanishes due to the semilocal cancellation of the interaction free energy. In this respect, we can conclude that  $K_{13}=0$  is a very general result, which applies not only to nematic liquid crystals but also cholesteric liquid crystals and a much wider class of mesophases.

The emergence of the apparent surfacelike bulk term Eq. (68) is actually an artifact of an improper application of gradient expansion at a boundary. The ambiguity associated with the parameter  $\gamma$  is a clear manifestation of this fact. To illustrate this point, let us consider a semi-infinite sample of a nematic liquid crystal having a sharp boundary at  $z=0$ . As schematically depicted in Fig. 2, the double integral of  $G(\mathbf{r}, \mathbf{r}')$  on  $\mathbf{r}$  and  $\mathbf{r}'$  runs over the region  $r_z, r'_z > 0$ . Because

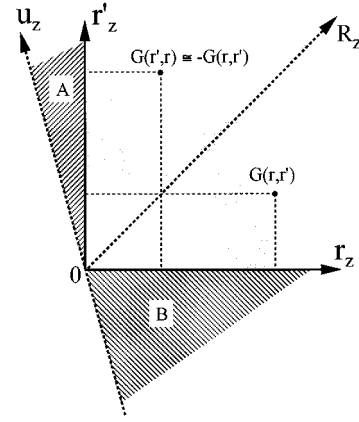


FIG. 2. Change in the range of integration associated with the application of a nonlocal-to-local mapping  $(r, r') \rightarrow (\mathbf{R}, u)$  for a semi-infinite nematic liquid crystal with a sharp boundary at  $z=0$ . The true integration region is the lightly shaded area occupying  $r_z, r'_z > 0$  and the hatched regions A and B are brought about by a mapping to the new integration variables  $(\mathbf{R}, u)$ . The  $R_z$  axis is fixed by the condition  $r_z = r'_z$ , whereas the inclination of the  $u_z$  axis is dependent on the mapping parameter  $\gamma$ . Only when  $\gamma=0$ , the regions A and B become exactly symmetrical about the  $R_z$  axis and the contributions from these regions cancel each other to make the integral agree with the original one. In this sense, the choice of  $\gamma=0$  may well be said to be the correct mapping for this particular case.

of the approximate antisymmetry of  $G(\mathbf{r}, \mathbf{r}')$  about the plane  $r_z = r'_z$ , the double integral over the entire semi-finite nematic liquid crystal vanishes to the order of  $O(\epsilon \xi^{-2})$  as shown above. However, when the mapping from  $(\mathbf{r}, \mathbf{r}')$  to  $(\mathbf{R}, u)$  is naively implemented for a natural range of integration  $R_z > 0$  and  $-\infty < u_z < +\infty$ , the integration on  $\mathbf{R}$  and  $u$  should also be performed on an additional region (A and B in Fig. 2) outside the integration range of the original double integral. Since this region is not in general symmetrical about the  $r_z = r'_z$  plane, except for the case of  $\gamma=0$ , the additional integral does not necessarily disappear, thereby leading to a fictitious surfacelike contribution given by Eq. (68). It is easy to confirm that if the real surface contribution is treated by consistently using the same mapping, the ambiguity associated with  $\gamma$  is rigorously canceled out [43].

## V. INTERFACIAL ELASTIC FREE ENERGY

The surfacelike elasticity embodied by  $K_{13}$  and  $K_{24}$  refers, in principle, to a fictitious boundary taken in a bulk nematic liquid crystal. In an attempt to measure these constants, however, it is inevitable to bring in a real physical boundary in the hope of mimicking this hypothetical surface. Nevertheless, these constants may be modified at the real interface, and even additional phenomenological constants may appear, depending on the nature of the interface in question. It must therefore be of interest to see how the present density-functional approach can be extended to the system with a real interface.

We consider a planar interface between a semi-infinite nematic liquid crystal and a rigid structureless substrate; we take the  $z$  axis along the interface normal. Then, the effect of the substrate may be represented by a fixed single-particle

external potential  $V_s(z, \boldsymbol{\omega})$ , which goes to infinity as  $z \rightarrow -\infty$  and approaches zero sufficiently rapidly as  $z \rightarrow \infty$ . In the absence of deformation, therefore, the density function gradually varies from its bulk form  $\rho_0(\boldsymbol{\omega})$  to zero as one goes across the interface from the nematic liquid crystal to the substrate. Let us denote the density function in equilibrium under the substrate potential in the absence of bulk distortions by  $\rho_g(z, \boldsymbol{\omega})$ . Then, it satisfies  $\lim_{z \rightarrow \infty} \rho_g(z, \boldsymbol{\omega}) = \bar{\rho}(\boldsymbol{\omega})$  and  $\lim_{z \rightarrow -\infty} \rho_g(z, \boldsymbol{\omega}) = 0$ . Now, the deformation free energy is defined as the free-energy increase associated with the deviation of the density function from the bulk-undistorted state described by  $\rho_g(z, \boldsymbol{\omega})$ . The quadratic expansion of the free-energy functional Eq. (32) is valid even in the presence of an interface, provided the ground-state density function  $\bar{\rho}(\boldsymbol{\omega})$  is replaced by  $\rho_g(z, \boldsymbol{\omega})$ , complying with the presence of the substrate, and the density deviation by that measured from  $\rho_g(z, \boldsymbol{\omega})$ ,

$$\begin{aligned} \delta F[\mathbf{n}] = & \frac{1}{2} k_B T \int d\mathbf{r} d\boldsymbol{\omega} d\mathbf{r}' d\boldsymbol{\omega}' C_2(\rho_g; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') \\ & \times \delta\rho(\mathbf{r}, \boldsymbol{\omega}) \delta\rho(\mathbf{r}', \boldsymbol{\omega}'). \end{aligned} \quad (32')$$

Note that this free energy increase is positive definite, so there is no way for a pathological behavior such as that due to Oldano and Barbero [10] to emerge.

The purpose of the curvature elastic description of a nematic interface is to formulate an expression of the interfacial elastic free energy as a functional of a given director field. Unlike the bulk elasticity, however, the director field could and is likely to lose its realistic meaning in the vicinity of the substrate, where the structure and properties of the nematic liquid should be drastically modified from the bulk state. Therefore, in order to define the director field even in the interfacial region, we need to employ a proper extrapolation scheme [16]. A normal way of extrapolation, which we shall also adopt here, is to first consider an infinite nematic medium with its undistorted orientation being identical to the easy direction  $\mathbf{n}_0$  brought about by the substrate. Next, an arbitrary infinitesimal director distortion field  $\delta\mathbf{n}(r)$  is introduced by means of a distorting external potential  $V_d(\mathbf{r}, \boldsymbol{\omega})$  as we have exploited in defining the bulk distortion. Finally, the medium is switched back to the nematic liquid crystal–substrate system in question in the presence of this external potential. If we denote the free-energy increase in the last situation from its field-free ground state by  $\delta F$ , it becomes a unique functional of  $V_d(\mathbf{r}, \boldsymbol{\omega})$ . Since the correspondence between  $\delta\mathbf{n}(\mathbf{r})$  and  $V_d(\mathbf{r}, \boldsymbol{\omega})$  can be made unique in the weak deformation limit via the density deviation  $\delta\rho(\mathbf{r}, \boldsymbol{\omega})$  as described earlier, we can now define  $\delta F$  as a unique functional of  $\delta\mathbf{n}(\mathbf{r})$  as implied in Eq. (32').

Let  $\delta\rho_b(\mathbf{r}, \boldsymbol{\omega}) = \rho'_0(\mathbf{n}_0 \cdot \boldsymbol{\omega}) \boldsymbol{\omega} \cdot \delta\mathbf{n}(r) + \Delta\rho(\mathbf{r}, \boldsymbol{\omega})$  be the density deviation in the extrapolated bulk nematic liquid crystal corresponding to the given fictitious director field. From the condition of equilibrium Eq. (12) applied to  $\delta F[\mathbf{n}]$  in Eq. (32) with  $\delta\rho(\mathbf{r}, \boldsymbol{\omega}) = \delta\rho_b(\mathbf{r}, \boldsymbol{\omega})$ , we find the hypothetical external potential conjugate to  $\delta\rho_b(\mathbf{r}, \boldsymbol{\omega})$  as

$$V_d(\mathbf{r}, \boldsymbol{\omega}) = -k_B T \int d\mathbf{r}' d\boldsymbol{\omega}' C_2(\bar{\rho}; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') \delta\rho_b(\mathbf{r}', \boldsymbol{\omega}'). \quad (79)$$

Finally, by applying this potential to the real nematic liquid crystal–substrate system, we find the variation in the density function pertaining to the real boundary as

$$\begin{aligned} \delta\rho(\mathbf{r}, \boldsymbol{\omega}) = & \int d\mathbf{r}' d\boldsymbol{\omega}' d\mathbf{r}'' d\boldsymbol{\omega}'' C_2^{-1}(\rho_g; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') \\ & \times C_2(\bar{\rho}; \mathbf{r}', \boldsymbol{\omega}', \mathbf{r}'', \boldsymbol{\omega}'') \delta\rho_b(\mathbf{r}'', \boldsymbol{\omega}''). \end{aligned} \quad (80)$$

Substituting this equation into Eq. (32'), we obtain

$$\begin{aligned} \delta F[\mathbf{n}] = & \frac{1}{2} k_B T \int d\mathbf{r} d\boldsymbol{\omega} d\mathbf{r}' d\boldsymbol{\omega}' d\mathbf{r}'' d\boldsymbol{\omega}'' d\mathbf{r}''' d\boldsymbol{\omega}''' \\ & \times K(\mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') \delta\rho_b(\mathbf{r}, \boldsymbol{\omega}) \delta\rho_b(\mathbf{r}', \boldsymbol{\omega}'), \end{aligned} \quad (81)$$

where the kernel function is defined by

$$\begin{aligned} K(\mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') = & \int d\mathbf{r}'' d\boldsymbol{\omega}'' d\mathbf{r}''' d\boldsymbol{\omega}''' C_2^{-1}(\rho_g; \mathbf{r}'', \boldsymbol{\omega}'', \mathbf{r}''', \boldsymbol{\omega}''') \\ & \times C_2(\bar{\rho}; \mathbf{r}'', \boldsymbol{\omega}'', \mathbf{r}, \boldsymbol{\omega}) C_2(\bar{\rho}; \mathbf{r}''', \boldsymbol{\omega}''', \mathbf{r}', \boldsymbol{\omega}'). \end{aligned} \quad (82)$$

Clearly, the kernel inherits the invariance for permutation of molecules and also satisfies

$$\begin{aligned} \lim_{z, z' \rightarrow \infty} K(\mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') = & C_2(\bar{\rho}; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}'), \\ \lim_{z, z' \rightarrow -\infty} K(\mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') = & 0. \end{aligned} \quad (83)$$

Separating the bulk density deviation into the quasihomogeneous and correction parts, i.e.,  $\delta\rho_b(\mathbf{r}, \boldsymbol{\omega}) = \delta\rho_0(\mathbf{n} \cdot \boldsymbol{\omega}) + \Delta\rho(\mathbf{r}, \boldsymbol{\omega})$ , we can rewrite Eq. (81) as

$$\begin{aligned} \delta F[\mathbf{n}] = & \frac{1}{2} k_B T \int d\mathbf{r} d\boldsymbol{\omega} d\mathbf{r}' d\boldsymbol{\omega}' K(\mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') \\ & \times [\delta\rho_0(\mathbf{n}(\mathbf{r}) \cdot \boldsymbol{\omega}) \delta\rho_0(\mathbf{n}(\mathbf{r}') \cdot \boldsymbol{\omega}') \\ & - \Delta\rho(\mathbf{r}, \boldsymbol{\omega}) \Delta\rho(\mathbf{r}', \boldsymbol{\omega}')]. \end{aligned} \quad (84)$$

Here we have used Eq. (A13), following the same procedure taken in Appendix A.

With the help of the algebraic identity Eq. (36) used for the evaluation of bulk elastic constants, the above expression allows us an unambiguous identification of interfacial contributions. The quasihomogeneous part in Eq. (84) is now reduced to

$$\begin{aligned} \delta F_h[\mathbf{n}] = & \frac{1}{2} k_B T \int d\mathbf{r} d\boldsymbol{\omega} d\mathbf{r}' d\boldsymbol{\omega}' K(\mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') \\ & \times \delta\rho_0(\mathbf{r}, \boldsymbol{\omega}) \delta\rho_0(\mathbf{r}', \boldsymbol{\omega}') \\ & + \frac{1}{4} k_B T \int d\mathbf{r} d\boldsymbol{\omega} d\mathbf{r}' d\boldsymbol{\omega}' [K(\mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') \\ & - K(\mathbf{r}, -\boldsymbol{\omega}', \mathbf{r}', -\boldsymbol{\omega})] \delta\rho_0(\mathbf{r}, \boldsymbol{\omega}) \delta\rho_0(\mathbf{r}', \boldsymbol{\omega}') \\ & + \frac{1}{4} k_B T \int d\mathbf{r} d\boldsymbol{\omega} d\mathbf{r}' d\boldsymbol{\omega}' K(\mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') \\ & \times [\delta\rho_0(\mathbf{r}, \boldsymbol{\omega}) - \delta\rho_0(\mathbf{r}', \boldsymbol{\omega}')] \\ & \times [\delta\rho_0(\mathbf{r}', \boldsymbol{\omega}') - \delta\rho_0(\mathbf{r}, \boldsymbol{\omega}')]. \end{aligned} \quad (85)$$

As already pointed out, the first two integrals disappear in the bulk due to the Nambu-Goldstone degeneracy and the inversion symmetry, respectively. So these contributions are essentially interfacial. The last integral, on the other hand, contains the bulk Oseen-Frank elastic contribution, which must be subtracted in obtaining the interfacial elastic free energy by the introduction of the Gibbs dividing surface [16,53]. The remaining part in Eq. (84) coming from the density correction is also made up of the bulk Oseen-Frank plus interfacial contributions, as readily appreciable from the linear dependence of the density correction on the director gradient.

To cope with the bulk contributions, we take arbitrarily the Gibbs dividing surface at  $z_d$ . Then, substituting the specific functional form for the quasihomogeneous density function and retaining all the contributions up to the order of  $\xi^{-2}$ , we obtain the interfacial elastic free energy as

$$\begin{aligned} \delta F^s[\mathbf{n}] = & \frac{1}{2} \int d\mathbf{R} W_{ij} \delta n_i(\mathbf{R}) \delta n_j(\mathbf{R}) \\ & + \frac{1}{2} \int d\mathbf{R} H_{ijk} \left( \frac{\partial n_j}{\partial R_i} \right) \delta n_k + \frac{1}{2} \int d\mathbf{R} [M_{ijkl}(\mathbf{R}) \\ & - \Delta M_{ijkl}(\mathbf{R}) - s(R_z - z_d)(M_{ijkl}^0 - \Delta M_{ijkl}^0)] \left( \frac{\partial n_k}{\partial R_i} \right) \\ & \times \left( \frac{\partial n_l}{\partial R_j} \right), \end{aligned} \quad (86)$$

where

$$\begin{aligned} W_{ij}(\mathbf{R}) = & k_B T \int d\mathbf{u} d\boldsymbol{\omega} d\boldsymbol{\omega}' K(\mathbf{R}, \boldsymbol{\omega}, \mathbf{R} + \mathbf{u}, \boldsymbol{\omega}') \\ & \times \rho'_0(\mathbf{n}_0 \cdot \boldsymbol{\omega}) \rho'_0(\mathbf{n}_0 \cdot \boldsymbol{\omega}') \omega_i \omega'_j, \end{aligned} \quad (87)$$

$$\begin{aligned} H_{ijk}(\mathbf{R}) = & \frac{1}{2} k_B T \int d\mathbf{u} d\boldsymbol{\omega} d\boldsymbol{\omega}' [K(\mathbf{R} - \frac{1}{2}\mathbf{u}, \boldsymbol{\omega}, \mathbf{R} + \frac{1}{2}\mathbf{u}, \boldsymbol{\omega}') \\ & - K(\mathbf{R} - \frac{1}{2}\mathbf{u}, -\boldsymbol{\omega}', \mathbf{R} + \frac{1}{2}\mathbf{u}, -\boldsymbol{\omega})] \\ & \times \rho'_0(\mathbf{n}_0 \cdot \boldsymbol{\omega}) \rho'_0(\mathbf{n}_0 \cdot \boldsymbol{\omega}') u_i \omega_j \omega'_k, \end{aligned} \quad (88)$$

and  $M_{ijkl}$  and  $\Delta M_{ijkl}$  can be found by properly replacing the bulk correlation functions in Eqs. (41) and (52) by the kernel function  $K$ . In deriving this formula, the choice of nonlocal-to-local mapping is immaterial since surface integrals can be safely ignored in this continuous system with the boundary taken at infinity; in the evaluation of  $\mathbf{H}$ , for example, the mapping,  $\mathbf{r} \rightarrow \mathbf{R} - \mathbf{u}/2$  is automatically selected in the final expression, whatever mapping scheme has been adopted initially. The tensor coefficients  $\mathbf{W}$ ,  $\mathbf{H}$ ,  $\mathbf{M}$ , and  $\Delta \mathbf{M}$  are all position dependent and become a function of the separation from the substrate. Corresponding to the permutation symmetry of the kernel, we have the relations,

$$W_{ij} = W_{ji}, \quad H_{ijk} = -H_{ikj}. \quad (89)$$

$M_{ijkl}^0$  and  $\Delta M_{ijkl}^0$  refer to their corresponding values in the bulk phase and  $s(z)$  denotes the step function, which satisfies  $s(z) = 1$  for  $z > 0$  and  $s(z) = 0$  for  $z < 0$ .

The last term in Eq. (86) is first of all an expression of the fact that the Oseen-Frank elastic constants become position dependent near the substrate. As the definition of the kernel function implies, the width of this interfacial transition regions is not necessarily limited by the range of direct substrate potential, but it is dependent on the correlation range of the particular fluctuation mode other than that described by the director. In a macroscopic sense, the interfacial modification of the elastic constants can be renormalized into the macroscopic anchoring energy coefficient [54]. Moreover, due to the broken symmetry at the interface,  $M_{ijkl}$  and  $\Delta M_{ijkl}$  no longer have their symmetry characteristics in the bulk such as the rotational invariance about the director. Hence there may appear surface-specific components connected, for example, with the biaxiality and polarity. We shall not go into this point in further detail here, but limit ourselves to commenting on how the saddle-splay term will be modified. It follows from Eq. (86) that

$$\begin{aligned} \delta F_{24}^s[\mathbf{n}] = & \frac{1}{2} \int d\mathbf{R} \frac{d}{dR_z} [K_{22}(\mathbf{R}) + K_{24}(\mathbf{R})] \\ & \times \mathbf{e}_z \cdot (\mathbf{n} \nabla \cdot \mathbf{n} + \mathbf{n} \times \nabla \times \mathbf{n}) - \frac{1}{2} (K_{22}^0 + K_{24}^0) \\ & \times \mathbf{e}_z \cdot (\mathbf{n} \nabla \cdot \mathbf{n} + \mathbf{n} \times \nabla \times \mathbf{n})|_{z_d}, \end{aligned} \quad (90)$$

where  $\mathbf{e}_z$  is a unit vector along the  $z$  axis and the translational invariance in the  $x$ - $y$  plane has been taken into account. The first term is the  $K_{24}$ -like elastic contribution pertaining to a real physical interface; the second term coming from the bulk will be canceled out on summation with the bulk elastic free energy and is taken over by the first, which has quantitatively nothing to do with the bulk saddle-splay constant. In this term, the contribution is not localized at the interface, but distributed over the entire interfacial transition region, wherein the gradient of the relevant elastic constants is acting as a local orientational field conjugate to the saddle-splay mode. The conventional phenomenological expression is recovered in the limit of an infinitely thin transition region, although the effective saddle-splay constant is no longer an intrinsic property of the nematic liquid alone.

The first term in Eq. (86),  $\delta F_1^s[\mathbf{n}]$ , represents the microscopic anchoring energy, which results from the breaking of Nambu-Goldstone degeneracy occurring over a finite interfacial transition region. The symmetry of  $W_{ij}$  for  $i \leftrightarrow j$  ensures the existence of a local intrinsic anchoring energy function  $w_a(\mathbf{n}, \mathbf{R})$ , satisfying  $W_{ij} = \partial^2 w_a / \partial n_i \partial n_j$  at each point. An easy connection with the macroscopic anchoring energy function  $W_a(\mathbf{n})$  can be made by Taylor expanding the director field at the Gibbs dividing surface:

$$\delta \mathbf{n}(\mathbf{R}) = \delta \mathbf{n}_d(R_x, R_y) + (R_z - z_d) \frac{\partial}{\partial R_z} n_d + \dots,$$

where the subscript  $d$  indicates that the quantity must be evaluated at the dividing surface. Using this expansion,  $\delta F_1^s[\mathbf{n}]$  reduces to

$$\begin{aligned} \delta F_1^s[\mathbf{n}] = & \frac{1}{2} \left[ \int d\mathbf{R} W_{ij}(\mathbf{R}) \right] \delta n_{di} \delta n_{dj} \\ & + \left[ \int d\mathbf{R} (R_z - z_d) W_{ij}(\mathbf{R}) \right] \delta n_{di} \frac{\partial n_{dj}}{\partial R_z} + \dots \end{aligned} \quad (91)$$

up to the first order in the director gradients. From this expression, we may identify the anchoring energy function as

$$W_a(\mathbf{n}_d) = \frac{1}{2} \left[ \int d\mathbf{R} W_{ij}(\mathbf{R}) \right] n_{di} n_{dj}. \quad (92)$$

Note that  $W_a(\mathbf{n}_d)$  is solely a function of  $\mathbf{n}_d$  without a direct dependence on the location of the dividing surface. This is an indication of the originally interfacial nature of this contribution. As already mentioned, this is not the only source of the macroscopic anchoring energy; other terms such as the surface-excess Oseen-Frank elastic energy can make a significant contribution, which is dependent on the choice of the dividing surface [16,54,55]. Finally, a comment may be in order about the second term in  $\delta F_1^s[\mathbf{n}]$ , which looks similar to the  $K_{13}$  term for its linear dependence on the normal derivative of the director. In contrast to the true  $K_{13}$  term, however, this contribution is variationally well behaved since this is a product of the gradient and the director deviation and hence is in second order in the distortion amplitude. Furthermore, it should also be worth noting that this term can be eliminated at all for a given director field by a choice of the dividing surface at an appropriate point inside the transition region.

From the viewpoint of surface elasticity, a particularly important feature of the formula for the interfacial elastic free energy Eq. (86) is the presence of the second term, which is linear in the director gradient. This linear term, involving the normal as well as tangential gradients of the director, yields a term formally similar to the  $K_{24}$  as well as  $K_{13}$  surfacelike bulk contributions. This term arises from the broken inversion symmetry, and as pointed out by Faetti and Riccardi [39] in their remarkable paper, should disappear when the inversion symmetry still prevails at the interface. To consider more specifically the nature of this contribution, let us assume a situation relevant to a pretilted homogeneous alignment toward the  $x$  direction. Further assuming the presence of a mirror plane perpendicular to  $y$  axis, we are left with the four nonzero tensor components

$$\begin{aligned} H_{yxy} &= -H_{yyx}, & H_{yzy} &= -H_{yyz}, \\ H_{xzx} &= -H_{xxz}, & H_{zxx} &= -H_{zxx}. \end{aligned} \quad (93)$$

Note that if the system has an up-down symmetry (mirror plane perpendicular to the  $z$  axis), all the first three components associated with the tangential gradients also disappear.

In view of the above symmetry relation, the corresponding free energy is written as

$$\begin{aligned} \delta F_2^s[\mathbf{n}] = & \frac{1}{4} \int d\mathbf{R} (H_{yyz} + H_{xxz}) \mathbf{e}_z \cdot (\mathbf{n} \nabla \cdot \mathbf{n} + \mathbf{n} \times \nabla \times \mathbf{n}) \\ & + \frac{1}{2} \int d\mathbf{R} (H_{yyz} - H_{xxz}) n_z \left( \frac{\partial n_y}{\partial R_y} - \frac{\partial n_x}{\partial R_x} \right) \\ & + \frac{1}{2} \int d\mathbf{R} H_{zxx} \left( \delta n_x \frac{\partial n_z}{\partial R_z} - \delta n_z \frac{\partial n_x}{\partial R_z} \right). \end{aligned} \quad (94)$$

If the interface is conically degenerate so that we have  $H_{yyz} = H_{xxz}$ , the contribution from the tangential gradients of director reduces simply to a term of  $K_{24}$  form. In the more general case considered here, however, an additional contribution exists, reflecting the in-plane anisotropy. As mentioned above, the broken up-down symmetry at the interface is essential for the appearance of these contributions.

Regarding the normal gradient contributions, we must first realize that they are variationally well behaved for the same reason as for the similar term in  $\delta F_1^s[\mathbf{n}]$ . This property is independent of the width of the transition region, so we can freely take the complete localization limit without jeopardizing the mathematical tractability. We may thus conclude that even at a real physical interface, no  $K_{13}$ -like elastic *excess* free energy exists [56].

## VI. CONCLUDING REMARKS

We have developed a microscopic formalism for the surfacelike elasticity of nematic liquid crystals on the basis of the density-functional theory. Although still formal, it could provide a few qualitatively significant results concerning the nature of the surfacelike bulk elastic constants. It has in particular been shown that the splay-bend elastic constant  $K_{13}$  must be zero. This result immediately resolves the mathematical difficulty associated with a nonzero  $K_{13}$ , the so-called Oldano-Barbero paradox, and also offers a rationale for overwhelming majority of continuum theoretic studies ignoring the surfacelike elasticity. The absence of  $K_{13}$  parallels the famous Cauchy relation established in the ordinary elasticity theory of solids, in the sense that it is not directly rooted in any of the macroscopic symmetries existing in nematic liquid crystals; but is a general consequence of the type of microscopic structure responsible for this particular term. In this respect,  $K_{13}=0$  applies to a wider range of phases including cholesteric liquid crystals. It has also been shown that the saddle-splay constant satisfies, under an approximate yet plausible condition, the extended Nehring-Saupe relation  $K_{24} \geq (K_{11} - K_{22})/2$ , taking into account the correction of the density function beyond the quasihomogeneous approximation.

We have also formulated a curvature elastic expression for the interfacial elastic free energy in the presence of a real substrate. The formula consists of the anchoring energy,  $K_{24}$ -like term, surface-excess Oseen-Frank elastic energy, and additional contributions connected with the surface-specific symmetries at the interface that have no counterparts in the bulk phase. The interfacial elastic free energy retains the equivalence of  $\mathbf{n}$  and  $-\mathbf{n}$  as in the bulk elastic energy, regardless of the actual symmetry at the interface; indeed,

even if the interface does not have an inversion symmetry, the interfacial free energy as a functional of  $\mathbf{n}$  has the  $\mathbf{n} \leftrightarrow -\mathbf{n}$  invariance. This paradoxical situation is a natural consequence of the way in which the bulk nematic liquid crystal is extrapolated to the interfacial region in Gibbs sense. In defining the elastic free energy as a functional of the director field, we consistently employed a hypothetical external one-body potential, which is infinitesimally weak on the order of  $\xi^{-2}$ , with  $\xi$  being the distortion wavelength, i.e., the same order of magnitude as the Oseen-Frank elastic free energy itself. This potential is able to couple, on the required order of  $\xi^{-2}$ , only with a continuously degenerate variable, the director, in the nematic phase, thereby making the elastic free energy a unique functional of the director field independent of the external potential used. We extended this approach to the interfacial elastic problem and obtained the interfacial free energy with  $\mathbf{n} = -\mathbf{n}$  symmetry. In view of the current interest in the curvature elastic treatment of nematic interfaces involving only deformations weak from the molecular standpoint, this approach seems to be general enough to cover all these realistic cases. Although it is in principle straightforward to employ a stronger external potential at the interface that is to radically modify the microscopic liquid structure, the interface can no longer allow a description only in terms of the director.

Finally, we would like to comment on the experimental measurement of the bulk  $K_{24}$ . As mentioned above, in contrast to the illusive  $K_{13}$ , the reality of  $K_{24}$  as an intrinsic material parameter of the nematic liquid crystal is now indisputable. However, a separate determination of  $K_{24}$  will always entail a real physical boundary, which carries its own interfacial  $K_{24}$ -like or more general elastic free-energy contributions depending linearly on the director gradients. Since these contributions always come together and there is no way of separation within the realm of the linear curvature elasticity, an independent measurement of bulk  $K_{24}$  will not be experimentally feasible. Nevertheless, it may well be possible if we become able to enter the strong distortion regime beyond the director functional description.

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#### APPENDIX A: DERIVATION OF THE DENSITY CORRECTION

On the basis of Eq. (32), the external potential conjugate to a given density deviation is given by

$$V_d(\mathbf{r}, \boldsymbol{\omega}) = -k_B T \int d\mathbf{r}' d\boldsymbol{\omega}' C_2(\bar{\rho}; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') \delta\rho(\mathbf{r}', \boldsymbol{\omega}'). \quad (\text{A1})$$

If only a quasihomogeneous density function is used for  $\delta\rho(\mathbf{r}', \boldsymbol{\omega}')$  in this equation, the condition  $V_d(\mathbf{r}, \boldsymbol{\omega}) = O(\xi^{-2})$ , as required by the uniqueness of  $\delta F[\mathbf{n}]$  as a functional of only

the director field, is not in general satisfied. The role of the density correction is to get rid of this discrepancy so as to achieve

$$\int d\mathbf{r}' d\boldsymbol{\omega}' C_2(\bar{\rho}; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') [\rho'_0(\mathbf{n}_0 \cdot \boldsymbol{\omega}') \boldsymbol{\omega}' \cdot \delta\mathbf{n}(\mathbf{r}') + \Delta\rho(\mathbf{r}', \boldsymbol{\omega}')] = O(\xi^{-2}). \quad (\text{A2})$$

This equation must be solved for  $\Delta\rho(\mathbf{r}, \boldsymbol{\omega})$  under the condition that the density correction should not change the given director field.

We must note that due to the Nambu-Goldstone degeneracy, if  $\Delta\rho(\mathbf{r}', \boldsymbol{\omega}')$  satisfies the above equation, then  $\Delta\rho(\mathbf{r}', \boldsymbol{\omega}') + \rho'_0(\mathbf{n}_0 \cdot \boldsymbol{\omega}') \boldsymbol{\omega}' \cdot \mathbf{a}(\mathbf{r}')$  also satisfies the same equation regardless of the vector field  $\mathbf{a}(\mathbf{r}')$  normal to  $\mathbf{n}_0$ . Hence, to obtain the density correction with the desired property, we can regard  $\mathbf{a}(\mathbf{r}')$  as a Lagrange multiplier, then solve for the density correction involving  $\mathbf{a}$ , and finally determine  $\mathbf{a}$  to meet the above requirement. As confirmed *a posteriori*, the choice of  $\mathbf{a}(\mathbf{r}') = -\delta\mathbf{n}(\mathbf{r})$  gives us a correct answer. Based on this choice, we can rewrite Eq. (A2) as

$$\int d\mathbf{r}' d\boldsymbol{\omega}' C_2(\bar{\rho}; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') \{ \rho'_0(\mathbf{n}_0 \cdot \boldsymbol{\omega}') \boldsymbol{\omega}' \cdot [\mathbf{u} \cdot \nabla \mathbf{n}(\mathbf{r})] + \Delta\rho(\mathbf{r}', \boldsymbol{\omega}') \} = O(\xi^{-2}), \quad (\text{A3})$$

where  $\mathbf{u} = \mathbf{r}' - \mathbf{r}$ . This equation can be readily solved for the density correction to give

$$\Delta\rho(\mathbf{r}, \boldsymbol{\omega}) = - \int d\mathbf{u} d\mathbf{u}' d\boldsymbol{\omega}' d\boldsymbol{\omega}'' C_2^{-1}(\bar{\rho}; \mathbf{u}', \boldsymbol{\omega}, \boldsymbol{\omega}'') \times C_2(\bar{\rho}; \mathbf{u}, \boldsymbol{\omega}'', \boldsymbol{\omega}') \rho'_0(\mathbf{n}_0 \cdot \boldsymbol{\omega}') \boldsymbol{\omega}' \cdot [\mathbf{u} \cdot \nabla \mathbf{n}(\mathbf{r})], \quad (\text{A4})$$

where  $C_2^{-1}(\bar{\rho}; \mathbf{u}, \boldsymbol{\omega}, \boldsymbol{\omega}') \equiv C_2^{-1}(\bar{\rho}; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}')$  is the inverse of  $C_2(\bar{\rho}; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}')$  or, equivalently, the density-density correlation function [45] connected to the total correlation function  $h(\bar{\rho}; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}')$  by

$$C_2^{-1}(\bar{\rho}; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') = \rho_0(\mathbf{n}_0 \cdot \boldsymbol{\omega}) \rho_0(\mathbf{n}_0 \cdot \boldsymbol{\omega}') h(\bar{\rho}; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') + \rho_0(\mathbf{n}_0 \cdot \boldsymbol{\omega}') \delta(\mathbf{r} - \mathbf{r}') \delta(\boldsymbol{\omega} - \boldsymbol{\omega}'). \quad (\text{A5})$$

By applying the inversion to all the integration variables in Eq. (A4), we find that the density correction is antisymmetrical for inversion of the molecular orientation

$$\Delta\rho(\mathbf{r}, -\boldsymbol{\omega}) = -\Delta\rho(\mathbf{r}, \boldsymbol{\omega}), \quad (\text{A6})$$

which ensures the orthogonality of the density correction to the quasihomogeneous density function and, equivalently, the invariance of the initial director field.

The above derivation of the density correction is essentially equivalent to the results by Somoza and Tarazona [21]. However, they took an alternative route to expand the density correction into an infinite series on an appropriate complete set of orthonormal basis functions such as the spherical harmonics and then to directly minimize the free-energy functional with respect to the expansion coefficients, from

which the terms affecting the director field have been omitted in prior. Due to the difficulty in summation of the resultant series expansion, they did not reach the general compact formula Eq. (A4), except for the case of the ideal gas approximation [neglecting the total correlation function in Eq. (A5) to allow an easy summation].

In order to get more detailed information about the density correction, let us take the  $z$  axis along  $\mathbf{n}_0$  and define a matrix  $\mathbf{J}(\boldsymbol{\omega})$  by

$$J_{ij}(\boldsymbol{\omega}) = - \int d\mathbf{u} d\mathbf{u}' d\boldsymbol{\omega}' d\boldsymbol{\omega}'' C_2^{-1}(\bar{\rho}; \mathbf{u}', \boldsymbol{\omega}, \boldsymbol{\omega}'') \times C_2(\bar{\rho}; \mathbf{u}, \boldsymbol{\omega}'', \boldsymbol{\omega}') \rho'_0(\mathbf{n}_0 \cdot \boldsymbol{\omega}') u_i \omega'_j. \quad (\text{A7})$$

If we take the  $x$  axis along the projection of  $\boldsymbol{\omega}$  on the  $x$ - $y$  plane, we have a symmetry relation

$$J_{xy} = J_{yx} = J_{zy} = 0. \quad (\text{A8})$$

Hence we see that there are only three independent components  $J_1(\omega_z) = J_{xx}/2$ ,  $J_2(\omega_z) = J_{yy}/2$ , and  $J_3(\omega_z) = J_{zx}$ , which make nonvanishing contributions to the density correction. For a general choice of the  $x$  axis making an angle  $\phi$  with the projection of  $\boldsymbol{\omega}$ , the tensor components can be written in terms of these constants

$$\begin{aligned} J_{xx}(\boldsymbol{\omega}) &= J_{12}^+(\omega_z) + J_{12}^-(\omega_z) \cos 2\phi, \\ J_{xy}(\boldsymbol{\omega}) &= J_{yx}(\boldsymbol{\omega}) = -J_{12}^-(\omega_z) \sin 2\phi, \\ J_{yy}(\boldsymbol{\omega}) &= J_{12}^+(\omega_z) - J_{12}^-(\omega_z) \cos 2\phi, \end{aligned} \quad (\text{A9})$$

where  $J_{12}^+(\omega_z) = J_1(\omega_z) + J_2(\omega_z)$  and  $J_{12}^-(\omega_z) = J_1(\omega_z) - J_2(\omega_z)$ . If we can ignore the short-range correlation between the molecular orientations within the plane perpendicular to the director, we have  $J_{xy} = 0$  and  $J_{xx} = J_{yy}$  so that the density correction assumes a particularly simple form, reminiscent of the flexoelectric contributions, as

$$\Delta\rho(\mathbf{r}, \boldsymbol{\omega}) = A_S \boldsymbol{\omega} \cdot (\mathbf{n} \nabla \cdot \mathbf{n}) + A_B \boldsymbol{\omega} \cdot (\mathbf{n} \times \nabla \times \mathbf{n}), \quad (\text{A10})$$

where  $A_S$  and  $A_B$  are functions of  $(\mathbf{n} \cdot \boldsymbol{\omega})^2$ .

We now calculate the correction to the elastic free energy  $\Delta F_c[\mathbf{n}]$  resulting from the density correction. Substituting

$$\begin{aligned} &\delta\rho(\mathbf{r}, \boldsymbol{\omega}) \delta\rho(\mathbf{r}', \boldsymbol{\omega}') \\ &= \delta\rho_0(\mathbf{r}, \boldsymbol{\omega}) \delta\rho_0(\mathbf{r}', \boldsymbol{\omega}') + \delta\rho_0(\mathbf{r}, \boldsymbol{\omega}) \Delta\rho(\mathbf{r}', \boldsymbol{\omega}') \\ &\quad + \Delta\rho(\mathbf{r}, \boldsymbol{\omega}) \delta\rho_0(\mathbf{r}', \boldsymbol{\omega}') + \Delta\rho(\mathbf{r}, \boldsymbol{\omega}) \Delta\rho(\mathbf{r}', \boldsymbol{\omega}') \end{aligned} \quad (\text{A11})$$

into Eq. (32), we find the free-energy correction as

$$\begin{aligned} \Delta f_c[\mathbf{n}] &= \frac{1}{2} k_B T \int d\mathbf{r} d\boldsymbol{\omega} d\mathbf{r}' d\boldsymbol{\omega}' C_2(\bar{\rho}; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') \\ &\quad \times [2 \delta\rho'_0(\mathbf{n}_0 \cdot \boldsymbol{\omega}') \delta\mathbf{n}(\mathbf{r}') \Delta\rho(\mathbf{r}, \boldsymbol{\omega}) \\ &\quad + \Delta\rho(\mathbf{r}, \boldsymbol{\omega}) \Delta\rho(\mathbf{r}', \boldsymbol{\omega}')]. \end{aligned} \quad (\text{A12})$$

Note that Eq. (A3) is identical to the stationary condition of  $\Delta F_c[\mathbf{n}]$  with respect to the density correction, i.e.,

$0 = \delta\Delta F_c / \delta\Delta\rho(\mathbf{r}, \boldsymbol{\omega})$ . The negligence of the distorting external potential is justified by the fact that the coupling between this external potential and the density correction is on the order of  $\xi^{-3}$ . For the equilibrium density correction, substitution of Eq. (A3) into Eq. (A12) yields

$$\begin{aligned} \Delta F_c[\mathbf{n}] &= -\frac{1}{2} k_B T \int d\mathbf{r} d\boldsymbol{\omega} d\mathbf{r}' d\boldsymbol{\omega}' C_2(\bar{\rho}; \mathbf{r}, \boldsymbol{\omega}, \mathbf{r}', \boldsymbol{\omega}') \\ &\quad \times \Delta\rho(\mathbf{r}, \boldsymbol{\omega}) \Delta\rho(\mathbf{r}', \boldsymbol{\omega}'). \end{aligned} \quad (\text{A13})$$

This formula demonstrates that

$$\Delta F_c[\mathbf{n}] \leq 0, \quad (\text{A14})$$

which manifests the nature of the density correction as a structural relaxation agent. Using the matrix  $\mathbf{J}$  given above, the correction to the elastic constant tensor Eq. (52) can be written as

$$\Delta M_{ijkl} = k_B T \int d\mathbf{u} d\boldsymbol{\omega} d\boldsymbol{\omega}' C_2(\bar{\rho}; \mathbf{u}, \boldsymbol{\omega}, \boldsymbol{\omega}') J_{ik}(\boldsymbol{\omega}) J_{jl}(\boldsymbol{\omega}'). \quad (\text{A15})$$

Using Eq. (A9) in Eq. (A15), we obtain

$$\begin{aligned} \Delta M_{xxxx} &= \Delta M_{yyyy} = 2 \langle J_{12}^+(\omega_z) J_{12}^+(\omega'_z) \rangle \\ &\quad + \langle J_{12}^-(\omega_z) J_{12}^-(\omega'_z) \cos 2\alpha \rangle, \end{aligned} \quad (\text{A16a})$$

$$\begin{aligned} \Delta M_{xxyy} &= \Delta M_{yyxx} = \Delta M_{xyyx} = \Delta M_{yxyx} \\ &= \langle J_{12}^-(\omega_z) J_{12}^-(\omega'_z) \cos 2\alpha \rangle, \end{aligned} \quad (\text{A16b})$$

$$\begin{aligned} \Delta M_{xyxy} &= \Delta M_{yxyx} = 2 \langle J_{12}^+(\omega_z) J_{12}^+(\omega'_z) \rangle \\ &\quad - \langle J_{12}^-(\omega_z) J_{12}^-(\omega'_z) \cos 2\alpha \rangle, \end{aligned} \quad (\text{A16c})$$

$$\Delta M_{zzxx} = \Delta M_{zzyy} = 2 \langle J_3(\omega_z) J_3(\omega'_z) \rangle, \quad (\text{A16d})$$

where  $\alpha$  is the angle between the  $x$ - $y$  plane projections of  $\boldsymbol{\omega}$  and  $\boldsymbol{\omega}'$  and the operator  $\langle \rangle$  is defined by

$$\begin{aligned} \langle H(\omega_z, \omega'_z, \alpha) \rangle &\equiv \pi k_B T \int d\omega_z d\omega'_z d\alpha \\ &\quad \times \left[ \int d\mathbf{u} C_2(\bar{\rho}; \mathbf{u}, \omega_z, \omega'_z, \alpha) \right] \\ &\quad \times H(\omega_z, \omega'_z, \alpha). \end{aligned} \quad (\text{A17})$$

Since there are only three independent parameters for at least four elastic constants, there appears a Cauchy relation as given by Eqs. (A16b) and (53). Equations (A16a)–(A16d) also show that if the flexoelectric form Eq. (A10) holds or, equivalently,  $J_{12}^-(\omega_z) = 0$ , the effect of density correction applies only to  $K_{11}$  and  $K_{33}$ .



**APPENDIX B: DENSITY CORRECTION  
IN THE GRADIENT EXPANSION**

Here we show that the inclusion of the density correction does not affect our conclusion of  $K_{13}=0$ . In order to get the correction to the intrinsic free energy up to the order of  $\xi^{-2}$  in the presence of  $\Delta\rho(\mathbf{r},\boldsymbol{\omega})$ , we need to take account of not only the second integral but also the first in Eq. (61), since the free-energy density for a local homogeneous state is no longer a constant throughout the nematic liquid crystal, but contains a contribution to the elastic excess free energy due to the density correction.

We begin with the expansion of the first member of the direct correlation function about the quasihomogeneous density  $\bar{\rho}(\mathbf{r},\boldsymbol{\omega})=\rho_0(\mathbf{n}(\mathbf{r}),\boldsymbol{\omega})$ ,

$$\begin{aligned} c(\rho_{\alpha;\mathbf{r}};\mathbf{r},\boldsymbol{\omega}) &= c(\bar{\rho}_{\alpha;\mathbf{r}};\mathbf{r},\boldsymbol{\omega}) \\ &+ \alpha \int d\mathbf{r}' d\boldsymbol{\omega}' \Delta\rho(\mathbf{r},\boldsymbol{\omega}') c(\bar{\rho}_{\alpha;\mathbf{r}};\mathbf{r},\boldsymbol{\omega},\mathbf{r}',\boldsymbol{\omega}') \\ &+ \frac{\alpha^2}{2} \int d\mathbf{r}' d\boldsymbol{\omega}' d\mathbf{r}'' d\boldsymbol{\omega}'' \Delta\rho(\mathbf{r},\boldsymbol{\omega}') \\ &\times \Delta\rho(\mathbf{r},\boldsymbol{\omega}'') c(\bar{\rho}_{\alpha;\mathbf{r}};\mathbf{r},\boldsymbol{\omega},\mathbf{r}',\boldsymbol{\omega}',\mathbf{r}'',\boldsymbol{\omega}'') + \dots \end{aligned} \quad (\text{B1})$$

Using this formula in the first integral of Eq. (61) for the local homogeneous state, we obtain the desired expansion in powers of  $\Delta\rho(\mathbf{r},\boldsymbol{\omega})$ ; after some manipulations involving the exchange of integration variables such as  $(\mathbf{r},\boldsymbol{\omega})\leftrightarrow(\mathbf{r}',\boldsymbol{\omega}')$  to make a local-to-nonlocal conversion, the expansion is reduced to

$$\begin{aligned} \Phi_1[\rho_d] &= \Phi_1[\rho_0] + k_B T \int d\mathbf{r} d\boldsymbol{\omega} \Delta\rho(\mathbf{r},\boldsymbol{\omega}) c(\bar{\rho}_{\mathbf{r}};\mathbf{r},\boldsymbol{\omega}) - k_B T \int_0^1 \alpha d\alpha \int d\mathbf{r} d\boldsymbol{\omega} d\mathbf{r}' d\boldsymbol{\omega}' \delta\rho_0(\mathbf{r},\boldsymbol{\omega}) \\ &\times [\Delta\rho(\mathbf{r}',\boldsymbol{\omega}') - \Delta\rho(\mathbf{r},\boldsymbol{\omega}')] c(\bar{\rho}_{\alpha;\mathbf{r}};\mathbf{r},\boldsymbol{\omega},\mathbf{r}',\boldsymbol{\omega}') + k_B T \int_0^1 \alpha d\alpha \int d\mathbf{r} d\boldsymbol{\omega} d\mathbf{r}' d\boldsymbol{\omega}' \Delta\rho(\mathbf{r},\boldsymbol{\omega}) \\ &\times [\rho_0(\mathbf{r}',\boldsymbol{\omega}') - \rho_0(\mathbf{r},\boldsymbol{\omega}')] c(\bar{\rho}_{\alpha;\mathbf{r}};\mathbf{r},\boldsymbol{\omega},\mathbf{r}',\boldsymbol{\omega}') + k_B T \int_0^1 \alpha^2 d\alpha \\ &\times \int d\mathbf{r} d\boldsymbol{\omega} d\mathbf{r}' d\boldsymbol{\omega}' d\mathbf{r}'' d\boldsymbol{\omega}'' c(\bar{\rho}_{\alpha;\mathbf{r}};\mathbf{r},\boldsymbol{\omega},\mathbf{r}',\boldsymbol{\omega}',\mathbf{r}'',\boldsymbol{\omega}'') \delta\rho_0(\mathbf{r}',\boldsymbol{\omega}') \\ &\times [\rho_0(\mathbf{r}',\boldsymbol{\omega}'') - \rho_0(\mathbf{r},\boldsymbol{\omega}'')] \Delta\rho(\mathbf{r},\boldsymbol{\omega}) + \frac{1}{2} k_B T \int d\mathbf{r} d\boldsymbol{\omega} d\mathbf{r}' d\boldsymbol{\omega}' c(\bar{\rho}_{\mathbf{r}};\mathbf{r},\boldsymbol{\omega},\mathbf{r}',\boldsymbol{\omega}') \Delta\rho(\mathbf{r},\boldsymbol{\omega}) \Delta\rho(\mathbf{r}',\boldsymbol{\omega}') \\ &+ \frac{1}{2} k_B T \int_0^1 \alpha^2 d\alpha \int d\mathbf{r} d\boldsymbol{\omega} d\mathbf{r}' d\boldsymbol{\omega}' d\mathbf{r}'' d\boldsymbol{\omega}'' c(\rho_{\alpha;\mathbf{r}};\mathbf{r},\boldsymbol{\omega},\mathbf{r}',\boldsymbol{\omega}',\mathbf{r}'',\boldsymbol{\omega}'') [\delta\rho_0(\mathbf{r},\boldsymbol{\omega}'') \Delta\rho(\mathbf{r},\boldsymbol{\omega}) \Delta\rho(\mathbf{r},\boldsymbol{\omega}') \\ &- \delta\rho_0(\mathbf{r},\boldsymbol{\omega}) \Delta\rho(\mathbf{r},\boldsymbol{\omega}') \Delta\rho(\mathbf{r},\boldsymbol{\omega}'')]. \end{aligned} \quad (\text{B2})$$

The second term in Eq. (B2) disappears due to  $\Delta\rho(\mathbf{r},-\boldsymbol{\omega})=-\Delta\rho(\mathbf{r},\boldsymbol{\omega})$ . Also owing to  $\Delta\rho(\mathbf{r}',\boldsymbol{\omega}')=\Delta\rho(\mathbf{r},\boldsymbol{\omega})+O(\xi^{-2})$ , the last integral turns out to be of the order of  $\xi^{-3}$ , so it can be omitted.

Similarly, the second integral in Eq. (61) can be expanded to give

$$\begin{aligned} \Phi_2[\rho_d] &= \Phi_2[\rho_0] \\ &+ k_B T \int_0^1 \alpha d\alpha \int d\mathbf{r} d\boldsymbol{\omega} d\mathbf{r}' d\boldsymbol{\omega}' \delta\rho_0(\mathbf{r},\boldsymbol{\omega}) \\ &\times [\Delta\rho(\mathbf{r}',\boldsymbol{\omega}') - \Delta\rho(\mathbf{r},\boldsymbol{\omega}')] c(\bar{\rho}_{\alpha;\mathbf{r}};\mathbf{r},\boldsymbol{\omega},\mathbf{r}',\boldsymbol{\omega}') \\ &+ k_B T \int_0^1 \alpha d\alpha \int d\mathbf{r} d\boldsymbol{\omega} d\mathbf{r}' d\boldsymbol{\omega}' \Delta\rho(\mathbf{r},\boldsymbol{\omega}) \\ &\times [\rho_0(\mathbf{r}',\boldsymbol{\omega}') - \rho_0(\mathbf{r},\boldsymbol{\omega}')] c(\bar{\rho}_{\alpha;\mathbf{r}};\mathbf{r},\boldsymbol{\omega},\mathbf{r}',\boldsymbol{\omega}') \\ &+ k_B T \int_0^1 \alpha^2 d\alpha \int d\mathbf{r} d\boldsymbol{\omega} d\mathbf{r}' d\boldsymbol{\omega}' d\mathbf{r}'' d\boldsymbol{\omega}'' c \end{aligned}$$

$$\begin{aligned} &(\bar{\rho}_{\alpha;\mathbf{r}};\mathbf{r},\boldsymbol{\omega},\mathbf{r}',\boldsymbol{\omega}',\mathbf{r}'',\boldsymbol{\omega}'') \delta\rho_0(\mathbf{r},\boldsymbol{\omega}) [\rho_0(\mathbf{r}',\boldsymbol{\omega}') \\ &- \rho_0(\mathbf{r},\boldsymbol{\omega}')] \Delta\rho(\mathbf{r},\boldsymbol{\omega}'). \end{aligned} \quad (\text{B3})$$

Combining these expansions, we obtain

$$\begin{aligned} \Phi_1[\rho_d] + \Phi_2[\rho_d] &= \Phi_1[\rho_0] + \Phi_2[\rho_0] \\ &+ k_B T \int d\mathbf{r} d\boldsymbol{\omega} d\mathbf{r}' d\boldsymbol{\omega}' \Delta\rho(\mathbf{r},\boldsymbol{\omega}) \\ &\times [\rho_0(\mathbf{r}',\boldsymbol{\omega}') - \rho_0(\mathbf{r},\boldsymbol{\omega}')] c(\bar{\rho}_{\mathbf{r}};\mathbf{r},\boldsymbol{\omega},\mathbf{r}',\boldsymbol{\omega}') \\ &+ \frac{1}{2} k_B T \int d\mathbf{r} d\boldsymbol{\omega} d\mathbf{r}' d\boldsymbol{\omega}' c(\bar{\rho}_{\mathbf{r}};\mathbf{r},\boldsymbol{\omega},\mathbf{r}',\boldsymbol{\omega}') \\ &\times \Delta\rho(\mathbf{r},\boldsymbol{\omega}) \Delta\rho(\mathbf{r}',\boldsymbol{\omega}'). \end{aligned} \quad (\text{B4})$$

This result is in perfect agreement with Eq. (A12), the master equation for determining the density correction for a given quasihomogeneous density distribution. It follows immedi-

ately from this result that the density correction does not generate a surfacelike elastic term.

### APPENDIX C: AMBIGUITY IN THE NONLOCAL-TO-LOCAL MAPPING

In a critique against Somoza and Tarazona's argument, Teixeira, Pergamenschik, and Sluckin [26] ruled out, on a rather general ground, the existence of ambiguity in the nonlocal-to-local mapping that ruins the uniqueness of the surfacelike bulk elastic constant as discussed in Sec. IV. Their claim is that the particular mapping with  $\gamma=\frac{1}{2}$  in our notation is the only physically acceptable mapping scheme, so that the  $K_{13}$  resulting from this mapping must be regarded as a well-defined material parameter. For a Gay-Berne model nematic liquid crystal, they carried out a microscopic calculation of  $K_{13}$  and found a nonzero value on the same order of magnitude as the ordinary Frank elastic constants. Since this result presents a fundamental contradiction with our result of  $K_{13}=0$ , it must be worthwhile to clarify where this discrepancy came from and how it can be corrected.

After Somoza and Tarazona, Teixeira, Pergamenschik, and Sluckin adopted a mean-field approach using  $f(\mathbf{r}'-\mathbf{r}, \mathbf{n}(\mathbf{r}), \mathbf{n}(\mathbf{r}'))$  as the angle-averaged interaction potential between molecules at  $\mathbf{r}$  and  $\mathbf{r}'$ . The free energy  $F$  of a volume of a nematic liquid crystal is thus given by a double integral

$$F = \int d\mathbf{r} d\mathbf{r}' f(\mathbf{r}'-\mathbf{r}, \mathbf{n}(\mathbf{r}), \mathbf{n}(\mathbf{r}')). \quad (\text{C1})$$

If we imagine an undistorted nematic liquid crystal oriented along  $\mathbf{n}$ , the free energy reduces to

$$F_u = \int d\mathbf{r} d\mathbf{r}' f(\mathbf{r}'-\mathbf{r}, \mathbf{n}, \mathbf{n}). \quad (\text{C2})$$

Since  $\mathbf{n}$  is not a function of position here, it is perfectly legitimate to regard

$$g_u(\mathbf{n}) = \int d\mathbf{u} f(\mathbf{u}, \mathbf{n}, \mathbf{n}) \quad (\text{C3})$$

as a free-energy density in the undistorted state. Locally subtracting this contribution, we can rewrite Eq. (C1) as

$$F = \int d\mathbf{r} d\mathbf{r}' f(\mathbf{r}'-\mathbf{r}, \mathbf{n}(\mathbf{r}), \mathbf{n}(\mathbf{r})) + \int d\mathbf{r} d\mathbf{r}' [f(\mathbf{r}'-\mathbf{r}, \mathbf{n}(\mathbf{r}), \mathbf{n}(\mathbf{r}')) - f(\mathbf{r}'-\mathbf{r}, \mathbf{n}(\mathbf{r}), \mathbf{n}(\mathbf{r}))]. \quad (\text{C4})$$

When the nematic liquid crystal is undistorted, the second integral automatically disappears. This is an expression corresponding to the density-functional formula Eq. (61).

On the basis of this equation, Teixeira, Pergamenschik, and Sluckin considered the function

$$g(\mathbf{r}) = \int d\mathbf{r}' [f(\mathbf{r}'-\mathbf{r}, \mathbf{n}(\mathbf{r}), \mathbf{n}(\mathbf{r}')) - f(\mathbf{r}'-\mathbf{r}, \mathbf{n}(\mathbf{r}), \mathbf{n}(\mathbf{r}))] \quad (\text{C5})$$

as the *unique* physically legitimate elastic free-energy density, to which all other permissible elastic free-energy densi-

ties, if any, should be isomorphic by a one-to-one correspondence requiring the retrievability of  $g(\mathbf{r})$ . This is, however, too strong a condition, going far beyond the ordinary requirements in constructing a local thermodynamic function [50]. Quite the contrary, indeed, the heart of the nonlocal-to-local mapping issue lies essentially in the loss of a one-to-one correspondence between equally acceptable free-energy densities as pedagogically described by Rowlinson and Widom in their monograph [50]. Then, only those properties that are immune to this mapping issue can be regarded as physically well defined. Requiring the availability of a one-to-one correspondence leads to an automatic prohibition of mapping ambiguity, tautologically resulting in the uniqueness of the density function.

Teixeira, Pergamenschik, and Sluckin's objection to applying a general mapping scheme, as we have used in Sec. IV, to Eq. (C5) stems from the seeming shift of the reference state from an "undistorted" to a "distorted" one. As is clear from Eq. (C4), however,  $g(\mathbf{r})$  comes from the second integral in Eq. (C4), which is just the remainder of total free energy after the local homogeneous contribution (the first integral) has been subtracted. Consequently, there is inherently no such concept as the pointwise reference state in the second integral, provided the first integral takes correct care of the homogeneous local *reference* state. In fact, the recipe of gradient expansion only demands that the total free energy be decomposed in such a way that

$$F = \int d\mathbf{R} g_u(\mathbf{n}(\mathbf{R})) + \int d\mathbf{R} g(\partial\mathbf{n}(\mathbf{R})), \quad (\text{C6})$$

where  $g_u(\mathbf{n}(\mathbf{R}))$  is the homogeneous free-energy density at  $\mathbf{R}$  evaluated for the local director at this point and  $g(\partial\mathbf{n}(\mathbf{R}))$  is the gradient-dependent part that should be zero when the gradients locally vanish. This condition is fulfilled by using a mapping  $\mathbf{R}=\mathbf{r}$  and  $\mathbf{u}=\mathbf{r}'-\mathbf{r}$  only in the first integral; further imposing this mapping to the second integral is another source of flaw in Teixeira, Pergamenschik, and Sluckin's argument. The second integral can be subjected to any mapping as long as the resultant elastic free-energy density remains finite.

Although the discrepancy between Teixeira, Pergamenschik and Sluckin and Somoza and Tarazona can be traced back to the erroneous handling of gradient expansion by the former authors, it should be of interest to see how the result  $K_{13}=0$  generally follows in the present mean-field context beyond Somoza and Tarazona's *ad hoc* argument. Due to the inversion symmetry in the real and the director isotopic spaces, the interaction potential has a symmetry

$$f(\mathbf{r}'-\mathbf{r}, \mathbf{n}, \mathbf{n}') = f(\mathbf{r}'-\mathbf{r}, \mathbf{n}', \mathbf{n}) = f(\mathbf{r}-\mathbf{r}', \mathbf{n}', \mathbf{n}). \quad (\text{C7})$$

It follows from this relation that

$$\left( \frac{\partial f}{\partial n_i} \right)_{\mathbf{n}=\mathbf{n}'} = \left( \frac{\partial f}{\partial n'_i} \right)_{\mathbf{n}=\mathbf{n}}. \quad (\text{C8})$$

We define a function

$$G(\mathbf{r}, \mathbf{r}') = f(\mathbf{r}'-\mathbf{r}, \mathbf{n}(\mathbf{r}), \mathbf{n}(\mathbf{r}')) - f(\mathbf{r}'-\mathbf{r}, \mathbf{n}(\mathbf{r}), \mathbf{n}(\mathbf{r})). \quad (\text{C9})$$

Then, we find from the above symmetry relation that

$$G(\mathbf{r}, \mathbf{r}') = -G(\mathbf{r}', \mathbf{r}) + O(|\delta n|^2), \quad (\text{C10})$$

which is the counterpart of Eq. (76). Using this equation in Eq. (C4), we obtain

$$\int d\mathbf{r} d\mathbf{r}' [f(\mathbf{r}' - \mathbf{r}, \mathbf{n}(\mathbf{r}), \mathbf{n}(\mathbf{r}')) - f(\mathbf{r}' - \mathbf{r}, \mathbf{n}(\mathbf{r}), \mathbf{n}(\mathbf{r}))] = O(|\delta n|^2). \quad (\text{C11})$$

This shows that the term linear in  $\delta \mathbf{n}$ , from which  $K_{13}$  emerges, is deemed to disappear on integration for symmetry reasons even before the gradient expansion is applied, so we must have  $K_{13} = 0$  also in this mean-field context.

As in the rigorous density-functional theory, a formal gradient expansion of Eq. (C5) using a general mapping scheme Eq. (65) yields a surface integral as

$$\delta F = 2 \int d\mathbf{R} \frac{\partial}{\partial R_i} \left[ \int d\mathbf{u} \gamma(u^2) \left( \frac{\partial f(\mathbf{u}, \mathbf{n}, \mathbf{n})}{\partial n_k} \right)_{\mathbf{n}(\mathbf{R})} u_i u_j \frac{\partial n_k}{\partial R_j} \right], \quad (\text{C12})$$

which is the mean-field version of Eq. (68) and gives rise to a formal expression for  $K_{13}$ . A combination of Eqs. (C11)

and (C12) clearly reveals the surface origin of  $K_{13}$ , which arises in fact as an artifact of the gradient expansion when it is applied formally to a system with a boundary as discussed in detail in Sec. IV.

We consider briefly the effect of applying an arbitrary mapping to the first integral in Eq. (C4). As noted by Teixeira, Pergamenschik, and Sluckin, this is an invalid procedure since the general mapping leads to the loss of a one-to-one correspondence between the local director and the free-energy density. It is interesting to note that, due to the Nambu-Goldstone degeneracy,  $g_u(\mathbf{n})$  is in fact a constant independent of the direction of  $\mathbf{n}$ . Hence, regardless of the mapping used, the volume contribution to the first integral is a constant, as a signature of its physical well definability. However, there also arises an apparent surfacelike contribution of the  $K_{13}$  form, which depends on the mapping parameter. Just as shown above, this is also an artifact resulting from an inconsistent change of the integration volume at the boundary. Although there is, as noted by Teixeira, Pergamenschik, and Sluckin, a coincident condition whereby this  $K_{13}$  term cancels the similar term coming from the higher-order contribution, one should clearly realize that this is absolutely not the reason why  $K_{13}$  should generally disappear.

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