Surface free energies for nematic shells

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(Received 10 November 2011; published 1 June 2012)

We propose a continuum model to describe the molecular alignment in thin nematic shells. By contrast with previous accounts, the two-dimensional free energy, aimed at describing the physics of thin films of nematics deposited on curved substrates, is not postulated, but it is deduced from the conventional three-dimensional theories of nematic liquid crystals. Both the director and the order-tensor theories are taken into account. The so-obtained surface energies exhibit extra terms compared to earlier models. These terms reflect the coupling of the shell extrinsic curvature with the nematic order parameters. As expected, the shape of the shell plays a key role in the equilibrium configurations of nematics coating it.

DOI: 10.1103/PhysRevE.85.061701 PACS number(s): 61.30.Dk, 68.35.Md, 61.30.Jf

I. INTRODUCTION

Nematic liquid crystals are aggregates of rodlike molecules that tend to align parallel to each other along a given direction [1]. Due to their easy response to externally applied electric, magnetic, optical, and surface fields, liquid crystals are of greatest potential for scientific and technological applications. Currently there is an increasing interest in soft matter physics on small spherical colloidal particles or droplets coated with a thin layer of nematic liquid crystal [2,3]. The hope is to build *mesoatoms* with controllable valence [4]. We refer to these coating layers as *nematic shells*.

When nematic liquid crystals are constrained to a curved surface, the geometry induces a distortion in the molecular orientation. The possibility to have an in-plane order rather than a spatial distribution of the molecules depends on the shell thickness [2,5,6]. In ultra-thin shells, the interaction with the colloid surface enforces a sort of degenerate anchoring, i.e., the tendency of the molecules to align along any direction parallel to the surface. Thus, unavoidable defects arise when nematic order is established on a surface with the topology of the sphere. The number of defects is a consequence of the Poincaré-Hopf theorem, which states that any configuration must have a total topological charge equal to the Euler-Poincaré characteristic of the surface. For instance, on a sphere whose characteristic is $+2$, we can have two diametrically opposite $+1$ defects or four $+1/2$ defects located at the vertices of a tetrahedron [5]. This tetrahedral defect structure is of great interest in material science because defects regions can be functionalized to serve as bonds [4]. This could lead to tetravalent mesoatoms with sp^3-like directional bonding like carbon. Theoretical studies have emphasized the possibility to control the location of the defects, and hence the valence of mesoatoms, by varying the shell geometry [7] or by tuning the elastic constants of the nematic [8,9].

Most theoretical studies on nematic liquid crystals are framed within the classical *director theory* (see, for instance, Refs. [1,10]). In this setting, the local properties of the nematic liquid crystal are described through a unit vector, the director, parallel to the local molecular direction. The equilibrium configurations of the nematics minimize the Frank's free energy, with respect to all configurations that satisfy the boundary conditions. However, the director description of a nematic configuration misses a relevant information at the mesoscopic level: the dispersion of the molecules around the director. The *order-tensor theory*, put forward by de Gennes (see Refs. [1,10]), overcomes this gap by introducing a richer kinematic description. Within this theory the free energy to minimize is the Landau–de Gennes free energy.

Theories for two-dimensional nematic order have been proposed in both director and order-tensor schemes [7,11–15] and use free energies derived by symmetry arguments or mesoscopic properties. By contrast, our approach derives the surface free energy for thin films as limiting cases of the well-established three-dimensional theories of nematic liquid crystals. The main concern is how classical theories (Frank and Landau–de Gennes theories) reduce when the nematic molecules, confined within a thin region, align in the direction parallel to the underlying surface. A prominent role is played by the ratio between the thickness of the shell, denoted by h, and the minimum radius of curvature of the entire shell, denoted by ℓ. In fact, the surface versions of Frank and Landau–de Gennes free energies can be deduced from the three-dimensional models under the assumption of smallness of the ratio h/ℓ.

Conversely to existing models, we find that in the two-dimensional directory theory the twist term does not vanish. Actually, it expresses the tendency of the molecular axis to align with the curvature principal directions. Moreover, our analysis provides a coherent way to obtain the two-dimensional order-tensor theory. As a result, we retrieve the quadrupolar coupling between the two-dimensional order tensor and the curvature tensor already obtained by the authors of Ref. [15] using mesoscopic arguments.

The paper is organized as follows. In Sec. II we introduce the mathematical notations and terminology. Sections III and IV are devoted to obtain surface free energies from Frank and Landau–de Gennes theories, respectively. Mathematical topics employed in these sections and some details of the calculations are reported in the Appendixes. Finally, we draw our concluding remarks in Sec. V.

II. GEOMETRICAL PRELIMINARIES

We first introduce the terminology and establish some preliminary notations. First, three-dimensional vectors are denoted by lower-case boldface letters, whereas second order tensors are denoted by upper-case boldface letters. The scalar, vector, and tensor products between two vectors $\mathbf{u}$ and $\mathbf{v}$ are indicated by $\mathbf{u}\cdot\mathbf{v}$, $\mathbf{u}\times\mathbf{v}$, and $\mathbf{u}\otimes\mathbf{v}$, respectively. In cartesian components, $\mathbf{u}\cdot\mathbf{v}=u_iv_i$, $(\mathbf{u}\times\mathbf{v})_i=\epsilon_{ijk}u_jv_k$, $(\mathbf{u}\otimes\mathbf{v})_{ij}=u_iv_j$, where summation is understood over repeated indices, and the third-order tensor $\boldsymbol{\epsilon}=\epsilon_{ijk}$ is the Ricci alternator. The composition between two second-order tensors $\mathbf{A}$ and $\mathbf{B}$ is the tensor $\mathbf{C}=\mathbf{AB}$ with components $C_{ij}=A_{ih}B_{hj}$. For the compositions of tensors of different orders, it is agreed that the lower-order tensor is on the right and all its indexes are saturated. For instance, the composition between a second-order tensor $\mathbf{A}$ and a vector $\mathbf{u}$ gives the vector $\mathbf{v}=\mathbf{Au}$ with components $v_i=A_{ij}u_j$. Finally, the scalar product between $\mathbf{A}$ and $\mathbf{B}$ is the scalar $\mathbf{A}\cdot\mathbf{B}=A_{ij}B_{ij}$, whereas, given the third-order tensors $\mathbb{A}$ and $\mathbb{B}$, we set $\mathbb{A}\cdot\mathbb{B}=A_{ijk}B_{ijk}$ and $\mathbb{A}\cdot\mathbb{B}^t=A_{ijk}B_{ikj}$.

Let us assume that the nematic shell occupies a thin region V of thickness h around a regular compact surface $\mathcal{S}$. Let $\boldsymbol{\nu}_s$ be the normal unit vector field to $\mathcal{S}$. We parametrize points in the bulk through a coordinate set (u,v,ξ) such that

$$p(u,v,\xi)=p_S(u,v)+\xi\boldsymbol{\nu}_s(u,v), \tag{1}$$

where p_S is the normal projection of p onto $\mathcal{S}$, and $|\xi|$, with $\xi\in[-h/2,h/2]$, is the distance of p from the same surface. Such a coordinate set is well defined in a finite neighborhood of $\mathcal{S}$. More precisely, we introduce the principal curvatures $c_{1s}(p_S)$ and $c_{2s}(p_S)$ of $\mathcal{S}$ at point p_S, and assume

$$h\ll\min_{p_S\in\mathcal{S}}(\max\{|c_{1s}(p_S)|,|c_{2s}(p_S)|\})^{-1}=\ell. \tag{2}$$

For every fixed $\xi\in[-h/2,h/2]$, Eq. (1) defines a parallel surface $\mathcal{S}_\xi=\{p_S+\xi\boldsymbol{\nu}_s(p_S):p_S\in\mathcal{S}\}$ at distance $|\xi|$ from $\mathcal{S}$ with the vector field $\boldsymbol{\nu}:p\in\mathcal{S}_\xi\mapsto\boldsymbol{\nu}_s(p_S)$ as unit normal vector field. In such a way, the unit vector field $\boldsymbol{\nu}$ is defined on the entire region V. The second-order tensor $\nabla\boldsymbol{\nu}$ is symmetric. Its eigenvectors are $\boldsymbol{\nu}$ (with a null eigenvalue) and the unit vector fields

$$\mathbf{e}_i(p)=\mathbf{e}_{is}(p_S)\quad(i=1,2),$$

where $\mathbf{e}_{1s}$ and $\mathbf{e}_{2s}$ represent the tangent principal directions fields on $\mathcal{S}$. The spatial gradient for each eigenvector is

$$\nabla\boldsymbol{\nu}=-\frac{c_{1s}}{1-\xi c_{1s}}\mathbf{e}_1\otimes\mathbf{e}_1-\frac{c_{2s}}{1-\xi c_{2s}}\mathbf{e}_2\otimes\mathbf{e}_2, \tag{3}$$

$$\nabla\mathbf{e}_1=\kappa_1(\xi)\mathbf{e}_2\otimes\mathbf{e}_1+\kappa_2(\xi)\mathbf{e}_2\otimes\mathbf{e}_2+\frac{c_{1s}}{1-\xi c_{1s}}\boldsymbol{\nu}\otimes\mathbf{e}_1, \tag{4}$$

$$\nabla\mathbf{e}_2=-\kappa_1(\xi)\mathbf{e}_1\otimes\mathbf{e}_1-\kappa_2(\xi)\mathbf{e}_1\otimes\mathbf{e}_2+\frac{c_{2s}}{1-\xi c_{2s}}\boldsymbol{\nu}\otimes\mathbf{e}_2, \tag{5}$$

where the functions $\kappa_1(\xi)$ and $\kappa_2(\xi)$ are given in Appendix A. We refer the reader to Ref. [16] for a more comprehensive treatise of the geometry of surfaces.

Let Φ be a smooth field defined on $\mathcal{S}$. Assume Φ scalar, vector, or tensor valued. Then the surface gradient of Φ is defined (see Ref. [17]) as

$$\nabla_s\Phi=(\nabla\Phi)\mathbf{P},$$

where $\mathbf{P}=\mathbf{I}-\boldsymbol{\nu}_s\otimes\boldsymbol{\nu}_s$ represents the projection onto the tangent plane of $\mathcal{S}$. The trace of the surface gradient of a vector field $\mathbf{u}$ defines the surface divergence of $\mathbf{u}$: $\mathrm{div}_s\mathbf{u}=\mathrm{tr}\nabla_s\mathbf{u}=\nabla_s\mathbf{u}\cdot\mathbf{P}$, which is a scalar field. On the other hand, the surface curl of $\mathbf{u}$ is defined as twice the skew-simmetric part of the surface gradient:

$$\mathrm{curl}_s\mathbf{u}=-\boldsymbol{\epsilon}\nabla_s\mathbf{u}.$$

Let $\mathbf{n}$ denote a unit vector field defined on V such that $\mathbf{n}(p)=\mathbf{n}(p_S)$ and $\mathbf{n}\cdot\boldsymbol{\nu}=0$ at each point p. Next, by introducing the *conormal* unit vector field $\mathbf{t}=\boldsymbol{\nu}\times\mathbf{n}$, we write the spatial gradient of $\mathbf{n}$ (see Appendix A for calculation details):

$$\begin{aligned}\nabla\mathbf{n}=J_\xi^{-1}\big\{&\big[\kappa_{\mathbf{n}_s}-\xi\boldsymbol{\nu}_s\cdot\mathrm{curl}_s(\mathbf{Ln}_s)\big]\mathbf{t}\otimes\mathbf{n}\\&+\big[\kappa_{\mathbf{t}_s}-\xi\boldsymbol{\nu}_s\cdot\mathrm{curl}_s(\mathbf{Lt}_s)\big]\mathbf{t}\otimes\mathbf{t}\\&+\big(c_{\mathbf{n}_s}-\xi K\big)\boldsymbol{\nu}\otimes\mathbf{n}-\tau_{\mathbf{n}_s}\boldsymbol{\nu}\otimes\mathbf{t}\big\},\end{aligned} \tag{6}$$

where $\mathbf{n}_s$ and $\mathbf{t}_s$ represent the restrictions of $\mathbf{n}$ and $\mathbf{t}$ on $\mathcal{S}$, respectively. The tensor $\mathbf{L}=-\nabla_s\boldsymbol{\nu}_s$ represents the extrinsic curvature tensor of $\mathcal{S}$. Its trace gives twice the mean curvature H, while its second invariant gives the Gaussian curvature K. The quantities $c_{\mathbf{n}_s}=\mathbf{n}_s\cdot\mathbf{Ln}_s$, $\tau_{\mathbf{n}_s}=-\mathbf{t}_s\cdot\mathbf{Ln}_s$ represent the normal curvature and the geodesic torsion of the flux lines of $\mathbf{n}_s$ on $\mathcal{S}$, respectively. The latter is zero whenever $\mathbf{n}_s$ is a principal direction. The quantities $\kappa_{\mathbf{n}_s}$ and $\kappa_{\mathbf{t}_s}$ denote the geodesic curvature of the flux lines of $\mathbf{n}_s$ and $\mathbf{t}_s$ on $\mathcal{S}$, respectively [18,19]. The geodesic curvature $\kappa_{\mathbf{n}_s}$ (respectively, $\kappa_{\mathbf{t}_s}$) measures the deviance of the flux lines of $\mathbf{n}_s$ (respectively, $\mathbf{t}_s$) from following a geodesic on $\mathcal{S}$. Finally, we have set $J_\xi=1-2H\xi+K\xi^2$.

The divergence and the curl of $\mathbf{n}$ are the trace of $\nabla\mathbf{n}$ and the axial-vector associated with twice the skew-symmetric part of $\nabla\mathbf{n}$, respectively. Thus, from (6) it follows that

$$\mathrm{div}\mathbf{n}=J_\xi^{-1}\big[\kappa_{\mathbf{t}_s}-\xi\boldsymbol{\nu}_s\cdot\mathrm{curl}_s(\mathbf{Lt}_s)\big], \tag{7}$$

$$\begin{aligned}\mathrm{curl}\mathbf{n}=J_\xi^{-1}\big\{&-\tau_{\mathbf{n}_s}\mathbf{n}-\big(c_{\mathbf{n}_s}-\xi K\big)\mathbf{t}\\&+\big[\kappa_{\mathbf{n}_s}-\xi\boldsymbol{\nu}_s\cdot\mathrm{curl}_s(\mathbf{Ln}_s)\big]\boldsymbol{\nu}\big\}.\end{aligned} \tag{8}$$

We observe that the normal curvatures, the geodesic torsion, the geodesic curvatures, and the surface gradients introduced above are quantities related to the surface $\mathcal{S}$, and, therefore, they do not depend on ξ. Instead, although $\mathbf{n}$ has been supposed constant along normal directions within the thickness, its spatial gradient depends on ξ.

Finally, since $\kappa_{\mathbf{n}_s}=\mathbf{t}_s\cdot(\nabla_s\mathbf{n}_s)\mathbf{n}_s$ and $\kappa_{\mathbf{t}_s}=\mathbf{t}_s\cdot(\nabla_s\mathbf{n}_s)\mathbf{t}_s$ (see Ref. [18]), the surface gradient of $\mathbf{n}_s$ is given by

$$\nabla_s\mathbf{n}_s=\kappa_{\mathbf{n}_s}\mathbf{t}_s\otimes\mathbf{n}_s+\kappa_{\mathbf{t}_s}\mathbf{t}_s\otimes\mathbf{t}_s+c_{\mathbf{n}_s}\boldsymbol{\nu}_s\otimes\mathbf{n}_s-\tau_{\mathbf{n}_s}\boldsymbol{\nu}_s\otimes\mathbf{t}_s,$$

and consequently

$$\mathrm{div}_s\mathbf{n}_s=\kappa_{\mathbf{t}_s},\quad\mathrm{curl}_s\mathbf{n}_s=-\tau_{\mathbf{n}_s}\mathbf{n}_s-c_{\mathbf{n}_s}\mathbf{t}_s+\kappa_{\mathbf{n}}\boldsymbol{\nu}_s. \tag{9}$$

Unlike flat surfaces, the surface curl of $\mathbf{n}_s$ possesses nonvanishing in-plane components.

III. TWO-DIMENSIONAL DIRECTOR THEORY

The classical elastic continuum theory is based on the pioneering works of Oseen, Zocher, and Frank (OZF) published between the 1930s and 1950s. We refer the reader to

Ref. [10] for a detailed mathematical treatment. The average alignment of the molecules is represented by a unit vector $\mathbf{n}$, called the director, where $\mathbf{n}$ is physically equivalent to $-\mathbf{n}$. The expression for the elastic energy density (per unit of volume) associated with the director distortion consists of four terms:

$$2w_{\mathrm{OZF}} = K_1(\mathrm{div}\mathbf{n})^2 + K_2(\mathbf{n}\cdot\mathrm{curl}\mathbf{n})^2 + K_3|\mathbf{n}\times\mathrm{curl}\mathbf{n}|^2 + (K_2+K_{24})\mathrm{div}[(\nabla\mathbf{n})\mathbf{n} - (\mathrm{div}\mathbf{n})\mathbf{n}], \quad (10)$$

where the constants K_1, K_2, K_3, and K_{24} are called the splay, twist, bend, and saddle-splay moduli, respectively. To ensure a stable undistorted configuration of a nematic liquid crystal in the absence of external fields or confinements, the three moduli $K_i (i = 1,2,3)$ must be non-negative, whereas the elastic saddle-splay constant must obey Ericksen's inequalities [6]:

$$|K_{24}| \leqslant K_2, \quad K_2 + K_{24} \leqslant 2K_1.$$

In the absence of external actions, the equilibrium configurations are stationary points of the total energy

$$W = \int_V w_{\mathrm{OZF}}(\mathbf{n}, \nabla\mathbf{n})\, dV, \quad (11)$$

according to the boundary conditions. These may consist in fixing $\mathbf{n}$ at the boundary (strong boundary conditions) or in allowing $\mathbf{n}$ to rotate freely (free boundary conditions). Intermediate situations, known as *weak anchoring* boundary conditions, can be envisaged by including an anchoring energy that penalizes the deviation of the molecules at the boundary from a given direction. Furthermore, the free energy density may account for extra terms in order to describe, for instance, the interaction of the nematic with external electric or magnetic fields.

Let us introduce the small parameter $\varepsilon = h/\ell$. The smallness of ε on the one hand ensures that the parametrization (1) is properly defined, and on the other hand, with the aid of Proposition 2 (see Appendix B), it allows us to approximate the OZF free energy as follows:

$$W_{\mathrm{OZF}} \approx W^S_{\mathrm{OZF}} = \frac{1}{2}\int_{\mathcal{S}} [k_1(\mathrm{div}_s\mathbf{n}_s)^2 + k_2(\mathbf{n}_s\cdot\mathrm{curl}_s\mathbf{n}_s)^2 + k_3|\mathbf{n}_s\times\mathrm{curl}_s\mathbf{n}_s|^2]dA, \quad (12)$$

where $k_i = hK_i$ $(i = 1,2,3)$. Observe that the saddle-splay term has disappeared in this approximation since $\mathbf{n}$ is assumed independent of ξ. In fact, from (6) it follows

$$\mathrm{div}[(\nabla\mathbf{n})\mathbf{n} - (\mathrm{div}\mathbf{n})\mathbf{n}] = \mathrm{tr}(\nabla\mathbf{n})^2 - (\mathrm{tr}\nabla\mathbf{n})^2 = 0. \quad (13)$$

Comparing Eqs. (12) and (10) we remark that (1) W^S_{OZF} involves a surface integral rather than a volume integral, thus we can refer to W^S_{OZF} as a *surface free energy*; (2) the surface elastic constants k_i are obtained by multiplying K_i and the thickness h, and, hence, by virtue of Ericksen's inequalities, they must be non-negative; (3) the surface free energy involves surface differential operators instead of spatial ones.

It is worth mentioning a peculiarity of curved substrates with respect to planar nematics. Unlike the planar case, the twist term cannot be *a priori* neglected. Indeed, as it has been already observed, $\mathrm{curl}_s\mathbf{n}_s$ is not orthogonal to $\mathbf{n}_s$. In fact, by using formulas (9), Eq. (12) reduces to

$$W^S_{\mathrm{OZF}} = \frac{1}{2}\int_{\mathcal{S}} \left[k_1\kappa^2_{\mathbf{t}_s} + k_2\tau^2_{\mathbf{n}_s} + k_3\left(c^2_{\mathbf{n}_s} + \kappa^2_{\mathbf{n}_s}\right)\right]dA, \quad (14)$$

which shows that the twist free energy density is proportional to $\tau^2_{\mathbf{n}_s}$. The latter vanishes if and only if the flux lines of $\mathbf{n}_s$ lie along principal directions. Thus, the twist free energy can be disregarded whenever spherical shells are concerned [9] or whenever the director lies along meridians or parallels of an axisymmetric shell [20].

In light of Eq. (14), we can give the following intuitive interpretation for the shell-nematic interaction. The arrangement of the molecules on a surface is the result of the competition between the bend and the splay free energies that try to put the flux lines of $\mathbf{n}_s$ and $\mathbf{t}_s$ along geodesics of $\mathcal{S}$, and the twist term that tries to align the flux lines of $\mathbf{n}_s$ with the curvature lines of $\mathcal{S}$. Furthermore, the term proportional to the square of the normal curvature expresses the tendency of the flux lines of $\mathbf{n}_s$ to align with the principal direction of minimal curvature.

From Eq. (14) it follows that within the *one constant approximation* $(k_1 = k_2 = k_3 = k)$, the surface OZF free energy becomes

$$W^S_{\mathrm{OZF}} = \frac{k}{2}\int_S |\nabla_s\mathbf{n}_s|^2 dA. \quad (15)$$

A key feature of the free energy (15) is that it differs from the one used in earlier works [5,11,21]. Indeed, by denoting α the angle between the principal direction $\mathbf{e}_{1s}$ and $\mathbf{n}_s$, Eq. (15) reduces to

$$W^S_{\mathrm{OZF}} = \frac{k}{2}\int_S \left(|\nabla_s\alpha - \boldsymbol{\omega}|^2 + c^2_{\mathbf{n}_s} + \tau^2_{\mathbf{n}_s}\right) dA,$$

where $\boldsymbol{\omega}$ represents the *spin connection field* [22,23]. A glance at Eq. (21a) of Ref. [22] shows that the terms proportional to $\tau^2_{\mathbf{n}_s}$ and $c^2_{\mathbf{n}_s}$ were neglected. Clearly, this mismatch stems from the fact that free energy density in Eq. (15) is proportional to the square of the surface gradient of $\mathbf{n}_s$ rather than proportional to the square of covariant derivative of $\mathbf{n}_s$ as it is customary to assume (see, for instance, Ref. [22] or [21]).

IV. TWO-DIMENSIONAL ORDER-TENSOR THEORY

The director theory describes only states with a single optical axis. For closed shells whose topology is different from that of a torus, the tangent vector field $\mathbf{n}$ exhibits singular points, i.e., regions where the local orientational order of the nematic is undefined. As a result, the shell often incorporates so-called topological defects. These mathematical singularities can be avoided by introducing a tensorial-order parameter, that describes defects as those points in which the nematic melts into a liquid phase (isotropic states). Hereinafter we illustrate the geometrical meaning of that order parameter.

We now recall the order-tensor theory for the usual three-dimensional nematics. Let us suppose that the orientation of a single molecule is represented by a unit vector $\mathbf{m}$. Microscopic disorder is taken into account by introducing a probability measure $f_p : \mathbb{S}^2 \to \mathbb{R}^+$, such that $f_p(\mathbf{m})$ describes the probability that a molecule placed in p is oriented along $\mathbf{m}$. The orientation of the molecular axis is described at each point in space by a point of the unit sphere $\mathbb{S}^2$ (or by a unit vector).

Thus, if Ω is any subset of $\mathbb{S}^2$, the probability of finding in p one molecule oriented within Ω is given by

$$P\{\Omega\} = \int_\Omega f_p(\mathbf{m}) d\sigma,$$

where σ denotes the area measure on $\mathbb{S}^2$. Nematics posses a molecular mirror symmetry; i.e., the *head* and *tail* of a molecule can be changed without experiencing any change in the probability distribution. Thus, the probability measure is even, $f_p(\mathbf{m}) = f_p(-\mathbf{m})$, and the first moment of the distribution f_p is zero.

The second moment of the distribution is the variance tensor $\mathbf{M} = \langle \mathbf{m} \otimes \mathbf{m} \rangle$, where the brackets denote averaging with respect to f_p. By definition, $\mathbf{M}$ is unit trace symmetric and semidefinite positive. The spectral decomposition theorem ensures that $\mathbf{M}$ can be put in the diagonal form:

$$\mathbf{M} = \lambda_1 \mathbf{e}_1 \otimes \mathbf{e}_1 + \lambda_2 \mathbf{e}_2 \otimes \mathbf{e}_2 + \lambda_3 \mathbf{e}_3 \otimes \mathbf{e}_3,$$

and, since the eigenvalues of $\mathbf{M}$ sum up to one, its spectrum is bounded by $\mathrm{sp}(\mathbf{M}) \subset [0,1]$.

Nematic liquid crystals may then exhibit three different states: isotropic, uniaxial, and biaxial. It is customary to define these states by using the *order tensor* $\mathbf{Q} = \mathbf{M} - \frac{1}{3}\mathbf{I}$. Thus, we can have the following:

(1) The eigenvalues of $\mathbf{Q}$ are equal, which implies $\mathbf{Q}_{\mathrm{iso}} = \mathbf{0}$; in this case we label the nematic as *isotropic*.

(2) At least two eigenvalues are equal, the nematic is called *uniaxial*. Simple algebraic manipulation allows us to write

$$\mathbf{Q}_{\mathrm{uni}} = s\left(\mathbf{u} \otimes \mathbf{u} - \tfrac{1}{3}\mathbf{I}\right).$$

The scalar parameter $s \in [-\frac{1}{2}, 1]$ is called the *degree of orientation*, and the unit vector $\mathbf{u}$ is the optical axis. We retrieve the isotropic phase when $s = 0$, while the perfect alignment of the molecules is obtained for $s = 1$. The case $s = -\frac{1}{2}$ represents flat isotropic distributions, in the plane orthogonal to $\mathbf{u}$.

(3) When the eigenvalues of the order tensor are all different, the nematic is labeled as *biaxial*. Then we can write the general expression for the order tensor

$$\mathbf{Q}_{\mathrm{bia}} = s\left(\mathbf{u} \otimes \mathbf{u} - \tfrac{1}{3}\mathbf{I}\right) + \lambda(\mathbf{e}_+ \otimes \mathbf{e}_+ - \mathbf{e}_- \otimes \mathbf{e}_-),$$

where λ denotes the degree of biaxiality and $s \in [-\frac{1}{2}, 1]$ as above. The sign of λ is unessential, since it involves only an exchange between $\mathbf{e}_+$ and $\mathbf{e}_-$. The degree of biaxiality does always satisfy $|\lambda| \leqslant \frac{1}{3}(1 - s)$. Even for biaxial nematic, $s = -\frac{1}{2}$ represents flat (not necessarily isotropic) distributions.

The free energy comprises two terms: the elastic energy and the Landau–de Gennes potential. Following Ref. [24], the most general quadratic elastic energy can be written as

$$W_{\mathrm{el}}(\nabla\mathbf{Q}, \mathbf{Q}) = \int_V \{L_1 |\nabla\mathbf{Q}|^2 + L_2 (\nabla\mathbf{Q}) \cdot (\nabla\mathbf{Q})^t + L_{24} \mathrm{div}[(\nabla\mathbf{Q})\mathbf{Q} - \mathbf{Q}\mathrm{div}\mathbf{Q}]\} dV, \quad (16)$$

where L_1, L_2, and L_{24} are constants. This energy expresses the tendency of the molecules to arrange parallel one to each other in a homogeneous state.

The Landau–de Gennes potential W_{LdG} is a temperature-dependent thermodynamic contribution that takes into account the material tendency to spontaneously arrange in ordered or disordered states. Its density is of the form (see Ref. [1])

$$w_{\mathrm{LdG}}(\mathbf{Q}) = F(A,B,C) + \frac{A}{2}\mathrm{tr}\mathbf{Q}^2 - \frac{B}{3}\mathrm{tr}\mathbf{Q}^3 + \frac{C}{4}(\mathrm{tr}\mathbf{Q}^2)^2, \quad (17)$$

where $A = A_0(T - T_c)/T_c$, A_0 is a material-dependent positive constant, T is the absolute temperature, and T_c is a characteristic temperature; B and C are material-dependent positive constants and $F(A,B,C)$ is a positive constant that accounts for the free energy of the isotropic phase. We observe that $F(A,B,C)$ plays no role in the minimization of the Landau–de Gennes energy density, and the stationary points of w_{LdG} correspond to either isotropic tensors or, whenever $B^2 - 24AC \geqslant 0$, uniaxial tensors of the form

$$\mathbf{Q}_{\mathrm{cr}} = \tilde{s}\left(\mathbf{u} \otimes \mathbf{u} - \tfrac{1}{3}\mathbf{I}\right),$$

with

$$\tilde{s} = \frac{B + \sqrt{B^2 - 24AC}}{4C},$$

and $\mathbf{u} \in \mathbb{S}^2$. In addition to the supercooling temperature T_c below which the isotropic state loses its stability, there are two other characteristic temperatures for w_{LdG}: the nematic-isotropic transition temperature $(1 + \frac{B^2}{27A_0C})T_c$ at which the nematic and the isotropic phase have the same energy, and the superheating temperature $(1 + \frac{B^2}{24A_0C})T_c$ above which the isotropic phase is the unique stationary point of w_{LdG}. The resulting seven characteristic temperature regimes for w_{LdG} are discussed in detail in Ref. [25].

A. Degenerate states

The procedure to derive the two-dimensional free energy for nematic shells is performed in two subsequent steps: (a) we have to specialize the free energy to describe degenerate planar distributions, where the eigenvector of $\mathbf{M}$ with null eigenvalue coincides with $\boldsymbol{\nu}$; then, (b) as for the OZF free energy, we approximate the three-dimensional free energy under the assumption of smallness of the parameter ε.

To describe a degenerate anchoring throughout the shell, let us suppose the nematic molecules are orthogonal to $\boldsymbol{\nu}$ and $\mathbf{m}(p(u,v,\xi)) = \mathbf{m}(p_S(u,v))$. Since at each point the probability to find $\mathbf{m}$ in the direction $\boldsymbol{\nu}$ is zero, it follows that $\mathbf{M}\boldsymbol{\nu} = \mathbf{0}$. This means that no isotropic spatial states are allowed. Let us introduce $\mathbf{n}$ and $\mathbf{t}$ the eigenvectors of $\mathbf{M}$ orthogonal to $\boldsymbol{\nu}$. We write the variance tensor in the form [7]

$$\overline{\mathbf{M}} = \tfrac{1}{2}(\mathbf{I} - \boldsymbol{\nu} \otimes \boldsymbol{\nu}) + \lambda\left(\mathbf{n} \otimes \mathbf{n} - \mathbf{t} \otimes \mathbf{t}\right),$$

where $\lambda \in [-\frac{1}{2}, \frac{1}{2}]$. We recognize that two kinds of uniaxial states are allowed: (1) $\lambda = 0$, then $\boldsymbol{\nu}$ is the optical axis and the molecules are randomly distributed orthogonally to $\boldsymbol{\nu}$; and (2) $\lambda = \pm\frac{1}{2}$ and the molecules are perfectly ordered along a direction orthogonal to $\boldsymbol{\nu}$. The latter case coincides with the directory theory analyzed in the previous section. Note that the sign of λ is inessential since, the order tensors associated with negative values of λ and director $\mathbf{n}$ coincide with the order tensors associated with the positive degree of order $-\lambda$ and director $\mathbf{t}$.

An alternative and equivalent parametrization of the variance tensor is the following [15]:

$$\overline{\mathbf{M}} = q\,(\mathbf{n}\otimes\mathbf{n}) + \tfrac{1}{2}(1-q)(\mathbf{I}-\boldsymbol{\nu}\otimes\boldsymbol{\nu}), \tag{18}$$

with $q = 2\lambda \in [-1,1]$.

It is worth noting that this parametrization can be also obtained from the three-dimensional order parameter $\mathbf{M}$ by imposing $s = -\frac{1}{2}$, by taking $\mathbf{u}$ along the normal surface and by choosing $\mathbf{n}$ along one of the two tangential eigenvectors of $\mathbf{M}$.

B. Elastic energy

Now, let us introduce the traceless tensor $\overline{\mathbf{Q}}$, associated with $\overline{\mathbf{M}}$, in the usual way: $\overline{\mathbf{Q}} = \overline{\mathbf{M}} - \frac{1}{3}\mathbf{I}$. With the aim of adapting the elastic free energy to the case of degenerate states, we replace $\mathbf{Q}$ by $\overline{\mathbf{Q}}$. Since $\overline{\mathbf{Q}}$ and $\overline{\mathbf{M}}$ (as well as $\mathbf{Q}$ and $\mathbf{M}$) differ up to a constant, we have $\nabla\overline{\mathbf{Q}} = \nabla\overline{\mathbf{M}}$; thus, in the elastic energy, $\overline{\mathbf{Q}}$ can be replaced by $\overline{\mathbf{M}}$ leading to

$$W_{el}(\iota_1,\iota_2,\iota_3) = \int_V [L_1\iota_1 + L_2\iota_2 + L_{24}(\iota_2-\iota_3)]dV, \tag{19}$$

where $\iota_1 = |\nabla\overline{\mathbf{M}}|^2$, $\iota_2 = (\nabla\overline{\mathbf{M}})\cdot(\nabla\overline{\mathbf{M}})^t$, and $\iota_3 = |\mathrm{div}\overline{\mathbf{M}}|^2$ are scalar invariants of $\overline{\mathbf{M}}$. On the other hand, by using the parametrization (18) and with the aid of equations (3)–(5), the following identities hold:

$$\begin{aligned}\iota_1 &= 2q^2\{(\mathrm{div}\mathbf{n})^2 + |\mathbf{n}\times\mathrm{curl}\mathbf{n}|^2 + (\mathbf{n}\cdot\mathrm{curl}\mathbf{n})^2\}\\ &\quad + \frac{1}{2}|\nabla q|^2 + 2J_\xi^{-2}(1-q)(H-K\xi)\big[(1-q)H\\ &\quad + 2qc_{\mathbf{n}_s} - (1+q)K\xi\big] - J_\xi^{-2}(1-q^2)K, \qquad (20a)\\ \iota_2 &= \mathrm{div}\left\{\frac{1-q}{2J_\xi}\big[(1-q)H + 2qc_{\mathbf{n}_s} - (1+q)K\xi\big]\boldsymbol{\nu}\right\}\\ &\quad + J_\xi^{-2}(1-q)(H-K\xi)\big[(1-q)H + 2qc_{\mathbf{n}_s}\\ &\quad - (1+q)K\xi\big] + q^2[(\mathrm{div}\mathbf{n})^2 + |\mathbf{n}\times\mathrm{curl}\mathbf{n}|^2] + \frac{1}{4}|\nabla q|^2\\ &\quad + q\nabla q\cdot[(\nabla\mathbf{n})\mathbf{n} - (\mathrm{div}\mathbf{n})\mathbf{n}], \qquad (20b)\\ \iota_3 &= q^2[(\mathrm{div}\mathbf{n})^2 + |\mathbf{n}\times\mathrm{curl}\mathbf{n}|^2] + \frac{1}{4}|\nabla q|^2\\ &\quad + J_\xi^{-2}(1-q)(H-K\xi)\big[(1-q)H + 2qc_{\mathbf{n}_s} - (1+q)K\xi\big]\\ &\quad - q\nabla q\cdot[(\nabla\mathbf{n})\mathbf{n} - (\mathrm{div}\mathbf{n})\mathbf{n}]. \qquad (20c)\end{aligned}$$

As for the director theory, in order to obtain the elastic surface free energy, we expand the volume free energy as a power series in the small parameter ε and consider only the leading-order term. Thus, by means of Proposition 1 in Appendix B and since Euler's formulas (A15) lead to $H = \frac{1}{2}(c_{\mathbf{n}_s} + c_{\mathbf{t}_s})$, we obtain

$$\begin{aligned}W_{\mathrm{el}}^S &= \int_{\mathcal{S}} l_1\left[q^2\big(\kappa_{\mathbf{t}_s}^2 + \kappa_{\mathbf{n}_s}^2\big) + \frac{1}{4}|\nabla_s q|^2 + \left(H + q\frac{c_{\mathbf{n}_s} - c_{\mathbf{t}_s}}{2}\right)^2\right]dA\\ &\quad + \int_{\mathcal{S}} l_2 q\nabla_s q\cdot\big(\kappa_{\mathbf{n}_s}\mathbf{t}_s - \kappa_{\mathbf{t}_s}\mathbf{n}_s\big)dA\\ &\quad - \int_{\mathcal{S}} l_3(1-q^2)A - \int_{\mathcal{S}}(l_1+l_2-4l_3)q^2\tau_{\mathbf{n}_s}^2\,dA, \qquad (21)\end{aligned}$$

where $l_1 = h(2L_1+L_2)$, $l_2 = h(L_2+2L_{24})$, $l_3 = h(2L_1 + L_2 + L_{24})/2$. In the next section we show that these elastic constants are subject to restrictions in order to guarantee the positiveness of the elastic free energy.

In order to interpret the contributions of the different terms, we first examine the special case where the perfect uniaxial nematic order ($q = 1$ everywhere) is enforced on the entire shell. Equation (21) reduces to

$$W_{el}^S(q=1) = \int_{\mathcal{S}}\big[l_1\big(\kappa_{\mathbf{t}_s}^2 + \kappa_{\mathbf{n}_s}^2 + c_{\mathbf{n}_s}^2\big) - (l_1+l_2-4l_3)\tau_{\mathbf{n}_s}^2\big]dA,$$

that represents a Frank-like surface free energy [to be compared with Eq. (14)]. The ratio between the twist and the splay constants can be tuned acting on the constants l_i ($i = 1,2,3$). In particular, when $L_2 = 0$, then $4l_3 = 2l_1 + l_2$, and we retrieve the one constant approximation of the Frank's energy (15).

By denoting $\mathbf{M}_s = q(\mathbf{n}_s\otimes\mathbf{n}_s) + \frac{1}{2}(1-q)\mathbf{P}$ the restriction of $\overline{\mathbf{M}}$ to $\mathcal{S}$, the following identity holds:

$$l_1\left(H + q\frac{c_{\mathbf{n}_s} - c_{\mathbf{t}_s}}{2}\right)^2 = l_1(\mathbf{M}_s\cdot\mathbf{L})^2; \tag{22}$$

the right-hand side of this identity is the quadrupolar coupling between the curvature tensor and the surface-order tensor derived in Ref. [15] employing quasi-microscopic arguments. When q is different from zero, this term express the tendency of $\mathbf{n}_s$ to align along one of the two principal directions depending on the sign of the mean curvature.

The energy term proportional to the square of the surface gradient of q clearly expresses the tendency of the nematic to arrange in states with constant order parameter. It is worth to note that, for topological reasons, states with nonzero uniform q are not always allowed. This is the case of closed surfaces with the topology of the sphere.

The term proportional to Gaussian curvature K was already obtained in Ref. [7]. It is a constant term only when q is homogeneous on a fixed surface, by virtue of Gauss-Bonnet theorem.

Concerning the second integral of the right-hand side of Eq. (21), we find the following identity (see Appendix C):

$$\begin{aligned}&\int_{\mathcal{S}} q(\nabla_s q)\cdot\big(\kappa_{\mathbf{n}_s}\mathbf{t}_s - \kappa_{\mathbf{t}_s}\mathbf{n}_s\big)dA\\ &\quad = \frac{1}{2}\int_{\partial S} q^2(\nabla_s\alpha - \boldsymbol{\omega})\cdot d\mathbf{l} - \frac{1}{2}\int_{\mathcal{S}} q^2K\,dA, \qquad (23)\end{aligned}$$

with α and $\boldsymbol{\omega}$ as in previous section. Thus, for closed shells, the density free-energy density associated with this term is even proportional to the Gaussian curvature.

To better compare our results with earlier models, we rewrite Eq. (21) in terms of $\mathbf{M}_s$. By introducing

$$\iota_{1s} = |\nabla_s\mathbf{M}_s|^2, \quad \iota_{2s} = (\nabla_s\mathbf{M}_s)\cdot(\nabla_s\mathbf{M}_s)^t, \quad \iota_{3s} = |\mathrm{div}_s\mathbf{M}_s|^2,$$

a straightforward calculation, exploiting identities (B14), yields

$$W_{\mathrm{el}}^S(\iota_{1s},\iota_{2s},\iota_{3s}) = \int_S[\mu_1\iota_{1s} + \mu_2\iota_{2s} + \mu_{24}(\iota_{2s}-\iota_{3s})]da, \tag{24}$$

where $\mu_i = hL_i$ ($i = 1,2,24$).

By introducing $\mathbf{Q}_s = \mathbf{M}_s - \frac{1}{2}\mathbf{P} = q(\mathbf{n}_s\otimes\mathbf{n}_s - \frac{1}{2}\mathbf{P})$, we notice that energy (24) reduces to Eq. (6) of Ref. [7] provided that $\mathbf{M}_s$ is replaced by $\mathbf{Q}_s$. However, it is worth noting that,

unlike the usual tensors $\mathbf{M}$ and $\mathbf{Q}$, the surface tensors $\mathbf{M}_s$ and $\mathbf{Q}_s$ differ for a *nonconstant* tensor field. As a consequence, Eqs. (24) and (6) of Ref. [7] *do not represent* the same surface free energy. Indeed, a direct calculation yields the following identities:

$$\begin{aligned}\iota_{1s} &= |\nabla_s \mathbf{Q}_s|^2 + 2\mathbf{Q}_s \cdot \mathbf{L}^2 + \tfrac{1}{2}|\mathbf{L}|^2,\\ \iota_{2s} &= (\nabla_s \mathbf{Q}_s)\cdot(\nabla_s \mathbf{Q}_s)^t + \mathbf{Q}_s \cdot \mathbf{L}^2 + \tfrac{1}{4}|\mathbf{L}|^2,\\ \iota_{2s} - \iota_{3s} &= (\nabla_s \mathbf{Q}_s)\cdot(\nabla_s \mathbf{Q}_s)^t - |\mathrm{div}_s \mathbf{Q}_s|^2 - \tfrac{1}{2}K,\end{aligned}$$

that allows us to state that the elastic energy (24) includes the one reported in Ref. [7] supplemented by additional terms describing the coupling of the shell extrinsic curvature with the nematic ordering. Finally, since

$$\mathbf{Q}_s \cdot \mathbf{L}^2 = 2H\varsigma \cos 2\alpha, \tag{25}$$

where $\varsigma = \frac{1}{2}(c_1 - c_2)$ is the local asphericity, we can conclude that (24) reduces (up to constant terms) to Eq. (6) of Ref. [7] if and only if the shell is a minimal surface or spherical.

The positiveness of the free energy imposes suitable restrictions to the free energy coefficients. Following the approach pursued in Ref. [7], let us decompose the surface elastic free energy density $w_{\mathrm{el}}^{\mathcal{S}}$ as follows:

$$w_{\mathrm{el}}^{\mathcal{S}} = w_{\mathrm{el}1}^{\mathcal{S}} + w_{\mathrm{el}2}^{\mathcal{S}} + w_{\mathrm{el}3}^{\mathcal{S}}, \tag{26}$$

with

$$\begin{aligned} w_{\mathrm{el}1}^{\mathcal{S}} &= l_1\left[q^2\left(\kappa_{\mathbf{t}_s}^2 + \kappa_{\mathbf{n}_s}^2\right) + \frac{1}{4}|\nabla_s q|^2\right]\\ &\quad + l_2 q\left(\kappa_{\mathbf{n}_s}\mathbf{t}_s - \kappa_{\mathbf{t}_s}\mathbf{n}_s\right)\cdot\nabla_s q, \qquad (27a)\\ w_{\mathrm{el}2}^{\mathcal{S}} &= \frac{l_1}{4}\left[(1+q)^2 c_{\mathbf{n}_s}^2 + 2(1-q^2)c_{\mathbf{n}_s}c_{\mathbf{t}_s} + (1-q)^2 c_{\mathbf{t}_s}^2\right]\\ &\quad - l_3(1-q^2)c_{\mathbf{n}_s}c_{\mathbf{t}_s}, \qquad (27b)\\ w_{\mathrm{el}3}^{\mathcal{S}} &= [l_3 - (l_1 + l_2 - 3l_3)q^2]\tau_{\mathbf{n}_s}^2, \qquad (27c)\end{aligned}$$

where the identity $K = c_{\mathbf{n}_s}c_{\mathbf{t}_s} - \tau_{\mathbf{n}_s}^2$ has been used. Then we recognize that $w_{\mathrm{el}1}^{\mathcal{S}} = \mathbf{v}_1 \cdot \mathbf{A}_1\mathbf{v}_1$ and $w_{\mathrm{el}2}^{\mathcal{S}} = \mathbf{v}_2 \cdot \mathbf{A}_2\mathbf{v}_2$, with

$$\mathbf{A}_1 = \begin{pmatrix} l_1 & l_2/2 & 0 & 0\\ l_2/2 & l_1/4 & 0 & 0\\ 0 & 0 & l_1 & -l_2/2\\ 0 & 0 & -l_2/2 & l_1/4\end{pmatrix},$$

$$\mathbf{A}_2 = \frac{1}{4}\begin{pmatrix} l_1 & l_1 - 2l_3\\ l_1 - 2l_3 & l_1\end{pmatrix},$$

$$\mathbf{v}_1 := \left(q\kappa_{\mathbf{n}_s}, \nabla_s q\cdot\mathbf{t}_s, q\kappa_{\mathbf{t}_s}, \nabla_s q\cdot\mathbf{n}_s\right),$$

$$\mathbf{v}_2 := \left[(1+q)c_{\mathbf{n}_s}, (1-q)c_{\mathbf{t}_s}\right].$$

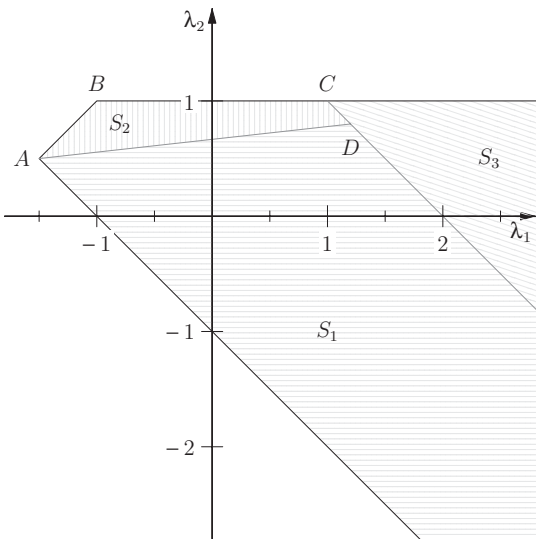

FIG. 1. We have set $\lambda_1 = L_2/L_1$, $\lambda_2 = L_{24}/L_1$. S_1 is the region in which the elastic energy density in Eq. (16) is nonnegative (see Ref. [24]). $S_1 \cup S_2$ represent the domain in which the surface elastic free energy in Ref. [7] is non-negative. $S_1 \cup S_2 \cup S_3$ is the region where inequalities (28) hold. $A \equiv (-3/2,1/2)$, $B \equiv (-1,1)$, $C \equiv (1,1)$, $D \equiv (6/5,4/5)$.

Hence, it can be easily proved that $w_{\mathrm{el}}^{\mathcal{S}} \geqslant 0$ if and only if

$$l_1 \geqslant 0, \quad |l_2| \leqslant l_1, \quad 0 \leqslant l_3 \leqslant l_1, \quad l_1 + l_2 \leqslant 4l_3,$$

or, equivalently,

$$\begin{aligned} &\mu_1 \geqslant 0, \quad 2\mu_1 + \mu_2 \geqslant 0, &(28a)\\ &|\mu_{24}| \leqslant 2\mu_1 + \mu_2, \quad |\mu_2 + 2\mu_{24}| \leqslant 2\mu_1 + \mu_2. &(28b)\end{aligned}$$

By assuming $L_1 > 0$ and introducing the ratios $\lambda_1 = \mu_2/\mu_1$ and $\lambda_2 = \mu_{24}/\mu_1$, the admissible region in the (λ_1,λ_2) plane in which the surface elastic energy density (21) is positive semidefinite is sketched in Fig. 1. It is worth noting that the domain in which the elastic free energy density (26) is positive semidefinite contains the domain of nonnegativeness of the surface energy density introduced in Ref. [7]. This in turn contains the domain of nonnegativeness of the elastic energy density (16).

C. Landau–de Gennes potential

Let us consider the Landau–de Gennes free energy density (17), where $\mathbf{Q} = \overline{\mathbf{Q}}$. A straightforward calculation gives

$$\mathrm{tr}(\overline{\mathbf{Q}}^2) = \tfrac{1}{6} + \tfrac{1}{2}q^2, \quad \mathrm{tr}(\overline{\mathbf{Q}}^3) = -\tfrac{1}{36} + \tfrac{1}{4}q^2.$$

Following the same arguments given in Appendix B, we readily derive the surface Landau–de Gennes free energy

$$W_{\mathrm{LdG}} \approx W_{\mathrm{LdG}}^{\mathcal{S}} = \int_{\mathcal{S}}\left(d + \frac{a}{4}q^2 + \frac{c}{8}q^4\right)dA \quad \text{for} \quad \varepsilon \ll 1,$$

where

$$d = h\left[F(A,B,C) + \frac{A}{12} + \frac{B}{108} + \frac{C}{144}\right],$$
$$a = a_0\frac{T - T_c^*}{T_c}, \quad a_0 = hA_0,$$
$$c = h\frac{C}{2}, \quad T_c^* = \left(1 + \frac{B}{3A_0} - \frac{C}{6A_0}\right)T_c.$$

We then obtain a Landau–de Gennes potential with two constants in which the cubic term vanishes. An analogous expression is proposed in Refs. [7,15]. It is worth noting that homogenous states with $q \neq 0$ are allowed only on surfaces with zero Euler-Poincaré chracteristic. In fact, only in this case does it make sense to define a critical temperature that generally depends on the shell curvature. For instance, in the case of a cylindrical shell of radius R, the elastic free energy produces terms proportional to q/R^2 and q^2/R^2 that can be viewed as effective contributions to the Landau–de Gennes potential.

V. CONCLUDING REMARKS

We have deduced the two-dimensional versions of Frank and Landau–de Gennes free energies needed to treat the equilibrium of thin nematic films, coating curved surfaces. These models have been obtained as limiting cases of the respective three-dimensional models. The formalism proposed applies to rigid shells as well as to flexible surfaces with two-dimensional nematic order. Obviously, in the latter case additional energy terms are required to describe the elasticity of the shell. The problem of equilibrium can be framed in the general variational scheme proposed in Ref. [26]. However, the resulting equations for this complex problem are strongly nonlinear and demand a numerical treatment.

Our rigorous procedure predicts the existence of new terms in the free energy, with respect to earlier models. The physical interpretation of these extra terms is widely discussed in Secs. III and IV. The key results of our analysis are as follows:

(1) In the context of the director theory for curved nematic thin films, the twist free energy does not vanish. This free energy, coupled with the term proportional to $c_{\mathbf{n}_s}^2$, expresses the tendency of the molecules to align along the principal direction of the surface with minimal (in modulus) curvature. Thus, the extrinsic geometry of the shell influences the molecular alignment in agreement with the results announced in Ref. [27]. In a forthcoming work, we show how the twist term influences the stability of a nematic on a cylindrical surface.

(2) In the context of Landau–de Gennes theory, we establish a coherent framework to develop a two-dimensional order-tensor theory. As a result, we obtain the coupling term (22). This term has been already proposed in Ref. [15], but it required an additional phenomenological constant in the model. By contrast, since we deduce that the coefficient of this energy is the elastic constant l_1, no further phenomenological constants should be introduced. Finally, we notice that, within the model proposed in Ref. [7], the quadrupolar coupling (22) does not appear.

Our approach offers the twofold advantage of being based on well-established theories and, at same time, to avoid the proliferation of phenomenological coefficients in the free energy expression. Therefore, our models describe in an *economical* and *exhaustive* manner the equilibrium configuration of in-plane curved nematics. Obviously, our procedure can be extended to more complicated models as that proposed in Ref. [24].

We believe that the results outlined in this paper are the basis to study the arrangement of two-dimensional curved nematics. We envisage a series of future studies to establish the influence of external actions (temperature, electric, or magnetic fields), of the shell geometry, and of the material coefficients on the nematic shell texture.

ACKNOWLEDGMENT

The authors thank Stefano Turzi for useful discussions on the topics of this paper. This research has been supported by the Italian Ministry of University and Research Grant No. 200959L72B 004, "Mathematics and Mechanics of Biological Assemblies and Soft Tissues"

APPENDIX A: DERIVATION OF THE SPATIAL GRADIENTS OF ν, $\mathbf{e}_1$, $\mathbf{e}_2$, AND $\mathbf{n}$

Let $\boldsymbol{\varphi} = \boldsymbol{\varphi}(u,v)$ an orthogonal parametrization of $\mathcal{S}$ such that

$$\frac{\boldsymbol{\varphi}_{,u}}{|\boldsymbol{\varphi}_{,u}|} = \mathbf{e}_{1s} \quad \text{and} \quad \frac{\boldsymbol{\varphi}_{,v}}{|\boldsymbol{\varphi}_{,v}|} = \mathbf{e}_{2s}.$$

Then, for any fixed $\xi \in [-h/2,h/2]$, $\boldsymbol{\varphi}_\xi = \boldsymbol{\varphi}(u,v) + \xi\boldsymbol{\nu}_s(u,v)$ is an orthogonal parametrization of $\mathcal{S}_\xi$ such that

$$\boldsymbol{\varphi}_{\xi,u} = (1 - \xi c_{1s})\boldsymbol{\varphi}_{,u} \quad \text{and} \quad \boldsymbol{\varphi}_{\xi,v} = (1 - \xi c_{2s})\boldsymbol{\varphi}_{,v}.$$

As consequences of assumption (2), $\{\mathbf{e}_1,\mathbf{e}_2\}$, with

$$\mathbf{e}_1(p) := \frac{\boldsymbol{\varphi}_{\xi,u}}{|\boldsymbol{\varphi}_{\xi,u}|} = \frac{\boldsymbol{\varphi}_{,u}}{|\boldsymbol{\varphi}_{,u}|} = \mathbf{e}_{1s}(p_{\mathcal{S}}) \quad \forall p \in V, \quad \text{(A1a)}$$
$$\mathbf{e}_2(p) := \frac{\boldsymbol{\varphi}_{\xi,v}}{|\boldsymbol{\varphi}_{\xi,v}|} = \frac{\boldsymbol{\varphi}_{,v}}{|\boldsymbol{\varphi}_{,v}|} = \mathbf{e}_{2s}(p_{\mathcal{S}}) \quad \forall p \in V, \quad \text{(A1b)}$$

is a local orthonormal basis of the space of tangent vectors $\mathfrak{X}(\mathcal{S}_\xi)$, whereas

$$\boldsymbol{\nu}(p) := \frac{\boldsymbol{\varphi}_{\xi,u} \times \boldsymbol{\varphi}_{\xi,v}}{|\boldsymbol{\varphi}_{\xi,u} \times \boldsymbol{\varphi}_{\xi,v}|} = \frac{\boldsymbol{\varphi}_{,u} \times \boldsymbol{\varphi}_{,v}}{|\boldsymbol{\varphi}_{,u} \times \boldsymbol{\varphi}_{,v}|} = \boldsymbol{\nu}_s(p_{\mathcal{S}}) \quad \forall p \in V \quad \text{(A2)}$$

is the unit normal vector field on $\mathcal{S}_\xi$. We now introduce the following quantities:

$$e_\xi = -\boldsymbol{\nu}_{s,u} \cdot \boldsymbol{\varphi}_{\xi,u} = c_{1s}(1 - \xi c_{1s})\boldsymbol{\varphi}_{,u} \cdot \boldsymbol{\varphi}_{,u} = c_{1s}(1 - \xi c_{1s})E,$$
$$f_\xi = -\boldsymbol{\nu}_{s,u} \cdot \boldsymbol{\varphi}_{\xi,v} = 0 = -\boldsymbol{\nu}_{s,v} \cdot \boldsymbol{\varphi}_{\xi,u},$$
$$g_\xi = -\boldsymbol{\nu}_{s,v} \cdot \boldsymbol{\varphi}_{\xi,v} = c_{2s}(1 - \xi c_{2s})\boldsymbol{\varphi}_{,v} \cdot \boldsymbol{\varphi}_{,v} = c_{2s}(1 - \xi c_{2s})G,$$
$$E_\xi = \boldsymbol{\varphi}_{\xi,u} \cdot \boldsymbol{\varphi}_{\xi,u} = (1 - \xi c_{1s})^2\boldsymbol{\varphi}_{,u} \cdot \boldsymbol{\varphi}_{,u} = (1 - \xi c_{1s})^2 E,$$
$$F_\xi = \boldsymbol{\varphi}_{\xi,u} \cdot \boldsymbol{\varphi}_{\xi,v} = (1 - \xi c_{1s})(1 - \xi c_{2s})\boldsymbol{\varphi}_{,u} \cdot \boldsymbol{\varphi}_{,v} = 0,$$
$$G_\xi = \boldsymbol{\varphi}_{\xi,v} \cdot \boldsymbol{\varphi}_{\xi,v} = (1 - \xi c_{2s})^2\boldsymbol{\varphi}_{,v} \cdot \boldsymbol{\varphi}_{,v} = (1 - \xi c_{2s})^2 G,$$

where $E = \boldsymbol{\varphi}_{,u} \cdot \boldsymbol{\varphi}_{,u}$ and $G = \boldsymbol{\varphi}_{,v} \cdot \boldsymbol{\varphi}_{,v}$.

We first derive the gradient of $\boldsymbol{\nu}$. From Eq. (A2) it follows that

$$(\nabla\boldsymbol{\nu})\boldsymbol{\nu} = \mathbf{0}, \tag{A3}$$

and, since it is a unit vector field,

$$\boldsymbol{\nu}\cdot(\nabla\boldsymbol{\nu})\mathbf{e}_i = 0 \quad \forall i = 1,2.$$

Moreover, for any fixed ξ, $-\nabla\boldsymbol{\nu}$ restricted to the space of tangent vectors $\mathfrak{X}(\mathcal{S}_\xi)$ represents the extrinsic curvature tensor of $\mathcal{S}_\xi$. Therefore, following do Carmo [16]:

$$\mathbf{e}_1\cdot(\nabla\boldsymbol{\nu})\mathbf{e}_1 = -\frac{f_\xi F_\xi - e_\xi G_\xi}{E_\xi G_\xi - F_\xi^2} = -\frac{c_{1s}}{1-\xi c_{1s}}, \tag{A4a}$$

$$\mathbf{e}_1\cdot(\nabla\boldsymbol{\nu})\mathbf{e}_2 = -\frac{g_\xi F_\xi - f_\xi G_\xi}{E_\xi G_\xi - F_\xi^2} = 0, \tag{A4b}$$

$$\mathbf{e}_2\cdot(\nabla\boldsymbol{\nu})\mathbf{e}_1 = -\frac{e_\xi F_\xi - f_\xi E_\xi}{E_\xi G_\xi - F_\xi^2} = 0, \tag{A4c}$$

$$\mathbf{e}_2\cdot(\nabla\boldsymbol{\nu})\mathbf{e}_2 = -\frac{f_\xi F_\xi - g_\xi E_\xi}{E_\xi G_\xi - F_\xi^2} = -\frac{c_{2s}}{1-\xi c_{2s}}, \tag{A4d}$$

by which we deduce that $\mathbf{e}_1$ and $\mathbf{e}_2$ are the tangent principal directions on $\mathcal{S}_\xi$. Finally, (A3) and (A4) yield (3). Let us now calculate $\nabla\mathbf{e}_i$ $(i = 1,2)$. From Eqs. (A1) and since $\mathbf{e}_i$ $(i = 1,2)$ are unit vector fields, we deduce that

$$(\nabla\mathbf{e}_i)\boldsymbol{\nu} = \mathbf{0} = (\nabla\mathbf{e}_i)^T\mathbf{e}_i \quad \forall i = 1,2. \tag{A5}$$

Next, since $\{\mathbf{e}_1,\mathbf{e}_2,\boldsymbol{\nu}\}$ is a local orthonormal basis

$$(\nabla\mathbf{e}_i)^T\mathbf{e}_j = -(\nabla\mathbf{e}_j)^T\mathbf{e}_i \quad \forall i,j = 1,2, \quad i \neq j, \tag{A6}$$

$$\boldsymbol{\nu}\cdot(\nabla\mathbf{e}_i)\mathbf{e}_j = -\mathbf{e}_j\cdot(\nabla\boldsymbol{\nu})^T\mathbf{e}_i = \delta_{ij}\frac{c_i}{1-\xi c_i} \quad \forall i,j = 1,2, \tag{A7}$$

where δ_{ij} denotes the Kronecker symbol. By means of Eq. (A6),

$$\mathbf{e}_2\cdot(\nabla\mathbf{e}_1)\mathbf{e}_1 = -\mathbf{e}_1\cdot(\nabla\mathbf{e}_2)\mathbf{e}_1 = \kappa_1(\xi), \tag{A8a}$$

$$\mathbf{e}_2\cdot(\nabla\mathbf{e}_1)\mathbf{e}_2 = -\mathbf{e}_1\cdot(\nabla\mathbf{e}_2)\mathbf{e}_2 = \kappa_2(\xi), \tag{A8b}$$

where $\kappa_1(\xi)$ and $\kappa_2(\xi)$ are the geodesic curvatures of the lines of curvature on $\mathcal{S}_\xi$. Hence, by following Ref. [16] and since the surface gradient of a scalar-valued function f defined in a neighborhood of $\mathcal{S}$ may be written as

$$\nabla_s f = \frac{f_{,u}}{\sqrt{E}}\mathbf{e}_{1s} + \frac{f_{,v}}{\sqrt{G}}\mathbf{e}_{2s}, \tag{A9}$$

the geodesic curvatures of the lines of curvature on $\mathcal{S}_\xi$ are found to be

$$\begin{aligned}\kappa_1(\xi) &= -\frac{E_{\xi,v}}{2E_\xi\sqrt{G_\xi}} = -\frac{E_{,v}}{2(1-\xi c_{2s})E\sqrt{G}} + \frac{\xi c_{1,v}}{(1-\xi c_{1s})(1-\xi c_{2s})\sqrt{G}} \\ &= \frac{\kappa_{1s}}{1-\xi c_{2s}} + \frac{\xi\nabla_s c_{1s}\cdot\mathbf{e}_{2s}}{(1-\xi c_{1s})(1-\xi c_{2s})},\end{aligned} \tag{A10a}$$

$$\begin{aligned}\kappa_2(\xi) &= \frac{G_{\xi,u}}{2G_\xi\sqrt{E_\xi}} = \frac{G_{,u}}{2(1-\xi c_{1s})G\sqrt{E}} - \frac{\xi c_{2,u}}{(1-\xi c_{1s})(1-\xi c_{2s})\sqrt{E}} \\ &= \frac{\kappa_{2s}}{1-\xi c_{1s}} - \frac{\xi\nabla_s c_{2s}\cdot\mathbf{e}_{1s}}{(1-\xi c_{1s})(1-\xi c_{2s})},\end{aligned} \tag{A10b}$$

where

$$\kappa_{1s} = -\frac{E_{,v}}{2E\sqrt{G}} \quad \text{and} \quad \kappa_{2s} = \frac{G_{,u}}{2G\sqrt{E}}$$

are the geodesic curvatures of the lines of curvature on $\mathcal{S}$. Therefore, (A5)–(A10) give (4) and (5).

We are now in position to derive the gradient of the director field $\mathbf{n}$. Since $\mathbf{n}$ is a unit vector field that does not vary with ξ and is pointwise orthogonal to $\boldsymbol{\nu}$, we get

$$(\nabla\mathbf{n})\boldsymbol{\nu} = \mathbf{0} = (\nabla\mathbf{n})^T\mathbf{n}. \tag{A11}$$

Next, we introduce the angle α that $\mathbf{n}$ form with $\mathbf{e}_1$ so that we may write

$$\mathbf{n} = \cos\alpha\mathbf{e}_1 + \sin\alpha\mathbf{e}_2, \tag{A12a}$$

$$\mathbf{t} = -\sin\alpha\mathbf{e}_1 + \cos\alpha\mathbf{e}_2, \tag{A12b}$$

and

$$\nabla\mathbf{n} = -\sin\alpha\mathbf{e}_1\otimes\nabla\alpha + \cos\alpha\nabla\mathbf{e}_1 + \cos\alpha\mathbf{e}_2\otimes\nabla\alpha + \sin\alpha\nabla\mathbf{e}_2. \tag{A13}$$

Since $\mathbf{n}$ and $\mathbf{e}_1$ does not depend on ξ, the scalar field α also satisfies the equality $\alpha(p) = \alpha(p_S)$ for all $p \in V$. Therefore, in view of Eq. (A9) the spatial gradient of the scalar field α is

$$\begin{aligned}\nabla\alpha &= \frac{\alpha_{,u}}{(1-\xi c_{1s})\sqrt{E}}\mathbf{e}_1 + \frac{\alpha_{,v}}{(1-\xi c_{2s})\sqrt{G}}\mathbf{e}_2 \\ &= \frac{\nabla_s\alpha\cdot\mathbf{e}_{1s}}{1-\xi c_{1s}}\mathbf{e}_1 + \frac{\nabla_s\alpha\cdot\mathbf{e}_{2s}}{1-\xi c_{2s}}\mathbf{e}_2.\end{aligned}$$

Thus,

$$\boldsymbol{\nu}\cdot(\nabla\mathbf{n})\mathbf{n} = -\mathbf{n}\cdot(\nabla\boldsymbol{\nu})\mathbf{n} = \frac{c_{1s}\cos^2\alpha + c_{2s}\sin^2\alpha - \xi c_{1s}c_{2s}}{(1-\xi c_{1s})(1-\xi c_{2s})} = \frac{c_{\mathbf{n}_s} - \xi K}{1-2\xi H+\xi^2 K}, \tag{A14a}$$

$$\boldsymbol{\nu}\cdot(\nabla\mathbf{n})\mathbf{t} = -\mathbf{n}\cdot(\nabla\boldsymbol{\nu})\mathbf{t} = \frac{(c_{2s}-c_{1s})\sin\alpha\cos\alpha}{(1-\xi c_{1s})(1-\xi c_{2s})} = -\frac{\tau_{\mathbf{n}_s}}{1-2\xi H+\xi^2 K}, \tag{A14b}$$

$$\begin{aligned}\mathbf{t}\cdot(\nabla\mathbf{n})\mathbf{n} = {}& \frac{(\nabla_s\alpha\cdot\mathbf{e}_{1s})\cos\alpha + (\nabla_s\alpha\cdot\mathbf{e}_{2s})\sin\alpha + \kappa_{1s}\cos\alpha + \kappa_{2s}\sin\alpha}{(1-\xi c_{1s})(1-\xi c_{2s})} \\ & - \xi\frac{c_{1s}\kappa_{1s}\cos\alpha + c_{2s}\kappa_{2s}\sin\alpha + \nabla_s c_{2s}\cdot\mathbf{e}_{1s}\sin\alpha - \nabla_s c_{1s}\cdot\mathbf{e}_{2s}\cos\alpha}{(1-\xi c_{1s})(1-\xi c_{2s})} - \xi\frac{c_{2s}\cos\alpha\nabla_s\alpha\cdot\mathbf{e}_{1s} + c_{1s}\sin\alpha\nabla_s\alpha\cdot\mathbf{e}_{2s}}{(1-\xi c_{1s})(1-\xi c_{2s})}\end{aligned}$$

$$= \frac{\nabla_s\alpha\cdot\mathbf{n}_s + \kappa_{1s}\cos\alpha + \kappa_{2s}\sin\alpha - \xi\,\mathrm{div}_s(c_{2s}\sin\alpha\mathbf{e}_{1s} - c_{1s}\cos\alpha\mathbf{e}_{2s})}{1-2H\xi+K\xi^2} = \frac{\kappa_{\mathbf{n}_s} - \xi\boldsymbol{\nu}_s\cdot\mathrm{curl}_s(\mathbf{L}\mathbf{n}_s)}{1-2H\xi+K\xi^2}, \tag{A14c}$$

$$\mathbf{t}\cdot(\nabla\mathbf{n})\mathbf{t} = \frac{-(\nabla_s\alpha\cdot\mathbf{e}_{1s})\sin\alpha + (\nabla_s\alpha\cdot\mathbf{e}_{2s})\cos\alpha - \kappa_{1s}\sin\alpha + \kappa_{2s}\cos\alpha}{(1-\xi c_{1s})(1-\xi c_{2s})}$$
$$-\xi\frac{-c_{1s}\kappa_{1s}\sin\alpha + c_{2s}\kappa_{2s}\cos\alpha + \nabla_s c_{2s}\cdot\mathbf{e}_{1s}\cos\alpha + \nabla_s c_{1s}\cdot\mathbf{e}_{2s}\sin\alpha}{(1-\xi c_{1s})(1-\xi c_{2s})} + \xi\frac{c_{2s}\sin\alpha\nabla_s\alpha\cdot\mathbf{e}_{1s} - c_{1s}\cos\alpha\nabla_s\alpha\cdot\mathbf{e}_{2s}}{(1-\xi c_{1s})(1-\xi c_{2s})}$$
$$= \frac{\nabla_s\alpha\cdot\mathbf{t}_s - \kappa_{1s}\sin\alpha + \kappa_{2s}\cos\alpha - \xi\,\mathrm{div}_s(c_{2s}\cos\alpha\mathbf{e}_{1s} + c_{1s}\sin\alpha\mathbf{e}_{2s})}{1-2H\xi+K\xi^2} = \frac{\kappa_{\mathbf{t}_s} - \xi\boldsymbol{\nu}_s\cdot\mathrm{curl}_s(\mathbf{L}\mathbf{t}_s)}{1-2H\xi+K\xi^2}, \tag{A14d}$$

where $\mathbf{n}_s = \cos\alpha\mathbf{e}_{1s} + \sin\alpha\mathbf{e}_{2s}$ and $\mathbf{t}_s = \boldsymbol{\nu}_s\times\mathbf{n}_s$ are the restrictions of $\mathbf{n}$ and $\mathbf{t}$ on $\mathcal{S}$, respectively, and $\mathbf{L} = c_{1s}\mathbf{e}_{1s}\otimes\mathbf{e}_{1s} + c_{2s}\mathbf{e}_{2s}\otimes\mathbf{e}_{2s}$ is the extrinsic curvature tensor on $\mathcal{S}$. The quantities

$$c_{\mathbf{n}_s} = c_{1s}\cos^2\alpha + c_{2s}\sin^2\alpha, \tag{A15a}$$
$$c_{\mathbf{t}_s} = c_{1s}\sin^2\alpha + c_{2s}\cos^2\alpha \tag{A15b}$$

are the normal curvatures of the flux lines of $\mathbf{n}_s$ and $\mathbf{t}_s$, respectively, whereas

$$\tau_{\mathbf{n}_s} = (c_{1s} - c_{2s})\sin\alpha\cos\alpha$$

is the geodesic torsion of the flux lines of $\mathbf{n}_s$. In deriving (A14c) and (A14d) we have made use of the Lioville's formula (see Ref. [16], p. 253) for the calculation of the geodesic curvatures $\kappa_{\mathbf{n}_s}$ and $\kappa_{\mathbf{t}_s}$, i.e.,

$$\kappa_{\mathbf{n}_s} = \nabla_s\alpha\cdot\mathbf{n}_s + \kappa_{1s}\cos\alpha + \kappa_{2s}\sin\alpha, \quad \kappa_{\mathbf{t}_s} = \nabla_s\alpha\cdot\mathbf{t}_s - \kappa_{1s}\sin\alpha + \kappa_{2s}\cos\alpha,$$

and have employed the identity

$$\mathrm{div}_s(\boldsymbol{\nu}_s\times\mathbf{u}) = -\boldsymbol{\nu}_s\cdot\mathrm{curl}_s\mathbf{u} \tag{A16}$$

that holds true for any smooth field $\mathbf{u}$ defined on $\mathcal{S}$. We may then conclude that (A11)–(A14) yield (6).

APPENDIX B: DERIVATION OF W^S_{OZF} AND W^S_{el}

In this section we derive the approximations of the energies (10) and (16) that are valid for a homogeneous nematic whenever $\varepsilon \ll 1$.

Proposition 1. Let $\mathbf{n}$ and q be smooth fields defined on V. Assume $\mathbf{n}$ to be a unit vector field such that

$$\mathbf{n}(p)\cdot\boldsymbol{\nu}(p) = 0 \quad \forall p\in V \quad \text{and} \quad \mathbf{n}[p_{\mathcal{S}} + \xi\boldsymbol{\nu}_s(p_{\mathcal{S}})] = \mathbf{n}(p_{\mathcal{S}}) \quad \forall p_{\mathcal{S}}\in\mathcal{S}, \quad \forall\xi\in[-h/2,h/2],$$

and q a scalar-valued field such that

$$q[p_{\mathcal{S}} + \xi\boldsymbol{\nu}_s(p_{\mathcal{S}})] = q(p_{\mathcal{S}})\in[-1,1] \quad \forall p_{\mathcal{S}}\in\mathcal{S}, \quad \forall\xi\in[-h/2,h/2].$$

Then, denoting by $\mathrm{vol}(V)$ the volume of V,

$$\lim_{\varepsilon\to0}\int_V\frac{\iota_1}{\mathrm{vol}(V)}dV = \int_{\mathcal{S}}\frac{q^2[(\mathrm{div}_s\mathbf{n}_s)^2 + |\mathbf{n}_s\times\mathrm{curl}_s\mathbf{n}_s|^2 + (\mathrm{curl}_s\mathbf{n}_s\cdot\mathbf{n}_s)^2]}{\mathrm{area}(\mathcal{S})}dA$$
$$+\int_{\mathcal{S}}\frac{\frac{|\nabla_s q|^2}{2} + 2(1-q)H\big[(1-q)H + 2qc_{\mathbf{n}_s}\big] - (1-q^2)K}{\mathrm{area}(\mathcal{S})}dA, \tag{B1a}$$

$$\lim_{\varepsilon\to0}\int_V\frac{\iota_2}{\mathrm{vol}(V)}dV = \int_{\mathcal{S}}\frac{q^2[(\mathrm{div}_s\mathbf{n}_s)^2 + |\mathbf{n}_s\times\mathrm{curl}_s\mathbf{n}_s|^2]}{\mathrm{area}(\mathcal{S})}dA$$
$$+\int_{\mathcal{S}}\frac{\frac{|\nabla_s q|^2}{4} - q\nabla_s q\cdot\big[(\mathrm{curl}_s\mathbf{n}_s\cdot\boldsymbol{\nu}_s)\mathbf{t}_s - (\mathrm{div}_s\mathbf{n}_s)\mathbf{n}_s\big] + (1-q)H[(1-q)H + 2qc_{\mathbf{n}_s}]}{\mathrm{area}(\mathcal{S})}dA, \tag{B1b}$$

$$\lim_{\varepsilon\to0}\int_V\frac{\iota_2-\iota_3}{\mathrm{vol}(V)}dV = \int_{\mathcal{S}}\frac{2q\nabla_s q\cdot[(\mathrm{curl}_s\mathbf{n}_s\cdot\boldsymbol{\nu}_s)\mathbf{t}_s - (\mathrm{div}_s\mathbf{n}_s)\mathbf{n}_s]}{\mathrm{area}(\mathcal{S})}dA - \int_{\mathcal{S}}\frac{(1-q^2)}{2\mathrm{area}(\mathcal{S})}A. \tag{B1c}$$

Proof. We observe that

$$\mathrm{vol}(V) = h\left[\mathrm{area}(\mathcal{S}) + \frac{h^2}{12}\int_{\mathcal{S}}A\right]. \tag{B2}$$

With the aid of Eq. (7),

$$\int_V \frac{q^2(\mathrm{div}\mathbf{n})^2}{\mathrm{vol}(V)}\,dV = \int_{-h/2}^{h/2} d\xi \int_{\mathcal{S}_\xi} \frac{q^2\left[\kappa_{\mathbf{t}_s} - \xi \boldsymbol{\nu}_s \cdot \mathrm{curl}_s(\mathbf{L}\mathbf{t}_s)\right]^2}{J_\xi^2 \mathrm{vol}(V)}\,dA = \int_{-h/2}^{h/2} d\xi \int_{\mathcal{S}} \frac{q^2\left[\kappa_{\mathbf{t}_s} - \xi \boldsymbol{\nu}_s \cdot \mathrm{curl}_s(\mathbf{L}\mathbf{t}_s)\right]^2}{J_\xi \mathrm{vol}(V)}\,dA = \int_{\mathcal{S}} \left\{ \int_{-h/2}^{h/2} \frac{q^2\left[\kappa_{\mathbf{t}_s} - \xi \boldsymbol{\nu}_s \cdot \mathrm{curl}_s(\mathbf{L}\mathbf{t}_s)\right]^2}{J_\xi \mathrm{vol}(V)} d\xi \right\} dA. \quad \text{(B3)}$$

Since q, $\kappa_{\mathbf{t}_s}$, and $\boldsymbol{\nu}_s \cdot \mathrm{curl}_s(\mathbf{L}\mathbf{t}_s)$ do not depend on ξ, by means of Eq. (B2) we deduce that

$$\int_{-h/2}^{h/2} \frac{q^2\left[\kappa_{\mathbf{t}_s} - \xi \boldsymbol{\nu}_s \cdot \mathrm{curl}_s(\mathbf{L}\mathbf{t}_s)\right]^2}{J_\xi h\left[\mathrm{area}(\mathcal{S}) + \frac{h^2}{12}\int_{\mathcal{S}} A\right]} d\xi \to \frac{q^2\kappa_{\mathbf{t}_s}^2}{\mathrm{area}(\mathcal{S})}$$

uniformly in $\mathcal{S}$ as $\varepsilon \to 0$. Therefore, recalling $(9)_1$,

$$\lim_{\varepsilon\to 0} \int_V \frac{q^2(\mathrm{div}\mathbf{n})^2}{\mathrm{vol}(V)} dV = \int_{\mathcal{S}} \frac{q^2(\mathrm{div}_s \mathbf{n}_s)^2}{\mathrm{area}(\mathcal{S})} dA. \quad \text{(B4)}$$

We now use Eq. (8) to obtain

$$\int_V \frac{q^2(\mathrm{curl}\mathbf{n}\cdot\mathbf{n})^2}{\mathrm{vol}(V)} dV = \int_{\mathcal{S}} dA \int_{-h/2}^{h/2} \frac{q^2\tau_{\mathbf{n}_s}^2}{J_\xi \mathrm{vol}(V)} d\xi$$

and

$$\int_V \frac{q^2|\mathbf{n}\times\mathrm{curl}\mathbf{n}|^2}{\mathrm{vol}(V)} dV = \int_{\mathcal{S}} dA \int_{-h/2}^{h/2} \frac{q^2\left(c_{\mathbf{n}_s} - K\xi\right)^2 + \left[\kappa_{\mathbf{n}_s} - \xi \boldsymbol{\nu}_s \cdot \mathrm{curl}_s(\mathbf{L}\mathbf{n}_s)\right]^2}{J_\xi \mathrm{vol}(V)} d\xi. \quad \text{(B5)}$$

Considering that q, $c_{\mathbf{n}_s}$, $\tau_{\mathbf{n}_s}$, $\kappa_{\mathbf{n}_s}$, and $\boldsymbol{\nu}_s \cdot \mathrm{curl}_s(\mathbf{L}\mathbf{n}_s)$ do not depend on ξ, by means of Eq. (B2), we have

$$\int_{-h/2}^{h/2} \frac{q^2\tau_{\mathbf{n}_s}^2}{J_\xi h\left[\mathrm{area}(\mathcal{S}) + \frac{h^2}{12}\int_{\mathcal{S}} A\right]} d\xi \to \frac{q^2\tau_{\mathbf{n}_s}^2}{\mathrm{area}(\mathcal{S})}$$

uniformly in $\mathcal{S}$ as $\varepsilon \to 0$ and

$$\int_{-h/2}^{h/2} q^2 \frac{\left(c_{\mathbf{n}_s} - K\xi\right)^2 + \left[\kappa_{\mathbf{n}_s} - \xi \boldsymbol{\nu}_s \cdot \mathrm{curl}_s(\mathbf{L}\mathbf{n}_s)\right]^2}{J_\xi h\left[\mathrm{area}(\mathcal{S}) + \frac{h^2}{12}\int_{\mathcal{S}} A\right]} d\xi \to \frac{q^2\left(c_{\mathbf{n}_s}^2 + \kappa_{\mathbf{n}_s}^2\right)}{\mathrm{area}(\mathcal{S})} \quad \text{(B6)}$$

uniformly in $\mathcal{S}$ as $\varepsilon \to 0$. Thus, from Eq. (9) we deduce that

$$\lim_{\varepsilon\to 0} \int_V \frac{q^2(\mathbf{n}\cdot\mathrm{curl}\mathbf{n})^2}{\mathrm{vol}(V)} dV = \int_{\mathcal{S}} \frac{q^2(\mathbf{n}_s\cdot\mathrm{curl}_s\mathbf{n}_s)^2}{\mathrm{area}(\mathcal{S})} dA \quad \text{(B7)}$$

and

$$\lim_{\varepsilon\to 0} \int_V \frac{q^2|\mathbf{n}\times\mathrm{curl}\mathbf{n}|^2}{\mathrm{vol}(V)} dV = \int_{\mathcal{S}} \frac{q^2|\mathbf{n}_s\times\mathrm{curl}_s\mathbf{n}_s|^2}{\mathrm{area}(\mathcal{S})} dA. \quad \text{(B8)}$$

By following the same arguments which lead to Eqs. (B4)–(B8) and by taking into account that

$$\nabla q = \frac{\nabla_s q\cdot\mathbf{e}_{1s}}{1-\xi c_{1s}}\mathbf{e}_1 + \frac{\nabla_s q\cdot\mathbf{e}_{2s}}{1-\xi c_{2s}}\mathbf{e}_2,$$

one can easily prove that

$$\lim_{\varepsilon\to 0} \int_V \frac{|\nabla q|^2}{\mathrm{vol}(V)} dV = \int_{\mathcal{S}} \frac{|\nabla_s q|^2}{\mathrm{area}(\mathcal{S})} dA, \quad \text{(B9a)}$$

$$\lim_{\varepsilon\to 0} \int_V \frac{(1-q)(H-K\xi)}{J_\xi^2 \mathrm{vol}(V)}\left[(1-q)H + 2qc_{\mathbf{n}_s} - (1+q)K\xi\right] = \int_{\mathcal{S}} \frac{(1-q)H}{\mathrm{area}(\mathcal{S})}\left[(1-q)H + 2qc_{\mathbf{n}_s}\right] dA, \quad \text{(B9b)}$$

$$\lim_{\varepsilon\to 0} \int_V \frac{(1-q^2)K}{J_\xi^2 \mathrm{vol}(V)} dV = \int_{\mathcal{S}} \frac{(1-q^2)K}{\mathrm{area}(\mathcal{S})} dA, \quad \text{(B9c)}$$

$$\lim_{\varepsilon\to 0} \int_V \frac{q\nabla q\cdot[(\nabla\mathbf{n})\mathbf{n} - (\mathrm{div}\mathbf{n})\mathbf{n}]}{\mathrm{vol}(V)} dV = \int_{\mathcal{S}} \frac{q\nabla_s q\cdot[(\mathrm{curl}_s\mathbf{n}_s\cdot\boldsymbol{\nu}_s)\mathbf{t}_s - (\mathrm{div}_s\mathbf{n}_s)\mathbf{n}_s]}{\mathrm{area}(\mathcal{S})} dA. \quad \text{(B9d)}$$

Now, let us assume now that $\mathcal{S}$ is a regular surface whose boundary $\partial\mathcal{S}$ is a regular curve, and let $\boldsymbol{\tau}$ be the tangent unit vector field to $\partial\mathcal{S}$. Then the normal unit vector field to the surface

$$\mathcal{S}_l := \{p_{\partial\mathcal{S}} + \xi\boldsymbol{\nu}_s(p_{\partial\mathcal{S}}) : p_{\partial\mathcal{S}} \in \partial\mathcal{S}, \xi \in [-h/2, h/2]\}$$

is

$$\mathbf{N} = \frac{(\boldsymbol{\tau} - \xi\mathbf{L}\boldsymbol{\tau})\times\boldsymbol{\nu}}{|(\boldsymbol{\tau} - \xi\mathbf{L}\boldsymbol{\tau})\times\boldsymbol{\nu}|}.$$

Therefore, by means of the divergence theorem we deduce that

$$\begin{aligned}
&\int_V \mathrm{div}\left\{J_\xi^{-1}(1-q)\left[(1-q)H + 2qc_{\mathbf{n}_s} - (1+q)K\xi\right]\boldsymbol{\nu}\right\} dV \\
&= \int_{\mathcal{S}_{h/2}} (1-q)J_{h/2}^{-1}\left[(1-q)H + 2qc_{\mathbf{n}_s} - (1+q)K\frac{h}{2}\right] dA \\
&\quad - \int_{\mathcal{S}_{-h/2}} (1-q)J_{-h/2}^{-1}\left[(1-q)H + 2qc_{\mathbf{n}_s}\right. \\
&\quad \left. + (1+q)K\frac{h}{2}\right] dA + \int_{\mathcal{S}_l} J_\xi^{-1}(1-q)[(1-q)H \\
&\quad + 2qc_{\mathbf{n}_s} - (1+q)K\xi]\boldsymbol{\nu}\cdot\mathbf{N}\,dA \\
&= \int_{\mathcal{S}} (1-q)\left[(1-q)H + 2qc_{\mathbf{n}_s} - (1+q)K\frac{h}{2}\right] dA \\
&\quad - \int_{\mathcal{S}} (1-q)\left[(1-q)H + 2qc_{\mathbf{n}_s} + (1+q)K\frac{h}{2}\right] dA \\
&= -\int_{\mathcal{S}} h(1-q^2)A. \quad \text{(B10)}
\end{aligned}$$

By means of Eq. (B2) we may conclude that

$$\lim_{\varepsilon\to 0}\int_V \mathrm{div}\left\{\frac{(1-q)}{J_\xi \mathrm{vol}(V)}\left[(1-q)H+2qc_{\mathbf{n}_s}-(1+q)K\xi\right]\boldsymbol{\nu}\right\}dV$$
$$=-\lim_{\varepsilon\to 0}\int_{\mathcal{S}}\frac{(1-q^2)K}{\mathrm{area}(\mathcal{S})+\frac{h^2}{12}\int_{\mathcal{S}}A}\,dA$$
$$=-\int_{\mathcal{S}}\frac{(1-q^2)K}{\backslash,\mathrm{area}(\mathcal{S})}\,dA. \tag{B11}$$

We arrive at (B11) also whenever $\mathcal{S}$ is a geometrically closed surface, i.e., $\partial\mathcal{S}=\emptyset$.

Finally, Eqs. (B1) immediately follows from Eqs. (20) and (B4)–(B11).

From Eq. (B2) it follows that

$$\lim_{\varepsilon\to 0}\mathrm{vol}(V)=h\,\mathrm{area}(\mathcal{S}). \tag{B12}$$

As an immediate consequence of Proposition 1 and (B12), for $\varepsilon\ll 1$ we have

$$W_{\mathrm{el}}=\mathrm{vol}(V)\int_V\frac{L_1\iota_1+L_2\iota_2+L_{24}(\iota_2-\iota_3)}{\mathrm{vol}(V)}dV\approx W_{\mathrm{el}}^{\mathcal{S}}, \tag{B13}$$

with $W_{\mathrm{el}}^{\mathcal{S}}$ as in Eq. (21). Finally, with the aid of the following identities:

$$\iota_{1s}=2q^2\left(c_{\mathbf{n}_s}^2+\tau_{\mathbf{n}_s}^2+\kappa_{\mathbf{n}_s}^2+\kappa_{\mathbf{t}_s}^2\right)+\tfrac{1}{2}|\nabla_s q|^2+2q(1-q)$$
$$\times\left(c_{\mathbf{n}_s}^2+\tau_{\mathbf{n}_s}^2\right)+(1-q)^2(2H^2-K), \tag{B14a}$$
$$\iota_{2s}=\iota_{3s}+2q\nabla_s q\cdot\left(\kappa_{\mathbf{n}_s}\mathbf{t}_s-\kappa_{\mathbf{t}_s}\mathbf{n}_s\right)-\tfrac{1}{2}(1-q^2)K, \tag{B14b}$$
$$\iota_{3s}=q^2\left(\kappa_{\mathbf{n}_s}^2+\kappa_{\mathbf{t}_s}^2\right)+\tfrac{1}{4}|\nabla_s q|^2+(\mathbf{L}\cdot\mathbf{M}_s)^2$$
$$-q\nabla_s q\cdot\left(\kappa_{\mathbf{n}_s}\mathbf{t}_s-\kappa_{\mathbf{t}_s}\mathbf{n}_s\right), \tag{B14c}$$

surface free energy (21) can be recast in the form (24).

On taking $q\equiv 1$ in Eqs. (B4)–(B8) we have the following.

Proposition 2. Let $\mathbf{n}$ be a smooth unit vector field defined on V such that

$$\mathbf{n}(p)\cdot\boldsymbol{\nu}(p)=0\quad\forall p\in V$$

and

$$\mathbf{n}(p_{\mathcal{S}}+\xi\boldsymbol{\nu}_s)=\mathbf{n}(p_{\mathcal{S}})\quad\forall p_{\mathcal{S}}\in\mathcal{S},\quad\forall\xi\in[-h/2,h/2].$$

Then

$$\lim_{\varepsilon\to 0}\int_V\frac{(\mathrm{div}\mathbf{n})^2}{\mathrm{vol}(V)}dV=\int_{\mathcal{S}}\frac{(\mathrm{div}_s\mathbf{n}_s)^2}{\mathrm{area}(\mathcal{S})}dA,$$
$$\lim_{\varepsilon\to 0}\int_V\frac{(\mathbf{n}\cdot\mathrm{curl}\mathbf{n})^2}{\mathrm{vol}(V)}dV=\int_{\mathcal{S}}\frac{(\mathbf{n}_s\cdot\mathrm{curl}_s\mathbf{n}_s)^2}{\mathrm{area}(\mathcal{S})}dA,$$
$$\lim_{\varepsilon\to 0}\int_V\frac{|\mathbf{n}\times\mathrm{curl}\mathbf{n}|^2}{\mathrm{vol}(V)}dV=\int_{\mathcal{S}}\frac{|\mathbf{n}_s\times\mathrm{curl}_s\mathbf{n}_s|^2}{\mathrm{area}(\mathcal{S})}dA.$$

Therefore, from Eq. (13), Proposition 2 and (B12), it follows that

$$W_{\mathrm{OZF}}=\mathrm{vol}(V)$$
$$\times\int_V\frac{K_1(\mathrm{div}\mathbf{n})^2+K_2(\mathbf{n}\cdot\mathrm{curl}\mathbf{n})^2+K_3|\mathbf{n}\times\mathrm{curl}\mathbf{n}|^2}{\mathrm{vol}(V)}dV$$
$$\approx W_{\mathrm{OZF}}^{\mathcal{S}}$$

for $\varepsilon\ll 1$, with $W_{\mathrm{OZF}}^{\mathcal{S}}$ as in Eq. (14).

APPENDIX C: GEOMETRICAL IDENTITIES

Let us consider the orthogonal parametrization of $\mathcal{S}$ introduced in Appendix A and set

$$x_1=u,\quad x_2=v,$$
$$\mathbf{g}_1=\boldsymbol{\varphi}_{,u}=\sqrt{E}\mathbf{e}_{1s},\quad\mathbf{g}_2=\boldsymbol{\varphi}_{,v}=\sqrt{G}\mathbf{e}_{2s}.$$

The metric tensor induced on $\mathcal{S}$ by the Euclidean metric tensor, written with respect to the system of local coordinates (x_1,x_2), is

$$g=Edx^1\otimes dx^1+Gdx^2\otimes dx^2.$$

The Levi-Cività connection associated with the metric g is defined by the Christoffel symbols

$$\Gamma_{11}^1=\frac{E_{,u}}{2E},\quad\Gamma_{11}^2=-\frac{E_{,v}}{2G}=\frac{E}{\sqrt{G}}\kappa_{1s}, \tag{C1a}$$
$$\Gamma_{12}^1=\Gamma_{21}^1=\frac{E_{,v}}{2E}=-\sqrt{G}\kappa_{1s}, \tag{C1b}$$
$$\Gamma_{12}^2=\Gamma_{21}^2=\frac{G_{,u}}{2G}=\sqrt{E}\kappa_{2s}, \tag{C1c}$$
$$\Gamma_{22}^1=-\frac{G_{,u}}{2E}=-\frac{G}{\sqrt{E}}\kappa_{2s},\quad\Gamma_{22}^2=\frac{G_{,v}}{2G}. \tag{C1d}$$

Then, the (0,4) curvature tensor of $\mathcal{S}$ has components

$$R_{\beta\gamma\delta\rho}=g_{\rho\mu}\left(\frac{\partial\Gamma_{\beta\delta}^{\mu}}{\partial x_\gamma}-\frac{\partial\Gamma_{\gamma\delta}^{\mu}}{\partial x_\beta}+\Gamma_{\beta\delta}^{\lambda}\Gamma_{\gamma\lambda}^{\mu}-\Gamma_{\beta\lambda}^{\mu}\Gamma_{\gamma\delta}^{\lambda}\right)$$
$$=-EG\left(\nabla_s\kappa_{2s}\cdot\mathbf{e}_{1s}-\nabla_s\kappa_{1s}\cdot\mathbf{e}_{2s}+\kappa_{1s}^2+\kappa_{2s}^2\right)\epsilon_{\beta\gamma}\epsilon_{\delta\rho}$$
$$=EG\,(\boldsymbol{\nu}_s\cdot\mathrm{curl}_s\boldsymbol{\omega})\epsilon_{\beta\gamma}\epsilon_{\delta\rho}\quad(\beta,\gamma,\delta,\rho,\mu,\lambda=1,2), \tag{C2}$$

where $\epsilon_{\beta\gamma}=\delta_{1\beta}\delta_{2\gamma}-\delta_{1\gamma}\delta_{2\beta}$ is the antisymmetric symbol and $\boldsymbol{\omega}=-(\kappa_{1s}\mathbf{e}_{1s}+\kappa_{2s}\mathbf{e}_{2s})$ is the vector that parameterizes the spin connection $\Omega_{\beta\gamma\delta}$ (see Ref. [23]), that is,

$$\Omega_{\beta\gamma\delta}=\mathbf{e}_\gamma\cdot(D\mathbf{e}_\delta)\mathbf{e}_\beta=\omega_\beta\epsilon_{\gamma\delta}\quad(\beta,\gamma,\delta=1,2),$$

where $D=\mathbf{P}\nabla_s$ is the usual covariant derivative (see Ref. [17]). It is well known that the Gaussian curvature of a surface equals the scalar curvature (see Ref. [28]). Therefore

$$K=\frac{1}{2}\sum_{\beta\neq\gamma}\frac{R_{\beta\gamma\beta\gamma}}{\det g}=\boldsymbol{\nu}_s\cdot\mathrm{curl}_s\boldsymbol{\omega}. \tag{C3}$$

By means of Eq. (C3) we can prove identity (23). We first observe that $\kappa_{\mathbf{n}_s}\mathbf{n}_s+\kappa_{\mathbf{t}_s}\mathbf{t}_s=\nabla_s\alpha-\boldsymbol{\omega}$, by which $\kappa_{\mathbf{n}_s}\mathbf{t}_s-\kappa_{\mathbf{t}_s}\mathbf{n}_s=\boldsymbol{\nu}_s\times(\nabla_s\alpha-\boldsymbol{\omega})$, with α as in Sec. III. Next, we recall the identity

$$\boldsymbol{\nu}_s\cdot\mathrm{curl}_s(\nabla_s f)=0, \tag{C4}$$

that is valid for any smooth scalar field f defined on $\mathcal{S}$. Then, applying the surface divergence theorem and identities (A16),

(C3) and (C4) lead to

$$\begin{aligned}\int_{\mathcal{S}} q(\nabla_s q)\cdot\left(\kappa_{\mathbf{n}_s}\mathbf{t}-\kappa_{\mathbf{t}_s}\mathbf{n}\right)dA &= \frac{1}{2}\int_{\mathcal{S}}\mathrm{div}_s[q^2\boldsymbol{\nu}_s\times(\nabla_s\alpha-\omega)]\,dA-\frac{1}{2}\int_{\mathcal{S}}q^2\mathrm{div}_s[\boldsymbol{\nu}_s\times(\nabla_s\alpha-\boldsymbol{\omega})]\,dA\\ &= \frac{1}{2}\int_{\partial\mathcal{S}}q^2[\boldsymbol{\nu}_s\times(\nabla_s\alpha-\boldsymbol{\omega})]\cdot\mathbf{k}\,dl+\frac{1}{2}\int_{\mathcal{S}}q^2\boldsymbol{\nu}_s\cdot\mathrm{curl}_s(\nabla_s\alpha-\boldsymbol{\omega})\,dA\\ &= \frac{1}{2}\int_{\partial\mathcal{S}}q^2(\nabla_s\alpha-\boldsymbol{\omega})\cdot d\mathbf{l}-\frac{1}{2}\int_{\mathcal{S}}q^2K\,dA,\end{aligned}\tag{C5}$$

where $\mathbf{k}$ is the outward normal to the boundary $\partial\mathcal{S}$ lying on the tangent plane. Finally, combining (B14b) and (C5) yields

$$\int_{\mathcal{S}}(\iota_{2s}-\iota_{3s})\,dA=\int_{\partial\mathcal{S}}q^2(\nabla_s\alpha-\boldsymbol{\omega})\cdot d\mathbf{l}-\int_{\mathcal{S}}\mathrm{tr}\mathbf{M}_s^2K\,dA.$$

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