Liquid crystal model of membrane flexoelectricity

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An interfacial liquid crystal model is formulated and used to derive a membrane shape equation that takes into account pressure, tension, bending, torsion, and flexoelectric forces. Flexoelectricity introduces electric field-induced curvature and is of relevance to the study and characterization of biological membranes. It is shown that flexoelectricity renormalizes the membrane mechanical tension, shear, and bending effects, and hence it offers diverse pathways to manipulate the membrane's shape. The derived electroelastic shape equation provides systematic guidance on how to use electric fields in membrane studies.

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I. INTRODUCTION

Piezoelectric solids are materials that exhibit electroelastic couplings, such that under an imposed electric field the generated stress varies linearly with the imposed field [1,2]. This effect is the basis of a wide range of application of piezoelectric solids in generators, filters, and sensors. Liquid crystals are materials that also exhibit electroelastic couplings, but in this case it is the torque that varies linearly with an imposed electric field [3]. This so-called flexoelectric effect is the basis for a range of phenomena and applications of flexoelectric liquid crystals. A key difference between these two effects is that while in piezoelectrics the imposed electric field produces positional strain, in liquid crystals it produces orientational strains. The effect of the electric field on strain/orientation is known as the converse effect, while the production of an electric field by a positional/orientational strain is known as the direct effect [4]. This paper is restricted to the converse flexoelectric effect observed when subjecting a flexoelectric material to an external electric field [4].

Electroelastic couplings in solids and liquid crystals can be manifested in the bulk and on interfaces. Piezoelectric shells and membranes of elastic solids have been widely studied for their use as wave-propagation media [2]. Likewise, flexoelectricity in fluid membranes have been widely studied for its relevance in biological function. Petrov and co-workers have developed the basic nature, use, and applications of membrane flexoelectricity and demonstrated its relevance to biological function [4–6]. This paper seeks to contribute to the further development of membrane flexoelectric physics by formulating generalized covariant models that lack restrictions from specific geometries and can eventually take into account dissipative dynamics.

Piezoelectricity in solids and flexoelectricity in liquid crystals arise due to the absence of a center of symmetry, and the phenomenological coefficient linking the external field vector to the symmetric distortion tensor is a tensor of third rank [2]. For transversely isotropic surfaces, whose distinguishing direction is surface unit normal $\mathbf{k}$, the only possible material property third-rank tensor, which is linear in $\mathbf{k}$ and symmetric in the last two indices, is $\mathbf{c}=\mathbf{c}^T=c\mathbf{k}\mathbf{I}_s$ [2]. Although both piezoelectricity and flexoelectricity involve a third-rank tensor, flexoelectricity leads to richer phenomena, as shown in what follows, by considering the generated surface stresses $\mathbf{t}$ and their corresponding capillary pressures p (i.e., normal forces to the interface). In transversely isotropic interfaces, the piezoelectric contribution to the electromechanical Helmholtz free energy per unit area $\rho\hat{A}_{\text{piezo}}$ under an external electric field $\mathbf{E}$ ($\mathbf{E}=E^\alpha\mathbf{a}_\alpha+E^n\mathbf{k}$) is [2],

$$\rho\hat{A}_{\text{piezo}}=-c_p^{n\alpha\beta}d_{\alpha\beta}E^n=-c_p a^{\alpha\beta}d_{\alpha\beta}E^n=-\frac{\mathbf{P}_{\text{piezo}}\cdot\mathbf{E}}{\rho}, \quad (1)$$

where the symbol ˆ denotes per unit mass, c_p is the piezoelectric electroelastic coefficient, $d_{\alpha\beta}$ is the symmetric tangential deformation tensor, $a^{\alpha\beta}$ is the reciprocal surface metric tensor, $\mathbf{P}_{\text{piezo}}=c_p(\mathbf{I}_s:\mathbf{d})\,\mathbf{k}$ is the piezoelectric vector, and ρ is the surface density. An external field $\mathbf{E}$ acting on a piezoelectric surface generates a surface stress $\mathbf{t}_{\text{piezo}}$ given by [2],

$$\mathbf{t}_{\text{piezo}}=\frac{\rho\partial\hat{A}_{\text{piezo}}}{\partial\mathbf{d}}=-c_p(\mathbf{k}\cdot\mathbf{E})\mathbf{I}_s, \quad (2)$$

and an $\mathbf{E}$-dependent capillary pressure p_{piezo},

$$p_{\text{piezo}}=-(\nabla\cdot\mathbf{t}_{\text{piezo}})\cdot\mathbf{k}=2c_p(\mathbf{k}\cdot\mathbf{E})H, \quad (3)$$

where $H=\mathbf{I}_s:\mathbf{b}/2$ is the average curvature, and $\mathbf{b}=-\nabla_s\cdot\mathbf{k}$ is the symmetric curvature tensor; $\nabla_s(\cdot)=\mathbf{I}_s\cdot\nabla(\cdot)$ is the surface gradient operator, and $\mathbf{I}_s=\mathbf{I}-\mathbf{k}\mathbf{k}$ is the surface unit tensor. Equations (2) and (3) show that piezoelectricity generates tangential stresses and capillary pressures proportional to the curvature, or in other words, it just renormalizes the interfacial tension effects,

$$\mathbf{t}=\gamma\mathbf{I}_s\rightarrow\mathbf{t}_{\text{piezo}}=[\gamma-c_p(\mathbf{k}\cdot\mathbf{E})]\mathbf{I}_s, \quad (4a)$$

$$p_c=2\gamma H\rightarrow p_{c\text{piezo}}=[2\gamma+2c_p(\mathbf{k}\cdot\mathbf{E})]H, \quad (4b)$$

where γ is the interfacial tension. In fluid membranes, an imposed external electric field $\mathbf{E}$ couples with bending distortions [4–6],

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$$\rho\hat{A}_{\text{flexo}} = -c_{\text{flexo}}^{n\alpha\beta}b_{\alpha\beta}E^n = -c_{\text{flexo}}a^{\alpha\beta}b_{\alpha\beta}E^n$$
$$= -c_{\text{flexo}}2H(\mathbf{k}\cdot\mathbf{E}) = -\mathbf{P}_{\text{flexo}}\cdot\mathbf{E}, \quad (5)$$

where $\rho\hat{A}_{\text{flexo}}$ is the Helmholtz free energy per unit area due to flexoelectricity, $c_{\text{flexo}}^{n\alpha\beta}=c_{\text{flexo}}a^{\alpha\beta}$ is the third-order flexoelectric tensor, c_{flexo} is the flexoelectric coefficient, and $\mathbf{P}_{\text{flexo}}=c_{\text{flexo}}(\mathbf{I}_s:\mathbf{b})\ \mathbf{k}$ is the flexoelectric polarization vector. Typical values of c_{flexo} for dipolar lipid membranes are 10^{-20} C [4]; the convention for the sign of c_{flexo} used here is that when $H>0$, a $c_{\text{flexo}}>0$ means that $\mathbf{P}_{\text{flexo}}$ is along $\mathbf{E}$. Since both unit normal ($\mathbf{k}$) and average curvature (H) enter in the interfacial flexoelectric effect ($\hat{A}_{\text{flexo}}=\hat{A}_{\text{flexo}}(\mathbf{k},H)$), we now have to consider both stress and bending moment contributions. The symmetric flexoelectric bending moment tensor $\mathbf{M}_{\text{flexo}}$, analogous to the piezoelectric stress [Eq. (2)], is

$$\mathbf{M}_{\text{flexo}} = \frac{\rho\partial\hat{A}_{\text{flexo}}}{\partial\mathbf{b}} = -c_{\text{flexo}}(\mathbf{k}\cdot\mathbf{E})\mathbf{I}_s. \quad (6)$$

As shown below, the flexoelectric membrane stress contributions will contain extension, shear, and bending stresses,

$$\mathbf{t}_{\text{flexo}} = \rho\hat{A}_{\text{flexo}}\mathbf{I}_s - \mathbf{M}_{\text{flexo}}\cdot\mathbf{b} - \frac{\delta A_{\text{flexo}}}{\delta\mathbf{k}}\mathbf{k}, \quad (7)$$

where $\delta(A)/\delta\mathbf{k}$ denotes the variational derivative of the Helmholtz free energy A, and $A=\int\rho\hat{A}\ \text{dS}$. Comparing $\mathbf{t}_{\text{flexo}}$ [Eq. (7)] with $\mathbf{t}_{\text{piezo}}$ [Eq. (2)], it is seen that interfacial flexoelectricity leads to a wider range of phenomena. The corresponding flexoelectric capillary pressure $p_{\text{flexo}}=-(\nabla_s\cdot\mathbf{t}_{\text{flexo}})\cdot\mathbf{k}$ due to its dependence on the nondiagonal 2×3 stress tensor $\mathbf{t}_{\text{flexo}}$ will now be a nonlinear function of curvature and its gradients.

$$p_{\text{flexo}} = -\left[\nabla_s\left(\rho\hat{A}_{\text{flexo}}\mathbf{I}_s - \mathbf{M}_{\text{flexo}}\cdot\mathbf{b} - \frac{\delta A_{\text{flexo}}}{\delta\mathbf{k}}\mathbf{k}\right)\right]\cdot\mathbf{k}. \quad (8)$$

Since the capillary pressure is the decisive factor in shape selection [7,8], we conclude from these simple observations that flexoelectricity in transversely anisotropic fluid membranes has the ability to change the surface geometry under the action of external electric fields through extension, shear, and bending stresses, and offer a nontrivial window of opportunity to membrane characterization and functionalization. For experimental measurements and quantitative studies of membrane flexoelectricity, the reader is referred to Petrov [4]. The main motivation of this paper is to develop a covariant membrane shape model that includes the flexoelectric pressure given in Eq. (8). Most of the existing works in membrane flexoelectricity are devoted to specific geometries and no coordinate-free approach based on the liquid crystal model seems to be available.

This paper presents an electroelastic model based on the liquid crystal membrane model [9–11]. Liquid crystals of the nematic type are sometimes referred to as transversely isotropic materials, since the average molecular orientation of the rodlike molecules singles out the unique direction of the phase. In liquid crystal membranology, the transversely isotropic nature of the membrane is incorporated through the outward unit normal $\mathbf{k}$. In bulk liquid crystal statics [3], the equations of equilibrium are described using the molecular field $\mathbf{h}$, which is the negative of variational derivative of the elastic free-energy density: $\mathbf{h}=-\delta A_{\text{bulk}}/\delta\mathbf{n}$. In fluid membranes, the equations of equilibrium are derived using the interfacial molecular field which is now the negative of the variational derivative of the free energy with respect to the unit normal $\mathbf{h}_{\text{surface}}=-\delta A_{\text{surface}}/\delta\mathbf{k}$. Previous work using this approach was applied to the surfactant-laden liquid-liquid crystal interface, and shown to lead to equations fully compatible with shape equations of membranes and vesicles.

The objective of this paper are (i) to derive a covariant membrane shape equation that includes the flexoelectric effect, using the liquid crystal membranology approach, and (ii) to identify the main mechanisms of electric field driven-shape changes in flexoelectric membranes.

In this initial effort, we assume that the electric field $\mathbf{E}$ is a known constant and that the membrane order parameter is the outward unit normal $\mathbf{k}$; for a discussion on how to asses $\mathbf{E}$, see Ref. [4]. Other models using tensorial order parameters that take into account ordoelectric effects can be formulated using a similar approach. The approach used in this paper extends previous models of liquid crystal surface mechanics [12–25], and builds on previous works on membrane mechanics [26–30] and flexoelectric membranes [4–6,31].

The organization of this paper is as follows. Appendix A presents the thermodynamics of polarized surfaces used in the derivation of the stress tensor needed in this paper. Section II A presents the well-known interfacial force balance equation in terms of the divergence of the membrane stress tensor T_s. Section II B uses the results of Appendix A to reformulate the membrane stress tensor $\mathbf{T}_s$ using the liquid crystal membranology approach; in this model T_s is expressed in terms of the membrane molecular field $\mathbf{h}$ [3], bending moment tensor $\mathbf{M}$ [2], and capillary vector $\mathbb{Q}_{\|}$. Appendix B shows the variational derivation of the complete interfacial stress tensor $\mathbf{T}_s$ discussed in Sec. II B. Section III A expresses the membrane stress tensor $\mathbf{T}_s$ in terms of the capillary vector $\boldsymbol{\Xi}$, which makes the derivation of the shape equation simple and transparent. Section III B uses classical membrane elasticity and flexoelectricity to formulate a shape equation in terms of tension, shear, bending, torsion, and electric-field effects; validation procedures are implemented. Appendix C presents a discussion of boundary conditions relevant to real experiments and derives the integral shape equation. Section IV provides an illustrative example of the application of the integral shape equation to field-induced curvature; validation of the results is implemented by comparison with the experimental and theoretical results of Ref. [4]. Finally, Sec. V gives the conclusions.

II. LIQUID CRYSTAL MEMBRANOLOGY

In this work we consider the isothermal electromechanics of a thermodynamically closed membrane phase separating two fluid phases; the membrane is geometrically open and has an edge C. The model is based on the static limit of the linear momentum balance equation in terms of the membrane stress tensor $\mathbf{T}_s$, and its functional dependence on the bending moment tensor $\mathbf{M}$ [see Eq. (16b) below] and membrane molecular field $\mathbf{h}_{\parallel}$ [see Eq. (17) below].

A. Interfacial stresses and interfacial force balance equation

In this section the basic force balance is introduced [32,33] and the nature of the stress tensors is defined. The 3×3 stress tensors in the bulk phases are denoted by $\mathbf{T}_{b(1)}$, $\mathbf{T}_{b(2)}$ and the 2×3 membrane stress tensor $\mathbf{T}_s$ is given by the sum of a tangential contribution and a bending contribution,

$$\mathbf{T}_s = \mathbf{T}_{s\parallel} + \mathbf{T}_{s\perp}, \tag{9a}$$

$$\mathbf{T}_{s\parallel} = T_s^{\alpha\beta}\mathbf{a}_\alpha \mathbf{a}_\beta, \quad \alpha,\beta = 1,2, \tag{9b}$$

$$\mathbf{T}_{s\perp} = T_s^{\alpha(n)}\mathbf{a}_\alpha \mathbf{k}, \tag{9c}$$

where $\parallel$ denotes the tangential plane, $\perp$ denotes the interface normal direction, and $\mathbf{a}_i$ are covariant surface base vectors.. The 2×2 tangential stress tensor $T_s^{\alpha\beta}$ describes normal-(stretching) and shear stresses, while $T_s^{\alpha(n)}$ is the 2×1 bending stress tensor [7].

The interfacial static force balance equation is the balance between membrane forces and the bulk stress jump [7,8,32,33],

$$\nabla_s \cdot \mathbf{T}_s + \mathbf{k}\cdot[\mathbf{T}_{b(2)} - \mathbf{T}_{b(1)}] = 0. \tag{10}$$

Expressing $\nabla_s . \mathbf{T}_s$ in component form, Eq. (10) becomes [27,28,32,33]

$$(T_{s\ |\alpha}^{\alpha\beta} - T_s^{\alpha(n)} b_\alpha^\beta)\mathbf{a}_\beta + (T_s^{\alpha\beta} b_{\alpha\beta} + T_{s\ |\alpha}^{\alpha(n)})\mathbf{k} + \mathbf{k}\cdot[\mathbf{T}_{b(2)} - \mathbf{T}_{b(1)}] = 0, \tag{11}$$

where $|_\alpha$ denotes covariant derivative. Projecting Eq. (11) into tangential and normal components yields the interfacial force balances [27,28,32,33]

$$(T_{s\ |\alpha}^{\alpha n} + T_s^{\alpha\beta} b_{\alpha\beta}) + [T_{b(2)}^{nn} - T_{b(1)}^{nn}] = 0, \tag{12}$$

$$(T_{s\ |\alpha}^{\alpha\beta} - T_s^{\alpha n} b_\alpha^\beta) + [T_{b(2)}^{n\beta} - T_{b(1)}^{n\beta}] = 0, \quad \alpha,\beta = 1,2. \tag{13}$$

Equation (12) is used to derive the shape equation. Equation (13) is the tangential force balance equation.

B. Membrane molecular field and bending moment

The liquid crystal description of membrane electromechanics is based on the expression of the membrane stress tensor $\mathbf{T}_s$ in terms of the membrane molecular field $\mathbf{h}_{\parallel}$ and bending moment tensor $\mathbf{M}$. The membrane molecular field $\mathbf{h}_{\parallel}$ gives the changes in electroelastic energy due to changes in surface tilting ($\delta\mathbf{k}$) and surface bending ($\delta\mathbf{b}$). For brevity we use $\mathbf{P}=\mathbf{P}_{\text{flexo}}$.

According to Appendix A [Eq. (A13)], the Helmholtz free energy per unit mass $\hat{A}$ is given by

$$\hat{A} = \mu + \frac{\gamma}{\rho} + \hat{A}_e, \tag{14a}$$

$$\hat{A}_e = \hat{A}_{\text{flexo}} - \frac{\boldsymbol{\varepsilon}:\mathbf{EE}}{8\pi\rho}, \tag{14b}$$

$$\hat{A}_{\text{flexo}} = -\frac{\mathbf{P}\cdot\mathbf{E}}{\rho}, \tag{14c}$$

where μ is the Gibbs function per unit mass, ρ is the surface mass density, γ is the membrane tension, $\hat{A}_e$ is the electric Helmholtz free energy per unit mass, $\hat{A}_{\text{flexo}}$ is the flexoelectric Helmholtz free energy per unit mass, $\mathbf{P}$ is the polarization, $\mathbf{E}$ is the electric field, and $\boldsymbol{\varepsilon}$ is the dielectric tensor. Appendix A [Eq. (A3)] shows that at constant electric field $\mathbf{E}$, the total differential of $\hat{A}$ is

$$d\hat{A} = -\left(\gamma - \mathbf{P}\cdot\mathbf{E} - \frac{\boldsymbol{\varepsilon}:\mathbf{EE}}{8\pi}\right)\frac{d\rho}{\rho^2} - \frac{\mathbf{M}}{\rho}:d\nabla_s\mathbf{k} + \frac{\mathbb{Q}_{\parallel}}{\rho}\cdot d\mathbf{k}, \tag{15}$$

where the membrane tension γ [Eq. (A5)], bending moment tensor $\mathbf{M}$ [27,28], the tangential component of the local electrocapillary vector $\mathbb{Q}_{\parallel}$ are

$$\gamma = -\rho^2\frac{\partial\hat{A}}{\partial\rho} + \mathbf{P}\cdot\mathbf{E} + \frac{\boldsymbol{\varepsilon}:\mathbf{EE}}{8\pi}, \tag{16a}$$

$$\mathbf{M} = \mathbf{M}^{\mathrm{T}} = -\left(\rho\frac{\partial\hat{A}}{\partial\nabla_s\mathbf{k}}\right)_{\rho,\mathbf{k}} = \left(\rho\frac{\partial\hat{A}}{\partial\mathbf{b}}\right)_{\rho,\mathbf{k}}, \tag{16b}$$

$$\mathbb{Q}_{\parallel} = \left(\rho\mathbf{I}_s\cdot\frac{\partial\hat{A}}{\partial\mathbf{k}}\right)_{\rho,\nabla_s\mathbf{k}}, \tag{16c}$$

where the superposed T in Eq. (16b) denotes transpose. Equation (15) shows that $(\gamma-\mathbf{P}\cdot\mathbf{E}-\boldsymbol{\varepsilon}:\mathbf{EE}/8\pi)/\rho^2$ is the conjugate to ρ, $\mathbf{M}/\rho$ is the conjugate of curvature $\nabla_s\mathbf{k}$, and the local electrocapillary vector $\mathbb{Q}_{\parallel}/\rho$ is the conjugate to $\mathbf{k}$.

Following previous work on anisotropic interfaces [34], the tangential membrane molecular field $\mathbf{h}_{\parallel}$ is defined as the variational derivative of the Helmholtz free energy A,

$$\mathbf{h}_{\parallel} = -\mathbf{I}_s\cdot\frac{\delta A}{\delta\mathbf{k}} = \mathbf{I}_s\cdot\left(-\frac{\rho\partial\hat{A}}{\partial\mathbf{k}} + \nabla_s\cdot\frac{\rho\partial\hat{A}}{\partial\nabla_s\mathbf{k}}\right) \tag{17}$$

$$\mathbf{h}_{\parallel} = -[\mathbb{Q}_{\parallel} + \mathbf{I}_s\cdot(\nabla_s\cdot\mathbf{M})], \tag{18}$$

where we used definitions (16c) and (16b) for $\mathbb{Q}_{\parallel}$ and $\mathbf{M}$, respectively. The membrane molecular field $\mathbf{h}_{\parallel}$ is a tangential vector, and expresses the changes in energy due to surface tilting and surface bending.

Appendix B shows that the tangential $\mathbf{T}_{s\parallel}$ and bending $\mathbf{T}_{s\perp}$ components of the membrane stress tensor $\mathbf{T}_s$ are given in terms of the free energy $(\hat{A}-\mu)\rho$, bending moment tensor $\mathbf{M}$, and molecular field $\mathbf{h}_{\parallel}$, as follows:

$$\mathbf{T}_{s\parallel} = (\hat{A}-\mu)\rho\mathbf{I}_s - \left(\rho\frac{\partial\hat{A}}{\partial\nabla_s\mathbf{k}}\right)_{\rho,\mathbf{k}}\cdot\nabla_s\mathbf{k} \tag{19}$$

$$= \left(\gamma - \mathbf{P}\cdot\mathbf{E} - \frac{\boldsymbol{\varepsilon}:\mathbf{EE}}{8\pi}\right)\mathbf{I}_s - \mathbf{M}\cdot\mathbf{b}, \tag{20}$$

$$\mathbf{T}_{s\perp} = -\mathbf{I}_s \cdot \frac{\rho\delta\hat{A}}{\delta\mathbf{k}}\mathbf{k} = \mathbf{h}_{\parallel}\mathbf{k}. \tag{21}$$

Extracting the trace from the $\mathbf{M}\cdot\mathbf{b}$ contribution to $\mathbf{T}_{s\parallel}$, the total interfacial stress tensor $\mathbf{T}_s$ now reads

$$\mathbf{T}_s = \left(\gamma - \mathbf{P}\cdot\mathbf{E} - \frac{\boldsymbol{\varepsilon}{:}\mathbf{EE}}{8\pi} - \frac{1}{2}(\mathbf{M}{:}\mathbf{b})\right)\mathbf{I}_s - \overline{\mathbf{M}\cdot\mathbf{b}} + \mathbf{h}_{\parallel}\mathbf{k}, \tag{22}$$

where the overbar on the second term $(\overline{\mathbf{M}\cdot\mathbf{b}})$ denotes a traceless tensor. The first term in Eq. (22) are the extension stresses, the second the shear stresses, and the third the bending stresses. Splitting the electroelastic stress tensor $\mathbf{T}_s$ into dielectric-elastic and flexoelectric $\mathbf{T}_{\text{sflexo}}$ contributions, we find that the latter are given by

$$\mathbf{T}_{\text{sflexo}} = \left[\rho\hat{A}_{\text{flexo}} - \frac{1}{2}\left(\frac{\rho\partial\hat{A}_{\text{flexo}}}{\partial\mathbf{b}}{:}\mathbf{b}\right)\right]\mathbf{I}_s - \overline{\frac{\rho\partial\hat{A}_{\text{flexo}}}{\partial\mathbf{b}}{:}\mathbf{b}} - \frac{\delta A_{\text{flexo}}}{\delta\mathbf{k}}\mathbf{k}, \tag{23}$$

which is in contrast to piezoelectricity in transversely isotropic materials that exhibit only extensional stresses.

III. ELECTROELASTIC SHAPE EQUATION

A. Generic shape equation

Assuming that the bulk fluid stresses are pure pressures

$$\mathbf{T}_1 = -P_1\mathbf{I}, \tag{24a}$$

$$\mathbf{T}_2 = -P_2\mathbf{I}, \tag{24b}$$

the normal force balance Eq. (12) becomes

$$\Delta P \equiv P_2 - P_1 = T^{\alpha\beta}b_{\alpha\beta} + T^{\alpha(n)}{}_{|\alpha}. \tag{25}$$

Using Eq. (21) to express $\mathbf{T}_{s\perp}$ in terms of the molecular field $\mathbf{h}_{\parallel}$, the pressure jump ΔP becomes

$$\Delta P = \mathbf{T}_{s\parallel}{:}\mathbf{b} + \nabla_s\cdot\mathbf{h}_{\parallel} = \mathbf{T}_{s\parallel}{:}\mathbf{b} - \nabla_s\cdot[\mathbb{Q}_{\parallel} + (\nabla_s\cdot\mathbf{M})]\cdot\mathbf{I}_s. \tag{26}$$

Replacing the tangential stress $\mathbf{T}_{s\parallel}$ expression [Eq. (19)] into Eq. (26) gives a compact form of the generic shape equation

$$\Delta P = -D\overline{\mathbf{M}\cdot\mathbf{b}}{:}\mathbf{q} - \nabla_s\cdot\boldsymbol{\Xi}, \tag{27a}$$

where the new vector $\boldsymbol{\Xi}$ is the electrocapillary vector for curved interfaces,

$$\boldsymbol{\Xi} = \left[\gamma - \mathbf{P}\cdot\mathbf{E} - \frac{\boldsymbol{\varepsilon}{:}\mathbf{EE}}{8\pi} - \frac{1}{2}(\mathbf{M}{:}\mathbf{b})\right]\mathbf{k} + [\mathbb{Q}_{\parallel} + (\nabla_s\cdot\mathbf{M})]\cdot\mathbf{I}_s, \tag{27b}$$

D is the deviatoric curvature, and $\mathbf{q}$ is the deviatoric curvature tensor, given by $D\mathbf{q}=\mathbf{b}-H\mathbf{I}_s$ [26]. Equation (27a) is the most compact and revealing form of the shape equation and shows that interfacial pressure jumps are due to shear $(-D\mathbf{M}\cdot\mathbf{b}{:}\mathbf{q})$ and the divergence of the capillary vector $(-\nabla_s\cdot\boldsymbol{\Xi})$. For spherical interfaces $(D=0)$, the shape equation (27a) reduces to

$$\Delta P = -\nabla_s\cdot\boldsymbol{\Xi}. \tag{28}$$

B. Shape equation for the electroelastic Helfrich interface

The Helfrich free energy per unit area [26,29] widely used to describe the elasticity of membranes and surfactant-laden interfaces reads

$$\rho\hat{A}_{\text{curvature}}(H,K) = 2k_c(H-H_o)^2 + \bar{k}_cK, \tag{29}$$

where k_c is bending elastic moduli, H_o is the spontaneous curvature, and $\bar{k}_c$ is the torsion elastic moduli. Under an external electric field $\mathbf{E}$, Eqs. (31) and (A13) show that the total Helmholtz free energy per unit area $\rho\hat{A}$ is

$$\rho\hat{A}(H,K) = 2k_c(H-H_o)^2 + \bar{k}_cK - 2c_{\text{flexo}}(\mathbf{k}\cdot\mathbf{E})H - \frac{\boldsymbol{\varepsilon}{:}\mathbf{EE}}{8\pi}. \tag{30}$$

To derive an expression of the shape equation (27a) using (30), we next find expressions for the primary quantities (i) membrane tension γ, (ii) bending moment tensor $\mathbf{M}$, (iii) electrocapillary vector $\boldsymbol{\Xi}$, and (iv) the membrane stress tensor $\mathbf{T}_s$.

Using the surface Euler equation [Eq. (A13)], the membrane tension γ is

$$\gamma = \gamma_o + 2k_c(H-H_o)^2 + \bar{k}_cK, \tag{31}$$

where γ_o is the tension at zero field $(\mathbf{E}=0)$ and zero curvature $(H=K=0)$. Expressing $\mathbf{M}$ in terms of unit tensor $\mathbf{I}_s$ and curvature tensor $\mathbf{b}$, we find

$$\mathbf{M} = \frac{\rho\partial\hat{A}}{\partial\mathbf{b}} = \left(\frac{C_1}{2} + 2C_2H\right)\mathbf{I}_s - C_2\mathbf{b}, \tag{32}$$

where the bending coefficients $\{C_1, C_2\}$ are

$$C_1 = \left(\frac{\rho\partial\hat{A}}{\partial H}\right)_{K,\mathbf{k}} = 4k_c(H-H_o) - 2c_{\text{flexo}}(\mathbf{k}\cdot\mathbf{E}), \tag{33a}$$

$$C_2 = \left(\frac{\rho\partial\hat{A}}{\partial K}\right)_{H,\mathbf{k}} = \bar{k}_c, \tag{33b}$$

which shows that $C_1=f(H,\mathbf{k}\cdot\mathbf{E})$ is a function of the external field $\mathbf{E}$. Using Eqs. (32) and (33), we find that $\mathbf{M}{:}\mathbf{b}/2=C_1H/2+C_2K$, which upon introduction into Eq. (31) yields the membrane tension in terms of three tension coefficients $[\gamma_o+\gamma_1(H)+\gamma_{\text{flexo}}(H,\mathbf{k})]$ and the bending stress trace $\mathbf{M}{:}\mathbf{b}/2$,

$$\gamma = \gamma_o + \gamma_1(H) + \gamma_{\text{flexo}}(H,\mathbf{k}) + \frac{1}{2}\mathbf{M}{:}\mathbf{b}, \tag{34}$$

where $\gamma_1(H)$ and $\gamma_{\text{flexo}}(H,\mathbf{k})$ are the curvature-dependent tension coefficients given by

$$\gamma_1 = -2k_c H_o(H - H_o); \quad \gamma_{\text{flexo}} = c_{\text{flexo}} H(\mathbf{k}\cdot\mathbf{E}). \tag{35}$$

Using Eqs. (16c) and (30), it is found that the local electrocapillary vector $\mathbb{Q}_{\parallel}$ for this interface is linear in the average curvature H,

$$\mathbb{Q}_{\parallel} = \left(\mathbf{I}_s \cdot \frac{\rho \partial \hat{A}}{\partial \mathbf{k}}\right)_{\rho,\nabla_s \mathbf{k}} = -2c_{\text{flexo}} H \mathbf{E}_{\parallel}, \tag{36}$$

where $\mathbf{E}_{\parallel}=\mathbf{I}_s\cdot\mathbf{E}$. Replacing Eqs. (32)–(36) into (27b) we find the electrocapillary vector $\boldsymbol{\Xi}$,

$$\Xi_{\perp} = \gamma_o + \gamma_1 + \gamma_{\text{flexo}} - \mathbf{P}\cdot\mathbf{E} - \frac{\boldsymbol{\varepsilon}:\mathbf{EE}}{8\pi}, \tag{37}$$

$$\boldsymbol{\Xi}_{\parallel} = \nabla_s\left(\frac{C_1}{2}\right) - (\mathbf{b} - 2H\mathbf{I}_s)\cdot\nabla_s C_2 + \mathbb{Q}_{\parallel}. \tag{38}$$

According to Eqs. (37) and (38), the flexoelectric contributions appear in tangential and normal components of $\boldsymbol{\Xi}$,

$$\Xi_{\perp\text{flexo}} = -c_{\text{flexo}} H(\mathbf{k}\cdot\mathbf{E}), \tag{39}$$

$$\boldsymbol{\Xi}_{\parallel\text{flexo}} = -\mathbf{h}_{\parallel\text{flexo}} = -2c_{\text{flexo}} H\mathbf{E}_{\parallel} - c_{\text{flexo}}\nabla_s(\mathbf{k}\cdot\mathbf{E}), \tag{40}$$

indicating that the energy associated with surface stretching is affected by $\mathbf{E}_{\perp}=\mathbf{kk}\cdot\mathbf{E}$ and for tilting it is affected by $\mathbf{E}_{\parallel}=\mathbf{I}_s\cdot\mathbf{E}$ and by gradients of $\mathbf{E}_{\perp}=\mathbf{kk}\cdot\mathbf{E}$.

Using Eqs. (22), (32), (37), and (38), the total interface stress tensor $\mathbf{T}_s$ is found to be

$$\mathbf{T}_s = \left(\gamma_o + \gamma_1 + \gamma_{\text{flexo}} - \mathbf{P}\cdot\mathbf{E} - \frac{\boldsymbol{\varepsilon}:\mathbf{EE}}{8\pi}\right)\mathbf{I}_s - \frac{C_1}{2}D\mathbf{q} - \left\{\left[\nabla_s\left(\frac{C_1}{2}\right)\right] - [(\mathbf{b} - 2H\mathbf{I}_s)\cdot\nabla_s C_2] + \mathbb{Q}_{\parallel}\right\}\mathbf{k}. \tag{41}$$

According to Eq. (41), the three flexoelectric stress contributions are

$$\mathbf{T}_{s\text{flexo}} = \underbrace{(+c_{\text{flexo}}(\mathbf{k}\cdot\mathbf{E})H)\mathbf{I}_s}_{\text{extension}} + \underbrace{c_{\text{flexo}}(\mathbf{k}\cdot\mathbf{E})D\mathbf{q}}_{\text{shear}} + \underbrace{c_{\text{flexo}}\{2H\mathbf{E}_{\parallel} + [\nabla_s(\mathbf{k}\cdot\mathbf{E})]\}\mathbf{k}}_{\text{bending}}, \tag{42}$$

where the underbracket defines the stress type. Electric stress is thus a function of $[\mathbf{E}_{\parallel}, \mathbf{E}_{\perp}, \nabla_s(\mathbf{k}\cdot\mathbf{E})]$ for a spherical interface $D=0$, and where there is no shear stress. If $\mathbf{E}$ is tangential, the only stress is of the bending type, $\mathbf{T}_s = 2c_{\text{flexo}} H\mathbf{E}_{\parallel}\mathbf{k}$. Thus interfacial flexoelectricity, in contrast to piezoelectricity [Eq. (2)], affects all stress components.

The shape equation, obtained by introducing Eqs. (32), (37), and (38) into (27a), gives

$$\Delta P = 2H\left(\gamma_o + \gamma_1 + \gamma_{\text{flexo}} - \mathbf{P}\cdot\mathbf{E} - \frac{\boldsymbol{\varepsilon}:\mathbf{EE}}{8\pi}\right) - \nabla_s\cdot\mathbb{Q}_{\parallel} + C_1(K - H^2) - \nabla_s^2\left(\frac{C_1}{2}\right) + (\mathbf{b} - 2H\mathbf{I}_s):\nabla_s\nabla_s C_2. \tag{43}$$

According to Eq. (36), the local electrocapillary vector $\mathbb{Q}_{\parallel}$ is a function of $(H,\mathbf{k})$, and hence its divergence is

$$-\nabla_s\cdot(\mathbb{Q}_{\parallel}) = -4c_{\text{flexo}} H^2\mathbf{k}\cdot\mathbf{E} + 2c_{\text{flexo}}\mathbf{E}_{\parallel}\cdot\nabla_s H. \tag{44}$$

Using the expression (44) for the bending coefficients $\{C_1, C_2\}$, the flexoelectric shape equation (43) reduces to

$$\Delta P = \left\{\gamma_o - 2k_c H_o(H - H_o) - c_{\text{flexo}}\mathbf{k}\cdot\mathbf{E}H - \frac{\boldsymbol{\varepsilon}:\mathbf{EE}}{8\pi}\right\}(2H) + \{4k_c(H - H_o) - 2c_{\text{flexo}}\mathbf{k}\cdot\mathbf{E}\}(K - H^2) - \{[\nabla_s^2(2k_c(H - H_o) - c_{\text{flexo}}(\mathbf{k}\cdot\mathbf{E}))] - 2c_{\text{flexo}}\mathbf{E}_{\parallel}\cdot\nabla_s H\}, \tag{45}$$

where the first bracket is the effective extensional stress, the second the shear stress, and the last the bending stress contribution to the normal force. Equation (45) is the main result of this paper. The equation can be used, in conjunction with experiments, to determine elastic (γ_o, k_c) and electrical properties (c_{flexo}), to design experiments without trial and error, and to explore new field-induced shaping methodologies. Equation (45) shows that the presence of membrane flexoelectricity renormalizes shear and the bending effects by

$$2k_c(H - H_o) \rightarrow 2k_c(H - H_o) - c_{\text{flexo}}(\mathbf{k}\cdot\mathbf{E}), \tag{46}$$

and extensional effect by

$$2k_c H_o(H - H_o) \rightarrow 2k_c H_o(H - H_o) + c_{\text{flexo}}(\mathbf{k}\cdot\mathbf{E})H. \tag{47}$$

Extracting the $\mathbf{E}$-related contributions from (45) reveals all the possible ways available to manipulate membrane shapes,

$$\Delta P_{\text{flexo}} = \left\{ -c_{\text{flexo}} \mathbf{k} \cdot \mathbf{E} H - \frac{\boldsymbol{\varepsilon}:\mathbf{EE}}{8\pi} \right\} (2H) - \{2c_{\text{flexo}} \mathbf{k} \cdot \mathbf{E}\} \times (K - H^2) + c_{\text{flexo}} \nabla_s^2 (\mathbf{k} \cdot \mathbf{E}) + 2c_{\text{flexo}} \mathbf{E}_{\parallel} \cdot \nabla_s H, \tag{48}$$

which include homogeneous normal fields $(\mathbf{k}\cdot\mathbf{E})$, gradient normal fields $[\nabla_s^2(\mathbf{k}\cdot\mathbf{E})]$, and tangential fields $(\mathbf{E}_{\parallel})$. In the absence of electric effects ($c_{\text{flexo}}=0$, $\boldsymbol{\varepsilon}=0$) and constant k_c, Eq. (45) reduces to the Ou-Yang-Helfrich vesicle shape equation [26,29,35] for curved interfaces,

$$\Delta P = 2H[\gamma_o - 2k_c H_o (H - H_o)] + 4k_c (H - H_o)(K - H^2) - 2k_c \nabla_s^2 H. \tag{49}$$

Finding a membrane shape by solving Eq. (45) subjected to edge conditions is not always feasible under constant curvature. This is due to the fact that under constant curvature spatial gradients vanish $(\nabla_s H=0)$ from the shape equation (45) and therefore edge information cannot be incorporated into the solution. Appendix C uses Eq. (45) to derive the following integral model for constant curvature

$$\Delta P = \left(\gamma_o - \frac{\boldsymbol{\varepsilon}:\mathbf{EE}}{8\pi} \right) 2H - (\boldsymbol{\eta} \cdot \mathbf{M} \cdot \boldsymbol{\eta}) \frac{GL}{V}, \tag{50}$$

where V is the displaced volume due to the normal displacement, L is the edge length, and G the slope at the edge. The use of the integral model is discussed below and its validity established by comparison with previous results [4].

IV. APPLICATION

Consider an initially flat membrane subjected to an external constant field $\mathbf{E}$, under hinged edge conditions. Assuming that the response to an imposed constant $\mathbf{E}$ field creates a constant-curvature spherical distortion ($D=0$, $H^2=K$), and further assuming $H_o=0$, Eqs. (10), (32), (33a), and (33b) yield

$$\Delta P = \left(\gamma_o - \frac{\boldsymbol{\varepsilon}:\mathbf{EE}}{8\pi} \right) 2H - \{(2k_c + \bar{k}_c) H - c_{\text{flexo}} (\mathbf{k} \cdot \mathbf{E})\} \frac{GL}{V}. \tag{51}$$

For a spherical cap of base radius a, the edge length is $L=2\pi a$. If the sphere radius is R and the height of the cap is h, the displaced volume V is

$$V = \frac{1}{6}\pi h (3a^2 + h^2) \approx \frac{1}{2}\pi h a^2, \tag{52}$$

where we assumed that $a \gg h$. The slope of the normal displacement at the edge is $G=-a/R$. Then, using the fact that for a spherical cap of $R \gg h$, $a^2=2Rh$, the geometric factor becomes

$$\frac{GL}{V} = -\frac{4}{Rh} = -\frac{8}{a^2}. \tag{53}$$

Introducing this result in (51), we arrive at the expression for the radius of the membrane

$$R = \frac{\left(2\gamma_o - \frac{\boldsymbol{\varepsilon}:\mathbf{EE}}{4\pi} \right) a^2 + 8(2k_c + \bar{k}_c)}{[-\Delta P a^2 + 8c_{\text{flexo}} (\mathbf{k} \cdot \mathbf{E})]}. \tag{54}$$

If we neglect $\boldsymbol{\varepsilon}:\mathbf{EE}/4\pi$ and $\bar{k}_c$, this expression is in agreement with Eq. (7.37) of Ref. [4], which was derived using a direct energy minimization approach and includes a gravitational term. The decrease of interfacial tension γ_o by $(\boldsymbol{\varepsilon}:\mathbf{EE}/8\pi)$ is known as the Lippmann equation [4]. The numerator of Eq. (54) is the resistance to deformation of an initially planar membrane. The denominator is the driving force for the deformation. The sign of the denominator determines the sign of R. The initial size of the circular membrane a appears in the tension term, indicating an increase in resistance and in the driving pressure, indicating an increase in area under same pressure drop decreases the deflection. Order of magnitude analysis of the different terms is given in Ref. [4]. Usually the bending and torsion moduli are negligibly in previously used material andexperimental setups, and the dominant effects are interfacial tension in the numerator and flexoelectricity in the denominator of (54). Other material systems or geometric parameters may change the role of the elastic moduli. As an example of the application of (54), for typical values quoted in Ref. [4], $E=25$ mV/nm, $\gamma_o=5$ mN/m, $a=0.5$ mm, $c_{\text{flexo}}=20\times10^{-18}$ C, $k_c=\boldsymbol{\varepsilon}:\mathbf{EE}=\bar{k}_c=\Delta P=0$, it is found that $R\approx 0.5$ m.

V. CONCLUSIONS

This paper presents the formulation of a membrane shape equation (45) that includes tension, bending, pressure, and flexoelectric effects. Flexoelectricity in membranes has been shown to create polarization under curvature (direct effect) and curvature under externally imposed electric fields (converse effect). This paper focused on the latter effect. Liquid crystal membranology was used to efficiently incorporate electroelastic effects in the stress tensor formulation. Flexoelectricity is shown to contribute to extensional, shear, and bending stresses. This is in stark contrast to piezoelectricity in transversely isotropic materials under external electric fields, where only extensional stresses arise. The electroelastic shape equation (45) was shown to converge to classical shape equation (49) for surfactant-laden interfaces, vesicles, and membranes. The description of constant curvature spherical membranes under hinged edge conditions, a situation of interest to real experiments, requires the integration of surface and edge effects. The integrated model (50) leads to a shape equation (54) that is consistent with previously derived equations, and captures the creation of membrane curvature under an external electric field resisted by tension, curvature, and torsion.

The covariant form of shape equation [Eq. (45)] is formulated in a transparent form that can guide systematic exploration of other field effects, such as tangential field effects $(\mathbf{E}_{\parallel})$ and field gradient effects $[\nabla_s^2(\mathbf{k}\cdot\mathbf{E})]$, and lead to further understanding of biological membranes. Lastly, the covariant approach used here can be extended to dynamical situations, nonspherical geometries, and to flexoelectric fibers.

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APPENDIX A: THERMODYNAMICS OF POLARIZED INTERFACES

The purpose of Appendix A is to present the thermodynamics of polarized interfaces and membranes relevant to the derivation of the electroelastic shape equation (48). Here we use the approach of Ref. [8] and work with the Helmholtz free energy. Assuming that the Helmholtz free energy per unit mass $\hat{A}$ and that the Helmholtz free energy per unit area $\bar{A}$ are given by

$$\hat{A} = \hat{A}\left(\frac{1}{\rho}, T, \mathbf{E}, \mathbf{k}, \nabla_s \mathbf{k}\right), \tag{A1}$$

$$\bar{A} = \bar{A}(\rho, T, \mathbf{E}, \mathbf{k}, \nabla_s \mathbf{k}), \tag{A2}$$

and their differentials read

$$d\hat{A} = \left(-\gamma + \mathbf{P}\cdot\mathbf{E} + \frac{\boldsymbol{\varepsilon}:\mathbf{EE}}{8\pi}\right)\frac{d\rho}{\rho^2} - \hat{S}dT - \frac{\mathbf{D}}{4\pi\rho}\cdot d\mathbf{E} - \frac{\mathbf{M}}{\rho}:d\nabla_s\mathbf{k} + \frac{\mathbb{Q}_\parallel}{\rho}\cdot d\mathbf{k}, \tag{A3}$$

$$d\bar{A} = -\bar{S}dT + \mu d\rho - \frac{\mathbf{D}}{4\pi}\cdot d\mathbf{E} - \mathbf{M}:d\nabla_s\mathbf{k} + \mathbb{Q}_\parallel\cdot d\mathbf{k}, \tag{A4}$$

where the membrane tension γ, entropy per unit mass $\hat{S}$, Gibbs free energy per unit mass μ, electric displacement $\mathbf{D}$, bending moment tensor $\mathbf{M}$, local electrocapillary vector $\mathbb{Q}_\parallel$, and polarization $\mathbf{P}$ are

$$\gamma = -\rho^2\left(\frac{\partial\hat{A}}{\partial\rho}\right)_{T,\mathbf{E},\nabla_s\mathbf{k},\mathbf{k}} + \mathbf{P}\cdot\mathbf{E} + \frac{\boldsymbol{\varepsilon}:\mathbf{EE}}{8\pi}, \tag{A5}$$

$$\mu = \left(\frac{\partial\bar{A}}{\partial\rho}\right)_{\rho,\mathbf{E},\nabla_s\mathbf{k},\mathbf{k}}, \tag{A6}$$

$$\mu = \left(\frac{\partial\bar{A}}{\partial\rho}\right)_{\rho,\mathbf{E},\nabla_s\mathbf{k},\mathbf{k}}, \tag{A7}$$

$$\mathbf{D} = -\frac{1}{4\pi}\left(\frac{\partial\bar{A}}{\partial\mathbf{E}}\right)_{\rho,T,\nabla_s\mathbf{k},\mathbf{k}}, \tag{A8}$$

$$\mathbf{M} = -\left(\rho\frac{\partial\hat{A}}{\partial\nabla_s\mathbf{k}}\right)_{\rho,\mathbf{k},\mathbf{T},\mathbf{E}} = \left(\rho\frac{\partial\hat{A}}{\partial\mathbf{b}}\right)_{\rho,\mathbf{k},\mathbf{T},\mathbf{E}}, \tag{A9}$$

$$\mathbb{Q}_\parallel = \left(\rho\mathbf{I}_s\cdot\frac{\partial\hat{A}}{\partial\mathbf{k}}\right)_{\rho,\nabla_s\mathbf{k},\mathbf{T},\mathbf{E}}, \tag{A10}$$

$$4\pi\mathbf{P} = \mathbf{D} - \boldsymbol{\varepsilon}\cdot\mathbf{E}. \tag{A11}$$

Re-writing $d\bar{A}$ in Eq. (A4) in terms of $d\hat{A}$, we find

$$d\hat{A} = -\hat{S}dT + \frac{1}{\rho}(\mu - \hat{A})d\rho - \frac{\mathbf{D}}{4\pi\rho}\cdot d\mathbf{E} - \frac{\mathbf{M}}{\rho}:d\nabla_s\mathbf{k} + \frac{\mathbb{Q}_\parallel}{\rho}\cdot d\mathbf{k}. \tag{A12}$$

Comparing Eq. (A12) with Eq. (A3), we find the surface Euler equation

$$\hat{A} = \mu + \frac{\gamma}{\rho} - \frac{\mathbf{P}\cdot\mathbf{E}}{\rho} - \frac{\boldsymbol{\varepsilon}:\mathbf{EE}}{8\pi\rho}. \tag{A13}$$

The surface Euler equation is used to define the interfacial stress tensor in Eq. (B6), which in part is based on the variation of $\hat{A}$ with density ρ.

Next we validate the form of the differentials (A3) and (A4) by using the Maxwell relations involving second partial derivatives. The Maxwell relation of interest to flexoelectricity is obtained from Eq. (A4),

$$\left(\frac{\partial^2\bar{A}}{\partial\mathbf{b}\partial\mathbf{E}}\right)_{\rho,T,\mathbf{k}} = \left(\frac{\partial^2\bar{A}}{\partial\mathbf{E}\partial\mathbf{b}}\right)^T_{\rho,T,\mathbf{k}}, \tag{A14}$$

where the superposed T denotes the transpose and where for brevity we used the definition $-\nabla_s\mathbf{k}=\mathbf{b}$. Using (A4) leads to the equality between changes of electric displacement vector $\mathbf{D}$ with curvature tensor $\mathbf{b}$ and changes of moment tensor $\mathbf{M}$ with electric field $\mathbf{E}$,

$$\left(\frac{\partial\mathbf{D}}{\partial\mathbf{b}}\right)_{\rho,T,\mathbf{k}} = 4\pi\left(\frac{\partial\mathbf{M}}{\partial\mathbf{E}}\right)^T_{\rho,T,\mathbf{k}}. \tag{A15}$$

Using Eqs. (A11) and (5), the displacement is $\mathbf{D}=4\pi\mathbf{P}+\boldsymbol{\varepsilon}\cdot\mathbf{E}=c_{\text{flexo}}4\pi(\mathbf{I_s}:\mathbf{b})\mathbf{k}+\boldsymbol{\varepsilon}\cdot\mathbf{E}$, and the left-hand side of Eq. (A15) yields a third-order tensor symmetric in its first two indices,

$$\left(\frac{\partial\mathbf{D}}{\partial\mathbf{b}}\right)_{\rho,T,\mathbf{k}} = c_{\text{flexo}}4\pi\mathbf{I_s}\mathbf{k}. \tag{A16}$$

Using Eq. (34), the right-hand side of (A15) gives

$$4\pi\left(\frac{\partial\mathbf{M}}{\partial\mathbf{E}}\right)^T_{\rho,T,\mathbf{k}} = 4\pi c_{\text{flexo}}\mathbf{I_s}\mathbf{k}. \tag{A17}$$

Comparing Eqs. (A16) and (A17) shows that Eq. (A14) is satisfied.

The Maxwell relation of interest to piezoelectricity is obtained from Eq. (A3),

$$\left(\frac{\partial^2\hat{A}}{\partial\rho\partial\mathbf{E}}\right)_{\mathbf{b},T,\mathbf{k}} = \left(\frac{\partial^2\hat{A}}{\partial\mathbf{E}\partial\rho}\right)_{\mathbf{b},T,\mathbf{k}}. \tag{A18}$$

Using Eqs. (A3) and (A18) leads to the equality between changes of electric displacement vector per unit mass $\mathbf{D}/4\pi\rho$ with density ρ and changes of effective tension $(-\gamma+\mathbf{P}\cdot\mathbf{E}+\boldsymbol{\varepsilon}:\mathbf{EE}/8\pi)$ with electric field $\mathbf{E}$,

$$-\left(\frac{\partial}{\partial\rho}\frac{\mathbf{D}}{4\pi\rho}\right)_{\mathbf{b},T,\mathbf{k}} = \frac{1}{\rho^2}\left[\frac{\partial}{\partial\mathbf{E}}\left(-\gamma+\mathbf{P}\cdot\mathbf{E}+\frac{\boldsymbol{\varepsilon}:\mathbf{EE}}{8\pi}\right)\right]_{\mathbf{b},T,\mathbf{k}}, \tag{A19}$$

which upon direct differentiation leads to

$$\left(\frac{\partial^2\hat{A}}{\partial\rho\partial\mathbf{E}}\right)_{\mathbf{b},T,\mathbf{k}} = \frac{1}{\rho^2}\frac{\mathbf{D}}{4\pi}, \tag{A20}$$

$$\left(\frac{\partial^2\hat{A}}{\partial\mathbf{E}\partial\rho}\right)_{\mathbf{b},T,\mathbf{k}} = \frac{1}{\rho^2}\frac{\partial}{\partial\mathbf{E}}\left(\mathbf{P}\cdot\mathbf{E}+\frac{\boldsymbol{\varepsilon}:\mathbf{EE}}{8\pi}\right) = \frac{1}{\rho^2}\frac{\mathbf{D}}{4\pi}, \tag{A21}$$

and hence the piezoelectric Maxwell relation (A18) is upheld.

APPENDIX B: MEMBRANE STRESS TENSOR

The purpose of Appendix B is to present the derivation of the membrane stress tensor $\mathbf{T}_s$, shown in equation (22). It proves convenient to introduce the following decomposition:

$$\mathbf{T}_s = \mathbf{T}_{\|\mathrm{iso}} + \mathbf{T}_{\|\mathbf{b}} + \mathbf{T}_{\perp\mathbf{b}} + \mathbf{T}_{\perp\mathbf{k}}, \tag{B1}$$

$$\mathbf{T}_{\|\mathrm{iso}} = \left(\gamma - \mathbf{P}\cdot\mathbf{E} - \frac{\boldsymbol{\varepsilon}:\mathbf{EE}}{8\pi}\right)\mathbf{I}_s, \tag{B2}$$

$$\mathbf{T}_{\|\mathbf{b}} = -\mathbf{M}\cdot\mathbf{b}, \tag{B3}$$

$$\mathbf{T}_{\perp\mathbf{b}} = -(\nabla_s\cdot\mathbf{M})\mathbf{k}, \tag{B4}$$

$$\mathbf{T}_{\perp\mathbf{k}} = -\mathbb{Q}_{\|}\mathbf{k}, \tag{B5}$$

where "iso" denotes isotropic, $\|$ denotes tangential and $\perp$ normal components, and the subscripts $(\mathbf{k},\mathbf{b})$ denote whether surface tilting or bending is involved, respectively.

At constant $\mathbf{E}$ and T, the variation of the total Helmholtz free energy A is

$$\delta\int_S \rho\hat{A}dS = \int_S \rho\delta\hat{A}dS = \int_S \rho\left(\frac{\partial\hat{A}}{\partial\rho}\cdot\delta\rho + \left(\mathbf{I}_s\cdot\frac{\partial\hat{A}}{\partial\mathbf{k}}\right)\cdot\delta\mathbf{k} + \left(\mathbf{I}_s\cdot\frac{\partial\hat{A}}{\partial\nabla_s\mathbf{k}}\cdot\mathbf{I}_s\right):\delta\nabla_s\mathbf{k}\right)dS$$
$$= \int_S \rho\left(\frac{\partial\hat{A}}{\partial\rho}\delta\rho + \mathbb{Q}_{\|}\cdot\delta\mathbf{k} + \mathbf{M}:\delta\mathbf{b}\right)dS, \tag{B6}$$

where $(\delta\rho,\delta\mathbf{k},\delta\mathbf{b})$ are variations in areal density, unit normal, and curvature tensor, respectively. To proceed further we need to find $(\delta\rho,\delta\mathbf{k},\delta\mathbf{b})$ in terms of the interfacial displacement vector $\delta\mathbf{R}$ that creates the energy change. In the following derivation we use the fact that a small displacement $\delta\mathbf{R}$ can be expressed in terms of the surface velocity $\delta\mathbf{R}=\mathbf{v}\delta t$, where $\mathbf{v}$ is the surface velocity and t is time, as done in Ref. [26]. Expressing the displacement $\delta\mathbf{R}$ in terms of tangential $\mathbf{u}_{\|}$ and normal $\zeta\mathbf{k}$ components, we find

$$\delta\mathbf{R} = \mathbf{u}_{\|} + \zeta\mathbf{k}, \quad \mathbf{u}_{\|} = \mathbf{v}_{\|}\delta t, \quad \zeta\mathbf{k} = \mathbf{v}_{\perp}\delta t, \tag{B7}$$

where $(\mathbf{v}_{\|},\mathbf{v}_{\perp})$ are the tangential and normal velocities.

(i) Variation in areal density $(\delta\rho)$: Using the interfacial mass balance equation $(\partial\rho/\partial t+\mathbf{v}\cdot\nabla_s\rho=-\rho\nabla_s\cdot\mathbf{v})$, we find

$$\delta\rho = \delta\rho_{\|} + \delta\rho_{\perp}, \tag{B8}$$

$$\delta\rho_{\|} = -\rho\mathbf{I}_s:\nabla_s\mathbf{u}_{\|}, \tag{B9}$$

$$\delta\rho_{\perp} = -\rho\nabla_s\cdot(\zeta\mathbf{k}). \tag{B10}$$

(ii) Variation in unit normal $(\delta\mathbf{k})$: The velocity of the surface unit normal is according to transport law [32],

$$\frac{\partial\mathbf{k}}{\partial t} = -(\nabla_s\mathbf{v})\cdot\mathbf{k}, \tag{B11}$$

which yields the variations

$$\delta\mathbf{k}_{\|} = -\mathbf{k}\cdot(\nabla_s\mathbf{u}_{\|})^T, \tag{B12}$$

$$\delta\mathbf{k}_{\perp} = -\nabla_s\zeta. \tag{B13}$$

(iii) Variation in curvature tensor $(\delta\mathbf{b})$: According to transport law, the time derivative of the curvature tensor $\mathbf{b}$ is [32]

$$\frac{\partial\mathbf{b}}{\partial t} = -(\nabla_s\mathbf{v})\cdot\mathbf{b} + \nabla_s\{[(\nabla_s\mathbf{v})\cdot\mathbf{k}]\}\cdot\mathbf{I}_s + \mathbf{b}\cdot\frac{\partial\mathbf{I}_s}{\partial t} + \frac{\partial\mathbf{I}_s}{\partial t}\cdot\mathbf{b}, \tag{B14}$$

where the last two terms are changes due to spatial orientation of $\mathbf{b}$ given by [32],

$$\mathbf{b}\cdot\frac{\partial\mathbf{I}_s}{\partial t} + \frac{\partial\mathbf{I}_s}{\partial t}\cdot\mathbf{b} = \mathbf{kb}\cdot(\nabla_s\mathbf{v})\cdot\mathbf{k} + \mathbf{b}\cdot(\nabla_s\mathbf{v})\cdot\mathbf{kk}. \tag{B15}$$

The variations $\delta\mathbf{b}$ due to the displacements, then, are

$$\delta\mathbf{b}_{\|} = -(\nabla_s\mathbf{u}_{\|})\cdot\mathbf{b}, \tag{B16}$$

$$\delta\mathbf{b}_{\perp} = \nabla_s\{[(\nabla_s\zeta\mathbf{k})\cdot\mathbf{k}]\}\cdot\mathbf{I}_s = \nabla_s\nabla_s\zeta. \tag{B17}$$

To derive the stress tensor due to dilation,

$$\mathbf{T}_{\|\mathrm{iso}} = \left(\gamma - \mathbf{P}\cdot\mathbf{E} - \frac{\boldsymbol{\varepsilon}:\mathbf{EE}}{8\pi}\right)\mathbf{I}_s,$$

we use a density variation due to tangential displacements,

$$\int_S \rho\frac{\partial\hat{A}}{\partial\rho}\cdot\delta\rho_{\|}dS = \int_S \mathbf{T}_{\mathrm{iso}\|}:(\nabla_s\mathbf{u}_{\|})^T dS. \tag{B18}$$

Using expression (B9) for surface density changes $\delta\rho_{\|}$ into the integrand of Eq. (B18) gives

$$\rho\frac{\partial\hat{A}}{\partial\rho}\delta\rho_{\|} = \left(-\rho^2\frac{\partial\hat{A}}{\partial\rho}\right)\mathbf{I}_s:(\nabla_s\mathbf{u}_{\|})^T. \tag{B19}$$

Replacing Eq. (B19) into (B18) leads to

$$\mathbf{T}_{\mathrm{iso}\|} = \left(-\rho^2\frac{\partial\hat{A}}{\partial\rho}\right)\mathbf{I}_s = \left(\gamma - \mathbf{P}\cdot\mathbf{E} - \frac{\boldsymbol{\varepsilon}:\mathbf{EE}}{8\pi}\right)\mathbf{I}_s. \tag{B20}$$

To find the tangential stress tensor due to bending $\mathbf{T}_{\|\mathbf{b}}$, we use a variation $\delta\mathbf{b}_{\|}$ due to tangential displacements,

$$\int_S \rho\frac{\partial\hat{A}_{\text{flexion}}}{\partial\mathbf{b}}:\delta\mathbf{b}_{\|}dS=\int_S \mathbf{T}_{\|\mathbf{b}}:(\nabla_s\mathbf{u}_{\|})^T dS. \quad \text{(B21)}$$

Using expression (B16) for $\delta\mathbf{b}_{\|}$ into the integrand in Eq. (B21) gives

$$\rho\frac{\partial\hat{A}}{\partial\mathbf{b}}:\delta\mathbf{b}_{\|}=\left(-\rho\frac{\partial\hat{A}}{\partial\mathbf{b}}\cdot\mathbf{b}\right):(\nabla_s\mathbf{u}_{\|})^T. \quad \text{(B22)}$$

Replacing Eq. (B22) into (B21) leads to

$$\mathbf{T}_{\|\mathbf{b}}=-\rho\frac{\partial\hat{A}}{\partial\mathbf{b}}\cdot\mathbf{b}=-\mathbf{M}\cdot\mathbf{b} \quad \text{(B23)}$$

To find the bending stress due to bending $\mathbf{T}_{\perp\mathbf{b}}$, we use a variation due to normal displacements,

$$\int_S \rho\frac{\partial\hat{A}_{\text{flexion}}}{\partial\mathbf{b}}:\delta\mathbf{b}_{\perp}dS=\int_S (\mathbf{T}_{\perp\mathbf{b}}\cdot\mathbf{k})\cdot(\nabla_s\zeta)dS. \quad \text{(B24)}$$

Using expression (B17) for $\delta\mathbf{b}_{\perp}$ into the integrand in Eq. (B24) gives

$$\rho\frac{\partial\hat{A}}{\partial\mathbf{b}}:\delta\mathbf{b}_{\perp}=\left(\rho\frac{\partial\hat{A}}{\partial\mathbf{b}}\right):(\nabla_s\nabla_s\zeta)=\nabla_s\cdot\left[\left(\rho\frac{\partial\hat{A}}{\partial\mathbf{b}}\right)\cdot(\nabla_s\zeta)\right]$$
$$-\left(\nabla_s\cdot\rho\frac{\partial\hat{A}}{\partial\mathbf{b}}\right)\cdot(\nabla_s\zeta). \quad \text{(B25)}$$

Replacing the last term in Eq. (B25) into (B24) leads to

$$\mathbf{T}_{\text{surf}\perp}=-\left(\nabla_s\cdot\rho\frac{\partial\hat{A}}{\partial\mathbf{b}}\right)\mathbf{k}=-(\nabla_s\cdot\mathbf{M})\mathbf{k}. \quad \text{(B26)}$$

The term $\nabla_s\cdot[(\rho\partial\hat{A}/\partial\mathbf{b})\cdot(\nabla_s\zeta)]$ in Eq. (B25) is integrated out into an edge term, which is discussed in Ref. [26].

To find the interface stress tensor $\mathbf{T}_{\perp\mathbf{k}}$, we use a variation of the energy due to changes in the outward unit normal $\delta\mathbf{k}$ due to normal displacements $(\nabla_s\zeta\mathbf{k})$ and find

$$\int_S \rho\mathbf{I}_s\cdot\frac{\partial\hat{A}}{\partial\mathbf{k}}\cdot\delta\mathbf{k}_{\perp}dS=\int_S \mathbf{T}_{\perp\mathbf{k}}:(\nabla_s\zeta\mathbf{k})^T\,dS$$
$$=\int_S (\mathbf{T}_{\perp\mathbf{k}}\cdot\mathbf{k})\cdot(\nabla_s\zeta)dS. \quad \text{(B27)}$$

Replacing Eq. (B13) into the first integrand in Eq. (B27) gives

$$\mathbf{I}_s\cdot\rho\frac{\partial\hat{A}}{\partial\mathbf{k}}\cdot\delta\mathbf{k}_{\perp}=-\mathbf{I}_s\cdot\rho\frac{\partial\hat{A}}{\partial\mathbf{k}}\cdot\nabla_s\zeta. \quad \text{(B28)}$$

Replacing (B28) into the first integrand of (B27) yields upon comparison with the last integrand in (B27) the expression

$$\mathbf{T}_{\perp\mathbf{k}}=-\mathbf{I}_s\cdot\rho\frac{\partial\hat{A}}{\partial\mathbf{k}}\mathbf{k}=-\mathbb{Q}_{\|}\mathbf{k}. \quad \text{(B29)}$$

Summing the four stress tensors [Eqs. (B20), (B23), (B26), and (B29)], we find, after making the expression in Eq. (B23) traceless, the expression for the membrane stress $\mathbf{T}_s$ given in Eq. (22).

APPENDIX C: INTEGRAL SHAPE EQUATION

Here we derive Eq. (50). To solve practical problems in membrane flexoelectricity, Eq. (45) must be satisfied subjected to edge conditions. According to classical membrane and plate mechanics [26,36], the edge conditions are imposed according to the edge displacements

$$\delta\mathbf{R}=\mathbf{u}_{\|}+\zeta\mathbf{k}, \quad \text{(C1)}$$

where $\mathbf{u}_{\|}$ is the tangential displacement vector and $\zeta\mathbf{k}$ is the normal displacement vector. The common edge conditions are (i) free edge conditions $\mathbf{u}_{\|}\neq 0$, $\zeta\neq 0$, and $\nabla_s\zeta\neq 0$, (ii) clamped edge conditions $\mathbf{u}_{\|}=0$, $\zeta=0$, and $\nabla_s\zeta=0$, and (iii) hinged edge conditions $\mathbf{u}_{\|}=0$, $\zeta=0$, and $\nabla_s\zeta\neq 0$. A full discussion of all edge conditions is beyond the scope of this paper; here we briefly discuss hinged edge conditions since they are relevant to important flexoelectric measurements [4]; a complete discussion is given in Ref. [26]. According to (B25), the normal force due to $(\nabla_s\zeta)$ is

$$\int_S \rho\frac{\partial\hat{A}}{\partial\mathbf{b}}:\delta\mathbf{b}_{\perp}dS=\int_S \mathbf{M}:(\nabla_s\nabla_s\zeta)dS. \quad \text{(C2)}$$

Since the total normal force balance is given in terms of ζ, the surface gradients in the second integrand in Eq. (55) must be shifted to $\mathbf{M}$. Using the identity $\mathbf{M}:(\nabla_s\nabla_s\zeta)=\nabla_s\cdot[\mathbf{M}\cdot(\nabla_s\zeta)]-\nabla_s\cdot[(\nabla_s\cdot\mathbf{M})\zeta]+\zeta(\nabla_s\nabla_s:\mathbf{M})$ and the surface divergence theorem leads to [26],

$$\int_S \mathbf{M}:(\nabla_s\nabla_s\zeta)dS=\int_S \zeta(\nabla_s\nabla_s:\mathbf{M})dS-\oint_C \boldsymbol{\eta}\cdot(\nabla_s\cdot\mathbf{M})\,\zeta d\ell$$
$$+\oint_C \boldsymbol{\eta}\cdot\mathbf{M}\cdot(\nabla_s\zeta)d\ell, \quad \text{(C3)}$$

where the term $(\nabla_s\nabla_s:\mathbf{M})$ in the first integrand is the negative of the normal force due to bending stresses that appears in Eq. (45), and $\boldsymbol{\eta}$ is normal to the edge and tangential to the membrane surface. For a hinged edge of a flexoelectric Helfrich interface, we find

$$\int_S \mathbf{M}:(\nabla_s\nabla_s\zeta)dS=\int_S \zeta\nabla_s^2[2k_c(H-H_o)-c_{\text{flexo}}(\mathbf{k}\cdot\mathbf{E})]dS$$
$$+\oint_C \boldsymbol{\eta}\cdot\mathbf{M}\cdot(\nabla_s\zeta)d\ell, \quad \text{(C4)}$$

and hence in the absence of external edge couples we must impose [26]

$$\boldsymbol{\eta}\cdot\mathbf{M}\cdot\boldsymbol{\eta}=0 \quad \text{(C5)}$$

at the hinged edges [36].

The canonical approach to membrane shape determination under hinged conditions involves solving Eq. (45) subjected to (58),

$$\boldsymbol{\eta}\cdot\mathbf{M}\cdot\boldsymbol{\eta}=-2k_cH_o-c_{\text{flexo}}(\mathbf{k}\cdot\mathbf{E})+2k_cH+\bar{k}_c(H-D)=0, \tag{C6}$$

where we note that the torsion modulus $\bar{k}_c$ appears in the boundary condition because $\bar{k}_cK$ [Eq. (32)] is a nilpotent energy not discardable in open surfaces under hinged edge conditions. The role of torsion on edge conditions was previously identified in Ref. [26]. In the literature of closed membranes, the torsion term $\bar{k}_cK$ is usually discarded at the outset.

Finding a membrane shape by solving Eq. (45) subjected to edge conditions is not always feasible under constant curvature. This is due to the fact that under constant curvature spatial gradients vanish ($\nabla_sH=0$) from the shape equation (45) and therefore edge information, such as Eq. (58), cannot be incorporated into the solution. For spherical interfaces, such as spherical caps of crucial importance in flexoelectric membranes under a constant $\mathbf{E}$ and $H_o=0$, the governing equation becomes algebraic in H, and the surface and edge model equations (45) and (58) lead to a redundancy since we have the following two equations for just one unknown (H),

$$\Delta\text{P}-\left(2\gamma_o-\frac{\boldsymbol{\varepsilon}:\mathbf{EE}}{4\pi}\right)H=0,$$

$$-c_{\text{flexo}}(\mathbf{k}\cdot\mathbf{E})+(2k_c+\bar{k}_c)H=0. \tag{C7}$$

To remove the unavoidable redundancy, one can use an integral balance approach. The integral normal force model is obtained by multiplying the electroelastic shape equation (45) [or Eq. (27a) for brevity] by ζ, integrating over the area S and adding the result to the edge term [Eq. (58)],

$$\int_S\{\Delta P+D\overline{\mathbf{M}\cdot\mathbf{b}}:\mathbf{q}+\nabla_s\cdot\boldsymbol{\Xi}\}\zeta dS+\oint_C\boldsymbol{\eta}\cdot\mathbf{M}\cdot(\nabla_s\zeta)d\ell=0. \tag{C8}$$

For a spherical interface ($D=0$), the integral shape equation (63) reduces to

$$\int_S\left[\Delta P-\left(\gamma_o-\frac{\boldsymbol{\varepsilon}:\mathbf{EE}}{8\pi}\right)(2H)\right]\zeta d\,S+\oint_C\boldsymbol{\eta}\cdot\mathbf{M}\cdot(\nabla_s\zeta)d\ell=0. \tag{C9}$$

Under constant curvature the integrands are constant and the integrals yield

$$\int_S\left[\Delta P-\left(\gamma_o-\frac{\boldsymbol{\varepsilon}:\mathbf{EE}}{8\pi}\right)(2H)\right]\zeta d\,S=\left[\Delta P-\left(\gamma_o-\frac{\boldsymbol{\varepsilon}:\mathbf{EE}}{8\pi}\right)(2H)\right]V, \tag{C10a}$$

$$\oint_C\boldsymbol{\eta}\cdot\mathbf{M}\cdot(\nabla_s\zeta)d\ell=(\boldsymbol{\eta}\cdot\mathbf{M}\cdot\boldsymbol{\eta})GL, \tag{C10b}$$

where V is the displaced volume V due to the normal displacement, L is the edge length, and G the slope at the edge. The integral shape equation for spherical membranes then is given by Eq. (50):

$$\Delta P=\left(\gamma_o-\frac{\boldsymbol{\varepsilon}:\mathbf{EE}}{8\pi}\right)2H-(\boldsymbol{\eta}\cdot\mathbf{M}\cdot\boldsymbol{\eta})\frac{GL}{V},$$

where the edge contribution $\boldsymbol{\eta}\cdot\mathbf{M}\cdot\boldsymbol{\eta}$ is found by using Eqs. (32) and (33).

[1] W. P. Mason, *Piezoelectric Crystals and Their Application to Ultrasonics* (D. Van Nostrand Company, New York, 1950).

[2] K. C. Le, *Vibrations of Shells and Rods* (Springer-Verlag, Berlin, 1999).

[3] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, 2nd ed. (Oxford University Press, London, 1993).

[4] A. G. Petrov, *The Lyotropic State of Matter* (Gordon and Breach Science Publishers, Amsterdam, 1999).

[5] A. G. Petrov, Biochim. Biophys. Acta **85535**, 1 (2001).

[6] A. G. Petrov, in *Dynamics and Defects in Liquid Crystals*, edited by P. E. Cladis and P. Palffy-Muhoray (Gordon and Breach, Amsterdam, 1998), 255–262.

[7] D. A. Edwards, H. Brenner, and D. T. Wasan, *Interfacial Transport Processes and Rheology* (Butterworth, Boston, MA, 1991).

[8] J. C. Slattery, *Interfacial Transport Phenomena* (Springer-Verlag, New York, 1990).

[9] O.-Y. Zhong-Can, L. Ji-Xing, and X. Yu-Zhang, *Geometric Methods in the Elastic Theory of Membranes in Liquid Crystal Phases* (World Scientific, Singapore, 1999).

[10] A. D. Rey, Rheol. Acta **40**, 507 (2001).

[11] A. D. Rey, Langmuir **17**, 1922 (2001).

[12] H. Yokoyama, *Handbook of Liquid Crystal Research*, edited by P. J. Collins and J. S. Patel (Oxford University Press, New York, 1997), chap. 6, p. 179.

[13] A. D. Rey, Langmuir **22**, 219 (2006).

[14] T. J. Sluckin and A. Poniewierski, in *Fluid Interfacial Phenomena*, edited by C. A. Croxton (Wiley, Chichester, 1986), chap. 5.

[15] S. Faetti, in *Physics of Liquid Crystalline Materials*, edited by I.-C. Khoo and F. Simoni (Gordon and Breach, Philadelphia, 1991), chap. 12, p. 301.

[16] G. Barbero and D. Durand, in *Liquid Crystals in Complex Geometries*, edited by G. P. Crawford and S. Zumer (Taylor and Francis, London, 1996), 21.

[17] M. A. Osipov and S. Hess, J. Chem. Phys. **99**, 4181 (1993).

[18] A. K. Sen and D. E. Sullivan, Phys. Rev. A **35**, 1391 (1987).

[19] C. Papenfuss and W. Muschik, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A **262**, 561 (1995).

[20] E. B. Kim, O. Guzmán, S. Grollau, N. L. Abbott, and J. J. de Pablo, J. Chem. Phys. **121**, 1949 (2004).

[21] E. G. Virga, *Variational Theories for Liquid Crystals* (Chap-

man Hall, London, 1994).
[22] J. T. Jenkins and P. J. Barrat, Appl. Math. Optim. **27**, 111 (1974).
[23] M. G. Forest and Q. Wang, Phys. Lett. A **245**, 518 (1998).
[24] P. T. Yue, J. J. Feng, C. Liu, and C. Shen, J. Fluid Mech. **515**, 293 (2004).
[25] P. Cermelli, E. Fried, and M. E. Gurtin, Arch. Ration. Mech. Anal. **174**, 151 (2004).
[26] S. Ljunggren, J. C. Eriksson, and P. Kralchevsky, J. Colloid Interface Sci. **191**, 424 (1997).
[27] P. A. Kralchevsky, J. C. Eriksson, and S. Ljunggren, Adv. Colloid Interface Sci. **48**, 19 (1994).
[28] P. A. Kralchevsky and K. Nagayama, *Particles at Fluids Interfaces and Membranes* (Elsevier, Amsterdam, 2001).
[29] J. C. Eriksson and S. Ljunggren, in *Surface and Interfacial Tension*, edited by S. Hartland, Surfactant Science Series 119 (Marcel Dekker, New York, 2004), 547.
[30] J. T. Jenkins, SIAM J. Appl. Math. **32**, 755 (1977).
[31] E. Glassinger, A. C. Lee, and R. M. Raphael, Phys. Rev. E **72**, 041926 (2005).
[32] J. D. Eliassen, PhD Thesis, Univerity of Minnesota, 1962.
[33] A. M. Waxman, Stud. Appl. Math. **70**, 63 (1984).
[34] A. D. Rey, J. Chem. Phys. **120**, 2010 (2004).
[35] Z. Ou-Yang and W. Helfrich, Phys. Rev. A **39**, 5280 (1989).
[36] J. N. Reddy, *Elastic Plates* (Taylor and Francis, Philadelphia, 1999).