PHYSICAL REVIEW E **73**, 051706 (2006)

Nematic membranes: Shape instabilities of closed achiral vesicles

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(Received 27 April 2005; revised manuscript received 16 September 2005; published 16 May 2006)

We consider the coupling between the local curvature tensor of a membrane and the local two-dimensional nematic order parameter, deriving it from a quasi-microscopic argument. This coupling makes the nematic director aligned along the lowest curvature eigenvector in a local metric. Local bending of a membrane may then generate nematic ordering. Alternatively, emerging nematic order leads to shape instabilities of closed vesicles. The theory is applied to a spherical isotropic vesicle, which turns into a prolate shape with two +1 disclinations on its poles as the nematic order sets in the membrane, described within the Landau-de Gennes continuum model.

DOI: 10.1103/PhysRevE.73.051706 PACS number(s): 61.30.Dk, 87.16.Dg, 61.30.Cz

I. INTRODUCTION

Membranes with vanishing surface tension represent a large and well-developed field of study, motivated by mathematical elegance and applications in soft-matter and life sciences. The generic physical system is a bilayer of amphiphilic molecules aggregated such that they are allowed to take up their preferred area, thus rendering surface tension irrelevant and dominated by bending rigidity. Since Helfrich has derived the continuum curvature-elasticity Hamiltonian of such a membrane [1], a vast literature has emerged on all aspects of physical behavior: remarkable fluctuation spectra [2], local two-dimensional (2D) hexatic ordering [3], interaction between inclusions [4], and shapes of closed vesicles [5]. The reader should consult key reviews [6–8] for details.

The two-dimensional nematic order (uniaxial breaking of local rotational symmetry in the plane, as opposed to the hexatic bond-orientational order) has many interesting aspects, making it distinct from the classical uniaxial liquid crystal order in 3D [9]. Still described as the traceless second-rank tensor order parameter, the phase transition of a 2D mesogenic liquid is continuous, allowing for critical phenomena and Landau-level mean field theory to be applied.

An early look at the orientational bias in a membrane arose from the experimental observation of chiral lipid tubules [10–12]. In the theoretical models [13–15] the tilt of the tails of molecules forming a bilayer was described by a plane-projection vector $\mathbf{m}$. Due to the chiral nature of the lipid tubules involved, this orientational variable was assumed to couple to the membrane curvature tensor $\mathbf{H}$ in a uniform quadrupolar form $\sim \mathbf{m}\cdot\mathbf{H}\cdot\mathbf{m}$, and also through a gradient $\sim \mathbf{H}:\nabla\mathbf{m}$, in addition to a Landau-style potential for the powers of $|\mathbf{m}|$, penalizing the magnitude of local molecular tilt. These ideas were subsequently developed in a number of seminal works [16–20], describing fluctuation anomalies and shape instabilities. Importantly, apart from the original work of Lubensky and MacKintosh, the principal axis of uniaxial ordering in the plane was the only variable, while the degree of orientation is clearly a significant parameter, especially for closed vesicles that inherently contain topological singularities in $\mathbf{m}(\mathbf{x})$. Most authors used the linear coupling of ordering tensor to the curvature, which is appropriate for the original idea of *tilted* molecules or, in general, in the presence of chiral bilayers, since the linearity in the curvature tensor breaks the bilayer up-down symmetry. Only Powers and Nelson [17] considered a quadratic achiral term $\sim(\mathbf{m}\cdot\mathbf{H}\cdot\mathbf{m})^2$. We refer the reader to [21] for a far more complete review of the chiral elastic membrane models, and their comparison with experimental observations of cylindrical tubules and helical ribbons.

In this paper we consider an achiral 2D nematic order emerging on the surface of a membrane, regarding the molecules as rods confined to the local plane. This model may describe the membrane perturbations induced by interfacially adsorbed rodlike molecules, such as polymers [22,23] or amphipathic peptides [24–26]. Tracking both the director orientation and the variation of the nematic order parameter allows the description of curvature-induced ordering and topological defects in closed vesicles. We focus on the shape-order interaction when a membrane is closed into a vesicle, topologically equivalent to a sphere.

In the next section we derive the local coupling term from a quasimicroscopic model. Then we use symmetry arguments to analyze how this specific (quadratic) coupling term is able to deal with all limiting cases of membrane curvature (in particular, saddle points). In the continuum approach, with the zero membrane thickness, we shall disregard a possibility put forward by Fournier and Galatola [20] when the two surfaces may have a different nematic order. Finally, we have to distinguish from the recent works on nematic elastomer membranes [27,28], which are very different from the ones generically controlled by the Helfrich Hamiltonian of an inextensible membrane.

In Sec. III we apply the previously derived coupling term to study the stability of a spherical isotropic configuration against the settling of a nematic phase, accompanied by either ellipsoidal or tetrahedral shape perturbations. The type of shape modifications suffered by the closed vesicle depends on how the nematic chooses to satisfy the constraint

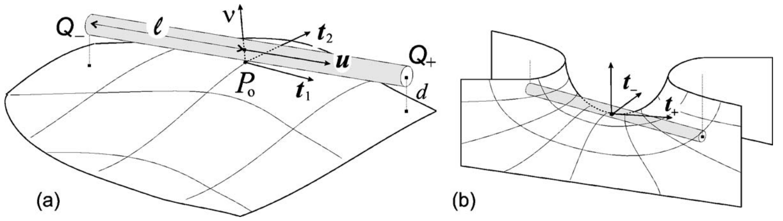

FIG. 1. (a) The local metric on a curved surface, illustrating the origin of coupling to the 2D nematic order. (b) A case of opposite principal curvatures, along $\mathbf{t}_+$ and $\mathbf{t}_-$, illustrating the requirement for the quadratic coupling (5).

on the total topological defect charge. In fact, any 2D nematic order spread on a closed vesicle topologically equivalent to a sphere is forced to give rise to a number of defects carrying a +2 total topological charge. In the absence of any nematic-membrane coupling, four $+\frac{1}{2}$ defects are expected to form at the vertices of a tetrahedron [29]. Even if this possibility stands when the liquid crystal is deep in the nematic region, we will show that our proposed interaction induces the formation of two +1 defects at the poles of an axially perturbed sphere even *above* the isotropic-nematic transition temperature. Section IV is devoted to the discussion of the derived results.

II. NEMATIC-MEMBRANE COUPLING

Consider a point P_o on a nematic membrane, described through the regular surface Σ, with two unit-vectors $\mathbf{t}_1, \mathbf{t}_2$, in the tangent plane at P_o, along the principal curvature directions. The unit normal at P_o, $\boldsymbol{\nu}$, completes an orthogonal basis. Let $\mathbf{H}=c_1\mathbf{t}_1\otimes\mathbf{t}_1+c_2\mathbf{t}_2\otimes\mathbf{t}_2$ be the (symmetric) curvature tensor, where c_1, c_2 denote the principal curvatures, Fig. 1(a).

The orientation of any molecule, whose center of mass lies in (an arbitrarily small neighborhood of) P_o, is identified by a tangent unit vector $\mathbf{u}$. Then, if 2ℓ denotes the rod length, the molecule end points are $Q_\pm(\mathbf{u})=P_o\pm\ell\mathbf{u}$. The surface points closest to $Q_\pm(\mathbf{u})$ are separated from the rod ends by a distance $d(\mathbf{u})\approx\frac{1}{2}\ell^2|\mathbf{u}\cdot\mathbf{H}\cdot\mathbf{u}|$. We assume that the resulting interaction can be described through a potential which penalizes the microscopic detachment of the rod end points from the membrane by a potential energy quadratic in d:

$$U_\mathrm{m}(\mathbf{u}) := pd^2 \approx \frac{p\ell^4}{4}(\mathbf{u}\cdot\mathbf{H}\cdot\mathbf{u})^2. \tag{1}$$

To obtain the macroscopic continuum coupling potential we need to evaluate the average of U_m over the local probability distribution of molecular orientations:

$$\langle U_\mathrm{m}(\mathbf{u})\rangle = P\langle(\mathbf{u}\cdot\mathbf{H}\cdot\mathbf{u})^2\rangle, \tag{2}$$

where $P=\frac{1}{4}p\ell^4$ is the essential coupling strength. It has the dimensions of an elastic constant and critical phenomena will arise when it becomes of the order of the average nematic elastic constants. Equation (2) can be written in terms of the fourth-order nematic tensor $\mathbf{N}=\langle\mathbf{u}\otimes\mathbf{u}\otimes\mathbf{u}\otimes\mathbf{u}\rangle$, such that $\langle U_\mathrm{m}(\mathbf{u})\rangle=P(\mathbf{H}:\mathbf{N}:\mathbf{H})$. By a dimensional estimate, we expect the magnitude of P to be related to the main bending modulus of the membrane, $P\sim\kappa(\ell/X)$, where ℓ is the characteristic length of the nematic rodlike molecule and X the membrane thickness. One expects in many cases $\ell\sim X$ and therefore $P\sim\kappa\sim kT$.

Let us now define the 2D uniaxial orientational averages, starting from the "standard" nematic order parameter

$$\mathbf{Q} := \langle\mathbf{u}\otimes\mathbf{u}\rangle - \frac{1}{2}\mathbf{I} = q\left(\mathbf{n}\otimes\mathbf{n} - \frac{1}{2}\mathbf{I}\right), \tag{3}$$

here $\mathbf{n}$ is the nematic director, $\mathbf{I}$ is the two-dimensional identity tensor, and the scalar nematic order parameter $q=2\langle(\mathbf{u}\cdot\mathbf{n})^2\rangle-1\in[-1,1]$. Note that the order tensors associated with negative values of q and director $\mathbf{n}$ coincide with the order tensors associated with the positive degree of order $-q$ and director $\boldsymbol{\nu}\wedge\mathbf{n}$, orthogonal to $\mathbf{n}$. Thus, without loss of generality, we restrict our analysis to non-negative values of q. Now the 2D second- and fourth-order moments of the molecular probability distribution take the form

$$\mathbf{M} := \langle\mathbf{u}\otimes\mathbf{u}\rangle = q\mathbf{n}\otimes\mathbf{n} + \tfrac{1}{2}(1-q)\mathbf{I},$$

$$\begin{aligned}\mathbf{N} = {}& q_4\mathbf{n}\otimes\mathbf{n}\otimes\mathbf{n}\otimes\mathbf{n} + \tfrac{1}{6}(q-q_4)\{\mathbf{n}\otimes\mathbf{n}\otimes\mathbf{I}\}_\mathrm{sym} \\ & + \tfrac{1}{24}(3-4q+q_4)\{\mathbf{I}\otimes\mathbf{I}\}_\mathrm{sym},\end{aligned} \tag{4}$$

where $\{\cdots\}_\mathrm{sym}$ denotes the combination symmetric with respect to all of its indices. The fourth order nematic order parameter $q_4=8\langle(\mathbf{u}\cdot\mathbf{n})^4\rangle-8\langle(\mathbf{u}\cdot\mathbf{n})^2\rangle+1\in[-1,1]$ is usually much smaller than q.

Although it is not strictly necessary (the theory is well-defined in its full form), it is common to neglect the small contribution from the fourth-order nematic parameter and apply a closure of the form $\mathbf{N}\approx\mathbf{M}\otimes\mathbf{M}$. In doing so one does not lose any significant symmetries in the system, acquires only a very small quantitative error, but gains a theory fully determined within second-order tensor fields. In particular, the essential nematic-membrane coupling now takes the form

$$U_\mathrm{NM}(\mathbf{H},\mathbf{M}) := P(\mathbf{H}:\mathbf{M})^2. \tag{5}$$

A useful representation can be obtained by identifying an angle of director orientation with respect to the frame $\{\mathbf{t}_1,\mathbf{t}_2\}$, $\mathbf{n}=\cos\alpha\mathbf{t}_1+\sin\alpha\mathbf{t}_2$, and using the eigenvalues of the second-moment $\mathbf{M}$, $\{\frac{1}{2}(1+q),\frac{1}{2}(1-q)\}$, so that

$$(\mathbf{H}:\mathbf{M}) = \tfrac{1}{2}(c_1+c_2) + \tfrac{1}{2}(c_1-c_2)q\cos 2\alpha, \tag{6}$$

where $\frac{1}{2}(c_1+c_2)=h$ is the mean membrane curvature and $\Delta=\frac{1}{2}(c_1-c_2)$ the local asphericity.

The potentials (2) and (5) share the same qualitative features. Both are non-negative and are minimized when the nematic molecules are completely aligned along a null-curvature direction. Any alignment along any curved direction is penalized, regardless of the sign of the curvature. These features make U_NM intrinsically different from most interaction potentials used in the literature, which are usually proportional to ($\mathbf{H}:\mathbf{M}$), or ($\mathbf{H}:\mathbf{Q}$). Figure 1(b) pictures a situation in which these differences are particularly evident. It illustrates a hyperbolic surface point P_o, where the principal curvatures c_1 and c_2 are opposite in sign. Any linear interaction term would tend to orient the nematic molecules along one of the curved directions (the choice depending on the sign of the coupling constant). In fact, a linear coupling between $\mathbf{H}$ and $\mathbf{M}$ *maximizes* the detachment of the rods, instead of inducing the rodlike nematic molecules to lay on the surface. However, the linear ($\mathbf{H}:\mathbf{M}$) coupling may well be physically appropriate for the model of tilted membranes used in [14,16–18], aligning the tilt along the maximal curvature direction.

For the 2D nematic order of rods confined to the interface, the coupling potential U_{NM} and its microscopic counterpart (2) favor the orientation along a direction oblique to $\{\mathbf{t}_+,\mathbf{t}_-\}$ axes [directly seen by minimization of Eq. (6) for $c_1=-c_2$], where the surface remains almost flat. This saddle-point example allows one to compare and distinguish our proposed coupling $(\mathbf{H}:\mathbf{M})^2$ from some previously used expressions. Let us, for example, consider the term ($\mathbf{H}^2:\mathbf{M}$) [30,31]. This potential is achiral and complies with the bilayer up-down symmetry as well. (The free-energy functional considered in [30] was indeed chiral, but chirality was introduced through a different term, linear in the curvature tensor.) However, when the principal curvatures are opposite in sign, the coupling (5) attains its minimum when the nematic molecules orient themselves in the oblique direction along which the surface is maximally flat. In contrast, the term ($\mathbf{H}^2:\mathbf{M}$) does not carry information on the curvature signs and just pushes the nematic molecules towards the direction of the smaller curvature (in absolute value).

III. SHAPE INSTABILITY

Let us now consider a closed membrane (vesicle) topologically equivalent to a sphere. Let (r,θ,ϕ) denote the standard spherical coordinates with origin $\mathbf{O}$. We may parametrize the points on any star-shaped surface Σ as $\mathbf{r}(\theta,\phi)=\mathbf{O}+r(\theta,\phi)\mathbf{e}_r(\theta,\phi)$. In the following, we will mainly deal with axisymmetric vesicles, in which the *shape function* r depends only on the polar angle θ. We denote by c_1 and $c_2 \geqslant c_1$ the principal curvatures along Σ, and by $\{\mathbf{t}_1,\mathbf{t}_2\}$ the unit vectors along the corresponding principal tangent directions. We refer the reader to, e.g., [32] for a detailed treatment of the technical differential geometry topics involved in our calculations.

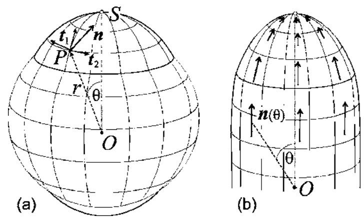

FIG. 2. (a) Spherical vesicle, with its ellipsoidal perturbation (the nematic director determines an angle α with $\mathbf{t}_1$). (b) A developed asphericity, illustrating the +1 disclination at a pole $\theta=0$.

We describe the nematic order of rodlike molecules lying on Σ through the tensors $\mathbf{Q}$ and $\mathbf{M}$ defined above, and represent the local director as $\mathbf{n}=\cos\alpha\mathbf{t}_1+\sin\alpha\mathbf{t}_2$, see Fig. 2(a). To simplify the following calculations, we adopt the one-constant approximation for the elastic nematic free energy density:

$$\sigma_{\mathrm{el}} = K|\boldsymbol{\nabla}_{\mathrm{s}}\mathbf{Q}|^2 = 2K\left(q^2|\boldsymbol{\nabla}_{\mathrm{s}}\mathbf{n}|^2+\frac{1}{4}|\boldsymbol{\nabla}_{\mathrm{s}}q|^2\right), \tag{7}$$

where $\boldsymbol{\nabla}_{\mathrm{s}}$ denotes the surface gradient. In the 2D case, the usual Landau-de Gennes' potential becomes

$$\sigma_{\mathrm{LdG}} = a\ \mathrm{tr}\ \mathbf{Q}^2 + c\ \mathrm{tr}\ \mathbf{Q}^4 = \frac{aq^2}{2}+\frac{cq^4}{8}. \tag{8}$$

Note the absence of the cubic term since for a 2D nematic field $\mathrm{tr}\ \mathbf{Q}^3=0$. We further assume that both a and c are positive, in order to stress that any possibly induced nematic order is not a consequence of the nematic molecular interactions: the system is kept above the nematic-isotropic transition.

If we collect Helfrich's elastic potential, together with the nematic-membrane coupling (5) and the nematic contributions (7) and (8) we arrive at the free energy functional to be minimized:

$$\mathcal{F}[\Sigma,\mathbf{Q}] = \int_{\Sigma}\Big[\kappa(h-\sigma_0)^2+P(h+\Delta q\cos 2\alpha)^2 + 2K\big(q^2|\boldsymbol{\nabla}_{\mathrm{s}}\mathbf{n}|^2+\tfrac{1}{4}|\boldsymbol{\nabla}_{\mathrm{s}}q|^2\big)+\tfrac{1}{2}aq^2+\tfrac{1}{8}cq^4\Big]dS, \tag{9}$$

where σ_0 is the membrane spontaneous curvature (added here for generality) and κ its bending modulus.

We now test the stability of the spherical, isotropic configuration against nematic perturbations. They will certainly increase both the Helfrich and nematic free energies. However, we will find that there is a particular perturbation that decreases the nematic-membrane potential (5). Consequently, there is threshold on the value of the coupling constant P above which the spherical isotropic configuration becomes unstable.

The topological theory of defects guarantees that, as soon as nematic order establishes on a surface of genus zero (i.e., a closed surface topologically equivalent to a sphere), point defects of total topological charge +2 must arise [29]. In the following, we will analyze the two lower-energy ways in which the nematic may fulfill the topological constraint. In the former, two +1 defects stand at opposite poles, while in the latter four $+\frac{1}{2}$ defects are placed at the vertices of a tetrahedron.

A. Ellipsoidal instability

We enforce axial symmetry by assuming that both the shape function r and the nematic variables q,α depend only on the polar angle θ. To study the stability of spherical isotropic configurations, we expand the shape function and the nematic degree of orientation around the isotropic sphere of radius R as

$$r(\theta,\phi) = R(1+\epsilon r_1(\theta)) \text{ and } q(\theta,\phi) = \epsilon q_1(\theta). \qquad (10)$$

When we expand $r_1(\theta)$ in Fourier series, the lowest-order shape perturbation that preserves the vesicle total area and is not singular at the poles is given by

$$r_1(\theta) = \eta\left(\cos 2\theta + \tfrac{1}{3}\right), \qquad (11)$$

with the amplitude $\eta \in \mathbb{R}$ acting as a spherical symmetry-breaking order parameter. Note that a perturbation such as Eq. (11) can be also retrieved by restricting the analysis to ellipsoidal shapes which preserve the total area.

Up to null Lagrangians and terms whose integrals vanish due to the conservation of the total area, the free-energy functional can be expanded as $\mathcal{F}=4\pi(\mathcal{F}_0+\epsilon^2\mathcal{F}_2+o(\epsilon^2))$, with $\mathcal{F}_0=\kappa(\gamma-1)^2+P$, and

$$\mathcal{F}_2 = \frac{32}{45}\kappa\eta^2(2\gamma^2-3\gamma+3) + 2P\eta\int_0^\pi (\eta\sin^2\theta - \cos 2\alpha(\theta) q_1(\theta))\sin^3\theta d\theta + K\int_0^\pi \left(\frac{q_1'^2}{4} + q_1^2\left(\alpha'^2 + \frac{1}{\sin^2\theta} + \frac{R^2}{\xi^2}\right)\right)\sin\theta d\theta, \qquad (12)$$

where $\xi := \sqrt{4K/|a|}$ is the nematic coherence length, and $\gamma = \sigma_0 R$. Since q_1 is non-negative, the minimum of the functional (12) is trivially attained when $\cos 2\alpha(\theta)=1$ for all θ, cf. Fig. 2. Letting $\alpha\equiv 0$ in Eq. (12) we can derive the Euler-Lagrange equation for $q_1(\theta)$,

$$q_1'' + q_1'\cot\theta - 4q_1\left(\frac{1}{\sin^2\theta} + \frac{R^2}{\xi^2}\right) + \frac{4P\eta}{K}\sin^2\theta = 0, \qquad (13)$$

which needs to be solved with the boundary conditions $q_1(0)=q_1(\pi)=0$, arising from the topological need for two isotropic defects placed at the poles. The simplest nontrivial solution that satisfies Eq. (13) and these boundary conditions is

$$q_1(\theta) = \frac{4P\eta}{6K+aR^2}\sin^2\theta, \qquad (14)$$

where the expression for coherence length ξ has been recovered. The induced nematic order is thus a consequence of both the nematic-membrane interaction (P) and of the non-sphericity of the vesicle (η). Note that in spherical geometry the decay of the nematic order towards the cores of two polar disclinations, Fig. 2(b), is continuous (in step with surface curvature), unlike the more sharp decay in $q(\boldsymbol{x})$ in cores of plane disclinations. Using Eq. (14), we find

$$\int_\Sigma (\mathbf{H}\cdot\mathbf{M})^2 dS = 1 + \frac{32}{15}\frac{6K+aR^2-4P}{6K+aR^2}\eta^2\epsilon^2 + o(\epsilon^2). \qquad (15)$$

Thus the ellipsoidal perturbation and the nematic order induce a gain in the nematic-membrane coupling term, if the coupling constant P is large enough. If we then take into account all the energy terms in Eq. (12), a stability condition for the shape perturbation parameter η can be derived. In the leading order, the sphere loses stability when the coupling constant exceeds the critical value

$$P_c = \frac{6K+aR^2}{4}\left(1 + \sqrt{1 + \frac{8(2\gamma^2-3\gamma+3)\kappa}{3(6K+aR^2)}}\right). \qquad (16)$$

Assuming, in a 2D nematic system, $K\sim\kappa$ as an order of magnitude estimate, and taking a vesicle with no spontaneous curvature ($\gamma=0$), this critical value of the coupling constant is $P_c\sim K$ for small vesicles with $R\sim\xi$, the nematic correlation length. Big vesicles, with $R\gg\xi$, will lose stability if $P_c\sim K(R/\xi)^2$.

B. Critical temperature shift

Far from the spontaneous nematic phase transition, one expects $aR^2\gg K$. Again, for simplicity, taking a case with no spontaneous membrane curvature and, by the order of magnitude, $\kappa\sim K\sim k_B T$, the critical coupling constant estimate is $P_c\sim k_B T(R/\xi)^2\sim aR^2$. This threshold seems high and so most vesicles (with membrane rods high above the nematic phase) should remain spherical. However, this threshold will fall dramatically near the nematic transition, where $a\to 0$ and then becomes negative. (Recall that the nematic transition is a continuous second order transformation in a 2D system.)

In an alternative analysis, if we optimize the functional (12) with respect to the shape parameter η first, we obtain a renormalized free energy density for the nematic phase transition, described by the order parameter magnitude $q(T)$. The result is a correction to the Landau expansion in powers of q, with the leading term $\tilde{a}q^2$ and the critical temperature shifted by a factor scaling as $1/R^2$. That is, $\tilde{a}=a_0(T-T_{\text{eff}})$ with

$$T_{\text{eff}} = T_c + \frac{6}{a_0R^2}\left[\frac{P^2}{(2\gamma^2-3\gamma+3)\kappa+3P} - K\right]. \qquad (17)$$

The P-coupling raises the critical temperature, favoring the nematic phase on uniaxially curved membranes. At sufficiently high P the vesicle of "mesogenic membrane" would find it difficult to stay in the isotropic spherical shape. However, the topological defects in spherelike shapes cost Frank energy (measured by K) and contribute to a negative shift in T_c. Comparing the temperature of the nematic transition in a flat membrane, T_c, with that in a closed vesicle, given by Eq. (17), could be the best way of finding the value of coupling constant P experimentally.

C. Fully developed tubules

Finally, it is interesting to briefly explore the case of high spontaneous nematic order, when the closed vesicle turns into a highly elongated tubule. The key point follows the discussion that led to Eq. (12) and is illustrated in Fig. 2(b). We break the tubule into two sections: the middle cylinder of length L and thickness d and the two semielliptical caps, with the area conservation requiring $L=2(R^2/d^2-1)$. When the nematic order $q_0^2=-2|a|/c$ [arising from σ_{LdG}, Eq. (8)] is well-established and the director is aligned at $\alpha=0$ in the uniform cylinder part, while in the caps the nematic order decreases towards the singular points as $q=q_0\sin^2\theta$. Integrating over the surface of such a tubule one obtains the full Landau-de Gennes part of the free energy

$$F_{\mathrm{LdG}} = -\frac{4\pi K q_0^4 R^2}{\xi^2}\left(1 - \frac{107 d^2}{315 R^2}\right). \tag{18}$$

This negative thermodynamic free energy is the driving force for the tubular shape. It is opposed by the Frank elasticity of the two defects and increasing free energy of membrane curvature which, again, combines the contribution from the middle cylinder and the two caps:

$$F_{\mathrm{el}} = \frac{\pi\kappa(R^2 - d^2)}{d^2} + 4\pi(\kappa + P) + \pi P(1 - q_0)^2\left(\frac{R^2}{d^2} - 1\right) + \frac{32}{5}\pi K q_0^2. \tag{19}$$

The balance between these opposing factors in the total free energy $\mathcal{F}(d, q_0)$ produces the optimal value for the tubule thickness d, which in the leading order yields:

$$\left(\frac{d}{R}\right)^4 \approx \frac{315}{428}\frac{\xi^2}{R^2}\frac{\kappa + P(1 - q_0)^2}{K q_0^4}. \tag{20}$$

Deep in the nematic phase, when $q_0 \approx 1$, this estimate reduces to

$$\left(\frac{d}{R}\right)^4 \sim \frac{\xi^2}{R^2}\frac{\kappa}{K} \ll 1. \tag{21}$$

For the aspect ratio of the nematic tubule we thus obtain:

$$\mathrm{AR} = \frac{L + 2d}{d} \approx \sqrt{\frac{5.43 K q_0^4}{\kappa + P(1 - q_0)^2}}\frac{R}{\xi} \sim \sqrt{\frac{K}{\kappa}}\frac{R}{\xi}. \tag{22}$$

Deep in the nematic phase, when one expects $R/\xi \gg 1$, this aspect ratio can become very large and the isotropic spherical vesicle turns into a long thin tubule with two caps containing localized +1 topological defects on the poles.

We have neglected a further interesting possibility for tubule formation. Were the curvature energy of the caps too high, the tubule may burst into an open tubule, by paying an extra energy due to the line tension at the open ends. We remark, however, that the defect energy stored in the caps does not yield a divergent contribution in the thin cap limit $d \to 0$. This fact can be seen in the last term of the free energy (19), which is indeed independent of d.

D. Tetrahedral instability

Let us now analyze the stability of the isotropic sphere against the formation of a nematic phase with four $+\frac{1}{2}$ defects, a possibility considered in [29] for a somewhat different physical system. Their principal interaction on the membrane is repulsive and, in order to minimize the overall elastic energy, the defects will certainly stand at the vertices of a tetrahedron. Let us introduce four unit-vectors, each pointing in the direction of a tetrahedron vertex:

$$\mathbf{e}_0 = \mathbf{e}_z, \quad \mathbf{e}_i = \mathbf{e}_r\left(\theta_0, \tfrac{2}{3}i\pi\right), \quad \text{for } i = 1,2,3, \tag{23}$$

where $\theta_0 = \arccos\left(-\frac{1}{3}\right)$, $\mathbf{e}_z$ is a unit-vector in the direction of the polar axis, and $\mathbf{e}_r(\theta, \phi)$ still denotes the radial unit-vector in the (θ, ϕ) direction. The lower-order spherical harmonic that guarantees tetrahedral symmetry is given by

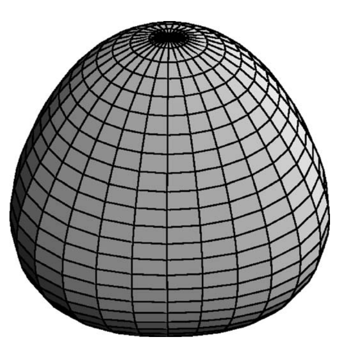

FIG. 3. Sphere perturbed with a shape function of the form (25). The plot corresponds to the value $\epsilon\eta = \frac{1}{4}$. The zeroth defect is placed on the top of the sphere.

$$\begin{aligned} f_{\mathrm{T}}(\theta, \phi) &= \prod_{i=0}^{3}(1 - \mathbf{e}_r(\theta, \phi)\cdot\mathbf{e}_i) \\ &= \frac{1 - \cos\theta}{54}((\cos\theta + 3)(7\cos 2\theta + 12\cos\theta + 13) \\ &\quad - 8\sqrt{2}\sin^3\theta\cos 3\phi). \end{aligned} \tag{24}$$

Consequently, we expand the shape function and the degree of nematic orientation as

$$\begin{aligned} r(\theta, \phi) &= R_\epsilon + \epsilon\eta f_{\mathrm{T}}(\theta, \phi), \text{ and} \\ q(\theta, \phi) &= \epsilon\chi f_{\mathrm{T}}(\theta, \phi), \end{aligned} \tag{25}$$

where the constant correction R_ϵ takes into account the fact that a shape perturbation proportional to f_{T} would not be area-preserving. Figure 3 illustrates how f_{T} modifies the sphere shape. In terms of the azimuthal angle ϕ, the only essential angular component that enters in Eq. (24) is $\cos 3\phi$, in agreement with the three-fold tetrahedral symmetry.

The orientation of the nematic director can be determined by using the complex-wave-function method, which is described in detail in [29]. Once we determine the principal directions along Σ, it turns out that the angle α between $\mathbf{n}$ and $\mathbf{t}_1$ satisfies

$$\cos 2\alpha = F_1(\theta)\cos\phi + F_2(\theta)\cos 2\phi. \tag{26}$$

There will be no need to give explicit expressions of the functions F_1, F_2. In terms of ϕ, Eq. (26) shows that α contains different Fourier components than all the other essential fields. This is related to the intrinsic symmetry of the $+\frac{1}{2}$ defects: If we follow the variation of both $\mathbf{n}$ and $\mathbf{t}_1$ along a closed path that surrounds a defect, we measure a π-turn in the director, while $\mathbf{t}_1$ performs a rotation of 2π. This disagreement induces the angular components in Eq. (26) that strongly influence the following considerations.

As a direct consequence of Eq. (26), when we estimate the coupling P-term $(\mathbf{H}:\mathbf{M})^2$ we find that its $O(\epsilon^2)$ contribution to the free energy is of the form

$$\int_0^{\pi} d\theta \int_0^{2\pi} d\phi (F_1(\theta)\cos\phi + F_2(\theta)\cos 2\phi)F_3(\theta,\cos 3\phi), \tag{27}$$

where F_3 is another complicated expression, which is a polynomial function of $\cos 3\phi$. As a result, the integral in $d\phi$ in Eq. (27) is null for any θ, because F_3 contains only terms proportional to $\cos 3n\phi$, which are all orthogonal to both $\cos\phi$ and $\cos 2\phi$.

Once we have proven that the P-term, describing the nematic-curvature coupling, yields no gain in the sphere perturbations of this symmetry, the stability analysis is completed. Since both the Helfrich and the nematic terms are separately minimized by the isotropic sphere, no tetrahedral instability may arise in the present theory.

IV. CONCLUSIONS

We have analyzed the effects of the nematic-membrane coupling (5) that is derived here from microscopic arguments. A number of previous studies of similar membrane systems, which are reviewed in the Introduction and throughout the text, mostly use phenomenological, symmetry motivated coupling terms. The first essential point in this paper is the discussion of merits and failings of different such terms. In addition we should also mention a very close set of ideas recently put forward to account for the long-range interaction between such intrinsically uniaxial membranes aligned in a lamellar stack [33]. Although we have not pursued the problem of a lamellar phase with our particular interaction, the interaction between anisotropic curvature tensors in a stack, suggested by Hamaneh and Taylor, would no doubt have interesting consequences.

Practical implementation of our model in this paper is the calculation of equilibrium vesicle shapes. There are several types of shape instabilities, which certainly can be observed experimentally. Probably, the long tubules of strongly nematic membranes have been seen already, but the most interesting regime would be in the vicinity of the 2D nematic critical point. Here we only mentioned the shift in the transition temperature, however, another fascinating question would be the effect of critical fluctuations on this transition in curved constrained spaces. This problem seems to be very much alive, both theoretically and experimentally, even after the number of years it has been looked upon.

ACKNOWLEDGMENT

This work was completed while the authors visited the Institute of Mathematics and Applications (IMA) at University of Minnesota, whose support is gratefully acknowledged.

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