

Orientational Order, Topology, and Vesicle Shapes

F. C. MacKintosh and T. C. Lubensky^(a)

Corporate Research Science Laboratories, Exxon Research and Engineering, Annandale, New Jersey 08801

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While ideal fluid membranes are characterized solely by curvature elasticity, many structural ("external") properties of real membranes are strongly influenced by internal degrees of freedom. Here, we consider, within mean-field theory, the effect of in-plane vector order (such as the molecular tilt in surfactant bilayers) on the shapes of closed vesicles with the topology of a sphere. We find that coupling between in-plane order and Gaussian curvature causes continuous shape changes from spherical to cylindrical vesicles as the degree of in-plane order increases.

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Two-dimensional fluid membranes occur in a wide variety of physical and biological systems. They are of fundamental physical interest, partly because they constitute examples of random surfaces. They also have many technological applications, such as in microencapsulation and chemical separation. Vesicles, composed of surfactant bilayers, are often used as model cell membranes. Most theories treat fluid membranes as structureless two-dimensional films, whose free energy depends principally on a local curvature tensor with constant bending moduli for mean and Gaussian curvatures [1]. The large-scale structural properties of many real membranes, however, are strongly influenced by internal degrees of freedom [2,3], such as density, relative concentration in two halves of a bilayer, or molecular orientation. This interplay between internal degrees of freedom and structure is believed to be responsible for the stability of mixed-surfactant vesicles observed in recent experiments [4] and for the formation of certain biological structures, such as tubules [5]. In this paper, we investigate shape changes in closed vesicles brought about by the development of orientational order in the fluid membrane of which they are composed. Within the mean-field approximation we use, shape changes occur continuously below a second-order phase transition.

Two-dimensional fluid films can exhibit various kinds of order, including quasi-long-range *orientational* order in the absence of positional order. Free-standing liquid-crystal films provide experimental examples of flat membranes that exhibit a variety of distinct thermodynamic phases characterized by varying degrees of quasi-long-range order (QLRO), including molecular tilt [6]. In the smectic-*A* (Sm-*A*) phase, the Frank director \mathbf{n} , specifying the direction of average molecular alignment, is parallel to the unit vector \mathbf{N} , normal to the plane. There is no in-plane positional order, and the film is essentially a two-dimensional fluid. In the smectic-*C* (Sm-*C*) phase, \mathbf{n} develops a nonvanishing component \mathbf{m} perpendicular to \mathbf{N} . This is depicted in Fig. 1 for a curved membrane. The component \mathbf{m} represents an in-plane vector order parameter in the fluid. Thermal fluctuations destroy *long-range* order in \mathbf{m} . The correlation function $\langle \mathbf{m}(\mathbf{r}) \cdot \mathbf{m}(0) \rangle$, however, dies as a power law in r at large separations,

and the two-dimensional Sm-*C* phase is characterized by QLRO, rather than long-range order. In the hexatic phase [7], there is a power-law decay in the bond-angle order parameter, $\psi_6 = e^{6i\theta}$, where θ is the angle (relative to some axis) of a bond formed by nearest-neighbor molecules. Sm-*F*, Sm-*I*, and Sm-*L* phases exhibit both hexatic and Sm-*C* order [8].

Noninteracting phospholipid bilayers in water provide another example of nearly flat two-dimensional films. In the L_α phase, these bilayers exhibit Sm-*A* order, whereas in the L_β phases, they exhibit Sm-*F*, Sm-*I*, or Sm-*L* order [8]. Under appropriate conditions, phospholipid bilayers in either the L_α or L_β phases can form closed vesicles [9].

Orientational order within a curved fluid membrane is coupled to the local geometry of the membrane and is strongly influenced by its global topology. This interplay between orientational order and the local geometry of a fluid membrane can have dramatic consequences for the structure and phase behavior of fluid membrane systems. Two-dimensional orientational order in a flat film, such as that of a Sm-*C* or a hexatic, becomes tangent-plane order in a curved surface. Gaussian (intrinsic) curvature introduces elastic deformations in the orientational order parameter and leads to an increase in the free energy of the membrane. Thus, tangent-plane order tends to expel Gaussian curvature, and vice versa. A particular manifestation of this effect is the reduced crumpling of a hex-

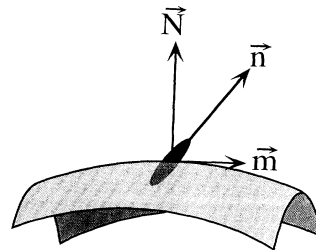


FIG. 1. Smectic-*C* order within a fluid membrane arises from a tilt of the constituent molecules (represented by the solid oval and unit director \mathbf{n}) relative to the unit surface normal \mathbf{N} . The surface component, $\mathbf{m} = \mathbf{n} - (\mathbf{N} \cdot \mathbf{n})\mathbf{N}$, represents a vector order parameter defined in the tangent plane perpendicular to \mathbf{N} .

atic membrane compared with a disordered fluid membrane [10].

The global topology of the surface has a profound effect on the interplay between orientational order and curvature, and thus on shape. The Euler number of a sphere is 2, and the total vorticity of a tangent-plane order parameter on its surface is 2 [11]. Like vortices repel each other. Thus, there will be two antipodal strength-1 vortices on a spherical membrane with vector order. Because the minimum vorticity of a hexatic field is $\frac{1}{6}$, a similar membrane with hexatic order will have twelve vortices at the vertices of an icosahedron in its ground state [12]. Additional vortex pairs will be created at finite temperatures, eventually leading to a Kosterlitz-Thouless transition [13,14].

In this paper, we investigate the simplest model of tangent-plane order that will lead to shape changes. From the above discussion, it is clear that the lowest-energy configuration for a spherical vesicle is characterized by order which is a maximum around the equator and zero in the disordered regions (vortex cores) located at opposite poles. The tangent-plane order at the equator tends to expel Gaussian curvature. Thus, the intrinsic curvature (the integral of which is a topological invariant) is increased in the disordered regions near the poles. As the temperature is lowered, the surface will become more and more cylindrical (for which the Gaussian curvature is zero) with decreasing radius and smaller vortex core regions. This is illustrated in Fig. 2. The elongated shape is shown, together with the corresponding (unnormalized) vector order parameter on the surface. In order to keep our treatment as simple as possible, we will assume that the vesicle is permeable so that it has only a surface energy and no volume energy, which, for exam-

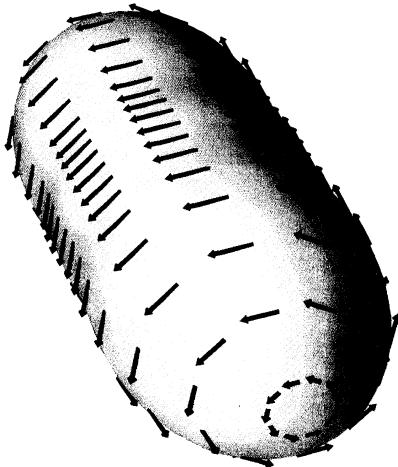


FIG. 2. In this view of an elongated vesicle, the tangent-plane order parameter corresponding to the represented shape has been depicted by the arrows. The tangent-plane order parameter is dimensionless, and its normalization has been chosen for clarity of presentation.

ple, might arise from a pressure difference across the vesicle membrane.

Our calculations are based on a phenomenological model on a fluctuating surface of arbitrary curvature. Consider, for example, the generalization of the Sm-*A*-to-Sm-*C* transition in a flat film. In the Sm-*C* phase of liquid crystals, the orientational order is manifested in the microscopic tilt of the constituent molecules relative to the smectic plane. As depicted in Fig. 1, we let \mathbf{n} denote the Frank director and \mathbf{N} the surface normal. The order parameter is \mathbf{m} , which is defined by $\mathbf{n} = \omega \mathbf{N} + \mathbf{m}$, where $\mathbf{m} \cdot \mathbf{N} = 0$ and $\omega^2 = 1 - m^2$. The two-component field \mathbf{m} is then a tangent vector. A Landau-Ginzburg free energy for the Sm-*A*-Sm-*C* transition in a flat film is then $F = F_m + F_{\mathbf{v}\mathbf{n}}$, where

$$F_m = \int d^2x \left(\frac{1}{2} \mu m^2 + \frac{1}{4} \lambda m^4 \right) \quad (1)$$

and

$$F_{\mathbf{v}\mathbf{n}} = \frac{1}{2} c \int d^2x (\partial_a n_b \partial_a n_b) \delta_{aa'} \delta_{bb'} \quad (2)$$

is the two-dimensional Frank free energy. Here, $\mu \sim T - T_c$ and $\delta_{aa'} = \delta_{aa'} - N_a N_{a'}$. For simplicity, we have used a single Frank elastic constant c . Throughout we shall make use of the convention that repeated indices are summed over.

Positions on a two-dimensional surface are specified by a three-component vector $\mathbf{X}(\sigma)$ that is a function of the two-dimensional surface coordinate σ . The vectors $\mathbf{e}_a = \partial \mathbf{X} / \partial \sigma^a$ form a basis for the tangent plane to the surface at σ , whose metric and curvature tensors are, respectively, $g_{ab} = \mathbf{e}_a \cdot \mathbf{e}_b$ and $K_{ab} = \mathbf{N} \cdot \partial_a \mathbf{e}_b$. Furthermore, the area of a surface element bounded by $d\sigma^1 \mathbf{e}_1$ and $d\sigma^2 \mathbf{e}_2$ is $|\mathbf{e}_1 \times \mathbf{e}_2| d\sigma^1 d\sigma^2 = \sqrt{g} d\sigma^1 d\sigma^2$, where $\sqrt{g} = |\det g_{ab}|^{1/2}$. The free energy of an ideal fluid membrane with fixed area is dominated by its curvature energy [1]

$$F_{\text{curv}} = \frac{1}{2} \kappa \int \sqrt{g} d^2\sigma (\text{Tr} K)^2 + \frac{1}{2} \kappa_G \int \sqrt{g} d^2\sigma (\det K), \quad (3)$$

where κ is an extrinsic curvature modulus with units of energy and κ_G is the Gaussian curvature modulus. The mean-curvature term tends to stabilize the vesicle against fluctuations or changes in shape, while the second term is a topological invariant for surfaces with fixed Euler number and can be ignored in our present calculation.

The generalization of Eq. (2) to lowest order in m on a curved surface is

$$F_{\mathbf{v}\mathbf{n}} = \frac{1}{2} c \int \sqrt{g} d^2\sigma (D_a m^b D_a m_b - 2K_b^a D_a m^b + K_b^a K_a^b). \quad (4)$$

There are corrections to this expression arising from gradients of ω , which are of order m^2 times each of the three terms. Here, $\mathbf{m} = m^a \mathbf{e}_a$, and $D_a m^c = \partial_a m^c + \Gamma_{ab}^c m^b$ is the covariant derivative, where $\Gamma_{ab}^c = \mathbf{e}^c \cdot \partial_a \mathbf{e}_b$ is the affine

connection. In this covariant notation, indices are "raised" and "lowered" with the metric g_{ab} and its matrix inverse g^{ab} ; e.g., $K_b^a = g^{ac}K_{bc}$. The last two terms come from gradients in the normal component of \mathbf{n} . The third term represents an effective bending rigidity of the membrane, which renormalizes the bending modulus κ . The second term reflects the fact that, by bending, the membrane is able to relieve stresses due to gradients in \mathbf{n} . This provides an explicit coupling between curvature and the spatial variations in \mathbf{m} . In this work, we shall focus on the first term, which is simply a generalization to a curved surface of the square gradient term in m . Such a term is common to all models which are characterized by a tangent-plane vector order parameter.

Because of the implicit coupling of the vector order to Gaussian curvature through the covariant derivatives, the development of order favors changes in the shape of vesicles. This competes with curvature energy terms, which favor uniform curvature. In order to study this competition, we consider the following simplified free energy:

$$F = \int \sqrt{g} d^2\sigma \left[\frac{1}{2} c D_a m^b D^a m_b + \frac{1}{2} \mu m^a m_a + \frac{1}{4} \lambda (m^a m_a)^2 + \frac{1}{2} \kappa (\text{Tr} K)^2 \right]. \quad (5)$$

This energy is identical to $F_m + F_{\text{curv}} + F_{\text{vn}}$ in Eqs. (1), (3), and (4) without the $K_b^a D_a m^b$ term and the topologically invariant Gaussian-curvature term. We shall treat κ and c as independent phenomenological parameters, although in specific models such as Eq. (4) they may be related. To carry out an explicit minimization of F , we find it convenient to use the spin connection for the covariant derivatives. Let $\hat{\mathbf{E}}_1(\sigma)$ and $\hat{\mathbf{E}}_2(\sigma)$ form an orthonormal basis for the tangent plane at σ . In this basis, the order parameter can be expressed in the noncovariant form, $\mathbf{m} = m_{(a)} \hat{\mathbf{E}}_a$, where $m_{(1)} = m(\sigma) \cos \alpha$ and $m_{(2)} = m(\sigma) \times \sin \alpha$. Here, α is the angle between $\hat{\mathbf{E}}_1$ and \mathbf{m} . In this representation, the square-gradient term becomes

$$D_a m^b D^a m_b = \partial^a m \partial_a m + g^{ab} m^2 (\partial_a \alpha - A_a) (\partial_b \alpha - A_b),$$

where $A_a = \hat{\mathbf{E}}_1 \cdot \partial_a \hat{\mathbf{E}}_2$. The spin connection [10] A_a expresses the gauge invariance of $D_a m^b D^a m_b$, under redefinition of the basis $\{\hat{\mathbf{E}}_a\}$. In the disordered phase, the vesicle assumes a spherical shape. We choose coordinates $\{\sigma^a\}$ corresponding to the usual polar and azimuthal coordinates $\{\theta, \phi\}$. We shall characterize the surface of the membrane by $\mathbf{X}(\theta, \phi) = R(\theta, \phi) \hat{\mathbf{r}}$. Without loss of generality, the lowest-energy state can be chosen such that the vector field is azimuthally symmetric and vanishes at the poles: $\theta = 0, \pi$. In the natural "gauge," corresponding to $\hat{\mathbf{E}}_1 = \hat{\boldsymbol{\theta}}$ and $\hat{\mathbf{E}}_2 = \hat{\boldsymbol{\phi}}$, α is constant. In other words, the vector field has a fixed orientation relative to the familiar latitude and longitude lines, and the magnitude of the field is a function only of the polar angle θ . Furthermore, the solution is symmetric about $\theta = \pi/2$.

Because of their symmetry, the order parameter $m(\theta)$ and shape function $R(\theta)$ can be expanded in the (associ-

ated) Legendre series

$$m(\theta) = \sum_{j=1}^{\infty} m_{2j-1} P_{2j-1}^1(\cos \theta) \quad (6)$$

and

$$R(\theta) = R_0 \left[1 + \sum_{j=1}^{\infty} \rho_{2j} P_{2j}(\cos \theta) \right]. \quad (7)$$

In equilibrium, the free energy F is a minimum with respect to $\{R_0, m_1, m_3, \dots, \rho_2, \rho_4, \dots\}$, subject to the constraint of fixed area, $\mathcal{A} = \int \sqrt{g} d^2\sigma$. One can easily express R_0 as a function of \mathcal{A} and $\{\rho_{2j}\}$. Thus, F can be expressed as a function of $\{\mathcal{A}, m_1, m_3, \dots, \rho_2, \rho_4, \dots\}$. The contributions to F from curvature and gradients in \mathbf{m} are independent of area. The remaining part of F can be written as

$$F_m = \mathcal{A} \left[\frac{1}{\int \sqrt{g} d^2\sigma} \int \sqrt{g} d^2\sigma \left(\frac{\mu}{2} m^2 + \frac{\lambda}{4} m^4 \right) \right], \quad (8)$$

where the factor multiplying \mathcal{A} is a function only of the $\{\rho_{2j}\}$.

Near the transition, the $j=1$ modes dominate. The energy can be evaluated analytically for small m_1 and ρ_2 , subject to the constraint of fixed area, with the result that

$$\frac{F}{c} \sim (1 + \hat{\mu}) m_1^2 + \frac{2}{5} \hat{\lambda} m_1^4 - \frac{4}{5} \rho_2 m_1^2 + \frac{36\kappa}{5c} \rho_2^2, \quad (9)$$

where $\hat{\mu} = \mathcal{A} \mu / 4\pi c$ and $\hat{\lambda} = \mathcal{A} \lambda / 4\pi c$. Note that the transition temperature has been depressed below its value for a flat membrane, i.e., $\mu_c < 0$, by an amount proportional to \mathcal{A}^{-1} , which vanishes in the thermodynamic limit. This is because the mode for which m is a constant cannot order on a sphere. The coupling of the shape to the order in the membrane leads to a continuous change in shape. For $\mu \lesssim \mu_c$, $m_1^2 \approx 5(\mu_c - \mu)/4\lambda$ and $\rho_2 \approx c m_1^2 / 18\kappa$.

Equation (5) can be evaluated numerically for arbitrary single-valued functions $m(\theta)$ and $R(\theta)$. We use a variational approach to find the minimum of Eq. (5). We parametrize the shape function $R(\theta)$ as in Eq. (7). For a given shape $R(\theta)$, minimization of Eq. (5) with respect to $m(\theta)$ is equivalent to solving a nonlinear differential equation for $m(\theta)$. The solution of this differential equation can be closely approximated by the following two-parameter variational function:

$$m(\theta) = m_0 \tanh[(\sin \theta) / \xi]. \quad (10)$$

Here, $R(0)\xi$ is the correlation length, which diverges near $\mu = \mu_c$. Equation (5) is then minimized with respect to $\{m_0, \xi, \rho_2, \rho_4, \dots\}$, subject to the constraint of fixed area \mathcal{A} . The results are shown in Fig. 3, where $m(\pi/2)$, ρ_2 , and ρ_4 are plotted versus $\hat{\mu}$. In the disordered phase, for $\mu > \mu_c$, the vesicle assumes a spherical shape. Below the transition, the vesicle shape becomes increasingly cylindrical in nature.

We have presented here a simple model for tangent

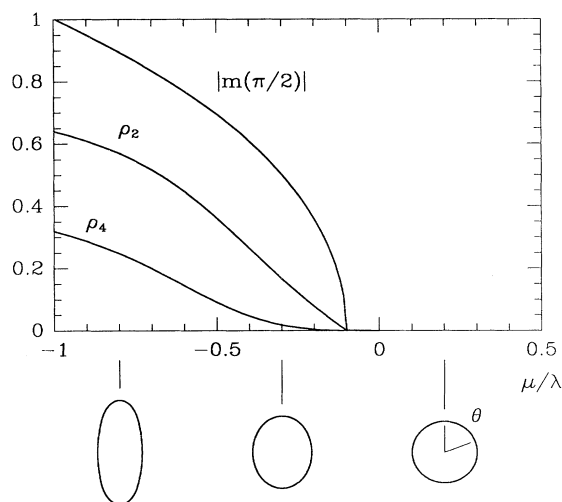


FIG. 3. The effect of vector order on the shape of vesicles. The magnitude of the order parameter at the equator, $m(\pi/2)$, is shown as a function of μ/λ . The resulting change in shape is characterized by the coefficients ρ_{2j} , as defined by Eq. (7). Only ρ_2 and ρ_4 have been plotted here, although the numerical minimization was performed through ρ_8 . Near the transition, $\rho_2 \sim m^2$. The shapes $R(\theta)$ for three specific values of μ/λ are drawn to the same scale. These results were obtained for $\hat{\lambda} = 10$ and $\kappa/c = 0.1$.

plane order in a vesicle with spherical topology and shown within mean-field theory how the development of such order leads to a change in the vesicle's shape. Clearly, it is important to determine how fluctuations will modify this result. At temperatures below the Kosterlitz-Thouless [13] (KT) transition of the surface, the shape of the equilibrium surface will be similar to that predicted here. Since there is a logarithmic repulsion between vortices, fluctuations in the positions of the vortices will be small. Above the KT transition, the repulsion between vortices is screened and fluctuations in the vortices will increase. For large fluctuations, the shape will be more spherical. If the internal volume as well as membrane area is fixed, shape changes can only occur if there is excess area. In this there are P_2 fluctuations [15] even in the absence of

vortices, and couplings between these and the vortex positions must be considered.

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(a)Permanent address: Department of Physics, University of Pennsylvania, Philadelphia, PA 19104.

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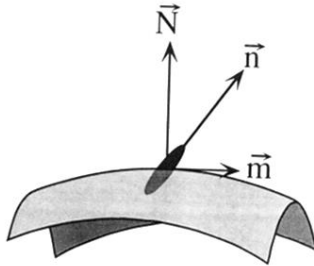


FIG. 1. Smectic-*C* order within a fluid membrane arises from a tilt of the constituent molecules (represented by the solid oval and unit director \mathbf{n}) relative to the unit surface normal \mathbf{N} . The surface component, $\mathbf{m} = \mathbf{n} - (\mathbf{N} \cdot \mathbf{n})\mathbf{N}$, represents a vector order parameter defined in the tangent plane perpendicular to \mathbf{N} .

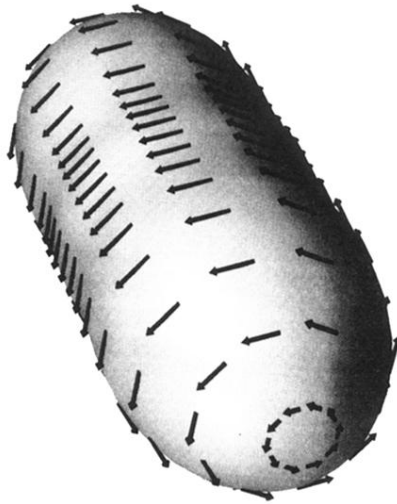


FIG. 2. In this view of an elongated vesicle, the tangent-plane order parameter corresponding to the represented shape has been depicted by the arrows. The tangent-plane order parameter is dimensionless, and its normalization has been chosen for clarity of presentation.