Composition-Driven Shape Transformations of Membranes of Complex Topology

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The shape of a phase-separated two-component membrane, which forms a square lattice of passages, is investigated in the strong-segregation limit. We employ a model, in which the composition of the membrane is coupled to the spontaneous curvature. The shapes of both the membrane and the interface between the two components are calculated as a function of composition. We predict a phase transition between two different domain morphologies. In the limit of vanishing line tension, we conjecture the existence of smooth, piecewise constant mean-curvature surfaces.

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Membranes made of amphiphilic molecules are present in many soft-matter systems [1,2]. Typical examples are surfactant monolayers, which assemble at the oil-water interface in microemulsions, and lipid bilayers, which form the walls of all biological cells. Membranes are often not homogeneous, but consist of two or more different components. These components can be either different species of amphiphiles [3,4]—in particular, phospholipids and cholesterol [5,6]—inclusions such as proteins which are embedded in an otherwise homogeneous amphiphile layer [7,8], or amphiphilic molecules with attached polymer chains [9,10].

The presence of several components in a membrane leads to the possibility of lateral phase separation. Since the composition and shape of a membrane are coupled locally, this leads to domain-induced shape changes or shape transitions. The effect of phase separation on the shapes of almost planar membranes [11–13] and of vesicles of spherical topology [14–18] has been studied recently in some detail. Here we study the effect of phase separation in a more complex topology, in which two membranes are connected by a lattice of passages. For homogeneous membranes, this type of topology has been observed in “catenoid” lamellar phases [19,20] of block-copolymer mixtures and in multilamellar vesicles of phospholipid membranes [21,22].

At low temperatures, the phase-separated domains consist almost exclusively of a single component, and the interface between the domains is very sharp. This is the strong-segregation limit we want to investigate in this paper, since the effect of phase separation on the membrane shape is most pronounced in this case. The strong-segregation limit has been investigated in Refs. [14,15,17] for vesicles, and in Ref. [13] for almost planar membranes [23]. At higher temperatures, the components begin to mix inside the domains, until the two-phase coexistence vanishes in a critical point.

Our calculations are based on the curvature Hamiltonian [13,14,17,24],

\[ \mathcal{H} = \kappa \int_S dx \, dy \sqrt{g(x,y)} [H(x,y) - H_0(x,y)]^2 + \lambda \int_{\partial S^\omega} dl, \]

where \( g(x,y) \) is the determinant of the metric tensor, \( H(x,y) \) the local mean curvature, \( H_0(x,y) \) a local spontaneous curvature, \( \kappa \) the bending rigidity, and \( \lambda \) the interface, or line, tension. We assume that the composition \( \phi \) is coupled to the local spontaneous curvature, but that the bending rigidity \( \kappa \) and the saddle-splay modulus \( \kappa_G \) are independent of \( \phi \). In the strong-segregation limit, the surface \( S \) consists of domains \( S^{(i)} \), which are composed entirely of component “\( i \)” (with \( i \in \{ \alpha, \beta \} \)). Within each domain \( S^{(i)} \), the spontaneous curvature is constant, \( H_0(x,y) = H_0^{(i)} \). For periodic membranes, the Gauss-Bonnet theorem implies that a Gaussian curvature term in the Hamiltonian gives a constant contribution to the energy in the case of a \( \phi \)-independent saddle-splay modulus; such a term is therefore omitted here. Finally, the line-tension integral is taken along the boundary \( \partial S^{(\alpha)} \) of the domains of component “\( \alpha \).”

We examine a square lattice of passages, with a passage in the center of the unit cell. The basic length and energy scales for the problem are set by the lattice constant \( L \) and the bending rigidity \( \kappa \). The values for the spontaneous curvatures are chosen to be significantly different for each component, \( LH_0^{(\alpha)} = 1.2 \) and \( LH_0^{(\beta)} = 0.4 \). The value of the reduced interface tension \( \lambda L / \kappa \) is set to \( 10^{-4} \), since we want to investigate the behavior of two-component membranes in the limit where the membrane shape is only weakly affected by the interface tension.

We consider membrane shapes which are symmetric with respect to the \( z = 0 \) plane, so that they can be described in the Monge representation by the ansatz

\[ \cosh^2(z) = B(x,y) \]

with \( B(x,y) \geq 0 \). This ansatz is motivated by the shape equation for the catenoid minimal surface, which is...
obtained from Eq. (2) by choosing $B(x, y) = x^2 + y^2$. For a lattice of passages, $B(x, y)$ is a periodic function. In this case, it can be expanded in the Fourier series

$$B(x, y) = a_0 + \sum_{i=1}^{N} a_i \sum_{j=1}^{N_{ij}} \cos(k_{ij} \cdot r),$$  \hspace{1cm} (3)

where $r = (x, y)$, and $N$ is the number of Fourier amplitudes. There are $N_{ij}$ reciprocal lattice vectors $k_{ij}$ in the $i$th shell. No $\sin(k_{ij} \cdot r)$ terms appear in the expansion (3) because we assume the full symmetry of the square lattice.

The shape of the domain boundary is written in cylindrical coordinates $(r, \theta, z)$ as

$$r(\theta) = r_0 + \sum_{i=1}^{N_{ij}} r_i \cos(4i\theta);$$  \hspace{1cm} (4)

the value of the $z$ coordinate follows directly from Eq. (2). We consider the two cases in which the center of the domain of one component [which is the origin of cylindrical coordinates of Eq. (4)] is located either at the middle or at the corner of the unit cell. In the former case, one of the components forms a ring-shaped domain inside the passage, and, in the latter, a caplet-shaped domain of circular topology forms outside the passages; compare Fig. 1. We denote these configurations “ring” and “caplet” morphologies, respectively.

The functional (1) is now minimized with respect to the coefficients $a_i$ and $r_i$ under the constraint of constant composition $\phi = S^\alpha/(S^\alpha + S^\beta)$. The number of coefficients $r_i$ is always the same ($N_{ij} = 5$). In order to check the accuracy of our numerical method, we have performed calculations for one-component membranes using Hamiltonian (1) with $H_0(\alpha) = H_0(\beta) = H_0$ and $\lambda = 0$. The computed energies for different $H_0$ in the range $0.25 < H_0 < 1.95$ are equal to zero within the numerical accuracy already for $N = 32$ in Eq. (3), indicating that the surfaces we have obtained for one-component systems are doubly periodic constant mean-curvature surfaces. For two-component membranes, such an accuracy cannot be easily achieved. One has to use a much larger number $N$ of coefficients $a_i$ because of the discontinuity of the mean curvature in the functional (1). The source of this discontinuity is the jump of the spontaneous curvature at the interface between the regions occupied by different components.

We have calculated the membrane shapes for different composition $\phi = S^\alpha/(S^\alpha + S^\beta)$ and various numbers of coefficients $a_i$, $N = 32, 49, 66,$ and $89$ (corresponding to lengths of the largest reciprocal lattice vector $k_{ij}^{(N)}$ equal to $8, 10, 12$, and $14$ in units of the $2\pi/L$). We want to emphasize that properties such as membrane area, the curvature energy depends significantly on $N$, and are already very accurately given for $N = 32$. However, the curvature energy depends significantly on $N$.

The form of the Hamiltonian (1) implies that the lowest energy is obtained when the mean curvature is locally as close as possible to the spontaneous curvature for each component, as long as the line tension is sufficiently small. However, membrane pieces of different composition have to fit together smoothly to form one differentiable surface without any holes or cusps [25].

Our data show that the free energy depends roughly linearly on the length $\ell$ of the domain boundary (for fixed $N$). This is demonstrated in Fig. 2, where we plot the (dimensionless) curvature energy—without the contribution of the line tension in Eq. (1)—per interface length, $E_{\omega}/L/k\ell$. The concentration dependence of this quantity shows some oscillations around the average value, the amplitude of which decreases with increasing $N$. More importantly, the increase of $N$ causes a decrease of the curvature energy. Both of these results can be attributed to the approximation of the discontinuity of the mean composition.
We observe that the curvature energy depends very little for an infinite number of the coefficients $a_i$ reduced line tension is of hypothesis. A linear extrapolation then gives values as a function of composition $\phi$ for different numbers $N$ of the coefficients $a_i$, as indicated. The reduced line tension is $\lambda L/\kappa = 10^{-1}$. The decrease of $E_b L/\kappa \ell$ with $N$ suggests that the energy for an infinite number of the coefficients $a_i$ could vanish.

We have therefore plotted the energy per unit interface length—averaged over all calculated concentrations—as a function of the inverse length of the largest reciprocal lattice vector for a given set of coefficients $a_i$ to test this hypothesis. A linear extrapolation then gives values $E_b L/\kappa \ell = (1.5 \pm 9.0) \times 10^{-5}$ (rings) and $E_b L/\kappa \ell = (6.5 \pm 9.0) \times 10^{-5}$ (caplets) for the reduced curvature energy in the limit $N \to \infty$. This result is very interesting from the point of view of differential geometry, since it suggests the existence of smooth piecewise constant mean-curvature (CMC) surfaces in the limit $\lambda \to 0$.

Less systematically, we have also done calculations for larger line tensions, with $\lambda L/\kappa = 10^n$ and $n \in [-3:1]$. We observe that the curvature energy depends very little on $\lambda$ for $\lambda L/\kappa \leq 10^{-1}$, and increases rapidly with $\lambda$ for $\lambda L/\kappa \geq 1$. This behavior is in good agreement with a simple scaling argument. The dimensionless curvature energy should only depend on the ratio of the two energy scales of the system, which is just the parameter $\lambda L/\kappa$. For $\lambda L/\kappa \ll 1$, the line tension should have little effect on the membrane shape, which is exactly what we find.

It is interesting to note that the existence of piecewise CMC surfaces for cylindrical vesicles (where one radius of curvature is infinite) of fixed area, and their generic absence for axially symmetric vesicles of spherical topology, has already been demonstrated in Ref. [17]. The doubly periodic lattice of passages considered here is the first example of a membrane geometry of nonzero Gaussian curvature, where piecewise CMC surfaces occur generically.

The fact that the total free energy depends primarily on the length of the domain boundary implies a phase transition between the caplet and ring morphologies as a function of concentration. This transition happens near the point where the interface lengths of the two morphologies are equal. The configurations shown in Figs. 1(b) and 1(c) demonstrate that the interface shape changes discontinuously at the transition. There is also a small jump of the total surface area of the membrane at the transition. However, no pronounced change of the radius of the passage at this first-order phase transition has been observed.

Another interesting phenomenon is the effect of the membrane topology on the shape of the domain boundary. For the ring morphology, the periodicity of the structure leads to deviations of the interface from a circular shape. The unit cell boundaries seem to act like a repulsive wall for the interface, so that the domain boundaries of neighboring passages do not merge. The deformations are larger the closer the interface approaches the boundaries of the unit cell; see Fig. 3. For caplets, the more the interface reaches into the inner part of the passages, the larger the deviations are from a circular shape. This is due to the competition between the formation of the shortest possible length of the interface and the adjustment of its shape to the topology of the membrane.

We have also studied changes of global properties of the membrane as a function of composition $\phi$. For the whole range of compositions, the shape of the passage in the $z = 0$ plane is circular, with negligible deviations. It is quite surprising to see that the radius of the passage in the $z = 0$ plane varies almost linearly with the composition $\phi$, for both rings and caplets. Moreover, the (average) radius is almost the same for caplets and rings of the same composition. Thus, the size of a passage can be changed easily by varying the composition. Figures 1(a) and 1(b) show configurations for small and large concentrations of the $\alpha$ component.
In summary, we have shown that the physics of multicomponent membranes of complex topology reveals new qualitative features which are absent in single-component systems. First, the shape of the domain boundary has been shown to be strongly influenced by the topology of the membrane. By changing the composition $\phi$, the membrane shape can be modified significantly. Second, the existence of smooth, periodic piecewise constant mean-curvature surfaces has been conjectured in the limit of zero line tension. Finally, a first-order phase transition between the caplet and ring morphologies has been found.

It is tempting to speculate that the mechanism of regulating the size of passages by changing the composition of a membrane may be used in cells or cell organelles. A possible application of two-component membranes could be the crystallization of membrane proteins in CMC surfaces [28], where the enrichment of one component near the protein provides an extra degree of freedom for optimal hydrophobic matching [29].

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[23] The case of a square or hexagonal lattice has been considered only approximately in Ref. [13], where the unit cell has been replaced by a circular disk of equal area.
[25] This follows directly from the form of the Hamiltonian (1), where the integral is over the whole surface (including the domain boundary).
[26] It can be shown analytically that in a Fourier representation of a surface with a discontinuity of the mean curvature along a line, the Fourier coefficients decay asymptotically as $|k|^3$ for wave vector $k \rightarrow \infty$. This implies that the domain-boundary contribution to the curvature energy decreases inversely proportional to the magnitude of the largest wave vector used in Eq. (3).
[27] In the case of adjustable area, we can show that piecewise CMC surfaces of spherical topology do exist in a limited range of concentrations and spontaneous curvatures.