

Mixed fluid bilayers: Effects of confinement

F. C. MacKintosh

Department of Physics, University of Michigan, Ann Arbor, Michigan 48109-1120

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A theoretical model for binary mixtures in fluid membranes is developed to study possible modulated phases in confined geometries. It is shown that two-component fluid bilayers can exhibit modulations of both membrane shape and composition when subject to confinement. In particular, lyotropic smectic phases can exhibit a transition to an undulated structure similar to that of the Helfrich-Hurault instability. In the case of binary mixtures, however, the resulting structure is stable. These results are also extended to freely suspended films, for which a transition to a modulated phase is predicted as a function of the film thickness.

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I. INTRODUCTION

Under a broad range of experimental conditions, amphiphiles such as phospholipids or surfactants can form bilayer membranes in water. These membranes are typically fluidlike—lacking any positional order of the constituent molecules. Such membranes are flexible and can form a variety of structures on length scales large compared with the individual amphiphilic molecules. Lamellar or smectic phases consist of ordered stacks of nearly flat bilayer “sheets.” These phases are studied experimentally both in bulk solutions and in freely suspended films of a few layers to hundreds of layers in thickness [1–3]. In solution, closed, single-bilayer or unilamellar vesicles can also form under certain conditions. In many cases of interest, mixtures of two surfactants or a surfactant and a cosurfactant have been studied. For instance, mixed-surfactant systems have been widely studied in connection with stable vesicles [4–7]. Single-surfactant vesicles appear to be possible (with or without cosurfactant) only in special cases [8–10].

The presence of more than one component in a fluid membrane leads to the possibility of phase separation or segregation within the two-dimensional membrane. An “internal degree of freedom,” such as composition, within the membrane can significantly influence the shapes and phase behavior of the membrane. A number of experimental and theoretical [5–7,11–15] studies have focused on the effects of segregation on the curvature properties of membranes. On the one hand, binary fluid mixtures provide a particularly simple example of a possible phase transition within a membrane. Such a phase transition is characterized by a single scalar order parameter ψ , which is the local composition of the two-dimensional fluid. On the other hand, this simple example would appear to be applicable to a variety of systems from the surfactant mixtures mentioned above to biological cell membranes involving multicomponent mixtures.

In this paper, we show that for mixtures of amphiphiles in membranes, lamellar phases can become unstable to modulations of both shape and composition. This is first

illustrated with an example of a single membrane confined between hard walls. We also consider the similar case of a stack of membranes either confined between walls or in a freely suspended film. The resulting instability is similar to the Helfrich-Hurault [16,17] effect in smectic liquid crystals subjected either to an applied magnetic field or an external tension. In contrast with the latter case, which is only metastable [17], however, the modulated structures of mixed bilayers can be stable.

Ordinary binary mixtures of simple liquids have been widely studied, in part, because of their critical behavior. Such mixtures are characterized by a single scalar order parameter ψ , which is the composition of the mixture. In the case of two-dimensional fluid membranes, however, the ability of the membrane to curve in the three dimensions in which it is embedded can lead to novel behavior for which there is no analog for ordinary fluids. Fluid membranes involving two or more components occur in a variety of systems from biological cell membranes to synthetic vesicles.

Several previous theoretical studies have concerned binary mixtures of surfactants or lipids in fluid membranes. Leibler and Andelman [12,13], for instance, showed that there can be phases of modulated composition and curvature of fluid monolayers. Such a phase can be stable in the case of a fluid film under tension because of the coupling of composition to curvature. Regions of different composition have different spontaneous curvatures.

In the case of a bilayer membrane, however, such a direct coupling of local composition of the bilayer to its curvature is not allowed by symmetry. Rather the curvature can couple to the local composition difference between the two halves (1 and 2) of the bilayer [5–7]. This is shown schematically in Fig. 1. Because regions of different average bilayer composition remain symmetric, such variations in the composition of a bilayer do not result in variations of the spontaneous curvature. (On time scales for which the exchange of surfactants between the two halves of the bilayer can be ignored, the composition of the bilayer can couple to the curvature of the membrane. This coupling can also arise if one of the surfactant components is constrained to only one side of the bilayer,

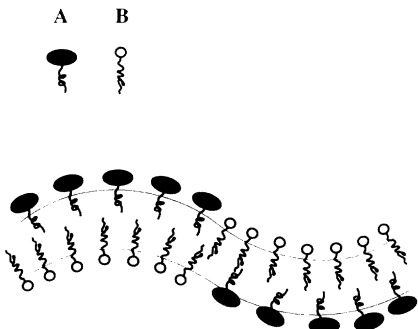


FIG. 1. Schematic view of a modulated bilayer composed of two surfactants A and B . If $\psi_{1,2}$ represent the relative concentrations of A in the top and bottom monolayers, respectively, then the composition asymmetry $\phi \propto \psi_1 - \psi_2$ is positive in the region on the left and negative in the region on the right. The presence of nonzero asymmetry ϕ results in curvature of the bilayer membrane.

in which case the bilayer symmetry is broken explicitly. Models based on such a constraint have been studied recently in the context of vesicles [15].) If, on the other hand, there is a difference in composition between the two halves of the bilayer, then this symmetry is broken and the bilayer can be curved. Thus $\phi \propto \psi_1 - \psi_2$, the difference in composition between the two halves of the bilayer, is the order parameter that has the strongest (i.e., lowest order) coupling to membrane shape.

II. MODEL

Below we assume the following Landau free energy per unit area at constant chemical potential μ for each half (monolayer) of the bilayer,

$$f_\psi = \frac{1}{2} \left[\frac{1}{2} c (\nabla \psi)^2 + \frac{1}{2} t \psi^2 + a \psi^3 + b \psi^4 - \mu \psi \right]. \quad (1)$$

Here ψ is the local composition of the monolayer. The normalization in Eq. (1) is chosen for simplicity of the resulting free energy per unit area of the bilayer. For a bilayer, there are two such contributions: one for each half of the bilayer. Thus

$$f_{\text{comp}} = \frac{1}{2} c [(\nabla \psi)^2 + (\nabla \phi)^2] + \frac{1}{2} t (\psi^2 + \phi^2) + a (\psi^3 + 3\psi\phi^2) + b (\psi^4 + 6\psi^2\phi^2 + \phi^4) - \mu \psi, \quad (2)$$

where the compositions of the two halves of the bilayer are $\psi_1 = \psi + \phi$ and $\psi_2 = \psi - \phi$. Here it is assumed that the interactions leading to eventual phase separation are primarily between the surfactant head groups. Thus, for instance, Eq. (2) is valid for a mixture of lipids with different polar head groups, but with the same hydrocarbon chains. From here on, we shall set $a = 0$, since it can be shown that the presence of the third-order terms in Eq. (2) will not affect the resulting phase diagrams in an es-

sentential way because of the absence of a third-order term in ϕ . For $a = 0$, the critical composition for the mixture is $\psi = 0$. Not only is there no third-order term in ϕ , but there is no chemical potential associated with the order parameter ϕ . For a bilayer, such terms can be present in the free energy only if the symmetry of the bilayer is explicitly broken. This would be the case, for instance, in a bilayer vesicle that has distinct “inside” and “outside” environments. Of course, such terms (as considered in Ref. [13]) must also be present for a fluid monolayer.

The sign of the order parameter ϕ depends on the orientation (choice of “inside” and “outside”) of the bilayer. Thus it is not strictly a scalar, but rather a pseudoscalar. [Note, for instance, the absence of a ϕ^3 term in Eq. (2).] These symmetry considerations alone would lead to a phenomenological model with each of the terms in Eq. (2), plus higher-order terms. The most general phenomenological model based on symmetry would have many more parameters than Eq. (2). The precise relationship between all of the parameters implied by Eq. (2) is not essential for the results derived below. For instance, the coefficients of ϕ^2 and ψ^2 need not be equal. In simple physical terms, this can arise from an interaction between the lipids on opposite sides of the bilayer. This might become important for short-chain surfactants. Provided that this interaction is not too strong, however, the phase diagrams predicted by the model in Eq. (2) will still be valid.

The curvature of the membrane also changes sign under inversion of the membrane. Therefore, the lowest-order coupling between composition and curvature is $\phi \nabla^2 h$, where $h(x, y)$ represents the height of the membrane above a reference plane. This Monge representation is valid for membranes that are nearly flat with only gradual variations of h . The mean curvature of the membrane in this representation is $H = \text{Tr} K_{ij} = \nabla^2 h$, where K_{ij} is the curvature tensor. [In contrast, the lowest-order coupling of average bilayer composition ψ to curvature is $\psi (\nabla^2 h)^2$.] From the symmetry considerations above, the leading curvature contributions to the free energy are given by

$$f_{\text{curv}} = \frac{1}{2} \kappa (\nabla^2 h)^2 + \gamma \phi \nabla^2 h. \quad (3)$$

Here κ is the bending elastic modulus for the bilayer. This curvature energy can also be motivated by consideration of the two monolayers that make up the bilayer, as was done for Eq. (2) above. The essential curvature properties of the two monolayers are summarized by

$$f_1 = \frac{1}{4} \kappa [H - H_0(\psi_1)]^2, \quad (4)$$

$$f_2 = \frac{1}{4} \kappa [-H - H_0(\psi_2)]^2.$$

Here $H_0(\psi)$ represents the preferred or spontaneous curvature of an individual monolayer. This spontaneous curvature depends on the composition ψ of the monolayer. Furthermore, because of the opposite orientation of the two halves of the bilayer, there is a relative sign difference

between the curvatures of the two halves represented by Eq. (4). Near the critical composition, H_0 can be expanded about the critical composition:

$$H_0(\psi) = c_0 + c_1\psi + \dots \quad (5)$$

Here only the leading terms have been retained. Higher-order terms have also been implicitly ignored in assuming that the bending modulus in Eq. (4) is independent of the composition. The resulting curvature energy for the bilayer, $f_1 + f_2$, is given by Eq. (3)—apart from terms that shift the energy, the chemical potential, or the transition temperature by constants. The coupling constant $\gamma = \kappa c_1$ has units of energy per length. The relevant energy scale is that of the bending modulus κ (typically several kT), while the length scale is given by spontaneous radius of curvature R_0 for an asymmetric distribution of the two surfactant components. Depending on the choice of the two surfactants, we expect this radius to be of order a few hundred angstroms. The other relevant parameters of the present model can also be estimated. For a binary fluid mixture that exhibits phase separation below a transition temperature T_c , the microscopic interaction energy is approximately kT_c . Equation (1) represents an energy per unit area of the membrane. Thus, if the area per molecule is $a_0^2 \simeq 40 \text{ \AA}^2$ [18], then $t \simeq a_0^{-2}(T - T_c)$. Furthermore, for a short-range interaction between head groups, $c \simeq kT_c$.

Strictly speaking, an additional Gaussian bending energy $\bar{\kappa} \det K_{ij}$ must be included. This contribution to the energy can be neglected for an asymptotically flat and homogeneous membrane, as it is a topological invariant. In the case of a mixed fluid membrane, this contribution can no longer be neglected in general since the Gaussian modulus $\bar{\kappa}$ may depend on the composition of the membrane. However, not only will this effect be of higher order than the terms in Eq. (3), but for the one-dimensional modulations considered here it can be neglected altogether.

III. CONFINEMENT OF A SINGLE MEMBRANE

As a simple illustration of the effects of confinement, we first consider the case of a single bilayer membrane confined between walls. This is sketched in Fig. 2. For a short-range interaction between the membrane and confining walls, the effect of the confinement can be modeled by the addition of a potential energy $V(h)$, which is a function of the membrane position $h(x, y)$ between the walls. For simplicity, we shall consider a harmonic potential, so that [19]

$$f = f_{\text{comp}} + f_{\text{curv}} + \frac{1}{2}kh^2. \quad (6)$$

The free energy density f_{curv} can easily be integrated over the area A of the membrane, with the result that

$$F_{\text{curv}} = \int f_{\text{curv}} dx dy \quad (7)$$

$$= A \sum_q \left[\frac{1}{2}(\kappa q^4 + k)|h_q|^2 - \gamma q^2 \phi_q h_{-q} \right]. \quad (8)$$

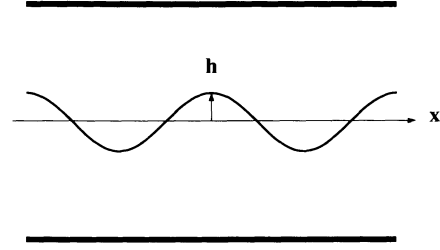


FIG. 2. The confinement of a single bilayer between hard walls is modeled by a potential $V(h)$ as a function of the height of the membrane above the midplane.

Within the mean field approximation, the effective free energy in terms of ψ and ϕ is determined by minimization of $F = \int f dx dy$ with respect to the amplitudes h_q , i.e., we set $\delta F / \delta h_q = 0$. This leads to

$$h_q = \frac{\gamma q^2 \phi_q}{\kappa q^4 + k}. \quad (9)$$

In the following, we consider $a = 0$ and $\mu = 0$. The effective free energy is

$$F_{\text{eff}} = A \sum_q \left[\frac{1}{2} \Gamma_q^{(2)} |\phi_q|^2 + b \int \phi^4 dx dy \right], \quad (10)$$

where

$$\Gamma_q^{(2)} = t + cq^2 - \frac{\gamma^2 q^4}{(\kappa q^4 + k)}. \quad (11)$$

In this model, three phases can occur. These are shown in the phase diagram as a function of t and γ in Fig. 3 for $\mu = 0$ and $a = 0$. At high temperatures t there is a single uniform flat phase. For $\gamma^2 < \gamma_0^2 = \sqrt{4c^2 k \kappa}$, ordinary phase separation (in this case of flat lamellae with $\phi = 0$) occurs for $t < 0$. This is the two-phase region indicated in Fig. 3. The two phases have compositions $\psi > 0$ and $\psi < 0$. For $\gamma^2 > \gamma_0^2$, there is an intermediate modulated phase for $\Gamma_q^{(2)} < 0$. On cooling, both transitions from the uniform phase are second order. The modulated phase is characterized by $\psi = 0$. Both ϕ and the membrane shape h are modulated. The wavelength $\lambda = 2\pi/q_0$ of the modulation is determined by minimizing $\Gamma_q^{(2)}$ with respect to q . In physical terms, this corresponds to the wavelength at which the uniform flat phase is most unstable. This analysis is valid near the transition, i.e., for $\Gamma_q^{(2)} \lesssim 0$. For $\gamma^2 \gtrsim \gamma_0^2$, this model predicts $q_0^2 \gtrsim \gamma^2 / (2c\kappa)$.

Near the transition, the modulated phase can be described in the single-mode approximation. The composition is assumed to have the simple form $\phi(x) \simeq \phi_0 \cos(qx)$, where it is also assumed that the modulation is in the x direction. The averaged free-energy density over one spatial period is

$$\langle f \rangle = \frac{1}{4} \Gamma_{q_0}^{(2)} \phi_0^2 + \frac{3}{8} b \phi_0^4. \quad (12)$$

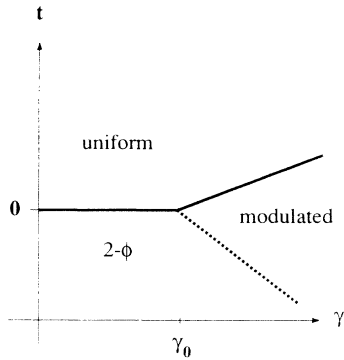


FIG. 3. The phase diagram for the model in Eq. (6) as a function of the reduced temperature t and the coupling γ for $a = 0$ and $\mu = 0$. The solid lines denote second-order transitions, while the broken line represents a first-order transition. There are three equilibrium phases. The *uniform* phase at high temperature is characterized by $\phi = 0$. For $\gamma < \gamma_0$, ordinary phase separation of two homogeneous phases occurs below $t = 0$. The two-phase region is indicated by $2 - \phi$. The two phases are flat ($h = 0$), but of different average composition ψ . For $\gamma > \gamma_0$, on the other hand, an intermediate *modulated* phase occurs in a temperature range near $t = 0$.

Within the mean field approximation, the free-energy density is

$$\langle f \rangle = -\frac{1}{48b} \left[\Gamma_{q_0}^{(2)} \right]^2. \quad (13)$$

As indicated in the phase diagram, for $\gamma^2 > \gamma_0^2$, the second-order transition from the uniform phase to the intermediate modulated phase occurs at a temperature $t > 0$. At a lower temperature, there is a first-order transition from the modulated phase to the two-phase region described above.

The phase diagram as a function of t and μ (or ψ) for fixed $\gamma^2 > \gamma_0^2$ is shown in Fig. 4. For $\mu \neq 0$, the equilibrium state is characterized by $\psi \neq 0$. For small enough $|\mu|$, the transition from the uniform phase to the modulated phase in the $t-\mu$ plane or the $t-\psi$ plane remains second order, but it is suppressed as shown in the figure. This transition becomes first order at tricritical points at $(t_0, \pm\mu_0)$ for $a = 0$. Below $t = t_0$, the modulated phase can coexist with either of two uniform flat phases.

IV. CONFINEMENT OF A SMECTIC DOMAIN

Consider an ideal single domain in the smectic- A phase. This is characterized by a stack of parallel membranes equally spaced in the direction perpendicular to the individual sheets. This defines the z direction. Thus the membranes are parallel to the x - y plane. Distortions of this ideal state can be described by the local displacement field $u(x, y, z)$, which represents the vertical (z) displacement of a membrane at (x, y, z) away from its ideal position. This is sketched in Fig. 5. The elastic energy

of distortions per unit volume can be described in terms of gradients of $u(x, y, z)$ [17,20]:

$$f_{\text{smectic}} = \frac{1}{2}K(\nabla^2 u)^2 + \frac{1}{2}\bar{B}\left(\frac{\partial u}{\partial z}\right)^2, \quad (14)$$

where ∇ refers to two-dimensional gradients in x and y . Here $K = \kappa/d$, where d is the average layer spacing and κ is the bending modulus of an individual membrane. The first term represents the curvature of the membranes at (x, y, z) , while the second term represents the compression of the stack. The phenomenological coupling of the curvature to $\phi(x, y, z)$, the local composition difference between halves of a bilayer at (x, y, z) , becomes

$$f_\gamma = \frac{\gamma}{d}\phi(x, y, z)\nabla^2 u(x, y, z). \quad (15)$$

Again, this is an energy per unit volume. Similarly, the

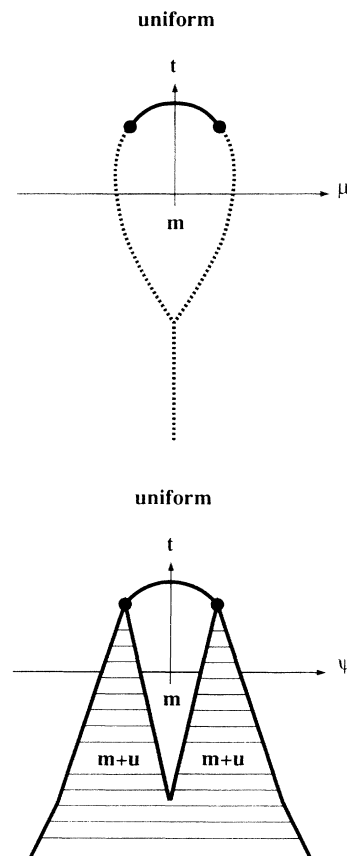


FIG. 4. (a) The phase diagram as a function of reduced temperature t and chemical potential μ for $\gamma > \gamma_0$. For a range of temperature t and chemical potential μ an equilibrium modulated phase m is predicted. This phase diagram exhibits both first- and second-order transitions. The solid line indicates a second-order transition from the high-temperature uniform phase to the modulated phase. The line of second-order transitions ends in a tricritical point, below which modulated and uniform flat phases coexist. (b) This coexistence is indicated by $m + u$. Here the phase diagram is shown in the t, μ plane.

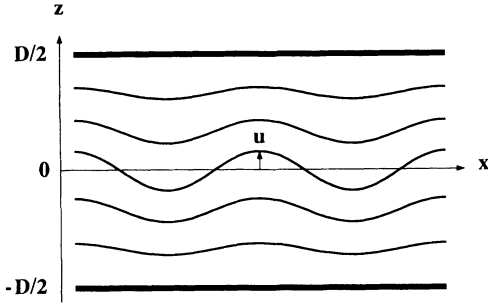


FIG. 5. For either a single smectic domain confined to a region $-D/2 < z < D/2$ or a freely suspended lyotropic film of thickness D a modulated phase can occur for increasing thickness or number of layers $n = D/d$.

mixing terms in the energy are

$$f_{\text{comp}} = \frac{1}{d} \left[\frac{1}{2} c (\nabla \phi)^2 + \frac{1}{2} t \phi^2 + b \phi^4 \right]. \quad (16)$$

As above, only the case $\psi = \mu = 0$ will be discussed in detail. The results are valid for compositions close to the critical composition. In Eqs. (15) and (16), only in-plane gradients of ϕ have been included. Thus direct interactions between adjacent membranes are not included. This should be valid, for instance, for lyotropic phases of phospholipids in water at sufficiently high water content.

For a stack of membranes confined between hard walls at $z = \pm D/2$, a modulation of u must satisfy the boundary conditions $u = 0$ at $z = \pm D/2$. Thus we assume a single undulation mode of the form [16,17]

$$u(x, y, z) = u_0 \cos(z\pi/D) \cos(qx). \quad (17)$$

We also assume a similar form for the accompanying modulation of the composition ϕ :

$$\phi(x, y, z) = \phi_0 \cos(z\pi/D) \cos(qx). \quad (18)$$

Within this single-mode approximation, the integrated free energy is given by

$$F = \frac{AD}{4} \left[\frac{1}{2} K q^4 u_0^2 + \frac{1}{2} \frac{\pi^2}{D^2} u_0^2 - \frac{\gamma}{d} q^2 \phi_0 u_0 + \frac{1}{2d} (t + c q^2) \phi_0^2 + \frac{9b}{16d} \phi_0^4 \right], \quad (19)$$

where A is the area of the sample in the x - y plane. The equilibrium amplitude of the modulation

$$u_0 = \frac{\gamma q^2 \phi_q}{d(Kq^4 + \bar{B}\pi^2/D^2)}. \quad (20)$$

Thus

$$F = \frac{AD}{d} \left[\frac{1}{8} \Gamma_q^{(2)} \phi_0^2 + \frac{9b}{64} \phi_0^4 \right], \quad (21)$$

where

$$\Gamma_q^{(2)} = t + c q^2 - \frac{\gamma^2 q^4}{(Kq^4 + \bar{B}\pi^2/D^2)d}. \quad (22)$$

As in Sec. III, there are three possible equilibrium phases. At high-temperatures t there is a single, uniform, flat phase. At lower temperatures, one of two flat phases can occur. These have different compositions ψ . In addition, an intermediate modulated phase can occur for $\gamma^2 > \frac{2\pi dc}{D} \sqrt{K\bar{B}}$. Thus, for example, as the thickness D of the sample is increased, there can be a transition from the high-temperature uniform phase to a modulated phase. For thick samples, this transition occurs for

$$t \simeq \gamma^2 / \kappa. \quad (23)$$

In this limit, the wavelength of the modulated phase is given approximately by

$$\lambda \simeq 2\pi \left(\frac{c\kappa}{\gamma^2} D^2 \lambda_0^2 \right)^{1/6} \lesssim \sqrt{D\lambda_0}, \quad (24)$$

where $\lambda_0 = \sqrt{K/\bar{B}}$ is the bare penetration length of the smectic. This is of order the layer thickness d . The phase diagram as a function of t and the number of layers $n = D/d$ is shown in Fig. 6. The transition occurs for

$$n > 2\pi \frac{c\kappa}{\gamma^2 d \lambda_0}. \quad (25)$$

While this phase diagram has been derived for the case of an oriented smectic domain between hard walls, a similar analysis can be done for a freely suspended film. In this case, instead of hard-wall boundary conditions, there is an excess free-energy proportional to the area of the top and bottom layers of the film, which we assume to be at $z = \pm D/2$. As in the case of the hard-wall boundary conditions, this also has the effect of suppressing undulations of the membranes. In fact, it can be shown that in the limit of thick films, the above results are applicable to

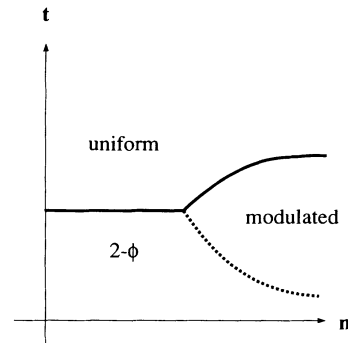


FIG. 6. The phase diagram for a confined smectic or a freely suspended film as a function of the reduced temperature t and the number of layers n . The solid lines denote second-order transitions, while the broken line represents a first-order transition. There are three equilibrium phases. The *uniform* phase at high temperature is characterized by $\phi = 0$. In thin films, for example, ordinary phase separation of two homogeneous phases is predicted below $t = 0$. The two phases are flat, but of different average composition ψ . For thick films, an intermediate *modulated* phase occurs in a temperature range near $t = 0$.

freely suspended films. For thin films, on the other hand, the finite compression modulus \bar{B} leads to a modulated phase characterized approximately by

$$u(x, y, z) = u_0 \cos(qx), \quad (26)$$

which is independent of z . The free energy in this case is

$$F = \frac{AD}{d} \left[\frac{1}{4} \Gamma_q^{(2)} \phi_0^2 + \frac{3b}{8} \phi_0^4 \right], \quad (27)$$

where

$$\Gamma_q^{(2)} = t + cq^2 - \frac{\gamma^2 q^4}{(Kq^4 + \frac{2\sigma}{D}q^2)d}. \quad (28)$$

This model is similar to that of Ref. [13], although no linear or third-order terms in ϕ are allowed by symmetry here. In this model, the intermediate modulated phase occurs for $\gamma^2 > 2\sigma cd/D$. Thus a transition is expected with increasing thickness D for a fixed value of γ . The optimal wave vector is given by

$$q_0^2 = \left(\gamma - \sqrt{\frac{2\sigma cd}{D}} \right) \sqrt{\frac{2\sigma d}{cD\kappa^2}}. \quad (29)$$

The transition is second order. At this transition, the wavelength of the modulation diverges. Furthermore, with increasing sample thickness D ,

$$q_0 \sim D^{-1/4}. \quad (30)$$

For thicker films, the effect of surface tension at the boundaries is to suppress undulations at $z = \pm D/2$. As $D \rightarrow \infty$, the effect of surface tension becomes the same as that of hard walls. This is because the hard-wall boundary conditions cost an elastic energy

$$\Delta f \sim \bar{B} \frac{\pi^2}{D^2} u_0^2 \sim D^{-2}, \quad (31)$$

averaged over the volume of the sample. For a modulation given by Eq. (26), however,

$$\Delta f \sim \frac{\sigma}{D} q_0^2 u_0^2 \sim D^{-3/2}. \quad (32)$$

Thus the amplitude of the undulation at the surface of the film is expected to decrease relative to the center of the film as the film thickness is increased. A similar effect has been reported for the amplitude of fluctuations in single-component films of varying thickness [21].

V. DISCUSSION

As the above shows, the coupling of membrane composition to curvature can lead to undulated membrane structures in confined geometries. In the case of a single, oriented smectic domain confined between hard walls, the resulting instability of the uniform flat smectic phase is reminiscent of the Helfrich-Hurault instability of single-component smectics under mechanical tension. This occurs if the separation between the confining plates is

increased. An undulated structure forms in order to achieve the ideal spacing between layers. However, this structure is only metastable, as the true constrained equilibrium structure can be achieved by changing the number of layers.

In the case of the two-component system studied above, the undulated structure is an equilibrium phase. Such modulated phases are also predicted for freely suspended films of mixed surfactants. In this case, for thin films the modulated phase is similar to that predicted for monolayers in Ref. [13] since the surface tension is responsible, in part, for the instability of the flat film. In contrast with the model of Ref. [13], however, no hexagonal modulated phase is expected here. This is because of the symmetry considerations for bilayers described above. In particular, no third-order term in ϕ is allowed by symmetry. Similarly, no chemical potential associated with ϕ is possible. This is analogous to the absence of a physically realizable staggered magnetic field conjugate to the staggered magnetization in magnetic systems. In the absence of such a "staggered chemical potential," only the stripe phase was predicted in Ref. [13]. Furthermore, as Sec. IV shows, with increasing thickness of a freely suspended film, the behavior of this model is expected to approximate that of the confined smectic domain. The finite compression modulus of the smectic allows the film to reduce the excess free energy of the top and bottom layers of the film. For typical values of the parameters

$$\kappa \simeq 10kT, \quad c \simeq kT, \quad \lambda_0 \simeq d \simeq 50 \text{ \AA},$$

$$R_0 = \kappa/\gamma \simeq 500 \text{ \AA}, \quad (33)$$

the modulated phase is predicted for $n \gtrsim 100$ layers. From Eq. (24) the corresponding wavelength is approximately $\lambda \simeq \sqrt{nd} \gtrsim 500 \text{ \AA}$. Furthermore, by Eq. (23), the temperature range of stability of the modulated phase is given by

$$\Delta t \simeq a_0^{-2} k \Delta T \simeq \gamma^2 / \kappa. \quad (34)$$

For the parameters given above, together with $T_c \simeq 300 \text{ K}$, this temperature range is about 1 K in thick films. For a greater asymmetry between the constituents, the characteristic radius of curvature is smaller. This would lead to a modulated phase for thinner films [22] and for a broader temperature range.

In contrast with both the confined smectics and freely suspended films considered above, similar modulated phases are not expected in *bulk* smectics within the model considered here. In the bulk, the wavelength of the resulting instability becomes infinite. (It can also be shown that the penetration length λ_0 diverges near the transition [17].) The resulting $q = 0$ instability, however, is not necessarily that of phase separation of flat lamellar phases. Rather it was shown in Ref. [7] that, in bulk solutions of sufficiently low concentration of surfactant, an equilibrium phase of vesicles is predicted for compositions near the critical composition for the mixture. In this case, the size of the vesicles is determined by the

amplitude of the instability.

The model described above has been treated within mean field theory. Thermal fluctuations, which have been ignored above, can significantly affect the stability of modulated phases. It is known [23] that in systems characterized by preferred fluctuations of finite wavelength [as illustrated by Eqs. (11), (22), and (28)], thermal fluctuations can destabilize the uniform phase relative to a modulated phase. Furthermore, the resulting transition is first order. Thus we expect that the presence thermal fluctuations may lead to first-order transitions from the high-temperature uniform phases to the modulated phases as the temperature is lowered in Figs. 3 and 4.

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