

Curvature interfacial transitions in amphiphile monolayers and their possible relation to the onset of micelle formation

A. Robledo

*Instituto de Física, Universidad Nacional Autónoma de México, Apartado Postal 20-364,
01000 México, Distrito Federal, Mexico*

C. Varea and V. Talanquer

*Facultad de Química, Universidad Nacional Autónoma de México, 04510 México, Distrito Federal, Mexico
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We describe two types of curvature-related interfacial transitions occurring in *soluble* amphiphile monolayers under compression. The first type corresponds to the buckling of areas with sizes up to the monolayer's de Gennes-Taupin persistence length squared, and starts to occur when the interfacial tension is about one-half its bare value. The second type corresponds to the transformation of the simply connected monolayer into either a dispersion of droplets or an interconnected bicontinuous structure. The resulting type of volume-spanning state is determined by the sign of the saddle-splay bending constant.

Two of the most familiar manifestations of the unique nature of amphiphiles—molecules with different attributes at opposite ends—are the formation of compact monolayers at interfaces and of micellar aggregates in the bulk phases. Although descriptions of the onset of micelle assemblage, at the so-called critical micellar concentration (CMC), are often preceded by that of the development of interfacial monolayers, these two forms of amphiphile collective configurations have not been explicitly characterized as states linked by a phase transition. Here we investigate a model amphiphile monolayer described by the Helfrich free energy and find two types of curvature-related transitions occurring under monolayer compression.

An important feature in our analysis is the consideration that the amphiphiles are soluble in the monolayer's supporting solvent or solvents and that the entire interface between, say, water and air, or water and oil, like in a simple test tube, is constituted by the monolayer. We assume that the projected area of the interface on a plane S_0 is fixed, and that compression of the monolayer takes place (below the CMC) by increments in the amphiphile bulk concentration, i.e., increments in interfacial adsorption produce a reduction of the interfacial area per surfactant molecule. We choose S_0 fixed because any change in S_0 will be accompanied by the transference of amphiphiles between the monolayer and the bulk phases, leaving the film pressure unchanged. In contrast, compression of an *insoluble* surfactant monolayer in a Langmuir trough is accomplished externally via the reduction of S_0 . In this case the total interfacial area is composed of two portions separated by an amphiphile barrier: the monolayer and the amphiphile-free interface. The reduction of S_0 by the displacement of the barrier produces by construction an increment of the same magnitude in the area of the amphiphile-free interface. As we see below, there is an important difference in the free-energy expressions, and in the properties derived from them, between these two physical situations.

We follow Helfrich,¹ and others,²⁻⁷ in considering a simple phenomenological model in which the monolayer formed at a water-vapor (or water-oil) interface is treated as a two-dimensional incompressible fluid film, $\zeta(x,y)$, embedded in three-dimensional space. This type of model membrane has been mostly employed in the description of sheetlike bilayer assemblies implanted in a single solvent, but regions of immiscible solvents separated from one another by amphiphile monolayers have been similarly treated.^{2,4,6,7} The free energy f_{film} per unit area that quantifies the curvature elastic energy of the system is

$$f_{\text{film}} = \frac{1}{2} \kappa (c - 2c_0)^2 + \bar{\kappa} C, \quad (1)$$

where κ and $\bar{\kappa}$ are, respectively, the splay and saddle-splay bending constants and c , c_0 , and C are, respectively, the mean, spontaneous, and Gaussian curvatures of the film. The Gauss-Bonnet theorem, stated below, tells us that it is not necessary to take the last term in Eq. (1) into account if one considers only variations of the film shape which do not change its topology, since the integral of C over the whole film area is a topological invariant. To study the shape response of the surface to compression, e.g., when the film amphiphile concentration is increased, additional contributions to the free energy need to be taken into account. These are the work of compression with its concomitant increment in surface energy that takes place whenever a local bending of the film occurs, i.e., there is a monolayer enlargement sustained by a net inflow of amphiphiles from the environment since no ruptures or pores are allowed. To write these contributions let

$$dS = \left[1 + \left(\frac{\partial \zeta}{\partial x} \right)^2 + \left(\frac{\partial \zeta}{\partial y} \right)^2 \right]^{1/2} dx dy$$

and $dS_0 = dx dy$ denote, respectively, area elements of the monolayer and its planar projection. The work of compression is $-\Pi(dS - dS_0)$, where Π is the Langmuir surface pressure of the film [$\Pi = \gamma_0 - \gamma > 0$, and γ and γ_0 are the actual interfacial tension and the bare (in the absence

of amphiphile) interfacial tension, respectively]. Now, a compact monolayer that maintains its area per amphiphile constant when it is deformed out of its planar shape will produce a bare area element $ds - dS_0$, which when filled with amphiphile contributes an amount $\gamma(ds - dS_0)$ to the monolayer's free energy. Therefore, the free energy in excess per unit area between bent and flat states f can be written as $f = f_{\text{film}} + f_{\text{comp}}$ where

$$f_{\text{comp}} = -\lambda \left\{ \left[1 + \left(\frac{\partial \zeta}{\partial x} \right)^2 + \left(\frac{\partial \zeta}{\partial y} \right)^2 \right]^{1/2} - 1 \right\}, \quad (2)$$

and where $\lambda = \Pi - \gamma = \gamma_0 - 2\gamma$.

Surfactant monolayers under compression have been recently⁷ studied with the employment of a similar free-energy expression. However, the system studied in Ref. 7 corresponds to insoluble amphiphiles on a Langmuir trough and, as mentioned, differs from ours in that reduction in the monolayer's projected area is accompanied by an equivalent increment in the trough's amphiphile-free surface area with bare tension γ_0 . Thus, instead of the monolayer enlargement term one must consider the contribution $\gamma_0(ds - dS_0)$, and λ in Eq. (2) becomes $\lambda = \Pi - \gamma_0 = -\gamma$. Insoluble monolayers have a fixed number of amphiphiles, whereas any departure in shape of a soluble monolayer with respect to the reference flat state $\zeta(x, y) = 0$ will lead to an increment in the film area, i.e., deformations are always accompanied by the creation (or destruction) of portions of monolayer through exchange of amphiphiles with the bulk.

The monolayer thermal shape fluctuations, or undulations, imply that normals to $\zeta(x, y)$ have their directions correlated only up to a length ξ which is called the de Gennes-Taupin persistence length,² therefore, the monolayer can be considered on average to consist of a collection of independent patches, or units, of sizes of $O(\xi^2)$ within each of which the film retains coherence. Film portions with areas increasingly smaller than the maximum size of $O(\xi^2)$ would appear to be more tightly bound objects since they have increasingly higher correlated orientations throughout. As suggested by Helfrich,⁸ and subsequently confirmed by renormalization-group calculations,³ the monolayer undulations produce a reduction of κ with increasing observation scale length l , or equivalently, with increasing membrane size l , according to the expression $\kappa(l) = \kappa_m + (3kT/4\pi)\ln(a/l)$, where κ_m is the microscopic scale-length value of κ , and a is some microscopic distance, e.g., the amphiphile size.⁹ At the scale-length equal to the persistence length ξ , given by $\xi = a \exp(4\pi\kappa_m/3kT)$,⁹ the effective rigidity $\kappa(\xi)$ vanishes, that is, *only sections or pieces of film with areas up to $O(\xi^2)$ are sustained as structural units with well-defined uniform and unbroken average shapes*. Undulations also lead to the renormalization of the tension and the saddle-splay constant, and for a membrane size or scale length l one obtains $\gamma(l) = \gamma_m [1 + (1/4\pi)\ln(l/a)] - akT[(1/a)^2 - (1/l)^2]$ and $\bar{\kappa}(l) = \bar{\kappa}_m + (5/6\pi)\ln(l/a)$, where γ_m and $\bar{\kappa}_m$ are the microscopic scale-length values of γ and $\bar{\kappa}$, and a is a constant.⁹ (The effect of the renormalization upon c_0 is not considered here.) It is important to notice that the derivation of the expressions for the re-

normalized $\kappa(l)$ and $\bar{\kappa}(l)$ do not require the microscopic tension γ_m to vanish.^{3,9}

Therefore, in order to examine the bending of coherent pieces of film at the chosen membrane portions of size l about their average or coarse-grained flat states, we minimize $F = \int f dS$, with $\kappa = \kappa(l)$, $\bar{\kappa} = \bar{\kappa}(l)$ and $\gamma = \gamma(l)$, $a < l < \xi$, only over an area of $O(l^2)$, say a circle of radius l with the boundary condition $(\partial\zeta/\partial r)_{r=l} = 0$. The problem is seen now to be analogous to that of the buckling under compression of an elastic plate, familiar in the theory of strength of materials. First, we consider the size dependence only on κ , and then comment on the modifications of our results for size-dependent γ (the dependence of $\bar{\kappa}$ on l is unimportant here). The Euler-Lagrange equation associated to Eq. (3) indicates that the interface remains flat provided $\lambda < \lambda_c$, but it bends progressively with increased compression when $\lambda < \lambda_c$. For the geometry we have chosen, solutions of the form $\partial\zeta/\partial r \sim J_1(\lambda^{1/2}\kappa^{-1/2}r)$ (where J_1 is the Bessel function of the first kind) bifurcate from the trivial solution $\partial\zeta/\partial r = 0$ when $J_1(\lambda_c^{1/2}\kappa^{-1/2}l) = 0$, this is $\lambda_c = 14.68\kappa l^{-2}$ or $\gamma_c = \gamma_0/2 - 7.34\kappa l^{-2}$. Buckling occurs first at the maximum scale length or portion size ξ when $\gamma = \gamma_0/2$ (which is often observed to be a rough value for γ at the CMC), followed with further amphiphile additions, by the buckling associated to smaller scale lengths or portion sizes. We obtain a line of self-similar buckling transitions for which the critical $\lambda_c(l)$ and the effective $\kappa(l)$ scale with the size l of the bulges or prominences created out of the flat surface (see Fig. 1). The critical value of the interfa-

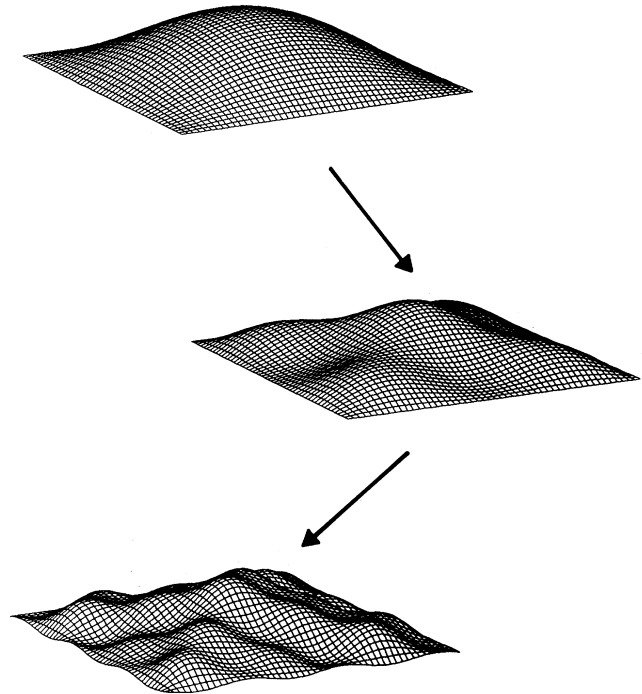


FIG. 1. When the monolayer is progressively compressed via amphiphile additions it buckles first at a critical value of the interfacial tension with sizes of the order of its persistence length. Further compression produces buckling at smaller scales.

cial tension γ_c decreases with decreasing l and vanishes at a limiting length ξ' given by $\gamma_0 = 14.68\xi'^{-2} [\kappa_m + (3kT/4\pi)\ln(a/\xi')]$. When a renormalized tension $\gamma(l)$ is considered the line of buckling, transitions may no longer show a monotonic decrement in bulge size with increasing compression, and appear with sizes smaller than $O(\xi^2)$.

In Ref. 7 a buckling instability for the entire macroscopic monolayer of size L in a Langmuir trough was found to occur, in the absence of gravity, at a negative tension $\gamma_c = -\pi^2\kappa_m/L^2$, or vanishing tension for an infinite monolayer. In Ref. 7 no undulations were considered, and therefore the buckling wavelength is of the order of the monolayer size. The consideration of gravity greatly reduces the buckling wavelength and also the absolute value of γ_c but it remains negative.⁷ The difference in the value of γ_c between the two types of monolayers, soluble and insoluble, is easily accounted for by their different definition of λ , $\gamma_0 - 2\gamma$, and $-\gamma$, respectively, in Eq. (2).

We now discuss the implications of the Gaussian term in f_{film} . For a system of surfaces that consists of a simply connected piece to which n_h handles have been attached and an n_s boundaryless disjoint pieces or spheres, the Gauss-Bonnet theorem states that

$$\int C dS = 2\pi(1 + 2n_s - 2n_h). \quad (3)$$

Thus, the free-energy cost f_{top} for creating a sphere of radius R (plus sign), or a handle of equivalent size and curvature (minus sign), out of the simply connected interface is

$$f_{\text{top}} = \left[\gamma + 2\kappa \left(\frac{1}{R} - c_0 \right) \pm \frac{\bar{\kappa}}{R^2} \right] 4\pi R^2. \quad (4)$$

Therefore, when f_{top} vanishes the interface undergoes a phase transition in which its connectivity changes, and according to the sign of $\bar{\kappa}$, the magnitude of $\int C dS$ jumps from a value of 2π to $\pm\infty$ (see Fig. 2). The gain in configurational entropy by fragmentation of spheres or proliferation of handles stabilizes the volume-filling phase. The size of the objects formed can be estimated from $f_{\text{top}} = 0$, e.g., when $c_0 \approx 0$, $R \approx [(2\kappa + \bar{\kappa})/\gamma]^{1/2}$. For micellar solutions formed in the presence of monolayers at water-vapor interfaces, $2\kappa + \bar{\kappa} \sim 10^{-12}$ erg and $\gamma \sim 10$

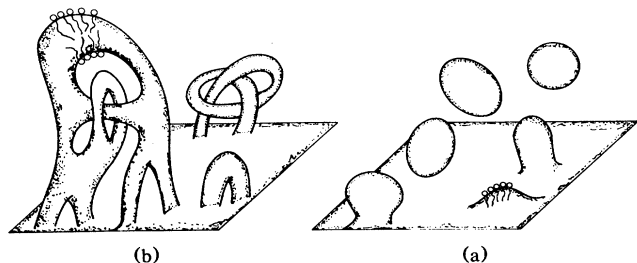


FIG. 2. Topologically driven interfacial transitions. (a) A dispersion of droplets is obtained when the saddle-splay constant $\bar{\kappa} < 0$. (b) Proliferation of handles produces a bicontinuous structure when $\bar{\kappa} > 0$.

erg/cm², then $R \sim 30 \text{ \AA}$ which is a reasonable value for empty micelles. On the other hand, for microemulsions formed in the presence of monolayers at water-oil interfaces (containing cosurfactants), $2\kappa + \bar{\kappa} \sim 10^{-13}$ erg and $\gamma \sim 10^{-2}$ erg/cm², one obtains $R \sim 300 \text{ \AA}$, and thus larger objects support the swollen micellar or bicontinuous microstructures of these systems. When undulations are taken into account [and f_{top} is minimized with size-dependent $\gamma(R)$, $\kappa(R)$, and $\bar{\kappa}(R)$] one obtains

$$R = [a'kT/(8\pi\gamma + \gamma_m)]^{1/2},$$

where $a' = 8\pi[a + (1/3\pi)]$, i.e., $\gamma R^2 \sim kT$. Hence, for given γ fluctuating structures produce objects larger than those quoted above if $a'kT/[8\pi + (\gamma/\gamma_m)] > -(2\kappa + \bar{\kappa})$. Recalling that buckling (at the scale of ξ) takes place when $\gamma \sim \gamma_0/2$, micellization can occur before buckling only if $\gamma_0 < (1/4\pi)(kTR^{-2} - \gamma_m)$, where R is determined from

$$2\kappa_m + \bar{\kappa}_m = (2kT)/(2\pi)\ln(R/a) + (1/8\pi)(\gamma_m R^2 - a'kT).$$

In contrast, since handles can be created with zero curvature, whenever $\bar{\kappa} > 0$, handles proliferate before buckling.

The possibility of topological changes governed by the Gaussian curvature have been discussed before,^{6,10,11} however, we specifically address here the case of the instability of a single interface consisting of a monolayer and stress its possible relation with the well-known phenomena that takes place at the so-called critical micellar concentration. To demonstrate the usefulness of this approach a description of the (incompletely understood) CMC phenomena associated to Winsor microemulsion phases¹² can be readily obtained in terms of the monolayer topologically driven transitions. A straightforward generalization of the bilayer expression for κ derived by Petrov, Mitov, and Derzhanski¹³ for monolayers leads to the following expressions for c_0 and $\bar{\kappa}$

$$c_0 = \frac{A_h A_c (1/A_h - 1/A_c) (k_h/A_h^2 + k_c/A_c^2)}{2d(k_h/A_h + k_c/A_c)} \quad (5)$$

and

$$\bar{\kappa} = \frac{k_h k_c (1/A_h - 1/A_c) (k_h/A_h^2 - k_c/A_c^2) d}{A_h A_c (k_h/A_h^2 + k_c/A_c^2)^2}, \quad (6)$$

where A_h and A_c are the mean area per head and per area of the amphiphile, respectively, k_h and k_c are positive constants defined in Ref. 13, and d is the monolayer thickness. An inspection of the factors in the expressions for c_0 and $\bar{\kappa}$ above indicates that increments in salinity of the aqueous solvent, or decrements in the length of the amphiphile hydrocarbon chain (which are likely to produce either monotonic increments in k_h and A_h or monotonic decrements in k_c and A_c) may lead to one change in the sign of c_0 and two changes in the sign of $\bar{\kappa}$,¹⁰ such that addition of amphiphile to bare water-oil interfaces prepared with different bulk salt concentration yield oil-in-water micellar, bicontinuous, or water-in-oil micellar microemulsion phases. The required equality of chemical potentials for phase coexistence between (one or two) bulk solvent phases and the incipient microemulsion phase formed from the fragmentation or handle proliferation of

the original monolayer is given by the soluble amphiphile factor $\lambda = \gamma_0 - 2\gamma$ in Eq. (2).

We remark here on a similarity between wetting and micellization phenomena. One of the wetting transitions takes place at the interface of a two-phase state when three-phase equilibrium is approached. There, the thickness of the interface diverges signaling an instability caused by the saturation of the species with smallest concentration in the interfacial region, and the alternative structure for this region is the appearance of the phase rich in this component in bulk. In a manner analogous to this wetting transition we found that the increment in amphiphile concentration eventually saturates the interfacial region forcing again its instability. The monolayer requires an alternative that would let it occupy volume, only now the appearance of a third phase, partially miscible in the former two, is not favored. The aggregation of the amphiphiles into volume-filling structures, micellar or bicontinuous, is the prevailing alternative. Wetting and curvature transitions relate, respectively, to area extension

and bending energy costs of interfacial fluctuations. Generally $\gamma > \gamma_0/2$, and the effects of the former type of fluctuations conceal the physical features of the latter; however, amphiphiles efficiently suppress interfacial tension and the latter type of transitions may occur in systems that contain them.

Our aim has been to offer a minimal model for the characterization of the curvature interfacial transitions (we have not considered at this stage possible transformations under compression of the monolayer internal structure that may arise from degrees of freedom such as amphiphile-tail conformations). Although the breakdown of Langmuir monolayers under compression is a well-known phenomenon, the experimental investigation of the interfacial transitions discussed here, do not correspond to those of an insoluble monolayer in a Langmuir trough.¹⁴

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