Curvature Instability of Diblock Copolymer Bilayers

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Received November 14, 1991; Revised Manuscript Received April 6, 1992

ABSTRACT: The curvature expansion of the free energy for diblock copolymers aggregated into bilayers is studied for strongly incompatible diblocks. It is shown that sufficient asymmetry in the diblock composition leads to an instability of the flat bilayer with respect to spherical or saddle-splay deformations: when the bilayer consists of two (diblock copolymer) monolayers each having a strong tendency to curve convexly toward the solvent, i.e., when the outer block is much larger than the inner block, spherical vesicles become favored by the curvature elastic free energy over flat bilayers. In the opposite case, saddle-splay deformations are favored.

Amphiphile molecules in solution can self-assemble to form a large array of structures,[1] including dispersed globular and wormlike micelles, spongelike bicontinuous phases, and lyotropic liquid-crystalline phases, such as lamellar, hexagonal, and cubic structures. In all cases, knowledge of the properties of the individual aggregates is a crucial first step toward a full understanding of the larger scale structures which result from the delicate balance between the intra- and interaggregate interactions.

In this paper, we study a bilayer membrane formed from polymeric amphiphiles, namely, A–B diblock copolymers. We focus on the stability of the bilayer with respect to small curvature deformations. Specifically, we address the question of whether a curved (uniformly curved or saddle-shaped) bilayer can be favored over the flat bilayer. The answer to this question bears obvious relevance to the spontaneous formation of vesicles and the bicontinuous phases; the latter are believed to consist of membranes that are saddle-shaped.[2-5]

To be concrete, consider A–B diblock copolymers in a B-like solvent. Then the bilayer membranes that are expected to form have the A-blocks in the interior of the bilayers and the B-blocks in the exterior. In the calculations which we present, we study the case where the A–B blocks are strongly incompatible and where the B-like solvents are homopolymers of large molecular weight, so that the two blocks are well separated with a sharp interface and there is little penetration of the solvent polymers into the B-layers.[6] The case of small B-solvent molecules which swell the B-layers is briefly discussed at the end of the paper.

Consider, then, a symmetric bilayer made up of two diblock copolymer monolayers. Now impose a (uniform) curvature deformation of the bilayer as shown in Figure 1. The free energy of each monolayer is a function of the curvature and the number of chains per unit area (*both measured with respect to the midsurface of the bilayer*) and depends on the molecular weights of the two blocks forming the monolayer. If we let x be the fraction of chains in the inner monolayer and $1 - x$ be the fraction of chains in the outer monolayer, we may write the free energy per chain as

$$F = xf(\sigma_i,-c) + (1-x)f(\sigma_o,c) \tag{1}$$

where $c = 1/R$ is the curvature, and σ_i and σ_o are, respectively, the number of chains per unit area in the inner and outer monolayers. Clearly, the assignment of the inner and outer monolayers is arbitrary, since by symmetry the free energy of the bilayer is invariant with respect to a change in the sign of the curvature.

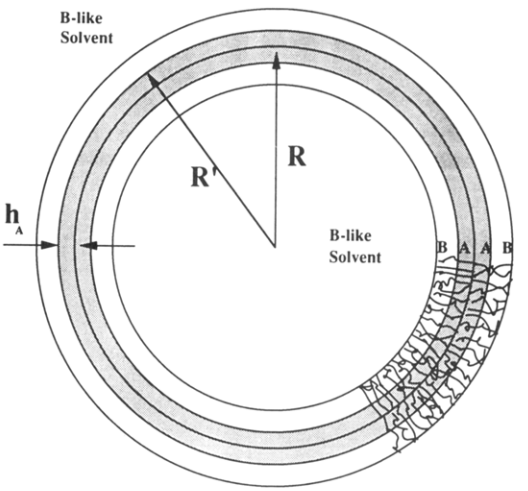

Figure 1. Schematic cross-sectional view of a uniformly-curved bilayer formed from A–B diblock copolymers. R is the radius of curvature for the bilayer, defined with respect to the midsurface of the bilayer, and R' is the radius of curvature for the outer monolayer, defined with respect to the A–B junction points in the outer monolayer.

The fraction x is simply related to σ_i and σ_o via $x = \sigma_i/(\sigma_i + \sigma_o)$. Hence, eq 1 becomes

$$F = \frac{\sigma_i}{\sigma_i + \sigma_o} f(\sigma_i,-c) + \frac{\sigma_o}{\sigma_i + \sigma_o} f(\sigma_o,c) \tag{2}$$

If we allow free exchanges of molecules between the two monolayers as well as between the bilayer and the reservoirs, then both σ_i and σ_o are variable. For a given curvature, the free energy is minimized with respect to these quantities. As a result, both σ_i and σ_o depend on the curvature, and the full curvature expansion will have contributions from this dependence. The stability of the flat bilayer can then be inferred from the sign of the quadratic term(s); the linear term vanishes by symmetry.

The symmetry of the bilayer implies that the functional form of the free energy (per chain) for the outer monolayer and that for the inner monolayer are the same. Therefore, we only need to consider one side of the bilayer. For concreteness, we choose to work out the free energy for the outer monolayer. We have included some details of the calculation in order to expose some subtleties in the curvature expansion that do not seem to have been given due attention by other researchers. However, readers who are not interested in these details may go directly to eq 15.

In the strongly-segregated limit, the free energy of a block copolymer monolayer consists of the interfacial

0024-9297/92/2225-3702$03.00/0

energy and the (entropic) stretching free energy of each block. (The two-dimensional translational entropy of the junction points are negligible compared to the dominant free energy contributions mentioned above, in the limit of very long chains.) The free energy for the monolayer has been calculated as a curvature expansion to second order in curvatures by Milner and Witten[7] and by Wang and Safran.[8,9] In the case of a monolayer, the radius of curvature is measured from the center of the curvature to the locus of *junction points* of the two blocks as indicated in Figure 1; the area per chain is also measured on this locus of junction points. Let $c' = 1/R'$ be the curvature and σ' be the number of chains per unit area, both measured on the locus of the *junction points* of the diblock (see Figure 1). The free energy for the outer monolayer is

$$f_o(\sigma',c') = g_A(\sigma',-c';N_A) + g_B(\sigma',c';N_B) + \gamma/\sigma' \quad (3)$$

where g_A (g_B) is the stretching free energy of the A (B) block with polymerization index N_A (N_B), and γ is the interfacial tension.

Using the result in ref 7, we find

$$g_A = (\pi^2/24)N_A b v \sigma'^2[1 + (3/2)N_A v\sigma' c' + (13/5)(N_A v\sigma' c')^2 + ...] \quad (4a)$$

for spherical geometry and

$$g_A = (\pi^2/24)N_A b v \sigma'^2[1 + (3/4)N_A v\sigma' c' + (3/4)(N_A v\sigma' c')^2 + ...] \quad (4b)$$

for cylindrical geometry. g_B can be obtained by replacing N_A with N_B and changing the sign of c' in eq 4.

In eq 4, v is the volume of a monomer, and b is a packing length[10] defined by $b = v/\lambda^2$ where λ is the length of a monomer (persistent length). We assume for simplicity that these geometrical parameters are the same for the two blocks, so that we may characterize the length of each block by the fraction $\phi = N_A/N$ where $N = N_A + N_B$ is the total polymerization index of the chain. In the following, we treat only the spherical geometry explicitly; the case of cylindrical symmetry proceeds similarly.

In order to obtain the free energy appropriate to the *bilayer*, we need to relate c' and σ' to c and σ, the latter being defined on the *midsurface of the bilayer*. For a spherical geometry, they are related as

$$\sigma' = \sigma R^2(R + h_A)^{-2} = \sigma(1 + h_A c)^{-2} \quad (5)$$

and

$$c' = R'^{-1} = (R + h_A)^{-1} = c(1 + h_A c)^{-1} \quad (6)$$

where h_A is the thickness of the A-block in the outer layer. Given the number of chains per unit area σ, h_A can be obtained from the incompressibility condition as

$$h_A = \phi N v\sigma[1 - \phi N v\sigma c + (5/3)\phi^2(N v\sigma)^2 c^2 + ...] \quad (7)$$

Substituting eqs 5 and 6 in eq 4a and making use of eq 7, we arrive at the following curvature expansion for g_A in terms of σ and c:

$$g_A = \phi(\pi^2/24)N b v\sigma^2[1 - (5/2)\phi N v\sigma c + (61/10)\phi^2(N v\sigma)^2 c^2 + ...] \quad (8)$$

We now define a dimensionless parameter q as $q = \sigma/\sigma^*$ where σ^* is the value of σ which minimizes the free energy of a monolayer in the flat geometry and is equal to $(12/\pi^2)^{1/3}\gamma^{1/3}b^{-1/3}v^{-1/3}N^{-1/3}$. Using q and σ^*, we can rewrite eq 8 as

$$g_A = \phi(\pi^2/24)N b v\sigma^{*2}q^2[1 - (5/2)\phi q\tilde{c} + (61/10)\phi^2 q^2\tilde{c}^2 + ...] \quad (9)$$

where we have defined the dimensionless curvature $\tilde{c} = N v\sigma^* c$. Using similar arguments for the stretching free energy of the B-block and for the interfacial free energy, we obtain

$$g_B = (1 - \phi)(\pi^2/24)N b v\sigma^{*2}q^2\{1 - [3/2 + (5/2)\phi]q\tilde{c} + [13/5 + (53/10)\phi + (61/10)\phi^2]q^2\tilde{c}^2 + ...\} \quad (10)$$

and

$$\gamma/\sigma' = \gamma\sigma^{*-1}q^{-1}[1 + 2\phi q\tilde{c} - \phi^2 q^2\tilde{c}^2 + ...] \quad (11)$$

Combining these results, we obtain the free energy of the outer monolayer as

$$f(q_o,\tilde{c}) = f^*[f_0(q_o) + f_1(q_o)\tilde{c} + f_2(q_o)\tilde{c}^2 + ...] \quad (12)$$

where

$$f_0(q_o) = (1/3)(q_o^2 + 2q_o^{-1}) \quad (13a)$$

$$f_1(q_o) = -(1/2 + \phi/3)q_o^3 + (4/3)\phi \quad (13b)$$

$$f_2(q_o) = [13/15 + (9/10)\phi + (4/15)\phi^2]q_o^4 - (2/3)\phi^2 q_o \quad (13c)$$

and where f^* is the minimized free energy (per chain) for a monolayer in the flat geometry and is equal to $(3/2)(\pi^2/12)^{1/3}\gamma^{-1/3}b^{1/3}v^{1/3}N^{1/3}$.[9] The free energy for the inner monolayer can be obtained simply by replacing $\tilde{c}$ with $-\tilde{c}$ and q_o with q_i in eqs 12 and 13. Then eq 2 becomes

$$F = \frac{q_i}{q_i + q_o}f(q_i,-\tilde{c}) + \frac{q_o}{q_i + q_o}f(q_o,\tilde{c}) \quad (14)$$

Minimization of eq 14 with respect to q_i and q_o and subsequent expansion of these quantities in powers of the (dimensionless) curvature yield

$$F_s = f^*\{1 + [-(2/15) + (9/10)\phi - (2/5)\phi^2]\tilde{c}^2 + O(\tilde{c}^4)\} \quad (15)$$

It can be seen that the coefficient of the quadratic term turns negative when $\phi < 0.16$, indicating that the flat geometry becomes unstable with respect to a spherical deformation.

A similar calculation can be performed for a cylindrical deformation, and the result is

$$F_c = f^*[1 + (1/16)\tilde{c}^2 + O(\tilde{c}^4)] \quad (16)$$

The coefficient of the quadratic term is always positive and is independent of ϕ!

The results in eqs 15 and 16 enable us to write the free energy (per diblock copolymer molecule) in the Helfrich form for a general deformation of (dimensionless) curvatures[11] $\tilde{c}_1$ and $\tilde{c}_2$ with (dimensionless) mean-curvature bending coefficient K and Gaussian (saddle-splay) bending coefficient $\bar{K}$:

$$F = f^*[1 + (1/2)K(\tilde{c}_1 + \tilde{c}_2)^2 + \bar{K}\tilde{c}_1\tilde{c}_2] \quad (17)$$

with

$$K = 1/8 \quad (18a)$$

and

$$\bar{K} = -23/60 + (9/10)\phi - (2/5)\phi^2 \qquad (18b)$$

We note that $\bar{K}$ becomes positive for $\phi > 0.57$, thus favoring a saddle-shaped deformation.

Equations 17 and 18a,b are the main results of this study. We now discuss the stability of a diblock copolymer bilayer with respect to small curvature deformations, based on these results. Clearly, the flat bilayer geometry is stable if the curvature deformation leads to an increase in the free energy or, equivalently, if the overall contribution from the curvature terms is positive; this is the case for a tubular deformation (see eq 16) regardless of the composition of the diblock. However, when the composition of the diblocks is sufficiently asymmetric with longer B-blocks, i.e., when each monolayer has a strong tendency to curve away from (i.e., convexly toward) the solvent, the flat bilayer becomes unstable with respect to a spherical deformation. In other words, spherical vesicles become favored over the flat bilayers. Though not shown here, we have also calculated the quartic term in the curvature expansion and found it to be always positive. Thus the transition from flat bilayers to spherical vesicles is "second order" as the relative molecular weights of the two blocks are varied. The scenario is rather analogous to the Landau theory of phase transitions for a magnet.[12] In the "symmetry-broken" phase, the vesicle has a well-defined size which is determined by the ratio of the quartic coefficient to the quadratic coefficient. We have also carried out a preliminary calculation for the case of swollen B-blocks, which obtains in a small-molecule solvent, and have come to the same qualitative conclusion. In this case, however, because a swollen block is effectively much bulkier than a melt block,[6,9] the above-mentioned instability can occur for much shorter B-blocks.

The fact that a spherical vesicle can have a lower free energy than the flat bilayer, can be understood roughly with the following argument. When each *monolayer* has a strong tendency to curve away from (i.e., convexly toward) the solvent, a curved geometry obviously decreases the free energy of the outer monolayer. It is true that the free energy of the inner monolayer increases at the same time, but this increase is partially alleviated if the number of molecules per unit area is allowed to vary (decrease) accordingly. Consequently, there are more molecules in the outer monolayer than there are in the inner layer, and, as a result, the decrease in the free energy of the outer layer more than compensates the increase in the free energy of the inner layer. However, the net gain in the free energy is a result of a delicate balance among several second-order curvature effects. Therefore, without going through the actual calculation, one cannot apply the above argument a priori to predicting whether a certain curvature deformation is favored over the flat geometry. Our calculation shows in fact that cylindrical (tubular) deformations are *never* favored (either for melt B-blocks or for swollen B-blocks).

We now consider saddle-shaped deformations. Of particular interest is a class of surfaces called minimal surfaces because these are believed to be the midsurface of the bilayer in ordered, bicontinuous structures.[2] On the minimal surface, the mean curvature $H = (1/2)(\tilde{c}_1 + \tilde{c}_2)$ is everywhere zero and the Gaussian curvature $G = \tilde{c}_1\tilde{c}_2$ is negative. Thus a positive Gaussian bending modulus $\bar{K}$ implies that a minimal surface has a lower free energy than the flat bilayer; this is the case when $\phi > 0.57$, i.e., when the inner A-block is sufficiently large. The physical reason for the formation of saddle-shaped surfaces is similar to that for the spherical vesicles. It arises from the frustration experienced by the two monolayers because of their inability to curve with their natural curvature.

After this work had been completed, we learned of some recent calculations by Ajdari and Leibler[13] on the curvature stability of copolymer bilayers. Their results show that the Gaussian bending modulus can become positive for asymmetric diblocks with a bulkier inner A-block, in agreement with our result. In fact the onset of the saddle-splay instability predicted by these authors occurs at $\phi = 0.58$, a value very close to ours. However, these authors argue that vesicles are always of higher free energy than flat bilayers, in direct contradiction to our prediction. This last discrepancy between their results and ours can be attributed to the difference between the choice of an appropriate free energy: they consider the free energy *per unit area* whereas we consider the free energy *per molecule*. In our opinion it is the free energy *per molecule* that should be the appropriate quantity,[14] since the number of molecules per unit area σ (or, equivalently, the area per molecule) is not fixed but rather changes with the curvatures.[9] If σ is defined on the midsurface of the bilayer, such a change is of second order in curvatures. However, it is precisely at this order that we study the curvature stability. Thus, even though it is meaningful to compute a free energy per unit area in a curvature expansion, such a free energy *cannot* be used to study the stability of phases.

In closing, we make a few remarks on the main results of this paper. First, we point out that our result concerning spherical vesicles should not be considered positive proof for the equilibrium formation of these objects. In a complete theory, we have to consider all types of aggregates with competing free energies. Indeed, when the inner A-block becomes sufficiently shorter than the outer B-block, it seems more natural that these copolymers would rather form micelles with A-blocks in the interior of the micelles. Nevertheless, if spherical vesicles have a lower free energy than the flat bilayers, these vesicles may exist as metastable states with sufficiently long lifetimes. Furthermore, it is possible that in some cases the vesicle geometry may indeed have the lowest free energy. Recent experiments on polystyrene–polyisoprene diblock copolymers in aniline[15] suggest a sharply-peaked distribution for the vesicle sizes, indicating that the vesicles are either stable or metastable objects. Since aniline is a good solvent for polystyrene, it is particularly interesting to explore the possibility of vesicle formation with swollen outer B-blocks. Spontaneous formation of vesicles has also been observed in systems containing surfactant *mixtures*.[16] However, the mechanism there is rather different[17] from that discussed in this paper.

Second, our result for a positive Gaussian bending modulus when $\phi > 0.57$ implies (within the framework of the free energy contributions considered in this paper) that the formation of bicontinuous structures can be due to an (linear) instability of the bilayer with respect to saddle-splay deformations. As pointed out by Ajdari and Leibler, these bicontinuous structures are more likely to be ordered, periodic phases than disordered, spongelike phases because of the large, positive value of the bending modulus K. Indeed, recent experiments by Winey, Thomas, and Fetters[18] have lent evidence to these ordered bicontinuous phases in systems of diblock copolymers + homopolymers. In order to determine the periodicity of the ordered structures, however, higher order curvature terms are required.

Last, we comment on the relevance of our results concerning saddle-shaped surfaces to the ordered, bicontinuous, double-diamond (OBDD) structures in the *solvent-free* diblock copolymer systems.[19,20] The OBDD structure in the solvent-free system can be thought of as a limiting case of the bilayer + solvent system with the solvent replaced by one of the two blocks. Of course, because of the requirement of space-filling, the bilayers are highly deformed and are nonuniform in thickness. Obviously, then, a full account of these structures has to include higher-order curvature terms as well as deformations/interactions arising from the requirement of space-filling. (In this connection, we mention a recent attempt by Fredrickson,[21] who studied a catenoid-lamellar phase[22] which also possesses saddle-shaped curvatures.) Nevertheless, the incipient tendency for a single, unconstrained bilayer to be saddle-shaped may well be an important factor for the formation of the OBDD structures in the solvent-free cases.

Acknowledgment. I thank S. A. Safran for helpful discussions and a critical reading of the manuscript. Financial support from the National Science Foundation (Grant CHE88-16059) through Professor W. M. Gelbart at the University of California, Los Angeles, CA, where part of this work was conducted, and from The Camille and Henry Dreyfus New Faculty Awards Program is gratefully acknowledged.

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