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Equilibrium Shape of Two-Component Unilamellar Membranes and Vesicles.

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Abstract. – We show that a strong segregation of a two-component surfactant system coupled to the local membrane curvature has a pronounced effect on the shape of unilamellae or closed vesicles. For an average flat lamella, the preferred periodicity in the local composition as well as the lamellar shape is calculated and depends on the ratio between surface tension and bending modulus. In the case of a closed visicle with a fixed total area, there is no selected periodicity in contrast to the unilamellar case. For vesicles subjected to positive or negative inner pressure, we calculate their shape numerically, whereas when there is no added inner pressure, the shape is found analytically to be composed of circular sections.

One of the most common structures formed when amphiphiles such as phospholipids or surfactants are dissolved in water is a bilayer membrane [1,2]. Such membranes are arranged either as a *lamellar* stack of bilayers that are planar on average or as closed-form *vesicles* [3-10]. Recently, an increased number of studies has focused on two-component surfactant solutions [11-18]. In some cases [11-13], vesicles can form spontaneously upon mixing surfactants with two oppositely charged head groups. In other cases [17, 18], mixing lipids with surfactants can induce a transition from a bilayer structure (either multi lamellar or vesicular) to a mixed micellar one.

Motivated by the above-mentioned experiments, we investigate in this paper the interplay between a heterogeneous composition of a membrane composed of two surfactants (amphiphiles) and *pronounced* changes in the vesicle or unilamellar shape. We employ a phenomenological coupling [10] between the local composition (of the two species) and the local curvature in the strong segregation limit of the two species. For example, this limit is achieved by a deep temperature quench far from the critical temperature. Results are obtained for unilamellae as well as for closed-form vesicles, for which large deviations from a spherical shape are calculated. Throughout this paper, we employ the mean-field approximation, where the thermal fluctuation effects are neglected. For simplicity, we look only at a two-dimensional geometry where the membrane fluctuates around a reference line

(flat case) or forms a closed curve. In the dilute-solution limit, only one such interface is considered and all inter-membrane interactions can be neglected.

Consider first a single lamella whose out-of-plane undulation with respect to a reference plane is $l(x)$, x being the coordinate along a reference plane. The total free-energy functional can be expressed [10] as a sum of three terms, $F = F_1 + F_2 + F_3$:

$$F_1 = \int \left[\frac{1}{2}\sigma \left(\frac{\mathrm{d}l}{\mathrm{d}x} \right)^2 + \frac{1}{2}\kappa c^2 \right] \mathrm{d}x + \ldots , \tag{1}$$

where σ is the surface tension, κ is the rigidity modulus and c is the local curvature, which can be well approximated by $c \simeq \mathrm{d}^2 l/\mathrm{d}x^2$ in this almost planar case. The second term in F is a Ginzburg-Landau expansion of the local order parameter $\phi(x)$:

$$F_2 = \int \left[\frac{1}{2} b(\nabla\phi)^2 + f(\phi) - \mu\phi \right] \mathrm{d}x + \ldots , \tag{2}$$

where $f(\phi) = (1/2)\, a_2 \phi^2 + (1/4)\, a_4 \phi^4$ and μ is the chemical potential. For an amphiphilic monolayer separating two solvents like water and oil, $\phi(x)$ is defined as $\phi(x) = \phi_A(x) - \phi_B(x)$, ϕ_A and ϕ_B being the concentrations of the A and B species, respectively. On the other hand, for lamellae or vesicles composed of bilayer membranes, $\phi(x)$ should be read as the composition difference between the two sides of the bilayer.

Finally, the coupling between the two degrees of freedom $\phi(x)$ and $l(x)$ is a coupling between the local membrane curvature c and the local composition

$$F_3 = \Lambda \int \phi(x)\, c(x)\, \mathrm{d}x + \ldots . \tag{3}$$

Note that when $\phi(x)$ is a constant as in the single-component case, F_3 is nothing else but the energy contribution of the average *spontaneous* curvature of the film, $c_0 = -\Lambda\phi/\kappa$.

Since in our approximation F contains terms only up to second order in $l(x)$ and its derivatives (1), it is possible to minimize F with respect to $l(x)$ or even more conveniently to go to a Fourier representation where $l_q = \int l(x) \exp[iqx]\, \mathrm{d}x$ is the Fourier transform of $l(x)$. Requiring $\delta F/\delta l_q = 0$, we can express l_q in terms of $\phi_q = \int \phi(x) \exp[iqx]\, \mathrm{d}x$ and substituting the relation back into F yields

$$F_{\mathrm{eff}} = \int \left(\frac{1}{2} b q^2 + \Gamma_q \right) \phi_q \phi_{-q} \mathrm{d}q + \int \left(f(\phi) - \mu\phi - \frac{1}{2} \frac{\Lambda^2}{\kappa} \phi^2 \right) \mathrm{d}x , \tag{4}$$

and

$$\Gamma_q = \frac{\sigma}{2\kappa} \frac{\Lambda^2}{\sigma + \kappa q^2} = \frac{1}{2\kappa} \frac{\Lambda^2}{1 + \xi^2 q^2} , \tag{5}$$

where the *correlation length* ξ is conveniently defined as $\xi \equiv \sqrt{\kappa/\sigma}$.

Beside an upward shift of the critical temperature proportional to $\Lambda^2/2\kappa$, the coupling term (3) introduces a mechanism of stabilizing modulated phases («meso-phases») such as the $P_{\beta'}$ phase (so-called ripple phase). It is instructive to investigate (4) in two limits. For a shallow temperature quench ($T \lesssim T_c$) an expansion of (5) in powers of q yields [10] a modulated structure [19-24] with $\phi(x) = \phi_q \cos qx$ and $l(x) = l_q \cos qx$. The preferred q value is $q^* =$

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(1) For simplicity, we neglect other terms in F that are considered in ref. [10]: $A(\nabla^2\phi(x))^2$ and $\lambda\nabla^4 l(x)$. They do not affect our results in any major way.

$= \sqrt{(\Lambda^2 - b\sigma)/2\Lambda^2\xi^2}$ and a necessary condition for the modulations is a negative coefficient of the q^2 term in (4), *i.e.* $\Lambda^2 - b\sigma > 0$.

We focus now on the other extreme limit of a deep temperature quench ($T \ll T_c$), where strong segregation occurs between A domains of concentration ϕ_0 and B domains of concentration $-\phi_0$. For simplicity, only the symmetric 1:1 mixture is considered for which the A and B domains have the same length. Instead of looking at the low-q expansion of the free energy, all q-modes must be retained in (4) in order to capture the behaviour at short distances due to the sharp domain walls between A and B domains.

The curvature-induced interaction of the membrane can then be simply expressed as

$$\int \Gamma_q \phi_q \phi_{-q} \, \mathrm{d}q = \int \Gamma(x - y)\, \phi(x)\, \phi(y) \, \mathrm{d}x \, \mathrm{d}y \,, \tag{6}$$

where $\Gamma(x) = (\Lambda^2/4\kappa\xi) \exp[-|x|/\xi]$. Assuming an alternating arrangement of n domains of A and n domains of B, each of length D, eq. (6) can be integrated exactly yielding a free-energy density $f = F/2nD$:

$$f = \frac{\gamma}{D} + \frac{\Omega}{D}(\exp[-d] + d - 1) - \frac{2\Omega}{D} \exp[-d/2] \sinh \frac{d}{2} \operatorname{tgh} \frac{d}{2} \,, \tag{7}$$

where $\Omega = (\Lambda^2 \xi/8\kappa)(\Delta\phi)^2$ and $d = D/\xi$ with $\Delta\phi = 2\phi_0$. The first term in (7) expresses the domain wall energy γ, while the second and third terms account for the intra- and inter-domain contributions from the effective long-range interaction, eq. (5), respectively. The optimal domain size D^* is obtained by the condition $\partial f/\partial d = 0$.

In the limit of large correlation length (large bending modulus), $D \ll \xi$ and $\gamma \ll \Omega$, $D^* = \xi(6\gamma/\Omega)^{1/3}$, whereas for small correlation length (small bending modulus) $D \gg \xi$, $\gamma/\Omega \to 1$, $D^* = \xi \log|1 - \gamma/2\Omega|$. For any configuration of $\phi(x)$, the shape profile $l(x)$ can be calculated from its Fourier components using the relation between l_q and ϕ_q as

$$l(x) = -\frac{\Lambda}{2\kappa} \xi \int \exp[-|x - y|/\xi] \, \phi(y) \, \mathrm{d}y \,. \tag{8}$$

Let us consider a periodic arrangement of alternating A and B domains, $\phi_A(x) = \phi_0$ for $2nD \leqslant x \leqslant (2n + 1)D$ and $\phi_B(x) = -\phi_0$ for $(2n + 1)D \leqslant x \leqslant (2n + 2)D$. Integrating eq. (8) gives

$$l_A(x) = l_0 \left(1 - \frac{\exp[x/\xi] + \exp[(D - x)/\xi]}{1 + \exp[D/\xi]}\right), \qquad 2nD \leqslant x \leqslant (2n + 1)D \,, \tag{9}$$

where $l_0 = -(\Lambda/\kappa)\xi^2\phi_0 = -(\Lambda/\sigma)\phi_0$. Similarly, for $(2n + 1)D \leqslant x \leqslant (2n + 2)D$, $l_B(x) = -l_A(x - D)$. Equation (9) has two simple limits: for small bending modulus, $\xi = \sqrt{\kappa/\sigma} \ll D$, and the lamellar shape follows the abrupt composition change from ϕ_0 to $-\phi_0$, by changing abruptly over a relatively short length ξ from l_0 to $-l_0$. On the other hand, in the limit of large bending modulus, $\xi \gg D$, the lamella has a parabolic profile where $\Delta l = l(D/2) - l(0) \simeq (l_0/8)(D/\xi)^2$ is much smaller than l_0. If the total (one-dimensional) area of the membrane is fixed, it is more convenient to use a natural coordinate, where each point on the membrane is specified by the distance s along the contour, $0 \leqslant s \leqslant L$, where L is the fixed contour length. Then, the curvature at point s can be expressed as $\mathrm{d}\theta/\mathrm{d}s \equiv \dot{\theta}(s)$, where θ is the angle between the tangent vector and some arbitrary fixed direction. Minimizing the free energy with respect to $\theta(s)$, we obtain the following condition for the membrane shape:

$$\frac{\delta F}{\delta\theta(s)} = -\kappa\ddot{\theta}(s) - \Lambda\dot{\phi}(s) = 0 \,. \tag{10}$$

Equation (10) is subject to the topological constraint of a closed shape of length L, $\boldsymbol{r}(L) = \boldsymbol{r}(0)$ and $\theta(L) = \theta(0) + 2\pi$, where $\boldsymbol{r}(s)$ is the position vector of the membrane element s. Note that expression (10) by itself is exact irrespective of whether the membrane is open or closed. In addition, eq. (10) should be supplemented by the variation condition of F with respect to the composition ϕ, $\delta F/\delta\phi = 0$.

Under the assumption of a strong segregation (deep quench—far from T_c), $\phi(s)$ takes a constant value $\phi_0 (-\phi_0)$ in the A (B) domain, separated by sharp domain walls where $\phi(s)$ changes discontinuously. Assuming that the membrane is composed of n domains of A and n of B arranged in a symmetrical way, eq. (10) can be solved exactly in the strong segregation limit for $n \geq 2$, whereas the case $n = 1$ is rather special and will be described in detail in our forthcoming paper [25]. For $n \geq 2$, eq. (10) simply reduces to $\ddot{\theta}(s) \equiv 0$ within a single domain, meaning that the curvature is constant throughout a single domain. Therefore, the membrane has an arclike shape in each one of the domains and the discontinuity of $\phi(s)$ at the domain walls leads to a discontinuity in the curvature $\dot{\theta}(s)$, while the tangent vector $\theta(s)$ remains continuous. Consequently, the global shape of the membrane is composed of consecutive arcs of alternating curvatures connected smoothly at the domain walls.

It can be shown for $n \geq 2$ that F_1 and F_3 do not depend on the domain configuration but only on the total length fraction of the A (or B) domains. Noting that F_2 accounts for the domain wall energy proportional to the total number of domain walls, the minimum free energy is obtained for the four-domain configuration (two of each species).

We also calculated the shape of the membrane under the condition that the inner enclosed volume is fixed. As we employed mean-field approximation, this can also be done by adding an appropriate pressure difference $\Delta P = P_o - P_i$ across the membrane, where P_o and P_i are the pressure outside and inside of the membrane, respectively. This pressure difference ΔP acts as *another* Lagrange multiplier related to the constraint on the total inner volume enclosed by the membrane. In fig. 1, we show typical examples of a membrane with $n = 2$ domains of each species. Negative, zero and positive pressure differences are shown in fig. 1*a*)-*c*), respectively. For cases *a*) and *c*), we have to rely on numerical solution of eq. (10) subject to the constraint of total inner volume. Case *b*) is the unconstrained one and is solved analytically along the lines indicated above. When comparing the three cases, it is important to recall that the total contour length is constrained to have the same length in all three cases. As the inner pressure becomes much larger than the external one, the vesicle shape tends towards a circular shape, which has the largest area of all shapes with the same perimeter length. Already in case *a*), the inner area is about 98.6% of a circle with the same perimeter length. Any other domain arrangement with $n \geq 2$ has very similar profile shape.

In conclusion, we have shown that strong segregation of two partially compatible

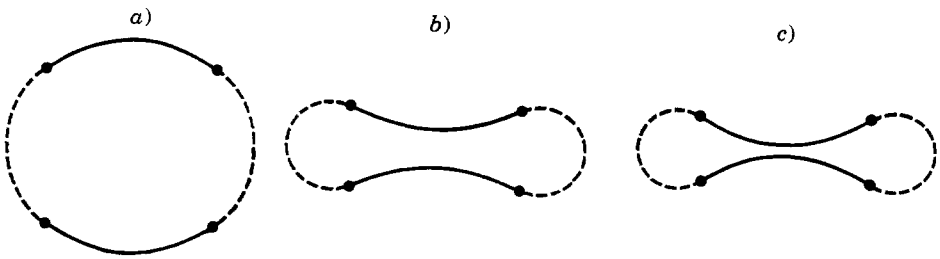

Fig. 1. – Typical examples of a membrane with $n = 2$ (two domains of each A and B phase). The pressure difference ΔP is negative, zero and positive in *a*), *b*) and *c*), respectively. Solid curves and broken curves show A domains [$\phi(s) = \phi_0$] and B domains [$\phi(s) = -\phi_0$], respectively. Solid circles indicate the location of the A/B domain walls.

surfactants leads to very strong shape modification of vesicles and unilamellae. They should be compared with analytical calculations and Monte Carlo simulations of *single*-component vesiscles [8, 26]. If the total contour length is fixed, both open and closed structures will separate into four large domains [25]. However, metastable solutions for closed vesicles include any number $n \geq 2$ of domains arranged in a symmetric way. For nearly flat but undulating unilamellar systems, a selected periodicity of the domain exists even in the strong segregation limit. Our results can be tested experimentally, for example, for mixed surfactant-lipid systems which couple differently to the local curvature [17, 18]. We are extending the present work to three-dimensional vesicles as well as to the nonsymmetric case which is equivalent to a system with an average nonzero spontaneous curvature.

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