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EQUILIBRIUM SHAPE DEFORMATIONS OF TWO-COMPONENT VESICLES

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We investigate the linear stability of two- and three-dimensional closed form vesicles which are composed of a partially miscible mixture of two amphiphiles. The shape of such vesicles is strongly influenced by the inplane phase separation of the amphiphiles. When the inner pressure of the vesicle is higher than the outer one, an instability of the vesicle shape occurs below the critical temperature due to a local spontaneous curvature induced by the coupling between the local curvature of the vesicle and the local composition of the amphiphiles. In addition, in two dimensions and within mean field approximation, we obtain equilibrium phase diagrams for temperatures close to the critical temperature T_c.
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In most existing theories of lamellar phases and vesicles, the membranes have been treated as an interface without any internal degrees of freedom. Recently, an increasing number of works have been devoted to the investigations of membranes with internal degrees of freedom such as the relative composition of mixtures of amphiphiles[1–4], the orientational order of the tilt angle of the amphiphiles with respect to the membrane plane[5], and quenched impurities embedded in a tethered membrane[6].

In this paper we investigate, within mean-field theory, the linear stability of two- and three-dimensional vesicles composed of a mixture of two-component amphiphiles, and obtain equilibrium phase diagram for the two-dimensional ($2d$) case. A vesicle in $2d$ can be represented by a closed contour line L in $2d$ space. The position vector $\mathbf{r}$ of a point on L is specified by a parameter u that labels the contour point $\mathbf{r}=\mathbf{r}(u)$. The total free energy functional H of such $2d$ vesicles can then be expressed as a sum of four terms[1-3]: $H = H_1 + H_2 + H_3 + PA$. The first term is the so-called Helfrich free energy coming from the rigidity of the membrane[7].

$$H_1 = \frac{1}{2}\kappa \int c^2 \, \eta du \tag{1}$$

where c is the curvature, ηdu denotes a line element of the membrane, κ is the bending elasticity and the integral is taken over the entire contour[8]. The second term, H_2, is the Ginzburg-Landau free energy expressed as a functional of the local relative concentration per unit contour length, $\phi = \phi_A - \phi_B$, where ϕ_A and ϕ_B are the concentrations of the "A" and "B" species of the amphiphiles, respectively;

$$H_2 = \int \{ \frac{1}{2}b\,(\nabla\phi)^2 + f(\phi) \}\eta du \tag{2}$$

and $f(\phi) = (a_2/2!)\phi^2 + (a_4/4!)\phi^4$ with $a_2 \equiv a(T - T_c)$, a and a_4 being positive constants. Note that this expansion is also valid for the case where $f(\phi)$ is asymmetric with respect to the exchange of ϕ_A and ϕ_B[9]. Depending on the sign of a_2, the homogeneous phase will be stable ($a_2 > 0$) or unstable ($a_2 < 0$). The third term, H_3, accounts for the coupling energy between the local curvature and the local composition of the amphiphiles[2];

$$H_3 = \Lambda \int \phi \, c \, \eta du \tag{3}$$

where Λ is the coupling constant. This term corresponds to an induced ϕ-dependent *local* spontaneous curvature. Finally, we introduce a pressure difference $P \equiv P_{out} - P_{in}$ between the outer and the inner regions of the vesicle, which results in the last term of H, that is, PA. This term couples the pressure difference P with the total enclosed inner area of the vesicle, A.

The equilibrium state of the vesicle is determined by minimizing the total free energy H under the following two constraints. The total contour length of the vesicle is constant, as is required by the condition of incompressibility of the membrane. In addition, the integral of ϕ over the contour, which gives the total composition difference between the two species on the membrane, is also constrained to be a constant in the absence of chemical reactions or exchange of matter between the vesicle and its surroundings. We choose the polar coordinate, $\mathbf{r}(u) = (r,\ \theta)$, to specify a position on the membrane, where θ is the polar angle and $r(\theta)$ is the radial distance from the origin. In this representation η and $|\nabla\phi|$ can be expressed as $\eta = (\dot{r}^2 + r^2)^{1/2}$ and $|\nabla\phi| = \dot{\phi}/\eta$, respectively, where the dot denotes the derivative with respect to θ. The curvature c is given by $(\ 2\dot{r}^2 + r^2 - r\ddot{r}\ )/(\dot{r}^2 + r^2)^{3/2}$, where we choose the sign of the curvature c to be positive when the vesicle is convex towards the external side. The total area A inside the vesicle is given by $A = \frac{1}{2}\int r^2 d\theta$. The total contour length L of the vesicle and the total amount of the matter M on the contour are given by $L = \int \eta d\theta = const.$, and $M = \int \phi \, \eta d\theta = const.$, respectively.

In what follows we limit our treatment to shallow temperature quenches close to T_c ($T \lesssim T_c$), where both the concentration difference ϕ and the shape deviation of the vesicle from a perfect circular shape are small. Namely, if we define $r(\theta) = r_0 + R(\theta)$, where r_0 is the radius of a reference circle, then the deviation $R(\theta)$ is much smaller than r_0[10]. One of the interesting questions is how a homogeneous distribution of A and B amphiphiles becomes unstable due to the coupling with the vesicle shape. To investigate the onset of such an instability it is enough to retain terms up to second order in both the deviation $R(\theta)$ and the order parameter ϕ in the above expressions for H, L and M. In particular, we will include only quadratic terms in $f(\phi)$ for the linear stability analysis. As L and M are kept constant, we obtain the relations: $\int R\, d\theta = -(1/2r_0)\int \dot{R}^2 d\theta$ and $\int \phi\, d\theta = -(1/r_0)\int R\phi\, d\theta + M$, respectively. The terms in H which are linear in R and ϕ can be eliminated using these relations. The resulting expression for H is quadratic in ϕ and R as follows

$$H = \int \left\{ \left(\frac{\kappa}{2r_0^3} + \frac{1}{2}P\right)R^2 + \frac{\kappa}{2r_0^3}\ddot{R}^2 - \left(\frac{\kappa}{r_0^3} + \frac{1}{2}P\right)\dot{R}^2 + \frac{b}{2r_0}\dot{\phi}^2 + \frac{1}{2}a_2 r_0 \phi^2 - \frac{\Lambda}{r_0}\phi\left(\ddot{R} + R\right) \right\} d\theta \qquad (4)$$

where we have omitted an irrelevant constant term. Since all the variables depend on R and ϕ which are 2π–periodic functions of θ, it is convenient to express H and the other quantities as sums over the *discrete* Fourier modes of R and ϕ: $R(\theta) = \sum_n' [c_n \cos n\theta + s_n \sin n\theta]$ and $\phi(\theta) = \sum_n [\phi_{cn} \cos n\theta + \phi_{sn} \sin n\theta]$, where $\sum'$ means that the n=1 term is omitted since it gives rise only to a translation mode of the vesicle as a whole. In addition, the $n = 0$ term is also omitted from these Fourier series and similar expressions hereafter, since it is already second order in the small deviations R and ϕ mentioned above, and contributes only to higher than second order in H [eq.(4)]. Substituting the Fourier series of R and ϕ into eq.(4) we find

$$H = \frac{\pi}{2}\sum_n \left\{ D_n(c_n^2 + s_n^2) + E_n(\phi_{cn}^2 + \phi_{sn}^2) + \frac{2\Lambda}{r_0}(n^2 - 1)(c_n\phi_{cn} + s_n\phi_{sn}) \right\}, \qquad (5)$$

with $D_n \equiv (n^2 - 1)\left[(\kappa/r_0^3)(n^2 - 1) - P\right]$ and $E_n \equiv (b/r_0)n^2 + a_2 r_0$.
A linear stability analysis can now be performed on (5). Two cases should be distinguished:

(a) $D_n > 0$ for all $n > 1$
In this case the circular vesicle shape is stable when the coupling between curvature and composition vanishes ($\Lambda = 0$). The condition $D_n > 0$ is satisfied for all pressure differences $P = P_{out} - P_{in}$ smaller than a threshold value $3\kappa/r_0^3$. On the other hand, if there is nonvanishing coupling ($\Lambda \neq 0$), an instability of the shape can take place. Such an instability is investigated by minimizing the free energy H in (5) with respect to c_n and s_n;

$$H = \frac{\pi}{2}\sum_n \Gamma_n(\phi_{cn}^2 + \phi_{sn}^2), \qquad (6)$$

with $\Gamma_n \equiv E_n - (\Lambda/r_0)^2(n^2 - 1)^2/D_n$. In this case we find that the instability occurs for all integer values of n satisfying $\Gamma_n < 0$.

(b) $D_n \leq 0$ for some n
In this case the circular shape is unstable even when the coupling term is zero ($\Lambda = 0$). This implies $Pr_0^3/\kappa \geq 3$ and the instability occurs for all integer n satisfying $4 \leq n^2 < 1 + Pr_0^3/\kappa$.

Whereas it was enough to retain only quadratic terms in ϕ for the study of the instabilities of a homogeneous circular vesicle shape, actual phase transitions can be calculated by re-including the quartic term $(a_4/4!)\phi^4$ in $f(\phi)$ and looking for the state with the minimum free energy among different modes. Here we assume that the equilibrium state is a pure state with a single n-mode. Namely, $R(\theta) = c_0 + c_n \cos n\theta + s_n \sin n\theta$ and $\phi(\theta) = \phi_{c0} + \phi_{cn} \cos n\theta + \phi_{sn} \sin n\theta$ ($n \neq 0$), where c_0 plays the role of a Lagrange multiplier which guarantees the condition that the total contour length is conserved. Using such an assumption, the relevant part of H is expressed as

$$H = \frac{\pi}{2}\{D_n(c_n^2 + s_n^2) + E_n(\phi_{cn}^2 + \phi_{sn}^2) + \frac{a_4 r_0}{16}(\phi_{cn}^2 + \phi_{sn}^2)^2 + \frac{2\Lambda}{r_0}(n^2 - 1)(c_n\phi_{cn} + s_n\phi_{sn})\}. \tag{7}$$

As mentioned above $\phi_{c0} = \int \phi d\theta$ is given by a sum of products of c_n (s_n) and ϕ_{cn} (ϕ_{sn}). Terms of order two or higher in ϕ_{c0} give higher-order couplings in H, and thus can be neglected.

In case (a) mentioned above, where $D_n > 0$ for all $n > 1$ ($Pr_0^3/\kappa < 3$), we can obtain an equilibrium state by minimizing the free energy H with respect to the variables c_n, s_n, ϕ_{cn} and ϕ_{sn}. The minimized free energy is then found to be $H = -2\pi\Gamma_n^2/a_4 r_0$ for $\Gamma_n < 0$, and H=0 for $\Gamma_n \geq 0$. In case (b), $Pr_0^3/\kappa \geq 3$ (or equivalently $D_{n=2} \leq 0$), and the circular shape is unstable due to the effect of pressure even without the coupling term[11]. A complete analysis of the shape stability is complicated since it requires the inclusion of $4th$ order terms in c_n and s_n, and will be presented elsewhere[12].

We show the calculated phase diagrams in Figs. 1 and 2. For $Pr_0^3/\kappa < 3$, equilibrium shape deformations with $n \geq 1$ occur and the bare T_c is renormalized upwards by $\Lambda^2/a\kappa$ [1] as is shown in Fig. 2. As the dimensionless coupling coefficient $(\Lambda^2 r_0^2/\kappa b)^{1/2}$, expressing the effective softness of the vesicle becomes larger, higher modes are selected (Figs. 1 and 2). The mechanism of such mode selections will be described in our forthcoming paper[12]. Note that the $n = 1$ mode found in Fig. 2 is rather special having an inplane phase separation of the A/B amphiphiles while preserving the circular vesicle shape, since the $n = 1$ mode of the vesicle shape (c_n and s_n) only gives rise to a translation of the circular vesicle as a whole.

We also investigate the stability of $3d$ vesicles with spherical topology[13]. The term PA in the free energy for $2d$ vesicles is replaced by PV, V being the volume inside the vesicle. The line element ηdu appeared in the integrals of H is replaced by an area element $\sqrt{g}d\mathbf{u}$, where $\mathbf{u} = (u^1, u^2)$ is an arbitrary parametrization of the two-dimensional membrane and g is the determinant of the metric tensor. Note that in $3d$ we can neglect the Gaussian curvature term in eq. (1) due to Gauss-Bonnet theorem, as long as we focus on vesicles with spherical topology. Hence, it is enough to retain the mean curvature c in eq. (1). We choose $\mathbf{u}$ to be $u^1 = \theta$, $u^2 = \varphi$, where θ and φ are the polar and azimuthal angles, respectively. Expanding the free energy up to second orders in R and ϕ and using spherical harmonics as the basis set of the expansion, the relevant part of the free energy is

$$H = \sum_{l=1}^{\infty} \sum_{m=-l}^{l} \left\{ \frac{D_l}{2} |C_{lm}|^2 + \frac{\Lambda}{2}(l(l+1)-2)C_{lm}\phi_{l-m} + \frac{bl(l+1)+a_2 r_0{}^2}{2} |\phi_{lm}|^2 \right\} \quad (8)$$

with $D_l \equiv (\kappa/4r_0{}^2)[l(l+1) - 2Pr_0{}^3/\kappa][\, l(l+1) - 2\,]$, where C_{lm} and ϕ_{lm} are expansion coefficients of $R(\theta,\varphi)$ and $\phi(\theta,\varphi)$, respectively. The results of the linear stability analysis for $3d$ vesicles exhibit almost the same features as those for the $2d$ case. The only important difference is the occurrence of an instability of the higher modes ($n > 2$) even for $P = 0$ (no pressure difference) when the dimensionless coupling coefficient $(\Lambda^2 r_0^2/\kappa b)^{1/2}$ is large[12].

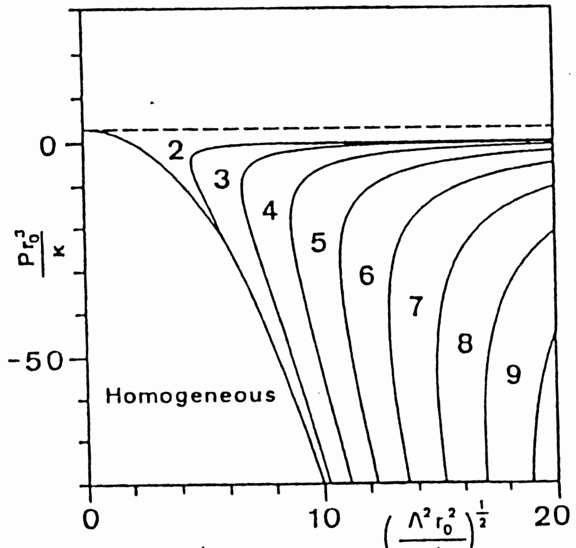

FIG. 1.

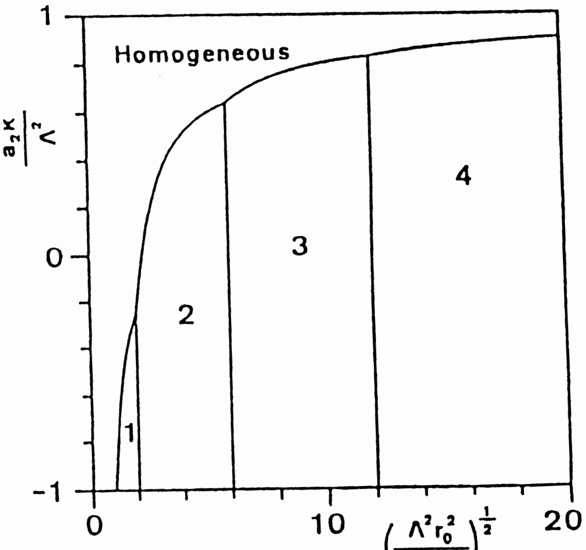

FIG. 2.

Fig. 1. Phase diagram for $2d$ vesicles plotted for the dimensionless pressure Pr_0^3/κ versus the dimensionless coupling coefficient $(\Lambda^2 r_0^2/\kappa b)^{1/2}$ at the bare critical temperature $T = T_c$ ($a_2 = 0$). The numbers indicate the values of the n-mode characterizing the shape deformation. The region above the dashed line corresponds to the unstable case (b) discussed in the text.

Fig. 2. Phase diagram for $2d$ vesicles plotted for the dimensionless temperature $a_2\kappa/\Lambda^2$ versus the dimensionless coupling coefficient $(\Lambda^2 r_0^2/\kappa b)^{1/2}$ at a pressure $Pr_0^3/\kappa = -1$. The numbers indicate the values of n.

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8. In general the curvature c in eq.(1) should be replaced by $c - c_{sp}$, c_{sp} being the spontaneous curvature. The spontaneous curvature term is important only in $3d$ case since the cross term $c_{sp} \int c\,\eta du$ only gives a constant for $2d$ case, whereas in $3d$ this integral depends on the shape. We neglect this contribution for $3d$ vesicles in this paper because we focus here on shape deformations due to the effect of induced local spontaneous curvature coming from H_3.
9. In such a case $f(\phi)$ generally includes first- and third-order terms in ϕ as well. However, we can eliminate the $3rd$ order term by replacing ϕ with $\phi + const.$ The $1st$ order term gives only a constant contribution to H due to the constraint that the total amount of surfactant molecules is fixed.
10. In a deep temperature quench ($T \ll T_c$), the equilibrium shape of $2d$ vesicles has been investigated in ref. 3. On the other hand, shallow temperature quenches ($T \simeq T_c$) for two-component unilamellar membranes have been considered in ref. 1.
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13. For one-component amphiphilic vesicles in $3d$, the phase diagram has been investigated by U. Seifert, K. Berndl and R. Lipowsky, *Phys. Rev. A* **44**, 1182 (1991).