Volume 8, Number 5 ACTA PHYSICA SINICA May, 1999
1004-423X/1999/08(05)/0321-05 (Overseas Edition) © 1999 Chin. Phys. Soc.

UNDULATION MODES IN BILAYER MEMBRANES*

ZHANG SHAO-GUANG(张劭光)[a)b)] and OUYANG ZHONG-CAN(欧阳钟灿)[b)]

[a)] *Department of Physics, Beijing Normal University, Beijing* 100875, *China*

[b)] *Institute of Theoretical Physics, Chinese Academy of Sciences, Beijing* 100080, *China*

(Received 28 July 1998)

Through the complete analysis of the solution for one dimensional bilayer membranes, it has been shown that under the Helfrich spontaneous curvature model, periodic shapes only exist in the case of $\overline{\Delta p}$=0. The undulation modes under force balance which correspond to positive, negative and zero tensile stresses have been given.

PACC: 0240; 6130; 8710; 8720

Bilayer lipid membranes may form vesicles spontaneously in aqueous solution. At high concentration of lipid molecules, vesicles will transform into extended structures. In the Helfrich spontaneous-curvature model[1,2], the equilibrium shape of a vesicle is determined by minimization of the free energy

$$F = \frac{1}{2}k_c \oint (c_1 + c_2 - c_0)^2 \mathrm{d}A + \Delta p \int \mathrm{d}V + \lambda \oint \mathrm{d}A \ , \tag{1}$$

where $\mathrm{d}A$ and $\mathrm{d}V$ are surface area and volume elements, respectively, c_1 and c_2 are the two principal curvatures of the surface of the vesicle, c_0 is the spontaneous curvature describing the intrinsic asymmetry in the amphiphilic molecules or the different aqueous environments on the two sides of the bilayer, k_c is the bending rigidity. The first term of Eq.(1) is the bending energy, while the second and the third terms take account of the constraints of constant volume and area. The pressure difference $\Delta p = (p_\mathrm{o} - p_\mathrm{i})$ between outer (p_o) and inner media (p_i) and the tensile stress λ serve as Lagrange multipliers. The Euler-Lagrange shape equation has been derived via variational calculus[3], which is also valid for periodic surfaces.

Periodic lamellar structures often appear in lipid bilayer systems. Among the periodic shapes, the undulation modes are very important because Harbich and Helfrich[4] have observed this kind of shape in their experiment of the swelling of egg lecithin in excess of water. What is more, there exhibit a variety of hydrodynamic modes in lamellar systems consisting of surfactant-stabilized layers of oil and water.[5] In Ref.[6] the equilibrium position of the surfactant is determined by the general shape equation[3] to give the relaxation time for various modes. However, it has never been checked whether the wavy kind of shape exists under pure consideration of force balance.

In this paper, from the analysis of the general one-dimensional(1D) solution to the Helfrich variation problem, we will give all the 1D periodic modes, especially the undulation modes within the spontaneous curvature model.

* Project supported by the Nonlinear Science Foundation of Institute of Theoretical Physics, China (Grant No. 98K103).

A 1D surface can be expressed by

$$z = f(x) \,. \tag{2}$$

The curvature of the curve is given by $t = \cos\psi \mathrm{d}\psi/\mathrm{d}x = \mathrm{d}\psi/\mathrm{d}s$, where s is the arc length under freely chosen origin, $\psi(s)$ is the angle between the x-axis and the tangent to the curve at point s. The curvature t satisfies the equation[7,8]

$$\frac{\mathrm{d}^2 t}{\mathrm{d}s^2} + \frac{1}{2}t^3 - \overline{\lambda}t - \overline{\Delta p} = 0 \,, \tag{3}$$

where $\overline{\lambda} = \lambda/k_c + c_0^2/2$, $\overline{\Delta p} = \Delta p/k_c$. The spontaneous curvature c_0 now appears only to contribute an effective tensile stress to $\overline{\lambda}$.

Equation (3) is the force balance equation of 1D memebranes (cylindrical membranes). The first integral of this equation is

$$\frac{\mathrm{d}t}{\sqrt{-t^4 + 4\overline{\lambda}t^2 + 8\overline{\Delta p}t + C}} = \frac{\mathrm{d}s}{2} = \frac{1}{2t}\mathrm{d}\psi \,, \tag{4}$$

where C is the constant of integration. Equation (4) shows that t is an elliptic function of arc length s. According to the fundamental theorem of plane curves, this function determines a unique plane curve except for an orientation-preserving Euclidean motion in R^2.

Althougth the curvature of the curve is a periodic function of the arc length s, it does not mean the curve is periodic. Only when a shape repeats periodically with Cartesian coordinates x and z, is the shape periodic.

Since t is a periodic function of s, we need only to consider one period of it. The angle ψ_0 turned in one period is

$$\psi_0 = \int_0^T t\mathrm{d}s \,, \tag{5}$$

where T is the period of $t(s)$, and ψ_0 can be expressed in terms of complete elliptic integral of the third kind. Detailed computation shows that ψ_0 are not equal to $2n\pi$ (n is an integer) in the case of $\Delta p \neq 0$, thus the shapes are not periodic in that case.

With $\overline{\lambda}$ and $\overline{\Delta p}$ given, ψ_0 can be viewed as a function of C. Though the constant C in Eq.(4) is an arbitrary integration constant, only when $\psi_0(C)$ satisfies certain conditions, is the curve closed. A complete classification of the types of closed shapes have been given in Ref.[8]. They are inward noduloids, outward noduloids, alternatively inward and outward noduloids and polygonal shapes.

In the following, we will prove that the shapes in general are periodic in the case of $\overline{\Delta p} = 0$. For $\overline{\Delta p} = 0$, Eq.(4) can be integrated to give

$$t = \frac{\mathrm{d}\psi}{\mathrm{d}s} = \frac{\sqrt{\pm 1 + \gamma\sin(\psi + \phi)}}{x_0} \,, \tag{6}$$

where γ and ϕ are integration constants and $\overline{\lambda} = \pm 1/(2x_0^2)$. The positive and negative signs correspond to the positive and negative tensile stresses respectively. As we have pointed out, λ takes account of the area constraint. The term λA can also be viewed as the energy

term. Positive λ means that this energy term increases with increasing area and negative λ means that it decreases with increasing area. It is clear that ϕ corresponds to a rotation of the axis, which can always be taken as zero. It can be proved that γ and $-\gamma$ give the same kind of shape and it is only necessary to consider positive γ.

For $\gamma \geq 1$, by a transformation $\sin\psi = 1 - 2k^2\sin^2\theta$, the integration of Eq.(6) can be reduced to Legendre's normal form

$$\int_{\psi}^{\pi/2} \frac{\mathrm{d}\psi}{\sqrt{\pm 1 + \gamma\sin\psi}} = g\int_0^{\theta} \frac{\mathrm{d}\theta}{\sqrt{1 - k^2\sin^2\theta}} = -s' \,, \tag{7}$$

where $s' = s/x_0$ is the dimensionless arc length, $g = \sqrt{2/\gamma}$ and $k^2 = (\pm 1 + \gamma)/2\gamma$; and the plus and minus sign correspond to positive and negative tensile stresses respectively. Here we have chosen the origin of s' such that $\psi(0) = \pi/2$. According to definition of Jacobian elliptic function, we have

$$\sin\theta = -\mathrm{sn}\left(\frac{s'}{g}, k\right) . \tag{8}$$

Thus

$$\sin\psi = 1 - 2k^2\mathrm{sn}^2\left[\frac{s'}{g}, k\right] , \tag{9}$$

$$c = \frac{\mathrm{d}\psi}{\mathrm{d}s'} = -\frac{2k}{g}\,\mathrm{cn}\left[\frac{s'}{g}, k\right] . \tag{10}$$

Here c is the curvature in units of the dimensionless arc length s'. Equation (10) shows that in one period the curvature c has two inflection points, i.e., two points with zero curvature. The angle rotated in one period is equal to

$$\psi_0 = \int_0^T c\mathrm{d}s' = \int_0^{4gK} -\frac{2k}{g}\,\mathrm{cn}\left[\frac{s'}{g}, k\right]\mathrm{d}s' = 0 \,, \tag{11}$$

where K is the complete elliptic integral of the first kind, $\mathrm{sn}(K, k)$=1, and $4gK$ is the period of $\mathrm{cn}\left(\frac{s'}{g}, k\right)$. Thus the curve rotates alternatively in two directions and maintains the angle turned in one period to be zero. Hence it is periodic in Euclidean space and represents an undulation shape.

For $0 < \gamma < 1$, $-1 + \gamma\sin\psi$ is always negative and only $1 + \gamma\sin\psi$ (which corresponds to positive $\overline{\lambda}$) is meaningful. In this case, Eq.(6) can be integrated to give

$$\sin\psi = 1 - 2\,\mathrm{sn}^2\left[\frac{s'}{g}, k\right] , \tag{12}$$

$$c = \frac{\mathrm{d}\psi}{\mathrm{d}s'} = -\frac{2}{g}\,\mathrm{dn}\left[\frac{s'}{g}, k\right] , \tag{13}$$

where $g = 2/\sqrt{1+\gamma}$, and $k^2 = 2\gamma/(1+\gamma)$. Equation (13) shows that c is a periodic function of s', ranging over $-2/g = -\sqrt{1+\gamma}$ and $-2\sqrt{1-k^2}/g = -\sqrt{1-\gamma}$, and is always negative (or equivalently positive) except in the limiting case of $\gamma = 1$, which corresponds to an

aperiodic case. So this kind of shape rotates towards one direction and has no inflection points. The angle rotated in one period is equal to

$$\psi_0 = \int_0^T c\mathrm{d}s' = \int_0^{2gK} -\frac{2k}{g}\,\mathrm{dn}\left[\frac{s'}{g},k\right]\mathrm{d}s' = 4\sin^-\left[\mathrm{sn}\left(\frac{s'}{g},k\right)\right]\Bigg|_0^{gK} = -2\pi\,, \tag{14}$$

where K is the complete elliptic integral of the first kind and $2gK$ is the period of $\mathrm{dn}\left(\dfrac{s'}{g},k\right)$. So this kind of shape is also periodic and rotates towards one direction. It is noduloid-like.[7]

To give the contour shapes of the solution, we come to the variable x. Equation (6) becomes

$$t = \cos\psi\frac{\mathrm{d}\psi}{\mathrm{d}(x/x_0)} = x_0\frac{\mathrm{d}\psi}{\mathrm{d}s} = \sqrt{\pm 1 + \gamma\sin\psi}\,. \tag{15}$$

Equation (15) can be integrated to give

$$\sin\psi = \frac{1}{4\delta}\left(\frac{x}{x_0} + B\right)^2 \mp \delta\,, \tag{16}$$

where $\delta = 1/\gamma$, the minus and plus signs correspond to the positive and negative tensile stresses respectively. B is a constant corresponding to a translation of the x-axis. With proper choice of the origin of the x-axis, we may have $B = 0$. From the above analysis, for $0 < \delta < 1$ ($\gamma > 1$), Eq.(16) describes undulation shapes and the amplitude of the surface is given by $x_\mathrm{A} = 2\sqrt{(1 \pm \delta)\delta}x_0$. With new variable $X = x/x_\mathrm{A}$, Eq.(16) can be written in the form

$$\sin\psi = (1+\delta)X^2 - \delta \qquad (-1 \le X \le 1) \tag{17}$$

for positive tensile stress, and

$$\sin\psi = (1-\delta)X^2 + \delta \qquad (-1 \le X \le 1) \tag{18}$$

for negative tensile stress. For the case of $\overline{\lambda} = 0$, Eq.(4) becomes

$$\frac{\mathrm{d}t^2}{\sqrt{C - t^4}} = \mathrm{d}\psi\,. \tag{19}$$

Integration of Eq.(19) gives

$$t = \cos\psi\frac{\mathrm{d}\psi}{\mathrm{d}x} = \sqrt{C^{1/2}\sin(\psi + \phi)}\,. \tag{20}$$

As we have pointed out, the integral constant ϕ corresponds to a rotation of the axis and can be taken as zero. With $x_\mathrm{A}^2 = 4/C^{1/2}$, Eq.(20) can be integrated to give

$$\sin\psi = X^2\,, \tag{21}$$

where $X = x/x_\mathrm{A}$. This is just Eq.(17) or Eq.(18) with $\delta = 0$.

The contour of the cross section can be obtained by calculating the integral

$$Z(X) - Z(X') = -\int_{X'}^{X}\tan\psi\mathrm{d}X\,, \tag{22}$$

where $Z = z/x_A$, so both x- and z-axes are scaled by x_A. Figure 1 displays the different undulation shapes corresponding to positive, negative and zero tensile stresses.

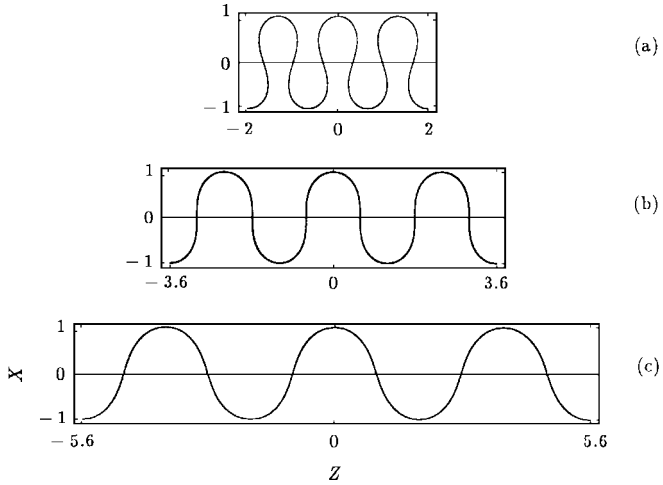

Fig.1. Undulation shapes for (a) $\overline{\lambda} < 0$ with $\delta = 0.3$; (b) $\overline{\lambda} > 0$ with $\delta = 0.3$ and (c) $\overline{\lambda} = 0$.

The period (actually period-amplitude ratio) of the cross section in the case of $\overline{\lambda} = 0$ is

$$Z_0 = 2\int_{-1}^{1} \frac{t^2}{\sqrt{1-t^4}}\,\mathrm{d}t \approx 2.4\,. \tag{23}$$

For negative $\overline{\lambda}$, the period increases with δ, and Z_0 is the lower limit of the period. When $\delta \to 1$, the shape degenerates into a plane.

For positive $\overline{\lambda}$ the period decreases with δ, and Z_0 is the upper limit of the period. For large δ, the shape will become self-intersected. And $\delta = 1$ corresponds to the aperiodic case, which is a special case of the noduloid-like shape.

In summary, we have shown that the shapes of 1D membranes are periodic only in the case of $\overline{\Delta p} = 0$. Three undulation modes exist corresponding to positive, negative and zero tensile stresses which are expressed in Eq.(17), Eq.(18) and Eq.(21) respectively. The undulation mode degenerates into a plane for negative tensile stress in the case of $\delta = 1$.

ACKNOWLEDGMENT

We are indebted to Prof. Peng Huan-wu for stimulating discussions and to Prof. Xie Yu-zhang for critical reading of the manuscript.

REFERENCES

[1] P. B. Canham, *J. Theor. Biol.*, **26**(1970), 61.
[2] W. Helfrich, *Z. Naturforsch.*, **C28**(1973), 693.
[3] Z. C. Ouyang, W. Helfrich, *Phys. Rev.*, **A39**(1989), 5280.
[4] W. Harbich, W. Helfrich, *Chem. Phys. Lipids*, **36**(1984), 39, Fig.11.
[5] F. Nallet, D. Roux, J. Prost, *J. Phys.(Paris)*, **50**(1989), 3147.
[6] E. V. D. Linden, F. M. Menger, *Langmuir*, **9**(1993), 690.
[7] S. G. Zhang, Z.C. Ouyang, *Phys. Rev.*, **E53**(1996), 4206.
[8] S. G. Zhang, *Acta Physica Sinica* (*Overseas Edition*), **6**(1997), 641.