

Elasticity of polymer vesicles by osmotic pressure: An intermediate theory between fluid membranes and solid shells

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The entropy of a polymer confined in a curved surface and the elastic free energy of a membrane consisting of polymers are obtained by scaling analysis. It is found that the elastic free energy of the membrane has the form of the in-plane strain energy plus Helfrich's curvature energy [Z. Naturforsch. C **28**, 693 (1973)]. The elastic constants in the free energy are obtained by discussing two simplified models: one is the polymer membrane without in-plane strains and asymmetry between its two sides, which is the counterpart of quantum mechanics in a curved surface [H. Jensen and H. Koppe, Ann. Phys. (N.Y) **63**, 586 (1971)]; the other is the planar rubber membrane with homogeneous in-plane strains. The equations to describe equilibrium shape and in-plane strains of the polymer vesicles by osmotic pressure are derived by taking the first-order variation of the total free energy containing the elastic free energy, the surface tension energy, and the term induced by osmotic pressure. The critical pressure above which a spherical polymer vesicle will lose its stability is obtained by taking the second-order variation of the total free energy. It is found that the in-plane mode also plays an important role in the critical pressure because it couples with the out-of-plane mode. Theoretical results reveal that polymer vesicles possess mechanical properties intermediate between those of fluid membranes and solid shells.

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I. INTRODUCTION

Thin structures exist widely in nature. Many things such as eggs, snails, airplanes, and so on in our daily life are covered with solid shells that play protective roles. In the realm that we cannot see with naked eyes, viruses usually have protein shells, and eukaryotic cells are enclosed by cell membranes that consist of lipids, proteins, and carbohydrates, etc. A lipid molecule has a polar hydrophilic head group and one or two hydrophobic hydrocarbon tails. When a quantity of lipid molecules disperse in water, they will assemble themselves into a lipid bilayer in which the hydrophilic heads shield the hydrophobic tails from the water surroundings because of the hydrophobic forces. Solid shells and lipid bilayers are, respectively, in the categories of hard and soft condensed matter. Their mechanical properties have attracted much attention for a long time [1–6].

The significant difference between solid shells and lipid bilayers is that the former can endure in-plane shear stress but the latter cannot. Due to this difference, solid shells and lipid bilayers have different forms of deformation energy. Under the assumption of homogenous and isotropic bulk materials and in the limit of thin thickness, the elastic free energy per unit area of a solid shell is expressed as [1]

$$\mathcal{E}_{sh} = \frac{D}{2}[(2H)^2 - 2(1 - \nu)K] + \frac{C}{2(1 - \nu^2)}[(2J)^2 - 2(1 - \nu)Q], \quad (1)$$

where $D = (1/12)Yh^3/(1 - \nu^2)$ and $C = Yh$ are the bending rigidity and in-plane stiffness of the shell. Y , ν , and h are, respectively, the Young's modulus, the Poisson ratio, and the thickness of the shell. $2J$ and Q are the trace and determinant of the in-plane strain tensor, respectively. For a spherical solid shell with radius R , the critical osmotic pressure (i.e., the pressure difference between the outer surface and inner one of the shell, above which the shell loses its stability) is [2]

$$p_{cs} = \frac{2Yh^2}{\sqrt{3(1 - \nu^2)}R^2}. \quad (2)$$

In 1973, Helfrich [3] recognized that the lipid bilayer was just like a liquid crystal in the smectic-A phase at room temperature. Based on the elastic theory of liquid crystals [7], he proposed the curvature energy per unit area of the bilayer

$$\mathcal{E}_{lb} = (k_c/2)(2H + c_0)^2 + \bar{k}K, \quad (3)$$

where k_c and \bar{k} are elastic constants, and H , K , and c_0 are the mean curvature, Gaussian curvature, and spontaneous curvature of the lipid bilayer, respectively. For phospholipid bilayers at room temperature T , the persistence length is usually much larger than the size of the membranes and the effect of shape fluctuations is negligible [4] because $k_c \approx 10^{-19}J \gg k_B T$ [8], where k_B is the Boltzmann factor. The free energy of a closed bilayer under the osmotic pressure p is written as $\mathcal{F}_{lb} = \oint (\mathcal{E}_{lb} + \lambda) dA + p \int dV$, where dA is the area element and V the volume enclosed by the closed bilayer. λ is the surface

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tension of the bilayer. The first-order variation of \mathcal{F}_{lb} gives the shape equation of the closed bilayer [9]:

$$p - 2\lambda H + k_c \nabla^2(2H) + k_c(2H + c_0)(2H^2 - c_0H - 2K) = 0. \quad (4)$$

For a spherical lipid bilayer with radius R , the critical osmotic pressure for stability is [10]

$$p_{cl} = \frac{2k_c(6 - c_0R)}{R^3}. \quad (5)$$

It follows that $p_{cl} \sim k_c/R^3$ because the typical value of c_0R is about 1. Therefore, a lipid bilayer is, indeed, much softer than a solid shell.

Are there membranes intermediate in state between Helfrich's fluid lipid bilayers and classical solid shells? The polymer vesicles discussed below may be an example. In the last decade, Decher invented the layer-by-layer assembling technique [11]. Following this technique, Caruso *et al.* made spherical polyelectrolyte capsules by the stepwise adsorption of polyelectrolytes onto charged colloidal templates and then decomposition of the templates [12,13]. The capsules were composed of about ten layers of alternating polystyrene sulfonate and polyallylamine hydrochloride. The thickness h of capsules was about tens of nanometers which was remarkably less than their radii R (several micrometers). Gao *et al.* [14] found that the spherical polyelectrolyte capsule lost its stability and changed its shape abruptly above some threshold of osmotic pressure p_c which was proportional to R^{-2} and h^2 . In their experiment, the thickness dependence of p_c might not be exact because the polyelectrolyte capsule with more than ten layers was chemically unstable as they claimed. They also explained their results through the stability theory of classical elastic solid shells [1,2]. But it is well known that the classical theory is based on the assumption of homogeneous and isotropic bulk materials which entirely ignores the characteristic of the polyelectrolyte capsule consisting of many polymers. If we consider the polymer structures of spherical polyelectrolyte capsule, can we still derive $p_c \sim R^{-2}$?

In this paper, we will answer the above questions. To do that, we derive the entropy of a polymer confined in a curved surface and the elastic free energy of a membrane consisting of polymers by scaling analysis. It is found that the elastic free energy of the polymer membrane has the form of the in-plane strain energy plus Helfrich's curvature energy. The elastic constants in the free energy are obtained by discussing two simplified models: one is the polymer membrane without in-plane strains and asymmetry between its two sides, which is the counterpart of quantum mechanics in a curved surface [15]; the other is the planar rubber membrane with homogeneous in-plane strains. The equations to describe the equilibrium shape and in-plane strains of polymer vesicles by osmotic pressure are derived by taking the first-order variation of the total free energy containing the elastic free energy, the surface tension energy, and the term induced by osmotic pressure. The critical pressure above which a spherical polymer vesicle will lose its stability is obtained by taking the second-order variation of the total free energy. It is

found that the in-plane mode also plays important role in the critical pressure because it couples with the out-of-plane mode. These theoretical results reveal that polymer vesicles possess mechanical properties being intermediate between those of Helfrich's fluid membranes and classical solid shells.

The following contents of this paper are organized as below. In Sec. II, we derive the free energy of polymer membrane by using scaling concepts [16]. In Sec. III, we obtain the shape and in-plane strain equations of closed polymer vesicles by using the surface variation theory developed in Refs. [17,18]. In Sec. IV, we discuss the mechanical stability of the spherical polymer vesicle by taking the second-order variation of the free energy. In Sec. V, we give a brief summary and discussion.

II. THE FREE ENERGY OF THE POLYMER MEMBRANE

The polymer membrane discussed in this paper is one or a few thin layers consisting of a cross-linked polymer structure like rubber [19] at molecular levels. It can be represented as a mathematical surface with curvature and strains. It is hard to derive its free energy in a strict way. But we can drive it by using scaling concepts in polymer physics proposed by de Gennes [16]. In the following, we take de Gennes' convention: the entropy S is a dimensionless quantity and the Boltzmann factor k_B is implicated in temperature T .

A. The free energy of the polymer membrane

If we take the Gaussian chain model [20], the root mean square end-to-end distance of a polymer is $R_0 \sim \sqrt{Nb_0}$, where b_0 is the segment length of the polymer and N is the number of segments. Assume that the principal radii of the surface are much larger than R_0 . If the in-plane strain tensor of the surface is denoted by ϵ which is assumed to be a small quantity, the entropy of the polymer confined to the surface must be the function of $2HR_0, KR_0^2, 2J$, and Q because it is a dimensionless invariant quantity under the transformation of coordinates, where $H, K, J = \text{tr}\epsilon$ and $Q = \text{tr}\epsilon$ are the mean curvature of the surface, the Gaussian curvature of the surface, the trace of the strain tensor, and the determinant of the strain tensor, respectively. Thus we can expand it as

$$S \sim A_1(2HR_0) + A_2(2HR_0)^2 + A_3KR_0^2 + B_2(2J)^2 + B_3Q \quad (6)$$

up to second-order terms, where A_1, A_2, A_3, B_2 , and B_3 are constants. In this expression, an unimportant constant term is neglected. Moreover, one must notice that generally we have $K \sim (2H)^2$ and $Q \sim (2J)^2$. Additionally, there is no first-order term of $2J$ in the expression of the entropy because we expect that $-\epsilon$ plays the same role as ϵ in the entropy. It is useful to write the entropy in another equivalent form:

$$S \sim A_2R_0^2(2H + c_0)^2 + A_3R_0^2K + B_2(2J)^2 + B_3Q, \quad (7)$$

where $c_0 = A_1/(2A_2)$ is a constant, the so called spontaneous curvature, which is expected to satisfy $|c_0R_0| \ll 1$. In fact, c_0 vanishes if there is no asymmetric factor between two sides

TABLE I. The correspondence principle between polymer statistics and path integral method in quantum mechanics.

Quantum mechanics	Polymer statistics
Time t	Number of segments N
i/\hbar	$-\beta = -1/T$
Lagrangian $\hat{L} = (m/2)(d\mathbf{r}/d\tau)^2 - V[\mathbf{r}(\tau)]$	Energy $E = (\eta/2)(d\mathbf{R}_n/dn)^2 + U(\mathbf{R}_n)$
Mass m	$\eta = 3/(\beta b_0^2)$
potential $V(\mathbf{r}(\tau))$	$-U(\mathbf{R}_n)$
Propagator $\hat{K} = \int \exp[(i/\hbar) \int_0^{\hat{L}} d\tau] D[\mathbf{r}(\tau)]$	Partition function $Z = \int \exp[-\beta \int_0^N E dn] D[\mathbf{R}_n]$
Hamiltonian $\hat{H} = -\hbar^2/2m \nabla^2 + V$	$\hat{P} = 1/2 \eta \beta^2 \nabla^2 - U$
$i\hbar \partial \hat{K} / \partial t = \hat{H} \hat{K} \quad (t > 0)$	$(1/\beta) \partial Z / \partial N = \hat{P} Z$

of the surface because H turns into $-H$ if we change the normal direction of the surface.

Assume h to be the membrane thickness and M the number of polymers per volume. Additionally, we neglect the the entanglement of polymers. Consequently, the free energy per unit area of a membrane consisting of polymers has the following form:

$$\mathcal{E}_{pm} = -(Mh)TS = \frac{k_d}{2}[(2J)^2 - \mu Q] + \frac{k_c}{2}(2H + c_0)^2 - \bar{k}K, \quad (8)$$

where $k_d = -2B_2MhT$, $\mu = -B_3/B_2$, $k_c = -2MhTA_2R_0^2$, and $\bar{k} = MhTA_3R_0^2$.

Obviously, Eq. (8) degenerates to Helfrich's curvature energy of fluid membranes if $k_d = 0$, and to the elastic energy of classical solid shells if $c_0 = 0$, $k_d = C/(1 - \nu^2)$, $k_c = D$, $\mu = 2(1 - \nu)$, and $\bar{k} = D(1 - \nu)$.

B. The elastic constants k_d, μ , and k_c

k_d, μ, k_c , and \bar{k} are unknown universal constants independent of the detailed shape and the small in-plane strains of the polymer membrane. If we only discuss closed polymer vesicles in this paper, we need not know \bar{k} because the integral of $\bar{k}K$ is an unimportant constant. To determine k_d, μ , and k_c , we will discuss two ideal cases: one is the cylinder polymer membrane without any strain and asymmetry between its two sides; the other is the planar membrane with homogeneous in-plane strains.

In the former case, we denote as ρ the radius of the cylinder. On the one hand, Eq. (8) is simplified as

$$\mathcal{E}_{pm} = \frac{k_c}{2\rho^2}. \quad (9)$$

On the other hand, we know there is a 1:1 correspondence relation between polymer statistics and the quantum path integral method [20] as shown in Table I. In 1971, Jensen and Koppe dealt with the quantum mechanics of a particle constrained in a curved surface and obtained a nontrivial conclusion [15]: the constraint would induce an effective potential $V_{eff} = -(\hbar^2/8m)[(2H)^2 - 4K]$ in the Schrödinger equation,

where m is the particle mass. In terms of the correspondence rules in Table I, there will be an effective potential $U_{eff} = (b_0^2/24\beta)[(2H)^2 - 4K]$ for a polymer confined in a curved surface. Especially, $U_{eff} = Tb_0^2/24\rho^2$ for the cylinder with radius ρ . We must pay more attention to the fact that there is a minus symbol in the potential term when we use the correspondence rules. In fact, Yaman *et al.* overlooked this fact in recent literature [21]. But this flaw cannot diminish the value of their pioneer work in the study of polymers confined in a curved surface. Thus their results can be safely transplanted only if we change the sign. Consequently, we obtain the free energy of the cylindrical membrane consisting of Mh polymers per unit area

$$\mathcal{E}_{pm} = \frac{MhTnb_0^2}{24\rho^2} = \frac{MhTR_0^2}{24\rho^2} \quad (10)$$

if we neglect the entanglement between polymers. Comparing Eq. (9) with Eq. (10), we obtain $k_c = MhR_0^2T/12$.

In the latter case, H, K , and c_0 are vanishing for planar membrane with symmetry between its two sides. On the one hand, Eq. (8) is simplified as

$$\mathcal{E}_{pm} = \frac{k_d}{2}[(2J)^2 - \mu Q]. \quad (11)$$

For homogeneous strain ϵ , we can express it by its components $\epsilon_{11}, \epsilon_{22}$, and $\epsilon_{12} = \epsilon_{21} = 0$ in some orthonormal coordinate system so that $2J = \epsilon_{11} + \epsilon_{22}$ and $Q = \epsilon_{11}\epsilon_{22}$.

On the other hand, we notice that there might be cross-linking joints between polymers in the membrane. This character suggests that the membrane should have the elastic properties of rubber materials. In terms of the elasticity theory of rubber [19], the deformation energy of a planar rubber per area can be expressed as $f_r = (MhT/2)[\lambda_1^2 + \lambda_2^2 + 1/(\lambda_1^2\lambda_2^2) - 3]$, where $\lambda_1 = 1 + \epsilon_{11}$ and $\lambda_2 = 1 + \epsilon_{22}$ are extensions. For small strains, it is expanded to the lowest order terms as

$$\mathcal{E}_{pm} = 2MhT(\epsilon_{11}^2 + \epsilon_{11}\epsilon_{22} + \epsilon_{22}^2) = 2MhT[(2J) - Q]. \quad (12)$$

Thus we can obtain $k_d = 4MhT$ and $\mu = 1$ by comparing Eq. (11) with Eq. (12).

Therefore, we obtain the free energy of a closed polymer vesicle under osmotic pressure p :

$$\mathcal{F} = \oint (k_d/2)[(2J)^2 - Q]dA + \oint [(k_c/2)(2H + c_0)^2 + \mu]dA + p \int dV, \quad (13)$$

where μ , A , and V are the surface tension, surface area, and volume enclosed by the vesicle, respectively. In this expression, the term related to the Gaussian curvature disappears because its integration $\oint K dA$ is a unimportant constant so that it is omitted. It is easy to see that Eq. (13) degenerates to the free energy of a closed lipid bilayer for $k_d=0$, and to the free energy of a solid shell with $\nu=1/2$ if $c_0=0$, $k_d=C/(1-\nu^2)$, and $k_c=D$.

III. THE SHAPE AND IN-PLANE STRAIN EQUATIONS OF CLOSED POLYMER VESICLES

In this section, we will give the shape and in-plane strain equations of closed polymer vesicles from the first-order variation of free energy (13). The method has been fully developed in Ref. [18], and the key elements and notations are shown in the Appendix.

If a point \mathbf{r}_0 in a surface undergoes a displacement \mathbf{u} to arrive at point \mathbf{r} , we have $d\mathbf{u}=d\mathbf{r}-d\mathbf{r}_0$ and naturally $\delta_i d\mathbf{u} = \delta_i d\mathbf{r}$ ($i=1, 2, 3$).

If we denote $d\mathbf{r}=\omega_1\mathbf{e}_1+\omega_2\mathbf{e}_2$ and $d\mathbf{u}=\mathbf{U}_1\omega_1+\mathbf{U}_2\omega_2$ with $|\mathbf{U}_1|\ll 1, |\mathbf{U}_2|\ll 1$, we can define the in-plane strains [22]

$$\epsilon_{11} = \left[\frac{d\mathbf{u} \cdot \mathbf{e}_1}{|d\mathbf{r}_0|} \right]_{\omega_2=0} \approx \mathbf{U}_1 \cdot \mathbf{e}_1, \quad (14)$$

$$\epsilon_{22} = \left[\frac{d\mathbf{u} \cdot \mathbf{e}_2}{|d\mathbf{r}_0|} \right]_{\omega_1=0} \approx \mathbf{U}_2 \cdot \mathbf{e}_2, \quad (15)$$

$$\epsilon_{12} = \frac{1}{2} \left[\left(\frac{d\mathbf{u} \cdot \mathbf{e}_2}{|d\mathbf{r}_0|} \right)_{\omega_2=0} + \left(\frac{d\mathbf{u} \cdot \mathbf{e}_1}{|d\mathbf{r}_0|} \right)_{\omega_1=0} \right] \approx \frac{1}{2} (\mathbf{U}_1 \cdot \mathbf{e}_2 + \mathbf{U}_2 \cdot \mathbf{e}_1). \quad (16)$$

Using $\delta_i d\mathbf{u} = \delta_i d\mathbf{r}$ and the definitions of strains (14)–(16), we can obtain the leading terms of variational relations:

$$\delta_i \epsilon_{11} \omega_1 \wedge \omega_2 = \delta_i \omega_1 \wedge \omega_2, \quad (17)$$

$$\delta_i \epsilon_{12} \omega_1 \wedge \omega_2 = \frac{1}{2} [\omega_1 \wedge \delta_i \omega_1 + \delta_i \omega_2 \wedge \omega_2], \quad (18)$$

$$\delta_i \epsilon_{22} \omega_1 \wedge \omega_2 = \omega_1 \wedge \delta_i \omega_2. \quad (19)$$

Please note that the symbol \wedge in this paper expresses the exterior (or wedge) product [18].

From Eqs. (17)–(19) and (A12)–(A21), we have

$$\delta_1 \mathcal{F} = \oint k_d \left(-d(2J) \wedge \omega_2 - \frac{\epsilon_{11} d\omega_2 - \epsilon_{12} d\omega_1}{2} + \frac{d(\epsilon_{12}\omega_1 + \epsilon_{22}\omega_2)}{2} \right) \Omega_1, \quad (20)$$

$$\delta_2 \mathcal{F} = \oint k_d \left(d(2J) \wedge \omega_1 - \frac{\epsilon_{12} d\omega_2 - \epsilon_{22} d\omega_1}{2} - \frac{d(\epsilon_{11}\omega_1 + \epsilon_{12}\omega_2)}{2} \right) \Omega_2, \quad (21)$$

$$\delta_3 \mathcal{F} = \oint \left(k_c(2H + c_0)(2H^2 - c_0H - 2K) + k_c \nabla^2(2H) + p - 2H(\mu + k_d J) - \frac{k_d}{2}(a\epsilon_{11} + 2b\epsilon_{12} + c\epsilon_{22}) \right) \Omega_3 dA. \quad (22)$$

Thus the Euler-Lagrange equations corresponding to the functional (13) are

$$k_d \left(-d(2J) \wedge \omega_2 - \frac{1}{2}(\epsilon_{11}d\omega_2 - \epsilon_{12}d\omega_1) + \frac{1}{2}d(\epsilon_{12}\omega_1 + \epsilon_{22}\omega_2) \right) = 0, \quad (23)$$

$$k_d \left(d(2J) \wedge \omega_1 - \frac{1}{2}(\epsilon_{12}d\omega_2 - \epsilon_{22}d\omega_1) - \frac{1}{2}d(\epsilon_{11}\omega_1 + \epsilon_{12}\omega_2) \right) = 0, \quad (24)$$

$$p - 2H(\mu + k_d J) + k_c(2H + c_0)(2H^2 - c_0H - 2K) + k_c \nabla^2(2H) - \frac{k_d}{2}(a\epsilon_{11} + 2b\epsilon_{12} + c\epsilon_{22}) = 0. \quad (25)$$

Equations (23) and (24) are called the in-plane strain equations because they describe the in-plane strains of polymer vesicles under the pressure p . Equation (25) is called the shape equation because it describes the equilibrium shape of polymer vesicles under the pressure p .

Obviously, if $k_d=0$, then Eqs. (23) and (24) are two identities while Eq. (25) degenerates into the shape equation (4) of closed lipid bilayers. Generally speaking, it is difficult to find the analytical solutions to Eqs. (23)–(25). But it is easy to verify that $\epsilon_{11}=\epsilon_{22}=\epsilon$ (a constant), $\epsilon_{12}=0$ satisfy Eqs. (23)–(25) for a spherical vesicle with radius R if the following equation is valid:

$$pR^2 + (2\mu + 3k_d\epsilon)R + k_c c_0(c_0R - 2) = 0. \quad (26)$$

IV. MECHANICAL STABILITY OF SPHERICAL POLYMER VESICLES

Now we will calculate the second-order variation of functional (13) and discuss the mechanical stability of a spherical polymer vesicle.

In Ref. [18], only the term $\delta_3^2 \mathcal{F}$ related to the out-plane mode $\{\Omega_3\}$ is calculated. Here we also consider the contribu-

tion of the in-plane mode $\{\Omega_1, \Omega_2\}$. Due to the notation of exterior differential d and Hodge star $*$, Ω_1 and Ω_2 can be expressed as

$$\Omega_1 \omega_1 + \Omega_2 \omega_2 = d\Omega + *d\chi \quad (27)$$

by two scalar potential functions Ω and χ for a two-dimensional manifold [23]. Using Eqs. (17)–(19) and (A12)–(A21), we can calculate $\delta_1^2 \mathcal{F}$, $\delta_2^2 \mathcal{F}$, $\delta_3^2 \mathcal{F}$, $\delta_1 \delta_2 \mathcal{F}$, $\delta_1 \delta_3 \mathcal{F}$, and $\delta_2 \delta_3 \mathcal{F}$ from Eqs. (20)–(22) and (26) for Spherical polymer membrane. Eventually, we arrive at

$$\begin{aligned} \delta^2 \mathcal{F} = & \delta_1^2 \mathcal{F} + \delta_2^2 \mathcal{F} + \delta_3^2 \mathcal{F} + 2\delta_1 \delta_2 \mathcal{F} + 2\delta_1 \delta_3 \mathcal{F} + 2\delta_2 \delta_3 \mathcal{F} \equiv G_1 \\ & + G_2, \end{aligned} \quad (28)$$

where

$$\begin{aligned} G_1 = & \oint \Omega_3^2 \{3k_d/R^2 + (2k_c c_0/R^3) + p/R\} dA \\ & + \oint \Omega_3 \nabla^2 \Omega_3 \{k_c c_0/R + 2k_c/R^2 + pR/2\} dA \\ & + \oint k_c (\nabla^2 \Omega_3)^2 dA + \frac{3k_d}{R} \oint \Omega_3 \nabla^2 \Omega dA \\ & + k_d \oint (\nabla^2 \Omega)^2 dA + \frac{k_d}{2R^2} \oint \Omega \nabla^2 \Omega dA, \end{aligned} \quad (29)$$

$$G_2 = \frac{k_d}{4} \oint (\nabla^2 \chi)^2 dA + \frac{k_d}{2R^2} \oint \chi \nabla^2 \chi dA. \quad (30)$$

If we take $\kappa = k_c/2$, $K = 3k_d/2$, $\mu = k_d/2$, $w = \Omega_3$, and $\Psi = \Omega$ in Eq. (6) and (7) of Zhang *et al.*'s paper [24], then G_1 and G_2 correspond to $F_1[w, \Psi]$ and $F_2[\chi]$ in that paper under the conditions of $p=0$ and $c_0 R=2$. Obviously, there is no coupling between modes $\{\chi\}$ and $\{\Omega, \Omega_3\}$; but there is coupling between in-plane mode $\{\Omega\}$ and out-of-plane mode $\{\Omega_3\}$. We will show that in-plane modes have quantitative effect on the stability of the cell membrane although they cannot qualitatively modify the results of Ref. [18].

Because G_2 is obviously positive definite, we merely need to discuss G_1 . Ω_3 and Ω in the expression of G_1 can be expanded by spherical harmonic functions [25] as $\Omega_3 = \sum_{l=0}^{\infty} \sum_{m=-l}^{m=l} a_{lm} Y_{lm}(\theta, \phi)$ and $\Omega = \sum_{l=0}^{\infty} \sum_{m=-l}^{m=l} b_{lm} Y_{lm}(\theta, \phi)$ with $a_{lm}^* = (-1)^m a_{l,-m}$ and $b_{lm}^* = (-1)^m b_{l,-m}$. It follows that

$$\begin{aligned} G_1 = & \sum_{l=0}^{\infty} \sum_{m=0}^l 2|a_{lm}|^2 \{3k_d + [l(l+1) - 2][l(l+1)k_c/R^2 - k_c c_0/R \\ & - pR/2]\} - \sum_{l=0}^{\infty} \sum_{m=0}^l \frac{3k_d}{R} l(l+1) (a_{lm}^* b_{lm} + a_{lm} b_{lm}^*) \\ & + \sum_{l=0}^{\infty} \sum_{m=0}^l \frac{k_d}{R^2} [2l^2(l+1)^2 - l(l+1)] |b_{lm}|^2. \end{aligned} \quad (31)$$

We find that if $p < p_l = 3k_d/[2l(l+1) - 1]R + (2k_c[l(l+1) - c_0 R])/R^3$ ($l=2, 3, \dots$), then G_1 is positive definite, i.e., the vesicle is stable. We must take the minimum of p_l to obtain the critical pressure:

$$p_c = \min\{p_l\} = \begin{cases} \frac{3k_d}{11R} + \frac{2k_c[6 - c_0 R]}{R^3} < \frac{k_c[23 - 2c_0 R]}{R^3} & (3k_d R^2 < 121k_c), \\ \frac{2\sqrt{3k_d k_c}}{R^2} + \frac{k_c}{R^3} (1 - 2c_0 R) & (3k_d R^2 > 121k_c). \end{cases} \quad (32)$$

But if we do not consider the in-plane mode $\{\Omega\}$, we will obtain the critical pressure [18]

$$p_c = \begin{cases} \frac{3k_d}{2R} + \frac{2k_c(6 - c_0 R)}{R^3} < \frac{2k_c(10 - c_0 R)}{R^3} & (3k_d R^2 < 16k_c), \\ \frac{4\sqrt{3k_d k_c}}{R^2} + \frac{2k_c}{R^3} (2 - c_0 R) & (3k_d R^2 > 16k_c). \end{cases} \quad (33)$$

Comparing Eq. (32) with Eq. (33), we find that the in-plane modes have a qualitative effect on the stability of the polymer vesicles although the qualitative result absence of these modes is unchanged.

Now we test the validity of Eq. (32) by considering two special cases. The first case, $k_d=0$, corresponds to a lipid bilayer. In this case, Eq. (32) is exactly reduced to Eq. (5), the critical pressure for a spherical lipid bilayer. The second case, $c_0=0$, $k_d=Yh/(1-\nu^2)$, and $k_c=Yh^3/[12(1-\nu^2)]$ with

$\nu=1/2$, corresponds to the solid shell with Young's modulus Y , Poisson ratio ν , and shell thickness h . Under the condition of $h \ll R$, Eq. (32) gives $p_c = (4/3)Yh^2/R^2$ which is exactly the result of Eq. (2) with $\nu=1/2$. Thus we are sure of the validity of Eq. (32).

Now we turn to the polymer vesicle consisting of poly-electrolytes. In the experiment by Gao *et al.* [14], its thickness is $h \sim 20$ nm which is much smaller than its radius $R \sim 2$ μ m. The segment length is taken as three times the

carbon-carbon bond length, i.e., $b_0 \sim 4.2 \text{ \AA}$. The number of segments per polymer are about $N \sim 200$ due to the molecule weight 70 000. Thus $R_0 \sim \sqrt{N}b_0 \sim 60 \text{ \AA}$, which is less than R . Considering $k_d = 4MhT$ and $k_c = MhR_0^2T/12$, we arrive at $3k_dR^2/(121k_c) = (12R)^2/(11R_0)^2 \gg 1$, i.e., $3k_dR^2 \gg 121k_c$. Under this condition, Eq. (32) is reduced to

$$p_c = \frac{2MTR_0h}{R^2}. \quad (34)$$

The above equation can explain the experimental result $p_c \sim R^{-2}$ obtained by Gao *et al.* But their result $p_c \sim h^2$ is inconsistent with our theoretical result $p_c \sim h$. The main reason for this discrepancy is that the membrane consisting of polyelectrolytes is chemically unstable if its layer number is more than 10, which will prevent a test of the exact relation between critical pressure p_c and thickness h .

V. CONCLUSION

In the above discussion, we briefly introduce the polymer statistics and the correspondence principle (shown in Table I) between it and the path integral method in quantum mechanics. We derive the entropy of a polymer confined in a curved surface and the elastic energy of a membrane consisting of polymers by scaling analysis. It is found that the elastic energy of the polymer membrane has the form of the in-plane strain energy plus Helfrich's curvature energy as shown in Eq. (8). The elastic constants k_d, k_c, μ in the free energy are obtained by discussing two simplified models: one is the polymer membrane without in-plane strains and asymmetry between its two sides, which is the counterpart of quantum mechanics in a curved surface; another is the planar rubber membrane with homogeneous in-plane strains. The equations to describe equilibrium shape and in-plane strains of polymer vesicles by osmotic pressure are derived by taking the first order variation of the total free energy (13) containing the elastic free energy, the surface tension energy, and the term induced by osmotic pressure. The critical pressure (32), above which the spherical polymer vesicle will lose its stability, is obtained by taking the second-order variation of the total free energy (13). It is found that the in-plane mode $\{\Omega\}$ also plays an important role in the critical pressure because it couples with the out-of-plane mode $\{\Omega_3\}$.

We estimate that $p_c = 2MTR_0h/R^2$ through the experiment by Gao *et al.* This result is qualitatively intermediate between $p_{cl} = 2k_c(6 - c_0R)/R^3$ for the lipid bilayer and $p_{cs} = 2Yh^2/\sqrt{3(1 - \nu^2)}R^2$ for a solid shell. Therefore polymer vesicles possess mechanical properties intermediate between those of Helfrich's fluid membranes and classical solid shells. But is it reasonable to use the present theory for polyelectrolyte membranes? We discuss two points. (i) The derivation of the bending rigidity of the polymer membrane uses results for the quantum mechanics of a particle constraint in a curved surface. The results can only apply to polymers that are much more constrained perpendicular to the membrane in than their lateral size. It seems that the polymer vesicles in the experiment by Gao *et al.* do not satisfy this condition since $R_0 \sim 6 \text{ nm}$ and $h \sim 20 \text{ nm}$. But in fact, the vesicles con-

tain ten layers and the thickness of each layer is about 2 nm which is much smaller than R_0 and the total length of a polymer. That is, the strong constraint in the normal direction of the membrane is satisfied. (ii) The Gaussian chain model is used in the present work. However, the polymers in polyelectrolyte membranes may be nonideal. This is indeed a difficulty. But the present theory is focused on small deformations of polymer vesicles; the model of the ideal polymer should give approximate results due to the lessons in classical theory of rubber elasticity [19]. Additionally, we indeed obtain the relation $p_c \sim R^{-2}$ observed by the experiment.

It is a nontrivial thing that we analysis the mechanical stabilities directly from second-order variations of the free energy (13). In the classical literature on stabilities of shells, such as Refs. [1,2], the critical pressure (2) is obtained under a special assumption of the unstable mode that the concave part after instability is the mirror image of its initial one. Therefore, the present work implies that we can also analyze the mechanical stabilities of solid shells directly from second-order variations of free energy (1) without the special assumption in conventional literature.

It is well known that cell membranes contain lipid bilayers and membrane skeleton. Our theory of polymer membranes may be applicable for the membrane skeleton because it is also a cross-linking structure at molecular levels. In the future, we can turn to the elasticity of cell membranes after we have fully studied the elasticity of the lipid bilayer and membrane skeleton.

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APPENDIX: SURFACE VARIATION THEORY

Here we briefly review the surface variation theory originated in Ref. [17] and fully developed in Ref. [18].

We use a smooth and closed surface \mathcal{M} in three-dimensional Euclid space \mathbb{E}^3 to represent a membrane. As shown in Fig. 1, we can construct a right-hand orthonormal system $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$ at any point \mathbf{r} in the surface and call $\{\mathbf{r}; \mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$ a moving frame. The differential of the frame is denoted by

$$\begin{cases} d\mathbf{r} = \omega_1 \mathbf{e}_1 + \omega_2 \mathbf{e}_2, \\ d\mathbf{e}_i = \omega_{ij} \mathbf{e}_j (i = 1, 2, 3), \end{cases} \quad (A1)$$

where ω_1, ω_2 , and $\omega_{ij} = -\omega_{ji}$ ($i, j = 1, 2, 3$) are one-forms. The structure equations of the surface are

$$d\omega_1 = \omega_{12} \wedge \omega_2, \quad (A2)$$

$$d\omega_2 = \omega_{21} \wedge \omega_1, \quad (A3)$$

$$\omega_{13} = a\omega_1 + b\omega_2, \quad \omega_{23} = b\omega_1 + c\omega_2, \quad (A4)$$

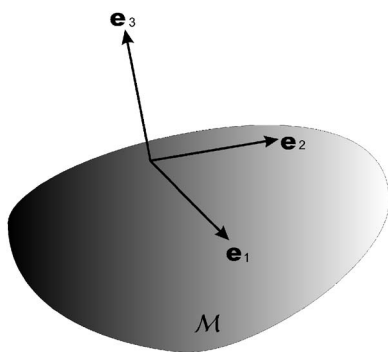


FIG. 1. Smooth and orientable surface M . We can construct a right-hand orthonormal system $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$ at any point \mathbf{r} in the surface and call $\{\mathbf{r}; \mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$ a moving frame.

$$d\omega_{ij} = \omega_{ik} \wedge \omega_{kj} (i, j = 1, 2, 3). \quad (\text{A5})$$

Readers should notice that the operator “ d ” is an exterior differential operator [18] in this paper. The area element, mean curvature, and Gaussian curvature are, respectively, expressed as

$$dA = \omega_1 \wedge \omega_2, \quad (\text{A6})$$

$$H = (a + c)/2, \quad (\text{A7})$$

$$K = ac - b^2. \quad (\text{A8})$$

If M undergoes an infinitesimal deformation such that every point \mathbf{r} in M has a displacement $\delta\mathbf{r}$, we obtain a new surface $M' = \{\mathbf{r}' | \mathbf{r}' = \mathbf{r} + \delta\mathbf{r}\}$. $\delta\mathbf{r}$ is called the variation of surface M and can be expressed as

$$\delta\mathbf{r} = \delta_1\mathbf{r} + \delta_2\mathbf{r} + \delta_3\mathbf{r}, \quad (\text{A9})$$

$$\delta_i\mathbf{r} = \Omega_i\mathbf{e}_i (i = 1, 2, 3), \quad (\text{A10})$$

where the repeated subindices do not represent Einstein summation. Due to the deformation of M , $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$ also change. We denote the change as

$$\delta_i\mathbf{e}_i = \Omega_{lij}\mathbf{e}_j, \quad \Omega_{lij} = -\Omega_{lji}. \quad (\text{A11})$$

Using the commutativity between δ_i ($i = 1, 2, 3$) and d , we obtain the fundamentally variational identities of the moving frame [18]:

$$\delta_1\omega_1 = d\Omega_1 - \omega_2\Omega_{121}, \quad (\text{A12})$$

$$\delta_1\omega_2 = \Omega_1\omega_{12} - \omega_1\Omega_{112}, \quad (\text{A13})$$

$$\Omega_{113} = a\Omega_1, \quad \Omega_{123} = b\Omega_1, \quad (\text{A14})$$

$$\delta_2\omega_1 = \Omega_2\omega_{21} - \omega_2\Omega_{221}, \quad (\text{A15})$$

$$\delta_2\omega_2 = d\Omega_2 - \omega_1\Omega_{212}, \quad (\text{A16})$$

$$\Omega_{213} = b\Omega_2, \quad \Omega_{223} = c\Omega_2, \quad (\text{A17})$$

$$\delta_3\omega_1 = \Omega_3\omega_{31} - \omega_2\Omega_{321}, \quad (\text{A18})$$

$$\delta_3\omega_2 = \Omega_3\omega_{32} - \omega_1\Omega_{312}, \quad (\text{A19})$$

$$d\Omega_3 = \Omega_{313}\omega_1 + \Omega_{323}\omega_2, \quad (\text{A20})$$

$$\delta_l\omega_{ij} = d\Omega_{lij} + \Omega_{lik}\omega_{kj} - \omega_{ik}\Omega_{lkj}. \quad (\text{A21})$$

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- [1] L. D. Landau and E. M. Lifshitz, *Theory of Elasticity*, 3rd ed. (Butterworth-Heinemann, Oxford, 1997).
- [2] A. V. Pogorelov, *Bendings of Surfaces and Stability of Shells* (RI, AMS, Providence, 1989).
- [3] W. Helfrich, *Z. Naturforsch. C* **28**, 693 (1973).
- [4] R. Lipowsky, *Nature (London)* **349**, 475 (1991).
- [5] U. Seifert, *Adv. Phys.* **46**, 13-137 (1997).
- [6] Ou-Yang Zhong-can, *Thin Solid Films* **393**, 19 (2001).
- [7] P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon Press, Oxford, 1975).
- [8] M. Mutz and W. Helfrich *J. Phys. (France)* **51**, 991 (1990).
- [9] Ou-Yang Zhong-can and W. Helfrich, *Phys. Rev. Lett.* **59**, 2486 (1987); *Phys. Rev. A* **39**, 5280 (1989).
- [10] Z. C. Ou-Yang, J. X. Liu, and Y. Z. Xie, *Geometric Methods in the Elastic Theory of Membranes in Liquid Crystal Phases* (World Scientific, Singapore, 1999).
- [11] G. Decher, *Science* **277**, 1232 (1997).
- [12] F. Caruso, R. A. Caruso, and H. Möhwald, *Science* **282**, 1111 (1998).
- [13] E. Donath, G. Sukhorukov, F. Caruso, S. Davis, and H. Möhwald, *Angew. Chem., Int. Ed.* **37**, 2201 (1998).
- [14] C. Gao, E. Donath, S. Moya, V. Dudnik, and H. Möhwald, *Eur. Phys. J. E* **5**, 21 (2001).
- [15] H. Jensen and H. Koppe, *Ann. Phys. (N.Y.)* **63**, 586 (1971); P. C. Schuster and R. L. Jaffe, *ibid.* **307**, 132 (2003).
- [16] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY, 1979).
- [17] Z. C. Tu and Z. C. Ou-Yang, *Phys. Rev. E* **68**, 61915 (2003).
- [18] Z. C. Tu and Z. C. Ou-Yang, *J. Phys. A* **37**, 11407 (2004).
- [19] L. R. G. Treloar, *The Physics of Rubber Elasticity*, 3rd ed. (Clarendon Press, Oxford, 1975).
- [20] M. Dio and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon Press, Oxford, 1986).
- [21] K. Yaman, P. Pincus, F. Solis, and T. A. Witten, *Macromolecules* **30**, 1173 (1997).
- [22] J. K. Wu and M. Z. Wang *Introduction to Elastic Theory* (Peking University Press, Beijing, 1981).
- [23] C. V. Westenholtz, *Differential Forms in Mathematical Physics* (North-Holland, Amsterdam 1981).
- [24] Z. Zhang, H. T. Davis, and D. M. Kroll, *Phys. Rev. E* **48**, R651 (1993).
- [25] Z. X. Wang and D. R. Guo, *Introduction to Special Function* (Peking University Press, Beijing, 2000).