VESICLES

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Shape Fluctuations of Vesicles

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I. INTRODUCTION

Membranes that I consider in this chapter are extremely thin and highly flexible sheets made of amphiphilic molecules. Due to these features, they can deform very easily from the microscopic small-length scale to macroscopic large-length scale. Properties of such membranes have attracted great interests in connection with various fields such as the statistical physics, quantum field theory, physical chemistry or biophysics [1]. In fact, the behavior of amphiphilic systems exhibits various aspects; they behave as biological systems, molecule-aggregates, two-dimensional systems, elastic sheets or random surfaces. Among these features, attention is paid to the restricted class of problems which have to do with the energy and the entropy of the membrane shape—in other words, the statistical mechanics of membranes.

It is widely recognized that the deformation of the membrane is mainly governed by the elastic bending energy rather than the surface tension which is usually zero or practically zero [2]. As we notice in the case of thin plates or shells, however, amphiphilic systems are not the only systems dominated by the bending energy. The essential difference between such mechanical plates and membranes is that the associated bending rigidity of the latter is known to be the order of k_BT. Hence membranes can easily fluctuate due to thermal agitations and one has to consider this object from the point of view of statistical mechanics. This is the main spirit of this chapter.

Before going into the details of this central subject, a brief overview on the general background of the membrane is given in the following section as well as the orders of magnitude of related physical quantities. Most of Sec. II follows the unpublished lecture notes by R. Lipowsky, written in German [3]. For more general and detailed reviews, the readers are referred to Refs. [1, 4–7]. In describing the conformation of membranes, one has to introduce some theoretical concepts such as the bending elasticity or curvature. For this purpose, several formulas from differential geometry are provided in Sec. III. In Sec. IV, starting from the description of the curvature model, the general shape equation of the fluid vesicles is discussed. The expected fluctuation amplitudes is calculated under the constraint of constant enclosed volume. In Sec. V, the shape fluctuations of polymerized vesicles are investigated within the framework of shell theory. The intrinsic curvature of the vesicle leads to an enhanced coupling between bending and stretching modes which acts to suppress the shape fluctuations on large scales. This effect is explicitly calculated for a spherical shape of the vesicle. Section VI is concerned with the hydrodynamics of compressible fluid vesicles. The compressibility is taken into account by allowing the molecular density to vary on the surface. We calculate the sequence of the stress relaxation times for a small deformation. The diffusion coefficient of the droplet and the complex effective viscosity of the droplet dispersion are also obtained. In the last section, comparing various char-

acteristic time scales both for vesicles and microemulsions, we discuss the detectable relaxation modes in the experiments.

II. GENERAL PROPERTIES OF MEMBRANES

In this section, some general properties of membranes are roughly surveyed following the unpublished lecture notes by R. Lipowsky [3].

Biological membranes such as *plasma membranes* are universal structural components constructing complex cellular architectures of biological systems. Moreover, most of the cells in plants or animals contain many intracellular organs inside, such as, cell nuclei or mitochondrias which are also enclosed by specific membranes. There are indeed many important physiological functions where biological membranes play important roles, e.g., (i) they operate as a selective barrier during the exchange of molecules between the inside and outside of the cell; (ii) they provide a two-dimensional environment for the catalytic reactions taking place in macromolecules; (iii) they constitute a two-dimensional supporter for protein molecules penetrating through the membranes. A rich variety of macromolecules are assigned to realize these important functions and each biomembrane can be regarded as a specific complex multicomponent alloy of different lipids and proteins.

In spite of the complex combinations of the chemical compositions in the real biomembranes, one can still extract a general common structure which maintains the essential features of biomembranes. Singer and Nicolson introduced such a general picture where lipid molecules form a double layer in which protein molecules are embedded like ships floating on the ocean [8,9]. The simplest membrane without any proteins is a single component lipid bilayer which assembles spontaneously from independent lipid molecules dissolved in water. Such a simple model membrane still posseses the following two fundamental properties. (i) Due to the hydrophobic effects, membranes tend to form closed shapes which are called *vesicles*. A simple explanation why membranes form vesicles will be discussed later. (ii) Lipid molecules can move around (diffuse) rather rapidly and freely within the membranes since they are usually in the fluid state. Membranes in this state are called *fluid membranes*. The measured diffusion constant of a lipid is typically $\simeq 10^{-7}$–10^{-8} cm^2/s. This implies that a lipid molecule sweeps the area of $\simeq 1$ μm^2 per second which is comparable to the typical biomembrane size.

Lipids are one of the most typical amphiphilic molecules which has two conflicting well-defined parts in one molecule. In an aqueous solution of lipids, the polar head group prefers a highly polarizable water environment (*hydrophilic*), whereas two hydrocarbon chains prefer oil (*hydrophobic*). A typical example of a lipid is a phospholipid whose head part consists of a phosphate molecule with ionic

feature. Amphiphilic molecules order in a such a way that the contact area between hydrocarbon chains and water can be as small as possible. Surface-active materials such as soap or detergent also belong to the family of amphiphilic molecules and they are called *surfactants*. Since surfactants are typically smaller than lipids in size and have only one hydrocarbon chain, they are usually less hydrophobic than lipids.

Depending on the concentration or the temperature, amphiphilic molecules in an aqueous solution exhibit a surprisingly rich variety of phases. At extremely low concentrations, molecules are dispersed in the water independently. When the concentration exceeds a certain value called the *critical micelle concentration*, c^*, molecules start to assemble spontaneously, constructing the macromolecular structure. Typical values of c^* are $c^* \simeq 1$ molecule/μm^3 for lipids and $c^* \simeq 10^5$–10^7 molecules/μm^3 for surfactants [10]. A micelle is a small sac-like aggregate in spherical form. When the concentration becomes much larger, one can observe various lyotropic phases such as the hexagonal phase or the lamellar phase.

The aggregation process of amphiphilic molecules takes place due to the hydrophobic effect which is purely of entropic origin. The configurational entropy of water molecules is decreased by the direct contact with hydrocarbon chains. This situation costs free energy and hence hydrocarbon chains dislike water. It turns out that the hydrophobic effect induces a strong attractive force between nonpolar hydrocarbon chains.

The reason why bilayer membranes form vesicles is as follows. Consider a membrane segment of linear size L. If this segment is planar, the membrane costs the edge energy since the hydrocarbon chains at the edges are forced to come in direct contact with the neighboring water. The total edge energy is proportional to L in this case. If we close this membrane into a spherical shape and let the edges disappear, we have to now take into account the contribution from the curvature energy (see Sec. IV). Nevertheless, the curvature energy does not depend on the radius L of the spherical vesicle. Therefore, for large L, membranes can always lower their shape energy by forming closed surfaces. The above mechanism of vesicle formation according to the hydrophobic effect is quite general and can be found in various biological systems as well. The fact that bilayers usually do not exhibit any holes or pores can also be explained by the same effect. In this chapter, I shall consider mainly spherically closed membranes.

One well-known fact about lipid bilayer systems, related to the internal degrees of freedom, is the presence of a first-order phase transition associated with the melting of the hydrocarbon chains, separating a high-temperature disordered fluid phase called the L_α phase and a low-temperature ordered gel phase called the L_β phase. The fluid membrane mentioned above corresponds to the L_α phase in which hydrocarbon chains are quite flexible and entropically shortened. In the gel L_β phase, on the other hand, they are more rigid and longer than in the fluid phase. This phase is one of the examples of *polymerized membranes* discussed in Sec. V.

Between these two flat phases, an intermediate structurally modulated (rippled) phase has been detected in a few phospholipids. This phase is termed the P_β phase and has stimulated considerable theoretical interest [11].

III. PREPARATIONS

First, we will collect some formulas from differential geometry [12]. One can, in general, parameterize a two-dimensional membrane in a three-dimensional space by two real inner coordinates $s = (s^1, s^2)$. The shape of the membrane is then described by a three-dimensional vector $\boldsymbol{r} = \boldsymbol{r}(s)$. At each point on the membrane, there are two tangent vectors $\boldsymbol{r}_i \equiv \partial \boldsymbol{r}/\partial s^i$ with $i = 1,2$. The outward unit normal vector $\boldsymbol{n}$ is perpendicular to these tangent vectors; i.e., $\boldsymbol{n} = (\boldsymbol{r}_1 \times \boldsymbol{r}_2)/|\boldsymbol{r}_1 \times \boldsymbol{r}_2|$.

All properties related to the intrinsic geometry of the membrane are expressed in terms of the metric tensor defined by the inner product of the tangential vectors:

$$g_{ij} = \boldsymbol{r}_i \cdot \boldsymbol{r}_j \tag{3.1}$$

Two important quantities are the determinant and the inverse of the metric tensor which will be denoted by

$$g = \det(g_{ij}) \qquad \text{and} \qquad g^{ij} = (g_{ij})^{-1} \tag{3.2}$$

In addition, one has to consider the (extrinsic) curvature tensor given by

$$h_{ij} = \boldsymbol{n} \cdot \boldsymbol{r}_{ij} = -\boldsymbol{n}_i \cdot \boldsymbol{r}_j \tag{3.3}$$

where $\boldsymbol{r}_{ij} = \partial^2 \boldsymbol{r}/\partial s^i \partial s^j$ and $\boldsymbol{n}_i = \partial \boldsymbol{n}/\partial s^i$. The third expression follows from the partial derivative of $\boldsymbol{n} \cdot \boldsymbol{r}_j = 0$. Similar to Eq. (3.2), the determinant and the inverse of the curvature tensor are denoted by

$$h = \det(h_{ij}) \qquad \text{and} \qquad h^{ij} = (h_{ij})^{-1} \tag{3.4}$$

The mean curvature H and the Gaussian curvature K are calculated according to

$$H = \frac{1}{2} g^{ij} h_{ij} = -\frac{1}{2}(c_1 + c_2) \tag{3.5}$$

and

$$K = \frac{h}{g} = c_1 c_2 \tag{3.6}$$

respectively, where c_1 and c_2 are two principle curvatures.

The covariant derivative D_j of f^i and f_i are

$$D_j f^i = \partial_j f^i + \Gamma^i_{kj} f^k \qquad \text{and} \qquad D_j f_i = \partial_j f_i - \Gamma^k_{ij} f_k \tag{3.7}$$

respectively, with the Christoffel symbols Γ_{ij}^{k} defined

$$\Gamma_{ij}^{k} = g^{kl}\boldsymbol{r}_l \cdot \boldsymbol{r}_{ij} \tag{3.8}$$

and $\partial_i \equiv \partial/\partial s^i$.

The metric and the curvature tensors are determined by the vector $\boldsymbol{r}(s)$ and consist of six independent functions since both tensors are symmetric. In order to solve the inverse problem, namely, to determine the function $\boldsymbol{r}(s)$ from the fundamental tensors, one has to solve the following equations [13];

$$\boldsymbol{n}_i = -h_i^j \boldsymbol{r}_j \tag{3.9}$$

and

$$\boldsymbol{r}_{ij} = \Gamma_{ij}^{k}\boldsymbol{r}_k + h_{ij}\boldsymbol{n} \tag{3.10}$$

which are called the Weingarten equation and the Gaussian equation, respectively.

IV. FLUID VESICLES

A. Curvature Model

As described in the previous section, lipid bilayers tend to form vesicles in water and are in the fluid state since the molecules can diffuse freely to adapt themselves to a particular membrane configuration. Shape transformation among various conformations can be caused by changing, e.g., the osmotic conditions, the temperature or the composition of the lipids. These properties might be closely related to the physiological functions of biomembranes described in the previous section. Similar system is also realized in a microemulsion system being homogeneous mixtures of oil, water and surfactants. In both cases, amphiphilic molecules orient their polar heads toward water and their aliphatic tails away from it, decreasing the surface tension drastically to the level of practically zero. In place of the surface tension, it is widely understood that the deformation of the membrane is mainly governed by the elastic bending energy. Although microemulsion droplets differ from vesicles by several decades in length scale (see the discussion in Sec. VII), the ruling physics behind is expected to be qualitatively similar.

From the theoretical point of view, the features of fluid membranes can be summarized in the following way: (i) since the surface tension is extremely small, the elastic bending energy determines the membrane shape primarily; (ii) since the membrane is in the fluid state at room temperature, it supports no in-plane shear resistivity. (iii) in most cases, one can also assume that the fluid membrane is incompressible, although the compressibility can be generally introduced and turns out to play an important role when we discuss the hydrodynamic effect (see Sec. VI.B). The curvature model was originally proposed for such a membrane by Hel-

frich according to a phenomenological consideration [2,3]. We shall briefly follow his argument.

In accordance with the above assumptions, the free energy is considered to be in the form which depends only on the membrane shape; i.e.,

$$H_f = \oint f(h_i{}^j)\, dA \tag{4.1}$$

In the above, $dA = \sqrt{g}\, ds^1\, ds^2$ is the surface element and f is a scalar function of matrix elements $h_i{}^j$. (We use $\oint$ for the surface integral in order to distinguish from the volume integral $\int$.) There are only two independent scalars that can be constructed from the 2×2 matrix $h_i{}^j$: the mean curvature and the Gaussian curvature defined by Eqs. (3.5) and (3.6), respectively. Up to second order in the principal curvatures, the scalar function f can be expanded using the coefficients a_0 to a_3 in the following way:

$$f \approx a_0 + a_1(c_1 + c_2) + a_2(c_1 + c_2)^2 + a_3 c_1 c_2 \tag{4.2}$$

or alternatively, by introducing four new coefficients Σ, κ, c_0 and κ_G, we have

$$f \approx \Sigma + \frac{1}{2}\kappa(c_1 + c_2 - c_0)^2 + \kappa_G c_1 c_2 \tag{4.3}$$

This is the *curvature model* first proposed by Helfrich [2]. The constant Σ is the lateral *surface tension* of the membrane and c_0 is called the *spontaneous curvature* which is, in general, nonzero whenever both sides of the membrane are not identical. Two elastic constants κ and κ_G are called *bending rigidity* and *Gaussian curvature modulus*, respectively. The surface tension Σ can, in general, depend on the molecular density of the membrane, which leads to the introduction of the membrane compressibility into the model and will be discussed in Sec. VI.B. In this and next sections, we assume that Σ is a negligibly small constant although it is left in the subsequent equations.

For a closed surface, the surface integral over the Gaussian curvature, $c_1 c_2$, turns out to be a constant number which depends only on the topology of the surface or, more precisely, on its Euler characteristic, χ. Euler characteristic is an integer number which can be known by breaking up the surface into an arbitrary polyhedron. Then it is given by $\chi = \#(V) - \#(E) + \#(F)$ where $\#(V)$, $\#(E)$ and $\#(F)$ are numbers of vertices, edges and faces of the polyhedron, respectively. When a given surface is topologically identical to a sphere with G handles (*genus*), $\chi = 2 - G$. According to the Gauss-Bonnet theorem in differential geometry [12], the surface integral over the Gaussian curvature simply yields

$$\oint c_1 c_2\, dA = 2\pi\chi \tag{4.4}$$

for a surface without edge. Accordingly, concerning the membrane deformation that maintains its topology, the term Eq. (4.4) can be usually discarded.

The equilibrium shape of a fluid vesicle is then determined by the shape energy such that

$$H_f = \oint \Sigma \, dA + H_b = \oint \Sigma \, dA + \oint \frac{1}{2}\kappa(c_1 + c_2 - c_0)^2 \, dA \tag{4.5}$$

where H_b stands for the bending energy.

By calculating the first variation of Eq. (4.5) with respect to an infinitesimal displacement ϵ normal to the membrane, we obtain the following restoring force per unit membrane area [14,15]:

$$\begin{aligned} F_\parallel &= -\frac{\delta H_f}{\delta \epsilon} \\ &= 2\Sigma H - \kappa(2H + c_0)(2H^2 - 2K - c_0 H) - 2\kappa \nabla_{LB}^2 H \end{aligned} \tag{4.6}$$

where ∇_{LB}^2 is the Laplace-Beltrami operator on the surface given by

$$\nabla_{LB}^2 = \frac{1}{\sqrt{g}} \partial_i (g^{ij} \sqrt{g} \, \partial_j) \tag{4.7}$$

In equilibrium, this restoring force balances with the (osmotic) pressure difference $P - P'$ between the outside and the inside of the membrane; i.e., $P - P' = F_\parallel$. (Here and below we shall use the prime in order to distinguish the quantities of the fluid inside of the membrane from the corresponding quantities of the fluid outside.) In this way, Zhong-can and Helfrich obtained the following nonlinear equilibrium shape equation in general coordinates [15]:

$$(P - P') - 2\Sigma H + \kappa(2H + c_0)(2H^2 - 2K - c_0 H) + 2\kappa \nabla_{LB}^2 H = 0 \tag{4.8}$$

In order to make this chapter self-contained, we show a concise derivation of Eq. (4.6) in Appendix A. Eq. (4.8) reduces to the well-known Laplace formula when $\kappa = 0$. The more general case will be discussed in Sec. VI.

Meanwhile $P - P'$ can be also interpreted as the Lagrange multiplier associated with the constraint of constant enclosed volume, i.e., $\delta \, dV = 0$ where dV is the volume element. Mathematically, the variation of the energy of the fluid vesicle may be given by

$$\delta H_f + \int (P - P') \delta \, dV = \delta H_f + \oint (P - P') \epsilon \, dA \tag{4.9}$$

from which Eq. (4.8) can be also obtained.

B. Spherical Fluid Vesicles

For our later purpose, we summarize here several expressions related to a spherically closed fluid vesicle of radius r_0 at zero temperature. By specifying the internal coordinates as $(s^1, s^2) = (\theta, \phi)$, we introduce the following three unit vectors as a local basis:

$$\boldsymbol{e}_r = \begin{pmatrix} \sin\theta\cos\phi \\ \sin\theta\sin\phi \\ \cos\theta \end{pmatrix}, \quad \boldsymbol{e}_\theta = \begin{pmatrix} \cos\theta\cos\phi \\ \cos\theta\sin\phi \\ -\sin\theta \end{pmatrix}, \quad \boldsymbol{e}_\phi = \begin{pmatrix} -\sin\phi \\ \cos\phi \\ 0 \end{pmatrix} \tag{4.10}$$

With these notations, the undeformed reference state is described by

$$\boldsymbol{R} = r_0 \boldsymbol{e}_r \tag{4.11}$$

Now consider the membrane slightly distorted from the reference state. Any deformed state of the membrane without any overhangs can then be parameterized by using the normal vector $\boldsymbol{N}$ in the reference state ($\boldsymbol{N} = (\boldsymbol{R}_1 \times \boldsymbol{R}_2)/|\boldsymbol{R}_1 \times \boldsymbol{R}_2| = \boldsymbol{e}_r$) in the following way:

$$\boldsymbol{r} = \boldsymbol{R} + \ell(\theta,\phi,t)\boldsymbol{N} = [r_0 + \ell(\theta,\phi,t)]\boldsymbol{e}_r \tag{4.12}$$

here the variable $\ell(\theta,\phi,t)$ represents the transverse (out-of-plane) displacement field which can generally depend on time t. A straightforward calculation up to first order in terms of the out-of-plane displacement ℓ yields the following expression for the normal vector:

$$\boldsymbol{n} \approx \boldsymbol{e}_r - \frac{1}{r_0}\frac{\partial \ell}{\partial \theta}\boldsymbol{e}_\theta - \frac{1}{r_0 \sin\theta}\frac{\partial \ell}{\partial \phi}\boldsymbol{e}_\phi, \tag{4.13}$$

and for twice the mean curvature H and the Gaussian curvature K:

$$2H \approx -\frac{2}{r_0} + \frac{1}{r_0^2}(2 + \nabla_\perp^2)\ell(\theta,\phi,t) \tag{4.14}$$

and

$$K \approx \frac{1}{r_0^2} - \frac{1}{r_0^3}(2 + \nabla_\perp^2)\ell(\theta,\phi,t) \tag{4.15}$$

respectively, where

$$\nabla_\perp^2 = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \tag{4.16}$$

For our later calculations, it is convenient to expand the function $\ell(\theta,\phi,t)$ in terms of the spherical harmonics $Y_{nm}(\theta,\phi)$:

$$\ell(\theta,\phi,t) = \sum_{n,m} \ell_{nm}(t) Y_{nm}(\theta,\phi) \tag{4.17}$$

As usual, we have $\ell_{nm}^*(t) = (-1)^m \ell_{n,-m}(t)$ in order to ensure that the displacement field is real (the asterisk denotes the complex conjugate value) and the summation runs over $n = 0,1,2,\ldots$ and $|m| \le n$. Hereafter, the well-known relation

$$\nabla_\perp^2 Y_{nm}(\theta,\phi) = -n(n+1)Y_{nm}(\theta,\phi) \tag{4.18}$$

will be used frequently.

The change in the bending energy H_b (see Eq. (4.5)) and the area A due to the deformation Eq. (4.12) have been calculated by several authors [14–18]. Up to second order in terms of ℓ_{nm}, the results are summarized as

$$H_b \approx 2\pi\kappa(c_0r_0 - 2)^2 + \sqrt{4\pi}\kappa c_0r_0(c_0r_0 - 2)\frac{\ell_{00}}{r_0} + \sum_{n,m}\frac{1}{2}\kappa\left\{[n(n+1)]^2 - \left(2 + 2c_0r_0 - \frac{1}{2}c_0^2r_0^2\right)n(n+1) + c_0^2r_0^2\right\}\frac{|\ell_{nm}|^2}{r_0^2} \tag{4.19}$$

and

$$A \approx A_0 + 2\sqrt{4\pi}r_0\ell_{00} + \sum_{n,m}\left[1 + \frac{1}{2}n(n+1)\right]|\ell_{nm}|^2 \tag{4.20}$$

where $A_0 = 4\pi r_0^2$. On the other hand, the volume V is given by

$$V \approx V_0 + \sqrt{4\pi}r_0^2\ell_{00} + r_0\sum_{n,m}|\ell_{nm}|^2 \tag{4.21}$$

with $V_0 = (4\pi/3)r_0^3$.

Although many arguments concerning the constraint will be discussed in Sec. VI.A, we shall consider here the case where the total volume is kept constant during the shape deformation. This can be easily incorporated by using Eq. (4.21) for the volume, where we require $V - V_0 = 0$. Then we have

$$\sqrt{4\pi}\ell_{00} \approx -\sum_{n,m}{}'\frac{|\ell_{nm}|^2}{r_0} \tag{4.22}$$

where the prime in the summation indicates that $(n, m) = (0,0)$-mode is excluded. Hence the constant volume constraint leads to the elimination of the ℓ_{00}-terms. Inserting this into Eqs. (4.19) and (4.20), the shape energy Eq. (4.5) can be calculated apart from the constant terms as [19]

$$H_f \approx \sum_{n,m}{}'\frac{1}{2}(n-1)(n+2)S_{nm}|\ell_{nm}|^2 \tag{4.23}$$

where

$$S_{nm} = \Sigma + \frac{\kappa}{r_0^2}\left[n(n+1) - 2c_0r_0 + \frac{1}{2}c_0^2r_0^2\right] \tag{4.24}$$

is the effective surface tension and will be more generally introduced in Sec. VI.B. Since Eq. (4.23) depends only on n but not on m, the shape energy has $(2n + 1)$-fold degeneracy.

With the use of equipartition theorem (or straightforward Gaussian integrations), the average fluctuation amplitudes are easily estimated from Eq. (4.23) as

$$\langle |\ell_{nm}|^2 \rangle = \frac{k_B T}{(n-1)(n+2)S_{nm}} \tag{4.25}$$

where k_B is the Boltzmann constant and T is the temperature. It is important to realize that Eq. (4.25) is valid only for $n \geq 2$, since $n = 1$ corresponds to the simple translational sideways displacement of the droplet as a whole requiring no energy. This mode is essentially related to the Brownian motion of the vesicle and will be discussed in Sec. VI.E.

V. POLYMERIZED VESICLES

A. Polymerized Membranes

Recently, the properties of polymerized membranes have attracted a lot of attention. In these membranes, the molecules form a two-dimensional network of fixed connectivity. In biomembranes, these networks often consist of semiflexible polymers and then have a relatively large mesh size. One example is the network of spectrin molecules which is attached to the plasma membrane of erythrocytes; the latter network has a mesh size of 100–200 nm [20]. A polymerized network with a much smaller mesh size is contained in the cell wall of bacterial cells. These networks are composed of peptidoglycan molecules and are capable of resisting great stress since bacteria exhibit an internal turgor pressure [21]. Artificial polymerized membranes can be also synthesized from bilayers of polymerizable lipids by irradiating ultraviolet light [22]. This technique typically produces network patches whose lateral extension is the order of 10–20 nm.

So far, the theoretical work has focused on polymerized membranes which are *flat* in their undeformed state. It has been found that, in spite of their two-dimensional character, these membranes exhibit a low temperature phase which is rough but not crumpled [23]. The energy of an undulation mode with wave vector q is expected to scale as $q^{4-\eta}$ with $\eta > 0$. The existence of such an uncrumpled phase has been confirmed by many computer simulations for open polymerized membranes [24–27]. The value of η is still a matter of some controversy [28–30]. Likewise, Monte Carlo simulations of polymerized vesicles showed that flaccid vesicles exhibit uncrumpled configurations and the mean-squared radius of gyration is proportional to the number of monomers on the membrane [31,32].

In the present section, we investigate the shape fluctuations of polymerized vesicles (or shells) which are *curved* in the undeformed state. For such a shell, the stretching deformation which accompanies the bending deformation is a first-order effect while it is only a second-order effect for a flat plate. Thus, for a dis-

placement ℓ along the normal direction, the strain tensor is proportional to ℓ and ℓ^2 for shells and plates, respectively. Therefore, one expects that the shape fluctuations of polymerized vesicles will be effectively suppressed. For mathematical simplicity, we investigate this coupling between bending and stretching modes primarily for the case of spherical vesicles. However, one should keep in mind that this coupling is present for arbitrarily curved polymerized membranes.

It has been argued that a polymerized or solidlike membrane with a relatively small shear modulus or a relatively large bending rigidity should exhibit a pronounced crossover between fluidlike behavior on small scales to solidlike behavior on large scales [28]. For membranes which are flat in their undeformed state, this crossover is again a consequence of the nonlinear terms in the strain tensor. Here we will show that, for curved shells, such a crossover behavior arises already within the linearized theory.

B. Stretching Energy

By regarding the polymerized membrane as an elastic shell, its elastic deformation energy is derived here in accordance with classical shell theory [13,33,34].

At zero temperature, the membrane is supposed to be in the (undeformed) reference state described by $\boldsymbol{r} = \boldsymbol{R}$. If the membrane is stretched, the distance between two neighboring points in the membrane is changed. This change can be expressed by the strain tensor u_{ij} defined by

$$u_{ij} \equiv \frac{1}{2}(g_{ij} - G_{ij}) \tag{5.1}$$

where G_{ij} represent the metric tensor in the reference state; i.e., $G_{ij} = \boldsymbol{R}_i \cdot \boldsymbol{R}_j$. The mixed strain tensor is obtained by raising one of the indices according to

$$u_i{}^j = u_{ik}g^{kj} \tag{5.2}$$

According to the elasticity theory of thin elastic sheets conventionally known as *shell theory*, the deformation energy of an isotropic sheet is given by

$$H_p = H_f + H_s \tag{5.3}$$

where

$$H_s = \oint \left[\frac{1}{2}\lambda(u_i{}^i)^2 + \mu u_i{}^j u_j{}^i\right] dA \tag{5.4}$$

is the stretching energy. The parameters λ and μ are two-dimensional Lamé coefficients. As a generalization of Eq. (4.12), the deformed state of the shell can be parameterized in general by

$$\boldsymbol{r} = \boldsymbol{R} + u^i(s)\boldsymbol{R}_i + \ell(s)\boldsymbol{N} \tag{5.5}$$

The variables $u^i(s)$ represent two lateral (in-plane) displacement fields and $\ell(s)$ represents the transverse (out-of-plane) displacement field as before. The strain tensor can be expressed in terms of the components of these displacement fields. Up to first order in the displacement $\boldsymbol{r} - \boldsymbol{R}$, the mixed strain tensor turns out to be [13].

$$u_i{}^j \approx \frac{1}{2}(D^j u_i + D_i u^j) - \ell H_i{}^j \tag{5.6}$$

where $H_i{}^j$ is the mixed curvature tensor in the reference state; i.e., $H_i{}^j = \boldsymbol{N} \cdot \boldsymbol{R}_{ik} G^{kj}$. Here we see that the strain tensor is proportional to ℓ provided $H_i{}^j \neq 0$.

C. Spherical Polymerized Vesicles

We now consider spherical vesicles as one of the simplest nontrivial examples which exhibit the intrinsic curvature effect. The case of cylindrical polymerized vesicles was discussed by Komura and Lipowsky, and they derived essentially the same results as here [35].

Let the radius of a polymerized sphere r_0. Equation (4.10) is again employed as a local basis. The stress tensor for a sphere is known as [13,36]

$$u_i{}^j \approx \frac{1}{2}(D^j u_i + D_i u^j) + \delta_i^j \frac{\ell}{r_0} \tag{5.7}$$

where δ_i^j is the Kronecker delta. In calculating the stretching energy H_s, it is convenient to use the decomposed form of the in-plane displacement such that [13]

$$u_i = D_i \Psi + \varepsilon_{ji} D^j \Upsilon \tag{5.8}$$

where Ψ and Υ are scalar functions and ε_{ij} is the alternating tensor. It is defined through the alternating symbol e_{ij} as

$$\varepsilon_{ij} = \sqrt{g} e_{ij} \tag{5.9}$$

whereas e_{ij} is

$$e_{12} = -e_{21} = 1, \qquad e_{11} = e_{22} = 0 \tag{5.10}$$

Using Eq. (5.8), Zhang, Davis and Kroll calculated the stretching energy in the form [36]

$$\begin{aligned} H_s &= H_s\{\ell, \Psi\} + H_s\{\Upsilon\} \\ &\approx \oint \left[\frac{2(\lambda + \mu)}{r_0^2} \ell^2 + \frac{2(\lambda + \mu)}{r_0^3} \ell(\nabla_\perp^2 \Psi) + \frac{\lambda + 2\mu}{2r_0^4} (\nabla_\perp^2 \Psi)^2 + \frac{\mu}{r_0^4} \Psi(\nabla_\perp^2 \Psi) \right] dA \\ &\quad + \oint \left[\frac{\mu}{2r_0^4} (\nabla_\perp^2 \Upsilon)^2 + \frac{\mu}{r_0^4} \Upsilon(\nabla_\perp^2 \Upsilon) \right] dA \end{aligned} \tag{5.11}$$

It is important to realize here that there is no coupling term between $\{\ell,\Psi\}$ and Υ while ℓ and Ψ couples through the term $\ell(\nabla_\perp^2\Psi)$, which vanishes in the limit of $r_0 \to \infty$. This reflects the intrinsic curvature effect.

On the other hand, as far as bending energy is concerned, we assume that the spontaneous curvature takes the value $c_0 = 2/r_0$ for the sake of the simplicity in the following argument. In this case, although we start from Eq. (5.5), only out-of-plane displacement ℓ is relevant within the linear approximation. Hence, from Eq. (4.19) the bending energy H_b is

$$H_b \approx \sum_{n,m} \frac{1}{2}\kappa[(n-1)(n+2)]^2 \frac{|\ell_{nm}|^2}{r_0^2} \tag{5.12}$$

Also by using Eq. (5.8), the area A and the volume V of the deformed sphere are expressed as

$$\begin{aligned} A &= A_0 + A\{\ell,\Psi\} + A\{\Upsilon\} \\ &\approx A_0 + \oint\left[\frac{2\ell}{r_0} + \frac{\ell^2}{r_0^2} - \frac{1}{2}\ell(\nabla_\perp^2\ell) + \frac{2}{r_0^3}\ell(\nabla_\perp^2\Psi) - \frac{1}{r_0^4}\Psi(\nabla_\perp^2\Psi)\right] dA \\ &\quad - \oint \frac{1}{r_0^4}\Upsilon(\nabla_\perp^2\Upsilon)\, dA \end{aligned} \tag{5.13}$$

and

$$\begin{aligned} V &= V_0 + V\{\ell,\Psi\} + V\{\Upsilon\} \\ &\approx V_0 + \oint\left[\ell + \frac{\ell^2}{r_0} + \frac{1}{r_0^2}\ell(\nabla_\perp^2\Psi) - \frac{1}{2r_0^3}\Psi(\nabla_\perp^2\Psi)\right] dA \\ &\quad - \oint \frac{1}{2r_0^3}\Upsilon(\nabla_\perp^2\Upsilon)\, dA \end{aligned} \tag{5.14}$$

up to second order in the displacement fields. Again there is no coupling term between $\{\ell,\Psi\}$ and Υ, so we shall ignore the terms including Υ hereafter.

In order to decompose the displacements in terms of appropriate eigenmodes, we use the following expansion of Ψ in addition to Eq. (4.17):

$$\Psi(\theta,\phi) = \sum_{n,m} \Psi_{nm} r_0 Y_{nm}(\theta,\phi) \tag{5.15}$$

If the stretching energy as given by Eq. (5.11) is expressed in terms of ℓ_{nm} and Ψ_{nm}, one obtains

$$\begin{aligned} H_s\{\ell,\Psi\} \approx \sum_{n,m} \Big\{ & 2(\lambda+\mu)|\ell_{nm}|^2 - 2(\lambda+\mu)n(n+1)\ell_{nm}^*\Psi_{nm} \\ & + \frac{1}{2}n(n+1)[(\lambda+2\mu)n(n+1) - 2\mu]|\Psi_{nm}|^2 \Big\} \end{aligned} \tag{5.16}$$

In this expression, the Ψ_{00}-mode does not enter since the corresponding energy is identically zero (in field-theoretic language, this mode is called "zero mode"). This implies that the ℓ_{00}-mode is completely decoupled from all other modes. Likewise, the area A and volume V are expressed as

$$A \approx A_0 + 2\sqrt{4\pi} r_0 \ell_{00} + \sum_{n,m} \left\{ \left[1 + \frac{1}{2} n(n+1) \right] |\ell_{nm}|^2 - 2n(n+1) \ell_{nm}^* \Psi_{nm} + n(n+1) |\Psi_{nm}|^2 \right\} \tag{5.17}$$

and

$$V \approx V_0 + \sqrt{4\pi} r_0^2 \ell_{00} + r_0 \sum_{n,m} \left\{ |\ell_{nm}|^2 - n(n+1) \ell_{nm}^* \Psi_{nm} + \frac{1}{2} n(n+1) |\Psi_{nm}|^2 \right\} \tag{5.18}$$

respectively. Notice that these two equations reduce to Eqs. (4.20) and (4.21), respectively, when $\Psi = 0$.

Notice that H_p is quadratic in the field Ψ corresponding to the phonon-like field. Performing the Gaussian functional integrations over all (n,m)-modes of Ψ with $(n, m) \neq (0, 0)$, one obtains

$$\int \mathcal{D}\{\Psi\} exp[-H_p\{\ell, \Psi\}/k_B T] \equiv exp[-H_{\text{eff}}\{\ell\}/k_B T] \tag{5.19}$$

where the new effective configuration energy H_{eff} now depends only on the transverse mode ℓ:

$$H_{\text{eff}}\{\ell\} = \sum_{n,m}{}' \frac{1}{2} \left[(n-1)(n+2) S_{nm} + 4(\lambda + \mu) - \frac{4(\lambda+\mu)^2 [n(n+1)]^2}{n(n+1)[(\lambda + 2\mu) n(n+1) - 2\mu]} \right] |\ell_{nm}|^2 \tag{5.20}$$

where

$$S_{nm} = \Sigma + \frac{\kappa}{r_0^2} (n-1)(n+2) \tag{5.21}$$

In the above, we have incorporated the constraint of constant volume; i.e., $V - V_0 = 0$. Similar to Eq. (4.22), this is essentially equivalent to the elimination of ℓ_{00}-terms as seen from Eq. (5.18). In addition, we do not include the ℓ_{10}-term since it corresponds to a simple translational motion of the sphere requiring no energy; i.e., $H_{\text{eff}}\{\ell = \ell_{10}\} = 0$.

For large n, Eq. (5.20) takes the simple form [36]

$$H_{\text{eff}}\{\ell\} = \sum_{n,m}{}' \frac{1}{2} [(n-1)(n+2) S_{nm} + Y] |\ell_{nm}|^2 \tag{5.22}$$

where the parameter

$$Y = \frac{4\mu(\lambda + \mu)}{\lambda + 2\mu} \tag{5.23}$$

is the two-dimensional Young modulus. This modulus describes the elastic response of the two-dimensional sheet when subjected to an uniaxial tension. It is interesting to note that the same modulus is also relevant if one considers a *flat* reference state and includes the leading *nonlinear* term in the strain tensor [23]. Again by using the equipartition theorem, the average mean-squared mode amplitude is

$$\langle |\ell_{nm}|^2 \rangle = \frac{k_B T}{(n-1)(n+2)S_{nm} + Y} \tag{5.24}$$

The case of zero shear modulus or $Y = 0$ corresponds to fluid membranes as studied previously. It follows from Eq. (5.24) that the presence of a finite shear modulus or $Y > 0$ reduces the amplitude of all shape fluctuations as expected. Hence, Y plays the role of the mass term. In the case of $\Sigma = 0$, the shape fluctuations exhibit the crossover scale

$$L^* \simeq \left(\frac{r_0^2 \kappa}{Y}\right)^{1/4} \tag{5.25}$$

according to Eq. (5.24). For $L \ll L^*$, the fluctuations are fluid-like but are strongly suppressed for $L \gg L^*$.

As shown in Ref. 28, the crossover length for plates arising from the nonlinear terms of the strain tensor depends on temperature. If the critical exponent is $\eta = 1$ as concluded from the Monte Carlo simulations in Ref. 28, the latter crossover length is given by $L^* \simeq \kappa/(k_B T Y)^{1/2}$. In contrast, the crossover length for shells as given by Eq. (5.25) is independent of temperature but depends explicitly on the curvature radius r_0.

In the rest of this section, we estimate the typical value of L^* for various cases. First, consider a polymerized membrane consisting of a thin solidlike sheet. In this case, the elastic moduli of the membrane can be estimated starting from the elastic properties of the bulk material. For an isotropic material in three dimensions, one has two three-dimensional Lamé coefficients λ_3 and μ_3. For a membrane of thickness a, one finds that the Lamé coefficients are

$$\lambda = a\frac{2\lambda_3\mu_3}{\lambda_3 + 2\mu_3} \qquad \text{and} \qquad \mu = a\mu_3 \tag{5.26}$$

while its bending rigidity κ is given by

$$\kappa = a^3 \frac{\mu_3(\lambda_3 + \mu_3)}{3(\lambda_3 + 2\mu_3)} = a^2 \frac{\lambda + 2\mu}{12} \tag{5.27}$$

This implies that

$$\frac{\kappa}{Y} \simeq a^2 \qquad \text{and} \qquad L^* \simeq (r_0 a)^{1/2} \tag{5.28}$$

These estimates should apply, for example, to the cell wall of bacteria. If the radius of the sphere is $r_0 \simeq 1$ μm and the thickness of the membrane is $a \simeq 5$ nm, one has $(r_0 a^2)^{1/2} \simeq 70$ nm which sets the scale for the crossover length L^*.

Next, consider the *tethered membranes* which have been studied in many computer simulations. For example, the networks studied in Ref. 24 are characterized by the values $Ya^2/k_BT \simeq 20$ and $\kappa/k_BT \simeq 1$, where a is the mesh size of the network. This implies that

$$\frac{\kappa}{Y} \simeq \frac{a^2}{20} \qquad \text{and} \qquad L^* \simeq \frac{1}{2}(r_0 a)^{1/2} \tag{5.29}$$

Thus, for the accessible sizes of networks with $r_0 \simeq 3a - 6a$, the crossover scale L^* is of the order of a, and all fluctuations will be suppressed by the polymerization.

Finally, it is instructive to consider the plasma membrane of red blood cells. The elastic moduli of this membrane are estimated to be $\kappa \simeq 3 \times 10^{-20}$ J and $Y \simeq 2 \times 10^{-5}$ J/m^2 [37–39]. This leads to $Y/\kappa \simeq 0.7 \times 10^{15}$ m^{-2}. Using an effective radius $r_0 = 1$ μm, one obtains the crossover length $L^* \simeq 0.2$ μm. The latter length scale is comparable to the mesh size of the spectrin network and somewhat smaller than the crossover length arising from the nonlinear terms of the strain tensor as estimated in Ref. 28.

Recently, Sackmann and co-workers have made a detailed comparison between experiment and theory for the flickering of red blood cells which have the shape of discocytes [40]. Somewhat surprisingly, they conclude that the experimentally observed flickering shows no effect of the small but finite shear modulus proportional to Y arising from the spectrin network. This is difficult to understand especially because the discocyte shape itself should be determined by this network.

VI. HYDRODYNAMIC EFFECTS

A. Dynamics of Membranes

In order to make our understanding of the bending energy more deeply, not only static measurements but also dynamical measurements of the membrane system are quite important. In fact, there have been several dynamical measurements of vesicles (fluorescence microscopy [14], optical videomicroscopy [41–47], reflection interference contrast microscopy [38,48,49] and microemulsions (neu-

tron scattering [50–52], dynamical Kerr effect [53]). By knowing the relaxation time of a small deformation of a droplet, one can determine the bending rigidity quantitatively.

Along with these experiments, several people calculated the time correlation function of the out-of-plane displacement for spherically closed fluid membranes. The first work by Shneider, Jenkins and Webb [14] was generalized by Milner and Safran to the case of nonzero spontaneous curvature [18]. The important assumption in their calculations is that the total area is a conserved quantity as well as the total volume both for vesicles and microemulsion droplets. In order to incorporate these two constraints simultaneously, they introduced the notion of "constant excess area" using the unknown Lagrange multiplier. They also assumed that the membrane is incompressible. On the other hand, Van der Linden, Bedeaux and Borkovec insisted that only the area should be kept constant for vesicles, whereas only the volume constraint is necessary for microemulsion droplets since the supply and the loss of surfactants from the bulk phase would take place in a short enough time scale compared to the deformation of droplets [19]. Van der Linden et al. or Komura and Seki [54] obtained different dynamical correlation functions from the previous result by assuming that only the total volume should be kept constant. Their calculations, however, correspond to the case of zero compressibility (fully compressible). Several others calculated the stress relaxation time upon taking the compressibility of the membrane into account [55–60].

Recently, Smeulders, Blom and Mellema performed a viscoelastic measurement on an emulsion of relatively small vesicles, $r_0 \simeq 40$–100 nm [61–63]. A distinct feature of their observation is that there exist two relaxation processes: one related to the translational ordering of the vesicles that are subjected to a shear flow, and the other, appearing at higher frequencies, has been attributed to the membrane deformation. From the characteristic time of the latter relaxation process, they determined several elastic constants and viscosities of the membrane as well as the bending rigidity by changing the size of the droplets. Their experimental data has been analyzed according to the theoretical prediction by Oldroyd with a modified relaxation time including the bending rigidity [64,65]. One of their interesting findings is the deformation mode dependent on the shear modulus, although Helfrich assumed vanishing of it in his original model (see Sec. IV.A). Viscosity of the *L_3-phase* in amphiphilic systems has been also reported [66,67].

In this section, we give a description of the compressible fluid membrane and the mechanical boundary condition at the interface. We show the sequence of the stress relaxation times for several limiting cases. These relaxation times show up in the real system as the diffusion coefficient of the droplet or complex effective viscosity of dispersions.

B. Compressible Fluid Membranes

Following the argument by Onuki and Kawasaki [68], the compressibility of the fluid membrane can be implicitly taken into account through the change of the areal density ρ_s of amphiphilic molecules on the membrane. As the generalization of Eq. (4.5), we start from the following shape energy:

$$H_f = \oint \sigma(\rho_s)\, dA + \oint \frac{1}{2}\kappa(c_1 + c_2 - c_0)^2\, dA \tag{6.1}$$

where $\sigma(\rho_s)$ is the *bare* surface tension.

It is important to mention that due to the incompressible assumption for the ambient fluids (see later Eq. (6.13)), the shape energy Eq. (6.1) should be minimized under the constraint of constant enclosed volume as before. (The ambient fluids can be, in general, compressible; see for instance Ref. 57.) In principle, one can also consider the situation in which κ and/or c_0 depend also on ρ_s. However, this effect is expected to be negligibly small compared to the *bare* surface tension, and we shall put these quantities as constants [55].

Exchange of molecules between the membrane and the ambient fluid takes place through desorption and adsorption. Desorption is a thermally activated process. The characteristic time for a molecule to remain in the membrane is proportional to $\exp(\Delta E/k_BT)$, where ΔE is the energy barrier per molecule associated with the desorption process. For a phospholipid in the bilayer membrane, the estimated typical sticking time (at room temperature) ranges from several hours to a couple of days, i.e., $\simeq 10^5$ s, which provides a measure of the time scale within which a new chemical equilibrium can be attained. This estimation implies that such a relaxation process takes rather long time in the case of bilayers made of lipids such as red blood cells. Hence one can assume that the number of molecules in the membrane remains almost constant during the time scale of the experiments which is much shorter than the sticking time [69,70]. Keeping these facts in mind, we assume throughout this chapter that the total number of amphiphilic molecules N is a conserved quantity. Here N is given by the integral of ρ_s over the whole surface of the membrane; i.e.,

$$N = \oint \rho_s\, dA \tag{6.2}$$

Several comments are necessary for the above assumption. Typical sticking time scale for a single-chain surfactant in micelles is much shorter compared to the lipids and is the order of 10^{-5}–10^{-3} s. Hence, for a supramolecular structure of surfactants, Eq. (6.2) holds only for a short time scale. One should note that there exists also an open system, such as *black films*, where the lipid bilayer exchanges molecules with the outer system. In this case, N is no longer a constant while ρ_s remains unchanged with respect to the small change in the total area [69].

Similar to Eq. (4.6), the normal restoring force due to the membrane under the constraint of fixed N is now given by

$$F_{\parallel} = 2\Sigma(\rho_s)H - \kappa(2H + c_0)(2H^2 - 2K - c_0H) - 2\kappa\nabla_{LB}^2 H \tag{6.3}$$

where $\Sigma(\rho_s)$ is the *apparent* surface tension defined by [68]

$$\Sigma(\rho_s) \equiv \sigma(\rho_s) - \rho_s \frac{\partial\sigma(\rho_s)}{\partial\rho_s} \tag{6.4}$$

The second term on the r.h.s. of Eq. (6.4) represents the reduction of the surface tension [70].

Due to the fluctuation of the local density $\delta\rho_s$ of amphiphilic molecules around the equilibrium (or mean) value of ρ_s denoted as ρ_{s0}, the *apparent* surface tension Eq. (6.4) can be different from point to point on the surface being expressed as $\Sigma(\rho_s) = \Sigma(\rho_{s0}) + \delta\Sigma(\rho_s)$, where [55,68,71,72]

$$\delta\Sigma(\rho_s) = -\frac{B}{\rho_{s0}}\delta\rho_s \qquad \text{with} \qquad B = \rho_{s0}^2\left(\frac{\partial^2\sigma(\rho_s)}{\partial\rho_s^2}\right)_{\rho_s=\rho_{s0}} \tag{6.5}$$

In the above, B is called the two-dimensional (in-plane) compression modulus and is put hereafter as a constant. The former relation in Eq. (6.5) can be also regarded as an equation of state of the membrane as a two-dimensional fluid [59].

It is known that the compressible nature of the membrane leads to a considerable effect on the hydrodynamical properties of the interface [73]. The change in the membrane shape due to the motion of the surrounding fluid is coupled to the change in ρ_s, which in turn affects the surface tension as seen by Eq. (6.5). If ρ_s varies over the surface, the *apparent* surface tension Eq. (6.4) is not constant as well and this fact gives rise to the tangential restoring force due to the membrane such that [74]

$$F_{\perp\alpha} = \mathrm{grad}_{\perp\alpha}\Sigma(\rho_s) \tag{6.6}$$

where $\mathrm{grad}_{\perp\alpha}$ is the α-component of the gradient operator on the surface given by

$$\mathrm{grad}_{\perp\alpha} = \frac{\partial}{\partial x_\alpha} - n_\alpha n_\beta \frac{\partial}{\partial x_\beta} \tag{6.7}$$

while n_α are components of the normal vector which should not be confused with $\boldsymbol{n}_i = \partial\boldsymbol{n}/\partial s^i$. (We shall use Greek indices for the range 1, 2 and 3.)

In order to construct the boundary condition that must be satisfied at the interface between two viscous fluids in motion, we follow the discussion by Landau and Lifshitz [73]. According to Eqs. (6.3) and (6.6), the balance of force per unit membrane area is expressed as

$$(\Pi_{\alpha\beta} - \Pi'_{\alpha\beta})n_\beta + F_{\parallel}n_\alpha + F_{\perp\alpha} = 0 \tag{6.8}$$

or more explicitly

$$(\Pi_{\alpha\beta} - \Pi'_{\alpha\beta})n_\beta + \mathrm{grad}_{\perp\alpha}\Sigma(\rho_s) + [2\Sigma(\rho_s)H - \kappa(2H + c_0)(2H^2 - 2K - c_0H) - 2\kappa\nabla^2_{LB}H]n_\alpha = 0 \quad (6.9)$$

where, as given in Sec. VI.C, $\Pi_{\alpha\beta}$ is the fluid stress tensor outside of the membrane and $\Pi'_{\alpha\beta}$ is that inside of the membrane.

In addition to the equation of motion for the ambient fluids subjected to the boundary condition Eq. (6.9), we need another equation since the variable ρ_s has been introduced in our problem. This is an equation of continuity of amphiphilic molecules, expressing the conservation of the local number of molecules. According to the hydrodynamics of two-dimensional fluids [59,75,76], this can be written in general as

$$\frac{\partial\rho_s}{\partial t} + \mathrm{div}_\perp(\rho_s v_s) + \frac{\rho_s}{2g}\frac{\partial g}{\partial t} = 0 \quad (6.10)$$

See Eq. (3.2) for g and v_s is the velocity of amphiphilic molecules composing the membrane and will be put equal to those of ambient fluids. (The allowance of the slippage between the membrane and the fluids was considered by Oldroyd [65] and recently by Onuki [58,75].) The precise mathematical definition of the term $\mathrm{div}_\perp(\rho_s v_s)$ in the language of differential geometry is given in Appendix B. The last term in Eq. (6.10) simply expresses the density fluctuation due to the local areal change.

We comment that another way of incorporating the membrane compressibility is to add a compressional energy term such as

$$H_c = \frac{1}{2}B\oint\left(\frac{\delta\rho_s}{\rho_{s0}}\right)^2 dA \quad (6.11)$$

to Eq. (6.1) if the surface tension $\sigma(\rho_s)$ in the first term is put as a constant (zero) [77–80]. However, the compressibility is more generally taken into account in Eq. (6.1) than by Eq. (6.11).

C. Hydrodynamic Equations

Here we shall give the hydrodynamic equations describing the motion of the surrounding fluids. Denoting the fluid velocity around the droplet by $v^{(\prime)}$, the flow field is assumed to be the *creeping flow* which satisfies the stationary Stokes equation [14,18,19,81]

$$\eta^{(\prime)}\nabla^2 v^{(\prime)} = \mathrm{grad}\, P^{(\prime)} \quad (6.12)$$

together with the incompressibility condition

$$\mathrm{div}\, v^{(\prime)} = 0 \quad (6.13)$$

Again quantities with prime refer to those of inside of the droplets while quantities without prime correspond to those of outside. In the above equations, both fluids are assumed to be Newtonian in its stress behavior and Eq. (6.13) yields

$$\Pi^{(')}_{\alpha\beta} = -P^{(')}\delta_{\alpha\beta} + \sigma^{(')}_{\alpha\beta} = -P^{(')}\delta_{\alpha\beta} + \eta^{(')}\left(\frac{\partial v^{(')}_{\alpha}}{\partial x_{\beta}} + \frac{\partial v^{(')}_{\beta}}{\partial x_{\alpha}}\right) \tag{6.14}$$

where $\eta^{(')}$ are the dynamic viscosities.

The solution of Eqs. (6.12) and (6.13) in spherical coordinates is expressed in terms of three scalar functions; $\psi(\boldsymbol{r}, t)$, $\chi(\boldsymbol{r}, t)$ and $P(\boldsymbol{r}, t)$ where ψ and χ give solutions to the homogeneous equation $\nabla^2 v = 0$. Since all of these functions satisfy the Laplace equation (obviously $\nabla^2 P = 0$), they can be expanded in terms of solid spherical harmonics:

$$\psi'(\boldsymbol{r}, t) = \sum_{n,m}{}' \psi'_{nm}(t)\left(\frac{r}{r_0}\right)^n Y_{nm}(\theta, \phi) \tag{6.15}$$

$$\chi'(\boldsymbol{r}, t) = \sum_{n,m}{}' \chi'_{nm}(t)\left(\frac{r}{r_0}\right)^n Y_{nm}(\theta, \phi) \tag{6.16}$$

$$P'(\boldsymbol{r}, t) = \sum_{n,m} P'_{nm}(t)\left(\frac{r}{r_0}\right)^n Y_{nm}(\theta, \phi) \tag{6.17}$$

and

$$\psi(\boldsymbol{r}, t) = \sum_{n,m}{}' \psi_{nm}(t)\left(\frac{r_0}{r}\right)^{n+1} Y_{nm}(\theta, \phi) \tag{6.18}$$

$$\chi(\boldsymbol{r}, t) = \sum_{n,m}{}' \chi_{nm}(t)\left(\frac{r_0}{r}\right)^{n+1} Y_{nm}(\theta, \phi) \tag{6.19}$$

$$P(\boldsymbol{r}, t) = \sum_{n,m} P_{nm}(t)\left(\frac{r_0}{r}\right)^{n+1} Y_{nm}(\theta, \phi) \tag{6.20}$$

describing inside and outside of the fluid, respectively. For the pressure fields P' and P, we included $(n, m) = (0, 0)$ mode (without prime in the summation) due to the existence of the finite nonfluctuating hydrostatic pressure which satisfies

$$(P_{00} - P'_{00})r_0^3 + 2\Sigma(\rho_{s0})r_0^2 + \kappa c_0 r_0(c_0 r_0 - 2) = 0 \tag{6.21}$$

This relation is called the *capillarity condition* [19,54], and comes from the requirement that the undeformed reference sphere Eq. (4.11) is always a solution of the equilibrium shape equation Eq. (4.8) after setting $\Sigma = \Sigma(\rho_{s0})$.

According to the general solution of the Stokes equation given by Lamb [82], the velocity field inside of the droplet is given by [81]

$$\boldsymbol{v}'(\boldsymbol{r},t) = \sum_{n,m}{}' \left[\psi'_{nm}(t)\mathrm{grad} + \chi'_{nm}(t)\mathrm{rot}\,\boldsymbol{r} + \frac{n+3}{2\eta'(n+1)(2n+3)} P'_{nm}(t) r^2 \mathrm{grad} \right.$$
$$\left. - \frac{n}{\eta'(n+1)(2n+3)} P'_{nm}(t)\boldsymbol{r} \right] \left(\frac{r}{r_0}\right)^n Y_{nm}(\theta,\phi) \tag{6.22}$$

while the corresponding solution for the outside the droplet is

$$\boldsymbol{v}(\boldsymbol{r},t) - \boldsymbol{v}^{\infty}(\boldsymbol{r},t) = \sum_{n,m}{}' \left[\psi_{nm}(t)\mathrm{grad} + \chi_{nm}(t)\mathrm{rot}\,\boldsymbol{r} - \frac{n-2}{2\eta n(2n-1)} P_{nm}(t) r^2 \mathrm{grad} \right.$$
$$\left. + \frac{n+1}{\eta n(2n-1)} P_{nm}(t)\boldsymbol{r} \right] \left(\frac{r_0}{r}\right)^{n+1} Y_{nm}(\theta,\phi) \tag{6.23}$$

where $\boldsymbol{v}^{\infty}(\boldsymbol{r},t)$ is the unperturbed flow given by the boundary condition at infinite distance from the droplet and will be set equal to zero here. In Eqs. (6.22) and (6.23), both the gradient and rotation operators act on the solid spherical harmonics outside the large parentheses as well. Lamb showed that the radial component of the velocity involves ψ and P while $\boldsymbol{r} \cdot \mathrm{rot}\,\boldsymbol{v}$ is only a function of χ [81,82] and the terms involving χ always separate out in the course of the calculation. Hence, as far as our present purpose is concerned, we can ignore $\chi^{(')}$ without loss of generality and this simplifies the problem to some extent [14,18,19,81].

D. Stress Relaxation Time

In this subsection, we calculate the sequence of the stress relaxation times for spherical fluid vesicles within which the motion of the membrane surface is overdamped. The restoring force of the membrane balances with the viscous resistance force due to the surrounding fluid after a short initial period of motion. In this case, the components of the out-of-plane displacement ℓ obey the equation

$$\frac{\partial}{\partial t}\ell_{nm}(t) = -\frac{1}{\tau_{nm}}\ell_{nm}(t) \tag{6.24}$$

Hence all the time dependence will be taken into account through the factor of $\exp(-t/\tau_{nm})$.

As for the boundary condition, we employ the *stick* boundary condition which was used by several authors before [19,54,59]. This condition requires that the velocity of the molecules composing the membrane and the fluid velocity on both sides of the membrane are equal. Hence, from Eq. (4.12), the condition is written as

$$\boldsymbol{v} = \boldsymbol{v}' = \boldsymbol{v}_s = \frac{\partial \boldsymbol{r}}{\partial t} \tag{6.25}$$

at the surface. Since the velocity field is linear in the fluctuating amplitude ℓ, one can impose the boundary conditions at $r = r_0$. For the purpose of writing down the boundary conditions explicitly, we should keep in mind that the gradient operator in Eqs. (6.22) and (6.23) in spherical coordinates takes the form

$$\text{grad} = \boldsymbol{e}_r \frac{\partial}{\partial r} + \boldsymbol{e}_\theta \frac{1}{r}\frac{\partial}{\partial \theta} + \boldsymbol{e}_\varphi \frac{1}{r \sin\theta}\frac{\partial}{\partial \phi} \tag{6.26}$$

The first set of boundary conditions come from the continuity of the velocity. In the $\boldsymbol{e}_r$-direction, this is written as

$$\begin{aligned} v_r(r = r_0) &= \frac{1}{r_0}\sum_{n,m}{}' \left[n\psi'_{nm} + \frac{n}{2\eta'(2n+3)} r_0^2 P'_{nm} \right] Y_{nm}(\theta,\phi) e^{-t/\tau_{nm}} \\ &= -\frac{1}{r_0}\sum_{n,m}{}' \left[(n+1)\psi_{nm} - \frac{n+1}{2\eta(2n-1)} r_0^2 P_{nm} \right] Y_{nm}(\theta,\phi) e^{-t/\tau_{nm}} \\ &= -\sum_{n,m}{}' \frac{1}{\tau_{nm}} \ell_{nm} Y_{nm}(\theta,\phi) e^{-t/\tau_{nm}} \end{aligned} \tag{6.27}$$

where the last equation has been obtained by taking the time derivative of Eq. (4.17). Likewise, the continuity of the velocity in the $\boldsymbol{e}_\theta$-direction leads to

$$\begin{aligned} v_\theta(r = r_0) &= \frac{1}{r_0}\sum_{n,m}{}' \left[\psi'_{nm} + \frac{n+3}{2\eta'(n+1)(2n+3)} r_0^2 P'_{nm} \right] \frac{\partial Y_{nm}}{\partial \theta} e^{-t/\tau_{nm}} \\ &= \frac{1}{r_0}\sum_{n,m}{}' \left[\psi_{nm} - \frac{n-2}{2\eta n(2n-1)} r_0^2 P_{nm} \right] \frac{\partial Y_{nm}}{\partial \theta} e^{-t/\tau_{nm}} \end{aligned} \tag{6.28}$$

The continuity condition in the $\boldsymbol{e}_\phi$-direction results in the equivalent condition as Eq. (6.28). From Eqs. (6.27) and (6.28), we obtain the following relations among coefficients of the spherical harmonics:

$$\begin{aligned} n\psi'_{nm} + \frac{n}{2\eta'(2n+3)} r_0^2 P'_{nm} &= -(n+1)\psi_{nm} + \frac{n+1}{2\eta(2n-1)} r_0^2 P_{nm} \\ &= -\frac{r_0}{\tau_{nm}} \ell_{nm} \end{aligned} \tag{6.29}$$

and

$$\psi'_{nm} + \frac{n+3}{2\eta'(n+1)(2n+3)} r_0^2 P'_{nm} = \psi_{nm} - \frac{n-2}{2\eta n(2n-1)} r_0^2 P_{nm} \tag{6.30}$$

at $r = r_0$.

Additional set of boundary conditions follow from the balance of force on the membrane presented by Eq. (6.9). By noticing that the Laplace-Beltrami operator is now the usual Laplacian operator on the sphere

$$\nabla_{LB}^2 = \frac{\nabla_\perp^2}{r_0^2} \tag{6.31}$$

the force balance equations in the e_r and e_θ-directions up to first order in terms of ℓ are given by

$$(P - P') - \left(2\eta\frac{\partial v_r}{\partial r} - 2\eta'\frac{\partial v_r'}{\partial r}\right) + \frac{2}{r_0}\delta\Sigma(\rho_s) - \frac{1}{r_0^4}\left[\Sigma(\rho_{s0})r_0^2 - \kappa\left(\nabla_\perp^2 + 2c_0 r_0 - \frac{1}{2}c_0^2 r_0^2\right)\right](2 + \nabla_\perp^2)\ell(\theta, \phi, t) = 0 \tag{6.32}$$

and

$$-\eta\left(\frac{1}{r_0}\frac{\partial v_r}{\partial \theta} + \frac{\partial v_\theta}{\partial r} - \frac{v_\theta}{r_0}\right) + \eta'\left(\frac{1}{r_0}\frac{\partial v_r'}{\partial \theta} + \frac{\partial v_\theta'}{\partial r} - \frac{v_\theta'}{r_0}\right) - \frac{1}{r_0}\frac{\partial}{\partial \theta}\delta\Sigma(\rho_s) = 0 \tag{6.33}$$

at $r = r_0$, respectively. In the above, we used the capillarity condition Eq. (6.21). Notice also that $n_r \approx 1$ while $n_\theta \approx -(1/r_0)(\partial\ell/\partial\theta)$ which is proportional to ℓ to the lowest order.

In order to eliminate $\delta\Sigma(\rho_s)$ from the above equations, we notice that the linearized equation of continuity can be written from Eq. (6.10) as [59]

$$\frac{\partial}{\partial t}\delta\rho_s \approx -\rho_{s0}\,\mathrm{div}_\perp \boldsymbol{v}_s - \frac{2\rho_{s0}}{r_0}\frac{\partial \ell}{\partial t}. \tag{6.34}$$

where

$$\mathrm{div}_\perp \boldsymbol{v}_s = \frac{1}{r_0 \sin\theta}\left[\frac{\partial}{\partial\theta}(\sin\theta v_{s\theta}) + \frac{\partial}{\partial\varphi}v_{s\varphi}\right] \tag{6.35}$$

is the usual two-dimensional divergence of $\boldsymbol{v}_s$ in the spherical coordinate. From Eqs. (6.5), (6.25) and (6.34), we have

$$\begin{aligned}\frac{\partial}{\partial t}\delta\Sigma(\rho_s) &= B\,\mathrm{div}_\perp \boldsymbol{v}' + \frac{2B}{r_0}\frac{\partial \ell}{\partial t} \\ &= -\frac{B}{r_0^2}{\sum_{n,m}}' n(n+1)\left[\psi_{nm}' + \frac{n+3}{2\eta'(n+1)(2n+3)}P_{nm}' r_0^2\right]Y_{nm}(\theta,\phi)e^{-t/\tau_{nm}} \\ &\quad -\frac{2B}{r_0}{\sum_{n,m}}'\frac{1}{\tau_{nm}}\ell_{nm}Y_{nm}(\theta,\phi)e^{-t/\tau_{nm}}\end{aligned} \tag{6.36}$$

at $r = r_0$. Substitution of Eq. (6.36) into the time derivative of Eqs. (6.32) and (6.33) yields

$$\frac{1}{\tau_{nm}}\left[P'_{nm} - \left(2\eta' n(n-1)\frac{\psi'_{nm}}{r_0^2} + \frac{n(n+1)}{2n+3}P'_{nm}\right)\right]$$
$$-\frac{1}{\tau_{nm}}\left[P_{nm} - \left(2\eta(n+1)(n+2)\frac{\psi_{nm}}{r_0^2} - \frac{n(n+1)}{2n-1}P_{nm}\right)\right]$$
$$-\frac{1}{\tau_{nm}}\frac{1}{r_0^4}(n-1)(n+2)\left\{\Sigma(\rho_{s0})r_0^2 + \kappa\left[(n+1) - 2c_0r_0 + \frac{1}{2}c_0^2r_0^2\right]\right\}\ell_{nm}$$
$$-\frac{2B}{r_0^3}n(n+1)\left(\psi'_{nm} + \frac{n+3}{2\eta'(n+1)(2n+3)}P'_{nm}r_0^2\right) - \frac{1}{\tau_{nm}}\frac{4B}{r_0{}^2}\ell_{nm} = 0 \tag{6.37}$$

and

$$\frac{1}{\tau_{nm}}\left[2\eta'(n-1)\frac{\psi'_{nm}}{r_0^2} + \frac{n(n+2)}{(n+1)(2n+3)}P'_{nm}\right]$$
$$+\frac{1}{\tau_{nm}}\left[2\eta(n+2)\frac{\psi_{nm}}{r_0^2} - \frac{(n-1)(n+1)}{n(2n-1)}P_{nm}\right]$$
$$-\frac{B}{r_0^3}n(n+1)\left[\psi'_{nm} + \frac{n+3}{2\eta'(n+1)(2n+3)}P'_{nm}r_0^2\right] - \frac{1}{\tau_{nm}}\frac{2B}{r_0^2}\ell_{nm} = 0 \tag{6.38}$$

respectively, for $n \geq 1$.

Combining Eqs. (6.29), (6.30), (6.37) and (6.38), one has five homogeneous equations for five unknowns P'_{nm}, ψ'_{nm}, P_{nm}, ψ_{nm} and ℓ_{nm}. The nontrivial solutions can be found when $1/\tau_{nm}$ satisfies the following quadratic equation for each set of (n, m) [59]:

$$A_{nm}\left(\frac{1}{\tau_{nm}}\right)^2 - B_{nm}\left(\frac{1}{\tau_{nm}}\right) + C_{nm} = 0 \tag{6.39}$$

where

$$A_{nm} = [2(n-1)(n+1)E + 2n^2 + 1][(2n^2 + 4n + 3)E + 2n(n+2)] \tag{6.40}$$

$$B_{nm} = \frac{S_{nm}}{\eta r_0}(n-1)n(n+1)(n+2)(2n+1)(E+1)$$
$$+\frac{B}{\eta r_0}n(n+1)[(n-1)(2n^2 + 5n + 5)E + (n+2)(2n^2 - n + 2)] \tag{6.41}$$

$$C_{nm} = \frac{BS_{nm}}{\eta^2 r_0^2}(n-1)n^2(n+1)^2(n+2) \tag{6.42}$$

where $E = \eta'/\eta$ and the effective surface tension S_{nm} is now

$$S_{nm} = \Sigma(\rho_{s0}) + \frac{\kappa}{r_0^2}\left[n(n+1) - 2c_0 r_0 + \frac{1}{2}c_0^2 r_0^2\right] \tag{6.43}$$

Notice that this equation is the generalization of Eq. (4.24).

We list below the limiting expressions of τ_{nm} according to the relation between B and S_{nm}.

1. $B \gg S_{nm} > 0$: This limit corresponds to the case where the membrane is incompressible. Taking the limit of $B/S_{nm} \to \infty$, we find

$$\frac{1}{\tau_{nm}} = \frac{S_{nm}}{\eta r_0}\frac{(n-1)n(n+1)(n+2)}{(n-1)(2n^2+5n+5)E + (n+2)(2n^2-n+2)} \tag{6.44}$$

2. $S_{nm} \gg B > 0$: In the limit of $S_{nm}/B \to \infty$, we have

$$\frac{1}{\tau_{nm}} = \frac{B}{\eta r_0}\frac{n(n+1)}{(2n+1)(E+1)} \tag{6.45}$$

3. $S_{nm} > B = 0$: In this limit the membrane is fully compressible:

$$\frac{1}{\tau_{nm}} = \frac{S_{nm}}{\eta r_0}\frac{(n-1)n(n+1)(n+2)(2n+1)(E+1)}{[2(n-1)(n+1)E + 2n^2 + 1][(2n^2+4n+3)E + 2n(n+2)]} \tag{6.46}$$

4. $B > S_{nm} = 0$: In this case we have

$$\frac{1}{\tau_{nm}} = \frac{B}{\eta r_0}\frac{n(n+1)[(n-1)(2n^2+5n+5)E + (n+2)(2n^2-n+2)]}{[2(n-1)(n+1)E + 2n^2 + 1][(2n^2+4n+3)E + 2n(n+2)]} \tag{6.47}$$

Equation (6.44) was first derived by Schneider, Jenkins and Webb for $c_0 = 0$ and $E = 1$ [14] and generalized to $c_0 \neq 0$ by Milner and Safran [18] or by Onuki for $E \neq 1$ [58]. The more general case including the membrane viscosity was discussed by Fujitani [59]. Equation (6.46) was calculated by Lisy [56] or by Komura and Seki [54].

E. Diffusion Coefficient

In this subsection, we calculate the diffusion coefficient of a fluid vesicle. We follow the method by Edwards and Schwartz who proposed the theory of stochastic dynamics of a deformable membrane [83–85].

From Eq. (4.23), the equation for ℓ_{nm} should be of the form

$$\frac{\partial \ell_{nm}}{\partial t} = -K_{nm}\frac{\partial H_f}{\partial \ell_{n,-m}} = -K_{nm}(n-1)(n+2)S_{nm}\ell_{nm} \tag{6.48}$$

in the absence of thermal agitations. Combining this result with Eq. (6.24) and the expressions of τ_{nm} in Sec. VI.D, one can find K_{nm}. One of the important outcomes of K_{nm} is that the diffusion coefficient of the deformable droplet is identified with $n = 1$ mode as

$$D = k_B T\left(\frac{3}{4\pi} K_{n=1,m}\right) \tag{6.49}$$

Corresponding to the case of $B \gg S_{nm} > 0$ (see Eq. (6.44)), we have

$$K_{nm} = \frac{1}{\eta r_0} \frac{n(n+1)}{(n-1)(2n^2+5n+5)E + (n+2)(2n^2-n+2)} \tag{6.50}$$

with which the diffusion coefficient is

$$D = \frac{k_B T}{6\pi\eta r_0} \tag{6.51}$$

This is the well-known Stokes formula for a solid sphere, and does not depend on η'.

On the other hand, corresponding to the case of $S_{nm} > B = 0$ (see Eq. (6.46)), we see that

$$K_{nm} = \frac{1}{\eta r_0} \frac{n(n+1)(2n+1)(E+1)}{[2(n-1)(n+1)E + 2n^2 + 1][(2n^2+4n+3)E + 2n(n+2)]} \tag{6.52}$$

and hence

$$D = \frac{k_B T}{2\pi\eta r_0} \frac{E+1}{3E+2} \tag{6.53}$$

which coincides with the old result by Hadamard [86] and Rybczynski [87], who did not take into account the deformation of the droplet. Equation (6.52) was obtained by Edwards and Schwartz for $E = 1$ [85] and generally by Komura and Seki [54]. Notice also that Eq. (6.53) reduces to Eq. (6.51) when $E \to \infty$.

F. Complex Effective Viscosity

Dispersions of small spherical droplets can be regarded as a homogeneous fluid when we are concerned with the phenomena occurring in much larger length scale than the average size of the dispersed droplets. One example is the rheological behavior of dispersions where one asks the stress needed to cause a given bulk motion. On measuring the rheological property, a dispersion can be considered as a "homogeneous" fluid with an effective viscosity. Here we have addressed the term "homogeneous" in a statistical sense, since the exact position and motion of

droplets may differ for different realizations of experiments even if the macroscopic conditions such as the boundary conditions are prepared in the same manner. Hence we may observe, in principle, the ensemble average of the fluid velocity $\langle v \rangle$ instead of its exact value v. However, the ensemble average cannot be calculated directly and we assume the ergodicity property of the system, namely, the equality of the ensemble average and the volume average.

In fact, study of the effective viscosity of dispersions has a fairly long history and its theoretical basis has been well established. The first hydrodynamic calculation was given by Einstein for suspensions of solid spheres in the steady shear flow [88]. Taylor extended Einstein's approach to the liquid droplets in the continuous aqueous phase [89]. Later Frölich and Sack [90] and Oldroyd [64] argued the viscoelasticity of suspensions and emulsions, respectively. In this subsection, we show the results of the complex effective viscosity for an emulsion of fluid vesicles. Calculations shows that only $(n, m) = (2, 0)$ mode is relevant.

The effective viscosity η^* is defined as

$$\langle \Pi_{\alpha\beta} \rangle = \eta^* \left\langle \frac{\partial v_\alpha}{\partial x_\beta} + \frac{\partial v_\beta}{\partial x_\alpha} \right\rangle \tag{6.54}$$

where only the anisotropic part of the stress tensor is of our interest (compare with Eq. (6.14)). Batchelor derived the general constitutive equation in the form [73, 91]

$$\langle \Pi_{\alpha\beta} \rangle = \eta \left\langle \frac{\partial v_\alpha}{\partial x_\beta} + \frac{\partial v_\beta}{\partial x_\alpha} \right\rangle + c \oint [\Pi_{\alpha\gamma} x_\beta n_\gamma - \eta(v_\alpha n_\beta + v_\beta n_\alpha)] \, dA \tag{6.55}$$

where c is number of droplets per unit volume. In Eq. (6.55), the second term on the r.h.s. represents the extra stress due to the presence of the dispersed droplets. Since the detailed calculation is given in Refs. 60 and 92, we show here only the final result for dilute limit:

$$\frac{\eta^*}{\eta} = 1 + 5 \frac{24BS + [(23E - 16)B + 4(5E + 2)S]\Omega + (E - 1)(19E + 16)\Omega^2}{48BS + [2(23E + 32)B + 40(E + 1)S]\Omega + (2E + 3)(19E + 16)\Omega^2} \varphi \tag{6.56}$$

where $E = \eta'/\eta$, $\Omega = i\omega r_0 \eta$, $S = S_{20}$ and $\varphi = (4\pi/3) c r_0^3$ is the volume fraction of the total droplets.

The equation which determines the overdamped mode of the membrane deformation can be obtained by putting the denominator of the second term of Eq. (6.56) equal to zero. When neither B nor S is zero ($B \neq 0$ and $S \neq 0$), it exhibits, in general, two characteristic times. On the other hand, in the case of $B = S = 0$, we find a stationary η^* given by

$$\frac{\eta^*}{\eta} = 1 + \frac{5(E-1)}{2E+3}\varphi \tag{6.57}$$

which was first derived by Taylor [93]. In such a case there is no force due to the membrane and the fluid stress tensors balance at the interface. Hence the change in viscosity is proportional to $\eta - \eta'$ as it should be [74].

When either one of B or S is zero or tends to infinite, only a single characteristic time shows up. This case can be represented in general by the form

$$\eta^* = \eta_\infty + \frac{G\tau}{1 + i\omega\tau} \tag{6.58}$$

which coincides with the *Maxwell model* in the phenomenological rheology. In the above, τ is the relaxation time, G the relaxation strength and η_∞ is the constant viscosity when $\omega \to \infty$. τ represents the time scale dividing the short-time Hookian regime and the long time Newtonian regime. We shall collect the results of η_∞, τ, G and $\eta_0^* = \eta^*(\omega \to 0)$ for several cases depending on the relation between B and S.

1. $B \gg S > 0$:

$$\frac{\eta_\infty}{\eta} = 1 + \frac{5(23E-16)}{2(23E+32)}\varphi \tag{6.59}$$

$$\tau = \frac{\eta r_0}{S}\frac{23E+32}{24} \tag{6.60}$$

$$G = \frac{S}{r_0}\frac{2880}{(23E+32)^2}\varphi \tag{6.61}$$

and

$$\frac{\eta_0^*}{\eta} = 1 + \frac{5}{2}\varphi \tag{6.62}$$

Eq. (6.62) does not depend on the fluid viscosity and coincides with that of dilute suspensions of rigid particles [88].

2. $S \gg B > 0$:

$$\frac{\eta_\infty}{\eta} = 1 + \frac{5E+2}{2(E+1)}\varphi \tag{6.63}$$

$$\tau = \frac{\eta r_0}{B}\frac{5(E+1)}{6} \tag{6.64}$$

$$G = \frac{B}{r_0}\frac{9}{5(E+1)^2}\varphi \tag{6.65}$$

and η_0^* is identical to Eq. (6.62)

3. $S > B = 0$:

$$\frac{\eta_\infty}{\eta} = 1 + \frac{5(E-1)}{2E+3}\varphi \tag{6.66}$$

$$\tau = \frac{\eta r_0}{S}\frac{(2E+3)(19E+16)}{40(E+1)} \tag{6.67}$$

$$G = \frac{S}{r_0}\frac{20}{(2E+3)^2}\varphi \tag{6.68}$$

and

$$\frac{\eta_0^*}{\eta} = 1 + \frac{5E+2}{2(E+1)}\varphi \tag{6.69}$$

Eq. (6.69) was first derived by Taylor for the dispersions of almost undeformable liquid droplets with a large surface tension [89]. The case of $E = 1$ in Eq. (6.69) was also discussed by Schwartz and Edwards [84].

4. $B > S = 0$:

$$\frac{\eta_\infty}{\eta} = 1 + \frac{5(E-1)}{2E+3}\varphi \tag{6.70}$$

$$\tau = \frac{r_0\eta}{B}\frac{(2E+3)(19E+16)}{2(23E+32)} \tag{6.71}$$

$$G = \frac{B}{r_0}\frac{5}{(2E+3)^2}\varphi \tag{6.72}$$

and

$$\frac{\eta_0^*}{\eta} = 1 + \frac{5(23E-16)}{2(23E+32)}\varphi \tag{6.73}$$

Notice that all the relaxation times given above are recovered by calculating τ_{20} for the corresponding cases in Sec. VI.D.

Another limit can be taken in the small frequency limit by neglecting the Ω^2 terms in Eq. (6.56). In this case, the effective viscosity can be also expressed in terms of the Maxwell model, Eq. (6.58), with

$$\frac{\eta_\infty}{\eta} = 1 + \frac{5[(23E-16)B + 4(5E+2)S]}{2[(23E+32)B + 20(E+1)S]}\varphi \tag{6.74}$$

$$\tau = \frac{r_0 \eta}{BS} \frac{(23E + 32)B + 20(E + 1)S}{24} \tag{6.75}$$

$$G = \frac{BS}{r_0} \frac{720(4B + S)}{[(23E + 32)B + 20(E + 1)S]^2} \varphi \tag{6.76}$$

and η_0^* is identical to Eq. (6.62).

In all these cases, both η_∞ and η_0^* approach to the Einstein's result by taking the limit of $E \to \infty$. It should be emphasized that as long as the membrane is characterized by the nonzero B and S, the steady-state effective viscosity coincides with that of a suspension of solid particles [73, 94]. Moreover, neither B nor S appears in the steady-state viscosity, while the relaxation time and the relaxation strength depend explicitly on B and S. Hence an appropriate dynamical experiments should be performed in order to grasp the elastic properties of the membrane. Although these statements might appear obvious in the early calculations by Oldroyd [64,65], it should be stressed that he did not take into account the effect of the bending rigidity κ.

VII. DISCUSSION

In order to estimate the value of the bending rigidity κ from the observed characteristic time, we have to eliminate $\Sigma(\rho_{s0})$ from S in Eq. (6.43). (For the present discussion, we ignore the spontaneous curvature c_0.) This can be done by an independent observation of $\Sigma(\rho_{s0})$ according to the capillarity condition Eq. (6.21) [44]. In practice, however, it is difficult to perform such a measurement in a sufficient accuracy and many people assumed that $\Sigma(\rho_{s0}) \simeq 0$. In such a case, it is possible to estimate κ from the measured relaxation time of the membrane deformation [14,41–47]. Such a simplification can be justified provided $\Sigma(\rho_{s0}) \ll \kappa/r_0^2$ is satisfied. The quantitative estimation of this condition should be done separately for bilayer vesicles and for microemulsion droplets since they differ by several decades in length scale.

For a lipid vesicle of size $r_0 \simeq 10^{-5}$ m, various people observed that the bending rigidity is typically $\kappa \simeq 1 \times 10^{-19}$ J [14,41–47] and hence we have $\kappa/r_0^2 \simeq 1 \times 10^{-9}$ N/m. As for the surface tension, some people claim that it is less than 10^{-5} [95] or 10^{-8} N/m [44] while others insist $\Sigma \simeq 1 \times 10^{-8}$ N/m [45]. For a microemulsion droplet of size $r_0 \simeq 5 \times 10^{-9}$ m, the measured bending rigidities are $\kappa \simeq 1 \times 10^{-20}$ J by SANS technique [50–52] or $\kappa \simeq 1 \times 10^{-21}$ J by dynamic Kerr effect measurement [53] yielding $\kappa/r_0^2 \simeq 4 \times 10^{-4}$ or 10^{-5} N/m, respectively. (See Table 1.) These values can be compared with the relatively small two-dimensional pressure 7×10^{-5} N/m [51], although they claim that it is different from the macroscopic surface tension.

TABLE 1 Orders of Various Hydrodynamical Time Scales[a]

	Vesicle	Microemulsion droplet
r_0 (m)	10^{-5}	10^{-8}
B (N/m)	10^{-1}	[b]10^{-2}
κ (J)	10^{-19}	10^{-20}
κ/r_0^2 (N/m)	10^{-9}	10^{-4}
ω_c (1/s)	10^{8}	10^{11}
$1/\tau_\eta$ (1/s)	10^{4}	10^{10}
ω_B (1/s)	10^{6}	10^{10}
$1/\tau_B$ (1/s)	10^{7}	10^{9}
ω_s (1/s)	10^{6}	10^{9}
ω_κ (1/s)	10^{2}	10^{9}
$1/\tau_\kappa$ (1/s)	10^{-1}	10^{7}

[a]We used $v_c \simeq 10^3$ m/s, $\rho \simeq 10^3$ kg/m^3 and $\eta \simeq 10^{-3}$ Ns/m^2.
[b]See the text.

In either case, it is somewhat delicate to ignore the *apparent* tension $\Sigma(\rho_{s0})$ in Eq. (6.43). For the simplicity of the present argument, however, we assume here the tensionless case; i.e., $\Sigma(\rho_{s0}) \simeq 0$. In order to extract the property due to the bending rigidity in an emphasized way, it is recommended to prepare droplets of small size.

As we have done in Sec. VI.D, several limiting cases of the relaxation time have been considered according to the relation between B and $S \approx \kappa/r_0^2$. The question is, to which case does the real system correspond? By a mechanical experiment, Evans and co-workers found $B \simeq 0.14$ N/m for egg lecithin bilayers [95–97]. Therefore for a vesicle, we typically have $B/S \sim Br_0^2/\kappa \simeq 1.4 \times 10^8$, and the membrane can be considered to be almost incompressible. It should be noticed that even $S \sim \kappa/r_0^2$ is negligibly small compared to B; this does not mean $S = 0$ which corresponds to the different limiting case.

Another possible argument may be given as follows. Let us regard the membrane as a homogeneous elastic shell with a thickness a. According to the shell theory [13,33], two-dimensional compression modulus B is given by

$$B = a\frac{\mu_3(3\lambda_3 + 2\mu_3)}{\lambda_3 + 2\mu_3} = \lambda + \mu \tag{7.1}$$

respectively (see Sec. V.C). Then one can see from Eq. (5.27) that B/S is approximately determined by $B/S \approx (r_0/a)^2$ [46]. For a bilayer membrane, Evans took into account the fact that membrane is not a continuum in the thickness direction and obtained different thickness dependence of the bending rigidity as [97–99].

$$\kappa = \frac{Ba^2}{2} \tag{7.2}$$

In this case we also have the same scaling behavior as $B/S \approx (r_0/a)^2$. For a lipid vesicle of size $r_0 \simeq 10^{-5}$ m and $a \simeq 4 \times 10^{-9}$ m [46,62], one finds $B/S \simeq 6 \times 10^6$ corresponding to the incompressible case $B \gg S \neq 0$ as before. For a microemulsion droplet, however, since the size and thickness are typically $r_0 \simeq 5 \times 10^{-9}$ m and $a \simeq 2 \times 10^{-9}$ m, B and S take rather comparable values. Thus, we cannot simply employ the incompressible condition for the interface of microemulsion droplets and it might be better to take both B and κ into account in the consideration of the effective viscosity.

There are several time scales involved in the present problem; each of them reflecting the corresponding mode coupled to the ambient fluids. We consider now whether these time scales can be well separated from each other. As mentioned above, we ignore the time scales which come from the surface tension Σ. In Sec. VI.C, we used the stationary Stokes equation Eq. (6.12) to describe the creeping motion of the surrounding fluids. This can be justified as long as the Reynolds number of the fluids $R = \rho v r_0/\eta$ is sufficiently small (ρ is the fluid mass density). For a given frequency ω, Reynolds number can be given in terms of the viscous diffusion rate $1/\tau_\eta \sim \eta/\rho r_0^2$ as $R \sim \omega\tau_\eta$. Hence, the above condition sets the upper boundary value of the allowed frequency range such that $\omega \ll 1/\tau_\eta$. On the other hand, the incompressible condition of the fluids Eq. (6.13) requires $\omega \ll \omega_c \sim v_c/r_0$ where v_c is the speed of the sound.

For the modes related to the compression modulus B, we have the oscillating mode $\omega_B \sim (B/\rho r_0^3)^{1/2}$ and the overdamped decaying mode (or Lucassen mode [100–102]) $1/\tau_B \sim B/\eta r_0$. Moreover there exists an additional surface mode connected with the redistribution of ρ_s for compressible membranes. This mode is known to have an unusual dispersion law [55,56,71,72,75]:

$$\omega_s = \frac{\sqrt{3} - i}{2}\left(\frac{B^2}{\rho\eta r_0^4}\right)^{1/3} \tag{7.3}$$

For the bending modes, on the other hand, we have the oscillating mode $\omega_\kappa \sim (\kappa/\rho r_0^5)^{1/2}$ and the overdamped mode $1/\tau_\kappa \sim \kappa/\eta r_0^3$. Notice that Eq. (7.3) is derived in the limit of $\omega \gg 1/\tau_\eta, \omega_\kappa$ and may be irrelevant to the viscosity measurement. Order estimations of these time scales both for vesicles and microemulsion droplets are listed in Table 1. (Since there is no published experimental value of B for microemulsion droplets, as far as we know, it is roughly estimated by $B \sim \kappa/a^2$ with $a \simeq 10^{-9}$ m.) For the estimation of these quantities, we used $v_c \simeq 10^3$ m/s, $\eta \simeq 10^{-3}$ Ns/m^2 and $\rho \simeq 10^3$ kg/m^3.

For vesicles, bending modes are observable since $1/\tau_\kappa \ll 1/\tau_\eta$, while incompressible condition for the membrane is regarded to be reasonable since $\omega_B, 1/\tau_B, \omega_s \gg 1/\tau_\eta$. It can be also seen that the overdamped bending mode $1/\tau_\kappa$ is well

separated from oscillating bending mode ω_κ. In the microemulsion droplet case, although the allowed frequency range is rather high $\omega \ll 1/\tau_\eta \simeq 10^{10}\ s^{-1}$, several modes are in the same order close to $1/\tau_\eta$ and might be difficult to separate from each other. Moreover these frequency lie near the upper limit frequency which is measurable by mechanical experiments. The longest relaxation time $1/\tau_\kappa \simeq 10^7\ s^{-1}$ turns out be quite large compared to the vesicles and becomes rather comparable to $1/\tau_B \simeq 10^9\ s^{-1}$. Hence, both of the modes should be taken into account in this case as mentioned before.

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APPENDIX A: DERIVATION OF MEMBRANE FORCE

In this appendix, we briefly give the derivation of the restoring force due to the membrane Eq. (4.6), following mainly the calculation by Zhong-can and Helfrich [15]. We introduce a virtual displacement denoted by $\epsilon(s^1, s^2)$ which is the difference between a point on the actual surface and some point on the neighboring varied surface $\hat{\boldsymbol{r}}$:

$$\hat{\boldsymbol{r}} = \boldsymbol{r} + \epsilon \boldsymbol{n} \tag{A1}$$

Notice that $\boldsymbol{r}$ describes not only the undeformed surface but also the deformed shape and ϵ can be different from the actual displacement ℓ introduced in Eq. (4.12). Let us use $\hat{g}_{ij}$, $\hat{h}_{ij}$, $\hat{g}$ and $\hat{H}$ for the metric tensor, curvature tensor, determinant of the metric tensor and mean curvature of the varied surface, respectively. The tangent vector of the varied surface is

$$\hat{\boldsymbol{r}}_i = \boldsymbol{r}_i + \epsilon_i \boldsymbol{n} + \epsilon \boldsymbol{n}_i \tag{A2}$$

with which we find

$$\hat{g}_{ij} \approx g_{ij} - 2\epsilon h_{ij} \tag{A3}$$

Hence

$$\hat{g} \approx g(1 - 4\epsilon H) \tag{A4}$$

The local areal change is obviously

$$\sqrt{\hat{g}} \approx \sqrt{g}(1 - 2\epsilon H) \tag{A5}$$

In addition, we have

$$\hat{g}^{ij} \approx g^{ij} + 2\epsilon(2Hg^{ij} - Kh^{ij}) \tag{A6}$$

$$\hat{h}_{ij} \approx h_{ij} + \epsilon_{ij} + \epsilon(Kg_{ij} - 2Hh_{ij}) - \epsilon_k \Gamma^k_{ij} \tag{A7}$$

where the Christoffel symbols Γ^k_{ij} are defined in Eq. (3.8). In the above, we have used the Weingarten equation Eq. (3.9) and the relation

$$h_{ij}g^{jk}h_{kl} = 2Hh_{il} - Kg_{il} \tag{A8}$$

From Eqs. (3.5), (A6) and (A7), one can obtain the mean curvature of the varied surface as

$$\hat{H} \approx H + \epsilon(2H^2 - K) + \frac{1}{2}g^{ij}D_i\epsilon_j \tag{A9}$$

Next the first variation of H_f (Eq. (6.1)) is given by

$$\delta H_f = \oint \Sigma\delta \, dA + \delta H_b \tag{A10}$$

where

$$\begin{aligned}\delta H_b &= \delta \oint \frac{1}{2}\kappa(2H + c_0)^2 \, dA \\ &= \oint \frac{1}{2}\kappa[(2H + c_0)^2\delta \, dA + 4(2H + c_0)(\delta H) \, dA]\end{aligned} \tag{A11}$$

Using that that the first variation of A is

$$\delta \oint dA = -\oint 2\epsilon H \, dA \tag{A12}$$

and after the integration of ϵ_{ij} and ϵ_κ by parts, we obtain

$$\delta H_f = \oint \epsilon[-2\Sigma H + \kappa(2H + c_0)(2H^2 - 2K - c_0H) + 2\kappa\nabla^2_{LB}H] \, dA \tag{A13}$$

where ∇^2_{LB} is defined by Eq. (4.7). Finally the restoring force due to the membrane is calculated by

$$F_\parallel = -\frac{\delta H_f}{\delta\epsilon} \tag{A14}$$

which simply leads to Eq. (4.6).

APPENDIX B: DEFINITION OF DIVERGENCE OPERATOR

In this appendix, we give the mathematical definition of the divergence operator appearing in Eq. (6.10) in the general geometry [76]. First we raise the indices by

$$\boldsymbol{r}^i = g^{ij}\boldsymbol{r}_j \tag{B1}$$

with which we define –

$$v_s^i = \boldsymbol{v}_s \cdot \boldsymbol{r}^i \tag{B2}$$

Then the divergence operator stands for

$$\mathrm{div}_\perp(\rho_s \boldsymbol{v}_s) = \frac{1}{\sqrt{g}}\partial_i(\sqrt{g}\rho_s v_s^i) \tag{B3}$$

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