Dynamical fluctuations of droplet microemulsions and vesicles

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The hydrodynamic fluctuations of nearly spherical vesicles and microemulsion droplets are considered. The incompressibility of the enclosed fluid and surfactant or lipid layer imposes a constraint of constant droplet volume and area on the fluctuations. These overdamped modes, driven by bending energy and damped by viscosity of the surrounding fluids, change the shape of the surface and may scatter neutrons or light. A dynamical structure factor $S(q,t)$ is computed and a first frequency moment at fixed wave number $\omega_{\rm char}(q)$ obtained. In the limit of a stiff droplet at fixed "excess area," a new mode is obtained —an overdamped oscillation among ellipsoidal shapes about the minimum-energy (usually prolate) shape. Prospects for observing this fluctuation are discussed.

I. INTRODUCTION

The fluctuations of vesicles of droplet-phase microemulsions provide a dynamical probe of the bending stiffness of lipid bilayers and surfactant interfaces. Though the two systems are separated by several decades in length scale, they are described by very similar physics. In both cases, there is a convenient separation of energy scales which allows us to consider the fluctuations at constant volume and area of a "droplet" (nearly spherical in most cases) controlled only by the bending energy[1] of the surface.

Dynamical measurements of droplet microemulsions (by spin-echo neutron scattering[2]) and vesicles[3] (by video microscopy)[4,5] offer a more stringent test of our understanding of the bending energy and associated hydrodynamics than static measurements alone; in particular, values for the bending stiffness and spontaneous curvature can be extracted from the time dependence of the dynamic structure factor $S(q,t)$ as well as from the wave number dependence.

Any calculation of fluctuations for these systems must properly take into account the role of area conservation, so that predicted fluctuations are consistent with the "excess area" of the droplet. (The excess area is the area of the droplet beyond that of the sphere of equivalent volume.) The area of the droplet is conserved for vesicles (and for microemulsion droplets on time scales short compared to collision times), so the excess area is an important parameter in characterizing the shape and allowed fluctuations of the droplet. The fixed excess-area constraint must be present in dynamic as well as static calculations, so that the fluctuation-dissipation (FD) theorem can be satisfied.

In Sec. II we compute the equilibrium fluctuations of a single vesicle or droplet with fixed excess area. The area conservation is implemented approximately by a Lagrange multiplier (so that the average excess area is some prescribed value). We discuss the stiff and floppy limits for a droplet with a given excess area, and the limits of validity of the Lagrange multiplier approach. In Sec. III we extend the work of Schneider, Jenkins, and Webb (SJW) on the dynamics of droplet fluctuations[3] to the case of nonzero spontaneous curvature (appropriate for microemulsions) and make the connection to statics required by the FD theorem, which was unclear in the SJW treatment.

In Sec. IV we investigate a new "ellipsoidal mode" of droplets which occurs in the limit of stiff droplets at fixed excess area. (The possibility of such a mode was first discussed by Peterson,[6] who considered the bending energy of various ellipsoidal shapes.) The mode motion consists of overdamped oscillations about the minimum-energy shape (usually a prolate ellipsoid) at fixed area and volume. We derive a relaxation rate and amplitude for the mode.

In Sec. V we compute the dynamic structure factor $S(q,t)$ for droplet microemulsions and show how the bending constant and spontaneous curvature may be extracted from the initial decay rate of $S(q,t)$. In Sec. VI we discuss present and future vesicle experiments, where the ellipsoidal mode may be observed.

II. STATIC PROPERTIES OF DROPLETS

The fluctuations of nearly spherical droplets enclosed by surfactant molecules (droplet microemulsions) or lipid bilayers vesicles) can be understood in terms of a convenient separation of energy scales. The energy needed to compress the fluids inside or outside the drop, or to change the area per surfactant molecule is often much larger than the energy needed to bend the interface. (For rough estimates in terms of characteristic frequencies, see Appendix A.)

Thus we are led to consider the fluctuations of a droplet at constant area and volume, with energy given by the Helfrich expression:[1]

$$E_{\rm bend}=\frac{\kappa}{2}\int dS(H-H_s)^2 , \tag{1}$$

$$H=(1/r_1+1/r_2),\quad H_s=2/r_s , \tag{2}$$

where r_1 and r_2 are the principal curvature radii and r_s

is the spontaneous radius of curvature. The excess area of the droplet, defined as the area of the droplet less that of the sphere of the same volume, is a conserved quantity which characterizes the fluctuations of the droplet.

In practice, we describe the shape of the droplet by its deviation from some convenient sphere (e.g., the equivalent-volume sphere). We expand the bending energy, area, and volume of a surface described by $\mathbf{r}(\Omega)=r_0[1+u(\Omega)]\hat{\mathbf{r}}$ in powers of the deviation from the sphere to order u^2 $[o(u^2)]$ as follows:

$$r(\Omega)=r_0\left[1+\sum_{l,m} u_{lm}Y_{lm}(\Omega)\right], \tag{3}$$

$$\Delta E=\frac{\kappa}{2}\sum_{l,m}|u_{lm}|^2\{l(l+1)(l-1)(l+2) -4wl(l+1)+w^2[4+2l(l+1)]\} -16\pi\kappa w(1-w)u_0, \tag{4}$$

$$A=4\pi r_0^2(1+u_0)^2+r_0^2\sum_{l>0}|u_{lm}|^2[1+l(l+1)/2], \tag{5}$$

$$V=\frac{4\pi}{3}r_0^3(1+u_0)^3+r_0^3\sum_{l>0}|u_{lm}|^2, \tag{6}$$

where Ω is the solid angle, $w=r_0/r_s$, and $u_0=u_{00}/(4\pi)^{1/2}$. [These formulas follow from Ref. 7, Eqs. (A7) and (A8), except that we do not choose $r_0=\langle r\rangle_\Omega$.]

We may easily incorporate the constraint of constant volume to $o(u^2)$ by choosing u_0 to satisfy $V=4\pi r_0^3/3+o(u^3)$ (as in Ref. 8); this gives

$$(1+u_0)^3=1-\frac{3}{4\pi}\sum_{l>0}|u_{lm}|^2, \tag{7}$$

$$A=4\pi r_0^2+\frac{r_0^2}{2}\sum_{l>1}|u_{lm}|^2(l+2)(l-1), \tag{8}$$

$$\Delta E=\frac{\kappa}{2}\sum_{l>1}|u_{lm}|^2(l+2)(l-1)[l(l+1)-4w+2w^2], \tag{9}$$

with r_0 the equivalent-volume sphere radius.

In such a description, the constraint of constant excess area is intractable. Equation (8) implies that there is a constraint on the sum of the amplitudes of the u_{lm} which is difficult to eliminate, as we do not know beforehand where the excess area will be stored; no one mode or small subset of modes is known to serve as an area reservoir for the rest. Hence we employ a Lagrange multiplier for area, which ensures that the mean excess area of the fluctuating droplet is equal to some prescribed value.

The energy is now $E'=E-\gamma A$, with γ the Lagrange multiplier; equipartition gives the mean-square fluctuations as

$$\langle|u_{lm}|^2\rangle=\frac{kT}{\kappa}\{(l+2)(l-1) \times[l(l+1)-4w+2w^2-\tilde{\gamma}]\}^{-1}. \tag{10}$$

The mean excess area is then

$$\Delta=\delta A/A=\frac{kT}{8\pi\kappa}\sum_{l=2}^{l_{\max}}\frac{2l+1}{l(l+1)-4w+2w^2-\tilde{\gamma}}, \tag{11}$$

with the dimensionless Lagrange multiplier $\tilde{\gamma}=\gamma r_0^2/\kappa$. The upper cutoff $l_{\max}=r/a$, a being a microscopic length (otherwise the sum is logarithmically divergent).

We now illustrate the action of the Lagrange multiplier $\tilde{\gamma}$ with two limiting cases of stiffness at fixed excess area. In the limit of a floppy membrane, the fluctuation amplitudes would become unbounded if $\tilde{\gamma}$ were zero, thus constantly exceeding the available excess area; the multiplier must penalize these excursions. As $\kappa\to 0$, the bending energy becomes irrelevant for the fluctuation amplitudes, and each mode contributes equally to the excess area.

In the opposite limit of a stiff membrane, the fluctuations would vanish if $\tilde{\gamma}$ were zero; some mode must be forced to accept the excess area. It is clear that in this zero-temperature limit, the lowest mode of the droplet ($l=2$) will develop a large amplitude. The droplet will become an ellipsoid, the shape of lowest energy consistent with the required excess area. Within our expansion, this is manifested in a diverging amplitude for the $l=2$ modes.

In this limit, the lowest mode serves as an area reservoir for the higher modes, and the apparent tension takes the value which stabilizes the zero-temperature shape ($\gamma=6\kappa/r^2$ for the case of $H_s=0$). The Lagrange multiplier description of area conservation continues to work for the fluctuations of the higher modes, with the lowest mode treated separately. The description in terms of $\tilde{\gamma}$ suffers only when the lowest mode has a large share of the excess area, but not enough to be considered a reservoir for the other modes.

III. HYDRODYNAMICS OF THE DROPLET

The dynamical fluctuations of the droplet are assumed to take place at an ultralow Reynolds number, where both the convective and inertial terms in the Navier-Stokes (NS) equations can be neglected. In this limit (see Appendix A for a rough estimate of the validity of this approximation), the deterministic time evolution of the shape of the droplet is described by "creeping flow".[9]

The content of the deterministic dynamics, first worked out by Schneider, Jenkins, and Webb (SJW),[3] can be summarized as follows. Given a shape of the surface enclosing the droplet, bending forces on the surface can be computed. (We have extended SJW to the case of nonzero spontaneous curvature, which gives rise to new terms in the force; for details, refer to Appendix B.) Since the inertial terms in the NS equations have been dropped, forces must balance on the surface, hence the viscous stresses on the surface are known. From this and the no-slip boundary conditions on the incompressible flow of the fluids inside and outside of the drop, the flow fields can be calculated. From the normal component of the fluid velocities, the time rate of change of the droplet shape is determined.

The dynamical calculation is performed in a spherical

geometry, using the Lamb solution[10] for obtaining the fluid velocity fields from the surface stresses. This represents the lowest order in a systematic expansion in deviations from the sphere; since the velocities are all $o(u)$, the shape can be taken to be spherical.

The incompressibility of the fluid is enforced (within this approximation for the flow fields) by using a spatially varying pressure field, which cancels any compressional stresses set up by the fluid flow. The local incompressibility of the surface is enforced to lowest order in the displacements with a spatially varying "surface pressure" $\gamma(\Omega)$. This surface pressure is a Lagrange multiplier for local conservation of surface area just as the pressure is a Lagrange multiplier for local conservation of fluid volume.

Within the deterministic calculation of surface motion, the pressure $p(\mathbf{r})$ and surface pressure $\gamma(\Omega)$ have physical meaning as that which would be measured during the motion. The spatially varying parts of p and γ are purely functions of the distorted shape, since in the static limit global constraints on area and volume are sufficient.

The structure of the deterministic equations guarantees that all deviations from the sphere will relax in some finite time. The area conservation has not been (and cannot easily be) implemented to $o(u_{lm}^2)$, so that the long-time limit of the dynamics is a sphere, and not the lowest-energy ellipsoidal shape. However, our intent is to use the deterministic dynamics together with the fluctuation-dissipation theorem to obtain autocorrelation functions, i.e.,

$$\langle u_{lm}(t)u_{l'm'}(0)\rangle=\delta_{ll'}\delta_{mm'}\langle\,|u_{lm}|^2\rangle\exp(-\omega_{lm}t)\ . \tag{12}$$

The long-time average of the fluctuating dynamics gives the same mean-square amplitudes of the fluctuations as the static calculation if the random forces are chosen correctly and the same free energy is used; this is the content of the FD theorem. This means that we must choose the $\bar{\gamma}$ appearing in the dynamics to be the same as the $\bar{\gamma}$ which gave the correct mean excess area in the static calculation. Our description of the dynamical fluctuations of the droplet will be no worse than our equilibrium description.

The results of our generalization of the SJW calculation of the relaxational frequencies are (with $H_s\neq 0$; see Appendix B)

$$\omega_l=\frac{\kappa}{\eta r^3}\frac{l(l+1)-(\bar{\gamma}+4w-2w^2)}{Z(l)}\ , \tag{13}$$

$$Z(l)=\frac{(2l+1)(2l^2+2l-1)}{l(l+1)(l+2)(l-1)}\ . \tag{14}$$

It is interesting to look at the two limits of $\kappa\to 0$ and $\kappa\to\infty$ which we considered in the equilibrium discussion. In the floppy limit, the relaxation rate of the modes becomes independent of the stiffness,

$$\omega_l\sim\frac{kT\Delta}{NZ(l)},\quad N=\sum_{l>1}^{l_{\max}}(2l+1)\ . \tag{15}$$

In the stiff limit, the relaxation rate of the lowest ($l=2$) mode vanishes; the numerator of Eq. (13) is the denominator of Eq. (10). The physical reason for $\omega_2\to 0$ is that the restoring force from the fictitious energy $E'=E-\gamma A$ vanishes, so that the mean amplitude of the mode will be large enough to account for almost all of the excess area.

In principle, the various spherical-harmonic modes of the droplet could be dephased by thermally occurring random rotations of the droplet. We shall show that this effect can be neglected if $\kappa>kT$. We may estimate the effect of rotational diffusion by assuming the droplet rotates as a solid sphere, giving a drag coefficient ($\tau=\gamma_\theta\omega$) of $\gamma_\theta=8\pi\eta r_0^3$. Using the fluctuation-dissipation theorem to give the strength of the random torques acting on the droplet, we find the ensemble-averaged rotation operator is $\langle\hat{O}(t)\rangle=\exp[-(kT/\gamma_\theta)\mathbf{L}^2t]$. That is, distortions u_{lm} of the droplet are angularly dephased at a rate $\omega_\theta(l)=kTl(l+1)/(8\pi\eta r_0^3)$. For large l this is clearly smaller than the bending-driven relaxation of Eq. (13); we compare the two rates for the $l=2$ mode to find, for κ of a few times kT (and $w=\bar{\gamma}=0$ for simplicity),

$$\omega_\theta/\omega_{\text{bend}}=\frac{kT}{8\pi\kappa}\frac{55}{24}\ll 1\ .$$

IV. ELLIPSOIDAL SHAPE MODES

In the limit of stiff membranes and fixed excess area, a new mode of the system, which cannot be defined in terms of deviations from a sphere, becomes well defined. As we have seen, all $l=2$ distortions of the sphere have the same energy to $o(u^2)$; in particular, all ellipsoids, whether oblate or prolate or nonaxisymmetric, have the same bending energy to $o(u^2)$ at fixed volume and excess area. Terms of $o(u^3)$ break this symmetry, as first pointed out by Deuling and Helfrich.[11] If we expand to $o(u^3)$, and specialize to $l=2$ distortions only, we find (see Appendix C)

$$\Delta E=-\kappa C(w)[\,a_0^3+3(\tfrac{3}{2})^{1/2}(a_1^2a_{-2}+a_{-1}^2a_2)+3a_0|a_1|^2-6a_0|a_2|^2]\ , \tag{16}$$

where

$$u(\Omega)=\sum_m a_m Y_{2m}(\Omega),\quad C(w)=\frac{8}{7}\left[\frac{5}{\pi}\right]^{1/2}(1+5w/3)\ .$$

The number of parameters in the family of shapes available to us can be counted as follows. The general $l=2$ distortion has ten parameters; requiring $r(\Omega)$ to be real gives five constraints, choosing coordinates along the principal axes of the shape gives three constraints, and fixing the excess area gives one final constraint (the mean radius can be adjusted to fix the volume). Only one degree of freedom remains. It can be thought of as the "prolateness" of the ellipsoid; varying it takes us from prolate through nonaxisymmetric ellipsoids to an oblate ellipsoid.

We show in Appendix C that shapes corresponding to prolate ellipsoids have lower energy for $C(w)>0$, and oblate ellipsoids are favored for $C(w)<0$. Small, overdamped oscillations about the prolate shape are a new

ellipsoidal mode. The decay rate and mean-square amplitude of this mode can be calculated approximately by expanding the $o(u^3)$ expression for the bending energy about the prolate minimum in the bending energy and again using the Lamb hydrodynamic solution. (Again, we ignore the difference in shape as far as the flow fields are concerned.) The results of this calculation (contained in Appendix C) are, with

$$u = a_2(Y_{22}+Y_{2-2})+a_0 Y_{20}, \quad a_0^2+2a_2^2=2\pi\Delta ,$$

an equilibrium shape given by

$$a_0^{(\mathrm{eq})} = -(\pi\Delta/2)^{1/2}, \quad a_0 = a_0^{(\mathrm{eq})}+\epsilon_0 , \tag{17}$$

a relaxation rate of

$$\tau^{-1} = \frac{3456}{343}\frac{\kappa}{\eta r^3}(1+5w/3)(2\Delta/5)^{1/2} , \tag{18}$$

and a mean-square amplitude of

$$\langle \epsilon_0^2 \rangle = \frac{kT}{12(2\pi\Delta)^{1/2}\kappa C(w)} . \tag{19}$$

The mode can be visualized as follows. Push in on the long axis ($\hat{z}$) of a prolate ellipsoid (American football) and pull out a (arbitrary; say, $\hat{x}$) short axis. A nonaxisymmetric shape is obtained; if the process is continued, the pushed and pulled axes become of equal length, giving an oblate shape with symmetry axis $\hat{y}$.

Note that the mode frequency depends on the excess area and vanishes in the limit of zero excess area, becoming in some sense a Goldstone mode; this is reasonable in light of the energy difference involved. Such a Goldstone mode was first discussed by Peterson,[6] who considered the bending energy in precisely this limit. As $\Delta \to 0$, the mode becomes in a sense trivial—oblate, prolate, and spherical are indistinguishable, and the mode becomes invisible.

The expression for the mean-square amplitude of the mode is based on the expansion of the prolate minimum in the bending energy; this procedure breaks down in the zero-excess-area limit. Then we expect the ellipsoid to be found with equal probability in any ellipsoidal configuration.

A simple criterion for observing the ellipsoidal mode can be obtained by comparing the previously calculated relaxation rate for the $l=2$ mode with the ellipsoidal mode decay rate; if the $l=2$ mode within the extended SJW calculation does not decay within a characteristic time for the ellipsoidal mode, the ellipsoidal mode can be observed.

V. DROPLET-PHASE MICROEMULSIONS

In droplet-phase microemulsions, neutron spin-echo experiments can be performed[2] which probe length scales comparable to the droplet size (around 100 Å) and time scales appropriate for observing bending modes ($\omega \sim \kappa/\eta r^3$, or $\tau \sim 10^{-7}$ sec). If the concentration of the minority phase is kept low, the time for diffusing droplets to collide can be made much longer than the time for droplet fluctuations to occur.[12]

Under these conditions, the dynamic experiments are sensitive to fluctuations of a droplet typical of the equilibrium ensemble, but at fixed amount of internal phase and surfactant, and hence at fixed volume and excess area. The values (and variances) of the typical volume and excess area of such a droplet snatched from the equilibrium ensemble are, of course, equilibrium properties. Thus stiffness and excess area cannot be varied independently, because the excess area is determined in equilibrium by stiffness, spontaneous curvature, and volume fractions. For example, a stiffer surfactant interface will inhibit fluctuations away from spherical droplets and give a smaller excess area.

Safran[7] has calculated the equilibrium fluctuations of droplet-phase microemulsions, which we take as input to our calculations of the intermediate-time fluctuations of these systems. In the global equilibrium, droplets may collide and exchange surfactant and fluid; only the total amounts of fluid and surfactant are conserved. The fluctuation amplitudes, characterizing the fluctuations in shape and size of a typical droplet, are given by

$$\langle |u_{lm}|^2 \rangle = \frac{kT}{\kappa}\left[(l+2)(l-1)\left[l(l+1)-6+4w+\frac{3kT}{4\pi\kappa}h(\phi)\right]\right]^{-1} , \tag{20}$$

with the mixing entropy per drop given by

$$h(\phi) = -\frac{1}{\phi}[\phi\ln\phi+(1-\phi)\ln(1-\phi)] . \tag{21}$$

Using these results and formulas [Eqs. (5) and (6)] for the area and volume, one can show that the equivalence of the mean volume and excess area of the static and dynamic models implies

$$\tilde{\gamma} = 6+2w^2-8w-\frac{3kT}{8\pi\kappa}h(\phi) , \tag{22}$$

with the last term usually negligible. Thus the intermediate-time fluctuation amplitudes for the dynamical model are as in Eq. (20) and the decay rates for a typical microemulsion droplet are

$$\omega_l = \frac{\kappa}{\eta r^3}\frac{(l+3)(l-2)+4w+(3kT/8\pi\kappa)h(\phi)}{Z(l)} . \tag{23}$$

We now compute the structure factor $S(q,t)$ from scattering off of the thin shell of material (surfactant) at the interface, which will most clearly show the fluctuations of interest.[13] The result (see Ref. 14) is

$$S(q,t) = \langle \rho_q(t)\rho_{-q}(0)\rangle \propto \exp(-Dq^2t)\left[4\pi[j_0(qr)]^2+\sum F_l(qr)\langle u_{l0}(t)u_{l0}(0)\rangle\right] . \tag{24}$$

The weighting factor $F_l(qr)$ is defined by

$$F_l(z) = (2l+1)[(l+2)j_l(z)-zj_{l+1}(z)]^2 , \tag{25}$$

with $j_l(z)$ the spherical Bessel function of order l.

The sum-of-exponentials form of Eq. (24) is experimentally difficult to unfold; a convenient parameter is the initial slope of the decay (equal to the first frequency cumulant), written $\omega_{\rm char}(q)$ and defined by

$$\omega_{\rm char}(q)\equiv\frac{1}{S(q,0)}\frac{\partial S(q,t)}{\partial t}\bigg|_{t=0}=Dq^2+\left[\sum_{l>1}\omega_l F_l(qr)\langle\,|u_{lm}|^2\rangle\right]\left[4\pi[j_0(qr)]^2+\sum_{l>1}F_l(qr)\langle\,|u_{lm}|^2\rangle\right]^{-1}$$
$$\equiv Dq^2+\frac{\kappa}{\eta r^3}\langle\Sigma_N(qr)\rangle\left[\frac{4\pi\kappa}{kT}\langle j_0^2(qr)\rangle+\langle\Sigma_D(qr)\rangle\right]^{-1}. \tag{26}$$

Note that specifying the wave number does not in general select one or a few spherical harmonics to dominate the sum, even though there is a correspondence ($q\sim 2\pi l/r$) between the index l and the length scale q^{-1}. There is a special circumstance, however, where the sum is dominated by only two terms. For $qr=\pi$, the structure factor of the undistorted spherical shell vanishes, and the wave number is small enough that the $l=2$ mode has the largest weighting factor and also a large amplitude. Thus, in a narrow range of q around $qr=\pi$, $\omega_{\rm char}(q)$ will approximately equal the $l=2$ decay rate $\omega_{l=2}$; moving away from $qr=\pi$, $\omega_{\rm char}(q)$ will quickly drop to the center-of-mass diffusion rate Dq^2.

The function $S(q,t)$ should be averaged over the equilibrium ensemble of sizes, the mean and variance of which are given in Ref. 7. Details of the peak at $qr=\pi$ will be sensitive to the equilibrium polydispersity in the system, since a single choice of wave number cannot set $qr=\pi$ for all of the various-sized drops in the system. The main effect near the peak is to replace the vanishing $j_0^2(qr=\pi)$ with $\langle\delta r^2\rangle/r^2$. Using the theoretical polydispersity,[7] the numerical value for $\Sigma_N(\pi)$, and the fact that the $l=2$ term dominates $\Sigma_D(qr,w)$ for $qr\sim\pi$, we have

$$\omega_{\rm char}(qr=\pi)\approx D(\pi/r)^2+\frac{\alpha\kappa}{\eta r^3}\left[\frac{\pi/2}{3/2-w}+\frac{\beta}{w}\right]^{-1}, \tag{27}$$

with $\alpha\approx 0.53$ (from the numerator sum) and $\beta\approx 0.15$ (from the $l=2$ term in the denominator sum). The ratio of slow-decaying (center-of-mass diffusion mode) to fast-decaying ($l=2$ mode) signals in $S(q,t)$ is then roughly

$$S_{\rm slow}/S_{\rm fast}(qr=\pi)\approx\left[\frac{\pi/2}{3/2-w}\right]\left[\frac{(0.15)}{w}\right]^{-1}. \tag{28}$$

At large qr, the structure of the sum is not trivial; in particular, one cannot argue from dimensional analysis that the characteristic frequency is $\kappa/(\eta r^3)$ because this would multiply a function of qr, the behavior of which is not obvious. Asymptotic analysis of the sums in the numerator and denominator can be made (see Appendix D); they behave as

$$\Sigma_N(z)\sim N_1 z+N_2\cos(2z),$$
$$\Sigma_D(z,w)\sim D_1(w)+D_2(w)\cos(2z), \tag{29}$$

with coefficients $N_1\approx 0.2$, $N_2\approx 0.13$. D_1 and D_2 are functions of w which diverge as $w\to 0$, $w\to\frac{3}{2}$ (representing the limits of stability[7] of droplet microemulsions), but are weak functions of w for intermediate values. Equation (29) works well for $z=qr>5$ or so.

The averaging over polydispersity with a fixed variance in radius means smearing over a progressively wider range of q at large wave number, effectively destroying all sharp or oscillatory structure in q. The result of the averaging is

$$\langle\omega_{\rm char}(q)\rangle_r\sim Dq^2+\frac{\kappa}{\eta r^3}\frac{\alpha qr}{4\pi\kappa/[kT(qr)^2]+\beta(w)}, \tag{30}$$

where $\alpha\approx 0.2$ and $\beta(w)\approx 0.48$ for $w=\frac{1}{2}$. With $D/r^2=kT/(6\pi\eta r^3)$ and $\kappa/kT\sim 5$ or so, we have a range $4<qr<8$ or so where the second term in Eq. (30) dominates and gives an apparent $\omega_{\rm char}(q)\sim q^3$, which is experimentally observed.[2]

In principle, the entire line shape of $\omega_{\rm char}(q)$ could be fit by adjusting only stiffness and spontaneous curvature, thus giving well-characterized values for these fundamental interfacial parameters (efforts are under way to do this). Several words of caution are in order. First, the extreme sensitivity of the peak to small changes in the polydispersity suggests that polydispersity be taken as an independent parameter even though it is in principle a known function of κ, r_s, and volume fractions. (Of course, large deviations of the fitted polydispersity from the predicted value should be viewed with suspicion.) Second, when the thickness of the surfactant layer is comparable to the radius of the droplet, the approximations made in the bending energy and the hydrodynamics break down. Third, the experimental time resolution determines a cutoff to rates which should be included in the sum for $\omega_{\rm char}$; the "initial slope" of the data will not reflect more quickly decaying amplitudes.

VI. LIPID-BILAYER VESICLES

Lipid-bilayer vesicles typically have much larger sizes and longer time scales compared to droplet microemulsions. Nonetheless, they are described by much of the same physics. In addition, because the excess area can in principle be varied by the preparation technique (instead of being fixed at its global equilibrium value as in microemulsions), a greater variety of situations can be studied. Finally, the observation technique—video microscopy—can in principle provide a more direct measurement of the decay rates of individual fluctuation modes.

A few remarks are in order as to the role of the excess area in current experiments on vesicles. First, there is

probably some tendency to select for study vesicles which have by chance been produced with zero "apparent surface tension." Vesicles which are very floppy but have small excess area would not have large fluctuations, but would appear to be nearly "inflated" rigid spheres, and would be avoided. Vesicles which are stiff and ellipsoidal would also be avoided, because data from such vesicles has been difficult to analyze with previous theories. Second, the excess are is not directly measurable by the video microscopy experiments, because (1) only a cross section of the three-dimensional object is obtained and (2) the optical and time resolutions are not sufficient to see the short-length-scale fluctuations which can carry a significant part of the excess area. Thus the excess area might be well treated as a fitting parameter.

Of course, it is only in vesicles (not in droplet microemulsions) that the fluctuations of the ellipsoidal mode could possibly be observed, since the criterion for seeing them depends on being able to adjust the excess area independently of the stiffness. This would be an interesting phenomenon to search for.

Present experimental techniques could be extended to give information about the time autocorrelation of the vesicle modes, which of course gives a much stronger test of our understanding. Current experiments probe the autocorrelation times in a crude way by noting the dependence on observation time of the apparent mean-square fluctuation in the various modes of the vesicle.[4]

Up to now, most of the vesicle observations[4,5] have yielded only mean-square amplitudes of mode fluctuations (by time averaging); observations of, for example, Englehardt *et al.*[4] have been fit to the static predictions of SJW, with systematic discrepancies in the lower modes. These can be explained by two tendencies in the SJW formula. First, there is an arithmetic error in the SJW formula for $\langle |u_{lm}|^2 \rangle$ [which should be Eq. (10) with $w=0$ and $\bar{\gamma}=0$], which is most severe for the lowest modes. Second, as is evident from Eq. (10), the effect of $\bar{\gamma}$ is greatest for the lowest modes.

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APPENDIX A: TIME SCALE ESTIMATES

There is often a separation of characteristic frequency scales for sound, capillary waves, and bending modes. For a rough estimate, assume surface tension σ of a few kT/a^2 (a is some microscopic length, say, 10 Å), bending stiffness κ of a few kT, and sound speed $c \sim 10^5$ cm/sec. The characteristic length scale L is about 100 Å for microemulsion drops and about 10μ for vesicles.

We note that capillary waves propagate in vesicles and are overdamped in microemulsion droplets, while bending modes are overdamped in both cases. [We compare the assumed overdamped frequency to the viscous diffusion rate $\omega_\eta \sim \eta/\rho L^2$, with viscosity $\eta/\rho \sim 10^{-2}$ cm^2/sec and $\rho \sim 1$; the overdamped rates are $\omega_\sigma \sim \sigma/\eta L$ and $\omega_\kappa \sim \kappa/\eta L^3$. We find $\omega_\sigma/\omega_\eta \sim 10^{-2}$ and $\omega_\kappa/\omega_\eta \sim 10^{-4}$ for microemulsion drops, while we have $\omega_\sigma/\omega_\eta \sim 10$ and $\omega_\kappa/\omega_\eta \sim 10^{-7}$ for vesicles. Hence in vesicles, we shall write $\omega_\sigma \sim (\sigma/\rho L^3)^{1/2}$.]

Sound in fluids propagates down to molecular length scales. Hence we compare for microemulsion drops

$$\omega_s/\omega_\sigma \sim (c/L)/(\sigma/\eta L) \sim 10^7 ,$$

$$\omega_\sigma/\omega_\kappa \sim (\sigma/\eta L)/(\kappa/\eta L^3) \sim 10^2 ,$$

and for vesicles we obtain

$$\omega_s/\omega_\sigma \sim (c/L)/(\sigma/\rho L^3)^{1/2} \sim 10^4 ,$$

$$\omega_\sigma/\omega_\kappa \sim (\sigma/\rho L^3)^{1/2}/(\kappa/\eta L^3) \sim 10^7 .$$

To check the assertion that the convective and inertial terms in the dynamics can be neglected, we compute the Reynolds number and the ratio of inertial to viscous terms in the Navier-Stokes equations. The Reynolds number is $R=\rho v L/\eta$; with characteristic velocity $v \sim L\omega_\kappa \sim \kappa/\eta L^2$, we have $R \sim \kappa\rho/\eta^2 L \sim 10^{-4}$ for microemulsions and 10^{-7} for vesicles. The ratio of inertial $(\partial \mathbf{g}/\partial t)$ to viscous $(\eta \nabla^2 \mathbf{g}/\rho)$ terms is roughly $\omega_\kappa/\omega_\eta \sim \kappa\rho/\eta^2 L$ which is of order R.

APPENDIX B: BENDING FORCE FOR NONZERO SPONTANEOUS CURVATURE

To obtain the force on the surface due to bending, in the presence of spontaneous curvature, we follow Jenkins[15] in varying the bending energy with respect to the surface position. Using his methods, we derive

$$\delta \int H\, dS = -2 \int \bar{H}\hat{n}\cdot\delta\mathbf{r}\, dS , \tag{B1}$$

where $\bar{H}$ is the Gaussian curvature and $\hat{n}$ the surface normal. Hence we have for the variation of $E'=E_{\text{bend}}-\int \gamma\, dS$,

$$\begin{aligned}\delta E' &= \delta\left[\int dS\left[\frac{\kappa}{2}(H-H_s)^2-\gamma\right]\right] \\ &= \int dS\, \delta\mathbf{r}\cdot\{\nabla\gamma+\hat{n}[\kappa\nabla^2 H+H(\gamma-\kappa H_s^2/2) \\ &\qquad +2\kappa H_s\bar{H}]\} \\ &= -\int dS\, \delta\mathbf{r}\cdot\mathbf{F} .\end{aligned} \tag{B2}$$

Now $H^2=4\bar{H}+o(u^2)$, which we use to replace $\bar{H}$; $(H-H_0)^2$ is $o(u^2)$, and so we may replace $H^2 \approx 2HH_0-H_0^2$. Using these replacements we get

$$-\mathbf{F}=\nabla\gamma+\hat{n}[\kappa\nabla^2 H+H(\gamma-\kappa H_s^2/2+\kappa H_s H_0) -\kappa H_s H_0^2/2] . \tag{B3}$$

We can define a shifted Lagrange multiplier as

$$\gamma'=\gamma-\kappa H_s^2/2+\kappa H_s H_0 \tag{B4}$$

(and absorb the last term in the force into the pressure with $p'=p-\kappa H_s H_0^2/2$). This gives exactly the force expression in SJW with $H_s=0$,

$$-\mathbf{F}=\nabla\gamma'+\hat{n}(\kappa\nabla^2 H+H\gamma') \ . \tag{B5}$$

In the SJW calculation of mode frequencies, the pressure $p(\mathbf{r})$ and the apparent surface tension $\gamma(\Omega)$ are determined by constraints of constant droplet volume and surface area, leaving only γ_0 (the angle-independent part of γ) undetermined. Hence we may immediately write

$$\omega_l=\frac{\kappa}{\eta r_0^3}\frac{l(l+1)-\gamma' r_0^2/\kappa}{Z(l)} \ , \tag{B6}$$

with γ_0' given by Eq. (B4) and γ_0 determined by the requirement that the mean excess area in the dynamical model of the droplet is specified (by the kinetics of vesicle production or the global microemulsion equilibrium).

APPENDIX C: ELLIPSOIDAL MODE CALCULATIONS

1. Ellipsoids and bending energy

We extend the expansion of the bending energy to $o(u^3)$; after some algebra, we obtain

$$\begin{aligned}E=\frac{\kappa}{2}\int d\Omega[\,&4(1-w)^2+4(1-w)\xi L^2 u-8w(1-w)u\\&+2(1-w)\xi^2(r_0\nabla u)^2+\xi^2(L^2u)^2+4w^2u^2\\&-4\xi wuL^2u+2(1-w)(r_0\nabla u)^2L^2u\\&-4w(1-w)u(r_0\nabla u)^2]\ ,\end{aligned} \tag{C1}$$

with $w=r_0/r_s$ and $\xi=(1+u)^{-1}$.

Expanding ξ and integrating by parts, we obtain

$$\begin{aligned}E=\frac{\kappa}{2}\int d\Omega\{\,&4(1-w)^2-8w(1-w)u+8(1-w)\tilde{u}\\&+4[(1-w)^2-2]u\tilde{u}+4w^2u^2+4\tilde{u}^2\\&+4(1+w)\tilde{u}u^2-8w\tilde{u}^2u\\&-(1-w)u^2(L^2)^2u\}\ ,\end{aligned} \tag{C2}$$

where $\tilde{u}=L^2u/2$. [This agrees with the $o(u^2)$ expansion of Ref. 2.]

We want to consider the energy of various ellipsoids, i.e., $l=2$ deformations of the sphere, with fixed volume and excess area. To $o(u^3)$, the volume is

$$\begin{aligned}V=\tfrac{1}{3}\int r^3 d\Omega=\frac{4\pi}{3}r_0^3(1+u_0)^3\\+r_0^3\sum|u_{lm}|^2+\tfrac{1}{3}r_0^3\int u^3 d\Omega\ .\end{aligned} \tag{C3}$$

Fixing $V=4\pi r_0^3/3$ leads to

$$u_0=-\frac{1}{4\pi}\sum|u_{lm}|^2-\frac{1}{12\pi}\int u^3 d\Omega+o(u^4)\ . \tag{C4}$$

The area to $o(u^3)$ is

$$A=4\pi r_0^2(1+u_0)^2+r_0^2\sum|u_{lm}|^2[1+l(l+1)/2]\ . \tag{C5}$$

Using Eq. (C4) and defining the relative excess area $\Delta\equiv(A-4\pi r_0^2)/(4\pi r_0^2)$ gives

$$\sum|u_{2m}|^2=2\pi\Delta+\tfrac{1}{3}\int u^3 d\Omega\ , \tag{C6}$$

$$u_0=-\frac{1}{6\pi}\int u^3 d\Omega-\frac{\Delta}{2}+o(u^4)\ . \tag{C7}$$

Using Eqs. (C6) and (C7) in Eq. (C2) and specializing to $l=2$, we finally obtain

$$E=-8k(1+5w/3)\int u^3 d\Omega\ , \tag{C8}$$

with u restricted to the $l=2$ subspace.

To simplify the arithmetic, we shall write $u(\Omega)$ not as a general $l=2$ expansion, but as a real-valued ellipsoid with principal axes oriented along (x,y,z) and fixed excess area,

$$u=a_2(Y_{22}+Y_{2-2})+a_0Y_{20}\ , \tag{C9}$$

$$a_0^2+2a_2^2=2\pi\Delta\ . \tag{C10}$$

(One degree of freedom remains.)

The radial displacement $r(\Omega)=r_0[1+u(\Omega)]$ can be related to the solution of $(x/A)^2+(y/B)^2+(z/C)^2=1$ for A,B,C nearly equal, to show that Eq. (C9) describes an oriented ellipsoid as advertised. If we write $A=1+\alpha$, $B=1+\beta$, $C=1+\gamma$, we obtain

$$\begin{aligned}a_0&=(4\pi/5)^{1/2}(2\gamma-\alpha-\beta)/3\ ,\\a_2&=(2\pi/15)^{1/2}(\alpha-\beta)\ .\end{aligned} \tag{C11}$$

Substituting Eq. (C9) into Eq. (C8) and using the constraint Eq. (C10) gives

$$\begin{aligned}E&=-\kappa C(w)[a_0^3-6a_0a_2^2]=-kC(w)[4a_0^3-6\pi\Delta a_0]\ ,\\C(w)&=\frac{8}{7}\left[\frac{5}{\pi}\right]^{1/2}(1+5w/3)\ .\end{aligned} \tag{C12}$$

This calculation implies that prolate ellipsoids are stable for $w>-\frac{3}{5}$; this is not the value of Deuling and Helfrich,[11] who obtained $c_0R_0>-\frac{39}{23}$ ($c_0=2/r_s$), but agrees with a direct calculation in prolate and oblate coordinates.

This energy has two extrema at $a_0^2=\pi\Delta/2$, three roots at $a_0=0$, $a_0^2=3\pi\Delta/2$, and two endpoint extrema at $a_0^2=2\pi\Delta$. For $C>0$ (usual case, because $w>0$ for microemulsions and $w=0$ for bilayers) there are three minima: $a_0=-(\pi\Delta/2)^{1/2}$, $a_2=\pm(3\pi\Delta/4)^{1/2}$, and $a_0=(2\pi\Delta)^{1/2}$, $a_2=0$.

All three of the minimum-energy shapes are identical prolate ellipsoids. Using Eqs. (C11) and $V=4\pi ABC/3=4\pi/3$ so that $\alpha+\beta+\gamma=0$, we find the set $\{\alpha,\beta,\gamma\}=\{-1,-1,2\}\times(5\pi\Delta/4)^{1/2}$ which describes an ellipsoid with one long and two short axes, i.e., a prolate ellipsoid (albeit oriented with the long axis along $\hat{x}$, $\hat{y}$, or $\hat{z}$). To avoid singularities in perturbing about this lowest-energy shape, we will expand about $a_0=-(\pi\Delta/2)^{1/2}$, $a_2=(3\pi\Delta/4)^{1/2}$ when we consider overdamped shape oscillations in the next section.

2. Dynamics of the ellipsoidal mode

As we perturb the ellipsoidal shape within the $l=2$ subspace away from the prolate minimum at constant area and volume, we obtain nonaxisymmetric shapes. We consider the case of small oscillations to extract a relaxation rate and a mean-square amplitude.

The dynamics calculation is similar to that of SJW, with a few modifications. We derive the restoring force from Eq. (C12). The Lagrange multiplier γ is determined by the condition $\dot{\Delta}=0$. We need not consider the pressure as a constraint force because the constant-volume condition is built into our virtual displacements. We get around the need for computing flows in prolate spheroidal coordinates in a rough way, by mapping the normal component of bending force at (θ,ϕ) onto a spherical surface; we compute velocities in spherical geometry, and map back to the ellipsoid.

Formally, we are expanding in both $\Delta^{1/2}$ and deviations from the minimum-energy surface; we will find the force, pressure, and fluid velocities are $o(\Delta^{1/2}\delta u)$, and so corrections due to nonspherical geometry will be higher order. Following SJW with these modifications, we derive (setting $r_0=1$ until the end)

$$\begin{aligned} 0&=\tfrac{15}{7}p_2^{(i)}+F_n \quad \text{(normal)} , \\ 0&=-\tfrac{20}{7}p_2^{(i)}-6\gamma_2-2F_n \quad \text{(tangential)} , \\ F_n&=F_{\text{bend}}+F_\gamma-2\gamma_2 , \\ \mathbf{v}_2\cdot\hat{n}&=-\frac{2}{7\mu}p_2^{(i)} . \end{aligned} \tag{C13}$$

(The last term in F_n derives from the local incompressibility constraint as in SJW.)

Eliminate γ_2 in favor of F_{bend}, and F_γ, $p_2^{(i)}$ in favor of $\mathbf{v}_2$, to get

$$\mathbf{v}_2\cdot\hat{n}=\frac{6}{35\mu}(F_{\text{bend}}+F_\gamma) . \tag{C14}$$

The forces F_{bend} and F_γ derive from varying $E_{\text{bend}}-\gamma(a_0^2+2a_2^2)$; if we decompose $\mathbf{v}_2\cdot\hat{n}$ into velocities for a_0 and a_2, we get

$$\begin{aligned} \dot{a}_0&=-\frac{6}{35\mu}[-\kappa C(w)(3a_0^2-6a_2^2)-2\gamma a_0] , \\ \dot{a}_2&=-\frac{6}{35\mu}[-\kappa C(w)(-12a_0a_2)-4\gamma a_2] . \end{aligned} \tag{C15}$$

The equilibrium value of γ is fixed by requiring $\dot{a}_0=\dot{a}_2=0$ at the prolate configuration. This gives

$$\gamma_{\text{eq}}=-\tfrac{3}{2}\kappa C(w)(2\pi\Delta)^{1/2} .$$

Now we expand a_0, a_2, and γ about their equilibrium values; determine $\delta\gamma$ by requiring $\dot{\Delta}=0$ to linear order in δa_0 and δa_2; and relate δa_0 and δa_2 by $\Delta=0$, reducing to a single degree of freedom. This gives a single relaxation equation

$$\dot{a}_0=-\frac{6}{35\mu}[\kappa C(w)(2\pi\Delta)^{1/2}]\tfrac{72}{7}(a_0-a_0^{(\text{eq})}) , \tag{C16}$$

with a relaxation rate

$$\tau^{-1}=\frac{3456}{343}\frac{\kappa}{\mu r_0^3}(1+5w/3)(2\Delta/5)^{1/2} . \tag{C17}$$

If the expansion about the prolate minimum makes sense, we can apply equipartition; E_{bend} of Eq. (C12), with the constraint [Eq. (C10)] imposed, and $a_0=-(\pi\Delta/2)^{1/2}+\epsilon_0$ gives

$$\Delta E=\text{const}+6(2\pi\Delta)^{1/2}\kappa C(w)\epsilon_0^2+o(\epsilon_0^3) , \tag{C18}$$

$$\langle\epsilon_0^2\rangle=\frac{kT}{12(2\pi\Delta)^{1/2}\kappa C(w)} . \tag{C19}$$

For this to make sense, we need

$$\langle\epsilon_0^2\rangle\ll a_0^2$$

or

$$\frac{kT}{\kappa}\ll 3C(w)(2\pi\Delta)^{1/2} . \tag{C20}$$

APPENDIX D: LARGE-qr BEHAVIOR OF SUMS IN ω_{char}

The sums in the numerator and denominator of Eq. (26) are proportional to sums generically of the form

$$S_R(z)=\sum_{l\,(>l_0)}R(l)j_l^2(z) , \tag{D1}$$

with $R(l)$ a rational function of l, of leading degree $d(R)$ for large l.

1. Denominator sums

If $d(R)\le -2$, the sum $S_R(z)$ converges just because $j_l(z)\le 1$ and $\sum R(l)$ converge; hence for large z we can approximate

$$j_l(z)\sim z^{-1}\cos[z-(l+1)\pi/2] \tag{D2}$$

in all terms in the sum. Using the half-angle formula, we quickly reach

$$S_R(z)\sim\frac{1}{2z^2}\left[\sum_{l\,(>l_0)}R(l)+\cos(2z)\sum_{l\,(>l_0)}(-1)^{l+1}R(l)\right] . \tag{D3}$$

Using the functional relations for the $j_l(z)$, the factor $F_l(z)$ can be recast as

$$F_l(z)+\frac{z^2}{(2l+1)}[(l+2)j_{l-1}(z)-(l+1)j_{l+1}(z)]^2 . \tag{D4}$$

This equation and the asymptotic form for $j_l(z)$ quickly give us the result

$$\Sigma_D(z)\sim D_1(w)+D_2(w)\cos(2z) , \tag{D5}$$

where D_1 and D_2 are constants which depend on the parameter $w=r_0/r_s$.

2. Numerator sums

If $d(R)\ge -1$, the sum $S_R(z)$ converges only because $j_l(z)$ for $l\gg z$ vanishes sufficiently fast; this behavior is

more subtle. To extract large-z behavior of such sums, we use a differential equation for $S_R(z)$. Using the functional relations for $j_l(z)$, it can be shown that

$$\left[\frac{\partial}{\partial z}-\frac{d-1}{z}\right]S_R(z) = -\frac{1}{2}\frac{\partial}{\partial z}\sum_{l\,(\geq l_0)}\frac{1}{l}[dR(l)+Q(l)]j_l^2(z) + \frac{1}{z}\sum_{l\,(\geq l_0)}Q(l)j_l^2(z)+R(l_0)j_{l_0}(z)j_{l_0-1}(z)\ , \quad \text{(D6)}$$

where $d=d(R)$, $Q(l)$ is of leading degree $d-1$, and defined by

$$R(l+1)-R(l)=\frac{1}{l}[dR(l)+Q(l)]\ . \quad \text{(D7)}$$

In special cases, the right-hand side can be evaluated exactly and the differential equation solved; for example,

$$S_{R=1}(z)=\frac{\mathrm{Si}(2z)}{2z},\quad S_{R(l)=2l+1}(z)=1\ . \quad \text{(D8)}$$

As $\mathrm{Si}(2z)\sim\pi/2+\cos(2z)/2z$ for large z, we guess that

$$S_R(z)\sim c_1 z^{d-1}+[c_2+c_3\cos(2z)]z^{d-2}+o(z^{d-3})\ , \quad \text{(D9)}$$

which can be verified by induction on Eq. (D6).

The sum in the numerator of Eq. (26) can be written, using the functional relations, as the sum of such terms as in Eq. (D1), with some powers of z and $\partial/\partial z$ applied; the final result for large z is

$$\Sigma_N(z)\sim N_1 z+N_2\cos(2z)+o(z^{-1})\ . \quad \text{(D10)}$$

The coefficients in Eqs. (D5) and (D10) can be extracted from numerical evaluations of the sums; such evaluations suggest that the asymptotic formulas work well for $z>5$ or so. Rough numerical results for the sums (for typical values of w) appear in the main text.

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