Statistical mechanics of closed fluid membranes

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We discuss the statistical mechanics of systems, such as vesicle phases, that consist of many closed, disconnected fluid membranes. We show that the internal undulation free energy of a single such membrane always contains a logarithmically scale-dependent "finite-size" contribution, with a universal coefficient, that arises essentially from the absence of undulation modes of wavelength longer than the size of the surface. We show that the existence of this contribution is closely related to the existence of additional collective degrees of freedom, such as translations and polydispersity, that are present in a system of disconnected surfaces but absent in a system of infinite surfaces such as a lamellar or bicontinuous phase. The combination of undulation and collective mode free energy contributions found here is shown to yield thermodynamic properties (e.g., size distributions) for a vesicle phase whose parameter dependence is consistent with the scale invariance of the Helfrich bending energy. We briefly discuss the conceptually related problem of a polydisperse ensemble of fluctuating one-dimensional aggregates, such as rodlike micelles, for which we obtain the experimentally observed scaling of micelle size with concentration. We conclude by discussing the application of our results to the interpretation of recent experiments on equilibrium vesicle phases.

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I. INTRODUCTION

Certain types of surfactant molecules are known to self-assemble in solution to form bilayer membranes. Dilute solutions of such molecules can as a result often be sensibly described as ensembles of thin two-dimensional (2D) surfaces [1]. The thermodynamic behavior of such an ensemble of membranes is controlled by a competition between the bending energy of the membranes, which typically favors the formation of a lamellar structure, and the disordering effects of conformational entropy, which favor formation of isotropic bicontinuous [2–4] or vesicle phases [5–8]. Because of the importance of entropic effects in these systems, an accurate description of their thermodynamic behavior seems to require a rather detailed understanding of the configurational entropy associated with the fluctuations of semiflexible surfaces.

The starting point for a continuum description of a fluid membrane is the bending energy proposed by Canham [9] and Helfrich [10],

$$H = \int dA \, [\, \tfrac{1}{2}\kappa C^2 + \bar{\kappa} K \,] \quad , \tag{1}$$

in which dA is a surface area element, $C \equiv C_1 + C_2$ and $K \equiv C_1 C_2$ are the mean and Gaussian curvatures, C_1 and C_2 are principal curvatures, and κ and $\bar{\kappa}$ are, respectively, the mean and Gaussian rigidities. For simplicity, we will restrict ourselves in this paper to the case of symmetric bilayer membranes, and have therefore not included a spontaneous curvature term in the above. The total bending energy for such a bilayer is easily shown to be invariant under simple affine dilations or contractions that change the size but not the shape of the surface. One consequence of this scale invariance, and the absence of any energetically preferred length scale for a disconnected surface, is that the size distribution of an ensemble of such surfaces is found to be very sensitive to the presence of any scale-dependent entropic contributions to the free energy.

In the past decade, a great deal of work has been devoted to understanding the fluctuations of surfaces described by Eq. (1). Much of this work has focused more specifically upon understanding the effects of short-wavelength undulations, whose primary effect is to decrease the free energy cost of bending the membrane. The resulting change in the curvature dependence of the free energy can, it has been shown [11–15], be absorbed into renormalizations of a pair of scale-dependent elastic parameters $\kappa(R)$ and $\bar{\kappa}(R)$, that describe the resistance of a fluctuating membrane to the formation of curved regions of characteristic length scale R. These renormalized rigidities are found to vary with length scale R as

$$\kappa(R) \simeq \kappa - \frac{\alpha T}{8\pi} \ln\left(\frac{R^2}{a^2}\right) ,$$
$$\bar{\kappa}(R) \simeq \bar{\kappa} + \frac{\bar{\alpha} T}{8\pi} \ln\left(\frac{R^2}{a^2}\right) , \tag{2}$$

where a is a microscopic cutoff length, and $\alpha = 3$ [12–15] and $\bar{\alpha} = 10/3$ [15] are universal coefficients. The scale dependence of these renormalized rigidities suggests a description of the free energy of a fluctuating surface of characteristic length scale R (where R is, e.g., the radius

of a vesicle) in terms of a renormalized, or coarse-grained, bending energy

$$H_R = \int dA \, [\, \tfrac{1}{2}\kappa(R)C^2 + \bar{\kappa}(R)K \,] \quad , \tag{3}$$

which, as a result of the logarithmic scale dependence of the renormalized rigidities, also varies logarithmically with the size of the surface. The scale dependence of this effective elastic energy has played an important role in most recent models of membrane phase behavior, including both phenomenological models of the global phase behavior [16–20] and several more detailed treatments of the vesicle phase [18,14,21,22,8].

In the present paper, we consider the statistical mechanics of an equilibrium system of closed disconnected surfaces, such as a vesicle phase. The core of the paper is a systematic calculation to first order in temperature of the free energy F of a closed, finite membrane of fixed but arbitary topology and constrained area. This calculation is a generalization of our treatment in an earlier paper [23] of the case of simple spherical surfaces. We find here, as in Ref. [23], that the total internal free energy of a closed surface generally contains, in addition to contributions arising from the renormalization of the bending rigidities by short-wavelength undulations, other logarithmically size-dependent contributions that arise instead from a proper treatment of (i) the contributions of Goldstone modes such as translations, and (ii) the long-wavelength cutoff which must be imposed on the spectrum of undulation modes due to the finite size of the surface. We try, in what follows, to clarify the intimate physical relationship between these two aspects of the problem by discussing our results in terms of a competition between the loss of undulation entropy on a set of disconnected surfaces, relative to that of a single large surface, that arises from the destruction of undulation modes of wavelength longer than the size of the disconnected surfaces, and the corresponding gain in entropy that arises from the creation of new degrees of freedom, such as rigid translations, that are present only in a system of disconnected surfaces.

The issues emphasized here, of how one should treat the statistical mechanics of a finite object that exhibits both soft internal degrees of freedom (e.g., undulations) and Goldstone modes such as translations, are not peculiar to the problem discussed here, but seem to arise in the treatment of any system containing finite aggregates with many internal degrees of freedom. Many of the same questions have arisen previously (and often caused a great deal of confusion), in the context of models of nucleation [24–26], of micellar solutions [27–30], and of the droplet microemulsions phase of oil-water-surfactant mixtures [30–32]. Our treatment of the free energy of a spherical vesicle in Appendix C is actually quite similar to that given for the free energy of a critical nucleation drop in the field-theoretic approach to nucleation [24,25]. These issues are particularly important in the interpretation of experiments on systems of bilayer membranes, however, because the scale invariance of the bending energy, together with the rather small bending rigidities exhibited by most systems of interest, makes the equilibrium size distribution in such systems particularly sensitive to the effects of even small and weakly size-dependent entropic effects. There are two other surfactant systems for which we expect the resolution of these issues to be of similar importance. The first is the droplet microemulsion phase, which will be discussed in detail elsewhere [33]. The second is the micellar phase of linear (i.e., rodlike or wormlike) micelles, which are sometimes referred to as living polymers, found in some surfactant solutions [29]. A linear micelle has in common with a bilayer vesicle the mathematical property that the naive free energy cost to create a new micelle by breaking a larger micelle into two pieces, which is given by the free energy needed to create two new ends, is (like the bending energy cost of splitting a vesicle into two smaller vesicles) completely independent of the size of the parent or daughter aggregate. Consequently, the mathematics and the conceptual issues encountered in the calculation of the size distribution for a system of micelles are closely analogous to those encountered in the vesicle system. A brief treatment of the linear micelle phase is thus given in Sec. IV of this paper.

The structure of this paper is as follows. Section II contains our calculation of the free energy of a single membrane, of arbitrary shape, with either a fixed number of surfactant molecules or a constrained area, the results of which are summarized in subsection II E. Appendixes A and B contain some details of the calculation of the undulation free energy for a general surface. Appendix C contains a more direct calculation of the free energy of a simple spherical vesicle in which we analyze the sum over spherical harmonic undulation modes. In Sec. III, we calculate the size distribution of a polydisperse suspension of many surfaces (i.e., a vesicle phase) whose areas and particle numbers can fluctuate via exchange of surfactant molecules. In Sec. IV, we consider the behavior of an equilibrium phase of fluctuating one-dimensional micelles. A brief summary of our results, and a discussion of their relevance to the interpretation of existing experiments on vesicle phases, is given in Sec. V.

II. FREE ENERGY OF AN ISOLATED SURFACE

In this section we consider the statistical mechanics of a system containing a single closed membrane that contains a fixed number N of surfactant molecules. We calculate the Helmholtz free energy for a single membrane of fluctuating shape, but fixed topology, whose center-of-mass position is confined to a box of volume V.

The conformation of the surface defined by such a membrane can be described by a three-dimensional position vector $\mathbf{X}(\sigma)$ written as a function of a coordinate pair $\sigma = (\sigma^1, \sigma^2)$ that parametrizes positions within the surface. We will assume in what follows that the membrane fluctuates weakly around some equilibrium conformation $\mathbf{X}_0(\sigma)$ that is a local minimum of the bending energy and that has an area A equal to the unstretched area A_0 of the membrane, where $A_0 = a_s^2 N$ and where a_s^2 is an equilibrium area per surfactant molecule. We

also assume that the surface $\mathbf{X}_0$ can be characterized by some typical radius of curvature or structural length R, such as the equilibrium radius of a spherical vesicle or the "pore size" of a multiply connected surface typical of the bicontinuous (i.e., cubic or L_3) phases. We isolate the logarithmic size dependence of F by considering a family of equilibrium surfaces $\mathbf{X}_0$ that are related by scale transformations of the form

$$\mathbf{X}_0(\sigma) \to \lambda \mathbf{X}_0(\sigma) \quad , \tag{4}$$

which yields surfaces of the same shape and topology but different areas and particle numbers, and examining the dependence of F upon, equivalently, the structural length R or the scale factor λ.

A. Construction of a partition function

In this subsection, we discuss the construction of a continuum model for a closed, fluctuating membrane in which the membrane is described as an idealized surface. To begin, we discuss briefly how such a model might, at least formally, be derived from a more microscopic description.

We consider a membrane of N surfactant molecules immersed in a reservoir of solvent. Our starting point is thus the classical partition function Z of the entire system of surfactant and solvent, which can be expressed microscopically as a phase-space integral over the positions and momenta of both surfactant and solvent molecules. Integrating over all momenta for both solvent and surfactant molecules yields a corresponding configurational integral. Formally integrating over the positions of the solvent molecules while holding the positions of the surfactant molecules fixed then yields a configurational integral

$$Z = \frac{1}{N!} \prod_{i=1}^{N} \int \frac{d^3 r_i}{\lambda^3} \, e^{-\beta U(\{\mathbf{r}\})} \tag{5}$$

involving only the 3D positions $\mathbf{r}_i$ of the surfactant molecules, which, for simplicity, we have treated like point particles, where the effective potential $U(\{\mathbf{r}\})$ is given by the free energy of a constrained system in which the surfactant molecules are fixed to positions $\{\mathbf{r}\} = \{\mathbf{r}_1, \ldots, \mathbf{r}_N\}$. In the above, $\beta \equiv 1/T$, where we use a Boltzmann constant of $k_B = 1$, and $\lambda \equiv h/\sqrt{2\pi m T}$ is the thermal de Broglie wavelength for a surfactant molecule of mass m.

To obtain a continuum description of the membrane, we wish to convert this integral over molecular positions into an integral over possible conformations of a surface $\mathbf{X}$ defined by the locus of points occupied by the surfactant molecules. We will assume in what follows that this surface fluctuates only weakly around the equilibrium surface $\mathbf{X}_0$, thus allowing us to describe displacements of $\mathbf{X}$ relative to $\mathbf{X}_0$ by a small normal-displacement field $h(\sigma)$, where

$$\mathbf{X}(\sigma) = \mathbf{X}_0(\sigma) + \hat{\mathbf{n}}_0(\sigma) h(\sigma) \quad , \tag{6}$$

and where $\hat{\mathbf{n}}_0(\sigma)$ is a unit vector normal to $\mathbf{X}_0$ at point σ. The position $\mathbf{r}_i$ of the ith surfactant molecule can then be parametrized by its 2D position σ_i within surface $\mathbf{X}$, and by its normal displacement h_i from surface $\mathbf{X}_0$. To convert Eq. (5) into a continuum model for undulations of $\mathbf{X}(\sigma)$, we must integrate over the in-plane positions σ_i of the surfactant molecules while constraining their normal displacements h_i to follow a specified surface $h(\sigma_i)$, and then express the remaining integral over the different possible shapes of the surface as a path integral with respect to $h(\sigma)$. For a weakly fluctuating membrane, this separation into normal and tangential motions can be formally accomplished by inserting into Eq. (5) a representation of unity as the integral of a product of δ functions that constrain the height h_i of each particle to follow the surface $h(\sigma_i)$, yielding a path integral

$$Z \simeq \prod_{\sigma} \int \frac{dh(\sigma)}{\lambda} J[h] \, e^{-\beta H[h]} \quad , \tag{7}$$

in which

$$e^{-\beta H[h]} \simeq \frac{1}{J[h]} \frac{1}{N!} \prod_{i=1}^{N} \int \frac{d^3 r_i}{\lambda^2} \, \delta(h_i - h(\sigma_i)) \, e^{-\beta U(\{\mathbf{r}\})} \tag{8}$$

is the constrained partition function of an interacting 2D fluid of surfactant molecules that is constrained to lie on the surface $\mathbf{X}$, so that the effective Hamiltonian $H[h]$ is the corresponding constrained free energy. The canceling factors of J and J^{-1} in Eqs. (7) and (8) refer to the so-called Fadeev-Popov determinant

$$J[h] \equiv \prod_{\sigma} \hat{\mathbf{n}}(\sigma) \cdot \hat{\mathbf{n}}_0(\sigma) \tag{9}$$

discussed in Refs. [34,35], in which $\hat{\mathbf{n}}$ is the local normal to the physical surface $\mathbf{X}$ and $\hat{\mathbf{n}}_0$ is the normal to reference surface $\mathbf{X}_0$. The inclusion of these canceling factors guarantees that both the path integral measure used in Eq. (7) and the effective Hamiltonian $H[h]$ defined in Eq. (8) each have a physical meaning that is independent of one's choice of reference surface $\mathbf{X}_0$ or coordinate system σ [36]. The shape dependence of $J[\mathbf{X}]$ will not, however, play any role in the calculation of the free energy to the order in temperature that we will consider here.

The path integral in Eq. (7) has been expressed schematically as a product of integrals over the normal displacements $h(\sigma)$ measured at the center of N evenly spaced "patches" of membrane located at points σ. In the quasimicroscopic approach presented above, the number of independent degrees of freedom, or patches, needed to specify the shape of the surface was necessarily assumed to be equal to the number of surfactant molecules, implying the use of patches of area equal to the physical area a_s^2 occupied by a surfactant molecule within the membrane. In what follows, we will consider instead a coarse-grained model in which the molecular size a_s is generalized to an arbitrary cutoff length a, and in which each patch (or independent degree of freedom) of area a^2 is treated as a single coarse-grained "molecule." Con-

sistency with the underlying phase-space integral suggests that in the coarse-grained model $\lambda(a)$ should be taken to be the de Broglie wavelength for a patch of mass $m(a) = \varrho a^2$, where ϱ is the 2D mass density of the membrane. This yields a cutoff-dependent thermal de Broglie length

$$\lambda(a) = \nu^2/a \quad , \tag{10}$$

in which

$$\nu^2 \equiv h/\sqrt{2\pi\varrho T} \tag{11}$$

is a cutoff-independent constant with units of (length)^2.

Because the length λ depends upon the value of Planck's constant h, it can have no well-defined numerical value within a purely classical statistical mechanical treatment. Consequently, one's choice of a numerical value for λ should have no effect upon the physical predictions of the model. This is easily shown to be true for any system with a fixed total number of surfactant molecules by noting that, because λ (or ν^2) enters the partition function only via a multiplicative factor of λ^{-N}, it can enter the total free energy only via an additive constant

$$\delta F = NT\ln(\lambda^2) \tag{12}$$

which is simply proportional to the total number of surfactant molecules in the system. In any system, of either an isolated surface or an ensemble of many surfaces, with a fixed total number of surfactant molecules, such a constant free energy contribution per surfactant molecule can have no effect upon physically observable properties such as the size distribution [37]. In order to preserve this trivial dependence of the free energy upon λ (or ν) within the context of a continuum theory, we will insist in what follows that the continuum theory be regularized in a way that yields a total number of coarse-grained degrees of freedom that is strictly proportional to the unstretched area, and thus the number of microscopic degrees of freedom, of the surface of interest.

We assume that the effective Hamiltonian (or constrained free energy) $H[\mathbf{X}]$ of a surface of fixed particle number can be parametrized as a sum

$$H[\mathbf{X}] \equiv H_{bend}[\mathbf{X}] + H_{flat}(A) \tag{13}$$

of a bending energy $H_{bend}[\mathbf{X}]$ of form (1) plus a curvature-independent but area-dependent contribution $H_{flat}(A)$ that is given by the free energy of a flat membrane of particle number and area equal to those of the physical surface. The effective Hamiltonian for a surface $\mathbf{X}$ fluctuating weakly about an equilibrium surface $\mathbf{X}_0$ can then be expanded as

$$H = H[\mathbf{X}_0] + \delta H_{bend}[h] + \delta H_{flat}[h] \quad , \tag{14}$$

in which $\delta H_{bend}[h]$ is a change in bending energy, and $\delta H_{flat}[h]$ is a stretching energy that suppresses changes of area.

Given an expression for the effective Hamiltonian, a formal expansion of the free energy $F = -T\ln(Z)$ in powers of the temperature can then, in principle, be obtained by expanding $\delta H \equiv \delta H_{bend} + \delta H_{flat}$ in powers of the field h and calculating F in perturbation theory. In the case of an incompressible or nearly incompressible membrane, for which κ is the only relevant energy scale in the problem, this procedure leads naturally to an expansion of F/T in powers of the dimensionless ratio T/κ. In this article, as in all previous treatments of membrane fluctuations, we will assume that the membrane is in the "quasirigid" regime $\kappa \gg T$ and will calculate the fluctuation contributions to F only to lowest nontrivial order in T, giving contributions of $O(T)$ to the free energy. This $O(T)$ contribution to F can be obtained in a harmonic approximation in which we expand δH to harmonic order in h, thereby generating a set of harmonic undulation modes, and simply sum the fluctuation free energies of these (nearly) independent oscillators.

The effects of the Fadeev-Popov determinant can be absorbed into the Hamiltonian by adding to the Hamiltonian an additional term

$$\delta H_J[h] \equiv -T\ln(J[h]) \quad . \tag{15}$$

In the limit $h = 0$ (or $\mathbf{X} = \mathbf{X}_0$), $J[h] = 1$ and so $\delta H_J = 0$. Upon expanding δH_J in powers of h, one finds that, because of the different prefactors of T in δH_J and κ in δH_{bend}, harmonic and higher order contributions to δH_J are all smaller than the corresponding contributions to δH_{bend} by an overall factor of T/κ. When attempting to calculate only the dominant, $O(T)$ contributions to F within an expansion in powers of temperature, it is thus sufficient to ignore the h-dependent contributions to $\ln(J)$, and to approximate $J[h]$ by unity. Corrections to this approximation appear only in free energy contributions of order T^2/κ and higher, which we do not attempt to calculate.

Expanding the bending energy of Eq. (1) to quadratic order in $h(\sigma)$ yields an energy of the form

$$\delta H_{bend} = \tfrac{1}{2}\int dA_0\, h(\sigma)\mathcal{L}\, h(\sigma) + \cdots \quad , \tag{16}$$

in which dA_0 is the area element on surface $\mathbf{X}_0$ and $\mathcal{L} = \mathcal{L}[\mathbf{X}_0]$ is a differential operator. The form of $\mathcal{L}$ (which we discussed in more detail in subsection II B) will depend upon the curvature of the surface $\mathbf{X}_0$, but reduces to $\mathcal{L} = \kappa\nabla^4$ in the limit where $\mathbf{X}_0$ is flat. The harmonic bending modes of the membrane are the eigenfunctions $\psi_\alpha(\sigma)$ that satisfy

$$\mathcal{L}\psi_\alpha = \epsilon_\alpha\psi_\alpha \quad , \tag{17}$$

with eigenvalues ϵ_α. We expand $h(\sigma)$ in a basis of these eigenfunctions, writing

$$h(\sigma) = \sum_\alpha h_\alpha\psi_\alpha(\sigma) \ , \tag{18}$$

and assume a normalization for the ψ_α's in which [38]

$$\int dA_0\, \psi^*_\alpha(\sigma)\psi_\beta(\sigma) = \delta_{\alpha\beta} \ , \tag{19}$$

giving a harmonic bending energy

$$\delta H_{bend} \simeq \tfrac{1}{2} \sum \epsilon_\alpha |h_\alpha|^2 \quad . \tag{20}$$

In what follows, we sometimes adopt a bra-and-ket notation for normal displacements in which integration with respect to dA_0 is represented by an inner product, so that, e.g., normalization condition (19) is written as $\langle \psi_\alpha | \psi_\beta \rangle = \delta_{\alpha\beta}$.

To express Z as an integral over the mode amplitudes h_α rather than the patch heights $h(\sigma)$, we must apply transformation (18) to the measure in Eq. (7). The transformation of N_c such local coordinates (where $N_c \equiv A/a^2$ denotes the number of continuum or "coarse-grained" degrees of freedom in the model) into an equal number of collective-mode coordinates, with normalization condition (19), yields a measure

$$\prod_\sigma \int \frac{dh(\sigma)}{\lambda(a)} = \prod_\alpha \int \frac{dh_\alpha}{a\lambda(a)} \quad . \tag{21}$$

This, together with Eq. (10) for $\lambda(a)$, yields a collective-mode representation

$$Z \simeq \prod_\alpha \int \frac{dh_\alpha}{\nu^2} \, e^{-\beta H[h]} \, , \tag{22}$$

in which the cutoff a appears only via a restriction on the number of modes included in the product, and in which we have approximated $J[h]$ by unity [39].

Symmetry arguments indicate that the set of eigenmodes $\{\psi_\alpha\}$ for a closed surface must include several Goldstone modes, with eigenvalues $\epsilon_\alpha = 0$.

(i) Because the bending Hamiltonian H_{bend} is invariant under the scale transformation $\mathbf{X}(\sigma) \to \lambda \mathbf{X}(\sigma)$, there must exist one zero mode that generates an infinitesimal dilation of $\mathbf{X}$.

(ii) Because H_{bend} is invariant under rigid translations, there must exist three zero modes that generate infinitesimal translations of the surface.

(iii) Because H_{bend} is invariant under rigid rotations, there can exist up to three modes of h that generate infinitesimal rotations.

The dilation and three translation modes are always present, but the number of nontrivial rotation modes actually depends upon the symmetry of surface $\mathbf{X}_0$: If $\mathbf{X}_0$ is a surface of rotation, one or more of the physical rotations map the surface $\mathbf{X}_0$ onto itself, without generating any normal displacements. Such trivial rotations correspond to simple reparametrizations of the surface, or 2D fluid flow, and are thus already implicitly included within the constrained free energy $H[\mathbf{X}_0]$ of the 2D fluid constrained to surface $\mathbf{X}_0$. Consequently, rotations should not be treated as additional conformational degrees of freedom unless they induce a normal displacement of the membrane. For example, a spherical vesicle has one dilation mode (the $l = 0$ spherical harmonic) and three translation modes (the three $l = 1$ harmonics), but has no nontrivial rotation modes, whereas a completely asymmetric surface would have three nontrivial rotations. By convention, we will denote the dilation mode by ψ_0, the translation modes by $\psi_1 \ldots \psi_3$, and the rotation modes by $\psi_4 \ldots \psi_{N_0-1}$, where N_0 denotes the total number of zero modes.

We now consider the effects of area elasticity, which is given by the stretching energy $\delta H_{flat}(A)$. The in-plane elasticity of a nearly incompressible membrane can be approximated by a harmonic form

$$\delta H_{flat}[h] = B \frac{(A - A_0)^2}{2A_0} \quad , \tag{23}$$

where B is a 2D compression modulus and A_0 is the unstretched area of the membrane. We assume in what follows that B is finite (i.e., the membrane is compressible) but that the characteristic energy scales BA_0 and κ for changing, respectively, the area and curvature of the membrane by factors of order unity form a hierarchy

$$BA_0 \gg \kappa \gg T \quad , \tag{24}$$

so that the fractional changes in area are very small. The typical parameter values for real surfactant membranes are of order $B \sim T/a_s^2$, where a_s^2 is a molecular area and $\kappa \sim (1 - 50)T$. The area A is a functional of $h(\sigma)$, and can be expanded explicitly as a Taylor series

$$A[h] \simeq A_0 - \int dA_0 \, C_0 \, h + \int dA_0 \, h \, [-\tfrac{1}{2}\nabla_0^2 + K_0] \, h + \cdots \, , \tag{25}$$

where ∇_0^2 is the covariant Laplacian on surface $\mathbf{X}_0$, and where the local mean curvature $C_0(\sigma)$ is by convention positive wherever $\hat{\mathbf{n}}$ points towards the locally concave side of the surface. Examination of Eq. (25) shows that the energy δH_{flat} can involve contributions of all orders from all of the undulation modes, giving a combined harmonic contribution to $\delta H_{bend} + \delta H_{flat}$ whose eigenmodes are mixtures of the eigenmodes ψ_α of δH_{bend} alone, and, more importantly, producing anharmonic contributions that can become arbitrarily large in the limit of large B.

In order to bypass this problem, we first note that one mode, the dilation mode ψ_0, does not contribute either to the harmonic bending energy or to the translational and rotational entropy, but enters the harmonic Hamiltonian only through its effect on the area. It is therefore always possible, by an appropriate choice for the value of the mode amplitude h_0, to achieve any desired values of A at specified values of all of the other mode amplitudes, and to do so without affecting the harmonic bending energy. This observation suggests that we might think of the area as being regulated by the "breathing" mode amplitude h_0 alone, which in a nearly incompressible membrane must constantly adjust itself so as to compensate for the excess area associated with all of the other modes, and keep A always near A_0.

We implement this idea formally by changing our expansion of $h(\sigma)$ to one in which the coordinate h_0 is replaced by the area A, giving a new set of collective coordinates

$$\{h'_\alpha\} \equiv \{A, h_1, h_2, \ldots\} \quad , \tag{26}$$

with $h'_0 \equiv A$. This change of coordinates immediately diagonalizes the harmonic Hamiltonian and removes all anharmonic contributions to H_{flat}. The path integral measure is written in this coordinate system as

$$\prod_{\alpha\geq 0}\int \frac{dh_\alpha}{\nu^2} = \int \frac{dA}{\nu^2}\prod_{\alpha\geq 1}\int \frac{dh_\alpha}{\nu^2}\, J_A[h] \quad , \tag{27}$$

where the Jacobian $J_A[h]$ is the determinant of the transformation matrix $\partial h_\alpha/\partial h'_\beta$. While J_A is in general a functional of h, it is straightforward to show that it is sufficient when evaluating F only to $O(T)$ (i.e., in a harmonic approximation) to also approximate J_A by its value $J_A[h=0]$ evaluated for $\mathbf{X}=\mathbf{X}_0$. Furthermore, because the inverse transformation matrix $\partial h'_\alpha/\partial h_\beta$ differs from the identity only within the row associated with the area A, its determinant $J_A^{-1} = \det|\partial h'_\alpha/\partial h_\beta|$ is given exactly by the single partial derivative

$$J_A^{-1}[h] = \left.\frac{\partial A[h]}{\partial h_0}\right|_{h_1,h_2,\ldots} \quad . \tag{28}$$

The value of this derivative at $h=0$ can be obtained by inspection of the Taylor expansion (25) for the area, which yields an approximation for J_A as a dimensionless constant

$$J_A^{-1} \simeq -\int dA_0\, C_0(\sigma)\psi_0(\sigma) \quad , \tag{29}$$

in which $\psi_0(\sigma)$ is the dilation mode eigenfunction and $C_0(\sigma)$ is the mean curvature of the reference surface. This constant depends upon the shape, but not the overall size, of surface $\mathbf{X}_0$. The partition function can thus be written to the required accuracy as an integral

$$Z_N \simeq J_A \int \frac{dA}{\nu^2}\prod_{\alpha\geq 1}\int \frac{dh_\alpha}{\nu^2}\, e^{-\beta H} \quad , \tag{30}$$

which we will hereafter denote Z_N to indicate that it is the partition function for a membrane with a fixed number N of surfactant molecules.

Use of the harmonic approximation for H, with harmonic forms (16) and (23) for H_{bend} and H_{flat}, then allows Z_N to be factorized as a product

$$Z_N \simeq e^{-\beta H[\mathbf{X}_0]} Z_{area} Z_{trans} Z_{rot} Z_{und} \tag{31}$$

in which Z_{area} is associated with area fluctuations, Z_{trans} with rigid translations, Z_{rot} with nontrivial rotations, and Z_{und} with undulations. The corresponding free energy

$$F_N \equiv -T\ln(Z_N) \tag{32}$$

can thus be expressed as a sum

$$F_N = H[\mathbf{X}_0] + F_{area} + F_{trans} + F_{rot} + F_{und} \ , \tag{33}$$

in which $F_{und} \equiv -T\ln(Z_{und})$, etc. Each of these contributions will be considered separately in the following subsections.

An alternative approach to the calculation of F, and the one taken by most previous work, is to replace the area-dependent energy $H_{flat}(A)$ used in the above by a simple constraint on the area, and to thereby treat a compressible membrane of fixed particle number as an idealized surface of constrained area. The effective Hamiltonian for such an idealized surface is assumed to be of the form

$$H[\mathbf{X}] = H_{bend}[\mathbf{X}] + rA \quad , \tag{34}$$

where r is the free energy per unit area of a flat surface. To make contact between this approach and the above treatment of a membrane of fixed particle number, we define a corresponding partition function and free energy

$$\begin{aligned} Z_{A'} &\simeq \prod_\alpha \int \frac{dh_\alpha}{\nu^2}\,\delta\left(\frac{A[\mathbf{X}]-A'}{\Delta A}\right) e^{-\beta H[\mathbf{X}]} \ , \\ F_{A'} &= -T\ln(Z_{A'}) \ , \end{aligned} \tag{35}$$

for a surface of constrained area $A[\mathbf{X}] = A'$, where H is the effective Hamiltonian of Eq. (34). We denote these quantities Z_A and F_A to distinguish them from the partition function and free energy Z_N and F_N of a real membrane with fixed particle number N. The quantity ΔA that appears in the denominator of the δ function in the above is an arbitrary area element that has been introduced in order to obtain a dimensionless partition function, and that we will assume has been assigned a small value $\Delta A \ll A$. The quantities Z_A and F_A have a natural physical interpretation as, respectively, the partition function and free energy for a surface whose area is constrained to lie within a narrow range of values of width ΔA surrounding the specified value A.

Within the harmonic approximation used above to calculate Z_N, Z_A can be factorized as a product

$$Z_A = e^{-\beta H[\mathbf{X}_0]} Z_{\Delta A} Z_{trans} Z_{rot} Z_{und} \tag{36}$$

where Z_{trans}, Z_{rot}, and Z_{und} have the same meaning as in Eq. (31), and

$$Z_{\Delta A} = \Delta A\, J_A/\nu^2 \tag{37}$$

is a prefactor associated with fluctuations of the area over a range ΔA, which is calculated by using the change of variables of Eq. (26) and integrating with respect to A.

B. Undulations

The undulation free energy F_{und} is obtained by integrating over the amplitudes h_α with $\alpha \geq N_0$ in Eq. (30), yielding a sum

$$F_{und} = \frac{T}{2}\sum_{\alpha\geq N_0} \ln\left(\epsilon_\alpha \frac{\nu^4}{2\pi T}\right) \ , \tag{38}$$

over harmonic oscillator contributions.

Before attempting to evaluate Eq. (38) on a finite curved surface, it is instructive to consider first the sim-

pler case of a finite but completely flat background surface of linear size R and area $A \propto R^2$. Here, we can take the mode amplitudes to be Fourier components $h(q)$, with corresponding eigenvalues $\epsilon(q) = \kappa q^4$. We can thus approximate the free energy per unit area by a Fourier-space integral

$$\frac{F_{flat}}{A} \simeq \frac{T}{2}\int_{1/R}\frac{d^2q}{(2\pi)^2}\ln\left(\kappa q^4\frac{\nu^4}{2\pi T}\right)\tilde{\Psi}(q^2b^2) \qquad (39)$$

in which the presence of a finite size has been crudely represented by a lower limit of $1/R$ on q. For generality, the presence of a short-wavelength cutoff has been introduced through the use of a somewhat arbitrary weighting function $\tilde{\Psi}(q^2b^2)$, in which b is a cutoff length of magnitude similar to the "patch size" a, and in which the form of the function $\tilde{\Psi}(q^2b^2)$ is chosen so as to strongly suppress the contributions of wave numbers $qb \gg 1$ and to approach unity for $qb \ll 1$. The above integral yields a total free energy of the form

$$F_{flat} \simeq Af_{und} + BT\ln\left(\frac{R^2}{\nu^2}\right) , \qquad (40)$$

in which f_{und} is the free energy density for the corresponding infinite surface, and B is a constant of order unity whose value depends here on the exact manner in which the long-wavelength cutoff is introduced. The appearance of a logarithmic finite-size contribution is a simple result of the logarithmic low-q divergence of the integrand in Eq. (39). Equivalently, it can be understood as a consequence of the facts that each mode of wave number $q \sim R^{-1}$ makes a contribution of order $\ln(R/\nu)$ to F_{und}, and that the low-q cutoff excludes a finite number (of order unity) such modes from a surface of area R^2. We thus see immediately that on any finite surface the calculated coefficient of any logarithmic contribution to F_{und} will depend sensitively upon one's treatment of the few longest-wavelength modes.

To calculate F_{und} for an arbitrary closed surface, we must first take into account the curvature dependence of the operator $\mathcal{L}$. The explicit form of $\mathcal{L}[\mathbf{X}_0]$ has been calculated previously by several authors [13–15,40], who obtained (in standard differential geometric notation)

$$\begin{aligned}\mathcal{L} &= \kappa(\nabla^4 + \mathcal{L}_2^{ij}\nabla_i\nabla_j + \mathcal{L}_0) ,\\ \mathcal{L}_2^{ij} &= (\tfrac{1}{2}C^2 - 4K)g^{ij} + 2CK^{ij} ,\end{aligned} \qquad (41)$$

where $K_{ij} = \hat{\mathbf{n}}_0 \cdot \partial_i\partial_j\mathbf{X}_0$ is the curvature tensor, $g_{ij} \equiv \partial_i\mathbf{X}_0\cdot\partial_j\mathbf{X}_0$ is the metric tensor, and where the mean and Gaussian curvatures

$$C \equiv K_i^i, \qquad K \equiv \tfrac{1}{2}\varepsilon_k^i\varepsilon_l^j K_{ij}K^{kl} \qquad (42)$$

are given, respectively, by the covariant trace and determinant of K_{ij}. The curvature dependence of $\mathcal{L}_0$ is more complicated [40] but is not needed for what follows, and so is not displayed. In the above, we have left the subscript 0 on most geometrical quantities implicit, and will asssume in the rest of this subsection that all gradients, curvatures, and area elements are defined on the surface $\mathbf{X}_0$ unless otherwise noted.

To make Eq. (38) meaningful on a closed surface, we next express (39) as an operator expression

$$F_{und} = \frac{T}{2}\mathrm{Tr}'\left[\ln\left(\mathcal{L}\frac{\nu^4}{2\pi T}\right)\Psi\right] , \qquad (43)$$

in the Hilbert space of functions living on the surface $\mathbf{X}_0$, where Tr′ denotes a restricted trace

$$\mathrm{Tr}'[\cdots] \equiv \sum_{\beta=N_0}^{\infty}\langle\psi_\alpha|\cdots|\psi_\alpha\rangle \qquad (44)$$

over the subspace of undulation modes only, explicitly excluding the N_0 zero modes $\beta = (0, 1, \ldots, N_0 - 1)$. In Eq. (44), we have used bra-and-ket notation for the undulation eigenmodes ψ_α, in which the inner product is defined by an integral with respect to surface area. The quantity Ψ in the above is a regularization operator that acts to suppress the contributions of short-wavelength undulations, and that is understood to be an operator generalization of the scalar function $\tilde{\Psi}$ used in Eq. (39) to describe a flat surface. The simple regularization scheme used in Eq. (39) can be described in terms of a regularization operator Ψ that is diagonal in a basis of plane waves, giving a translationally invariant operator, with diagonal elements given by the scalar function $\tilde{\Psi}(q^2b^2)$. It will be enough in much of what follows to assume that Ψ is some appropriate generalization of this operator that is chosen to give the same effective area per degree of freedom, in a sense defined below, when applied to different surfaces, and that it reduces to the simple form used above, with some specified choice for the function $\tilde{\Psi}(q^2b^2)$, when applied to a flat surface. The problem of constructing an explicit form for Ψ on a curved surface that satisfies these conditions is deferred to Appendix A.

We wish to express F in what follows as a function of the value of a cutoff or patch area a^2 that is defined by the ratio

$$a^2 \equiv A_0/N_c \qquad (45)$$

where N_c is the total number of continuum, or coarse-grained, degrees of freedom in the model, including both undulation and zero modes. The appropriate definition of the number of degrees of freedom in the regularized theory is given by an unrestricted trace

$$N_c \equiv \mathrm{Tr}[\,\Psi\,] \qquad (46)$$

of the regularization operator Ψ. This definition of N_c has the properties that

(i) it reduces to the naive definition of N_c as the number of modes in the simple case in which, as on a flat surface, Ψ and $\mathcal{L}$ can be simultaneously diagonalized in terms of plane waves and $\tilde{\Psi}$ can be taken to be a sharp cutoff on wave number, and

(ii) it, like this naive definition of N_c, gives the overall coefficient of $T\ln(\nu^2)$ in the *total* free energy F, as defined by Eq. (33).

On a flat surface, definition (45) gives an inverse patch area, or density of degrees of freedom, of the form

$$\frac{1}{a^2} \equiv \int \frac{d^2q}{(2\pi)^2} \tilde{\Psi}(q^2 b^2) \quad , \tag{47}$$

which yields a patch area $a^2 \propto b^2$, with a constant of proportionality that depends upon the form of $\tilde{\Psi}(x)$. For simplicity, we will hereafter assume that the form of $\tilde{\Psi}(x)$ has been chosen to yield $a = b$, or, equivalently, that $\int \frac{dx}{4\pi} \tilde{\Psi}(x) = 1$.

We wish to express the undulation free energy F_{und} of a family of surfaces $\mathbf{X}_0$ as a function of the physical parameters R, a, ν, κ, and T. Examining definition (43), we note that the parameters ν, κ, and T appear within F_{und}/T only in the combination

$$\hat{\nu}^4 \equiv \frac{\kappa \nu^4}{2\pi T} \quad , \tag{48}$$

implying that F_{und}/T can be expressed as a function of the length scales R (or A), a, and $\hat{\nu}$ alone. Because we expect a logarithmic dependence on R, we will assume, and later confirm, that this scale dependence can be expressed as an expansion of the form

$$\frac{F_{und}}{T} = A\frac{f_{und}}{T} + B_a \ln\left(\frac{R^2}{a^2}\right) + B_\nu \ln\left(\frac{R^2}{\hat{\nu}^2}\right) + C \quad . \tag{49}$$

In the above, $A \propto R^2$ is the unstretched area, f_{und} is an asymptotic free energy density, whose value depends upon the parameters a and $\hat{\nu}$, and B_a, B_ν, and C are scale-independent but possibly shape-dependent constants. This is the most general form for the logarithmic contributions that satisfies the requirement that arguments of the logarithms be dimensionless ratios. The first logarithmic contribution in Eq. (49), which depends explicitly upon the cutoff length a, is of the form normally associated with a renormalization of κ and $\bar{\kappa}$. The second logarithmic term, which, like the logarithmic contribution in Eq. (40), is independent of the cutoff, is of the form expected from such a finite-size contribution. Distinguishing the dependence of F_{und} on the cutoff length a from its dependence on the physically irrelevant length ν thus provides a convenient way of distinguishing between the effects of the short-wavelength and long-wavelength cutoffs of the undulation spectrum.

The value of the coefficient f_{und} in Eq. (49) can be determined by considering the behavior of F_{und} in the limit of large R, i.e., large dilation. In this limit, the curvature of $\mathbf{X}_0$ vanishes everywhere as $1/R$ while all internal distances diverge as R. Consequently, the local environment of any point on $\mathbf{X}_0$ asymptotically approaches that of a point within an infinite flat surface. We thus expect the limiting value

$$f_{und} = \lim_{R\to\infty} \frac{F_{und}}{A} \tag{50}$$

of the free energy per unit area to be given by the free energy density

$$f_{und} \equiv \frac{T}{2} \int \frac{d^2q}{(2\pi)^2} \ln(q^4\hat{\nu}^4)\tilde{\Psi}(q^2a^2) \tag{51}$$

of an infinite flat surface.

The value of the coefficient B_ν can then be determined by considering the dependence of F_{und} upon the arbitrary length scale $\hat{\nu}$. We first note that $\hat{\nu}$ enters definition (43) for F_{und} only via an additive constant

$$\delta F_{und} = T N_{und} \ln(\hat{\nu}^2) \quad , \tag{52}$$

where

$$N_{und} \equiv N_c - N_0 \tag{53}$$

is the total number of *undulation* modes in the continuum free energy, excluding the N_0 zero modes. In expansion (49), where $\hat{\nu}$ appears both via the second logarithmic term and via the explicit $\hat{\nu}$ dependence of f_{und} in Eq. (51), it is straightforwared to show that F_{und} depends upon $\hat{\nu}$ only through an additive contribution

$$\delta F_{und} = T(N_c - B_\nu) \ln(\hat{\nu}^2) \quad , \tag{54}$$

in which the term proportional to N_c comes from the Af_{und} term in the free energy expansion, and where we have used Eqs. (45) and (47) to relate A to N_c. Upon equating the right-hand sides (RHS's) of Eqs. (52) and (54), we immediately find that

$$B_\nu = N_0 \quad , \tag{55}$$

i.e., that the correct dependence on $\hat{\nu}$ is obtained only if the coefficient B_ν is exactly equal to the number of zero modes excluded from the sum over undulations.

This result implies that the sensitivity of F_{und} on a closed surface to the low-q end of the spectrum is actually a sensitivity only to the *number* of modes included within F_{und}, and not to the details of the undulation spectrum. To show that this is at least plausible, we consider the effects of a continuous deformation of some surface $\mathbf{X}_0$ that substantially changes the undulation spectrum but that does not, like the extraction of a finite surface, change the total number of undulation modes per unit area. For the sake of concreteness, consider the deformation of an infinite flat membrane into a periodic rippled structure with a periodicity and typical radius of curvature both of magnitude R. If we can somehow make a one-to-one correspondence between the eigenvalues of the original and deformed surfaces, we can write the difference in undulation free energy as a sum

$$\Delta F_{und} = \frac{T}{2} \sum_\alpha \ln\left(\frac{\epsilon'_\alpha}{\epsilon_\alpha}\right) \tag{56}$$

involving logarithms of the ratios of corresponding eigenvalues. The ratio ϵ'/ϵ can differ significantly from unity only for modes of wave number $qR \lesssim 1$, for which the curvature-dependent contributions to $\mathcal{L}$ in Eq. (41) are seen to become comparable to the ∇^4 term, and is expected to approach unity algebraically for modes of wave number $qR \gg 1$. We focus on the contribution of the long-wavelength modes, since it is these that, on a closed surface, give rise to a finite-size contribution to F_{und}. The number of modes of wave number $qR \lesssim 1$ is of or-

der 1 per area R^2, so the total contribution to ΔF_{und} due to changes by factors of $O(1)$ in the eigenvalues of these modes is only a number of order T per area R^2. This stands in contrast to the larger contribution of order $T\ln(R^2/\nu^2)$ per area R^2 which is introduced in F_{und} if, by breaking up the surface into many disconnected pieces of area R^2, we instead *remove* several modes per area R^2 from the undulation spectrum. This suggests, in agreement with Eq. (55), that only such a discontinuous change of the number of undulation modes can produce a logarithmic finite-size contribution.

Having determined f_{und} and B_ν by relatively simple physical arguments, it remains for us to determine the coefficient B_a that controls the dependence of F_{und} upon the cutoff length a. This will require a direct calculation of the dependence of F_{und} upon the short-wavelength cutoff, which will in turn require us to be more specific about the form of operator Ψ which is used to impose this cutoff. Because our final results for B_a, which can be expressed in terms of a renormalization of the rigidities κ and $\bar{\kappa}$, are identical to those obtained by David [15], the details of this calculation are relegated to a pair of Appendixes. Appendix A contains a discussion of the problem of choosing a physically consistent regularization scheme for use on a curved surface. Appendix B contains a direct calculation of F_{und}. Our final result for F_{und} can be expressed as an expansion of the form (49), with a coefficient $B_\nu = N_0$, as expected, and

$$B_a = \frac{1}{8\pi}\int dA\{-\tfrac{1}{2}\alpha C^2 + \bar{\alpha}K\} \quad , \tag{57}$$

where

$$\alpha = 3, \qquad \bar{\alpha} = 10/3 \tag{58}$$

are the coefficients that determine the cutoff dependence of $\kappa(R)$ and $\bar{\kappa}(R)$ in Eq. (2), and are the same as those obtained previously by David [15]. The coefficient $\alpha = 3$ is also the same as that obtained by most other authors [12–15], with the notable exception of Helfrich [11,21].

By combining Eqs. (55) and (57), and absorbing the curvature-dependent logarithmic contributions into renormalizations of the scale-dependent rigidities, we can express $F_{und} + H_{bend}[\mathbf{X}_0]$ in the compact form

$$F_{und} + H_{bend}[\mathbf{X}_0] = Af_{und} + H_R[\mathbf{X}_0] + TN_0\ln\left(\frac{R^2}{\hat{\nu}^2}\right) + TC \quad , \tag{59}$$

in which $H_R[\mathbf{X}]$ is a renormalized bending energy of the form given in Eq. (3), with renormalized rigidities of form (2) evaluated at a length scale R. The value of the constant C in the above depends upon both the shape of the surface $\mathbf{X}_0$ and the conventions used in defining the structural length R.

The final expression (59) for F_{und} differs from that obtained previously by David [15] only by the inclusion of a finite-size contribution of magnitude

$$\delta F \simeq TN_0\ln\left(\frac{R^2}{\nu^2}\sqrt{\frac{T}{\kappa}}\right) \tag{60}$$

associated with the existence of N_0 zero modes per disconnected surface, where the dependence on T/κ comes from our use of definition (48) for $\hat{\nu}$. This finite-size contribution is expected to be unimportant in systems, such as bicontinuous phases, which contain a small number density of disconnected surfaces and a large number of handles, but has already been shown [23] to play a crucial role in the thermodynamics of systems, such as the vesicle phase [23], that contain a large number of disconnected surfaces.

C. Translations and rotations

In this subsection we discuss the free energy contributions F_{trans} and F_{rot} associated with overall translations and nontrivial rotations of the membrane. After discussing first translations and then rotations, we also make some more general comments on the contributions of such collective modes and their relationship to the finite-size contributions discussed in subsection II B.

An infinitesimal translation of the membrane's center of mass by a displacement $d\mathbf{X}_{c.m.} = dX^\alpha_{c.m.}\hat{\mathbf{e}}_\alpha$ (where the $\hat{\mathbf{e}}_\alpha$'s are three Cartesian unit vectors) can be generated by a normal displacement

$$\mathbf{X}(\sigma) \to \mathbf{X}(\sigma) + \hat{\mathbf{n}}(\sigma)[d\mathbf{X}_{c.m.}\cdot\hat{\mathbf{n}}(\sigma)] \ . \tag{61}$$

We can expand this in terms of normalized eigenmodes of the form

$$\psi_\alpha(\sigma) = \frac{1}{\sqrt{As_\alpha}}\,\hat{\mathbf{n}}(\sigma)\cdot\hat{\mathbf{e}}_\alpha \ , \tag{62}$$

in which $s_\alpha \equiv \int dA(\hat{\mathbf{e}}_\alpha\cdot\hat{\mathbf{n}})^2/A$ is a normalization constant of order unity. The three eigenmodes $\psi_\alpha(\sigma)$ ($\alpha = 1,\ldots,3$) can always be made orthogonal in the sense of Eq. (19) by choosing the unit vectors $\hat{\mathbf{e}}_\alpha$ to lie parallel to the eigenvectors of the Cartesian tensor

$$S_{ij} \equiv \frac{1}{A}\int dA\ \hat{n}_i\hat{n}_j \quad , \tag{63}$$

in which case the coefficients s_α are given by the eigenvalues of S_{ij}. With this convention, we obtain mode amplitudes

$$h_\alpha = dX^\alpha_{c.m.}\sqrt{s_\alpha A} \ . \tag{64}$$

Integrating over the mode amplitudes for a situation in which the membrane's center of mass is confined to a box of volume V then yields a free energy

$$F_{trans} = -T\ln\left(\frac{VA^{3/2}s^{3/2}}{\nu^6}\right) , \tag{65}$$

in which $s^3 = s_1s_2s_3$ is the determinant of S_{ij}. Note that this free energy depends explicitly upon the size of the membrane as well as upon the size of the box.

This dependence of F_{trans} upon the membrane area can also be obtained by a heuristic argument that was presented in Ref. [23], in which we treated the membrane

as a point particle with a mass equal to that of the entire membrane. The translational free energy of a particle or rigid body of total mass m_{tot} whose center of mass is confined within a box of volume V is given, either classically or quantum mechanically, by the free energy

$$F_{trans} = -T \ln(V/\lambda_{tot}^3) \tag{66}$$

where $\lambda_{tot} = h/\sqrt{2\pi m_{tot} T}$ is the center-of-mass thermal de Broglie wavelength. The de Broglie length for a surface of total mass $m_{tot} = \varrho A$ scales as $\lambda_{tot} = \nu^2/\sqrt{A}$ with the area, which, when substituted in Eq. (66), yields the same size dependence as that of Eq. (65).

This analogy between the excess translational free energy F_{trans} of a closed fluid membrane and the total translation free energy of a point particle or rigid body is, however, only of heuristic value, and can be misleading if taken too seriously. Comparing Eqs. (65) and (66), we see that the translational free energy of the membrane actually does differ somewhat from that of the corresponding point mass, as indicated by the presence of the geometrical factor $s^{3/2}$ that appears in (65) but not in (66). Each factor of $s_\alpha^{1/2}$ within F_{trans} weights the magnitude of center-of-mass motion along direction $\hat{\mathbf{n}}_\alpha$ by a factor related to the extent to which motion in this direction translates different patches of membrane along their local normal direction rather than simply generating fluid flow within the local tangent plane of the membrane. The inclusion of such a factor is necessary to avoid double counting of the free energy contributions associated with tangential displacements of the surfactant molecules *within* the membrane surface, which are already included in the constrained free energy H of the 2D surfactant fluid on a fixed surface. It is for the same reason that, when calculating the free energy F_{rot} arising from rotations of the surface, we will not include any rigid rotations that map the surface $\mathbf{X}_0$ itself, since all free energy contributions that arise from purely tangential displacements of the surfactant molecules within the membrane are already included within the definition of H. Serious errors of a similar nature can arise from the naive use of center-of-mass coordinates to describe, e.g., the excess translational entropy of a three-dimensional nucleation or microemulsion droplet [26,30], or the excess translational and rotational free energy [28] of a rodlike micelle. The translational and rotational free energies defined here should therefore *not* be understood as being the free energies associated with simple rigid translations or rotations, but as excess free energies arising from purely normal displacements of the surface.

The rotational free energy F_{rot} of a fluid membrane can be calculated in a manner analogous to that used above to treat translations. A rigid rotation of $\mathbf{X}$ around an axis $d\mathbf{\Omega}$, where $|d\mathbf{\Omega}|$ is an infinitesimal angle of rotation, is generated by a normal displacement

$$h(\sigma) = \hat{\mathbf{n}}_0(\sigma) \cdot [d\mathbf{\Omega} \times \mathbf{X}_0(\sigma)] \ . \tag{67}$$

The corresponding normalized eigenmodes can be written as

$$\psi_\alpha(\sigma) = c_\alpha \hat{\mathbf{n}}(\sigma) \cdot [\hat{\mathbf{\Omega}}_\alpha \times \mathbf{X}_0(\sigma)]/A \tag{68}$$

where c_α is a normalization constant of order unity, and $\hat{\mathbf{\Omega}}_\alpha$ is a unit vector along rotation axis α, where α indexes the different axes. This gives mode amplitudes of order

$$h_\alpha \propto |d\mathbf{\Omega}_\alpha| \, R^2 \ . \tag{69}$$

Integrating over rotation angles $|d\mathbf{\Omega}_\alpha|$ of order unity then gives a free energy with a scale dependence of the form

$$F_{rot} \simeq -T N_{rot} \ln\left(\frac{R^2}{\nu^2}\right) \ , \tag{70}$$

where N_{rot} is the number of physical rotation modes. Note that the R dependence of this contribution exactly cancels that arising from the part of the finite-size contribution to F_{und} that arises from the existence of N_{rot} undulation modes. The presence or absence of nontrivial rotation modes will thus have no effect upon the scale dependence of the total free energy.

The forms obtained above for the scale dependence of free energy contributions arising from translations and rotations can be understood most simply in terms of a simple relationship between the free energy contribution of a given mode and the magnitude of the surface displacements arising from it. The value of the factor Z_α in the partition function (e.g., Z_{trans}, Z_{rot}, etc.) that arises from fluctuations of a particular mode amplitude h_α can be related, to within factors of order unity, to the rms fluctuations of h_α by writing

$$Z_\alpha \sim \frac{\sqrt{\langle h_\alpha^2 \rangle}}{\nu^2} \ . \tag{71}$$

To relate the fluctuations in h_α to the resulting physical displacements of the surface, we define a spatially averaged mean-squared normal displacement,

$$\Delta_\alpha \equiv \left[\frac{1}{A}\int dA \, |\psi_\alpha(\sigma)|^2 \langle h_\alpha^2 \rangle\right]^{1/2} \ , \tag{72}$$

so that Δ_α is a measure of the typical surface displacements induced by thermal excitation of mode α alone. Using normalization condition (19), we find that $\Delta_\alpha = \sqrt{\langle h_\alpha^2 \rangle / A}$, which yields

$$Z_\alpha \sim \frac{\Delta_\alpha R}{\nu^2} \ , \tag{73}$$

and a corresponding free energy contribution of order

$$F_\alpha \simeq -T \ln\left(\frac{\Delta_\alpha R}{\nu^2}\right) \ , \tag{74}$$

where $R \sim A^{1/2}$.

The forms of the translational, rotational, and finite-size free energy contributions obtained above can all be understood as immediate consequences of Eq. (74). Equation (65) for F_{trans} is obtained by assuming a normal surface displacement

$$\Delta_{trans} \propto V^{1/3} \tag{75}$$

that is controlled by the size of the volume to which the

surface's center of mass is confined. Equation (65) for F_{rot} is given by assuming that each nontrivial rotation mode yields a surface displacement

$$\Delta_{rot}(R) \propto R \tag{76}$$

proportional to the size of the surface. Finally, Eq. (60) for the finite-size contribution to F_{und} can be obtained by assuming that this contribution is a change in F arising from the destruction of N_0 undulation modes, each with a corresponding surface displacement

$$\Delta_{und}(R) \sim R\sqrt{\frac{T}{\kappa}} \quad , \tag{77}$$

characteristic of undulation modes of wavelength R.

Because of the one-to-one correspondence between the N_0 collective-mode contributions to F and the corresponding finite-size contributions to F_{und}, it is also possible to define, for each collective mode, a total free energy contribution ΔF_α that gives the difference between the actual free energy contribution F_α of the mode in question and the corresponding contribution of the undulation mode that was "destroyed" in order to create it, thus isolating the total change in free energy that is, in some sense, attributable to the existence of that collective mode. This free energy difference is given by the logarithm $\Delta F_\alpha = -T\ln(\Delta Z_\alpha)$, where ΔZ_α is the ratio of partition function factors for mode α and the corresponding undulation mode, which can be approximated by the corresponding ratio

$$\Delta Z_\alpha \sim \frac{\Delta_\alpha}{\Delta_{und}(R)} \tag{78}$$

of rms surface displacements. The total free energy difference arising from translation modes, defined in this way, is roughly

$$\Delta F_{trans} \sim -T\ln\left(\frac{V}{\Delta^3_{und}(R)}\right) , \tag{79}$$

and thus depends upon both volume V and, through the size dependence of $\Delta_{und}(R)$, the size of the surface. The corresponding total free energy difference arising from nontrivial rotation modes is roughly

$$\Delta F_{rot} \sim \tfrac{1}{2}TN_{rot}\ln\left(\frac{T}{\kappa}\right) . \tag{80}$$

The quantity ΔF_{rot} is independent of the size of the surface because the surface displacements induced by rotation and long-wavelength undulation modes both scale linearly with R, but depends upon T/κ because the surface displacements arising from undulations are smaller than those arising from nontrivial rotations by a factor proportional to $\sqrt{T/\kappa}$.

D. Compressible vs incompressible membranes

In this subsection we consider the contributions F_{area} and $H_{flat}(A_0)$ that arise directly from a treatment of the membrane as a compressible fluid of fixed particle number, rather than as an idealized surface of constrained area. In so doing, we establish the equivalence of these two models.

We first consider the contribution F_{area} associated with fluctuations of the area in a membrane of fixed particle number. Evaluating the partition function factor

$$Z_{area} \equiv J_A \int \frac{dA}{\nu^2} e^{-\frac{1}{2}\beta B(A-A_0)^2/A_0} \quad , \tag{81}$$

yields the harmonic oscillator free energy

$$F_{area} \simeq \frac{T}{2}\ln\left(\frac{B\nu^4}{2\pi T A_0 J_A^2}\right) . \tag{82}$$

Taken alone, this contribution has two rather disturbing features:

(i) it contains a logarithmic dependence upon the area (or the structural length R, where $A_0 \propto R^2$) that arises from area fluctuations but that remains nonzero even in the limit $B \to \infty$ in which such fluctuations are completely suppressed, and

(ii) it contains a logarithmic dependence on B that diverges in the same limit of an incompressible fluid.

We now show that both the scale dependence and the B dependence of F_{area} are canceled in any real system by a subtle logarithmic contribution to the free energy $H_{flat}(A_0)$ of a flat, unstretched membrane.

The free energy $H_{flat}(A)$ about which the effective Hamiltonian H has been expanded is itself the total free energy of an interacting 2D fluid of fixed particle number on a finite surface of fixed area. The most obvious approximation for the scale dependence of H_{flat} would be to assume that it is extensive in N and A, which would capture the dominant behavior of the fluid free energy in the thermodynamic limit in which $N, A \to \infty$ at fixed N/A. We must consider the possibility, however, that this free energy might also contain subthermodynamic contributions that, like the other free energies of interest in this problem, are either logarithmically size dependent or size independent. Such contributions are subthermodynamic in the sense that they make a negligible contribution to the free energy per area of a large surface, but must nonetheless be considered here because they make a nonvanishing contribution to the free energy of the surface as a whole.

To determine whether any such contributions exist, we must isolate the dominant subthermodynamic contributions to the free energy of an interacting 2D fluid on a finite surface. To this end, it will be useful to consider the relationship in a finite system between the canonical partition function $Z_N(A)$ or Helmholtz free energy $F_N(A) \equiv -T\ln r[(Z_N(A)]$ of a 2D fluid of exactly N particles on a finite surface of area A and the corresponding grand canonical partition function and grand potential

$$\Xi(A,\mu) = \sum_{N=0}^{\infty} Z_N(A) e^{\beta\mu N} , \tag{83}$$

$$\Omega(A,\mu) \equiv -T\ln(\Xi) \tag{84}$$

of the same fluid evaluated in an ensemble of fixed area A but fluctuating particle number, in which the number density is controlled by a chemical potential μ. (These quantities, which are used in this subsection to describe the statistical mechanics of a hypothetical two-dimensional fluid, should not be confused with the thermodynamic potentials used in the rest of this paper to describe a fluctuating three-dimensional membrane.)

We first consider the unrealistic, but instructive, case of a 2D ideal gas. To obtain the Helmholtz free energy we use Stirling's formula to expand the exact free energy $F = T\ln(N!\lambda^2/A)$, where λ is the thermal de Broglie wavelength, giving

$$F_N(A) = Af_{ideal}(n) + T\ln(2\pi N) + \cdots , \tag{85}$$

where $f_{ideal}(n) = Tn[\ln(n\lambda^2) - 1]$ is the Helmholtz free energy per unit area in the thermodynamic limit, and where $n \equiv N/A$. The logarithmic term in the above is obtained by simply retaining one more term in the expansion of $\ln(N!)$ than is necessary when calculating the extensive term alone [41]. The corresponding grand potential Ω can be obtained directly as the continuum limit of an ideal lattice-gas model, which yields a grand potential

$$\Omega(A,\mu) = Af_{ideal}(\langle n\rangle) - \mu\langle N\rangle \tag{86}$$

that is rigorously extensive in the area, and is given by the Legendre transform of the extensive part of F_N. Thus, at least for an ideal gas, the thermodynamic potential of a finite system is extensive (to the accuracy required here) only for a system with a fluctuating particle number, and contains a logarithmic contribution for a system with a fixed particle number.

To generalize this result to the case of an interacting fluid, we use Eq. (83) to obtain a general relationship between the dominant subthermodynamic parts of F and Ω. We first Taylor-expand F_N as

$$F_N \simeq F_{\langle N\rangle} + \frac{\partial F_N}{\partial N}\,\delta N + \frac{1}{2}\frac{\partial^2 F_N}{\partial N^2}(\delta N)^2 + \cdots \tag{87}$$

around the expectation value $\langle N\rangle$ in the grand canonical ensemble, where $\delta N \equiv N - \langle N\rangle$, and where $\langle N\rangle$ is determined by the saddle-point equation

$$\mu = \left.\frac{\partial F_N}{\partial N}\right|_{N=\langle N\rangle} . \tag{88}$$

In order to relate the second derivative $\partial^2 F_N/\partial N^2$ to the 2D compression modulus B, defined by

$$B \equiv A\frac{\partial^2 F_N}{\partial A^2} , \tag{89}$$

we approximate $F_N \simeq Af(n)$ by its dominant extensive part and differentiate twice with respect to both A and N to obtain

$$\frac{\partial^2 F_N}{\partial N^2} \simeq \frac{BA}{N^2} + \cdots . \tag{90}$$

Approximating the sum in Eq. (83) by an integral and integrating over particle number fluctuations within a Gaussian approximation then yields a grand canonical potential

$$\Omega(\mu) = F_{\langle N\rangle} - \mu\langle N\rangle - \frac{T}{2}\ln\left(\frac{2\pi TN^2}{BA}\right) + \cdots , \tag{91}$$

which agrees with Eqs. (85) and (86) for the simple case of an ideal gas, for which $B = TN/A$. The above derivation of the logarithmic factor from a consideration of the effects of fluctuations in N indicates that the extra logarithmic contribution to F is caused by the loss of entropy associated with the suppression of these fluctuations.

The above argument shows only that the thermodynamic potentials F and Ω of an interacting fluid, like those of an ideal gas, differ by a nontrivial logarithmic contribution. In order to complete the analogy to the situation found above for an ideal gas, we now argue on physical grounds that the grand canonical free energy Ω will remain extensive in the presence of interactions, so that the only logarithmic contribution to the Helmholtz free energy F will be the one given explicitly in Eq. (91). We note that a large surface in contact with an infinite particle reservoir can be broken into subsystems, each of which is effectively also in contact with an infinite reservoir consisting of the original reservoir plus the other subsystems. For subsystems much larger than the range of interparticle correlations, fluctuations of the internal states of different subsystems, including their particle number, must become uncorrelated, so that the total grand potential Ω can be written as a sum of free energies for the different subsystems. This additivity implies a free energy that is strictly extensive in the area or average particle number, with no logarithmic contributions. The same argument cannot, however, be applied to a system of fixed particle number precisely because the particle number fluctuations in different subsystems are always correlated due to the constraint on the total particle number. It is apparently the reduction of entropy associated with this correlation of particle number fluctuations which gives rise to the logarithmic contribution to F.

The constrained free energy $H_{flat}(A_0)$ for the unstretched surfactant fluid is, by definition, the free energy for a fluid containing a fixed number of molecules. Its size dependence is thus of the form

$$H_{flat}(A_0) = Af_{flat} + \frac{T}{2}\ln\left(\frac{2\pi TN}{Ba_s^2}\right) \tag{92}$$

expected of a Helmholtz free energy, where f_{flat} is the free energy density per unit area of an infinite, flat unstretched membrane, and $a_s^2 = A_0/N$ is the area per surfactant molecule in such a membrane.

The total free energy contribution of interest in this subsection is the combination

$$\Delta F_N \equiv H_{flat}(A_0) + F_{area} , \tag{93}$$

which gives the free energy of a 2D surfactant fluid with fixed particle number but fluctuating area. Upon com-

paring Eqs. (82) and (92), we see that the logarithmic area and B dependences of H_{flat} and F_{und} exactly cancel, leaving a combined contribution

$$\Delta F_N = A_0 f_{flat} - T \ln\left(\frac{a_s^2 J_A}{\nu^2}\right) \tag{94}$$

with no logarithmic dependence on either R or B.

We now consider the corresponding contribution to the free energy F_A of an idealized surface whose area is allowed to fluctuate over a narrow range of values between A and $A+\Delta A$. The total free energy F_{A_0} for a completely idealized surface of area A_0 is given by the sum

$$F_{A_0} = H_{bend}[\mathbf{X}_0] + F_{trans} + F_{rot} + F_{und} + \Delta F_A \tag{95}$$

in which

$$\Delta F_A \equiv A_0 r - T \ln\left(\frac{\Delta A J_A}{\nu^2}\right) \tag{96}$$

is the counterpart within F_A to the contribution ΔF_N considered above. The logarithmic term in Eq. (96) is, like F_{area} in F_N, a free energy contribution arising from small fluctuations of the area.

Upon comparing the corresponding contributions ΔF_N and ΔF_A, we note that both quantities are of the same form, i.e., the sum of an extensive term plus a scale-independent term, and that they differ only by replacement of the physical parameters f_{flat} and a_s^2 appearing in δF_N by the phenomenological parameters r and ΔA appearing in F_A. The constrained-area free energy F_A thus becomes exactly equal to the physical free energy F_N only if F_A is evaluated using the parameter values

$$\begin{aligned} r &= f_{flat} \ , \\ \Delta A &= a_s^2 \ . \end{aligned} \tag{97}$$

The identification of r with f_{flat}, which serves to equate the extensive parts of F_N and F_A, is primarily a matter of convention, since f_{flat} can itself be set to any value one wishes simply by choosing an appropriate reference state when defining F_N. The identification of ΔA with a_s^2, however, which affects the subthermodynamic part of F_A, is physically meaningful, since it is the magnitude of the subthermodynamic part of the free energy that controls physical properties such as the size distribution of an ensemble of surfaces. The physical content of Eq. (97) is thus that the free energy F_N of a compressible membrane is equal (to within a thermodynamically irrelevant contribution proportional to the area) to the free energy F_A of an idealized surface whose area is allowed to fluctuate over a range of values equal to the average area a_s^2 per surfactant molecule within the membrane. We emphasize that this result for F_N is different from that obtained by simply adding a harmonic stretching energy to the bending energy of an idealized surface (and thus ignoring the logarithmic contribution to H_{flat}), which would instead yield the free energy of an idealized surface whose area is allowed to fluctuate over the much larger range of values $\langle (A - A_0)^2 \rangle \sim \sqrt{A_0 T/B}$.

We now show that the relationship between F_N and F_A obtained in Eq. (97) is precisely that which is needed in order to guarantee that a model of idealized surfaces of continuously variable area will actually yield the correct size distribution for a system of real membranes. We consider a system containing a dilute suspension of surfactant membranes, each containing an integer number of molecules that can vary via exchange of surfactant molecules with a reservoir. The average number $M_N(V)$ of membranes of particle number N whose center-of-mass positions lie within a region of volume V is given by a Boltzmann weight

$$M_N(V) = e^{-\beta[F_N(V) + \mu_s N]} \ , \tag{98}$$

in which $F_N(V)$ is the Helmholtz free energy for a membrane of N surfactant molecules whose position is confined to a box of volume V, and μ_s is a surfactant chemical potential. The corresponding quantity in a system containing a gas of idealized surfaces of continuously variable area is the total number of surfaces $M_A(V, a_s^2)$ whose positions lie within a region of volume V and whose areas lie within the range between $A = N a_s^2$ and $(N+1)a_s^2$. This quantity is given by the Boltzmann weight

$$M_A(V, a_s^2) = e^{-\beta[F_A(V, a_s^2) + \sigma A]} \ , \tag{99}$$

in which $-\sigma \equiv \mu_s / a_s^2$ is the chemical potential for the area, and in which $F_A(V, \Delta A)$ denotes the free energy for a surface whose position is confined to a region of volume V and whose area is allowed to fluctuate over a range of values of width ΔA. The continuum size distribution, as characterized by, e.g., the total number density of surfaces $d\rho/dA$ per unit volume and unit surface area, will be the same in the two models only if $M_N(V) = M_A(V, a_s^2)$. The quantities $M_N(V)$ and $M_A(V, a_s^2)$ will be equal *only* if the corresponding free energies satisfy $F_N(V) = F_A(V, a_s^2)$, as found above.

The results of this subsection thus provide a rigorous (but somewhat subtle) justification for the use of a model of idealized surfaces to describe properties of an ensemble of real, compressible membranes.

E. Total free energy for fixed N or A

Combining the results of subsections II A–II D, we can express the total free energy $F_A = F_A(V, \Delta A)$ of an idealized surface of constrained area, as defined in Eq. (35), as a sum

$$F_A = F_{int} + F_{trans} \tag{100}$$

of an "internal" free energy $F_{int} \equiv H[\mathbf{X}_0] + F_{\Delta A} + F_{rot} + F_{und}$ plus a translational free energy F_{trans}, which are of the form

$$\begin{aligned} F_{int} &\simeq A f_{tot} + H_R[\mathbf{X}_0] - T \ln\left(\frac{\nu^6 \Delta A}{R^8}\right) \\ &\quad - \tfrac{1}{2} T N_0 \ln\left(\frac{\kappa}{T}\right) \ , \\ F_{trans} &\simeq -T \ln\left(\frac{V R^3}{\nu^6}\right) \ , \end{aligned} \tag{101}$$

where

$$f_{tot} \equiv r + f_{und} \tag{102}$$

is the total free energy per unit area of an infinite sheet fluctuating about a planar equilibrium state. It is convenient to remove the extensive part of the free energy by defining the free energy per molecule (or unit area) relative to that in such a fluctuating planar surface, thereby setting $f_{tot} \equiv 0$ as a matter of convention. With this convention, the remaining nonextensive free energy can be written as a sum

$$F_A = H_R[\mathbf{X}_0] - T\ln\left(\frac{V\Delta A}{R^5}\right) - \tfrac{1}{2}TN_0\ln\left(\frac{\kappa}{T}\right) + TC \tag{103}$$

in which the value of the constant C will depend in detail upon the shape of the surface, the convention used to define the structural length R, and even the form of the regularization function used to calculate F_{und}. In Appendix C, where we calculate the free energy of a spherical vesicle by directly analyzing the sum over undulation modes, we obtain a free energy of the above form and calculate numerical values for C and related numerical constants.

The corresponding results for the free energy $F_N(V)$ of a compressible membrane of fixed particle number are obtained by simply setting $\Delta A = a_s^2$ and $r = f_{flat}$ in Eqs. (101), (102), and (103), as discussed in subsection II D.

It has been emphasized in several papers by Porte and co-workers [42–45] that the symmetry of the Helfrich bending energy with respect to scale transformations imposes some rather strong constraints on the types of scale dependence which can appear in the thermodynamic properties of a system of membranes. Porte *et al.*'s arguments in their original form applied primarily to a bicontinuous phase comprised of a single multiply connected membrane. We now show that most of the information in Eq. (103) can be derived by applying a similar symmetry argument to the free energy of a single disconnected surface.

It is convenient, for this purpose, to take definition (35) for the free energy F_A of an idealized surface of constrained area as our starting point. This free energy can, by construction, depend only upon the dimensionless parameters κ and $\bar{\kappa}$ and upon the length scales $A^{1/2}$, $V^{1/3}$, $\Delta A^{1/2}$, a, and ν. We know from the mode-counting arguments given in subsections II A and II B that the arbitrary length scale ν can appear in F_A only within a thermodynamically irrelevant term proportional to A. We know that the partition function Z_A must be proportional to V. We also know that Z_A must be proportional to the magnitude ΔA of the range of values over which the area of the membrane is allowed to fluctuate, as can be seen by applying the identity $\delta(A - A_0/\Delta A) = \Delta A\, \delta(A - A_0)$ to the δ function in Eq. (35). The free energy F_A must therefore depend on V and ΔA only via an additive logarithmic contribution of the form

$$\delta F \simeq -T\ln(V\,\Delta A)\ . \tag{104}$$

Finally, we know as a consequence of the scale invariance of the bending energy that the nonextensive parts of F_A must be invariant under a simultaneous rescaling

$$A \to \lambda^2 A, \quad \Delta A \to \lambda^2 \Delta A\ , \qquad a \to \lambda a,\ V \to \lambda^3 V \tag{105}$$

of the four remaining length scales in the problem. If we then assume, based on the results of earlier calculations of the cutoff dependence of the renormalized rigidities, that the dependence of the $O(T)$ contribution to F_A upon the cutoff length a is also logarithmic, but that this dependence can be completely absorbed into a renormalization of the bending energy, then we are forced to conclude that, to $O(T)$, the nonextensive part of the free energy must be of the form

$$F_A \simeq H_R[\mathbf{X}_0] - T\ln\left(\frac{V\,\Delta A}{A^{5/2}}\right) + Tf(\kappa/T)\ , \tag{106}$$

where $f(\kappa/T)$ is some dimensionless function of κ/T. This dimensional argument does not give the value of the coefficient B_a that controls the dependence of H_R upon the cutoff, nor the form of the function $f(\kappa/T)$, both of which must be calculated explcitly. What it does tell us, however, is that the form of the logarithmic dependence on A in the second term in Eq. (106) is dictated by the dependence of F_A upon V and ΔA, together with the requirement that F_A be invariant under an overall length rescaling of form (105).

III. A DILUTE SUSPENSION OF SURFACES

In the preceding section, we considered the free energy of an isolated membrane of fixed particle number N or area A. Physical situations in which this quantity is of interest, however, typically involve not just an isolated surface, but an equilibrium state of many disconnected surfaces, such as a vesicle phase, in which the areas of individual surfaces may fluctuate through the exchange of surfactant molecules. In this section we use the results of the previous subsection for the constrained area free energy of a single surface in order to calculate the thermodynamic properties of a dilute, polydisperse suspension of surfaces.

We consider a dilute suspension of many surfaces, all of which are assumed to be of the same topology and equilibrium shape, and treat the physically relevant case of spherical vesicles as a special case. The total Helmholtz free energy density F for a system of noninteracting surfaces in a box of volume V is given by the ideal gas free energy

$$\beta F = \sum_{N=N_{min}}^{\infty} M_N[\,\ln(M_N) - 1 + F_N(V)\,]\ , \tag{107}$$

where $F_N(V)$ is the free energy for a single surface of particle number N whose center of mass is constrained

to lie within a volume V, and M_N is the total number of surfaces of particle number N. The sum in Eq. (107) has been taken to include only surfaces of area greater than a cutoff size N_{min} as a way of crudely representing the facts that the harmonic bending energy used in deriving F_N cannot accurately describe the free energy of membranes of dimensions smaller than some molecular length scale of order of the bilayer thickness, and that the density of such very small surfaces will be strongly suppressed by molecular packing effects.

We obtain the equilibrium size distribution by minimizing F_{tot} with respect to M_N in the presence of a constraint on the total number of surfactant molecules. This yields

$$M_N(V) = e^{-\beta[F_N(V)+\mu_s N]} \quad , \tag{108}$$

where μ_s is a surfactant chemical potential that has been introduced as a Lagrange multiplier to constrain the total number of surfactant molecules in the system. To make contact with the description of the membranes as idealized surfaces, this distribution can be reexpressed as a differential number density

$$\frac{d\rho}{dA} \equiv \frac{1}{V a_s^2} e^{-\beta[F_N(V)+\sigma A]} \tag{109}$$

of surfaces per unit volume and unit surface area, in which

$$\sigma \equiv -\mu_s / a_s^2 \tag{110}$$

is a chemical potential for the area, or bare surface tension, and $A = N a_s^2$. Using Eq. (103) for $F_N(V)$ then yields

$$\frac{d\rho}{dA} \simeq \frac{(\beta\kappa)^{N_0/2}}{R^5} e^{-\beta[H_R(R)+\sigma' A]} \quad , \tag{111}$$

where $H_R(A)$ is the renormalized bending energy of a surface of structural length $R \sim A^{1/2}$, and where

$$\sigma' \equiv \sigma + f_{tot} \tag{112}$$

is the difference between the value of the chemical potential σ in the system of interest and that in a reference system consisting of an infinitely large surface fluctuating about a planar background state, or (equivalently) a single infinitely large vesicle. The physical state of the system is controlled by the value of this chemical potential difference.

As expected, this size distribution depends upon the cutoff length a only through the cutoff dependence of the renormalized bending energy $H_R(A)$ and of the reference free energy f_{tot}, so that the effects of changes in the cutoff length can always be absorbed into corresponding changes in the values of the bare parameters κ, $\bar{\kappa}$, and σ which are used to produce a given large-scale behavior for $H_R(A)$ and a given value for σ'. Similarly, this size distribution depends upon the length scale ν [or $\lambda(a)$] only through the trivial ν dependence of the reference free energy f_{tot}, so that changes in ν affect only the value of the (unobservable) bare parameter σ. Finally, we note that this result is completely independent of the molecular area a_s^2, or any other molecular length, since, as discussed in subsection II D, the size distribution is identical to that produced by the model of idealized surfaces of continuously variable areas.

It can be shown by a straightforward dimensional analysis that Eq. (111) is actually the only physically allowable form for the area dependence of $d\rho/dA$. More specifically, it is the only form allowable within the context of a model in which the membrane is treated as a surface of continuously variable area whose shape is controlled by the Helfrich bending energy. We know that in such a theory $d\rho/dA$ must be a function of the bending rigidities, the cutoff length a, the area A, and the surface tension σ alone. The dependence on the surface tension σ is determined by the requirement that the vesicles are in chemical equilibrium with respect to exchange of surfactant molecules, and must therefore be of the trivial form given above. We know that, if physical quantities such as $d\rho/dA$ are to remain unchanged under a coarse-graining transformation (i.e., under a simultaneous change of the cutoff length and of the corresponding elastic parameters of the membrane), then the cutoff length a can appear only within a renormalization of the bending rigidities, which we expect to appear in a Boltzmann factor $e^{-\beta H_R(A)}$. The dimensionful prefactor of $A^{-5/2}$ is then required by the facts that $d\rho/dA$ has units of $(\text{length})^{-5}$, and that, once the cutoff length a has been absorbed into a renormalization of the bending rigidities, the surface size $A^{1/2}$ is the only other length scale in the problem. It is this size-dependent prefactor that has been here obtained by a proper treatment of finite-size effects and of translational entropy.

In the physically relevant case of spherical vesicles, Eq. (111) yields a size distribution

$$\frac{d\rho}{dA} = C_\rho \frac{(\beta\kappa)^2}{R^{7/3} a^{8/3}} e^{-\beta\{H_{bend}[\mathbf{X}_0]+\sigma' A\}} \tag{113}$$

of the form obtained previously in Ref. [19], where $H_0 \equiv H_{bend}[\mathbf{X}_0] = 4\pi(2\kappa + \bar{\kappa})$ is the unrenormalized bending energy of a sphere, $R = \sqrt{A/4\pi}$ is the equilibrium radius, and C_ρ is a numerical constant. Numerical values for C_ρ, which depends somewhat upon the form chosen for the regularization function, are given at the end of Appendix C. By changing variables from the area A to the mechanical equilibrium radius $R \equiv \sqrt{A/4\pi}$ of the sphere, and using definition (77) for $\Delta_{und}(R)$, one can rewrite this as a simple expression

$$\frac{d\rho}{dR} \propto \frac{1}{\Delta_{und}^4(R)} e^{-\beta[H_R(R)+\sigma' A]} \tag{114}$$

for the number density per unit radius as a function of the renormalized bending energy $H_R(R)$ and the length scale $\Delta_{und}(R)$ alone, where $\Delta_{und}(R)$ is proportional to the rms normal displacement (i.e., the "roughness") of a surface of radius R due to thermal undulations.

An alternative way of calculating the size distribution of an ensemble of surfaces is to treat the area A of each

surface as a fluctuating internal degree of freedom, which can fluctuate due to exchange of area elements (i.e., surfactant molecules) with a reservoir, and thereby treat fluctuations of area on the same footing as fluctuations of position, orientation, and shape. We will briefly summarize this alternative in order to make contact with an earlier treatment of the vesicle problem by Huse and Leibler (HL) [18]. We consider the grand canonical partition function

$$\Xi(V,\sigma) \equiv \int D[\mathbf{X}]\, e^{-\beta\{H_{bend}[\mathbf{X}]+\sigma A)\}} \tag{115}$$

of a single surface whose position is confined to a volume V, and whose area fluctuates through exchange of material with a reservoir of chemical potential $-\sigma$, where $D[\mathbf{X}]$ denotes the path integral measure for a strongly fluctuating surface, which is a generalization of the approximate measure used in Sec. II. This single-surface grand canonical partition function can be expressed in terms of the free energy $F_A(V,\Delta A)$ calculated above as an integral

$$\Xi(V,\sigma) = \int \frac{dA}{\Delta A}\, e^{-\beta[F_A(V,\Delta A)+\sigma A]} \quad . \tag{116}$$

Comparing this to Eq. (109) for the size distribution in a system of many surfaces, we see that

$$\frac{\Xi(V,\sigma)}{V} = \int dA\, \frac{d\rho}{dA} \quad , \tag{117}$$

implying that the integrand in Eq. (116), i.e., the contribution to Ξ from surfaces of a given area, is simply equal to the total number of such surfaces.

Huse and Leibler, who considered the size distribution of an ensemble of spherical vesicles, suggested the following simple and intuitively appealing prescription for the radial size distribution. They noted that the radius and position of a fluctuating vesicle are "naturally viewed as uncertain" over distances less than approximately the thermally induced "roughness," or rms normal displacement, $\Delta_{und} \sim R\sqrt{T/\kappa}$ of the vesicle surface. They then suggested (to paraphrase) that the grand canonical partition function should thus be given by an integral of the form

$$\Xi(V,\sigma) = \int \frac{dR\, V}{\Delta_{und}^4(R)} e^{-\beta[H_R(R)+\sigma' A]} \quad , \tag{118}$$

in which $e^{-\beta[H_R(A)+\sigma' A]}$ is used as a coarse-grained Boltzmann weight, but in which the position and radius of the surface are effectively coarse grained over a length scale Δ_{und}, i.e., in which any two configurations for which the radii or center-of-mass positions differ by less than Δ_{und} should be regarded as identical within a coarse-grained sum over configurations. Upon comparing Eqs. (118) and (114), and using Eq. (117) to relate Ξ to the size distribution, we see that our and HL's results for the size distribution are identical.

Most easily measurable properties of a vesicle phase can be expressed as moments of the size distribution of the form

$$\rho_n \equiv \int_{A_{min}}^{\infty} dA\, A^n \frac{d\rho}{dA} \quad , \tag{119}$$

in which $A_{min} \equiv N_{min} a_s^2$ is a minimum allowable surface area. Quantities of interest include the total number density ρ_0 of disconnected surfaces per unit volume, the total concentration

$$c \equiv \rho_1 \tag{120}$$

of area per unit volume (which is proportional to the total number density c/a_s^2 of surfactant molecules), the total volume fraction

$$\phi \propto \rho_{3/2} \tag{121}$$

of space that is enclosed by the surfaces, and various higher-order moments that can, in principle, be determined by scattering experiments [32].

We are interested primarily in the behavior of these moments in the limit $A_{min} \ll T/\sigma'$ in which the surface area T/σ' characteristic of the exponential falloff of $d\rho/dA$ is much larger than the cutoff area A_{min}, so that our use of a harmonic bending energy remains valid for surfaces of typical size. Using the explicit size dependence of $H_R(R)$, it is straightforward to show that, in this limit, all moments of order $n > B_a + 3/2$ will be dominated by surfaces of area $A \sim T/\sigma'$, and will vary with σ' as

$$\rho_n \propto a^{2n-3} \left(\frac{A_\sigma}{a^2}\right)^{n-\frac{3}{2}-B_a} e^{-H_{bend}[\mathbf{X}_0]/T} \quad , \tag{122}$$

where

$$A_\sigma \equiv T/\sigma' \ . \tag{123}$$

Moments of order $n < B_a + 3/2$, however, will be dominated by surfaces of area $A \sim A_{min}$, and thus will depend sensitively upon the value of A_{min}.

For the physically relevant case of spherical surfaces, for which $B_a + 3/2 = 1/6$, this implies that the enclosed volume fraction ϕ and area density c will remain convergent in the limit $A_{min} \to 0$, but that the total number density ρ_0 of disconnected surfaces will not. The dependence of the characteristic area A_σ upon the total surfactant concentration can thus be obtained by using Eq. (122) to calculate c as a function of σ and then inverting to obtain

$$A_\sigma \sim a^2 (c\, a\, e^{H_0/T})^{6/5} \ . \tag{124}$$

The predicted $A_\sigma \propto c^{6/5}$ dependence of the average surface size upon concentration is probably the most easily testable and sensitive prediction of this theory, since the value of 6/5 for the exponent depends directly upon the value obtained for the prefactor of the logarithmic contribution to the single-surface free energy F_N. Models which ignore all logarithmic contributions to F_N instead yield $A_\sigma \propto c^{1/2}$, and models which take into account the renormalization of the bending energy but ignore all other logarithmic contributions yield $A_\sigma \propto c^{3/10}$.

The total volume fraction $\phi \propto \rho_{3/2}$ enclosed by an ensemble of spherical surfaces can be expressed, according to Eq. (122), by a simple Boltzmann weight

$$\phi \propto e^{-\beta H_R(A_\sigma)} \quad , \tag{125}$$

in which A_σ depends implicitly upon the surfactant concentration via Eq. (124). This expression for ϕ leads immediately to the conclusion that the value of surfactant concentration for which an initially dilute suspension of surfaces will begin to overpack (i.e., for which ϕ approaches unity) is roughly equal to that for which the vesicles have grown to an average radius $R \propto A_\sigma^{1/2}$ such that the renormalized bending energy $H_R(A_\sigma)$ for a sphere of this size vanishes. Increasing the concentration much beyond this overpacking concentration is believed to lead to a transition to a lamellar phase [22,23,19,20], with a lamellar spacing d at the transition that is of the order of the radii of the vesicles in the competing vesicle phase. The conclusion that $H_R(R \sim d)$ is nearly vanishing near this transition is consistent with the simple idea that, upon dilution, the lamellar phase should become unstable towards the formation of vesicles at roughly the lamellar spacing d for which the renormalized bending energy of a sphere of size d vanishes, as discussed previously in Refs. [23,19,20].

The total Helmholtz free energy of a dispersion of surfaces can be obtained by substituting the equilibrium size distribution back into Eq. (107). Doing so yields a total Helmholtz free energy per unit volume (measured relative to a reference state consisting of a planar fluctuating surface) of

$$F/V = -T[\rho_0 + \sigma' \rho_1] \quad . \tag{126}$$

For the physically relevant case of spherical surfaces, the number density of vesicles ρ_0 is much larger in the limit $A_{min} \ll A_\sigma$ of interest than the quantity $\sigma\rho_1$, and is dominated by the contributions of very small vesicles, of area $A \sim A_{min}$, even though most of the area of the system is in much large surfaces, of area $A \sim A_\sigma$. This leads to a free energy density

$$\begin{aligned} F/V &\simeq -T\rho_0 \\ &\simeq \frac{-T}{A_{min}^{1/6} a^{8/3}} e^{-H_0/T} \end{aligned} \tag{127}$$

of roughly $-T$ per vesicle. This free energy density is approximately independent of the value of σ, and thus independent of the total concentration c, throughout the region of validity of Eq. (127), that is, for all concentrations high enough so that $A_\sigma \gg A_c$ but low enough so that $\phi \lesssim 1$, so that the vesicles can be regarded as dilute. At higher concentrations, the free energy density of the vesicle phase is expected to rise rather sharply due to packing constraints, thus leading to the transition to a lamellar phase.

One unexpected feature of the above analysis is the observation that, for spherical vesicles, certain physical quantities (i.e., the number density of vesicles and the free energy density) are divergent in the absence of a lower cutoff on the surface area. It is interesting to ask whether this behavior will also appear in systems involving surfaces of more complicated topology. The convergence or divergence of a given moment ρ_n depends upon both the order n of the moment and the value of the coefficient B_a for the surfaces of interest. Because $\mathbf{X}_0$ is assumed to be the surface that minimizes the bending energy for a given topology, a single equilibrium shape and a single value of B_a can in principle be specified for each topology. An upper bound can be placed on the value of B_a for a specified topology by using the Gauss-Bonnet theorem $\int dA\ K = 4\pi(1-g)$ (where g is the number of handles) to evaluate the term in Eq. (57) involving the Gaussian curvature K, and by noting that the remaining term proportional to $\int dA\ C^2$ is always negative. The resulting inequality,

$$B_a \leq \frac{5}{3}(1-g) \quad , \tag{128}$$

is sufficient to guarantee that $B_a < -3/2$ for all surfaces of genus $g \geq 2$, and thus that for these high-genus surfaces all moments of order $n \geq 0$ will remain convergent in the limit $A_{min} \to 0$. The equilibrium shapes for the remaining cases of low-genus $g = 1$ (toroidal) and $g = 0$ (spherical) surfaces are known, so that values of B_a can be easily calculated, and yield $B_a + 3/2 = -(3/2)(\pi - 1) < 0$ for toroids and $B_a + 3/2 = +1/6 > 0$ for spheres. We thus conclude that $B_a + 3/2 < 0$ for all surfaces with genus $g > 0$, and, consequently, that all moments of order $n \geq 0$ will thus be convergent in the limit $A_{min} \to 0$ for all surfaces of nonspherical topology. This divergence of the number density of surfaces thus appears to be peculiar to spheres.

IV. LINEAR MICELLES

Many of the issues raised here regarding the relationship between internal and collective modes of a flexible aggregate have been raised previously, but not satisfactorily answered, in the context of discussions of rodlike micelles. A long, rodlike or wormlike micelle has in common with a closed two-dimensional membrane the mathematical property that, in the absence of conformational fluctuations, its free energy can be approximated as the sum

$$F_0(N) = N\mu_\infty + \Delta \tag{129}$$

of a term proportional to the number of molecules N in the micelle, where μ_∞ is the free energy per molecule for an infinitely long micelle, plus a length-independent contribution Δ. The contribution Δ arises in a rodlike or wormlike micelle from the defect energy associated with the two ends of the micelle, where the surfactant molecules are packed in a different, and presumably less favorable, environment than in the body of the micelle.

The size independence of the nonextensive part of the free energy makes the thermodynamic properties of a solution of rodlike micelles, like those of a solution of vesicles, extremely sensitive to the presence of any logarithmically size-dependent entropic contributions to the free energy. It has been noted by McMullen, Gelbart, and

Ben-Shaul (MGB) [28] that, if the free energy of a rodlike micelle is formally decomposed as the sum of an internal free energy plus a sum of center-of-mass translational and rigid rotational factors, then the translational and rotational contributions will, like those of a closed membrane, introduce free energy contributions that vary logarithmically with the size of the micelle. If the remaining internal free energy of a rodlike micelle with constrained center-of-mass position and constrained orientation is assumed (incorrectly, as we will show) to be of the form (129), then one obtains a free energy for the unconstrained rod of the form

$$F_N(V) \simeq N\mu_\infty + \alpha T \ln(N) + \Delta - T\ln(V) \qquad (130)$$

where V is the volume of some region to which the center of mass is confined, and where $\alpha = -5$ in the MGB model, in which the micelle is treated in essence as a rigid rod with rotations about all three principal axes. The average aggregation number $\bar{N}$ obtained from a free energy of form (130) is found to vary [28,23] as

$$\bar{N} \propto \rho_{tot}^{1/(2-\alpha)} \qquad (131)$$

with changes in total concentration ρ_{tot}, which yields an extremely slow

$$\bar{N}_{MGB} \propto \rho_{tot}^{1/7} \qquad (132)$$

growth with concentration in the MGB model. Our experience in the preceding sections with the problem of a closed membrane suggests, however, that it is possible for logarithmic contributions to the remaining internal free energy of such an aggregate to reduce or, as in the case of a spherical vesicle, even reverse the sign of the logarithmic size dependence which would be derived from consideration of the collective modes alone. A detailed thermodynamic analysis by Missel *et al.* [29] of dynamic light scattering experiments on suspensions of rodlike sodium dodecyl sulfate micelles showed, moreover, that the concentration dependence of the measured hydrodynamic radius can be fitted quite well by assuming a free energy of form (130) with no logarithmic contribution, i.e., with $\alpha = 0$, which yields an average aggregation number that varies as

$$\bar{N}_{experiment} \propto \rho_{tot}^{1/2} \qquad (133)$$

with concentration.

In order to clarify the relationship between internal and collective degrees of freedom of a one-dimensional aggregate such as a micelle, we consider a simple, exactly solvable model of the micelle as a one-dimensional collection of beads and springs. In considering such a model, we assume that it is not necessary, in order to obtain the correct logarithmic contribution to the free energy, to have an accurate molecular model of the micelle, but that it is sufficient to give a rigorous treatment of the internal degrees of freedom within a simple phenomenological model. We consider here a string of N particles with positions $\mathbf{x}_i$ $(i = 1, \ldots, N)$ that are connected into a chain by an elastic energy of the form

$$H = \sum_{i=2}^{N} v(r_i) - \kappa \sum_{i=2}^{N-1} \hat{\mathbf{r}}_i \cdot \hat{\mathbf{r}}_{i+1} \quad , \qquad (134)$$

in which $\mathbf{r}_i \equiv \mathbf{x}_i - \mathbf{x}_{i-1}$, $r_i \equiv |\mathbf{r}_i|$, $\hat{\mathbf{r}}_i \equiv \mathbf{r}_i/r_i$, κ is a dimensionless bending rigidity, and $v(r)$ is an arbitrary two-body potential. The corresponding partition function is written as

$$Z_N = \prod_{i=1}^{N} \int \frac{d^3x_i}{\lambda^3} e^{-\beta H[\mathbf{x}]} \quad , \qquad (135)$$

where λ is the thermal de Broglie wavlength for a single particle. The above model is sufficiently general to interpolate between the limit of a very rigid rod, which is described by taking $v(r)$ to have a sharp minimum at some nonzero preferred bond length $r = a$ and taking κ to be large, and of a completely flexible Gaussian chain, which is described by taking $\kappa = 0$ and taking $v(r)$ to be a harmonic potential with a minimum at $r = 0$.

The above partition function can be evaluated exactly by an iterative procedure of integrating over the positions of successive monomers. Integrating first over monomer N, while holding the other $N-1$ positions fixed, yields a multiplicative factor

$$q_\kappa \equiv \int \frac{d^3r}{\lambda^3} e^{-\beta[v(r) - \kappa \hat{\mathbf{z}} \cdot \hat{\mathbf{r}}]} \qquad (136)$$

where $\hat{\mathbf{z}}$ is an arbitrary unit vector. Because the three-body term in Hamiltonian (134) was chosen to couple only the directions, and not the magnitudes, of neighboring bond vectors, this factor is independent of the bond vector connecting particles $N-1$ and $N-2$. Consequently, the procedure can be repeated iteratively to remove the first $N-2$ particle on the chain, giving a multiplicative factor of q_κ for each particle, and eventually leaving two particles interacting through a two-body potential $v(\mathbf{r})$ alone. Integrating over the positions of these remaining two particles then gives a total partition function

$$Z = (V/\lambda^3) q_0 q_\kappa^{N-2} \qquad (137)$$

where q_0 is the value of q_κ evaluated with $\kappa = 0$, and V is a volume to which the position of the end particle is confined. This gives a total free energy

$$F = -TN\ln(q_\kappa) + T\ln(q_\kappa^2/q_0) - T\ln(V/\lambda^3) \qquad (138)$$

for the freely rotating and freely translating chain that contains only extensive and N-independent contributions, but no logarithmic contribution, in complete agreement with the experimental results of Missel *et al.* [29]. This result does not depend upon any assumptions about the degree of flexibility of the micelle (i.e., the magnitude of κ), and thus applies equally well to rodlike and wormlike systems.

The underlying reason for the absence of logarithmic terms in Eq. (138) is the separability of the free energy for a one-dimensional system with free ends. The partition function of a long, one-dimensional aggregate for which the position and (for a semiflexible aggregate) the

orientation of one end are constrained can be divided at any point along the chain into the product of corresponding constrained partition functions for the two segments that meet at the chosen point. This property implies that the total free energy of such an aggregate can contain only an extensive contribution and a size-independent contribution arising from the existence of the two ends.

If, however, following MGB, one insists on using a conventional center-of-mass coordinate system to formally decompose the partition function of a rodlike micelle into a product of translational, rotational, and internal factors, then the absence of a logarithmic term in this exact result for the total free energy must be intepreted as the result of an exact cancellation between the calculated logarithmic dependence produced by the translational and rotational contributions and an *inferred* logarithmic finite-size contribution to the remaining internal fluctuation free energy of a micelle with a fixed center-of-mass position and fixed orientation.

That this exact cancellation is a rather special property of quasi-one-dimensional aggregates with *free* ends can be shown by considering the free energy of a completely flexible, one-dimensional *ring* polymer. The free energy of such an object is easily shown to exceed that of a corresponding polymer with free ends by a contribution of order

$$\Delta F_{ring} \sim \frac{3}{2} T \ln(N) \ , \tag{139}$$

which is simply the free energy cost associated with forcing a three-dimensional random walk to return to its origin, and which yields a total free energy with a logarithmic scale dependence. Similarly, no such cancellation was found for the closed two-dimensional surface considered in Sec. II.

One essential physical assumption made in the above is that the micelle is flexible enough so that its longest-wavelength undulation modes can be treated using classical, rather than quantum mechanical, statistical mechanics. The free energy will reduce to that of a truly rigid rod, as assumed by MGB, only in the case of a rod in which the longest-wavelength internal degrees of freedom are quantum mechanically frozen out, i.e., in which their quantum mechanical excitation energies become large compared to T. This situation is rather unlikely to be realized for a large, comparatively weakly bound aggregate such as a micelle, but can be realized for, e.g., a covalently bound diatomic molecule.

V. SUMMARY AND CONCLUSIONS

In the above, we have calculated the size-dependent free energy of a closed undulating membrane, such as a spherical vesicle, and derived the size distribution of a dilute suspension of such surfaces.

Focusing first on the effects of undulations, we used a simple mode-counting argument to show that the undulation contribution F_{und} to the free energy of a single surface contains, in addition to the previously calculated logarithmic contributions arising from the renormalization of the bending rigidities, a universal "finite-size" contribution of magnitude

$$\delta F_{und} \simeq T N_0 \ln\left(\frac{R^2}{\nu^2}\right) \ , \tag{140}$$

in which R is a structural length, ν is an arbitrary configurational space measure, and in which N_0 is the number of Goldstone modes of the surface (i.e., translations, rotations, and polydispersity) for which the bending energy provides no restoring force. The explicit dependence of this contribution upon the number of such zero modes was given a simple physical interpretation in terms of a loss of undulation entropy of order $\ln(R^2/\nu^2)$ per collective mode, due to the destruction of one long-wavelength undulation mode for each collective mode created.

After taking into account the effects of overall translations, we find that the nonextensive part of the total free energy of a spherical surface whose center of mass is confined to a region of volume V and whose area is allowed to fluctuate over a narrow range of values between A and $A + \Delta A$ has a scale dependence of the form

$$F_A \simeq H_R(R) - T \ln\left(\frac{V \, \Delta R}{\Delta_{und}^4(R)}\right) \ , \tag{141}$$

where $H_R(R)$ is a renormalized bending energy for a sphere of equilibrium radius $R \propto (A/4\pi)^{1/2}$, $\Delta R = \Delta A/(8\pi R)$ is the variation in radius which is induced by a variation of magnitude ΔA in area, and

$$\Delta_{und}(R) \sim R\sqrt{T/\kappa} \tag{142}$$

is a length scale of order of the thermal "roughness" of the vesicle's surface R due to thermal undulations. The corresponding results for an asymmetric surface (e.g., a toroid) would differ only through the addition of free energy contributions of order $T \ln(\kappa/T)$ due to the presence of nontrivial rotation modes. The free energy for a physical membrane containing a fixed, integer number N of surfactant molecules is obtained by setting the arbitrary parameter ΔA equal to the average area $a_s^2 = A/N$ occupied by a surfactant molecule within the membrane.

By using the above results for the single-surface free energy to describe a dilute phase of noninteracting spherical vesicles, we obtain a number density of surfaces per unit volume and unit radius of the form

$$\frac{d\rho}{dR} \sim \frac{1}{\Delta_{und}^4(R)} e^{-[H_R(R)+\sigma' A]/T} \ , \tag{143}$$

in which σ' is a chemical potential for the area defined relative to that in a reference state given by a system consisting of a single infinite surface. This is completely identical to the form assumed by Huse and Leibler [18], but differs from that used in a number of other treatments of the vesicle phase [21,14,22,8] in which it was assumed that either $d\rho/dA$ or $d\rho/dR$ was given by the simple Boltzmann factor $e^{-[H_R+\sigma A]/T}$, without the R-dependent prefactor found here. The size dependence of this prefactor is precisely that which is necessary to allow $d\rho/dR$, which has units of (length)$^{-4}$, to be ex-

pressed as a function of the renormalized bending energy and the radius of the surface alone, as expected on physical grounds. The obvious physical interpretation of this result is the one originally proposed by Huse and Leibler: that the renormalized bending $H_R(A)$ of a disconnected surface should be interpreted as the coarse-grained Hamiltonian (i.e., free energy) for a surface whose position and radius are left uncertain (i.e., are allowed to vary) over distances of the order of the typical roughness $R\sqrt{T/\kappa}$ of the surface due to thermal undulations. The contribution of the present analysis has been to put this idea, which was originally proposed on purely heuristic grounds, on a firm footing by deriving it from a quasimicroscopic treatment of the Helfrich Hamiltonian. The crucial element in this analysis has been a clarification of the role of finite-size contributions to the undulation free energy in determining the final size distribution.

Upon taking into account the scale dependence of both $H_R(A)$ and $\Delta_{und}(R)$, Eq. (143) yields a size distribution for a dilute phase of spherical vesicles of the form

$$\frac{d\rho}{dR} \sim \frac{1}{R^{4/3}} e^{-[H_0+\sigma' A]/T} \quad , \tag{144}$$

where $H_0 = 4\pi(2\kappa + \bar{\kappa})$ is the unrenormalized bending energy of a sphere. The divergence at small radii is the result of the dominant influence of the finite-size contribution to F_{und}, and must be cut off by the introduction of some sort of lower cutoff on the vesicle radius. This result is quite different from that of several earlier models [21,14,22,8] in which the algebraic prefactor was assumed to arise only from the renormalization of the bending rigidities, which by itself would yield a prefactor that *vanishes* algebraically at small R, thus producing a broad peak in the distribution at radii of order $\sqrt{T/\sigma'}$. The above size distribution yields a typical vesicle radius $\bar{R} \sim \sqrt{T/\sigma'}$ that grows as

$$\bar{R} \propto c^{3/5} \tag{145}$$

with changes in total surfactant concentration c, in contrast to earlier predictions [22,8] of a much weaker $\bar{R} \propto c^{3/20}$ concentration dependence.

What can these results tell us about the existing experiments on vesicle phases? To date, dilute, thermodynamically stable phases of unilamellar vesicles have been observed in at least three classes of systems:

(i) mixtures of cationic and anionic surfactants with brine [5],

(ii) mixtures of ionic surfactants and alcohol cosurfactant with brine [7,8], and

(iii) a single example of a quasibinary mixture of surfactant (the ganglioside GM3) and brine [6].

Two distinct sets of theoretical ideas have been proposed to explain why equilibrium vesicle phases might be formed.

(i) "Enthalpic stabilization"—by this we mean any mechanism in which a bilayer will bend spontaneously in order to minimize its internal free energy. The most important such mechanism is the one proposed by Safran *et al.* [46], in which it is suggested that the free energy of a two-component bilayer may sometimes be minimized by a state of nonzero preferred curvature, due to the spontaneous formation of different chemical compositions in the top and bottom monolayers.

(ii) "Entropic stabilization"—this is the phenomenon described in this paper, in which the internal free energy of the bilayer is assumed to be lowest in a flat conformation, but in which vesicles can nonetheless be formed at sufficiently low surfactant concentrations and low rigidity due to the combined effects of translational entropy and renormalization of the bending elasticity.

The thermodynamic behaviors predicted from these two kinds of model differ qualitatively in the form of the predicted vesicle size distribution and, most importantly, in the predicted variation of the average vesicle size under changes in total surfactant concentration ρ_{tot}. In an enthalpically stabilized vesicle phase, for which there is some preferred vesicle radius set by the curvature that minimizes the internal free energy per molecule of the membrane, one expects a size distribution with a peak at or near this preferred radius, and, consequently, an average radius that changes very little with changes in ρ_{tot}. In contrast, the above analysis of an entropically stabilized phase predicts a broad distribution of sizes peaked at some microscopic cutoff size, and an "average" radius $\bar{R} \propto \sqrt{T/\sigma}$ (as given experimentally by, e.g., the ratio of the enclosed volume fraction to the surfactant concentration c) that, when $\bar{R}$ is substantially larger than the cutoff size, should vary comparatively rapidly with changes in concentration.

Of the three classes of vesicle-forming systems mentioned above, it is only for the first two (cationic-anionic surfactant mixtures and surfactant-alcohol mixtures) that enough data exist to allow a meaningful comparison of theory and experiment. The properties of the GM3-brine system have been studied [6] by light scattering only at a single concentration, for which the vesicle phase was found to coexist with a more concentrated (possibly lamellar) surfactant phase. Thus no information exists regarding the variation of vesicle size with concentration.

The various systems of mixed cationic-anionic vesicles studied by Kaler *et al.* [5] have been found to exhibit average radii of $\bar{R} \sim$ 200–800 Å that, for fixed relative concentrations of the two surfactant species and concentrations and at concentrations above the critical micellar concentration of both species [47], seem to be nearly independent of total surfactant concentration. Preliminary measurements of the size distribution by analysis of freeze-fracture images seem to exhibit a peak centered near this average size. The behavior of these systems thus seems to be broadly consistent with that expected for an enthalpically stabilized phase. This conclusion is consistent with the analysis of Safran *et al.* [46], whose theoretical work on enthalpically stabilized mixed-surfactant systems was motivated by the existence of these systems.

Our own interest in vesicle phases was originally motivated by the work of Hervé *et al.* [8] on an equilibrium vesicle phase found in a mixture of an ionic surfactant [sodium dodecyl sulfate (SDS)], an alcohol (octanol), and brine. A unilamellar vesicle phase is found to exist in this system within a very narrow range of relative concentra-

tions of surfactant and alcohol, and within a range of surfactant concentrations between a few hundredths of a percent and 4% by weight, above which the enclosed volume fraction approaches the close-packed limit of 60–70 % and the system begins to form multilamellar vesicles. A measurement of the radial size distribution of vesicles, as determined from freeze-fracture images at 2% concentration, indicated the existence of a broad peak centered at a radius $R \simeq 350$ Å with a strongly suppressed density of vesicles for $R \lesssim 200$ Å. By fitting the variation of the enclosed volume fraction (as extracted from conductivity measurements) with surfactant concentration to a power law form for surfactant concentrations of 0.1–1.0 % by weight, Hervé *et al.* found that the average vesicle radius $\bar{R}$ varies as $\bar{R} \propto c^{0.05\pm0.5}$, i.e., that it shows little or no dependence on concentration. Similarly, dynamic light-scattering measurements yielded a hydrodynamic radius of 700 ± 100 Å that was also found to show no noticeable variation with concentration. This is in strong contrast to the $\bar{R} \propto c^{3/5}$ behavior predicted above, which predicts a variation of $\bar{R}$ over roughly a factor of 4 when c is varied over a decade. This observed behavior is thus clearly incompatible with that predicted for a dilute entropically stabilized phase of large surfaces, and is actually much more consistent with that expected for a system with an enthalpically preferred vesicle size. The original analysis of the SDS-octanol vesicle phase by Hervé *et al.* [8] as an entropically stabilized system was based upon an earlier, and flawed, model of such a system.

We wish to suggest two possible explanations for the behavior observed by Hervé *et al.* First, it is possible that the vesicle phase is stabilized in this system by an enthalpic mechanism similar to that proposed for the mixed surfactant membranes, in which the surfactant and alcohol could partially demix within the membrane to produce top and bottom monolayers with slightly different chemical compositions. Such a spontaneous phase separation of alcohol and surfactant would, however, be completely unexpected, since the addition of an alcohol cosurfactant has thus far been assumed to modify the elastic properties of a membrane but to leave unchanged the validity of a description of the bilayer in terms of a simple Helfrich bending energy. Alternatively, it is also possible that the vesicle phase is entropically stabilized but that the effects of anharmonic contributions to the bending energy, which we have mimicked above through the use of a lower cutoff on the allowed range of vesicle sizes, are much larger than one might naively expect, and are large enough to produce an effective lower cutoff radius of about 200 Å. The existence of such a large cutoff radius could (if the number density of vesicles was sufficiently high, as would be caused by a low value for the harmonic bending energy) cause the average radius to remain near this cutoff value throughout the range of concentrations for which the system remains dilute.

For the sake of simplicity, we have restricted ourselves in the above to bilayer membranes, or monolayers with zero spontaneous curvature. Essentially identical considerations apply, however, to droplet microemulsion phases, for which there is a much larger body of experimental data. Future work [33] will aim to clarify the interpretation of experiments that attempt to extract the monolayer elastic parameters, and particularly the value of the Gaussian rigidity $\bar{\kappa}$, from measurements of various thermodynamic properties of droplet microemulsions.

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APPENDIX A: REGULARIZATION ON A CURVED SURFACE

In this Appendix, we consider the problem of choosing a regularization operator Ψ for use on a curved surface. We begin by considering the physical requirements that our choice of Ψ should, if possible, satisfy.

Any proposed choice for Ψ can, as an operator in the Hilbert space of functions on the surface $\mathbf{X}_0$, be represented in coordinate space as a function $\Psi(\sigma, \sigma')$ of two positions on this surface. On a flat surface, where Ψ is chosen to be diagonal in a basis of plane waves, the function $\Psi(\sigma, \sigma')$ can always be expressed as a localized function $\Psi(|\sigma - \sigma'|/a)$ of the separation between points σ and σ', where $\Psi(|\sigma - \sigma|'/a)$ is simply the 2D Fourier transform of $\tilde{\Psi}(q^2a^2)$ with respect to q. Similarly, we expect that on a curved surface $\Psi(\sigma, \sigma')$ will continue to be a localized distribution function for which the value of $\Psi(\sigma, \sigma')$ is large only for points separated by a distance $|\sigma - \sigma'| \lesssim a$. The additional physical conditions which must be satisfied by this distribution function can, we now argue, be expressed by requirements that

$$\int dA\ \Psi(\sigma, \sigma') = 1\ , \tag{A1}$$

$$\Psi(\sigma, \sigma')|_{\sigma=\sigma'} = \frac{1}{a^2} \tag{A2}$$

for all σ and σ', where $dA \equiv d^2\sigma\sqrt{g}$ is the surface element for point σ.

The first condition, Eq. (A1), is simply an expression of the requirement that, if the operator Ψ is not to affect the contributions of very-long-wavelength undulations, it should act like the unity operator (i.e., like a δ function) when convoluted with height functions that vary smoothly over distances large compared to a. This immediately yields the above requirement that Ψ should have the same normalization as a δ function. On a flat surface, this is simply equivalent to the requirement that the function $\tilde{\Psi}(q^2a^2)$ should approach unity for vanishing q, since only the uniform $q = 0$ component of $\Psi(\sigma, \sigma')$ contributes to the integral in Eq. (A1).

The second condition, Eq. (A2), is an expression of the requirement that the local effective patch size, as defined by the local area per independent degree of freedom, be spatially homogenous and everywhere equal to

some specified value a^2. The identification of $1/\Psi(\sigma,\sigma)$ as the appropriate definition of the local effective patch area follows immediately from the coordinate space representation

$$N = \int dA\ \Psi(\sigma,\sigma')|_{\sigma=\sigma'} \tag{A3}$$

of the trace in Eq. (46), in which the total number of modes N is expressed as the surface integral of a local mode density given by $\Psi(\sigma,\sigma)$. On a flat surface, this condition simply yields Eq. (47) for the mode density on such a surface.

The most natural generalization of the regularization scheme used on a flat surface is obtained by defining Ψ on a curved surface to be an operator function $\Psi \equiv \tilde{\Psi}(-\nabla^2 a^2)$ of the Laplacian operator ∇^2 for the surface in question. This form for Ψ, which we will call Ψ_{naive}, can be expressed as an expansion

$$\Psi_{naive}(\sigma,\sigma') \equiv \sum_{\beta=0}^{\infty} \phi_\beta(\sigma)\tilde{\Psi}(q_\beta^2 a^2)\phi_\beta^*(\sigma') \tag{A4}$$

in a basis of eigenfunctions of the Laplacian which satisfy

$$-\nabla^2\phi_\beta(\sigma) = q_\beta^2\phi_\beta(\sigma) \quad , \tag{A5}$$

where the generalized "wave numbers" appearing in $\tilde{\Psi}(q_\beta^2 a^2)$ are defined in terms of the corresponding eigenvalues of ∇^2, and where, as elsewhere in this article, we will assume that the form of $\tilde{\Psi}$ has been chosen to satisfy Eq. (47) on a flat surface with a cutoff parameter $b = a$. The above form of Ψ is the one used in essentially all previous calculations [13–15], and is the most practical choice for calculation.

We now consider whether an operator of form (A4) can satisfy Eqs. (A1) and (A2). An operator of this form will satisfy condition (A1) as long as $\tilde{\Psi}(q_\beta^2 a^2)$ approaches unity as q_β approaches zero, since, as on a flat surface, only the uniform $q_\beta = 0$ component of Ψ_{naive} contributes to the integral in Eq. (A1). To determine whether an operator of this form can also satisfy Eq. (A2), we consider a specific form

$$\Psi_{naive}(\sigma,\sigma') = \sum_{\beta=0}^{\infty} \phi_\beta^*(\sigma)\phi_\beta(\sigma')e^{-q_\beta^2 a^2/(4\pi)} \tag{A6}$$

for Ψ, in which $\tilde{\Psi}(x)$ is an exponential, so that Ψ is simply the diffusion propagator for the surface of interest, where b^2 is proportional to an imaginary diffusion time. The behavior of this function in the physically relevant limit $a \ll R$ corresponds to the "short-time" behavior of the propagator, which has been discussed previously in the mathematical and field-theory literature [15,48,49]. It is known [15] that the desired value $\Psi(\sigma,\sigma)$ can be expressed in the limit $a \ll R$ as an expansion

$$\Psi_{naive}(\sigma,\sigma) = \frac{1}{a^2} + \frac{K(\sigma)}{12\pi} + \cdots \ , \tag{A7}$$

in which the first nontrivial term is proportional to the local Gaussian curvature. Integrating with respect to area then gives a corresponding total number of degrees of freedom

$$N_{naive} = \frac{A}{a^2} + \frac{1}{12\pi}\int dA\ K + \cdots \tag{A8}$$

that differs by a number of $O(1)$ from that expected on a flat surface of equal area.

This curvature dependence of $\Psi(\sigma,\sigma)$ can be understood in terms of the modified relationship between area and distance on a curved surface: The locus of points that are within a fixed distance b (as measured along a geodesic) of a point σ' has a slightly smaller area on a surface of positive curvature K, such as a sphere, than it does on a flat surface, and a slightly larger area on a surface of negative K, such as a saddle point. Correspondingly, there is somewhat less area for the diffusion propagator to explore on a surface of positive K after a given "time" a^2, and so the propagator remains slightly more localized on such a surface than on a surface of zero curvature, leading to a larger value of $\Psi(\sigma,\sigma)$ and a smaller effective patch area.

We now show that the curvature dependence of $\Psi(\sigma,\sigma)$ found above is not specific to the diffusion propagator, but is instead a general property of operators of the form Ψ_{naive}. To do this, it is useful to construct a representation of N as an integral over contributions with different wave numbers rather than as a surface integral. We define a density of states per unit area

$$\rho(\omega) \equiv \frac{1}{A}\sum_\beta \delta(\omega - q_\beta^2) \tag{A9}$$

as a function of the squared wave number $\omega \equiv q^2$. We can express N in terms of this quantity as an integral

$$N_{naive} = A\int_0^\infty d\omega\ \rho(\omega)\tilde{\Psi}(\omega b^2) \quad . \tag{A10}$$

In the limit of an infinite planar surface, it is straightforward to show that $\rho(\omega)$ approaches an ω-independent constant

$$\lim_{R\to\infty}\rho(\omega) = \frac{1}{4\pi} \tag{A11}$$

for all $\omega > 0$. On a curved surface with typical radius of curvature R, the behavior of $\rho(\omega)$ depends upon the ratio of the wavelength q^{-1} of interest and the structural length R. For $qR \gg 1$, the membrane appears nearly flat over the length scales of interest, and ρ is expected to approach the value $1/(4\pi)$ characteristic of a planar surface. For $qR \lesssim 1$, however, the nontrivial structure of the surface $\mathbf{X}_0$ can strongly affect the spectrum of ∇^2, and so the density of states can deviate significantly from that of a planar surface. If we assume that the deviation

$$\delta\rho(\omega) \equiv \rho(\omega) - \frac{1}{4\pi} \tag{A12}$$

from planar behavior is significant (i.e., of order unity) only for wave numbers $q \lesssim R^{-1}$, we can rewrite N as

$$N_{naive} \simeq \frac{A}{a^2} + A\int_0^\infty d\omega\ \delta\rho(\omega) \quad , \tag{A13}$$

where we have used the assumption that $\delta\rho(\omega)$ is significant only for long-wavelength modes, and the fact that $\Psi(qa) \to 1$ for wave numbers $qa \ll 1$, in order to remove the $\tilde{\Psi}$ dependence of the second term on the RHS. By equating expressions (A8) and (A13) for N, we see that, at least for the diffusion operator,

$$\frac{1}{12\pi}\int dA\, K = A\int_0^\infty d\omega\ \delta\rho(\omega)\ . \tag{A14}$$

The fact that the RHS of this equation is actually independent of our choice of $\tilde{\Psi}$ then implies that the curvature-dependent contribution to N found in Eqs. (A7) and (A8) must also be independent of the form of $\tilde{\Psi}$, and is not specific to the diffusion operator alone.

The existence of this curvature dependence of the naive density of modes implies that the use of the same naive regularization operator on different surfaces can yield different effective patch areas, thus making it unphysical to compare the corresponding naive free energies. This problem is similar in some respects to the one discussed in Ref. [35], in which the authors carry out a Monge-gauge treatment of a membrane fluctuating about a planar equilibrium, and show that the most obvious cutoff scheme gives a local patch area that varies with the instantaneous orientation of the surface. The most conceptually straightforward way of fixing such a problem, and the one we will use here, is to invent a modified regularization scheme that, to the required accuracy, does preserve the local patch area. To do so, we define a spatially inhomogeneous cutoff parameter

$$b_\sigma^2(\sigma) = a^2\left[1 + \frac{a^2}{12\pi}K(\sigma) + \cdots\right] \tag{A15}$$

that gives the value of the parameter b which would yield the desired value of $\Psi_{naive}(\sigma,\sigma) = 1/a^2$ at some specified point σ. We then formally define a modified operator

$$\Psi \equiv \tilde{\Psi}(-b_\sigma^2\nabla^2) \tag{A16}$$

in which we simply replace the parameter a^2 appearing in Ψ_{naive} by the spatially varying function b_σ^2 defined above. This simple substitution of a function for a parameter makes sense because the inhomogeneous part of $b^2(\sigma)$ is both very small and very slowly varying over distances of order a, so that the quantity $b^2(\sigma)$ can to a very good accuracy be treated as a constant in determining its effect upon the rapidly varying function $\Psi(\sigma,\sigma')$.

In order to calculate with this operator, we simply Taylor-expand it as power series in $a^2K(\sigma)$. Expanding to first order as

$$\Psi = \Psi_{naive} + \delta\Psi\ , \tag{A17}$$

we obtain a correction term

$$\delta\Psi = -\tilde{\Psi}'(-\nabla^2 a^2)\frac{a^4K}{12\pi}\nabla^2\ , \tag{A18}$$

in which $\tilde{\Psi}'$ denotes the function $\tilde{\Psi}'(x) \equiv d\tilde{\Psi}(x)/dx$. To calculate the free energy, we make a corresponding expansion

$$F_{und} = F_{naive} + \delta F \tag{A19}$$

as the sum of the naive free energy F_{naive}, calculated using $\Psi = \Psi_{naive}$ and $b = a$, and a correction term

$$\delta F \equiv \frac{T}{2}\mathrm{Tr}'\left[\ \ln\left(\mathcal{L}\frac{\nu^4}{2\pi T}\right)\ \delta\Psi\ \right] \tag{A20}$$

involving $\delta\Psi$.

We now extract the dominant behavior of δF in the limit $a \ll R$. Because of the extra factor of a^2K that appears in definition (A18) for $\delta\Psi$, the corresponding correction δF_{und} to the free energy is smaller by a factor of $O(a^2/R^2)$ than that given by F_{naive}. As a result, we need consider only the dominant contribution to F_{und}, which is R independent, and which is dominated by the contributions of short-wavelength modes, with $q \gg R^{-1}$. This dominant contribution to δF_{und} can be obtained by treating K as a slowly varying quantity and treating the eigenfunctions of ∇^2 locally as plane waves, giving a contribution

$$\delta F_{und} = \frac{\partial f_{und}}{\partial a^2}\frac{a^4}{12\pi}\int dAK \quad . \tag{A21}$$

It is clear from the dependence of the above upon the Euler characteristic $\int dAK$ that this free energy contribution can be regarded as a contribution to the renormalization of $\bar{\kappa}$. As we show in Appendix B, it is the existence of this contribution that accounts for the difference between the value of $\bar{\alpha} = 4$ originally obtained by Kleinert [14] for the renormalization coefficient of $\bar{\kappa}$ and the (correct) value of $\bar{\alpha} = 10/3$ obtained by David [15].

It is straightforward to show that this value for δF_{und} could also have been obtained by the simpler procedure of using the naive form for the regularization operator but choosing the value of the global parameter b so as to give the correct total number (rather than local number density) of modes for each surface. By conserving the local density of modes, we have thus been somewhat more careful than was strictly necessary, since the correct final answers for B_a and B_ν can apparently be obtained by the use of any cutoff scheme that keeps the total number of degrees of freedom proportional to the area of the surface.

APPENDIX B: CALCULATION OF F_{und}

In this Appendix, we carry out an explicit calculation of the undulation free energy F_{und} for a general closed surface. Our calculation proceeds by two steps. We first calculate an undulation free energy F_{naive} which is defined by using a naive regularization operator of form (A4) in Eq. (43). We then calculate the correction term δF_{und} defined in Eq. (A20) and add this to F_{naive}.

To calculate F_{naive}, we first assume that it, like F_{und}, can be expressed as an expansion of the form

$$\frac{F_{naive}}{T} = A\frac{f_{und}}{T} + B'_a \ln\left(\frac{R^2}{a^2}\right) + B'_\nu \ln\left(\frac{R^2}{\hat{\nu}^2}\right) + C' \ , \tag{B1}$$

where B'_b, B'_ν, and C' are scale-independent constants, and where F_{naive} and f_{und} are evaluated with $b = a$.

We calculate the coefficient B'_ν by comparing the dependence of Eqs. (43) and (B1) upon the parameter $\hat{\nu}$, as done in subsection II B to determine the parameter B_ν in the physical free energy F_{und}. Expansion (B1) depends upon $\hat{\nu}$ through an additive contribution

$$\delta F_{naive} = T\left(\frac{A}{a^2} - B'_\nu\right)\ln(\hat{\nu}^2) \ , \tag{B2}$$

whereas definition (43) contains a corresponding contribution

$$\delta F_{naive} = T N_{und} \ln(\hat{\nu}^2) \ , \tag{B3}$$

where $N_{und} = N_{naive} - N_0$ is the number of undulation modes obtained with a naive regularization. Equating these two contributions, and using Eq. (A8) for N_{naive}, gives a coefficient

$$B'_\nu = N_0 - \frac{1}{12\pi}\int dA K \ . \tag{B4}$$

This coefficient differs from the value of N_0 predicted in Sec. II B precisely because the naive regularization used to calculate it gives an area per degree of freedom which depends upon the curvature of the surface, as discussed in Appendix A.

To calculate the coefficient B'_b we must examine the dependence of F_{naive} upon the cutoff b. This can be accomplished by examining the derivative of $\hat{F}_{und}$ with respect to a, as done in several previous treatments [13–15]. We first expand the logarithm in Eq. (43) in powers of the curvature-dependent contributions to the operator $\mathcal{L}$ defined in Eq. (41). Keeping only those terms that contribute in the limit $b/R \to 0$, we obtain an expansion

$$F_{naive} \simeq \frac{T}{2}\mathrm{Tr}'[\ \ln(\nabla^4\hat{\nu}^4)\Psi\ ] + \frac{T}{2}\mathrm{Tr}'\left[\ \frac{\mathcal{L}_2^{ij}\nabla_i\nabla_j}{\nabla^4}\Psi\ \right] + T(\mathrm{const}) \ . \tag{B5}$$

The first term in the above can be shown to diverge as A/a^2, yielding the extensive contribution in Eq. (B1), while the second term yields the $\ln(R/a)$ contribution. To obtain the coefficient of this logarithmic term, we differentiate Eq. (B5) with respect to a^2, which appears only in the weighting function η, yielding an expression that is dominated by the contributions of modes of wave number $q \sim a^{-1}$. By approximating these short-wavelength modes locally as plane waves, thus converting the trace to a Fourier integral, and treating $\mathcal{L}_2^{ij}(\sigma)$ as a slowly varying function of position, we obtain

$$\frac{\partial F_{naive}}{\partial a^2} \simeq A\frac{\partial \hat{f}_{und}}{\partial a^2} + \frac{T}{2a^2}\int dA\ \mathcal{L}_2^{ij}(\sigma)\int \frac{d^2k}{(2\pi)^2}\hat{k}_i\hat{k}_j\tilde{\Psi}'(k^2) \ , \tag{B6}$$

where $k \equiv qa$, $\hat{\mathbf{k}} \equiv \mathbf{k}/k$, and $\tilde{\Psi}'(x) \equiv d\tilde{\Psi}/dx$. Comparing Eqs. (B1) and (B6), we identify the second term in (B6) as the coefficient B'_b, and use the explicit curvature dependence of $\mathcal{L}_2^{ij}$ to obtain the coefficient

$$B'_a = \int dA\ \{\ -\tfrac{1}{2}\alpha' C^2 + \bar{\alpha}' K\ \} \tag{B7}$$

where

$$\alpha' = 3, \quad \bar{\alpha}' = 4 \ . \tag{B8}$$

The above values of α' and $\bar{\alpha}'$ are precisely those found previously by Kleinert [14], who equated these quantities with the coefficients α and $\bar{\alpha}$ that appear in the renormalization of κ and $\bar{\kappa}$. Like the above calculation of B'_b, however, Kleinert's calculation of the renormalized rigidities used a naive cutoff on generalized wave number and considered only the dependence of F_{naive} upon the cutoff length. He thus missed the additional curvature-dependent, but cutoff-independent, contribution to F_{naive} that appears in Eq. (B4) as part of B'_ν.

Our final result for F_{und} is obtained by adding the correction term δF_{und} calculated in Appendix A, as given in Eq. (A21), to the naive free energy obtained above. Explicitly differentiating the factor of f_{und} in Eq. (A21) yields

$$\delta F_{und} = \frac{-1}{12\pi}\left[D_0/4\pi + 1 + \ln\left(\frac{\hat{\nu}^2}{a^2}\right)\right]\int dA K \ , \tag{B9}$$

in which

$$D_0 \equiv \int dx \ln(x)\tilde{\Psi}(x) \tag{B10}$$

is a constant whose value depends upon the functional form of $\tilde{\Psi}$. We see from the above that, while δF_{und} is independent of R, it does contain a contribution proportional to $\ln(\hat{\nu}/a)$. Adding δF_{und} to F_{naive} can thus have no effect on the overall dependence on $\ln(R)$, which is determined by the sum of coefficients $B_R \equiv B'_a + B'_\nu$, but can and does affect the individual coefficients B_a and B_ν of $\ln(a)$ and $\ln(\nu)$.

Adding δF_{und} and F_{und}^{naive} yields a final result for F_{und} which can be expressed as an expansion of form (49), with coefficients given by Eqs. (55) and (57), and with a constant C given by

$$C = C' - \frac{\hat{f}+1}{12\pi}\int dA K \ . \tag{B11}$$

As noted in Sec. II, the resulting values for α and $\bar{\alpha}$ are the same as those obtained previously by David [15].

Since David, like Kleinert, used a naive regularization scheme, it is interesting to see why he nonetheless obtained the correct value of $\bar{\alpha}$. The reason is that David used a regularization scheme in which one implicitly sets $\nu \propto a$, thus giving a calculated free energy with a single logarithmic term of the form $\ln(R^2/a^2)$, with a coefficient

$$B_R = B'_a + B'_\nu = B_a + B_\nu \tag{B12}$$

whose value is the same in either naive or corrected regularization schemes. By correctly evaluating the total curvature dependence of this combined coefficient, he then obtained the correct value for $\bar{\alpha}$. The problems with the naive regularization scheme thus show up only if one attempts to calculate $\bar{\alpha}$ by a straightforward examination of the dependence of the free energy on the naive cutoff length, as done by Kleinert, or if one distinguishes between the lengths a and ν, as we have done here in order to distinguish contributions arising from the short-wavelength and long-wavelength cutoffs on the undulation spectrum.

APPENDIX C: FREE ENERGY OF A SPHERE

In this Appendix, we calculate the free energy of a simple spherical vesicle by directly analyzing the sum over spherical harmonic undulation modes. The normalized undulation modes on a spherical surface of radius R are given by functions

$$\psi_{lm}(\sigma) = Y_{lm}(\sigma)/R \tag{C1}$$

proportional to the spherical harmonics $Y_{lm}(\sigma)$, where σ represents a solid angle. The differential operator $\mathcal{L}$ of Eq. (41) is known to reduce on a spherical surface to

$$\mathcal{L} = \kappa\left(\nabla^4 + \frac{2}{R^2}\nabla^2\right) , \tag{C2}$$

yielding undulation eigenvalues

$$\epsilon_l = \kappa\omega_l\left(\omega_l - \frac{2}{R^2}\right) , \tag{C3}$$

where $-\omega_l \equiv -l(l+1)/R^2$ is an eigenvalue of the Laplacian operator ∇^2 on such a surface. Because of the translational and scale invariance of the bending energy, the above spectrum provides no restoring force either for the three $l = 1$ modes, which generate translations, or for the $l = 0$ dilation mode. The total free energy $F_A(V, \Delta A)$ for an idealized surface whose center-of-mass position is constrained to remain within a volume V and whose area is allowed to fluctuate over a small range of values between A and $A + \Delta A$ is given by a sum

$$F_A(V, \Delta A) = H[\mathbf{X}_0] + F_{\Delta A} + F_{trans} + F_{und} , \tag{C4}$$

where $H[\mathbf{X}_0]$ is the saddle-point value of Hamiltonian (34), $F_{\Delta A}$ arises from fluctuations of the area ($l = 0$), F_{trans} from overall translations ($l = 1$), and F_{und} from undulations ($l \geq 2$).

To calculate the undulation free energy on such a surface, we use a regularization operator of the form

$$\Psi(\sigma, \sigma') = \sum_{lm} \psi_{lm}(\sigma)\psi^*_{lm}(\sigma')\tilde{\Psi}(\omega_l b^2) , \tag{C5}$$

in which b is a parameter with units of length which must be adjusted to give the desired total density of modes. We assume here, as elsewhere in this paper, that the form of $\tilde{\Psi}(x)$ is chosen to give an area $a^2 = b^2$ per degree of freedom on an infinite flat surface. We will first calculate F_{und} as a function of b, R, and ν, and then relate b to the physical patch size a in order to reexpress F_{und} as a function of the physical parameters a, R, and ν.

The undulation free energy can be written as a sum

$$F_{und} = \frac{T}{2}\sum_{l=2}^{\infty}(2l+1)\ln\left(\epsilon_l\frac{\nu^4}{2\pi T}\right)\tilde{\Psi}(\omega_l b^2) . \tag{C6}$$

This is conveniently decomposed as a sum

$$F_{und} = F_1 + \ln\left(\frac{\hat{\nu}^2}{R^2}\right)(N_c - 4) \tag{C7}$$

in which

$$F_1 \equiv \frac{T}{2}\sum_{l=2}^{\infty}(2l+1)\ln[\hat{\omega}_l(\hat{\omega}_l - 2)]\tilde{\Psi}(\omega_l b^2) , \tag{C8}$$

$$N_c = \sum_{l=0}^{\infty}(2l+1)\tilde{\Psi}(\omega_l b^2) , \tag{C9}$$

where $\hat{\omega}_l \equiv \omega_l R^2 \equiv l(l+1)$ is a dimensionless squared wave number and $\hat{\nu^4} \equiv \kappa\nu^4/(2\pi T)$, N_c is the total number of continuum degrees of freedom in the problem, as defined in Eq. (46), and $N_c - 4$ is the total number of undulation modes.

To analyze the sums defining F_1 and N_c, we use the Euler-McLaurin equation

$$\sum_{l=a}^{\infty} g(l) = \int_a^{\infty} g(l)dl - \sum_{j=0}^{\infty}\frac{B_{j+1}}{(j+1)!}\left.\frac{d^j g}{dl^j}\right|_{l=a} , \tag{C10}$$

which relates the value of a discrete sum of an analytic function $g(l)$ to the value of the corresponding integral, and in which B_j are the Bernoulli numbers $B_1 = -1/2$, $B_2 = 1/6$, $B_3 = B_5 = 0$, etc.

We first apply Eq. (C10) to the evaluation of Eq. (C9) for N_c, in which $g(l) = (2l+1)\tilde{\Psi}(\omega_l b^2)$. We note that, because each differentiation of $\tilde{\Psi}(l) = \tilde{\Psi}(\hat{\omega}_l b^2/R^2)$ brings out a prefactor of b^2/R^2 that vanishes in the limit $b/R \to 0$, the derivatives of $g(l)$ that appear in the Euler-McLaurin series can be taken in this limit to act only on the degeneracy factor $2l + 1$. Because the second and higher derivatives of this factor vanish, the resulting series contains only zeroth and first order derivatives, and yields

$$N = A\int_0^{\infty}\frac{d\omega}{4\pi}\,\tilde{\Psi}(\omega b^2) + \frac{1}{3} \tag{C11}$$

where $A = 4\pi R^2$, and where we have defined a continuous function $\omega(l) = l(l+1)/R^2$ and used the fact that

$$d(\omega)R^2 = (2l+1)dl \tag{C12}$$

to simplify the integral. The R-independent contribution of $1/3$ agrees with that obtained by applying Eq. (A8) (which gives the number of degrees of freedom on an arbitrary surface) to a sphere.

Upon applying the Euler-McLaurin series to Eq. (C8) for F_1, we find that at the lower limit of $l = 2$ the func-

tion $\ln[\hat{\omega}_l(\hat{\omega}_l-2)]$ has derivatives of all orders that all remain nonzero in the limit $b \ll R$. We can thus conclude only that the difference between the discrete sum and the integral is a number of order unity whose value cannot be determined from the evaluation of a finite number of terms in Eq. (C10), or that

$$F_1 = A\frac{T}{2}\int_0^\infty \frac{d\omega}{4\pi}\ln[\hat{\omega}(\hat{\omega}-2)]\tilde{\Psi}(\omega b^2) + \text{const} \quad \text{(C13)}$$

where const denotes an unknown numerical constant. From the asymptotic behavior of the integral in the above in the limit $b/R \to 0$, we find that

$$F_1 = AT\int_0^\infty \frac{d\omega}{4\pi}\ln(\hat{\omega})\tilde{\Psi}(\omega b^2) - T\ln\left(\frac{R^2}{b^2}\right) + D_1[\tilde{\Psi}] + \text{const} \quad \text{(C14)}$$

in this limit, where const denotes a numerical constant, and

$$D_1[\tilde{\Psi}] \equiv \int_0^\infty dx\ \ln(x)\frac{d\tilde{\Psi}(x)}{dx} \quad \text{(C15)}$$

is a number whose value depends explicitly upon the functional form of function $\tilde{\Psi}$.

Combining Eqs. (C11) and (C14) then gives a total undulation free energy of the form

$$F_{und} = Af_{und}(b) - T\ln\left(\frac{R^2}{b^2}\right) + \frac{11}{3}T\ln\left(\frac{R^2}{\hat{\nu}^2}\right) + C' \quad \text{(C16)}$$

in which $f_{und}(b)$ is the value of the free energy density given in Eq. (51) evaluated with a replaced by b, and in which

$$C' = 0.1275 + D_1[\tilde{\Psi}] \quad . \quad \text{(C17)}$$

The value of the numerical constant in the above was obtained by numerically evaluating the sum in Eq. (C6) and subtracting the analytically calculated asymptotic form from the numerical free energy calculated for various choices of R, a, ν, κ, and $\tilde{\Psi}(x)$.

In order to compare free energies for spheres of different sizes, we wish to express this free energy as a function of the area per continuum degree of freedom $a^2 \equiv A/N_c$ rather than as a function of the parameter b. Using Eq. (C11) to relate b to a, while assuming that $\tilde{\Psi}$ is chosen to give $b = a$ on a flat surface, gives a parameter value

$$b^2 = a^2\left[1 + \frac{a^2}{12\pi R^2} + \cdots\right] . \quad \text{(C18)}$$

Using this to reexpress F_{und} as a function of a then yields

$$F_{und} = Af_{und}(b) - \frac{4}{3}T\ln\left(\frac{R^2}{a^2}\right) + 4T\ln\left(\frac{R^2}{\hat{\nu}^2}\right) + C_{und} \ , \quad \text{(C19)}$$

in agreement with Eqs. (57) and (55), with a constant

$$C_{und} = -0.2059 + D_1[\tilde{\Psi}] - \frac{1}{12\pi}D_0[\tilde{\Psi}] \ . \quad \text{(C20)}$$

The contribution F_{trans} of the $l = 1$ translational modes is most easily calculated using normalized eigenmodes of the form

$$\psi_\alpha(\sigma) = \sqrt{\frac{3}{4\pi R^2}}\,\hat{\mathbf{n}}_0(\sigma)\cdot\hat{\mathbf{e}}_\alpha \ , \quad \text{(C21)}$$

where $\hat{\mathbf{n}}_0(\sigma)$ denotes the unit normal to the sphere at solid angle σ, and $\hat{\mathbf{e}}_\alpha$ denotes one of three Cartesian unit vectors, with $\alpha = 1,2,3$. The variation in mode amplitude h_α that is induced by a rigid translation of the surface by a physical displacement dX_α in the direction α is given by $dh_\alpha = \sqrt{4\pi R^2/3}\,dX_\alpha$. The translational free energy F_{tran} for a vesicle whose center of mass is confined to a region of volume $V = dX_1dX_2dX_3$ is thus

$$F_{trans} = -T\ln\left[\frac{VR^3}{\nu^6}\left(\frac{4\pi}{3}\right)^{3/2}\right] \quad . \quad \text{(C22)}$$

The free energy contribution $F_{\Delta A}$ associated with fluctuations of the area is obtained by using the Jacobian

$$J_A^{-1} \equiv \partial A/\partial h_{00} = \sqrt{16\pi} \ , \quad \text{(C23)}$$

and letting A vary over a range of width ΔA, to obtain

$$F_{\Delta A} = -T\ln\left(\frac{\Delta A}{\sqrt{16\pi}\,\nu^2}\right) . \quad \text{(C24)}$$

Combining Eqs. (C19), (C22), and (C24) yields a total free energy

$$F_A(V,\Delta A) = Af_{tot}(a) + H_{bend}[\mathbf{X}_0] - \frac{4}{3}T\ln\left(\frac{R^2}{a^2}\right) - T\ln\left(\frac{V}{R^5}\frac{\Delta A}{T^2}\frac{\kappa^2}{T^2}\right) + C_F \ , \quad \text{(C25)}$$

in which $f_{tot} = r + f_{und}(a,\nu)$ and

$$C_F = 3.2799 + D_1[\tilde{\Psi}] - \frac{1}{12\pi}D_0[\tilde{\Psi}] \ . \quad \text{(C26)}$$

The dependence of C_F upon the form of the regularization function $\tilde{\Psi}$ can quite generally be absorbed into a corresponding dependence of the values of the phenomenological rigidities κ and $\bar{\kappa}$ on the form of the function $\tilde{\Psi}$ as well as the value of the nominal length a. The coefficient C_ρ that appears in size distribution (113) is given by $C_\rho \equiv e^{-C_F}$.

For the case where $\tilde{\Psi}(x)$ is taken to be the exponential function $\tilde{\Psi}(\omega b^2) = e^{-\omega b^2/4\pi}$ (i.e., a diffusion propagator), in which the factor of $1/4\pi$ in the exponential is included in order to set $a = b$ on a flat surface, we obtain

$$C_F = 0.6748, \quad C_\rho = 0.5092 \ . \quad \text{(C27)}$$

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[36] The inclusion of the factor of J in Eq. (7) converts the naive path integral measure $\prod dh(\sigma)$, which weights infinitesimal surface displacements by the degree of displacment measured along the direction $\hat{\mathbf{n}}_0$ normal to the reference surface into a covariant measure
$$D[\mathbf{X}] = \prod_\sigma \frac{dh(\sigma)\ \hat{\mathbf{n}}(\sigma)\cdot\hat{\mathbf{n}}_0(\sigma)}{\lambda} \quad ,$$
which instead weights displacements by the infinitesimal displacement $d\xi(\sigma) \equiv dh(\sigma)\ \hat{\mathbf{n}}(\sigma)\cdot\hat{\mathbf{n}}_0(\sigma)$ measured in the direction normal to the physical surface $\mathbf{X}$ [34,35]. Similarly, in Eq. (8) the inclusion of the factor of J^{-1} converts the naive δ function $\delta(h_i - h(\sigma_i))$ into a covariant δ function.
[37] Our identification of λ with a thermal de Broglie wavelength of a molecule or patch should therefore probably not be assigned much physical significance. Within the context of a continuum model, λ may be thought of instead as an arbitrary coarse-graining length for normal displacements, just as a is a coarse-graining length for distances within the local tangent plane of the membrane, so that a patch of membrane must be displaced by a distance λ or greater before its new position is treated as distinct from its old one in the sum over configurations of the membrane. Any free energy contributions arising from normal displacements of the surface over distances less than λ are, like the contributions of undulation modes of wavelength less than a, implicitly included within the values of the phenomenological parameters of the model, i.e., the bending rigidities and, for systems containing a variable number of surfactant molecules, the surfactant chemical potential. The values of these phenomenological parameters must therefore be understood to depend upon the values of λ and a in a way that leaves observable properties such as the size distributions invariant.
[38] This normalization is slightly different from that used in our calculation of Ref. [23] for a sphere, in which we used $\psi_\alpha = (a/R)Y_{lm}$, with Y_{lm} a spherical harmonic, which corresponds to a normalization condition of $\int dA\psi^*_\alpha\psi_\beta = a^2\delta_{\alpha\beta}$.
[39] This representation can be obtained more directly by starting with a partial phase-space integral which is written in terms of the continuum displacement field $h(\sigma)$ and its conjugate momentum $\pi(\sigma) \simeq \varrho\ dh(\sigma)/dt$. Integrating over the positions and momenta of the solvent molecules and over the in-plane positions and tangential momenta of the surfactant molecules yields an effective Hamiltonian of the form $H[h] + T[\pi]$ for the remaining normal displacement and momentum fields h and π, where $H[h]$ is a constrained free energy of the surface, and where $T \simeq \varrho^{-1}\langle\pi|\pi\rangle$ is the component of the kinetic energy which arises from the normal components of the surfactant molecule momenta. After transforming from a local to a collective-mode representation for the h and π fields, integrating over each component of the π field then yields a denominator of ν^2 for the corresponding component h_α of the h field.

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[41] See, e.g., R. K. Pathria, *Statistical Mechanics* (Pergamon, New York, 1972), p. 493. The common approximation of $\ln(n!) \simeq n[\ln(n) - 1]$ can be derived by evaluating the integral representiation $n! = \Gamma(n+1) = \int dx\ x^n e^{-x}$ in a saddle-point approximation, while the logarithmic contribution is obtained by including harmonic fluctuations about the saddle point.
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