The effect of thermal fluctuations on Schulman area elasticity

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Abstract. We study the elastic properties of a two-dimensional fluctuating surface whose area density is allowed to deviate from its optimal (Schulman) value. The behavior of such a surface is determined by an interplay between the area-dependent elastic energy, the curvature elasticity, and the entropy. We identify three different elastic regimes depending on the ratio $A_{\mathrm{p}}/A_{\mathrm{s}}$ between the projected (frame) and the saturated areas. We show that thermal fluctuations modify the elastic energy of stretched surfaces ($A_{\mathrm{p}}/A_{\mathrm{s}} > 1$), and dominate the elastic energy of compressed surfaces ($A_{\mathrm{p}}/A_{\mathrm{s}} < 1$). When $A_{\mathrm{p}} \sim A_{\mathrm{s}}$ the elastic energy is not much affected by the fluctuations; the frame area at which the surface tension vanishes becomes smaller than A_{s} and the area elasticity modulus increases.

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1 Introduction

Surfactant molecules are formed by chemically bonding two parts with different affinities to solvents — a hydrophilic head group (usually ionic or polar), and a hydrophobic tail (usually composed of non-polar hydrocarbon groups). When these molecules are placed in a mixture of water and oil they tend to rest at the water-oil interface and decrease the interfacial energy substantially [1]. An interface that is saturated by surfactants (as in the case of some surfactant mixtures) has a *nearly vanishing surface tension* [2]. Other interfacial systems which are frequently assumed to have zero surface tension are amphiphilic fluid bilayers [3]. Models ignoring surface tension effects (and relating the physical properties to the curvature energy only) have been very successful in describing many features of bilayer systems, such as the shapes of vesicles [4] and the entropic interactions between membranes [5].

The problem with the notion of vanishing surface tension is that it can be understood in two different ways, depending on the quantity in question. To demonstrate the two possible meanings of the term "surface tension", we consider a *flat* fluid membrane in an aqueous solution. Let us first assume that the total number N_{s} of amphiphilic molecules forming the membrane is fixed, *i.e.*,

we ignore the exchange of molecules between the surface (membrane) and the bulk (solution) [6]. This approximation may be relevant for highly insoluble amphiphiles, such as lipids, whose *critical micelle concentration (cmc)* is usually very low [7]. (Typical values of the cmc for bilayer-forming lipids are in the range 10^{-6}–10^{-10} M [8].) Lipid bilayers are also characterized by large "residence times" of the molecules within the aggregates [8,9]. The free energy of such a membrane depends only on the surface density of the amphiphiles $\Sigma \equiv N/A$, where A is the area of the membrane. It achieves a minimum at a certain area density Σ_0 which is determined by the intermolecular forces [8,10]. Small deviations from the equilibrium density can be described by a quadratic approximation of the Helmholtz free energy

$$\Omega_{\mathrm{C}} = \frac{K_A}{2A_{\mathrm{s}}} \left(A - A_{\mathrm{s}} \right)^2 , \qquad (1)$$

where $A_{\mathrm{s}} = N_{\mathrm{s}} \Sigma_0$ is called the *saturated area* of the membrane, and K_A is the stretching-compression modulus. Typical values of K_A for lipid bilayers are in the range $K_A \gtrsim 10^2$ ergs/cm^2 [8,11]. For such values of K_A, any appreciable deviation of A from A_{s} would involve an energy cost much larger than any other relevant energy scale such as the thermal energy and the energy associated with curvature deformations. Consequently, it is frequently assumed that the total area is effectively constrained to A_{s}

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and, therefore, the *surface pressure*

$$\Pi \equiv -\frac{\mathrm{d}\Omega_{\mathrm{C}}}{\mathrm{d}A} = 0. \tag{2}$$

It is the vanishing of Π for $A = A_{\mathrm{s}}$ which is usually described as the vanishing of the surface tension.

The ideas presented above are essentially due to Schulman [2,12], and so the saturated area is sometimes called *Schulman area*. However, a careful examination of Schulman's argument reveals that Π (which we referred to as the surface pressure) does not comply with our usual understanding of the concept of surface tension. The quantity called surface tension is supposed to describe the free energy required to remove molecules from the bulk and create a unit area of the surface [13]. It, therefore, cannot be discussed within a model that excludes the exchange of molecules between the membrane and the solution (like the one described above). This brings us to the second model: consider a membrane whose area density is fixed to Σ_0, but whose total number of molecules N_{s} may vary. The grand potential Ω_{G} of such a membrane can be described by

$$\Omega_{\mathrm{G}} = \mu N_{\mathrm{s}} = \mu \Sigma_0 A = \gamma A, \tag{3}$$

where the chemical potential μ is a Lagrange multiplier that fixes the average number of surface molecules. From the above equation we learn that a) the quantity γ, which truly deserves the name "surface tension", is proportional to the chemical potential of the molecules μ and b) that there is no special reason for γ to be equal to zero.

The differences between the above two examples can be viewed from a slightly different perspective: In both cases we deal with saturated surfaces. However, in the first example we deal with the response of the membrane to the variation of the area density of the molecules. The Helmholtz free energy Ω_{C} depicted by equation (1) is nothing but the *elastic free energy* of the membrane, which takes a quadratic form near the equilibrium (reference) state. In the second case, on the other hand, we look at the process of creating more saturated surface. The addition of molecules to the surface is governed by the *interfacial free energy* Ω_{G} described by equation (3), which is linear in A. Although we have just argued that γ and not $-\Pi$ should be regarded as the surface tension of the system we will adopt, in what follows, a unified approach: We will define the surface tension of a *flat* surface as $\sigma \equiv \mathrm{d}F/\mathrm{d}A$, where F (which we henceforth refer to as the *free energy*) is the relevant thermodynamic potential, *i.e.*, $F = \Omega_{\mathrm{C}}$ in the first case and $F = \Omega_{\mathrm{G}}$ in the second. (Note that Ω_{C} and Ω_{G} are *not* related by a Legendre transformation but rather describe two very distinct physical problems.) The differentiation with respect to A is taken while all the other state variables are held constant [14]. We get $\sigma = -\Pi$ when we apply our definition of the surface tension to equation (1), and $\sigma = \gamma$ when we apply it to equation (3). For a *fluctuating* surface we will use a generalized version of the above definition for σ (see Eq. (4), later in this section).

To fully describe the behavior of a thermally fluctuating surface we need to include both the elastic free energy (1) and the interfacial free energy (3) in our Hamiltonian. The above two models represent the two extreme cases of isolated elastic surfaces (first model) and incompressible surfaces (second model). There also exists a third model in which the surface is assumed to be both isolated and incompressible [15–17]. This last model has been successfully used in theoretical studies of bilayer vesicles [4]. As has been mentioned earlier, lipid membranes are usually considered as nearly incompressible due to the separation of energy scales between the stretching and bending energies. As a result, the behavior of bilayer systems had been hardly studied in the framework of the first model, and very little is known [2,18,19] about the effect of thermal fluctuations on the elastic free energy (1) (which have been described above for the case of a flat surface) and the corresponding surface tension. This should be compared to our very good understanding of the influence of temperature on the surface tension γ associated with incompressible surfaces [3,15,20–24]. The stretching elasticity contribution to the surface tension is usually described by the linear relation $\sigma = K_A(A - A_{\mathrm{s}})/A_{\mathrm{s}}$, and is simply added as a correction to γ [11,20].

The aim of the present paper is to fill the gap existing in the literature and to study the effect of thermal fluctuations on Schulman area elasticity. Understanding of this subject should improve our analysis of the results of stretching experiments of water-insoluble lipid bilayers [11,25]. It is also important for understanding the results of computer simulations where frequently the number of molecules forming the surface is fixed [26]. Most of the early work on this subject, which is of a semiquantitative nature, is summarized in the review by de Gennes and Taupin [2]. More recently [24], there has been an attempt to introduce the stretching elasticity into the problem in a non-*ad hoc* way, *i.e.*, without simply adding it as a correction to the surface tension γ. In ref. [24] the behavior of a membrane with a fixed microscopic area was investigated, and the surface tension was associated with the optically visible area. Here we consider a membrane which is elastic at the microscopic level and which is characterized by a finite compressibility.

In this work we carry out a statistical mechanical analysis of the behavior of a nearly flat fluid surface that spans a planar frame of a total area A_{p} (the "projected area") and consists of a fixed number of molecules N_{s}. We will calculate the free energy of a thermally fluctuating surface and extract the associated *frame tension* which is defined by

$$\sigma \equiv \frac{\mathrm{d}F}{\mathrm{d}A_{\mathrm{p}}}. \tag{4}$$

The latter quantity gives the force per unit length experienced by the frame holding the surface. The frame tension coincides with another quantity (which is denoted by r) that has the dimensions of a surface tension (*i.e.*, energy per unit area) —the "q^2 coefficient" [21,27,28]. The surface tension r is the one that is measured in flickering experiments [25], where the dependence of the mean-square amplitudes of the thermal fluctuations on

the wave number q is fitted to the formula

$$\langle |u_q|^2 \rangle = \frac{k_{\mathrm{B}}T}{A_{\mathrm{p}}\left[rq^2 + \mathcal{O}\left(q^4\right)\right]}, \qquad (5)$$

where k_{B} is the Boltzmann constant and T is the temperature. In order to investigate the elastic behavior of the system we first develop (in Sect. 2) a general formalism which can be applied to any fluctuating surface whose energy can be written as the sum of an area-dependent term and a curvature-dependent term. The validity of our formalism is demonstrated by applying it (in Sect. 3) to determine the surface tension of an incompressible surfaces whose area-dependent energy is depicted by equation (3). The well-known result [21] for the temperature-dependent surface tension is recovered. We then turn (in Sect. 4) to the main subject of the paper —the elastic behavior of compressible fluctuating surfaces. Our discussion of the subject is divided into three sections: In Section 4.1 we focus on the behavior of compressed surfaces with the projected area A_{p} smaller than the saturated (Schulman) area A_{s}. We will try to see the extent to which thermal fluctuations (which increase the total area compared to A_{p}) modify the Schulman elastic energy. In Section 4.2 we discuss the behavior of stretched surfaces with $A_{\mathrm{p}} > A_{\mathrm{s}}$. We will examine whether the thermal fluctuations reduce or increase the (zero temperature) elastic surface tension. The behavior of surfaces with $A_{\mathrm{p}} \sim A_{\mathrm{s}}$ is studied in Section 4.3. However, we must stress here that for very small values of the surface tension (which are encountered in part of this regime, close to the area where $\sigma = 0$) the elastic behavior is dominated by the interfacial free energy (3) and the associated surface tension γ rather than by the elastic free energy (1). The case when $A_{\mathrm{p}} = A_{\mathrm{s}}$ was investigated by Brochard *et al.* [18]. Their interpretation of the surface tension had been reexamined [3] because it is based on the calculation of the partition function at a single projected area. In Section 5 we summarize the results and discuss the other factors that might influence the elastic behavior of the surface.

2 The function Z(ΔA)

We consider a nearly flat surface that spans a planar frame of a total area A_{p}. To describe the microscopic configurations of the surface we use the Monge gauge $z = h(x,y)$, where h is the height of the surface above the frame reference plane [29]. We assume that the Hamiltonian that describes the elastic energy of each configuration can be decomposed into the sum of two terms:

$$\mathcal{H} = \mathcal{H}_1\left(A\left[h\right]\right) + \int_A \mathrm{d}S \frac{1}{2}\kappa H^2. \qquad (6)$$

The first term on the right-hand side (r.h.s) of the above equation describes the dependence of the elastic energy on the total area A of the surface and has yet to be specified. The second term is the bending energy associated with the curvature. It describes the energy difference between flat and curved surfaces with the same total

area. In equation (6) the bending energy is expressed using the quadratic approximation of the Canham-Helfrich Hamiltonian [30–32], where $\mathrm{d}S$ is a surface area element, $H \equiv c_1 + c_2$ is the sum of local principle curvatures (the total curvature), and κ is the associated bending modulus. For simplicity we will restrict our discussion in this paper to surfaces with no preferred (spontaneous) curvature, and to fluctuations which do not change the topology of the surface. For a nearly flat surface, *i.e.*, when the derivatives of the height function with respect to x and y are small —$h_x, h_y \ll 1$, we have

$$A \simeq A_{\mathrm{p}} + \int_{A_{\mathrm{p}}} \mathrm{d}x\mathrm{d}y \frac{1}{2}\left(\nabla h\right)^2 \equiv A_{\mathrm{p}} + \Delta A, \qquad (7)$$

and

$$\int_S \mathrm{d}S\, H^2 \simeq \int_{A_{\mathrm{p}}} \mathrm{d}x\mathrm{d}y \left(\nabla^2 h\right)^2, \qquad (8)$$

where the integral $\int_{A_{\mathrm{p}}}$ runs over the frame reference surface, and $\Delta A \geq 0$ (in Eq. (7)) denotes the excess area of the surface due to the fluctuations in the normal z-direction.

Using equations (6–8), we write the partition function of the system as

$$Z = \int \mathcal{D}\left[h\right]\exp\left\{ -\beta\left[\mathcal{H}_1\left(A_{\mathrm{p}} + \int_{A_{\mathrm{p}}}\mathrm{d}x\mathrm{d}y\frac{1}{2}(\nabla h)^2\right)\right.\right.$$
$$\left.\left. + \int_{A_{\mathrm{p}}}\mathrm{d}x\mathrm{d}y\frac{1}{2}\kappa\left(\nabla^2 h\right)^2\right]\right\}, \qquad (9)$$

where $\beta = 1/k_{\mathrm{B}}T$. The above partition function can also be written in the following form:

$$Z = \int_0^\infty \mathrm{d}\left(\Delta A\right)\exp\left[-\beta\mathcal{H}_1\left(A_{\mathrm{p}} + \Delta A\right)\right]$$
$$\times \int \mathcal{D}\left[h\right]\delta\left(\Delta A - \int_{A_{\mathrm{p}}}\mathrm{d}x\mathrm{d}y\frac{1}{2}(\nabla h)^2\right)$$
$$\times \exp\left[-\beta\kappa\int_{A_{\mathrm{p}}}\mathrm{d}x\mathrm{d}y\frac{1}{2}\left(\nabla^2 h\right)^2\right]$$
$$= \int_0^\infty \mathrm{d}\left(\Delta A\right)\exp\left[-\beta\mathcal{H}_1\left(A_{\mathrm{p}} + \Delta A\right)\right] \times Z\left(\Delta A\right), \quad (10)$$

where δ is the Dirac delta-function. The function $Z\left(\Delta A\right)$ can be identified as the partition function of a surface whose total area is constrained to the value $A = A_{\mathrm{p}} + \Delta A$. In other words, it reflects the probability density of the surface to have a total area A when the different configurations are weighted by their bending elasticity only. This probability density is determined by two opposite trends: Entropy favors strongly fluctuating configurations while the bending energy makes the configurations with moderate slopes more preferable. The contribution of the area-dependent term in the Hamiltonian (6) to the statistics is taken into account separately by the additional Boltzmann factor, $\exp\left[-\beta\mathcal{H}_1\left(A_{\mathrm{p}} + \Delta A\right)\right]$, in the integrand in equation (10). In order to calculate the function $Z\left(\Delta A\right)$ we

use the Fourier space representation of the delta-function

$$\delta(x - a) = \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} e^{\omega(x-a)} \mathrm{d}\omega, \qquad (11)$$

which when substituted in equation (10) yields

$$Z\left(\Delta A\right) = \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} \mathrm{d}\omega \, e^{\omega \Delta A}$$
$$\times \int \mathcal{D}\left[h\right] \exp\left\{-\frac{1}{2}\int_{A_{\mathrm{p}}} \mathrm{d}x\mathrm{d}y \left[\omega\left(\nabla h\right)^2 + \beta\kappa\left(\nabla^2 h\right)^2\right]\right\}. \qquad (12)$$

So far we have treated our surface as if it were a smooth continuous medium. One should not forget, however, that the Hamiltonian (6) is derived from a more microscopic description. This means that the conformations of the surface cannot be defined below some microscopic length scale: In the frame tangent plane we must use a coarse-graining length l comparable to the size of the constituent molecules, so that an area element ("patch") of linear size l contains at least one (preferably a few) molecules. Our choice of l (which is somewhat arbitrary) defines a coarse-graining length scale $\lambda(l)$ for the normal displacements of the membrane patches, where $\lambda(l) = \hbar\left(2\pi/mk_{\mathrm{B}}T\right)^{1/2}$ is the thermal de Broglie wavelength of a membrane patch, and m in the definition of λ is the mass of the patch which is proportional to the (mean) number of molecules forming it. The bending modulus κ is also scale dependent [33,34].

Details on length scale smaller than l are eliminated from our statistical mechanical treatment of the system by considering only those conformations of the surface $h(x,y) = h(\vec{r})$ with wave vectors in the range $|q| < \Lambda \equiv 2\sqrt{\pi}/l$:

$$h\left(\vec{r}\right) = \frac{\sqrt{A_{\mathrm{p}}}}{\left(2\pi\right)^2} \int_{|\vec{q}|\leq\Lambda} \mathrm{d}\vec{q}\, l\lambda h_q e^{i\vec{q}\cdot\vec{r}}. \qquad (13)$$

In the above equation h_q is the amplitude of the Fourier component corresponding to $\vec{q}$ [35]. The value of Λ had been chosen to set the number of modes included in the spectrum to be equal to the number of microscopic degrees of freedom N, i.e.,

$$N = \frac{A_{\mathrm{p}}}{l^2} = \frac{A_{\mathrm{p}}}{\left(2\pi\right)^2}\pi\Lambda^2. \qquad (14)$$

For simplicity we use a circular, rather than a square, region in q-space. The sets of height functions $h(\vec{r})$ in real space which can be generated by the modes included in the circular and square Brillouin zones are different only in the details on the microscopic length scale l. Therefore, both Brillouin zones are equally adequate in describing the macroscopic behavior of the system. With the Fourier modes representation, and using the identity

$$\int_{A_{\mathrm{p}}} \mathrm{d}\vec{r}\, e^{i(\vec{q}-\vec{p})\cdot\vec{r}} = \left(2\pi\right)^2 \delta(\vec{q}-\vec{p}), \qquad (15)$$

the excess area (Eq. (7)) is given by

$$\Delta A = \frac{A_{\mathrm{p}}}{\left(2\pi\right)^2} \int_{\Lambda_0}^{\Lambda} \mathrm{d}\vec{q} \frac{1}{2} q^2 l^2 \lambda^2 |h_q|^2, \qquad (16)$$

where $\Lambda_0 = 2\pi/\sqrt{A_{\mathrm{p}}} \simeq 0$, and the mode $q = 0$ has been excluded as it corresponds to a constant shift in h which does not contribute to the excess area. The second integral in equation (12) now reads

$$\int \mathcal{D}\left[h_q\right] \exp\left\{-\frac{A_{\mathrm{p}}}{\left(2\pi\right)^2} \int_{\Lambda_0}^{\Lambda} \mathrm{d}\vec{q} \frac{l^2\lambda^2}{2} \left[\omega q^2 + \beta\kappa q^4\right] |h_q|^2\right\}. \qquad (17)$$

Tracing over the surface profile h_q in equation (17), is straightforward, giving

$$\exp\left\{-\frac{A_{\mathrm{p}}}{\left(2\pi\right)^2} \int_{\Lambda_0}^{\Lambda} \frac{\mathrm{d}\vec{q}}{2} \ln\left[\frac{\left(\omega q^2 + \beta\kappa q^4\right) l^2\lambda^2}{2\pi}\right]\right\}. \qquad (18)$$

This result should be substituted back in equation (12). The first integral in equation (12) can be evaluated in the thermodynamic limit using the method of steepest descent. We find that (up to a constant factor)

$$Z\left(\Delta A\right) \equiv \exp\left\{\beta G\left(\Delta A\right)\right\}$$
$$\simeq \exp\left\{\omega_{\mathrm{s}}(\Delta A)\Delta A - \frac{A_{\mathrm{p}}}{\left(2\pi\right)^2}\right.$$
$$\left.\times \int_{\Lambda_0}^{\Lambda} \frac{\mathrm{d}\vec{q}}{2} \ln\left[\frac{\left(\omega_{\mathrm{s}}\left(\Delta A\right) q^2 + \beta\kappa q^4\right) l^2\lambda^2}{2\pi}\right]\right\}, \qquad (19)$$

where

$$\omega_{\mathrm{s}} = \beta\kappa\frac{\Lambda^2 - \Lambda_0^2 \exp\left(8\pi\beta\kappa\Delta A/A_{\mathrm{p}}\right)}{\exp\left(8\pi\beta\kappa\Delta A/A_{\mathrm{p}}\right) - 1}, \qquad (20)$$

satisfies

$$\frac{\partial G}{\partial \omega_{\mathrm{s}}} = 0, \qquad (21)$$

i.e., solves the equation

$$\Delta A - \frac{A_{\mathrm{p}}}{\left(2\pi\right)^2} \int_{\Lambda_0}^{\Lambda} \frac{\mathrm{d}\vec{q}}{2\left(\omega_{\mathrm{s}} + \beta\kappa q^2\right)} = 0. \qquad (22)$$

If we now substitute our expression for $Z\left(\Delta A\right)$ (19) in equation (10) and again use the saddle-point approximation, we obtain

$$Z \simeq \exp\left\{\beta\left[G\left(\Delta A^*\right) - \mathcal{H}_1\left(A_{\mathrm{p}} + \Delta A^*\right)\right]\right\}, \qquad (23)$$

where ΔA^* is the solution of the equation

$$-\frac{\partial\mathcal{H}_1}{\partial\Delta A} + \frac{\partial G}{\partial\left(\Delta A\right)} + \frac{\partial G}{\partial\omega_{\mathrm{s}}}\frac{\partial\omega_{\mathrm{s}}}{\partial\left(\Delta A\right)} = 0, \qquad (24)$$

and where the function $G\left(\Delta A, \omega_{\mathrm{s}}\left(\Delta A\right)\right)$ is defined by equation (19). The last term in the above equation vanishes by virtue of equation (21), while from equation (19) we have $\partial G/\partial\left(\Delta A\right) = \omega_{\mathrm{s}}/\beta$. We thus find that ΔA^* is the solution of

$$\omega_{\mathrm{s}}\left(\Delta A\right) = \beta\frac{\partial\mathcal{H}_1}{\partial\left(\Delta A\right)}. \qquad (25)$$

The free energy of the surface is given by

$$F = -k_{\mathrm{B}}T\ln\left(Z\right) = \mathcal{H}_1\left(A_{\mathrm{p}} + \Delta A^*\right) - G\left(\Delta A^*\right). \qquad (26)$$

The first term in the above expression is the area-dependent energetic contribution to the free energy. The second term can be regarded as the entropic part of the free energy, where the different configurations of the surface are weighted by their total bending elasticity.

3 Incompressible surfaces

In order to evaluate the free energy of the surface we now need to specify the area-dependent part $\mathcal{H}_1$ of the Hamiltonian (6). Let us first consider the extensively studied example of an incompressible surface (see discussion in Sect. 1). In this case, the area density of the surface is fixed, and any change in the total area due to thermal fluctuations must be matched by a change in the number of molecules that fixes the area per molecule. The fluctuations in the area are governed by the Hamiltonian (see Eq. (3))

$$\mathcal{H}_1 = \gamma A = \gamma \left(A_{\mathrm{p}} + \Delta A \right), \qquad (27)$$

where (as discussed in Sect. 1) γ is directly proportional to the chemical potential for the addition of molecules to the surface. From equations (25) and (27) we find that

$$\omega_{\mathrm{s}} = \beta\gamma. \qquad (28)$$

Using equations (19, 26), and (28) we obtain the expression for the free energy (consistent with [21])

$$
\begin{aligned}
F &= \gamma A_{\mathrm{p}} + k_{\mathrm{B}} T \frac{A_{\mathrm{p}}}{(2\pi)^2} \int_{\Lambda_0}^{\Lambda} \frac{\mathrm{d}\vec{q}}{2} \ln \left[\frac{\left(\beta\gamma q^2 + \beta\kappa q^4 \right) l^2 \lambda^2}{2\pi} \right] \\
&= A_{\mathrm{p}} \left\{ \gamma + \frac{k_{\mathrm{B}} T}{(2\pi)^2} \int_{\Lambda_0}^{\Lambda} \frac{\mathrm{d}\vec{q}}{2} \ln \left[\frac{\left(\beta\gamma q^2 + \beta\kappa q^4 \right) l^2 \lambda^2}{2\pi} \right] \right\},
\end{aligned}
$$
$$(29)$$

which is correct to the lowest order in an expansion in $(\beta\kappa)^{-1} = k_{\mathrm{B}} T/\kappa$. To find the surface tension, σ, we need to take the full derivative of F with respect to A_{p}. It is therefore important to examine the implicit dependence on A_{p} of the expression inside the braces in equation (29). One part of this expression that obviously depends on A_{p} is the lower limit of the integral $\Lambda_0 = 2\pi/\sqrt{A_{\mathrm{p}}}$. This dependence is associated with the logarithmic finite-size correction to the free energy, whose origin is the fact the variation of the linear size of the frame ($\sqrt{A_{\mathrm{p}}}$) leads to changes in the wave numbers of the long-wavelength modes. The contribution of this effect to σ is negligible in the thermodynamic limit. A more subtle issue is the possible dependence on A_{p} of the microscopic length l and of the quantities Λ and λ which are directly related to l. Recall that the patches have been identified as small sections of the surface containing, on average, a given number of (at least one) molecules. Since the area density of the surface is fixed, l can be derived from the constraint

$$\frac{\langle A \rangle}{N} = l^2 \frac{\langle A \rangle}{A_{\mathrm{p}}} = \mathrm{const}, \qquad (30)$$

where $\langle A \rangle$ is the mean total area of the surface. Using equation (29) and the relation $\langle A \rangle = \partial F/\partial\gamma$, we get [20]

$$\langle A \rangle = A_{\mathrm{p}} \left\{ 1 + \frac{1}{8\pi\beta\kappa} \ln \left[\frac{\gamma + \kappa\Lambda^2}{\gamma + \kappa\Lambda_0^2} \right] \right\}. \qquad (31)$$

For $\gamma \neq 0$ and in the limit $A_{\mathrm{p}} \to \infty$ ($\Lambda_0 = 2\pi/\sqrt{A_{\mathrm{p}}} \to 0$), we readily conclude that criterion (30) is obeyed by setting l to a constant value which does not depend on A_{p}. We thus find (ignoring the above-mentioned finite-size correction) in agreement with [21] that

$$
\begin{aligned}
\sigma &= \frac{\mathrm{d}F}{\mathrm{d}A_{\mathrm{p}}} \simeq \frac{F}{A_{\mathrm{p}}} = \\
&\gamma + \frac{k_{\mathrm{B}} T}{(2\pi)^2} \int_{\Lambda_0}^{\Lambda} \frac{\mathrm{d}\vec{q}}{2} \ln \left[\frac{\left(\beta\gamma q^2 + \beta\kappa q^4 \right) l^2 \lambda^2}{2\pi} \right].
\end{aligned}
$$
$$(32)$$

If $\gamma = 0$ we find l depending on A_{p}, what brings in another finite-size correction to the above result (32).

4 Compressible surfaces

We now turn to study a surface with a *fixed* number of molecules, whose area elasticity can be approximated by the harmonic form (see Eq. (1))

$$\mathcal{H}_1 = \frac{K_A}{2A_{\mathrm{s}}} \left(A - A_{\mathrm{s}} \right)^2 = \frac{K_A}{2A_{\mathrm{s}}} \left(\Delta A - \Delta A_{\mathrm{s}} \right)^2, \qquad (33)$$

where $\Delta A_{\mathrm{s}} \equiv A_{\mathrm{s}} - A_{\mathrm{p}}$. The system under consideration is characterized by three energy scales: $k_{\mathrm{B}} T = (\beta)^{-1}$, κ, and $K_A a_{\mathrm{s}}$, where $a_{\mathrm{s}} \equiv A_{\mathrm{s}}/N$ is the Schulman area of the surface patches (the microscopic degrees of freedom). In what follows we will assume that

$$\sqrt{\beta K_A a_{\mathrm{s}}} \gg \beta\kappa \gg 1. \qquad (34)$$

These relations are obeyed by typical values of the elastic moduli and the Schulman (saturated) area per lipid of phospholipid bilayers. We are interested in calculating the free energy of such a surface as a function of the ratio $A_{\mathrm{p}}/A_{\mathrm{s}}$ between the projected and the saturated areas. Combining equations (20, 25), and (33) we arrive to the following equation:

$$
\begin{aligned}
\omega_{\mathrm{s}} (\Delta A) &= \beta\kappa \frac{\Lambda^2 - \Lambda_0^2 \exp\left(8\pi\beta\kappa\Delta A/A_{\mathrm{p}} \right)}{\exp\left(8\pi\beta\kappa\Delta A/A_{\mathrm{p}} \right) - 1} = \\
&\beta\frac{K_A}{A_{\mathrm{s}}} \left(\Delta A - \Delta A_{\mathrm{s}} \right),
\end{aligned}
$$
$$(35)$$

whose solution ΔA^* should be substituted in expression (26) for the free energy of the surface. Three regimes can be distinguished as follows.

4.1 Floppy surfaces

Consider the case when $A_{\mathrm{p}} < A_{\mathrm{s}}$. The elastic energy caused by the mismatch between the frame area and the

saturated area can be relieved by thermal fluctuations which store the extra area needed to bring the total area A close to A_s. Let A_p^* be the projected area for which the solution of equation (35) coincides with the Schulman area

$$A^* = A_s, \tag{36}$$

so that

$$\omega_s = 0. \tag{37}$$

One can easily verify that

$$A_p^* = A_s \left[1 + \frac{1}{8\pi\beta\kappa} \ln\left(\frac{\Lambda^2}{\Lambda_0^2}\right)\right]^{-1} = A_s \left[1 + \frac{1}{8\pi\beta\kappa} \ln\left(\frac{N}{\pi}\right)\right]^{-1}. \tag{38}$$

For $A_p \sim A_p^*$ the corrections to equations (36) and (37) can be expressed as a power series in the variable $\epsilon_A \equiv A_p - A_p^*$ ($|\epsilon_A| < [\max(\ln N, 8\pi\beta\kappa)]^{-1} A_p^*$). The following relations can be derived:

$$A^* = A_s + \epsilon_A \frac{(2\pi)^2 \kappa A_s}{K_A A_p^{*2}} \left[\ln\left(\frac{N}{\pi}\right) + 1 - 8\pi\beta\kappa + \mathcal{O}\left(\frac{\epsilon_A}{A_p^*}\right)\right], \tag{39}$$

and

$$\omega_s = \frac{(2\pi)^2 \beta\kappa}{A_p^*} \left[\ln\left(\frac{N}{\pi}\right) + 1 - 8\pi\beta\kappa\right] \frac{\epsilon_A}{A_p^*} + \cdots, \tag{40}$$

which when used together with equations (19, 26), and (33), yield (after some straightforward, but lengthy calculation) the following expression for the free energy:

$$F = F_0 + F_1 + \cdots = k_B T \frac{A_p}{(2\pi)^2} \int_{\Lambda_0}^{\Lambda} \frac{d\vec{q}}{2} \ln\left[\frac{\beta\kappa q^4 l^2 \lambda^2}{2\pi}\right]$$
$$+ k_B T \left[\ln\left(\frac{N}{\pi}\right) + 1 - 8\pi\beta\kappa\right]$$
$$\times \left[\frac{3}{8\pi} \ln\left(\frac{N}{\pi}\right) + \frac{\pi}{2}\right] \frac{\epsilon_A}{A_p^*} + \cdots. \tag{41}$$

The form of the first term F_0 in free energy (41) is similar to (29) for an incompressible surface with $\gamma = 0$. The second term F_1 is the leading linear correction in the small variable ϵ_A/A_p^*. The harmonic (Schulman) elastic energy contributes only to the quadratic correction.

Our result (41) should be compared with the free energy (29) of an incompressible surface in the limit $\gamma \to 0$. As has been discussed in the literature [3] (see also our discussion in Sect. 1) and as evident from our equation (32), the vanishing of γ should not be confused with the vanishing of surface tension σ which occurs when $A_p \sim A_s$ (as we show in Sect. 4.3). In the derivation of equation (32), which applies for the case of an incompressible surface and for which the total number of surface molecules is *not* fixed, we have used relation (30), which enforces the conservation of mass of the surface patches. Here, we consider a different scenario, where the total number of molecules is fixed. Consequently, relation (30) should be replaced with

equation (14) in which we fix N, the number of patches dividing the surface. In order to calculate σ by differentiating F with respect to A_p, it is better to consider the explicit expression for F_0 and to perform the integral in equation (41). Setting the lower limit $\Lambda_0 = 0$ we get

$$F_0 \simeq k_B T \frac{A_p}{4\pi} \Lambda^2 \left[\ln\left(\frac{\beta\kappa\lambda^2 l^2 \Lambda^4}{2\pi}\right) - 2\right] = -N k_B T \left[\ln\left(\frac{A_p}{8\pi\beta\kappa\lambda^2 N}\right) + 2\right]. \tag{42}$$

Apart from the constant $-2N k_B T$ which can be discarded (if temperature is fixed), the free energy depicted by the above equation is reminiscent of the free energy $F = -N k_B T \ln\left(A_p/\lambda^2 N\right)$ of a two-dimensional ideal gas consisting of N particles confined in an area A_p. The only difference between the free energies of those two systems is that the *effective* de Broglie thermal wavelength in equation (42) is $\lambda^* = \lambda\sqrt{8\pi\beta\kappa}$. While λ is a constant that depends only on the mean number of molecules included in each patch (which is not affected by changes in A_p if we use Eq. (14) with a fixed value of N), the effective thermal wavelength λ^* may be area dependent. The origin of this dependence is the bending modulus κ appearing in the expression for λ^*. In the quadratic approximation of the Canham-Helfrich Hamiltonian (Eq. (6)), the elastic bending energy is expanded around the flat reference state of the area A_p and, in general, κ depends on the properties of the reference state. As the number of surface molecules is fixed, the variation of A_p leads to the variation of the area density of the reference state and, presumably, to the variation of κ. The exact calculation of κ requires the knowledge of the molecular interactions between the molecules [36,27], and is beyond the scope of this paper. We will, therefore, restrict our discussion in the reminder of this paper to surfaces for which the variation of κ (over the range of A_p of interest) is negligible. In such a case,

$$\sigma_0 \equiv \frac{dF_0}{dA_p} \simeq -\frac{N k_B T}{A_p}. \tag{43}$$

The first correction to this result is

$$\sigma_1 \equiv \frac{dF_1}{dA_p} = \frac{dF_1}{d\epsilon_A} = \left[\ln\left(\frac{N}{\pi}\right) + 1 - 8\pi\beta\kappa\right]$$
$$\times \left[\frac{3}{8\pi} \ln\left(\frac{N}{\pi}\right) + \frac{\pi}{2}\right] \frac{k_B T}{A_p^*}. \tag{44}$$

In the thermodynamic limit this is merely a logarithmic size correction to σ_0, and we thus conclude that for $A_p \sim A_p^*$

$$\sigma \simeq -\frac{N k_B T}{A_p}. \tag{45}$$

The negative surface tension implies that the surface opposes its contraction. This result is expected since reduction of A_p requires the surface to bend more and as a consequence pay a higher-energy cost in order to attain the Schulman area. Negative surface tension with

the same origin was previously explained in the context of vesicles in ref. [15], and has been also observed in simulations of bilayer membranes [37–39]. While the very fact that the surface tension becomes negative is not surprising, its magnitude (k_BT per microscopic unit area, *i.e.*, of the order of 1–10 ergs/cm^2), as predicted by equation (45), is strikingly large. Such a large and negative surface tension implies that undulations with wavelengths longer than $2\pi\sqrt{\beta\kappa(A_p/N)}$ should be unstable, because the coefficients of $|h_q|^2$ in the free energy become negative. This undulation instability will not show up in computer simulations where the size of the sample is small [37–39]. For real physical systems this highly compressed regime is unattainable. It can be preempted by a fluid-solid phase transition [37] (in which case the shear modulus of the solid surface may act against the increase in the total area), or by a transition of molecules from the surface to the solution [40]. It should be noted here that a large negative surface tension of the same order of magnitude is also predicted by the incompressible surface model (see Eq. (32), with $\gamma = 0$). However, it is probably worthwhile reemphasizing that surfaces are nearly tensionless for $\sigma \sim 0$ rather than for $\gamma \sim 0$.

4.2 Tense surfaces

Consider the case when $A_p > A_s$. In this regime the saturated area is not attainable because $A > A_p$. For

$$\frac{A_p}{A_s} - 1 \gg \sqrt{\frac{1}{2\beta K_A a_s}} \qquad (46)$$

(a condition which for $\sqrt{\beta K_A a_s} \gg 1$ excludes only a small regime of A_p close to A_s), *i.e.* for $\Delta A_s \ll -A_s (2\beta K_A a_s)^{-1/2}$, the optimal area is very close to A_p so that equation (35) can be approximated by

$$\omega_s (\Delta A) = \frac{\Lambda^2 A_p}{8\pi\Delta A} = -\beta\frac{K_A}{A_s}\Delta A_s. \qquad (47)$$

The above approximation is obtained by neglecting the exponent in the numerator of the expression in the central part of equation (35), and expanding the exponent in the denominator close to $\Delta A = 0$. We also omit the term ΔA on the r.h.s of equation (35). The solution of equation (47) is

$$\Delta A^* = -\frac{A_s A_p \Lambda^2}{8\pi\beta K_A \Delta A_s} = $$
$$-\frac{NA_s}{2\beta K_A \Delta A_s} = -\frac{A_s^2}{2\beta K_A a_s \Delta A_s}. \qquad (48)$$

(Note that for the range of ΔA_s considered here the solution satisfies $\Delta A^* \ll |\Delta A_s|$, and so our approximation of the r.h.s of Eq. (35) is justified.) Combining equations (19, 26, 33, 47), and (48), and recalling that

$\Delta A^* \ll |\Delta A_s|$, we find that the free energy is given by

$$F \simeq \frac{K_A}{2A_s}(\Delta A_s)^2 - \frac{Nk_BT}{2} + k_BT\frac{A_p}{(2\pi)^2}$$
$$\times \int_{\Lambda_0}^{\Lambda} \frac{d\vec{q}}{2} \ln\left[\frac{\left(\beta\left(K_A|\Delta A_s|/A_s\right) q^2 + \beta\kappa q^4\right) l^2\lambda^2}{2\pi}\right]. \quad (49)$$

If temperature is fixed then the second term in the above equation is a constant and can be ignored. The first term depicts the energetic contribution of Schulman elasticity to F. This is simply the elastic energy of a flat surface having been stretched to an area $A_p > A_s$. The surface tension experienced by such a flat surface is

$$\sigma_0 = -\frac{K_A}{A_s}\Delta A_s = \frac{K_A}{A_s}|\Delta A_s| > 0. \qquad (50)$$

The third term in equation (49) represents the entropic part of F. It is similar to the leading thermal correction to the free energy (29) of an incompressible surface, with $\gamma = \sigma_0$. The (full) derivative of this term with respect to A_p yields the correction to the linear relation $\sigma = \sigma_0$, between the surface tension and ΔA_s. It can be shown that for $K_A a_s/\kappa \gg 1$ (see relation (34)), the sign of this correction is positive which means that thermal fluctuations lead to a super-Hookean elasticity. This observation can be understood by noting (see Eq. (48)) that the optimal area A^* is independent of κ, and that it gets closer to A_p by increasing $|\Delta A_s|$. The approach of A^* to A_p involves a strong suppression of the thermal fluctuations, and that naturally reduces the entropy of the surface and thereby increases the surface tension. As already said, this entropic surface tension is also found for incompressible surfaces [15,20–24]. Stretching experiments of vesicles [11] are often analyzed assuming the decoupling of the elastic and entropic surface tensions. However, our equation (49) suggests the existence of a rather complicated interplay between the elastic and the entropic contributions, which is expressed by the fact that the stretching modulus K_A appears in the integral expression for the entropic component.

4.3 Schulman surfaces

Finally, we discuss the case when $A_p \sim A_s$. More precisely, we consider the regime where the projected and saturated areas are sufficiently close to each other that

$$|\Delta A_s| < \sqrt{\frac{1}{2\beta K_A a_s}} A_s \equiv \sqrt{D} A_s \ll A_s, \qquad (51)$$

where ΔA_s is either positive or negative. Instead of equation (47) we now have

$$\omega_s (\Delta A) = \frac{\Lambda^2 A_p}{8\pi\Delta A} = \beta\frac{K_A}{A_s}\left(\Delta A - \Delta A_s\right). \qquad (52)$$

Up to second order in the parameter $\Delta A_s/(\sqrt{D}A_s) < 1$, the solution of this equation is

$$\Delta A^* = \sqrt{D} A_s + \frac{\Delta A_s}{2} + \frac{(\Delta A_s)^2}{8\sqrt{D}A_s}, \qquad (53)$$

and hence

$$\omega_s\left(\Delta A^*\right) = \beta K_A \left(\sqrt{D} - \frac{\Delta A_s}{2A_s} + \frac{(\Delta A_s)^2}{8\sqrt{D}A_s^2}\right). \quad (54)$$

Equations (19, 26, 53), and (54) yield the following form for the free energy:

$$F \simeq \frac{K_A}{2A_s}(\Delta A_s)^2 - DK_A A_s + k_B T \frac{A_p}{(2\pi)^2}$$
$$\times \int_{A_0}^{\Lambda} \frac{d\vec{q}}{2} \ln\left[\frac{\beta l^2 \lambda^2 q^2}{2\pi}\left(K_A\sqrt{D} - \frac{K_A \Delta A_s}{2A_s}\right.\right.$$
$$\left.\left. + \frac{K_A(\Delta A_s)^2}{8\sqrt{D}A_s^2} + \kappa q^2\right)\right]. \quad (55)$$

The last three terms in the argument of the logarithmic function are smaller than the first one (see relations (34) and (51)). Using a Taylor expansion of the logarithm and keeping only terms up to first order in $\beta\kappa/\sqrt{\beta K_A A_s}$ and second order in $\Delta A_s/(\sqrt{D}A_s)$, we obtain

$$F \simeq \frac{K_A}{2A_s}(\Delta A_s)^2 - DK_A A_s + k_B T \frac{A_p}{(2\pi)^2}$$
$$\times \int_0^{\Lambda} \frac{d\vec{q}}{2} \ln\left(\frac{\beta l^2 \lambda^2 q^2}{2\pi}K_A\sqrt{D}\right) + k_B T \frac{A_p}{(2\pi)^2}\int_0^{\Lambda}\frac{d\vec{q}}{2}$$
$$\times \left[\frac{\frac{-K_A\Delta A_s}{2A_s}}{+ \frac{K_A(\Delta A_s)^2}{8\sqrt{D}A_s^2}}K_A\sqrt{D} + \frac{-\frac{(K_A\Delta A_s)^2}{8A_s^2}}{K_A^2 D} + \frac{\kappa q^2}{K_A\sqrt{D}}\right]$$
$$= \frac{K_A}{2A_s}(\Delta A_s)^2 - DK_A A_s + Nk_B T$$
$$\times \left[-1 + \ln\left(2\beta K_A \lambda^2\sqrt{D}\right)\right] + k_B T \frac{A_p}{(2\pi)^2}\int_0^{\Lambda}\frac{d\vec{q}}{2}$$
$$\times \left[\frac{\frac{-K_A\Delta A_s}{2A_s} + \frac{K_A(\Delta A_s)^2}{8\sqrt{D}A_s^2}}{K_A\sqrt{D}} + \frac{-\frac{(K_A\Delta A_s)^2}{8A_s^2}}{K_A^2 D} + \frac{\kappa q^2}{K_A\sqrt{D}}\right]. \quad (56)$$

If we fix the temperature and ignore the small dependence of κ on A_p, then the second and third terms on the r.h.s of equation (56) are constants which can be dismissed. The first term is the zero-temperature Schulman elastic energy, while the fourth term is the thermal correction. The integrals in the latter can be easily performed, and after several mathematical manipulations we find that (up to an irrelevant additive constant)

$$F \simeq \frac{K_A}{2A_s}(\Delta A_s)^2\left(1 + \frac{16\pi\kappa\sqrt{D}}{K_A a_s}\right)$$
$$+ K_A\sqrt{D}\Delta A_s\left(-\frac{1}{2} + \frac{8\pi\kappa}{K_A a_s}\right). \quad (57)$$

In the ΔA_s regime, which we discuss in this section (see Eq. (51)), the second term in equation (57) should not be considered as correction to the first, but rather as the dominant term in the free energy. From equation (57) we conclude that thermal fluctuations lead to a shift in the

value of the projected area at which the free energy is minimal. The free energy attains its minimum at

$$A_p = A_s\left\{1 - \sqrt{D}\left[\frac{1}{2} + \mathcal{O}\left(\frac{\kappa}{K_A a_s}\right)\right]\right\} \equiv A_s^{eff}, \quad (58)$$

which can be regarded as the effective Schulman area at which $\sigma = 0$. The very fact that $A_s^{eff} < A_s$ is not surprising since the total area is always larger than the projected area. For typical values of phospholipids: $\kappa = 10k_B T \sim 5 \times 10^{-13}$ ergs, $K_A \sim 200$ ergs/cm^2, and $a_s \sim 10^{-14}$ cm^2 (the area of a patch consisting of 1-2 molecules), we find that $\sqrt{D} \sim 0.1$ and so the shift in the equilibrium projected area is about 5% of A_s. We also conclude from equation (57) that thermal fluctuations increase the compression-stretching modulus K_A. The effective modulus is

$$K_A^{eff} \simeq K_A + \frac{16\pi\kappa\sqrt{D}}{a_s}. \quad (59)$$

For the values of the relevant quantities quoted above (characteristic of phospholipid bilayers) we find, quite surprisingly, that the magnitude of the thermal stretching modulus is comparable to the bare modulus K_A.

In the Evans-Rawicz experiment [11], linear elastic response was measured for areal strain $\eta \equiv (A_p - A_s^{eff})/A_s^{eff} < 0.05$. This is precisely the regime studied in the present section, and so our theoretical discussion explains well the experimental behavior. For extremely small values of the η (< 0.005) the surface tension grows exponentially with the strain. This elastic behavior has been recently explained in the framework of the incompressible surface model, and has been attributed to the dependence of the entropic surface tension on the optically visible area [24].

5 Summary

We have studied the elasticity of fluctuating two-dimensional compressible (elastic) surfaces. Starting with a Hamiltonian including the Canham-Helfrich bending energy and an area-dependent term, we have first developed a general formalism for analyzing the statistical-mechanical behavior of such systems. We have used the formalism to reproduce the expression for the temperature-dependent tension of incompressible surfaces. Our investigation of the elastic behavior of compressible surfaces reveals that the minimum of the free energy is obtained when the projected (frame) area $A_p = A_s^{eff}$, where A_s^{eff} is slightly smaller than the saturated area A_s. In the vicinity of A_s^{eff} the elastic energy is depicted by the Schulman quadratic form (33) with an area elasticity modulus K_A^{eff} larger than the bare modulus K_A. The response of the surface to compression and stretching away from A_s^{eff} is very different. The stretching behavior is dominated by the area elasticity. Thermal fluctuations introduce a correction to Hooke's law, which increases the surface tension. By contrast, area elasticity plays a very

small role in the compression behavior because the total area of the fluctuating surface is (effectively) constrained to A_s. The negative surface tension observed in this regime should be attributed to the fact that upon compression, the total area stored by the fluctuations (the excess area) grows. The enhancement of thermal fluctuations leads to an increase in the bending energy of the surface.

We conclude by briefly reviewing the factors which have been left out of our model, and which influence the elastic behavior of the surface. One of them is the exchange of molecules between the surface and the solution. It can be dealt with within the framework of a grand-canonical ensemble where both the area A and the number of patches N are allowed to fluctuate. Understanding the dependence of the bending modulus κ on the density of the reference state (*i.e.*, on the ratio A_p/A_s) is another challenge. This is a complicated matter since the values of the phenomenological parameters κ, A_s, and K_A are determined by the structure of the molecules and the interactions between them. It would therefore require a theoretical study at the molecular level (see, *e.g.*, [10,36,37]). For strongly fluctuating surfaces we should include corrections to the quadratic form of the Canham-Helfrich Hamiltonian and to go beyond the lowest order in $k_B T/\kappa$. In that case "measure factors" [21] which rather complicate the mathematical treatment must be introduced in order to correct the partition function. Finally, we mention the possibility that strongly stretched membranes can reduce their elastic energy by developing pores. A discussion on this subject can be found elsewhere [37,41–45].

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