Direct Calculation from the Stress Tensor of the Lateral Surface Tension of Fluctuating Fluid Membranes

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From the tangential and normal stresses associated with the Helfrich Hamiltonian, we calculate the lateral force per unit length, τ, exerted by a planar, fluctuating membrane, as a function of the membrane tension σ and bending rigidity κ. We unveil a confusion in the literature concerning the derivation of τ, and we argue, contrary to the present understanding, that τ should differ from the tensionlike coefficient of the fluctuation spectrum. Nontrivial implications concerning the Laplace pressure in vesicles and its relation with the excess area are discussed.

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The concept of surface tension for fluid membranes has always been a difficult one [1–8]. Membranes are thin, flexible, fluid two-dimensional sheets formed by the self-assembly into a bilayer of lipid molecules in water [9,10]. Their elasticity is well described by the Helfrich bending free-energy [11] supplemented by a surface tension term. An isolated piece of membrane possesses a fixed number of molecules and exhibits large fluctuations at room temperature. Hence, exerting a moderate lateral tension on it essentially reduces the amplitude of its fluctuations and extends its projected area, rather than stretches the bilayer surface itself [6]. It follows that there is a clear distinction between the tension σ conjugated with the actual membrane area A and the "frame" tension τ conjugated with the projected area A_p [3]. It is the tension τ, the lateral force per unit length, that is experimentally measurable, e.g., via the Laplace law in micropipette aspiration experiments [12–14]. The parameter σ is not directly measurable, but its large-scale counterpart r, renormalized by the fluctuations [2], is measurable through the q^2 squared wave vector dependence of the fluctuation spectrum [15]. When membrane tension is referred to, it is not always clear whether σ, τ or r is meant. A demonstration that $r = \tau$ in the thermodynamic limit was proposed in Ref. [4], but we shall question it.

In this Letter, we directly calculate the tension τ from the stress tensor associated with the Helfrich free-energy [16,17]. We obtain $\tau - \sigma$ (to lowest order in a temperature expansion) by thermally averaging the elastic force exchanged laterally through a membrane cut. We discuss several implications. For instance, we show that the well-known relation between the membrane tension and its excess area $(A - A_p)/A_p$, established by Helfrich [1], should be amended at low tension in order to refer to τ rather than σ. We argue that membranes can sustain moderate negative frame tensions. Importantly, we show that τ does not coincide with the (thermodynamic limit of) the free-energy per unit projected area, although it is usually defined this way [3,4]: it follows that r should not coincide with τ. We explain this point by comparing two calculations of τ, obtained by differentiating in different ways the total free-energy with respect to A_p: the one in the paper by Cai *et al.* [4] and a more recent one by Imparato [8]. We explain why only the latter agrees with our calculation. Finally, to defend our results, we numerically illustrate their validity in a Monte Carlo simulation of a one-dimensional ($1d$) discrete model of a fluid membrane.

Consider a piece of membrane either isolated or connected to a reservoir of lipids. We shall restrict our attention to applied lateral tensions $\tau \lesssim 10^{-4}$ N/m, for which the area per lipid remains essentially constant [13] (the tension only hinders the fluctuations). Hence, either the total area A is constant or there is a reservoir with some "area chemical potential" σ. In the limit of large systems, both ensembles are equivalent and the free-energy Hamiltonian can be expressed as [11]

$$\mathcal{H} = \sigma A + \int \frac{\kappa}{2}(c_\parallel + c_\perp)^2 dA. \qquad (1)$$

Here, $c_\parallel$ and $c_\perp$ are the membrane principal curvatures. The parameter σ is the (bare) membrane tension, conjugated with the actual area. We have omitted the Gaussian stiffness $\bar{\kappa}$, which enters only when topology changes are involved. As shown in [16,17], Eq. (1) implies that the force per unit length exchanged through a cut parallel to an axis of principal curvature has a tangential component perpendicular to the cut which is equal to $\sigma_t = \sigma + \frac{\kappa}{2}c_\parallel^2 - \frac{\kappa}{2}c_\perp^2$, where $c_\parallel$ is the curvature in the direction parallel to the cut, and a component normal to the membrane, $\sigma_n = \kappa\partial_{x'}(c_\parallel + c_\perp)$, where x' is perpendicular to the cut in the tangent plane. These quantities are the diagonal components of the stress tensor Σ.

We wish to calculate the force τ per unit length that must be applied to the membrane border in order to fix the mean projected area A_p. For this purpose, we consider an orthonormal basis (x, y) in the average plane P of the membrane, and we thermally average the force exchanged through a membrane cut whose projection onto P has a unit length and is parallel to y. Let the membrane deviation with respect to P be described by the function $z = h(x, y)$. As shown in Ref. [17], the component Σ^{xx} of the *projected* stress tensor, i.e., the stress tensor relative to the projected cut, takes the form

$$\Sigma^{xx} = \sigma + \frac{\sigma}{2}(h_y^2 - h_x^2) + \frac{\kappa}{2}(h_{yy}^2 - h_{xx}^2) + \kappa h_x \partial_x(\nabla^2 h) + \mathcal{O}(h^3), \tag{2}$$

where the subscripts represent partial differentiation. Since the fluctuations are symmetric with respect to P and to the plane perpendicular to P passing through the x axis, we have simply $\tau = \langle \Sigma^{xx} \rangle$, the brackets denoting thermal average. Let us comment on the form of Σ^{xx}. The first three terms arise from the tangential component of the stress tensor. With respect to the simpler expressions $\sigma_t = \sigma + \frac{\kappa}{2}c_\parallel^2 - \frac{\kappa}{2}c_\perp^2$ in the local tangent frame, the factor $1 - \frac{1}{2}h_x^2$ comes from projecting onto P while the factor $1 + \frac{1}{2}h_y^2$ comes from the fact that the actual cut is longer than the projected one. These corrective factors, like those arising from changing the coordinates from the local tangent basis to (x, y), do not affect the third term since it is already at second order: one may recognize the contribution h_{yy}^2 corresponding to the squared curvature in the y direction and h_{xx}^2 corresponding to the squared curvature in the x direction. The last and fourth term corresponds to the projection onto (x, y) of the normal component of the stress tensor. By symmetry, $\langle h_y^2 \rangle = \langle h_x^2 \rangle$ and $\langle h_{yy}^2 \rangle = \langle h_{xx}^2 \rangle$; hence, we are left with

$$\tau \simeq \sigma + \kappa \langle h_x \partial_x(\nabla^2 h) \rangle + \mathcal{O}(h^4). \tag{3}$$

To gain intuition into the physics of this contribution, consider a fluctuation mode $h = h_q \sin(qx + \phi)$. It yields $\kappa h_x \partial_x(\nabla^2 h) = -\kappa q^4 h_q^2 \cos^2(qx + \phi)$, which is always negative whatever the phase ϕ. Hence, we expect a reduction of the effective frame tension (Fig. 1).

To perform the thermal average in Eq. (3), we may restrict ourselves to the quadratic approximation of $\mathcal{H}$ [1]:

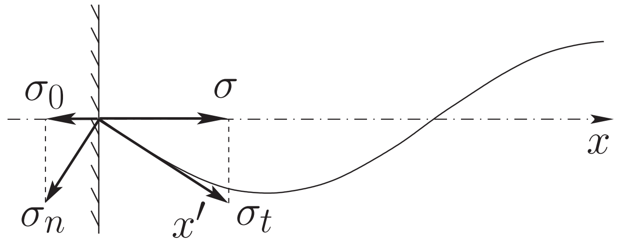

FIG. 1. Side view of a membrane fluctuation with a nonzero curvature gradient at the border. While the tangential stress σ_t gives an average projection onto x equal to σ, the normal stress $\sigma_n = \kappa \partial_{x'}(c_\parallel + c_\perp)$ gives an average projection $\approx \sigma_0$ reducing the effective tension exerted on the frame.

$$\mathcal{H}[h] \simeq \int_{A_p} dxdy \left[\frac{\kappa}{2}(\nabla^2 h)^2 + \frac{\sigma}{2}(\nabla h)^2 \right], \tag{4}$$

yielding, in Fourier series with periodic boundary conditions, the Gaussian approximation $\langle h_{\mathbf{q}} h_{\mathbf{k}} \rangle_0 = k_B T(\sigma q^2 + \kappa q^4)^{-1} \delta_{\mathbf{q}+\mathbf{k}}$. Note that the actual correlation function, renormalized by the fluctuations, involves $r = \sigma + \mathcal{O}(T)$ instead of σ, i.e., $\langle h_{\mathbf{q}} h_{\mathbf{k}} \rangle = k_B T[r q^2 + \mathcal{O}(q^4)]^{-1} \delta_{\mathbf{q}+\mathbf{k}}$. To lowest order, however, the Gaussian approximation is sufficient, yielding from Eq. (3),

$$\tau \simeq \sigma - \frac{k_B T}{2A_p} \sum_{\mathbf{q}} \frac{\kappa q^2}{\sigma + \kappa q^2}. \tag{5}$$

This equation actually gives the first term in an expansion in powers of T (taking into account fourth-order terms and measure corrections [4] would yield contributions $\sim T^2$). The wave vectors range from $q_{\min} \approx 2\pi / A_p^{1/2}$ (going to zero in the thermodynamic limit) to the upper cutoff $\Lambda \approx 1/a$ (up to some numerical factor), where $a \approx 5$ nm is the membrane thickness. Taking the thermodynamic limit and performing the corresponding integral yields (with $1/\beta = k_B T$)

$$\tau - \sigma \simeq -\frac{k_B T \Lambda^2}{8\pi} \left[1 - \frac{\sigma}{\sigma_r} \ln\left(1 + \frac{\sigma_r}{\sigma}\right) \right] \approx -\frac{\sigma_r}{8\pi\beta\kappa}, \tag{6}$$

where we have defined $\sigma_r = \kappa \Lambda^2$, of the order of the membrane rupture tension ($\kappa \approx 10^{-19}$ J [12] and the above value of Λ yields $\sigma_r \approx 5 \times 10^{-3}$ N/m, compatible with experiments [13]). The final approximation in Eq. (6) is valid for $\sigma \lesssim 10^{-2} \sigma_r$. Note that experimentally, for tensions $\tau \gtrsim 10^{-2} \sigma_r$, the stretching of the lipids (that we have neglected) should start playing a role [13], yielding further corrections to the bracket factor in Eq. (6).

Hence, for nonextreme tensions ($\sigma \lesssim 10^{-2} \sigma_r$), we obtain simply $\tau \simeq \sigma - \sigma_0$, with

$$\sigma_0 = \frac{\sigma_r}{8\pi\beta\kappa} \quad \left(= \frac{k_B T \Lambda^2}{8\pi} \right). \tag{7}$$

With the above values (yielding $8\pi\beta\kappa \approx 500$), we obtain $\sigma_0 \approx 5 \times 10^{-6}$ N/m (correct up to some numerical factor, given the inaccuracy on Λ^2). This is not a negligible correction, since the spontaneous tension of floppy vesicles can be as low as $r \approx 10^{-8}$ N/m, as measured by contour fluctuation analysis [15].

Whereas σ is not directly measurable, it may be related with the excess area $\alpha = (\langle A \rangle - A_p)/A_p \simeq \langle \frac{1}{2}(\nabla h)^2 \rangle$, which is observable [12–14]. As shown by Helfrich, using the Gaussian approximation of the correlation function (hence at first order in T) [1],

$$\alpha \simeq \frac{k_B T}{2A_p} \sum_{\mathbf{q}} \frac{1}{\sigma + \kappa q^2} \simeq \frac{k_B T}{8\pi\kappa} \ln\left(\frac{\sigma + \sigma_r}{\sigma + \kappa \frac{(2\pi)^2}{A_p}} \right). \tag{8}$$

One should remember that it is τ and not σ that one can measure or impose mechanically, e.g., by the Laplace pressure in micropipette experiments. Hence, since $\sigma \simeq \tau + \sigma_0$, we find, in the range of practical interest, $\kappa/A_p \ll \sigma \lesssim 10^{-2}\sigma_r$,

$$|\alpha| \simeq \frac{k_BT}{8\pi\kappa}\ln\frac{\sigma}{\sigma_r} \simeq \frac{k_BT}{8\pi\kappa}\ln\frac{\sigma_0+\tau}{\sigma_r}. \qquad (9)$$

Hence, micropipette experiments should reveal at very low tension (i.e., for $\tau \le 5\times 10^{-6}$ N/m) some deviation with respect to a linear relationship between α and $\ln\tau$. This effect has never been reported, but it might have been concealed by an underestimation of the tension produced by the minimum pressure allowing to grab the vesicle [18].

It follows from Eq. (9) that the natural excess area produced by a membrane subject to no external force, i.e., for $\tau = 0$, is given, within our approximations, by $\alpha_{\rm eq} \simeq \ln(8\pi\beta\kappa)/(8\pi\beta\kappa)$. This yields $\alpha_{\rm eq} \simeq 0.03$, 0.01, 0.005 for $\beta\kappa = 5, 25, 50$, respectively. Note that traditionally, one sets instead $\sigma = 0$ in Eq. (8), which yields $\alpha_{\rm eq} \simeq \ln[\Lambda\sqrt{A_p}/(2\pi)]/(4\pi\beta\kappa)$, displaying an explicit logarithmic dependence on the lateral size of the membrane. This result, however, is meaningless, because σ is not a control parameter. Actually, the question of the dependence of $\alpha_{\rm eq}$ on A_p is delicate, because renormalization group (RG) calculations show that κ effectively depends on the membrane size according to $\kappa \approx {\rm Cst} - [3k_BT/(8\pi)]\ln(A_p/a^2)$ [19]. This will yield, however, a much weaker dependence of $\alpha_{\rm eq}$ on A_p: a constant plus a very small logarithmic correction instead of a direct logarithmic dependence [20]. Note that $\alpha_{\rm eq}$ was obtained to lowest order in T; taking into account higher-order terms and measure corrections [4] should yield the secondary dependence in A_p compatible with the RG analysis.

In principle, the frame tension τ can also be calculated from $\tau = \partial F/\partial A_p$, where F is the total free-energy. This route, however, is very tricky. Starting from the Hamiltonian Eq. (4), both Refs. [4,8] show that F may be expressed, to lowest order in T, as

$$F = \sigma A_p + \frac{k_BT}{2}\sum_{\mathbf q}\ln\left[(\sigma q^2+\kappa q^4)\frac{\bar a^2\lambda^2}{2\pi k_BT}\right], \qquad (10)$$

where λ is a quantum discretizing the membrane vertical displacements and $\bar a^2 = A_p/N = 4\pi/\Lambda^2$, N being the total number of modes or degrees of freedom. As shown in Ref. [4], measure corrections and higher-order terms in the Hamiltonian give corrections of order T^2. Taking first the thermodynamic limit, then differentiating with respect to A_p, or doing the opposite, yields two different results. The former choice yields [4]

$$\frac{\partial F}{\partial A_p} = \sigma + \frac{k_BT}{2}\int\frac{d^2q}{(2\pi)^2}\ln\left[(\sigma q^2+\kappa q^4)\frac{\bar a^2\lambda^2}{2\pi k_BT}\right]. \qquad (11)$$

The latter choice, taking into account the quantification $\mathbf q = 2\pi A_p^{-1/2}(n,m)$, yields [8]

$$\left.\frac{\partial F}{\partial A_p}\right|_N = \sigma + \frac{k_BT}{2A_p}\sum_{\mathbf q}\frac{-\sigma q^2 - 2\kappa q^4}{\sigma q^2+\kappa q^4} + \frac{Nk_BT}{2A_p}, \qquad (12)$$

where the last term comes from $\partial(\ln\bar a^2)/\partial A_p|_N = 1/A_p$. This expression matches exactly the right-hand side of our Eq. (5), since $N = \sum_q$. The main difference between the approach of Ref. [8] and that of Ref. [4] is that the number of modes is kept fixed in the former and not in the latter. This result shows both the correctness of the approach of Ref. [8] and of our result obtained from the stress tensor. Another implication is that the demonstration of Ref. [4] that $r = \partial F_{\rm lim}/\partial A_p$, where $F_{\rm lim}$ is the thermodynamic limit of F, should not be interpreted as a demonstration that $r = \tau$. In general, one should thus expect $r \neq \tau \neq \sigma$.

In order to check the validity of our results, we have performed a Monte Carlo simulation of a discrete model of the Hamiltonian (1). We chose a $1d$ model in order to avoid the complex issue of the phase-space measure that arises when dealing with surfaces, while retaining all the essential features. The $1d$ membrane is a chain of N rodlike segments of length $\simeq a$, with bending rigidity in the joints, that is subject to an applied external force $\boldsymbol\tau$ (Fig. 2). The microstates are described by the variables $\{\theta_1,\ldots,\theta_N;\epsilon\}$, where θ_j is the angle between segment j and the reference x axis, and ϵ is a global variable used to let the membrane length $L = Na(1+\epsilon)$ fluctuate in the corresponding ensemble. The Hamiltonian is

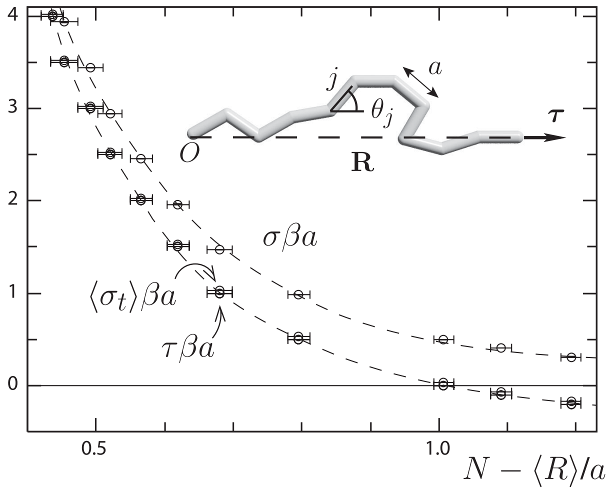

FIG. 2. Discrete $1d$-membrane model (inset). Numerical determination of the normalized membrane tension σ (upper data), tangential stress at the extremity $\langle\sigma_t\rangle \equiv \langle\sigma - \frac{1}{2}\kappa c_{N-1}^2\rangle$ (lower data) and imposed frame tension τ (lowest data, superimposed) *vs.* the shortening of the projected length $Na - \langle R\rangle$. Here, $N = 50$ and $\beta\kappa = 125a$ (persistence length). The dashed lines are guides for the eye.

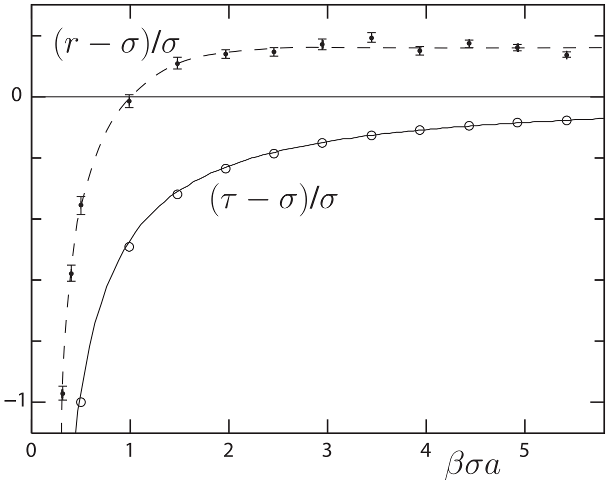

FIG. 3. Lower data: comparison between τ and σ (error bars given by the symbol size); the solid line is a fit using Eq. (14). Upper data: comparison between r and σ; the dashed line is a guide for the eye. N and κ are the same as in Fig. 2.

$$\mathcal{H}_1 = \sigma L + \frac{L}{N}\sum_{j=1}^{N-1}\frac{1}{2}\kappa c_j^2 - \tau R, \tag{13}$$

where $c_j = (\theta_{j+1} - \theta_j)/(L/N)$ and the end-to-end vector is given by $\mathbf{R} = (L/N)\sum_{j=1}^{N}\mathbf{u}(\theta_j)$, $\mathbf{u}(\theta)$ denoting the unit vector at the angle θ with respect to the x axis. We impose the boundary condition $\mathbf{u}(\theta_N) \parallel \mathbf{R}$; hence, both the applied force and the direction of the last segment are parallel to the end-to-end vector.

For each imposed value of τ, we adjust σ in order to fix $\langle L\rangle = Na$, i.e., $\langle\epsilon\rangle = 0$. In agreement with the previous $2d$ analysis, we obtain $\tau < \sigma$ (Fig. 2). Note that σ is strictly positive at zero applied force ($\tau = 0$) and that the membrane does not buckle for small negative values of τ (the buckling transition is outside the scope of this Letter). Now, in $1d$, the tangential stress reduces to $\sigma_t = \sigma - \frac{\kappa}{2}c^2$ [17]. If our analysis in terms of the stress tensor is correct, we must find $\tau \simeq \langle\sigma - \frac{\kappa}{2}c_{N-1}^2\rangle$, given the tangential boundary condition. This is indeed the case, as shown in Fig. 2, the very small discrepancy originating from the discreteness of the model.

We now reproduce in $1d$ the analytical calculation giving τ from the stress tensor. From $\tau = \langle\Sigma_{xx}\rangle \simeq \langle\sigma - \frac{\sigma}{2}h_x^2 - \frac{\kappa}{2}h_{xx}^2 + \kappa h_x h_{xxx}\rangle$, we obtain $\tau \simeq \sigma - \frac{1}{2}k_BTR^{-1}\sum_q(\sigma + 3\kappa q^2)/(\sigma + \kappa q^2)$, yielding

$$\tau - \sigma \simeq -\frac{3k_BT\Lambda}{2\pi}\left[1 - \frac{2}{3}\sqrt{\frac{\sigma}{\kappa\Lambda^2}}\arctan\sqrt{\frac{\kappa\Lambda^2}{\sigma}}\right]. \tag{14}$$

This equation is the equivalent of Eq. (6) in $1d$. As shown in Fig. 3, the agreement with the numerical data is excellent for $\Lambda = 1.1a^{-1}$ (one-parameter fit), which is a very reasonable value for the cutoff.

We now check the difference between σ and r. Following the normal gauge definition [4], we define, for any point x on the end-to-end axis $\{O;\mathbf{R}\}$, $\Theta(x) = \theta_i - \theta_N$, i being the segment whose projection onto $\{O;\mathbf{R}\}$ contains x. From $\Theta_n = \int_0^R dr\Theta(x)\exp(-in2\pi x/R)$, we fit $\langle|\Theta_n|^2\rangle^{-1} = \beta[r + \kappa q^2 + \mathcal{O}(q^4)]$, where $q = n2\pi/\langle R\rangle$. As shown in Fig. 3, r and σ are different in a nontrivial way: the sign of $r - \sigma$ changes at low tensions and $r \neq \sigma$ even at high tensions. A detailed study of this behavior is outside the scope of this Letter.

In conclusion, we have devised a new and efficient method to calculate the lateral frame tension τ of membranes. We showed that τ differs from the tensionlike coefficient r of the fluctuation spectrum, and we unveiled the correct way to derive τ from the free-energy. Our results could be checked experimentally by finely analyzing the membrane excess area of vesicles under very low Laplace pressures.

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[20] Note that there is no crumpling transition for $A_p \to \infty$ due to the frame boundary conditions.