Dynamics of a bound membrane

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The dispersion relation for the overdamped bending modes of a membrane bound to a substrate by an attractive potential is determined. The damping rate γ as a function of the wave vector q behaves, for small q, like $\gamma \sim q^2$ arising from the interplay between the hydrodynamic damping by the surrounding liquid and the restoring force in the binding potential. With increasing wave vector q, various crossovers can occur, leading to the possibility of nonmonotonic damping where γ *decreases* with q as $\sim 1/q$.

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The slow dynamics of membranes visible in the microscope as the flickering of giant vesicles [1,2] or red blood cells [3] has intrigued scientists for a long time. Indeed, the search for an explanation in the case of red blood cells may even be considered as one of the starting points of this rapidly developing field [4]. A quantitative analysis of these thermally excited shape fluctuations, however, is not trivial both for practical as well as theoretical reasons. For the giant vesicles, freely floating in a chamber, drift and rotation together with the fact that the flickering can be observed only in the equatorial plane lead to relatively large noise. The closed topology couples the shape fluctuations on long length scales through the constraint of a conserved area and enclosed volume. Likewise, in the case of red blood cells, their complicated membrane architecture as well as their nontrivial shape poses additional complications.

From a practical as well as a conceptual point of view, a big advantage arises from orienting the membrane in a well defined geometry through adhesion or interaction with a substrate [5–7]. Indeed, a new technique, reflection interference microscopy [8–10], allows quite precise measurements of the separation of a membrane from a substrate. Thus it has become possible to measure dynamical fluctuations of a bound membrane.

The purpose of this paper is to analyze this situation theoretically. So far, theoretical work on the dynamics of membranes has been focused on one planar membrane [11] and two almost planar (fluid [3] or polymerized [12]) membranes at a fixed separation used as a crude model for the thickness fluctuations of red blood cells. Fluctuations of free quasispherical vesicles have also been treated analytically [13]. The essential new effect arising for the dynamics of a bound membrane can be explained by first recalling the seminal study of Brochard and Lennon [3], who determine the damping rate for shape fluctuations of two planar incompressible membranes at a distance d. Their result for the dependence of the damping rate γ on the wave vector q can be written in the instructive form

$$\gamma(q,d) = \Gamma(q,d)E(q). \tag{1}$$

Here $E(q) = \kappa q^4$ is the well-known expression for the energy of a bending mode where κ is the bending rigidity. The kinetic coefficient $\Gamma(q,d)$ arises from the hydrodynamical damping within the surrounding liquid of viscosity η. It exhibits two different scaling regimes. (i) For $q \gg 1/d$, the two membranes are independent and the long-range hydrodynamic interaction along each of the bilayers leads to $\Gamma \sim 1/\eta q$ and thus to $\gamma \sim q^3$. (ii) For $q \ll 1/d$, $\Gamma(q,d) \sim q^2$, which can be understood [14] as the effect of conserving the enclosed incompressible volume. This leads to a quadratic behavior of the kinetic coefficient as familiar from other problems with conserved quantities. Consequently, the damping rate behaves like $\gamma \sim q^6$ in the small-q limit.

For a membrane bound at a distance $\bar{l}$ from a wall, a naive guess would be just to replace d by $\bar{l}$ in the relations given above. While this recipe indeed captures the influence of the hydrodynamic damping correctly, it is not the only modification. More importantly, the energy $E(q)$ for a bound membrane is different too, because of the potential which binds the membrane in the first place. Indeed, the full expression for the energy F of a membrane at $l(x,y)$ in a potential $V(l)$ reads [15,16]

$$\begin{aligned} F &= \int dxdy\ \tfrac{\kappa}{2}(\nabla^2 l)^2 + V(l) \\ &\approx \tfrac{\kappa}{2}\int dxdy\ (\nabla^2 h)^2 + \xi^{-4}h^2, \end{aligned} \tag{2}$$

Here I use a harmonic approximation for fluctuations $h(x,y) \equiv l(x,y) - \bar{l}$ around the minimum of the potential at $l = \bar{l}$ and define the parallel correlation length $\xi \equiv (\kappa/d^2V/dl|^2_{l=\bar{l}})^{1/4}$. For a plane-wave bending mode with wave-vector q and amplitude h_q,

$$F \equiv \tfrac{1}{2}E(q,\xi)h_q^2 = \tfrac{\kappa}{2}(q^4 + \xi^{-4})h_q^2. \tag{3}$$

Thus, for small q, the energy $E(q,\xi)$ is dominated by the term ξ^{-4} arising from the confining potential which is absent for a free membrane or two parallel membranes in the red blood cell geometry considered in Refs. [3,12]. Combining this behavior with the hydrodynamic damping, $\Gamma \sim q^2$ leads to the prediction $\gamma \sim \xi^{-4}q^2$ for a bound membrane and small q.

The expression for the damping rate γ over the full q range can be derived using the Stokes approximation for the surrounding incompressible liquid which implies

$$\nabla \cdot \mathbf{v} = 0, \quad \eta \nabla^2 \mathbf{v} = \nabla p \quad \text{for} \quad z \neq \bar{l}, \tag{4}$$

where z is the coordinate perpendicular to the substrate at $z = 0$. Using a Fourier ansatz in the x direction, the solution to these equations for the z component of the velocity with $\mathbf{v}(z = 0) = \mathbf{v}(z \to \infty) = 0$ reads

$$v_z(z) = \{A[\sinh(qz) - qz\cosh(qz)] + Bqz\sinh(qz)\}e^{iqx-\gamma t}, \ 0 \leq z \leq \bar{l} \tag{5}$$

$$v_z(z) = [Ce^{-q(z-\bar{l})} + Dq(z-\bar{l})e^{-q(z-\bar{l})}]e^{iqx-\gamma t}, \ \bar{l} \leq z, \tag{6}$$

with as yet undetermined coefficients A, B, C, and D and an undetermined damping rate γ. $v_x(z)$ and $p(z)$ follow easily from Eqs. (4) with $v_y \equiv 0$. Continuity of v_z and v_x at $z = \bar{l}$ yields two further conditions. Moreover, incompressibility of the membrane requires that the in-plane divergence of v_x vanishes at $z = \bar{l}$. Finally, as a fourth condition, the forces have to balance in the normal direction at the membrane which leads to

$$-T_{zz}^{+} + T_{zz}^{-} = -\delta F/\delta h_q = -Eh_q, \tag{7}$$

where $T_{zz}^{\pm}$ is the (z,z) component of the liquid stress tensor

$$T_{ij} \equiv -p\delta_{ij} + \eta(\partial_i v_j + \partial_j v_i) \tag{8}$$

at $z = \bar{l} \pm 0$. The amplitude h_q in the force balance (7) can be replaced by the normal velocity of the liquid at the membrane through $v_z(z = \bar{l}) = dh_q/dt$, i.e., $h_q = -v_z(z = \bar{l})/\gamma$. As trivial algebra then shows, the four conditions require for a nonvanishing solution that the damping rate is given by

$$\gamma(q, \bar{l}, \xi) = \Gamma(q, \bar{l})E(q, \xi) = \Gamma(q, \bar{l})\kappa(q^4 + \xi^{-4}) \tag{9}$$

with the kinetic coefficient

$$\Gamma(q, \bar{l}) \equiv \frac{1}{2\eta q} \frac{\sinh^2(q\bar{l}) - (q\bar{l})^2}{\sinh^2(q\bar{l}) - (q\bar{l})^2 + \sinh(q\bar{l})\cosh(q\bar{l}) + (q\bar{l})} \to \begin{cases} \bar{l}^3 q^2/12\eta, & q \ll 1/\bar{l} \\ 1/4\eta q, & q \gg 1/\bar{l}. \end{cases} \tag{10}$$

Depending on the relative size of the crossover length scale $\bar{l}$ of the kinetic coefficient and the crossover length scale ξ of the energy, two different cases have to be distinguished for the q dependence of the damping rate.

Monotonic damping. For $\bar{l} \ll \xi$, one finds from (9) and (10)

$$\gamma \approx \begin{cases} \kappa\bar{l}^3 q^2/12\eta\xi^4, & q \ll 1/\xi \\ \kappa\bar{l}^3 q^6/12\eta, & 1/\xi \ll q \ll 1/\bar{l} \\ \kappa q^3/4\eta, & 1/\bar{l} \ll q. \end{cases} \tag{11}$$

The small-q behavior has already been motivated qualitatively above as a result of conserving the volume between the membrane and the wall. The intermediate regime corresponds to the low-q limit of Brochard and Lennon since the potential has now become irrelevant. For large q, one recovers, of course, the behavior of a free membrane.

Nonmonotonic damping. For $\xi \ll \bar{l}$, the q dependence becomes

$$\gamma \approx \begin{cases} \kappa\bar{l}^3 q^2/12\eta\xi^4, & q \ll 1/\bar{l} \\ \kappa/4\eta\xi^4 q, & 1/\bar{l} \ll q \ll 1/\xi \\ \kappa q^3/4\eta, & 1/\xi \ll q. \end{cases} \tag{12}$$

The small- and large-q behavior remains the same as above. However, in the intermediate range, *the damping rate decreases with increasing wave vector* which is a very unusual feature. It arises from the fact that the potential confines the mean-square amplitudes $\langle h_q^2 \rangle$ to the value $\langle h_q^2 \rangle \approx T\xi^4/\kappa$ *independently* of q, while the hydrodynamic damping becomes less effective with increasing q.

The damping rate (9) with (10) as well as the identification of the two different dynamical scenarios (11) and (12) constitutes my main result. Whether any given potential $V(l)$ leads to monotonic or nonmonotonic damping depends on the two length scales $\bar{l}$ and ξ which are, of course, not independent but rather both determined by the potential. Before giving examples, one should also consider the effect of nonharmonic fluctuations which have been ignored so far. According to Lipowsky's general classification [17] of adhesion potentials based merely on *static* properties, three regimes for the influence of fluctuations have to be distinguished: (i) the mean-field regime, (ii) the weak-fluctuation regime, and (iii) the strong-fluctuation regime. I now discuss the *dynamical* behavior in these three cases by relating them to the two different dynamical regimes derived above using an illustrative example.

The mean-field regime. Consider a charged membrane pushed by an osmotic pressure p towards a substrate. In weak electrolytes, where the screening length is large compared to $\bar{l}$, fluctuations beyond the harmonic level can safely be ignored. The potential then reads [16]

$$V(l) = A/l + pl, \tag{13}$$

where $A \equiv (\pi T/2l_B)$ [18]. Here $l_B \simeq 0.7$ nm is the Bjerrum length in water and T the temperature (with Boltzmann's constant set to unity). One immediately gets $\bar{l} = (A/p)^{1/2}$ and $\xi = (\kappa/2A)^{1/4}\bar{l}^{3/4}$. In the small-$q$ range, this implies the damping rate $\gamma \approx (A/6\eta)q^2$, which does not depend on the mean separation $\bar{l}$ for this potential. For an estimate of the typical time scales involved, one finds $\gamma \approx (10^{-5}\ \mathrm{cm}^2/\mathrm{sec})q^2$, using the typical values $\kappa \simeq 10^{-12}$ erg$\simeq 25$ T for phospholipids and $\eta = 10^{-2}$ erg sec/cm^3 for water. For a wave length $\lambda = 1\ \mu\mathrm{m} = 2\pi/q$, this becomes $\gamma \simeq 6 \times 10^4\ \mathrm{sec}^{-1}$, which is too fast to be visible by videomicroscopy but will be accessible to dynamical light scattering. The criterion $\bar{l} \gg \xi$ implying nonmonotonic damping is met whenever $\bar{l} \gg \kappa l_B/\pi T \simeq 6$ nm. Thus one predicts a damping rate which decreases with q in the range $1/\bar{l} \ll q \ll 1/\xi$ for unscreened electrostatic interactions (and, quite generally, for adhesion potentials which belong to the mean-field regime). For $p \to 0$, which corresponds to the un-

binding transition [15,19], $\bar{l}$ becomes much larger than ξ. Thus the two crossover wave vectors $1/\bar{l}$ and $1/\xi$ separating the three regimes in (12) scale differently at the unbinding transition and the intermediate anomalous behavior of γ should, in principle, be clearly detectable.

The weak-fluctuation regime. In stronger electrolytes, the electrostatic repusion is screened and becomes exponential in l. Nonharmonic fluctuations can then no longer be neglected. In a self-consistent way they can be included by adding the steric interaction [5] $V_{FL} = c(T^2/\kappa)/l^2$ to the effective potential. Here c is a numerical coefficient of order one. (In the following, I use $c = 1$ for crude estimates.) Ignoring for simplicity the electrostatic repulsive part, the total potential now reads

$$V(l) = cT^2/(\kappa l^2) + pl. \tag{14}$$

The equilibrium separation is given by $\bar{l} = (2c/p)^{1/3}T^{2/3}/\kappa^{1/3}$. The relation between the correlation length $\xi = (\kappa/T)^{1/2}\bar{l}/(6c)^{1/4} \simeq 3\bar{l}$ and $\bar{l}$ becomes independent of the amplitude p of the linear attractive potential. Since $\xi > \bar{l}$, the weak-fluctuation regime will always be governed by monotonic damping. Note that even for $p \to 0$ the intermediate behavior $\gamma \sim q^6$ will be confined to the rather narrow interval $1/3\bar{l} \lesssim q \lesssim 1/\bar{l}$. For an estimate of the typical damping rates, I get, for small q, $\gamma \approx (cT^2/2\eta\kappa)q^2/\bar{l} \simeq (10^{-13}\ \mathrm{cm^3/sec})q^2/\bar{l}$. For $\bar{l} = 50$ nm and $\lambda = 2\ \mu$m, one obtains $\gamma \simeq 10/\mathrm{sec}$, which is below video frequency. Thus these fluctuations will be accessible to micro-optical techniques [8–10].

The strong-fluctuation regime. If both the attractive as well as the repulsive potential becomes short ranged, the nonharmonic fluctuations are so dominant that even the superposition of direct and steric interaction fails [15]. However, the scaling behavior of the damping rate as expressed by (9) and (10) should still hold, provided one uses the fully renormalized $\bar{l}$ and ξ.

I have treated the membrane as incompressible with no internal structure. The fact that it is a bilayer consisting of two compressible monolayers which can slip over each other has recently been shown to give rise to a second slow viscous mode [20]. This new mode can be understood as a fluctuation of the density difference between the two monolayers which is damped by intermonolayer friction [21]. For a free membrane, this slipping mode has the small-q behavior $\gamma \simeq kq^2/2b$, where k is the monolayer area elasticity modulus and b an intermonolayer friction coefficient. Reasonable estimates [20,21] lead to $k/2b \simeq 10^{-5}\ \mathrm{cm^2/sec}$, which shows that this slipping mode can be in the same range as the bending mode discussed above. Whenever the frequencies of both modes become comparable, the two modes will mix as it happens for the free membrane [20]. A detailed study of this effect will be pursued elsewhere [22].

For *polymerized membranes* [4], the theory developed in this paper can be applied too, provided two conditions are met: (i) the membrane is impermeable for the fluid and (ii) the membrane can still be considered as incompressible. Both conditions hold, e.g, for the compound red blood cell membrane as well as for phospholipids in the gel phase. The crucial difference between polymerized and fluid membranes arises from the renormalization of the bending rigidity by the coupling between the in-plane phonons and out-of-plane shape fluctuations [23]. This effect leads for free membranes to a crossover length ξ_*, which separates fluid behavior on small length scales from polymerized behavior on long length scales. Consequently, the energy $E(q,\xi)$ of a bound polymerized membrane [24] entering the expression (9) for the damping rate exhibits three scaling regimes [25]:

$$E(q,\xi) \approx \begin{cases} \kappa\xi_*^{2\zeta-2}\xi^{-(2+2\zeta)}, & q \ll 1/\xi \\ \kappa q^{2+2\zeta}\xi_*^{2\zeta-2}, & 1/\xi \ll q \ll 1/\xi_* \\ \kappa q^4, & 1/\xi_* \ll q, \end{cases} \tag{15}$$

where $\zeta \simeq 0.5-0.65$ is the roughness exponent. Thus, for small q, the damping rate is again given by the universal q^2 dependence. With increasing q, there is a whole set of possible crossover scenarios depending on the relative size of the three length scales $\bar{l}$, ξ, and ξ_* [26].

In most experimental setups, the bound membrane will be the bound part of an adhering vesicle. Even if only wavelengths much smaller than the size of the contact area are considered, one has to expect corrections arising from the constraint of a closed topology which preserves the enclosed volume and the total vesicle area. Approximatively, one can incorporate these effects by an effective tension Σ acting on the small-scale fluctuations [13]. Such a tension, quite generally, contributes a term Σq^2 to the energy E, which then reads for a fluid membrane

$$E(q,\xi) = \kappa(q^4 + \xi^{-4}) + \Sigma q^2. \tag{16}$$

While such a term neither modifies the small q nor the large q asymptotics, an even more complex crossover behavior emerges in the intermediate range if $\Sigma > \kappa/\xi^2$ [22]. I refrain from discussing the various cases for the sequence of crossovers theoretically. In practice, one should fit the measured dispersion relation against the theoretical expectation using Σ as a parameter [28]. With some optimism, one may then even contemplate to determine membrane adhesion potentials by carefully measuring the dynamical correlation function $\langle h_q(t)h_q(0)\rangle = [T/E(q,\xi)]\exp[-\gamma(q,\bar{l},\xi)t]$. A similar approach to determine the adhesion potential for rigid latex spheres has been used successfully indeed by Rädler and Sackmann [10].

In summary, the dispersion relation of the bending mode of a bound membrane shows rich behavior. The dominant effect on long length scales is the hydodynamical damping of the shape fluctuation taking place in a binding potential which leads to a quadratic dependence of the damping rate. This universal feature also holds for impermeable polymerized membranes and near the unbinding transition. For smaller wavelength a variety of crossover phenomena arises. Whenever nonharmonic fluctuations can be ignored, i.e., in the mean-field regime, the damping rate is predicted to decrease with increasing wave vector for an intermediate-q range. Estimates indicate that these effects should be accessible with available

techniques and yield further insight into the interaction of membranes with substrates.

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[25] In (15), it is implicitly assumed that the potential is weak enough so that the polymerized behavior can show up in an intermedate range, i.e., I assume $\xi > \xi_*$. For strong potentials, one would expect that the fluctuations are so confined that the intermediate regime in (15) is missing. In this case, the polymerized membrane will behave like a fluid one.
[26] As an example, consider the typical case $\xi_* < \bar{l} < \xi$. Then $\gamma \sim q^2$ crosses over at $q = 1/\xi$ to $\gamma \sim q^{4+2\zeta}$, at $q = 1/\bar{l}$ to $\gamma \sim q^{1+2\zeta}$, and finally at $q = 1/\xi_*$ to $\gamma \sim q^3$. The behavior in the two intermediate cases has been found previously for two parallel polymerized sheets by Frey and Nelson [12], while the free behavior $\gamma \sim q^{1+2\zeta}$ has also been obtained by simple scaling [27]. For $\bar{l} > \xi$, one can again obtain nonmonotonic behavior with $\gamma \sim 1/q$ in an intermediate-q range.
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