Nanoscale surface relaxation of a membrane stack

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Recent measurements of the short-wavelength (∼1–100 nm) fluctuations in stacks of lipid membranes have revealed two distinct relaxations: a fast one (decay rate of ∼0.1 ns⁻¹), which fits the known baroclinic mode of bulk lamellar phases, and a slower one (∼1–10 µs⁻¹) of unknown origin. We show that the latter is accounted for by an overdamped capillary mode, depending on the surface tension of the stack and its anisotropic viscosity. We thereby demonstrate how the dynamic surface tension of membrane stacks could be extracted from such measurements.

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Self-assembled stacks of membranes are encountered in various industrial and biological systems. They consist of parallel bilayers of amphiphilic molecules separated by microscopic layers of solvent — a structure with the symmetry of a smectic A liquid crystal [1]. Such stacks form lyotropic lamellar phases [2], on which many cleaning and cosmetic products are based. Lamellar bodies are found also in the lung [3] and as multilayer vesicles (“onions”) [4]. Membrane stacks made of phospholipids have been widely used to study properties of biological membranes, whereby the large number of identical, equally spaced membranes helps enhance the signal and allows the study of membrane–membrane interactions (e.g., [5]).

The elasticity of membrane stacks is equivalent to that of single-component (thermotropic) smectics [1] and has been extensively studied. The elastic moduli of the stack can be extracted from its equilibrium fluctuations using, e.g., x-ray line shape analysis [6]. By contrast, the hydrodynamics of membrane stacks [7, 8], because of their two micro-phase-separated components, differs from that of thermotropic smectics [9]. An additional hydrodynamic mode appears — the baroclinic (slip) mode — along with the known baroclinic mode of bulk lamellar phases, and a slower one (∼1–10 µs⁻¹) from that sampled by RHS. In that domain the slip dissipation dominates and, consequently, the surface relaxation is governed by an overdamped diffusive mode, whose decay rate Γ increases quadratically with the wavevector q. In this Brief Report we present a slight adaptation of that theory for a large-q, high-Γ regime such as that of RHS.

In a recent publication [12], we have addressed the surface dynamics of membrane stacks, highlighting the qualitative differences from the surface dynamics of both simple liquids and thermotropic smectics [13]. These differences arise from the slip dissipation mechanism, which is absent in simple liquids and thermotropic smectics but is usually dominant in lyotropic lamellar phases. Although the formulation in Ref. [12] is general, its analysis is focused on a very different domain (larger wavelengths and slower rates) from that sampled by RHS. In that domain the slip dissipation dominates and, consequently, the surface relaxation is governed by an overdamped diffusive mode, whose decay rate Γ increases quadratically with the wavevector q. In this Brief Report we present a slight adaptation of that theory for a large-q, high-Γ regime such as that of RHS.

The general surface dynamics of membrane stacks is quite complex, depending on several restoring and dissipation mechanisms [12]. Three moduli are associated with the restoring forces: the compression modulus B, bending modulus K, and surface tension γ. Viscous dissipation is characterized (in the limit of incompressible flow) by three viscosity coefficients [7], denoted ηM, ηγ, and ηT. The coefficient ηM, associated with differences in the lateral velocity across layers (sliding viscosity), is much smaller than the other two, which correspond to...
the viscous response to deformations of the lipid membranes. We use the parameter \( \Theta = 2(\eta_T + \eta_v) / \eta_M \) to characterize this viscosity anisotropy; it is typically of order \( 10^2 - 10^3 \) (see Fig. 1). The aforementioned slip motion requires another transport coefficient \( \eta \), \( \mu \simeq 2d^2 / (12\eta_0) \), where \( \eta_0 \) is the viscosity of the solvent (water) layer.

In view of this richness it is helpful to begin by identifying the dominant contributions to the slower mode of Ref. [14]. First, for the typical parameters of that case \( - q \sim 10^{-1} \) nm\(^{-1} \), \( \Gamma \sim 1 \) \( \mu s^{-1} \), \( \eta_M \sim 10^{-2} \) Pa s, and mass density \( \rho \sim 1 \) g/cm\(^3 \) — one gets a negligible Reynolds number, \( \text{Re} \sim \rho \Gamma / (\eta_M q^2) \sim 10^{-5} \), implying that inertial modes are irrelevant in the current case. Second, to determine the dominant dissipation mechanism one should compare the friction due to slip, \( \mu^{-1} v \) (\( v \) being a characteristic relative velocity), with that due to viscous stresses, \( \eta_T V q^2 v \), i.e., the dimensionless parameter \( S = (\eta_M \mu q^2)^{-1} \) is to be compared with \( \Theta \) [12]. We find \( S \sim 10 \ll \Theta \). Thus, unlike the mode focused on in Ref. [12], in the current large-\( q \) case viscous dissipation is dominant. Finally, the relative importance of the three restoring mechanisms depends not only on the surface perturbation wavevector \( q \) but also on its penetration depth \( \alpha^{-1} \). Since the value of \( \alpha \) is unknown a priori, all three mechanisms should be considered in principle. However, to keep the analysis as simple as possible we shall assume that the surface tension is the dominant factor. This ansatz is motivated by the experimental fact that the rate of RHS’s slower mode is linear in \( S \). This ansatz is motivated by the experimental fact that the rate of RHS’s slower mode is linear in \( S \).

For large wavelengths this dispersion relation becomes

\[
\Gamma(q) = \frac{2\gamma}{\Theta \eta_M d} \times 
\left[ \sinh^{-1} \left( \frac{1}{2} \Theta^{1/2} |q|d \right) + \sinh^{-1} \left( -\frac{1}{2} \Theta^{-1/2} |q|d \right) \right].
\] (2)

Equation (2) is the main result of our current analysis. For large wavelengths this dispersion relation becomes

\[
\Gamma(qd \ll \Theta^{-1/2}) \simeq \frac{\gamma}{2\eta_M (\eta_T + \eta_V)/2^{1/2}} |q|. \] (3)

Equation (3) is equivalent to the dispersion relation of an overdamped capillary mode at the surface of a simple liquid having effective viscosity \( \eta_{eff} = |\eta_M (\eta_T + \eta_V)/2|^{1/2} \). In the opposite, short-wavelength limit we get

\[
\Gamma(qd \gg \Theta^{1/2}) \simeq \frac{\gamma}{(\eta_T + \eta_V)d/2} \ln(|q|d). \] (4)

In this quasi-two-dimensional limit the dependence on the smaller (sliding) viscosity, \( \eta_M \), disappears, and an effective two-dimensional viscosity emerges, \( \eta_{2D} = (\eta_T + \eta_V)/2 \). Figure 1 shows fits of the dispersion relations for the slower mode, as measured by RHS, to Eq. (2) [10]. (The measurements for \( q > 0.5 \) nm\(^{-1} \) are considered less reliable due to scattering by defects in the stack.) The stack periodicity was measured as \( d = 5.4 \) and 5.6 nm at temperatures \( T = 30^\circ \)C (fluid membranes) and 19°C (gel-like membranes), respectively [10]. The value of the sliding viscosity at 30°C, \( \eta_M = 0.016 \) Pa s, was independently found from a fit of the faster mode [10]. We are thus left with two fitting parameters in Eq. (2), \( \Theta \) and \( \gamma \). For the fluid-membrane case we find \( \Theta = 110 \) and \( \gamma = 5.4 \) mN/m. It should be stressed that having two free parameters does not allow for accurate determination of both, and these values should be regarded merely as rough estimates. Nonetheless, the fitted values are of the correct scale. The value for \( \Theta \) implies \( \eta_T V \sim \Theta \eta_M \sim 1 \) Pa s, i.e., a viscosity 3 orders of magnitude larger than that of water, which matches the typical effective viscosity of lipid membranes [17]. It also implies an effective two-dimensional viscosity \( \eta_{2D} \sim \eta_T V d \sim 10^{-9} \cdot 10^{-8} \) Pa s m, which agrees well with measurements of the surface viscosity of fluid DMPC membranes [18].

The applicability of the theory to stacks of solid, gel-like membranes should be questioned, as such stacks have...
addition intra-membrane elasticity. The same concern, in fact, should be raised regarding the fluid-membrane case as well, since at the high frequencies considered here the individual membranes are expected to have a viscoelastic response. The fits obtained in Fig. 1 (in particular, the linear behavior for small \( q \)) suggest, however, that these additional restoring forces are negligible compared to the surface tension and do not affect the surface relaxation. The fit for \( T = 19^\circ C \) yields significantly larger values for both the viscosity anisotropy and the surface tension, \( \Theta = 350 \) and \( \gamma = 28 \text{ mN/m} \), which is the expected trend for stiffer membranes \[19\]. (In the fit we have assumed that the sliding viscosity \( \eta_M \) does not change much with temperature.)

The elasticity of membrane stacks gives rise to an effective static surface tension, \( \gamma_{el} = (KB)^1/2 \) \[1, 20, 21\]. The values of \( K \) and \( B \) in the fluid-membrane state were extracted by RHS from the fit of the faster mode as \( K \simeq 1.15 \times 10^{-11} \text{ N} \) (corresponding to a membrane bending modulus \( \kappa = Kd \simeq 14.8 \kappa_B T \)) and \( B \simeq 1.08 \times 10^7 \) Pa. This yields \( \gamma_{el} \simeq 11.1 \text{ mN/m} \), which is of the same order of magnitude as the high-frequency surface tension fitted above \[22\].

We now return to check the self-consistency of our assumptions. First, for a mode to be a surface one its penetration depth must be smaller than the total thickness of the sample. The penetration depth found in Eq. (1) is \( \alpha_{el}^{-1} < \Theta^{1/2}/q \lesssim 10^2 \text{ nm} \), which is at least 1–2 orders of magnitude smaller than the thickness of RHS’s films (\( \sim 10 \mu \text{m} \)). Second, for surface tension to be the dominant restoring force, one should have \( \gamma > \gamma_{el} \). This condition can be obtained rigorously \[21\] but is also realized upon demanding that the stress arising from surface tension, \( \gamma q^2 \alpha u \), be larger than both the compression one, \( B \alpha^2 u \), and the bending one, \( K \gamma q^4 u \). As described above, we actually have \( \gamma \sim \gamma_{el} \) and, thus, the assumption can be only marginally fulfilled. Moreover, the omission of the bending terms requires also that \( K \gamma q^2 / \eta_M \) be smaller than \( \Gamma \) \[12\], which is satisfied only for the lowest end of the sampled \( q \) range, \( q \lesssim 0.1 \text{ nm}^{-1} \). The apparent success of the simplified theory over the extended \( q \) range (Fig. 1), therefore, is somewhat surprising. We note that the stacks of RHS are densely packed. The thickness of a DMPC bilayer at \( 30^\circ C \) is 4.5 nm \[23\], implying that the solvent layers in-between membranes are only 1 nm thick. For such density and high-\( q \) surface perturbations the stack might not follow the usual description of linear smectic elasticity but respond merely as an anisotropic viscous liquid with surface tension.

In summary, the relaxation of nanoscale fluctuations in finite membrane stacks seems to occur via two distinct overdamped modes — a bulk baroclinic mode and a slower surface mode. The dispersion relation of the surface mode provides access to the dynamic surface tension of the stack, which should be hard to measure otherwise. Supplementing such an experiment with measurements at larger wavelengths (e.g., using dynamic light scattering), yielding a value for \( \Theta \), may allow the accurate extraction of the dynamic surface tension.

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