Undulations and Dynamic Structure Factor of Membranes

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We investigate the dynamic structure factor $S(q,t)$ of membrane phases at large wave numbers q which are sensitive to single membrane dynamics. Considering an ensemble of membrane plaquettes at random orientations, the effect of membrane thermal undulations is calculated. Their statistics is modeled by bending energy and standard hydrodynamic dispersion law. We predict a stretched exponential relaxation $S(q,t) \sim e^{-(\Gamma_q t)^{2/3}}$ with a relaxation rate $\Gamma_q \propto \kappa^{-1/2} q^3$ where κ is the bending modulus. Our results are in good agreement with recent dynamic light scattering spectra from dilute sponge phases obtained by Freyssingeas, Roux, and Nallet [(unpublished)]. [S0031-9007(96)01767-X]

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Surfactants in solutions self-assemble in a number of basic structures, of which membrane bilayer is a very common one [1,2]. Sponge and lamellar phases are two well known packing arrangements of these bilayers in the three-dimensional (3D) solvent. The sponge (or L_3) phase is isotropic with no long range order [3]. The membrane forms a random surface on a scale larger than a typical cell size ξ, resulting with finite (random) vesicles and one percolating membrane. In the lamellar phase [4], which has the symmetry of smectic-*A* liquid crystals, the membranes are arranged in a periodic stack with repeat distance which we also denote ξ. In practice the lamellar phase may be either fully oriented (i.e., a single "crystal") or powder (poly-"crystalline"), namely, composed of several lamellar grains, each having a different orientation.

On a length scale much shorter than ξ the membrane does not interact with neighboring membranes, and its behavior is similar in both phases. Scattering at such short wavelengths can thus probe the static and dynamic behavior of a single membrane, regardless of its long range order. In typical sponges, the regime of large wave numbers q, $q\xi \gg 1$, has been explored in the past by x-ray and neutron scattering [5] and yielded a static structure factor $S(q) \sim q^{-2}$, typical for an ensemble of nearly flat membrane pieces at random orientations. Recently, this regime has been exposed to light scattering using very dilute samples, giving rise to large ξ [6]. The dynamic light scattering from the sponge and powder lamellar is found anomalous. First, the relaxation profile cannot be fitted by a single exponential. A fit to a stretched exponential law $S(q,t) \sim e^{-(\Gamma_q t)^{\alpha}}$ yields an exponent $\alpha \simeq 0.7$. Second, in the sponge the relaxation rate Γ_q is found to depend on the bilayer material, which may be viewed as a dependence of Γ_q on the bending modulus κ. However, this plausible interpretation implies that, for the systems studied experimentally, Γ_q is decreasing with increasing κ, which is opposite to the trend expected from the dispersion relation for membrane undulations [7,8] $\omega(q) \sim \frac{\kappa}{\eta} q^3$ (where η is the viscosity).

On the other hand, the universal scaling law $\Gamma_q \sim q^3$ has been observed in both sponge and lamellar systems to a good accuracy. General mode coupling theories for systems where the hydrodynamic interaction dominates [9] predict $\Gamma_q \simeq \frac{k_B T}{16\eta} q^3$, so long as the wavelength is shorter than the characteristic correlation length. This result is consistent with the observed scaling with q, but inconsistent with the observed dependence of (the prefactor in) Γ_q on the specific system, since Γ_q is predicted by these theories to be independent of any free-energy parameters.

The purpose of this Letter is to resolve these apparent contradictions, which could raise some doubts in our current knowledge of membrane thermal undulations, and to explain the observed stretched exponential decay of the dynamic structure factor. We focus on one membrane plaquette of linear size ξ which is less than, or of the order of, the persistence length, making an arbitrary angle with the scattering wave vector $\vec{q}$, and consider the effect of thermal undulations on the resulting dynamic structure factor. The calculation of the latter is almost exact within the approximations made for calculating the statistics of thermal undulations. We do *not* assume, for instance, a linear relation between concentration fluctuations and membrane displacements, which is very common to the theory of smectic liquid crystals [10]. Nor do we assume that the average undulation amplitude, in a scattering blob of linear size q^{-1}, is small relative to q^{-1} [11]. We then make proper angular averaging to account for an isotropic ensemble of such plaquettes. This averaging should be suitable to describe both sponge and powder lamellar, as well as vesicle phases (see below). The result is a stretched exponential decay profile $S(q,t) \sim e^{-(\Gamma_q t)^{2/3}}$ with $\Gamma_q \sim (k_B T/\kappa)^{1/2} k_B T q^3/\eta$. The anomalous dependence on κ, $\Gamma_q \propto \kappa^{-1/2}$, is explained as a result of two competing effects. One is the *increase* of the undulations relaxation rate, and the other is the *decrease* of the average undulation amplitude, both with *increasing stiffness* κ. While a stiffer membrane, subject to a random (thermally activated) undulation, will relax faster to its flat state, it is less efficient in exploring volume, so that one has to wait a longer time for an empty solvent blob to be filled up by membrane material.

Other effects, such as the rotational and translational motion of plaquettes, will be considered in detail elsewhere [12]. Translational diffusion leads to an additional relaxation in the form of a multiplying factor e^{-q^2Dt} with a diffusion coefficient $D \sim k_BT/\eta\xi$. Comparing the two rates we conclude that, so long as $q\xi \gg 1$, the effect of translational diffusion is negligible. More precisely, this is true only for times $t \ll \eta\xi^3/\kappa$. However, for longer times $t \gtrsim \eta\xi^3/\kappa$, $S(q,t)$ has already decayed to vanishingly small, essentially unmeasurable, values. A similar conclusion is reached when we consider the effect of rotational diffusion. We note in passing that our results are not sensitive to the model of membrane plaquettes which we are using. Similar results can be obtained for a spherical vesicle of radius R, thereby significantly improving the study of Milner and Safran [11] in the scattering regime $qR \gg 1$.

We start with the general expression for the dynamic structure factor [13]

$$S(\vec{q},t) = \left\langle \sum_{i,j} e^{i\vec{q}\cdot[\vec{R}_i(t)-\vec{R}_j(0)]} \right\rangle, \qquad (1)$$

where$\vec{R}_i$'s are the coordinates of individual surfactant molecules building up the bilayer. The position of each molecule $\vec{R}_i(t)$ can be decomposed into a lateral, two-dimensional, coordinate $\vec{r}_i(t)$ on a reference flat surface, and a perpendicular position $z_i(t)$. The latter can be expressed by the function $h(\vec{r},t)$ which describes the deviation from flatness, $z_i(t) = h(\vec{r}_i(t),t)$. If membrane undulations are not too large, $\vec{r}_i(t)$ is roughly constant, with corrections being of order $\langle(\nabla h)^2\rangle$. We therefore replace $\vec{r}_i(t)$ by its average $\vec{r}$, assumed constant in time. The double sum in Eq. (1) is then transformed to

$$S(\vec{q},t) = \left\langle \frac{1}{a^4}\int d^2r\sqrt{g_r}\int d^2r' \times \sqrt{g_{r'}}\, e^{i\vec{q}_\parallel\cdot(\vec{r}-\vec{r}\,')} e^{iq_z[h(\vec{r},t)-h(\vec{r}\,',0)]} \right\rangle, \qquad (2)$$

where $\vec{q}_\parallel$ is the two-dimensional component of $\vec{q}$ parallel to the membrane average plane, a is a molecular length, and $g_r = 1 + [\nabla_r h(\vec{r},t)]^2$. We shall consider scattering geometries in which $q_z \gg (k_BT/\kappa)^{1/2}q_\parallel$. In an isotropic ensemble of plaquettes—our model of the sponge on short distances—$\vec{q}$ takes random values on different plaquettes. It can be shown, however, that the contribution to scattering from plaquettes oriented according to the reverse condition is negligible [12]. That is, density fluctuations in the parallel direction, in the form of excess area, can be neglected. Scattering from oriented lamellae is also easily performed at large q_z. When this is so, the main contribution to the integrals due to undulations comes from the exponential terms. Thus we may set g_r and $g_{r'}$ to unity and we are left to calculate the average of the second exponent in Eq. (2). We note that for the case $q_z = 0$, which has been studied in detail by Messager *et al.* [7], the entire effect of undulations is buried in the deviation of g_r and $g_{r'}$ from unity, and this approximation is not adequate.

Before we proceed to evaluate the average in Eq. (2), let us discuss the equilibrium statistics of the thermal undulations. These are assumed to follow the Helfrich bending Hamiltonian [14], which, for small deformations $\nabla h \ll 1$, is

$$H = \frac{1}{2}\kappa\int d^2r[\nabla^2 h(\vec{r})]^2 = \frac{1}{2}\kappa\sum_{\vec{k}} k^4 h_{\vec{k}} h_{-\vec{k}}\,, \qquad (3)$$

where κ is the bending modulus and $h_{\vec{k}}$ are the Fourier components of $h(\vec{r})$. With this free energy, standard hydrodynamic mode analysis [7,8] leads to the following relaxation rate of an amplitude $h_{\vec{k}}$

$$\omega(k) = \frac{\kappa}{4\eta}k^3, \qquad (4)$$

where η is the viscosity. This result for $\omega(k)$ can be rationalized using the Oseen hydrodynamic interaction [15] for the case of an almost flat membrane. Then $\omega(k) = \Lambda(k)\partial H/\partial h_{-\vec{k}}$ where $\Lambda(k) = 1/4\eta k$ is the two-dimensional Fourier transform of the Oseen interaction $1/8\pi\eta r$, leading immediately to Eq. (4)). The k^3 scaling of $\omega(k)$ is thus simply an outcome of the k^4 scaling of the energy and the long range, $1/k$, scaling of the hydrodynamic interaction. Using these, the time-dependent correlation function of $h_{\vec{k}}(t)$ is written as

$$\langle h_{\vec{k}}(t)h_{-\vec{k}}(0)\rangle = \frac{k_BT}{\kappa k^4}\,e^{-\omega(k)t}. \qquad (5)$$

The stochastic dynamics of $h_{\vec{k}}(t)$ can be described by a Langevin equation in which the random force is assumed to obey Gaussian statistics [16]. With this assumption, and the Gaussian (harmonic) approximation to the bending energy Eq. (3), it follows that the stochastic variable $h(\vec{r},t) - h(\vec{r}\,',0)$ also obeys Gaussian statistics [16]. As a result, the average in Eq. (2) can be performed exactly to give

$$S(\vec{q},t) = \frac{1}{a^4}\int d^2r\int d^2r' e^{i\vec{q}_\parallel\cdot(\vec{r}-\vec{r})} e^{-\frac{q_z^2}{2}\langle[h(\vec{r},t)-h(\vec{r}\,',0)]^2\rangle}. \qquad (6)$$

Equation (6) may be verified [12] by performing exact averaging in time over the random (white noise) force appearing the Langevin equation, and exact averaging over the initial (equilibrium) conditions, using a partition function with the Hamiltonian of Eq. (3).

Using Eq. (5), the real-space correlation function in Eq. (6) can be decomposed into static and dynamic parts

$$\langle[h(\vec{r},t) - h(\vec{r}\,',0)]^2\rangle = \Phi_o(r - \vec{r}\,') + \Phi(\vec{r} - \vec{r}\,',t) \qquad (7)$$

with the static membrane correlator

$$\Phi_o(\vec{r} - \vec{r}\,') = \langle [h(\vec{r}) - h(\vec{r}\,')]^2 \rangle$$

$$= \frac{1}{2\pi^2} \frac{k_B T}{\kappa} \int \frac{d^2 k}{k^4} (1 - e^{i\vec{k}\cdot(\vec{r}-\vec{r}\,')}) \qquad (8)$$

and a dynamic correlator

$$\Phi(\vec{r} - \vec{r}\,', t) = \frac{1}{2\pi^2} \frac{k_B T}{\kappa} \times \int \frac{d^2 k}{k^4} e^{i\vec{k}\cdot(\vec{r}-\vec{r}\,')} (1 - e^{-\omega(k)t}) \,. \qquad (9)$$

(The lower and upper limits for these integrals are $k = \pi/\xi$ and $k = \pi/a$, respectively.) The integral in Eq. (8) can be evaluated to give

$$\Phi_o(\vec{r} - \vec{r}\,') \simeq \frac{k_B T}{4\pi\kappa} |\vec{r} - \vec{r}\,'|^2 \ln\left(\frac{\xi}{|\vec{r} - \vec{r}\,'|} \right), \qquad (10)$$

showing the well known divergence with distance for surfaces dominated by bending energy [4], $\Phi_o(r) \sim r^2$.

Let us now turn to the time-dependent correlator which determines the relaxation profile of $S(q, t)$. The integral in Eq. (9) is calculated for $\eta a^3/\kappa \ll t \ll \eta \xi^3/\kappa$ to leading order [12] to give

$$\Phi(\vec{r} - \vec{r}\,', t) \simeq \left[0.069 \left(\frac{k_B T}{\kappa} \right)^{\frac{1}{2}} \frac{k_B T}{\eta} t \right]^{\frac{2}{3}} - \frac{1}{12\pi} \frac{k_B T}{\kappa} |\vec{r} - \vec{r}\,'|^2 \ln\left(\frac{\kappa}{4\eta a^3} t \right) + \phi_o(|\vec{r} - \vec{r}\,'|) \,. \qquad (11)$$

Here ϕ_o is a function only of $|\vec{r} - \vec{r}\,'|$ and thus contributes only to the static structure factor. The second term has a logarithmic dependence on time which would be extremely hard to detect in experiment. The dominant time dependence is thus described by the first term which increases with time as $\sim t^{2/3}$. This "anomalous diffusion" will subsequently give rise to the stretched exponential relaxation.

Using these results in Eq. (6), and performing the remaining integrals, we obtain the dynamic structure factor of plaquettes *at a given orientation* (e.g., an oriented lamellar phase) in the form $S(\vec{q}, t) = S(\vec{q}) e^{-(\Gamma_{q_z} t)^{2/3}}$ where $\Gamma_{q_z} = 0.025 (k_B T)^{3/2} / (\kappa^{1/2} \eta) q_z^3$ and where $S(\vec{q})$ is the static structure factor. Finally, in order to predict the relaxation profile for sponge, powder lamellar, and vesicle phases, we *average* over the angle between $\vec{q}$ and the surface normal. This average is dominated by the region near zero angle, i.e., when $q_\parallel \approx 0$ and $q_z \approx q$, but full integration is still required for an accurate description. The result, for $\kappa/k_B T \gtrsim 1$, can be well presented [17] by a *stretched exponential*

$$S(q, t) \simeq S(q) e^{-(\Gamma_q t)^{2/3}}, \qquad (12)$$

where

$$\Gamma_q = 0.025 \gamma_k \left(\frac{k_B T}{\kappa} \right)^{\frac{1}{2}} \frac{k_B T}{\eta} q^3. \qquad (13)$$

Here γ_k is a *weak*, monotonously increasing, function of $\kappa/k_B T$ and approaches unity for $\kappa/k_B T \gg 1$. [To lowest order $\gamma_k \simeq 1 - 3 \ln(q\xi) k_B T / 4\pi\kappa$.] Note the familiar scaling $\Gamma_q \sim q^3$ and the anomalous dependence on κ, $\Gamma_q \sim \kappa^{-1/2}$. $S(q) \sim q^{-2}$ is the sponge typical static structure factor [5] (in the regime $q\xi \gg 1$), describing also the scattering from an isotropic phase of large disks or large vesicles.

The result (13) can be justified using a simple handwaving, scaling-type, argument. We focus on one membrane plaquette which is oriented perpendicular to $\vec{q}$, i.e., with $q_z = q$. To significantly relax density correlations in the z direction, the membrane has to move in this direction a distance of order $1/q$, implying an average undulation amplitude $h \sim 1/q$. Since, from Eq. (10), $h \sim (\frac{k_B T}{\kappa})^{1/2} r$, the lateral distance corresponding to this amplitude is $r \sim (\frac{\kappa}{k_B T})^{1/2} q^{-1}$. As κ increases, one has to go further away along the membrane in order to obtain the desired amplitude. The Stokes-Einstein diffusion coefficient of a membrane sheet of this size is $D \sim k_B T / \eta r$ which leads to $D(q) \sim \frac{k_B T}{\eta} (\frac{k_B T}{\kappa})^{1/2} q$. The relaxation rate is, as usual, given by $\Gamma(q) \sim D(q) q^2$, which leads immediately to the same scaling as in Eq. (13).

The predicted stretching exponent $\alpha = 2/3$ is close to the experimental fit value $\alpha = 0.7$. The trend of Γ_q to decrease with increasing κ is also consistent with experiment. The latter behavior has been observed [6] using three different systems: (i) SDS/pentanol/water/dodecane, (ii) $C_{12}E_5$/hexanol/water, and (iii) SDS/octanol/brine, for which κ has been estimated independently from dynamic light scattering spectra of concentrated lamellar phases [6,18] (yielding the values 2, 3, and $4 k_B T$, respectively). The *small,* nontrivial, numerical prefactor in Eq. (13) is remarkably close to the experimental value (e.g., the agreement is within 20% for the system SDS/octanol/brine where $\kappa \simeq 4 k_B T$). This numerical factor is very different from the one predicted by the Kawasaki mode coupling theory (1/16, with no κ dependence). The experimental accuracy does not allow us, however, to quantitatively verify our prediction $\Gamma_q \sim \kappa^{-1/2}$. Our theory predicts a similar stretched exponential profile also for an *oriented* lamellar phase with $q_z \gg (k_B T/\kappa)^{1/2} q_\parallel$. Experiments on sufficiently dilute systems [6] at large q_z are not yet available.

It is interesting to note that the static structure factor ($t = 0$) obtained from Eqs. (6)–(10) is identical to the one derived by Ramaswamy, Prost, and Lubensky [19] for the single membrane contribution to the scattering from lamellar phases. However, Ramaswamy *et al.* [19] claim that, in order to discuss the *dynamics* of concentration fluctuations, the equations describing membrane undulations are not important since they have to be coupled to a membrane mass conservation law. Hence they conclude that the result of the mode coupling theory [9] $\Gamma_q \sim (k_B T/\eta) q^3$ is also correct for the sponge and lamellar phases in the limit $q\xi \gg 1$. Both our predictions and the experimental results [6] are at variance with this conclusion. Although we do not conserve exactly membrane material in each plaquette, in conjunction with the approximate transformation from Eq. (1) to Eq. (2), the error made in this approximation can be shown negligible. The general mode coupling approach *should* apply to the regime $q\xi \ll 1$ of the sponge where the wavelength is much longer than the individual cells building up the sponge. This regime has been studied elsewhere [20].

Another interesting point is that a similar stretched exponential decay of the dynamic structure factor, with an exponent $\alpha = 2/3$, appears for both *flexible* 1D [13] (linear) and 2D (membranelike) polymers [12] obeying the Zimm model. The counterpart of the undulations correlator $\langle [h(\vec{r}, t) - h(\vec{r}\,', 0)]^2 \rangle$ appearing in our calculation is the segment-segment correlator [13] $\langle [\vec{R}_m(t) - \vec{R}_n(0)]^2 \rangle$ (R_n is the position of polymer segment n). The expressions for the dynamic correlators are very similar in these three cases leading to the apparently universal decay law $e^{-(\Gamma_q t)^{2/3}}$. In fact, the expected scaling $\Gamma_q \sim q^3$ can be reconciled with Eq. (6), or with the analogous equations for flexible polymers [12,13], which are quite general and assume only Gaussian fluctuation statistics, only if α takes the value $2/3$. Yet for flexible polymers the effective relaxation rate has the more familiar temperature dependence $\Gamma_q \propto k_B T$. This is because in the Zimm model of polymers the segment spring constant is of entropic origin and is thus proportional to $k_B T$ with no dependence on any other free-energy parameters.

A somewhat different relaxation is found for semiflexible rodlike polymers [21], which are the 1D analog of the semiflexible membranes discussed here. The bending energy is described in a similar way to Eq. (3), with a 1D integral replacing the 2D integral and with a bending modulus κ which has dimensions of energy × length. Equation (5) still describes correctly the undulation correlation function $\langle h_{\vec{k}}(t) h_{-\vec{k}}(0) \rangle$ using, however, $\omega(k) \sim \frac{\kappa}{\eta} k^4$ instead of Eq. (4). Following the same approach as for membranes leads to [12,21] $S(q, t) \sim e^{-(\Gamma_q t)^{3/4}}$, where $\Gamma_q \sim (\frac{k_B T}{\kappa})^{\frac{1}{3}} \frac{k_B T}{\eta} q^{8/3}$.

To conclude, using the Helfrich bending free energy to describe membrane undulations we have explained both the stretched exponential decay of the sponge and powder lamellar dynamic structure factors, and the anomalous dependence of the effective relaxation rate on bending stiffness. A similar behavior is predicted for scattering from large vesicles and from an oriented lamellar phase at large q_z. Our predictions provide a novel quantitative method for measuring the bending stiffness of membranes in bulk phases. This can be extremely useful since knowledge of this quantity is often hampered by lack of accuracy and conflicting results from different techniques [22]. The structure factor can be often detected even outside the range of light scattering, e.g., by neutron spin echo which widens up the possible applicability of this method.

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Note Added.—Some of our results are similar to those obtained by Frey and Nelson [J. Phys. I France **1**, 1715 (1991)] using a renormalization group approach.

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