Bending Energy of Amphiphilic Films at the Nanometer Scale

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The diffuse scattering of x rays by the thermally excited out-of-plane fluctuations of different amphiphilic films was measured for in-plane wavelengths down to the nanometer range, giving access to nontrivial bending effects. The Helfrich Hamiltonian applies on pure water and in the solid phase of an arachidic acid monolayer a large bending rigidity constant was measured. When formed on a subphase containing divalent cadmium ions, the height-height fluctuation spectrum \( \langle z(q)z(-q) \rangle \) is greatly modified: no longer consistent with a \( q^{-4} \) law at large wavelengths but rather with a \( q^{-3.3 \pm 0.2} \) law, revealing a very different physical mechanism whose origin is discussed. [S0031-9007(97)02940-2]

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Amphiphilic molecules composed of a hydrophobic hydrocarbon moiety and a hydrophilic polar head adsorb at interfaces (forming monomolecular films) or self-assemble in bulk solutions where a variety of supramolecular structures ranging from microemulsions to cell membranes are obtained [1]. A success of recent years has been the ability to predict the topology and stability of the different supramolecular structures from the spontaneous curvature and the bending rigidity moduli for mean curvature \( K \) and Gaussian curvature \( K \) of the individual films, while ignoring their precise molecular structure [1]. However, whereas the corresponding Hamiltonian was given by Helfrich in 1973 on the basis of symmetry arguments [2], the associated fluctuation spectrum has never been measured, and the range of situations where the Helfrich Hamiltonian can be applied is still an open question from an experimental point of view. Indeed, the coupling of the out-of-plane fluctuations with the fluctuation modes of any quantity of suitable symmetry may modify the energy spectrum [3].

In addition to bending rigidity \( K \) at short length scales, the out-of-plane fluctuations of a film adsorbed at a liquid-gas or liquid-liquid interface are in general also limited by the surface tension \( \gamma \), and finally gravity at long length scales. The fluctuation spectrum including these effects of gravity, capillarity, and bending rigidity can be obtained by Fourier transforming the free energy and applying the equipartition theorem, namely,

\[
\langle z(q)z(-q) \rangle = \frac{k_B T}{\Delta \rho g + \gamma(q)q^2 + K(q)q^4}, \tag{1}
\]

where \( q \) is the (in-plane) wave-vector modulus of the fluctuation mode and \( \Delta \rho \) is the density gradient at the interface. Bending rigidity will therefore become important in limiting the out-of-plane fluctuations only at scales smaller than \( \sqrt{K/\gamma} \), i.e., in the nanometer range for films spread at the air-water interface. It has been made explicit in Eq. (1) that both \( \gamma(q) \) and \( K(q) \) should depend on the observation scale [4,5]. The renormalization of \( \gamma \) leads to terms in \( q^4 \) equivalent to a weak bending rigidity, whereas the renormalization of \( K \) depends on the nature of the film (fluid or solid) [4–7]. In the case of a tethered membrane having the elasticity of a solid, there can be a coupling between out-of-plane fluctuations and in-plane modes due to the fact that many configurations of the film with low bending energy per se imply stretching. This leads to a divergence of \( K(q) \) at large scale, or a rigidity term proportional to \( 1/q^{-\eta} \), \( 1/2 < \eta < 1 \) [8]. As mentioned above, out-of-plane fluctuations may also couple to the fluctuation modes of several different quantities. An interesting case is that of polarization for dipoles normal to the surface, always carried by classical amphiphiles, leading to a nontrivial \( q^{-3} \) dependence [3].

Among the different methods which have already been used to determine bending constants, reflectivity [9,10] and ellipsometric methods [4] measure an integral over modes and are therefore unable to give access to the most interesting power law, as is the Fourier analysis of the shape fluctuations of vesicles which relies on a given form of the Hamiltonian [11]. Small-angle x-ray scattering generally implies orientational averaging, making the extraction of information less direct [7]. In order to overcome these limitations and to get unambiguous information, the fluctuation spectra of oriented films with a well characterized structure must be measured. Langmuir films offer this possibility: molecular area, temperature, and surface pressure can be fixed, the structure can be determined by grazing-incidence x-ray diffraction and reflectivity, and the texture can be
observed in situ by Brewster angle microscopy or by atomic force microscopy (on transferred films). In this study, we directly measure the fluctuation spectra by grazing-incidence diffuse (off-specular) x-ray scattering [12–14]. In a Langmuir film, the scattering of x rays results from height fluctuations of the different interfaces (air/chain, chain/chain, chain/head, head/subphase), assumed in this study to fluctuate conformally. The interferences between beams scattered at the different interfaces, which can be accounted for within the distorted wave Born approximation taking into account refraction and absorption [14], give rise to the normal $q_z$ dependence. The $q_z$ dependence of the scattered intensity is concentrated in the form $\int dx dy \left\{ \left| e^{i q_z (x,y)} \right|^2 - 1 \right\} e^{i q_x x + i q_y y} \tilde{R}(x,y)$, where $\tilde{R}(x,y)$ is the Fourier transform of the resolution function.

The measurements were performed at the “Troika” beam line at the European Synchrotron Radiation Facility (ESRF) (Fig. 1). The desired radiation was selected using the (111) reflection of a diamond monochromator placed in the “white” beam in an asymmetric Laue geometry, and the grazing angle of incidence was fixed by tilting the monochromator. A SiC mirror was used in the monochromatic beam in order to eliminate higher order light. The intensity of the 0.4 × 0.2 mm$^2$ ($w \times h$) beam ($\Delta E/E = 6 \times 10^{-5}$) was approximately $10^{10}$ counts/s. The homemade Langmuir trough was mounted on a Nanofilm technologie GmbH active vibration isolation system on the sample circle of the three-axis diffractometer. Since the signal scattered by the interfacial fluctuations at large in-plane wave vectors $q_x$ is very low ($\approx 10^{-10}$ of the incident beam), extreme care was taken to limit the background by shielding the experimental device and by surrounding the Langmuir trough with helium. Another very important requirement is to fix the grazing angle of incidence below the critical angle for total external reflection in order to limit the evanescent wave penetration and therefore scattering in the bulk. Under total external reflection conditions the background could be measured by simply lowering the trough by 1 mm and scanning around the direct beam. The experiments consisted of $\theta_d$ detector scans in the plane of incidence at 12.9 keV ($\lambda = 0.096$ nm) with a fixed angle of incidence $\theta_i = 1.4 \times 10^{-3}$ rad, just below the critical angle for total external reflection [see Fig. 1]. With this geometry both $q_z = 2\pi/\lambda[\sin(\theta_i) - \sin(\theta_d)]$ and $q_x = 2\pi/\lambda[\cos(\theta_i) - \cos(\theta_d)]$ are varied jointly in an experiment.

We first measured the fluctuation spectrum of the bare water (from a Millipore purification system) surface [Fig. 2(a)]. In this case, the scattered intensity can be calculated without any adjustable parameter: the surface tension $\gamma_{H_2O} = 73$ mN/m is known, as well as the different parameters determining the resolution of the experiment (slit opening, footprint). The excellent agreement between the calculated intensity and the

![Fig. 2](image_url)

**FIG. 2.** Intensity scattered by the film as a function of the horizontal wave-vector transfer $q_x$. (a) Absolute scattered intensity multiplied by the in-plane wave-vector transfer $q_x$ as a function of $q_x$ (detector scans projected on $q_x$). Measured background for $s_3 = 1$ mm (empty squares) and 22 mm (diamonds). The grey solid line is a fit to the Gaussian tails of the direct beam for $q_x < 10^3$ m$^{-1}$ (does not contribute to the analysis) and $a \propto (q_x + C)^{-1}$ background at larger wave vectors. Bare water surface with $s_3 = 1$ mm (empty circles) and $s_3 = 10$ mm (empty triangles). Arachidic acid on pure water at 9°C at 25 mN/m (black filled circles) for $s_3 = 1$ mm. Arachidic acid on the CdCl$_2$ subphase for $s_3 = 22$ mm (filled squares); calculation with a pure $q^2$ spectrum (dot-dashed grey curve), best fit to a $q^{-1.3}$ power law (continuous line), and to a $q^{-3}$ power law with additional roughness (dashed grey curve). (b) Intensity scattered by the arachidic acid film on pure water at $\tau = 40$ mN/m divided by the intensity scattered at $\tau = 25$ mN/m in the S phase (circles) as a function of $q_x$. $K = 500 k_B T$ (black solid line), $K = 300 k_B T$ (grey dot-dashed line), and $K = 700 k_B T$ (grey dashed line).
experimental data for different resolution conditions demonstrates the ability of the method to determine fluctuation spectra very precisely. We also could extend the measurements of Ref. [13] towards much larger wave vectors by two decades.

In this first study, we limited the films investigated to different phases of a simple amphiphile: arachidic acid CH₂(CH₂)₁₈COOH at 9°C and a surface pressure of 1 mN/m in the so-called liquid-condensed \( L_2 \) mesophase and at 25 mN/m and 40 mN/m in the much less compressible (compressibility \( \approx 1 \) m/N) \( S \) solid phase [15]. In the presence of interfacial films it is necessary to strictly limit the number of adjustable parameters. We therefore always used the macroscopic surface tension measured by the Wilhelmy plate [16] and did not allow for values of the structural parameters outside the error bars determined from literature and complementary x-ray reflectivity experiments. Evidence that we are indeed observing scattering by the fluctuating film is provided by the interferences in Fig. 2(a) resulting from the interference of this phase, the structural contribution is the same in both cases and the quotient is only sensitive to the fluctuations (in fact, those of the film at 40 mN/m, which is the rougher one). We obtain \( K = 500 \pm 200k_BT \) for this film.

The values of the bending rigidity that we obtain in the \( S \) phase are much higher than the values found in the fluid phases of short chain surfactants [11], but compare well with previous indirect estimations [9]. As expected, \( K \) is found to increase when the compressibility of the film decreases. Simple models [10] for the bending of solid plates predict that the bending rigidity should be proportional to the compressibility, but more complicated behavior can be expected and will be investigated in future experiments. It is also interesting to note that the highest \( K \) values in the incompressible \( S \) phase are consistent with the bending stiffness of a solid plate having the elastic constants of polyethylene [11].

We also performed experiments with arachidic acid spread on a subphase containing \( 10^{-3}M \) CdCl₂, \( p\text{H} = 8.8 \) fixed by methylamine at a molecular area of 0.25 nm²/molecule (and zero pressure). In that case, a very stiff monolayer [19] is formed with partially covalent complex formation specific of the Cd²⁺ cation [19,20]. Its roughness measured by x-ray reflectivity is very low (0.2 ± 0.01 nm). The ordering of the Cd²⁺ counterions has been observed below 12°C with a coherence length larger than 100 nm [20]. In contrast to the films on pure water, the fluctuation spectrum of the film on the CdCl₂ subphase at high \( p\text{H} \) could not be fit using the \( q^{-4} \) law at large wave vectors, but rather with a term \( 8 \times 10^{-12}q^{-3.2±0.2} \) in Eq. (1) [Fig. 2(a)] [21]. Note that the best fit with a \( q^{-4} \) law using a possible additional roughness at the molecular scale (yielding \( K = 4000k_BT \), indicating that the film is indeed very stiff) is quite poor. We have no unique explanation for this nontrivial behavior. However, effects of nonconformal roughness or density fluctuations can be dismissed given the results of Ref. [20]. As explained above, there are at least two cases where such a power law can be expected: coupling of the out-of-plane fluctuations with dipoles born by the molecules or with phonons if the film were to be a true solid membrane. That the best fit is obtained with a
$q^{-3.3 \pm 0.2}$ power law rather than with a $q^{-3}$ law favors the second hypothesis of a solid membrane. Moreover, in the case of a dipolar origin, the prefactor of the $q^{-3}$ term should be $p_0^2/2\varepsilon$ where $p_0$ is the surface density of dipoles, and $\varepsilon$ intermediate between the values for water and air. A naïve estimation of this prefactor can be obtained from surface potential measurements, $\Delta V = p_0/\varepsilon$. With $\Delta V = 157\text{ mV}$ [22], the maximum value of the prefactor should be $\approx 10^{-14}N$, much smaller than any possible experimental value ($[5 \pm 3] \times 10^{-10}N$).

In conclusion, the possibility of measuring height fluctuation spectra down to molecular scales, thus enabling the determination of exponents and bending constants by means of x-ray surface scattering has been demonstrated in this paper. These results should open wide prospects in the study of simple liquid interfaces and membranes.

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[16] The value of the plateau in $q_x \times I$ of Fig. 2(a) $10^9 < q_x < 10^7 \text{ m}^{-1}$ is directly proportional to the surface tension.
[18] The sensitivity of the experiment is approximately $\gamma/q_x^{max}$, where $q_x^{max}$ is the position of the last interference maximum and is therefore $\approx 100k_BT$ for this curve.

The roughness of this film is so small that it is possible to develop the expression for the intensity to the lowest order in $q_x$. The scattered intensity is then proportional to the integral over the resolution of the Fourier spectrum Eq. (1), whose highest exponent can be varied.