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Letters

X-ray Study of the Fluctuations and the Interfacial Structure of a Phospholipid Monolayer at an Alkane–Water Interface

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The interfacial structure and fluctuations of a L- α -dipalmitoylphosphatidylcholine monolayer at the hexadecane/water interface were investigated using grazing-incidence surface scattering of X-ray synchrotron radiation. The interfacial structure of the densely packed monolayer is consistent with that of a similar monolayer at the air/water interface. The fluctuations are shown to be limited by interfacial tension on length-scales down to in-plane wavelengths of a few tens of nanometers. This result at the alkane/water interface demonstrates the power of the X-ray grazing-incidence technique applied to the study of liquid–liquid interfaces.

1. Introduction

The detailed understanding of liquid–liquid interfaces, which is of upmost importance for many industrial applications, still poses challenging problems to fundamental research, very often necessitating the precise structural and morphological characterization of well-defined interfaces. For example, a well-known property of surfactant molecules is their ability to compatibilize immiscible liquids by forming thermodynamically stable microemulsions with characteristic lengths in the sub-micrometer range, or metastable emulsions with larger characteristic lengths. Both of these structures find many important applications. One of the most fruitful approaches developed in recent years to understand the

range of microemulsion structures consists of comparing the relative interfacial energies of the different phase topologies (micellar, lamellar, and bicontinuous).¹ Because the formation of a microemulsion is accompanied by a dramatic lowering of the surface tension by up to several orders of magnitude, the interface fluctuations play a crucial role and the interfacial energies are mainly bending energies, depending on the monomolecular film spontaneous, mean and Gaussian curvatures.² Much theoretical effort has therefore been devoted to the understanding of bending constants in terms of the interfacial film structures,³ as well as their possible

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renormalization by thermal fluctuations.⁴ Experimentally, however, the accurate measurement of the interface position fluctuations at length scales ranging from the nanometer to the millimeter in order to determine the elastic constants remains a nontrivial problem. A very promising possibility has been opened by the recent development of grazing-incidence X-ray surface-scattering methods,^{5–7} but their reliable application to liquid–liquid interfaces has up to now still to be demonstrated. Similarly, many other problems, in particular those concerning complex interfaces (e.g., polymer or mixed polymer–surfactant films at interfaces, or the adsorbed structures they form at solid–liquid interfaces), require the precise structural or morphological characterization of well-defined buried fluid interfaces, and would greatly benefit from such developments. As a first step toward the study of such more complex interfaces, we have first investigated the bending energy of Langmuir films at the air–water interface.^{7,8} The advantage of this method is that well-controlled, well-oriented, macroscopically-flat films can be studied. In this letter, we describe a first extension toward the investigation of such films at submerged liquid–liquid interfaces.

The morphology of the liquid–liquid interface is mainly due to the capillary fluctuations of the interface position, best characterized by the interface height fluctuation spectrum $\langle z(q) z(-q) \rangle$ and can be determined in grazing-incidence surface-scattering experiments. The amplitude of thermally-excited interfacial undulations depends on the energy necessary to deform the film. According to the equipartition theorem

$$\langle z(q) z(-q) \rangle = k_B T / \mathcal{H}(q) \quad (1)$$

where $\mathcal{H}(q)$ is the Hamiltonian describing the energy necessary to deform the interface as a mode with wavelength $2\pi/q$. Considering the cost in energy due to the increase in gravitational energy and in area for the deformed surface: $\mathcal{H}(q) = \Delta\rho g + \gamma q^2$ where γ is the interfacial tension⁹ and $\Delta\rho$ the density difference between the two fluids. Using simple symmetry considerations,² an additional Kq^4 contribution should be included to account for bending effects, where K is the bending rigidity coefficient associated with mean curvature.

Since neutrons are generally less absorbed in condensed media than are X-rays, neutron reflectivity¹⁰ has first been applied to the study of submerged interfaces. However, the much higher flux of X-ray synchrotron sources might make them better suited to the investigation of interfacial structures and fluctuations, neutrons remaining unique in allowing the investigation of the dynamics of fluctuations.¹¹ Using fairly penetrating (≥ 18 keV) X-rays, both reflectivity experiments¹² probing the interfacial structure

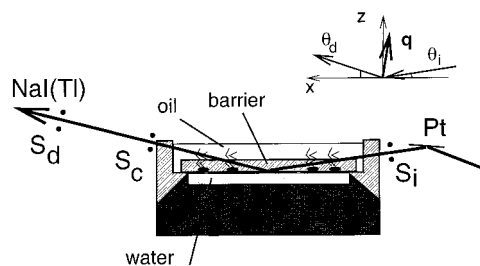


Figure 1. Experimental geometry. Pt is a platinum-coated mirror. Slits sizes are $s_i = (500 \times 15) \mu\text{m}^2$ ($H \times V$); $s_c = (5 \times 1) \text{mm}^2$ ($H \times V$); $s_d = (10 \times 0.1) \text{mm}^2$ ($H \times V$). The sample-to-detector distance is 720 mm and the slit s_c -to- s_d distance is 515 mm. NaI(Tl) scintillator. The glass parts of the modified Langmuir trough are indicated in dark gray and the Teflon parts are shaded. Inset: Scattering geometry.

normal to the interface and grazing-incidence diffraction experiments¹³ probing the in-plane order within the plane of the interfacial film have already been reported. To the best of our knowledge, the interface fluctuation spectrum was previously considered in only one case, that of an oil–water interface in equilibrium with a middle-phase microemulsion.¹⁴ In this very interesting study, the possibility of such experiments was demonstrated and the integrated interfacial roughness was measured. However, the measurement of diffuse scattering was only performed close to the specular reflection, limiting the investigation of interfacial ripples to in-plane wavelengths on the order or larger than $1 \mu\text{m}$. We demonstrate here that measurements using a carefully designed background subtraction procedure have allowed us to probe for the first time the interfacial roughness of an oil–water interface down to the 10-nm scale.

2. Experimental Details

For this study, we used ultrapure water (resistivity $> 18 \text{ M}\Omega\cdot\text{cm}$) from a Millipore MilliQ+ system and hexadecane (purity $> 99\%$) from Merck. The hexadecane–water interfacial tension at room temperature is 53.3 mN/m .¹⁵ The amphiphile chosen for this study was the phospholipid L- α -dipalmitoylphosphatidylcholine (DPPC) composed of two C_{16} hydrocarbon chains and a phosphocholine headgroup. The polymorphism of this phospholipid has been extensively investigated at the air–water interface¹⁶ as well as at the oil–water interface.^{17–19}

A Langmuir trough designed for X-ray studies at the oil–water interface was specially built for this experiment. The cell is composed of a lower glass trough containing the water phase on which a Teflon frame containing the oil phase is precisely mounted (Figure 1). The Teflon frame also guides the two symmetrical glass barriers, of which all faces except the bottom one are Teflon-coated. This configuration allows the efficient confinement and compression of an amphiphilic film at the oil–water interface. A Teflon Wilhelmy plate sits in a well in the glass trough, and two thin ($50 \mu\text{m}$) Teflon windows allow the passage

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of the X-ray beam through the cell. In this experimental cell, the DPPC film was first characterized by molecular area–surface pressure isotherm measurements and by fluorescence microscopy. The most interesting characteristic for the present study of DPPC films at the hexadecane–water interface is their stability. The film remains stable up to surface pressures larger than 40 mN/m; that is, interfacial tensions as low as 10 mN/m can be reached, from which a root mean square roughness of 1.1 nm is expected at the hexadecane–water interface by the integration of eq 1 (the density of hexadecane is 0.77 g/cm³).

The measurements were performed at the “CRG-IF BM32” beamline at the European Synchrotron Radiation Facility (ESRF). For the X-ray experiments, the cell was mounted on a Nanofilm technologie GmbH active vibration isolation system on the sample stage of the diffractometer. The energy of the X-ray beam was fixed at 18 keV ($\lambda = 0.0688$ nm) using a two-crystal Si(111) monochromator. A focusing mirror before the monochromator reduces the intensity of the higher harmonic reflections. As indicated above, the X-ray beam penetrates the alkane from the side and is then scattered by the interface. At 18 keV, the penetration length of X-rays through bulk hexadecane is about 5 cm. The transmission through the 7 cm wide experimental cell is only 26%. A grazing angle-of-incidence of $\theta_i = 0.45$ mrad was fixed below the critical angle for total external reflection at the hexadecane–water interface (0.5 mrad at 18 keV) by using a second platinum-coated glass mirror, which also serves to further eliminate the higher-order harmonics.

The scattering of X-rays in the experimental cell results from both bulk scattering in the alkane and interface height fluctuations. In fact, surface scattering occurs at the different hexadecane/chain, chain/head, and head/water interfaces, assumed to fluctuate conformally, and the corresponding scattered beams interfere with each other. The interferences between beams scattered at the different interfaces can be accounted for within the distorted wave born approximation taking into account refraction and absorption,^{20–22} and give rise to the normal q_z dependence of the scattered intensity. The in-plane (q_x, q_y) dependence of the scattered intensity is concentrated in the following form:

$$e^{-q_z^2 \langle z^2 \rangle} \int dx dy [e^{q_z^2 \langle z(0,0)z(x,y) \rangle} - 1] e^{i(q_x x + q_y y)} \tilde{R}(x, y) \quad (2)$$

where $\tilde{R}(x, y)$ is the Fourier transform of the resolution function.²¹ For small q_z values, the exponential can be developed to the first order in the above formula. This simplification is presented for illustrative purposes, and this rather crude approximation was not used in the analysis. Then, one simply obtains

$$I \propto S(q_z) \langle z(q_{xy}) z(-q_{xy}) \rangle$$

where $S(q_z)$ gives account of the normal interfacial structure.

A major difficulty of the experiment is the large bulk scattering in the upper phase. Fixing the grazing angle-of-incidence below the critical angle for total external reflection limits the penetration in the water subphase, and the background due to bulk scattering in the alkane

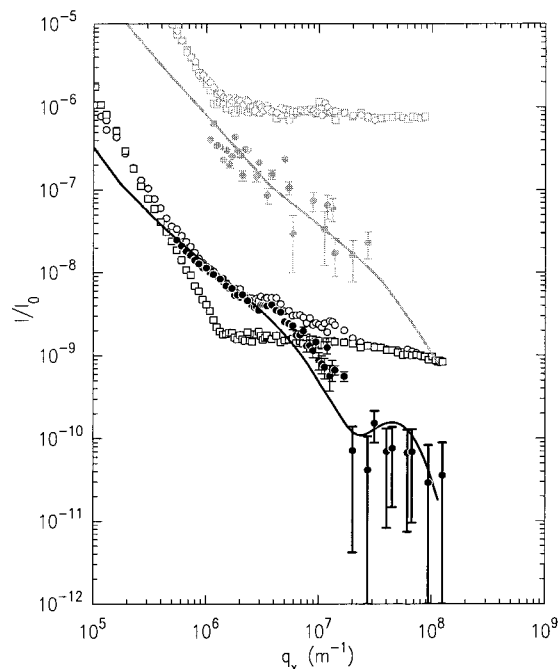


Figure 2. Diffuse X-ray scattering at the hexadecane–water interface: detector θ_d scans in the vertical plane-of-incidence. Gray symbols and curve: bare hexadecane–water interface ($\gamma = 53.3$ mN/m). Black symbols and curve: compressed L- α -dipalmitoylphosphatidylcholine film with $\gamma = 10$ mN/m (divided by a factor of 1000). Empty circles, signal; empty squares, background mainly due to bulk hexadecane scattering; filled circles, signal minus background.

can be very efficiently measured and subtracted by simply lowering the trough (by 1 mm) and repeating the measurement. With this constraint of fixed grazing incidence, essentially two types of scans can be performed:⁸ either detector θ_d scans in the vertical plane of incidence (see Figure 1) or in the horizontal plane of the sample. For this first experiment, we choose the first configuration because the fringes in $S(q_z)$ characteristic of the film thickness and structure allow one to verify that surface scattering is indeed observed. With this geometry both $q_x = 2\pi/\lambda[\cos(\theta_i) - \cos(\theta_d)]$ and $q_z = 2\pi/\lambda[\sin(\theta_i) + \sin(\theta_d)]$ are varied jointly in an experiment while $q_y = 0$.

It should be noted that due to the very small grazing angle-of-incidence, the required cell width results from a compromise between the absorption and the necessity of having a flat surface which is limited by the menisci. For example, a 2 cm wide cell did not yield a flat enough interface to allow us to measure any X-ray reflection. The width of 7 cm appears to be a good compromise. Another consequence of the small grazing angle-of-incidence is that the height of the incident beam must be very small. The intensity of the $500 \times 15 \mu\text{m}^2$ ($w \times h$) beam transmitted through the cell was only approximately 3×10^6 counts/s.

3. Results and Discussion

The main results of this paper are summarized in Figure 2. Significant interface scattering can be observed above the bulk scattering, and the background subtraction procedure is reliable enough that interface scattering intensities down to 10^{-8} of that of the incident beam were measured. With the compressed DPPC film at the interface, the increase in scattering cross-section was large enough that the interfacial fluctuations could be measured down to in-plane wavelengths on the order of 50 nm ($q_x \approx 10^8 \text{ m}^{-1}$).

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It is important to note that, in a diffuse scattering experiment, the scattered intensity is essentially proportional to the resolution volume, requiring a precise knowledge of the resolution function. The analytical dependence of the resolution function as a function of slit dimensions was the same as that used successfully for the analysis of previous experiments at the air–water interface.^{7,8} Using this resolution function, the diffuse scattering from the bare hexadecane–water interface (Figure 2) could be calculated without any adjustable parameter: The interfacial roughness was analyzed using the simple spectrum (eq 1) with only a γq^2 capillary wave contribution, and $\gamma = 53$ mN/m at the hexadecane–water interface, leading to a very good agreement with the experimental data. It was, in particular, not necessary to include an additional contribution to the rms roughness in the $e^{-q_z^2 \langle z^2 \rangle}$ prefactor in eq 2 to give account of the scattered intensity.

Similarly, the interfacial tension measured using the Wilhelmy balance (10 mN/m) was directly used in the analysis of the data for the compressed DPPC film. Whereas it is expected that this film should also exhibit some bending stiffness, the fits proved to be rather insensitive to the bending rigidity modulus K and a different scattering geometry will be used in future experiments to determine this parameter. However, the scattering geometry chosen for this experiment is interesting in that the measurements contain structural information equivalent to that obtained in reflectivity

experiments. A remarkably good agreement with the experimental data which extend up to $q_x = 10^8$ m⁻¹ was obtained using a two-slab model (aliphatic chains and headgroups) for the structural description in addition to the above-mentioned capillary wave height–height correlation function for the interface fluctuation description. The density and thickness of the slabs is respectively $(1.5 \pm 0.05)\rho_{\text{H}_2\text{O}}$ (thickness 0.7 ± 0.1 nm) for the headgroups and $(0.95 \pm 0.02)\rho_{\text{H}_2\text{O}}$ (thickness 1.7 ± 0.1 nm) for the chains (close to the length of the all-trans chains, 1.92 nm²³). All these parameters are consistent with those obtained for densely packed monolayers at the air–water interface.^{23,24}

As a conclusion, we have demonstrated in this paper that grazing-incidence surface scattering of synchrotron X-rays allows for the structural and morphological (the interfacial morphology being due, in the present case, to the thermally excited capillary waves) characterization of liquid–liquid interfaces. This experiment should be the first step toward the precise characterization of more and more complex interfaces, in particular, in soft-condensed matter.

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