



	Experiment title: STRUCTURE AND FLUCTUATIONS OF LIQUID SURFACES : SURFACE FLUCTUATIONS OF MONOLAYERS.	Experiment number: SC-688
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Report:

This experiment was the third part of the long term project "Structure and fluctuations of liquid surfaces", SC-688.

When a surfactant monolayer is present at the water surface, its first effect is to reduce the surface tension : $\gamma = \gamma_{H_2O} - \pi$, where π is the surface pressure. π can be easily determined, with a Wilhelmy plate for instance. A second effect, lower in magnitude, is the appearance of a bending rigidity κ that is more difficult to measure. The bending stiffness of the film is expected to modify the fluctuation spectrum $\langle h(-q_{||})h(q_{||}) \rangle$:

$$\langle h(-q_{||})h(q_{||}) \rangle = \frac{k_B T}{\Delta \rho g + \gamma q_{||}^2 + \kappa q_{||}^4},$$

where $\Delta \rho$ is the difference between the densities of the liquid and vapour phase, and g the gravitational constant.

The experiment consisted in measuring the diffuse intensity scattered by the film as a function of the horizontal $q_{||}$ or vertical q_z wave-vector transfer using a vertically mounted position sensitive detector (PSD), thus giving access to the roughness spectrum $\langle h(-q_{||})h(q_{||}) \rangle$ and to the monolayer's vertical structure. This gives access to a microscopic measurement of the surface tension (or the surface pressure) and allows a precise determination of the bending rigidity modulus (κ).

The energy was fixed to 8 keV, giving access to horizontal wave-vector transfert scanning from $10^7 m^{-1}$ to $10^{10} m^{-1}$. The size of the incident beam was fixed by a $250 \times 200 \mu m$ incidence slit. The horizontal resolution of the experiment was fixed by two slits : the slit placed just after the sample was $300 \mu m$ wide, the slit placed just before the PSD was $500 \mu m$ wide. Measurements were performed for water and behenic acid ($CH_3(CH_2)_{20}-COOH$), using a Langmuir trough mounted on a antivibration device.

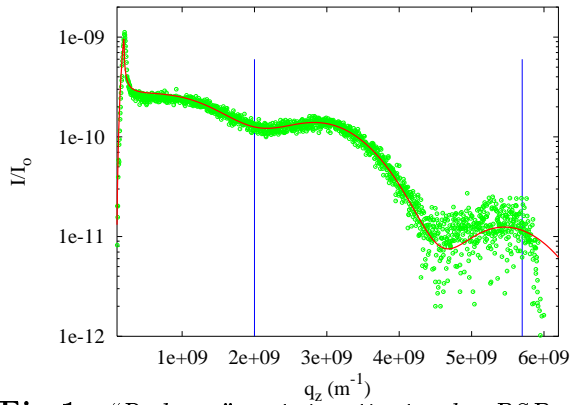


Fig.1- “Rodscan” : intensity in the PSD versus q_z (behenic acid, $\pi_w = 10 \text{ mN/m}$, $T=18^\circ \text{C}$). X-rays diffuse scattering gives information on the vertical structure of monolayer, and on surface tension π_x . Fits lead to the values of electronic densities, heights of the layers, and surface tension.

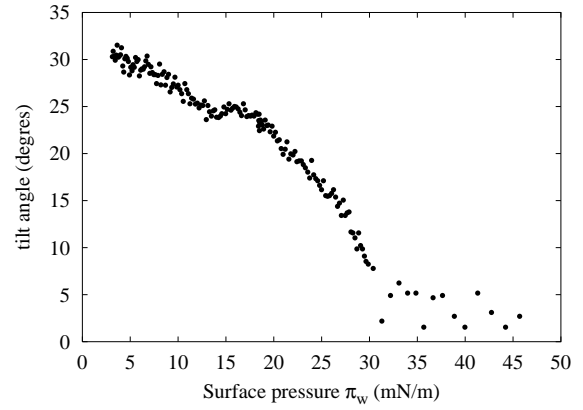


Fig.2- Tilt angle of amphiphilic molecules versus surface pressure : the intensity scattered by the film has been recorded during compression at fixed horizontal wave vector. Each dot corresponds to a rodscan whose fit gives the value of the film’s height.

The monolayer has been compressed, starting from $\pi = 0$ to $\pi \simeq 45 \text{ mN/m}$. π is measured with a Wilhelmy plate. We continuously recorded the intensity scattered by the film during compression at a fixed wave vector $q_{\parallel} = 10^8 \text{ m}^{-1}$. For this q_{\parallel} value, we expect the height fluctuation spectrum to be simply given by $\langle h(-q_{\parallel})h(q_{\parallel}) \rangle \simeq k_B T / (\gamma q_{\parallel}^2)$. Then, it is possible to measure the surface pressure versus molecular area from the scattered intensity (by fitting the curve $I(q_z)$, see fig.1). The vertical structure of the film can also be investigated (see fig.2). If one compares π_x from scattered intensity with π_w from Wilhelmy plate, it leads to the surprising conclusion that $\pi_w = \pi_x$ in liquid phases or in mesophases (L_2 or L'_2 for instance), **but** $\pi_w > \pi_x$ in solid phases (S or CS , fig.3), which obviously shows that the macroscopic surface tension (γ_w) differs from the microscopic one (γ_x). This may be due to the anisotropy of elastic moduli, or due to defects not seen when the surface is viewed at very little scale. The implications of such a result are of considerable importance.

When the in-plane wave vector transfer q_{\parallel} is varied, it appears (see fig.4) that for low q_{\parallel} values ($q_{\parallel} < 3 \cdot 10^8 \text{ m}^{-1}$) the intensity decreases like q_{\parallel}^{-2} . Then, with increasing q_{\parallel} , the intensity decreases faster than q_{\parallel}^{-2} (the q_{\parallel}^{-2} dependence is observed for water for these values of q_{\parallel}). This is due to the bending stiffness of the film. For instance, at 20°C and $\pi=20 \text{ mN/m}$ (L'_2 phase), we find $\kappa \simeq 40 k_B T$. When q_{\parallel} increases again, one can not reasonably expect a q_{\parallel}^{-4} dependence : even with pure water, short lengthscale phenomena make the spectrum different from the simple q_{\parallel}^{-2} law.

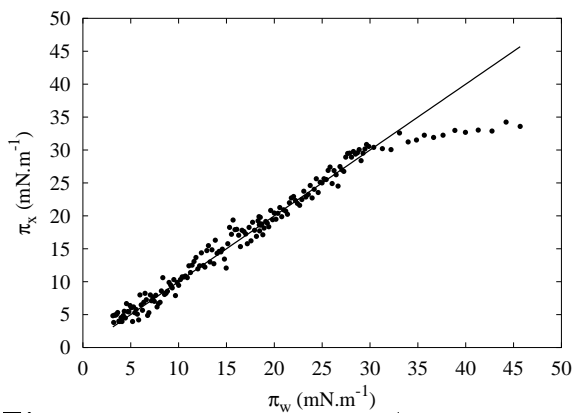


Fig.3- Surface pressure π_x (from x-ray scattering, black dots) versus π_w (from Wilhelmy plate) for behenic acid ($T=18^\circ \text{C}$) : if $\pi_w = \pi_x$, dots should superimposed with the line. This is the case for $\pi_w < 30 \text{ mN/m}$ which is the pressure for the phase transition $L'_2 \rightarrow S$ at this temperature. For $\pi_w > 30 \text{ mN/m}$ (solide phase), $\pi_w > \pi_x$.

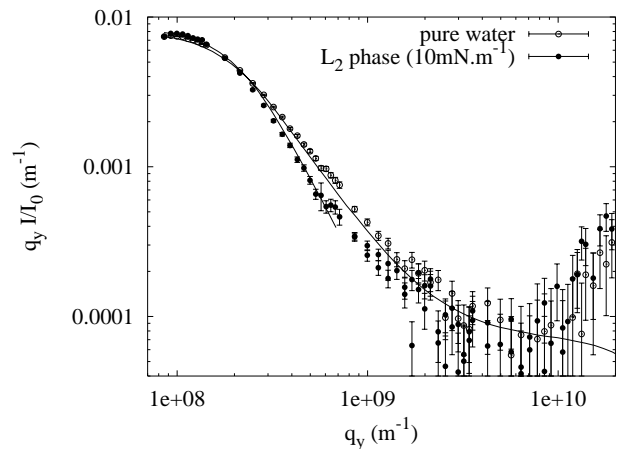


Fig.4- Intensity scattered by a behenic acid film as a function of the in-plane wave-vector transfer q_y . For $q_y \in [3 \cdot 10^8 : 10^9 \text{ m}^{-1}]$ intensity scattered by a bare water surface is higher. This is an effect of the bending stiffness of the film.