

	Experiment title: STRUCTURE AND FLUCTUATIONS OF LIQUID SURFACES : SIMPLE LIQUIDS.	Experiment number: SC-688
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Names and affiliations of applicants (*indicates experimentalists):

J. Daillant*, S. Mora*, A. Braslau*, M. Alba*, D. Luzet*.
 Service de Physique de l'Etat Condensé,
 Orme des Merisiers,
 CEA Saclay,
 F-91191 Gif sur Yvette Cedex.

Report:

This experiment was the second part of the long term project "Structure and fluctuations of liquid surfaces", SC-688. The aim of this experiment was to get a better understanding of the **molecular-scale fluctuations of amphiphilic monolayers on water**. According to the phenomenological description of Helfrich (1973), the (Fourier Transformed) Hamiltonian for interface deformation $\mathcal{H}(q)$ can be written as $\mathcal{H}(q) = \Delta\rho g + \gamma q^2 + \kappa q^4$. The bending rigidity κ is a parameter of theoretical and practical importance. An earlier experiment (SC-688 first part) demonstrated that bare water interfaces cannot be described at short length scales in terms of Helfrich's Hamiltonian with $\kappa \simeq 0$. This is perfectly explained by theoretical developments based on a density functional approach (S.Dietrich and K.Mecke, 2000). Since there is still no reliable experimental data, and no density functional theory available for monolayers, it was of crucial importance to measure monolayer Hamiltonians, to determine whether Helfrich's Hamiltonian is relevant for such systems and to measure the value of κ .

$\mathcal{H}(q)$ can be determined by **grazing-incidence surface scattering** following the method developed in previous experiments : Grazing incidence x-ray scattering allows the precise measurement of the surface fluctuation spectrum $\langle h(q)h(-q) \rangle$, which is the Fourier transform of the height-height correlation function. Since $\mathcal{H}(q) = k_B T / \langle h(q)h(-q) \rangle$, $\mathcal{H}(q)$ can therefore be precisely determined as a function of q .

The experimental setup was quite similar to those of the previous experiments (SC-441 and SC-688 first part). The detector was a vertically mounted gas-filled position sensitive detector (PSD), and the energy was fixed to 8keV. We put the angle of incidence below the critical angle for total external reflection in order to minimize penetration depth and so to be sensitive to interface fluctuations. Moving the horizontal scattering angle up to 20 degrees allowed us to reach wave vector transfers on the order of 2.10^{10}m^{-1} and therefore to detect the interface short-length scale structure.

Measurements were performed for water and behenic acid for different condensed phases : L₂ (10mN/m ; 15°C), S (30mN/m ; 15°C) and CS (20mN/m ; 5°C). The vertical structure of the monolayers has been successfully investigated (see Fig.1 and Fig.2).

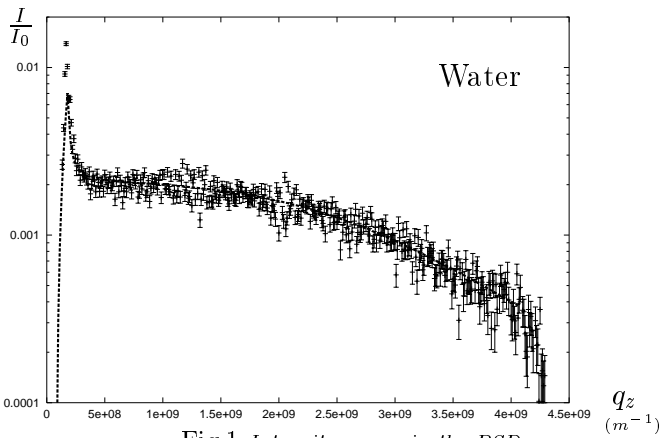


Fig.1 Intensity v.s q_z in the PSD

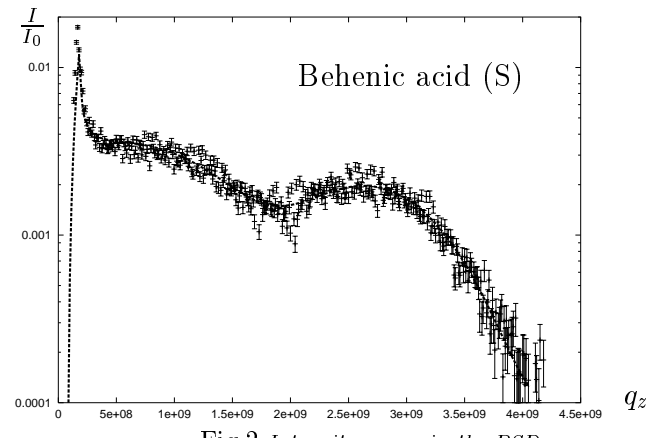


Fig.2 Intensity v.s q_z in the PSD

Fig.1 : Bare interface of water. Fig.2 : monolayer of behenic acid in the S phase. X-ray diffuse scattering gives information on the vertical structure of monolayers. Calculations show that the vertical structure is well understood.

Figure 3 is obtained by integration over suitable PSD's channels, after a very carefully background subtraction. Wave vector transfer q mainly depends on the horizontal scattering angle.

Calculations have been made using Helfrich's Hamiltonian : $\mathcal{H}(q) = \Delta\rho g + \gamma q^2 + \kappa q^4$. Fig.3 clearly shows that a **bending rigidity** of $\kappa \simeq 40k_B T$ is **necessary** to fit experimental data for $q < 8.10^8 m^{-1}$. However it seems that Helfrich's Hamiltonian doesn't succeed in describing the full experimental range of q .

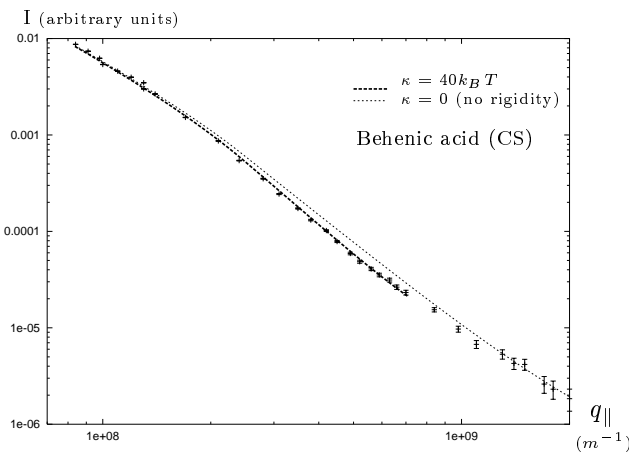


Figure 3 : Scattering by a behenic acid ($CH_3-(CH_2)_{20}-COOH$) film in the CS phase as a function of the in-plane wave-vector transfer q_{\parallel} (filled squares). Surface pressure = 20 mN/m ; $T=5^\circ C$.

Calculations (dashed lines) have been performed assuming Helfrich's Hamiltonian : $\mathcal{H}(q) = \Delta\rho g + \gamma q^2 + \kappa q^4$. Calculation for a zero-rigidity film ($\kappa = 0$) leads to too high intensities. Adding a bending rigidity (here, $\kappa = 40k_B T$) lowers scattered intensity (decreasing of height correlations). Calculations are now in good agreement with the experimental curve for $q < 8.10^8 m^{-1}$.

Further investigations are required to conclude and to give definitive values of bending rigidity for various fatty-acids in different condensed phases :

- Scattering due to bulk compressibility is not negligible at very large q_{\parallel} . For the moment, we can only approximate it, we can not therefore precisely investigate surface fluctuations for very large q_{\parallel}
- Since Helfrich's Hamiltonian is unable to fit data within the full range of q , we will test a new functional density approach as soon as it will be established (by K.Mecke).

It is clear that our experimental setup is good enough to give precise value of bending rigidity. Nevertheless, we must improve our understanding of physical properties of monolayers and make new experiments to confirm our promising conclusions.