



**Experiment title:** MOLECULAR ORIGIN OF THE BENDING RIGIDITY OF AMPHIPHILIC MONOLAYERS ON WATER.

**Experiment number:**

SC-440

**Beamline:**

ID10 A

**Date of Experiment:**

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18

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**Report:**

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 small scale fluctuations of amphiphilic films are limited by their bending rigidity which enters the (Fourier transformed) Hamiltonian for interface deformation  $\mathcal{H}(q)$  as a rapidly increasing  $q^4$  term which has to be added to the effects of gravity ( $\Delta\rho g$ ) and surface tension ( $\gamma q^2$ ):

$$\mathcal{H}(q) = \Delta\rho g + \gamma q^2 + K q^4,$$

where  $q$  is the in-plane wave-vector of the deformation,  $\gamma$  is the surface tension and  $K$  the bending rigidity modulus. Analysing the results of experiment SC-234 for short chain fatty acids (chain lengths ranging from 14 to 16 carbon atoms) in such a way, we found unexpectedly low  $K$  values on the order of a few  $k_B T$  in condensed phases. The aim of experiment SC-440 was therefore to investigate the case of longer chain-lengths (22 to 26 units) where stronger effects are expected ( $K$  is expected to scale with the third power of the film thickness). Another aspect of the elasticity of those films (in-plane compressibility) was previously investigated by grazing incidence diffraction (C. Fradin et al. Eur. Phys. **J. B** 1 (1998) p. 57).

$\mathcal{H}(q)$  can be precisely determined by grazing-incidence surface scattering following the method developed in previous experiments. We demonstrated in particular that grazing incidence x-ray scattering allows the precise measurement of the surface fluctuation spectrum  $\langle z(q)z(-q) \rangle$ , which is the Fourier transform of the height-height correlation function for wavevectors as large as  $10^{10} m^{-1}$  ( $z$  is the interface height). For thermally excited waves:

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

and  $\mathcal{H}(q)$  can therefore be precisely determined as a function of  $q$ .

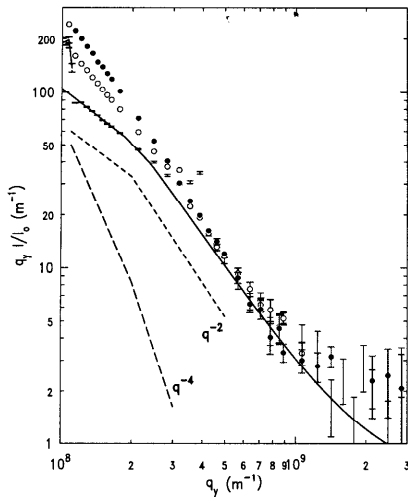


Figure 1: Intensity scattered by a behenic acid ( $CH_3-(CH_2)_{20}-COOH$ ) film as a function of the in-plane wave-vector transfer  $q_y$ . Dots: bare water surface and calculation (line). Circles: behenic acid at  $\Pi = 20 \text{ mN/m}$ ; Filled circles: behenic acid at  $\Pi = 26 \text{ mN/m}$ . Power laws corresponding to  $q^{-2}$  (dashed line) and  $q^{-4}$  (long-dashed line)  $\langle z(q)z(-q) \rangle$  spectra are indicated, taking into account a change in the resolution function dependence at  $q \approx 2 \times 10^8 \text{ m}^{-1}$ .

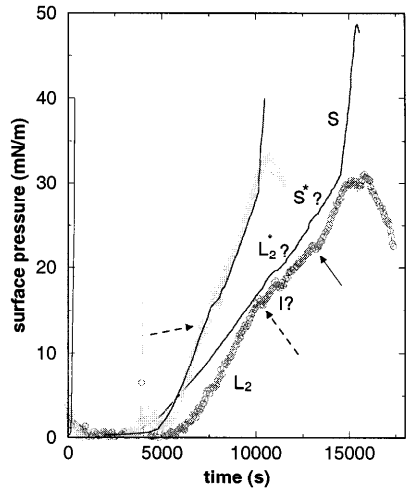


Figure 2: Surface pressure ( $\Pi$ )- molecular area (proportional to time for constant speed compression) isotherms for behenic acid at  $T = 15^\circ\text{C}$  (left) and  $T = 20^\circ\text{C}$  (right) determined by Wilhelmy balance measurements (lines) and surface scattering (circles). In the latter case  $\Pi(q)$  is determined by assuming that for the wave-vector considered  $\langle z(q)z(-q) \rangle \approx k_B T / \gamma(q) q^2$ . A continuous arrow indicates the  $L_2'$  to  $S^*$  phase transition, and dashed arrows indicate a reproducible unexplained feature attributed to a phase transition.

The experimental setup was similar to that used for previous experiments, including the improvements used in experiment SC-441 (see the attached report). Measurements were performed for different fatty-acids condensed phases:

behenic acid at  $5^\circ\text{C}$  at  $3 \text{ mN/m}$  in the  $L_2'$  phase and at  $15$ ,  $20$ , and  $25 \text{ mN/m}$  in the CS phase; at  $20^\circ\text{C}$  at  $15 \text{ mN/m}$  in the  $L_2$  phase, at  $25$ ,  $29$ , and  $29.5 \text{ mN/m}$  in the  $L_2'$  phase; at  $32$ ,  $35$  and  $43 \text{ mN/m}$  in the S phase.  
 \_ hexacosanoic acid at  $30^\circ\text{C}$  at  $15$  and  $25 \text{ mN/m}$  in the CS phase.

It is only possible to give a first, preliminary analysis of the results in this report. It appears that for low  $q$  values ( $< 10^8 \text{ m}^{-1}$ ), the increase in scattered intensity is consistent with the decrease in surface tension (increase in surface pressure). Then, with increasing  $q$ , the intensity decreases faster than  $q^{-2}$  (the  $q^{-2}$  dependence is observed for water, see Fig. 1), but certainly not as  $q^{-4}$  (in fact the power law seems to be close to  $q^{-3}$  for  $q \lesssim 2 \times 10^8 \text{ m}^{-1}$ ). This power law, already observed in a previous experiment could be due to a coupling between the in-plane elastic modes of the film and its height fluctuations.

In order to check the reliability of the method, we continuously recorded the intensity scattered by the film during compression at a fixed wave-vector  $q = 10^8 \text{ m}^{-1}$ . For this  $q$  value, we expect the height fluctuation spectrum to be simply given by  $\langle z(q)z(-q) \rangle = k_B T / \gamma(q) q^2$ . Then, it should be possible to reconstruct the compression isotherm from the scattering intensity. This was done in Fig. 2, and the results are extremely rich and interesting:

The reconstructed isotherm and the isotherm using a Wilhelmy balance are generally in good agreement. Small differences in compressibility can be understood due to the heterogeneous character of the film. Whereas the surface pressure measured by the Wilhelmy balance increases steeply in the solid S phase, the surface energy measured by the scattering experiment saturates, implying a very different physical state of the film compared to in the mesophases.

Even more surprisingly, additional phase transitions, not present in the standard phase diagram of fatty acids are revealed. It is interesting to note that some of them were claimed to be observed, or inferred from symmetry considerations. Such experiments should therefore provide new insight in the (local ?) thermodynamics of the 2-d polymorphism of amphiphilic monolayers.