

Experiment title: STRUCTURE AND FLUCTUATIONS OF LIQUID SURFACES : SIMPLE LIQUIDS.

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SC-688

Beamline:

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Report:

This experiment was the first part of the long term project "Structure and fluctuations of liquid surfaces", SC-688. The aim of this first experiment was to complement earlier liquid-vapour interface investigations (C. Fradin et al *Nature* **403**, p. 871, 2000) for liquids having different molecular sizes, strength of interactions, correlation lengths, surface tensions, or isothermal compressibilities, which are the parameters determining the surface structure. This was necessary in order to confirm our interpretation of the previous measurements (SC-441) using a modern density functional approach (S. Dietrich and K. Mecke, 1999) which gives a quantitative description of the liquid-vapor interfaces short-scale structure, which could be achieved neither by the van der Waals theory (1893) nor by the phenomenological capillary-wave models (1965). In addition, a first experiment on the surface of an electrolyte was planned to prepare future experiments.

The experimental setup (Fig. 1) was quite similar to the previous experiment (SC-441) : two mirrors were used as a deflector and to reject higher harmonic light. The detector was a vertically mounted gas-filled position sensitive detector, and the energy was fixed to 8keV. It was possible to reach wavenumber vector transfers on the order of $3.10^{10}m^{-1}$ and therefore to detect the interface short-length scale structure. Experiments with grazing angles of incidence below and above the critical angle for total external reflection (θ_c) were carried out for each liquid. The angle of incidence could be varied using the mirrors from 2mrad to 3.1mrad which was enough for liquids with $\theta_c \simeq 2.5mrad$. Above θ_c surface scattering is dominated by bulk scattering and bulk parameters like the compressibility which is important for the analysis can be deduced. Below θ_c the penetration length dramatically decreases and surface selectivity is enhanced; subtracting normalized bulk scattering leads to the scattering due to interface fluctuations. Their spectrum $\langle z(\mathbf{q}_{||}) z(-\mathbf{q}_{||}) \rangle$ gives access to the surface tension (for thermally excited waves):

$$\langle z(\mathbf{q}_{\parallel}) z(-\mathbf{q}_{\parallel}) \rangle = \frac{k_B T}{\Delta \rho g + \gamma(q_{\parallel}) q_{\parallel}^2}$$

where $\gamma(q_{\parallel})$ is the wave-vector dependent surface tension which directly depends on molecular interactions and molecular structure. The phenomenological capillary wave models assume a constant or increasing $\gamma(q_{\parallel})$ with q_{\parallel} whereas the new density functional approach predicts a non-monotonic behavior due to the effect of long range dispersion forces.

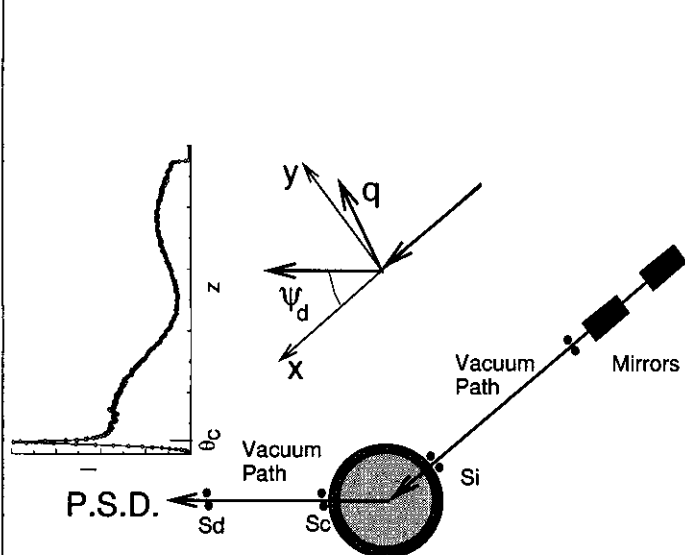


Figure 1 : Schematics of the experiment (top view). The (horizontal) slit sizes were : $s_i = 0.3\text{mm}$, $s_c = 0.3\text{mm}$, $s_d = 0.5\text{mm}$. Vertical scattering angle θ_d is varying between 0 and 150mrad, horizontal scattering angle ψ_d between 0 and 50°.

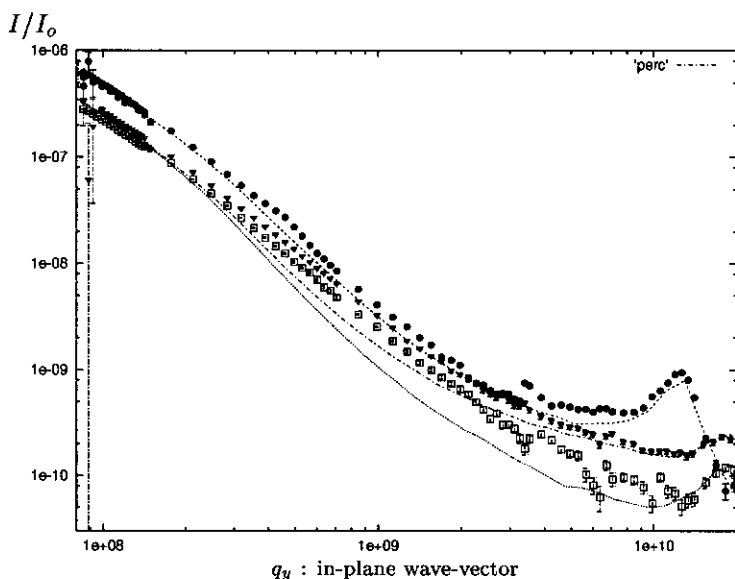


Figure 2 : Scattering by the water surface (empty squares), by the squalane surface (circles) and for perchloric acid (inverted triangles) for a grazing angle of incidence equal to 2.1mrad. Dotted lines represent calculations of surface scattering for a constant $\gamma(q_{\parallel})$. Intensity scattered by real interfaces is larger than the calculated one for q_y ($q_y > 2.10^8\text{m}^{-1}$). The larger scattered intensity is due to a larger amplitude of the fluctuations, that is to a decrease in the surface tension. The effect is more pronounced for water.

All the planned experiments could be performed. The investigated liquids were:

- water, in order to confirm the previous experiment,
- CCl_4 , a model tetrahedric molecule,
- octamethylcyclotetrasiloxane (OMCTS) : a nonpolar liquid with near-spherical molecules (diameter $\simeq 8\text{\AA}$) and a low surface tension,
- hexamethyltetracosane (squalane) : small balls of branched alkane with a medium surface tension,
- perchloric acid (1.5M) : to determine the height-height correlation function of an electrolyte, and to prepare further experiments on ionic solutions.

Experimental data provide a strong evidence for a huge dependence of $\gamma(q_{\parallel})$ on the liquid molecular structure (Fig. 2): the decrease of the microscopic surface tension is far more efficient for liquids with strong molecular interactions (compare water and OMCTS on Fig. 2). Preliminary theoretical analysis shows that this effect can even be quantitatively interpreted for water and CCl_4 using the density functional theory. An expected increase of γ at very large q_{\parallel} was also found.

The experimental data obtained with perchloric acid are also very encouraging since adding salt has an important effect on the short length scale structure (Fig.2). Further experiments (planned) will be necessary to investigate the specicity of each kind of ionic solutions and to determine the relationship between macroscopic and microscopic effects when salt is added.