



	Experiment title: WHAT ARE THE SHORT-SCALE CORRECTIONS TO THE SURFACE TENSION OF LIQUIDS.	Experiment number: SC-441
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Report:

The aim of this experiment was to elucidate still unanswered intriguing questions concerning the structure of the liquid-vapor interface dating back to the pioneering work of van der Waals (1893). Whereas it is now well established that the capillary wave model of Buff, Lovett and Stillinger (1965) gives an appropriate description of the liquid-vapor interface at the micrometer scale, its short-length scale (nanometer) intrinsic structure (as described for example by van der Waals) is still controversial. For example, the unfreezing of capillary waves must reduce the free energy, and, since the density of modes depends on the interface area, the interface free energy (i.e. the surface tension) should depend on the scale of observation. A larger effective short-scale surface tension is therefore expected from this argument. A mechanism for this renormalization of the surface tension based on the interaction between the modes was suggested by Meunier (1987). More recently, Dietrich and Niaporkowski (1993) demonstrated that, taking into account long-range dispersion forces, a smaller surface tension could be expected at short length-scales, i.e. a rougher configuration of the interface is stabilized. The solution of such problems has long been precluded by the absence of any experimental information at short length scales that the aim of this experiment was to surmount.

This experiment was also the first user experiment at the new ID10B beamline. Both the beamline optics and diffractometer proved to work quite well. The principle of the experiment was the following: we demonstrated in previous experiments SC-15, SC-54, SC-98, SC-234, SC-298 that grazing incidence x-ray scattering allows the precise measurement of an interface height-height correlation $\langle z(0,0)z(x,y) \rangle$ function or rather of its Fourier transform the surface fluctuation spectrum $\langle z(q)z(-q) \rangle$, where z is the interface height and q the in-plane wave-vector. For thermally excited capillary waves:

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

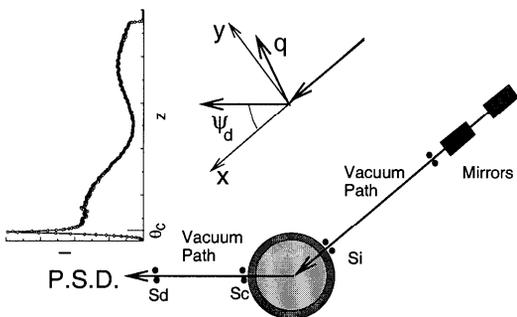


Figure 1: Schematics of the experiment (top view). The (horizontal) slit sizes were: $s_i = 0.3\text{mm}$, $s_c = 0.3\text{mm}$, $s_d = 0.5\text{mm}$. PSD is a vertically mounted gas-filled position sensitive detector, with the corresponding distribution of intensity given in the top-left inset.

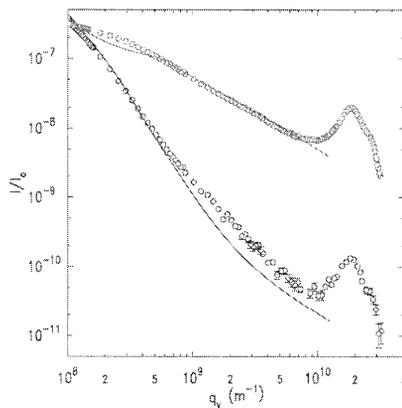


Figure 2: Below: Scattering by the water surface (circles) and calculations using a simple capillary wave model with a constant surface tension (line) for a grazing angle of incidence (2mrad) below the critical angle for total external reflection ($\theta_c = 2.5\text{mrad}$). Above: For a grazing angle of incidence larger than θ_c , the penetration length dramatically increases and bulk scattering dominates. In both cases the peak on the right is due to the short-range order in the liquid.

where the first term in the denominator is the increase in gravitational energy of the deformed interface, and $\gamma(q)$ is the wave-vector dependent surface tension. The precise measurement of surface scattering therefore allows the determination of $\gamma(q)$.

The experimental setup as used in previous runs was improved in two ways (Fig. 1):

- A larger experimental cell (35cm in diameter) was built to allow smaller grazing angles of incidence in order to reduce the penetration length and therefore increase the surface sensitivity.
- Two mirrors instead of only one were used for further harmonic rejection.

Another major improvement of the experimental method consisted in systematically taking data both below and above the critical angle for total external reflection θ_c . Below θ_c the penetration length is about 4nm and surface selectivity is high. It was however suspected in experiments SC-234 and SC-298 that the measurements were sensitive enough that bulk scattering in this thin layer could be evidenced. This must be subtracted if one wants to accurately determine the surface fluctuation spectrum. Taking data above θ_c allowed us to verify the consistency of this interpretation scheme. Another benefit is to allow a precise check of the resolution function used in the analysis because the scattering cross-section for bulk scattering (i.e. acoustic waves) has no dependence on q .

Four different liquids were studied giving a variety of surface tensions, isothermal compressibilities (for bulk scattering) and interactions (they have different polarisabilities, some bear a strong dipole or exhibit hydrogen bonding.):

- water,
- carbon tetrachloride,
- ethylene glycol,
- hexadecane.

Only the results for water will be discussed in this preliminary report (Fig. 2). It can be seen in Fig. 2 that the experimental scattering becomes increasingly larger than expected from a simple capillary wave theory with a constant q -independent surface tension, and that this effect saturates at about $5 \times 10^9 \text{m}^{-1}$. Whereas it is too early to draw definitive conclusions, this behavior nicely agrees with recent theoretical developments (Dietrich and Mecke, unpublished): The surface tension first decreases due to the effect of long-range dispersion forces before increasing due to the interface curvature at very short scale.