



	Experiment title: Structural study of buried ice and water interfaces (LTP)	Experiment number: SI-1164
Beamline: ID15A	Date of experiment: from: LTP 2005 to:	Date of report: 15.04.2006
Shifts: 72	Local contact(s): V. Honkimaki	<i>Received at ESRF:</i>
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Report:

The Max-Planck-Institute for Metal Research operates a long term program for the study of deeply buried solid-solid, solid-liquid, and liquid-liquid interfaces. For this purpose the new technique of high energy surface and interface microdiffraction has been developed over the past 5 years using prototype instrumentation at the high energy beamline ID15A supplied by the MPI. The method is now fully developed and the prototype instrument has been replaced by the user-proof permanent endstation (HEMD – **H**igh **E**nergy **M**icro**D**iffraction) at ID15A in January 2005 within the current long term project. The instrument has been commissioned in February/March 2005 and is fully operational (see Figure 1 and Figure 2). The instrument includes a new type of monochromator for liquid surface/interface spectrometers, which has been developed and installed in the first half year of the current LTP, and a vibration isolation stage for liquid sample environments.

First experiments have been performed using the new instrument. Solid-solid and solid-liquid interfaces could be studied readily. First experiments on liquid-liquid interfaces delivered promising results, although the procedures for data taking must be further refined. In addition, suitable sample cells for large area liquid-liquid interfaces should be developed in the future. The instrument exceeds its original specifications and has been tested in reflectivity, grazing incidence diffraction, and crystal truncation rod diffraction experiments. In order to take full advantage of the high microbeam for crystal truncation rod measurements, a large area 2D detector should be used. The limited availability of suitable CCD cameras is currently a bottle neck for the further development of this technique, especially for in-situ time-resolved surface diffraction experiments.

The instrument HEMD has already received its first users (SI-1094, SI-1095, SI-1253, MI-792). A postdoc (J.S. Okasinski), employed by the MPI in Stuttgart, has been stationed at the ESRF.

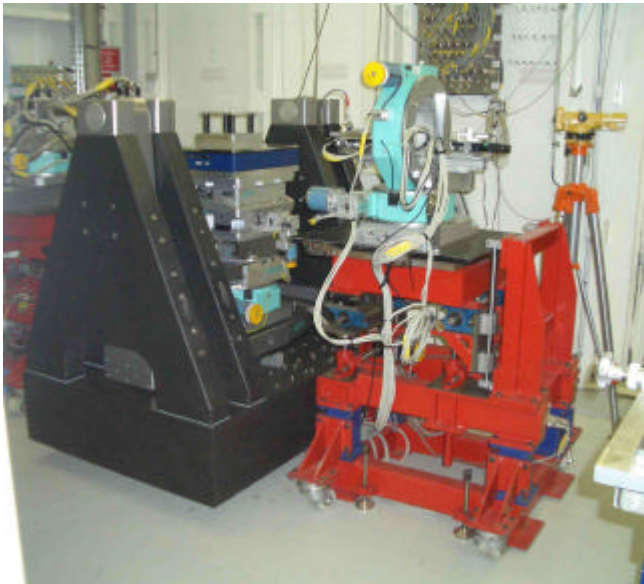


Figure 1: New instrument HEMD in the ID15A experimental hutch. The instruments includes focusing optics, a tilt monochromator stage for liquid surfaces/interfaces, a heavy duty sample tower, and a heavy duty detector tower.



Figure 2: Tilt monochromator stage installed before the sample tower. The stage allows to tilt the beam with respect to a liquid surface/ interface, while the sample is kept stationary .

Within the current long term project, we have used the instrument HEMD for investigations of deeply buried ice and water interfaces. We have performed systematic studies of the structural properties of water and ice at interfaces. These properties depend – in general – on many parameters, such as

- i) the interface potential (determined by the material adjacent to water/ice),
- ii) the surface orientation of the substrate material,
- iii) impurities at the interface,

and are of paramount interest for many different fields. We are running two parallel PhD projects (Project for S. Schoeder: melting behavior of ice at interfaces; project for M. Mezger: structure of water at interfaces) in order to address these questions. The results which have been obtained so far are summarized in the following.

Ice interfaces / Interfacial melting of ice:

Water is one of the materials whose solid-liquid phase transformation takes place at ambient temperatures. The phenomena that accompany this phase transformation play therefore an important role in our day to day life. Of special interest are the physics of the surface and interface of ice at conditions close to the melting point. Past studies have identified interesting phenomena like surface melting and roughening transitions at the surface of ice. Due to the lack of suitable probes, the physics of the interface between ice and other materials is largely unknown. These interface phenomena are thought to play important roles in the understanding of technical and natural phenomena like friction, adhesion and permafrost stability. The high penetration power of high energy x-rays at ID15 allow us to probe this hidden interfaces.

Our group has shown in previous studies [2] that interface melting can be observed at the interface between the natural grown silicon oxide and the basal plane of ice. At temperatures higher than -15 degrees C the first layers of the ice form a quasi-liquid state. This state is characterised by an increase in mobility and a loss of long-range order. The thickness of this disordered region increases as the temperature is increased closer to the melting point of the crystal.

The aim of this project is to identify the parameters that influence the interface melting in order to gain a deeper understanding of the physics behind this phenomenon.

We use different substrates to investigate the effects of changes in chemistry, structure and morphology. All substrates were contacted with the basal plane of an ice single crystal. During sample preparation great care was taken to preserve the crystalline structure of the ice while freezing it on the substrate.

We investigated the interface between ice and a metal surface. Because most metals form oxide layers in air the investigation could only be done with noble metals. For our experiment we have chosen silver because it is a good compromise between nobility and density. It is very difficult to polish Ag metal crystals to the roughness needed for our experiments. For this reason we have grown high quality Ag films (150 Å thick) on a 8 Å aluminium buffer layer on top of a sapphire substrate. This sample was frozen into the ice single crystal. The reflectivity curves for different temperatures are shown in Figure 1. The oscillations in the reflectivity are caused by the aluminium layer. No interface melting could be observed. Due to the high density of the metal it is very difficult to detect small changes in the density of the ice at the interface.

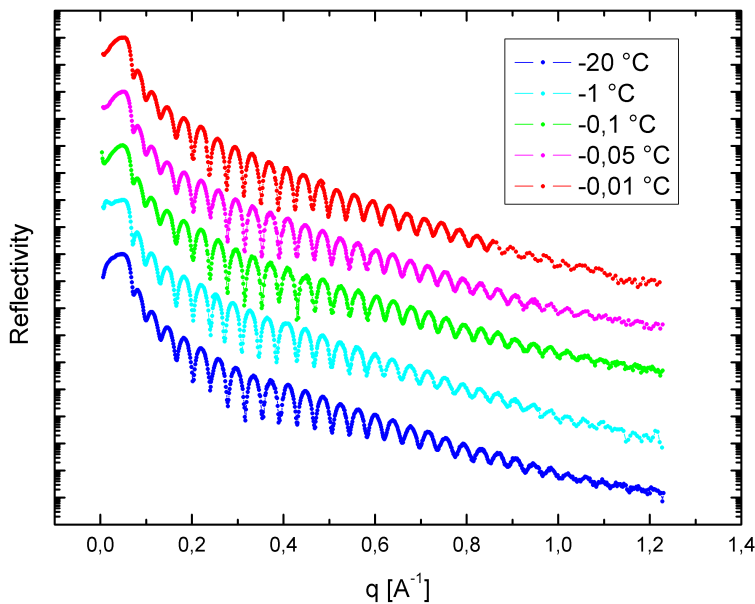


Figure 3: Temperature-dependent reflectivity from ice in contact with Ag(15nm)/Al(0.8nm)/Al₂O₃. No interface melting could be observed.

In previous studies [1,2] interface melting of ice was measured on amorphous silicon dioxide. In order to investigate the effects of crystallinity we prepared a single crystal of ice in contact with a single crystal of silicon dioxide (quartz). Both materials were contacted with their basal planes. The quartz sample was a 2 mm thin plate, which was slightly bent after the sample preparation. First measurements indicated no interface melting for this sample. The reflectivity curves are shown in Figure 4. Due to the bending of the substrate the edge of total reflection could not be measured for this sample.

In order to improve the quality of the data on the quartz-ice system a second sample was prepared. In order to prevent the substrate from bending a thick block of single crystalline quartz was used. The quality of the data could be improved significantly. In contrast to the first experiment interface melting was observed. The measured reflectivity curves are shown in Figure 5. The thickness of the quasiliquid layer between ice and quartz was comparable to values deduced in our earlier study [1,2]. The difference in melting behaviour between the two quartz samples remains unclear. Possible explanations include differences in the in-plane orientation of the crystals or different amounts of strain in the ice crystal (see below).

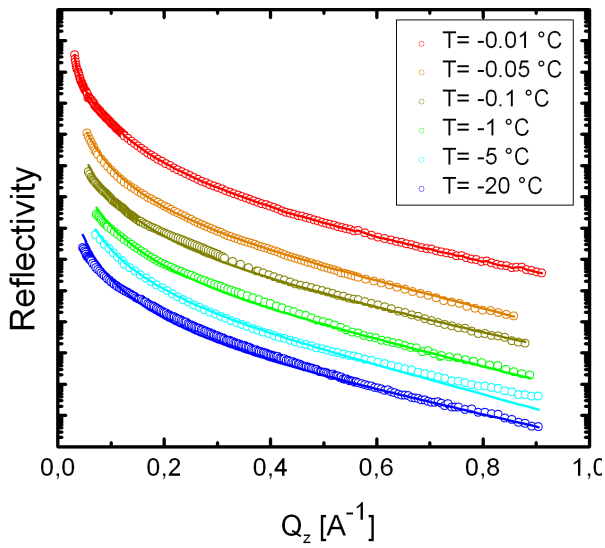


Figure 4: Temperature-dependent reflectivity of a ice-quartz sample. No interfacial melting is detected.

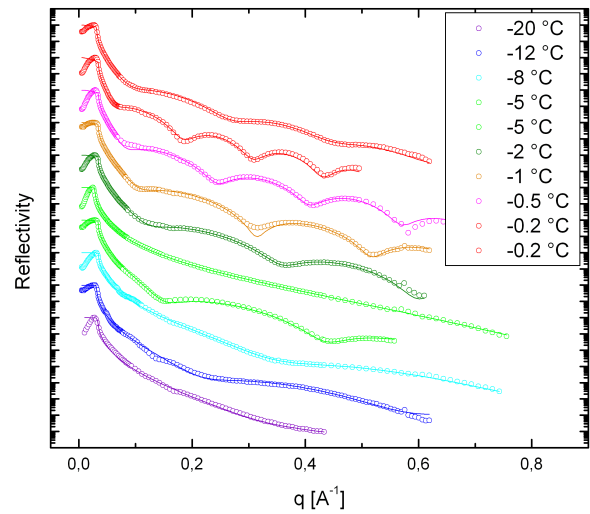


Figure 5: Temperature-dependent reflectivity of a ice-quartz sample. Interfacial melting is detected.

Finally, we explored the effects of strain and relaxation processes in the ice crystal. For this purpose a fused silica substrate was frozen into the ice. A first measurement was performed a few days after the preparation process. The reflectivity curves are shown in figure 6. Interface melting can be observed and the thickness of the quasi-liquid layer is in the same order of magnitude as measured in previous studies. The sample was then annealed for three months at temperatures 15 K below the melting point. Defects and strain from the sample preparation process are reduced during the annealing process. At the end of this relaxation period the sample was measured again. We took special care that the beam position on the sample was the same as in the previous experiment to rule out any differences by inhomogeneities in the sample. No interface melting could be detected in this second measurement. This leads to the conclusion that strain and defects may play an important role in interface phenomena. The results suggest that defects are required to increase the mobility of the interfacial water molecules in the ice crystal before a quasi-liquid layer can be formed.

/1/ S.Engemann et al., Phys. Rev. Lett. **92**, 205701 (2004).

/2/ S. Engemann et al. submitted to Geophys. Res. Lett.

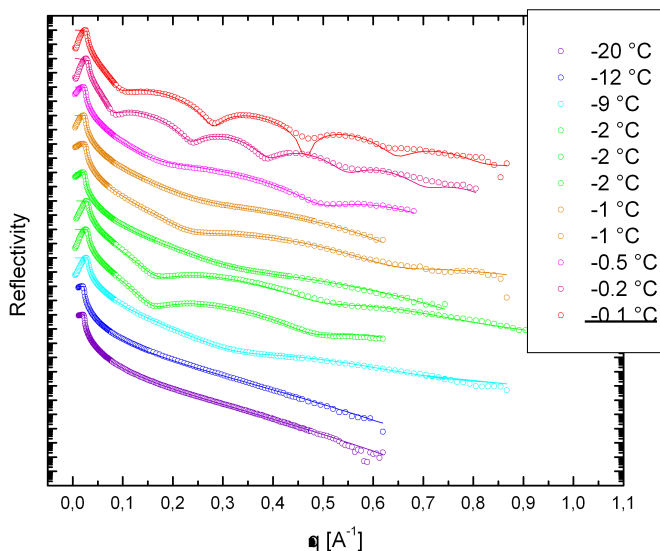


Figure 6: Temperature-dependent reflectivity from ice in contact with amorphous silica. Interface melting could be observed.

Water interfaces:

In order to explore the structure of water at interfaces, a systematic study of water at interfaces ranging from hydrophobic to hydrophilic has to be performed. Using Self Assembled Monolayers (SAM) of organic silanes the preparation of a large variety of well defined interfaces is possible. SAMs based on organic silanes can be prepared with a small RMS roughness of approx. 2Å, which is necessary to achieve high quality scattering data, from which structural information on a sub-nanometer length scale can be extracted. Since the index of refraction is similar to the one of water, interfacial density variations give a strong signal in x-ray reflectivity measurements. The comparison of experimental data measured on SAMs with a different carbon chain length but similar interfacial properties can help, therefore, to exclude artifacts in the data analysis by varying the interference pattern the signals from the substrate and the water adjacent to the interface. For the first experiments in December 2005 we have chosen OTS (OctadecylTrichloroSilane) and the perfluorinated silane FAS-17 (Heptadecafluoro-1,1,2,2-Tetrahydrodecyl)Trimethoxysilane.

Ultra-pure water (Millipore Gradient, ESRF Chemistry Lab) was used for the experiments. To remove dissolved gases, the water was heavily stirred under vacuum using a magnetic stirrer. For the experiment a new sample cell was designed. The cell was constructed from teflon and pure quartz glass parts only, in order to avoid contamination of the ultra-pure water. The high energy x-ray microbeam at ID15A can readily penetrate the sample cell and the water reservoir, while keeping the background scattering low.

A major experimental problem in x-ray scattering experiments on organic structures is beam damage. In air or in vacuum x-ray scattering experiments at photon energies around 70 keV can be performed readily without damage to the samples. In water the samples degrade on a timescale which is at least 2 orders of magnitude faster than in air. Figure 7 demonstrates the radiation damage at a FAS-17 monolayer, which was grown on SiO₂ and immersed in water.

The reflectivity curve in Fig. 7a has been recorded with a full-beam equivalent of less than 10 sec per measured data point. Fig. 7b shows the evolution of the scattered intensity in the minimum of the interference pattern under continuous irradiation intensity. The results demonstrate, that the maximum exposure of one single spot on the sample to the high energy x-ray beam should not exceed 10s. After a full-beam exposure of 10min we could clearly detect stripes on the sample where the originally hydrophobic surface turned hydrophilic.

Moving the sample perpendicular to the microbeam during the measurements enabled us to record high quality x-ray scattering data with negligible beam damage. This was verified by repeating multiple measurements on the same

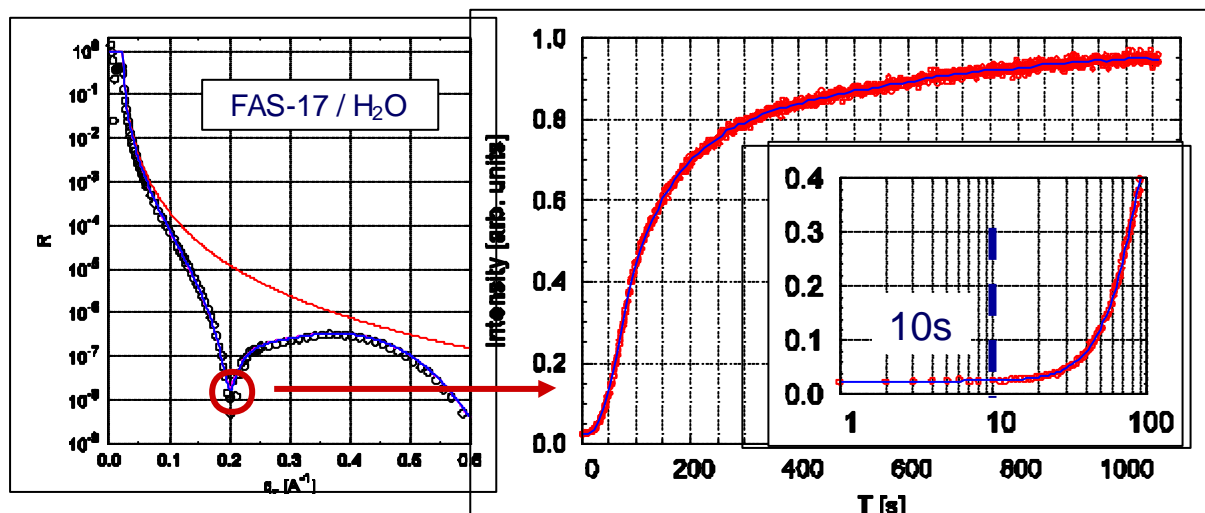


Figure 7: (a) Reflectivity from a FAS-17 layer immersed in water. (b) Radiation damage measured at the position of the deep minimum of the reflectivity in (a).

sample area where we found no deviations between consecutive runs.

Reflectivity curves of the bare Si-SiO₂ substrate were measured to determine the thickness and the roughness σ of the oxide layer. The density profile of the self assembled OTS film was determined from reflectivity measurements in air (Figure 8a). A box model including the silicon substrate (bulk), a thin oxide layer, the silane anchor group and the long chain carbohydrate tail was used for fitting using both, a Parratt and a master formalism. Both methods gave identical results in excellent agreement with the experimental data points. This allows to construct the scattering length density profile of the dry OTS depicted Fig 8b.

Starting from this, one can easily calculate the reflectivity curve for the sample immersed in water by exchanging the vacuum layer with water. Figure 9 demonstrates that the calculated reflectivity curve exhibits large deviations from the measured reflectivity curve, especially for large momentum transfer q_z . By introducing a single additional water layer with reduced density, as shown in Fig.10a, excellent agreement

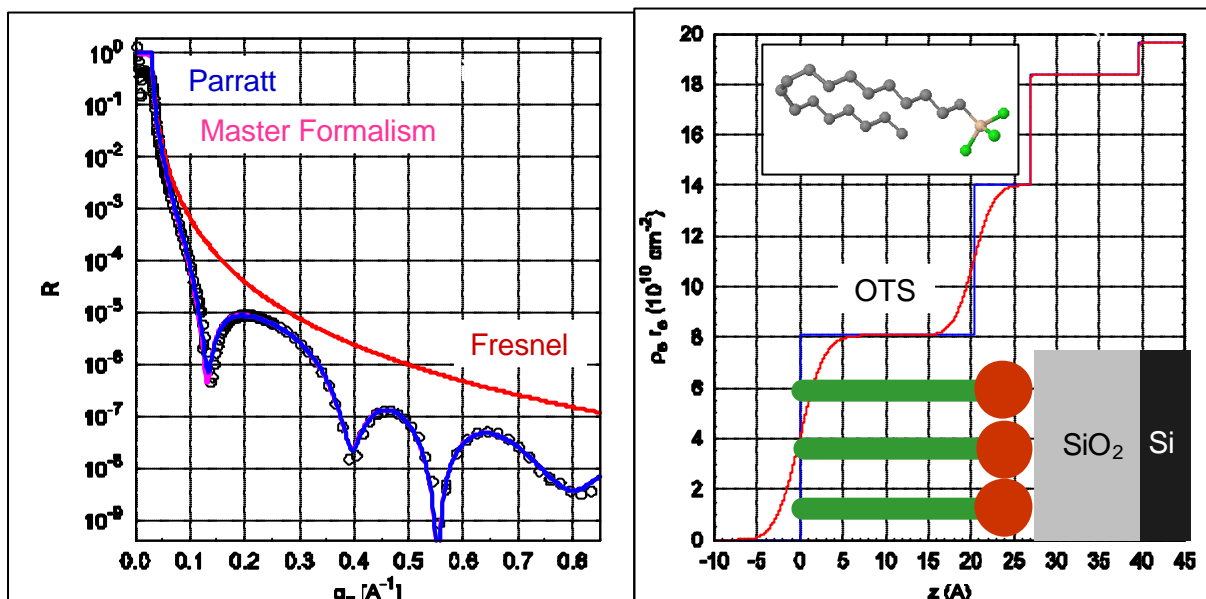


Figure 8: (a) Reflectivity from a OTS layer in air. The Fresnel reflectivity is shown for comparison. (b) Electron density profile for the OTS on top of the Si-SiO₂ substrate deduced from the fit shown in (a).

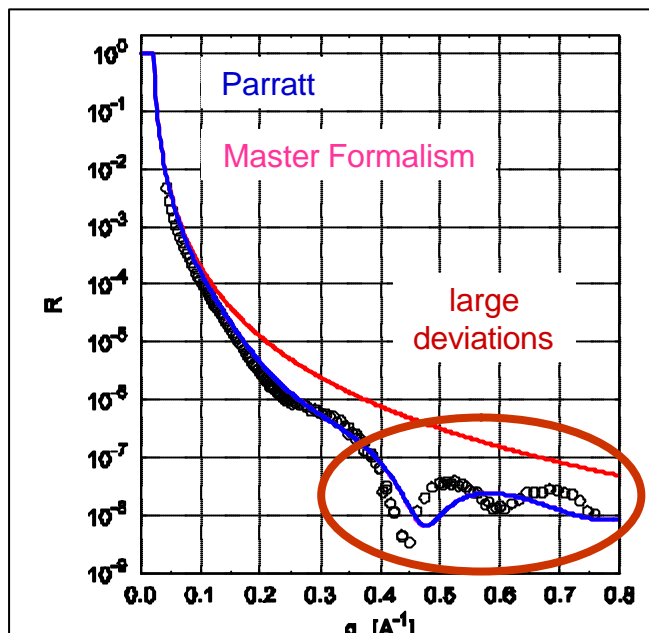


Figure 9: Reflectivity from a OTS layer in water. The Fresnel reflectivity is shown for comparison. The calculated curve assumes unmodified bulk water joining to the OTS interface.

between the measured and calculated reflectivity curve was found. The fitting parameters are summarized in the Table. Only the thickness and the density of the interfacial water layer no. 4 were optimized by fitting the measured data shown in Fig. 10a. All the remaining parameters were taken from the measurements on the dry sample (see Table). Due to the small thickness d of the interfacial layer (with $d \approx \sigma$), we can only determine the integral density deficit, $(\rho_{\text{H}_2\text{O}} - \rho) \cdot d$, which leads to a phase shift in the interference pattern from the different layers. The density

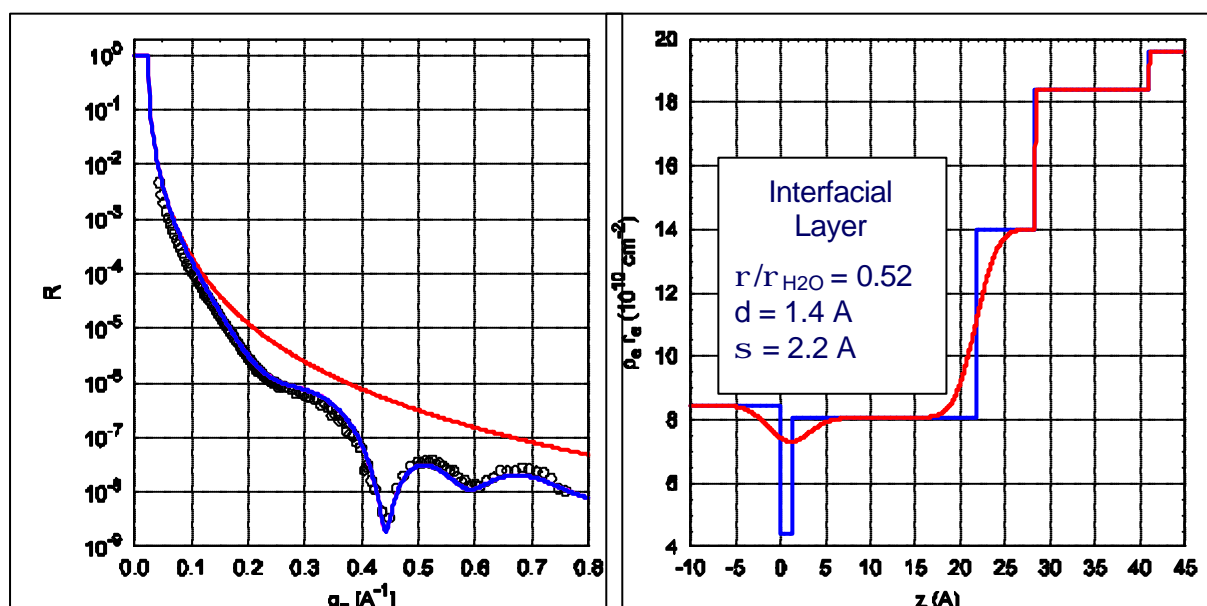


Figure 10: (a) Reflectivity from a OTS layer in water. The Fresnel reflectivity is shown for comparison. (b) Electron density profile for water on top of the OTS on deduced from the fit shown in (a).

profile of the OTS sample in water is summarized in Fig. 10b showing the intrinsic density profile in a box model as well as the density profile including roughness.

		$\rho/\rho_{\text{Reference}}$	$\rho_e r_e [10^{10} \text{cm}^{-2}]$	$d [\text{Å}]$	$\sigma [\text{Å}]$

5	H ₂ O	1.00	8.5	-	2.2
4	Interfacial Layer	0.52 (H ₂ O)	4.4	1.4	2.2
3	OTS-Tail	1.07 (C ₁₈ H ₃₈)	8.1	20.4	1.9
2	OTS-Head	0.65 (Quartz)	14.0	6.6	0.1
1	SiO ₂	0.86 (Quartz)	18.4	12.7	0.1
0	Si	1.00	19.6	-	-

Our results demonstrate that hydrophobic interfaces induce density depletion in water in a very thin layer adjacent to the interface. Due to the high quality of the high energy x-ray microbeam we were able to resolve this very thin layer at deeply buried interfaces. Furthermore, our results show that previous neutron reflectivity studies systematically overestimate the thickness of such a depletion layer due to the lack of resolution on the atomic length scale.

Outlook / further experiments:

In future experiments we plan to extend our studies to

- fluorinated silanes
- molecules with different carbon chain length
- quantitative measurements of the influence of dissolved gases (Noble gases, CO, CO₂, ...)
- other solvents (exchanging water with n-hexane or perfluorohexane)