



<b>Experiment Report</b>		<b>Experiment number:</b> HD200
<b>Experiment title:</b> High frequency dynamics of water in confined geometrie		
<b>Beamline:</b> ID28	<b>Date of experiment:</b> from: 12.09.07 to: 18.09.07	<b>Date of report:</b> 16.09.09
<b>Shifts:</b> 18	<b>Local contact(s):</b> M. Krisch	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): Dr. REICHERT Harald, M.P.I. fuer Metallforschung, Postfach 80 06 65, Heisenberg Strasse 1, D-70569 Stuttgart, Germany. Dr. DOURDAIN Sandrine, M.P.I. fuer Metallforschung, Postfach 80 06 65, Heisenberg Strasse 1, D-70569 Stuttgart, Germany.		

## Report:

In this project it was proposed to study by Inelastic X-ray Scattering the high frequency dynamics of water confined in nanopores. The dynamics in bulk liquids on inter atomic length scales can be studied by inelastic neutron (INS) or x-ray scattering (IXS) techniques. Many important insights have been gained concerning the nature of the acoustic-like (propagating) excitations, their relation to the local atomic structure, as well as the influence of relaxation phenomena on the excitation spectrum [1,2]. In contrast to this, the study of the high-frequency dynamics of liquids at surfaces, interfaces, or in confined geometries, represents a formidable challenge in condensed matter research. The dynamics of confined water in disordered porous structures is nowadays extensively investigated, experimentally as well theoretically via MD simulation techniques (see [3] and references therein). Experimentally a variety of probes have been applied ranging from infrared spectroscopy to quasielastic neutron scattering [4-6], revealing a strong influence of the confinement on the dynamics of water (slowing down). None of these experiments, however, accessed the mesoscopic regime, corresponding to phenomena at the interatomic distance and picosecond time scale.

For this project, we first planned to confine water in mesoporous silica thin films which were produced on Si substrates by template-assisted growth of a silica framework. It was finally decided to confine the water in bulk porous silicon wafers because they offer much bigger total porous volume than the silica thin films. These pores present the additional benefit to be aligned in the direction perpendicular to the wafer surface. The orientation of the nanopores allows one hence to select the momentum transfer along the long axis of the pores with a reflection geometry (unconfined), or perpendicular to the pores axis in transmission geometry (confined). The aim of the experiment was to derive dynamical properties of water such as the infinite-frequency sound velocity and characteristic relaxation times, for comparison to bulk water properties.

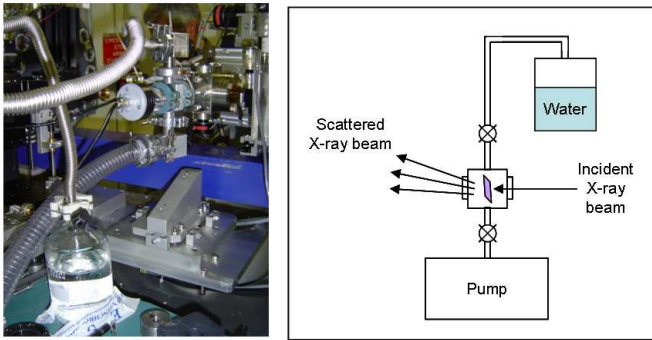
## Porous silicon description and previous characterization:

The porous silicon samples were provided by Patrick Huber and Anke Henschel from the University of Saarland in Germany. The pores, made of highly monodisperse nanometer-scaled pores, are obtained by electrochemical (anodic) etching of p-doped (100) silicon wafer with a resistivity of 0.01 to 0.02 Ohm.cm Depending on the etching time, the porous layer can have a thickness of 50 to 250 microns [7].

With this protocol, the pores have a radius in the range of 3.5 +- 0.5 nm and the average distance between the pores is around 10 nm. In order to adsorb water in the porous silicon sample, the pores surface was treated with H<sub>2</sub>O<sub>2</sub> in order to oxidize the hydrophobic silicon pore surface into hydrophilic silica. BET isotherm sorption of N<sub>2</sub>, showed that the radius was decreased from 3.5 to 3nm after the treatment. The pores are cylindrical, non-connected and oriented with their long axis normal to the (100) wafer surface, going through the whole thickness of the silicon layer.

## Experimental set up – Adsorption of water:

In order to extract the inelastic signal of water confined in the porous silicon samples, the measurements were achieved with and without water.



**Figure 1:** Picture and schematic illustration of the experimental set up.

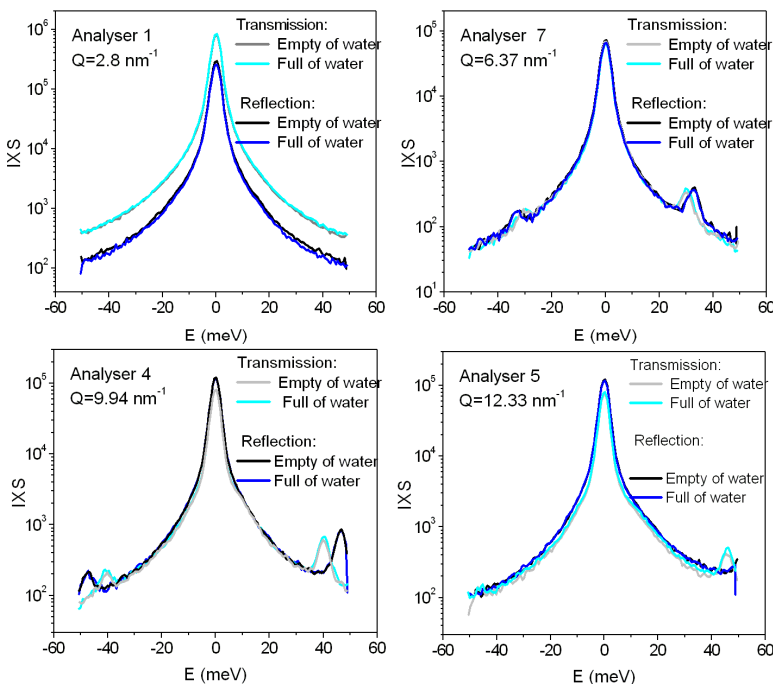
Concerning the measurement with water, it was important to make sure that the pores were not overfilled to avoid any bulk water layer formation at the top surface of the sample. It was then crucial to control properly the adsorption of water in the pores. Considering the Kelvin equation, cylindrical pores having a radius of 3nm need a relative humidity (RH)

of 85% to be filled by capillary condensation [8]. A RH of 90% was therefore adjusted to avoid the condensation of a water layer at the surface.

Moreover, as the signal of confined water was expected to be very small compared to the scattering of the silicon+silica porous network, a very good statistics was necessary. Therefore, the spectra were accumulated 8 hours and we chose to perform the measurements in vacuum condition. For this reason, the adsorption and desorption of water couldn't be simply achieved by controlling an ambient Relative Humidity (RH). The RH, being equal to the ratio between the pressure  $P$  and the vapor pressure of water  $P_0$ , was controlled from 0 to 1 by adjusting the pressure between  $P=0$  mbar and  $P=P_0=23.5$  mbar at  $T=20^\circ\text{C}$ . As the vapor pressure of water is strongly dependent on the temperature, the setup was moreover thermostatic. The porous sample empty of water was simply measured in vacuum. The experimental set up is presented at the figure 1.

## Experiments:

The measurements the IXS spectra were recorded with an energy resolution of 3 meV (utilising 17794 eV radiation), and at 10 different  $Q$ -values (two settings of the 5-Analyser spectrometer) between 4 and  $18\text{ nm}^{-1}$  with a scattering depth of approximately  $200\mu\text{m}$ . The porous silicon samples were measured filled with water and empty in order to extract the pure confined water contribution to the inelastic spectra. They were also measured in reflection and transmission geometry to observe the inelastic signal of the water in two confinement geometries. (Figure 2)



**Figure 2:** Selected raw IXS spectra.

The inelastic spectra show some features originating from excitations in the crystalline silicon. Inelastic peaks from phonons in the crystalline silicon can be observed. Their position is related to the sound velocity in silicon.

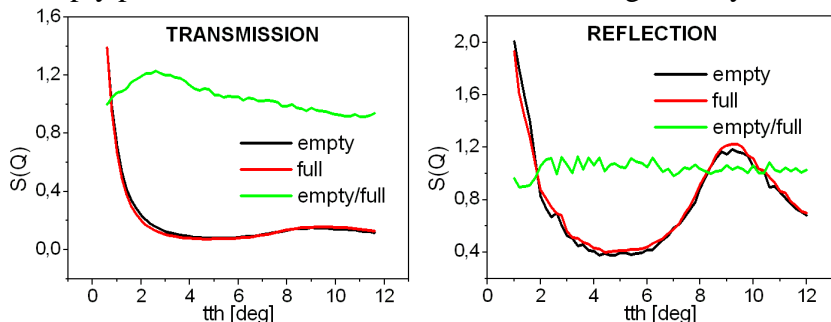
At a first glance, no clear signal of the confined water appears on the full of water spectra. Taking as reference the known spectra of bulk water, the inelastic signal of confined water is expected to be located around 10meV and to be very weak. This low intensity is moreover accentuated in the experiment by the very small amount of the scattered water in the sample.

The elastic peaks are here very broad and intense and may cover any signal from the confined water. A broadening of the elastic peak

can be expected from the broad inelastic scattering signal of amorphous silica. Silica is covering the whole surface of the porous silicon (owing to a treatment in  $\text{H}_2\text{O}_2$  to make the pores surface hydrophilic). Taking

into account a silica thickness of 2nm, equivalent as the usual native silica layer, it can be estimated that 50% of the porous matrix is made of silica.

Eventually, the high elastic contribution is due to the form factor of the pores, which is especially high at the small angles used in this experiment. As shown in the next figure this form factor is different in the filled or empty pores, and in transmission or reflection geometry.



**Figure 3:** Scattering of the pores measured in transmission and in reflection and for the states empty and full of water.

The ratio between the signals measured on the empty and the full of water sample (green curve) allows to show in transmission and at small angles the higher intensity of the scattering of the pores

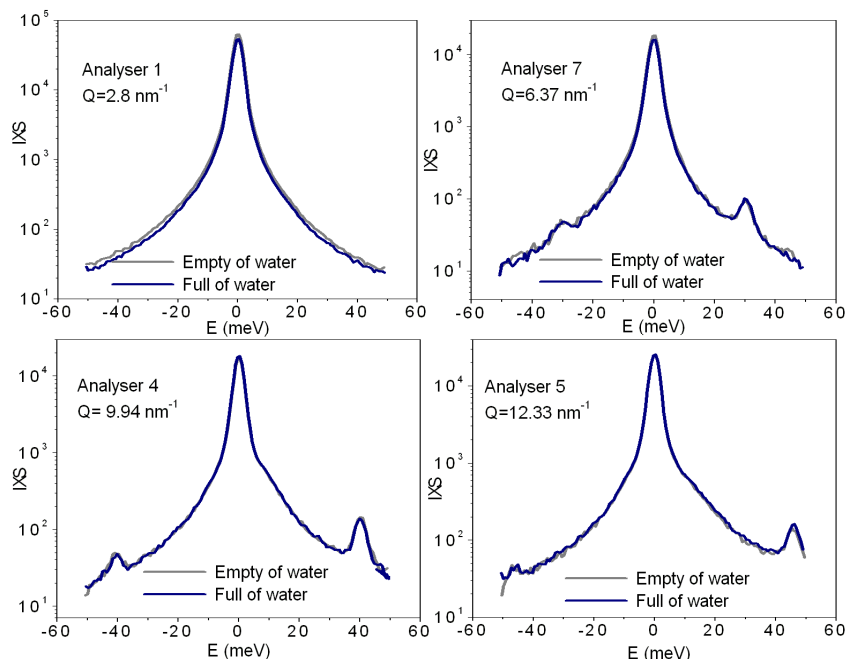
empty of water. In both transmission and reflection, the scattering of the signal appearing around  $tth=9^\circ$  is attributed to the silica scattering, confirming that an amorphous silica layer is covering the surface of the pores.

This difference in  $S(Q)$  must be taken into account carefully in the normalization of the inelastic scattering data before extracting the contribution of the confined water by subtracting the empty porous silicon spectra from the spectra of the filled pores.

Each IXS spectrum (integrated in energy) was therefore normalized by the corresponding value of the  $S(Q)$  :

$$\int I(Q, \omega)_{full} d\omega = S(Q)_{full} \quad \text{and} \quad \int I(Q, \omega)_{empty} d\omega = S(Q)_{empty}$$

The normalized spectra obtained in the reflection geometry are presented in Figure 4.



**Figure 4:** Spectra measured in reflection and normalized with the scattering of the pores.

The spectra in transmission are not shown here but give the same conclusions.

It appears that by subtracting the signal of the empty pores from the one of the full pores, no clear signal could be extracted that might be assigned to the confined water.

In conclusion, the elastic scattering contribution originating from the small angle scattering of the pores was completely dominating the signal. A

further problem was that the  $\text{SiO}_2$  coating of the pore walls, which was necessary to render the pore walls hydrophilic for filling with water, produced a similar IXS contribution as the water in the pores itself. A reliable extraction of the water IXS signal was therefore not possible. As we learned by now, experiments with identical results have also been performed at the APS and SPring-8. In order to overcome these problems we propose here to replace water with a liquid which is contrast-matched to the Si pore wall material, so that the dynamical properties of a liquid in confinement can be investigated.

#### References :

- [1] F. Sette, M.H. Krisch, C. Masciovecchio, G. Ruocco, and G. Monaco; Science 280 (1998) 1550.
- [2] G. Ruocco and F. Sette; J. Phys.: Cond. Matt. 11 (1999) R259.
- [3] H. Tanaka and K. Koga, Bull. Chem. Soc. Japan 79 (2006) 1621.
- [4] A.M. Dokter, S. Woutersen, H.J. Bakker, PNAS 103, 15355 (2006).
- [5] Takahara et al., Adsorption 11, 479 (2005).
- [6] F. Mansour, R.M. Dimeo, H. Peemoeller, Phys. Rev. E 66, 041307 (2002).
- [7] A. Henschel, T. Hofmann, P. Huber, K. Norr, Phys. Rev. E, 75 (2007) 021607.
- [8] K.S.W. Sing, D.H. Everett, R.A.W. Hual, L. mocsou, R.A Pierotti, J. Rouquerol, T. Siemienievska, IUPAC, Pure Appl. Chem., 57 (1985) 603.