EUROPEAN **S**YNCHROTRON **R**ADIATION **F**ACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

	Experiment title: **Liquids under Confinement in Slit Geometry**	**Experiment number**: SC/3900
Beamline: ID03	**Date of experiment**: from: 21.09.2014 to 25.09.2015 from: 11.03.2015 to: 14.03.2015	**Date of report**: 9.07.2015
Shifts: 9 + 9	**Local contact(s)**: Roberto Felici	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr. Milena LIPPMANN*, O. H. Seeck*, Dr. Florian BERTRAM*,

Photon Science, DESY, Notkestr. 85, 22607Hamburg

Dr. Kim NYGARD*, University of Gothenburg Department of Chemistry
Kemigarden 4, SE – GOETEBORG

Report

Background und motivation:

The investigations of the fluids at solid-liquid or liquid–liquid interface show that the liquid molecules arrange in the layers close to the interface [1, 2]. The ordering of the fluid at the interface is in the range of few molecular layers. Related experiments going for liquids confined in volume comparable to the molecular dimensions have established stronger deviations in comparison to the bulk liquid [3]. The main question that rises in those experiments is: how it should be understood the structure and properties of the confined fluids. Are they still fluids or reminisced the properties of solid materials? Moreover, the studies show that the properties of the confined fluids are dependent on different factor like substrates, strength of the confinement or the confined geometry [4].

In the present carbontethrachloride (CCl_4) was used as liquid and it was confined between two diamond culets (confinement in slit geometry). The advantage of the slit geometry against the confinement in porous material is the ability to increase the confinement strength by means of decreasing the gap size between the substrates. In addition the confinement in slits is a model system for theoretical investigation. Therefore, it is widely used in the computer experiments, and this geometry is a perfect base for comparison of the experimental and theoretical works.

The structure of the liquid confined in a slit is very well accessible by surface x-ray diffraction methods like reflectivity and in-plane scattering. Nevertheless the experiment is very challenging due to the strong requirements concerning the quality of the confined substrates and the very small sample volume. Microfocused, very stable beam is needed in order to deal with small volume sample.

The most experimental data in the literature are on confined fluids based on colloid system or liquid crystals. Structure measurements on real liquids with small molecular size are very rare. Therefore the goal of the experiment is to measure reflectivity curves of CCl_4 (molecular size 5 Å) at different gap sizes and calculate form them the electron density profile of the confined film in dependence of the confinement strength. Measurements in-plane direction has been also performed to resolve the in-plane structure.

Sample environment:
A special setup was developed to study confined liquids in slit geometry [5]. The setup was commissioned at PETRA III, DESY Hamburg and it has been used as sample environment for the current experiment. The diamond culets were with 300 µm diameter. CCl4 (1ml) was injected in to the liquid reservoir of the experimental cell and heated to 29°C. The liquid was evaporated and condensed at the substrates. The substrates are separated at distance of 20 µm in the beginning of the experiment. The energy of 18 KeV, beam size of 5-6 µm, and Maxipix (2x2 Modul, silicon detector) detector have been used. Before the experiment, with support from the beamline staff, a microscopes frame has been built for the diffractometer at EH1 (see Fig.1). Two microscopes for observation of the sample from the top and from the side have been mounted on the frame during the experiment. The microscopes are used to align the diffractometer and the sample to the x-ray beam with accuracy of few microns. The final sample alignment is done by means of the x-ray beam.

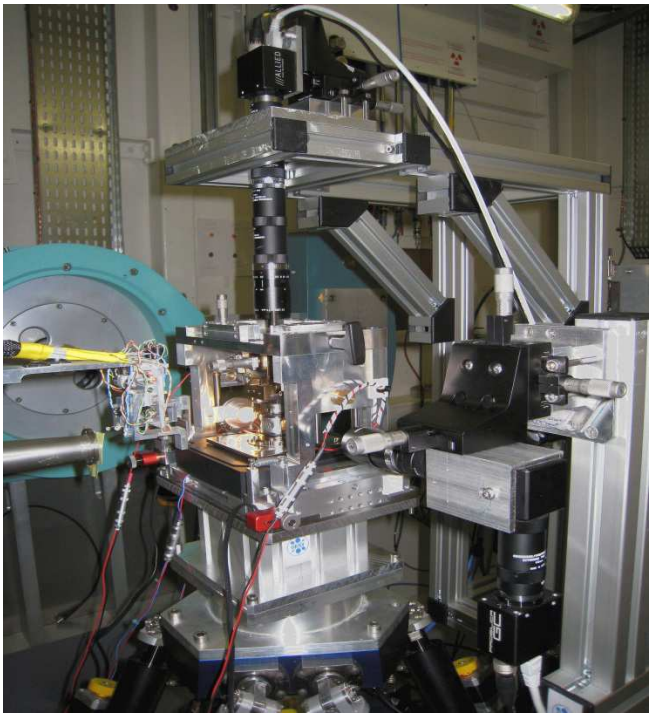

Fig 1. The microscope frame. The frame is committed to the ID03 beamline for further microfocus experiments.

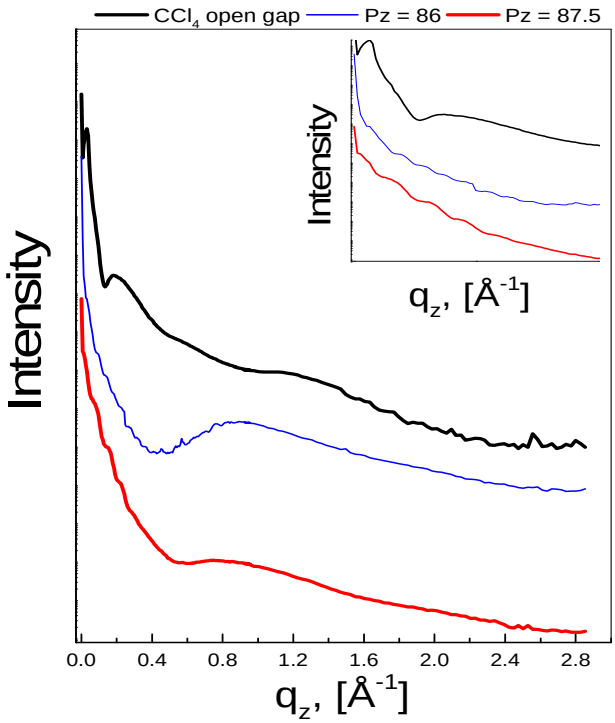

Fig. 2. Measured reflectivity curves. Pz is the monitoring value of the piezo stage that controls the gap size. The higher value corresponds to smaller gap sizes**.** The small angle part of the reflectivity curves are shown in the inset.

Results
The first reflectivity curve (from the top) is recorded at open gap after condensation of the liquid on the lower diamond substrate. The curve shows that on the bottom substrate there is a very thin liquid film. The position of the peak at high angle (1.2 $Å^{-1}$) correspond to the structure peak of CCl_4. Most probably the peak is due to already layer molecules at the surface. The last two curves are from confined films at different gap sizes. From the oscillations in smaller angle regime (see the inset) the gap sizes could be calculated. The confined films have a thickness of 250 Å and 100 Å for Pz=86 and Pz=87.5 respectively. The confinement leads to increasing of the peak at higher angels. The peak of the confined curves should not be directly associated with the structure factor of the CCl4 liquid. The preliminary data analysis shows that it could be a superposition of the electron density fluctuation in the gap profile, where the liquid close to the surface is layered but in the middle of the gap the electron density is almost constant.
The scans in the in-plane direction do not give usable information explaining the in-plane structure of the confined liquid. The small sample volume gives very low counting rate and the signal is lost in the background coming mainly from the scattering of the diamond substrates. The advantage to use the area detector against point detector is that the area detector gives additional information about the surface of the

diamond culets during the confinement. The last measurements indicated that the elastic deformations of the diamond substrate occur at higher values of Pz. These results in thinner and smoother confined film (see the second confined curve)

References:

[1] O. Shpyrko, M. Fukuto, P. Pershan, B. Ocko, I. Kuzmenko, Th. Gog, and M. Deutsch, *Surface layering of liquids: The role of surface tension,* Phys. Rev. B **69**, 245423 (2004)

[2] K. Nygård and O. Konovalov, *Decay of interfacial fluid ordering probed by X-ray reflectivity*. Soft Matter, **8**, 5180 (2012)

[3] K. Nygård, S. Sarman, and R. Kjellander, *Local order variations in confined hard-sphere fluid*. J. Phys. Chem. **139**, 164701 (2013)

[4] K. Kaneko, A. Watanabe, T. Iiyama, R. Radhakrishan, and K. E. Gubbins, *A Remarkable Elevation of Freezing Temperature of CCl4 in Graphitic Micropore*s. J. Phys. Chem. B, **103**, 7062 (1999)

[5] M. Lippmann, A. Ehnes, and O. H. Seeck**,** *An x-ray setup to investigate the atomic order of confined liquids in slit geometry*. Rev. Scientific Instrum. **85**, 015106 (2014)