Experimental evidence for confinement-induced crystallization.

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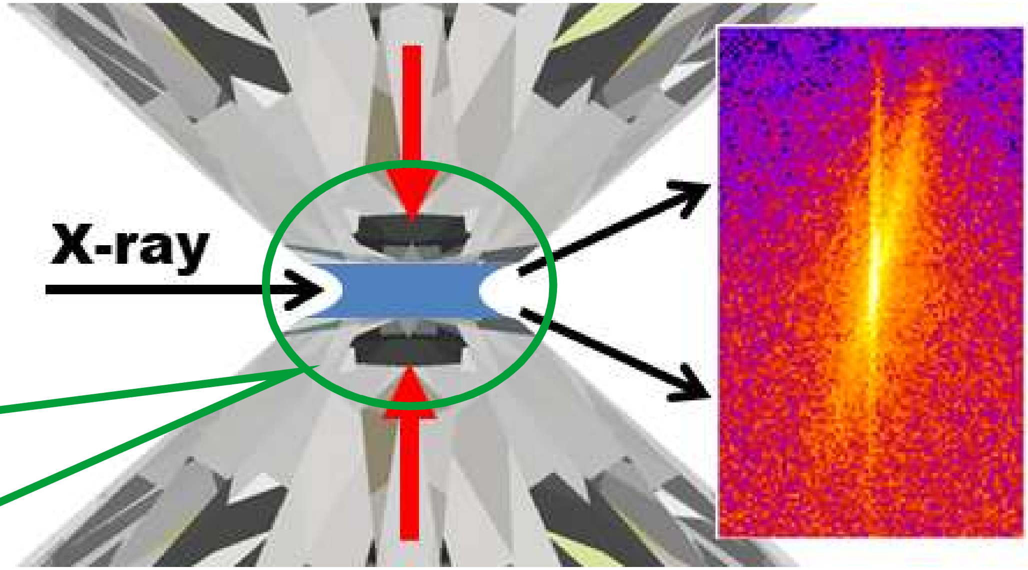
NWAT March-Meeting 2022



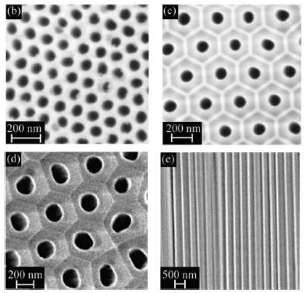
- Nano-scale gap ~ few tens to hundreds of nm
- Liquids with small molecules

HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

DESY.

Control of the properties of the condensed matter on nano-scale.

Applications:



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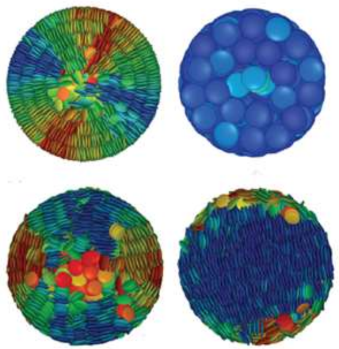

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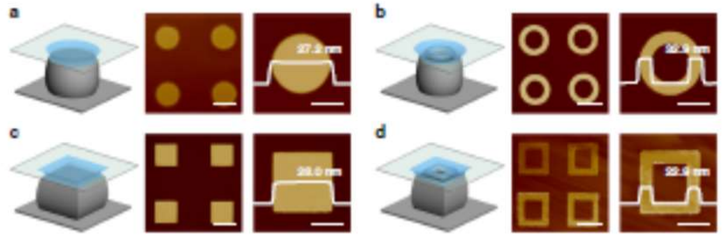
Metamaterials with tunable optical properties: **Kathrin Sentker, et al Phys. Rev. Lett. 120, 2018**

Crystallization control trough nano – confinement:

Hanfei Gao, et al.,. *Nat Commun* 10, 2019.



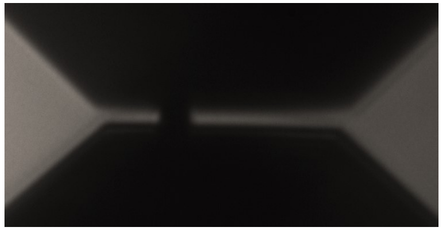
Confinement-induced crystallization

- Friction phenomena in lubricated contact
- Control of the chemistry on nano-scale
- Water desalination

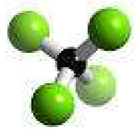
Confinement-induced crystallization

Klein, and Kumacheva, Science **269**, 816 (1995) observed **Solidification:**

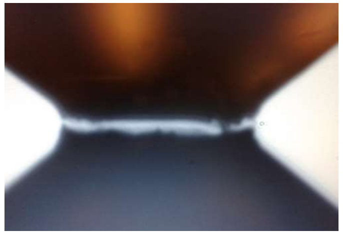
Before confinement



CCl_4



After confinement



Solidification due to the confinement is unambiguous establishment. It is observed in various experiments. SFA measurements and spectroscopy methods show strongly increase of the relaxation times.

and suggested: **The geometrical constrain of the fluid down to nano-scale can induce crystallization.**

What is the structure of the solid phase?

Heterogeneous:
- **Disordered structure**, similar to the glassy state
- **Layering parallel** to the surface
- **Crystals:**

- The matrix supports the crystallization and defines the shape/structure of the crystals

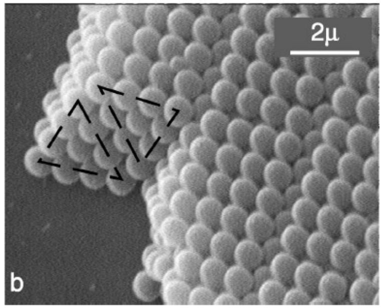
- **The confinement induces itself crystallization.**

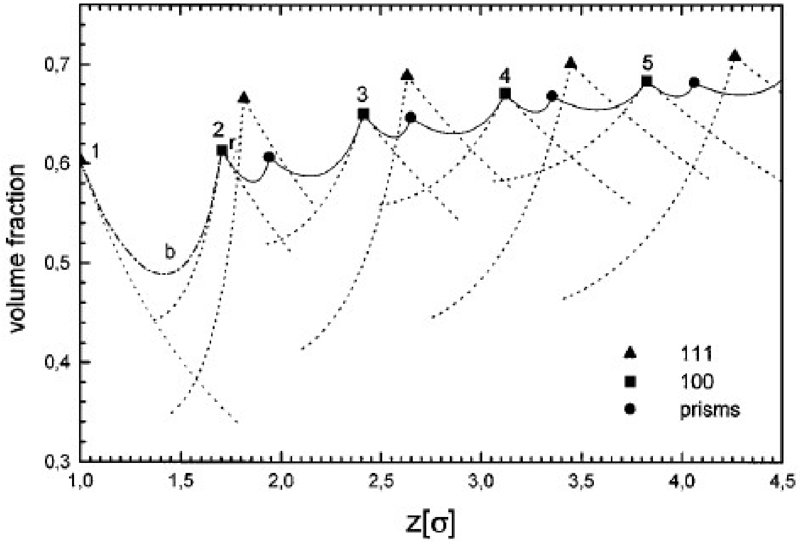
Studied Liquids: **OMCTS, TMS, CCl_4, and water**
no self-assembling properties
no strong interaction between the liquid and the surface

Simulations and theoretical investigations

A lot of simulation works and less experimental evidence. The tiny heterogenous confined sample put a strong demand on the sensitivity of the experimental methods.

Colloidal particles, optical microscopy:
S. Neser, et al. Phys. Rev. Letters, 1997

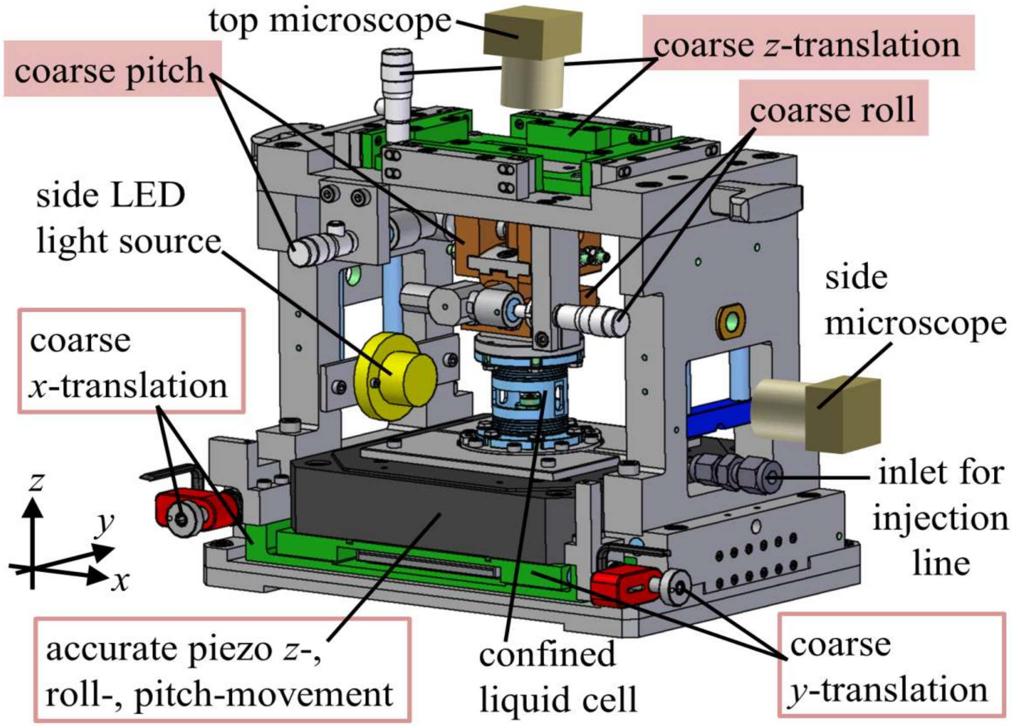




Entropy excess: The driving fore for the crystallization.
The roll of the pressure is not understood.

The simulations support the idea of crystallization induced by the confinement itself.
Experimental results are needed!

Experimental setup – Diamond Cell



The measurement are conducted at **P08** and **P23 beamlines**, Energy 18 KeV, beam size VXH=3X20 μm^2,
Diamond anvils: culet size 100 and 200 μm,
Max Pressure:
250 MPa @ 200 μm and 1000 MPa @ 100 μm
No pressure sensor.
The liquid film is created by liquid condensation at the top diamond substrate.

Image from the side microscope

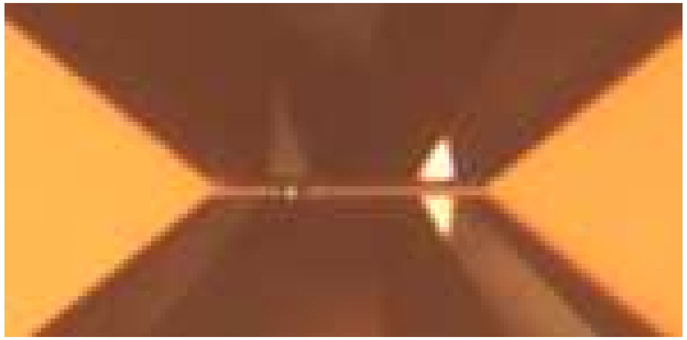
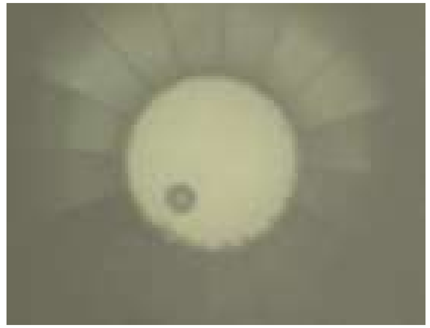
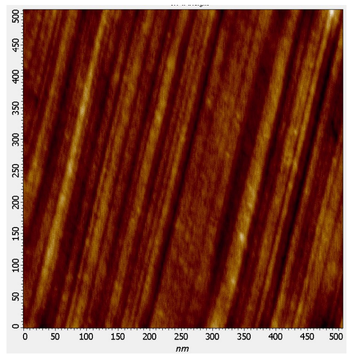


Image from the top microscope



AFM image of the diamond surface



Experimental setup – Stamp Cell

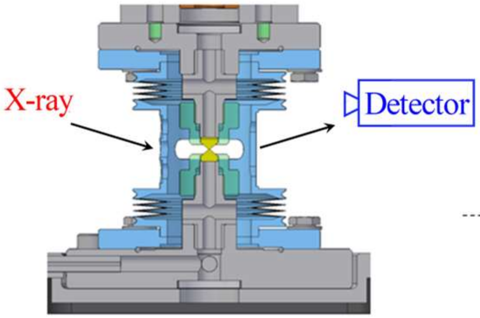
Sample-cell holder with two Si-wafer confining the liquid between.

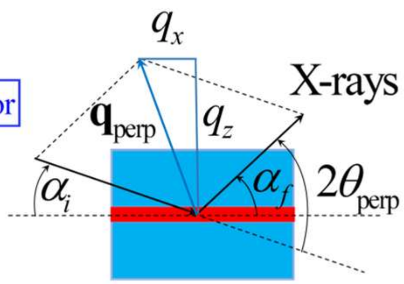
The measurement are conducted at **P23 beamline**, Energy 18 and 23 KeV, beam size VXH=3X20 μm^2,
sample size 5x5 mm, Different type substrates can be used,
Pressure sensor available,
Stepwise control of the pressure possible
Working pressure: 1.6 - 80 MPa
The liquid film is crated by drop-casting at the substrate.

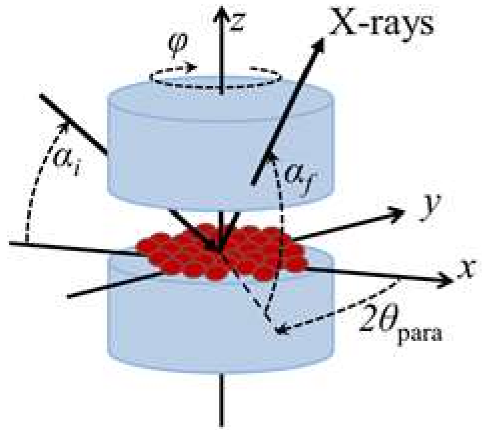
Experiment

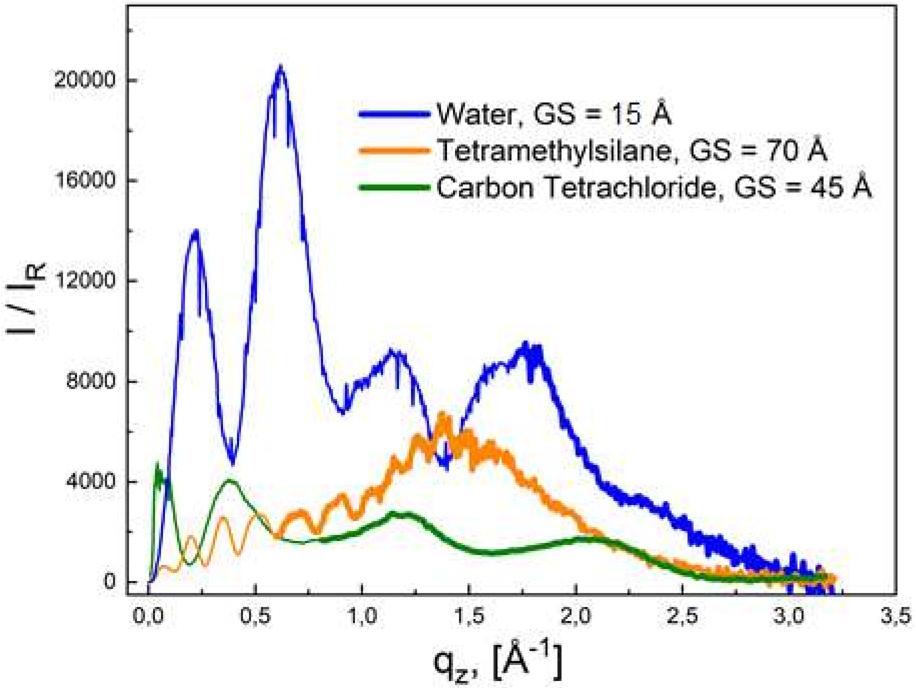
Reflectivity scans:

In-plane scattering:









Reflectivity up to 3Å^{-1}:

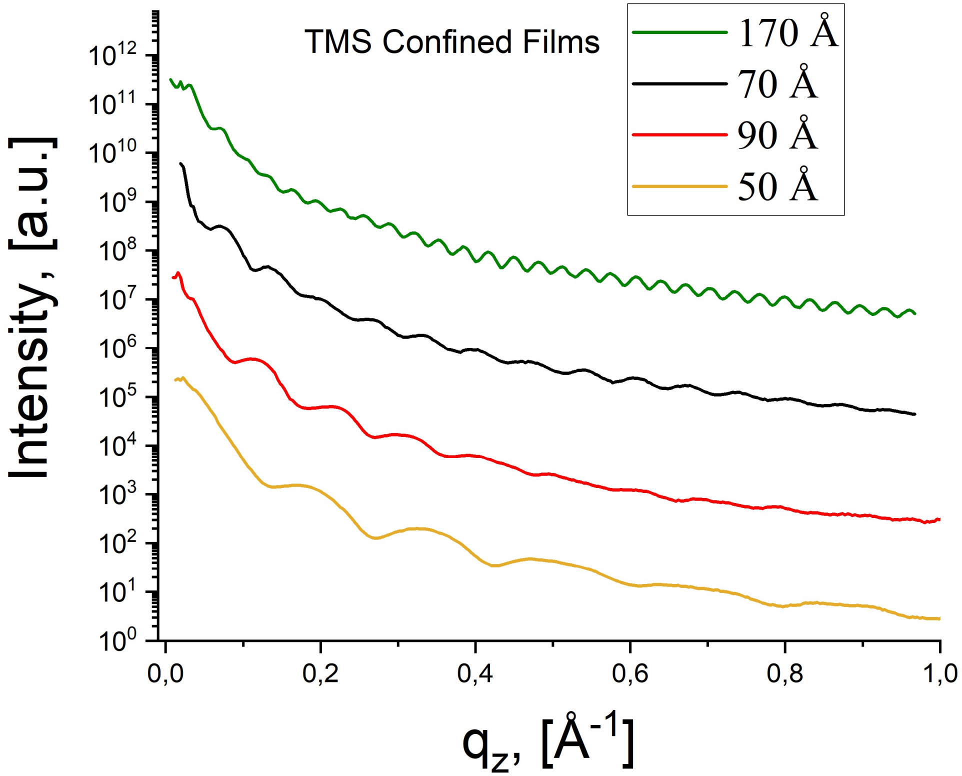
- Film thickness (lower q-range)
- Structure signal corresponding to the layering (higher q-range)

In-plane scattering:
Crystallization

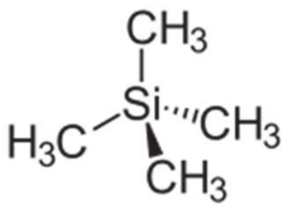
Crystallization under confinement: TMS and OMCTS

Diamond Cell:

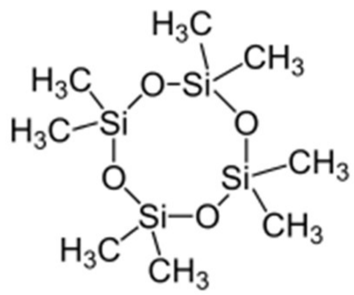
Diamond culet: 200 μm

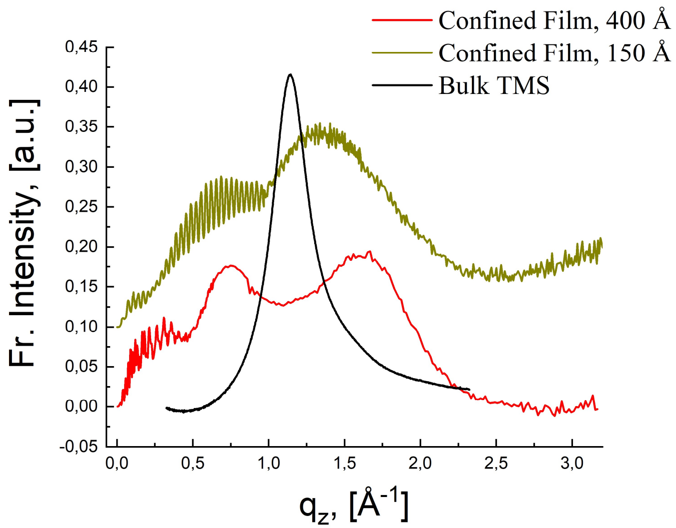


TMS



OMCTS





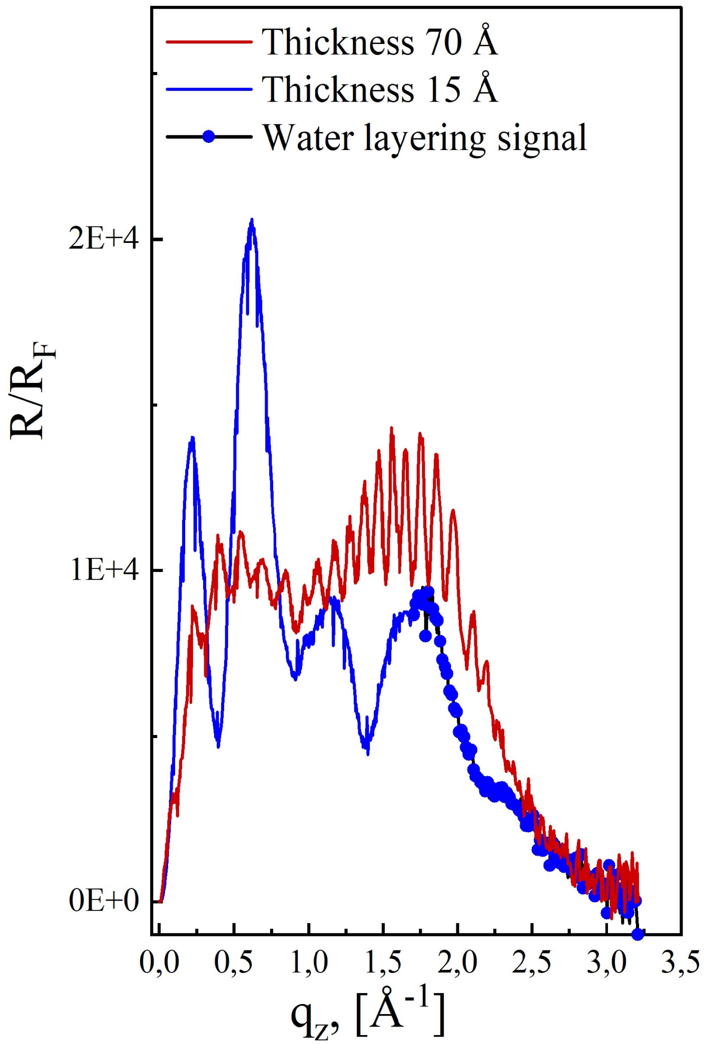
Very fast solidification, difficult to obtained thin films, film thickness > 50 Å

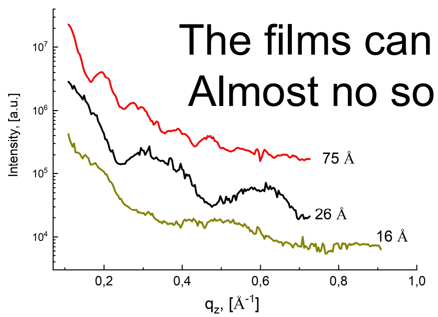
No crystal peaks are observed!

Crystallization under confinement: Water

Diamond Cell:

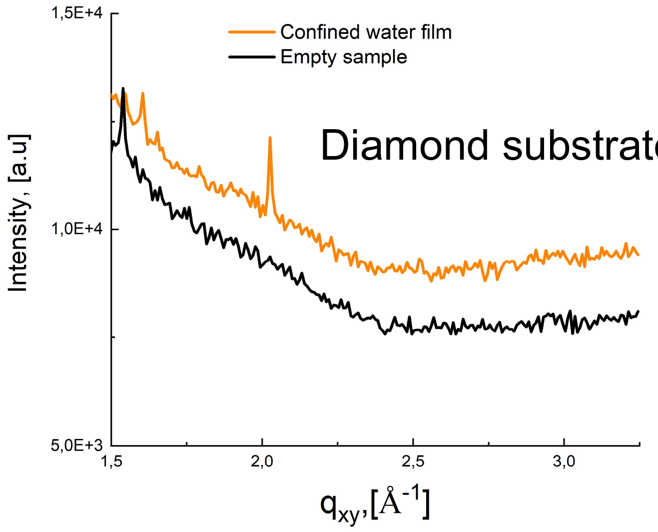
Reflectivity:





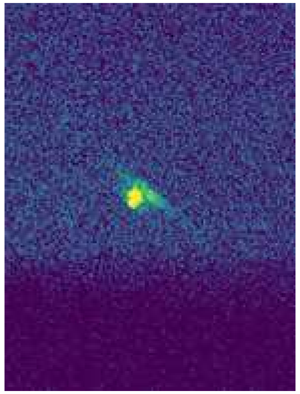
The films can be compressed!
Almost no solidification

In-plane scattering:



Stamp-Cell

Substrates: Si-wafers

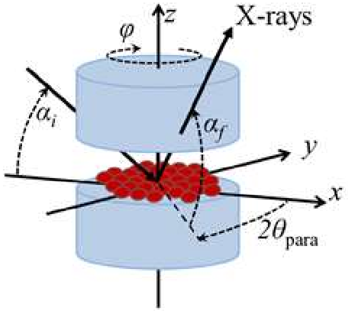


$q_{x,y}$=1.39 $Å^{-1}$; $q_{x,y}$=1.76 $Å^{-1}$

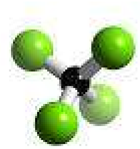
- Almost no solidification
- Single crystal reflections: evidence for crystallization,
- More experiments are needed!

Crystallization under confinement: Carbon tetrachloride, CCl_4

Stamp Cell:

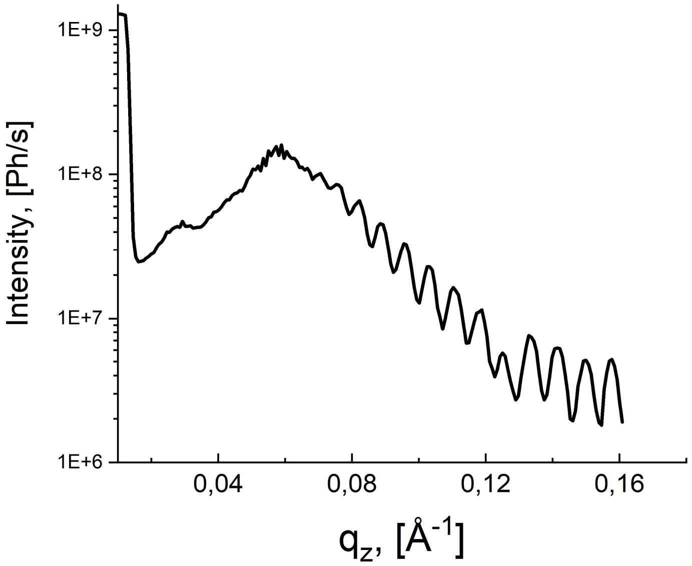


Substartes: Si-wafer
Liquid: CCl_4

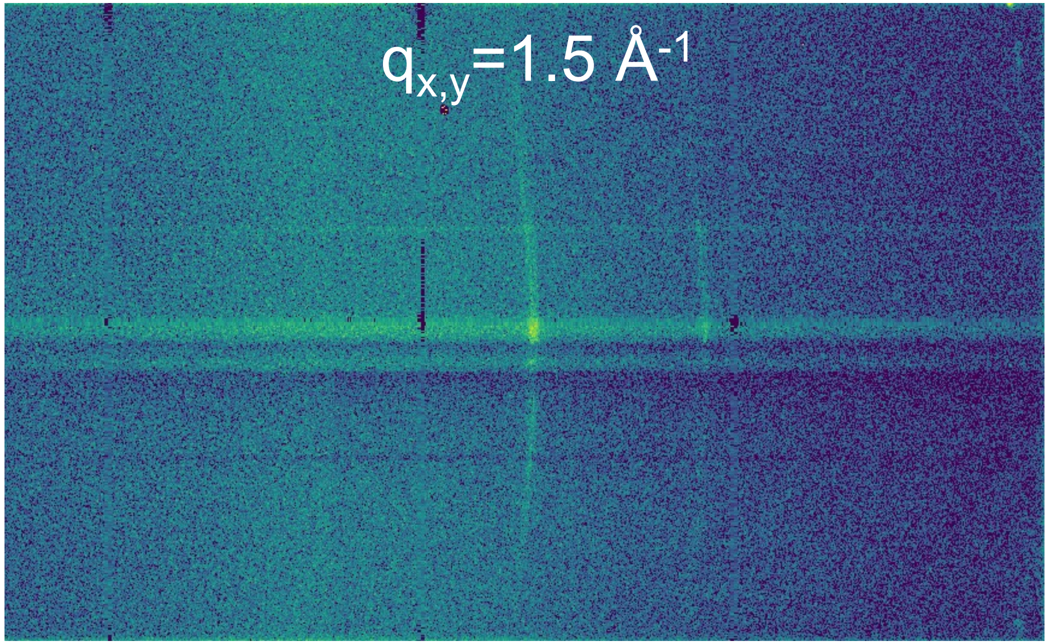


Reflectivity:

Film Thickness: 800 Å



In-plane scattering:

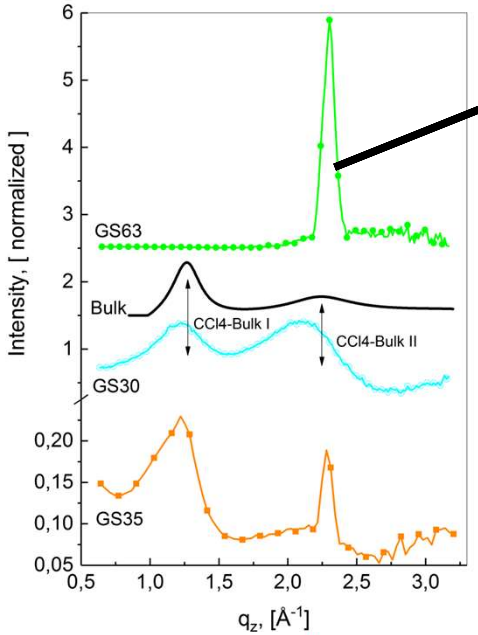


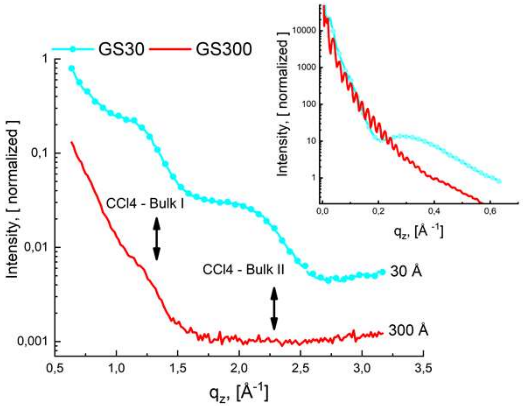
Crystallization under confinement: Carbon tetrachloride, CCl_4

Diamond Cell:

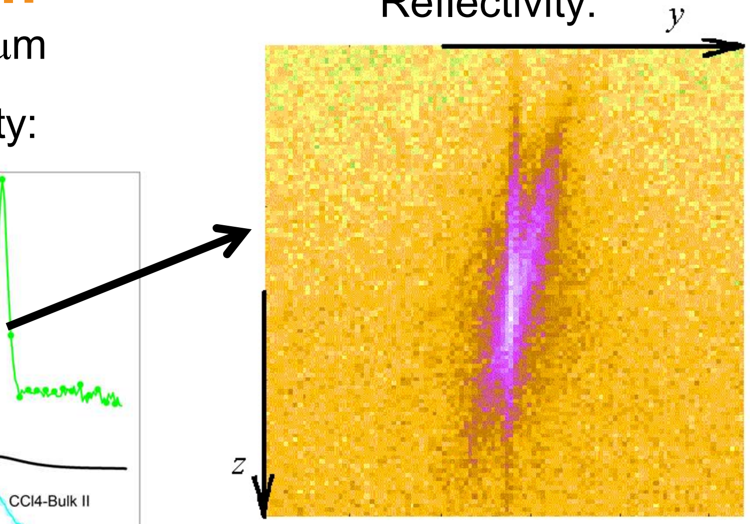
Diamond culet: 200 μm

Reflectivity:

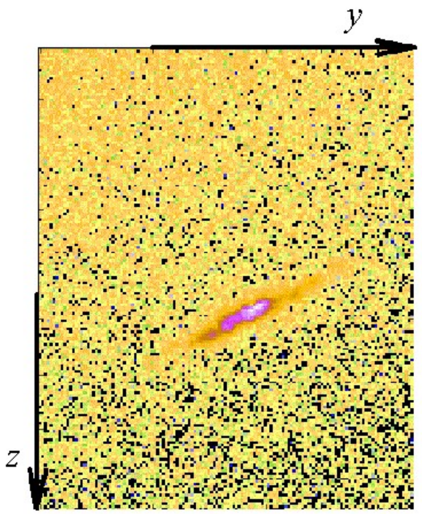




Reflectivity:



$q_z = 2,3$ Å^{-1}



$q = 1,2$ Å^{-1}

- Single crystals in thin films.
- Powder rings at thicker films.
- The observed reflections at single experiment are not enough to identify the crystal phase.
- It is very difficult to reproduce the single crystal reflections of the previous experiments.

Conclusions:

Experimental evidence for crystallization induced by the confinement in carbon tetrachloride films is observed. Single nanocrystals are supposed in the thin confined films and powder crystal rings are observed in the thicker samples.

In the case of the water a single crystal reflections are observed suggesting a crystallization. Nevertheless more experiments are needed.

The experimental data suggest no crystallization for OMCTS and TMS.

The single crystal reflections are not easy to be reproduced. We suppose that the observed crystal phase and the crystal orientation is strongly defined by the structure of the interfaces.

Thank you!

Oliver Seck, Anita Ehnes,
Rene Kirchhof and Florian Bertram, P08
Dmitri Novikov, P23

For the cooperation work with

Kim Nygård,

Patrick Huber,