Liquid structure in nano-space probed by x-ray scattering methods

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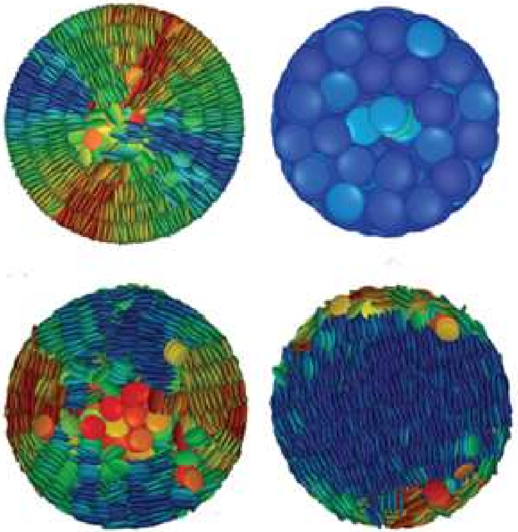
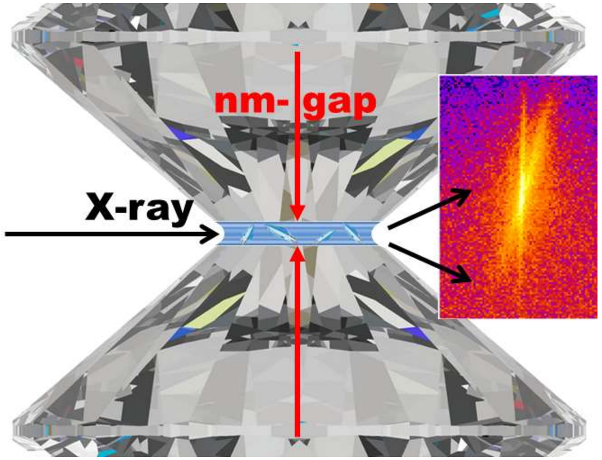
Analytical Tribology Network,
May 2021



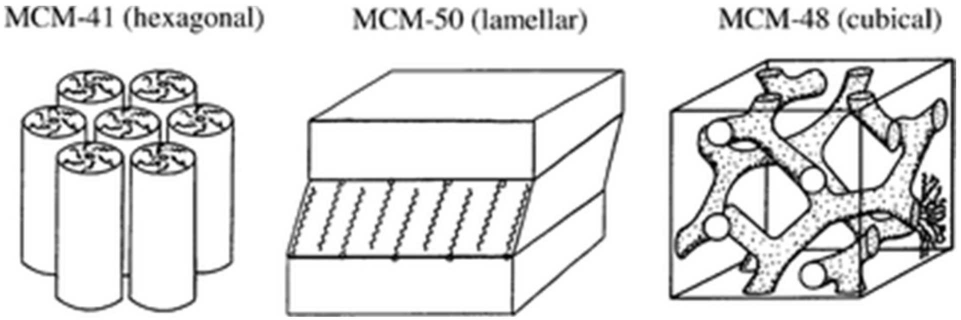
Fluids geometrically constrained in small volume. At least one of the volume dimensions is comparable to the molecular size of the liquid.

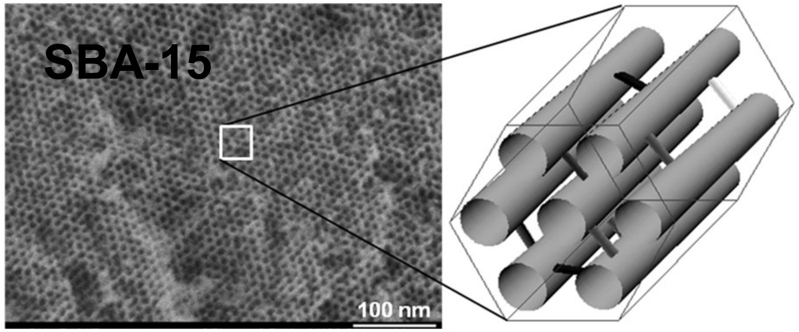


HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

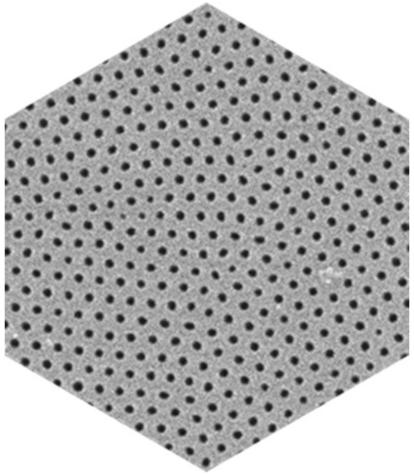
Template Materials – prose materials with pore size of ten to hundreds of nm

Silica Powder and Membranes

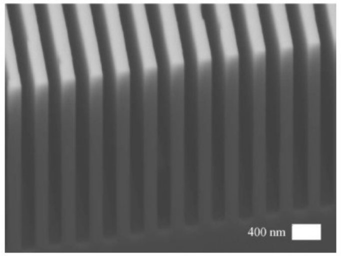




Alumina Membranes



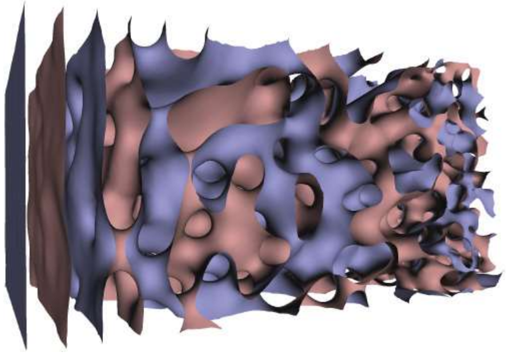
d~ 400nm



The filling of the fluids into the pores is via spontaneous imbibition.

Template Materials - micelles and slit-geometry

Micelles - soft confinement

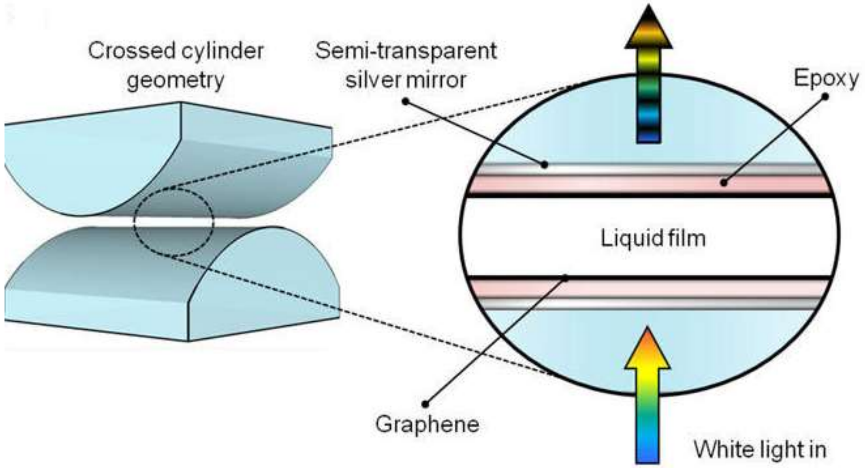


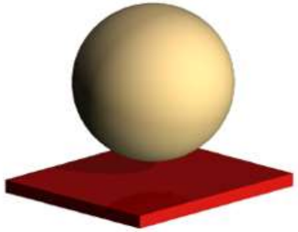
Applications in life science

confinement between two parallel substrates: slit-geometry setups

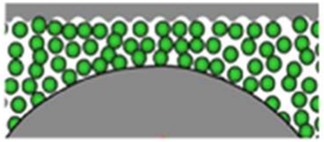
In-situ changing the gap size

Surface Force Apparatus (early 70s) -
(SFA) confined area -100 μm

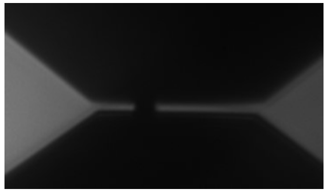




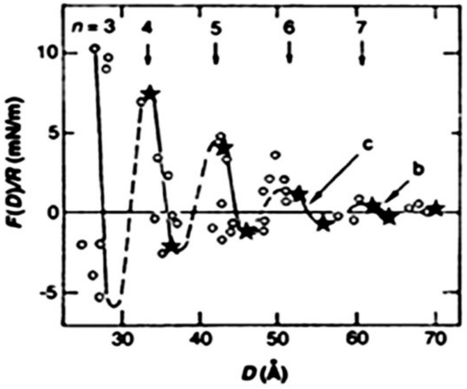
Atom Force Microscope
Very small confined area



X-ray Surface Force
Apparatus (XSFA)



Confined liquid setup
DESY

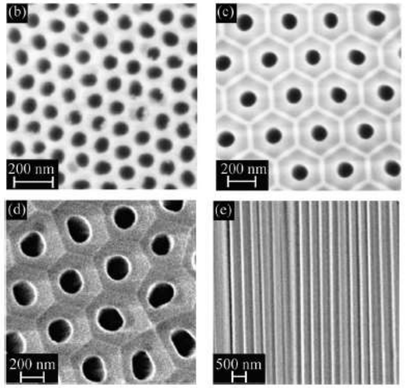


Liquids layer in confinement !

Applications

Confinement in porous membranes - Metamaterials

Reinforced materials



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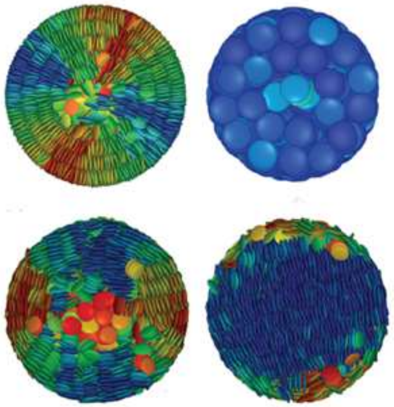


= **Metamaterials**

The pore size is smaller than the optical wavelength. Special optical properties tunable on the nanometer scale.

in material science and engineering

Confinement in slit is explored to study the friction reduction in sliding contact

decreasing of
energy losses

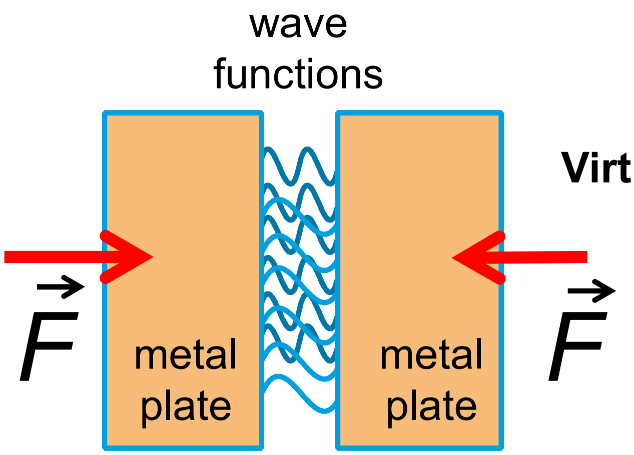
Increasing of the life time
of the artificial joints
The ageing causes inflammation

in tribology, lubrication in sliding contact

Properties of the confined fluids

Properties of the confined fluids

Casimir effect



Quantum field theory

➔ Space is filled with virtual particles (vacuum fluctuation)

Virtual particles

➔ wave functions have to fit in gap

➔ **less virtual particles in gap (compared to vacuum)**

➔ Casimir force drives plates on each other

For the fluids the confinement change the **conformation (reduce microscopic states) of the system**

Internal Energy in confined system is controlled by the entropy excess and surface potential

➔Confinement change strongly the Phase Diagram of the Liquids

It is manifested in:

➔ Deceasing / increasing of the freezing / melting temperatures

➔ Hysteresis in the Phase Diagram

➔ Confinement-Induced Crystallization

Surface Potential

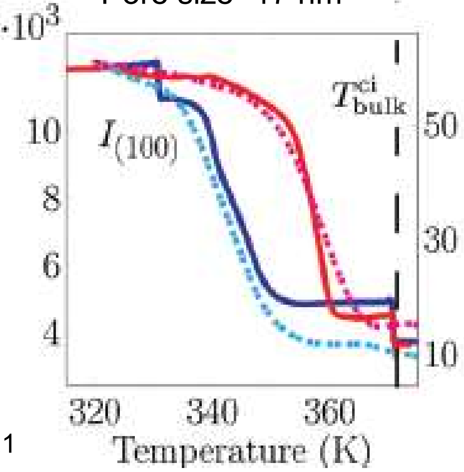
➔ Liquids layer at the interfaces in confinement

Dynamic in confinement

➔ Computer simulations predict continuous jamming of the confined system from liquid to solid phase and back.

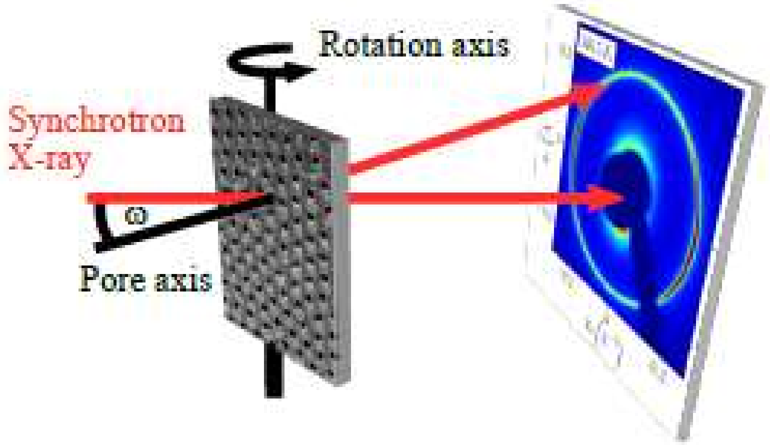
Kathrin Sentker, et al. *Nanoscale*, 2019

HAT6 - Liquid crystal
Pore size -17 nm

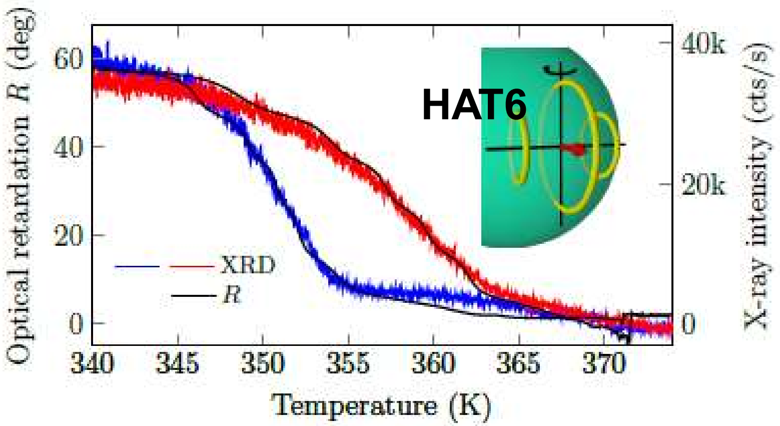


Phase Diagram of the liquid changes in confinement

P08, X-ray diffraction, beam size ca. 1 mm, Energy 18 keV



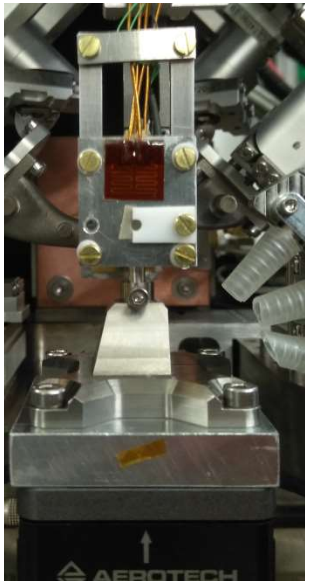
averaging over large amount of pores

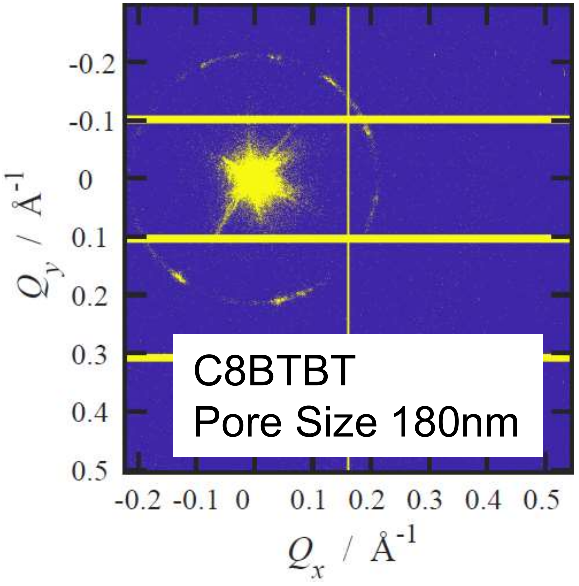


Kathrin Sentker, et al., PRL, **120**, 067801, (2018)

P06, X-ray nano-diffraction, beam size ~ 100nm , Energy 15 keV

X-ray diffraction from single pore
The samples are strongly textured



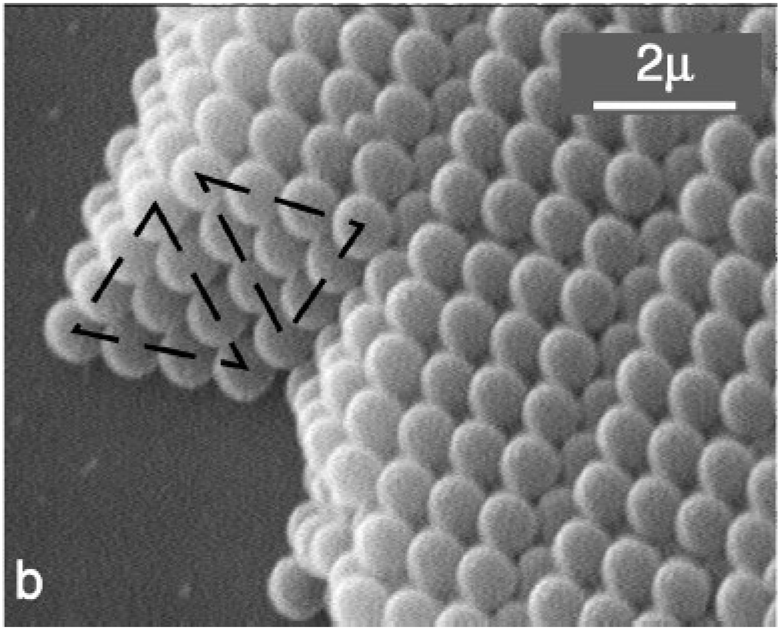


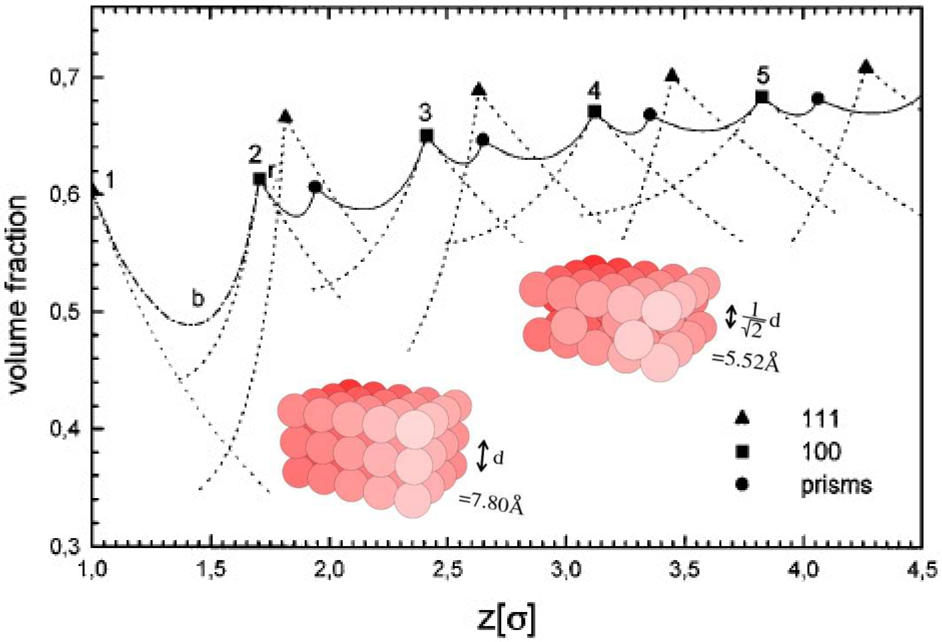
C8BTBT
Pore Size 180nm

Confinement-Induce Crystallization

Klein, and Kumacheva, Science **269**, 816 (1995) suggested: **The geometrical constrain drives a confinement-induced crystallization.** **In contradiction to:** The solidification on reduction of the confining gap is due to continuously approaching a glassy state.

The simulation of non-polar particles, with **Lennerd-Johns** or **Hard-Core** interacting potential and experimental work on confined colloid particles confirm the confinement-induce crystallization.



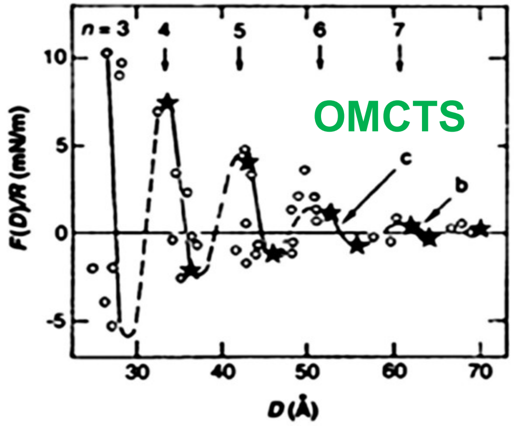


S. Neser, C Bechiner, P. Liedere, T. Palberg, Phys. Rev. Letters, 1997

Properties of the confined fluids

Liquids layer in confinement

SFA measurements



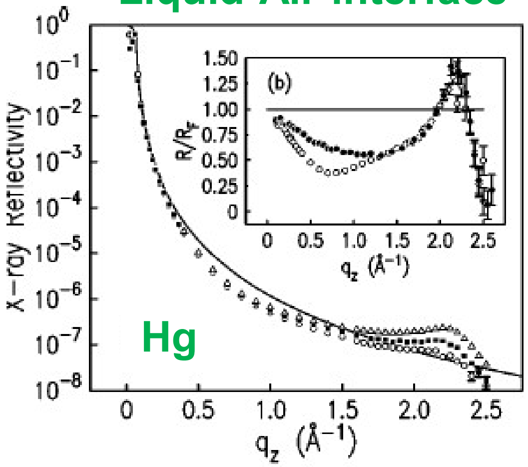
⬅ Mechanical measurements

J. N. Israelachvili, G. E. Adams, Nature **262**, 774 (1976).

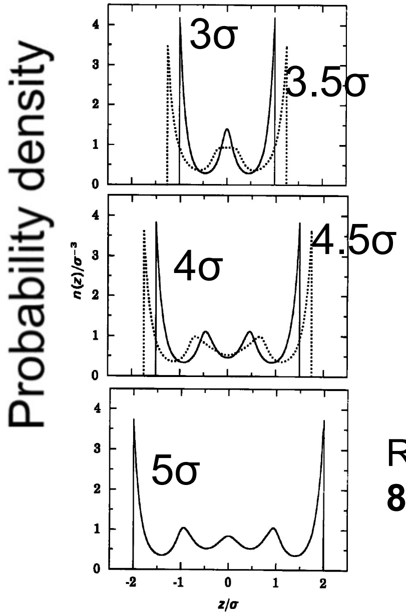
Liquid layers at single interface too!

Liquid-Air interface

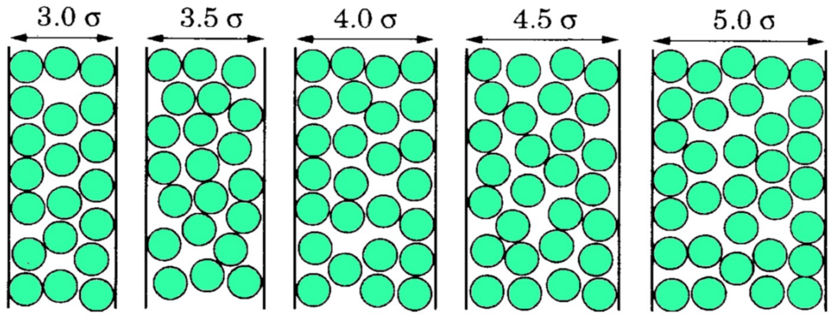
Reflectivity measurements ➡



Willem Jan Huisman et al., Nature, **390**,1997
E. DiMasi et al., Phys. Rev. B, **58**, 418 ,1998



Simulation:

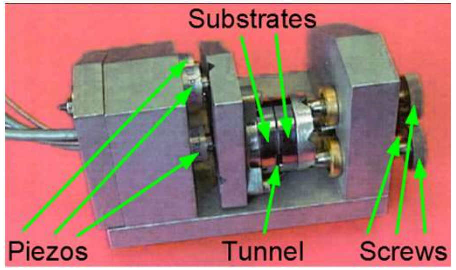


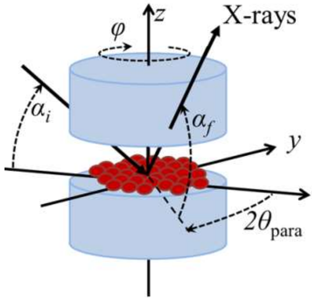
R. Kjellander & S. Sarman., *J. Chem. Soc. Faraday Trans.*, 1991, **87,** 1869-1881

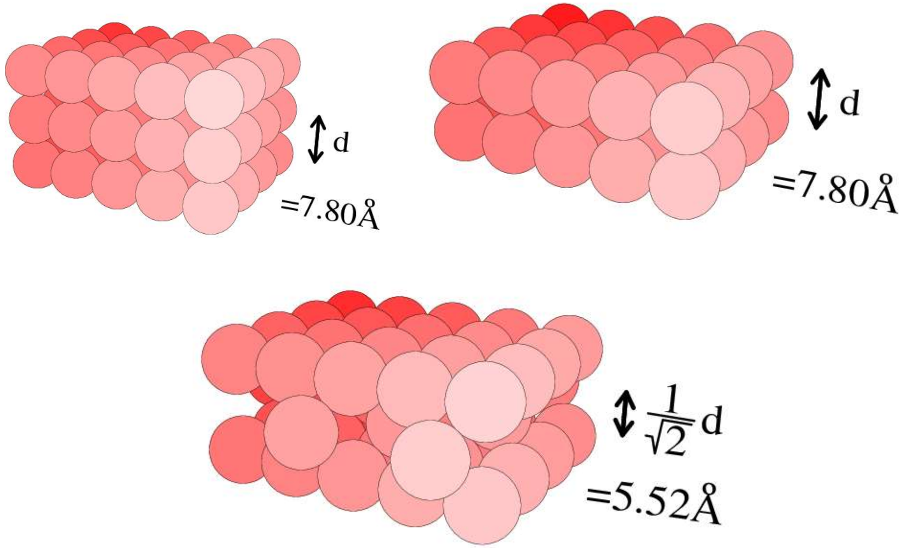
Liquids layer in confinement, slit geometry

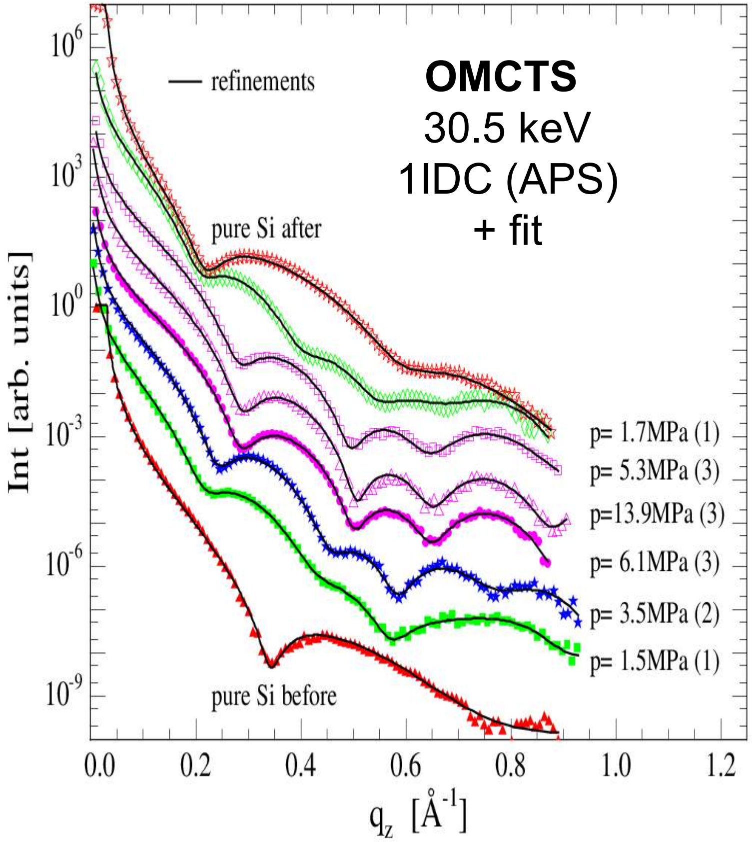
Experiment, x-ray reflectivity

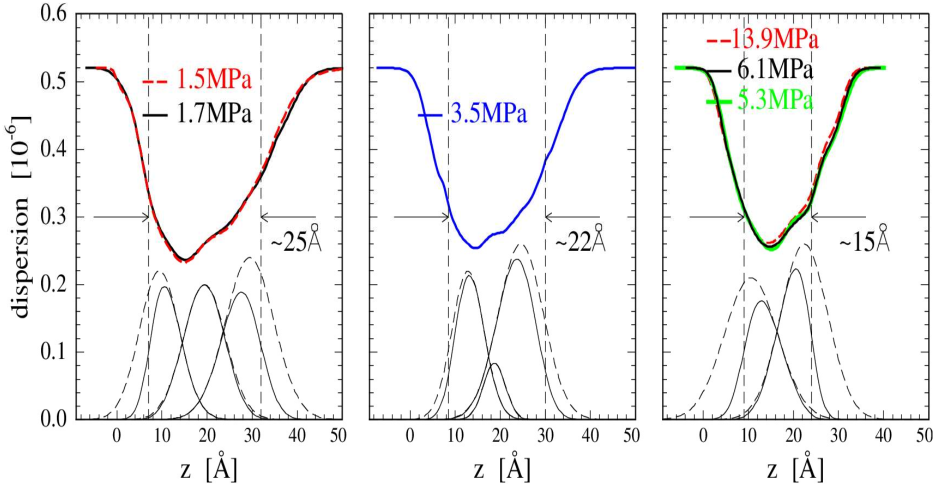
O. H. Seeck et al., *Euro Phys. Lett.*, 2002, **60**, 376-382









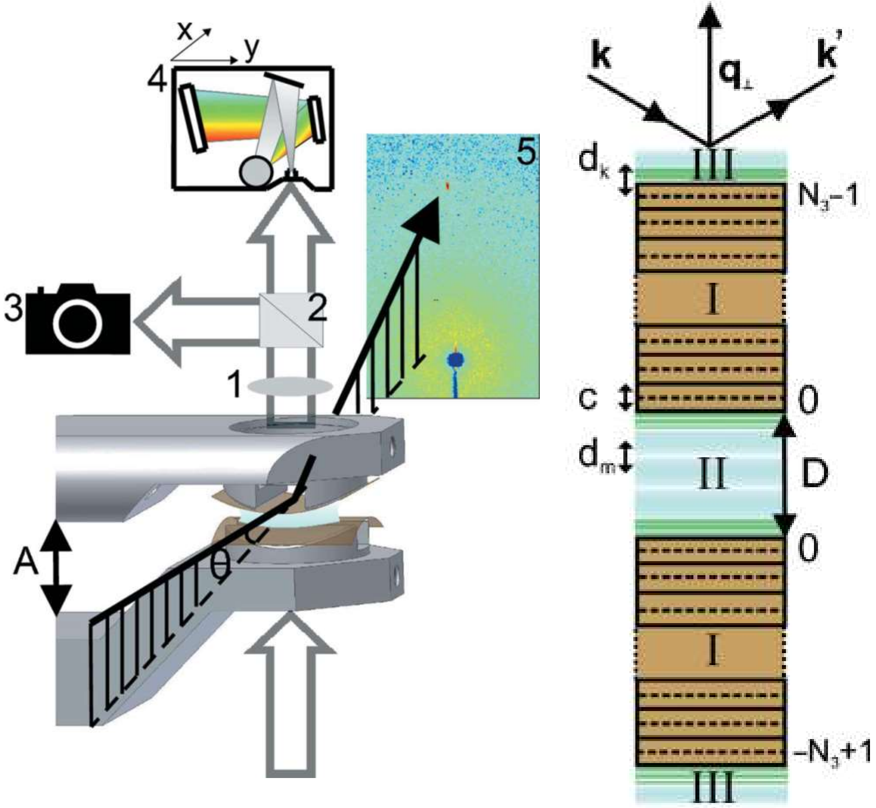


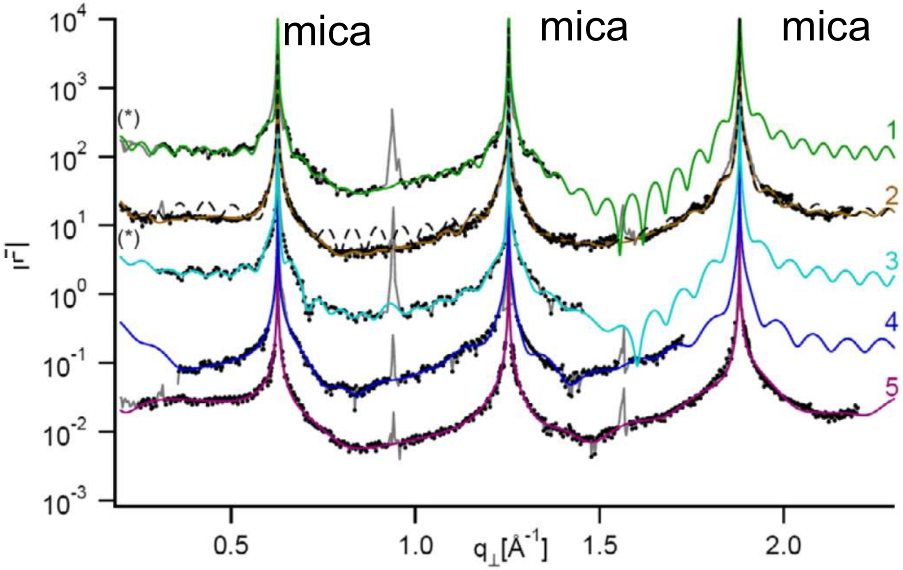
Liquids layer in confinement, slit geometry

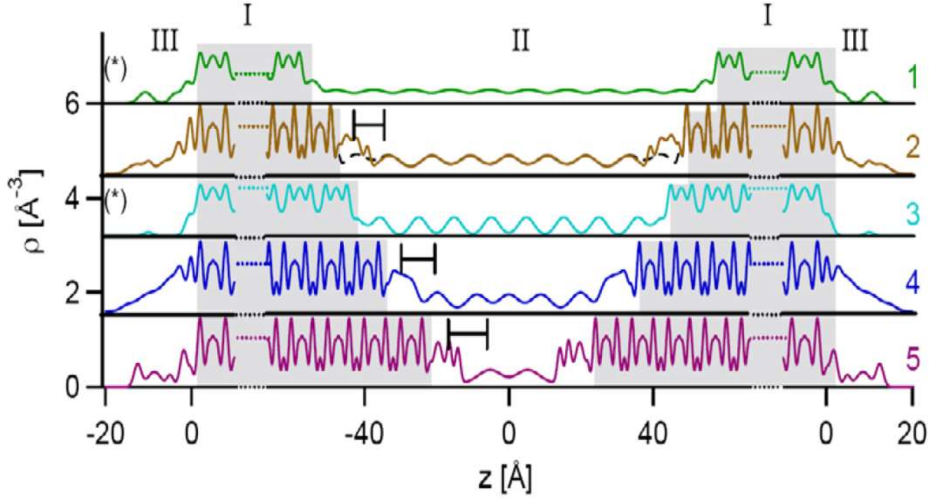
Experiment, x-ray reflectivity E. Perret et al., *J. Phys.: Condens. Matter,* 2010, **22**, 235102

Crossed mica cylinder X-ray SFA

Liquid: tetrakis(trimethyl)siloxysilane (TTMSS)
Molecular diameter 9 Å







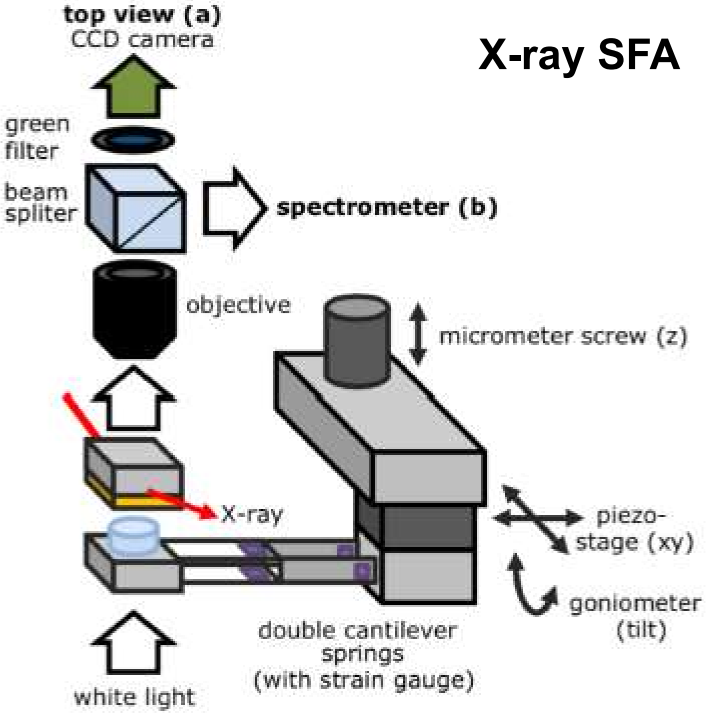
Liquids layer in confinement, slit geometry

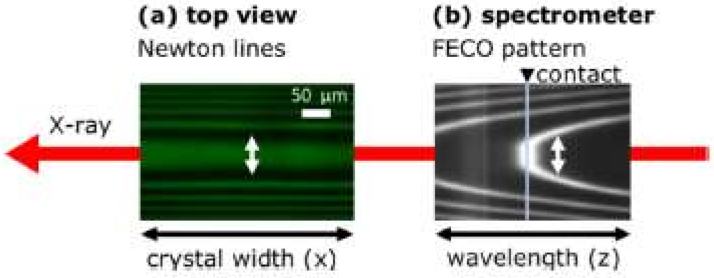
Experiment: x-ray reflectivity, in-plan scattering, Energy 40-80 keV

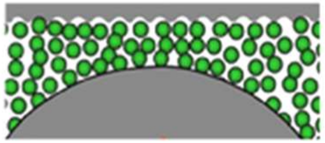
Liquid: 8CB liquid crystal, min Gap Size 100 nm

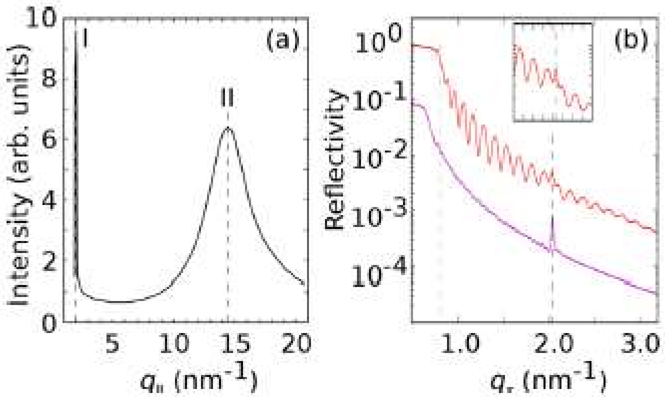
H. Weiss, *Langmuir* , 2019, **35**, 16679-16692

X-ray SFA

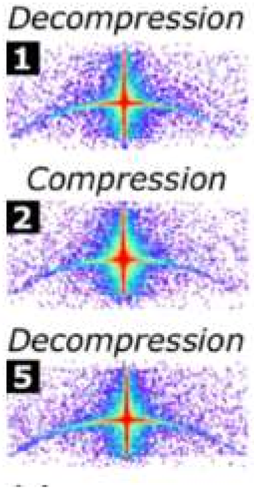


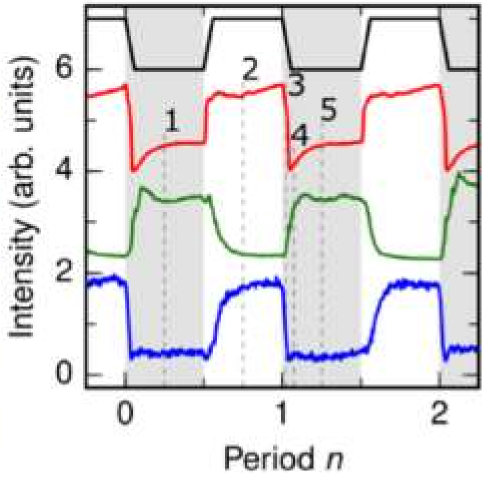






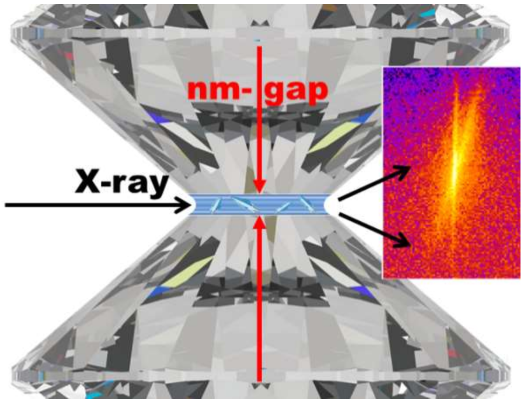
One Period 136s

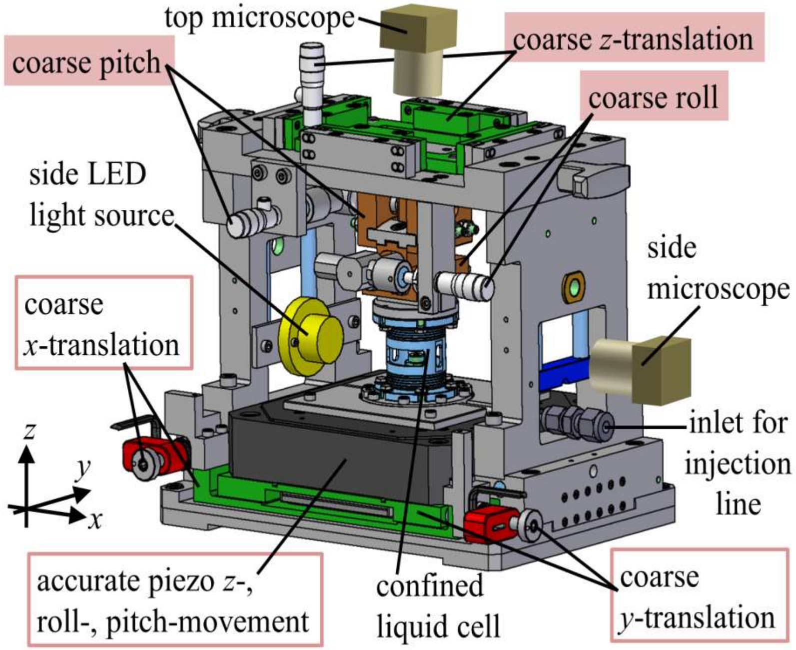




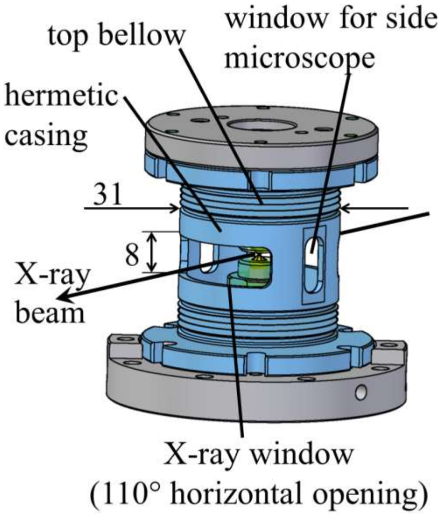
Confined-Induce Crystallization, slit-geometry

experimentally observed at P08, Energy 18 keV, x-ray reflectivity and in-plane scattering

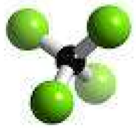


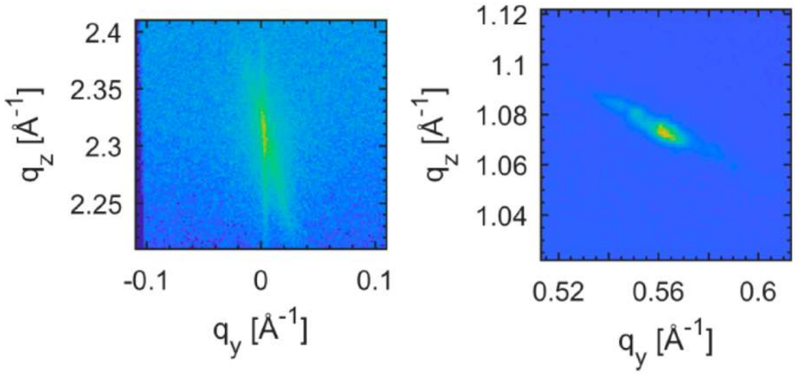


Inner cell



carbon tetrachloride

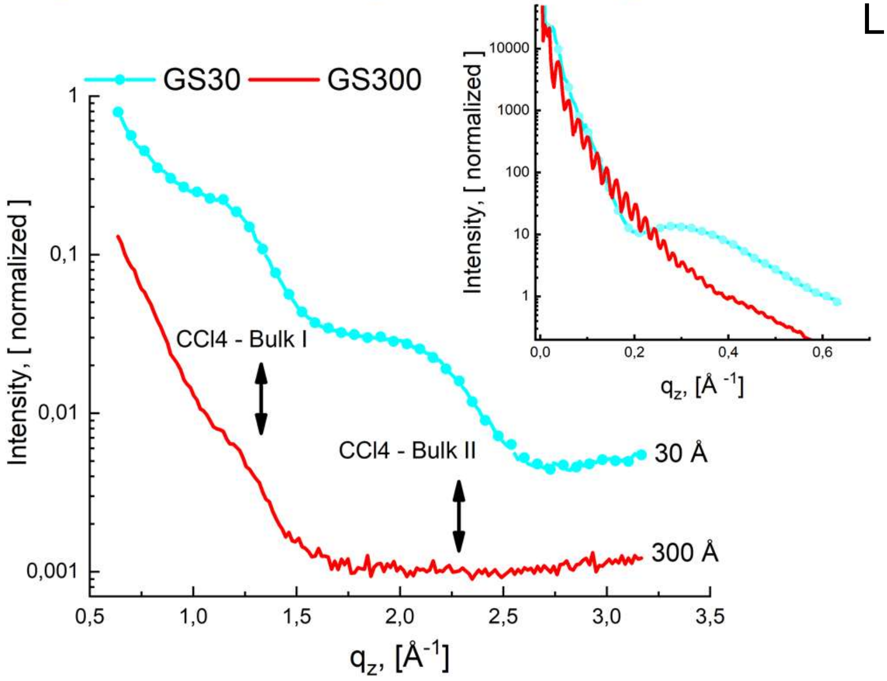




M. Lippmann et al., *JPCL.,* 2019, **10,** 1634-1638
M. Lippmann et al., *Rev. Sci. Instrum.,* 2014, **85**, 015106

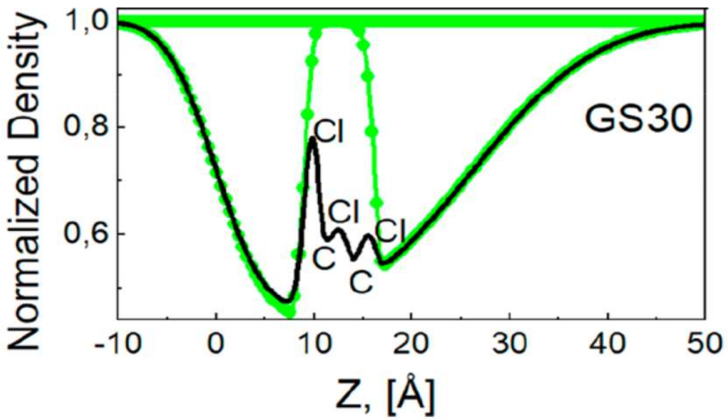
Liquids layer in confinement, slit geometry

Experiment, x-ray reflectivity, DESY

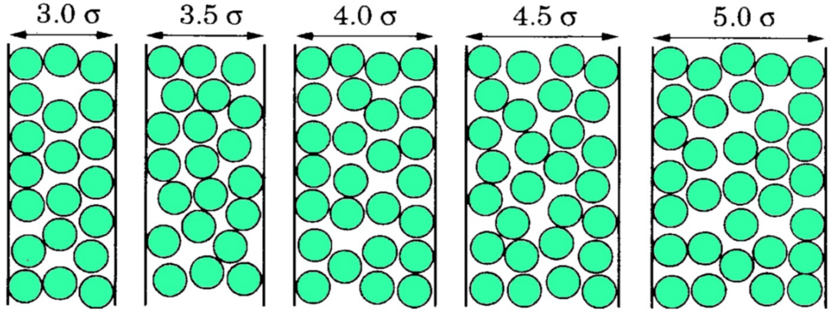


carbon tetrachloride

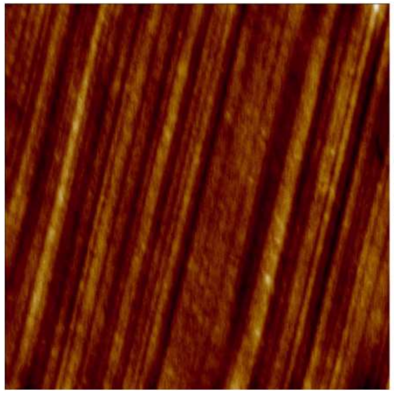
Lennard-Johns liquid, Molecular size 5 Å

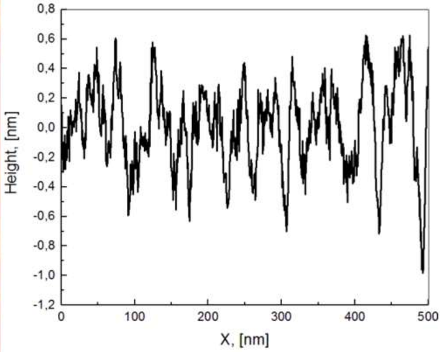


Simulation:



Diamond Surface, AFM measurements





Liquids layer in confinement also at rough surface !

Thank you!

Kim Nygård

MAX IV

Oliver Seeck,
Anita Ehnes
Anca Ciobau

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Rene Kirchhof
Florian Bertram

P23
Dimitry Novikov

P06 Nanoprobe
Andreas Schropp
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