

# Controlled self-organisation of Langmuir monolayers via the physical characteristics of a complex fluid

## A novel approach to crystal growth?



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### Introduction

Crystal growth is a surface process  
 => therefore Langmuir monolayers are ideal model systems

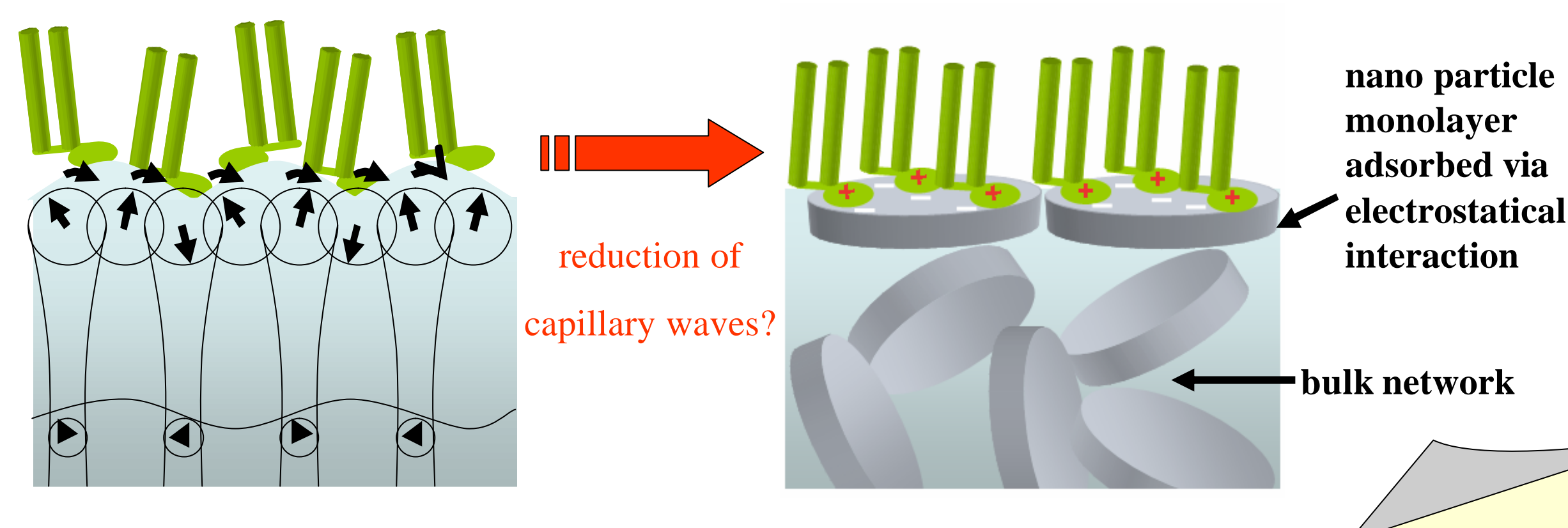
Thermally excited surface fluctuations (capillary waves) avert long range ordering of surfactant monolayers on liquid surfaces

Aim: higher ordering in the lipid lattice by stabilisation of the monolayer

Realisation: choose a complex fluid like a sol instead of water to make the substrate more viscous

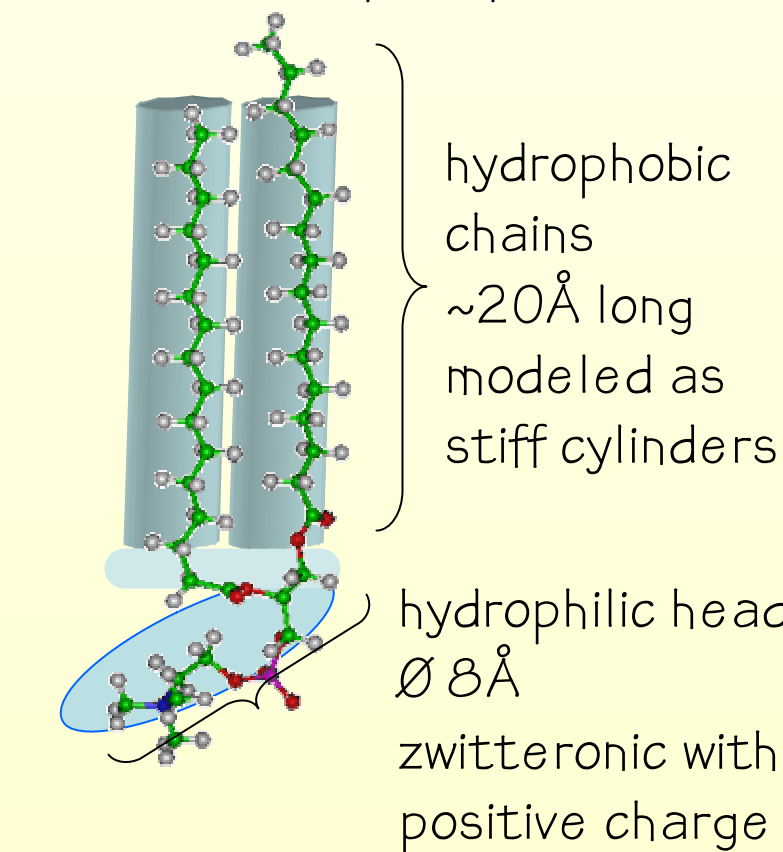
How are the structural and thermodynamical properties of the lipid monolayer influenced by the volume viscosity and the sol forming clay-nano particles?

The positive charge in the lipid headgroup tip and the negative charge excess on the mineral surface lead to an adsorbed mineral monolayer at the liquid air interface while the bulk viscosity is increased by a network of mineral particles.

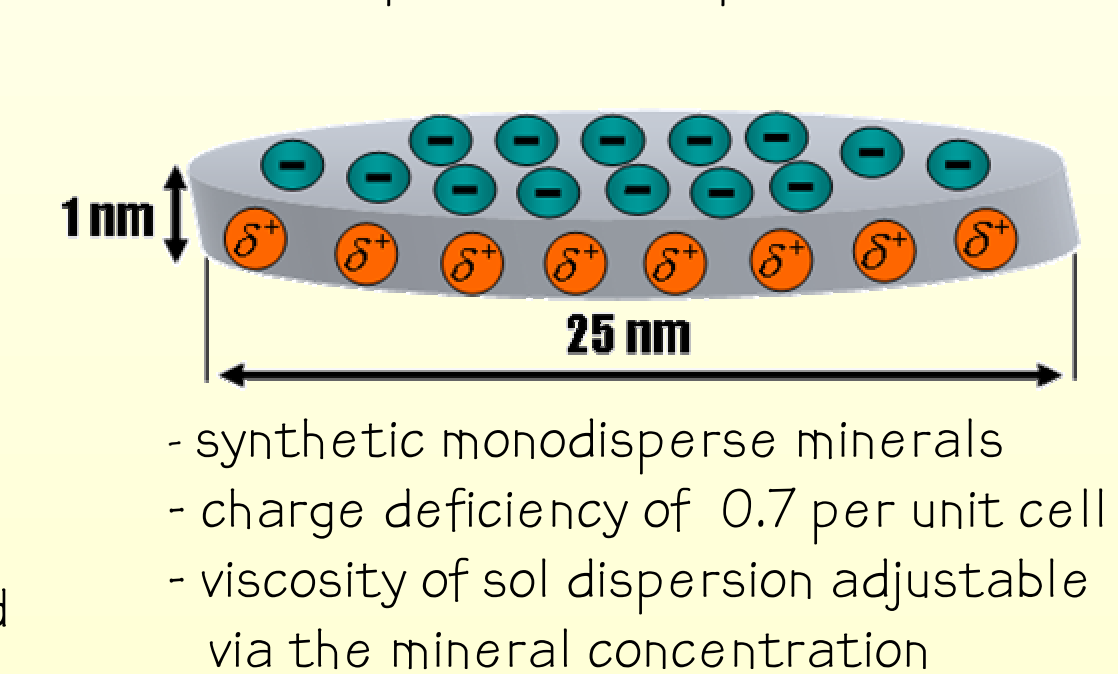


### The System

a Phospholipid: DPPC



clay nanoparticles: Laponite RD<sup>®</sup>



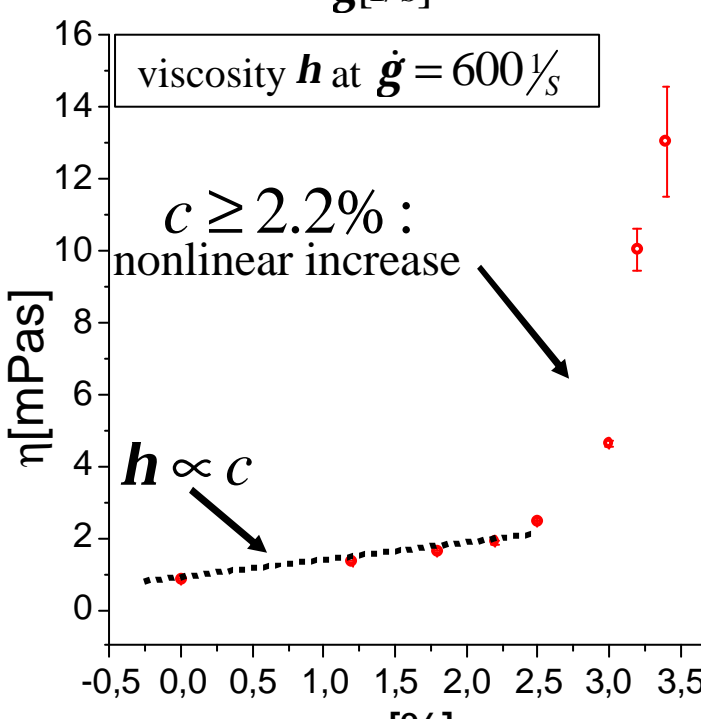
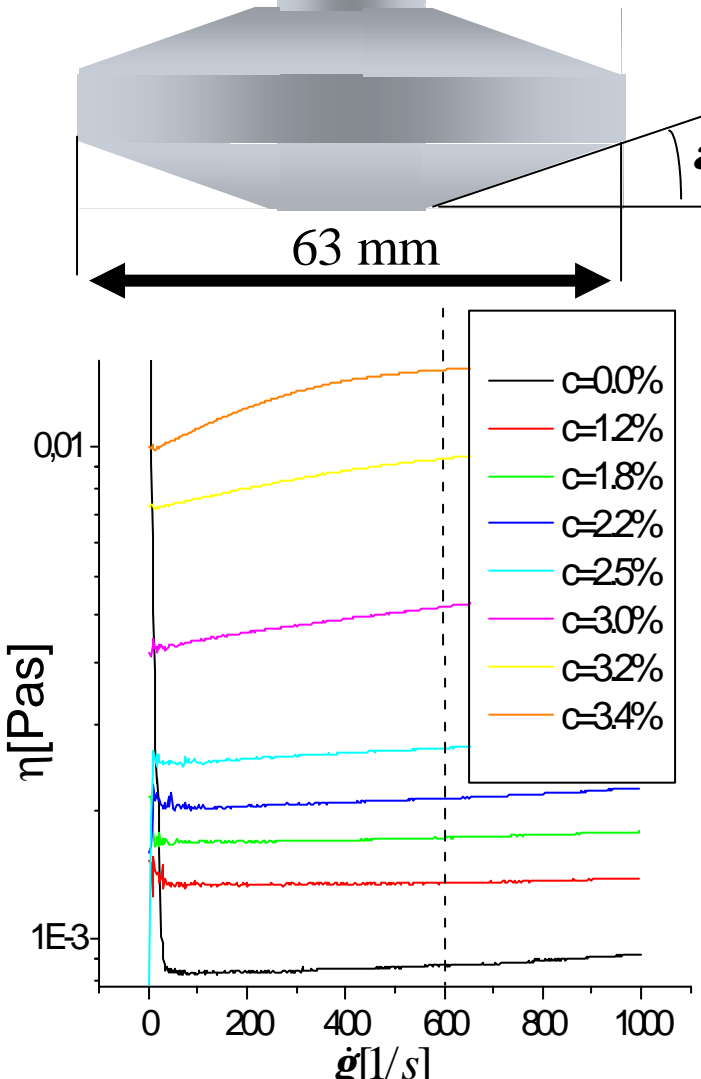
### Rheology

Double-Cone Geometry for high sensitivity to investigate liquid samples of low viscosity

shear rate  $\dot{\gamma} = a^{-1} \Omega$

63 mm

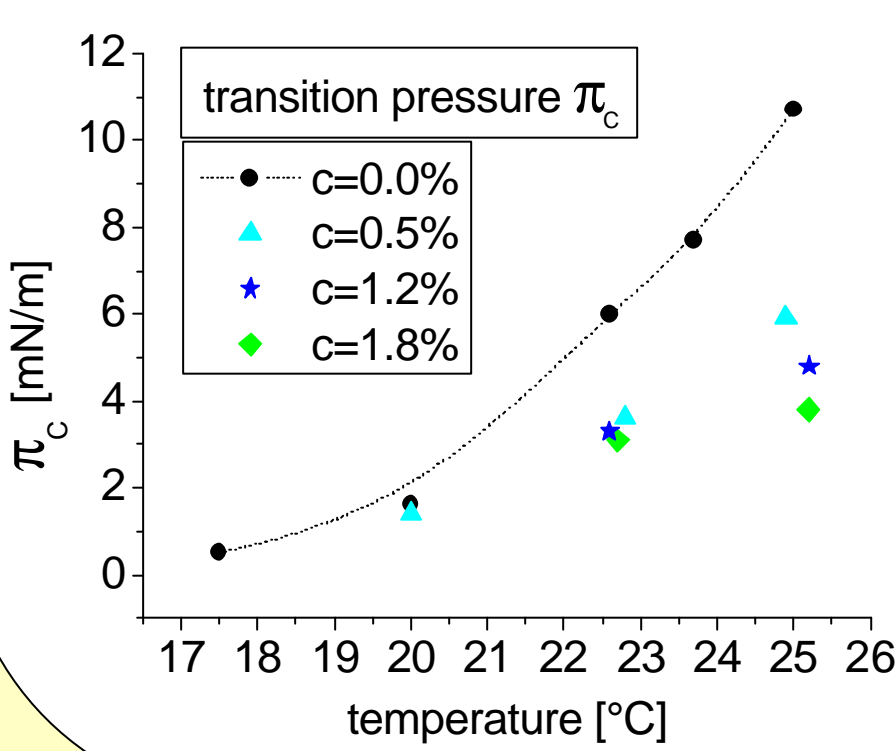
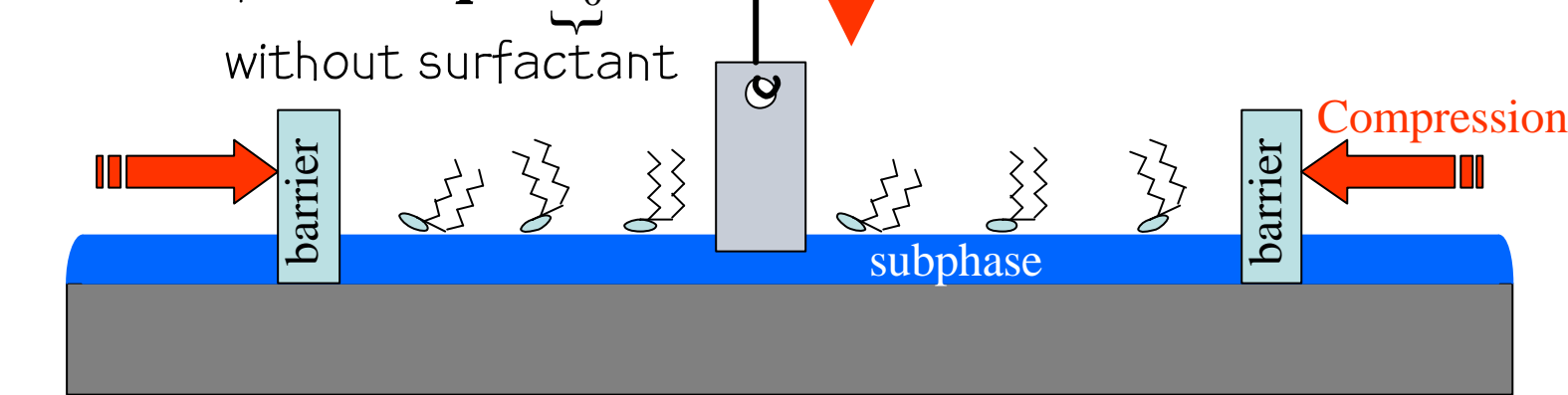
$\alpha = 1^\circ$



The nonlinear increase of the viscosity above 2.2% gives an explanation for the different behavior of these Langmuir isotherms

### The Langmuir Technique

A liquid tries always to reduce its surface area => surface tension  $\mathbf{S}$   
 surface pressure  $\mathbf{p} = \mathbf{S}_0 - \mathbf{S}$



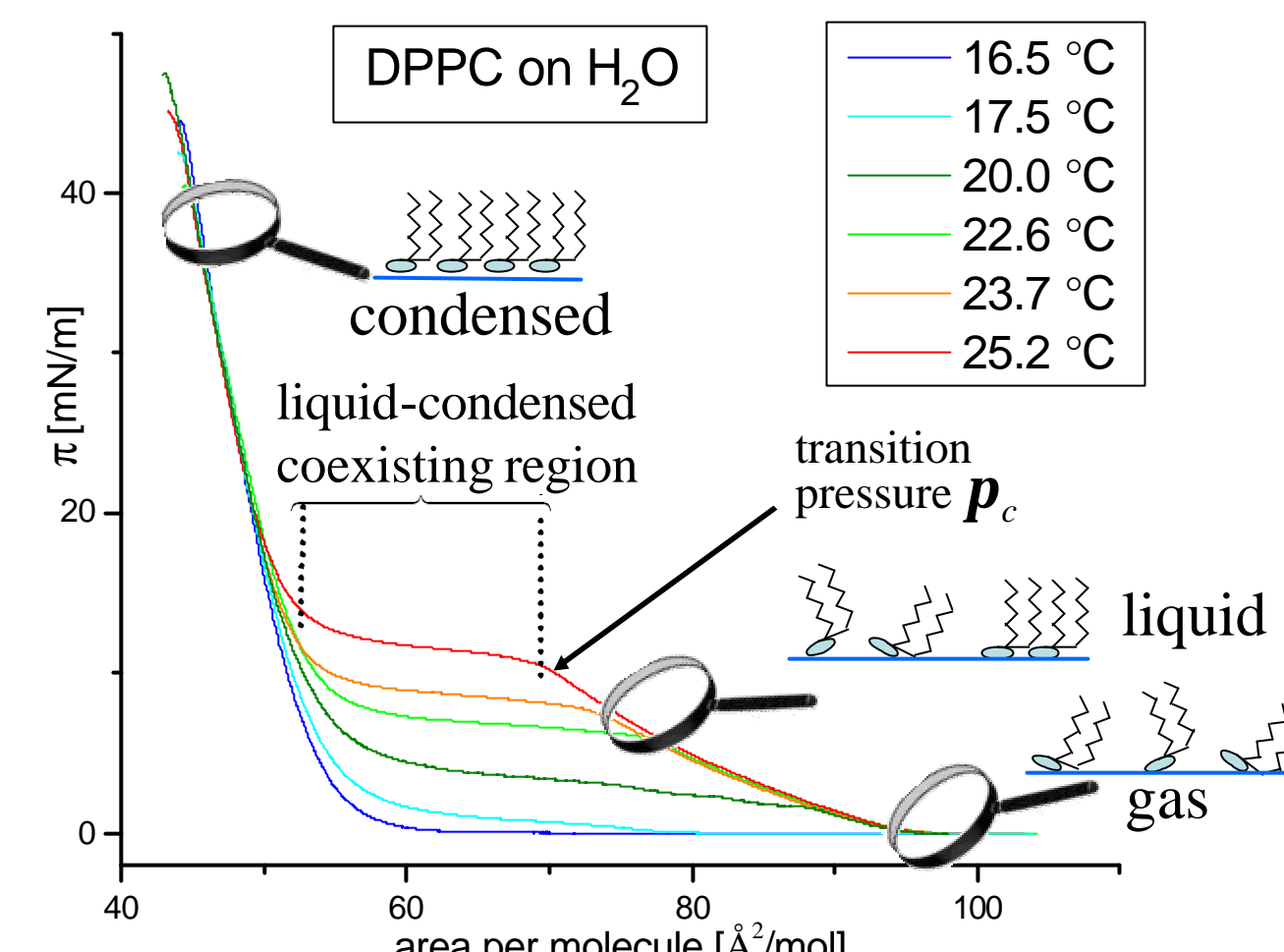
Phase diagram liquid-solid shift to lower  $p_c$  proportional to

- mineral concentration
- temperature

The DPPC isotherms on sols show a behavior quite similar to cooling on normal water. This demonstrates the increased van der Waals interaction between the lipid chains due to the reduced surface fluctuations. In addition the rigidity of the lipid monolayer is improved so that higher surface pressures are accessible.

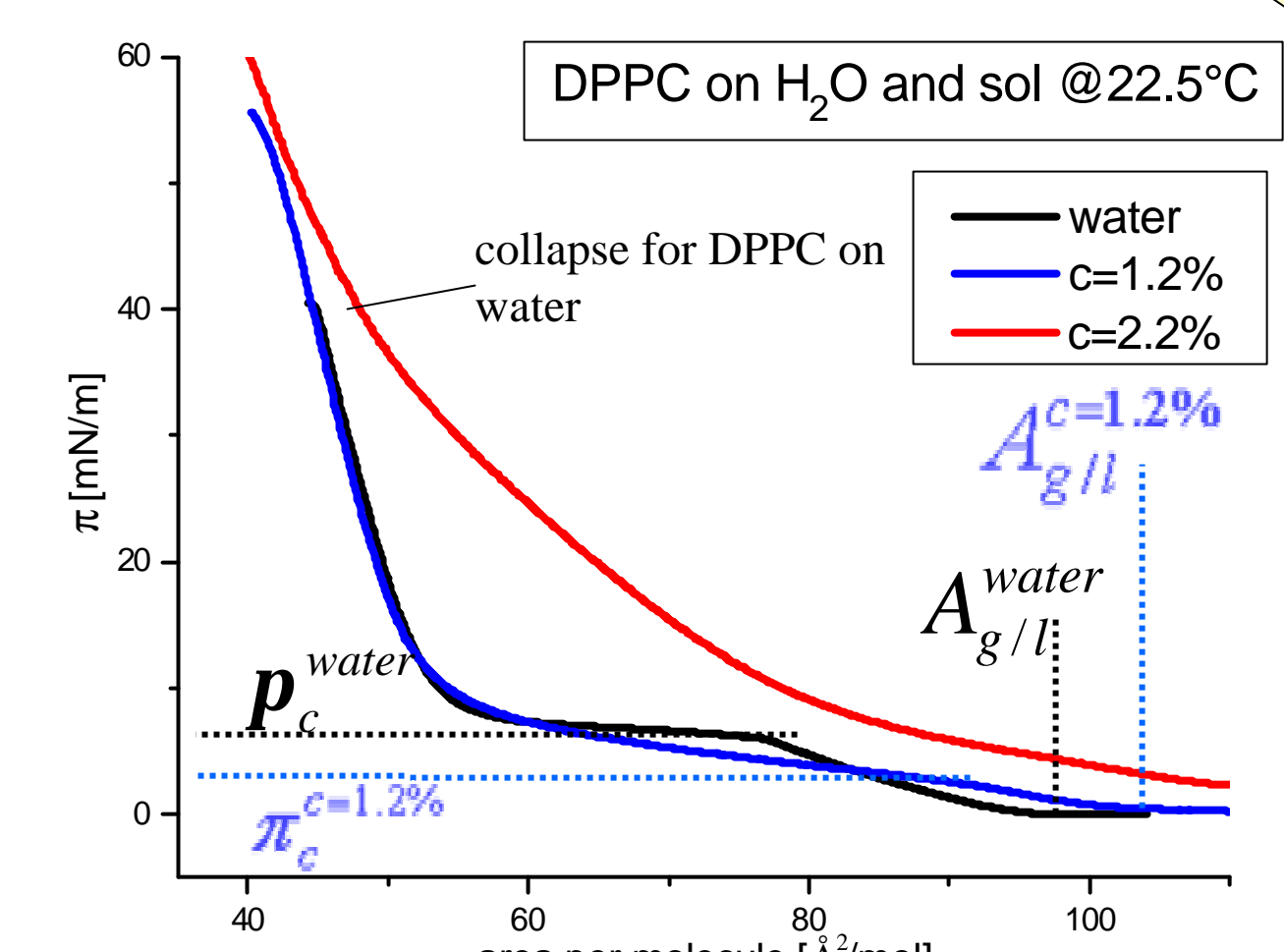
Pressure-Area-Isotherms

(2d analog of the pV-diagramm for the bulk)



Effect of cooling:

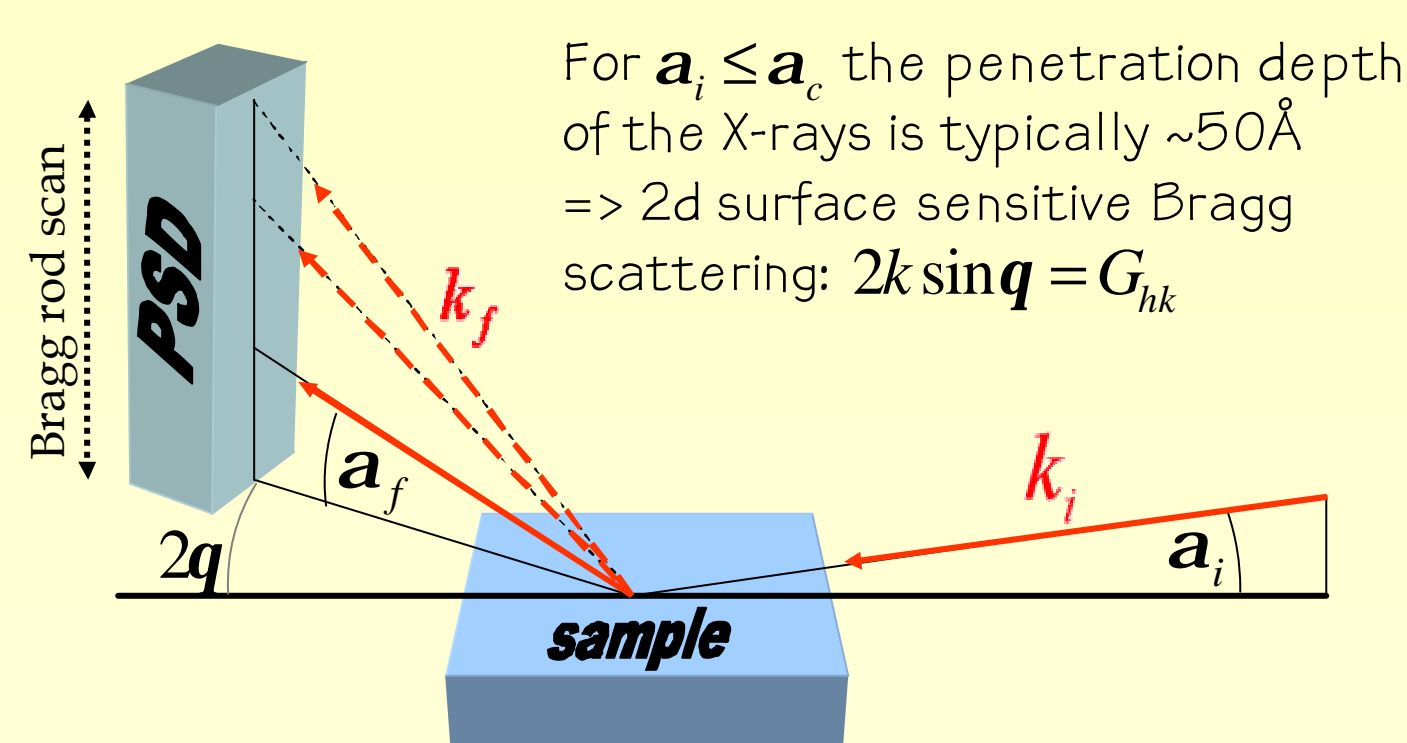
- shift of  $p_c$  to lower values
- decrease of the surface pressure in the liquid-condensed coexistence region



Influence of the sol:

- shift of  $p_c$  to lower values
- higher surface pressures accessible
- gas-liquid transition at lower area / molecule

### Grazing Incidence Diffraction (GID)

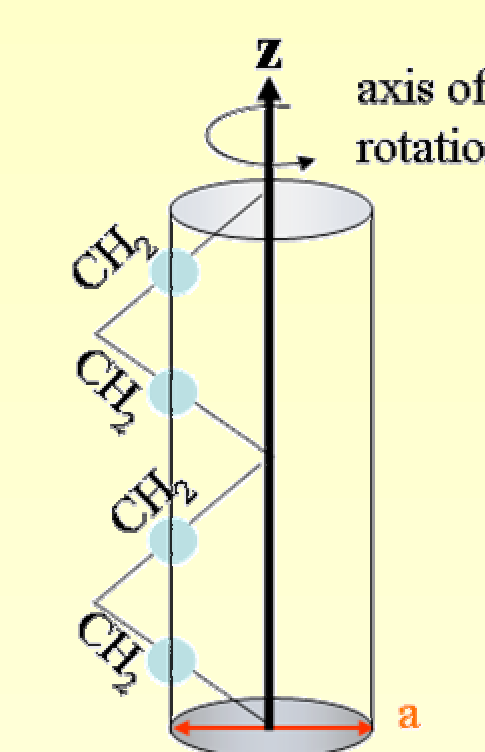


intensity of Bragg rod:  $I_{tot} = I_{mineral} + I_{lipid}$  → standardisation of intensities for mineral and lipid

$$\propto |F_{structure}(\vec{Q})|^2 \quad \propto |F_{molecule}(\vec{Q})|^2$$

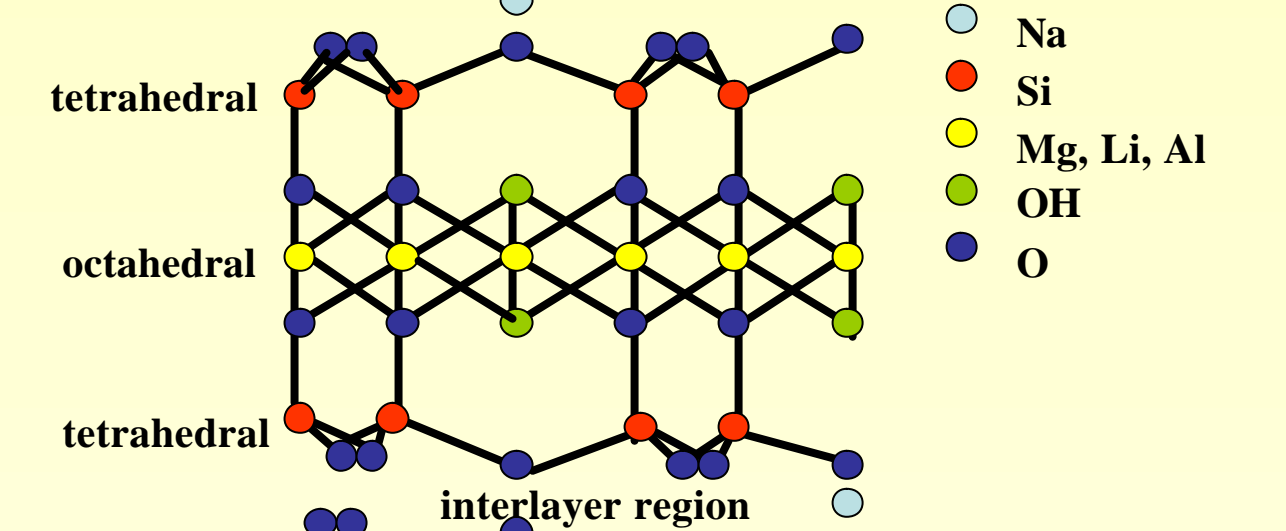
cylinder model for lipid chains

- free rotation of the chains
- substitution of the electron density of the chains with the electron density of an oxygen atom
- smearing out of the electron density over a cylindrical shell

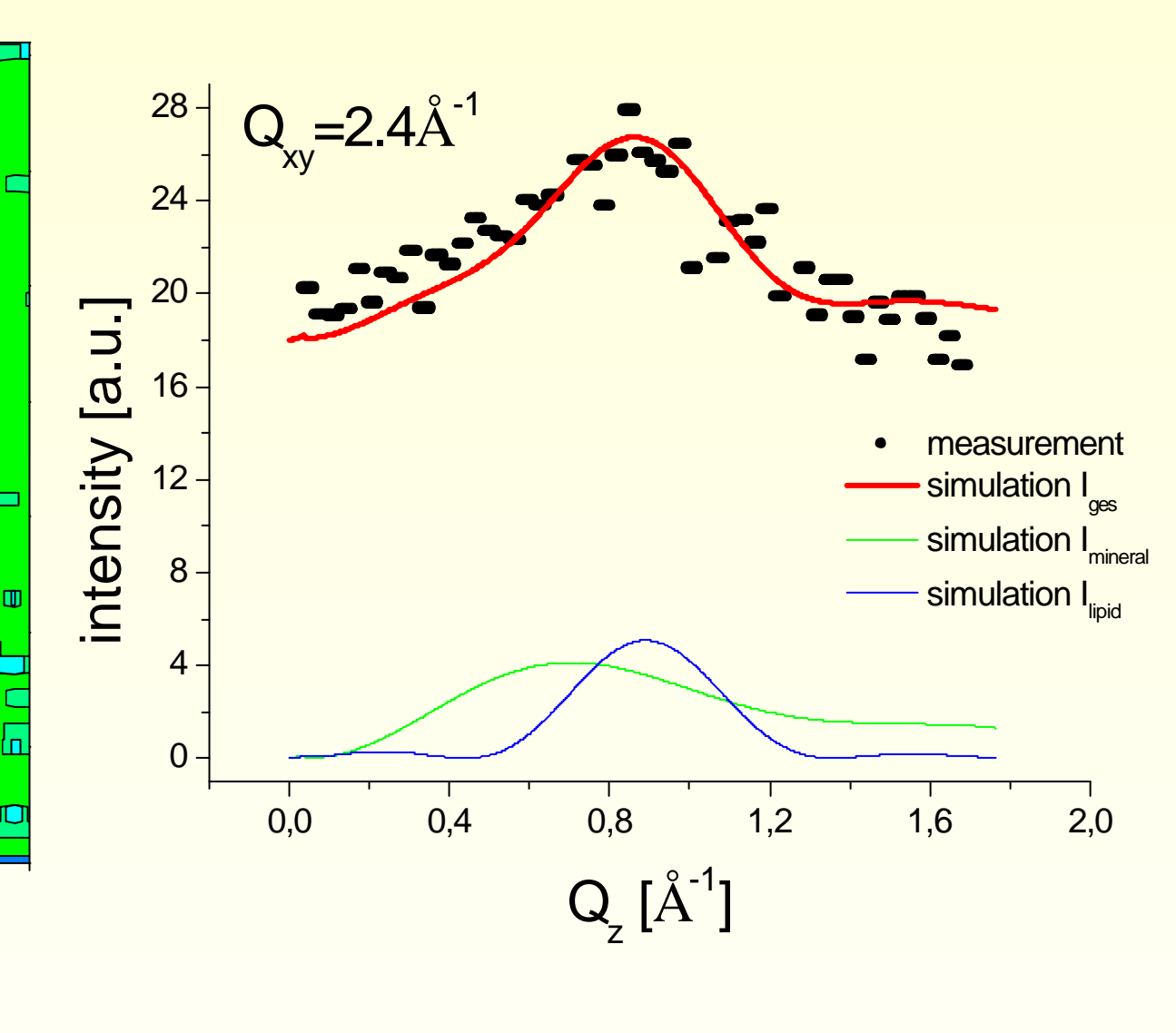
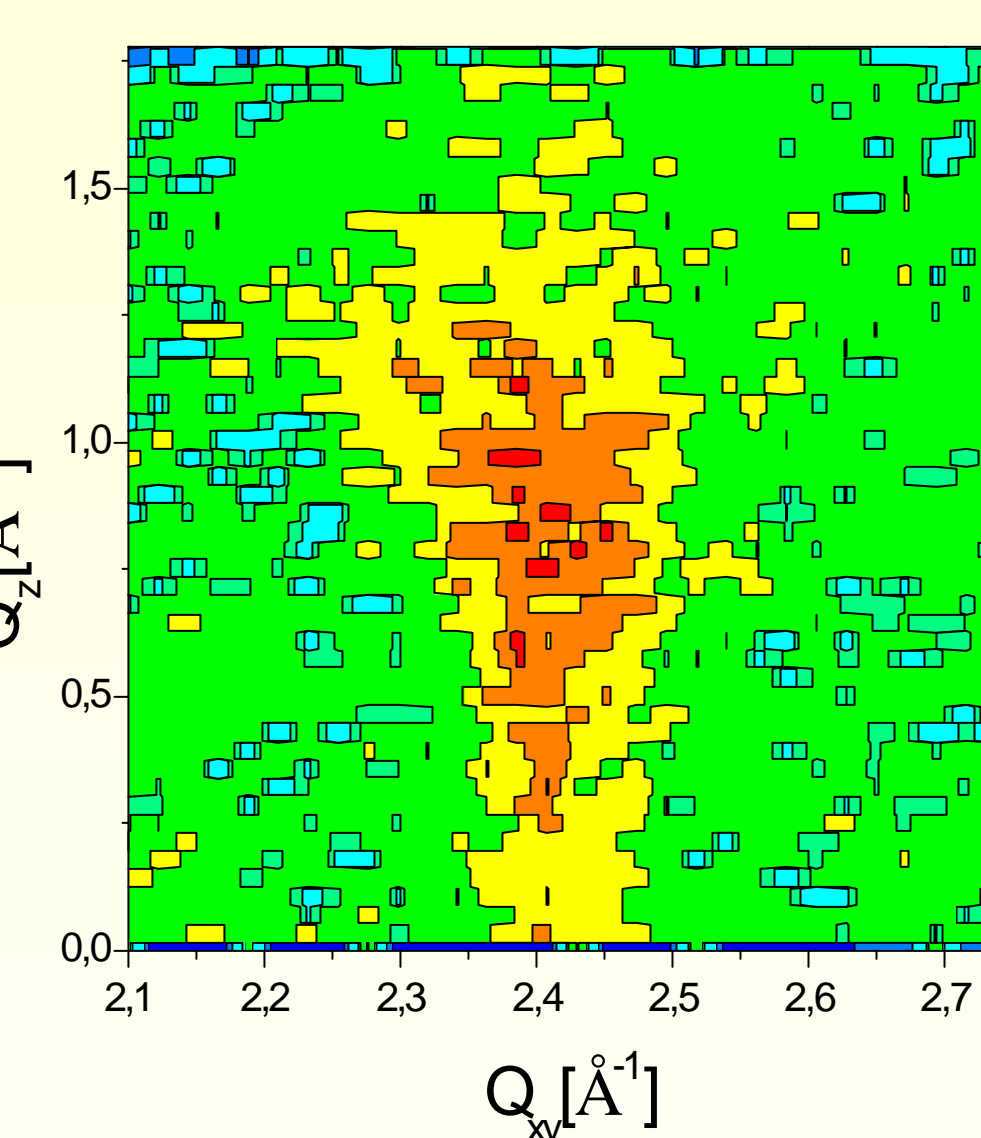
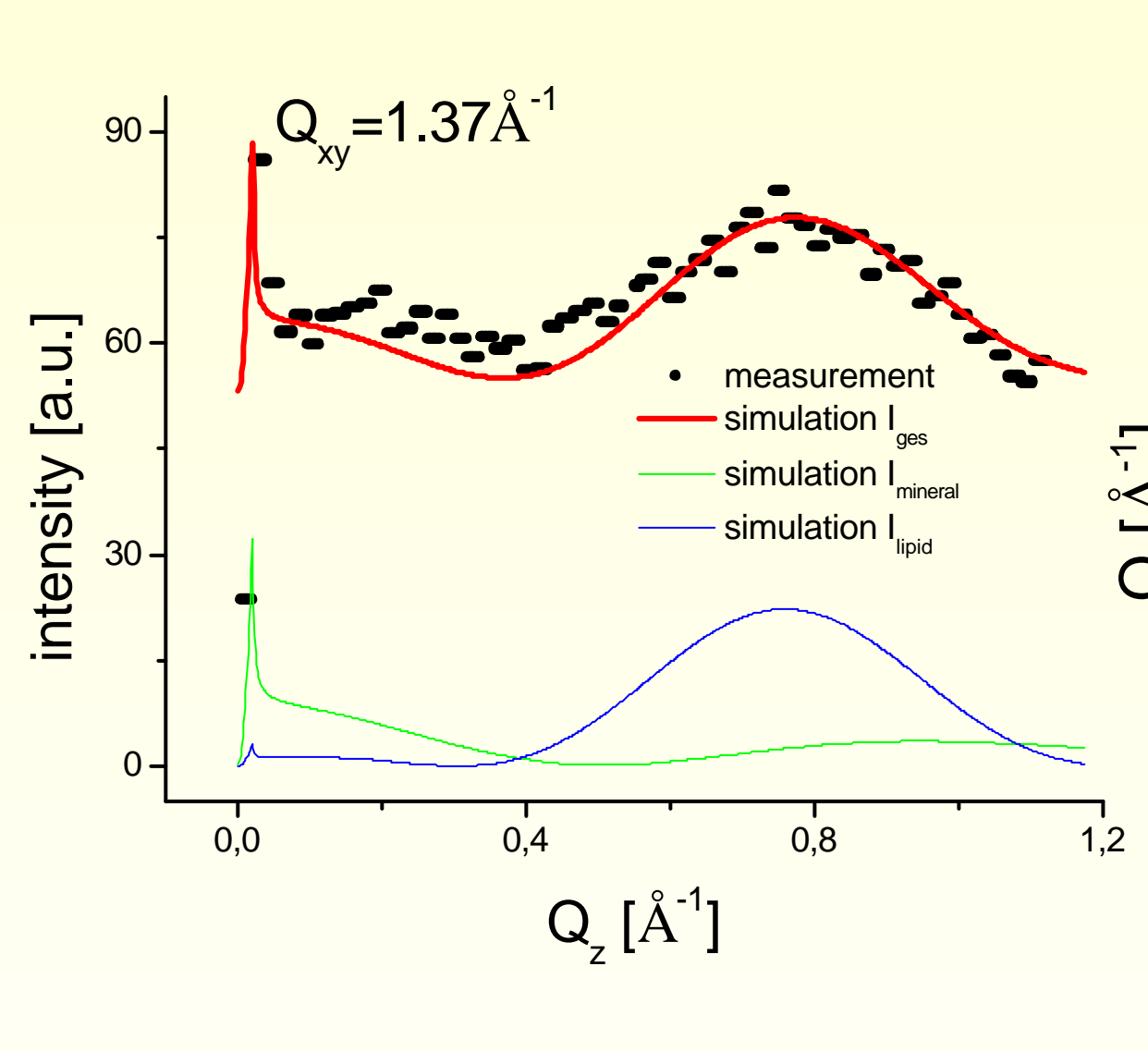
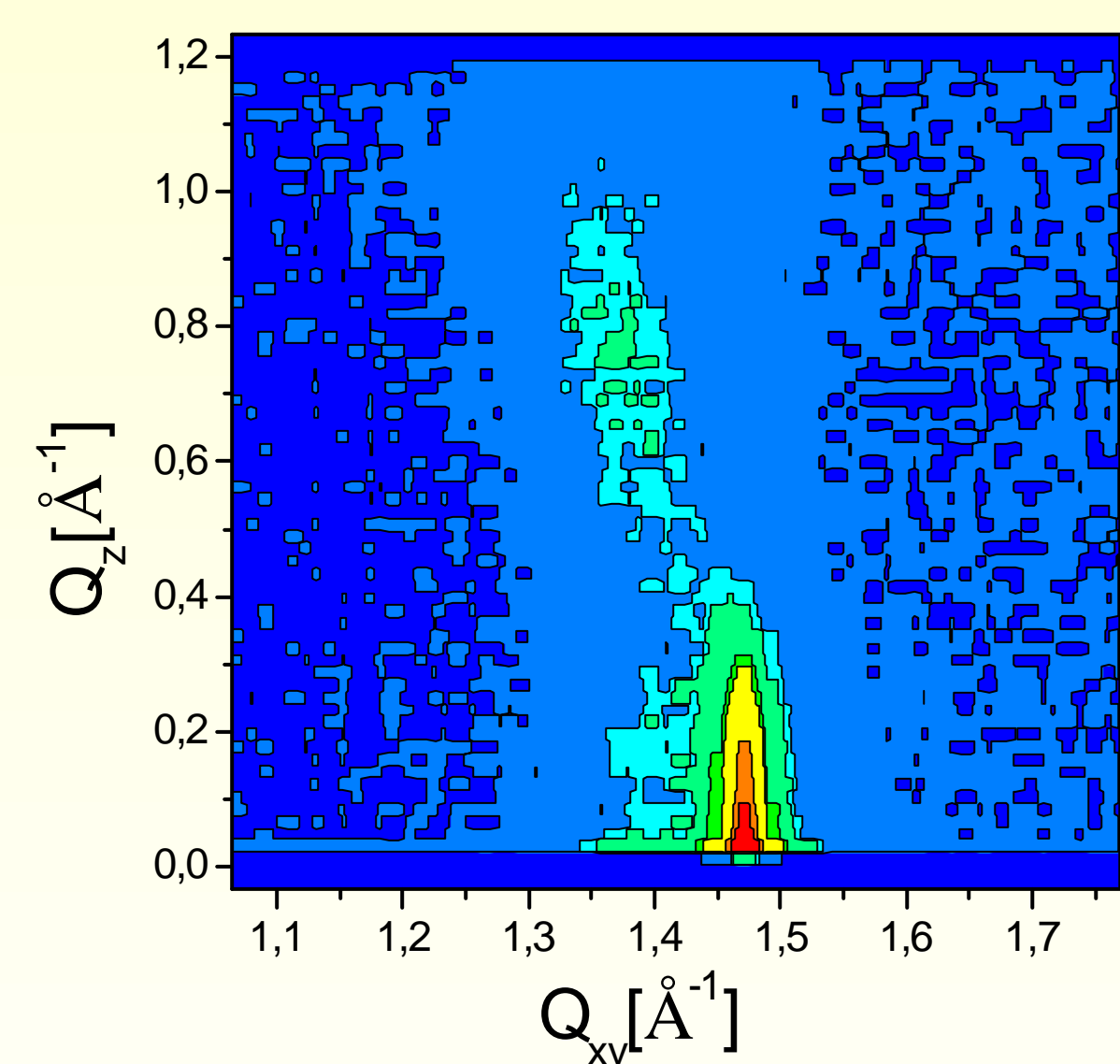
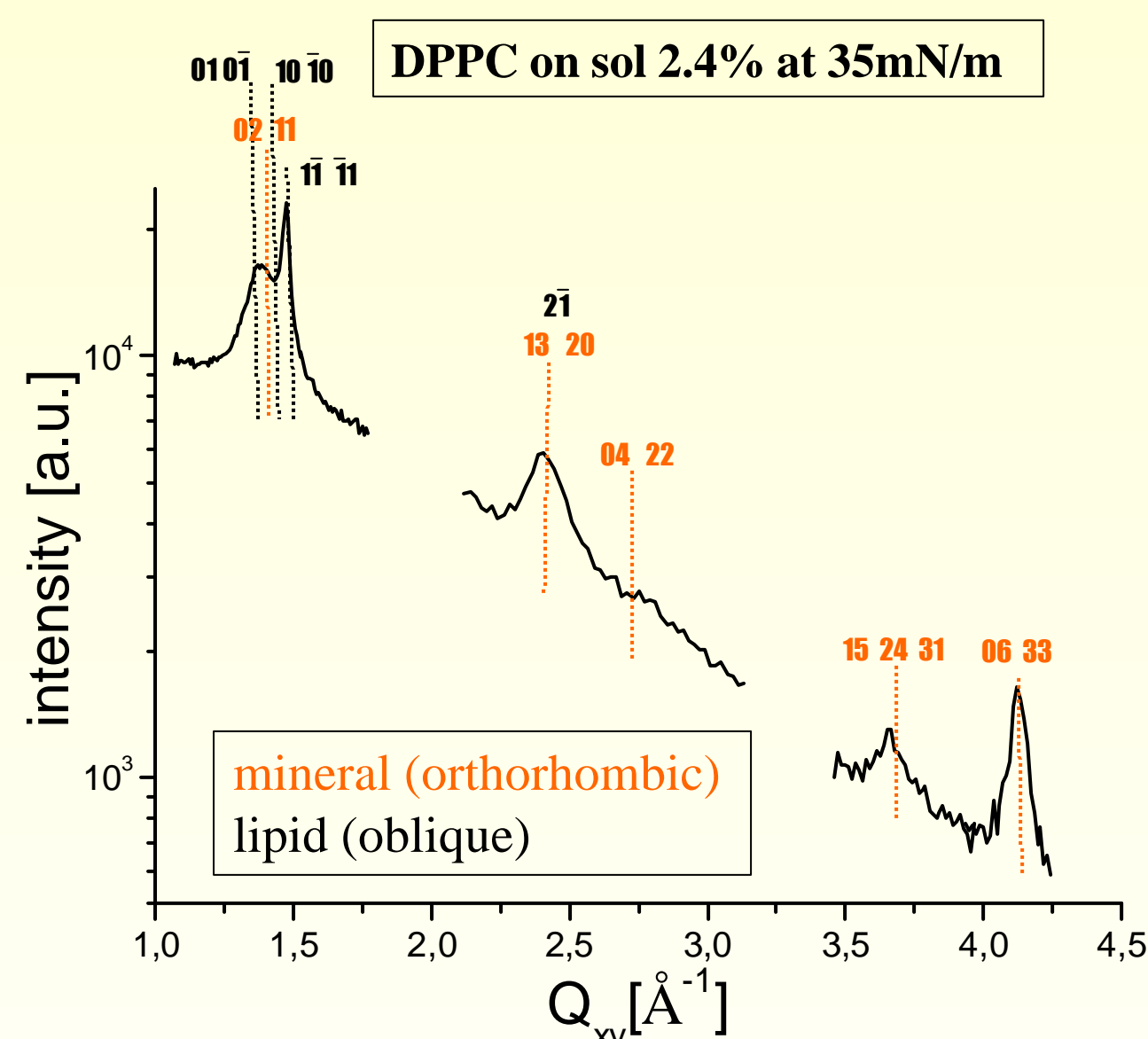


structure factor for the mineral:

$$F_{mineral}(\vec{Q})_{2d} = f_0(Q_{xy}) \exp[2\pi i(hx + ky + Q_z \frac{c}{2p} z)]$$



$$F_{mol}(\vec{Q}) \propto f_0(Q_{xy}) \frac{\sin(\frac{L}{2} Q_z)}{Q_z \cdot L} J_1(\frac{a}{2} Q_{xy})$$



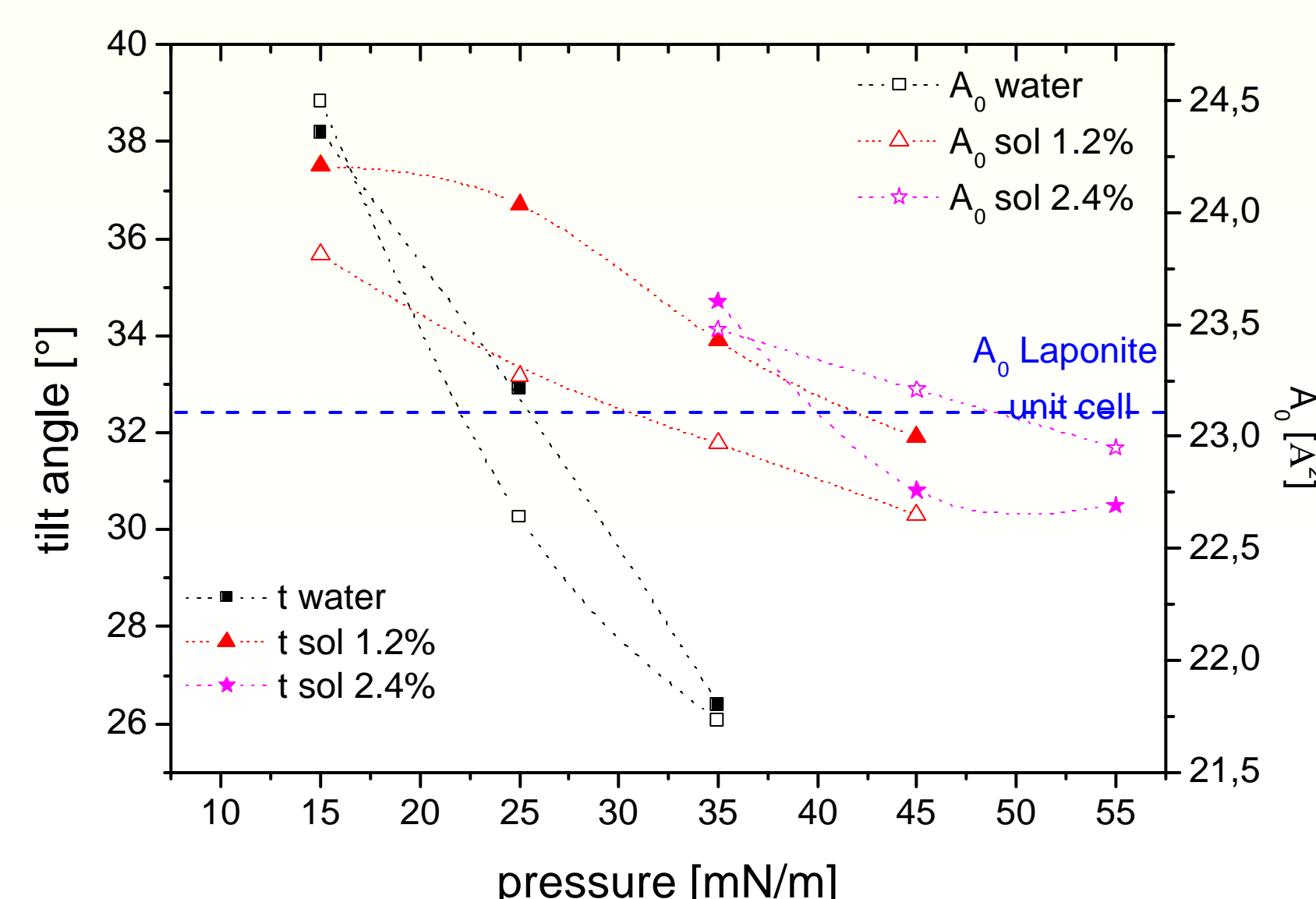
Lattice parameters of the mineral and the lipid lattice are similar => impossible to distinguish between scattering from mineral and lipid only from the position of their spectral peaks

Bragg rods: contain information about the form factor of the scatterer => lipid and mineral both contribute to the measured Bragg rods

Peak at  $Q_{xy} = 2.4 \text{ Å}^{-1}$  is a superposition of a lipid and a mineral reflection => for the first time a higher order reflection from a lipid monolayer is observed.

The area per lipid chain on a sol is closely related to the unit cell of the mineral. This is not the case on water => ordering is induced by the internal structure of single adsorbed mineral individuals

Tilt angle between chain and surface normal varies less with the surface pressure => electrostatic interaction reaches a maximum when the lipid structure is mapped to the mineral structure



### Conclusions

Viscosity and mineral layer exhibit an effect similar to cooling in isotherm measurements

Bulk viscosity measured by rheology gives a hint to explain the behaviour of isotherms for DPPC on sols with different mineral concentrations

For the first time a higher order reflection of a lipid monolayer was observed => increased van der Waals interactions due to reduced surface fluctuations

The lipid structure maps to the nano-particle structure

### Outlook

Could such processes induce nuclei formation and crystal growth in an inherently non ordering surfactant?