SAXS Under Extreme Conditions

H.Amenitsch

Outline:

-Why?

- What is extreme?
- Scientific case
- How it all began?

-How to trigger transitions?

- Jump-relaxation methods
- Other (oscillatory) methods

-Applications

- Biology and Biomedicine
- Physical Chemistry
- Material Science

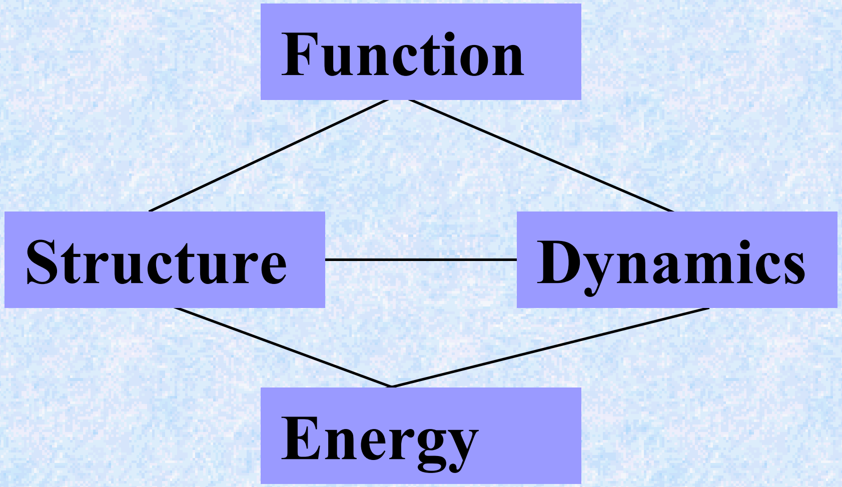
-Outlook

Why?

What is extreme?

-Temperature: mK, 10^3 K, 10^6 K
-Time scales: years,s, ms, µs
-Pressure: MPa, GPa
-Chemical potential
-Non equilibrium states => Transitions

Scientific Case:

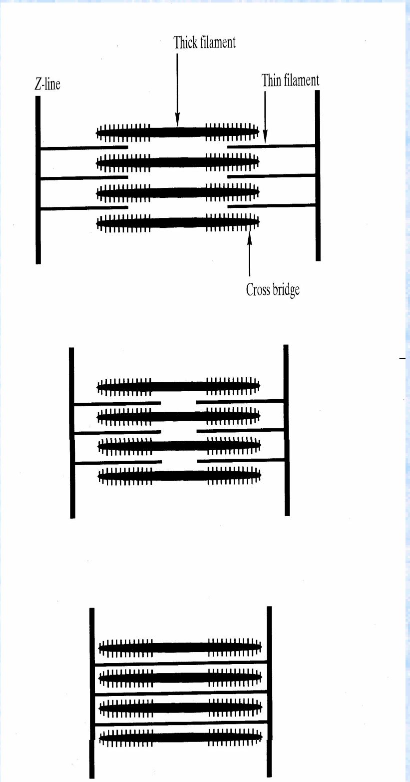


Biology and Biomedicine:
-understand molecular and cellular function
-find ways to cure diseases

Material Science:
-understand macro- and supramolecular assembly
-find new, purpose-designed materials

Why? - How it all began - Muscle Contraction

September 1970: DESY
Rosenbaum,Holmes & Witz, Nature (1971), **230**,434



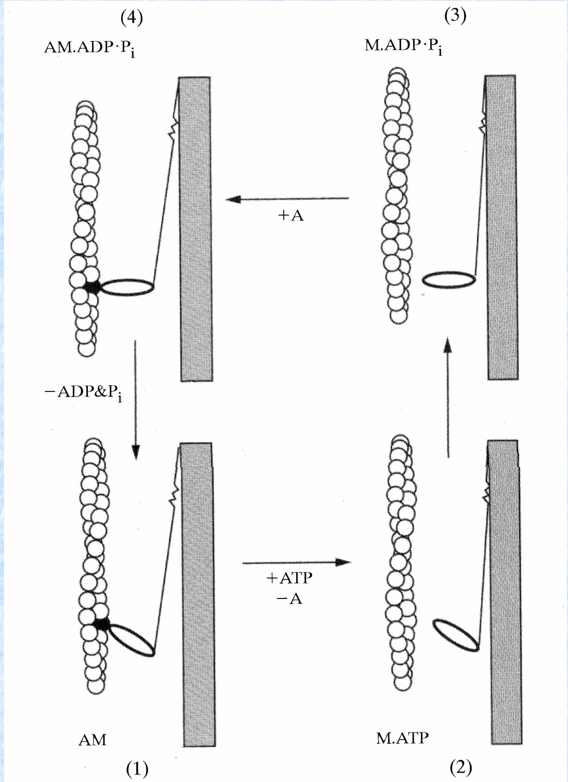


Fig. Muscle Contraction thick (myosin)-, thin-(actin) fibers are interdigitating
K.C Holms Acta Cryst. **A54**, (1997), 789

Fig. Lymn-Taylor cycle. (Lymn, Taylor Biochemistry, (1971)10, 4617 Mysoin-cross-bridge is bound in rigor (1) ATP binds->quick dissociation (2) ATP->ADP + P (hydrolysis) binding of myosin to actin 90 up (3) release of components, rowing to (1)

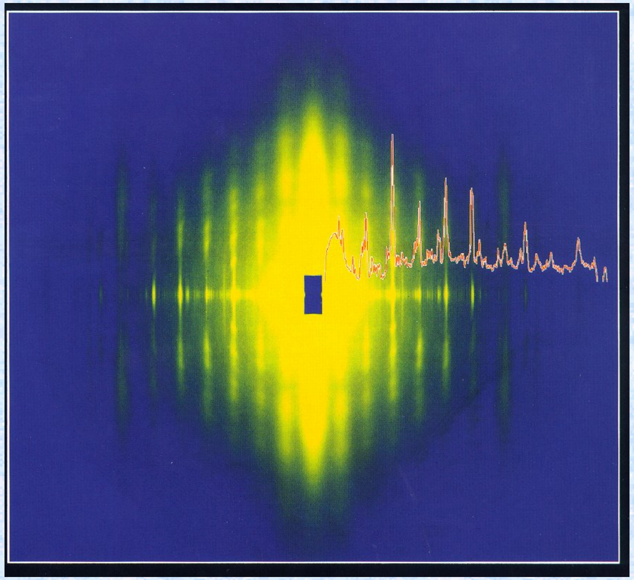


Fig. Diffraction pattern of life skeletal frog muscle Cover page: Yagi, et.al. J.Synchrotron. Rad (1996), 3,247

Why? - How it all began - Muscle Contraction

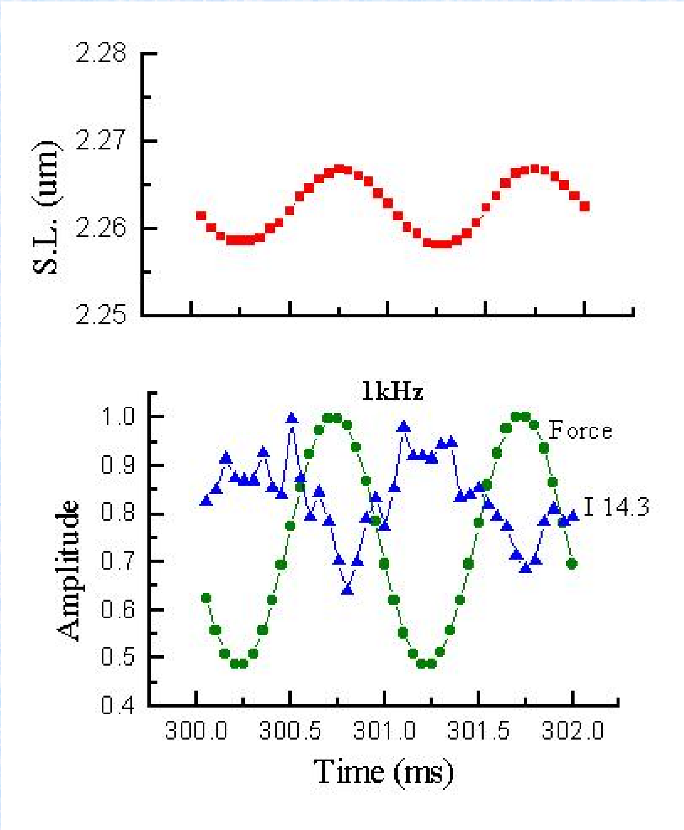


Fig.: Sarcomere length (S.L., filled squares), force (filled circles) and IM3 (I14.3, filled triangles) for a single fibre undergoing 1 kHz sinusoidal length oscillations

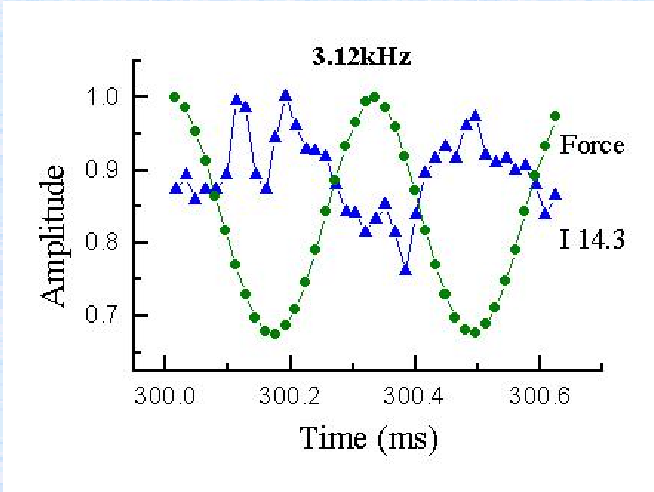


Fig.: IM3 (I14.3, filled triangles) and force (filled circles) for a two fibre bundle undergoing 3.12 kHz sinusoidal length oscillations. Sampling time 16 micro-seconds.

H. Amenitsch, C.C. Ashley, M.A. Bagni, S. Bernstorff, G. Cecchi, B. Colombini and P.J. Griffiths, Elettra News Letter, Number 26 (1), August 31, 1998

Literature:

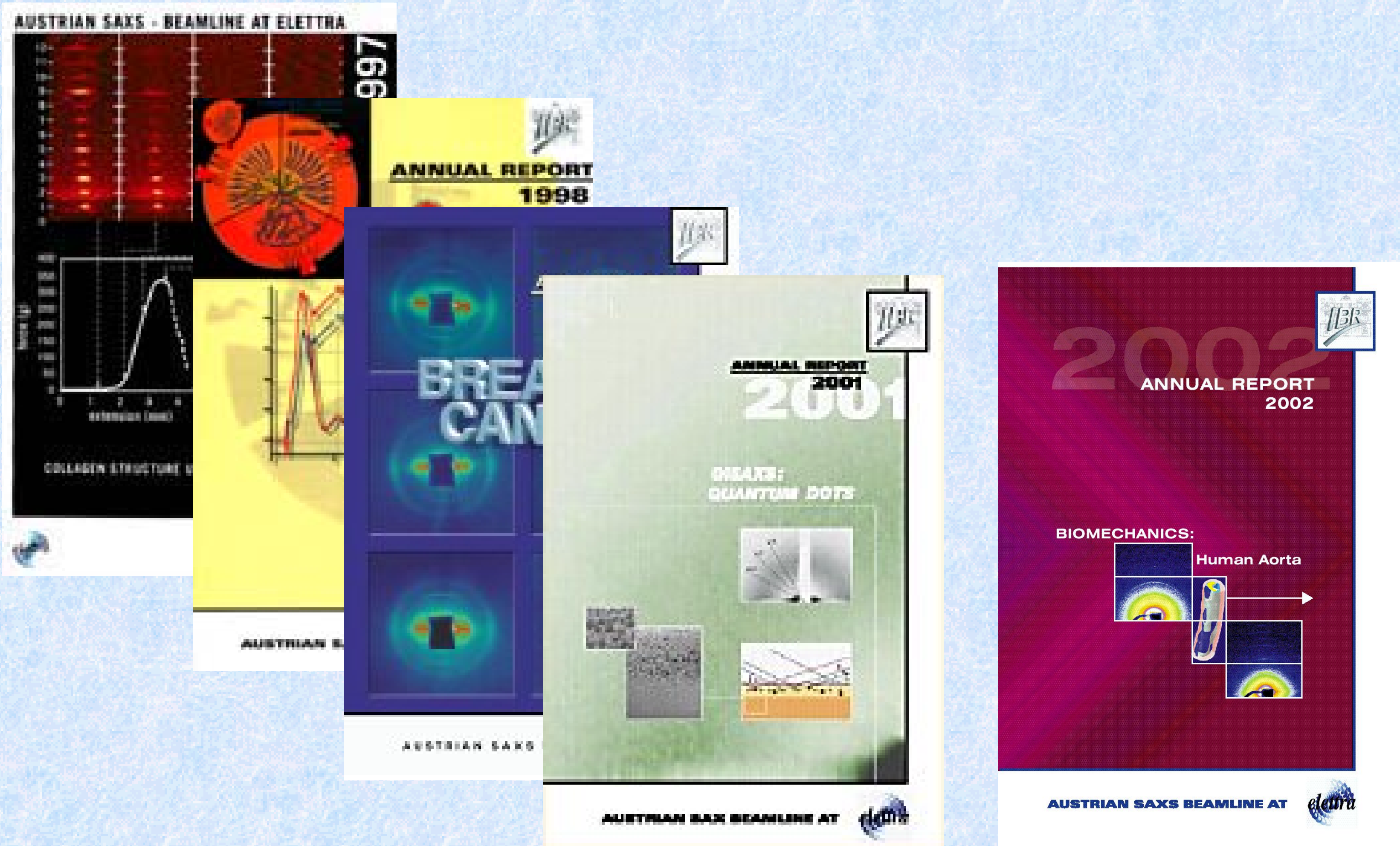
Bagni MA, et.al., BIOPHYSICAL JOURNAL **80**, 2809, (2001)

Piazzesi G, et.al. NATURE **415**, 659, (2002)

How to trigger transitions?

-T-jump (heating): Erbium Glass Laser
"heat exchanger"
-T-cool jump: "heat exchanger"
-p scans: High pressure cells
hydrostatic pressure
diamond anvil cells
-p-jumps
-Stopped-flow cells: -M.C.Ramachandra et.al. Biophysical Journal **74**, (1998), 2714
-Segel DJ, Bachmann A, Hofrichter J, Hodgson KO, Doniach S, Kiefhaber T, JOURNAL OF MOLECULAR BIOLOGY, 288, 489, (1999)
-Pollack L, Tate MW, Darnton NC, Knight JB, Gruner SM, Eaton WA, Austin RH, PNAS, 96,10115, (1999)
-Batch reactor
-Magnetic field
-Shear experiments

THE SAXS BEAMLINE: Output



AUSTRIAN SAXS - BEAMLINE AT ELETTRA

H. Amenitsch, S. Bernstorff, P. Dubcek, M. Rappolt & P. Laggner

SAXS - Applications: T-jump Device

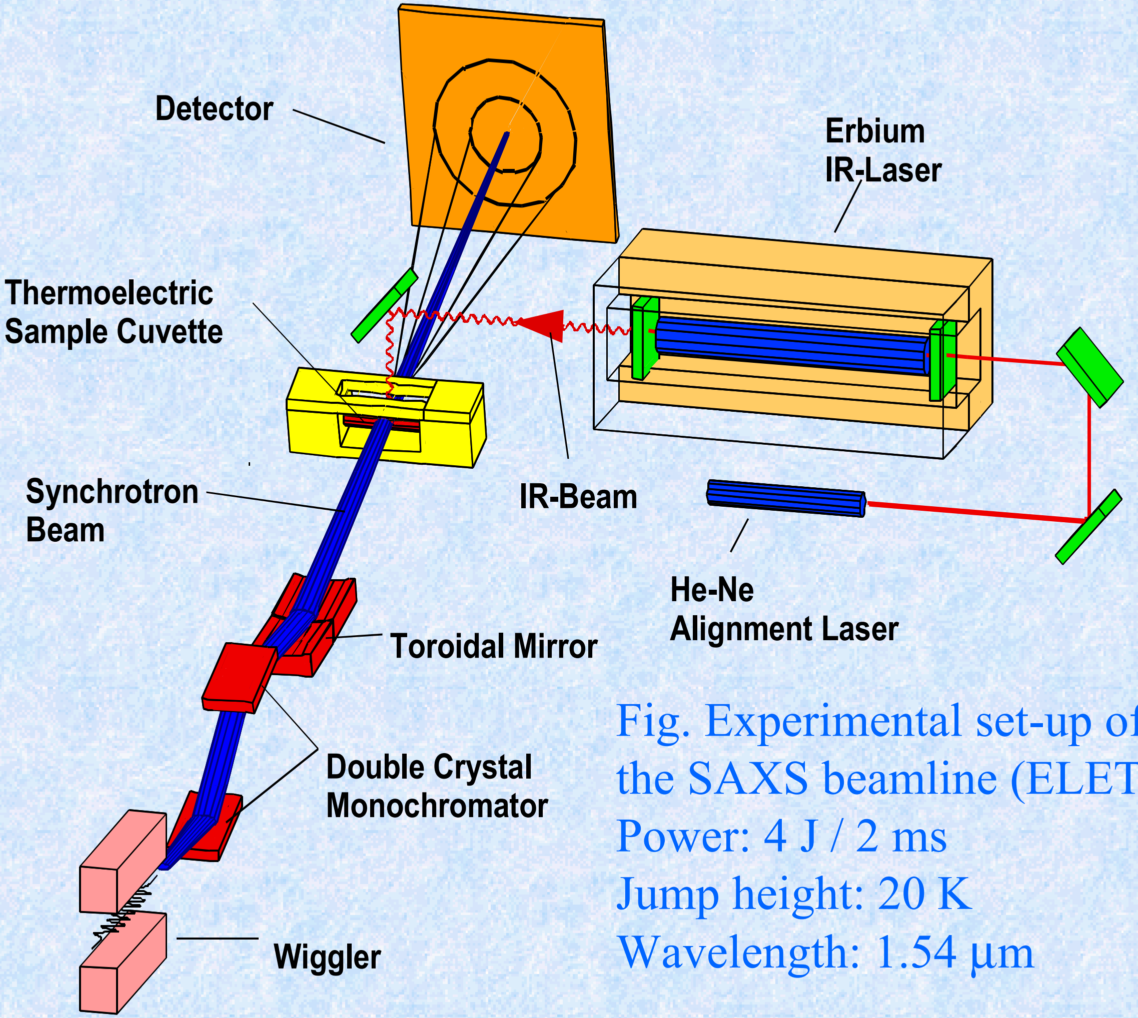


Fig. Experimental set-up of the T-jump device at the SAXS beamline (ELETTRA).

Power: 4 J / 2 ms

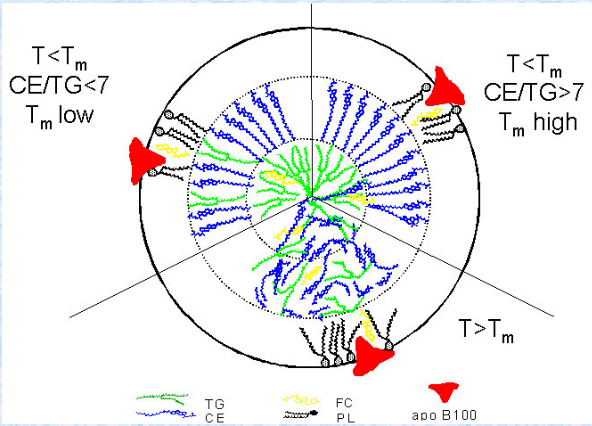
Jump height: 20 K

Wavelength: 1.54 µm

H. Amenitsch, S. Bernstorff, P. Dubcek, M. Rappolt & P. Laggner

T-jump on Low Density Lipoprotein

10 ms time-resolved x-ray diffraction of the core lipid transition of human Low Density Lipoproteins



Sketch of the LDL lipo-protein in the 3 different states:
-core liquid crystalline state
-core isotropic state TG, CE, FC, PL denotes triglycerides, esterified cholesterol, unesterified cholesterol, phospholipids.

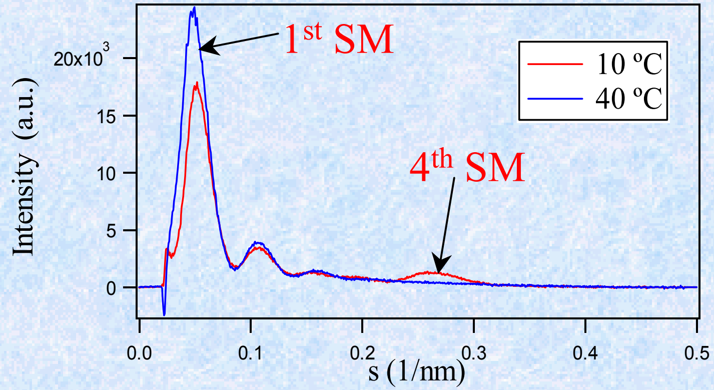


Fig. Static diffraction pattern at different temperatures

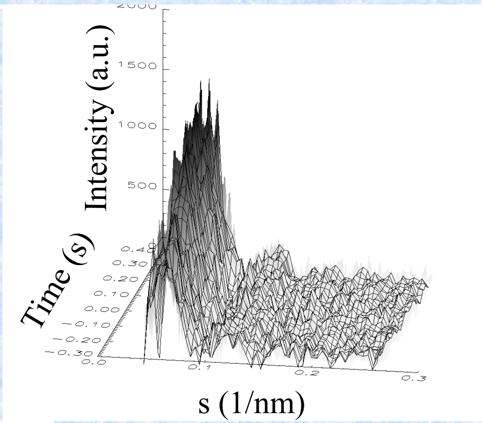
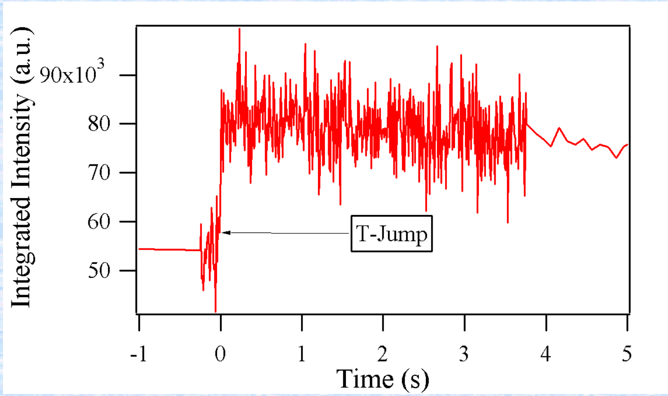


Fig. Time-resolved diffraction pattern during the T-jump left pattern – right integrated intensity 1st side maximum



AUSTRIAN SAXS - BEAMLINE AT ELETTRA

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Cool-jump on Low Density Lipoprotein

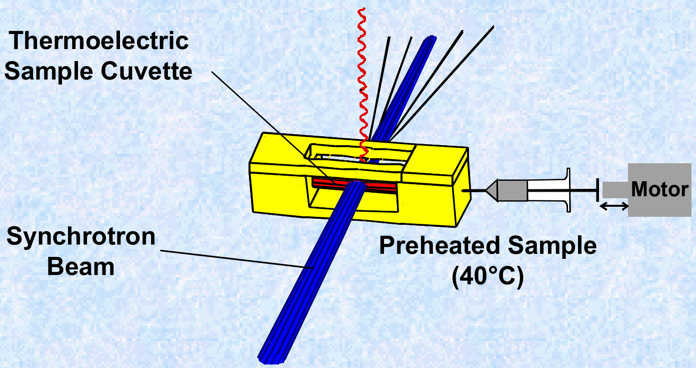


Fig. Sketch of cool-jump set-up

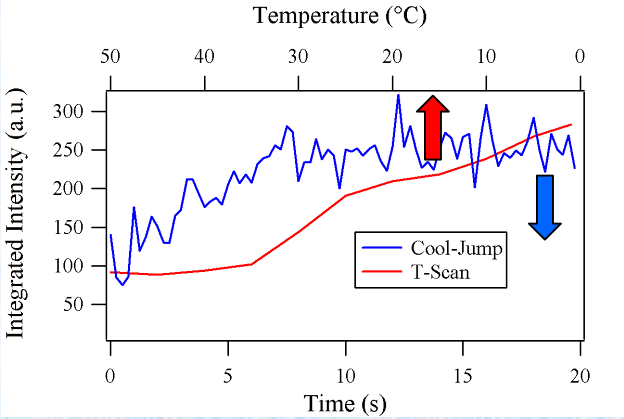


Fig: Integrated intensity 4th side maximum

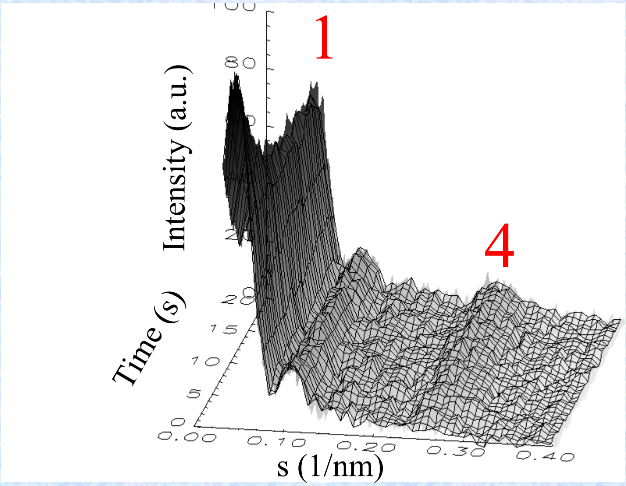


Fig. Time-resolved diffraction pattern during the cool-jump

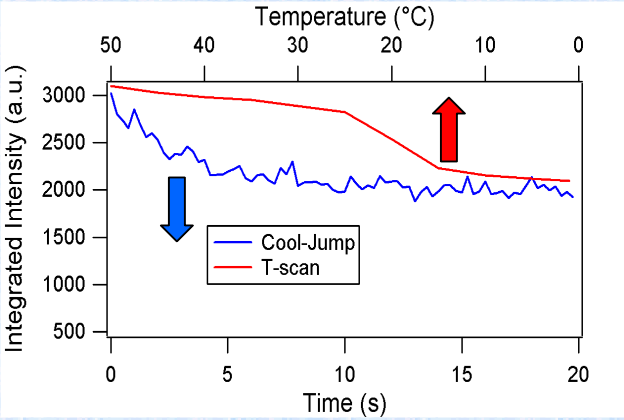
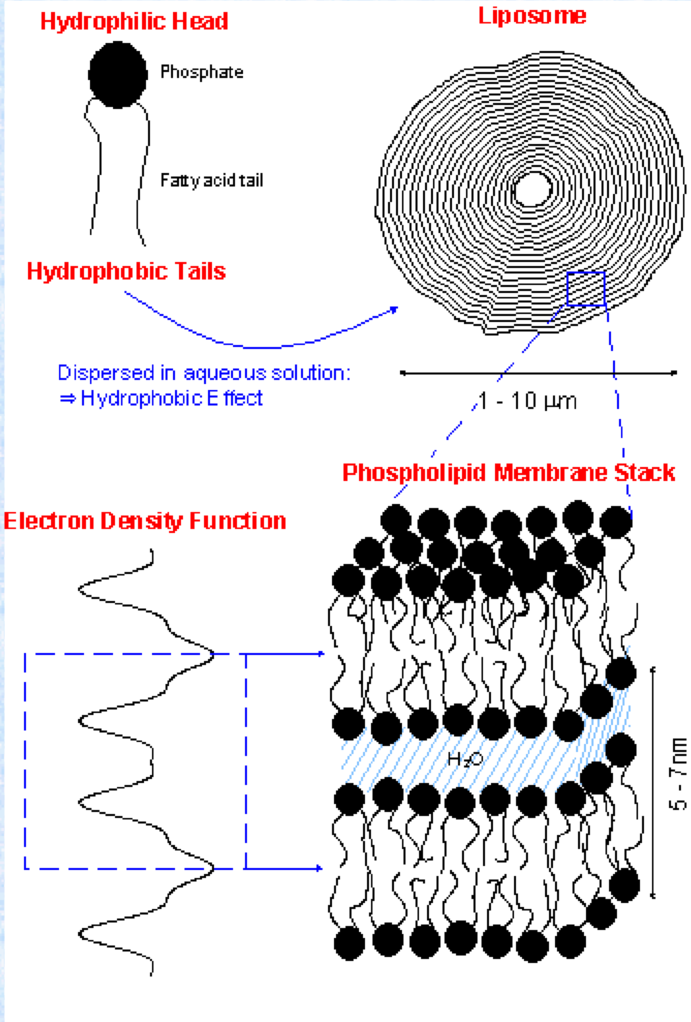


Fig: Integrated intensity 1st side maximum

H. Amenitsch, S. Bernstorff, P. Dubcek, M. Rappolt & P. Laggner

SAXS - Applications: T-jump Device



The formation of a phospholipid membrane. Phospholipids aggregate spontaneously into ordered supra-molecular structures in the presence of water. This can be explained in simple terms by the fact that phospholipids feature a hydrophilic headgroup (attracting water) and hydrophobic hydrocarbon-chains. The average 1- dimensional repeat distance d, i.e., bilayer plus waterlayer of the depicted liquid crystalline phase (La) is in the range of 5-7 nm. The electron density distribution of a bilayer (bottom left corner) has maxima in the headgroup regions and a minimum at the methyl terminus of the hydrocarbon-chains. The dashed rectangle marks the part of the electron density distribution shown in the fig below.

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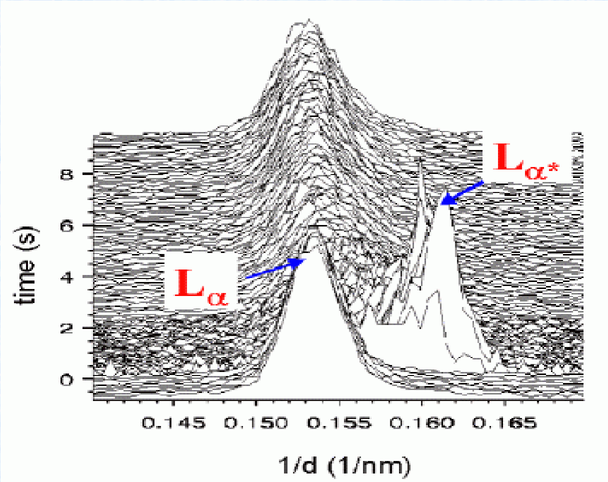
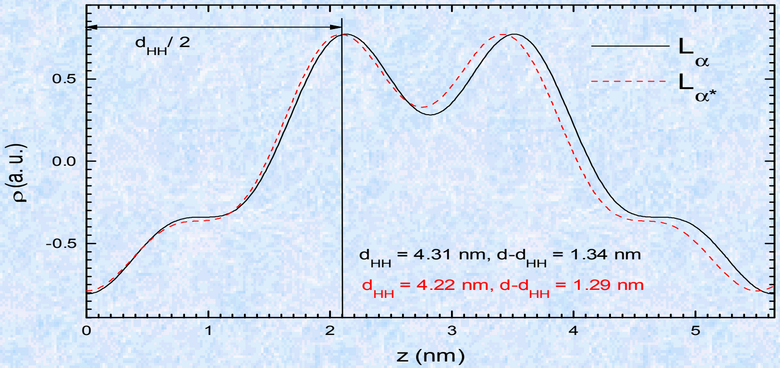
SAXS - Applications: T-jump Device



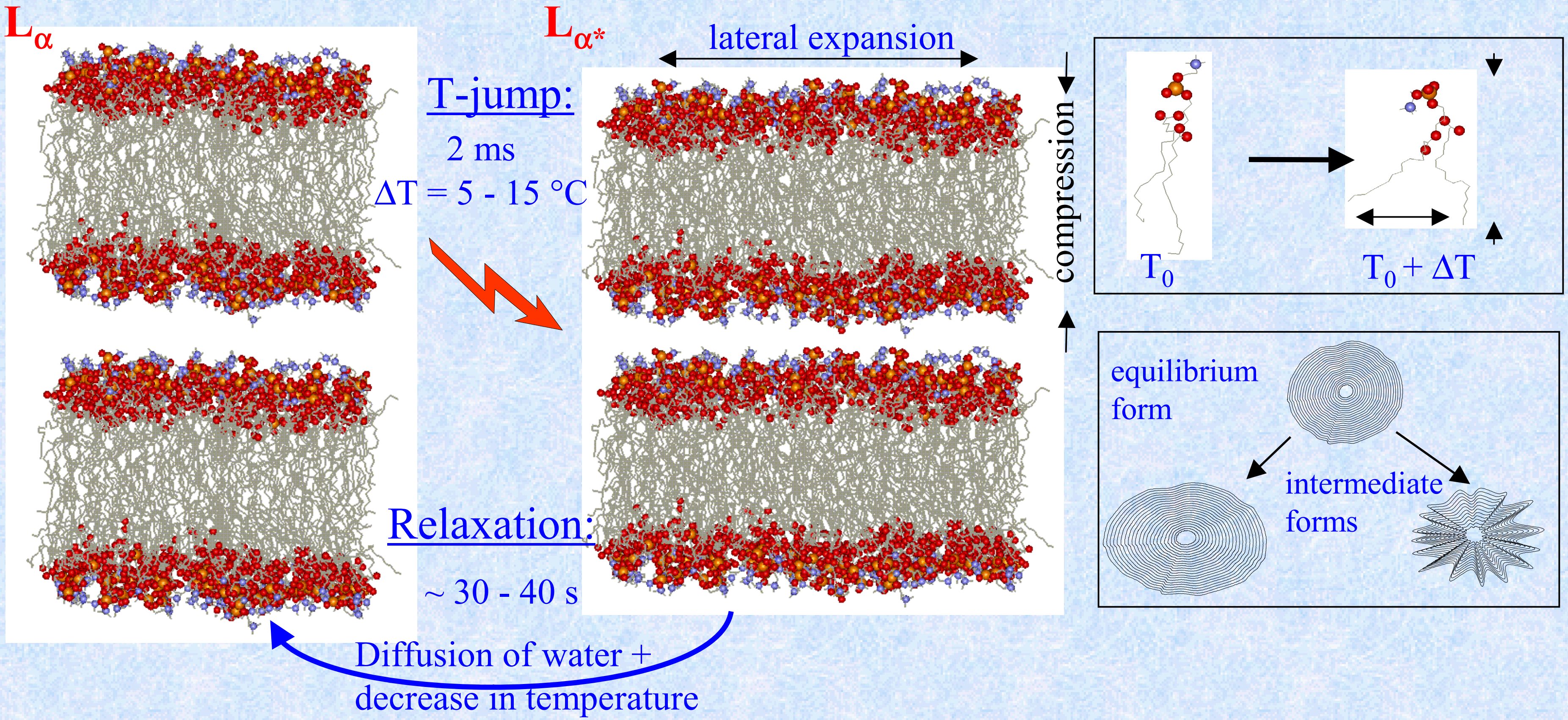
The first order diffraction peaks of a phospholipid sample during a T-jump experiment (time resolution = 5 ms). The IR-laser was triggered at time zero.



Superimposed electron density distributions of the original L_α-phase (straight line) and of the intermediate phase $L_{\alpha*}$ (dashed line) immediately after the laser flash

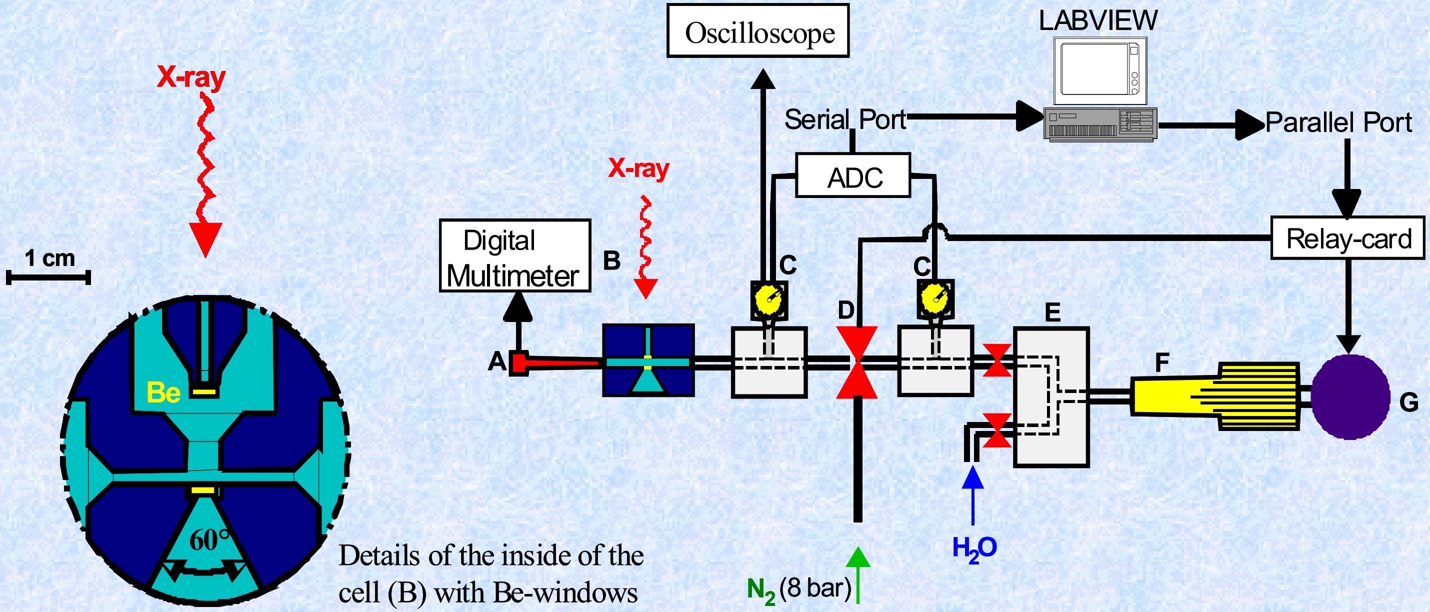
G. Pabst, M. Rappolt, H. Amenitsch, S. Bernstorff & P. Laggner (1998)

T-jumps: Phospholipid Phase Transition



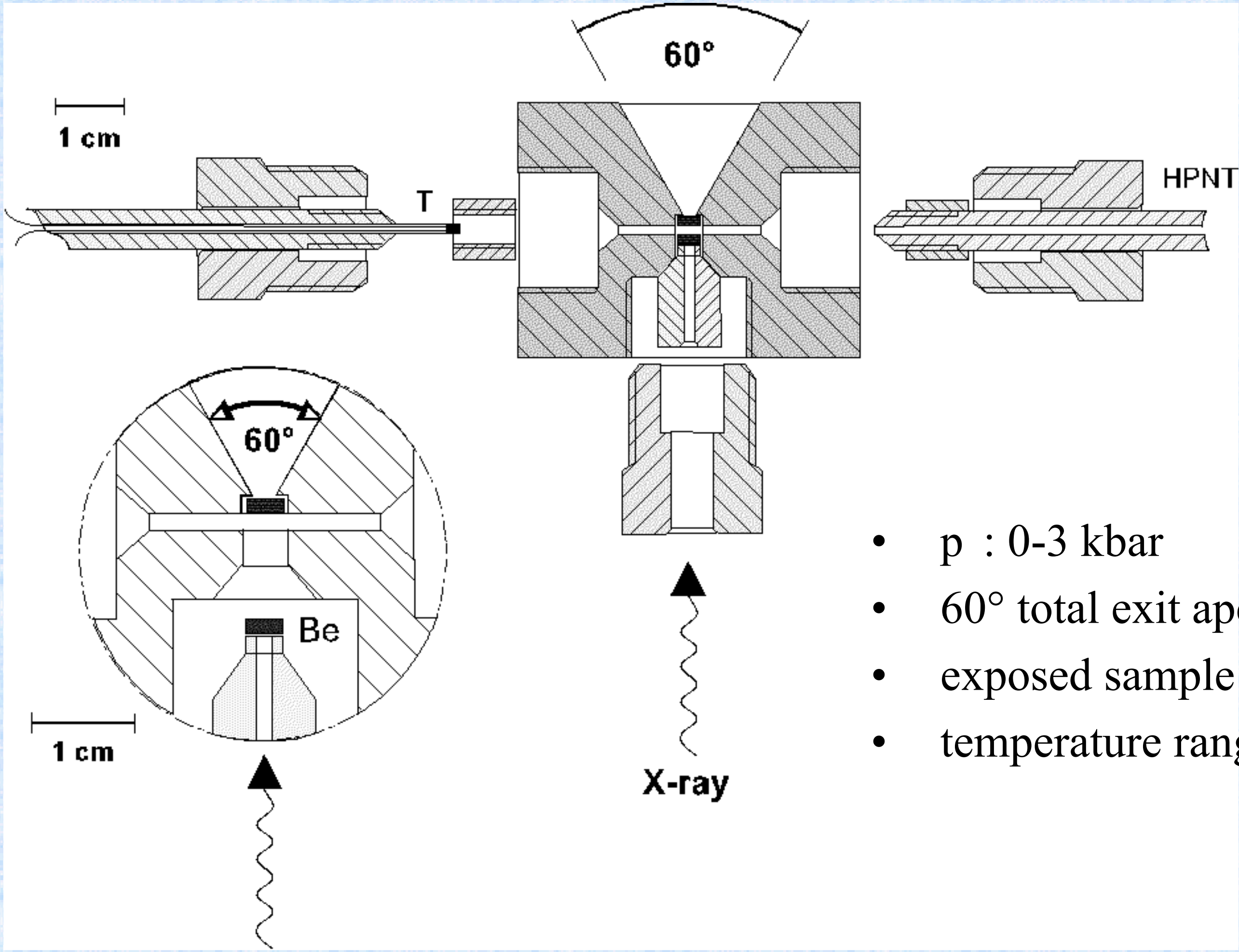
G. Pabst, M. Rappolt, H. Amenitsch, S. Bernstorff & P. Laggner, Biophys. J., (2000)

High Pressure Cell



M.Steinhart, M.Kriechbaum, K.Pressl, H.Amenitsch, P.Laggner and S.Bernstorff, Rev.Sci.Instrum. 70, 1540-1545 (1999).

SAXS - APPLICATIONS high pressure cell



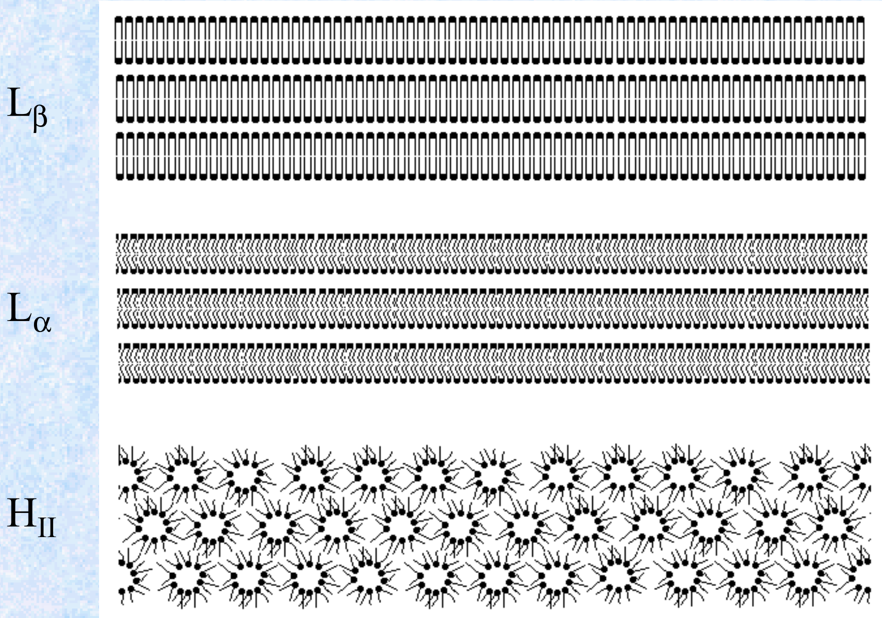
- p : 0-3 kbar
- 60° total exit aperture
- exposed sample volume: 1 ml
- temperature range: 0-80 °C

SAXS - APPLICATIONS high pressure cell

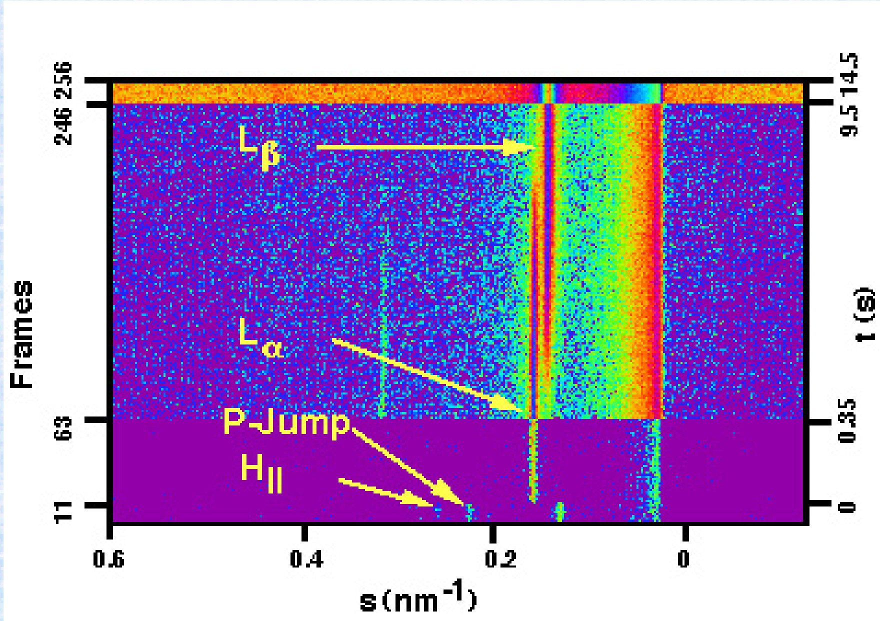
<u>EXAMPLE:</u> p-jump on DOPE (Dioleoylphosphatidylethanolamine) from *150 bar* to *2.3 kbar* at *20° C*. (A) Phases and (B) SAXS-pattern.

M. Kriechbaum, M. Steinhart, P. Laggner, H. Amenitsch and S. Bernstorff

A



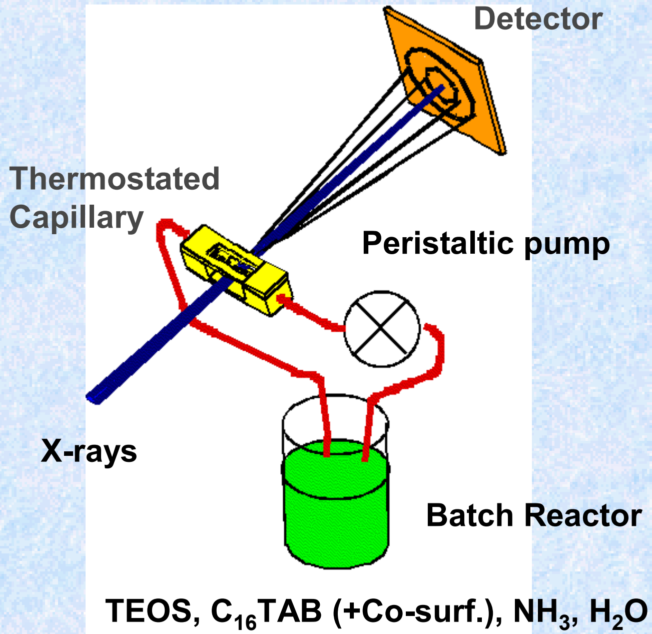
B



Mesoporous Materials: Bulk MCM-41

In-situ study of the Formation of the MCM-41 Structures using liquid crystal templating mechanism
P. Ågren, M. Linden, J.B. Rosenholm, R. Schwarzenbacher, M. Kriechbaum, H. Amenitsch, P. Laggner, J.Blanchard, F.Schüth, J.Phys. Chem. B, (1999), 103, 5943

Experimental set-up



Aim:

Influence of the co-surfactant and its concentration on the phase behaviour of the TEOS synthesis.

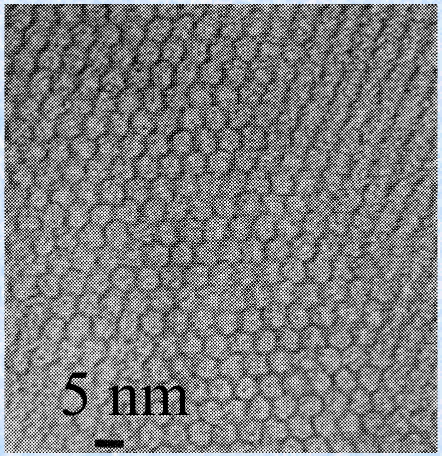


Fig. Representative electron transmission micrograph of a MCM41 structure depicting the mesoporous hexagonal nano-structure.

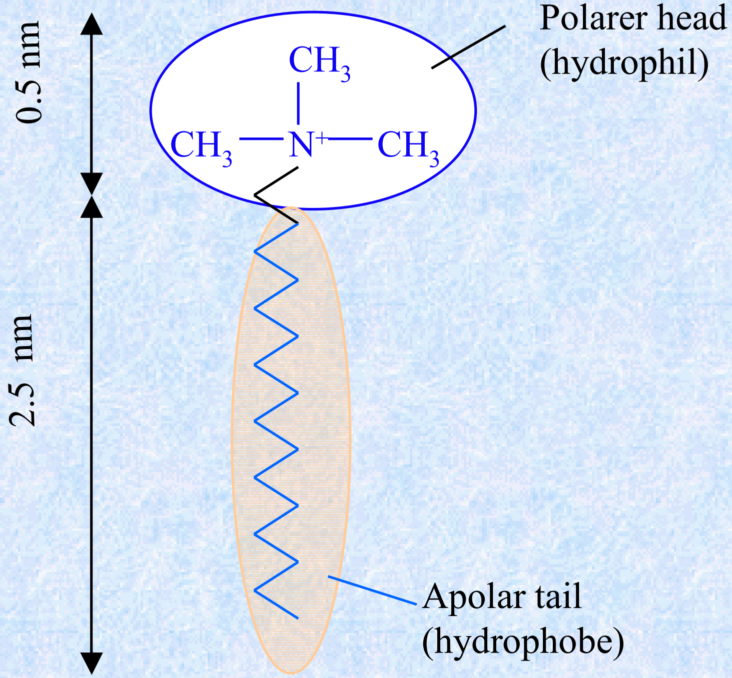
TEOS Tetraethylorthosilicate
C_{16}TAB Hexadecyltrimethylamonium bromide

Industrial applications: -adsorbents
-ion-exchangers
-catalysts

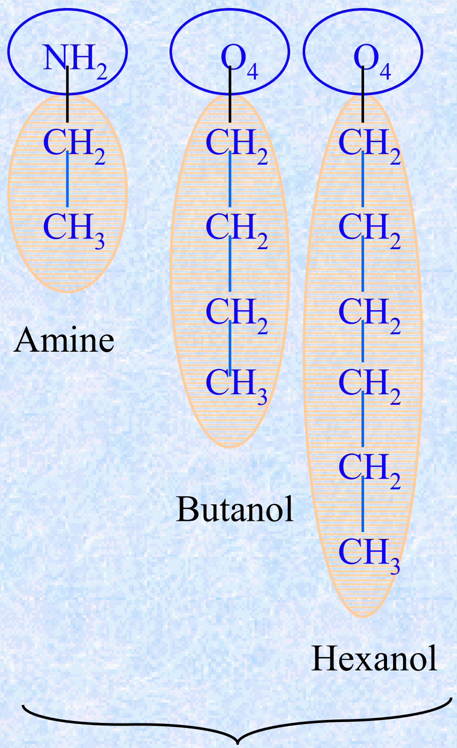
Hosts for technologically advanced materials

Mesoporous Materials: Bulk MCM-41

Amphiphilic Molecules:



Sufractant:
Hexadecyltrimethyl Amoniumbromid
(CTAB)



Co-surfactant

Mesoporous Materials: Bulk MCM-41

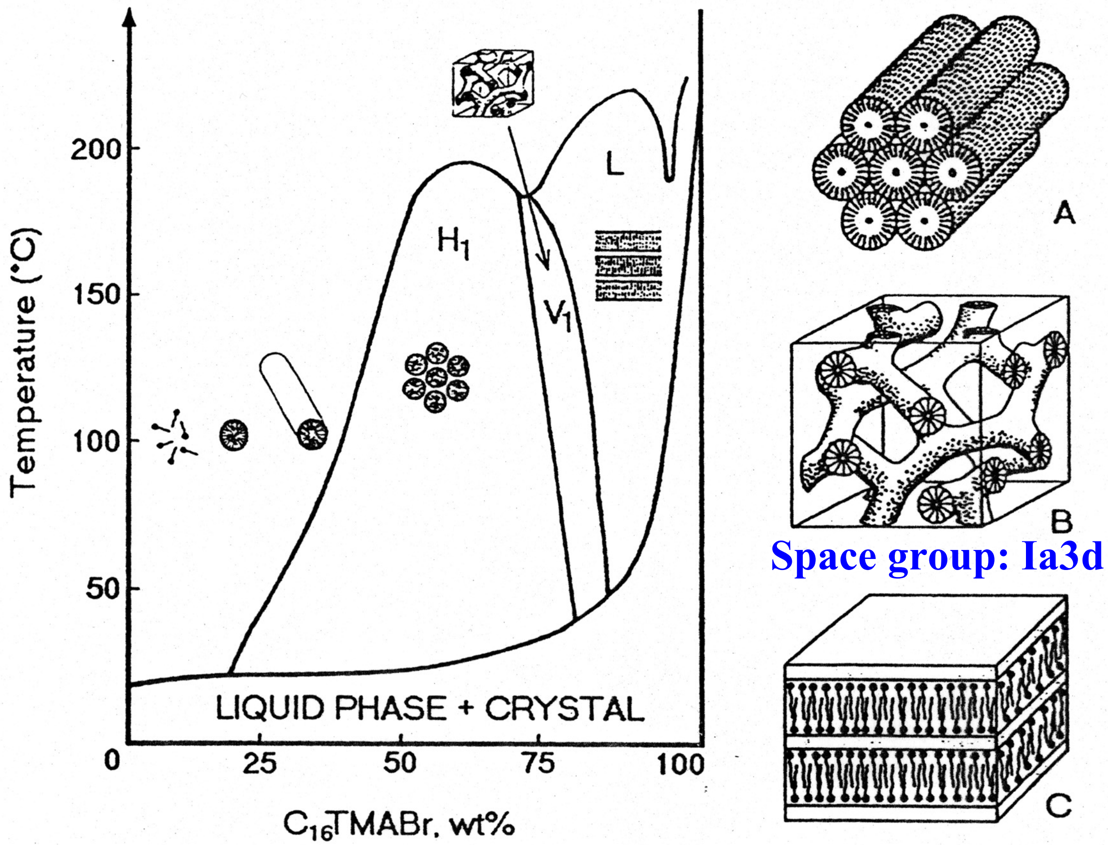


Figure 2. Schematic phase diagram of C_{16}TMABr in water [44].

Space group: Ia3d

Figure 3. Schematic representation of liquid-crystal structures, (A) hexagonal, (B) bicontinuous cubic, (C) lamellar.

MCM-41

MCM-48

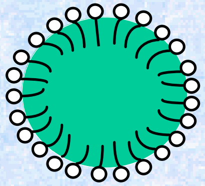
MCM-50

From: Sayari, Studies in Surface Science and Catalysis (1996), Vol 102, 1

Model for synthesis of mesophases in the system: TEOS/CTAB MCM-41

1

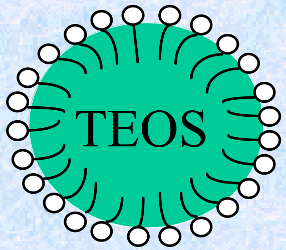
CTAB (surfactant) + H_2O



Spherical/elliptical Micells

2

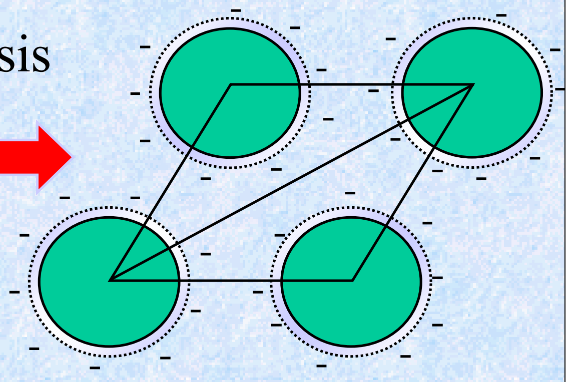
Micelles + H_2O + TEOS (oil)



Microemulsion

3

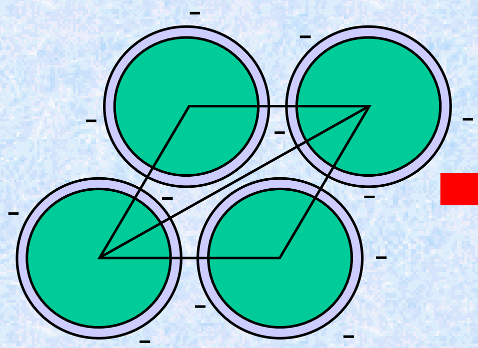
Silanhydrolysis on the surface of the micelles



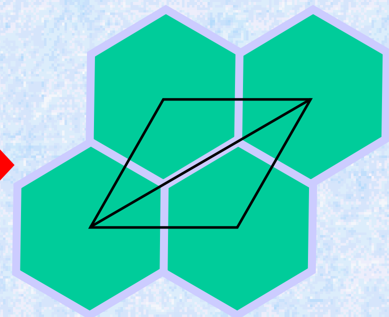
Formation of mesophases

4

condensation to poly-silicates between the aggregates of micelles



Inter-aggregat condenstation



Intra-aggregat condenstation

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Mesoporous Materials: Bulk MCM-41

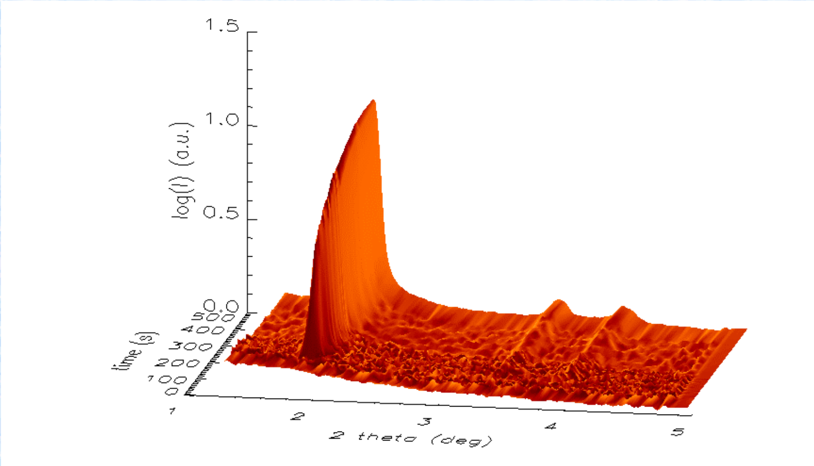
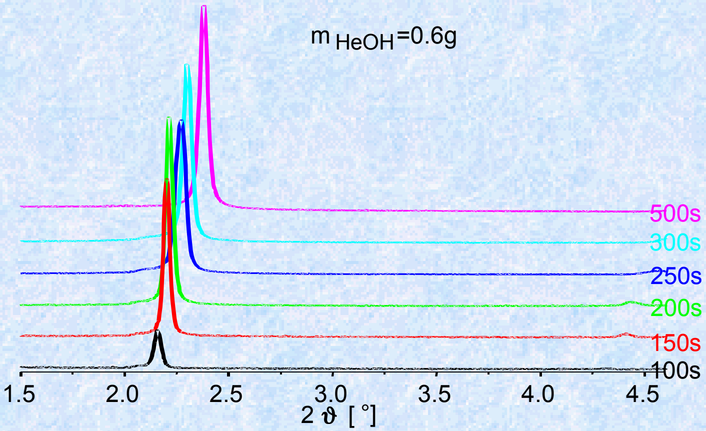
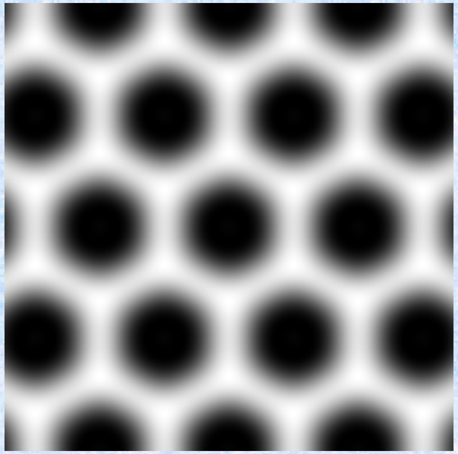


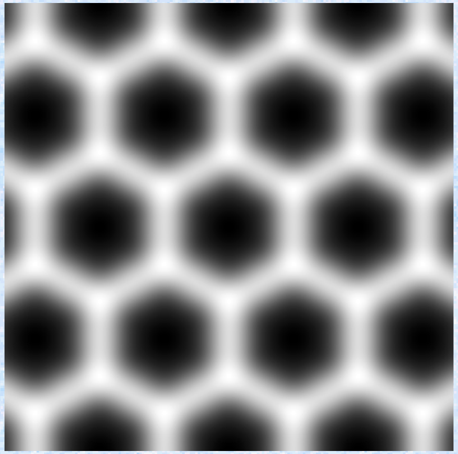
Fig. : Time-resolved diffraction pattern of the TEOS synthesis
Time resolution: 0.3 s/frame, Transition: micellar solution - ordered phases (standard synthesis: hexagonal D = 4.67 nm)



Calculated Electron Density



After 150s



Final Structure

AUSTRIAN SAXS - BEAMLINE AT ELETTRA
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Surface diffraction: Formation of aligned mesoporous thin films

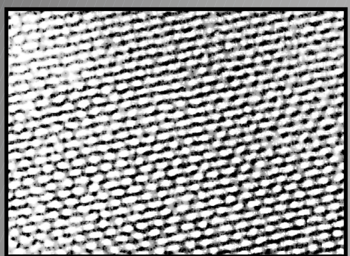
Sol-gel chemistry
+
surfactant mesophase

Self-assembly

Mesostructured hybrids

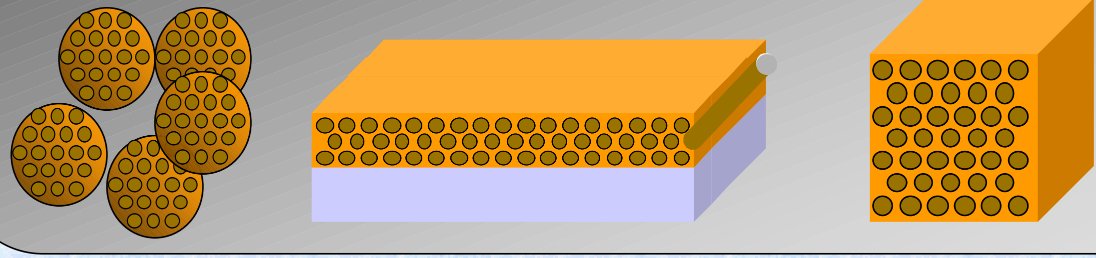
Treatment

Mesoporous materials with organised porosity

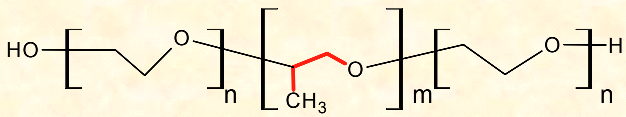


C. J. Brinker et al. Adv. Mater., 1999, 11, 579.

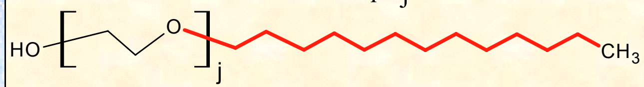
Particles made by aerosols | **Films** and **fibres** made by liquid deposition | **Monoliths** made by controlled evaporation



Triblocks POE-POP-POE



Diblocks C_iE_j



CTAB

SiO_2 : $Si(OR)_4$

TiO_2 : $TiCl_4$ - $Ti(OR)_4$

ZrO_2 : $ZrCl_4$ - $Zr(OR)_4$

Al_2O_3 : $AlCl_3$

VO_{2-x} : $VOCl_3$

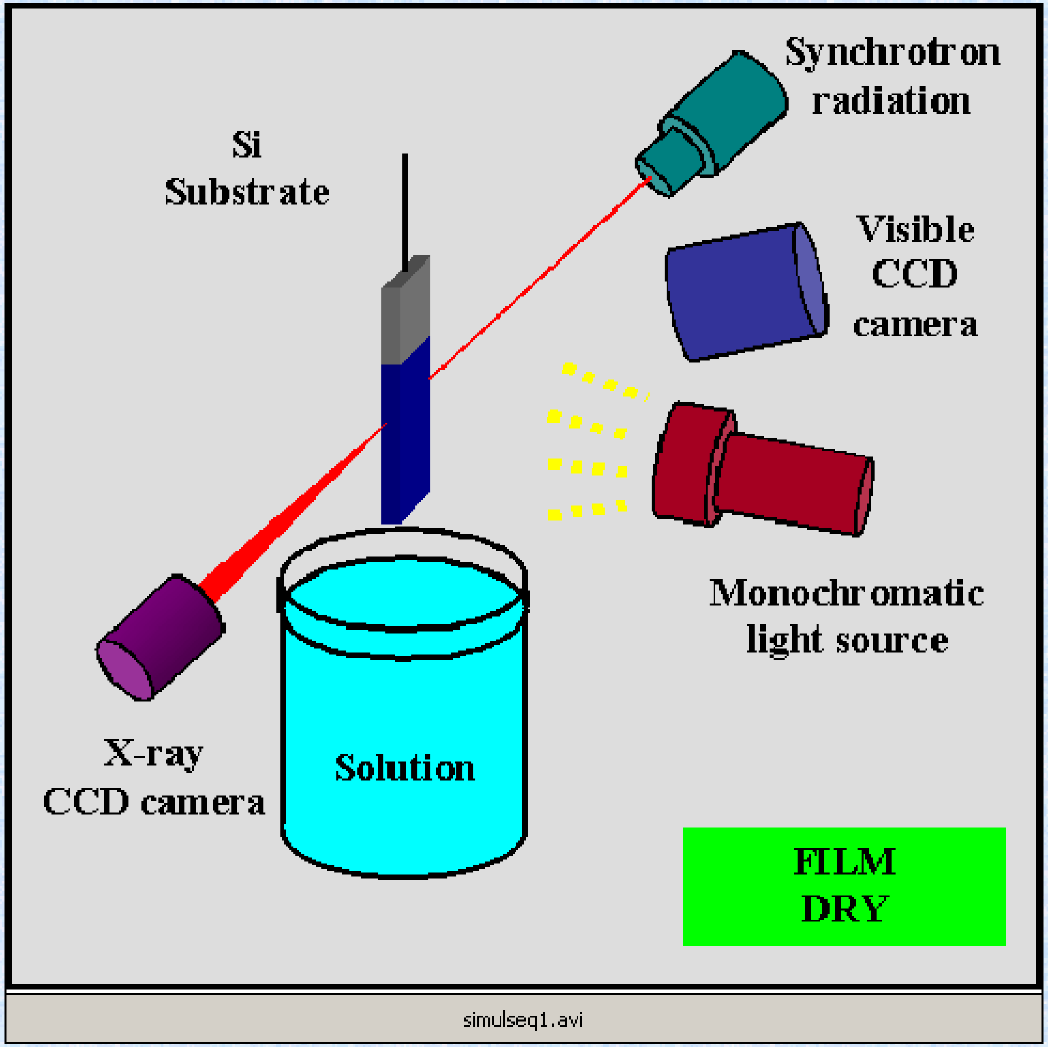
Y_2O_3 : YCl_3

Nb_2O_5 : $NbCl_5$

And binaries systems

The Self-Assembly of thin films as seen by In-Situ SAXS and interferometry

Film mesostructure



Film thickness profile

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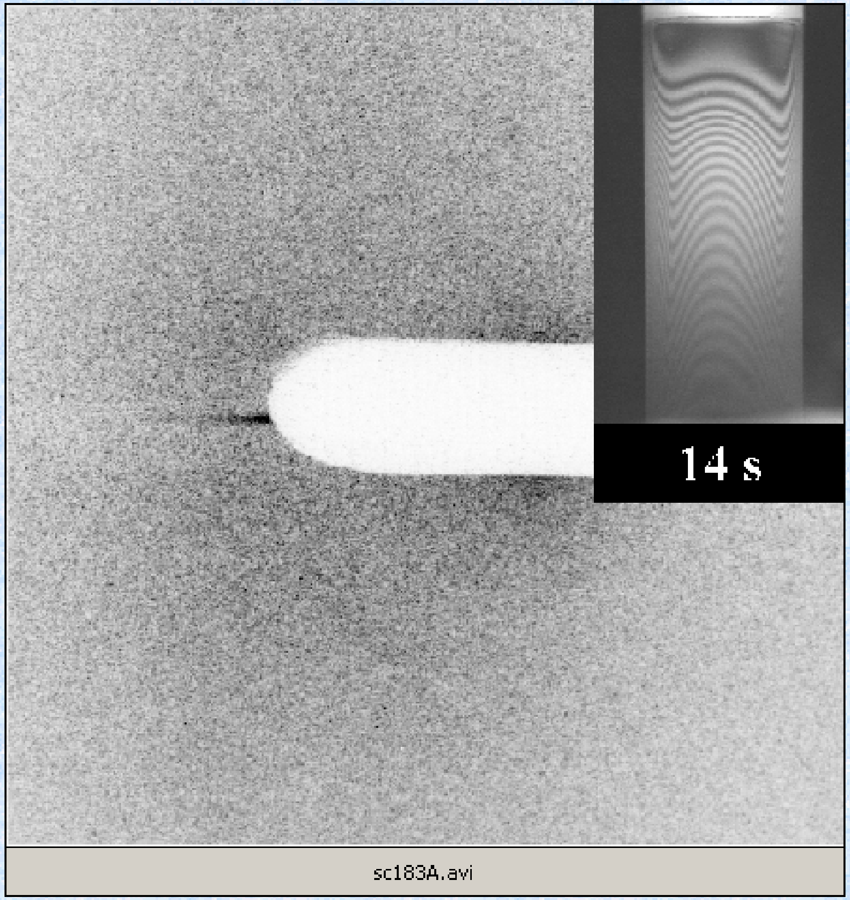
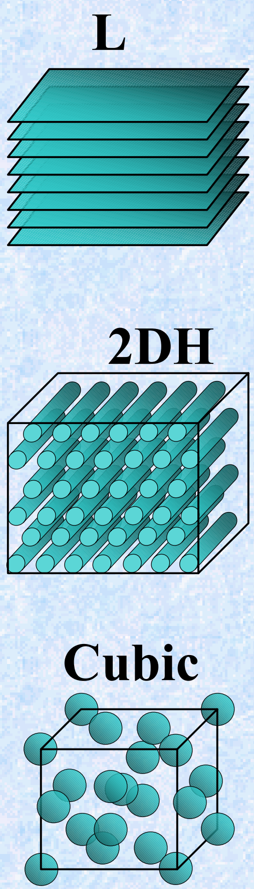
Surface diffraction: Formation of aligned mesoporous thin films

CTAB / Si = 0,18
H_2O / Si = 5
HCl / Si = 0.15
Ageing time
Relative Humidity



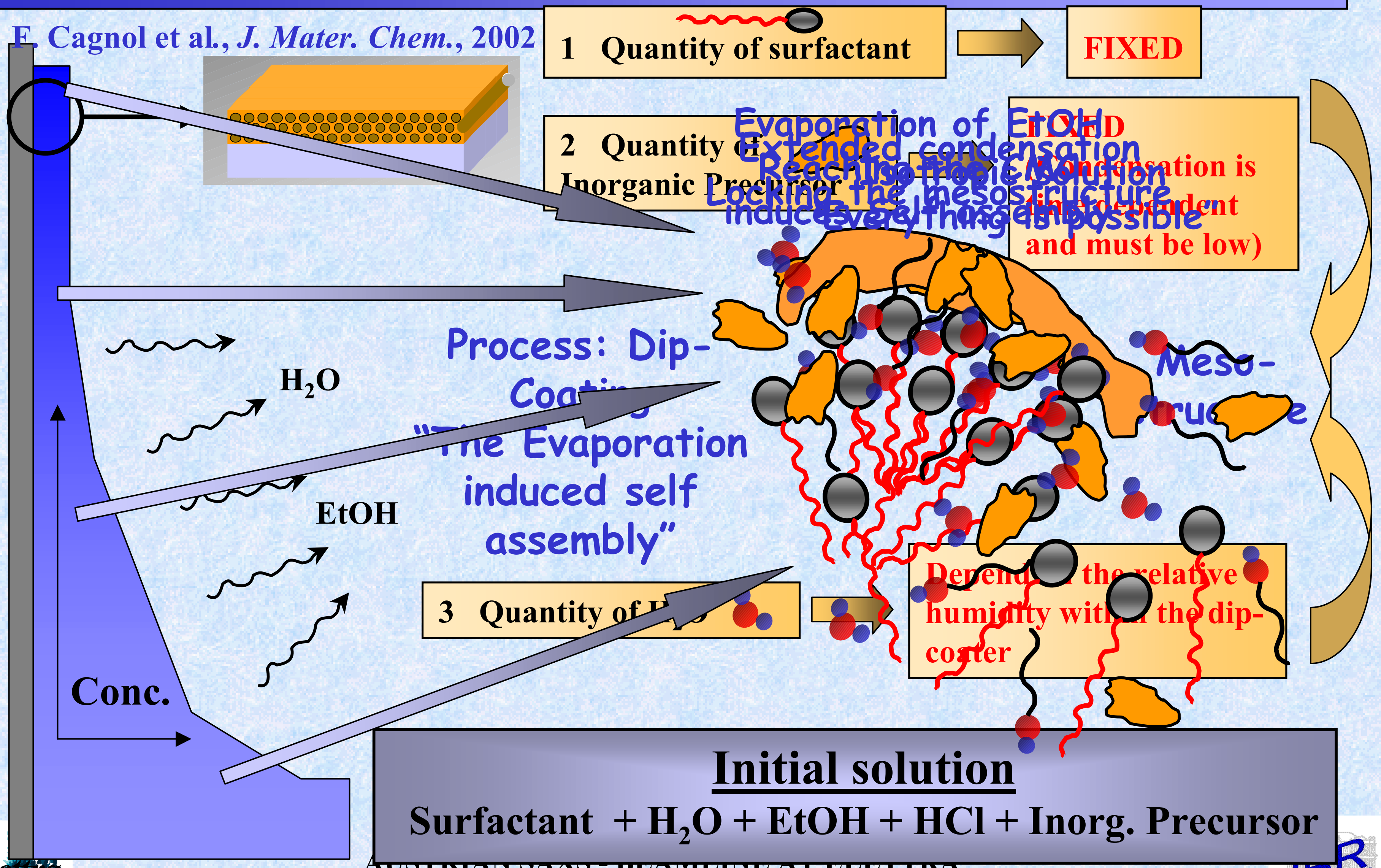


Grosso D, et.al., CHEMISTRY OF MATERIALS *14,* 931,(2002)

H. Amenitsch, S. Bernstorff, P. Dubcek, M. Rappolt & P. Laggner

The Modulable Steady State

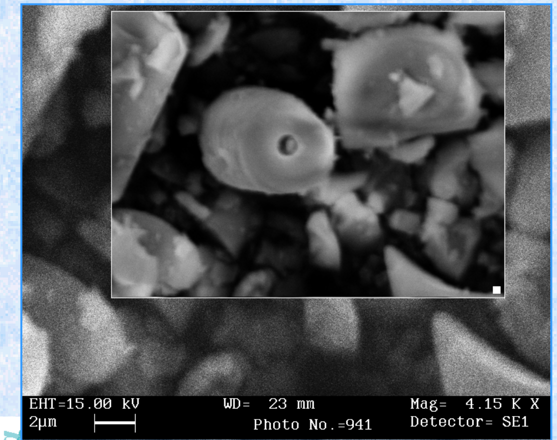
F. Cagnol et al., *J. Mater. Chem.*, 2002

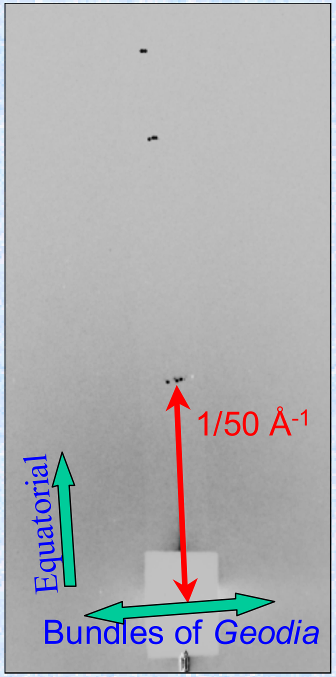


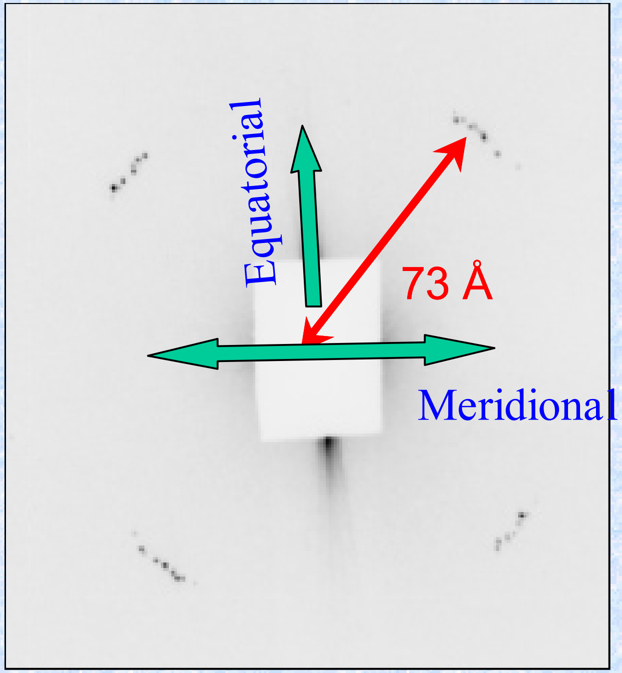
SAXS STUDY OF SPICULES FROM MARINE SPONGES

- The scientific name is "Porifera" which translates into "pore-bearing"

Biomineralisation



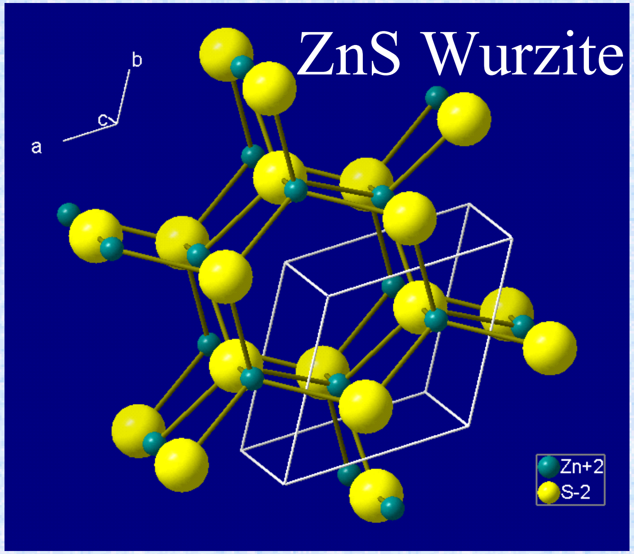




Geodia Scolimastra

Croce,G. et al., 2004. *Biophysical Journal* 86:526-534.
Croce,G., et al.,2003. *Microscopy Research and Technique* 62:378-381

ZnS precipitation Introduction



Precipitation in general:

-Industrial importance:

90% of industrial processes for solid products are precipitation from solutions

-No Theory available:

early stages are important for the precipitation of the final product

ZnS:

-II/VI semiconductor → size quantization → absorption edge higher

→ exciton excitations in UV/Vis spectra

→ Phosphor

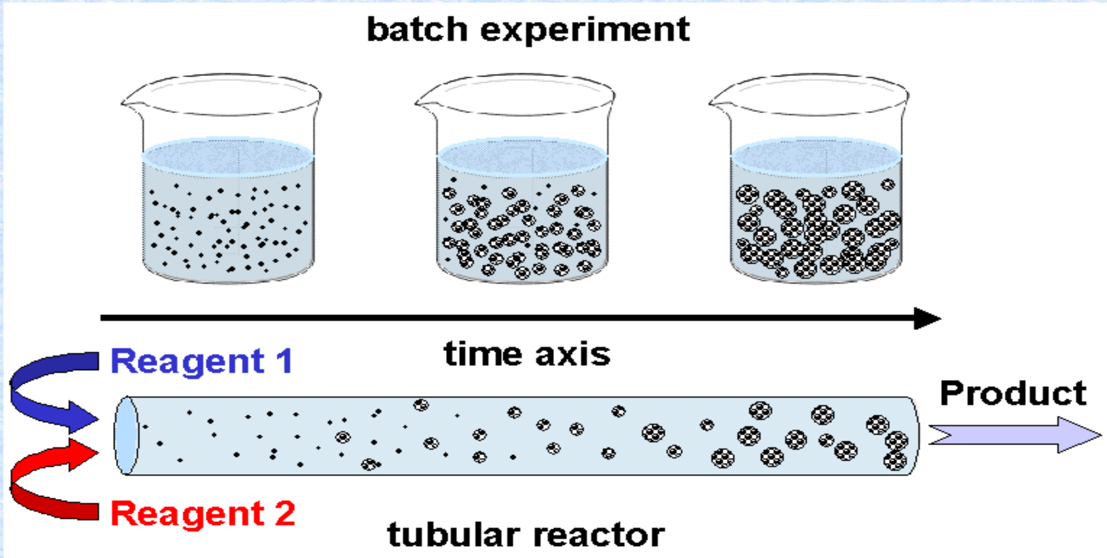
-Two modifications → cubic (sphalerit) and hexagonal structure (wurzite)

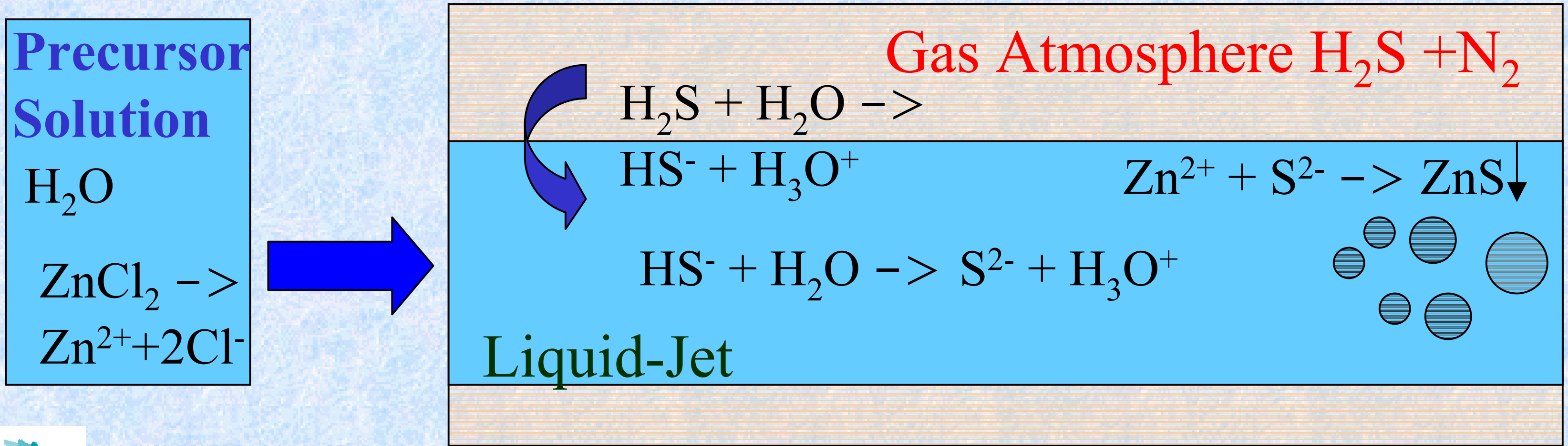
-Design of capping agents (e.g. Thioacetamine)

ZnS Tubular reactor - Liquid Jet-Experiments

Advantage:

- -higher time resolution
- -no fouling on walls
- -no clogging of the reactor





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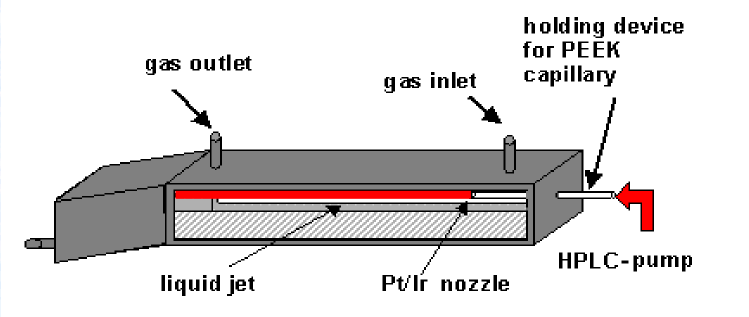
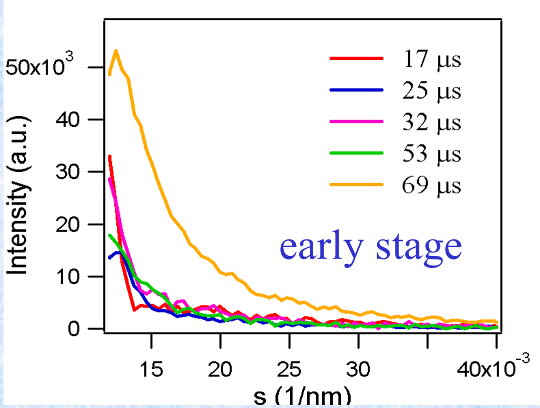
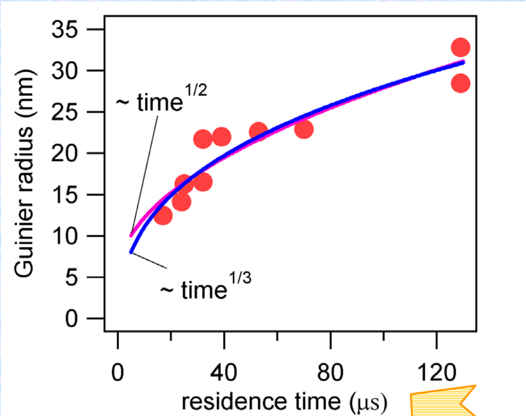
ZnS: Liquid Jet-Experiments

Set-up:

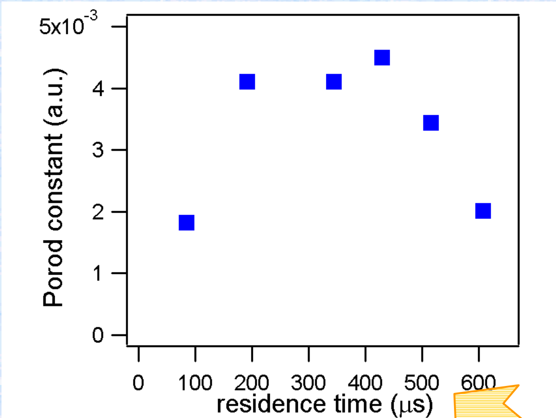


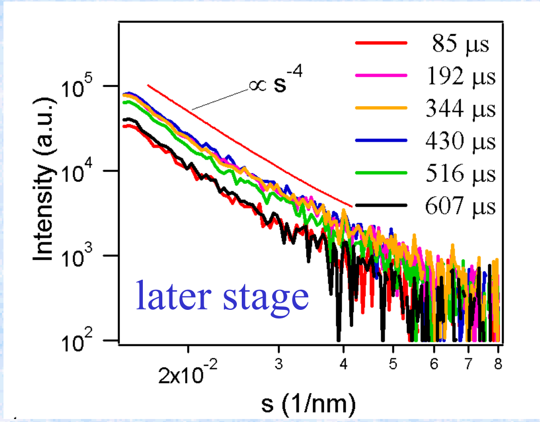


Guinier Regime



Porod Regime





Reaction limited process $R_g \propto time^{1/3}$

Diffusion limited process $R_g \propto time^{1/2}$

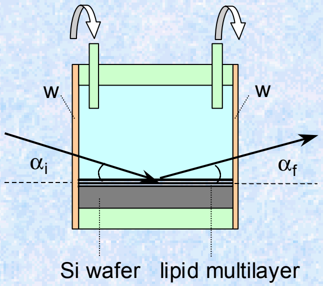
$$P \propto \frac{p \cdot \Delta\rho^2}{R}$$ Aggregation process dominating

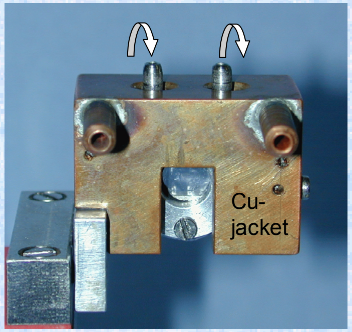
P.Bussian, P. Ågren, J.Andersson, M.Linden, W.Schmidt H.Amenitsch, F.Schüth, (2001)

AUSTRIAN SAXS - BEAMLINE AT ELETTRA

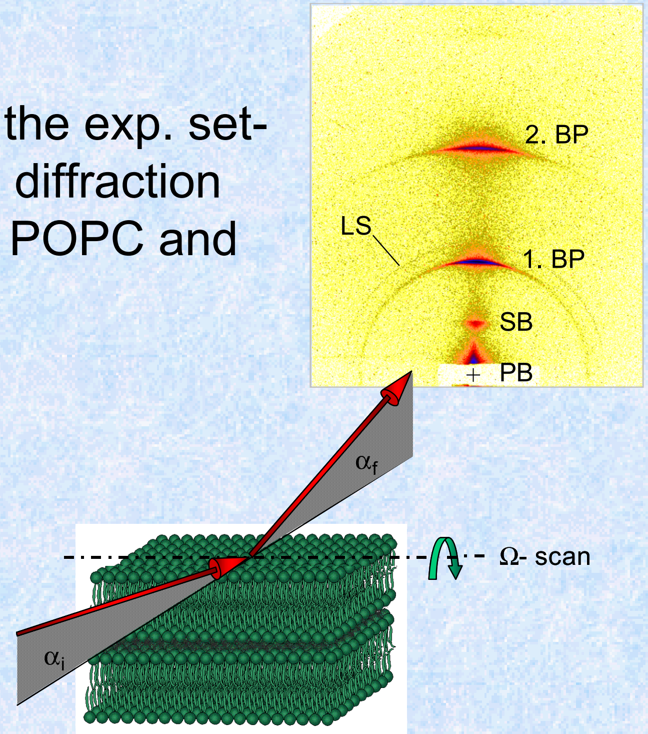
H. Amenitsch, S. Bernstorff, P. Dubcek, M. Rappolt & P. Laggner

Surface Diffraction Lipids – Surface Chemistry





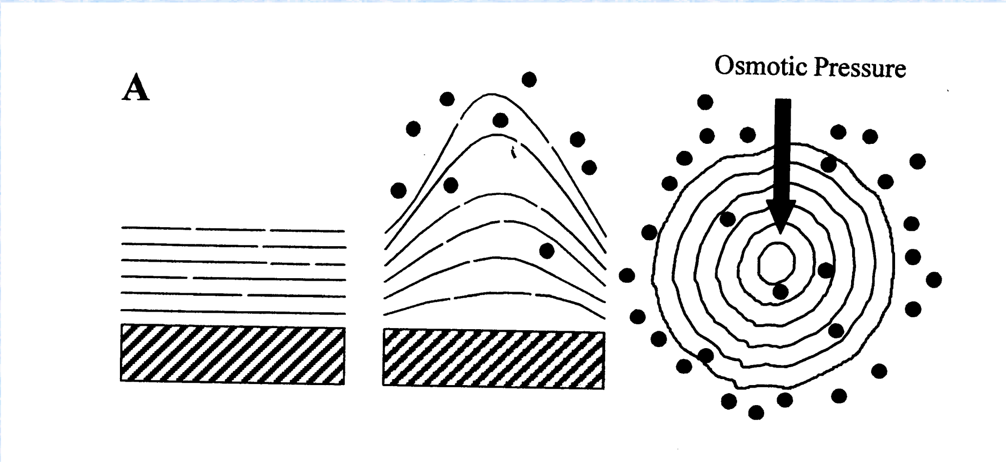
Sketch of the exp. set-up and 2D diffraction pattern of POPC and 0.5 M LiCl

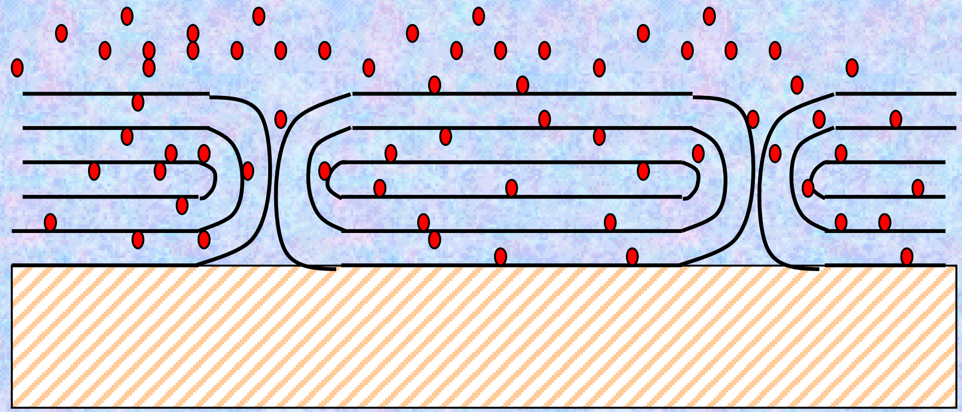


Sketch and photograph of the sample cell in transmission geometry for GISAXS.

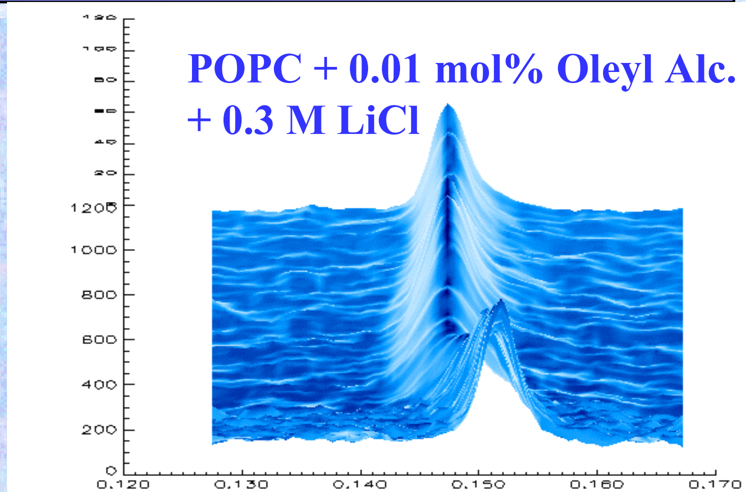
H. Amenitsch, S. Bernstorff, P. Dubcek, M. Rappolt & P. Laggner

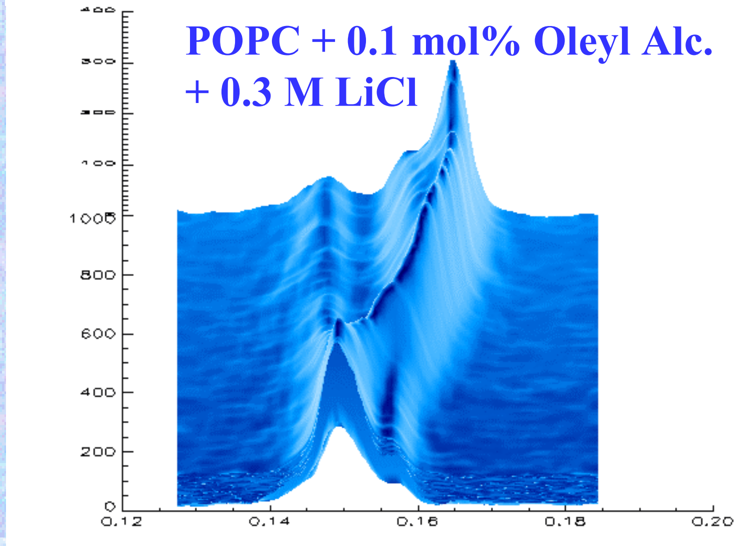
Surface Diffraction Lipids – Surface Chemistry





Amenisch, H., et al., (2004) Langmuir





Summary - Outlook

-Why? Extreme?

-How to trigger transitions?

-Applications

Biology and Biomedicine

Physical Chemistry

Material Science

"Frontiers in Material Science", Science, 277, (1997), 1213-1253

-Outlook: USE of NEW DETECTORS!

Use of coherence in SAXS!

(photon correlation spectroscopy)

Use of new sources FEL's!

Think for yourself of new ways

to use SAXS and SR