united nations
educational, scientific
and cultural
organization

international atomic
energy agency

the
abdus salam
international centre for theoretical physics

SMR/1270-28

SCHOOL ON SYNCHROTRON RADIATION

6 November – 8 December 2000

Miramare - Trieste, Italy

Supported in part by the Italian Ministry of Foreign Affairs in connection with the SESEME project

Co-sponsors: Sincrotrone Trieste, Società Italiana di Luce di Sincrotrone (SILS) and the Arab Fund for Economic and Social Development

SAXS applications for

time-resolved measurements

P. Laggner
Akademie Der Wissenschaften
Institut Fur Biophysik Und Rontgenstrukturforschung
Graz, Austria

[redacted]

P.Laggner

Outline:

-Why? Scientific case
How it all started?

-How to trigger transitions?
Jump-relaxation methods
Other (oscillatory) methods

-Applications
Biology and Biomedicine
Physical Chemistry
Material Science

Outlook

AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

Austrian SAXS Beamline at ELETTRA

Head of Project: Peter Laggner[1)]

Scientists: Heinz Amenitsch[1)]
Sigrid Bernstorff [2)]

Postdocs: Pavo Dubcek[2)]
Michael Rappolt[1)]

PhD-Student: Georg Pabst[1)]

1) Institute for Biophysics and X-ray Structure Research, Austrian Academy of Sciences, Schmiedlstrasse 6, 8042 Graz, Austria.

2) Sincrotrone Trieste, Strada Statale 14, km 163.5
34012 Basovizza (TS), Italy.

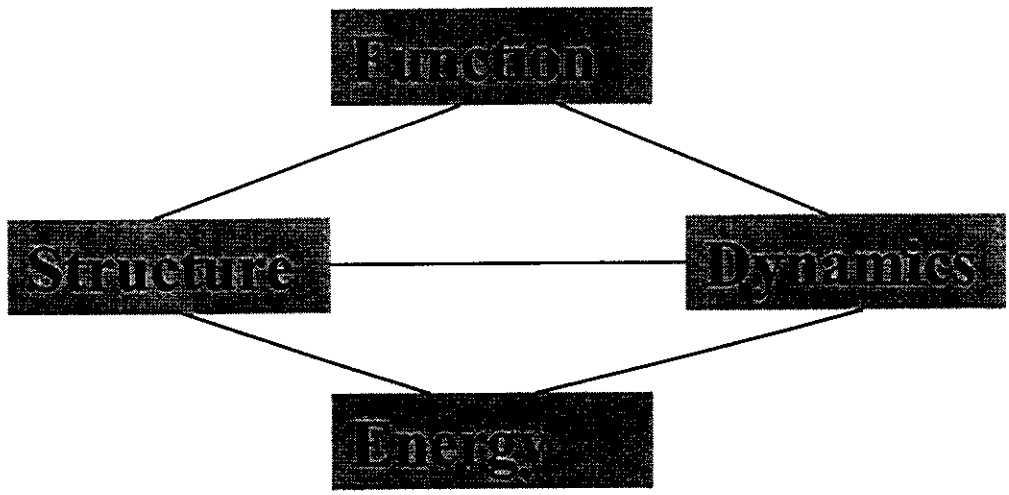
Collaborators: Ruth Prassl[1)]
Karl Lohner [1)]

Why?

What is extreme?

-Temperature: mK, 10^3 K, 10^6 K
-Time scales: years,s, ms, μs
-Pressure: μPa, 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

AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

Why? - How it all started I
Muscle Contraction

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

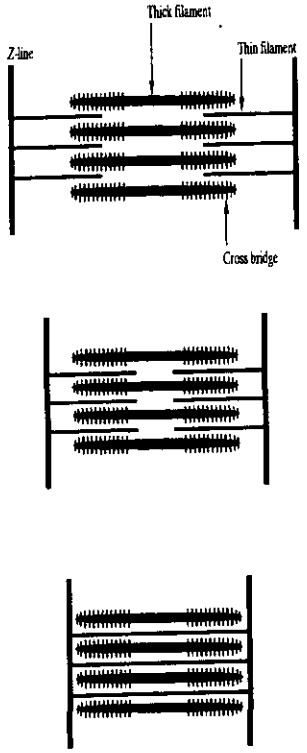
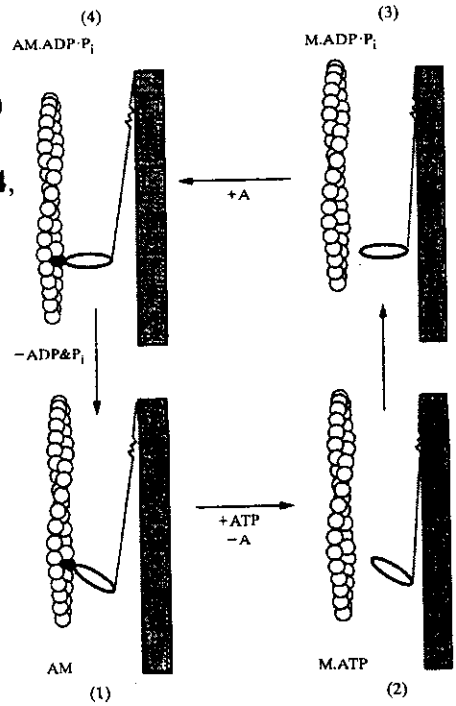


Fig. Muscle Contraction
thick (myosin)-, thin-(actin) fibers are interdigitating
K.C Holms Acta Cryst. **A54**, (1997), 789



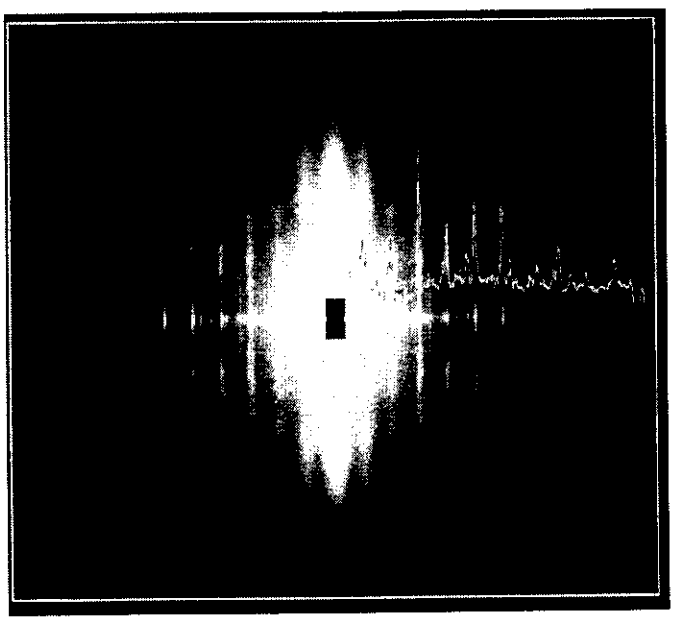


Fig. Lymn-Taylor cycle. (Lymn, Taylor Biochemistry, (1971)10, 4617
Mysoin-cross-bridge is bound in rigor (1)
ATP binds->quick dissociation (2)
ATP->ADP + P (hydrolysis) binding of myosin to actin 90 up (3)
release of components, rowing to (1)

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

AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

Why? - How it all started I
Muscle Contraction

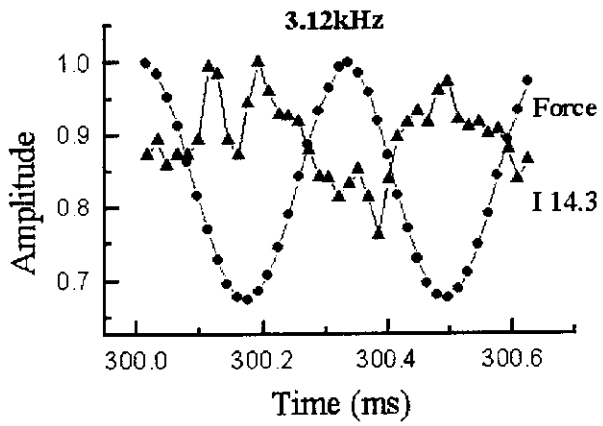


Fig.: IM3 (I14.3, filled triangles) and force (filled circles) for a two fibre bundle undergoing 3.12 kHz sinusoidal length oscillations. Sampling time 16 micro-seconds.

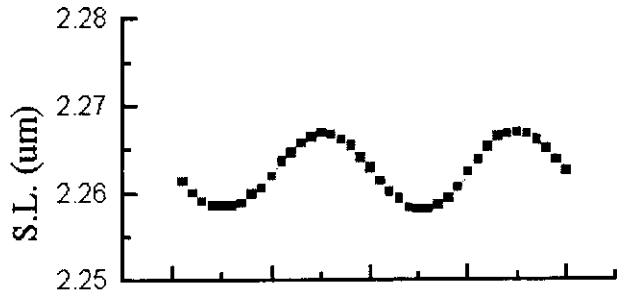
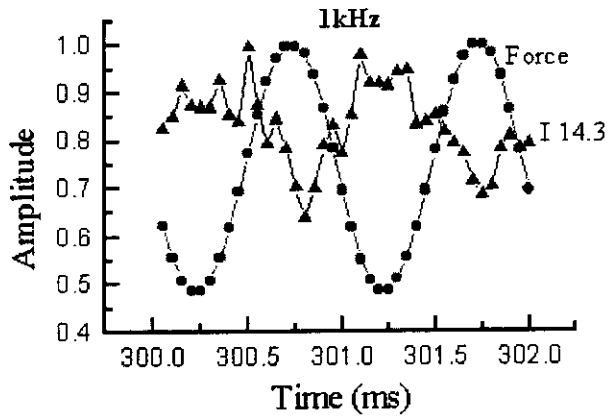


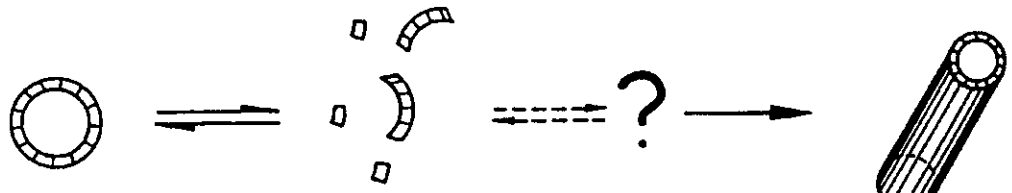
Fig.: Sarcomere length (S.L., filled squares), force (filled circles) and IM3 (I14.3, filled triangles) for a single fibre undergoing 1 kHz sinusoidal length oscillations. Amplitudes and time as in figure 1.



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

AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

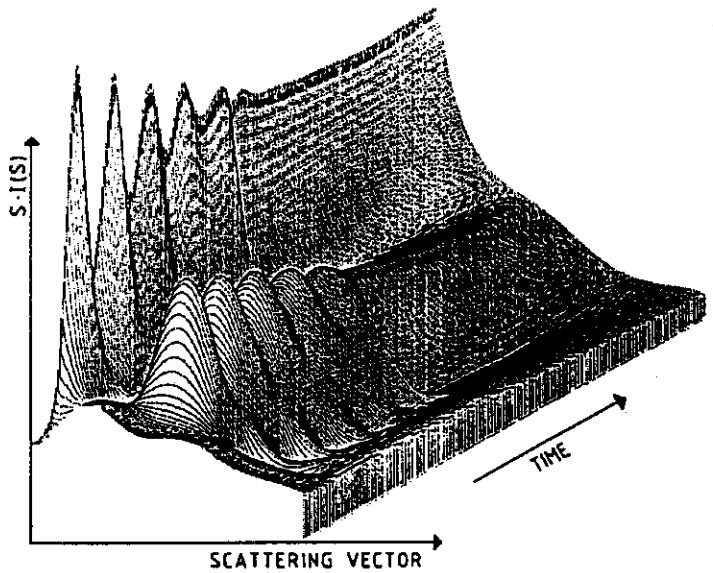
Why? - How it all started II
Microtubule Assembly



rapid equilibrium $t_{1/2}$ ≤s
Independent of GTP
Independent of nucleation

activation by GTP

slow nucleation & assembly $t_{1/2}$ ~30s
GTP hydrolysis



Reaction cycle

Subunits → Microtubules → Oligomers

From Mandelkow et.al., Top.Curr.Chem. 151 (1989), 10-29

AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

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 cell

M.C.Ramachandra et.al. Biophysical Journal **74**, (1998), 2714

-Batch reactor
-Magnetic field
-Shear experiments

SAXS - Applications: Stopped Flow Cell

EXAMPLE:

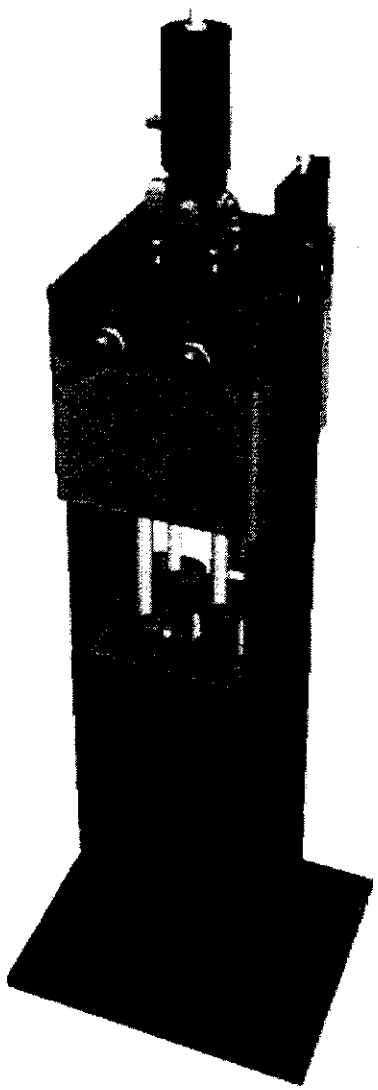
Protein denaturation of GroEL. to study the unfolding of the protein GroEL by the chemical denaturant guanidine hydrochloride monitored by time-resolved small-angle X-ray scattering with (milli)second time resolution.

M. Kriechbaum, P. Laggner, Y. Hiragi, H. Amenitsch & S. Bernstorff

Fig. 1: GroEL, a chaperonin protein which assists in protein folding contains 14 identical subunits (relative molecular mass of each is 58.000), that is assembled as 2 identical heptameric rings stacked back to back, forming roughly a hollow cylinder (length ~ 14.6 nm, outer diameter ~ 13.7 nm) with a hollow cavity of ~ 4.5 nm in diameter.

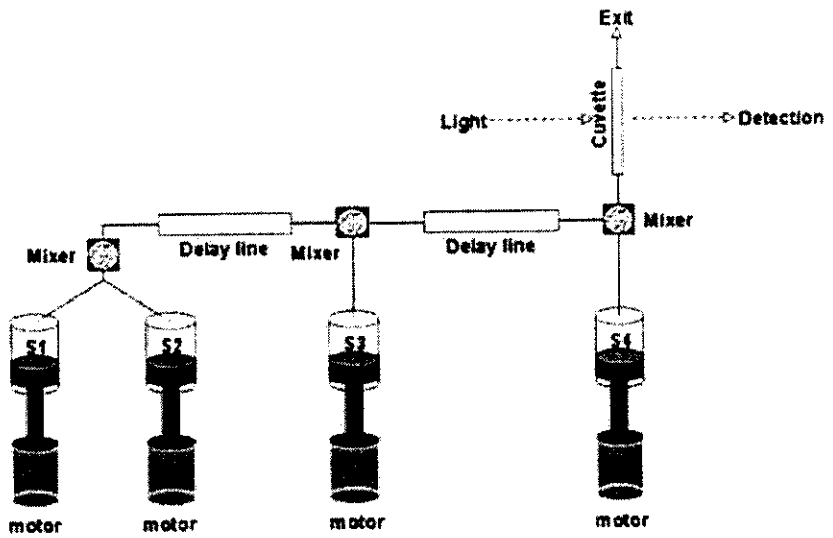
AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

SAXS - Applications: Stopped Flow Cell



Aim:

Time-resolved jump relaxations experiments on biological samples like proteins are a suitable method to elucidate the kinetics and dynamics governing the structural rearrangements during folding/refolding caused by temperature, pressure or chemical denaturation



AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

SAXS - Applications: Stopped Flow Cell

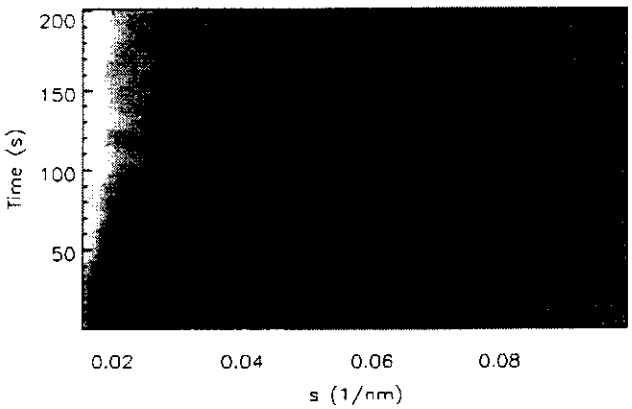
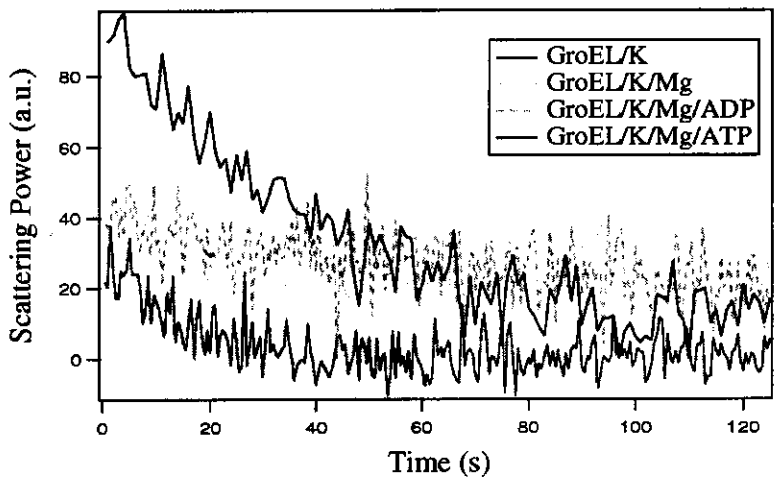
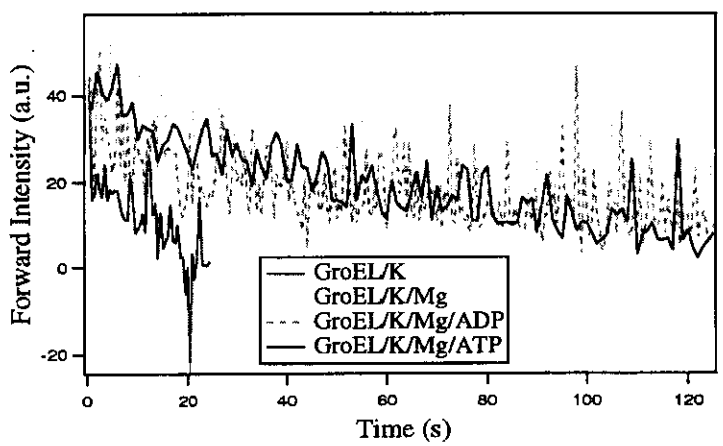


Fig. : Protein denaturation of GroEL (with K/Mg/ATP) by admixing 5M guanidine HCl in the stopped flow cell (<1 ms) recorded in time-sliced X-ray diffraction patterns with an exposure time of 1 s per frame





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

SAXS - Applications: Stopped Flow Cell

KINETICS OF MEMBRANE PERTURBATION AND DISRUPTION BY ANTIMICROBIAL PEPTIDES

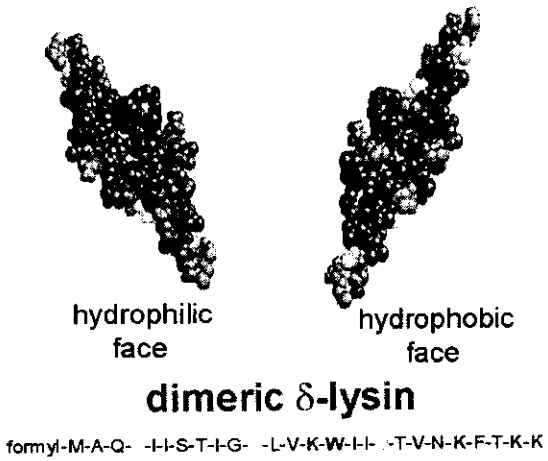


Fig: Space filling model of the dimeric δ-lysin molecule, a membranolytic toxin of *Staphylococcus aureus*

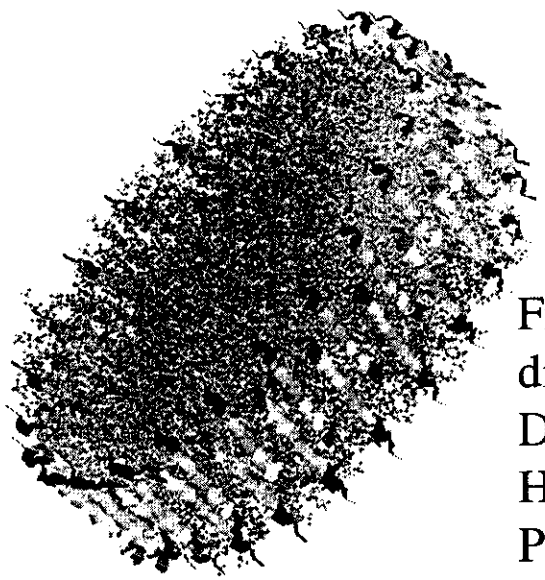


Fig.: Model from static data
discoidal lipid micelle
D = 14 nm
H = 5.2 nm
Peptide ring: 1 nm
Lipid disk: 12 nm

K.Lohner, et.al, Biochem. 38, 16544, (1999)

AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

SAXS - Applications: Stopped Flow Cell

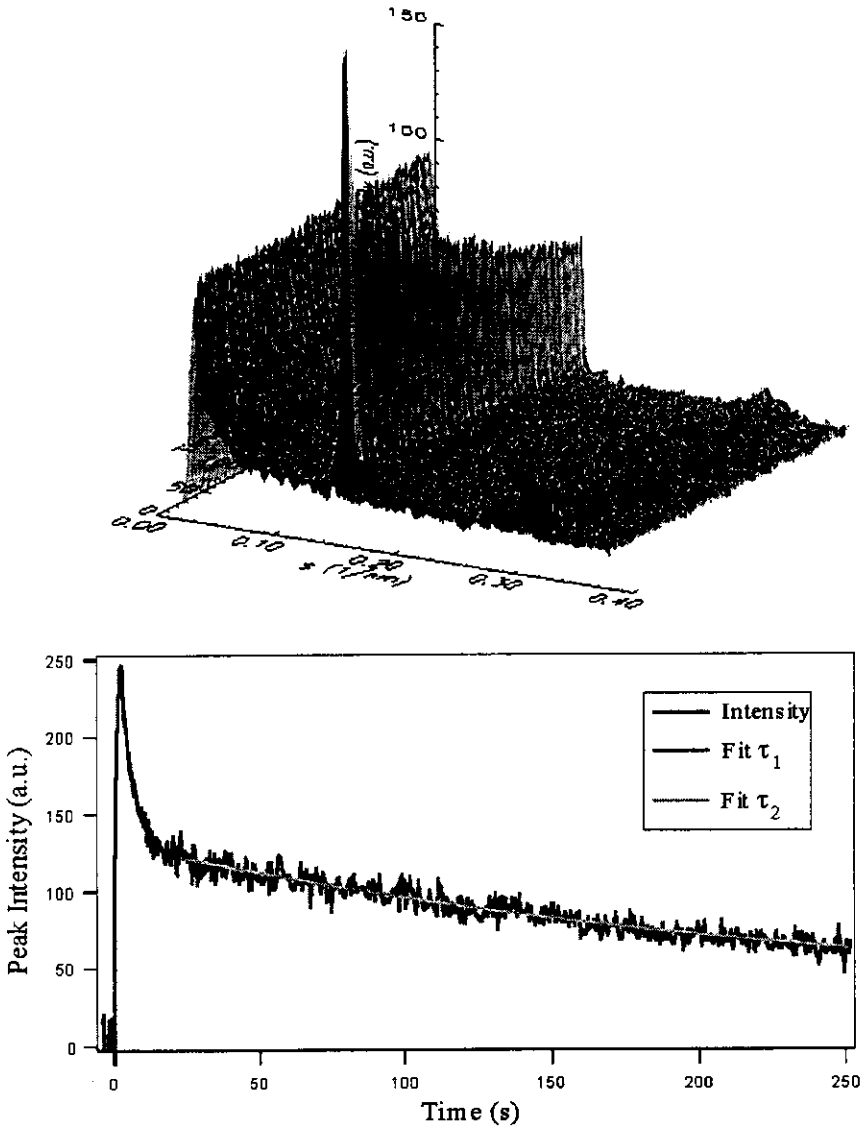


Fig. : Time resolved diffraction pattern (time resolution 0.5 s/frame) after admixing of delta-lysin (10 mg/ml) to DMPC (71 mg/ml) (1:1 by vol.). The decrease of the first and second order Bragg peaks, characteristic for multilamellar DMPC vesicles, are clearly visible.

K. Lohner, H. Amenitsch & E. Staudegger, (1998,1999)

AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

SAXS - Applications: T-jump Device

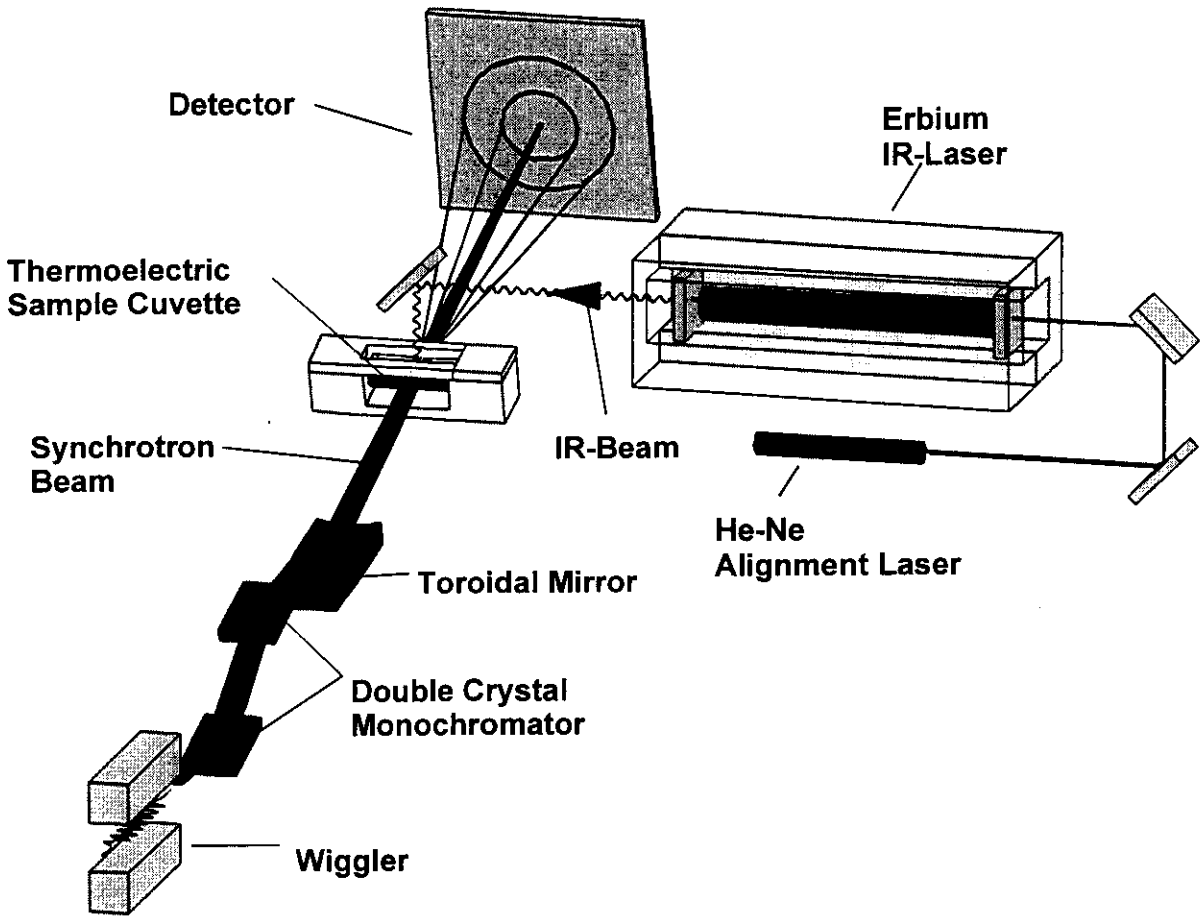
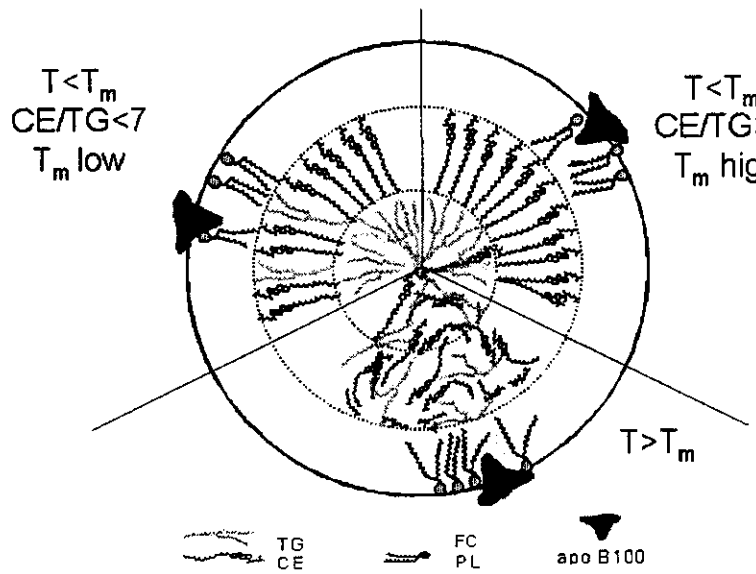


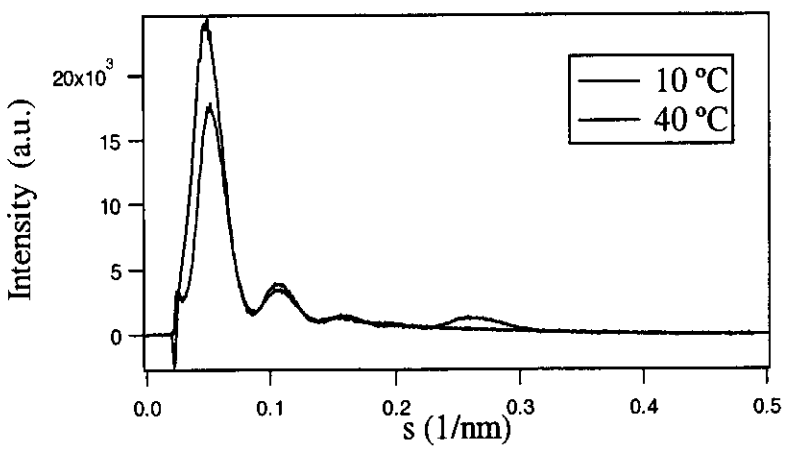
Fig. Experimental set-up of the T-jump device at the SAXS beamline (ELETTRA).
Power: 4 J / 2 ms
Jump height: 20 K
Wavelength: 1.54 μm

SAXS - Applications: T-jump Device

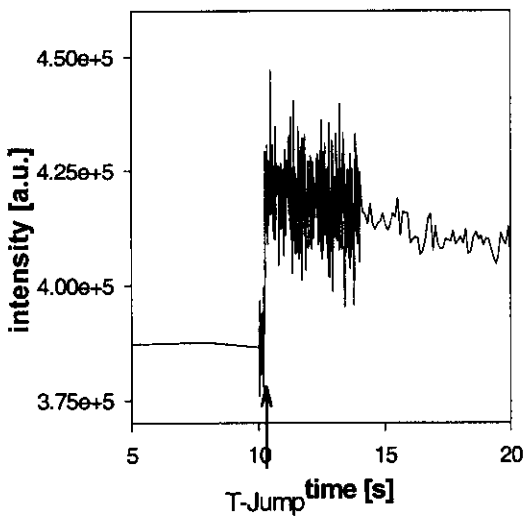
10 ms time-resolved x-ray diffraction of the core lipid transition of human Low Density Lipoproteins



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



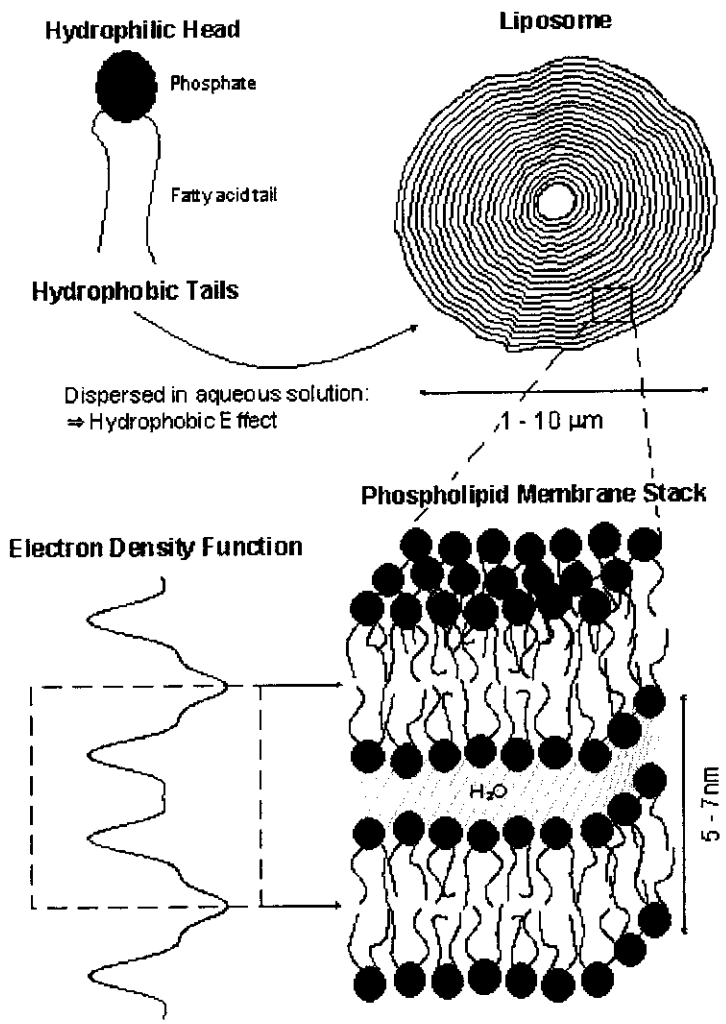
Static Diffraction pattern of LDL at 2 diff. Temperatures



Integrated intensity of the first side maximum versus time. The transition to an isotropic state of the LDL core (core-melting) occurs faster than the 10 ms time-resolution

AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

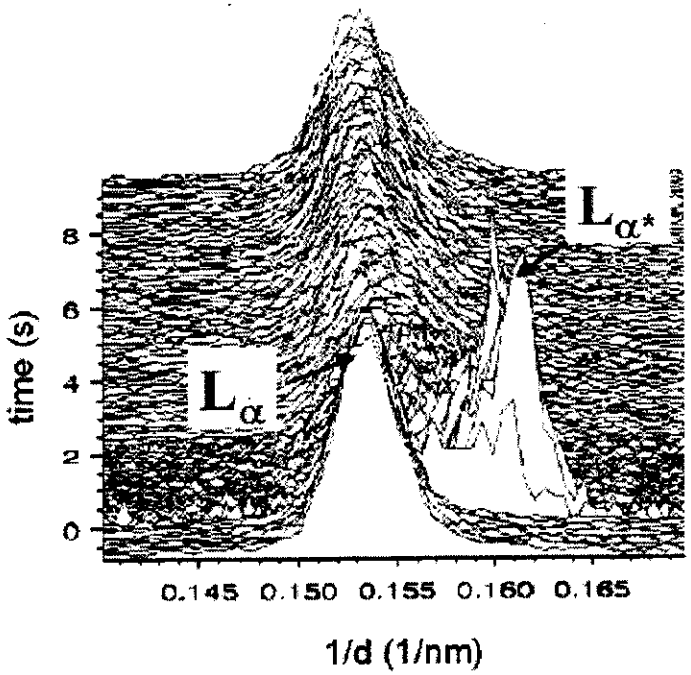
SAXS - Applications: T-jump Device



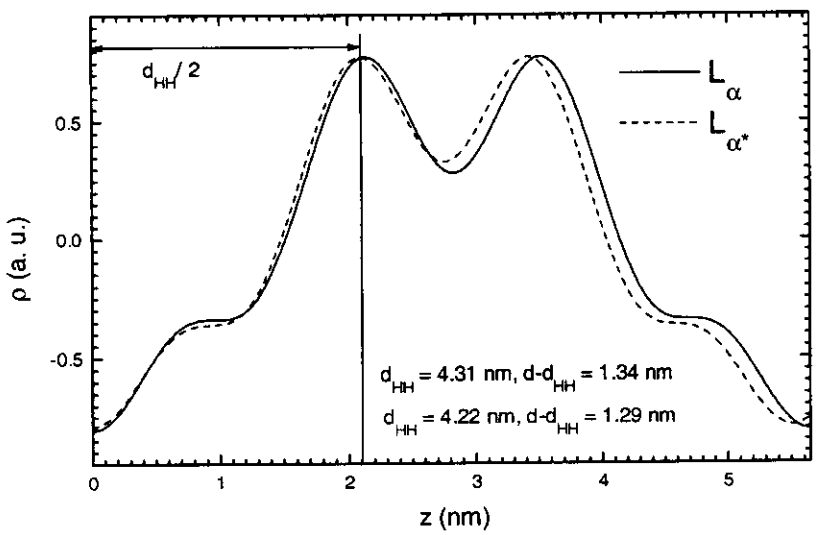
The formation of a phospholipid membrane. Phospholipids aggregate spontaneously into ordered supra-molecular structures in the presence of water. This can be explained in simple terms by the fact that phospholipids feature a hydrophilic headgroup (attracting water) and hydrophobic hydrocarbon-chains. The average 1- dimensional repeat distance d, i.e., bilayer plus waterlayer of the depicted liquid crystalline phase (L_α) 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.

AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

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.



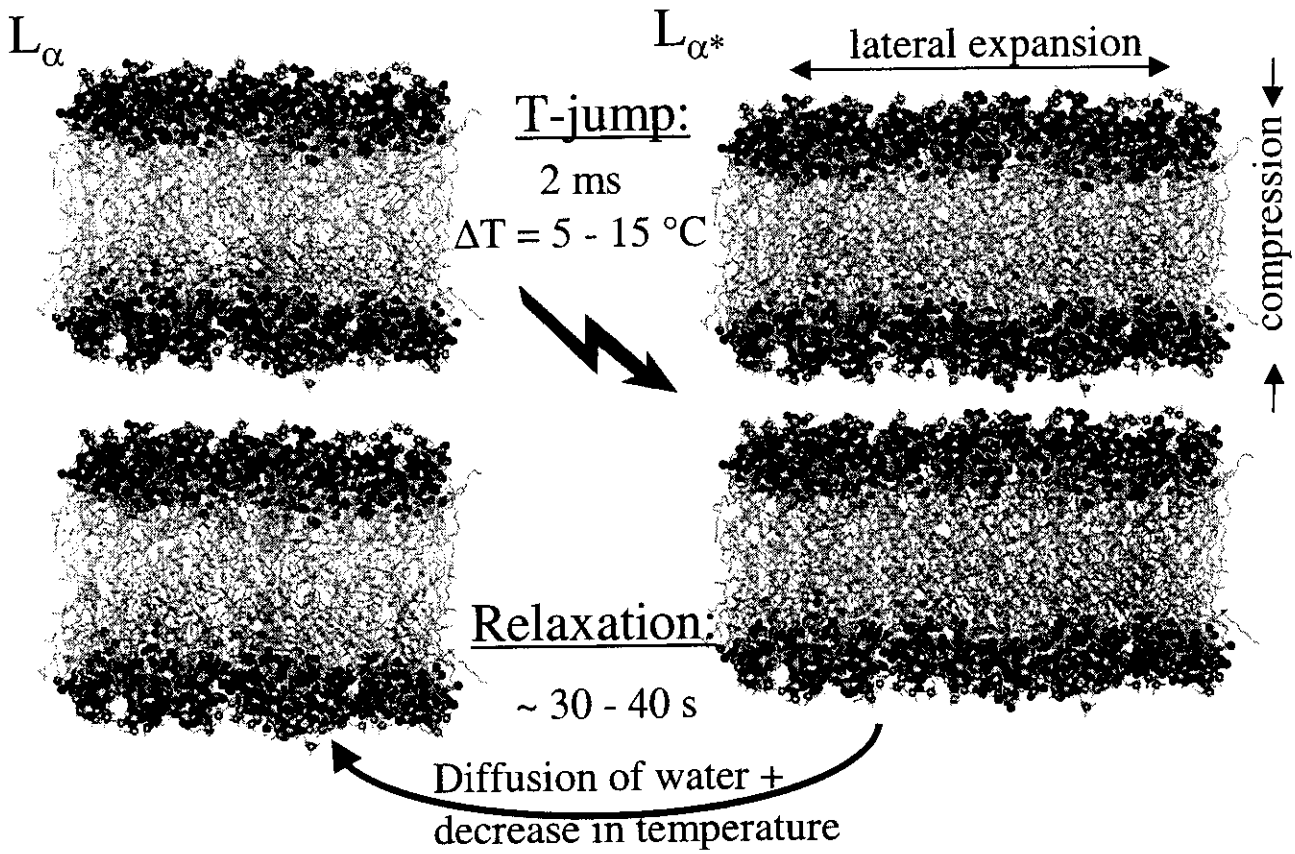
Superimposed electron density distributions of the original L_α-phase (straight line) and of the intermediate phase L_{α^*} (dashed line) immediately after the laser flash

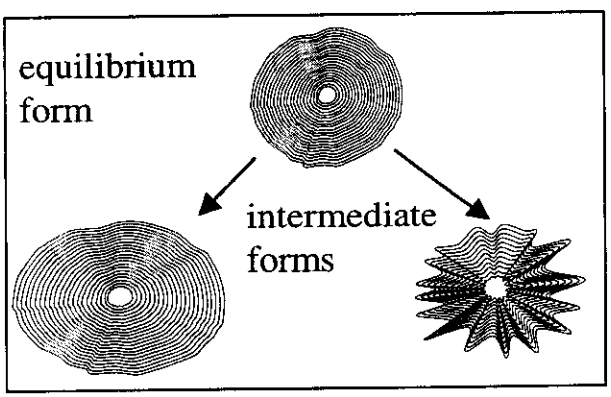
G. Pabst, M. Rappolt, H. Amenitsch, S. Bernstorff & P. Laggner (1998)

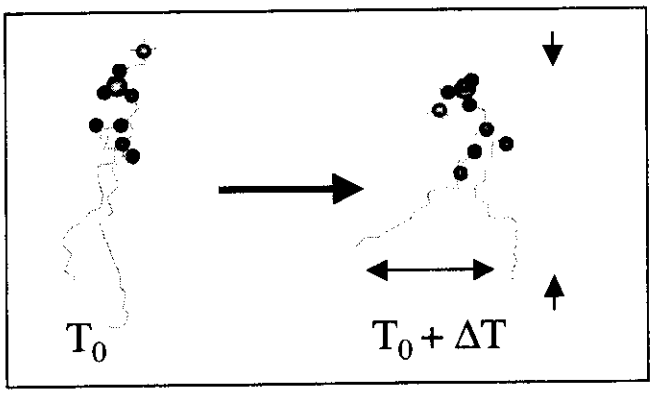
AUSTRIAN SAXS - BEAMLINE AT ELETTRA

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

T-jumps: Phospholipid Phase Transition





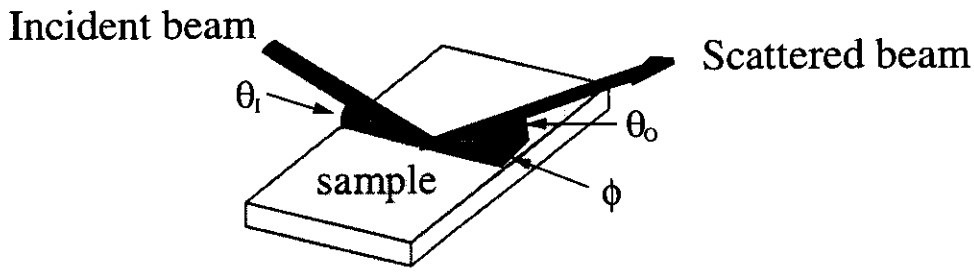


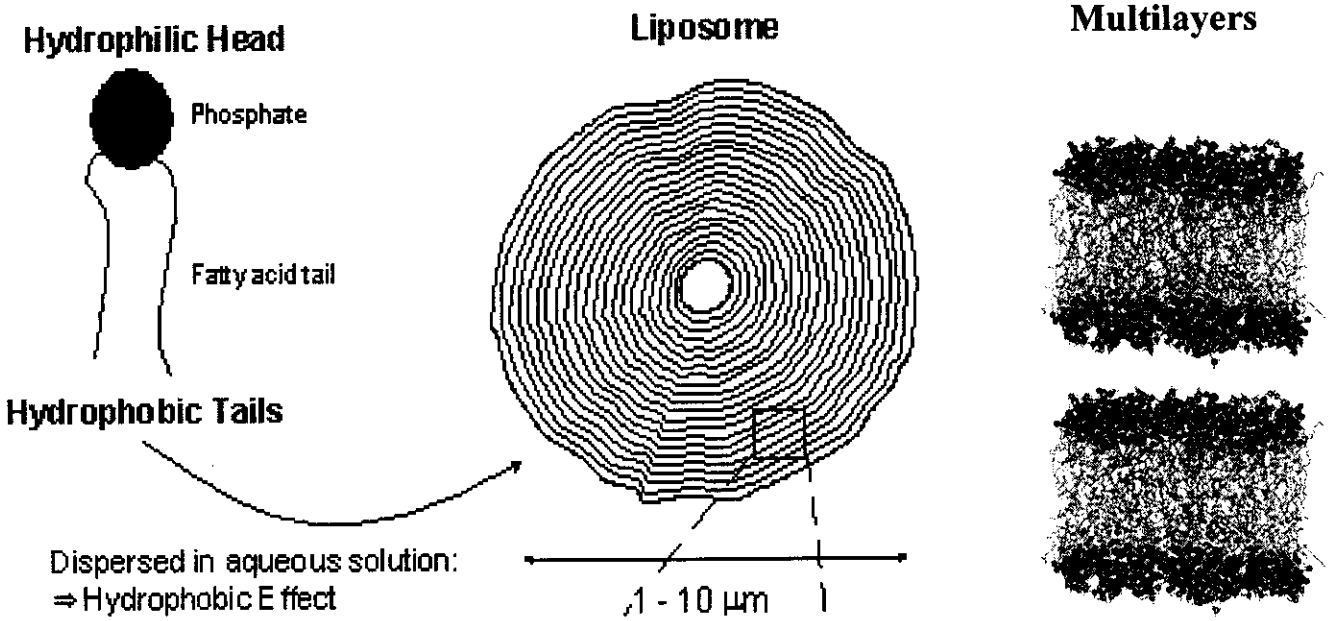
G. Pabst, M. Rappolt, H. Amenitsch, S. Bernstorff & P. Laggner,
sub. to. Biophys. J., (2000)

AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

Surface Diffraction: Introduction

Why Surface Diffraction?





-Higher Ordering (Lorentz factor) and
-High Intensity
-Differentiation In-plane and Out-of-plane
-Small Amounts of Sample needed

IBR

Surface Diffraction

Why Excess Water and not 100 % Humidity?

-Difficult to reach 100 % humidity
(Vapour pressure paradox)
-Difficult to prepare and stabilize the samples at 100 % humidity
-Excess Water => physiological conditions
-Interaction with Proteins and Peptides

History:

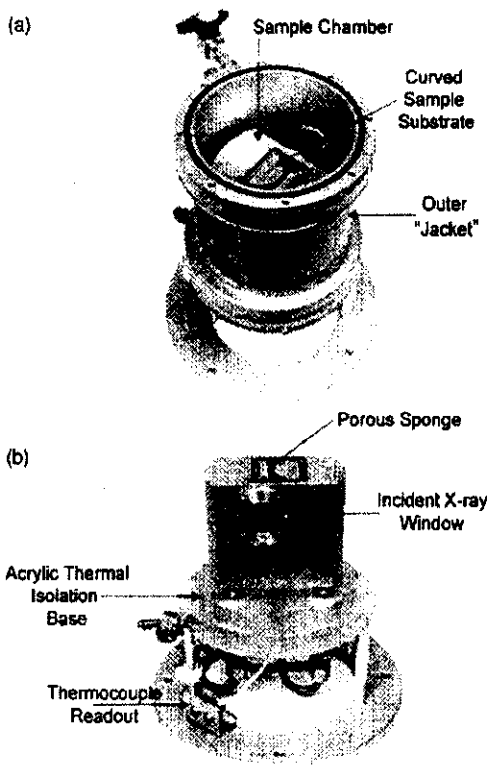
-Fringeli (1977), Bueldt et.al. (1978),
Sirota et.al. (1988),Smith et.al. (1988),
and.....
-J.Katsaras Biophysical Journal 73, 2924(1997)

AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

Surface Diffraction

Sample cell providing 100% relative humidity

(J.Katsaras, M.J.Watson, (2000) Rev.Sci.Instrum 71,1737



Sketch of the sample cell

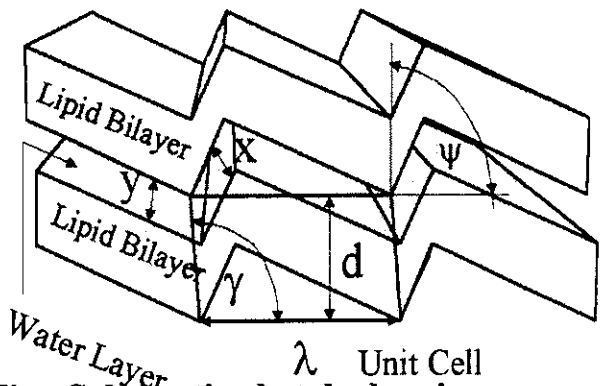
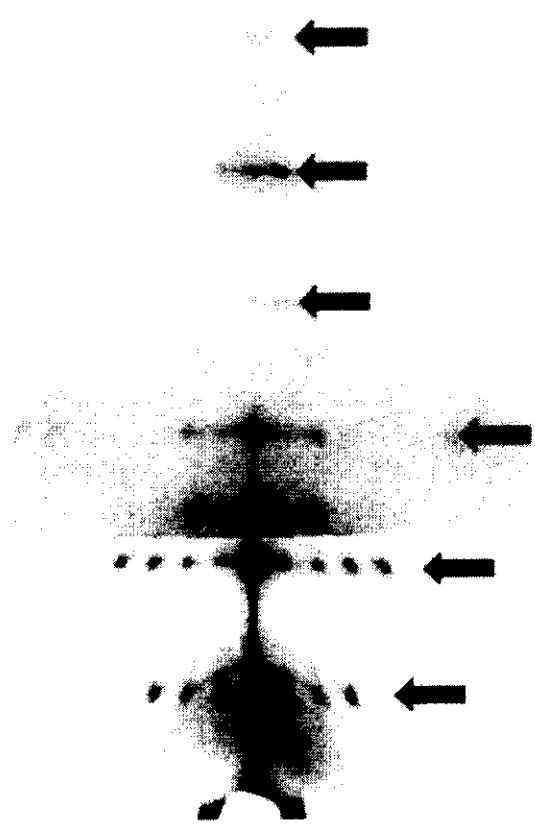


Fig. Schematic sketch showing asymmetric rippled bilayer,



Surface diffraction pattern of the ripple phase of DPPC at 39 °C: metastable (d=82.2 Å, λ=255 Å, g=90 °) and stable (d=68.3 Å, λ=144 Å, g=92 °) J.Katsaras et.al., (2000), Phys.Rev.E 61, 5668

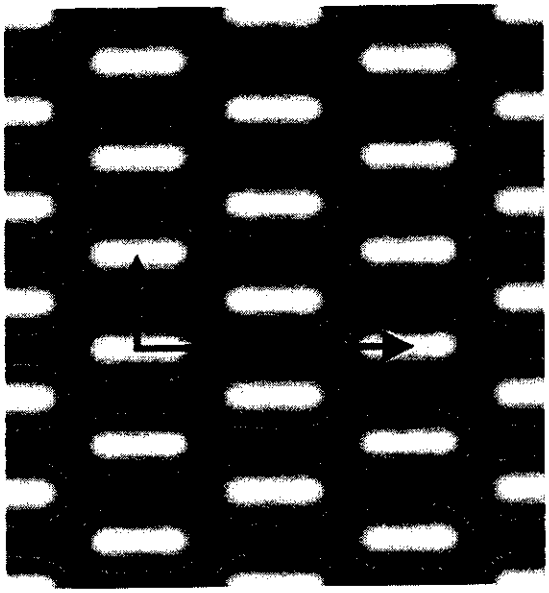
AUSTRIAN SAXS - BEAMLINE AT ELETTRA

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

Surface Diffraction

A. Tardieu, V. Luzzati and F.C. Reman (1973)*:

DLPC @ 121 °C; c = 100 %: The P_{δ}-Phase



a = 116.5 Å, b = 38.5 Å

a' = 61.2 Å, b' = b, γ = 109°

h, k	F(h,k)
2, 0	12.6
1 ,1 & 1, -1	18.5
4, 0	-6.6
3, 1 & 3, -1	-5.5
5, 1 & 5, -1	1.45
6, 0	2.1
0, 2	2.1
2, 2 & 2, -2	-0.85
4, 2 & 4, -2	0.55
7, 1 & 7, -1	-0.4

h, k	F(h,k)
1, 0	12.6
0, 1 & 1, -1	18.5
2, 0	-6.6
1, 1 & 2, -1	-5.5
2, 1 & 3, -1	1.45
3, 0	2.1
1, -2	2.1
0, 2 & 2, -2	-0.85
1, 2 & 3, -2	0.55
3, 1 & 4, -1	-0.4

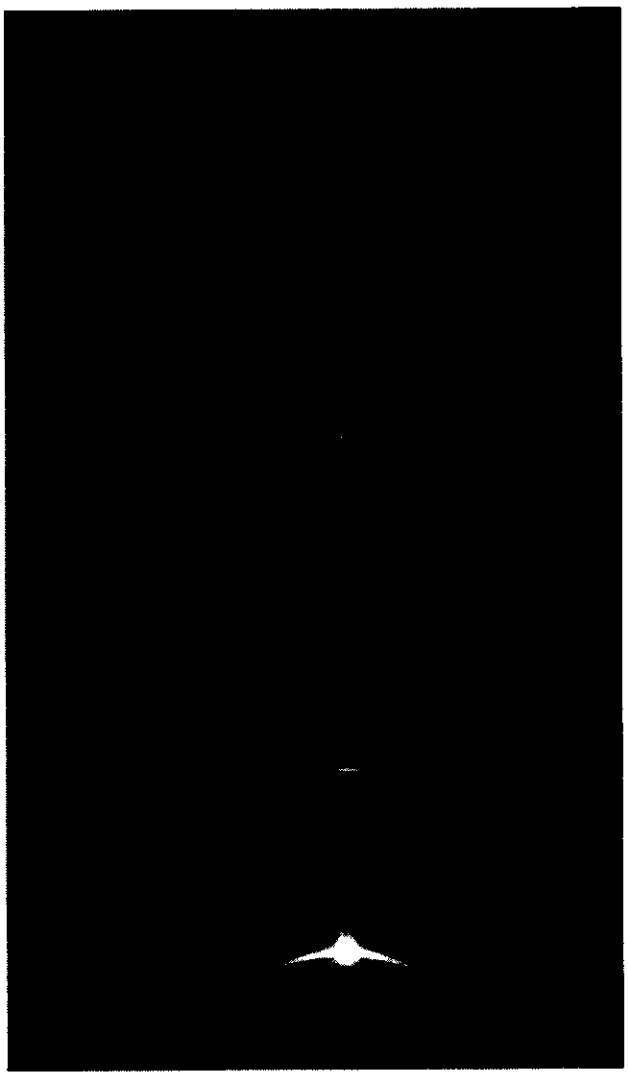
J. Mol. Biol.* **75: 711-733 (1973)

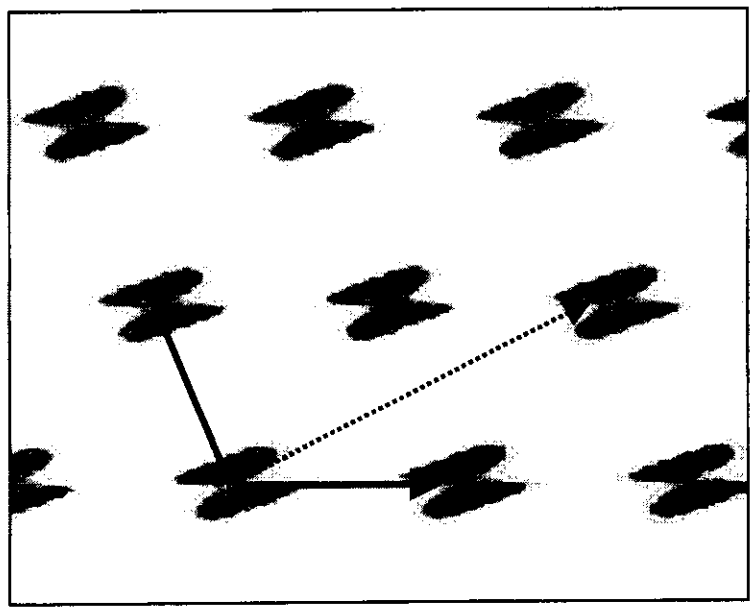
AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

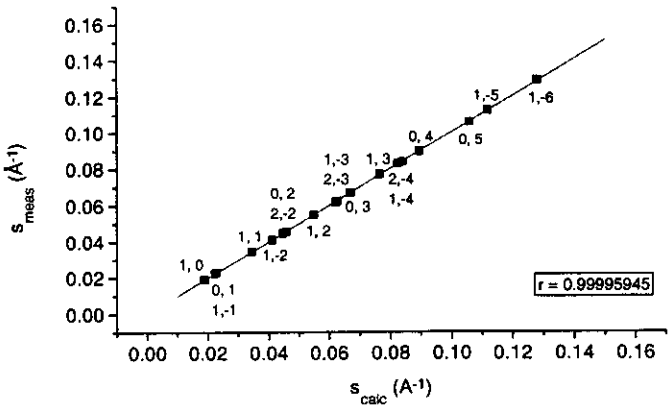
Surface Diffraction

H. Amenitsch, M. Rappolt & P.Laggner (2000)

DOPC @ RT ; c = 100 %: The P_{δ}-Phase







AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

Surface Diffraction Cell

Cell:

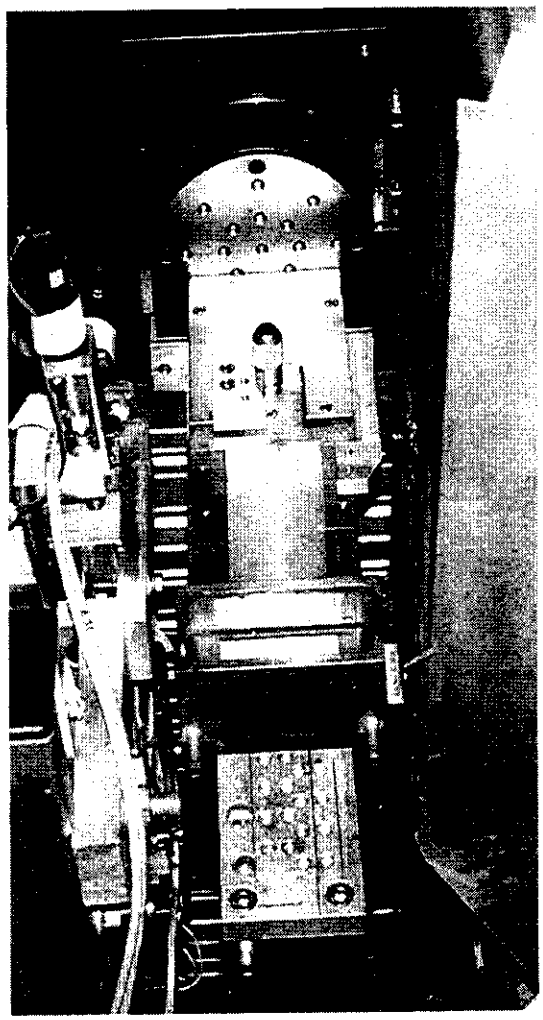


Fig.: Photo of surface diffraction cell at the Austrian SAXS beamline at ELETTRA, Trieste, Italy

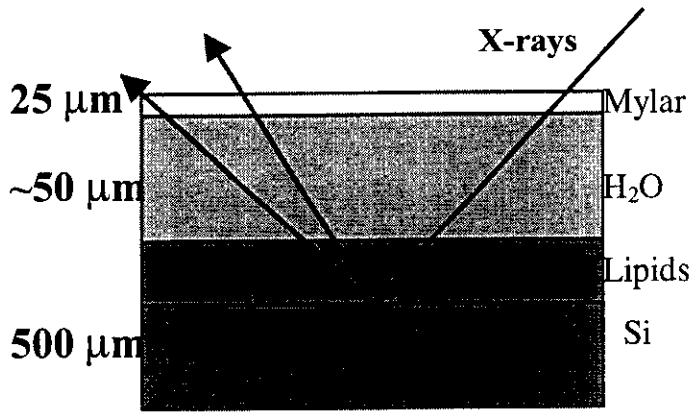
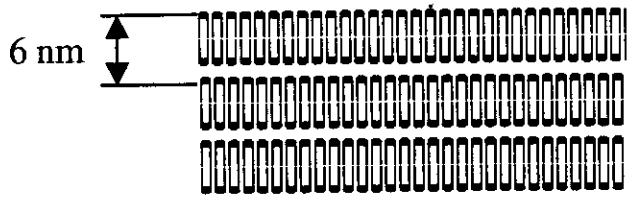


Fig.: Surface diffraction cell for studying aligned lipids under excess water conditions or varying solvent conditions (neutrons: J.Katsaras, (1997), Biophysical Journal, 73, 2924)

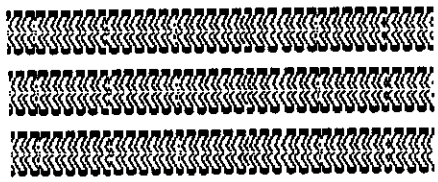
AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

Surface Diffraction Cell

L_β „Gel-Phase“



L_α „Liquidcrystaline-Phase“



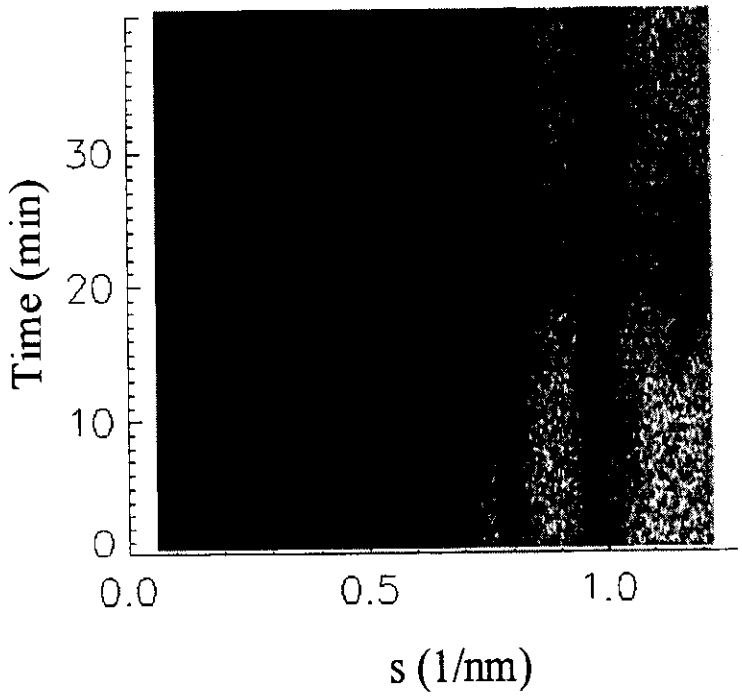
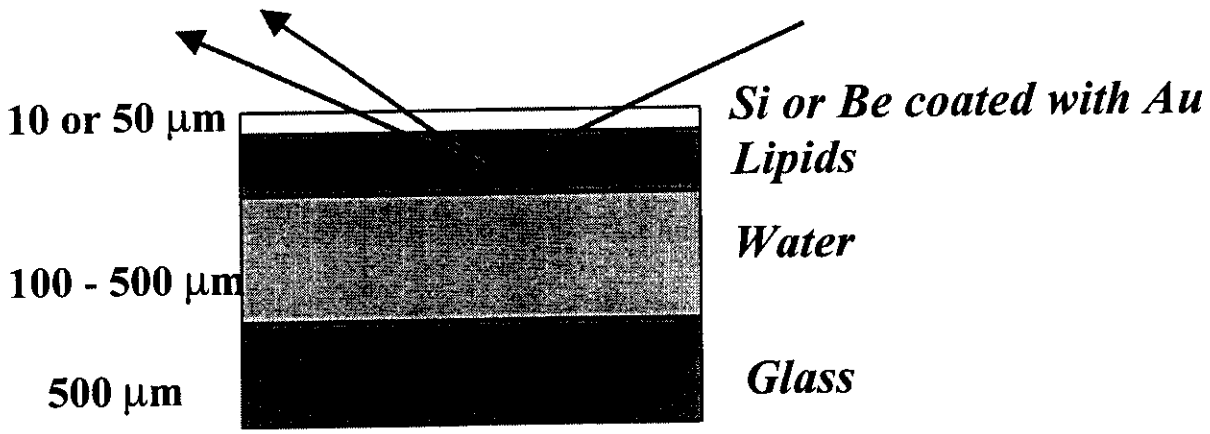
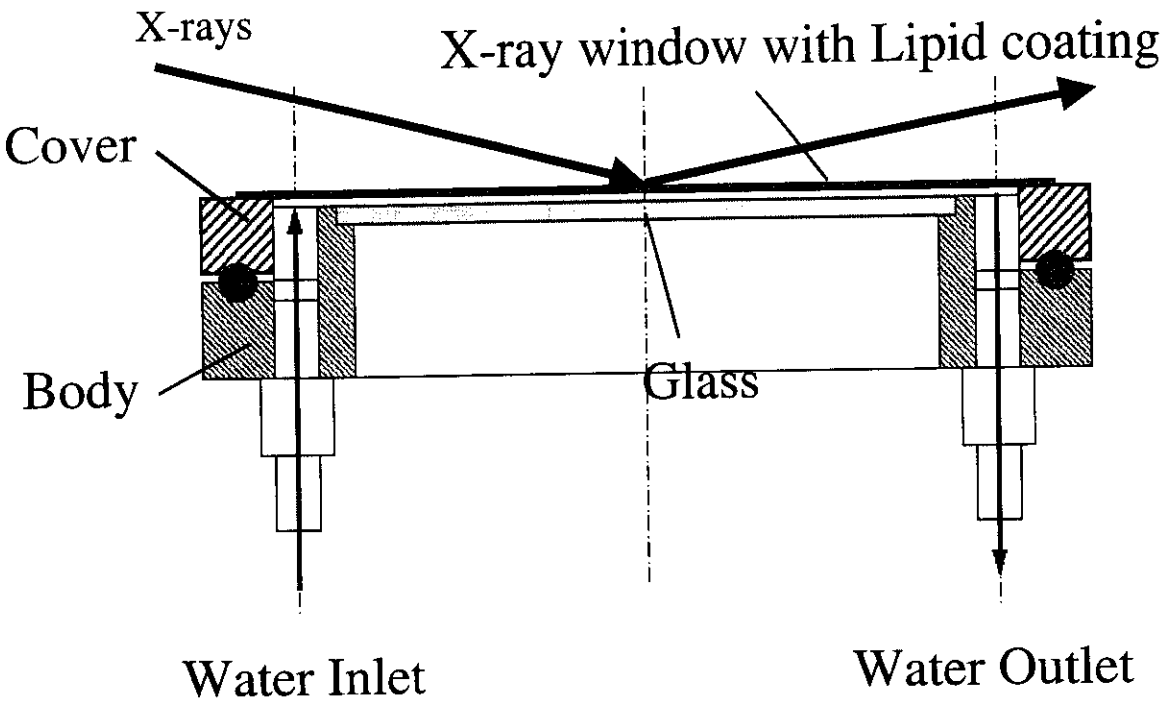


Fig.: Surface diffraction pattern of SOPE heated from 20 - 40 - 20 °C with a rate of 1°C/min showing the diffraction peaks from the 2nd to the 6th order at fixed incidence angle ω (1.2°). The upper resolution limit was just given by the dimension of the vacuum tube and the detector length. The phase transition L_β - L_α- L_β is clearly visible.

AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

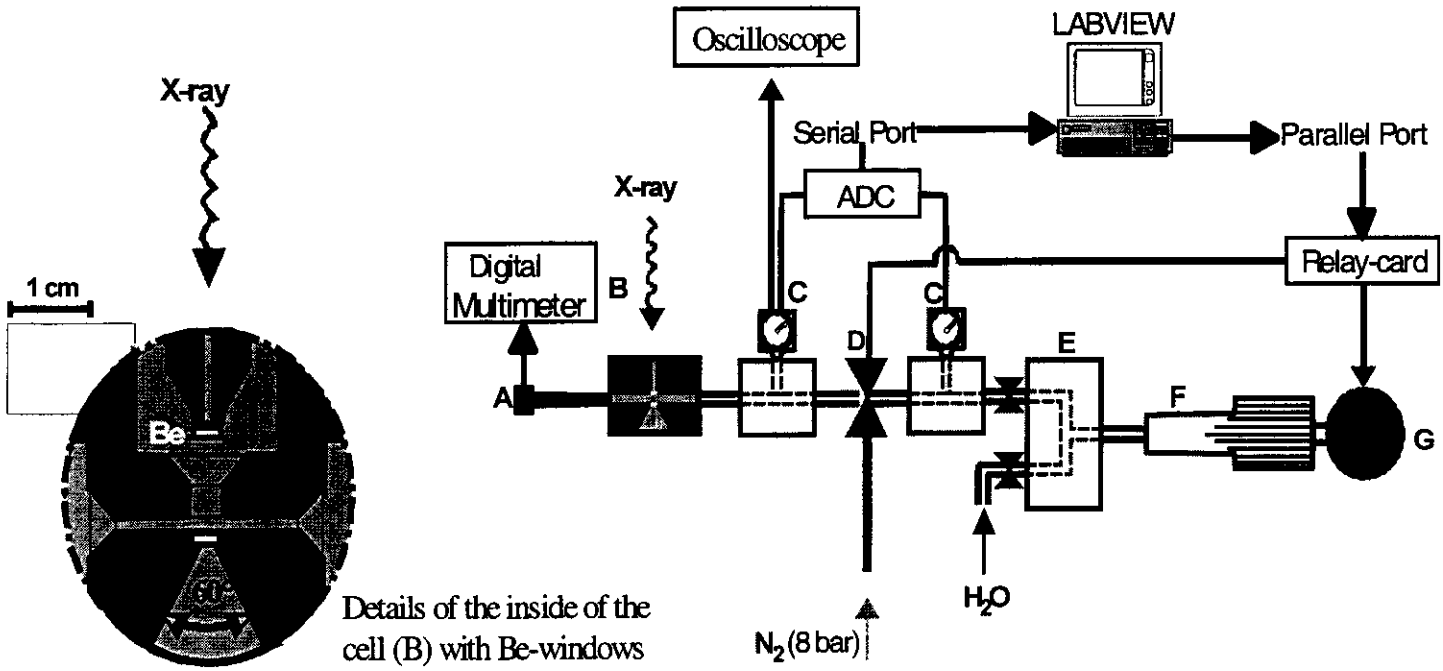
Surface Diffraction Cell





AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

High Pressure Surface Diffraction Cell

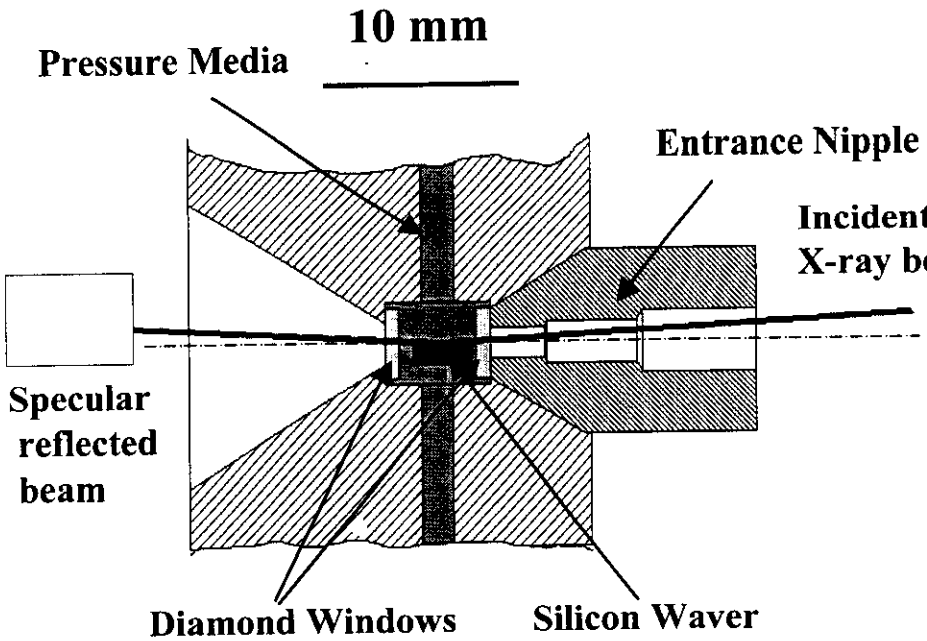


Set-up of the p-jump experiment: Thermocouple (A), high pressure X-ray cell (B), pressure sensors (C). Two pressure-circuits are separated by a pneumatic driven valve (D) and are kept at different pressure levels before activating a p-jump, which is accomplished by quickly opening the valve D, resulting in a quick pressure equilibration between both reservoirs within a few milli-seconds. Double-stem valve (E) and a motor(G)-driven pressure pump (F) are used for generating hydrostatic high pressures.

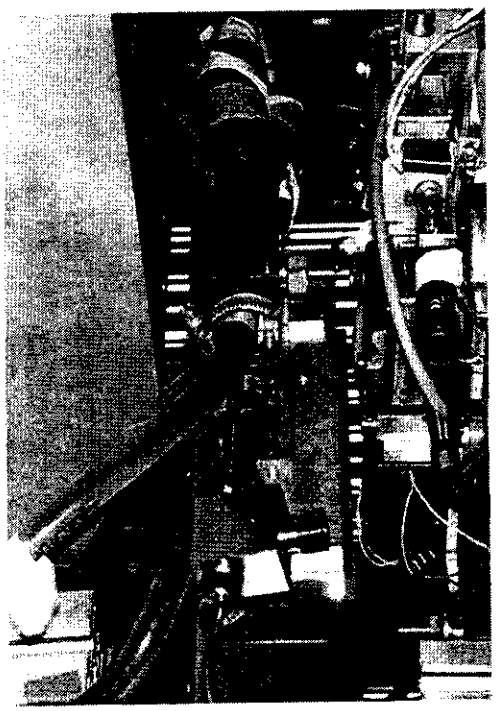
M.Steinhart, M.Kriechbaum, K.Pressl, H.Amenitsch, P.Laggner and S.Bernstorff, Rev.Sci.Instrum. 70, 1540-1545 (1999).

AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

High Pressure Surface Diffraction Cell



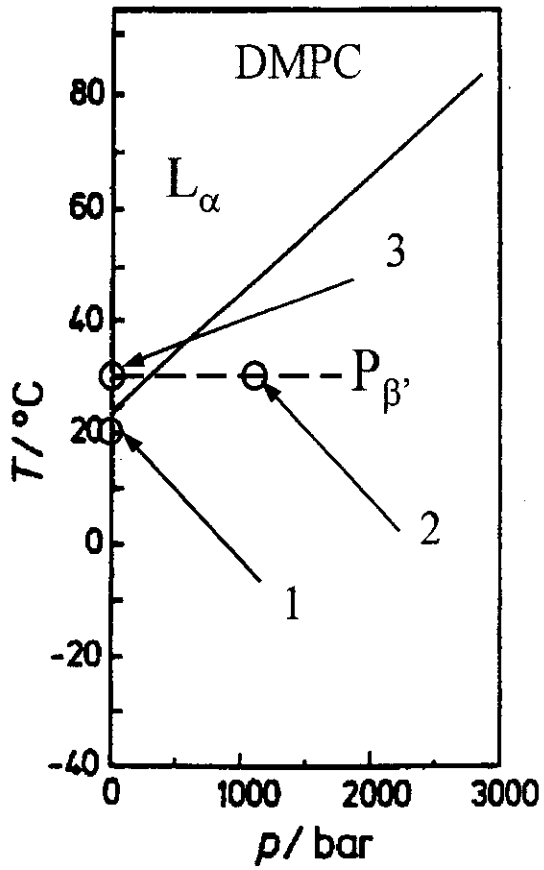
Sketch of the Surface Diffraction High Pressure Cell



- X-ray energy: 16 keV
- Diamond windows: 0.75 mm thick
- Beam size: 0.5 x 0.2 mm^2
- max incidence angle: 4°
- exit aperture: 60° total
- sample surface: 3 x 3 mm
- p : 0-3 kbar
- temperature range: 0-80 °C

AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

High Pressure Surface Diffraction Cell



P-T diagram for DMPC taken from:
R. Winter, A. Gabke, J. Erbes, and C. Czeslik. Pressure Effects on Lyotropic Lipid Mesophases and Model Membrane Systems - Effects on the Structure, Phase Behaviour and Kinetics of Phase Transformations. IN High Pressure Molecular Science, R. Winter and J. Jonas (Eds.). Kluwer Academic Publishers, Dordrecht, Netherlands, 1999, p 369-404.

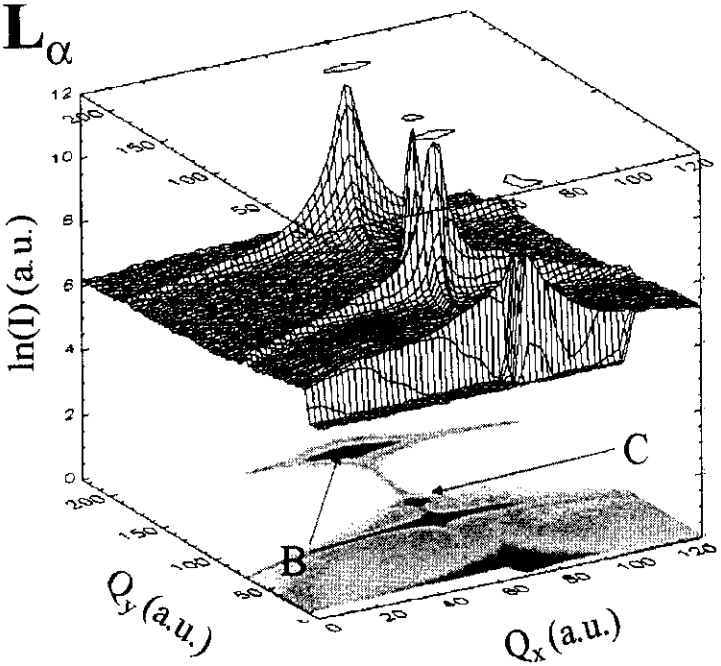
Phase of DMPC	Point	Temperature /°C	Pressure /bar	d-spacing /nm
L_α	3	30	1	6.47
$P_{\beta'}$ cooling from 30 °C	1	20	1	7.06
$P_{\beta'}$ pressurizing from 1 bar	2	30	1080	7.38

Table 1. Liquid crystalline and stable ripple phase of DMPC.

AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

High Pressure Surface Diffraction Cell

L_α



$P_{\beta'}$

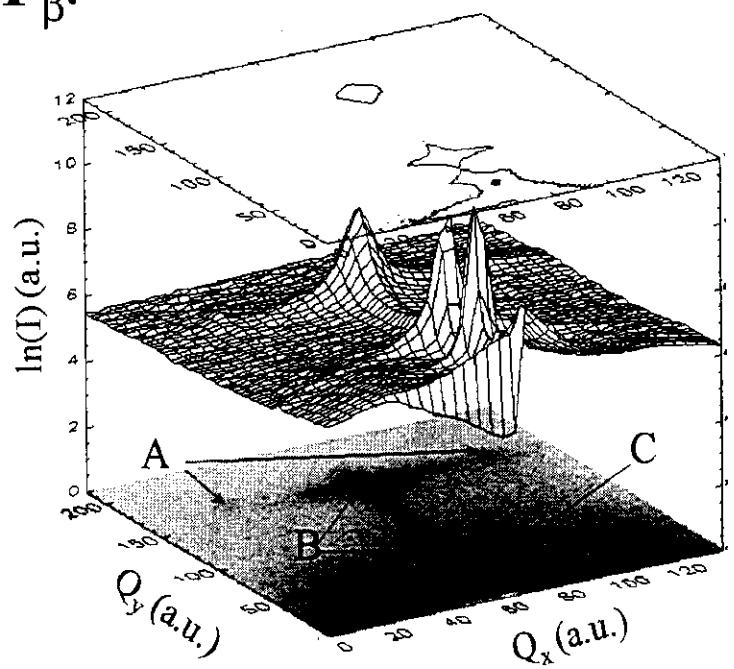


Fig.: Diffraction pattern of a highly aligned lipid (DMPC) in the L_α and $P_{\beta'}$ Phase at constant grazing angle at 30 °C and 20 °C.

A shows the in-plane reflections due to the ripple structure (distance λ)

B gives the off-plane reflections due to the lamellar repeat distance d

C denotes the specular reflectivity peak

AUSTRIAN SAXS - BEAMLINE AT ELETTRA

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

High Pressure Surface Diffraction Cell

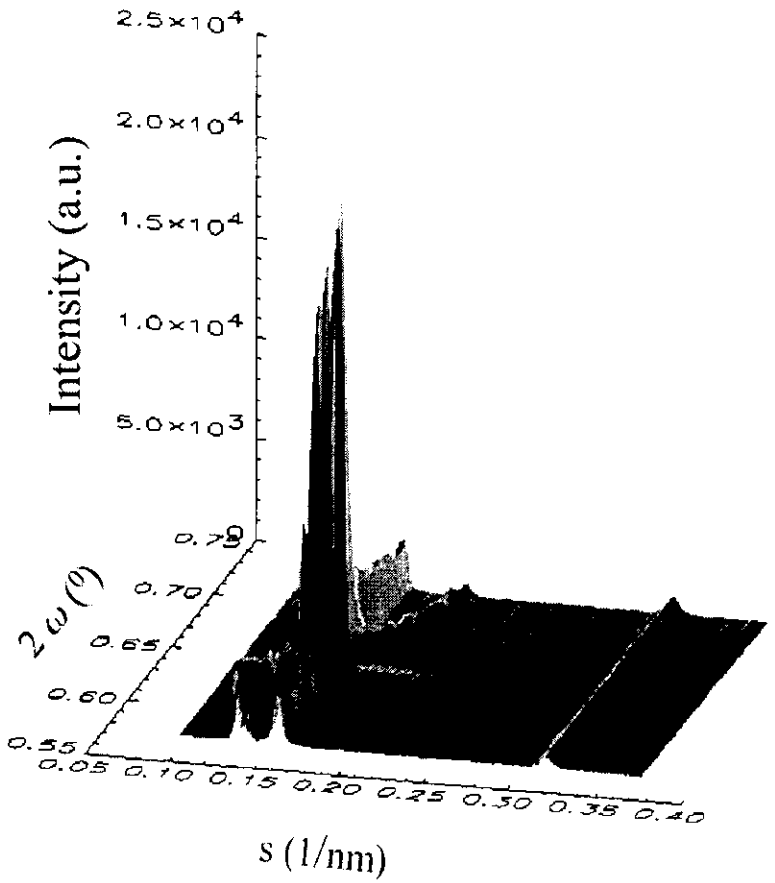


Fig.: Diffraction pattern of a highly aligned lipid (DMPC) in the L_α Phase at 30 °C during the ω-scan. FWHM of ω-scan: < 0.03°.

AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

High Pressure Surface Diffraction Cell

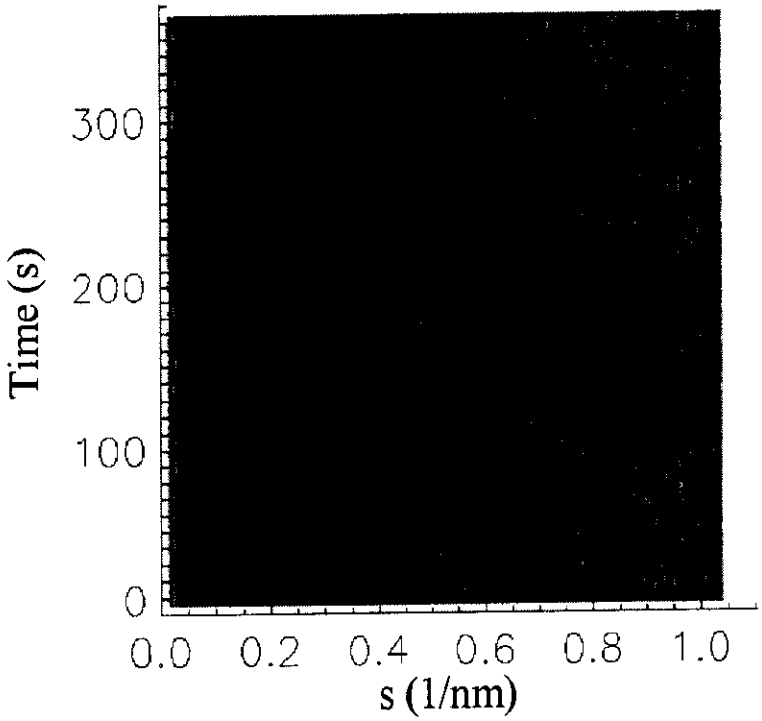
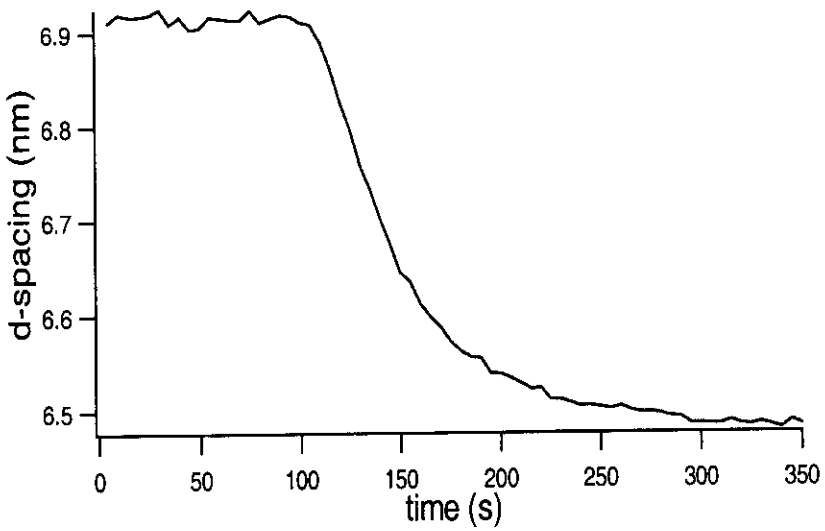


Fig.: Diffraction pattern of a highly aligned lipid (DMPC) in the L_α Phase on heating between 20 and 30 °C (at constant ω).



AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

High Pressure Surface Diffraction Cell

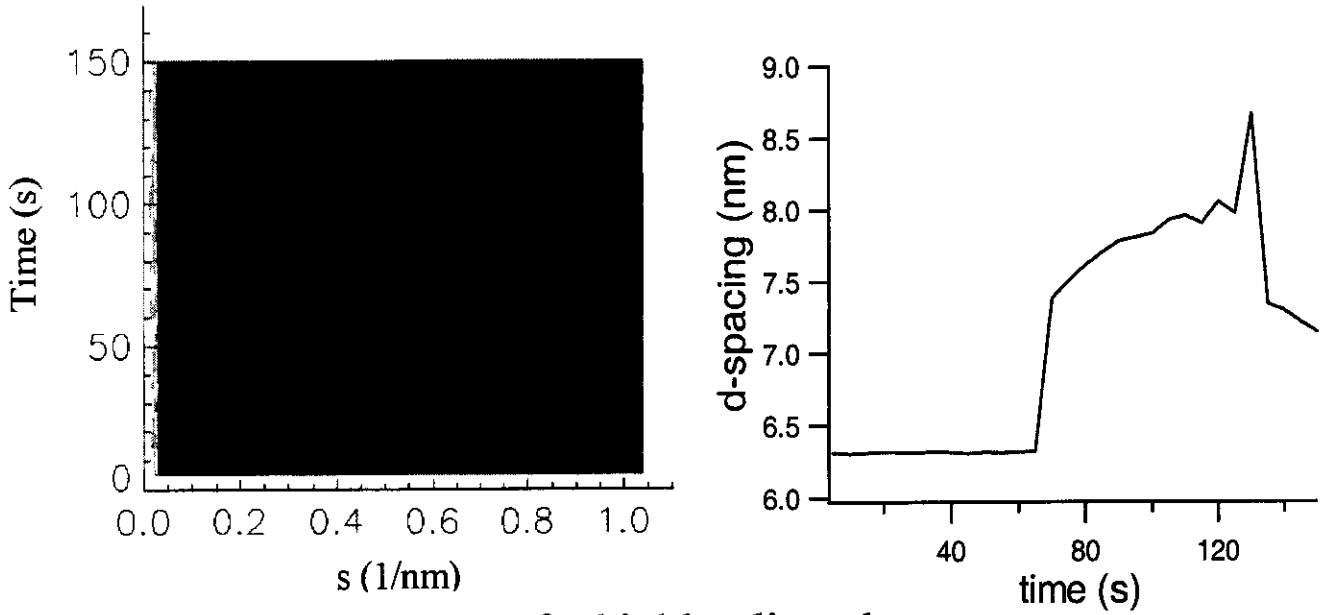
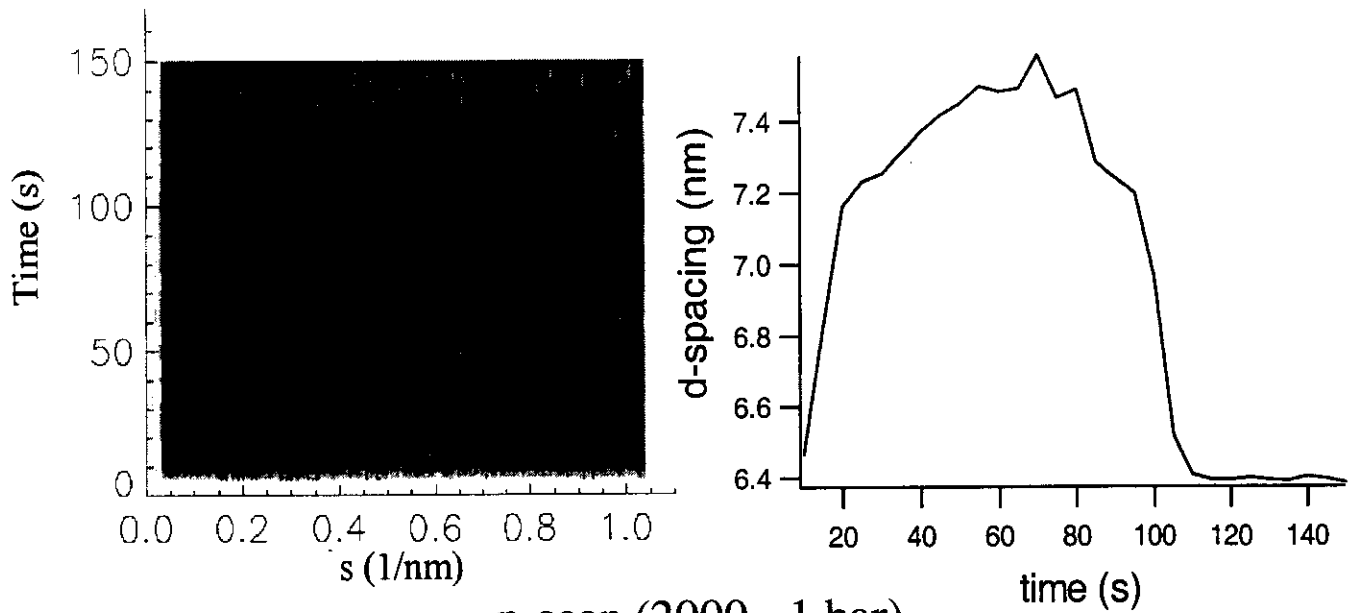


Fig.: Diffraction pattern of a highly aligned lipid (DMPC) at 30 °C: p-scan (1 - 1736 bar)



p-scan (2000 - 1 bar)

AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

High Pressure Surface Diffraction Cell

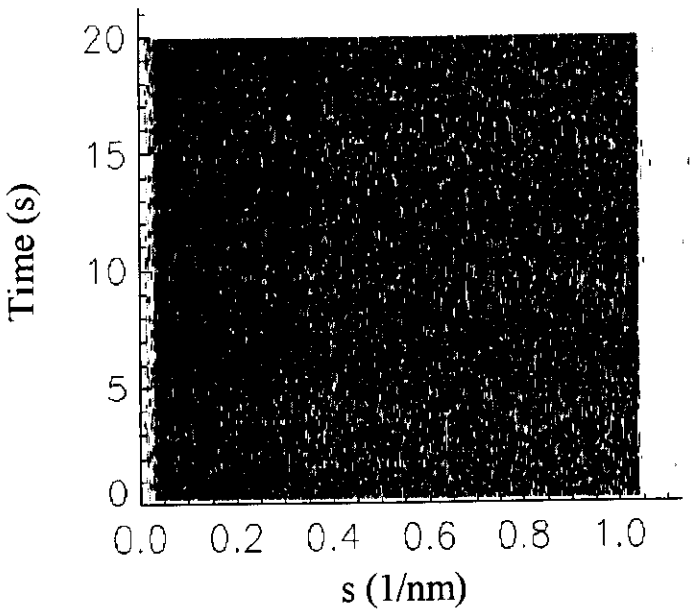


Fig.: Diffraction pattern of a highly aligned lipid (DMPC) at 25 °C on p-jump between 1700 - 1 bar.

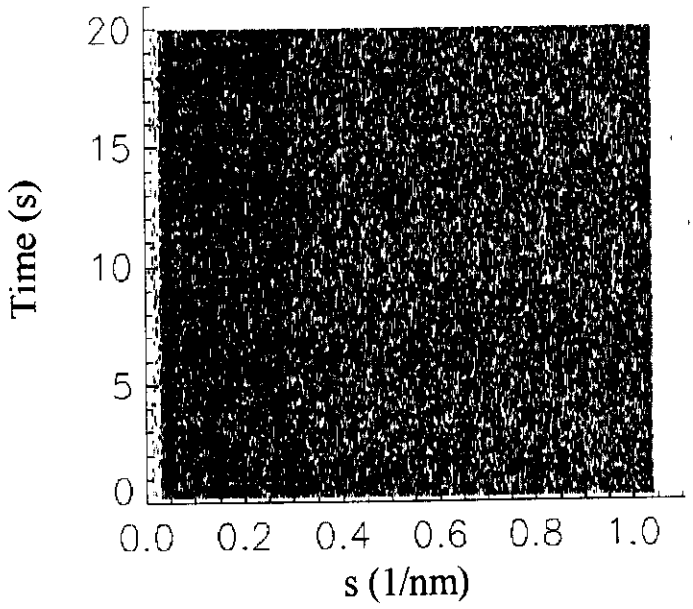


Fig.: Diffraction pattern of a highly aligned lipid (DMPC) at 25 °C on p-jump between 1 - 600 bar.

AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

Surface Diffraction: Conclusion

Why surface diffraction?

-additional information

-physiological conditions

-high pressure and aligned lipids

Future in surface diffraction?

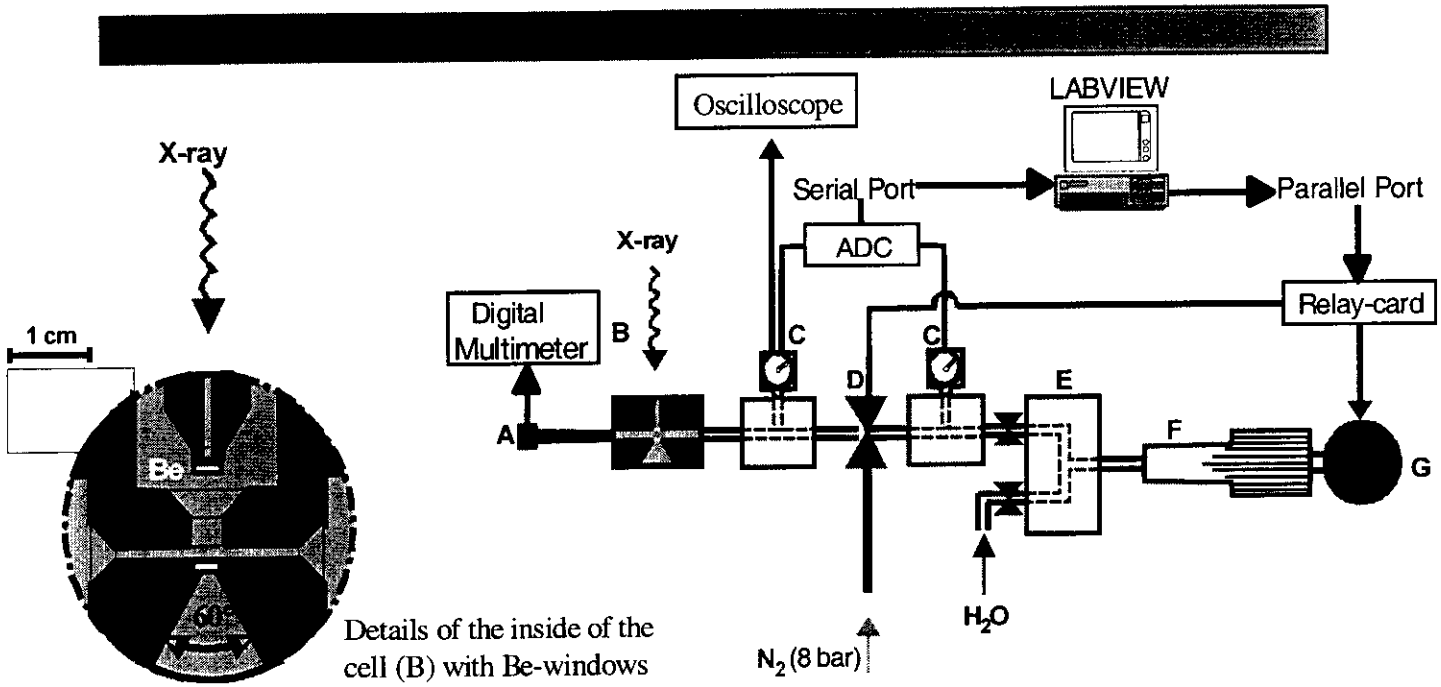
-self assembly of aligned systems

-flow shear alignment

-insertion of membrane active peptides or channel proteins and interaction

AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

High Pressure Cell



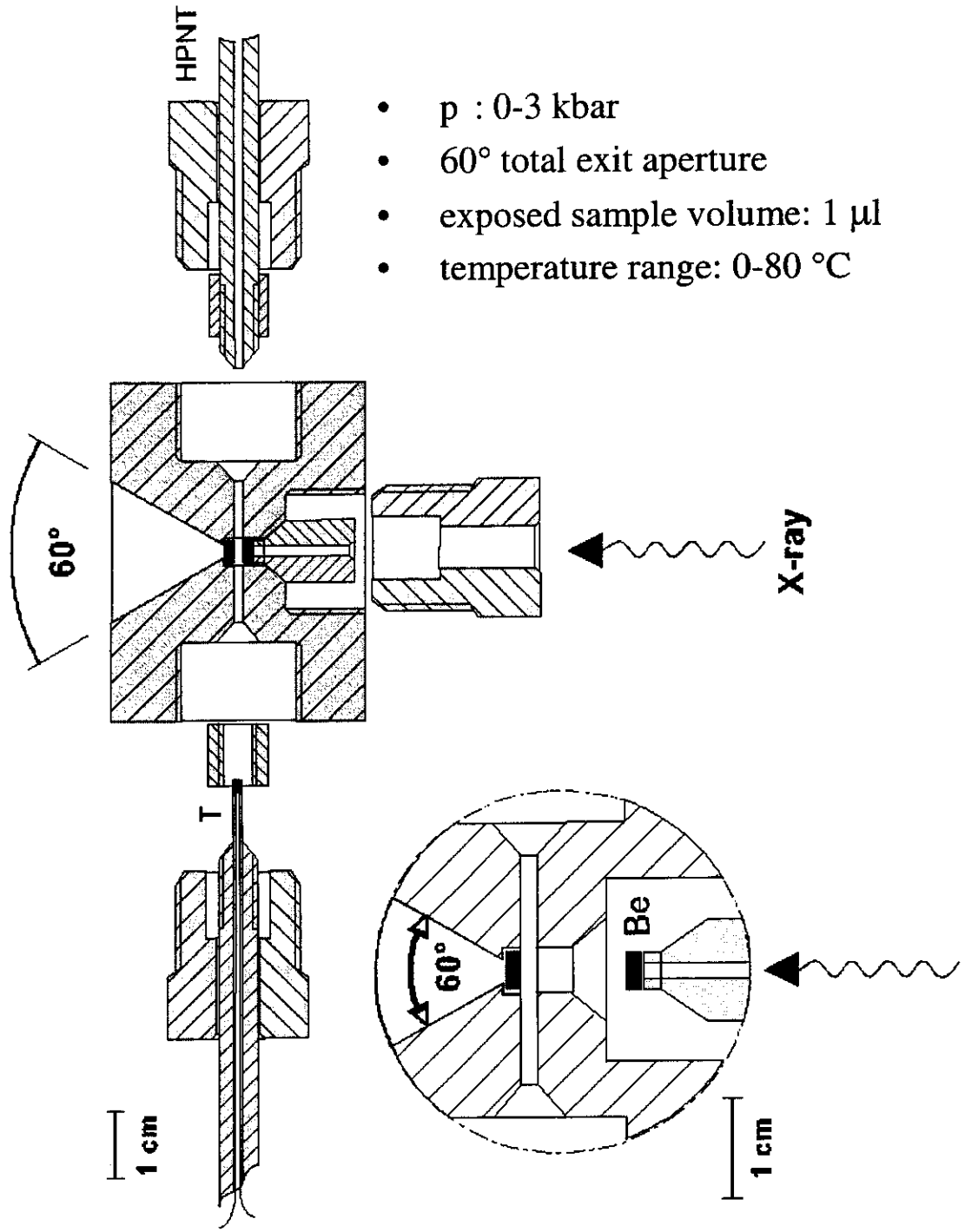
Set-up of the p-jump experiment: Thermocouple (A), high pressure X-ray cell (B), pressure sensors (C). Two pressure-circuits are separated by a pneumatic driven valve (D) and are kept at different pressure levels before activating a p-jump, which is accomplished by quickly opening the valve D, resulting in a quick pressure equilibration between both reservoirs within a few milli-seconds. Double-stem valve (E) and a motor(G)-driven pressure pump (F) are used for generating hydrostatic high pressures.

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

AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

SAXS - APPLICATIONS

high pressure cell



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

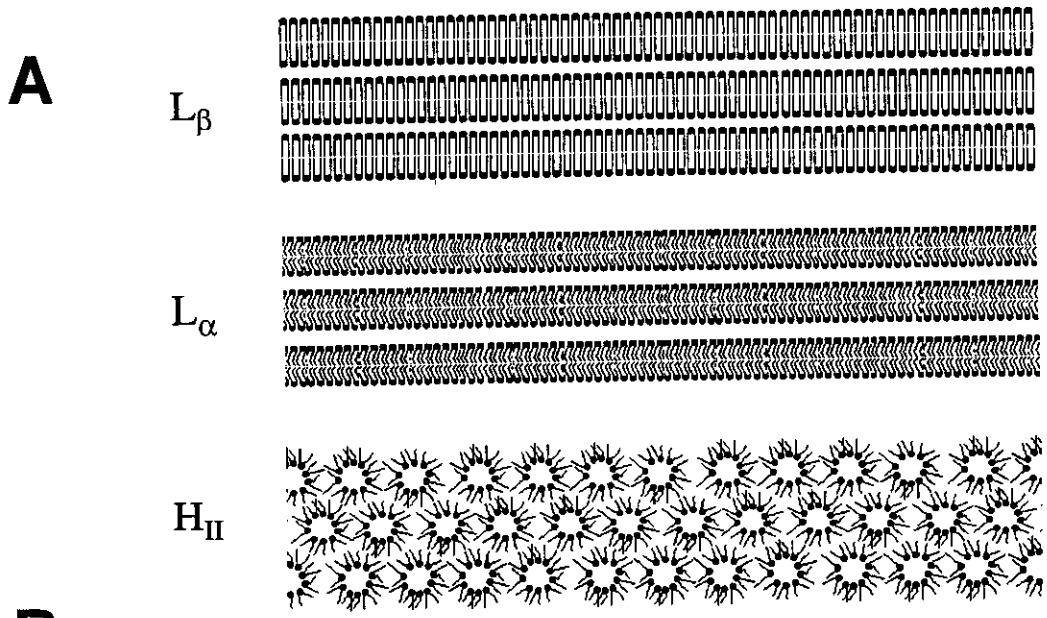
AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

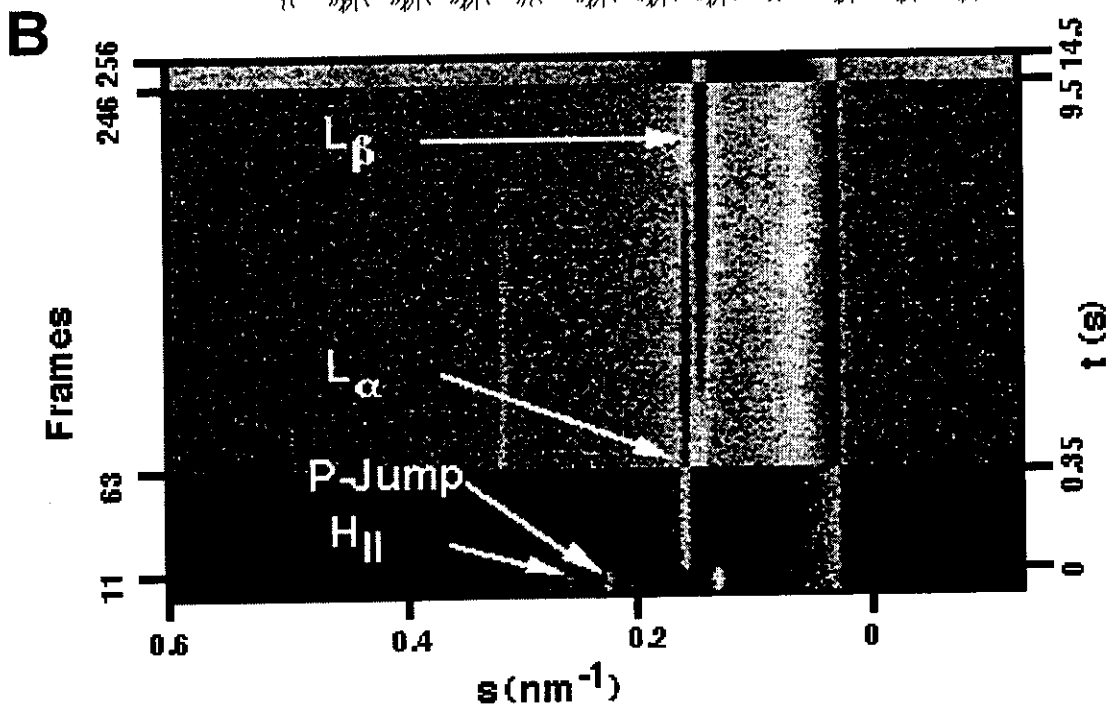
SAXS - APPLICATIONS

high pressure cell

EXAMPLE: 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





AUSTRIAN SAXS - BEAMLINE AT ELETTRA

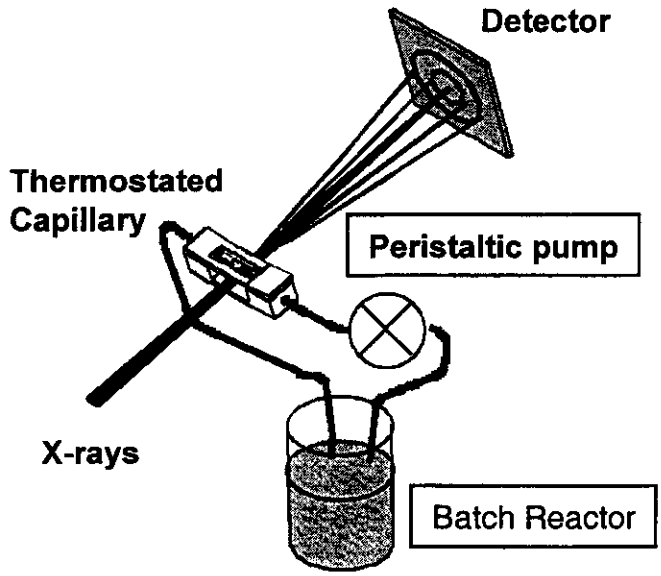
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

SAXS - APPLICATIONS
Batch Reactor

Insitu study of the Formation of the MCM-41 Structures
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

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

Experimental set-up



TEOS, C_{16}TAB (+Co-surf.), NH_3, H_2O

TEOS Tetraethylorthosilicate
C_{16}TAB Hexadecyltrimethylamonium bromide

Results:

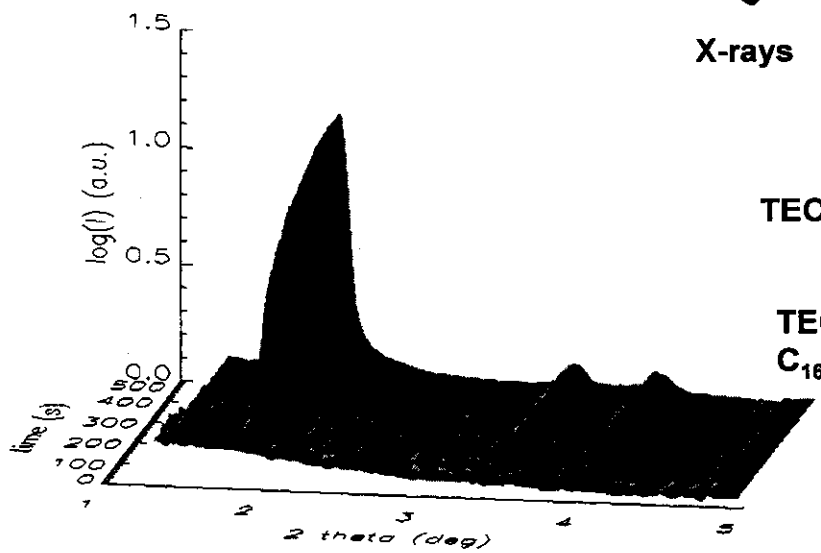


Fig. : Time-resolved diffraction pattern of the TEOS synthesis
Time resolution: 0.3 s/frame, Transition: micellar solution - ordered phases (standard synthesis: hexagonal D = 4.67 nm)

AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

MCM-41 and MCM-50

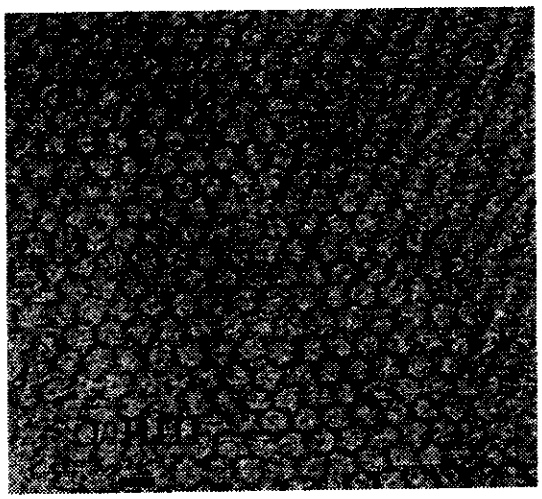


Fig. Representative electron transmission micrograph of a MCM41 structure depicting the mesoporous hexagonal nano-structure.

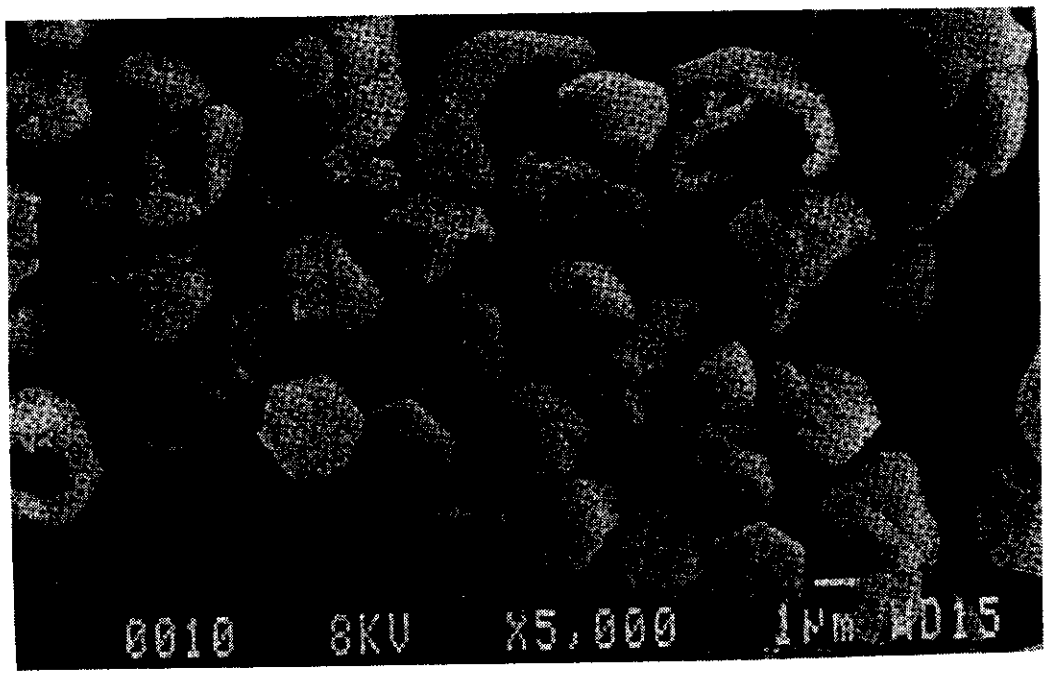


Fig. Scanning electron micrograph of a MCM-41 sample showing the micro-structure formed during the preparation of such Samples (both taken from C.T.Kresge, Nature (1992), 349, 710-712)

AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

MCM-41 and MCM-50

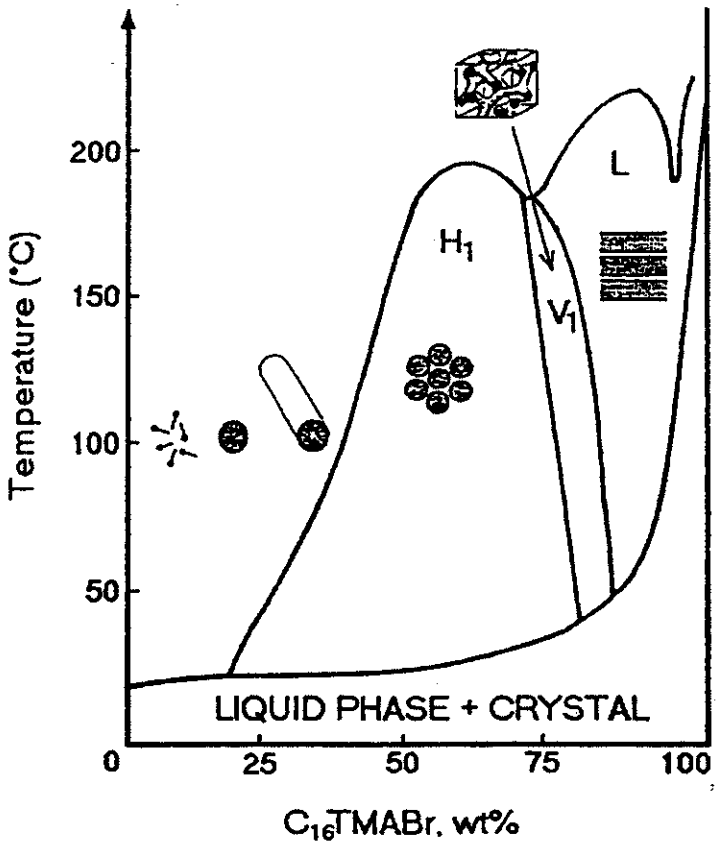


Figure 2. Schematic phase diagram of C_{16}TMABr in water [44].

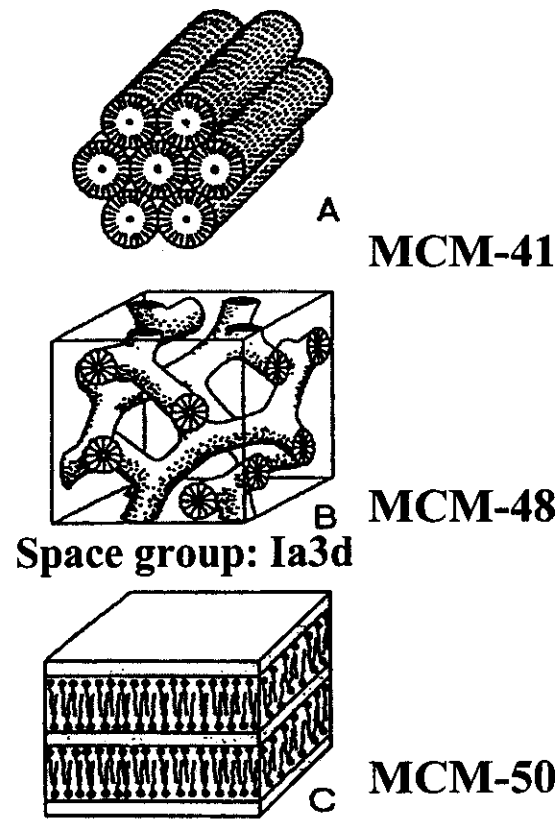


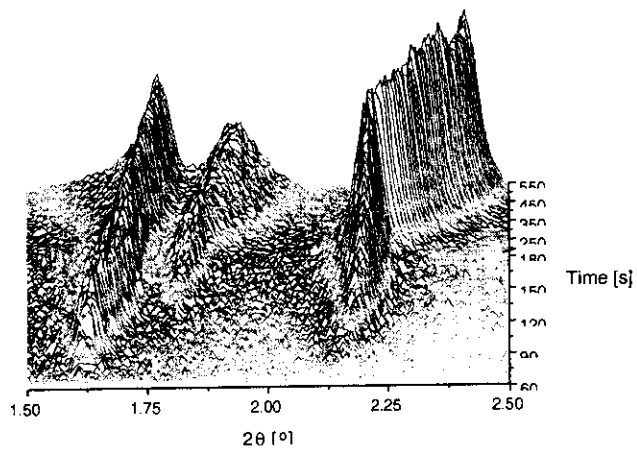
Figure 3. Schematic representation of liquid-crystal structures, (A) hexagonal, (B) bicontinuous cubic, (C) lamellar.

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

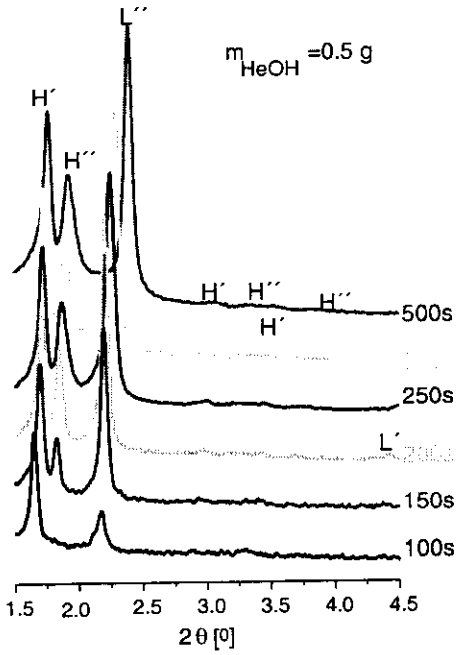
AUSTRIAN SAXS - BEAMLINE AT ELETTRA

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

MCM-41 and MCM-50: Measurements



a)

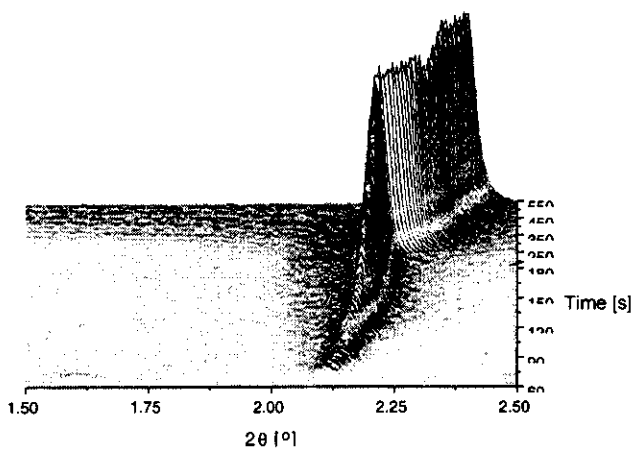


b)

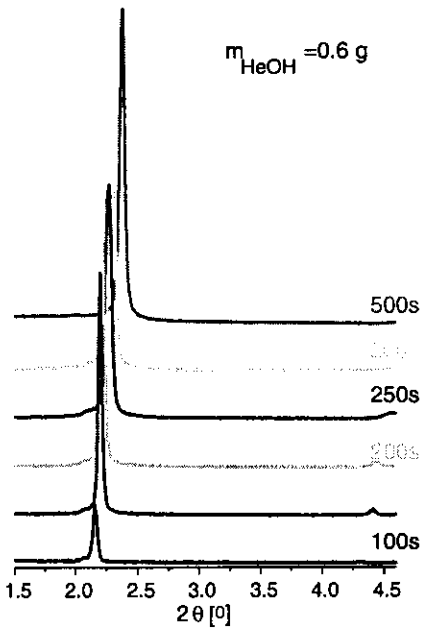
Fig. Diffraction pattern with 0.5 g hexanol as co-surfactant. H', H´´ denotes the hexagonal phases (MCM-41) and L' the lamellar phase (MCM-50).

AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

MCM-41 and MCM-50: Measurements



a.)



b)

Fig. Diffraction pattern with HeOH (0.6 g) as co-surfactant: lamellar phase (L', MCM-50)

AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

SAXS - APPLICATIONS
Batch Reactor: Model for MCM-41

Model for Mesophase Formation in the TEOS/CTAB system

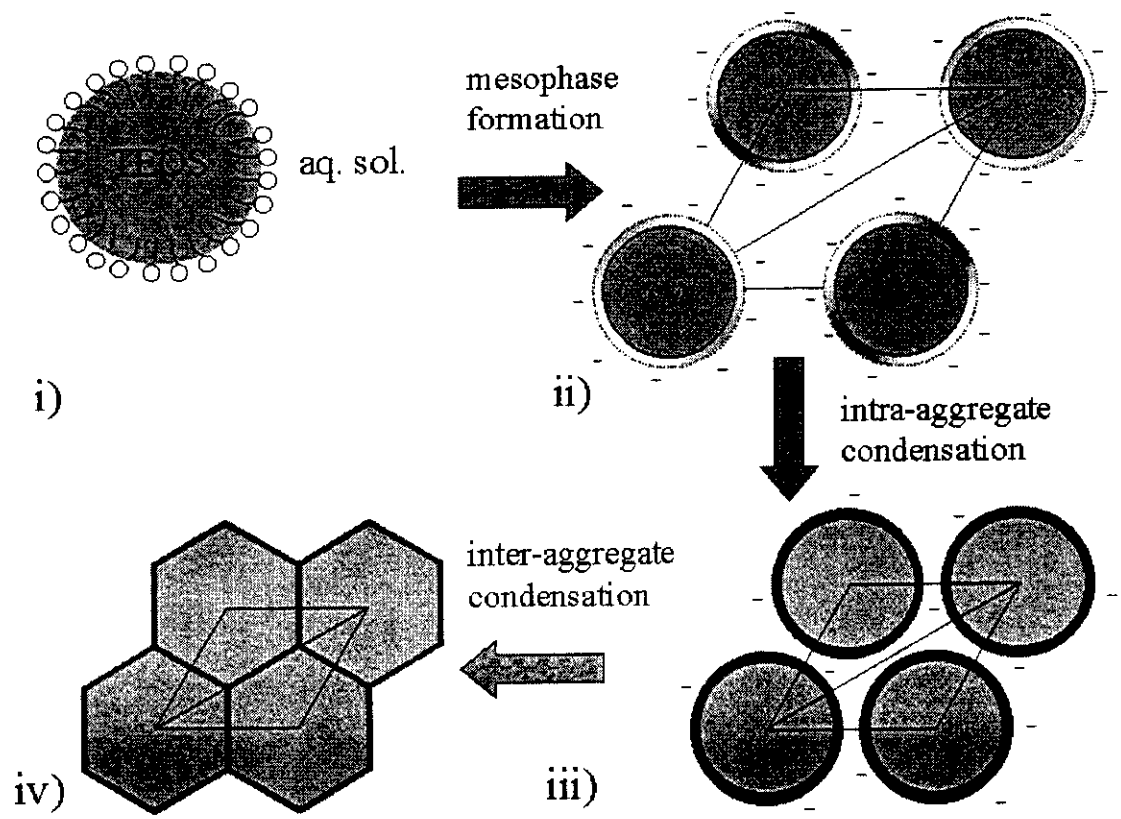


Fig. 5. Schematic presentation of the decrease of the unit cell. i) CTAB emulsifies TEOS in the aqueous solution. ii) Mesophase formation with partially condensed and highly ionized silicate around the surfactant aggregates. iii) Intra-aggregate condensation increases the degree of condensation around the surfactant aggreates and reduces the degree of ionization. iv) Inter-aggregate condensation maximize the inorganic-inorganic contact between the composite aggregates. The decrease of the unit cell has been exaggerated to be better visualized.

AUSTRIAN SAXS - BEAMLINE AT ELETTRA

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

MCM-41 and MCM-50: USANS

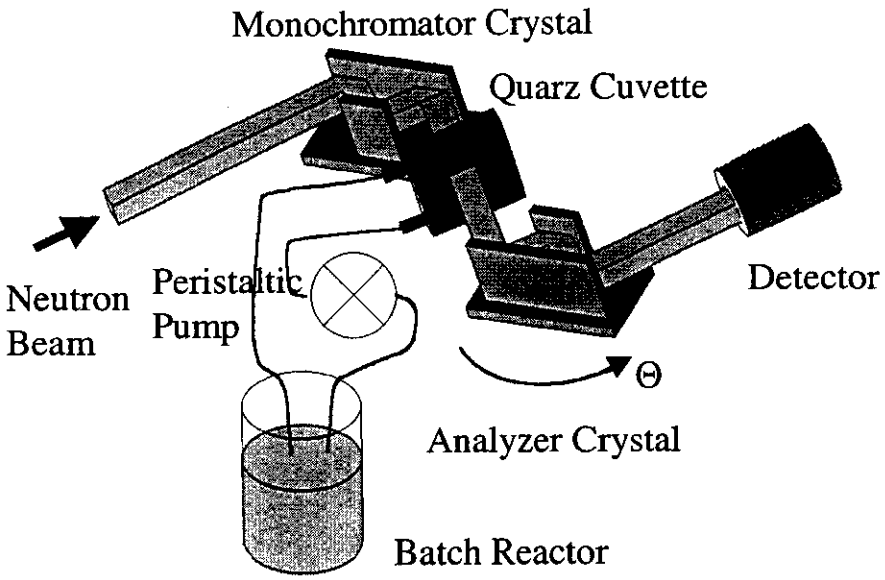


Fig. Schematic sketch of the USANS set-up, showing the Bonse Hart camera with the batch reactor

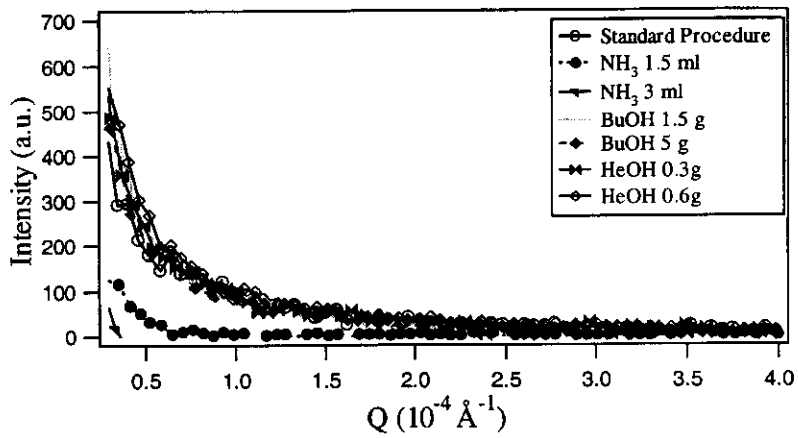


Fig.: Final diffraction pattern of the CTAB/TEOS synthesis of MCM-41(50) mesoporous materials with different cosurfactants

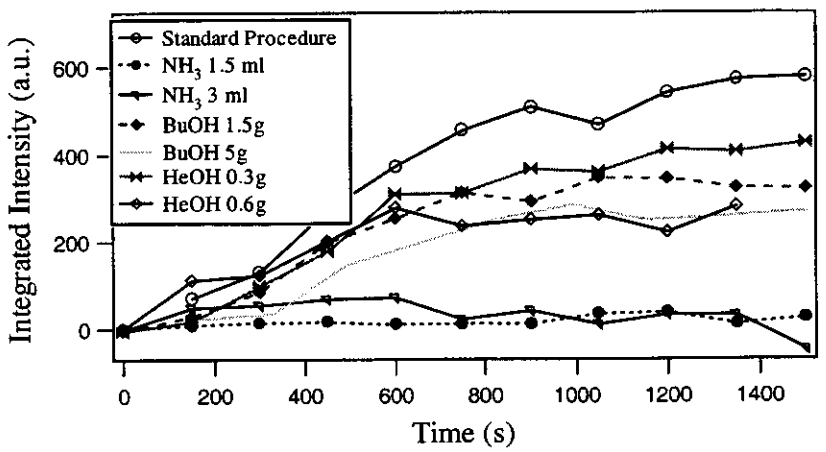
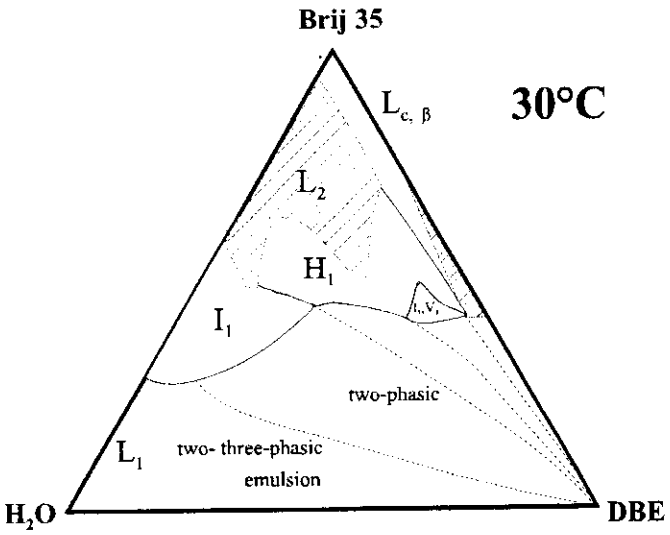
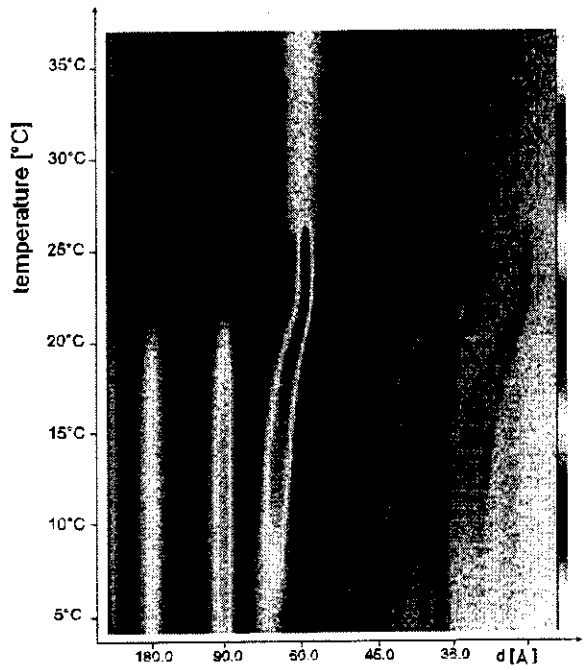


Fig.: Integrated intensities of the diffraction pattern versus time of the CTAB/TEOS synthesis of MCM-41(50) mesoporous materials with different cosurfactants.

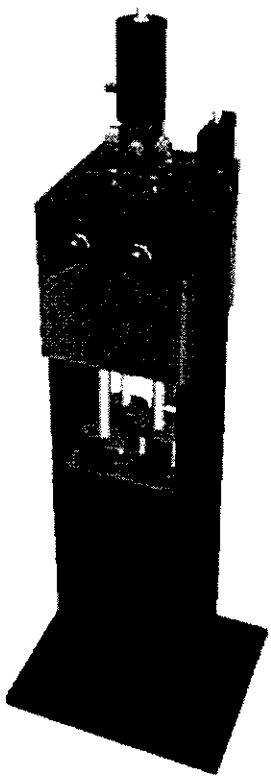
AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

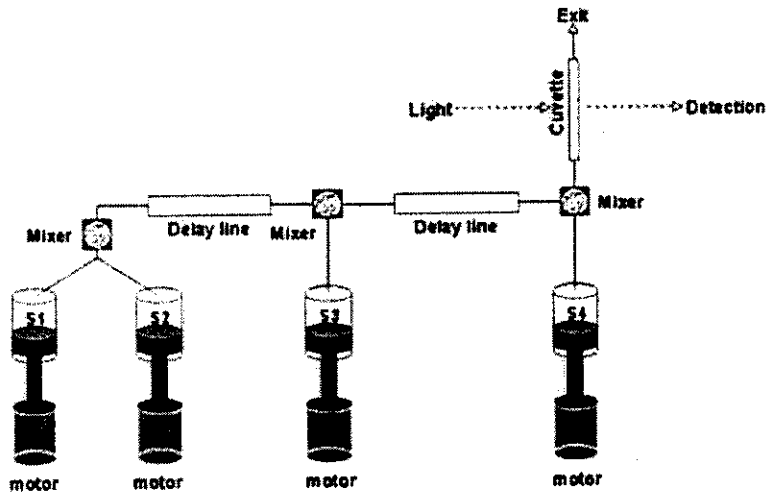
Trends: Combinatorial Supramolecular Chemistry





R.Schwarzenbacher et.al. (1998), J.Phys.Chem.B, 102, 9161





AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner

Summary - Outlook

-Why?

-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!

Think for yourself of new ways to use SAXS and SR

AUSTRIAN SAXS - BEAMLINE AT ELETTRA
H. Amenitsch, S. Bernstorff, P. Dubcek,
G. Pabst, M. Rappolt & P. Laggner