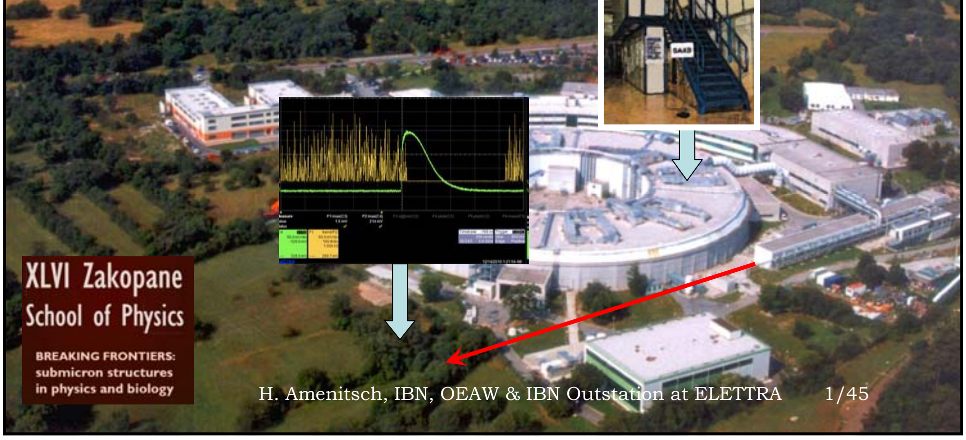
SMALL ANGLE SCATTERING FOR THE CHARACTERIZATION OF NANOSTRUCTURED (BIO-) MATERIALS

Heinz Amenitsch, IBN, Graz, Austria



Layout of Presentation

- What is S(W)AXS?
- How do we do S(W)AXS?

Applications:

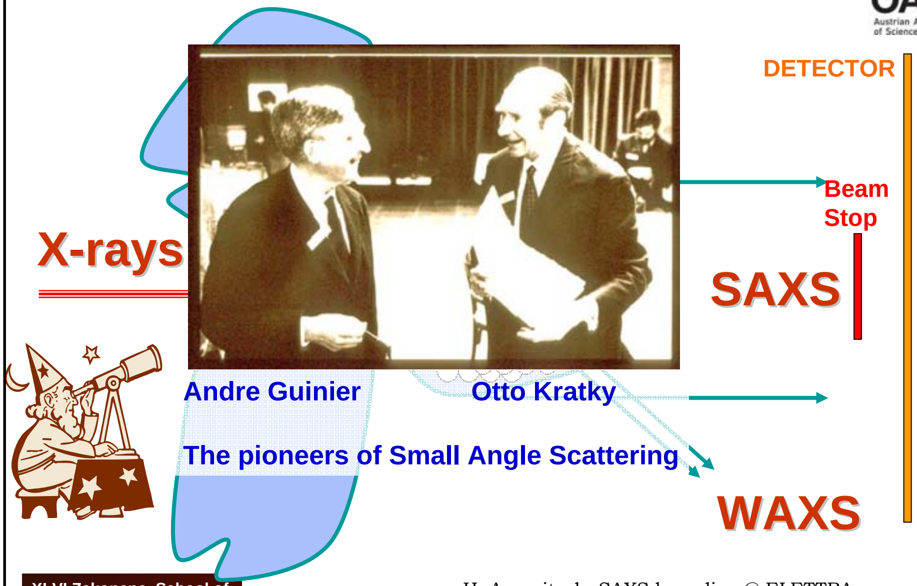
-Solution Scattering

-Model membranes

-Grazing Incidence Studies

-Hierarchical Materials

SAXS and WAXS



SAXS and WAXS

Small – Angle : Supramolecular Envelope

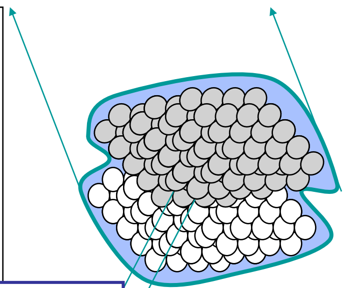
Bragg's law:

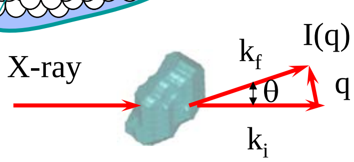
sin θ/2 = λ / 2d

small θ large d

For CuK$_\alpha$ 0.154 nm (8 keV)

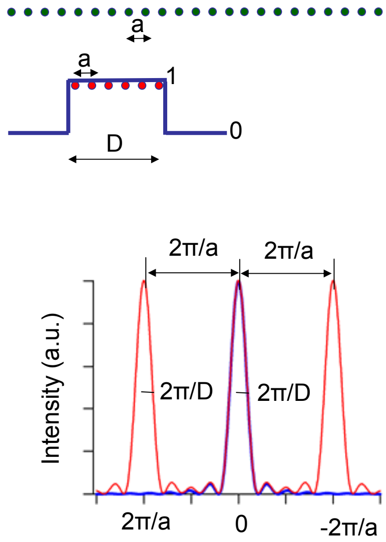
20 deg	0.5 nm
0.9 deg	10 nm
0.09 deg	100 nm



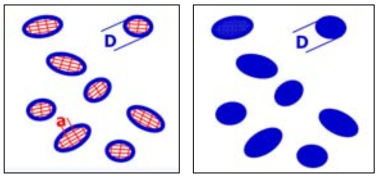


Molecular Lattice

SAXS and WAXS



$$q = \frac{4\pi}{\lambda} \cdot \sin(\theta/2)$$

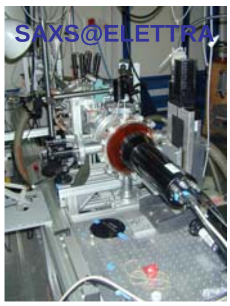


SAXS:
peak width (+ shape) → particle size

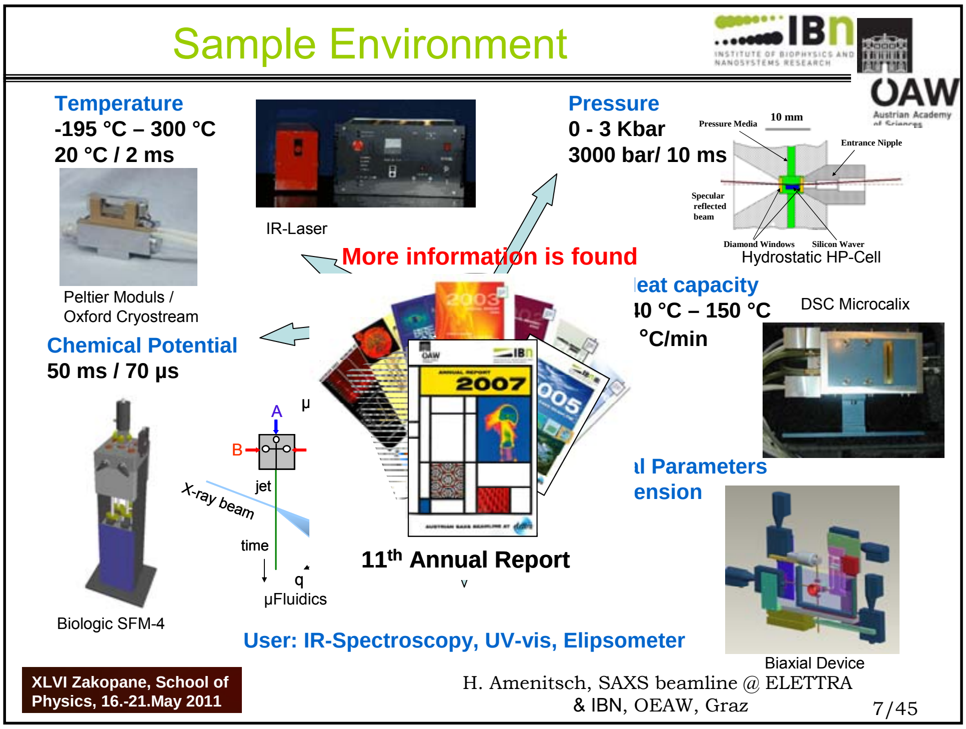
WAXS:
positions → lattice (type, spacings, strain)
width + shape → particle size
+ lattice strain fluctuations

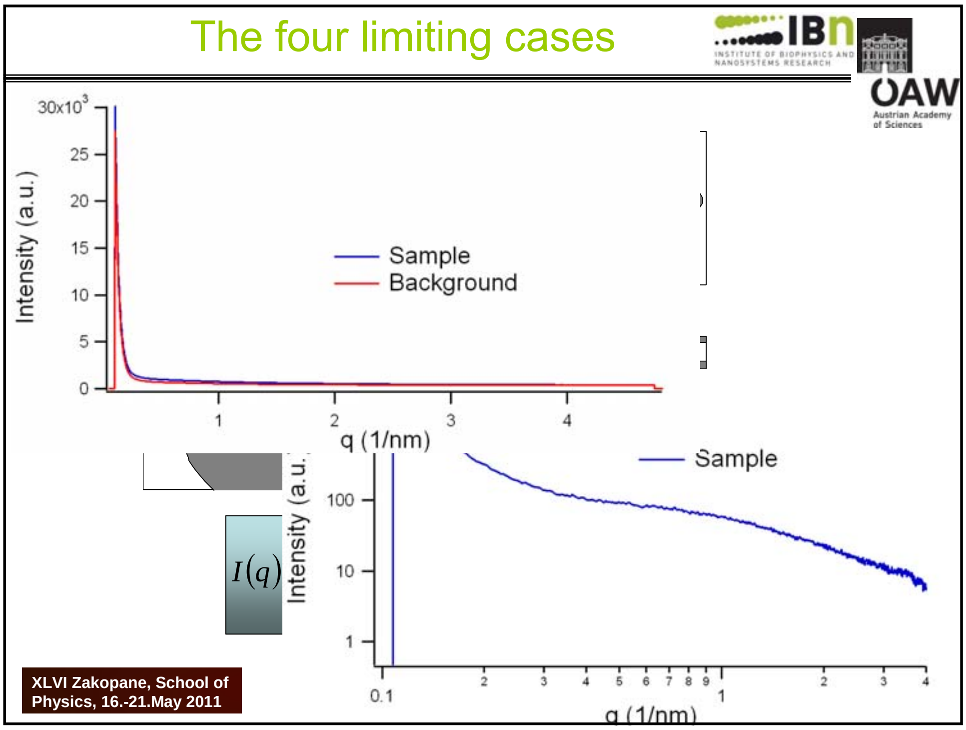
Courtesy of B. Aichmayer

How do we do the experiments?

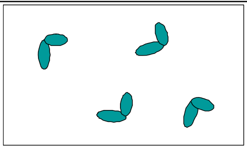
Laboratory	Synchrotron
S3 Micro 	

Time resolution	**200 s – 30 min**	**11 µs - 100 s**
Spatial resolution	**60 µm- 200 µm**	**0.1 µm – 1 µm**
Sample environment	**limited**	**almost no limit**
Availability	**40 weeks/year**	**2 – 4 weeks/year**


Sample Environment
Temperature
-195 °C – 300 °C
20 °C / 2 ms
Peltier Moduls /
Oxford Cryostream
IR-Laser
Pressure
0 - 3 Kbar
3000 bar/ 10 ms
Pressure Media
10 mm
Entrance Nipple
Specular reflected beam
Diamond Windows
Silicon Waver
Hydrostatic HP-Cell
More information is found
Chemical Potential
50 ms / 70 µs
eat capacity
0 °C – 150 °C
°C/min
DSC Microcalix
l Parameters
ension
11th Annual Report
A
B
jet
X-ray beam
time
q
µFluidics
Biologic SFM-4
Biaxial Device
User: IR-Spectroscopy, UV-vis, Elipsometer
XLVI Zakopane, School of Physics, 16.-21.May 2011
H. Amenitsch, SAXS beamline @ ELETTRA
& IBN, OEAW, Graz
7/45


The four limiting cases
Intensity (a.u.)
30x10³
25
20
15
10
5
0
Sample
Background
1
2
3
4
q (1/nm)
Sample
100
10
1
0.1
1
q (1/nm)
XLVI Zakopane, School of Physics, 16.-21.May 2011

Dilute Monodisperse Systems



Examples:

•Protein solutions

•Polymer solutions

•Nanoparticles

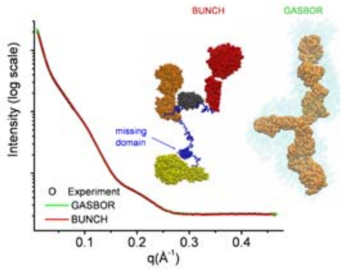
Parameters

•Radius of Gyration

•Particle weight

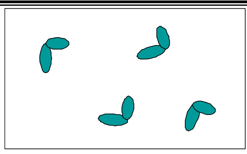
•Particle Volume

Particle Shape



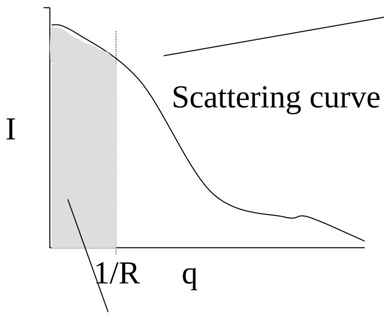
GASBOR, DAMMIN(F), Svergun D.I. et al.

Guinier's Law

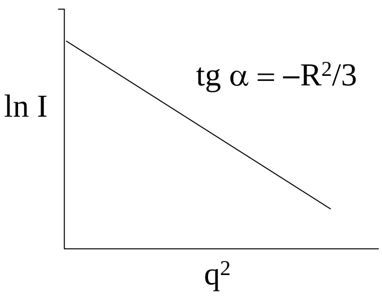


Radius of Gyration

$$I(q) = I(0) \cdot e^{-R^2 q^2 / 3}$$



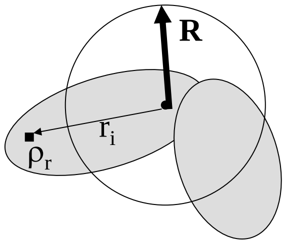
Guinier Plot



Guinier Range:

Limited to $q < 1/R$!

Guinier's Law



Radius of Gyration

$$R^2 = \frac{\int r^2 (\Delta\rho_r) d^3 r}{\int \Delta\rho_r d^3 r}$$

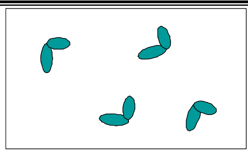
Ellipsoid with semiaxes a,b,c:

$$R = \sqrt{\frac{a^2 + b^2 + c^2}{5}}$$

Sphere with radius r:

$$R = \sqrt{\frac{3}{5}} \cdot r = 0.77 \cdot r$$

Real Space Function

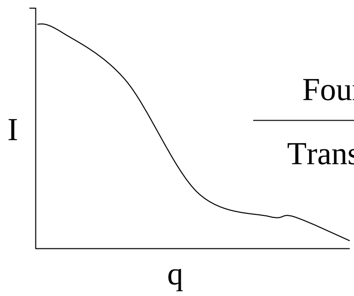


$$I(q) = |A(q)|^2 = V \cdot \int p(r) \cdot e^{-iqr} d^3 r$$

Scattering Space Function

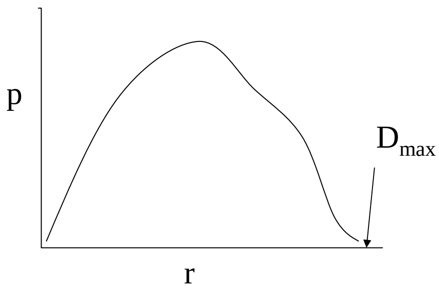
Real Space Function

$$p(r) = \frac{1}{V} \int \rho(r_0)\rho(r_0 + r) dr_0$$



Fourier

Transform

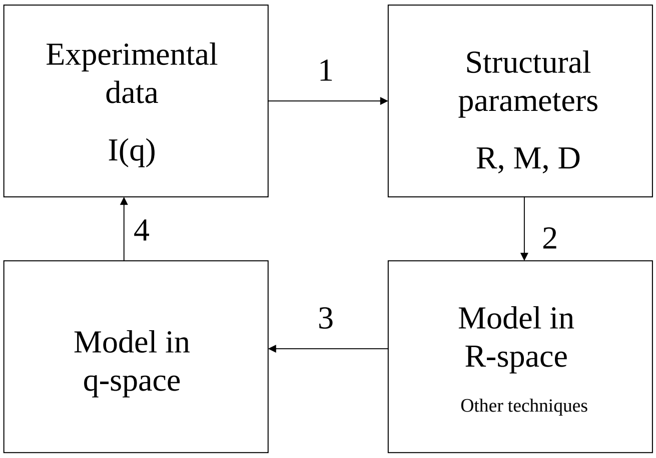


Scattering curve

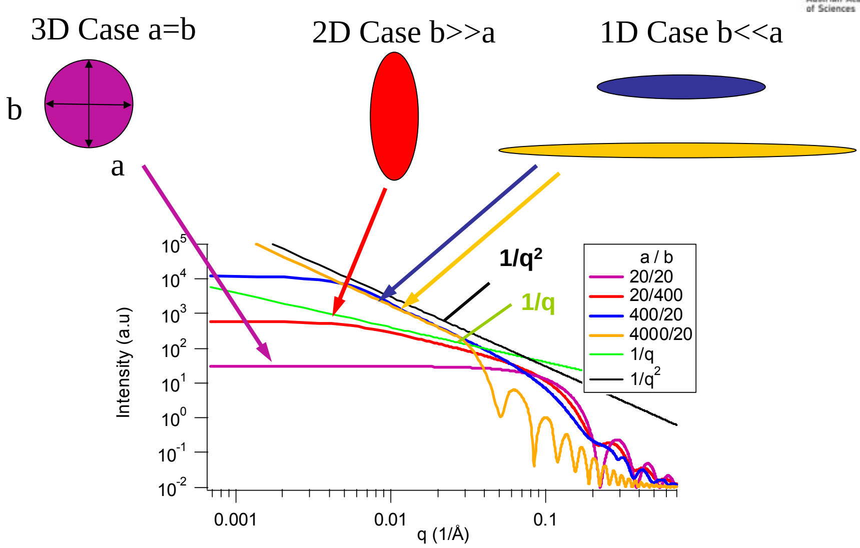
Electron Pair Distance Distribution

How Do You Obtain Information?

General strategy for solving
structural problems with SAXS



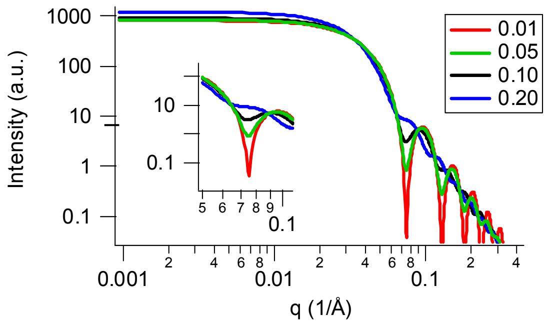
Globular and Non-Globular Particals



Size Distributions

$$I(q) = \int D_n(R) \cdot R^n \cdot i_o(qR) \cdot dq$$

$i_0(x)$ Formfactor
n=6: D_6 number distribution
n=3: D_3 volume distribution
n=0: D_0 intensity distribution



Scattered Intensity

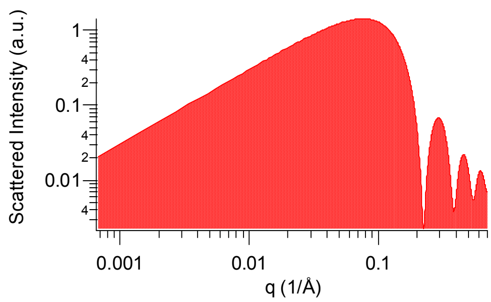
Scatter Probability

$$\Sigma \cdot D_s \propto \int I(q) \cdot q \cdot dq \propto p \cdot \Delta\rho^2 \cdot l_c$$

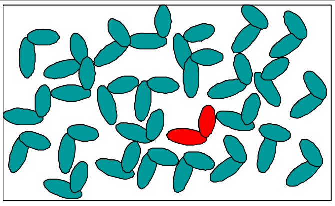
Makroscopic Cross Section
D_s Sample Thickness

Sphere: 20 Å, l_c= 3/2 R

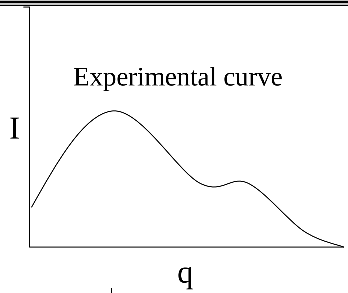
p Volume Fraction
Δρ Electron Density Contrast
l_c Correlation Lenght
R Radius

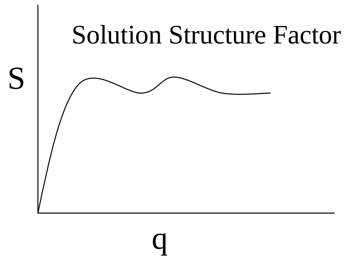


Interacting system

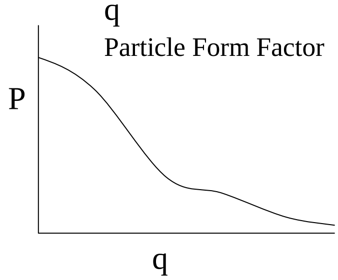


Dense particles

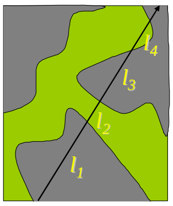




x



Random 2-phase System



Random porous/2-phase System

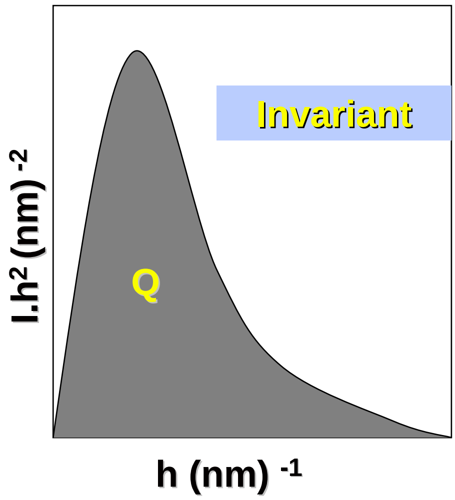
The “Invariant“ Q:

$$Q = \frac{1}{2\pi^2}\int_0^\infty I(q)q^2\,dq = V\langle\Delta\rho^2\rangle$$

The integral scattering, the ‚*Invariant*‘ , is equal to the total irradiated volume times the mean-square electron density fluctuation – independent of domain shape.

(Debye, Bueche)

Invariant



Q has the dimension of a reciprocal volume

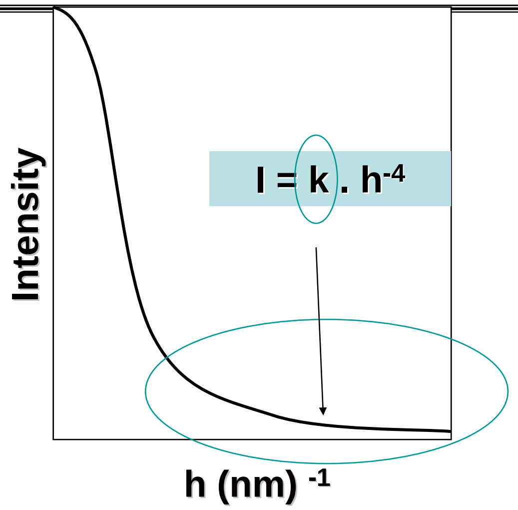
Invariant

In the case of a two-phase system (e.g. crystalline/ amorphous polymer), the invariant is related to the volume fractions ϕ, and the electron densities ρ_c and ρ_a

$$Q = V(\rho_c - \rho_a)^2 \cdot \phi_a \phi_c$$

total irradiated volume

Porods Law



Towards larger angles, the intensity decays with the fourth power of the angle (Porod's law)

Porods Law

The decay constant *k* from a two-phase system is given by

$$k = \lim_{h \to \infty} h^4 \cdot I(h) \quad = \quad 2\pi \cdot S \cdot (\rho_c - \rho_a)^2$$

K depends on the total inner surface and the mean-sqare electron density fluctuations

How Do You Use It?

Combining *Invariant Q* and *Tail-End Constant k*, obtained from one single measurement

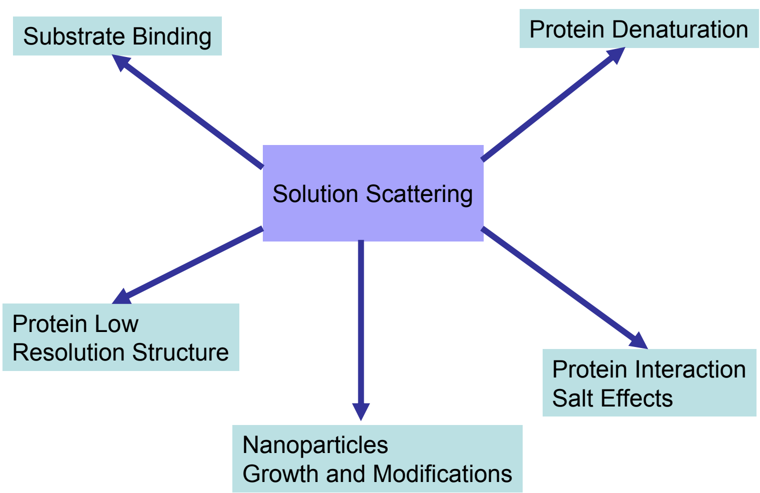
$$\frac{k}{Q} = \frac{2\pi \cdot S_i}{\phi(1-\phi)}$$

if ϕ is around 0.5, the value of S_i is not very sensitive to variations in ϕ.

Combining Scattered Intensity and *Invariant Q*

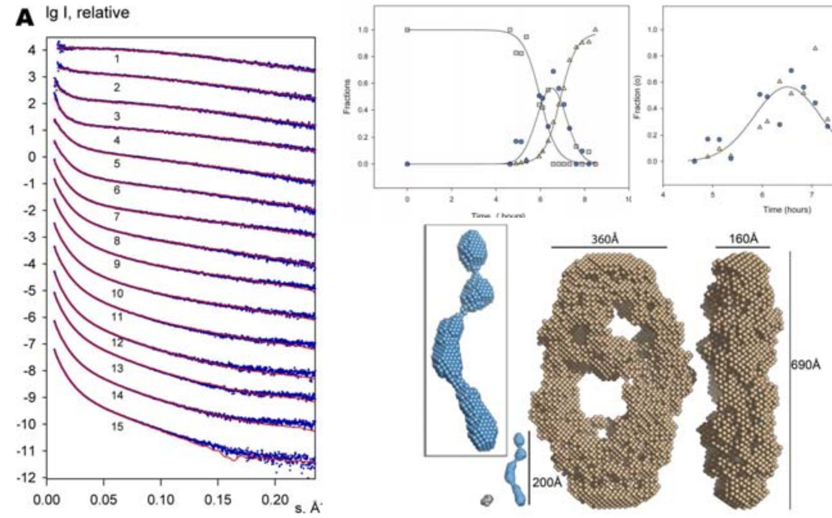
$$\frac{\Sigma \cdot D_s}{Q} = \frac{\int dq \cdot q \cdot I(q)}{\int dq \cdot q^2 \cdot I(q)} = \frac{1}{2 \cdot \pi} \cdot l_c$$

Solution Scattering



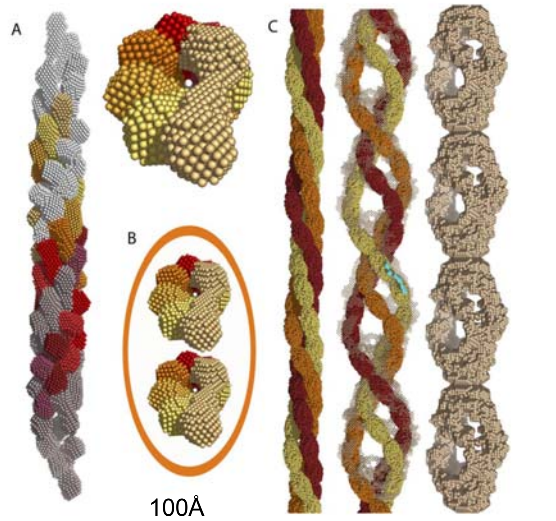
Insulin Amyloid Fibrils

5 mg/ml in 20% acetic acid with 0.5 M NaCl



B. Vestergaard et al., PLoS Biology **5**, e134 (2007)

Insulin Amyloid Fibrils



A 8 helical oligomers
=> **protofilament**

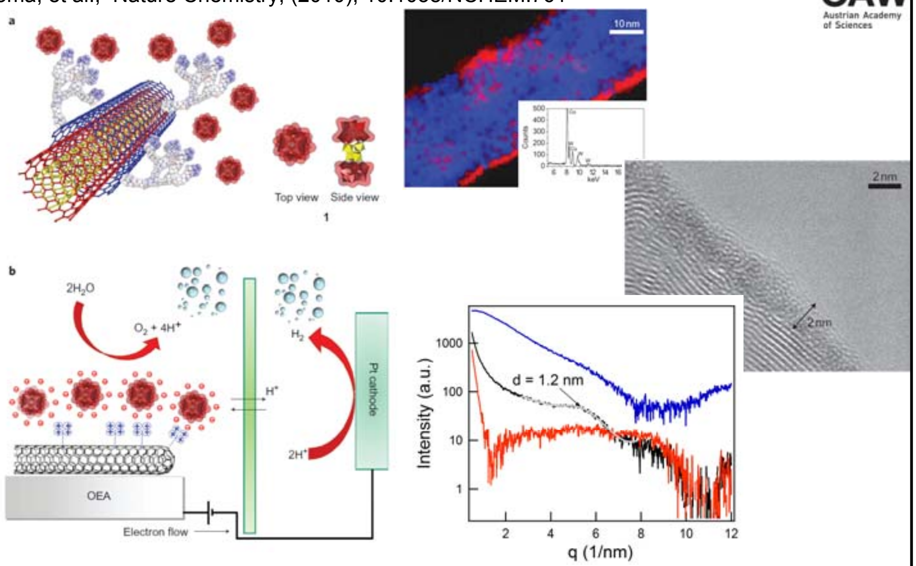
B 2 protofilaments
=> **protofibril**

C 3 protofibrils
=> **Insuline amyloid fibril**

B. Vestergaard et al., PLoS Biology **5**, e134 (2007)

Characterization of carbon nanotube–polyoxometalate electrocatalytic interfaces

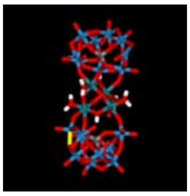
F.Toma, et al., Nature Chemistry, (2010), 10.1038/NCHEM.761



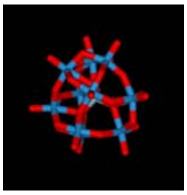
XLVI Zakopane, School of Physics, 16.-21.May 2011

H. Amenitsch, SAXS beamline @ ELETTRA & IBN, OEAW, Graz

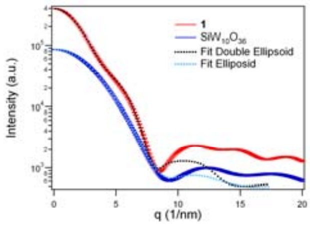
Characterization of carbon nanotube–polyoxometalate electrocatalytic interfaces



Ru4POM

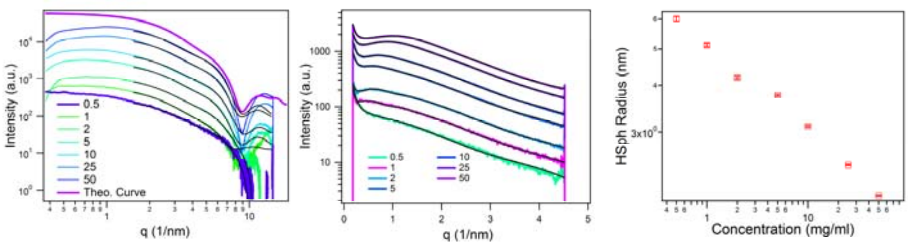


Precursor $SiW_{10}O_{36}$



Simulation Crysol ATSAS D.Svergun

Double ellipsoid model



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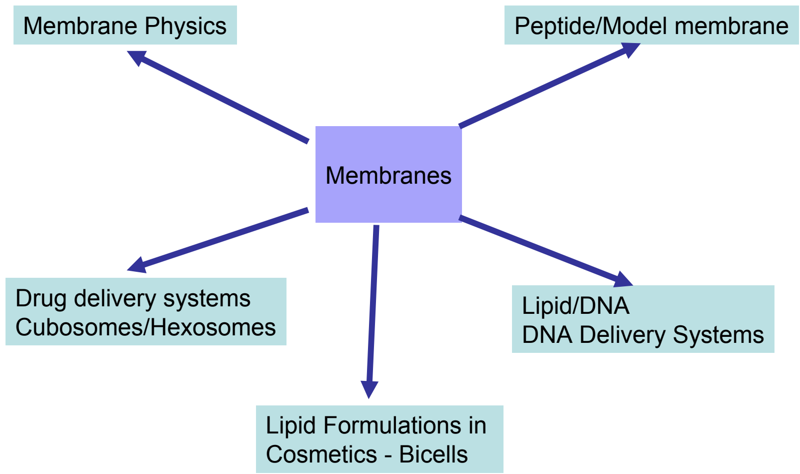
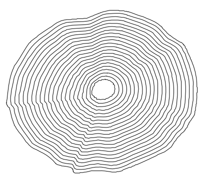
H. Amenitsch, SAXS beamline @ ELETTRA & IBN, OEAW, Graz

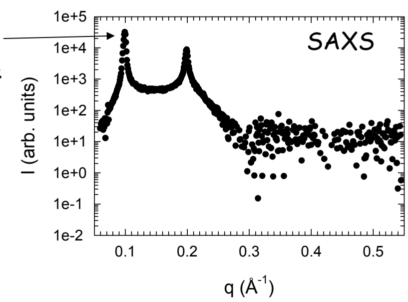
Membranes



Scattering from Multilamellar Vesicles



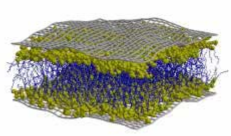
peaks from intraparticle correlations



multilamellar vesicle = 1d crystal

(consists of a stack of bilayers)

The problem: peaks + diffuse scattering



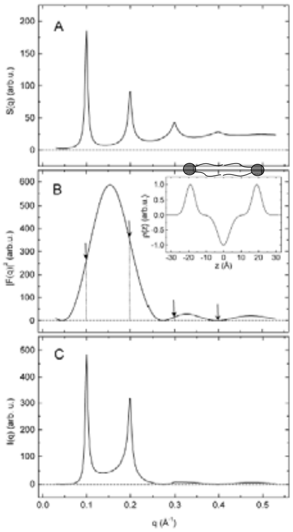
R. Böckmann, University of Zürich.

What we would like to know:

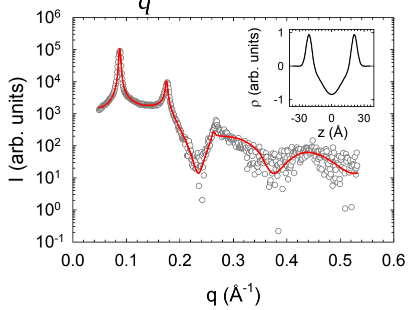
structure:
- membrane thickness
- water layer thickness
- lateral area per lipid

mechanical properties:
- flexibility (bending rigidity)

The Global Model



$$I(q) = \frac{S(q)|F(q)|^2}{q^2}$$



structure:
- membrane thickness
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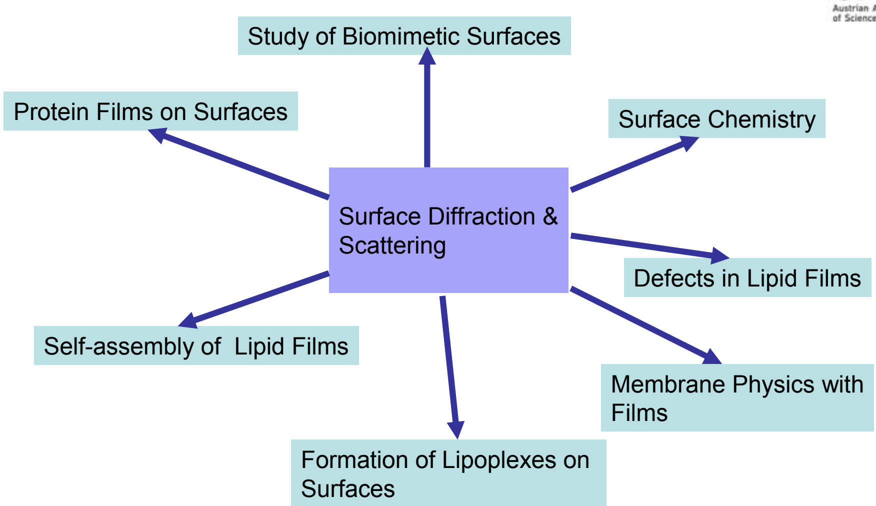
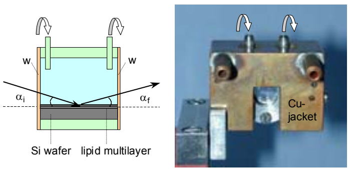
- lateral area per lipid

mechanical properties:
- flexibility (bending rigidity)

G. Pabst, M. Rappolt, H. Amenitsch, P. Laggner, Phys. Rev. E. **62**, 4000 (2000).

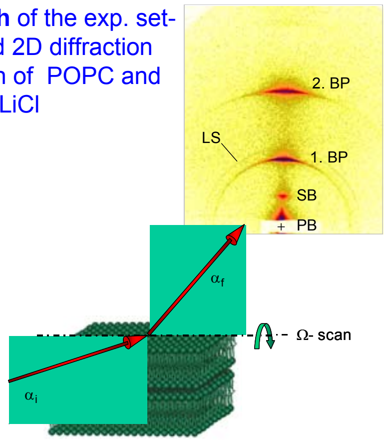
Surface Diffraction & Scattering

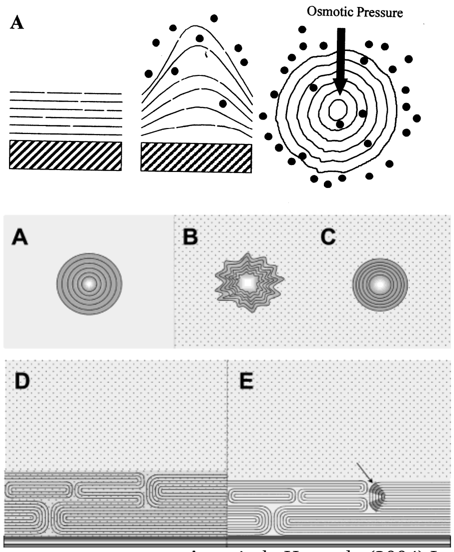


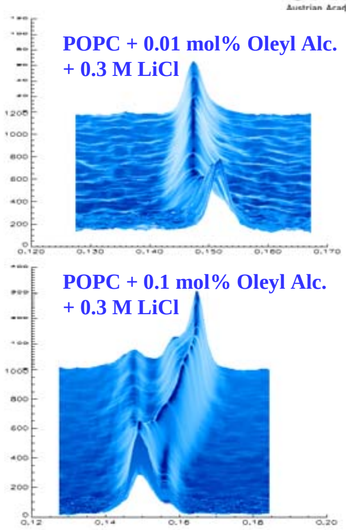


Sketch and photograph of the sample cell in transmission geometry for GISAXS.

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





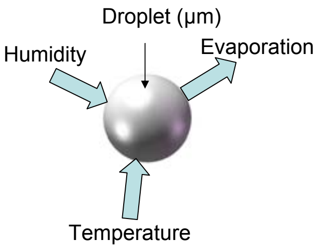


Amenisch, H., et al., (2004) Langmuir

In situ aerosol synthesis

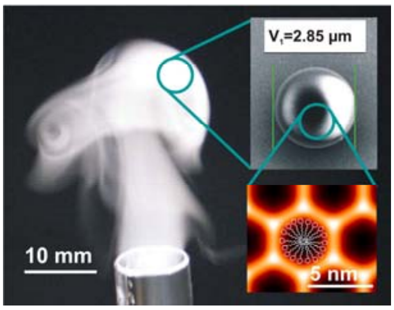
Scientific case

Aerosol-Microreactor



Mesostructured Si produced by Evaporation Induced Self Assembly (EISA)*

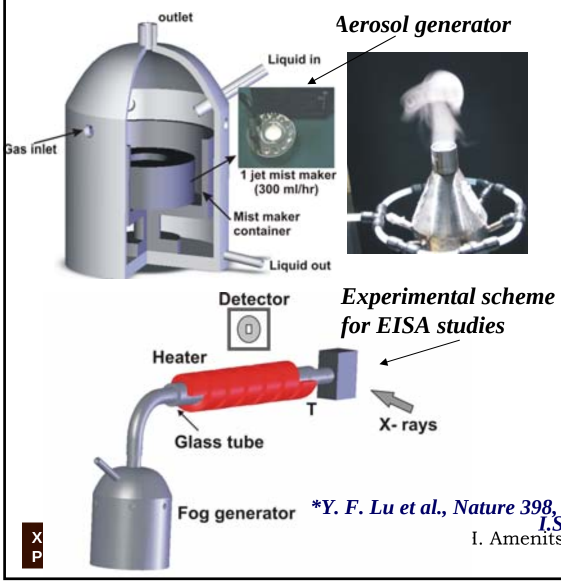
***Y. F. Lu et al., Nature 398, 223-226 (1999).**



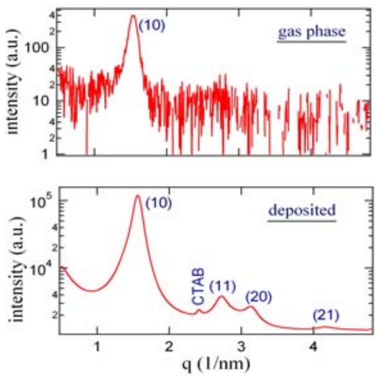
CTAB:TEOS:H_2O:HCl
molar ratio - 0.14:1:41:0.13

Gas phase study of Silica Self Assembly

Mesostructured Si produced by Evaporation Induced Self Assembly (EISA)*



CTAB:TEOS:H_2O:HCl
molar ratio - 0.14:1:41:0.13

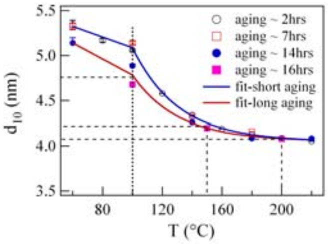


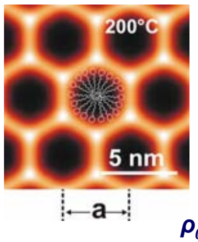
***Y. F. Lu et al., Nature 398, 223-226 (1999).**

I.Shyjumon et al. Rev.Sci.Ins. 79, 43905 (2008)

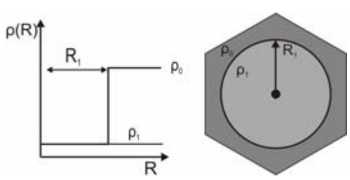
Electron density map & model fitting

electron density maps of (- + + -) phase from (10), (11), (20) & (21) integrated intensites





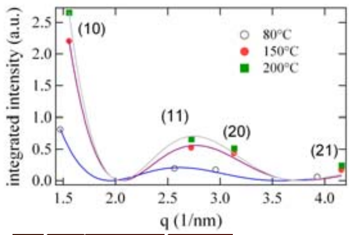
The two density regime model



ρ_0 - silica matrix
ρ_1 - inner core

$$I(q) = k\left[\frac{2J_1(qR_1)}{(qR_1)}\right]^2$$

model fit using the two density regime model



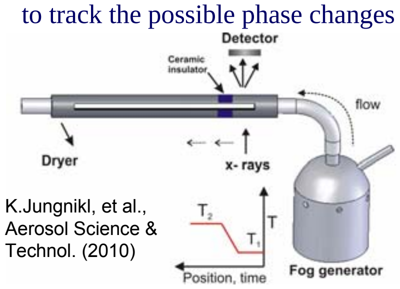
R_1 – radius of the core, a – cell parameter
& Silica matrix thickness = (a - 2R_1)

T (°C)	R_1 (nm)	a (nm)	Silica matrix(nm)
80	1.964±0.041	4.933±0.001	1.005 ±0.043
150	1.857±0.035	4.666±0.001	0.9516±0.037
200	1.868±0.037	4.664±0.001	0.9282±0.039

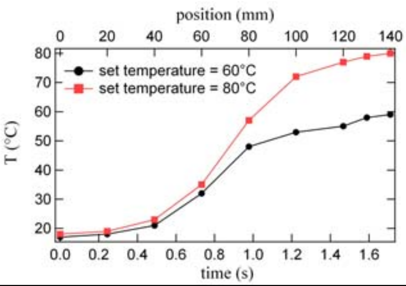
I.Shyjumon et al., Langmuir, 2011

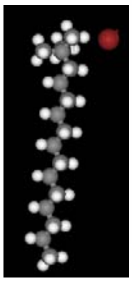
In situ analysis of Si mesophase formation

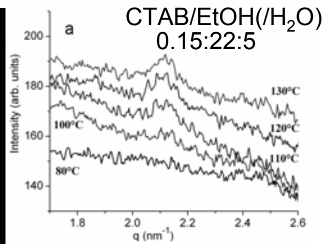
- Temperature profile inside the dryer is adjusted to track the possible phase changes of silica
- Test of Set-up Crystallization of CTAB

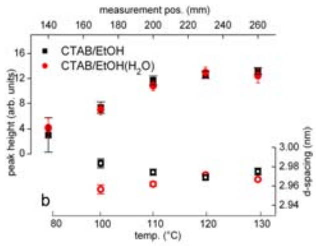


K.Jungnikl, et al., Aerosol Science & Technol. (2010)



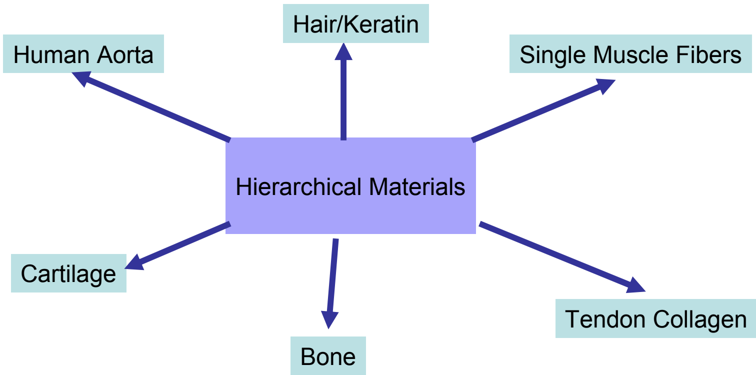






H. Amenitsch,
& IBN, OEAW, Graz

Hierarchical Materials

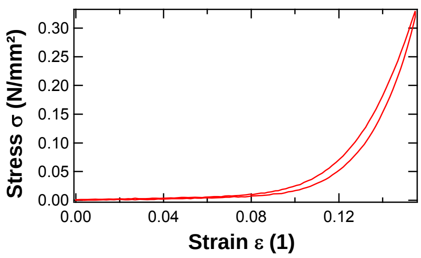


Human Aorta: Why

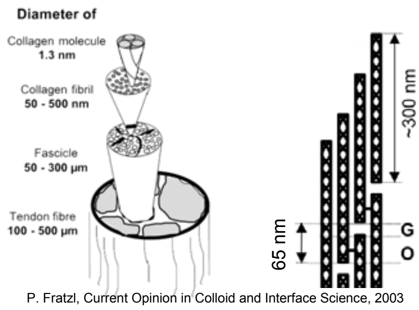
Macroscopic response ← Model → Micro- and nano-structure

- geometric deformation
- stress
- strain

- fiber – matrix composite
- fiber alignment
- fiber strain

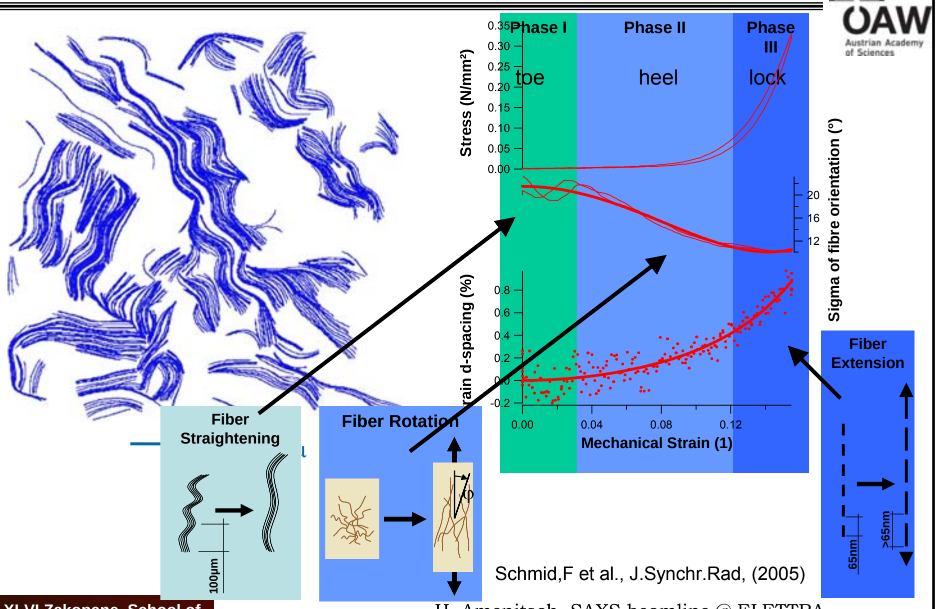


Collagen - The most abundant protein



P. Fratzl, Current Opinion in Colloid and Interface Science, 2003

Biomaterials: Human Arteries



Schmid,F et al., J.Synchr.Rad, (2005)

Who are we?

H.Amenitsch B.Sartori M.Rappolt S.Bernstorff C.Morello

Nuc.&Growth, Alig. Systems
Lipids, Biomaterials

Lipids, Non Lamellar Systems
Drug Delivery Systems

GISAXS,
Quantum Dots

F.Schmid* F.Cacho B.Marmiroli I.Shyjumon* K.Jungnikl* D. Jozić

NSF- Human Arteries

EU-Project SAXIER
Microfluidic

EU-Project NFFA
Scattering in Gasphase

Geopolymers

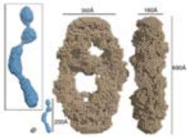
(*)former members of the group

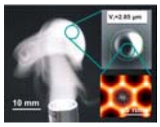
Conclusion & Outlook

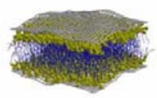
Conclusion

SAXS:
- What is S(W)AXS?
- How do we do S(W)AXS?

Applications:
- Solution Scattering
- Model membranes
- Grazing Incidence Studies
- Hierarchical Materials







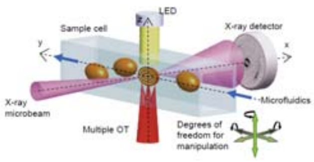
Human Arteries

Outlook

μFluidics

Channels 20 x 50 μm

Optical Tweezer



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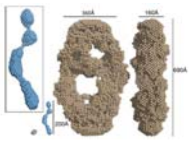
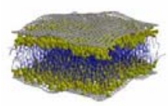
D.Grosso, C.Sanchez, Univ. Paris

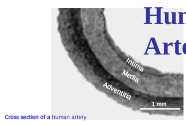
G. Holzapfel, TU-Graz, Stockholm



Insulin

Membranes





Human Arteries

11th Annual Report


Thank you for your attention
ÖAW
Austrian Academy of Sciences