The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
Cultural Organization

IAEA
International Atomic Energy Agency

2139-20

School on Synchrotron and Free-Electron-Laser Sources and their Multidisciplinary Applications

26 April - 7 May, 2010

Small angle x-ray scattering and applications

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Small angle x-ray scattering and applications

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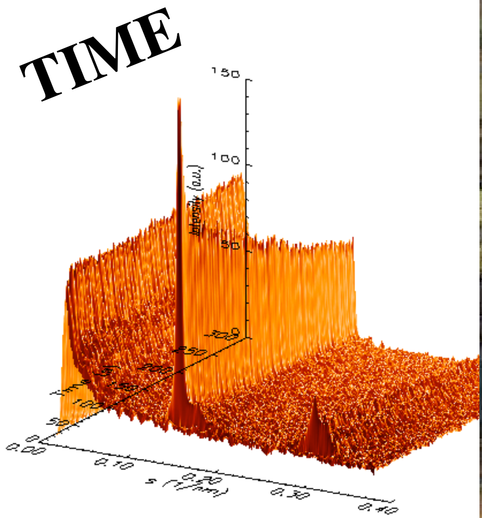
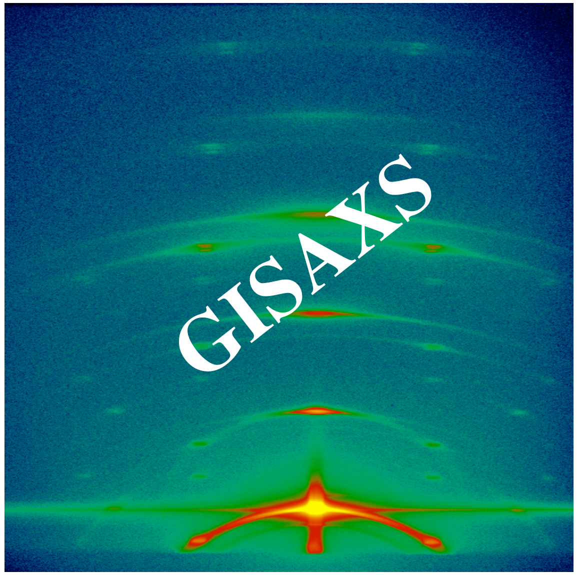




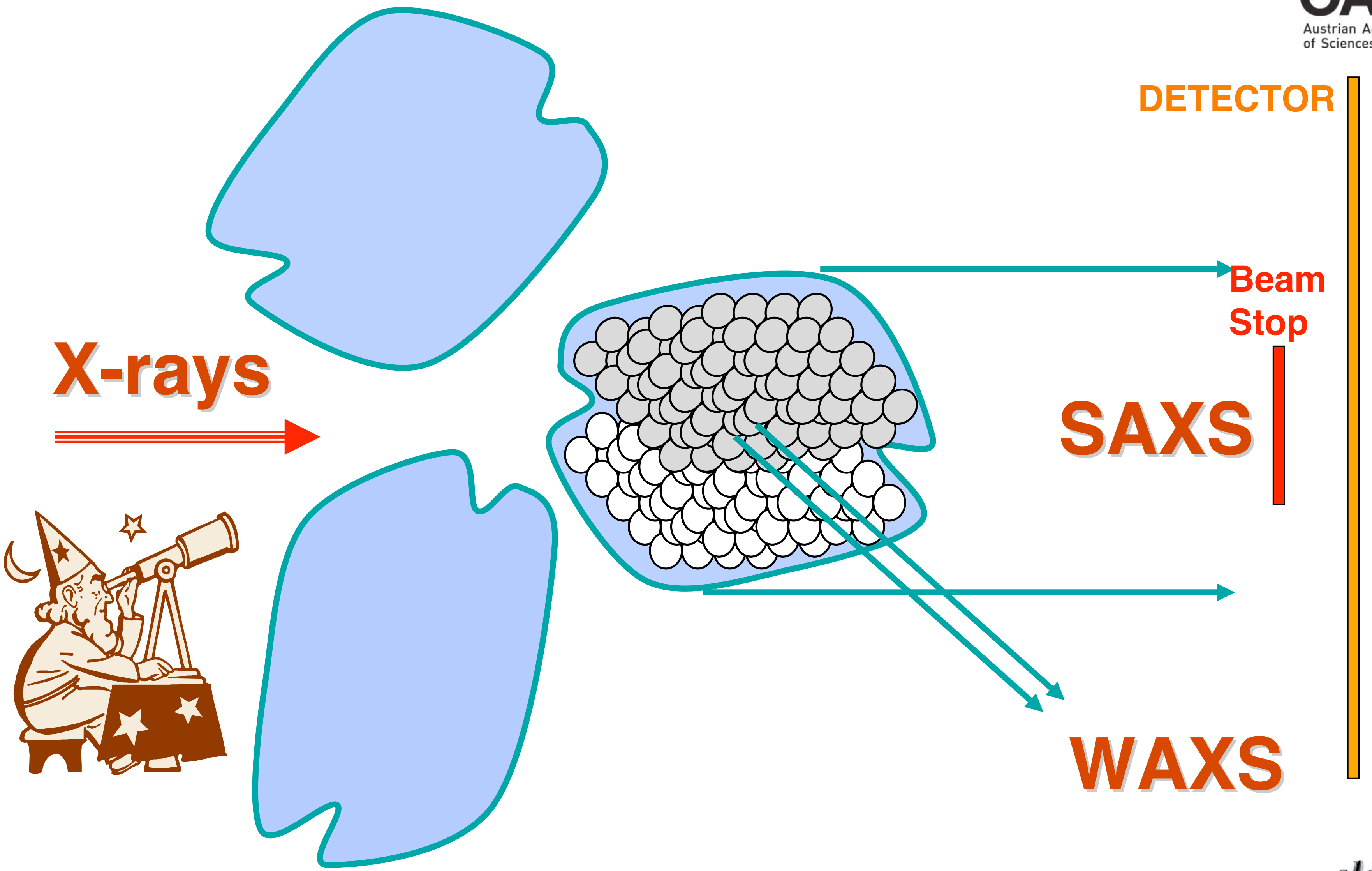
Outline

• Basics of small angle scattering
• Instrumentation for (*in situ*) small angle scattering
• What kind of information can be extracted from SAS?

• Examples from
growth of semiconducting nanoparticles,
Marine sponges

• Principles of GISAS
self assembly from mesoporous materials on surfaces
• Conclusion and outlook

SAXS and WAXS



Small – Angle : Supramolecular Envelope

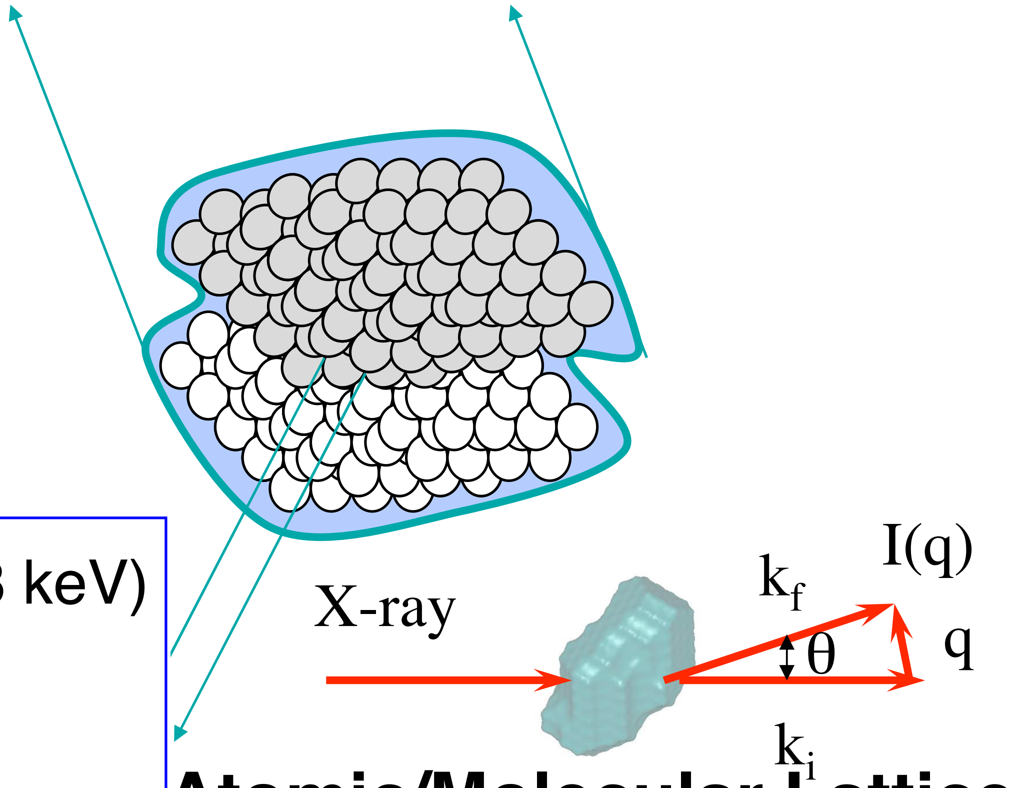
Bragg's law:

$$\sin \theta/2 = \lambda / 2d$$

small θ **large d**

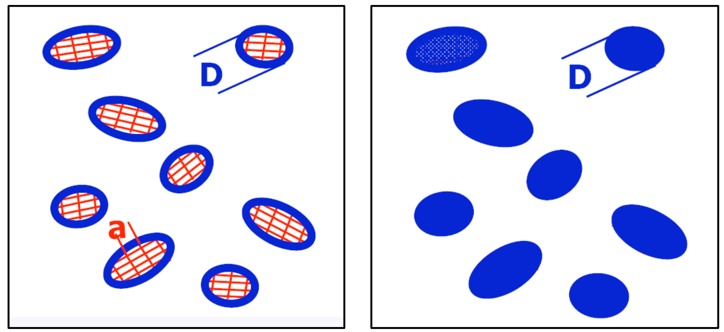
For CuK_α 0.154 nm (8 keV)

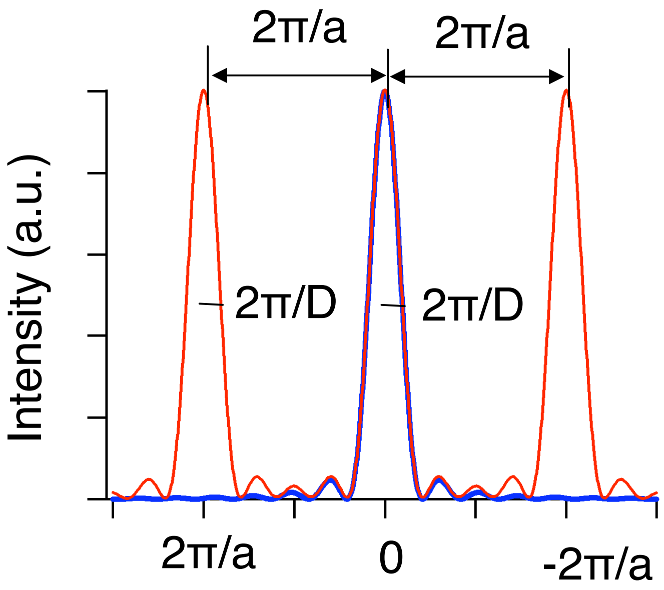
20 deg	0.5 nm
0.9 deg	10 nm
0.09 deg	100 nm



Atomic/Molecular Lattice

SAXS and WAXS



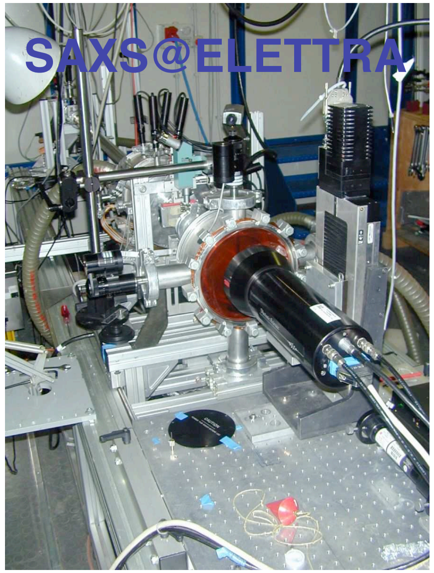


$$q = \frac{4\pi}{\lambda} \cdot \sin(\theta / 2)$$

SAXS:
peak width (+ shape) → particle size

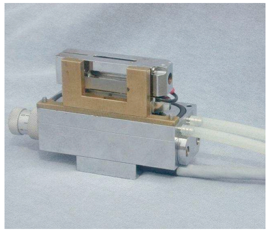
WAXS:
positions → lattice (type, spacings, strain)
width + shape → particle size
+ lattice strain fluctuations

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

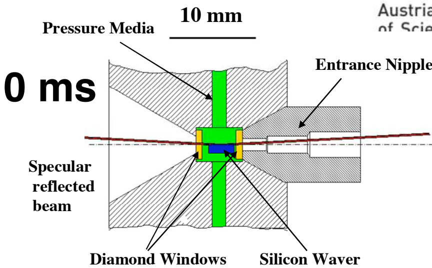
Temperature
-195 °C – 300 °C
20 °C / 2 ms



Peltier Moduls / Oxford Cryostream

IR-Laser

Pressure
0 - 3 Kbar
3000 bar/ 10 ms



Hydrostatic HP-Cell

More information is found

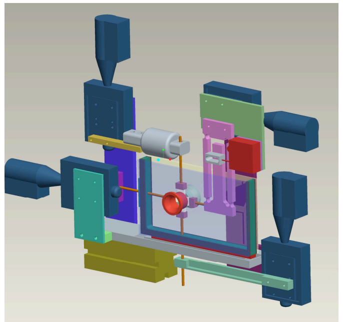
Chemical Potential
50 ms / 70 μs

11th Annual Report

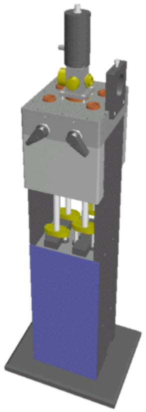
leat capacity
l0 °C – 150 °C
°C/min

DSC Microcalix

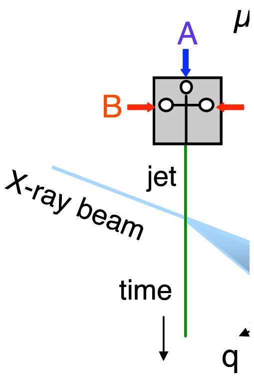
al Parameters
ension



Biaxial Device



Biologic SFM-4



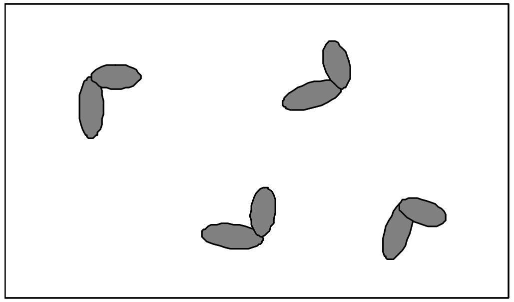
μFluidics

v

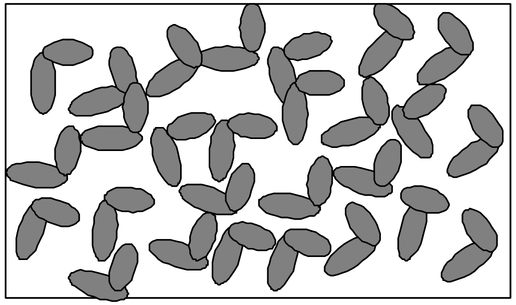
User: IR-Spectroscopy, UV-vis, Elipsometer

The four limiting cases

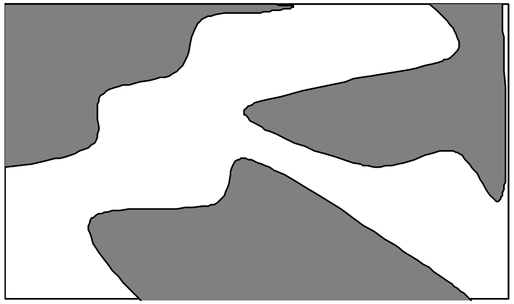
Dilute particles



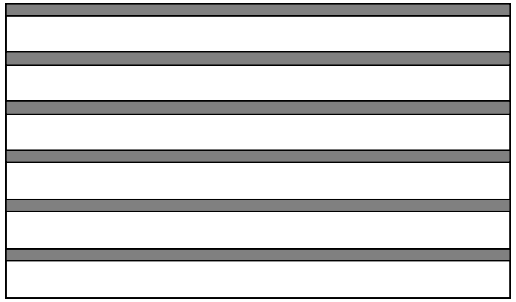
Dense particles



Random porous/2-phase

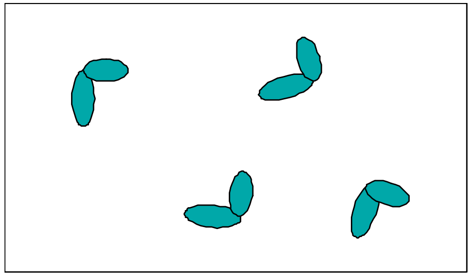


Highly ordered



$$I(q)=\left\langle\left|\int_V d^3r\cdot\rho(\vec{r})\cdot\exp(-i\cdot\vec{q}\cdot\vec{r})\right|^2\right\rangle_{rot}$$

Dilute Monodisperse Systems



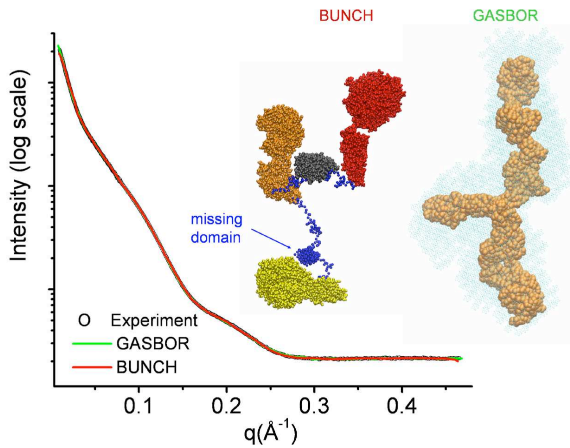
Examples:

- Protein solutions
- Polymer solutions
- Nanoparticles

Parameters

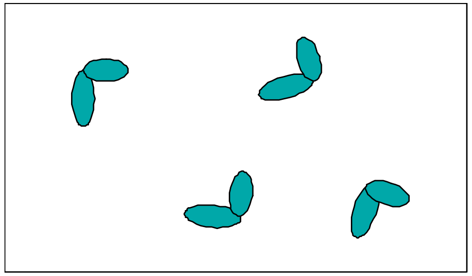
- Radius of Gyration
- Particle weight
- Particle Volume

Particle Shape



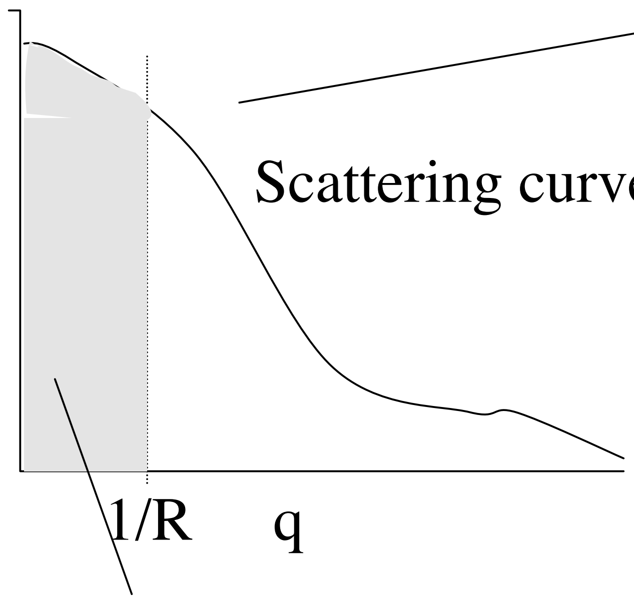
GASPOR, DAMMIN, Svergun D.I. et al.

Guinier's Law



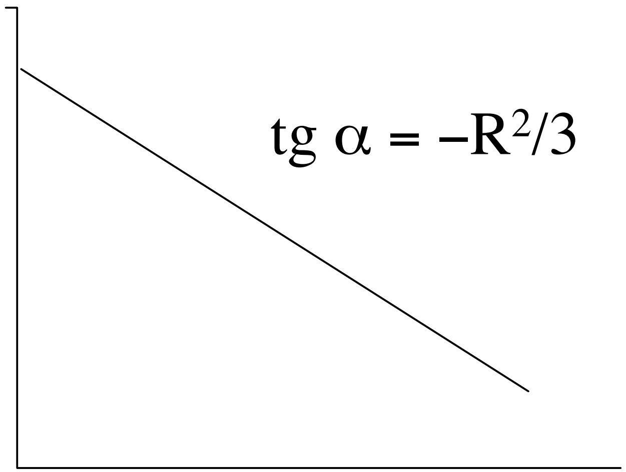
Radius of Gyration

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



Scattering curve

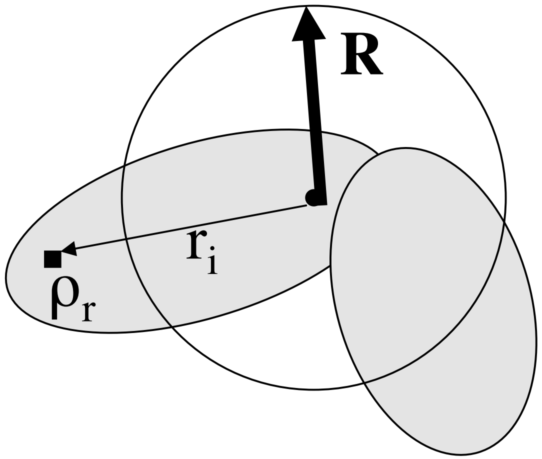
Guinier Plot



Guinier Range:

Limited to $q < 1/R$!

Guinier's Law



Radius of Gyration

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

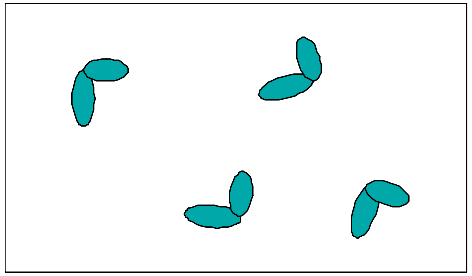
Ellipsoid with semiaxes a,b,c:

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

Sphere with radius r:

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

Real Space Function

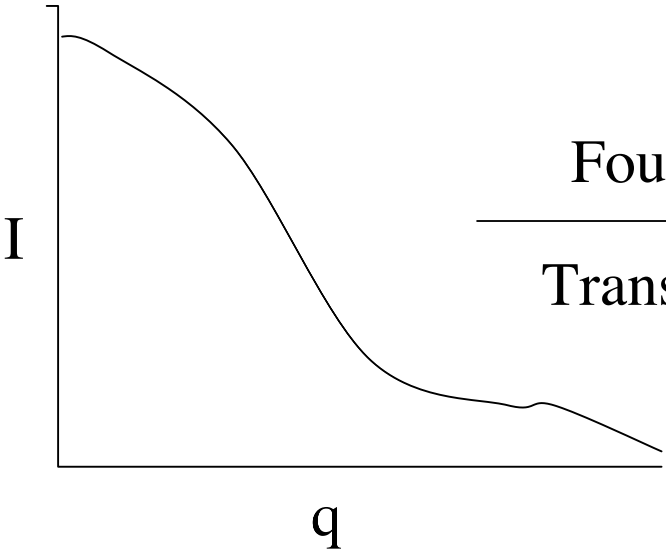


$$I(q) = |A(q)|^2 = V \cdot \int p(r) \cdot e^{-iqr} d^3r$$

Scattering Space Function

Real Space Function

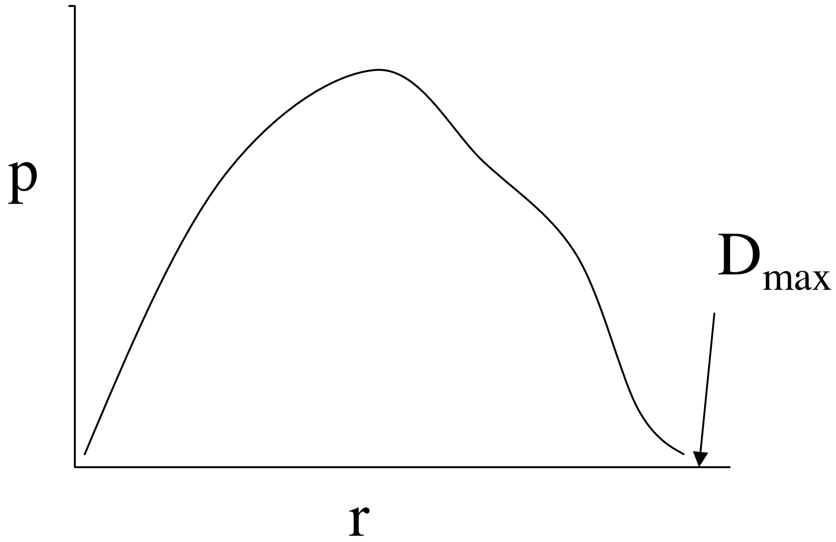
$$p(r) = \frac{1}{V} \int \rho(r_0)\rho(r_0 + r) dr_0$$



Scattering curve

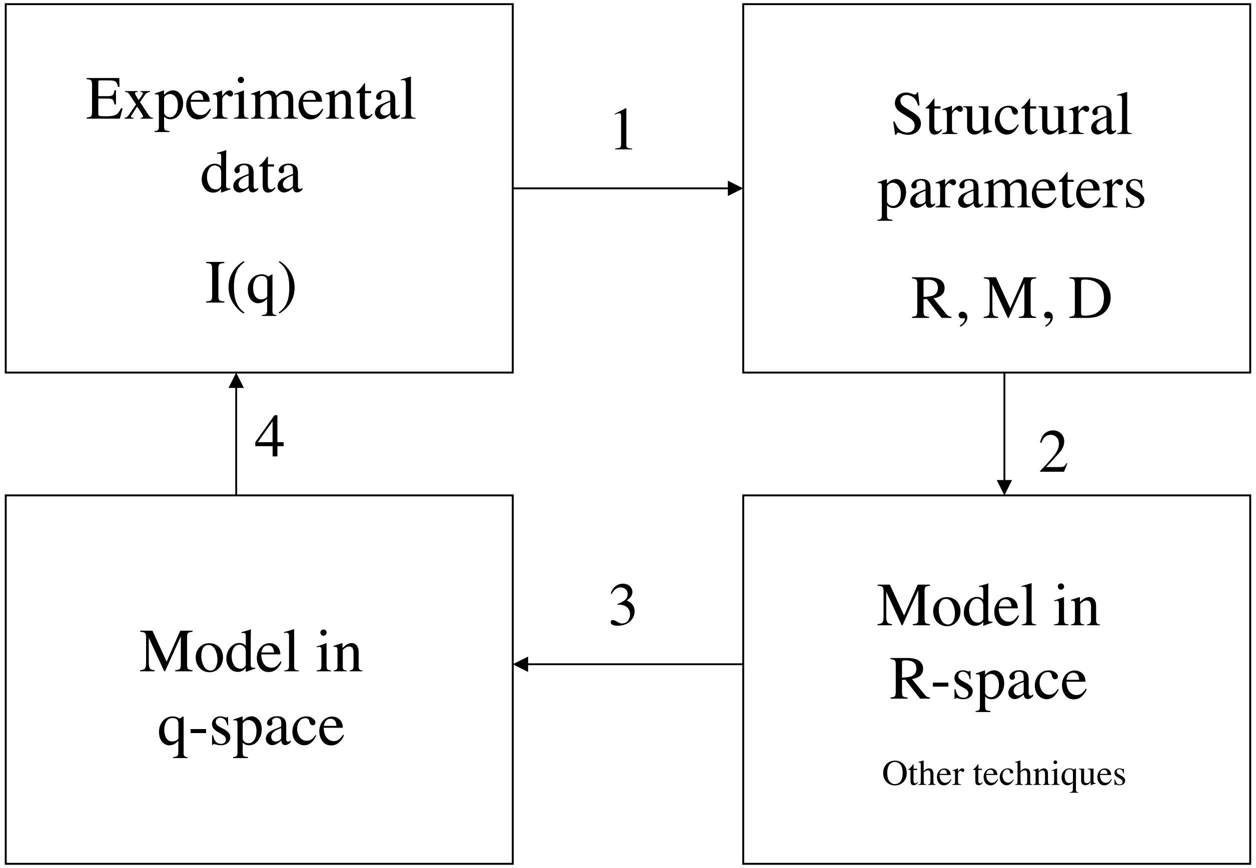
Fourier

Transform



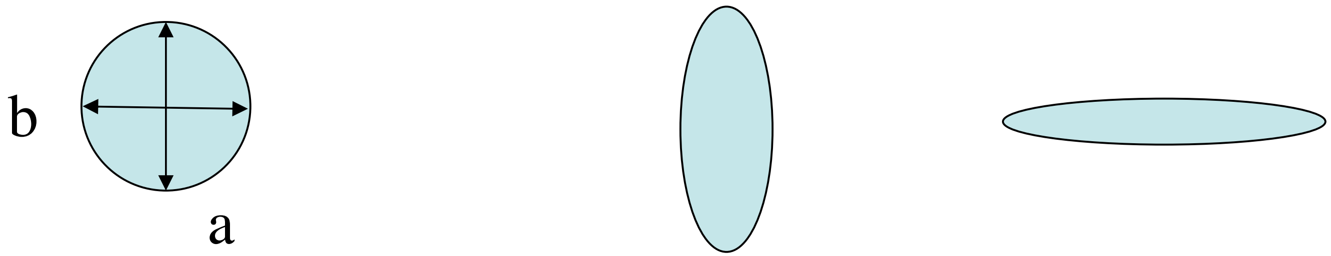
Electron Pair Distance Distribution

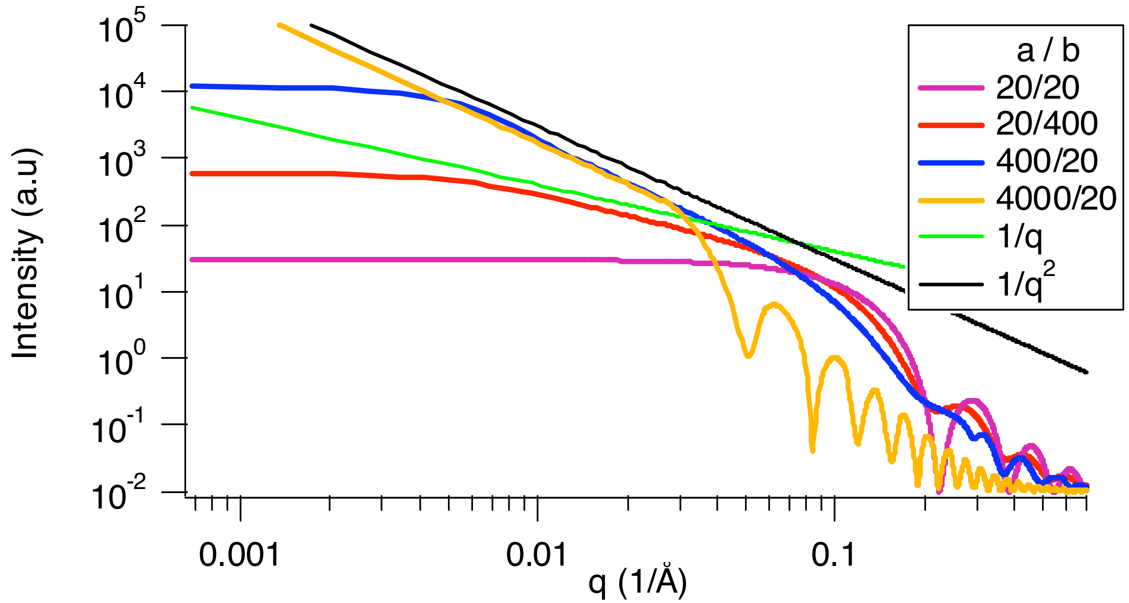
General strategy for solving structural problems with SAXS



Globular and Non-Globular Particals

3D Case a=b 2D Case b>>a 1D Case b<<a





Size Distriubtions

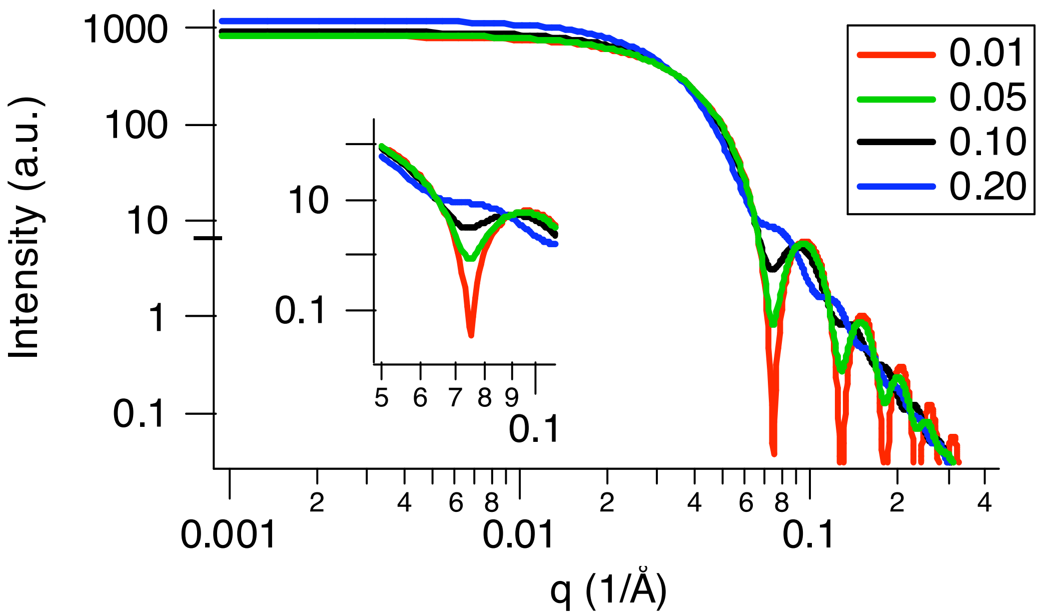
$$I(q) = \int D_n(R) \cdot R^n \cdot i_o(qR) \cdot dq$$

$i_0(x)$ Formfactor

n=6: D_6 number distribution

n=3: D_3 volume distribution

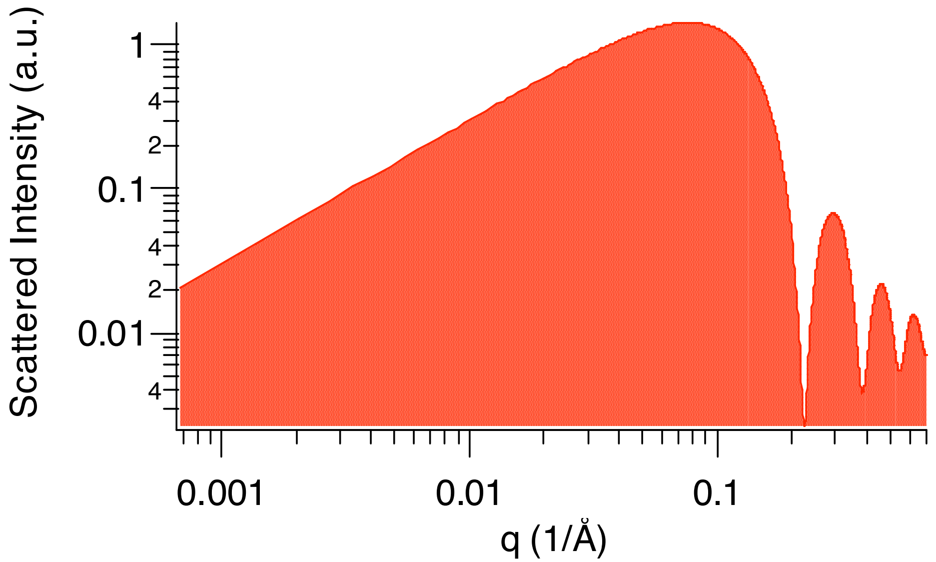
n=0: D_0 intensity distribution



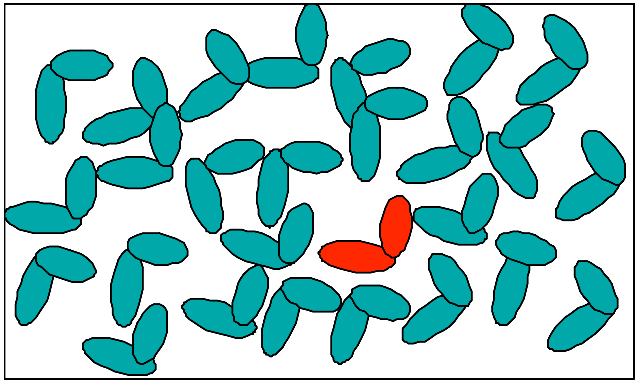
Scattered Intensity

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

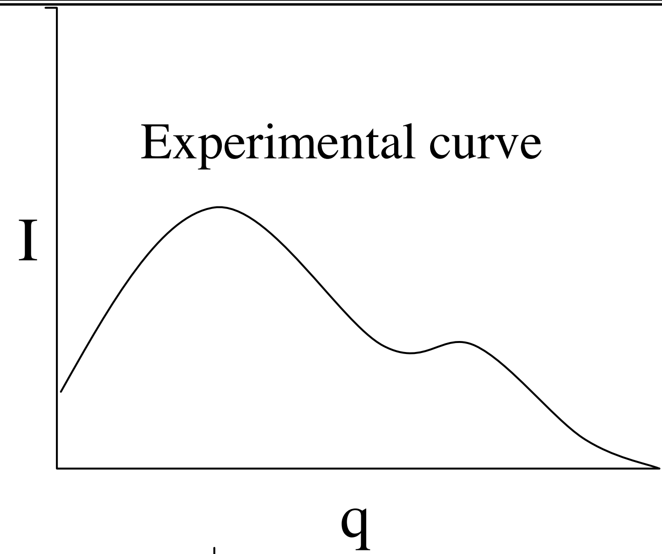
Sphere: 20 Å, l_c= 3/2 R

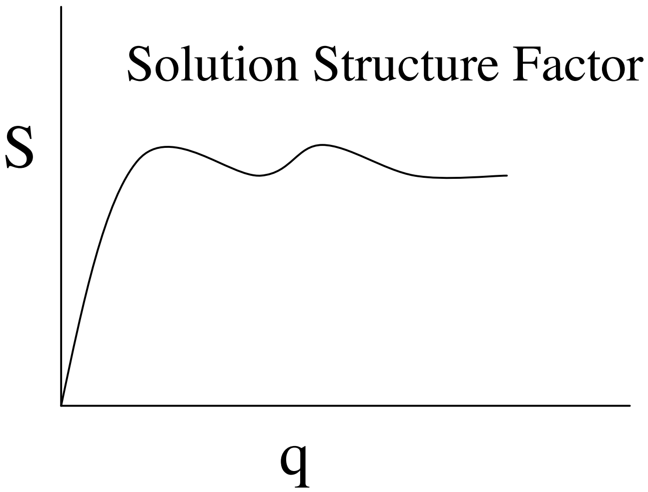


Interacting system

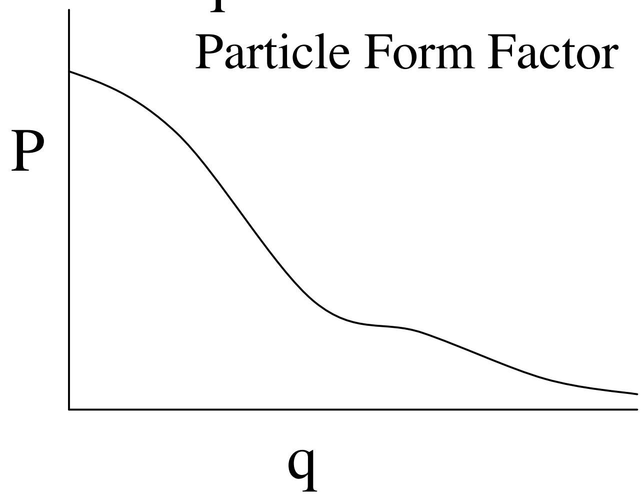


Dense particles

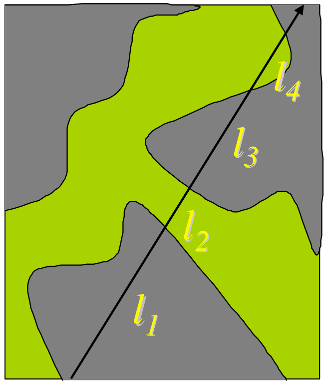




x



Random 2-phase System



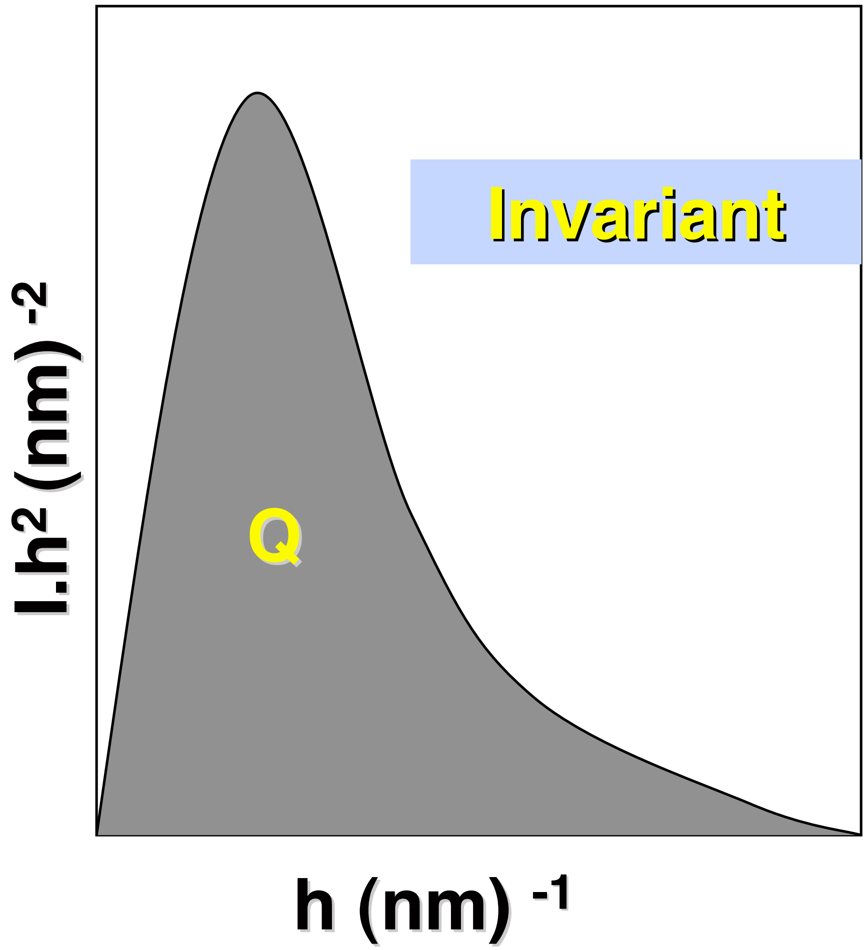
Random porous/2-phase System

The "Invariant" Q:

$$Q = \frac{1}{2\pi^2}\int_0^\infty I(h)h^2\,dh = V\langle\eta^2\rangle$$

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)



Q has the dimension of a reciprocal volume

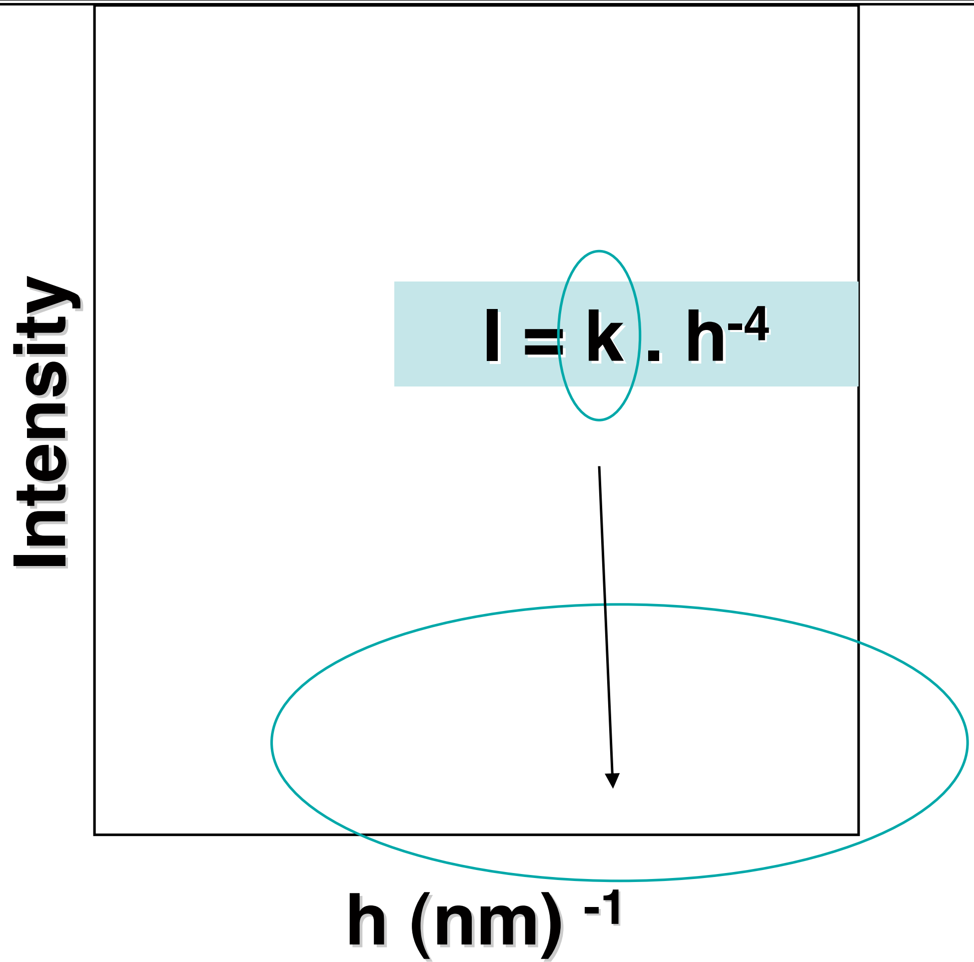
Invariant

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)

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

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

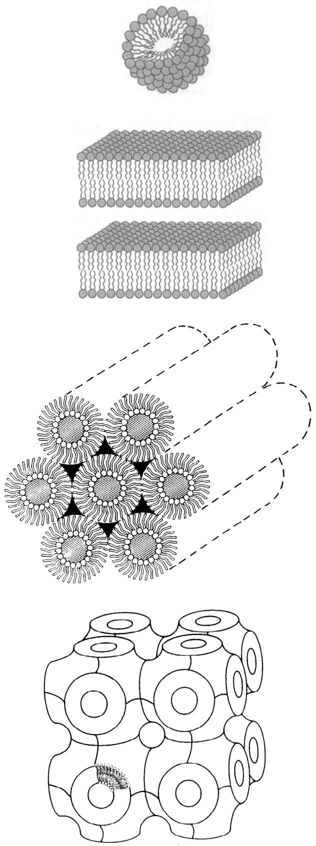
$$\frac{k}{Q} = \frac{2\pi \cdot S_i}{\phi(1-\phi)}$$

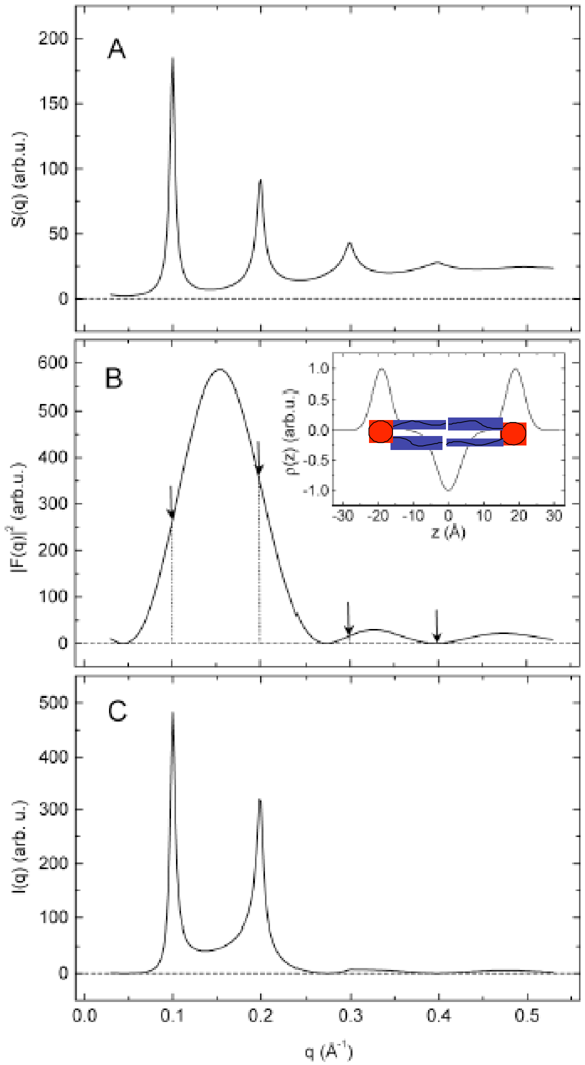
if ϕ is around 0.5, the value of S_i is not very sensitive to variations in ϕ.

Combining Scattered Intensity and *Invariant Q*

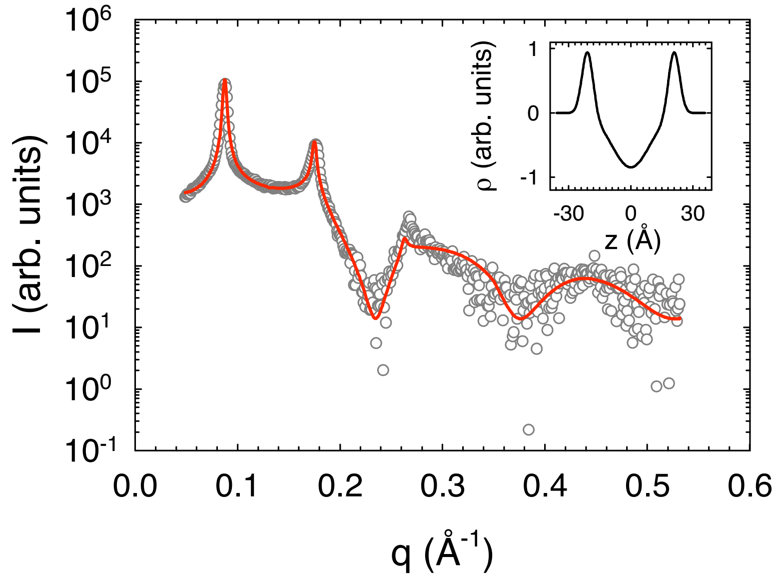
$$\frac{\Sigma \cdot D_s}{Q} = \frac{\int dq \cdot q \cdot I(q)}{\int dq \cdot q^2 \cdot I(q)} = \frac{1}{2 \cdot \pi} \cdot l_c$$

Liquid Crystalline Phase





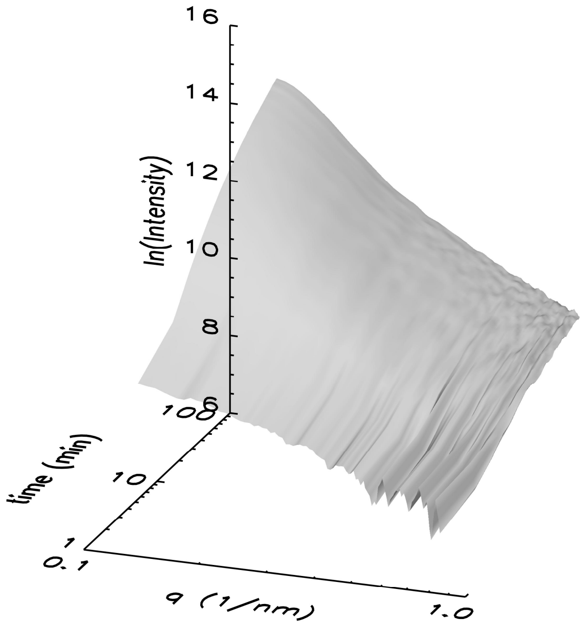
$$I(q) = \frac{S(q)\left|F(q)\right|^2}{q^2}$$

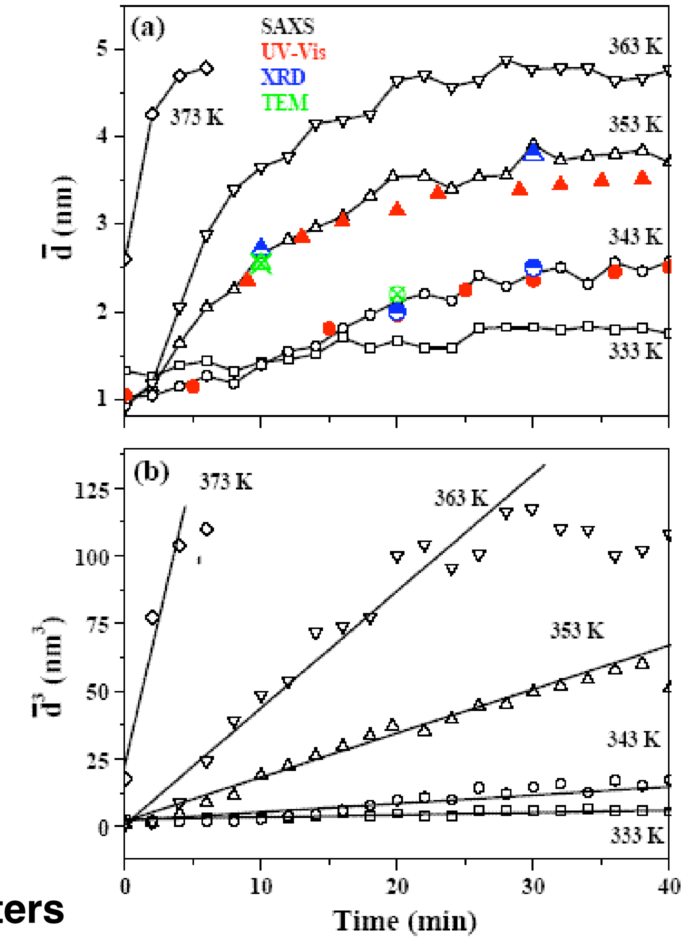


G. Pabst, M. Rappolt, H. Amenitsch, and P. Laggner, Phys. Rev. E. **62**, 4000 (2000).

CdS Nanoparticles

Cadmium acetate, Thiourea
in DMF => Temperature (60-100ºC)





„Ostwald Ripening"
Lifshitz-Slyozov-Wagner theory (1961)

$$\bar{d}^3 - \overline{d_0}^3 = Kt$$

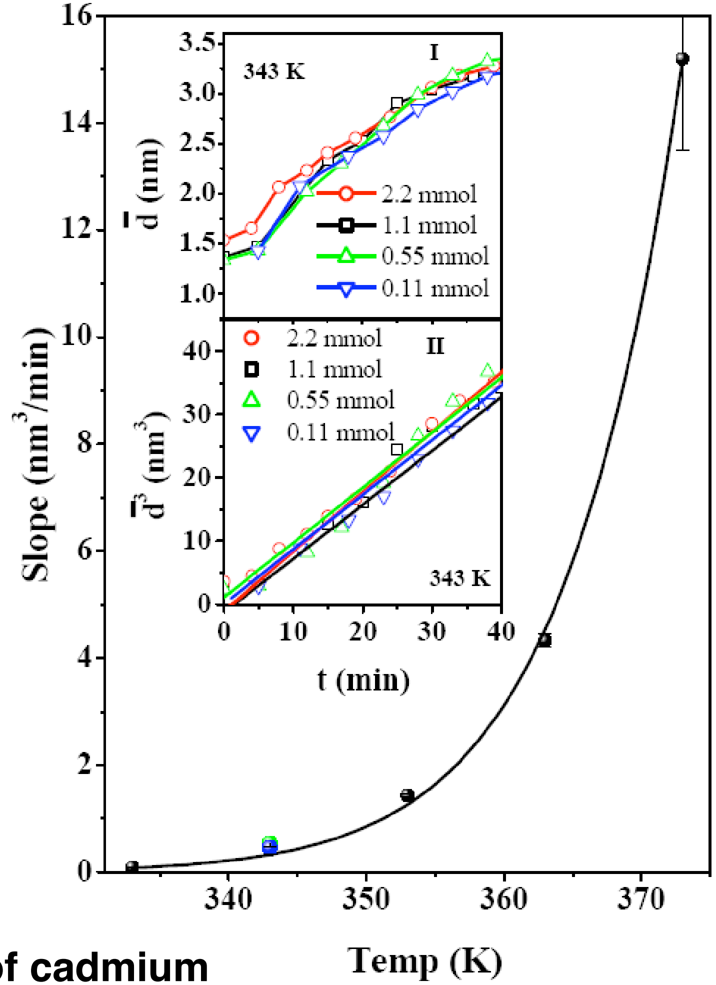
R. Viswanatha, D.D. Sarma et al. Chem Letters (2009)

CdS Nanoparticles

$$K = \frac{8 \cdot \gamma \cdot D \cdot V_m^2 \cdot C_\infty}{9 \cdot R \cdot T}$$

$$D = D_0 \cdot \exp(-E_a / kT)$$

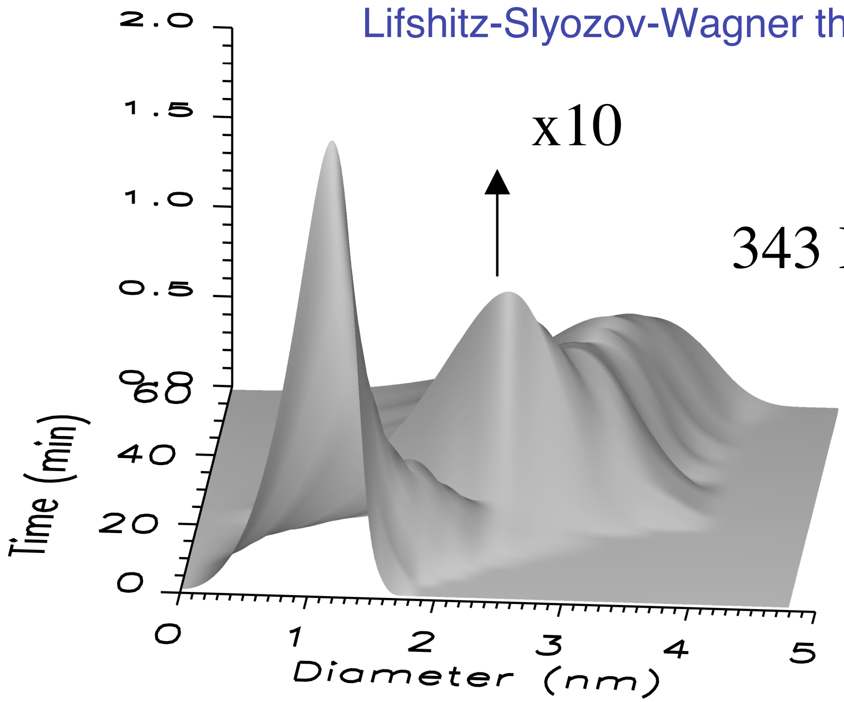
D	diffusion constant
V_m	molar energy
γ	surface energy
C_∞	equ. concentration at surface
E_a	activation energy



Viswanatha,R. *et al.* Growth mechanism of cadmium sulfide nanocrystals. *J. Phys. Chem. Lett.* 1, 304-308 (2010)

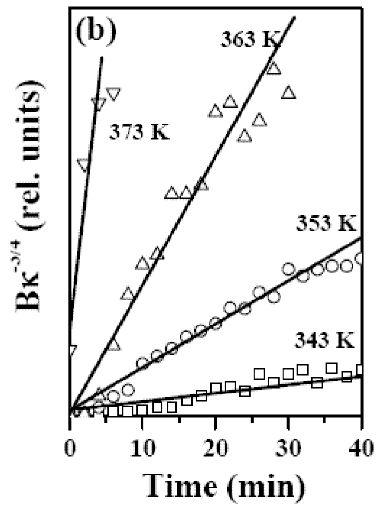
CdS Nanoparticles

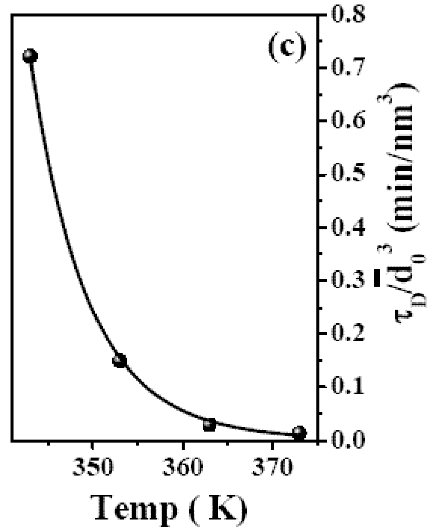
„Ostwald Ripening“
Lifshitz-Slyozov-Wagner theory (1961)



$$D(\xi) = \kappa\, \xi^2 \left(\frac{3}{3+\xi}\right)^{7/3} \left(\frac{1.5}{1.5-\xi}\right)^{11/3} exp\left(\frac{-\xi}{1.5-\xi}\right)$$

$$\kappa = \kappa_c/(1+t/\tau_D)^{4/3} \qquad \tau_D = \frac{9\bar{d}_0^3 RT}{64\gamma D C_\infty V_m^2} \qquad \frac{\tau_D}{\bar{d}_0^3} \propto T \cdot \exp(E_a/kT)$$



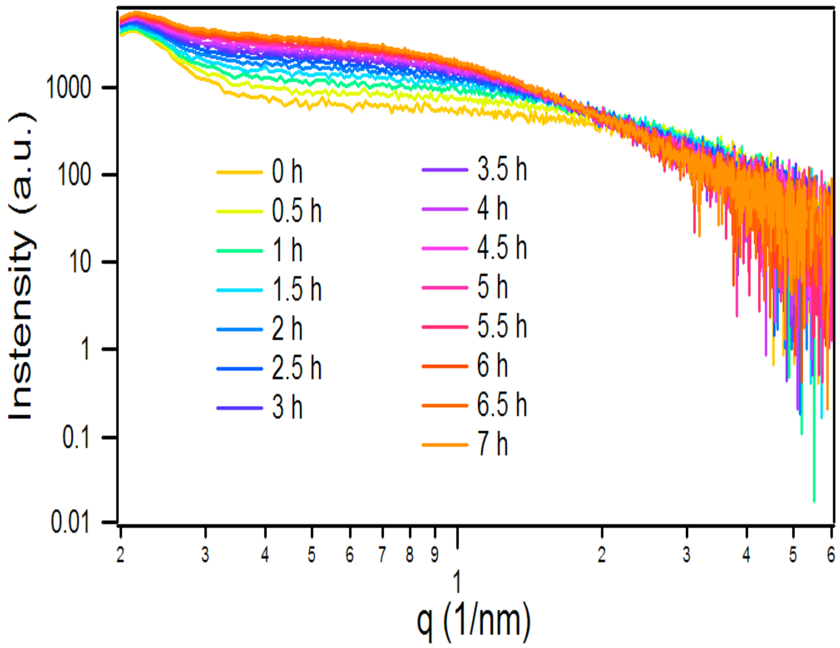


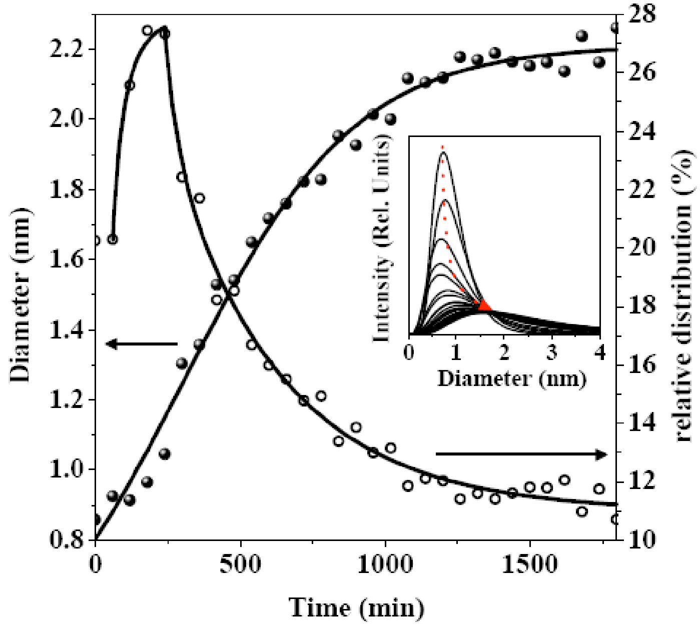
Viswanatha,R. *et al. J. Phys. Chem. Lett.* 1, 304-308 (2010)

CdS Growth

cadmium acetate/sodium sulphide in DMF
Capping agent: thioglycerol
Laboratory source

Cooked at 120°C



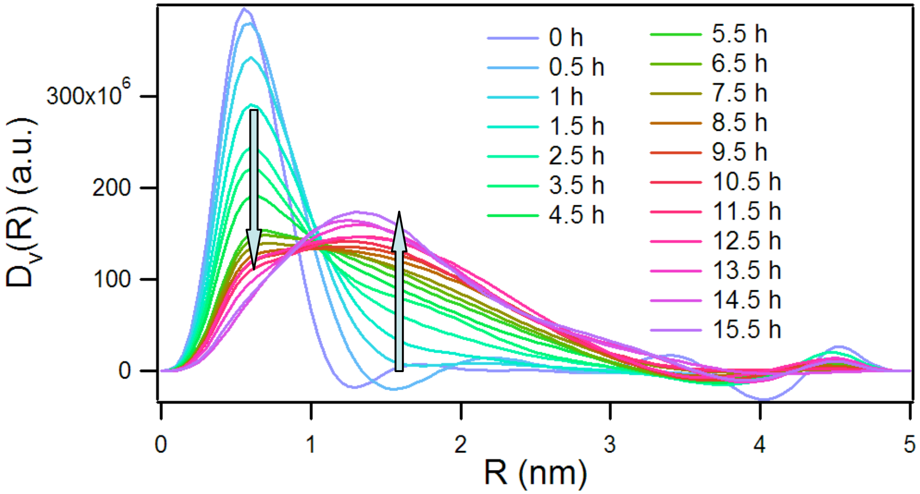


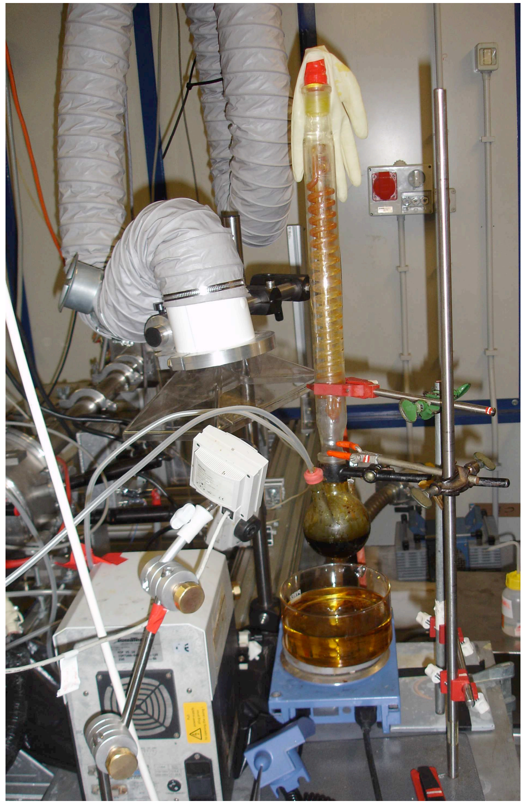
Viswanatha,R., Sapra,S., Amenitsch,H., Sartori,B. & Sarma,D.D. Growth of semiconducting nanocrystals of CdS and ZnS. *Journal of Nanoscience and Nanotechnology* **7**, 1726-1729 (2007).

CdS Growth

Model free determination of the size distribution (GIFT, Glatter O. et al.)

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



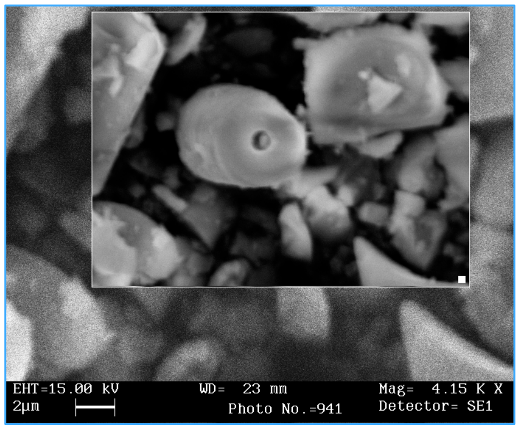


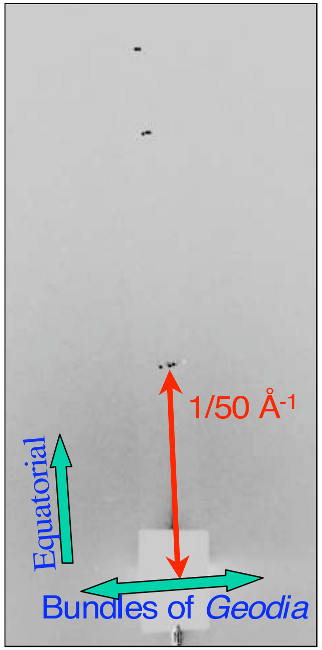
ZnS Synthesis
Trimmel et al. 2009

SAXS STUDY OF SPICULES FROM MARINE SPONGES

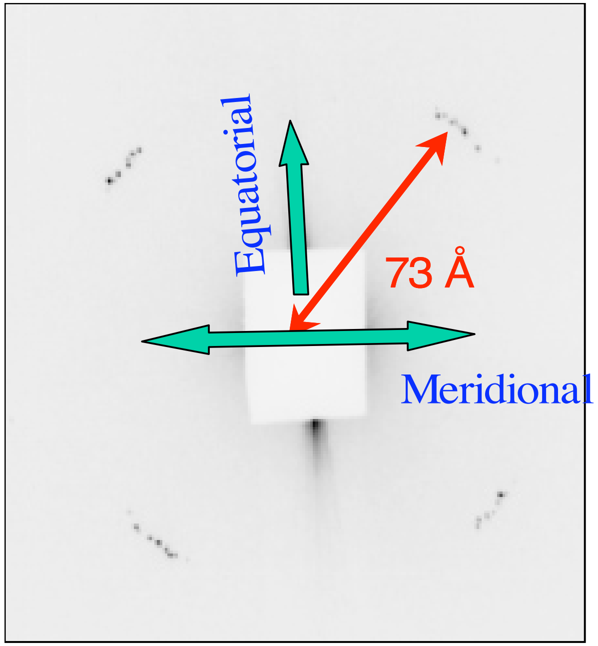
- The scientific name is “Porifera” which translates into “pore-bearing”

Biomineralisation





Geodia

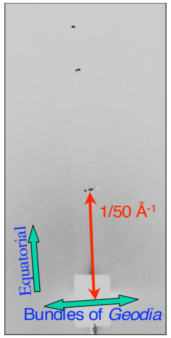


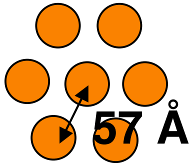
Scolimastra

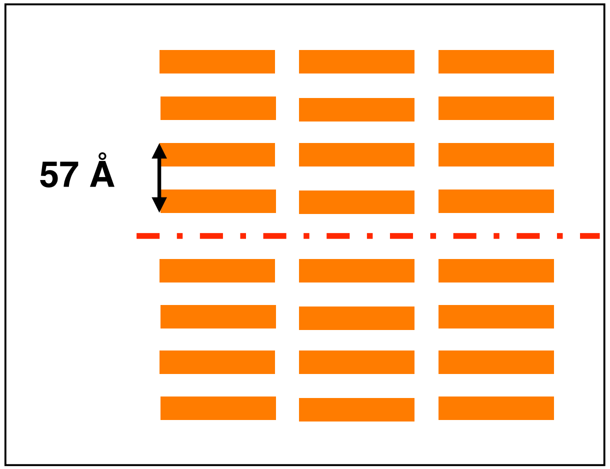
Croce,G. et al., 2004. *Biophysical Journal* 86:526-534.
Croce,G., et al.,2003. *Microscopy Research and Technique* 62:378-381

SAXS STUDY OF SPICULES FROM MARINE SPONGES

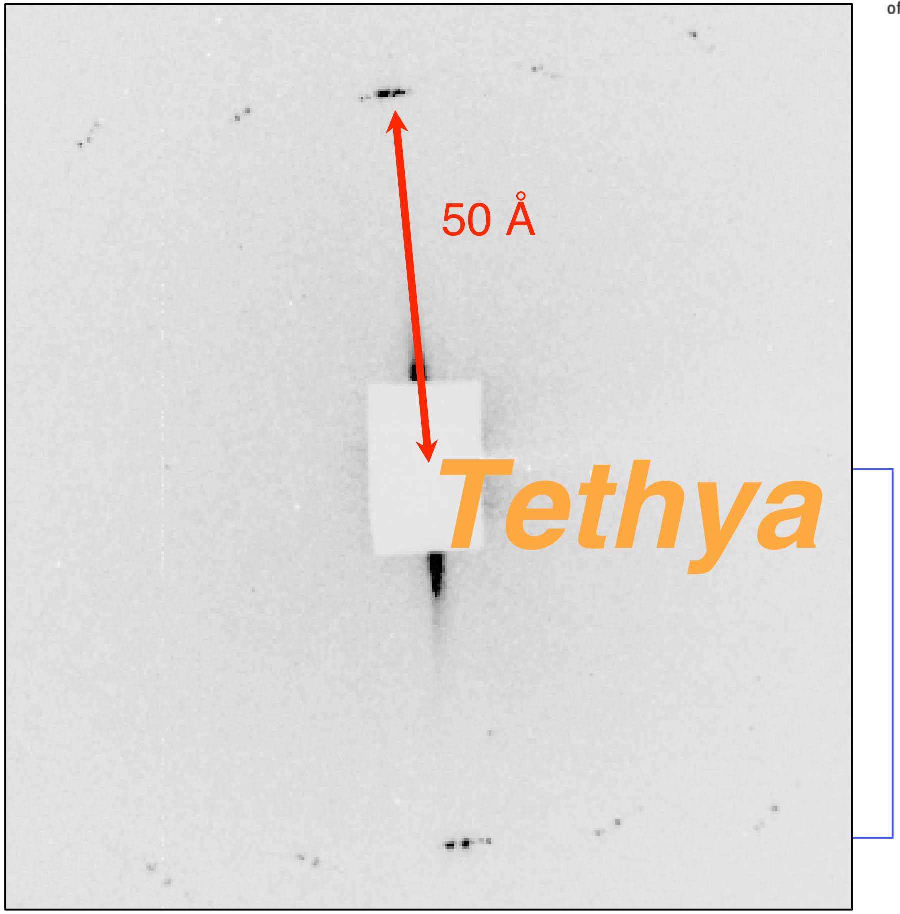
Geodia







Scolimastra



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

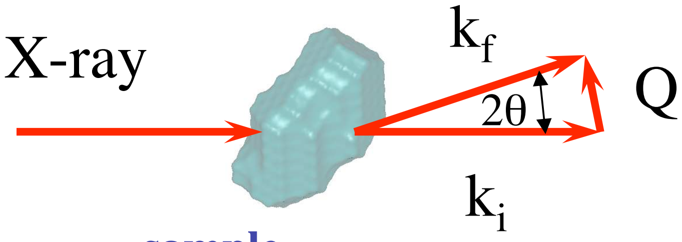
Outline

• Basics of small angle scattering
• Instrumentation for (*in situ*) small angle scattering
• What kind of information can be extracted from SAS?

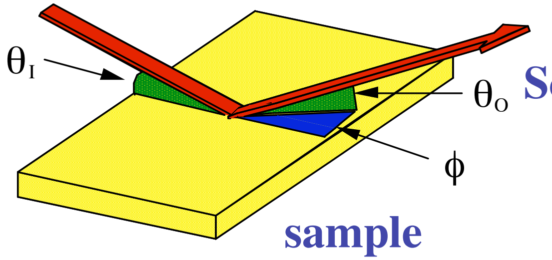
• Examples from
glass,
growth of semiconducting nanoparticles,
Marine sponges

• Principles of GISAS
self assembly from mesoporous materials on surfaces
• Conclusion and outlook

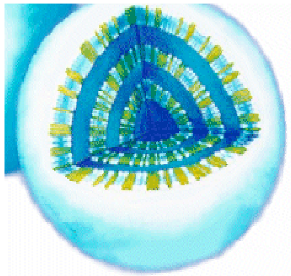
Small Angle Scattering - Surface Scattering

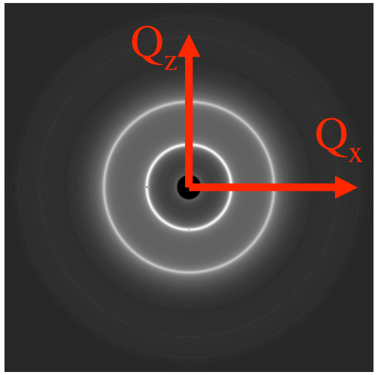


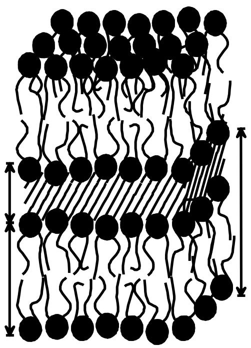
Small-Angle Scattering (Diffraction)

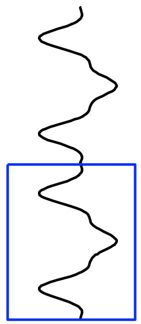


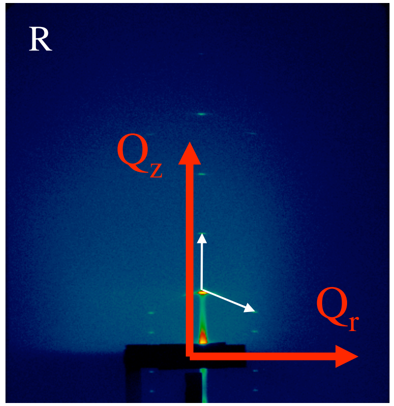
Grazing Incidence Small-Angle Scattering (GISAS) + Reflectometry









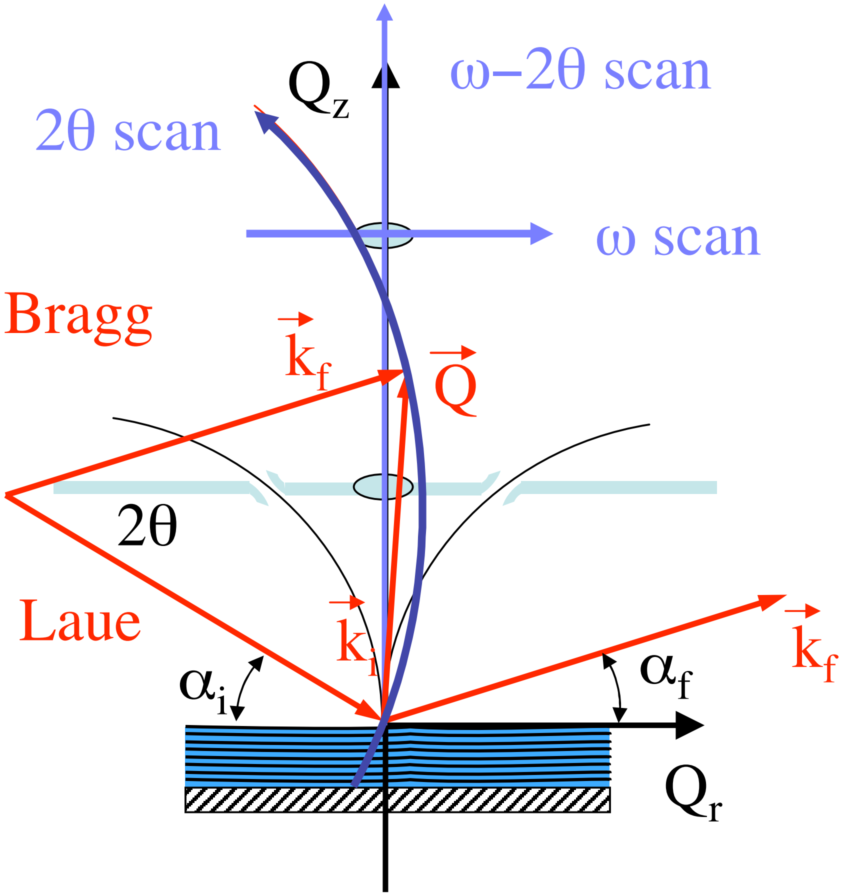


$$I(Q) = \left\langle \left| \int_V d^3r \cdot \rho(\vec{r}) \cdot \exp(-i \cdot \vec{Q} \cdot \vec{r}) \right|^2 \right\rangle \qquad I(Q_z, Q_r) = \left\langle \left| \int_V d^3r \cdot \rho(\vec{r}) \cdot \exp(-i \cdot \vec{Q} \cdot \vec{r}) \right|^2 \right\rangle$$

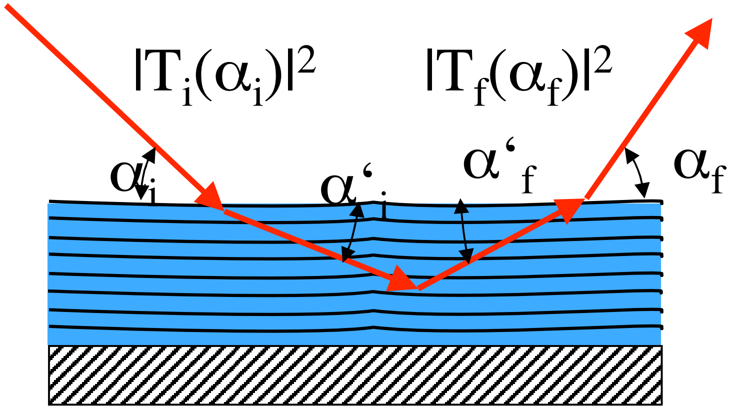
Distorted Wave Born Approximation

Vineyard (1982), Shinha et.al. (1988)

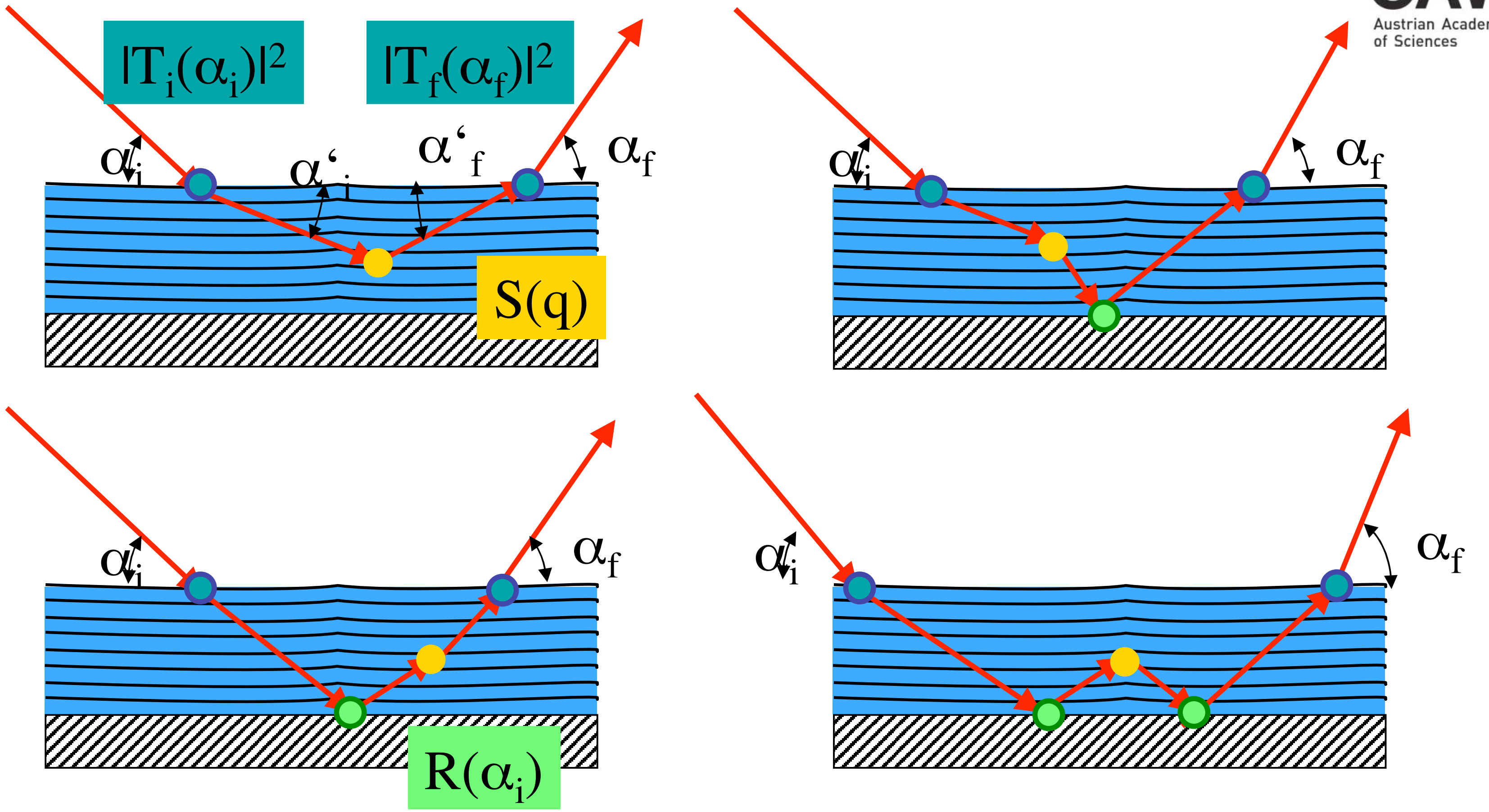
$$I(Q_z, Q_r) = |T_i(\alpha_i)|^2 \left\langle \left| \int_V d^3r \cdot \rho(\vec{r}) \cdot \exp(-i \cdot \vec{Q} \cdot \vec{r}) \right|^2 \right\rangle_r |T_f(\alpha_f)|^2$$



Refraction Effects



„Higher Orders“ of DWBA



Lazzari R, ISGISAXS: program, J APPL CRYSTALLOGR 35: 406, (2002)
http://www.esrf.fr/computing/scientific/joint_projects/IsGISAXS/isgisaxs.htm

M.P.Tate et al., J.Phys.Chem, 2006

Distorted Wave Born Approximation

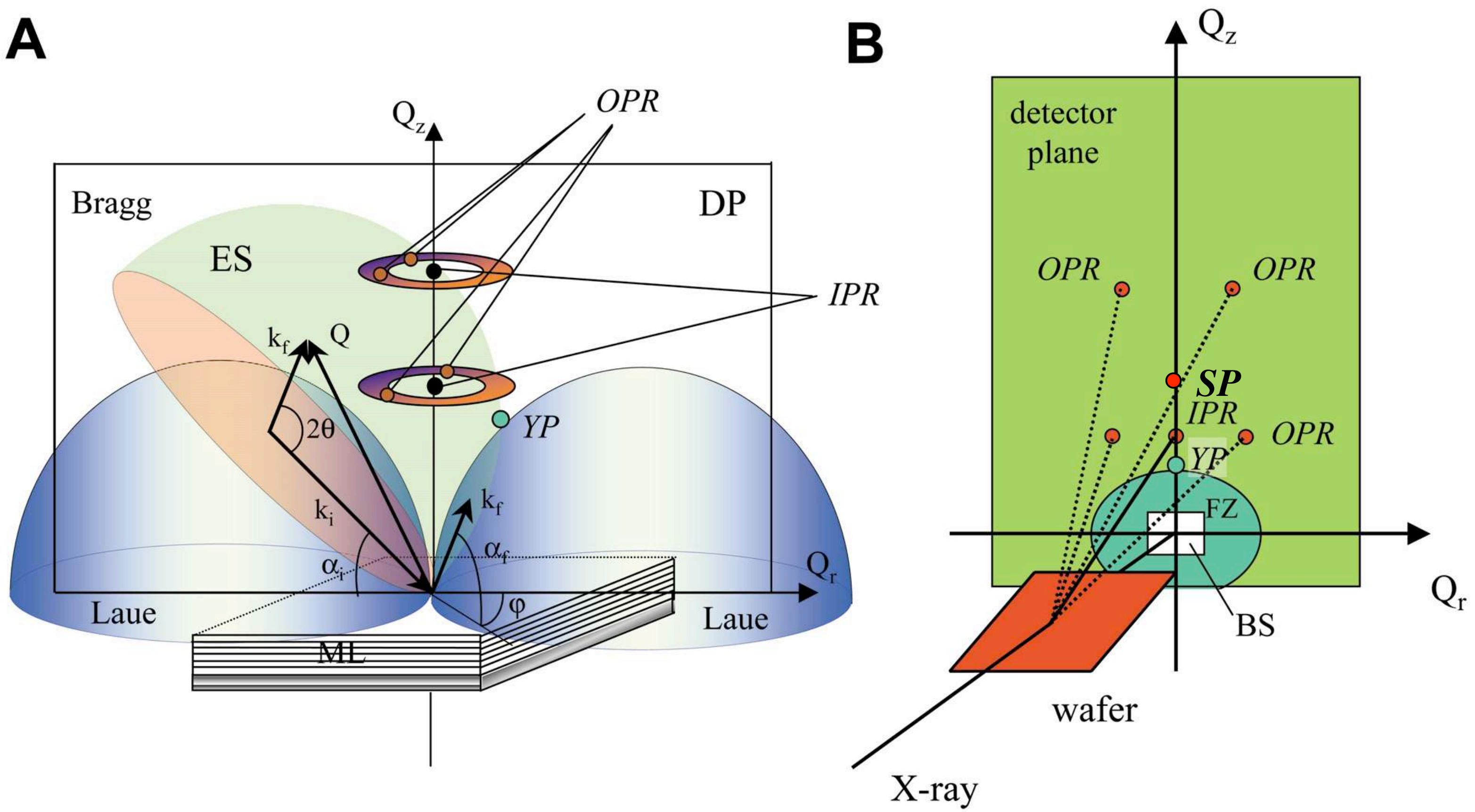


Fig. (A) the scattering geometry in reciprocal space. (B) Scattering geometry in real space. The abbreviations are: (ES) Ewald sphere, (DP) diffraction plane, (OPR) out-of plane reflections, (IPR) in-plane reflections, (ML) multi-layer, (FZ) forbidden zone, (BS) beam stop.

Surface diffraction: Formation of aligned mesoporous thin films

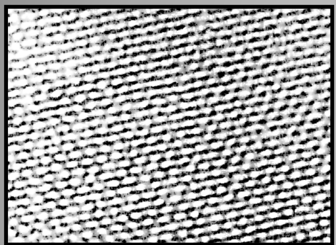
Sol-gel chemistry
+
surfactant mesophase

Self-assembly

Mesostructured hybrids

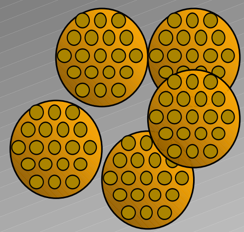
Treatment

Mesoporous materials with organised porosity

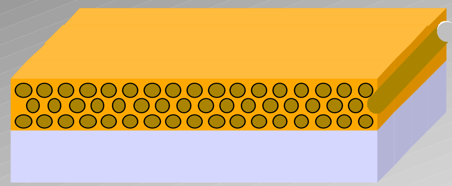


C. J. Brinker et al. Adv. Mater., 1999, 11, 579.

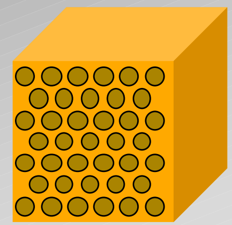
Particles made by aerosols



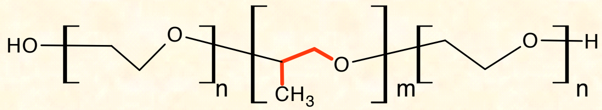
Films and **fibres** made by liquid deposition



Monoliths made by controlled evaporation

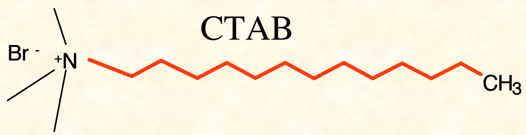


Triblocks POE-POP-POE



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} : $VOCl_3$

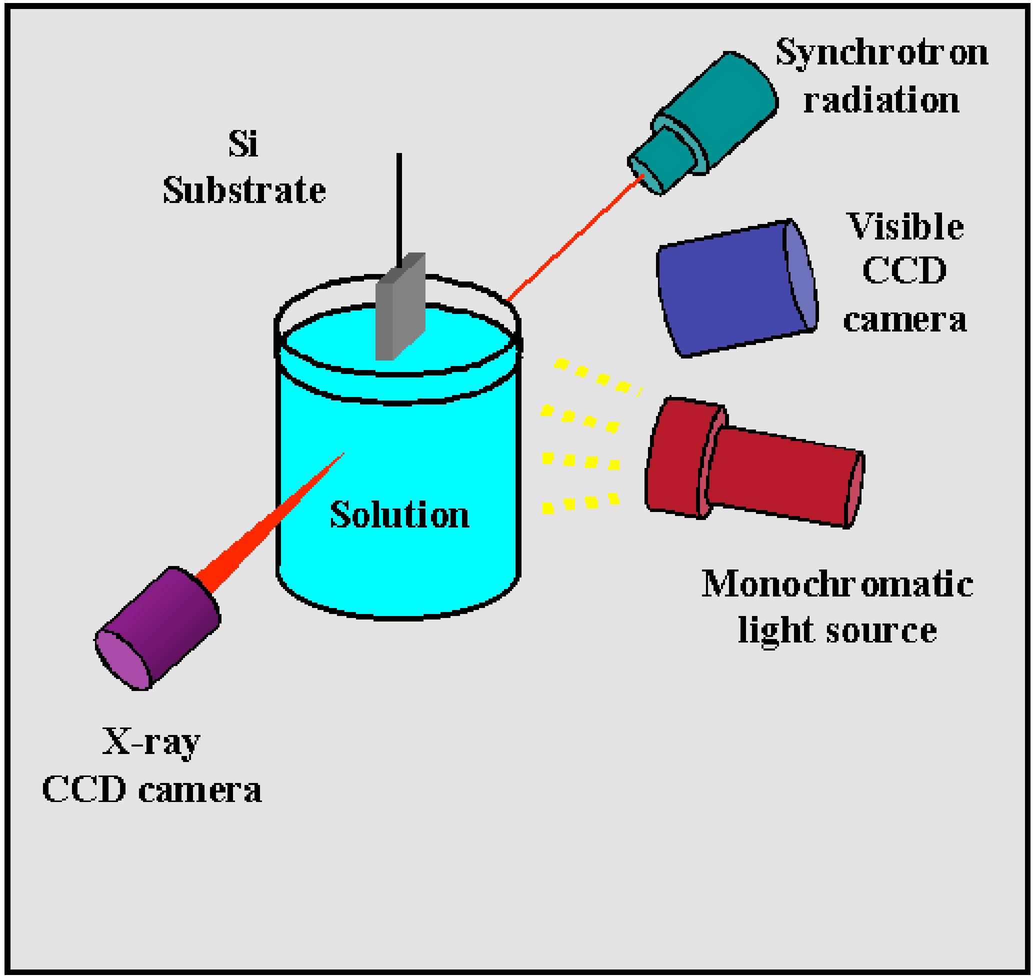
Y_2O_3 : YCl_3

Nb_2O_5 : $NbCl_5$

And binaries systems

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

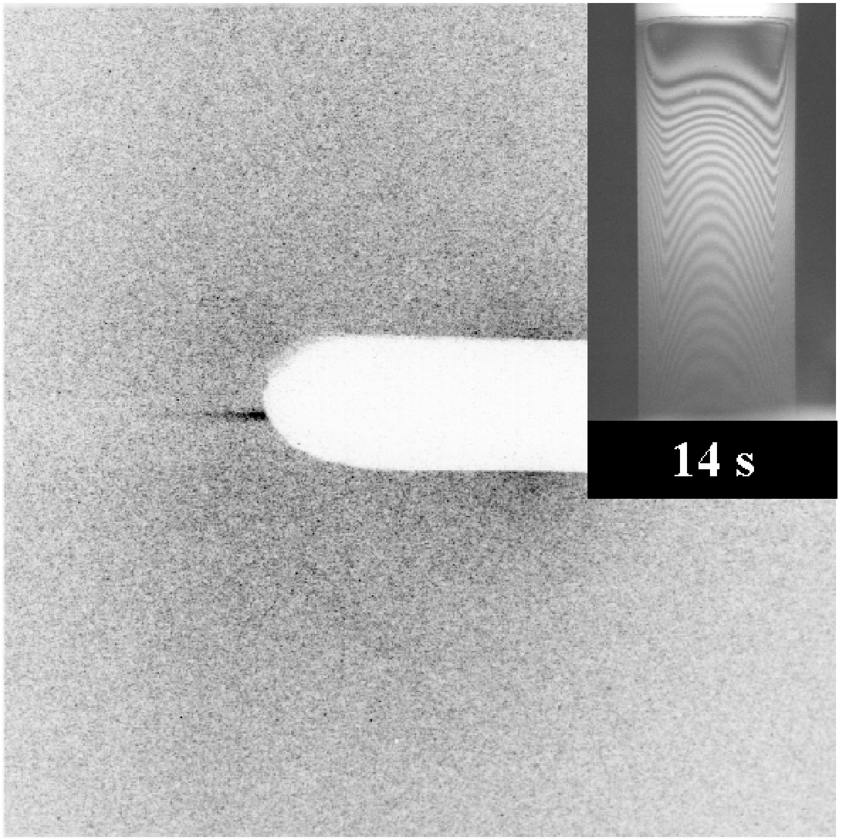
Film mesostructure

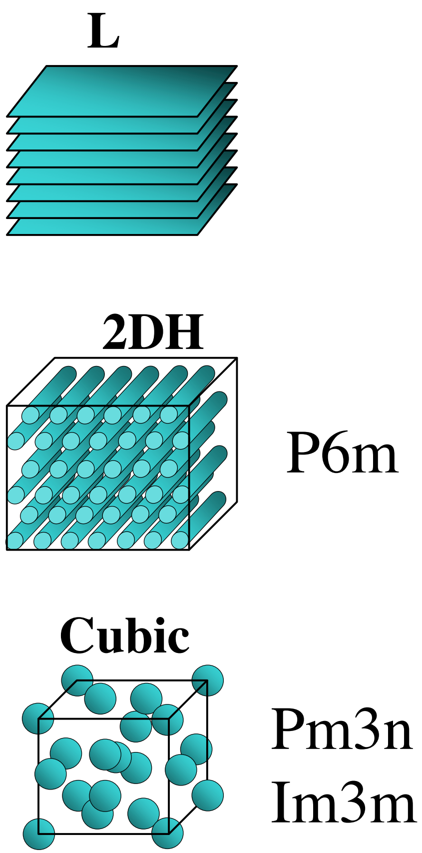


Film thickness profile

Surface diffraction: Formation of aligned mesoporous thin films

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

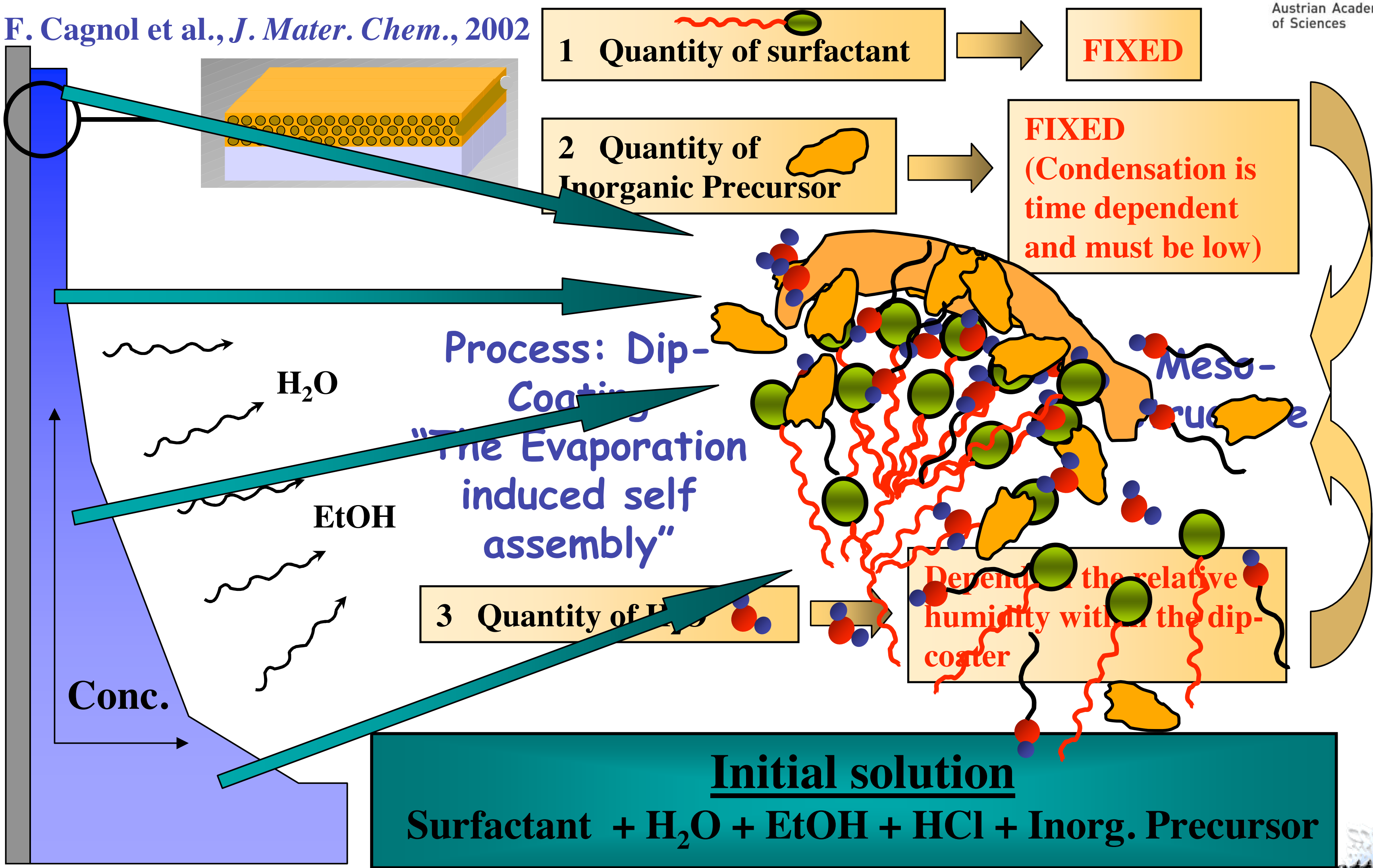




Grosso D, et.al., CHEMISTRY OF MATERIALS *14,* 931,(2002)

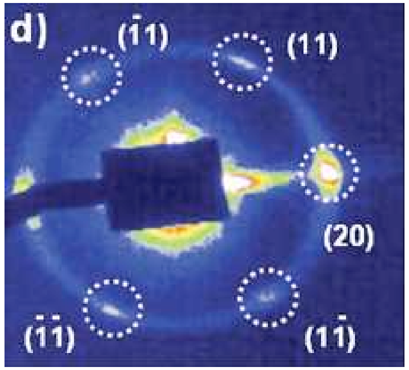
The Modulable Steady State

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

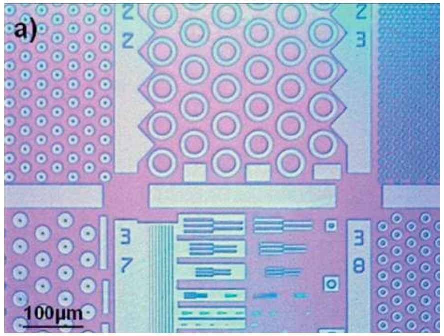


Combining bottom up/top down approaches

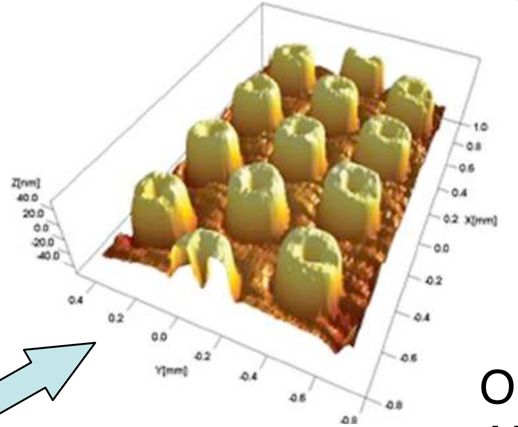
Mesoporous Functionalized nano/micro-Arrays



TRSAXS

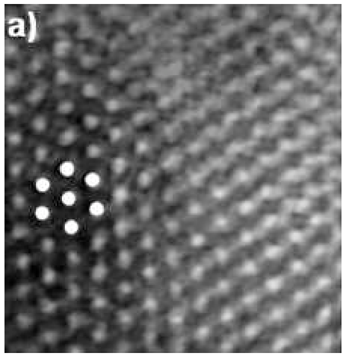


DXRL

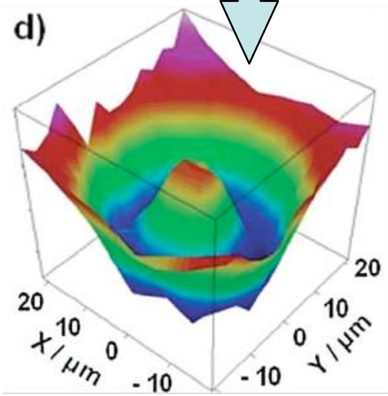


OPM/
AFM

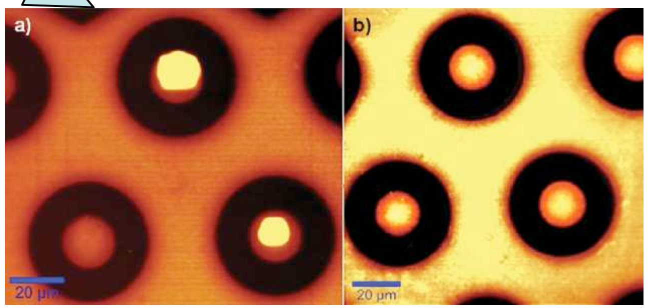
Multiscale Nano Surfaces



TEM



IR-Micr.



Flourescence-Micr.

P.Falcaro et al., *Adv.Mat.*,2008

Further Reading

11th Annual Report

Annual Reports SAXS Beamline:
-Time resolved studies
-Surface diffraction
-GISAXS

SAXS:

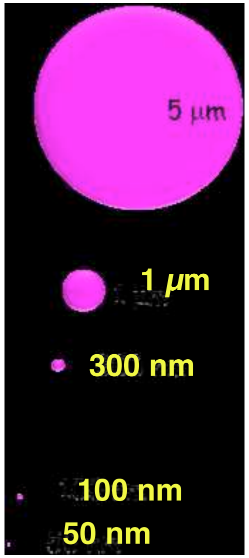
Programms:
Illiavsky J., IRENA
Glatter O., GIFT
Svergun D.I., ATSAS

Surface Diffraction/GISAXS

M. Tolan, X-ray scattering from soft-matter thin film. Springer Tracts in Modern Physics 148, Springer, Berlin, 1999.

Rauscher M, Salditt T, Spohn H, GISAXS –Distorted Born Wave Approximation PHYS REV B 52, 16855 (1995)

Future

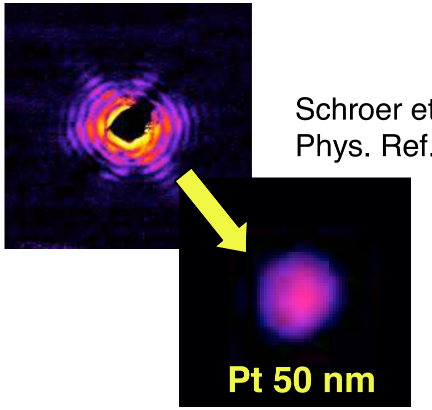


ID13 ESRF

NanoSpots (all SR)

Coherence (SAXS Imaging)

FEL (Single Particle Analysis)



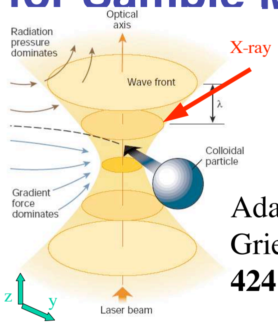
Schroer et al.
Phys. Ref. Lett. 2008

New Technologies for Sample Manipulation

Optical Tweezers

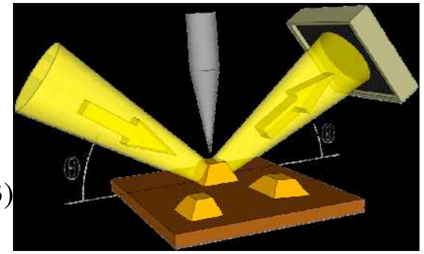
AFM

Microfluidics

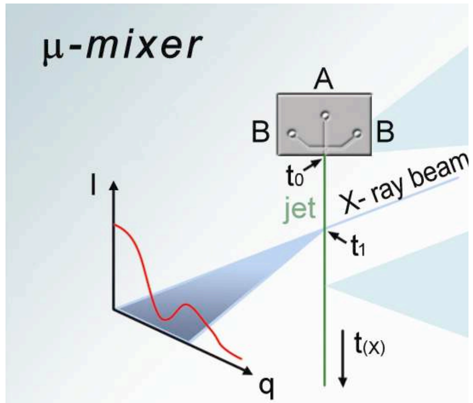


Adapted from:
Grier, Nature
424, 810 (2003)

TASC/IBN/ESRF



Development ESRF



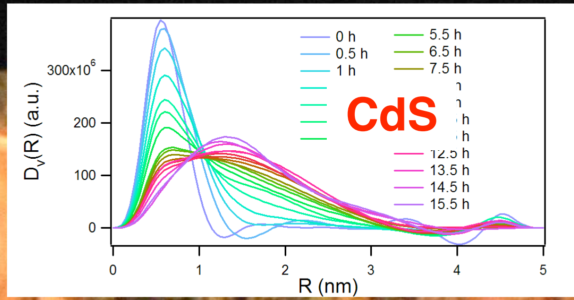
SAXS@ELETTRA

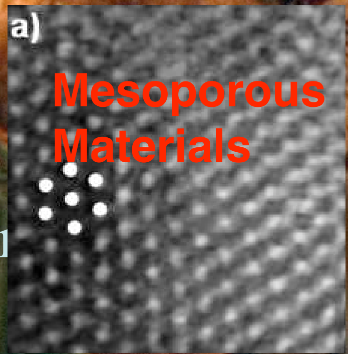
Acknowledgement

-IBN Graz: G. Pabst, R.Prassl, K.Lohner

-ext. Groups: D.D. Sarma
D.Viterbo, G.Croce
D.Grosso
P.Innocenzi

-Thanks for your attention





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Austro SAXS