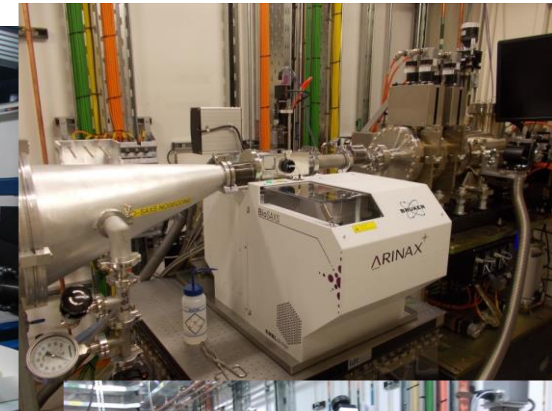
Small Angle X-ray Scattering

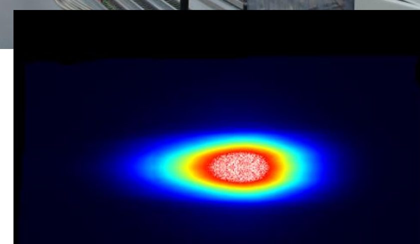
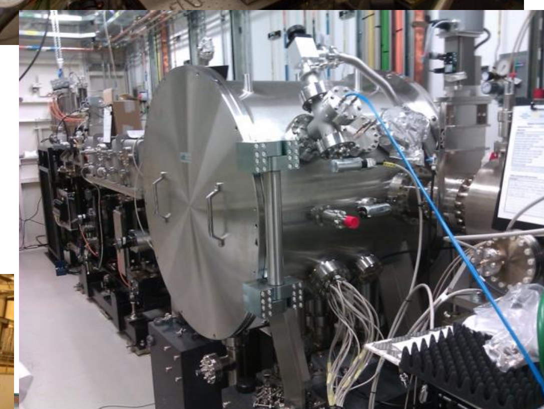
The last resort of the desperate!

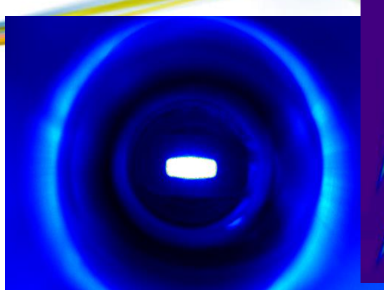
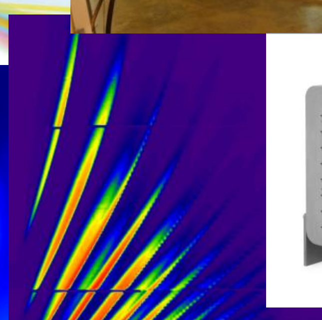
Nick Terrill – Principal Beamline Scientist, Scattering, Diamond

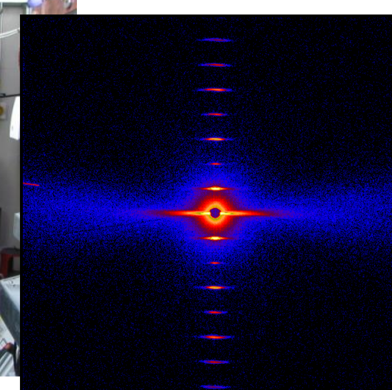
SAXS at Diamond
Beamline Progress and Science highlights

Small-angle, non-crystalline diffraction provides essential information on the structure and dynamics of large molecular assemblies in low ordered environments. These are characteristic of living organisms and many complex materials such as polymers and colloids.

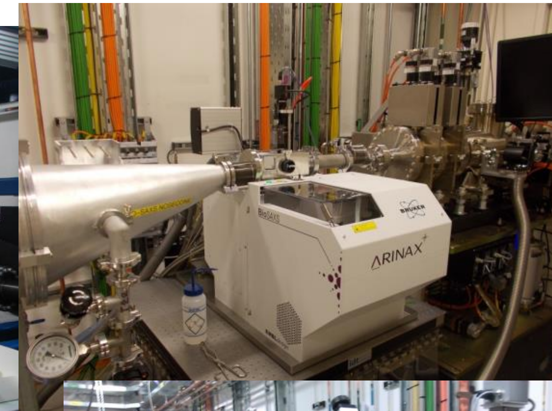



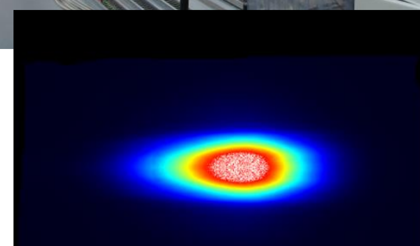
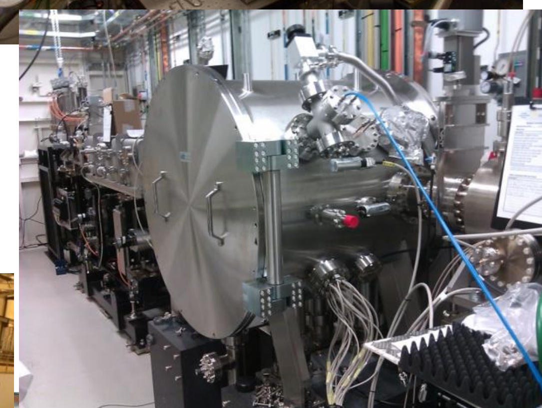



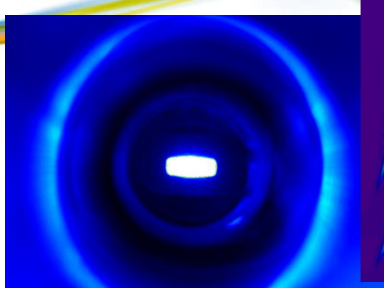
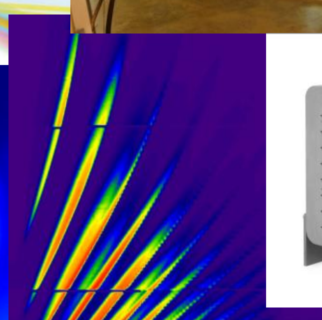



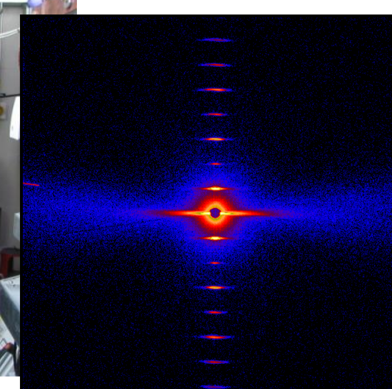
SAXS at Diamond
Beamline Progress and Science highlights

- Used for
  - Archaeology
  - Biology
  - Biomaterials
  - Ceramics
  - Colloids
  - Cultural heritage
  - Environmental science
  - Forensic science
  - Liquid crystals
  - Mineralised tissue
  - Polymers
  - Surfactants

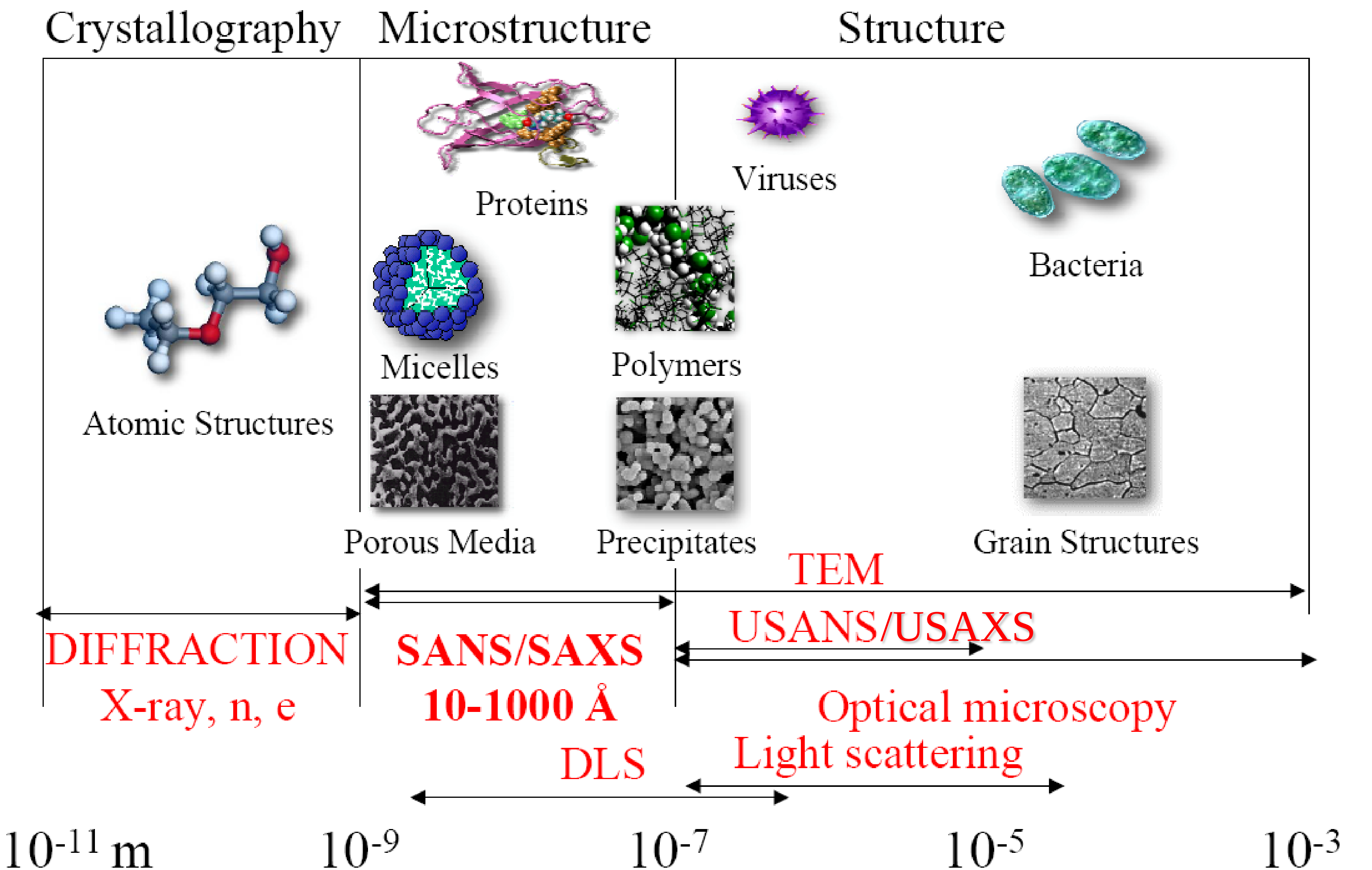



Probing the Length Scales



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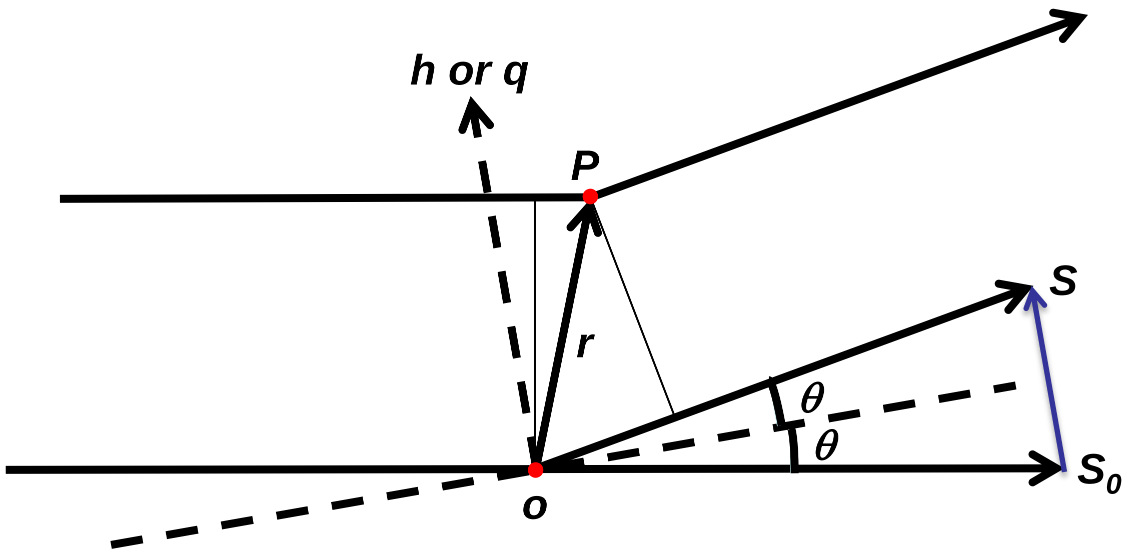
Scattering

X-ray scattering is probing distances that are large compared to inter-atomic distances. Characteristics are:

- Random orientation of particles (i.e. no long-range order) leads to scattering rather than diffraction (determination of size and shape)
- Electron density variations at the particle-matrix interface cause x-rays to scatter.
- The scattered intensity, $I(q)$, is measured in terms of the scattering vector, q.

Scattering by two point centres



From G. Porod, Ch2 in “Glatter and Kratky”

X-ray scattering

Amplitude: $A(q) = \int_{Vr} \rho(r) e^{-ir.q} dVr$ (Volume Integral)

Where ρ(r) is the relates to the electron density
and q is the scattering angle

Particle in solution => thermal motion => Particles have a random orientation/x-ray beam. The sample is **isotropic**. Only the **spherical average** of the scattered intensity is experimentally accessible.

Intensity: $I(q) = \langle A(q).A^*(q) \rangle$

Porod's law: specific surface and interface

- When two media are separated by a sharp interface, the scattered intensity follows an asymptotic law in the high q region:

$$I(q)=Aq^{-4}+B.$$

- This law is called the Porod's limit and has more sophisticated expressions in the case of complicated interfaces.
- The asymptotic value, when the electronic contrast of the sample is known, and when the intensity is expressed in absolute scale, allows the calculation of the specific surface S (in cm^2/cm^3) of the particles.

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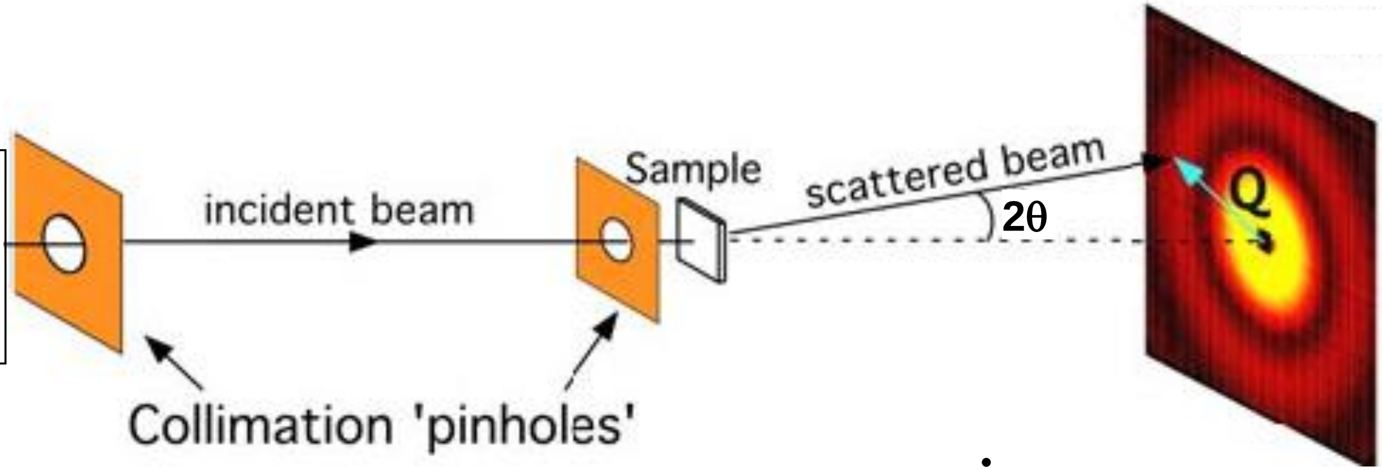
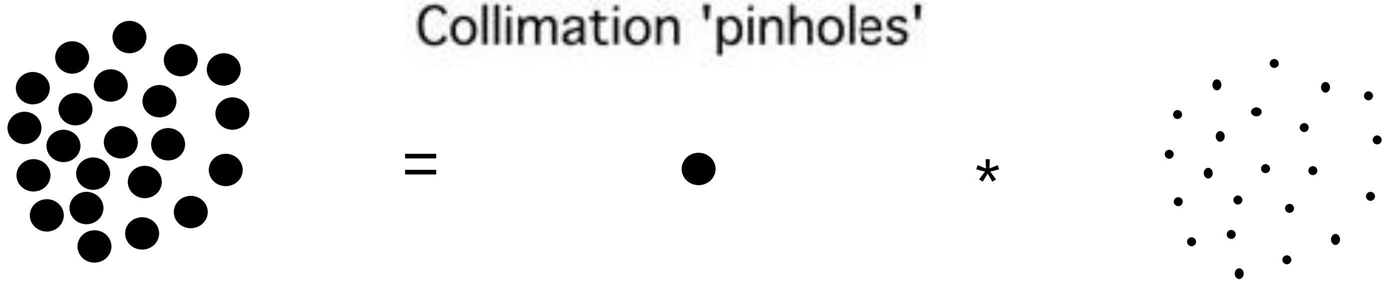
Surface Fractal Laws

- For a smooth surface $S(r) = r^2$, and for a rough surface $S(r) = r^{ds}$, where ds is the surface fractal dimension that varies from 2 to 3
  - $I(q)$ proportional to q^{ds-6}
- Surface fractals display power-law decays weaker than Porod's Law and are termed positive deviations from Porod's Law.

Source.
Monochromator,
Optics





Solution		Motif (Protein)	*	Lattice
I(c,q)		P(0,q)	.	S(c,q)

$$I(q) \propto \frac{d\sum(q)}{d\Omega} = \frac{N}{V} V_{particle}^{2} (\rho_{sample} - \rho_{matrix})^{2} P(q) S(q)$$

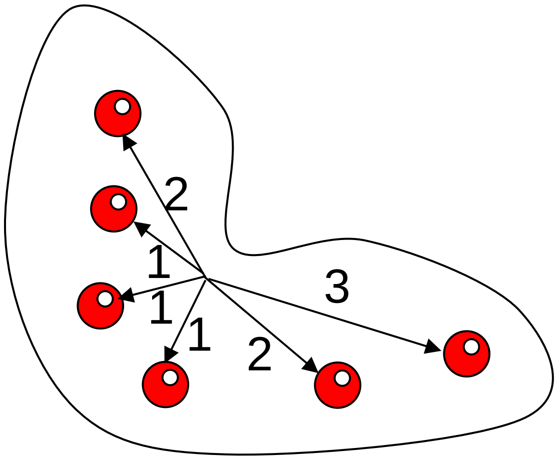
- 2θ = scattering angle, λ = radiation wavelength
- *N* = no. of scatterers in volume *V* of sample.
- $V_{particle}$ = volume of the individual scattering entity.
- ρ = density of the particle or the matrix
- *P(q)* = Form factor and *S(q)* = Structure Factor

- **From SAXS pattern:**
  - **Particle size**
  - **Particle shape**
  - **Polydispersity**
  - **Kinetics**

What do we mean by "size"?

Radius of gyration:

R_g^2 is the average squared distance of the scatterers from the centre of the object



$R_g^2 = (1^2 + 1^2 + 1^2 + 2^2 + 2^2 + 3^2)/6 = 20/6$

$R_g = \sqrt{3.333} = 1.82$

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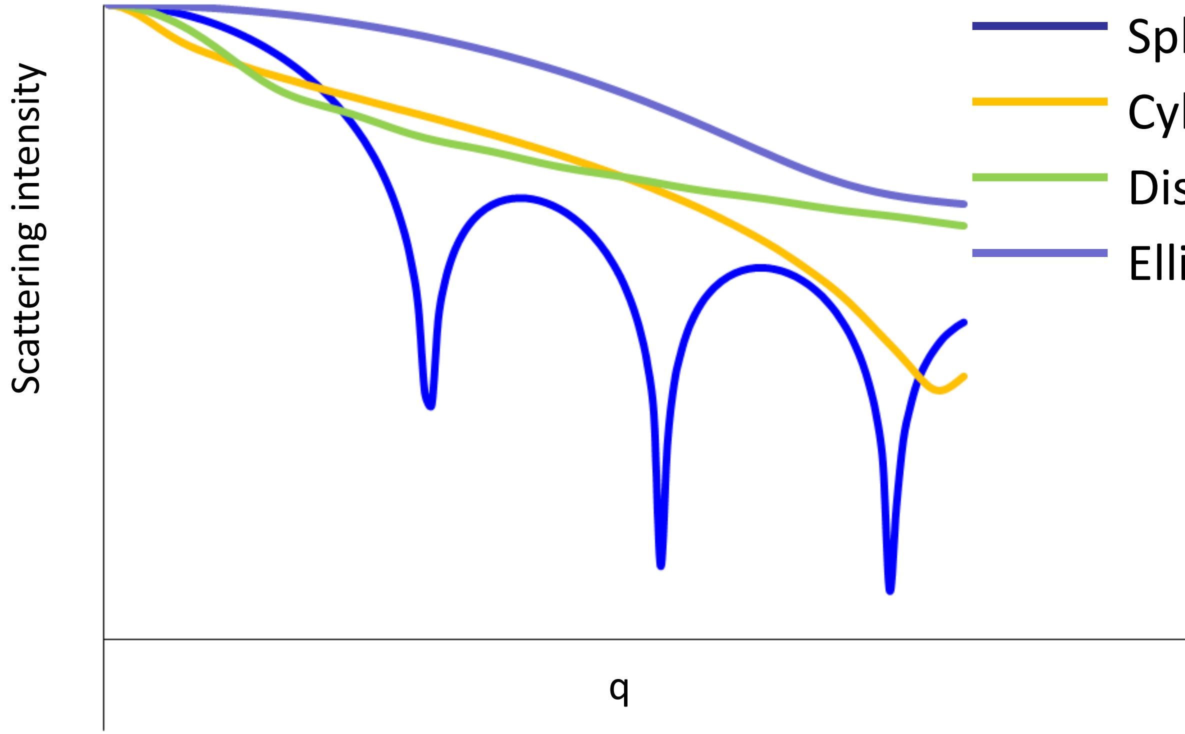
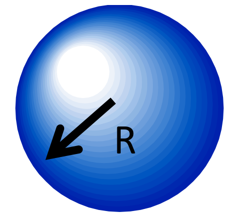
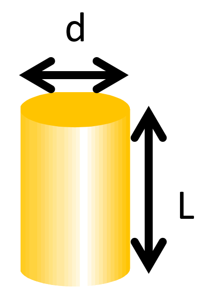
Form Factor for simple shapes

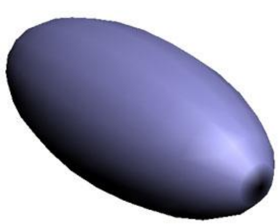




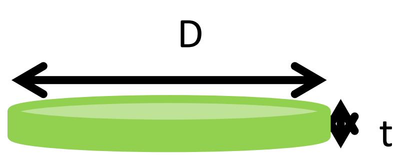
$$R_g = \sqrt{\frac{3}{5}}R$$



$$R_g = \frac{L}{\sqrt{12}}$$



$$R_g = \sqrt{\frac{1}{3}\left[\left(\frac{a}{b}\right)^{4/3} + 2\left(\frac{b}{a}\right)^{2/3}\right]}$$



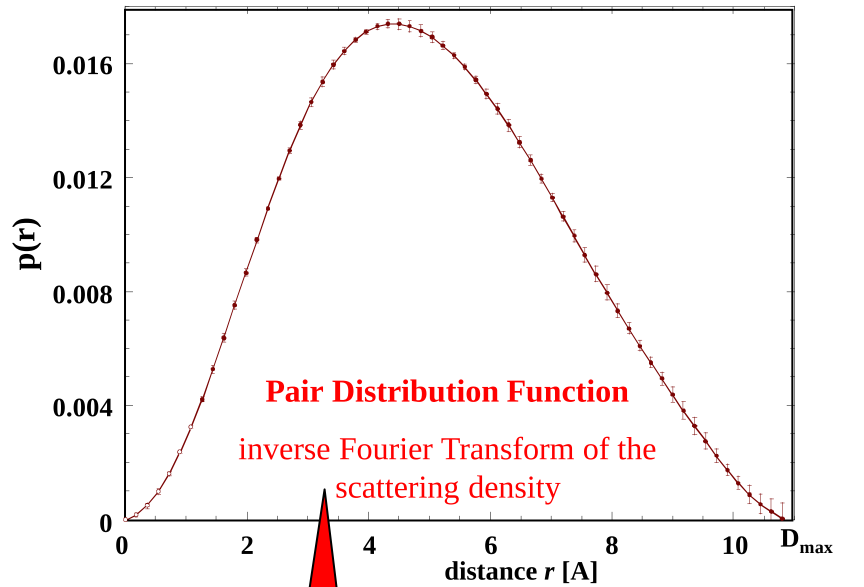
$$R_g = \frac{D}{2\sqrt{2}}$$

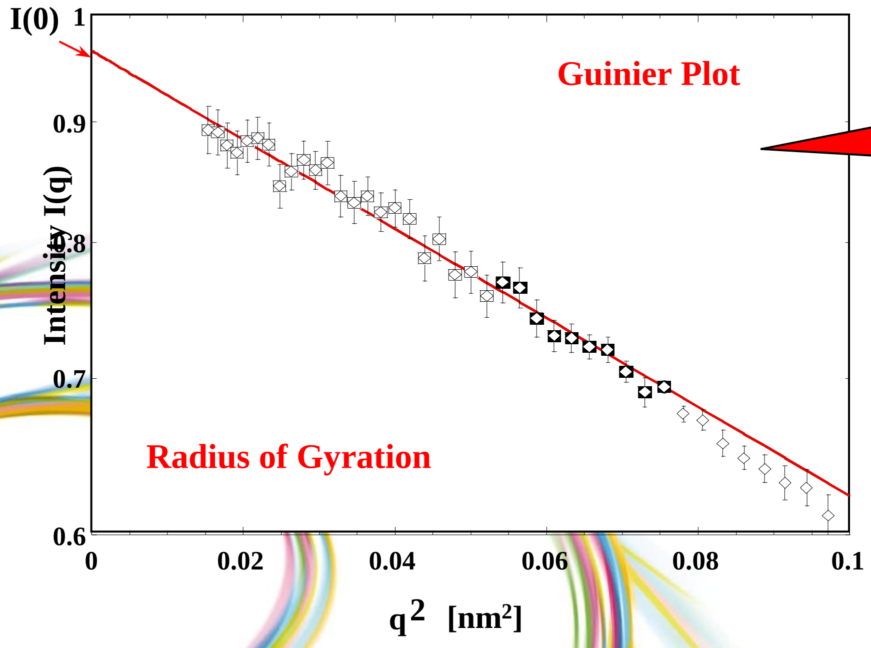
For more complicated shapes see reviews by J. S. Pedersen – http://www.chem.au.dk/~jansp/resdescription.html

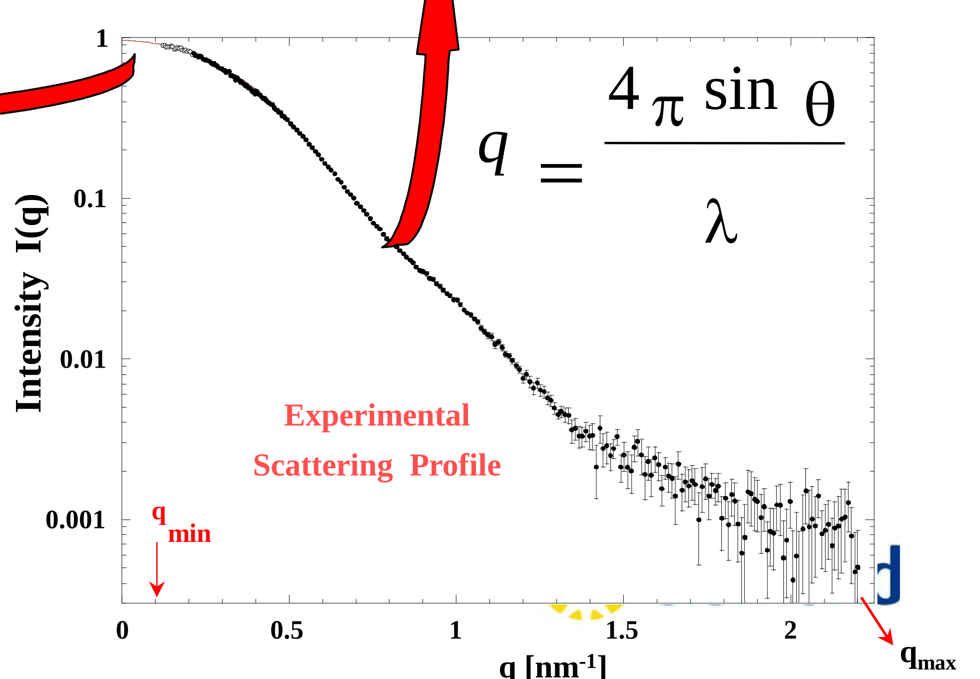
Solution SAXS: R_g, I_0 and P(r)

Rg = slope = shape function independent radius
I (at q=0) or intercept proportional to number of particles / volume of solution

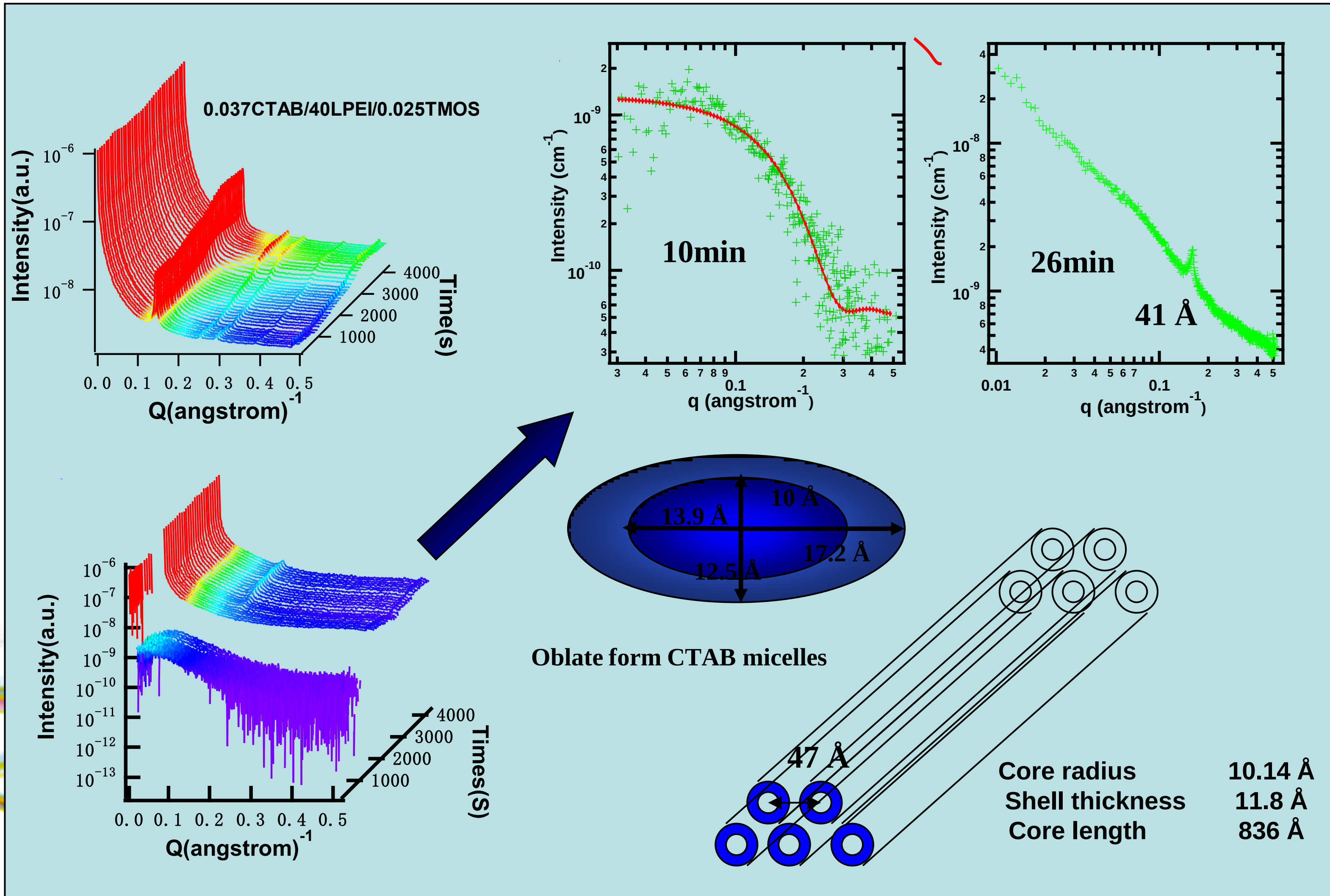
PDF = shape and size info





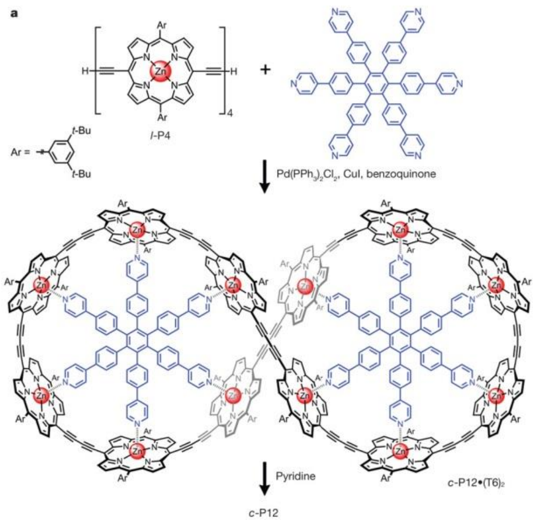


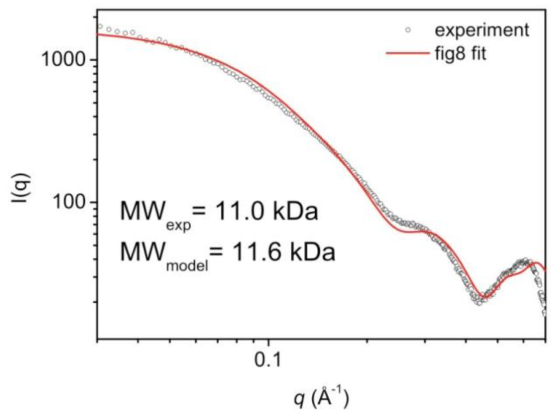
SAXS studies on silica templated with polyelectrolyte-surfactant complexes

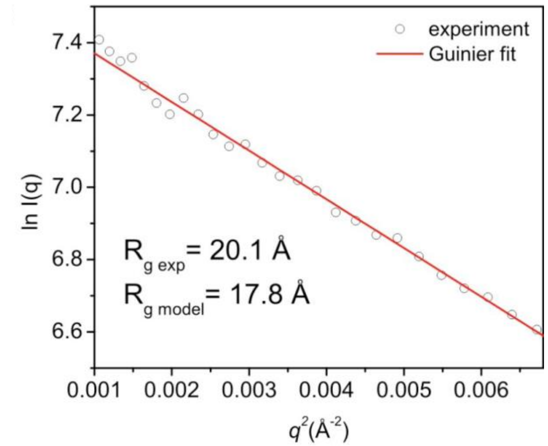


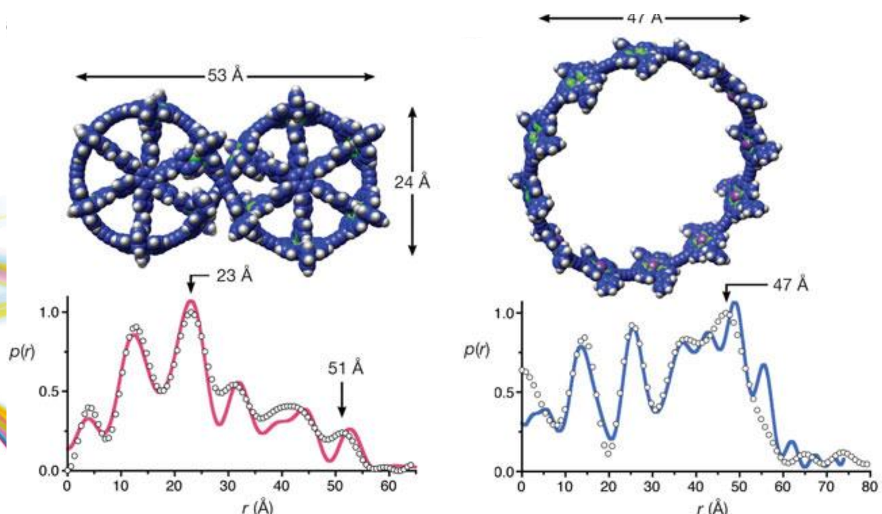
Bin Yang, Robben Jaber, and Karen J. Edler, **Langmuir**, 2012, 28 (22), 8337, DOI: 10.1021/la3014317

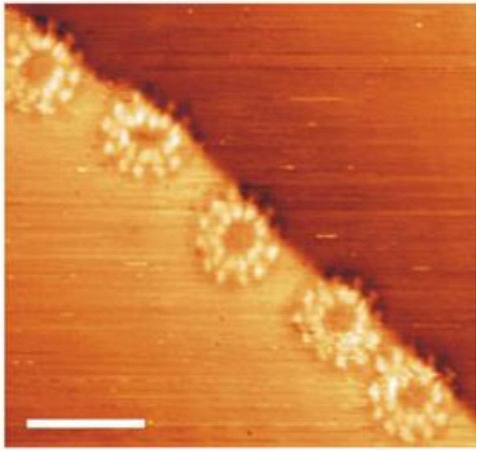
Vernier templating and synthesis of a 12-porphyrin nanoring.











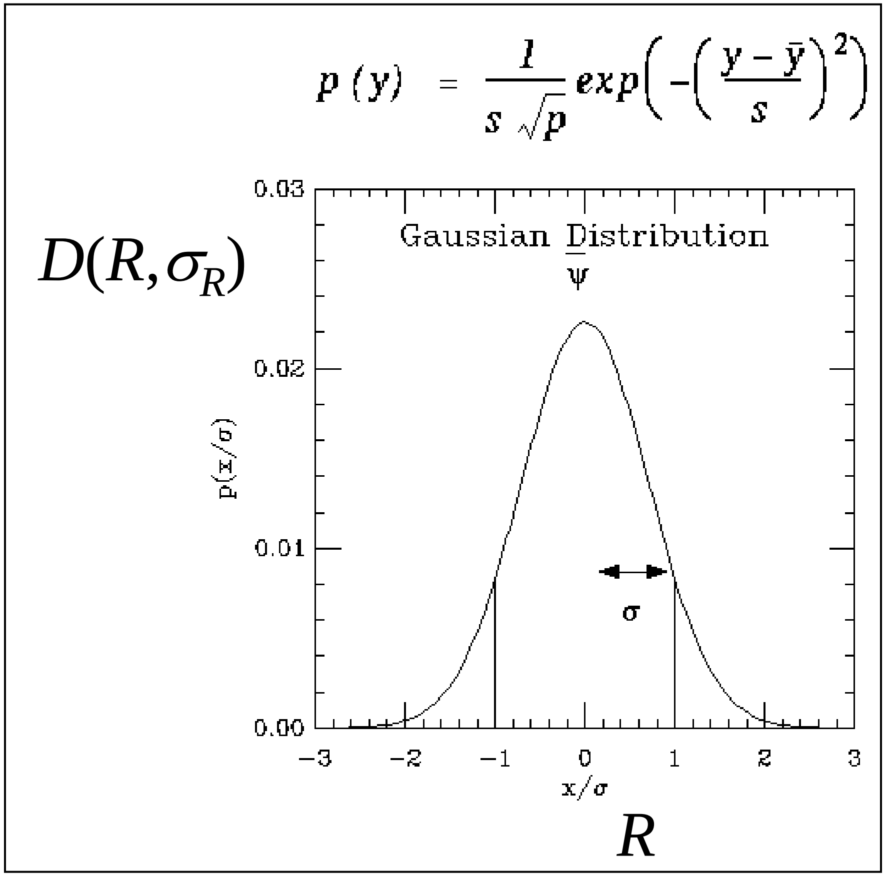
Melanie C. O'Sullivan, Johannes K. Sprafke, Dmitry Kondratuk, Corentin Rinfray, Timothy D. W. Claridge, Alex Saywell, Matthew O. Blunt, James N. O'Shea, Peter H. Beton, Marc Malfois, Harry L. Anderson,
Nature Letters Volume: 469, Pages: 72–75, 2011

Size polydispersity

$$I(q) = \Delta\rho^2 \int_0^\infty P(q,R) D(R,\sigma_R) dR$$

$$P(q,R) = \left[V \frac{3[\sin(qR) - qR\cos(qR)]}{(qR)^3} \right]^2$$

$$D(R,\sigma_R) = \frac{1}{\sigma_R \sqrt{2\pi}} \exp\left[-\frac{(R-R_a)^2}{2\sigma_R{}^2} \right]$$



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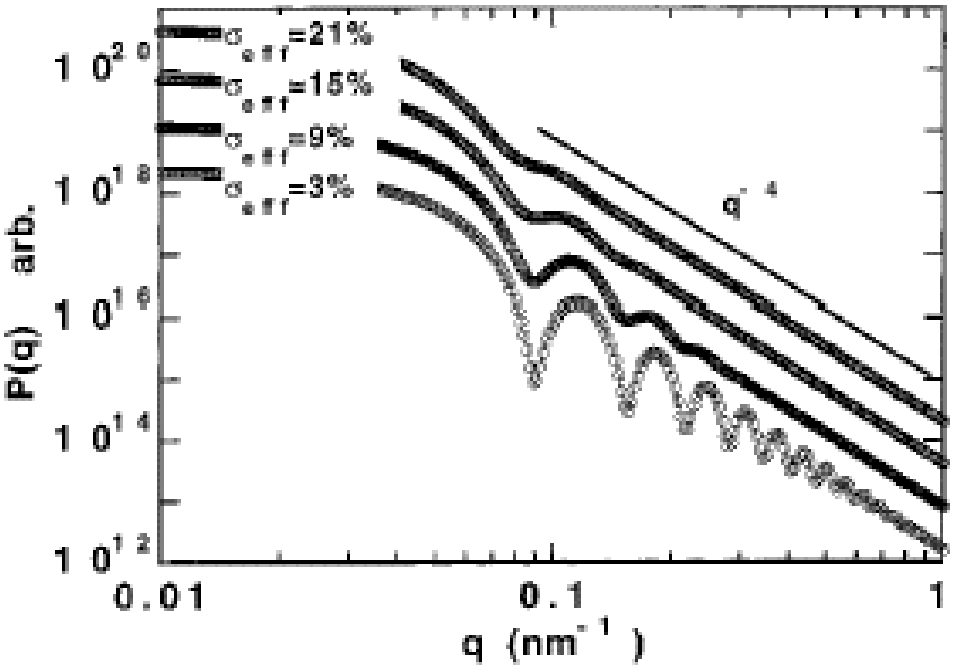
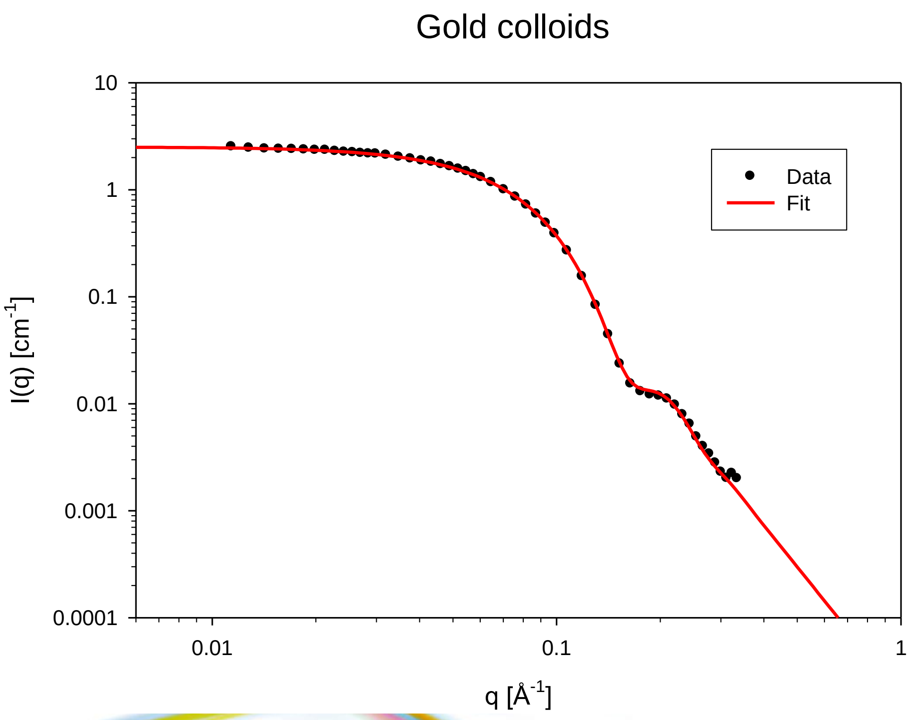
Size polydispersity

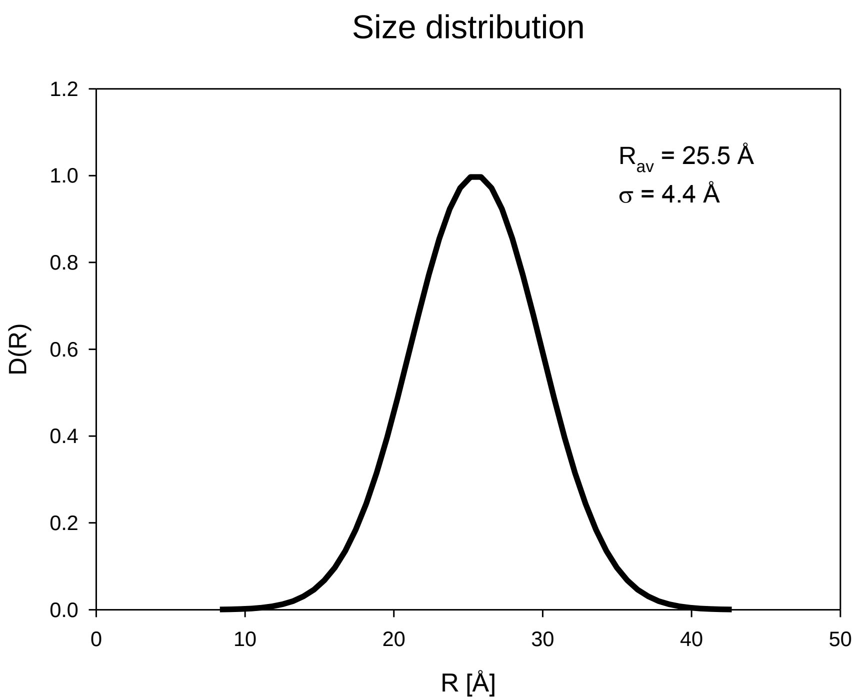


Smeared form factor P(q) for a sphere vs q showing the damping of Porod oscillation with increasing polydispersity (σ_{eff}). The oscillations disappear for σ_{eff} > ~0.21. The mean particle diameter a_0 = 100nm for all calculations. Note the overall q^{-4} power law for q >0.01nm^{-1}. The calculations terminate in the Guinier regime at low q.

Gold colloid

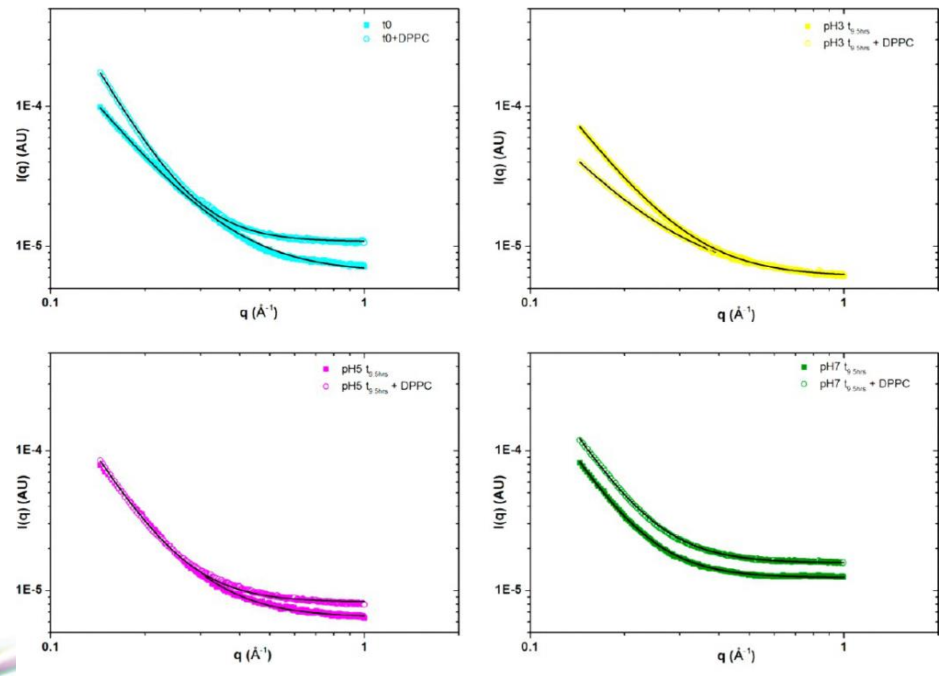
The spherical gold colloidal particles coated with thiols can be dissolved in an organic solvent like toluene



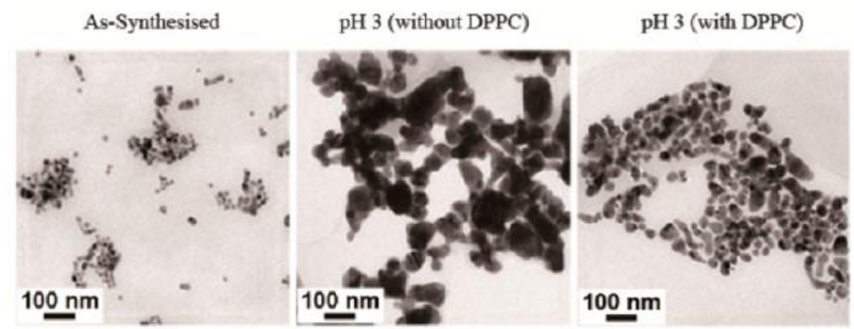


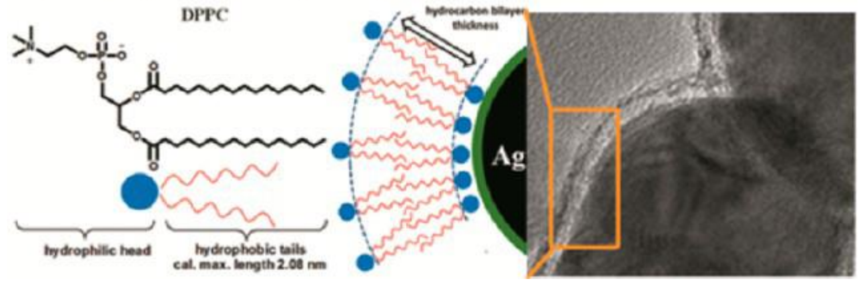
diamond

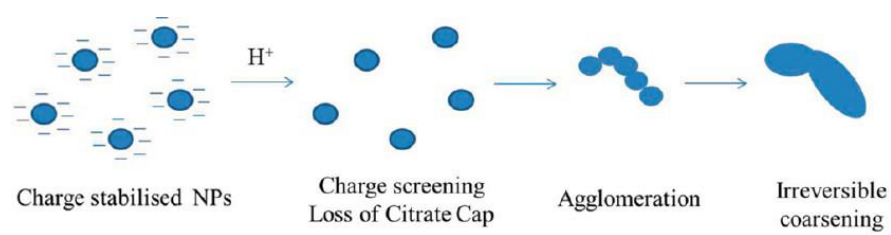
The Stability of Silver Nanoparticles in a Model of Pulmonary Surfactant



	As made, t=0		pH3, t=9.5 hrs		pH5, t=9.5 hrs		pH7, t=9.5 hrs	
	-DPPC	+DPPC	-DPPC	+DPPC	-DPPC	+DPPC	-DPPC	+DPPC
R_g (nm)	7.1	7.0	21.3	10.9	15.1	10.4	7.7	7.0
D (nm)	18.6	18.0	55.0	28.0	39.1	26.8	19.8	18.8
χ^2 (x 10^{-13})	1.2	2.3	0.5	0.5	1.0	1.3	0.6	1.6

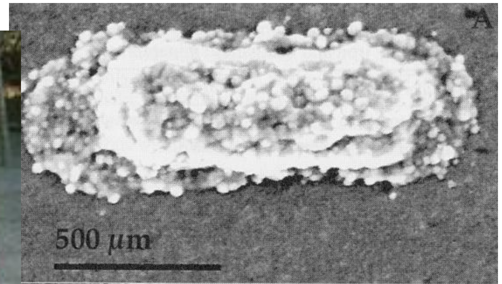






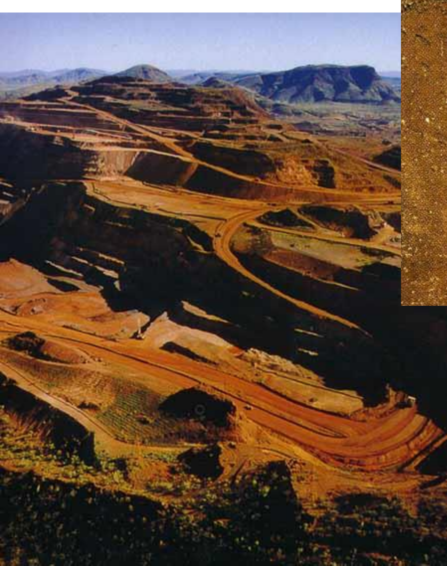
Bey Fen Leo, Shu Chen, Yoshihiko Kyo, Karla-Luise Herpoldt, Nicholas J. Terrill, Iain E. Dunlop, David S. McPhail, Milo S. Shaffer, Stephan Schwander, Andrew Gow, Junfeng Zhang, Kian Fan Chung, Teresa D. Tetley, Alexandra E. Porter, and Mary P. Ryan, **Environ. Sci. Technol.** 2013, 47, 11232−11240, DOI: 10.1021/es403377p front of the Huns local

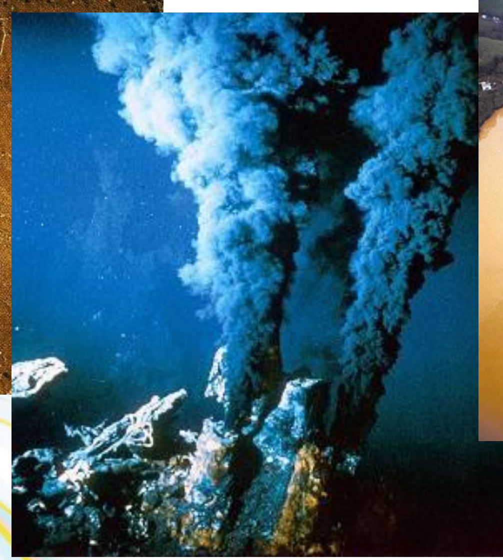
Iron oxyhydroxides in the environment



Thermodynamics vs. Kinetics

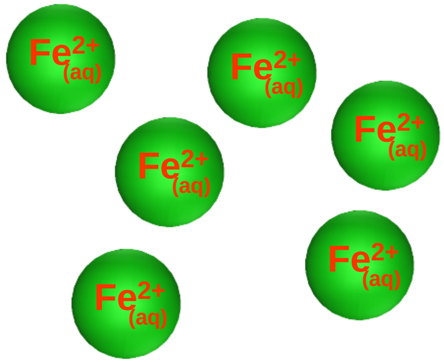
- Most stable phases are goethite (FeOOH) and hematite (Fe_2O_3)
- Poorly-ordered iron oxyhydroxide (ferrihydrite) very common in soils and sediments



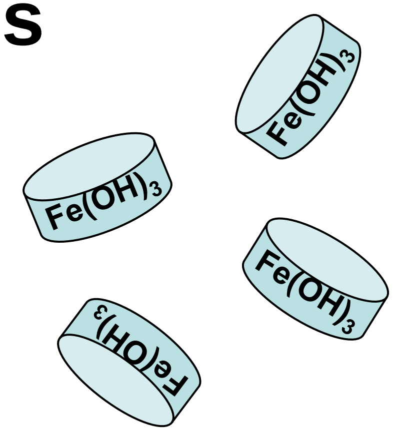


Iron oxyhydroxide bearing contaminant plume (Restronguet Creek, Cornwall) Acid mine drainage

Formation of ferric oxyhydroxide nanoparticles



oxidation & hydrolysis

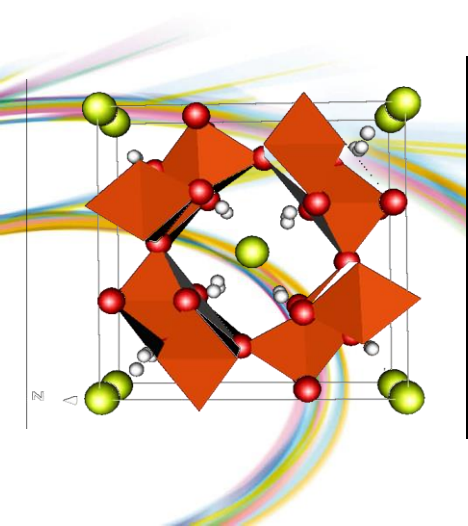


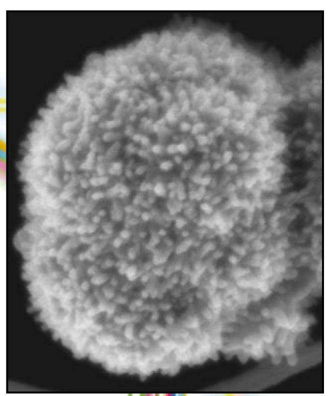
Dissolved ferrous iron

Poorly–ordered nanoparticles

Schwertmannite $Fe_{16}O_{16}(OH)_{12}(SO_4)_2$

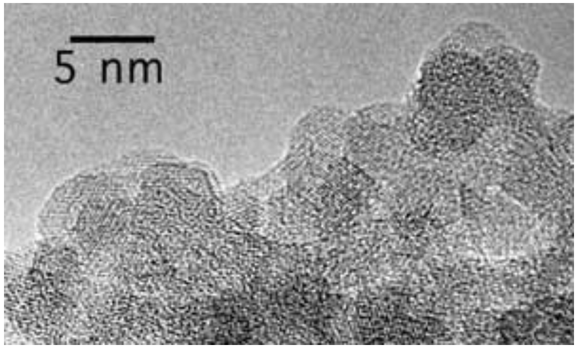
Ferrihydrite $Fe_xO_yOH_z.nH_3O$





Shaw et al

(Janney et al., 2000)



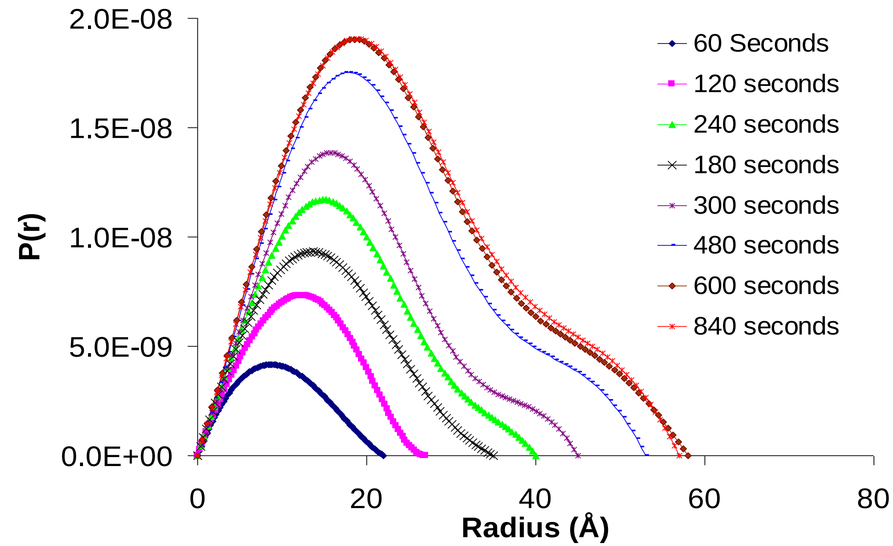
Pair/Size distribution function (pure) (PDF/SDF)

pH = 4

Pair distribution function

(Rg more accurate: based on full scattering pattern not only low q)

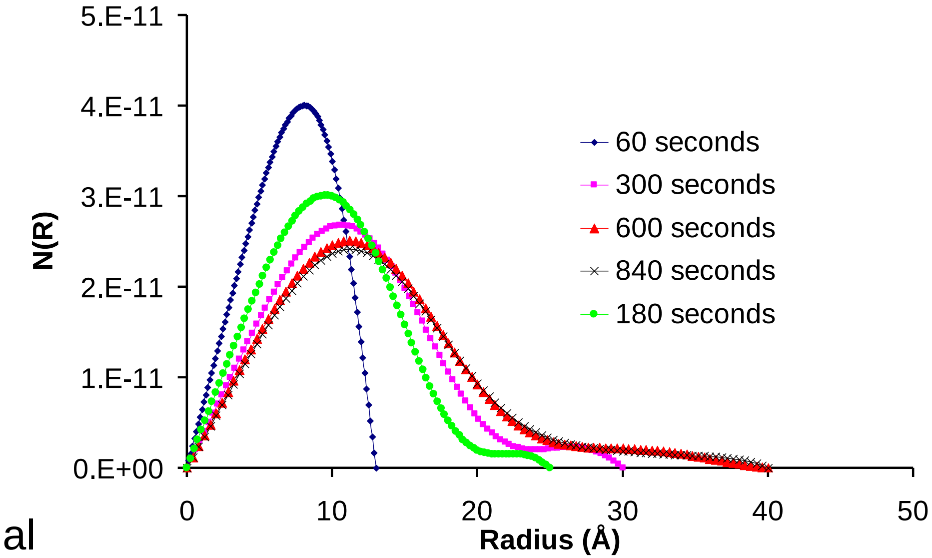
- Equant particle shape at beginning of reaction
- Elongated particles forming by end of reaction



Size distribution function

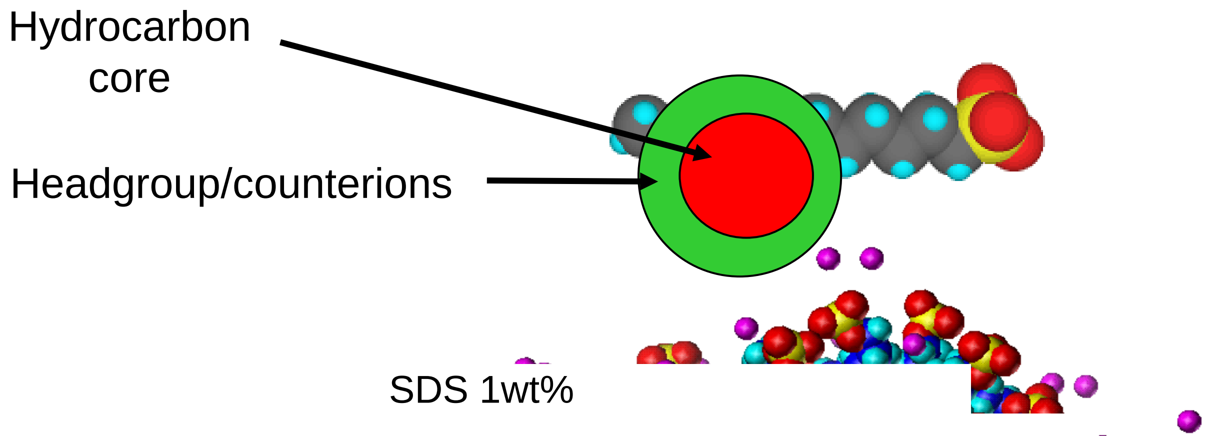
(degree of polydispersity)

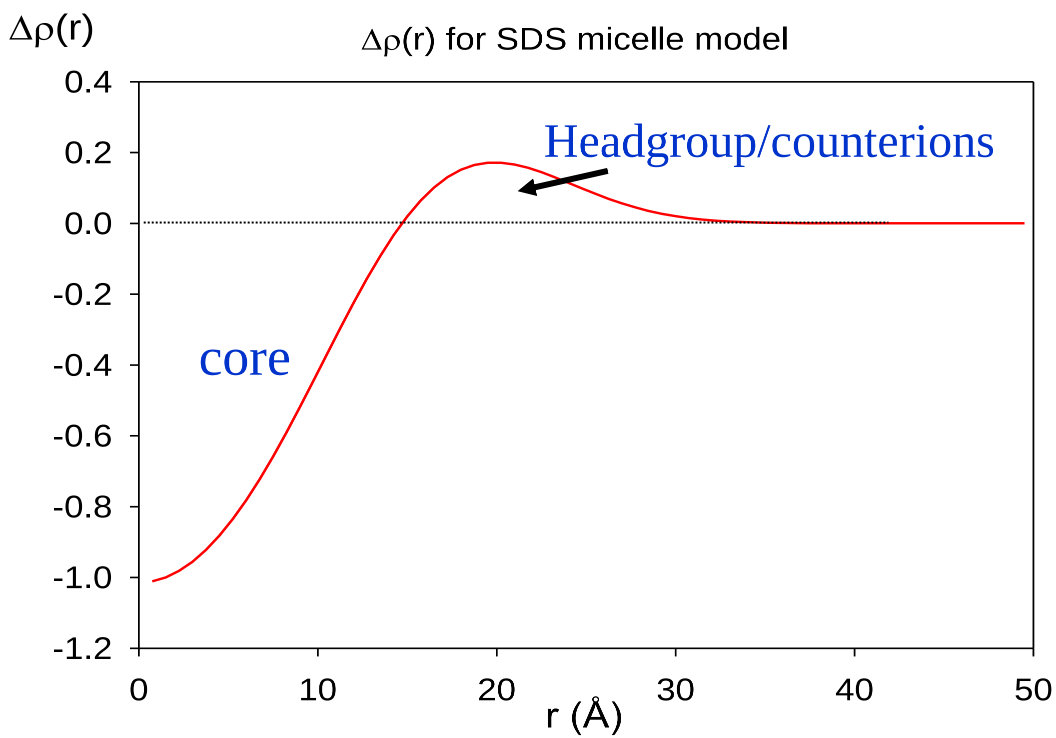
- Monodispersed system at beginning of reaction
- Slight increase in polydispersity with time



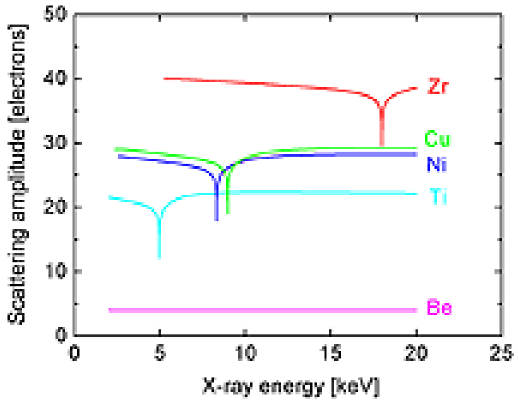
Shaw et al

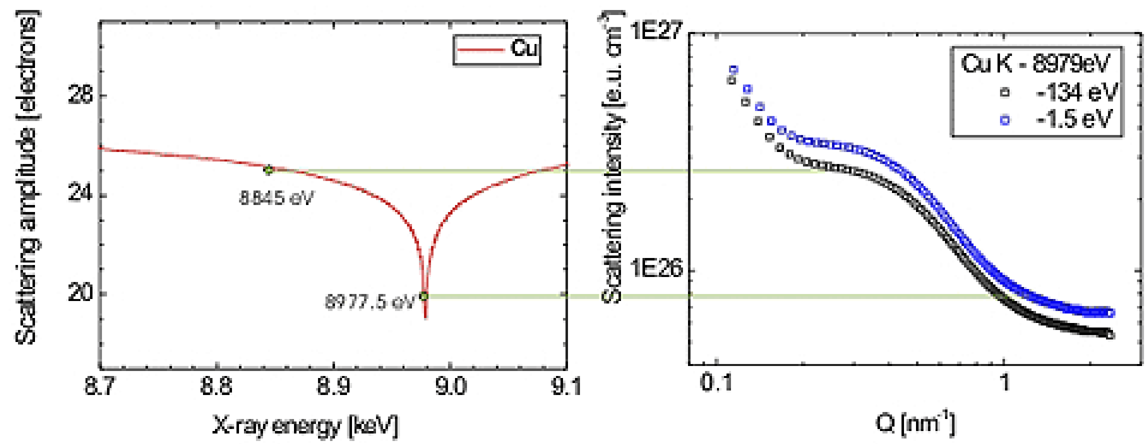
SDS micelle (Soap!)

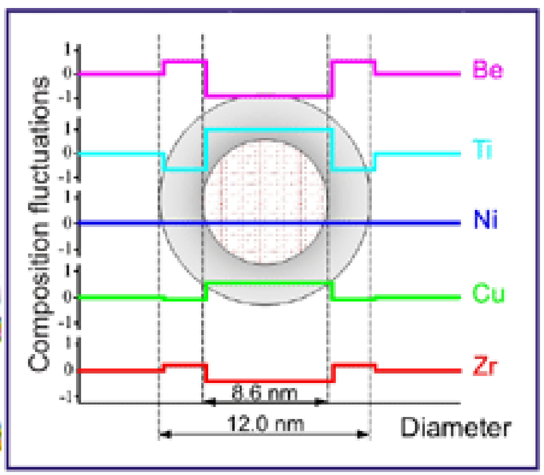




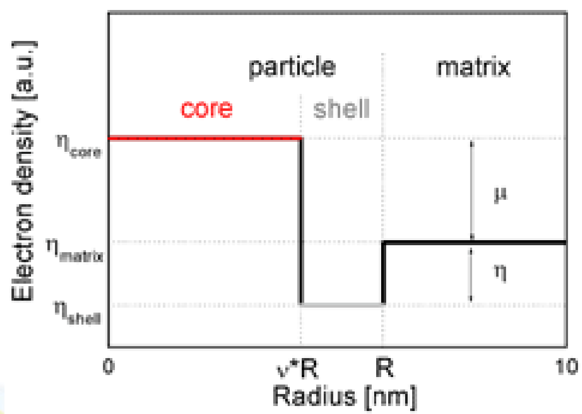
ASAXS example from BESSY (Berlin)

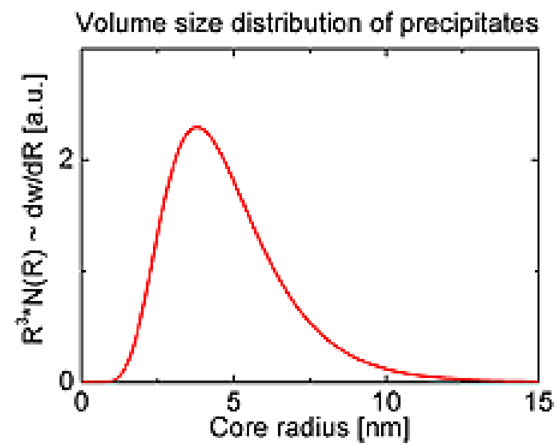






Relative composition changes in the precipitation and surrounding depletion zone.

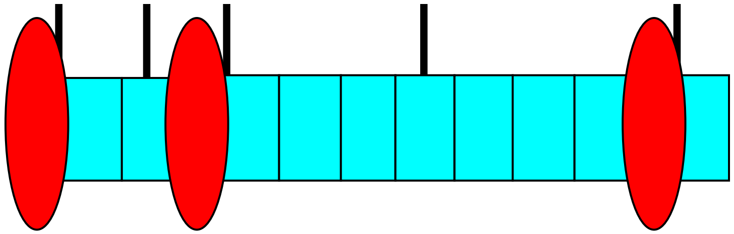


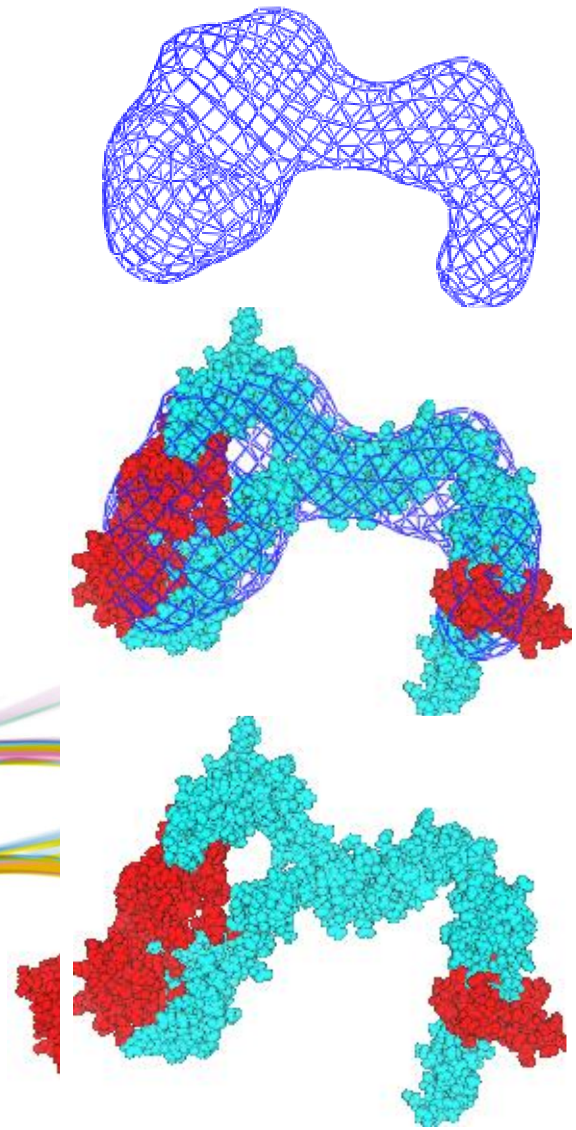


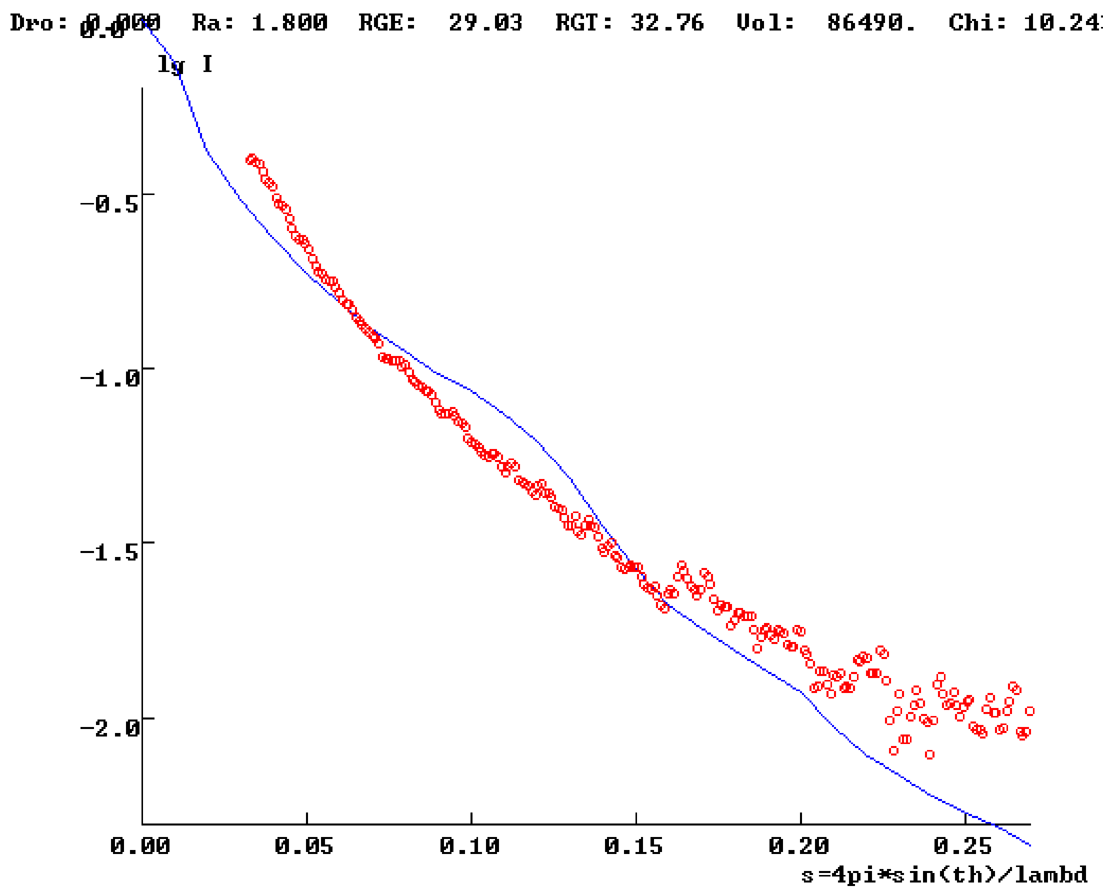
A. Hoell et al, Scripta mater 44 (2001) 2335

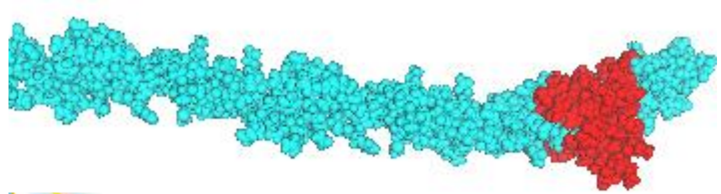
diamond

Fibrillin Protein Fragment 13





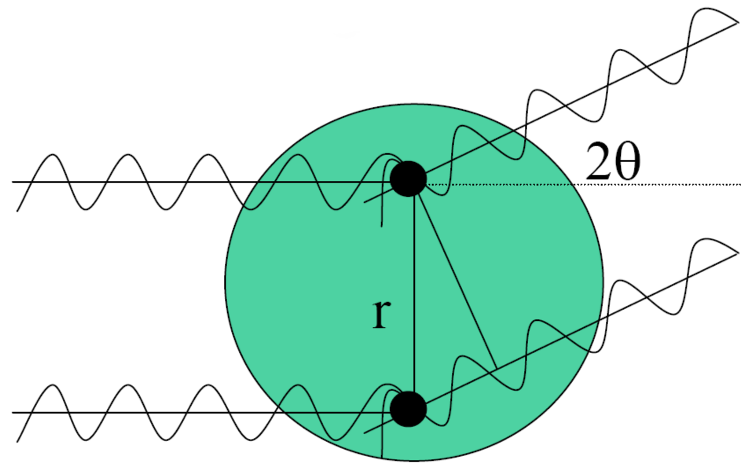


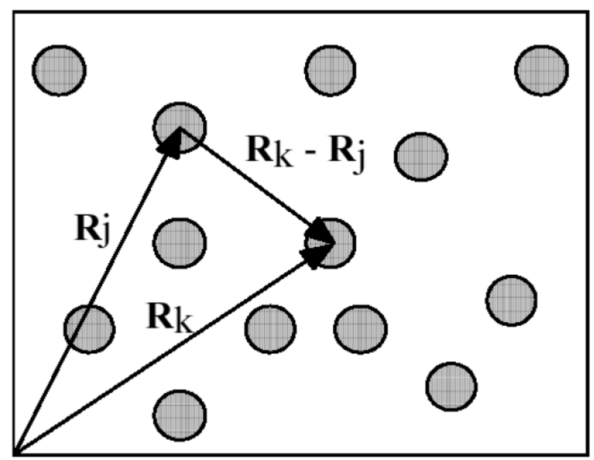


Wess et al – Cardiff

What if you have a Non-Dilute system?

- Scattering (Interference) determined by spatial dimensions
- Form Factor - P(q) - particle size and shape (intraparticle)
- **Structure Factor** - S(q) interparticle correlations function of local order and interaction potential; complex if correlation between position and orientation





diamond

Concentration effects (S_q)

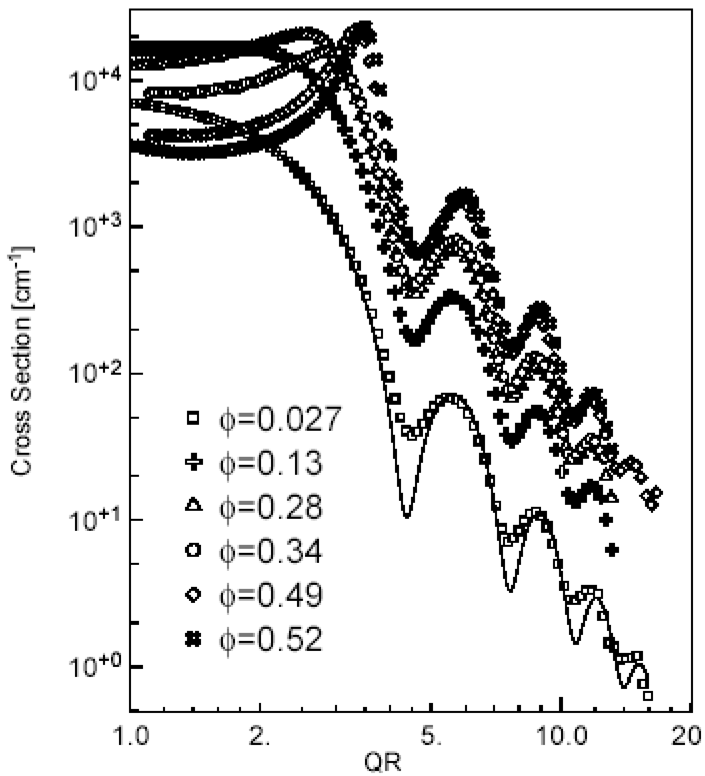


Figure 1: Cross-section for several different volume fractions of PS spheres in glycerol vs. *QR*.

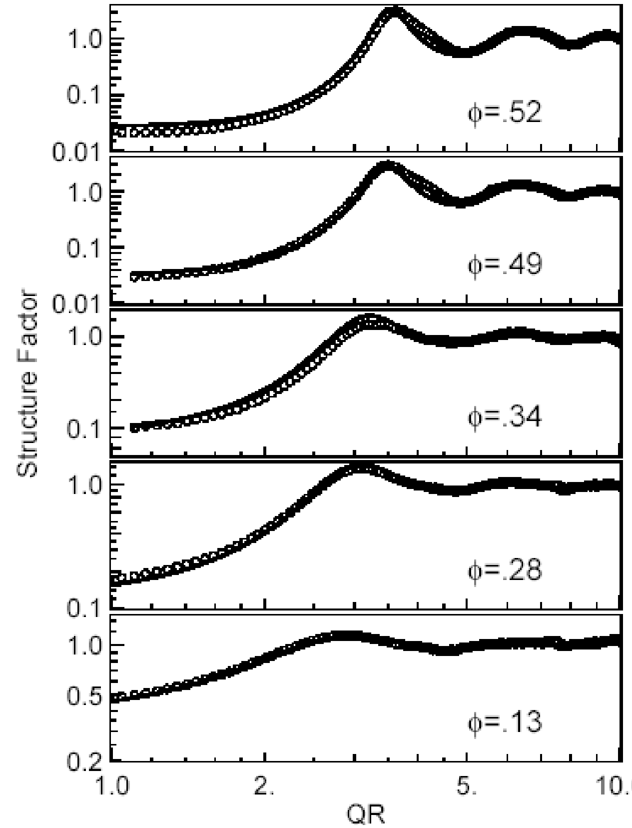


Figure 2: Measured and model structure factors, *S*(*Q*), (circles and dashed lines, respectively) vs. *QR* for PS spheres in glycerol.

Small Angle X-ray Scattering Study of a Hard-Sphere Suspension: Concentrated Polystyrene Latex Spheres in Glycerol

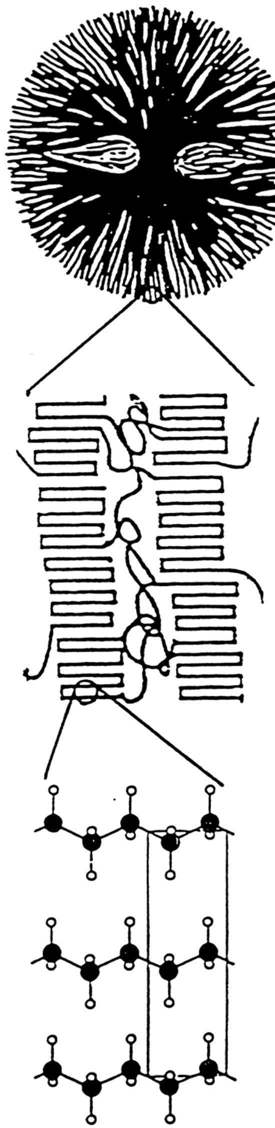
L. B. Lurio[1], D. Lumma[1], A. R. Sandy[1], M. A. Borthwick[1], P. Falus[1], S. G. J. Mochrie[1], J. F. Pelletier[2], M. Sutton[2], Lynne Regan[3], A. Malik[4] and G. B. Stephenson[4]

Semicrystalline Block Copolymers

- Few commercial examples
- Crystallisable end blocks
- PE-PEP-PE (hPB-hPI-hPB)
- Low crystallinity PE look-alike

- Metallocenes for multi-blocks

- Very complicated phenomenology
- Break-out & confined crystallisation depending on morphology and T_g of noncrystallising material.

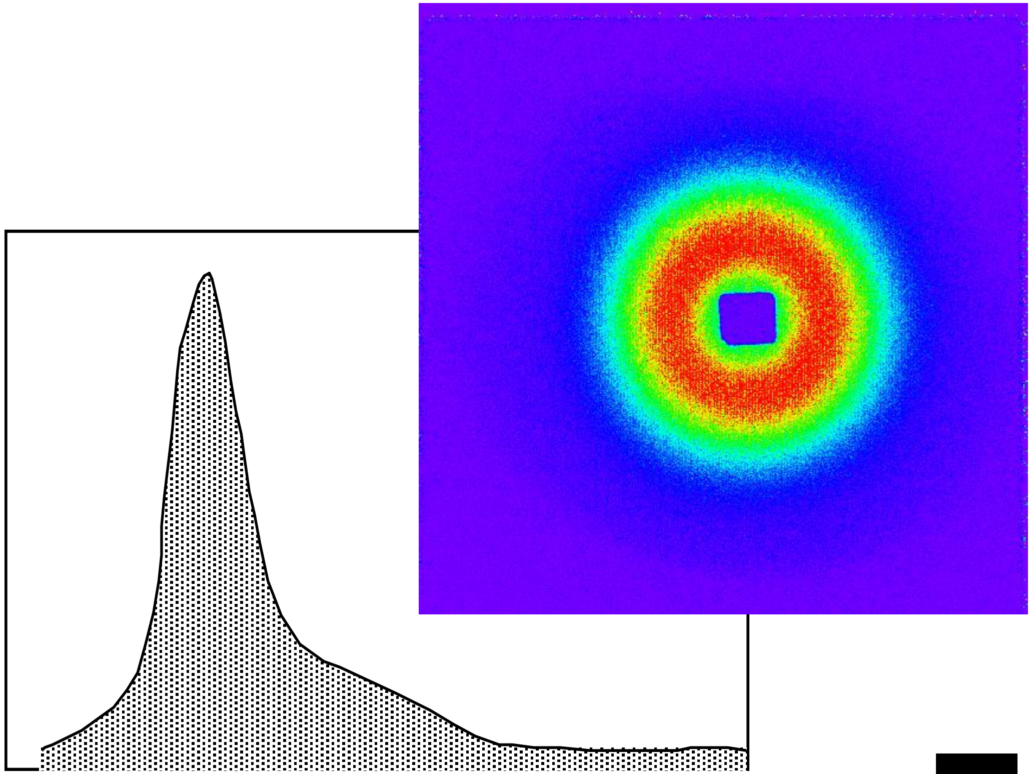


Spherulite
O(10 μm)

Lamella
O(10-100 nm)

Unit cell
O(1-10 Å)

Scattering at Small Angle

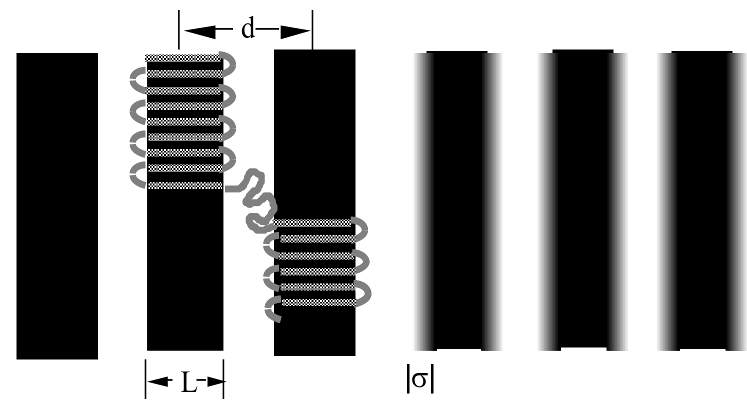


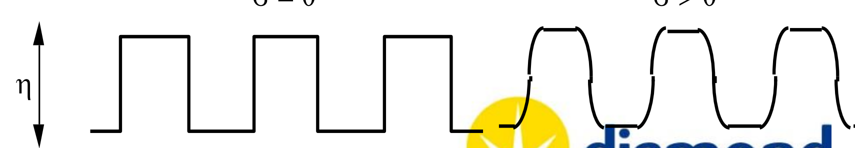
Bragg's law gives an estimate of interference function $d = 2\pi/q^*$ but how do we get the degree crystallinity and hence L?

The scattering invariant
$Q = \phi(1-\phi)\Delta\eta^2$
$Q = \int I(q)q^2 dq$ with limits $0 \le q \le \infty$

But the SAXS pattern has data in a range of q

semicrystalline lamellar stacks





electron density profile

SAXS Invariant

$Q = \phi(1-\phi)\Delta\eta^2$

ϕ and $\Delta\eta$ in a lamellar stack do not change during crystallisation but the crystalline volume increases so

$Q = X_s$

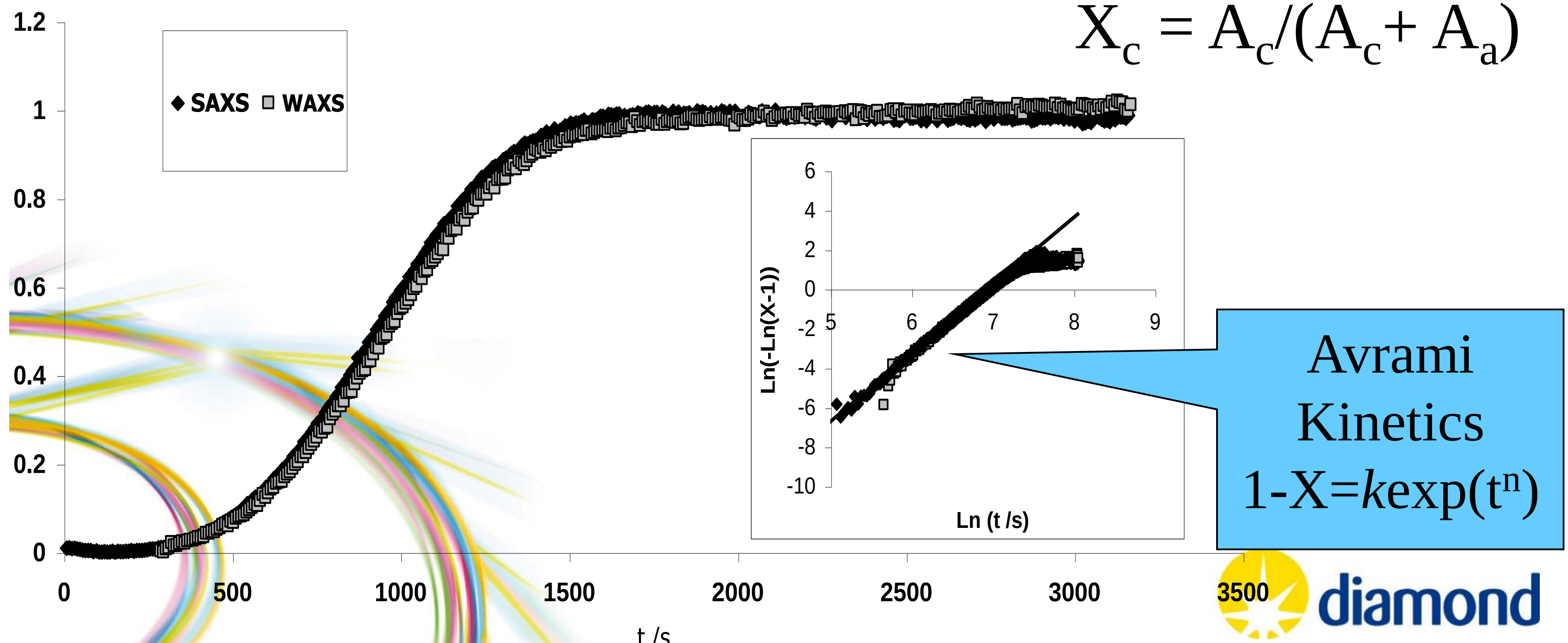
the volume fraction of spherulites

Kinetics from time-resolved (static) scattering

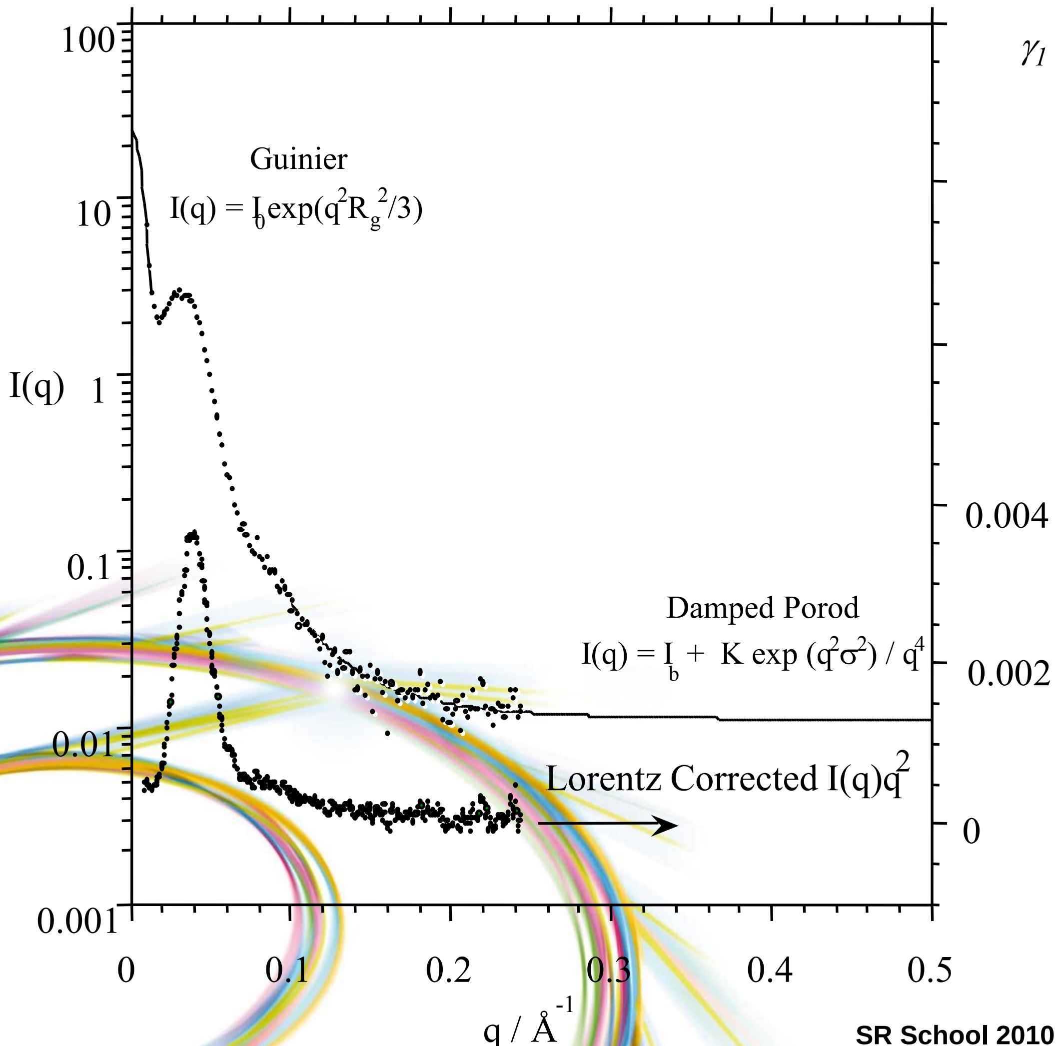
WAXS

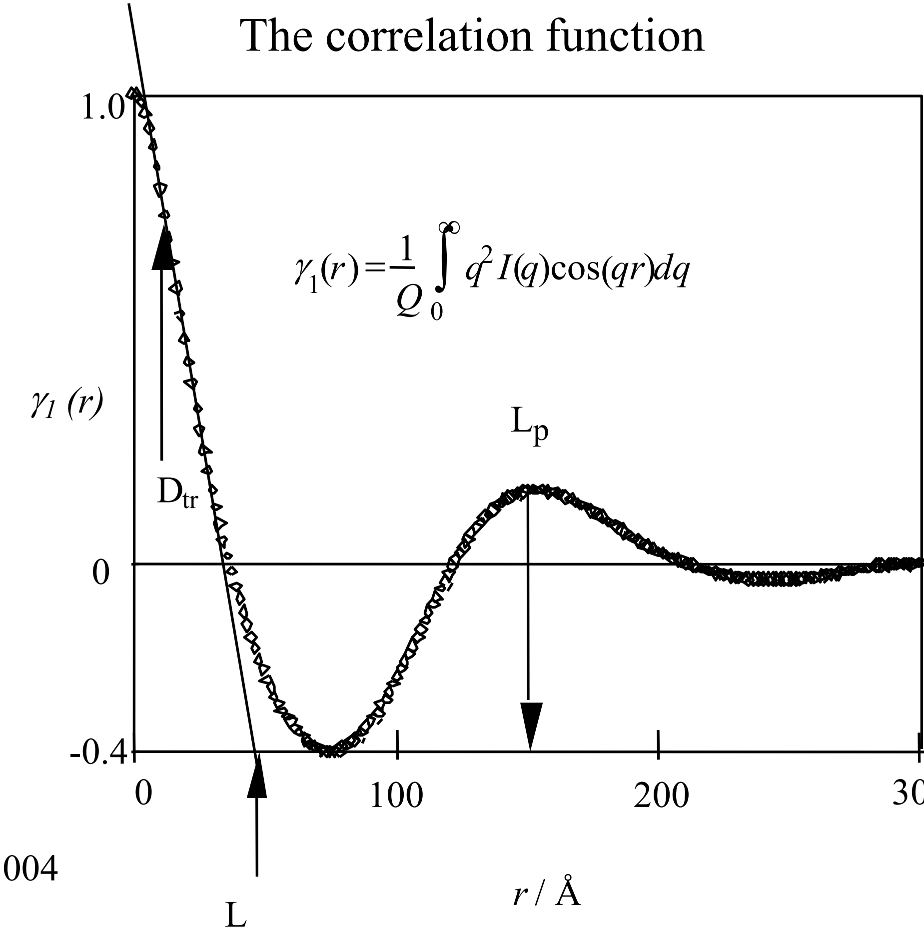
degree of crystallinity

$X_c = A_c/(A_c + A_a)$



For Lamellae there is more!





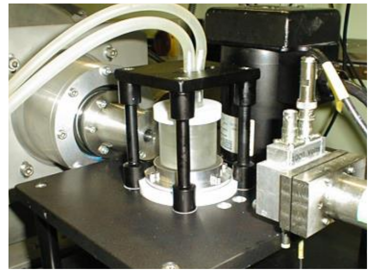
Correlation Function Analysis

diamond

How does it work?

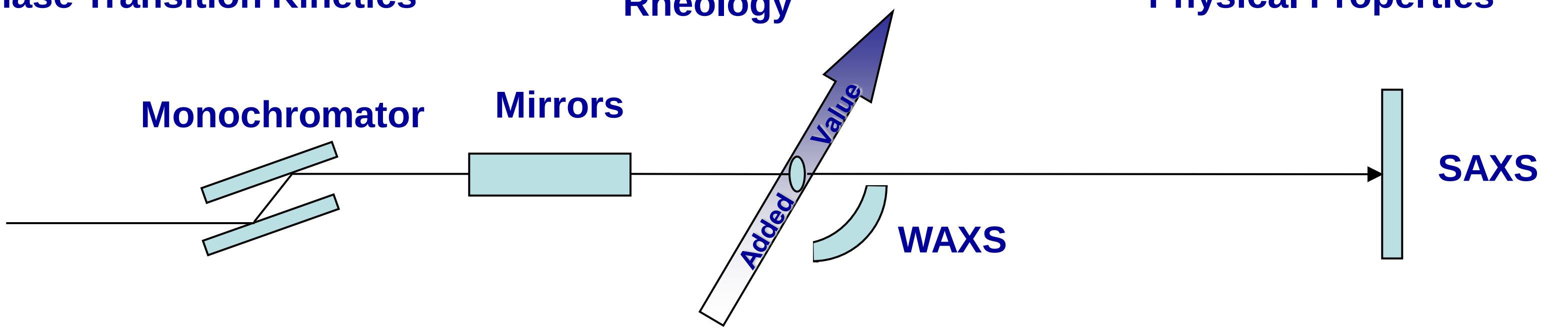
Added Value from the sample

Phase Transition Kinetics



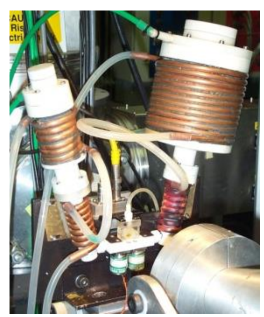
Rheology

Physical Properties

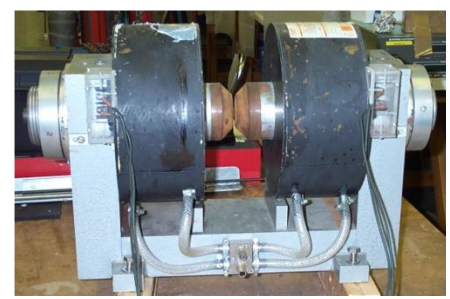


Processing

Reaction Kinetics



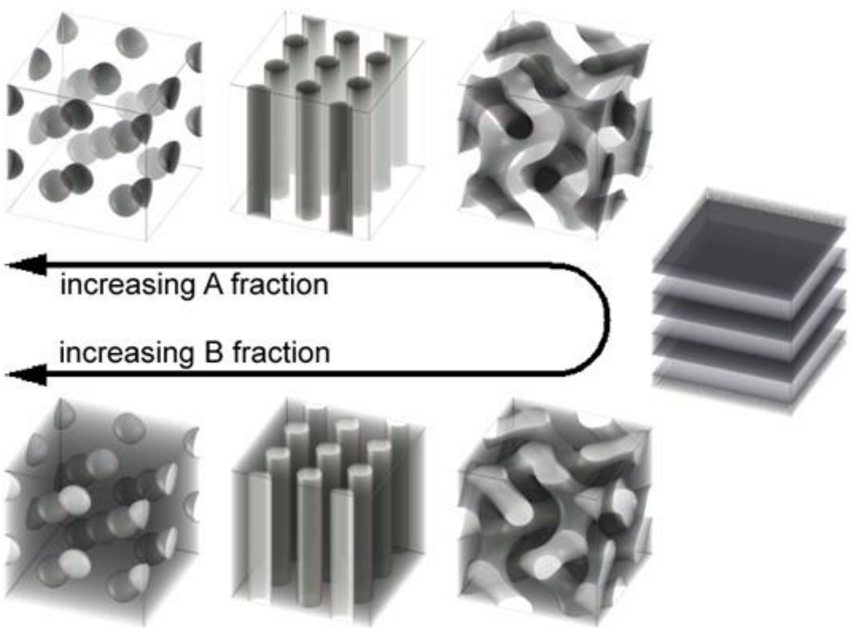
Alignment

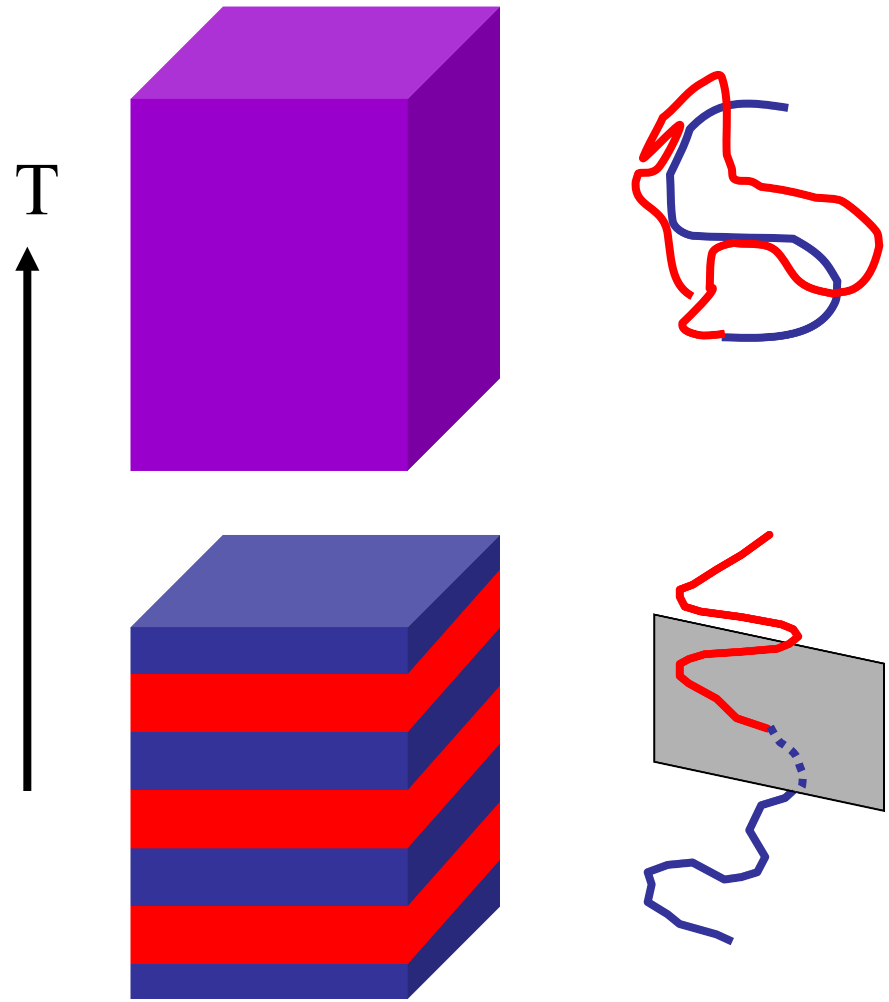


diamond

Block Copolymer Self Assembly

At high T thermal motion overcomes unfavourable interactions between blue and red segments

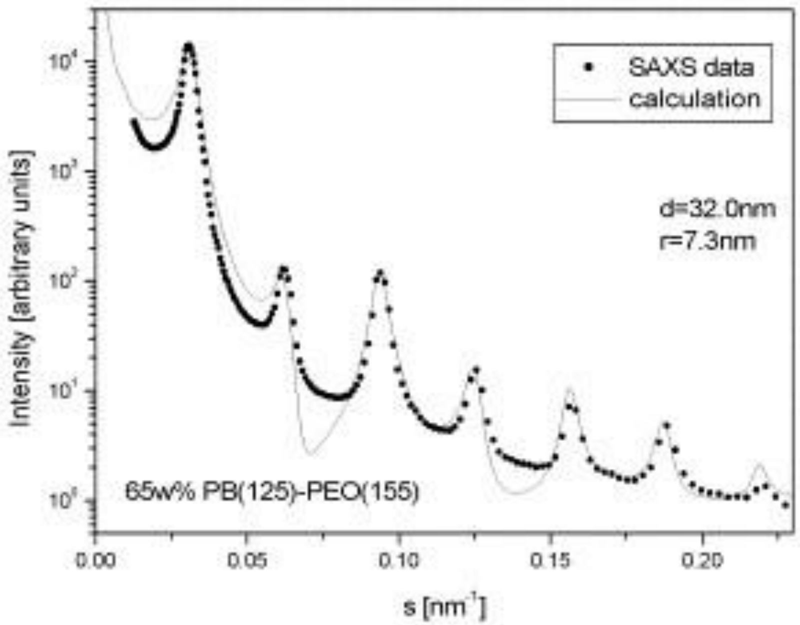


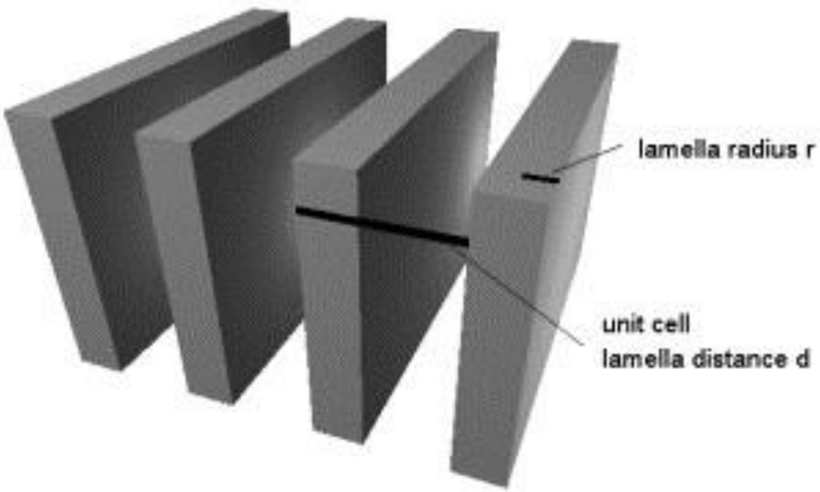


free energy = separation - stretching - interfacial energy

diamond

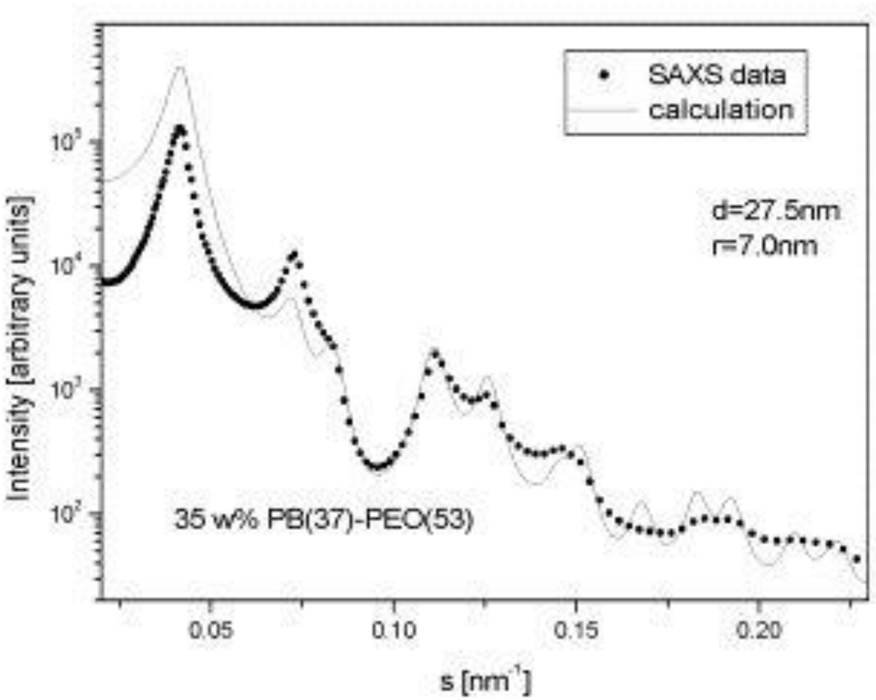
Lamellar phase

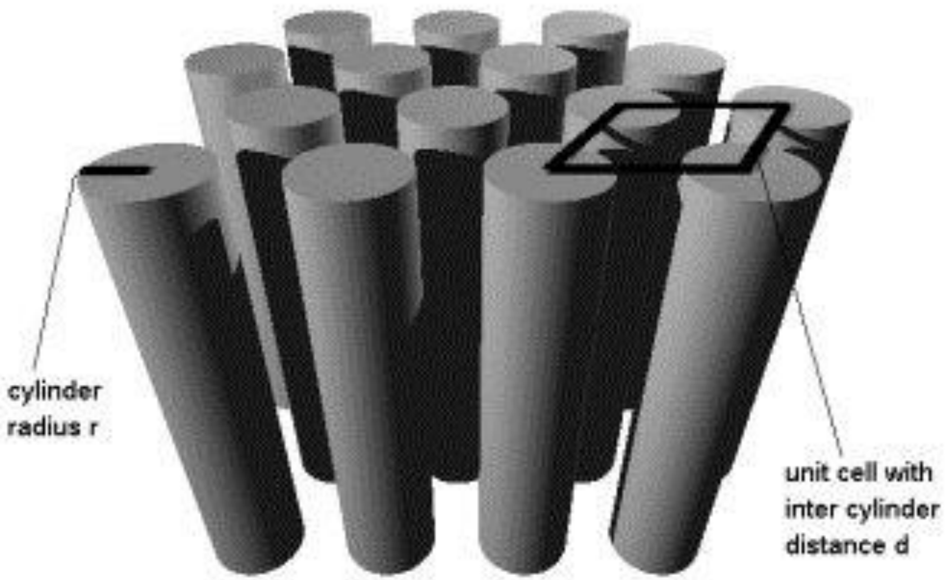




Peak order – q_0, $2q_0$, $3q_0$, $4q_0$

Hexagonal phase

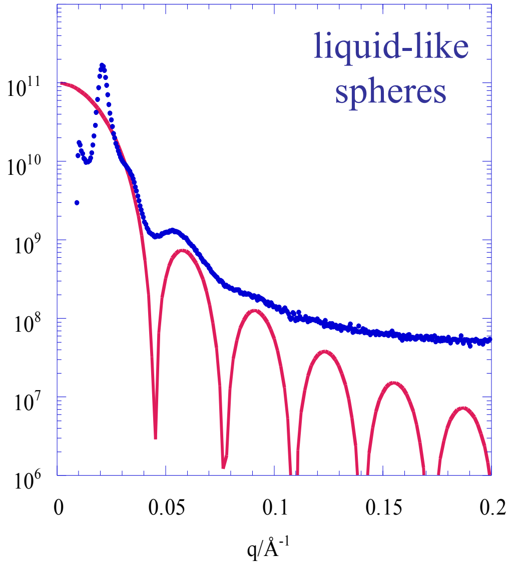


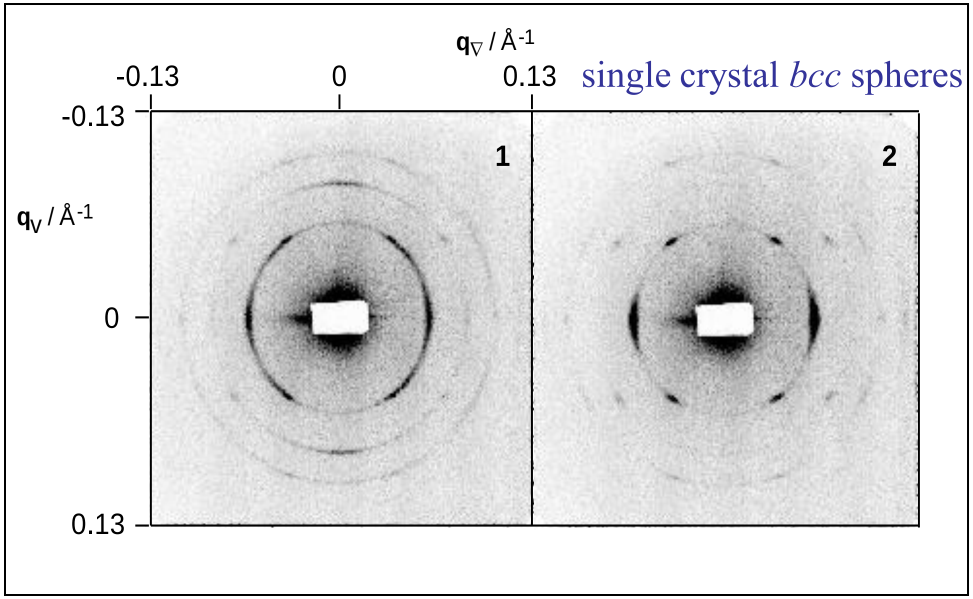


Hex Rods q_0 $\sqrt{3}q_0$ $\sqrt{4}q_0$

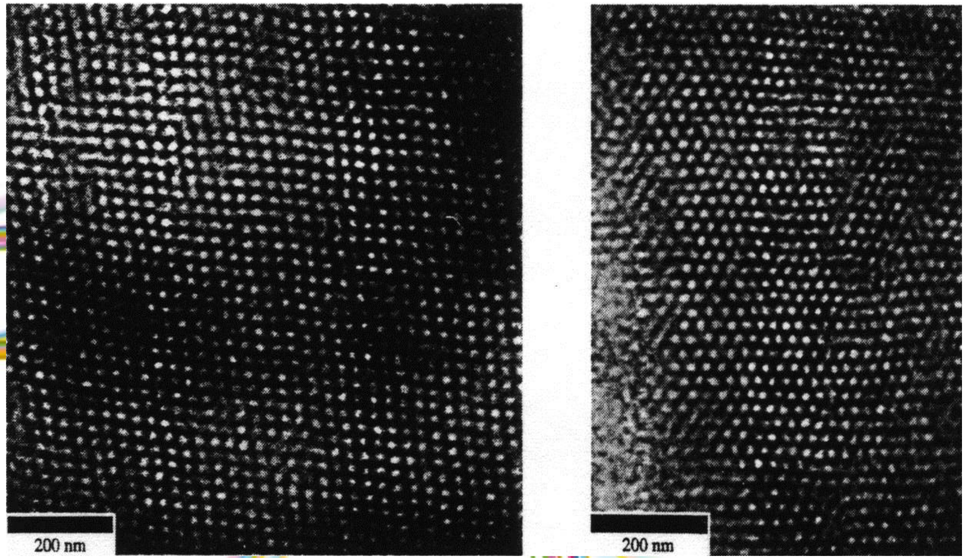
S. Förster

Body Centred Cubic

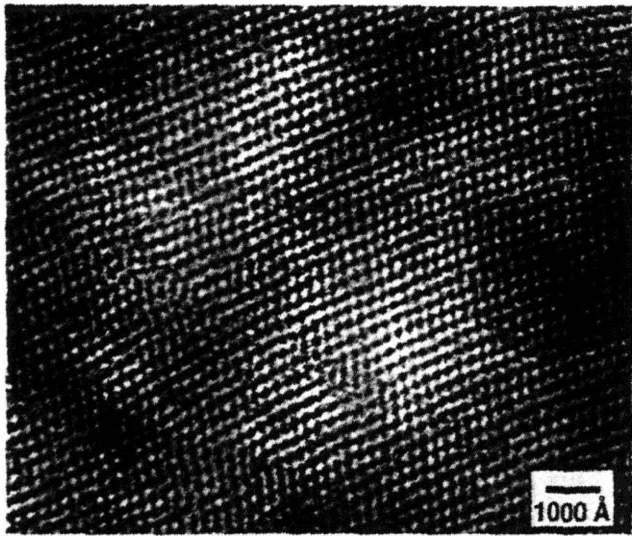




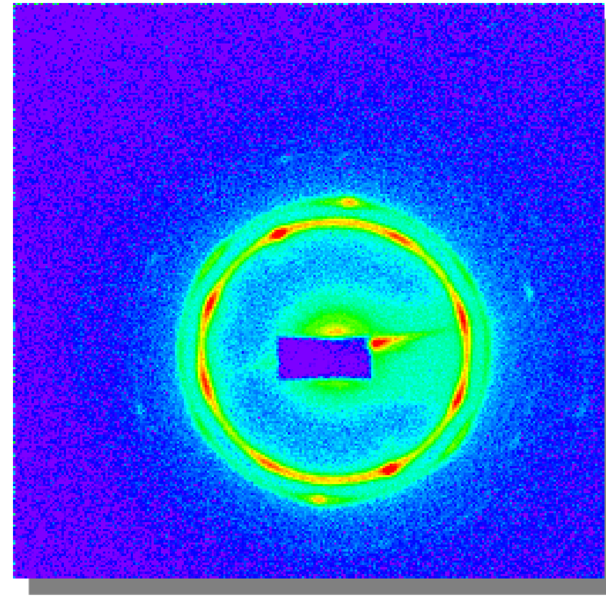
BCC Cubic q_0 $\sqrt{2}q_0$ $\sqrt{3}q_0$ $\sqrt{4}q_0$

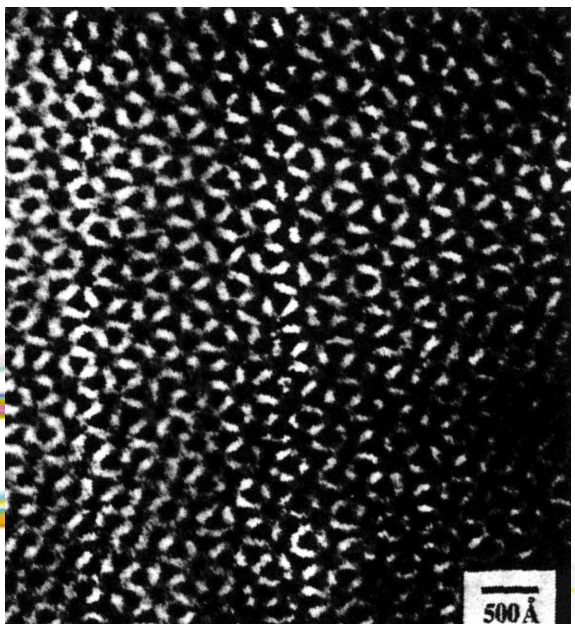


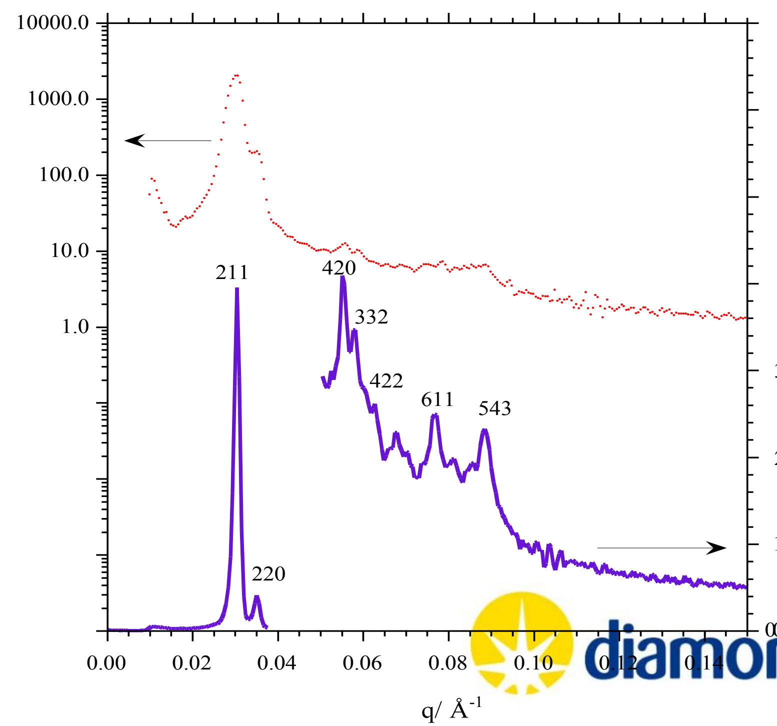
diamond



Ia3d Gyroid



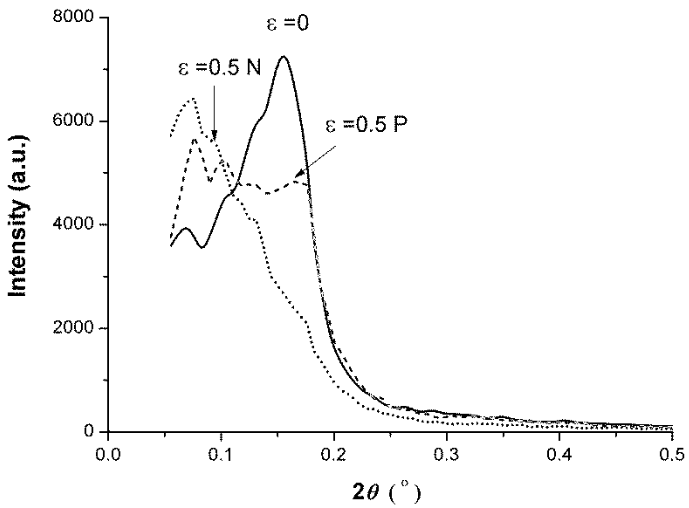


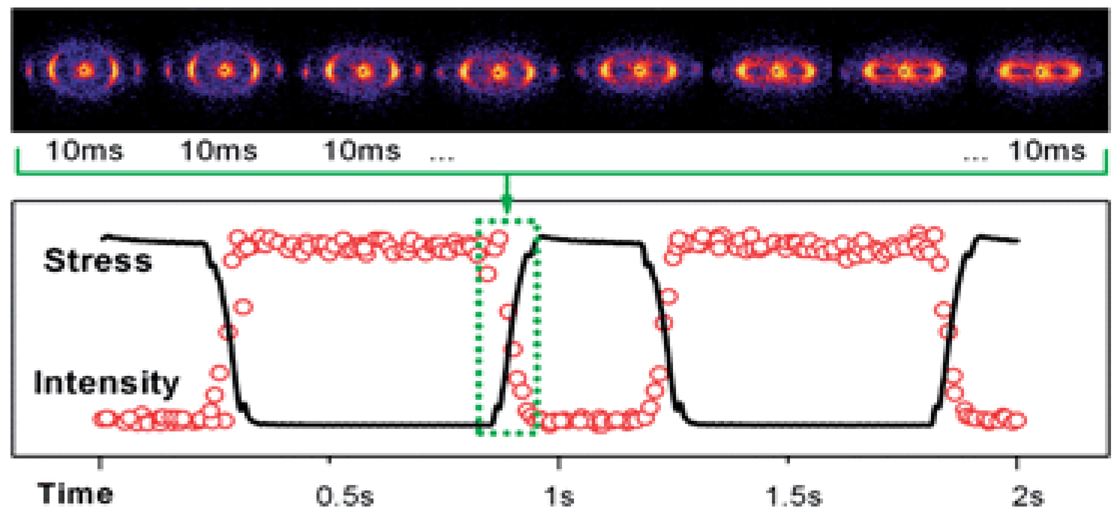


$\sqrt{6}q_0$ $\sqrt{8}q_0$ $\sqrt{14}q_0$ $\sqrt{16}q_0$ $\sqrt{20}q_0$ $\sqrt{22}q_0$

Khandpur et al Macromolecules 1995

A real time SAXS study of oriented block copolymers during fast cyclical deformation, with potential application for prosthetic heart valves

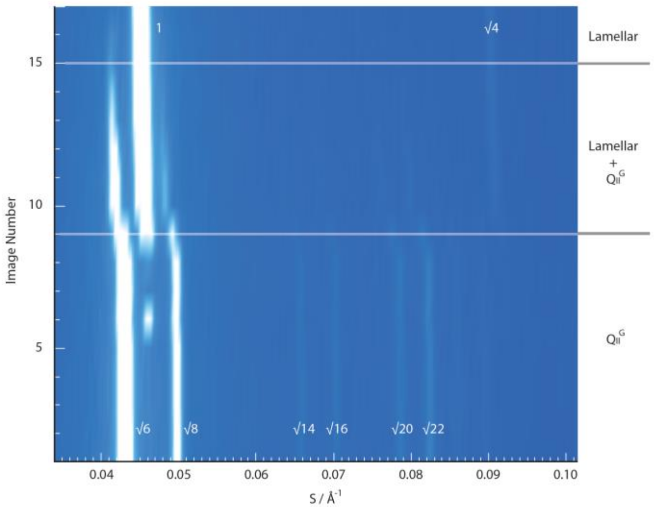


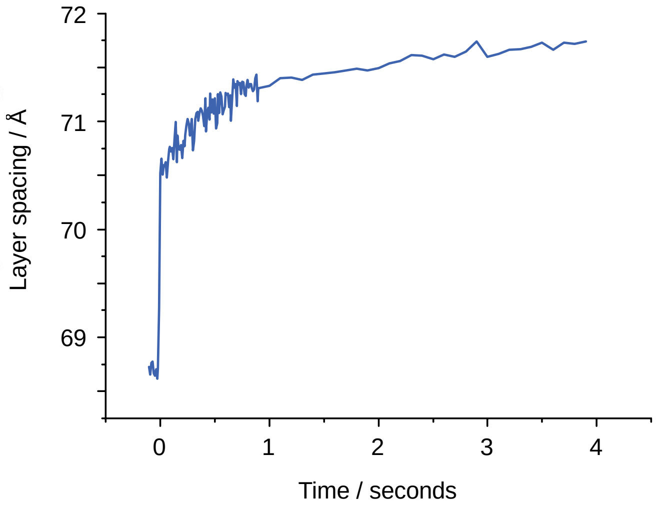


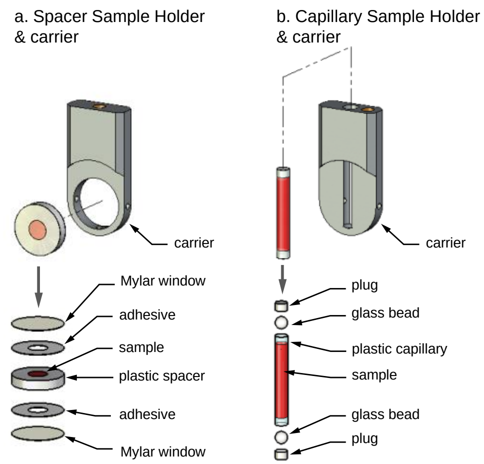
- Study of a range of thermoplastic elastomers with all rubbery components in the block copolymers
- Time resolution of RAPID 10ms used (although trials of <1ms also proved successful)
- Cycling used to mimic conditions for a prosthetic heat valve (10,000 cycles)

Joanna Stasiak, Adriano Zaffora, Maria Laura Costantino and Geoff D. Moggridge, **Soft Matter**, 2011

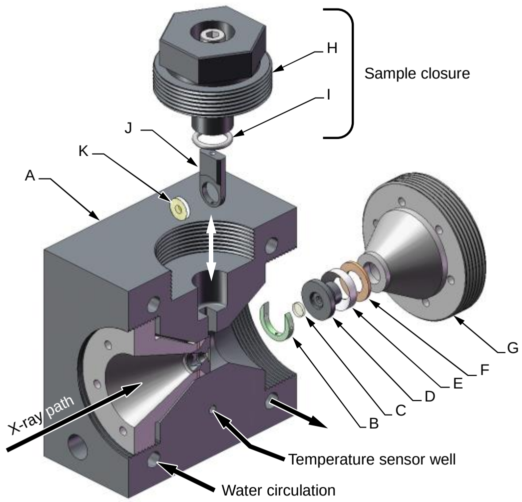
Time resolved X-ray diffraction studies of drug induced membrane degradation



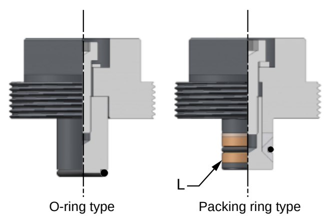


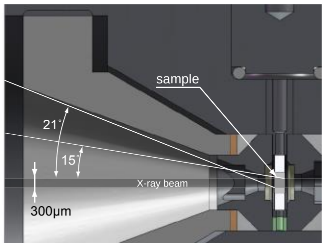


a. Partly exploded cross section of high pressure cell

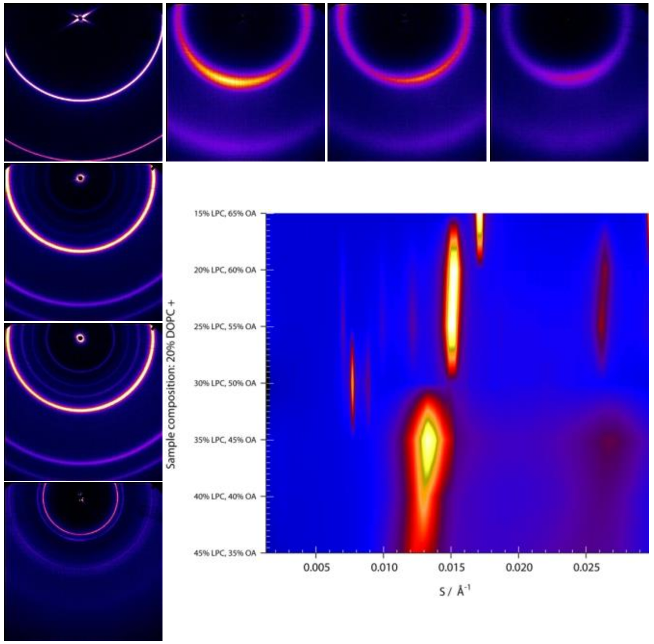


b. Sample closure type



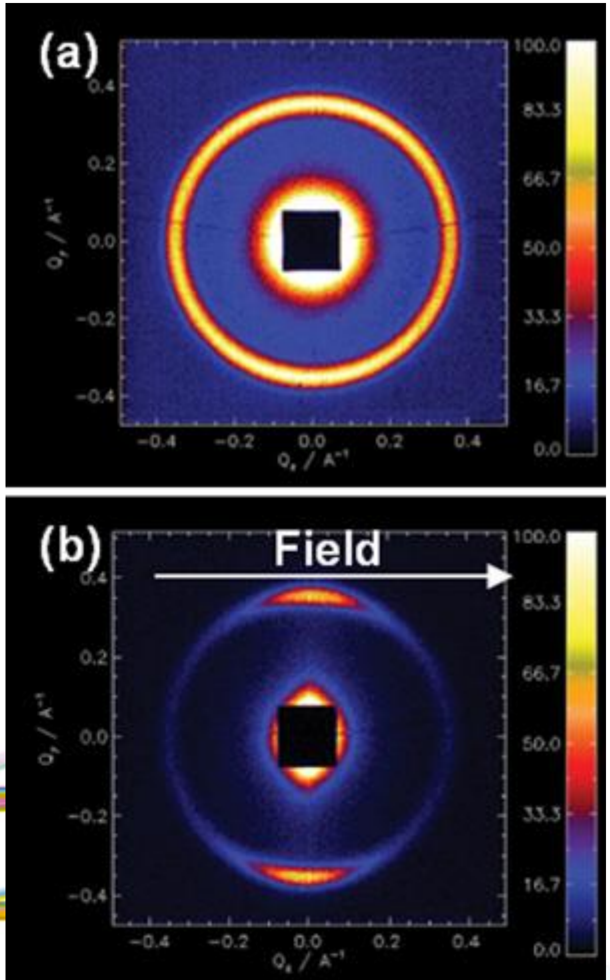


c. X-ray path & diffraction angles

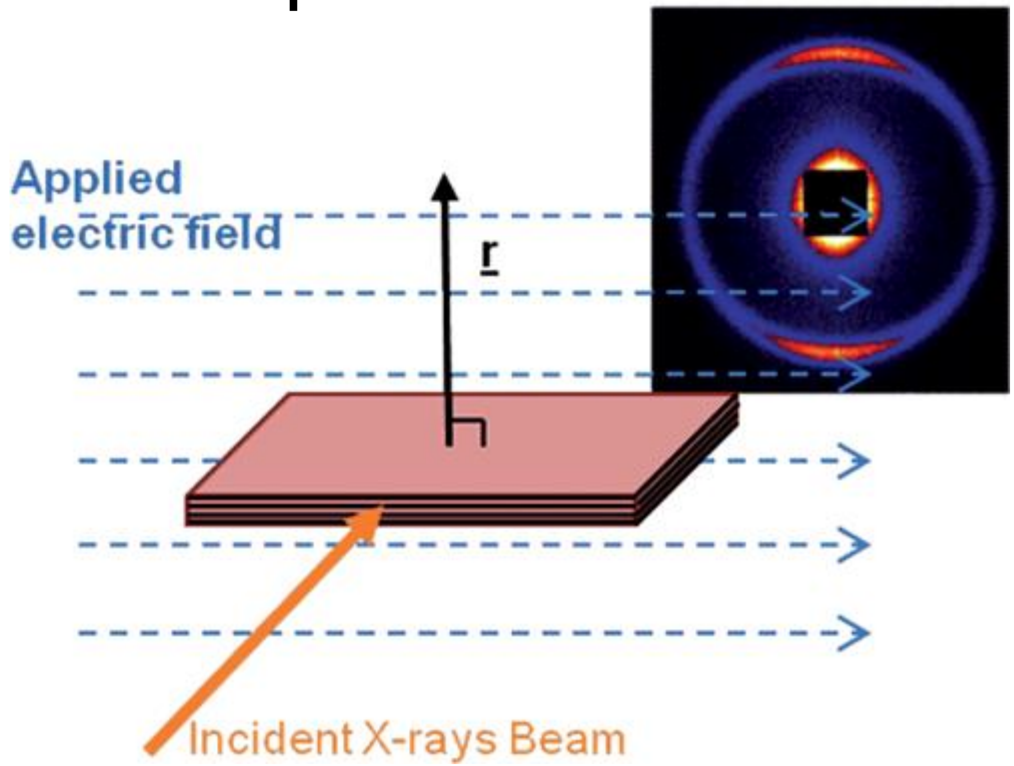


Automated high pressure cell for pressure jump x-ray diffraction, Nick Brooks, Beatrice Gauthe, Nicholas Terrill, Sarah Rogers, Richard Templer, Oscar Ces, John Seddon (2010) *Review of Scientific Instruments* **81**:064103 DOI: 10.1063/1.3449332

Electric Field Induced Orientational Order in Suspensions of Anisotropic Nanoparticles



2D Detector



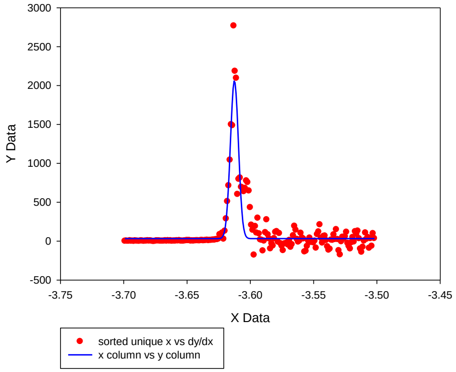
Scattering pattern obtained from Permanent Rubine in dodecane (30 wt%) using short camera length with (a) zero field (b) Electric field applied (4V=mm) giving nematic phase.

Robert Greasty, Jana Heuer, Susanne Klein, Claire Pizzey, and Robert Richardson
Mol. Cryst. Liq. Cryst., 545, 133

Microfocus End Station

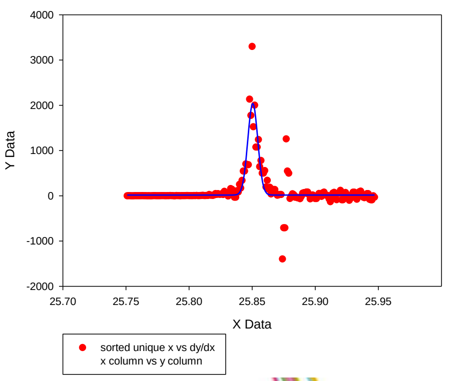
$FWHM_h = 12.7\mu m$

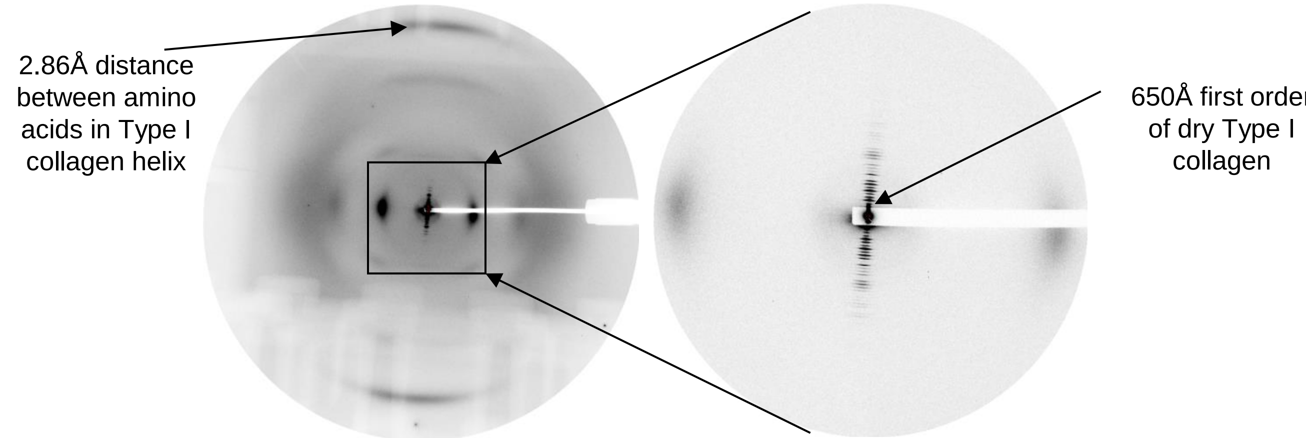
dx/dy
f=y0+a*exp(-.5*((x-x0)/b)^2)

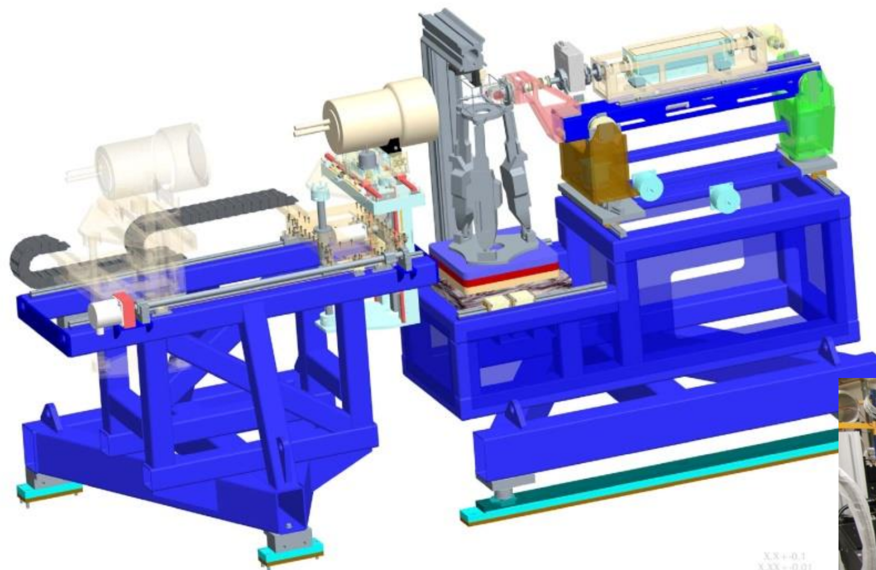


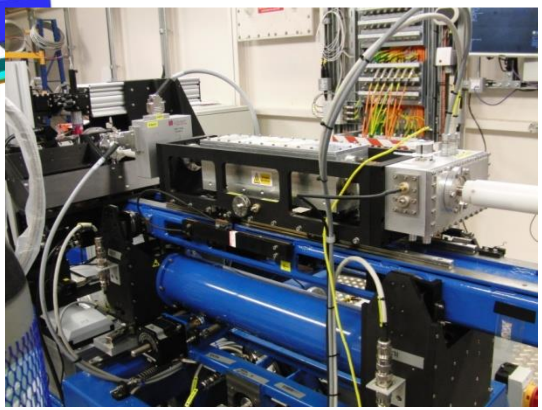
$FWHM_v = 10.4\mu m$

dx/dy
f=y0+a*exp(-.5*((x-x0)/b)^2)

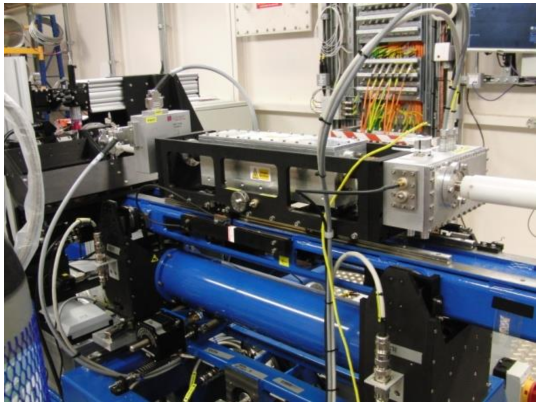


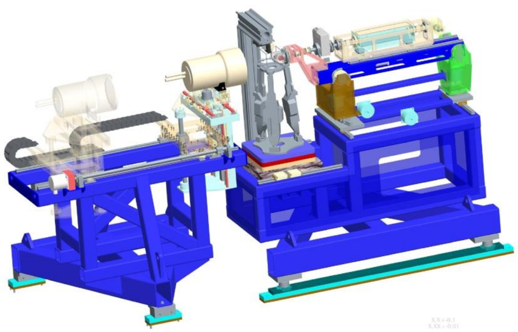


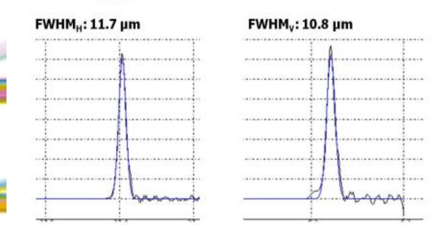




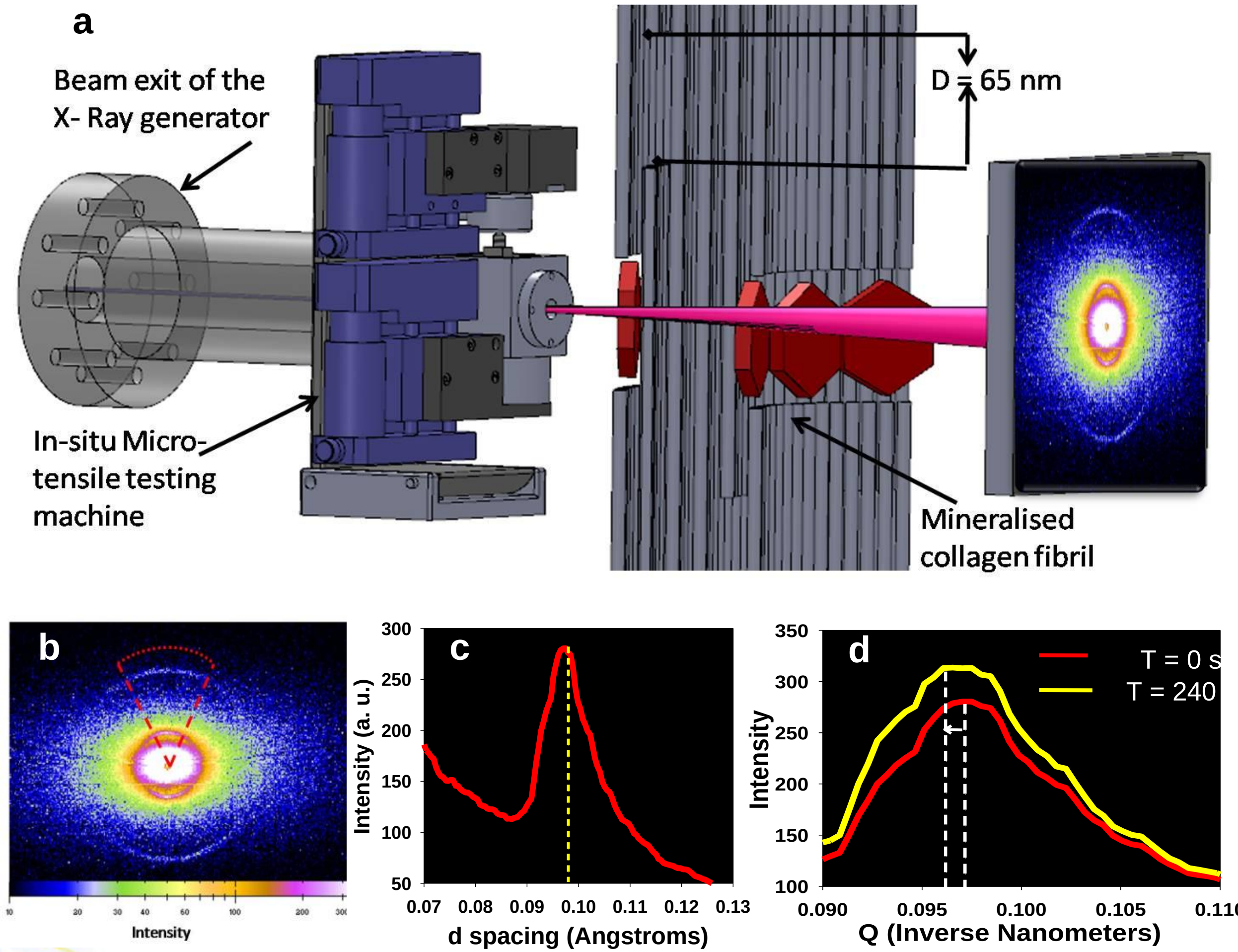
Nanoscale Fracture Mechanisms in Fibrolamellar Bone in Bending and Compression





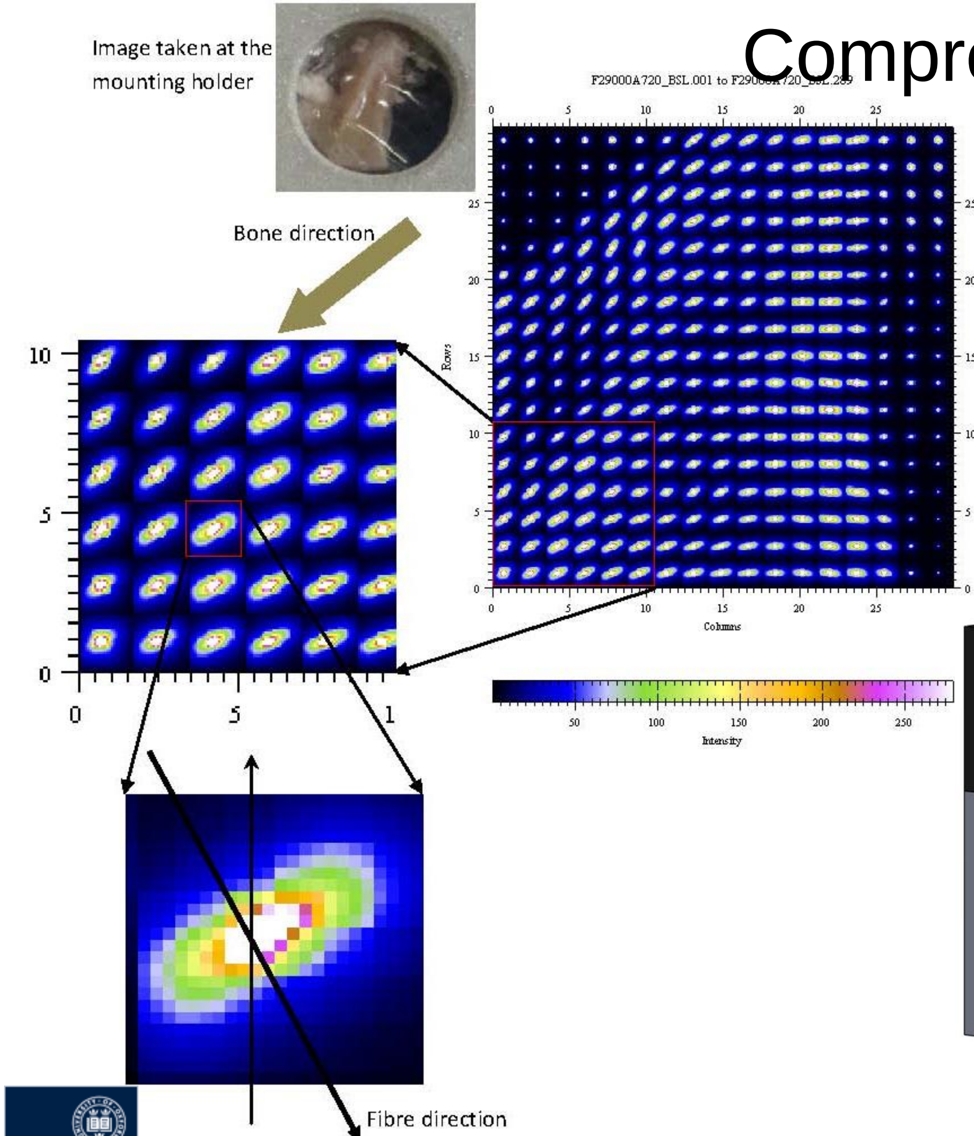


Microfocus spot obtained on I22 with CRL (90 lenses) at 14 keV

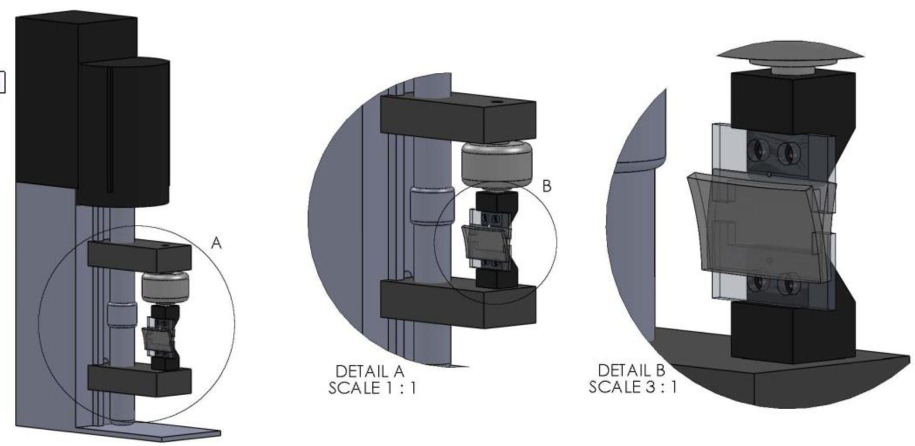


Angelo Karunaratne, Christopher R Esapa, Jennifer Hiller, Alan Boyde, Rosie Head, JH Duncan Bassett, Nicholas J Terrill, Graham R Williams, Matthew A Brown, Peter I Croucher, Steve DM Brown, Roger D Cox, Asa H Barber, Rajesh V Thakker, and Himadri S Gupta
, **Journal of Bone and Mineral Research**, Vol. 27, 2012, 876.

Nanoscale Fracture Mechanisms in Fibrolamellar Bone in Bending and Compression



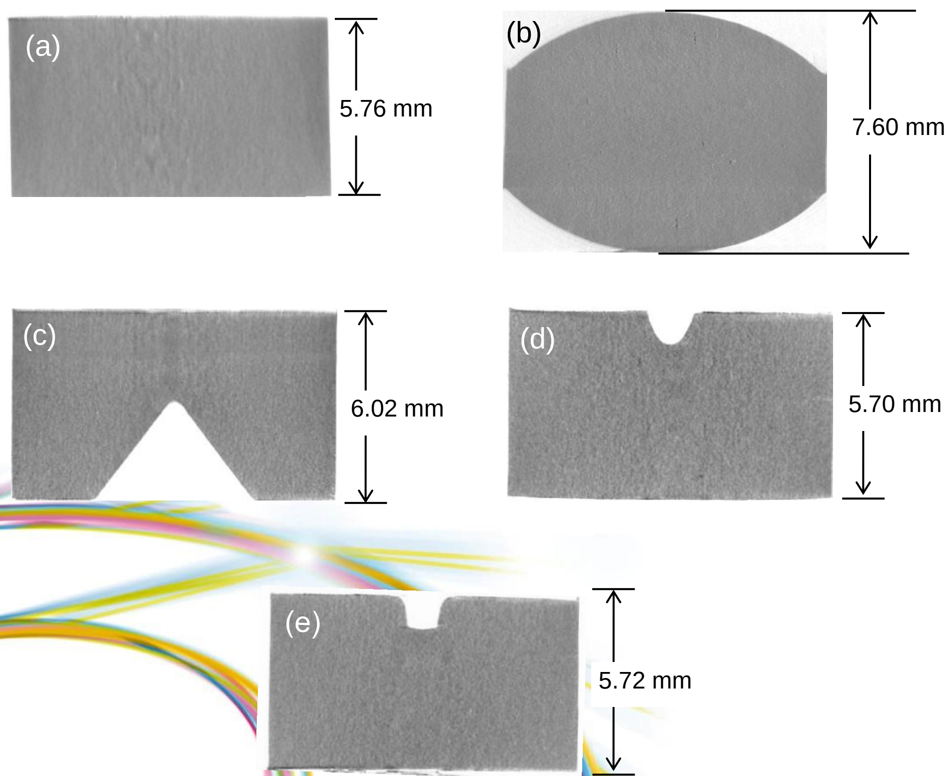
- Collagen Fibrillar strain
- Micro damage and cracking
- Mineral crystallite orientation

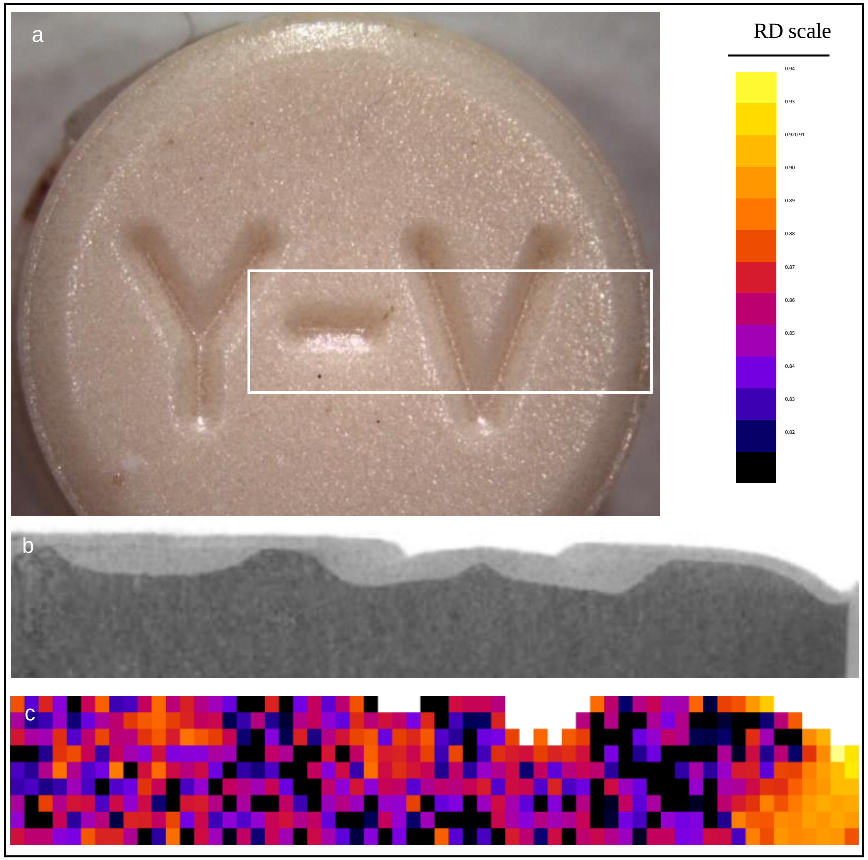


A. Karunaratne, J. Hiller, C. Esapa, A. Boyde, N.J. Terrill, A.H. Barber, R.V. Thakker, H.S. Gupta, Journal of Bone and Mineral Research, **2012**

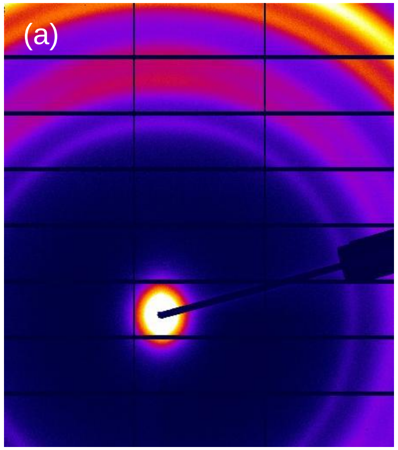
Tablet Compaction and its effect on pharmaceutical activity

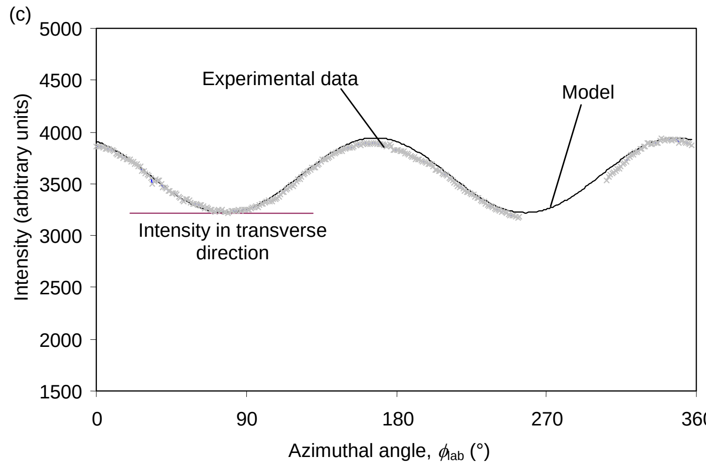
Tablet Test shapes including representative indentation types

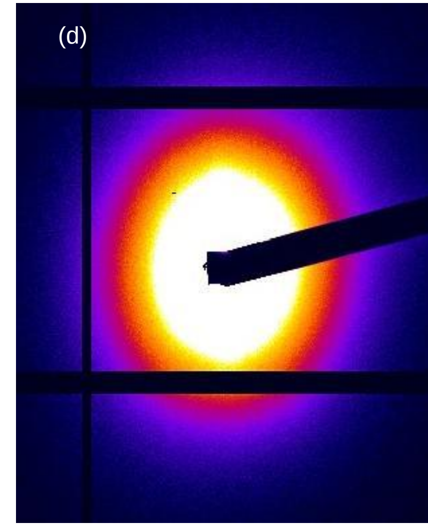


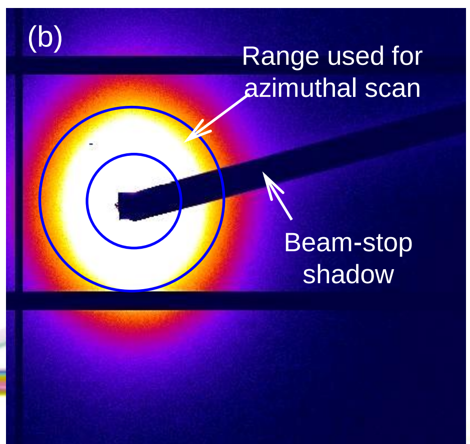


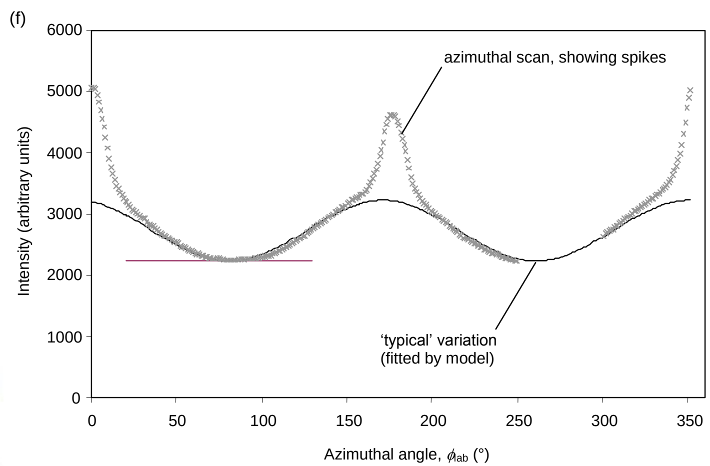
Compaction/ Morphology

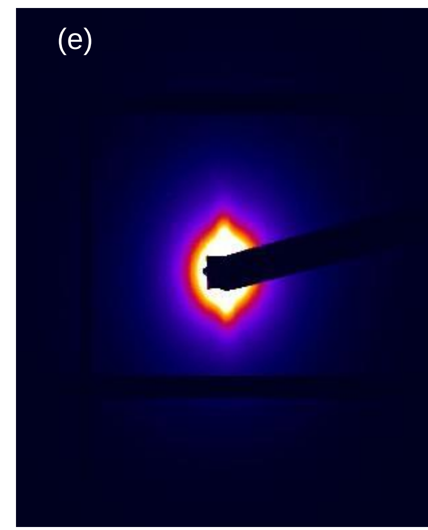












$$\langle \cos^2 \phi \rangle = \frac{\int_0^{180} I(\phi).\cos^2 \phi.\sin \phi.d\phi}{\int_0^{180} I(\phi).\sin \phi.d\phi}$$

$$H = \frac{3\langle \cos^2 \phi \rangle - 1}{2}$$

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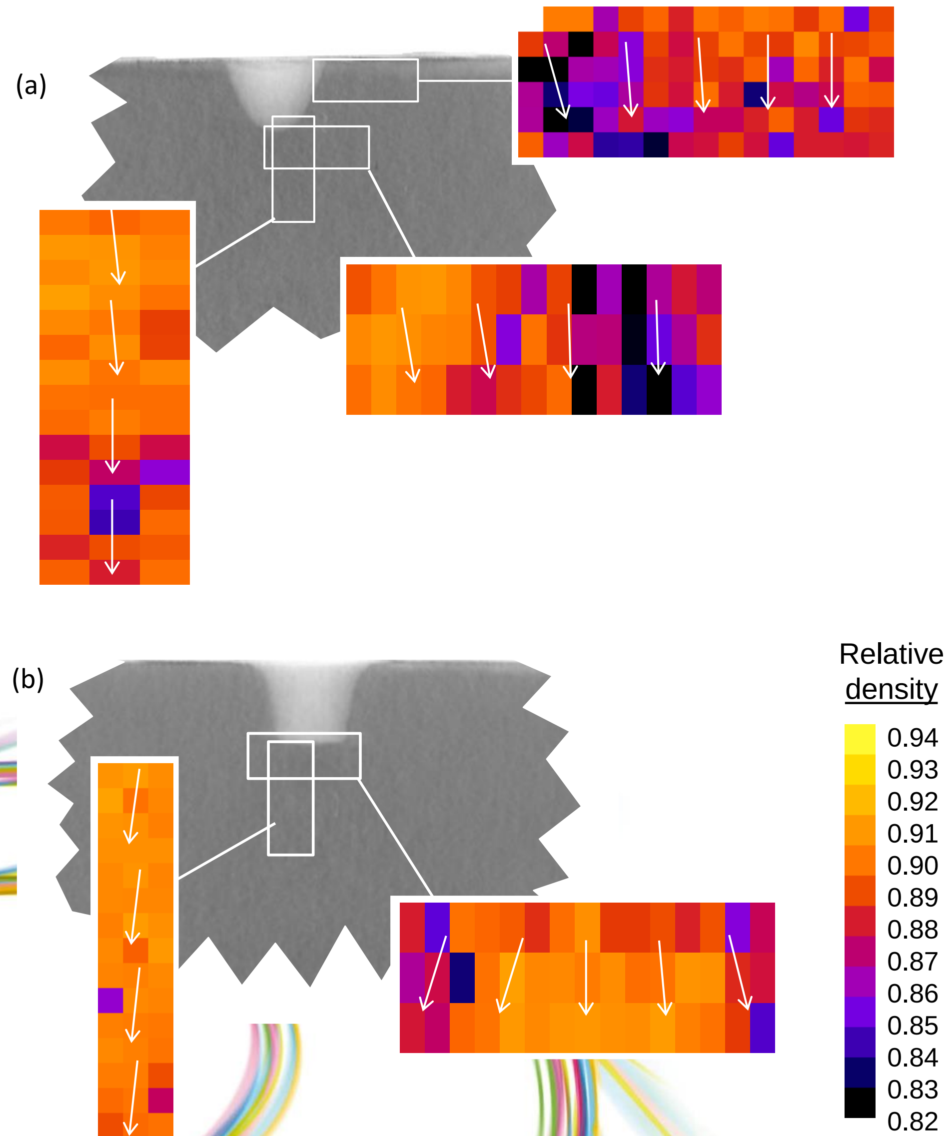
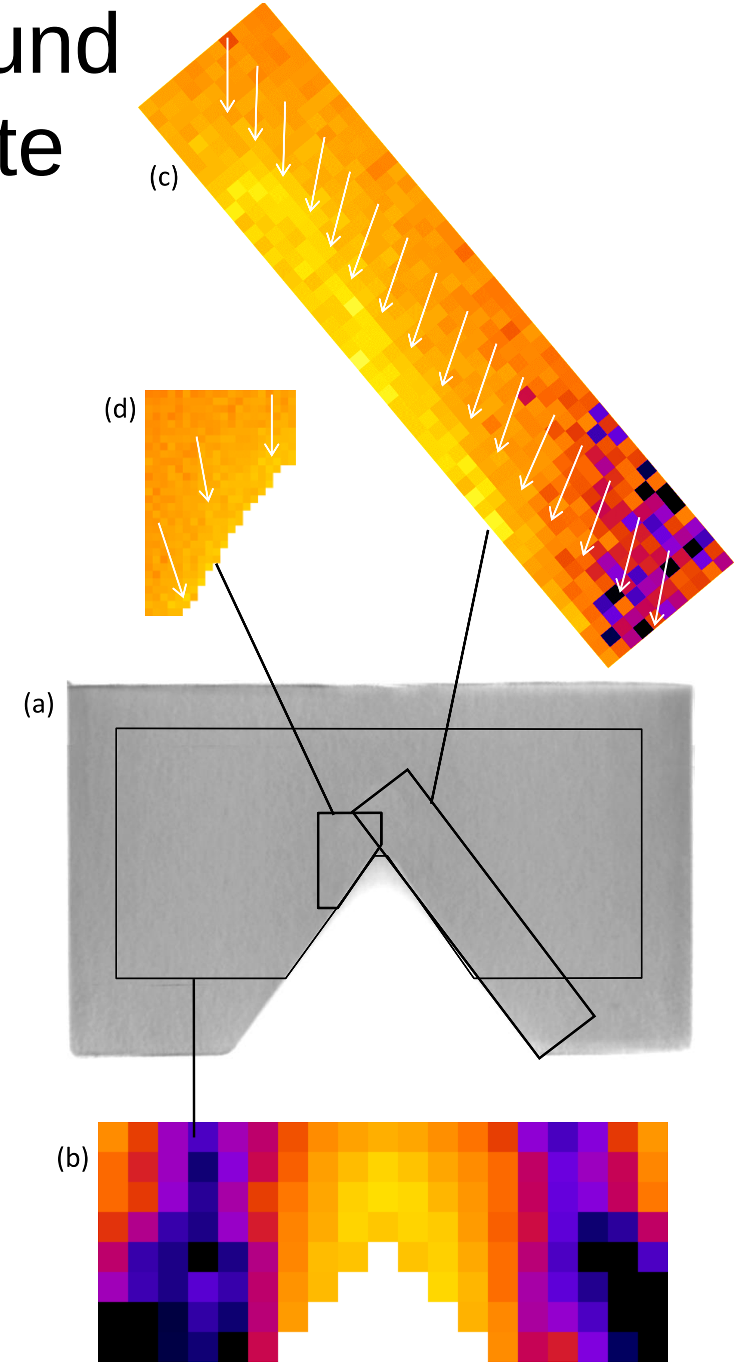
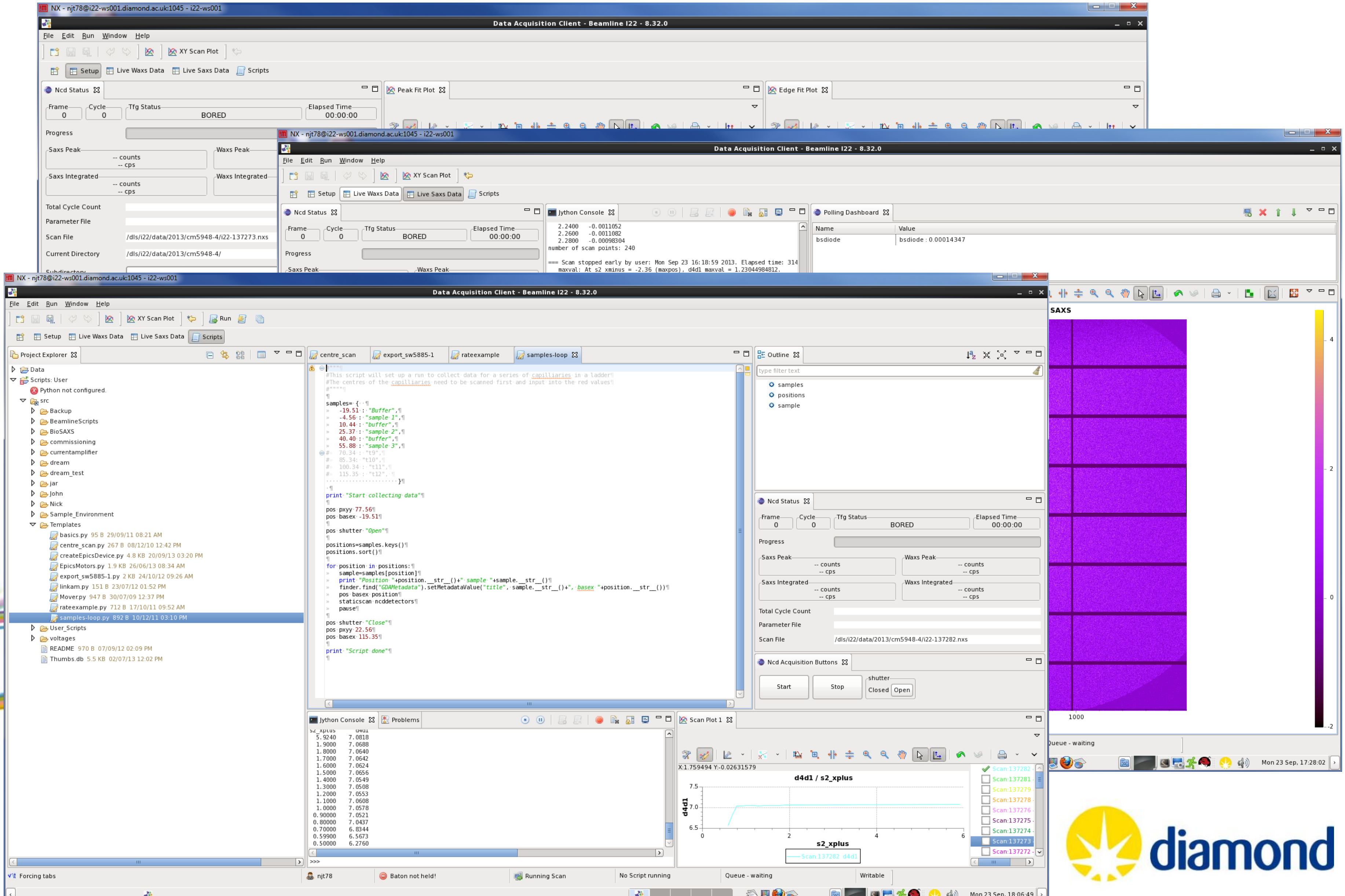
Orientation around compaction site





Data Collection *via* GDA



diamond

Data Reduction

Error Propogation

Normalisation 1D/2D	I_0/I_t
↓	↓
Detector Corrections 1D/2D	Dark Current, Detector Response, etc.
↓	↓
Background Subtractions 1D/2D	Sample cell, Porod, amorphous (variable)
↓	↓
Absolute intensity 1D/2D	By Cross calibration or directly
↓	↓
Radial Averaging 1D	Sector and full circle with masking

q Axis Propogation

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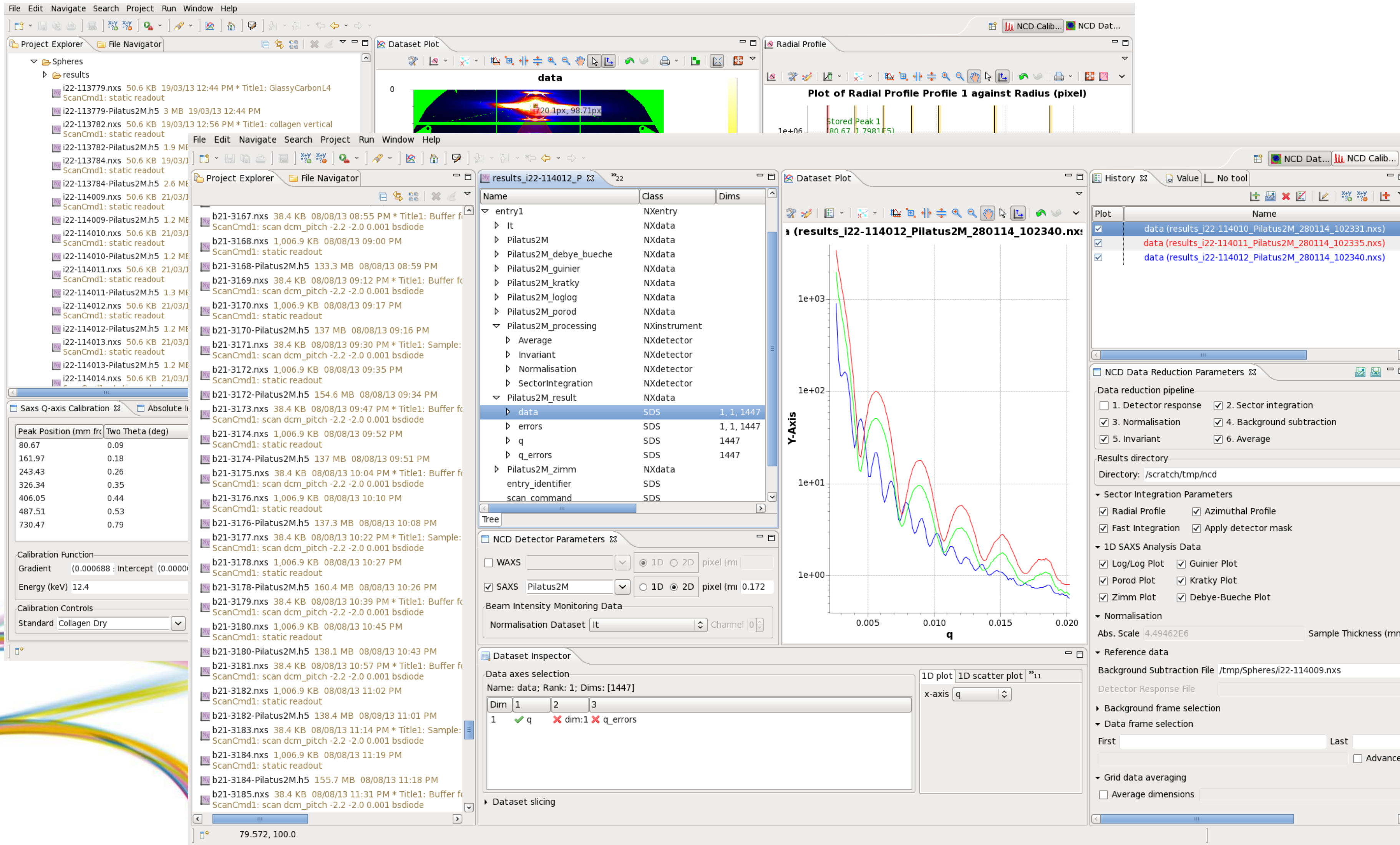
Data Calibration &Reduction in Dawn



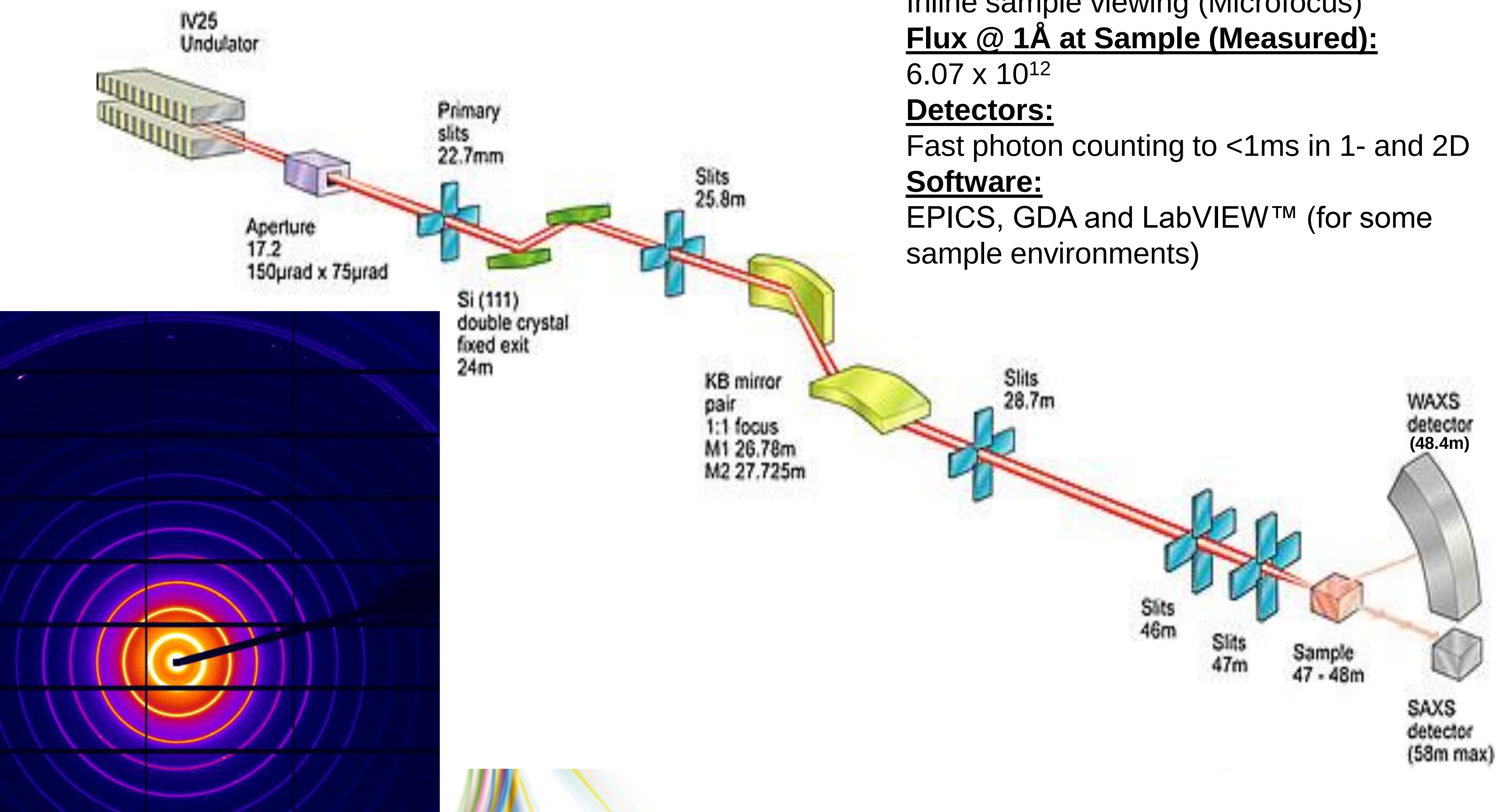
diamond

Data Analysis

- Peaks and single parameter values are being integrated into DAWN.
- More detailed analysis is available *via* a range of packages that have been developed to focus on particular areas of science or experiment.

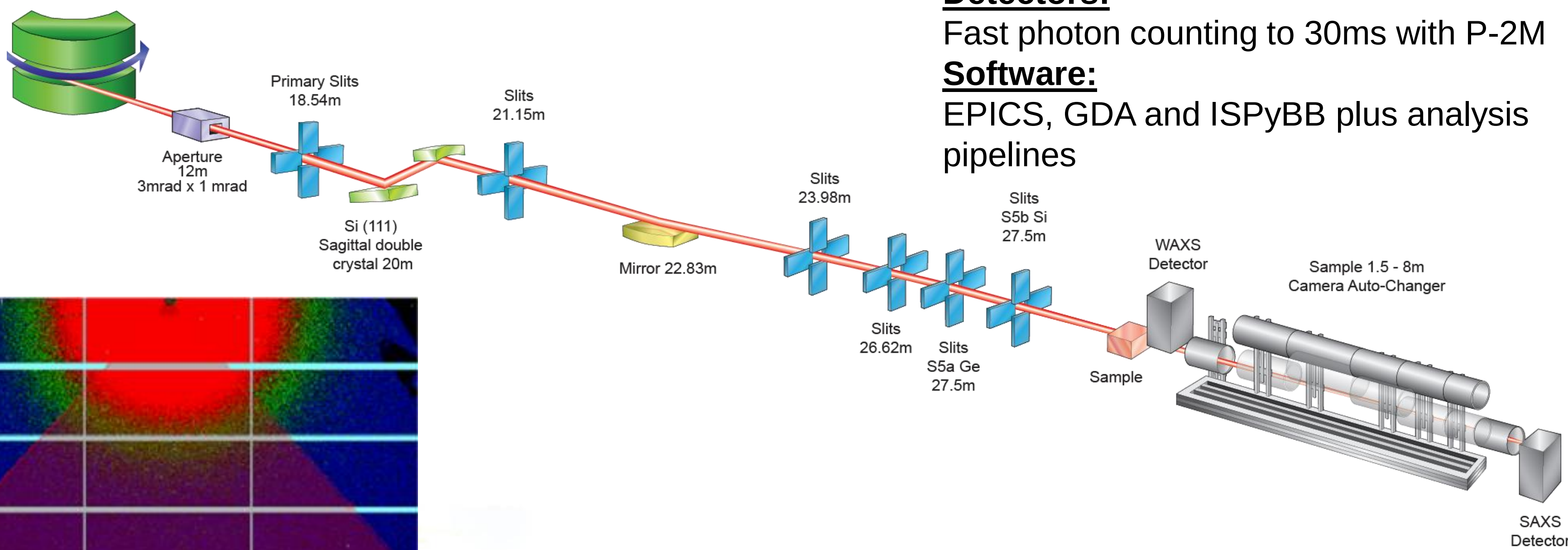
I22 – Small Angle X-ray Scattering for Diamond

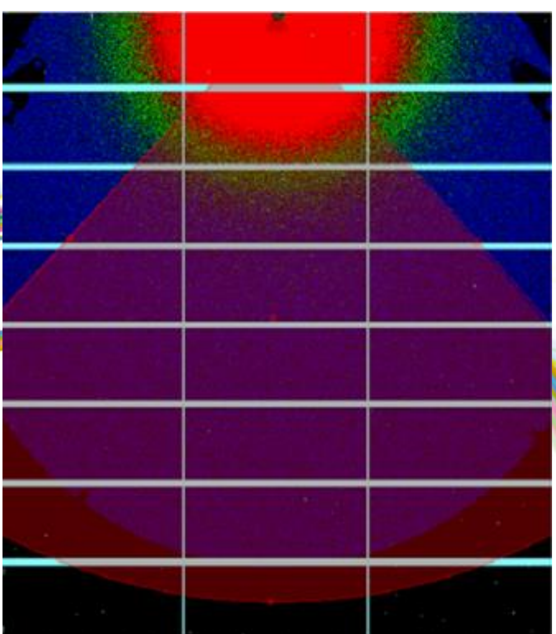
<u>Beamline:</u>
Energy Range 3.7-20keV
d/Å range 1-5000Å (probably >1mm)
<u>Beam size:</u>
70μm (V) – 330μm(H)
6μm x 7μm with microfocusing
<u>End Station:</u>
Flexible Sample platform
Inline sample viewing (Microfocus)
<u>Flux @ 1Å at Sample (Measured):</u>
6.07 x 10^{12}
<u>Detectors:</u>
Fast photon counting to <1ms in 1- and 2D
<u>Software:</u>
EPICS, GDA and LabVIEW™ (for some sample environments)



B21 – Solution SAXS for Diamond

Beamline:
Energy Range 6-23keV
d/Å range 1-2000Å
Beam size:
250µm (V) – 350µm(H)
End Station:
BioSAXS Robot for Solution Samples
Flux @ 1Å at Sample (Measured):
8 x 10^{11}
Detectors:
Fast photon counting to 30ms with P-2M
Software:
EPICS, GDA and ISPyBB plus analysis pipelines





Small Angle Scattering (SAXS)

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diamond

Thanks for your attention