

XIV Conference on Small Angle Scattering in Oxford



Sunday 13th - Friday 18th September, 2009



Satellite to SAS 2009

- *Synchrotron Radiation in Polymer Science IV*
- *Netherlands, 8th-11th September 2009*

- Co-organised by Eindhoven and Leuven University



Monastery of Rolduc



Near Maastricht, in the South of the Netherlands, close to the highest mountain in the Netherlands as well as close to the longest Dutch



So take your diary and write in it:

8th-11th September 2009

Rolduc

Synchrotron Radiation in Polymer
Science meeting



SAXS/WAXS

Wim Bras
DUBBLE @ ESRF
Netherlands Organization for Scientific Research (NWO)

NSLS2 workshop



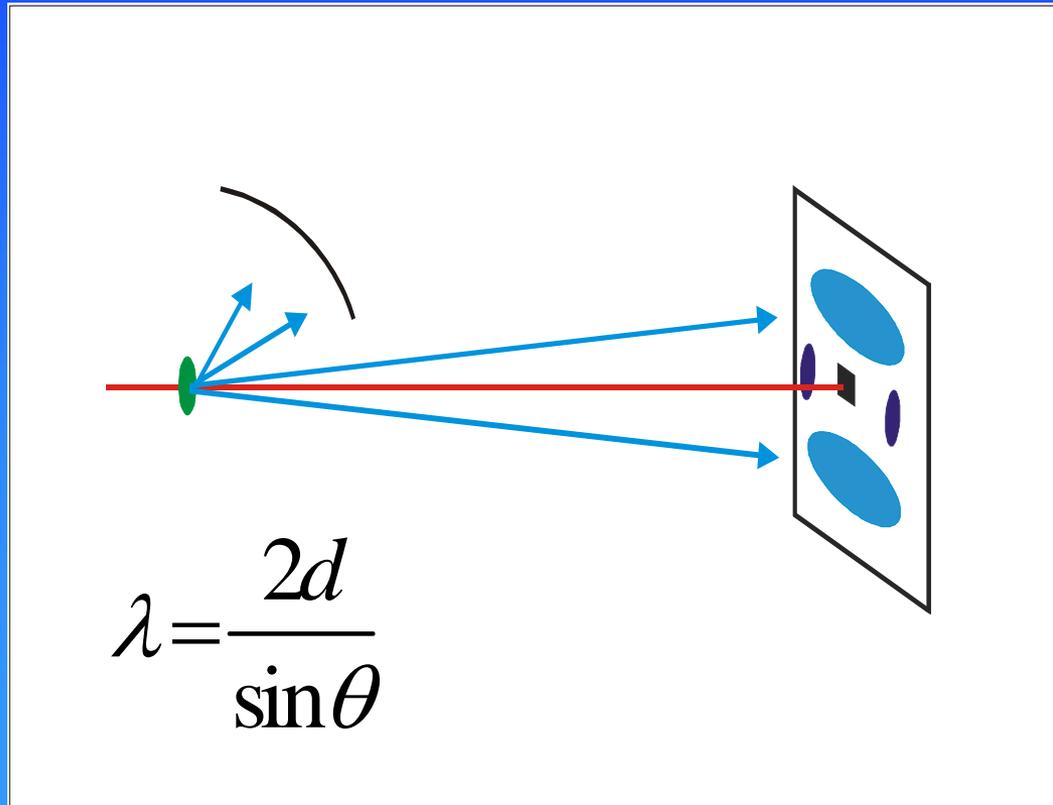
Outline

- Examples of what is presently possible
- Limitations
- ‘if I would build a beam line now....’
- Some key issues



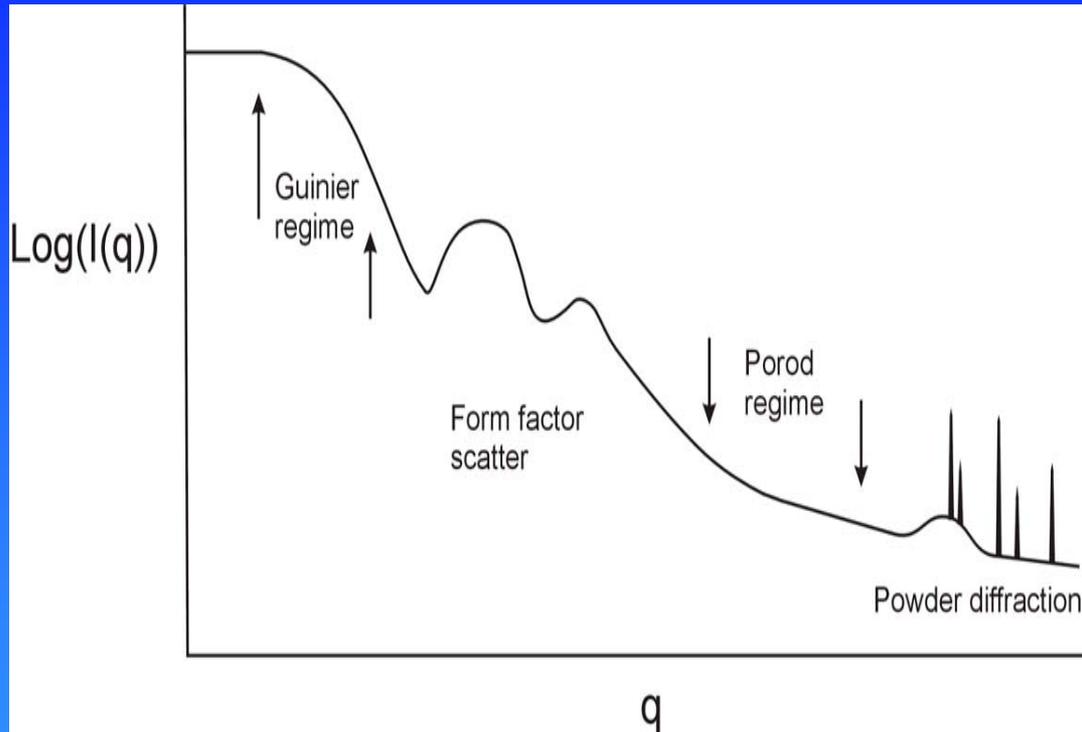
SAXS and WAXS

d small, θ large



θ small, d large

SAXS/WAXS



500 nm

0.2 nm

1 limit $q \rightarrow 0$
electron density contrast
density fluctuations
molecular weights

2 Guinier range
particle size
interparticle scattering

3 particle shape
large scale structures

4 Porod range
particle surface
Surface/volume

5 Intermolecular/atomic
ordering



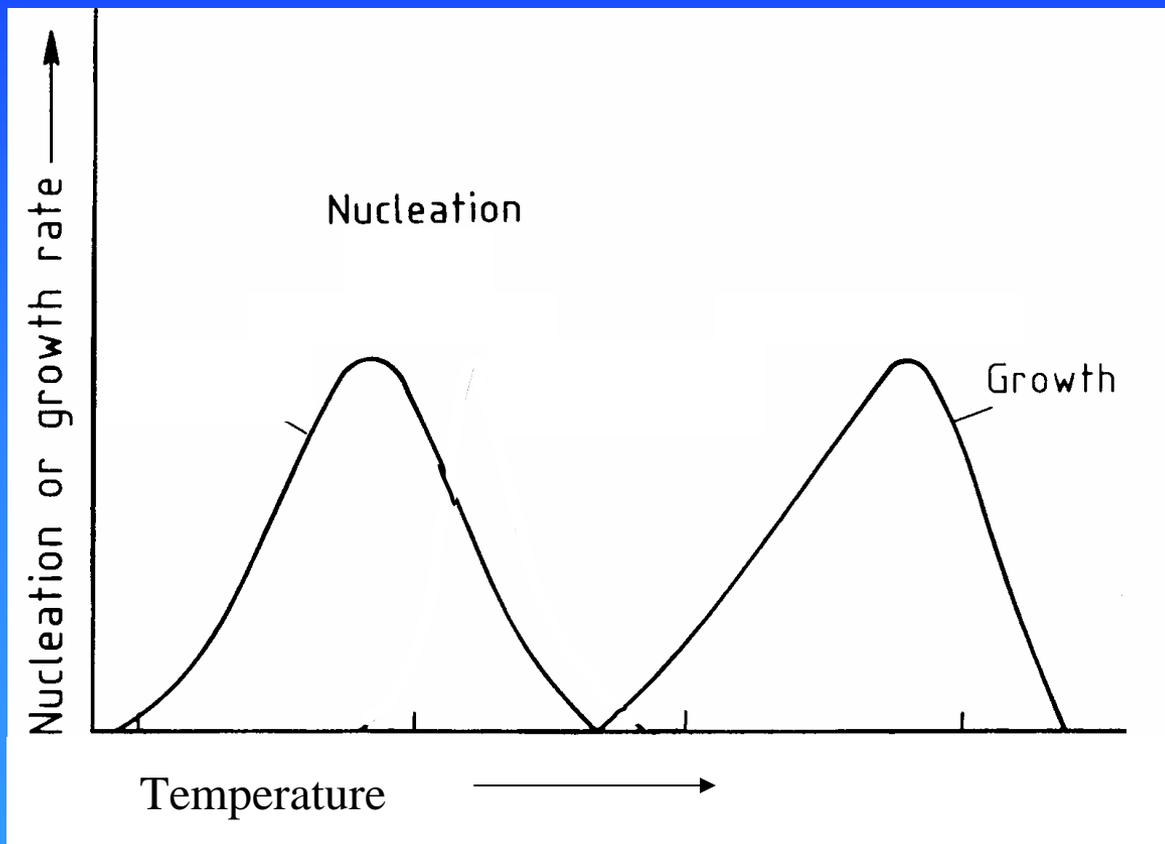
First example

- Devitrification of a glass sample in order to create a glass ceramic
- Time-resolution minutes/frame
- Reasonable amount of scatter
- Only complication 1000° C furnace
- Ideal for a bending magnet

On a second generation source.....

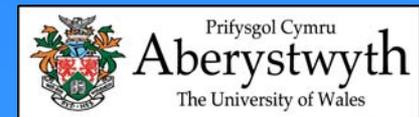


Cordierite glass devitrification



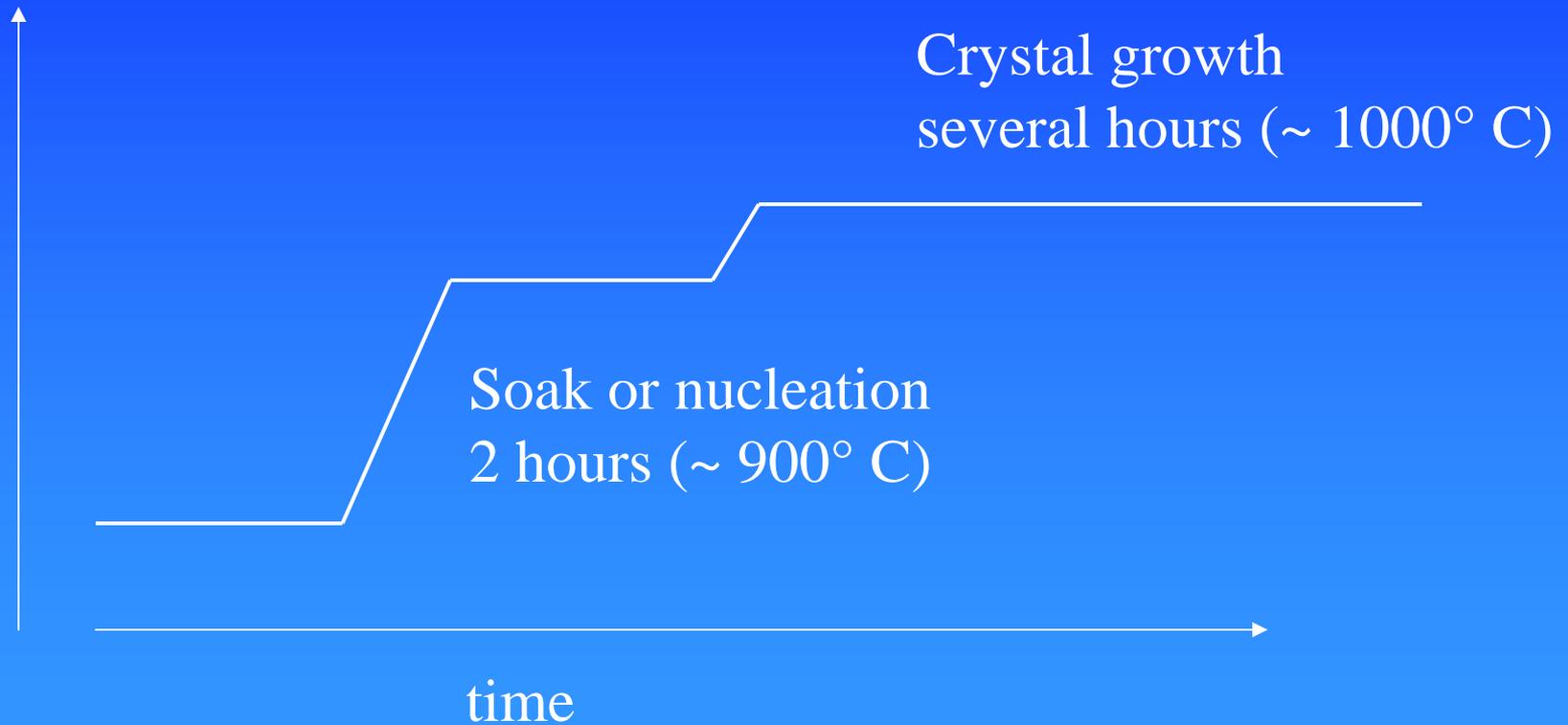
Cordierite
Glass with very low
expansion coefficient

$\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$
doped with
0.34 mol% Cr_2O_3
(crystallization enhancer)

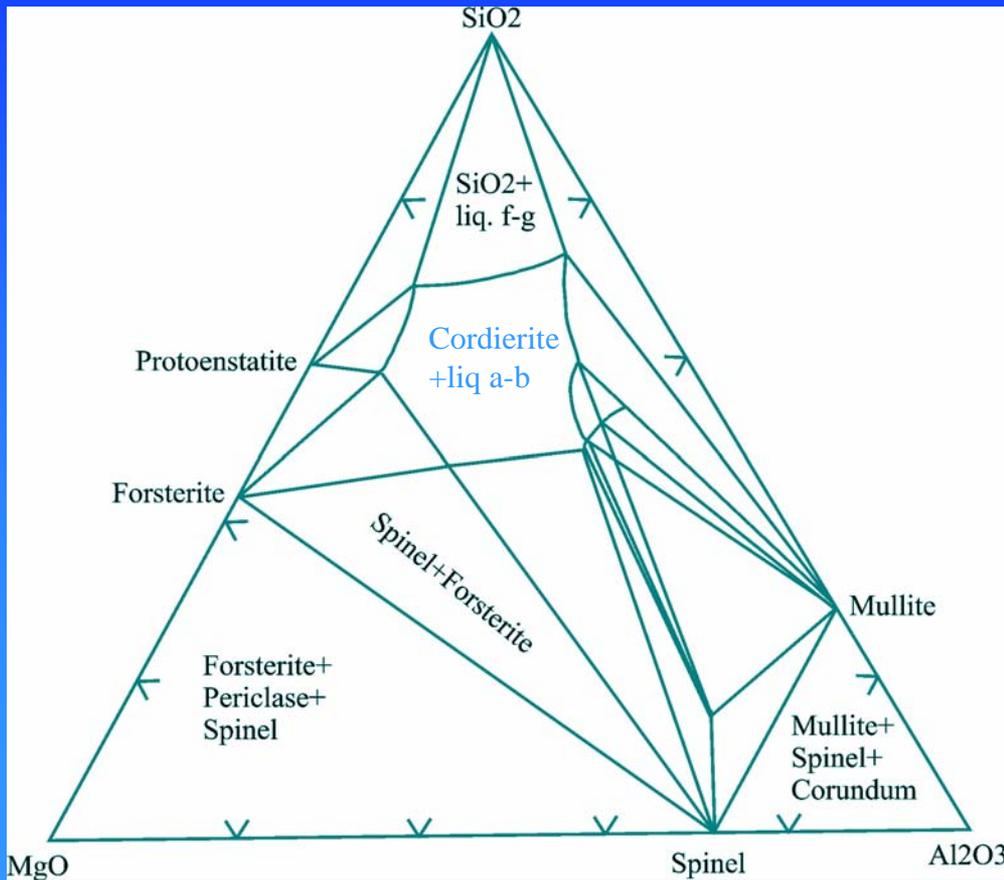


Experiment

temperature



Messy phase diagram



1460° C

Mullite $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$

Protoenstatite $\text{MgO} \cdot \text{SiO}_2$

Spinel $\text{MgO} \cdot \text{Al}_2\text{O}_3$

Forsterite $2\text{MgO} \cdot \text{SiO}_2$

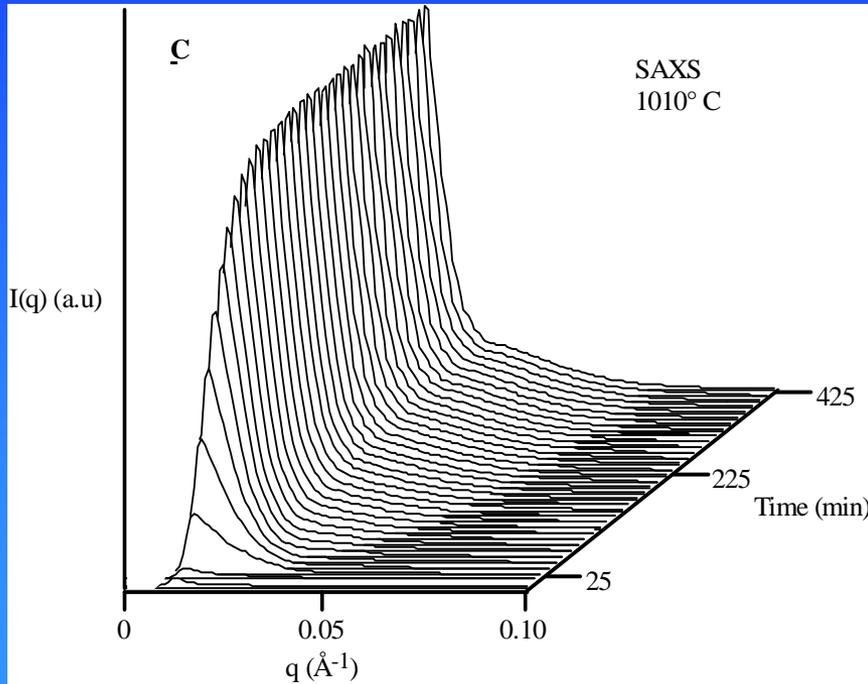
W. Schreyer, J.F. Schairer

J. Petrol., 2, 361, 1961

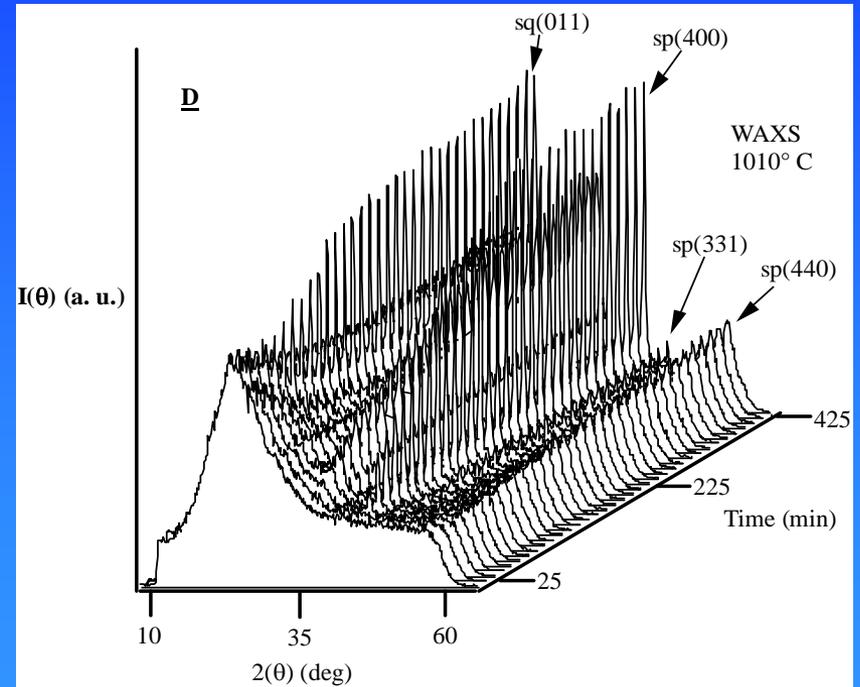


Structure development

Data taken at 1 minute/frame

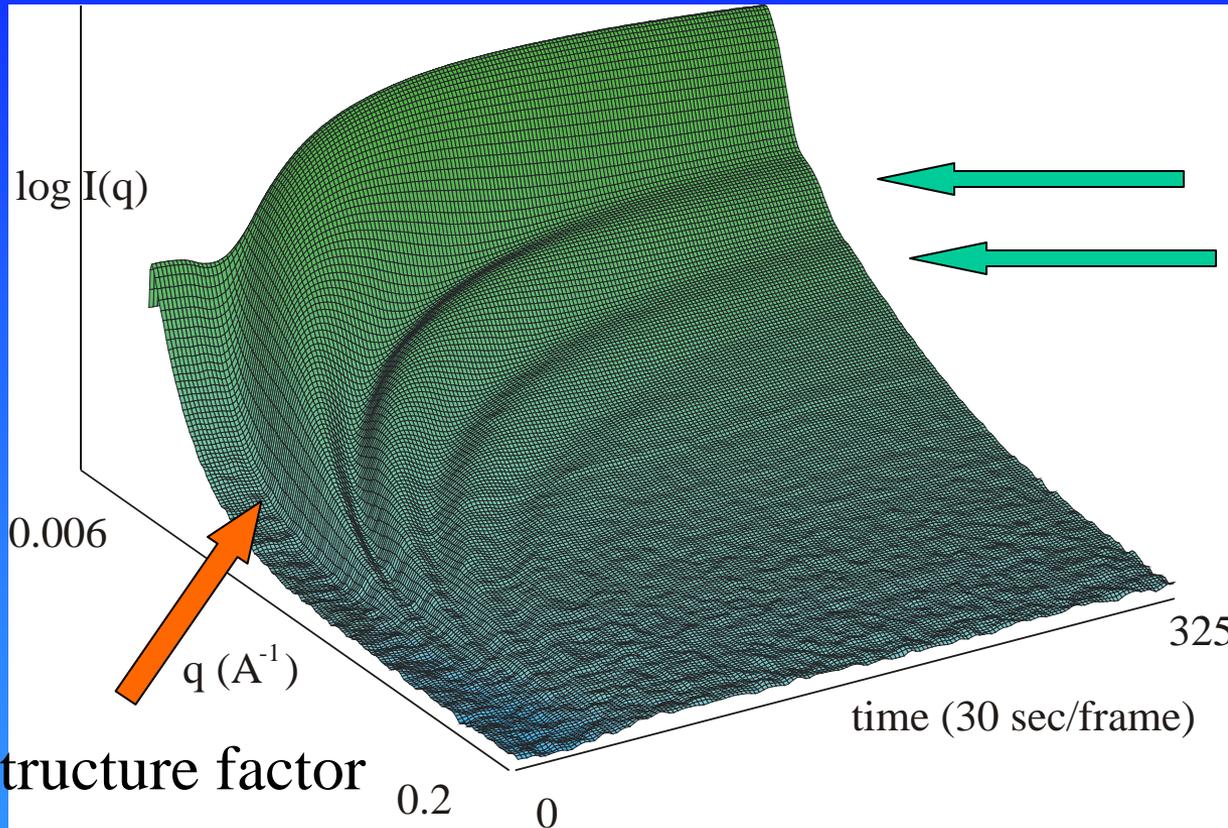


SAXS



WAXS



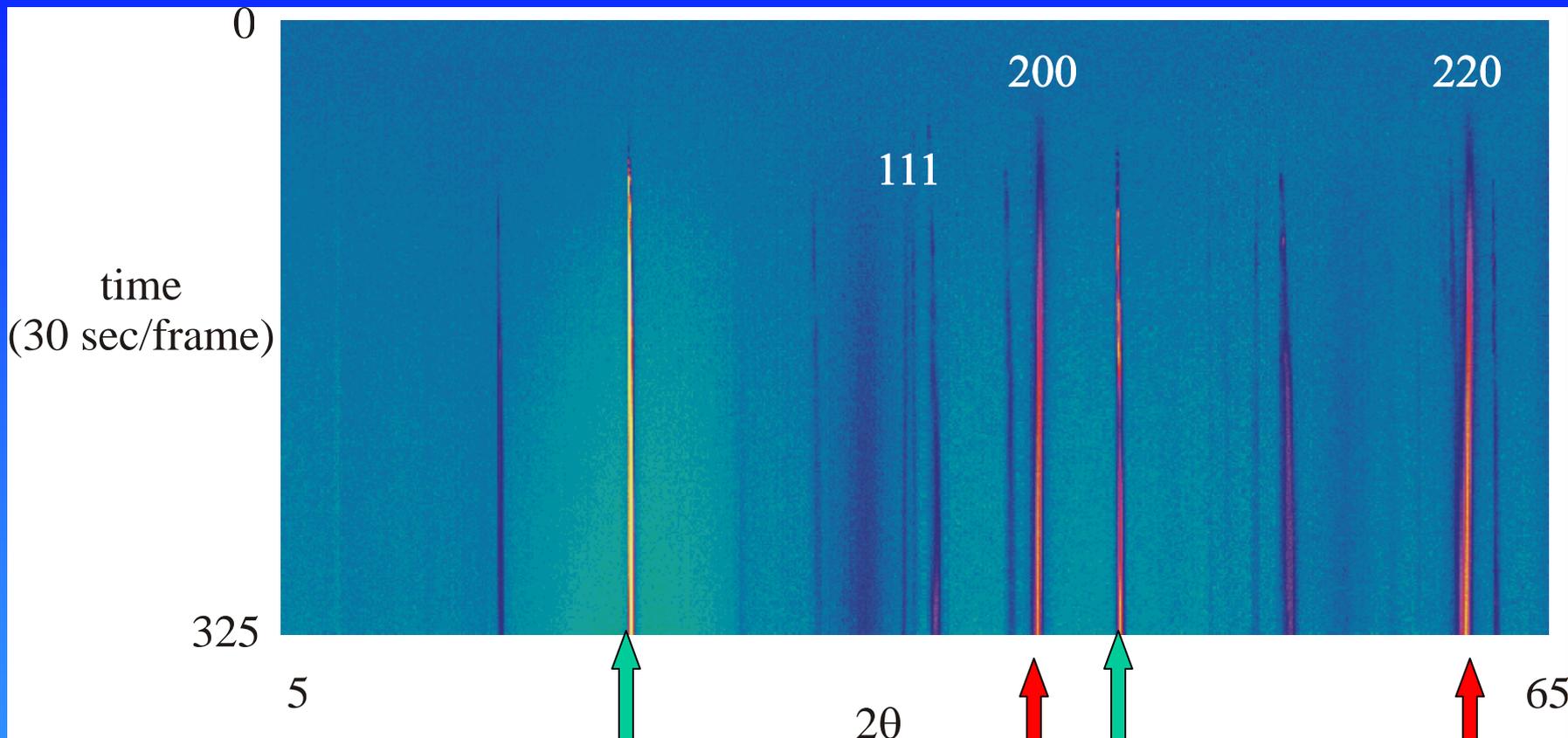


Form factor peaks
(up to 5th order)

The large number of form factor maxima indicate a very monodisperse sample



WAXS data



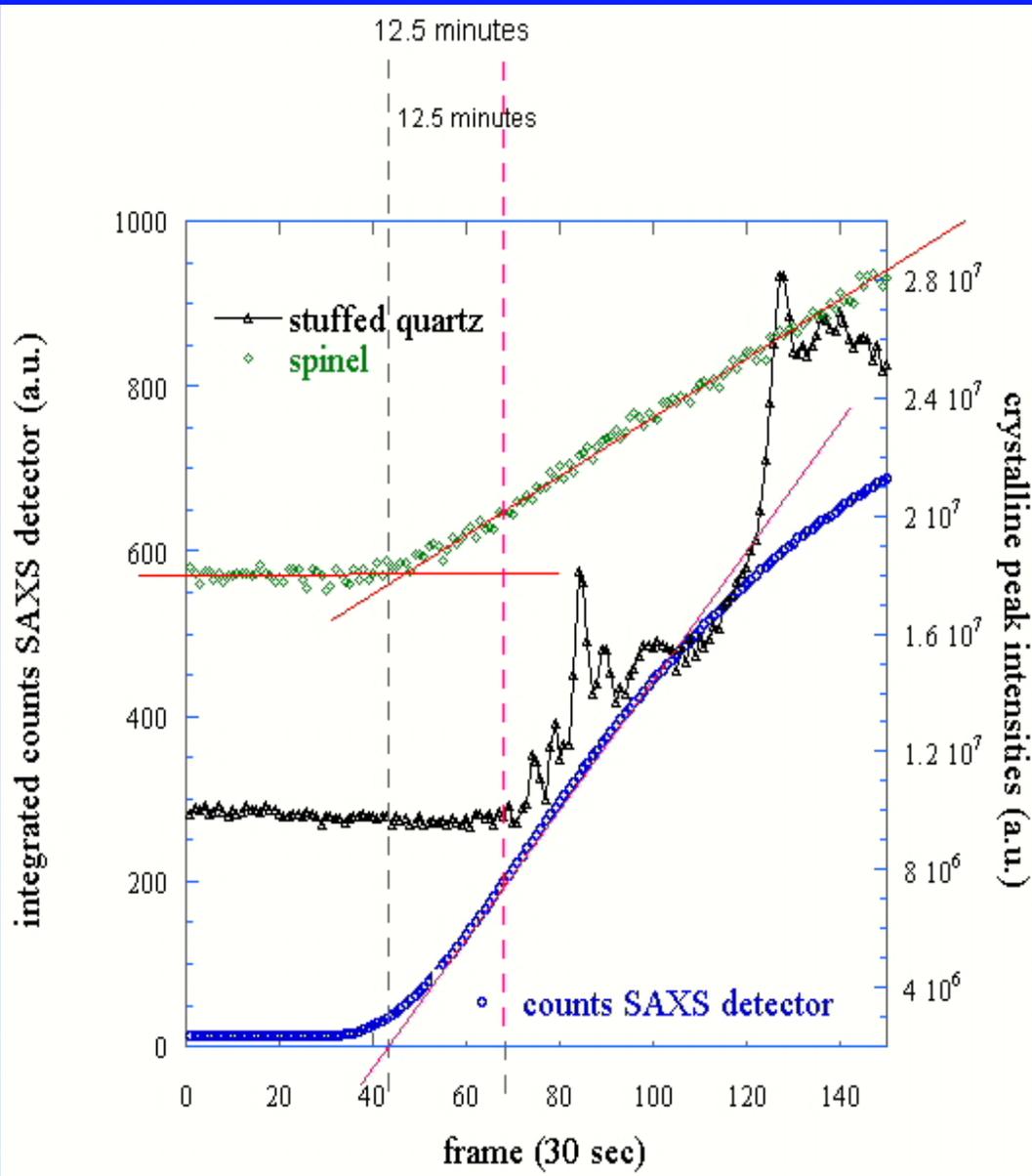
Stuffed quartz increases irregular

Spinel unit cell increases in time
 MgOAl_2O_3 FCC $a = b = c = 4.03 \text{ \AA}$

Spinel increases regularly

Stuffed quartz unit cell decreases in time
trigonal $a = b = 5.13 \text{ \AA}$ $c = 5.37 \text{ \AA}$





- Spinel increases regularly in time

- Stuffed quartz increases irregular

- Spinel starts at same time as particle growth observable in SAXS



What's the growth mechanism of the bulk crystallites ?

Conventional tool for solid state crystallization is Avrami analysis

Relates changing crystalline volume fraction to crystallization mechanism

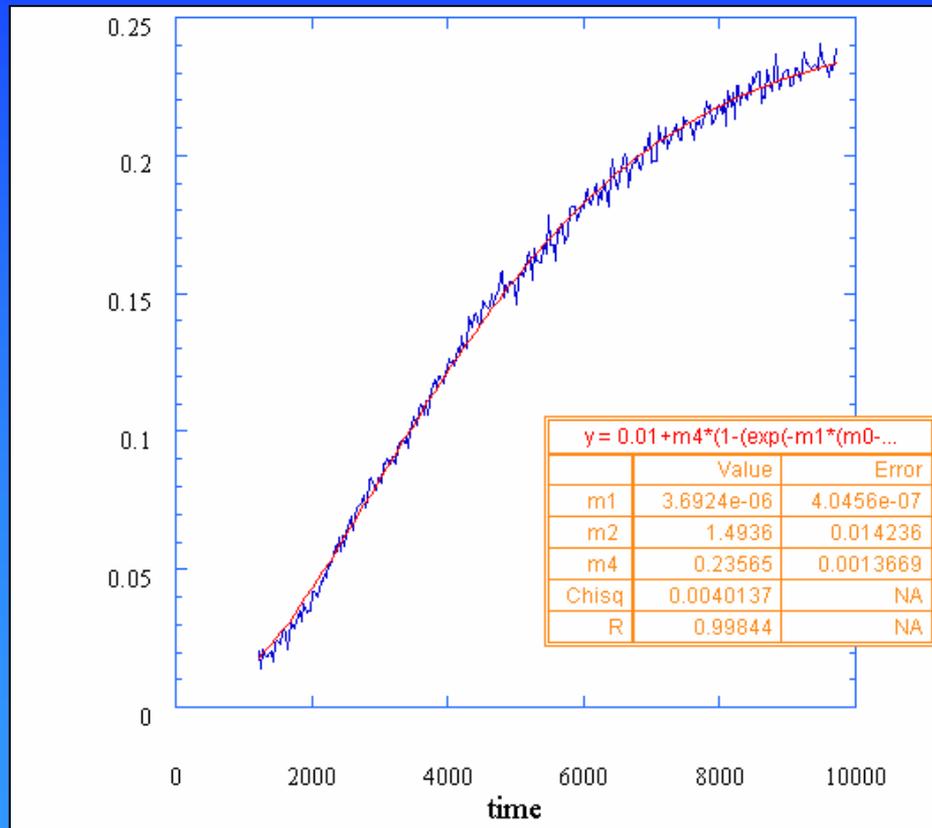
$$V_c = 1 - e^{(-Kt^n)}$$

The parameter n determines what the mechanism is (i.e. diffusion or reaction rate limited)



WAXS

Avrami coefficient
 1.49 ± 0.01



For SAXS data

- For fixed number of particles N which are monodisperse
- $N \times R^3$ is also related to the volume fraction

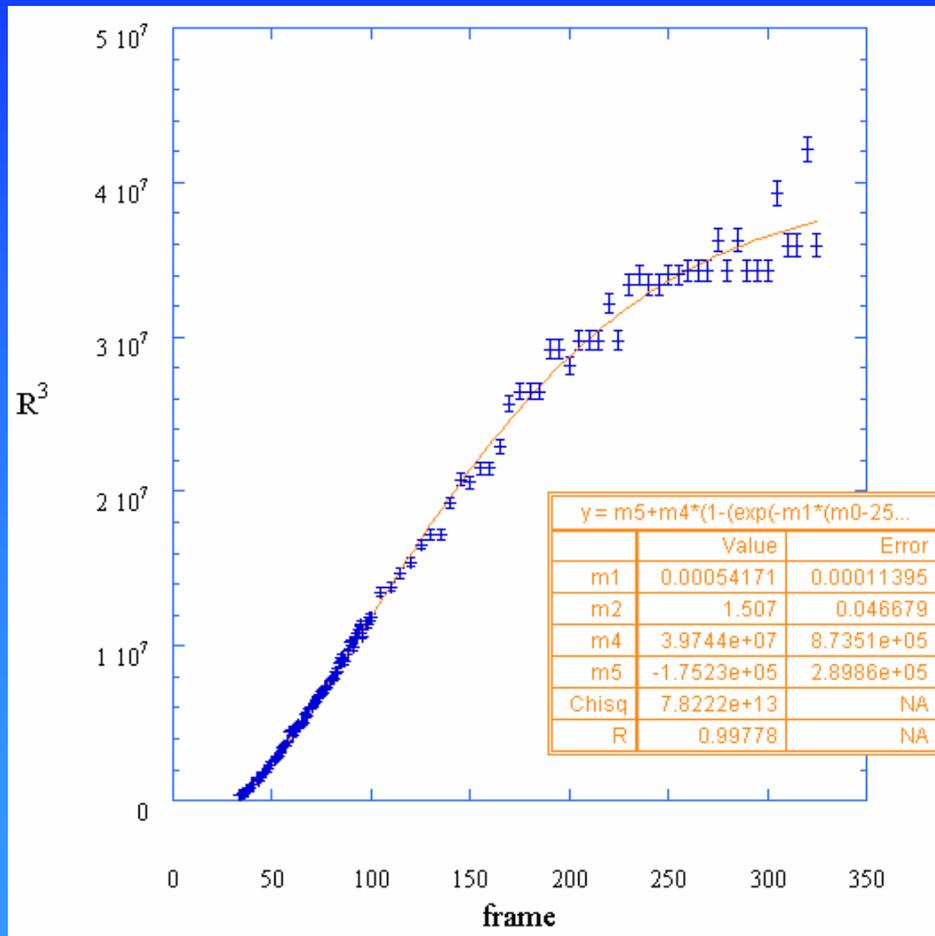


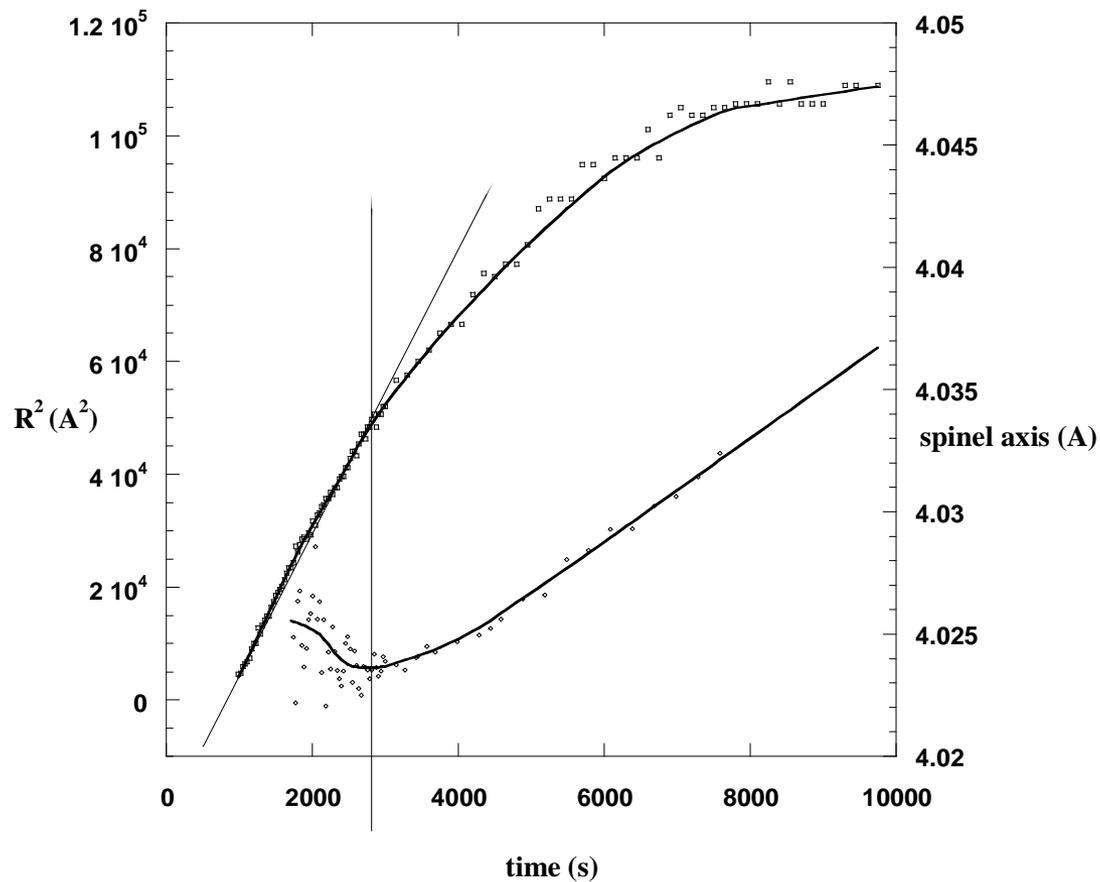
SAXS

Avrami coefficient

$$1.51 \pm 0.05$$

For the people with
poor memories:
from WAXS 1.49 ± 0.01





The increase in the spinel axis in time means that the crystal is slowly expanding

This can be translated to Pressure by Birch-Murnaghan equation of state

1.5 Gpa



Derived information:

- Bulk particle number density
- Bulk particle growth kinetics
- Distinguish between surface and bulk crystallisation
- Activation energy for crystallisation
- Stress profile around bulk crystallites
- Degree of polydispersity
- Crystalline volume fraction
- Electron density profile of crystallites
- Etc. etc.



In short:

- Simultaneous SAXS and WAXS crucial
- A large amount of information in a single experiment
- It took about 3 months work to retrieve all this information
- In effect it were only 8 data curves each obtained in about 2 hours, i.e. less than a day beam time
- Main problem: appropriate software



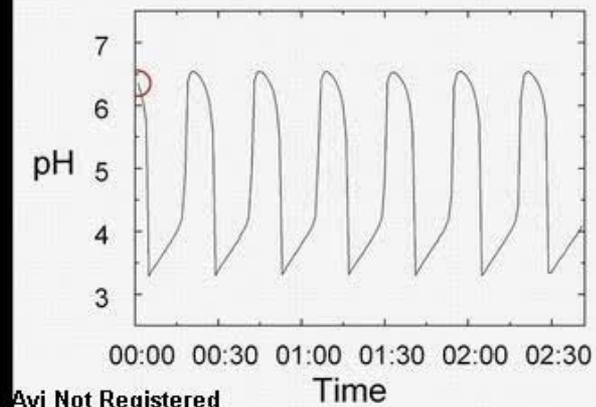
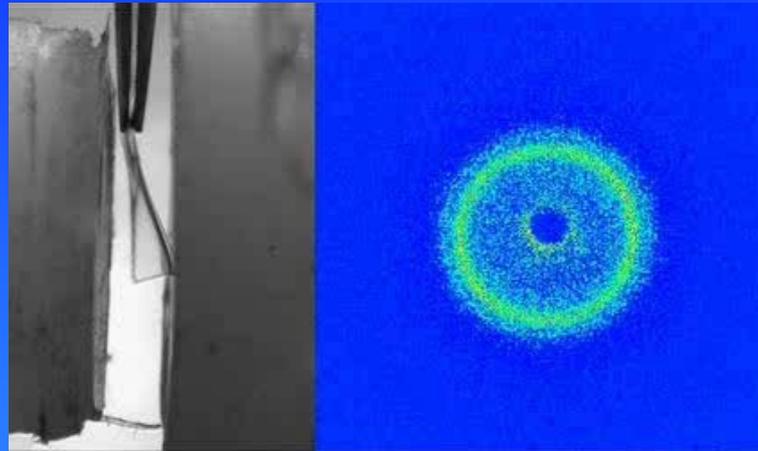
Second example

- Artificial 'muscle'
- Time resolution seconds
- Electron density contrast low
- Good for third generation bending magnet

- Main problem sample environment



The data:

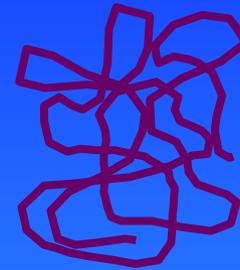


Avi Not Registered

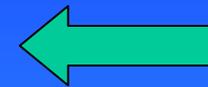


Responsive molecules change shape

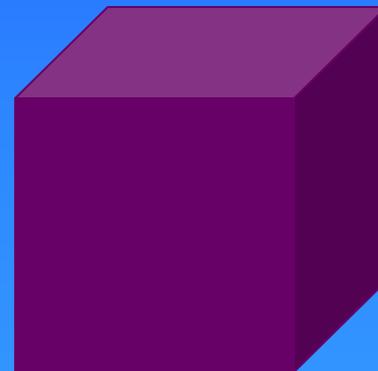
- Polyelectrolytes
- Responsive to solvent quality
- ON-OFF response
- Tunable polarity
- Self assembly available for processing
- Cheap and easy to synthesise



pH or ions



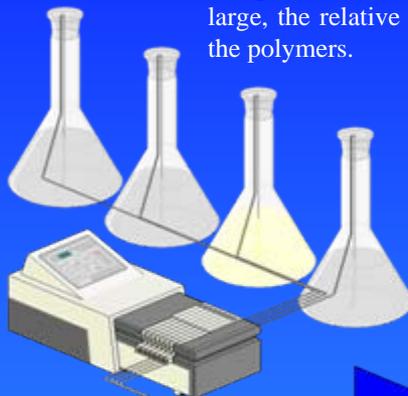
ON OFF



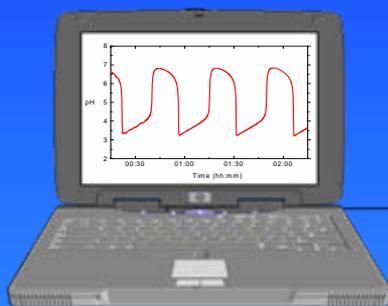
Macroscopic shape change for machines



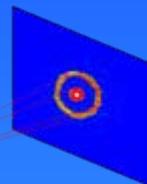
The reaction of bromate, sulfite and ferrocyanide ions in a continuously stirred tank reaction vessel exhibits sustained oscillations in pH^3 . A low acid input is also required. The pH oscillations display a sustained period. Since the amplitude of the pH change is large, the relative change in $[\text{H}^+]$ is dramatic and thus will affect the conformation of the polymers.



The pH meter was hooked up to a laptop computer with METTLER TOLEDO software which allows the variance of pH with time to be recorded and subsequently plotted.

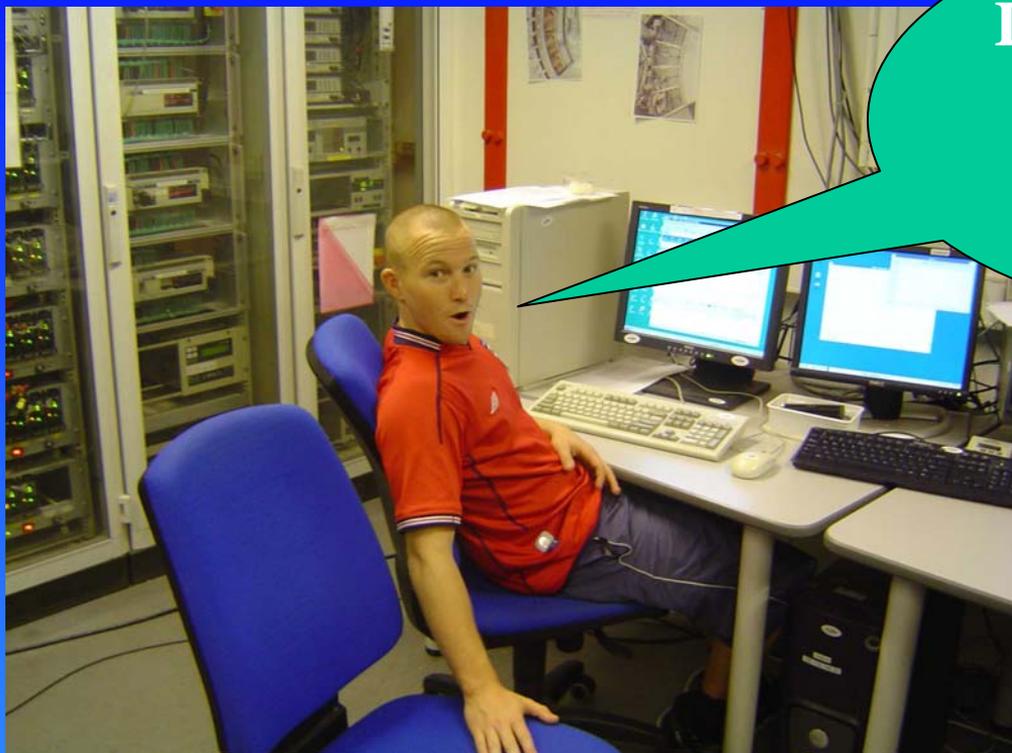


The 2D SAXS detector image featured a ring with an alternating radius, determined by the q value, which was dependent on the pH of the system. Radial integrals of each frame were taken to give a q value for every 60 seconds of data recorded.



A video camera was focussed on the hydrogel throughout the experiment and a small movie of the macroscopic volume change was recorded. Two still images are shown here, capturing the polymer at the extremes of the pH range.





If even I can make
it work, you
should be able as
well.....

Paul Topham is
actually smarter
than he looks !



Third example

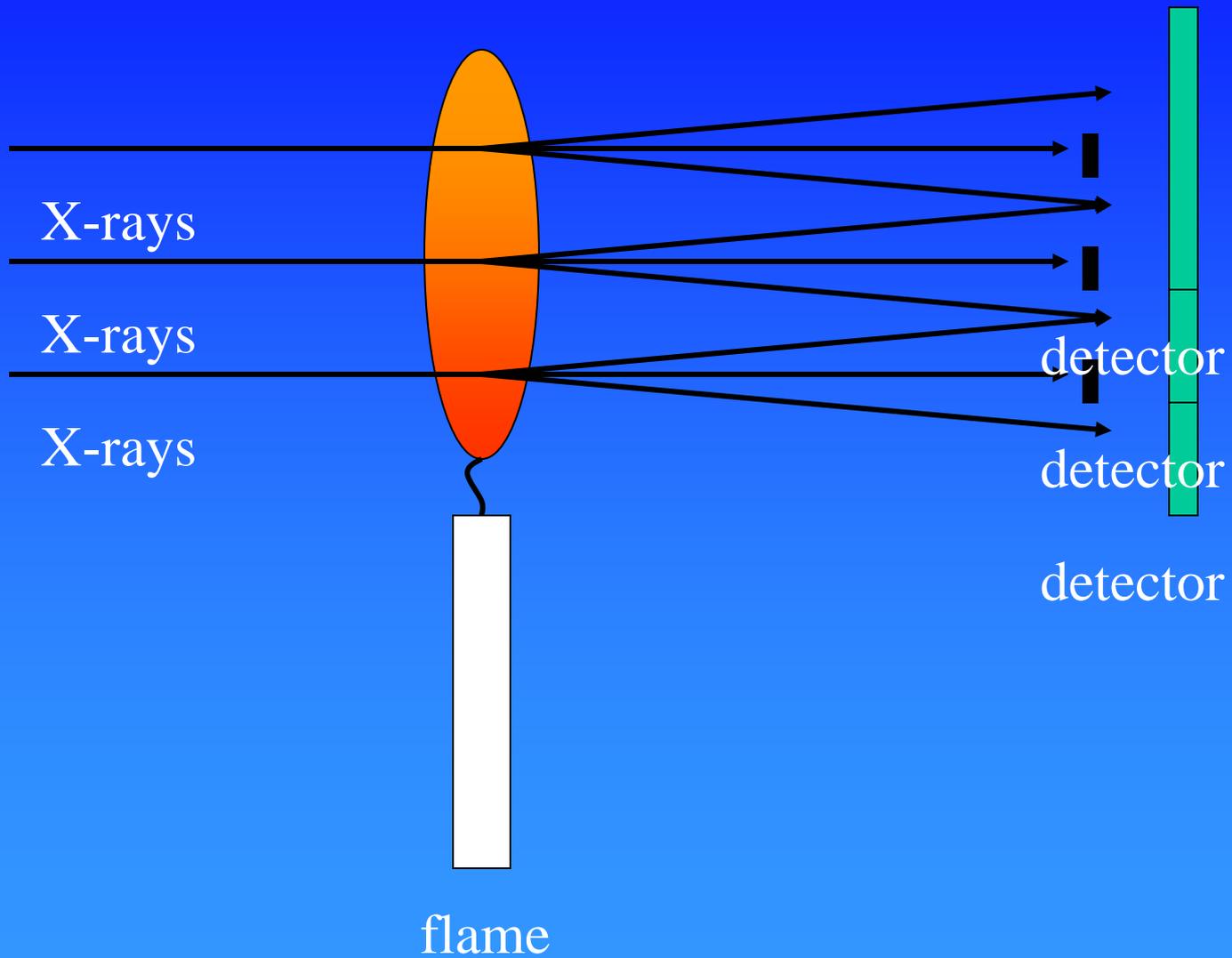
- Soot formation
- ‘Static’
- Electron density contrast very low
- Good for third generation bending magnet or undulator

- Main problem noise free detectors



On line barbecue





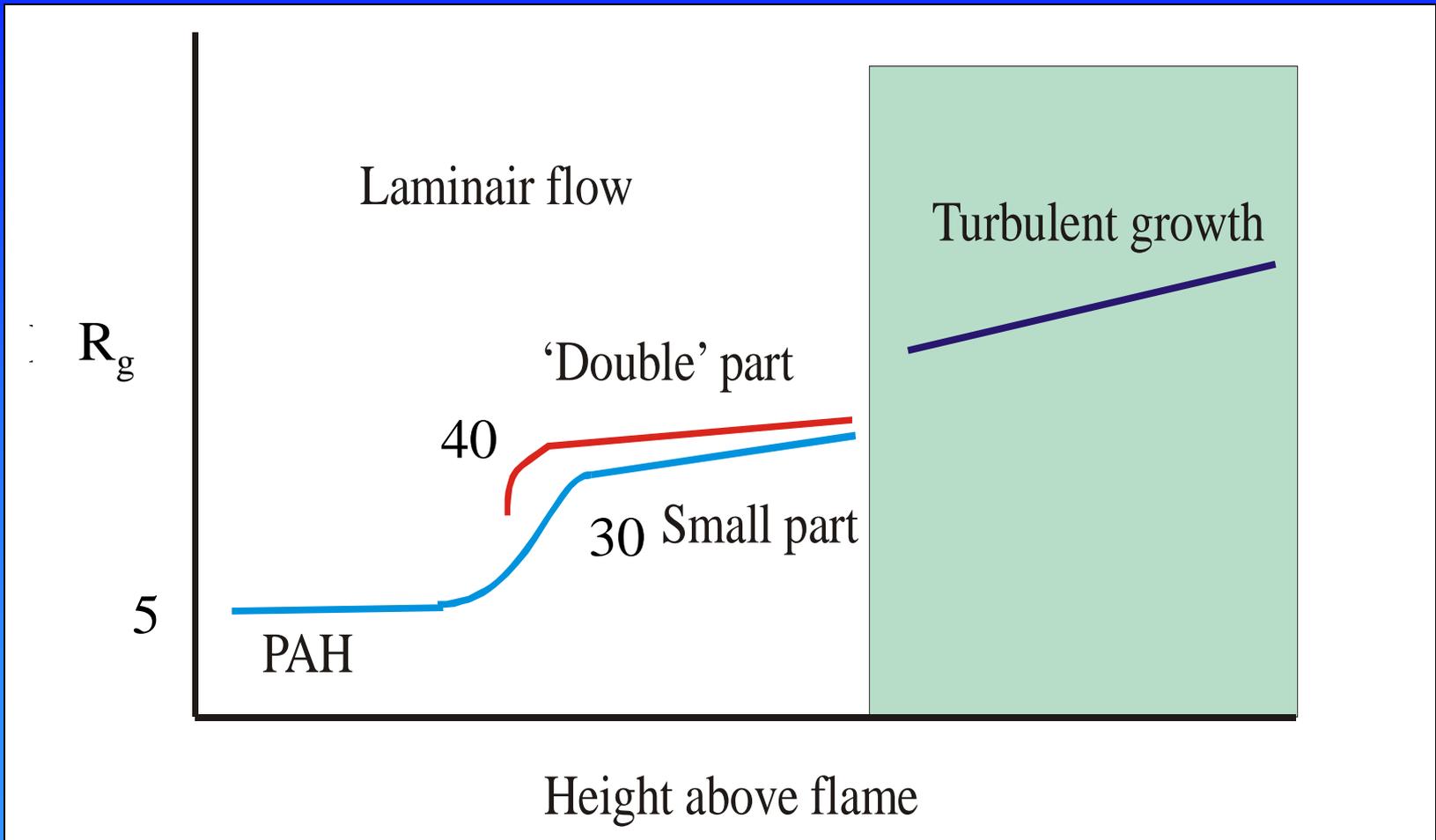
Experiment is simple enough

- Volume fraction of soot 0.001%
- Temperature flame $> 1400^{\circ}\text{C}$
- Temperature flame not constant as function of height
- Large path length required
- Multiple scattering is a problem even though it is near vacuum inside flame



- Crucial to have a laminar flow
- Turbulence will give a different growth pattern
- Crucial to minimise temperature gradients
- Small particles, very hot so: forget about powder diffraction (low count rate, Scherrer and thermal broadening)





Fourth example

- Muscle diffraction
- ‘Time resolved’
- Sample volume very small
- Third generation SR source undulator

- Main problem small sample and radiation damage



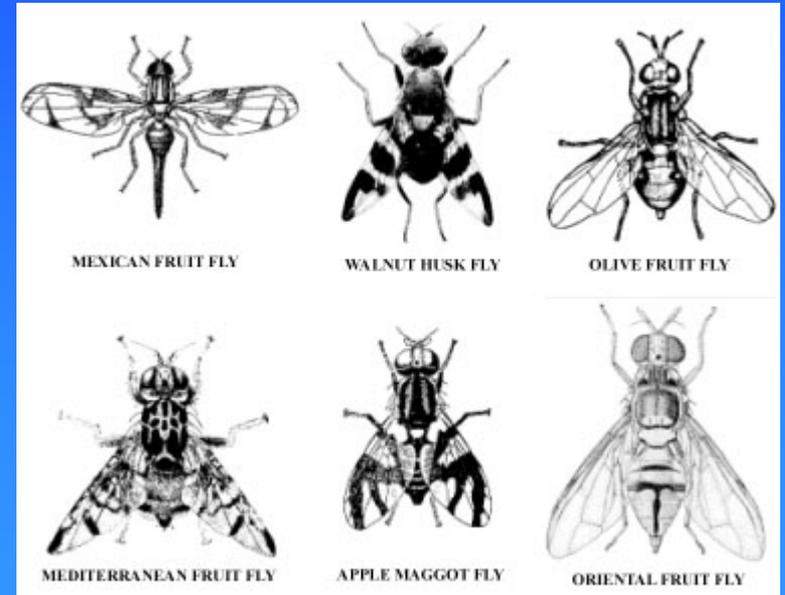
Muscle diffraction

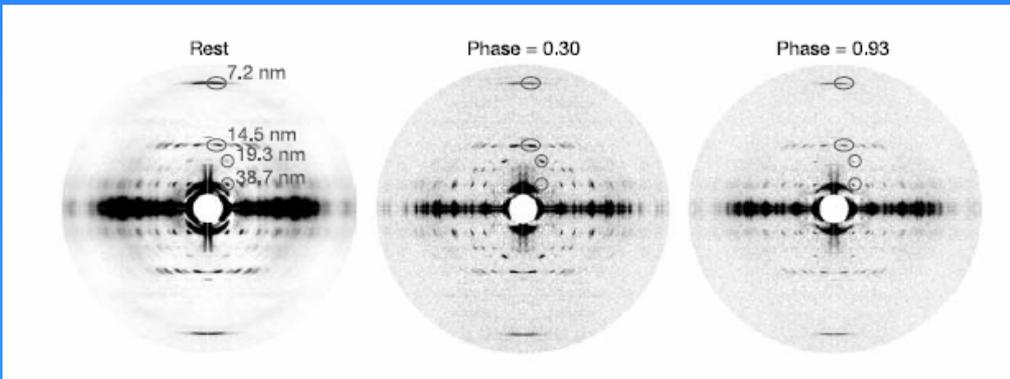
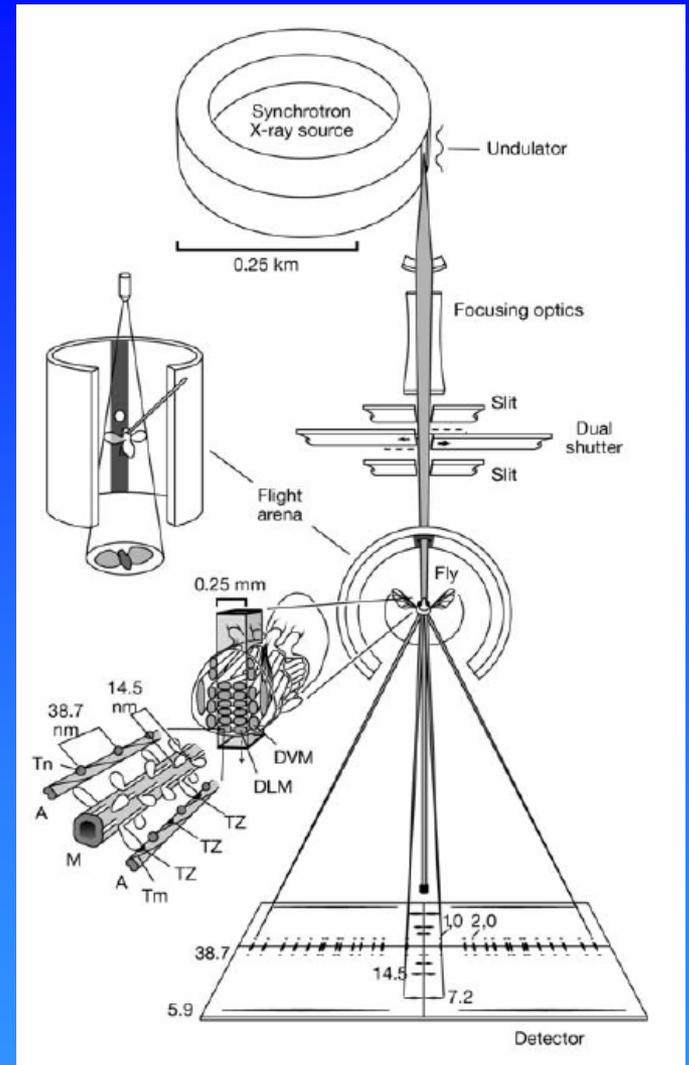
Ideally:
relatively large muscles



Arnie in better days

In this case:
relatively small muscles

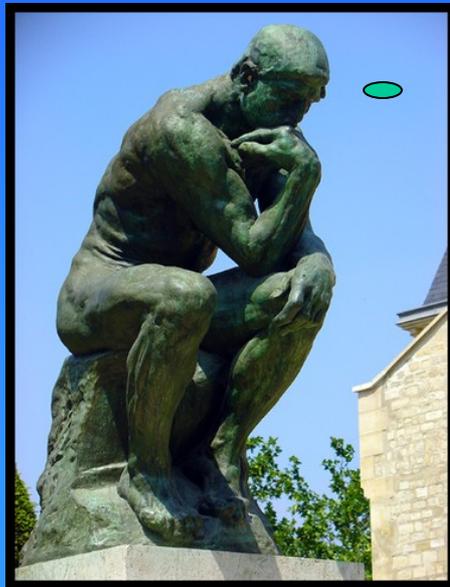




Tom Irving APS Biocat



- Very small sample volume
- Radiation damage
- Moving target



That doesn't
look easy....



And it certainly is not easy!!!

- But the crucial point is
- It might not be easy
- But it can be done
- Only the will to do it has to be there
- Technologically we can do this and other complicated experiments



State of play at present

- Generating flux is hardly a problem
 - 10^{11} - 10^{12} photons/sec sufficient for most problems
- Spot size is hardly a problem
 - Mostly required 200-300 micron, smaller means specialized beam line
- Low angle resolution
 - 2000 Å real space for oldies, 200 nm for younger people
- Time-resolution
 - Not determined by X-ray flux
 - Detectors first limiting step
 - Sample environments also rate limiting step
- Detectors
 - Pixel detectors/photon counting/1 ms minimum time frame length
 - Mainly out of our hands
- Radiation damage
 - It happens.....the more photons, the smaller spot size, the faster it occurs.....
 - It is in the hands of physics, 'nothing' we can do about it
- Data analysis
 - It happens..... the more accessible, the simpler the computer platform, the faster it happens.....



Detectors

- If you had asked me 5 years ago I would have been quite negative but things appear to change
- The new generation pixel detectors looks very promising
 - 3 ms time resolution
 - Photon counting
 - Individual pixel read-out/data processing
 - No parallax, so ok for WAXS
 - Large active areas possible
 - Cheap !!! (at least in a relative sense.....)



But remember the ‘SAXS-WAXS’ wars in polymer crystallisation

- If ‘spinodal’ then SAXS before WAXS
- If ‘nucleation and growth’ the SAXS and WAXS simultaneous
- What do we find now? WAXS before SAXS.....
(Panine et al, Polymer, 2008)
- The messages are:
 - Sloppy experiments will give you any answer you want
 - Even if detectors do exist you have to make them available



Health warning:

- One can always think of an experiment outside the parameter space sketched in the previous slide
- I'm aiming at 95% of the experiments
- In 20 years in this field I have not seen the demands change a lot



To satisfy 95% of the customers:

- 5×10^{11} photons/sec
- 200-300 micron spot size
- 7 -15 keV
- Detector framing 0.1 sec/frame
- Low angle resolution 2000 Å
- Good infrastructure
- Accessible software
- Reasonable volume of shifts available



But if I were a rich man:

- Beam line 1
 - 200 μm focus, $>10^{12}$ photons, 7-15 keV, large hutch, flexible infrastructure, 10 msec/frame
- Beam line 2
 - 1 micron, 10^{10} photons, 7- 40 keV (also high energy SAXS)
- Beam line 3
 - GISAXS, ASAXS
- Beam line 4
 - Biological solution scattering, 400 μm focus, 8 – 12 keV simple optical bench, black box approach



Remaining problems

- Software
- Sample environments
- Technique combinations
- Amount of available beam time



A software problem

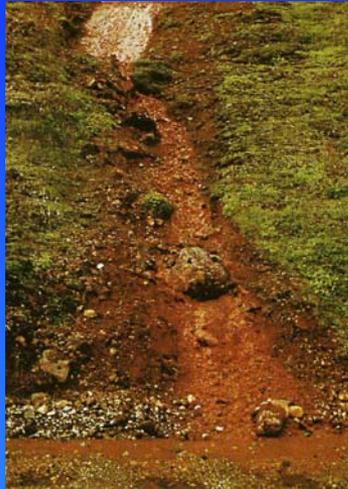


Nanoparticle formation in natural waters



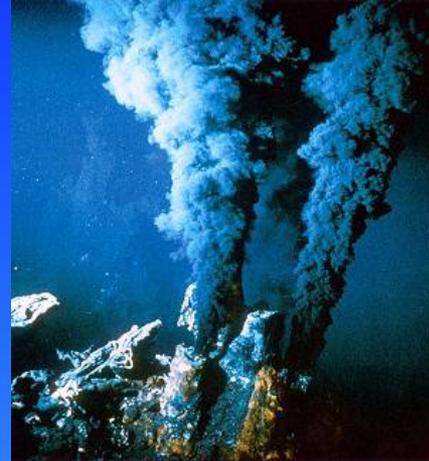
UNIVERSITY OF LEEDS

Terrestrial sediments



Oxidation of ferrous iron containing groundwater

Marine systems



Black smoker

Oxidation of iron sulphides formed in seawater

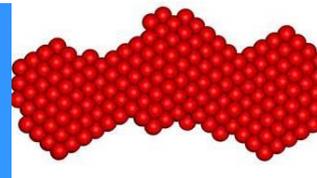
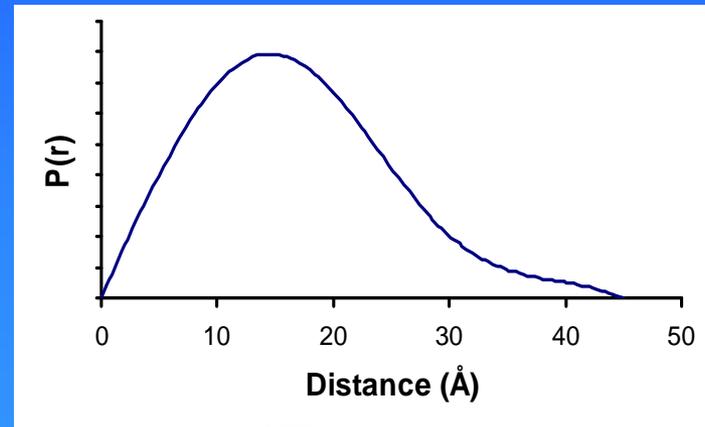
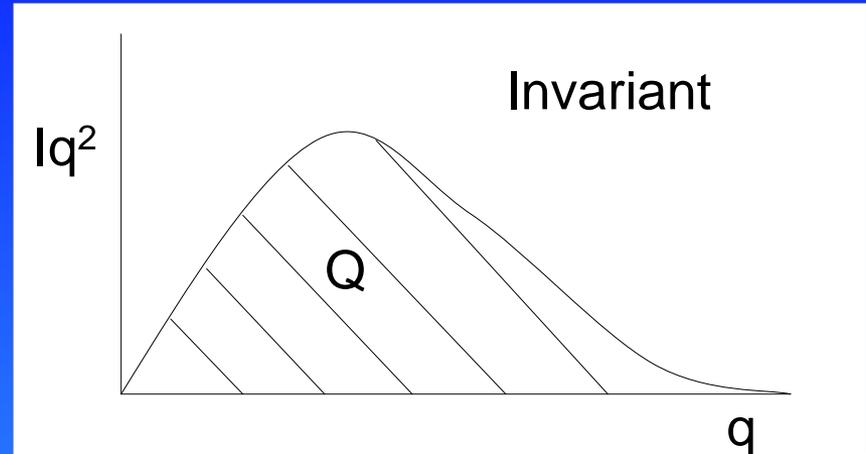
Contaminated mine systems

Acid mine drainage

Oxidation of ferrous iron from pyrite dissolution

SAXS analysis

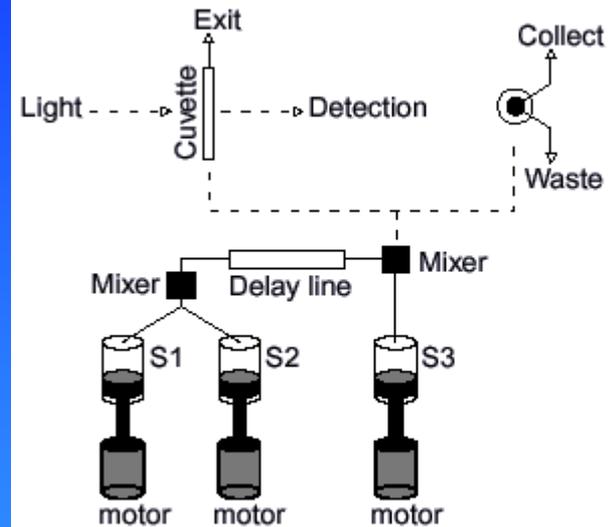
- Radius of Gyration
- $\ln I(q) = \ln I(0) - \frac{4\pi^2}{\lambda^2} \cdot RG \cdot (2\theta)^2$
- Intensity at $q = 0$
- $I(0) = (\Delta\rho)^2 V^2$
- Invariant
- $Q = (\Delta\rho)^2 (1-\phi)\phi$
- Pair/Size distribution function
- (GNOM)



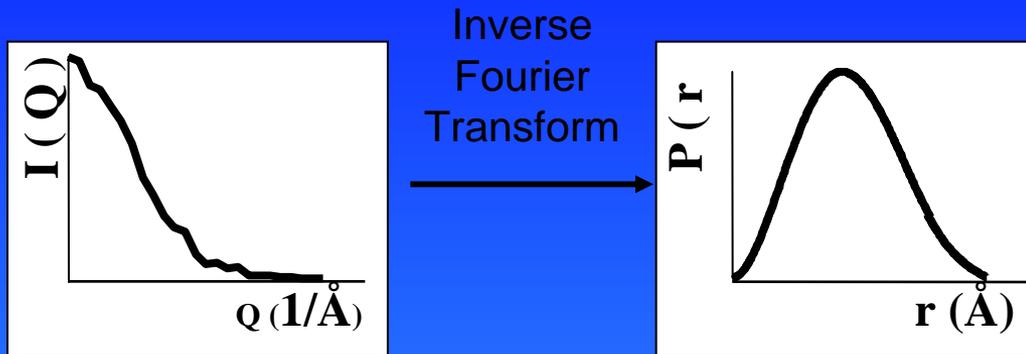
Stopped-flow apparatus



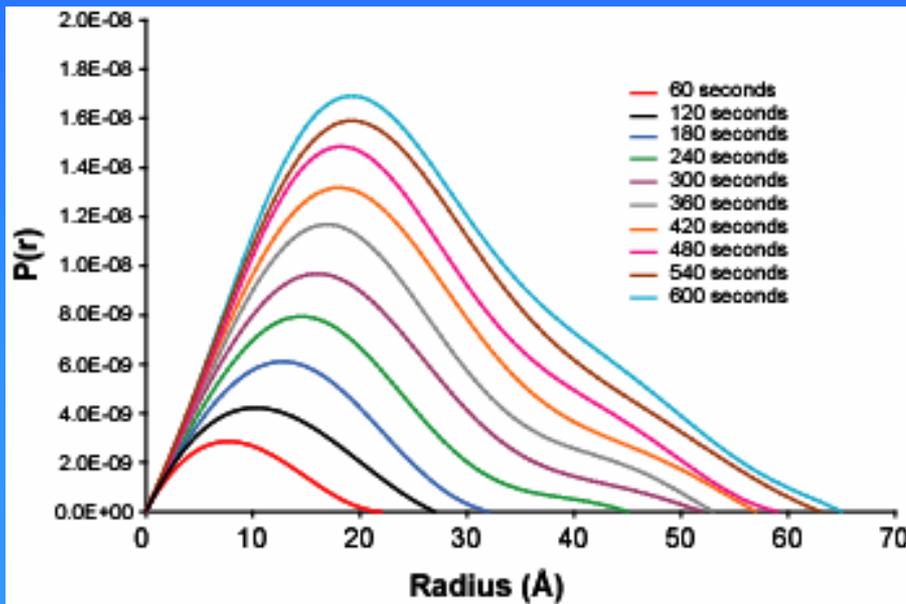
SFM-300



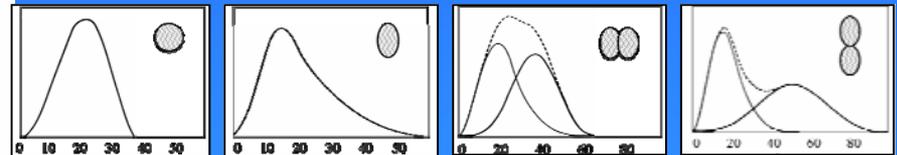
PDF analysis



$P(r)$ - Probability of finding two atoms at a distance (r) within a particle.



Idealised PDF Solutions

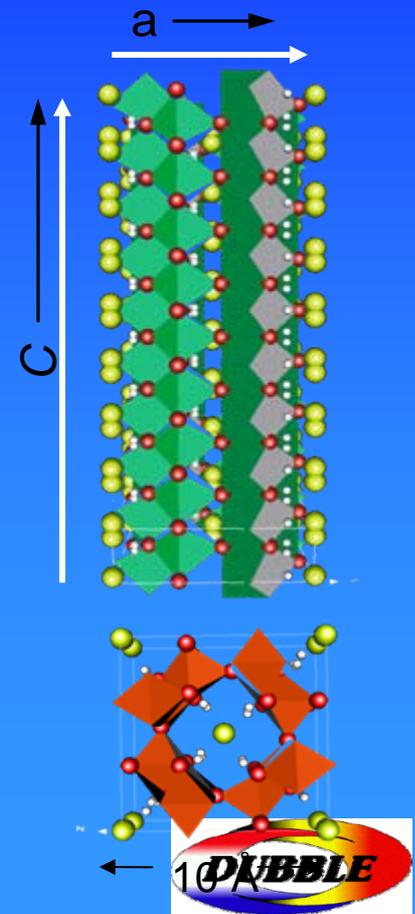
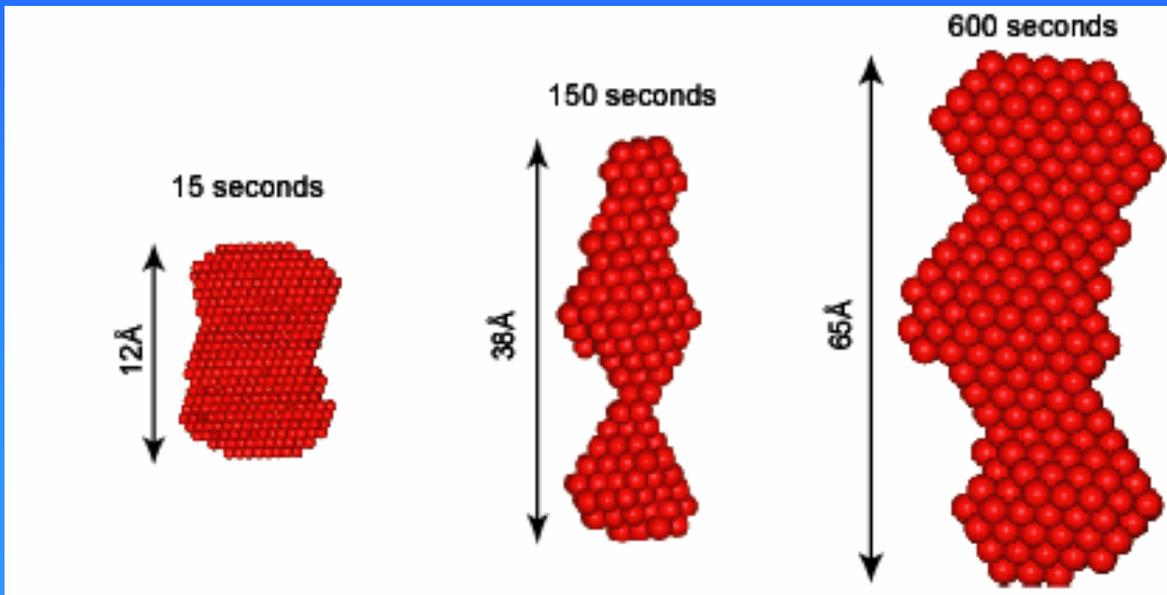


Skewed distributions suggest elongated particles



Shape Analysis

- *Ab-initio* shape determination by simulated annealing using a dummy atom model (Svergun, EMBL, Hamburg) DAMMIN



- This is use of analysis software routinely utilised in static biological SAXS (5 – 6 curves/day)*
- The number of frames is slightly different compared with static SAXS (5-6 /second, exp lasts 10 minutes, 24 exp/day.....
> 1000 frames/day)

*after data reduction



- One wants intelligent analysis
- Not just number crunching of individual frames
- This problem is solvable

- But in 20 years I have not seen an effort in this field from the Central Facilities for even isotropic scatterers

- And one would think that the powder diffractionists would have done something for WAXS.... Forget it!
- And the situation is even worse for non-isotropic time-resolved data



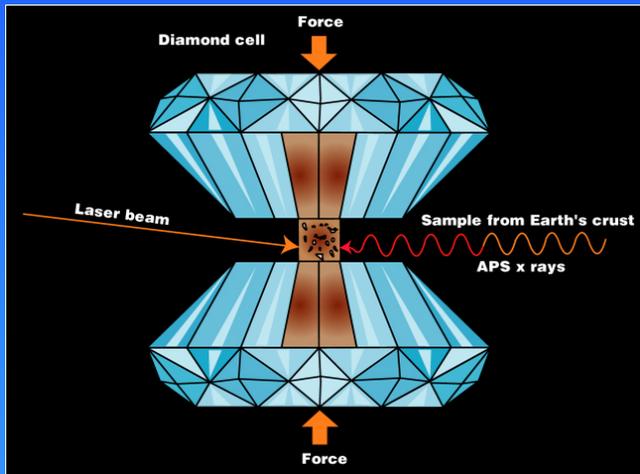
If we had widely available decent software

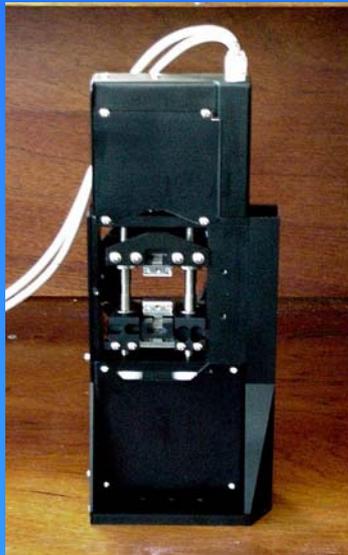
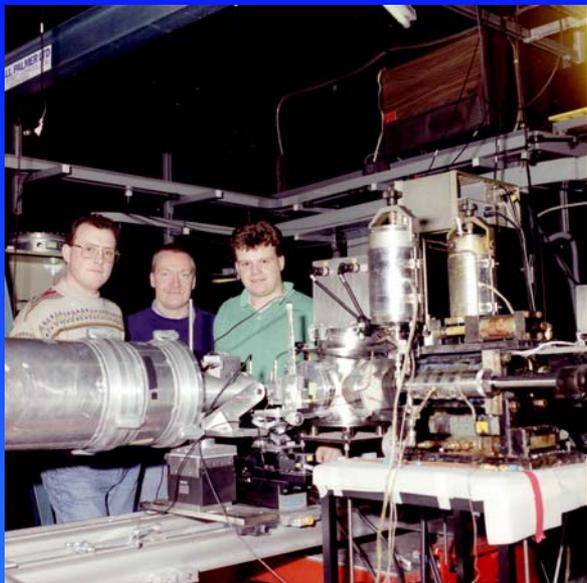
- Less data sets would be left un-analysed
- The real information content of the data could be used instead off:
 - “this peak moves from here to there and that could mean.....”
- The quality of our publications would go up
- The number of publications could go up by 50% for the same amount of beam time



Sample environments







Sample environments

- Stop flow/on-line chemistry/pressure jumps/magnetic fields/pulsed magnetic fields/high temperature laser furnaces/levitation cells/frog torture instruments/deformation etc.etc.



Based upon our soot work

- I calculated that we can do time-resolved experiments on soot formation in diesel engines
- Shine X-rays in a combustion cylinder with diamond windows
- Collect data in cyclic mode
- Construction would take about 200 k\$ according to Caterpillar



Sample environments

- These are getting more and more complicated
- Impossible to foresee what will come
- Infrastructure for easy physical mounting and interfacing to data acquisition software is crucial





However,.....

- Many people talk about millisecond time-resolution
- Our X-rays and detectors can do it
- But can our sample environments ????
 - Gradient free ??
 - Reproducible ??
 - Large enough volumes to avoid too much radiation damage ??



Technique combinations

dielectric



DSC

UV Vis

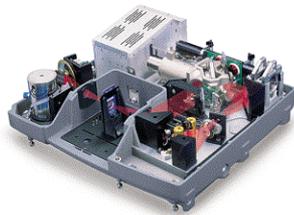


Thermo Nicolet

FT-IR System



Optical Bench



Raman



Technique combinations

- These have become a fact of life
- They are crucial for understanding more complicated problems
- Despite the problem that the data quality sometimes is not optimal
- There can be a lot of synergy in some technique combinations
- Please do not combine for combinations sake....
- Make sure that the infra structure to interface them is available



The most important issue

- Make sure you can generate the volume of shifts that is required
- Make sure that these are dedicated beam lines





*Thanks for your
attention*

