



**The Abdus Salam  
International Centre for Theoretical Physics**



**2031-5**

**Joint ICTP/IAEA School on Novel Synchrotron Radiation  
Applications**

*16 - 20 March 2009*

**Time-resolved SAXS/WAXS experiments in materials science**

Wim Bras

*Netherlands Organisation for Scientific Research*

# Time-resolved SAXS/WAXS experiments in materials science

**Wim Bras**

Netherlands Organisation for Scientific Research

# I work for the Dutch government





# I'm based at the ESRF in Grenoble



# Overview

- Materials science
- Time-resolved experiments
- Introduction to WAXS
- Introduction to SAXS
  
- Cordierite glass crystallisation

# Materials science

- Very wide ranging subject
  - Polymers
  - Ceramics
  - Food stuff
  - Nano-composites
  - Etc.

# A materials science chain

Special textiles

'Daily textiles'



Production of oil



Transport of oil

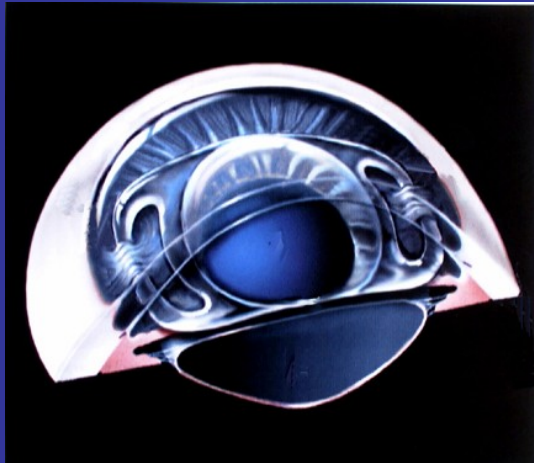


Oil chemistry



Oil products





Plastic eye lenses



Ceramic hip replacement



Carbon engine valves



Artificial colloidal crystals



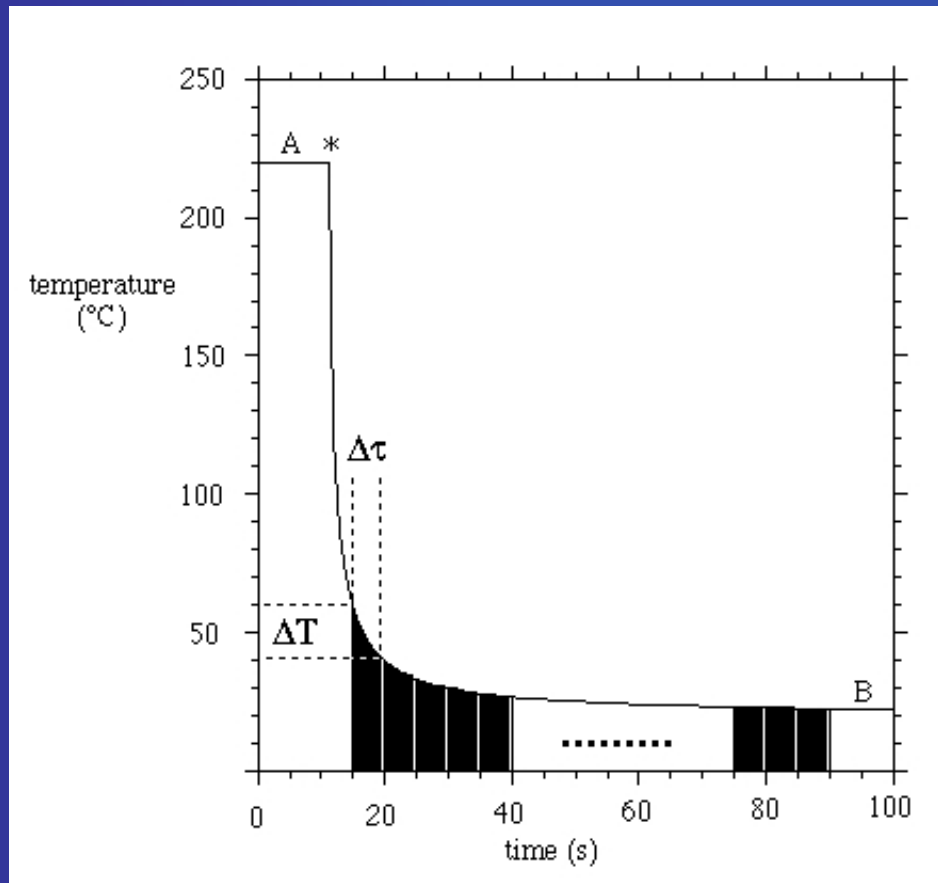
Bread and butter

- All these materials I have seen being investigated on my beam lines
- And even weirder ones for biological sciences



What does he mean by that?

# Time-resolved experiments



- Study of samples under changing conditions in a single experiment
- Variable parameters can be temperature, pressure, pH, etc.

# What time resolution?

- For different people time resolution means different things
- Someone studying high energy physics think femtoseconds
- For geologists studying plate tectonics think millions of years

# Time resolution in materials science

- Realistically limited to 0.1 second/frame or slower
- Why?
  - One deals with movements of large molecules (e.g. polymers)
  - One deals with diffusion processes (e.g. ceramics)

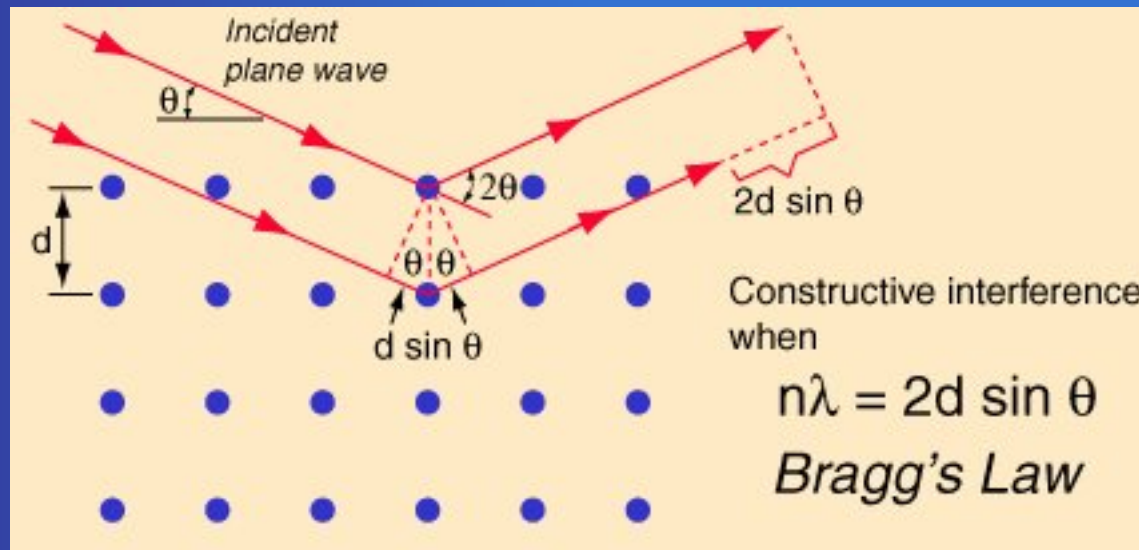
# WAXS

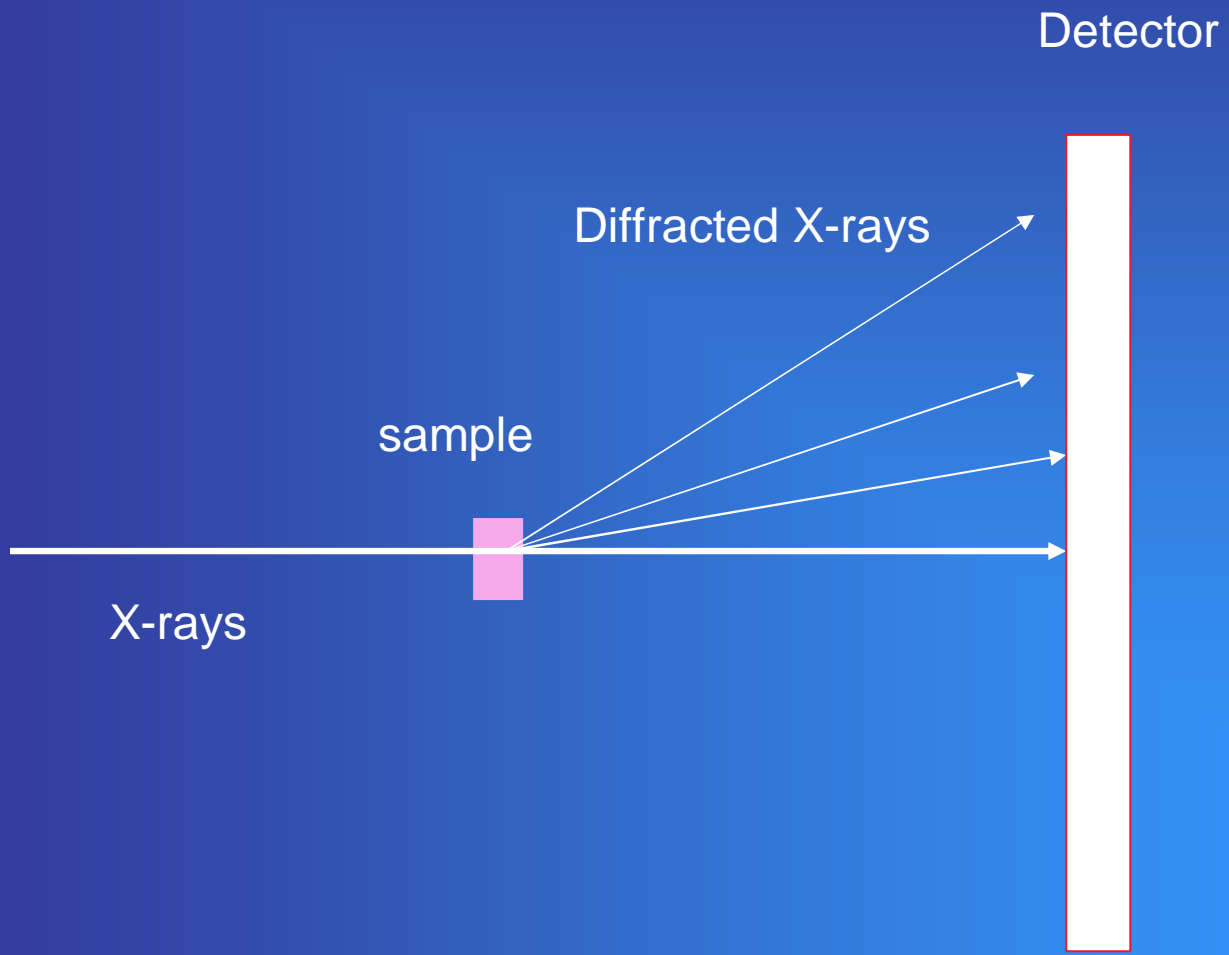
- Wide Angle X-ray Scattering
- Think of powder diffraction or diffraction on less ordered materials
- In this lecture it is a supporting technique for SAXS

Powder diffraction will be treated this afternoon by Paolo Scardi

# Bragg's law

- Crystalline materials

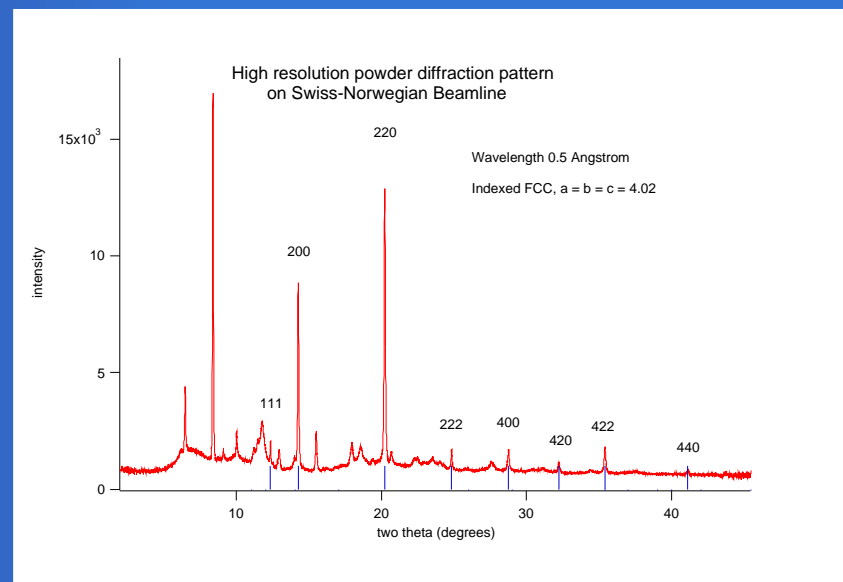
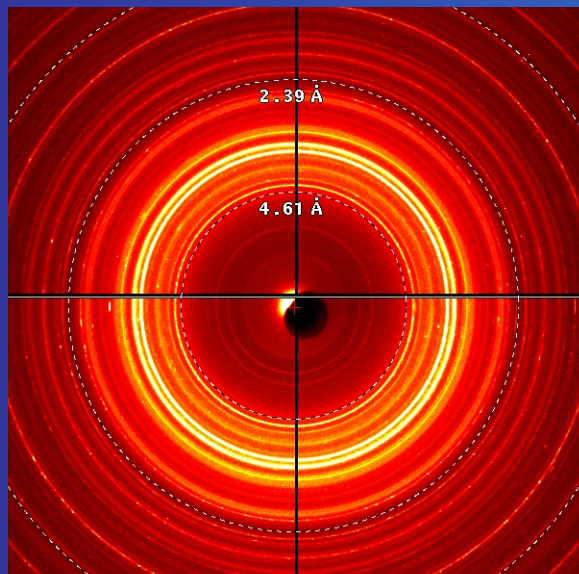




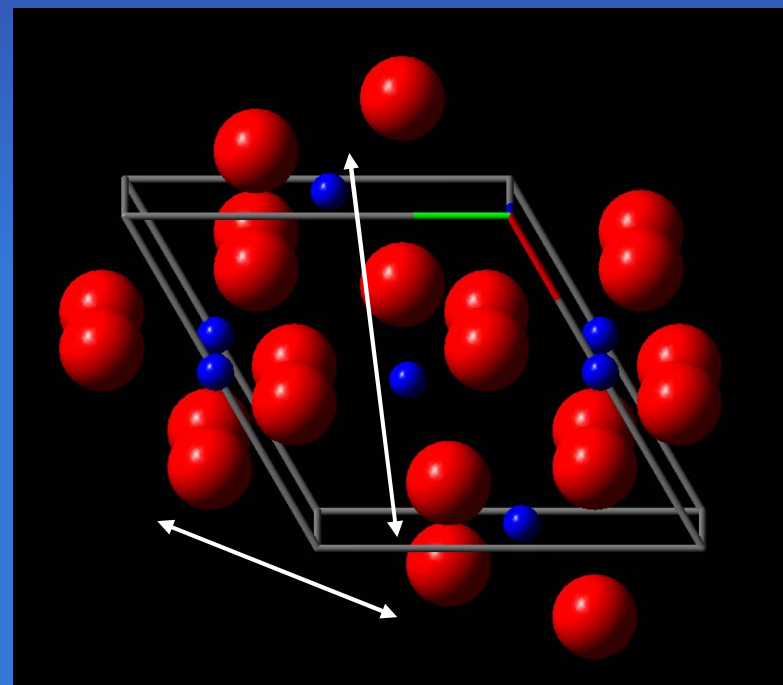
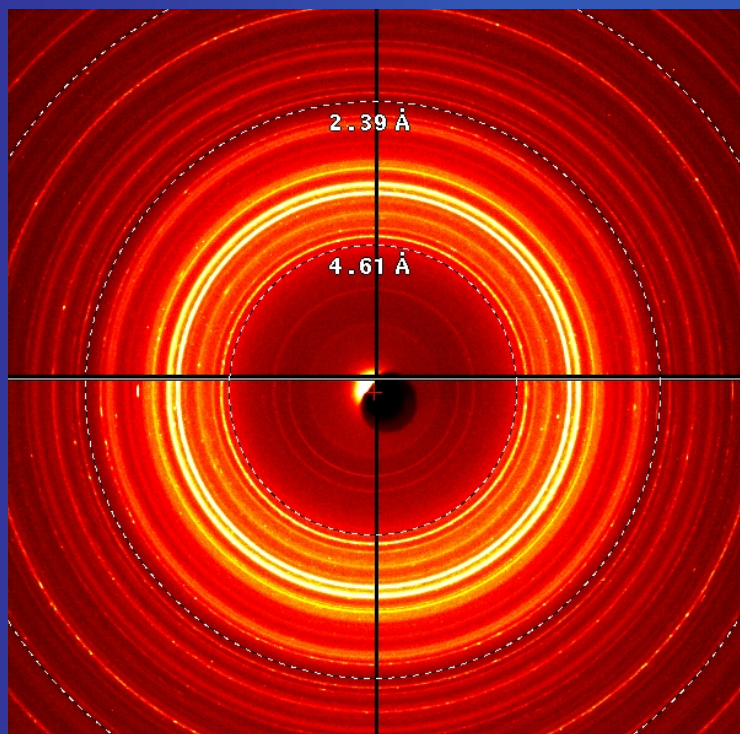


# WAXS experimental

- Assume sample is isotropic (powder with all grains having a random orientation)

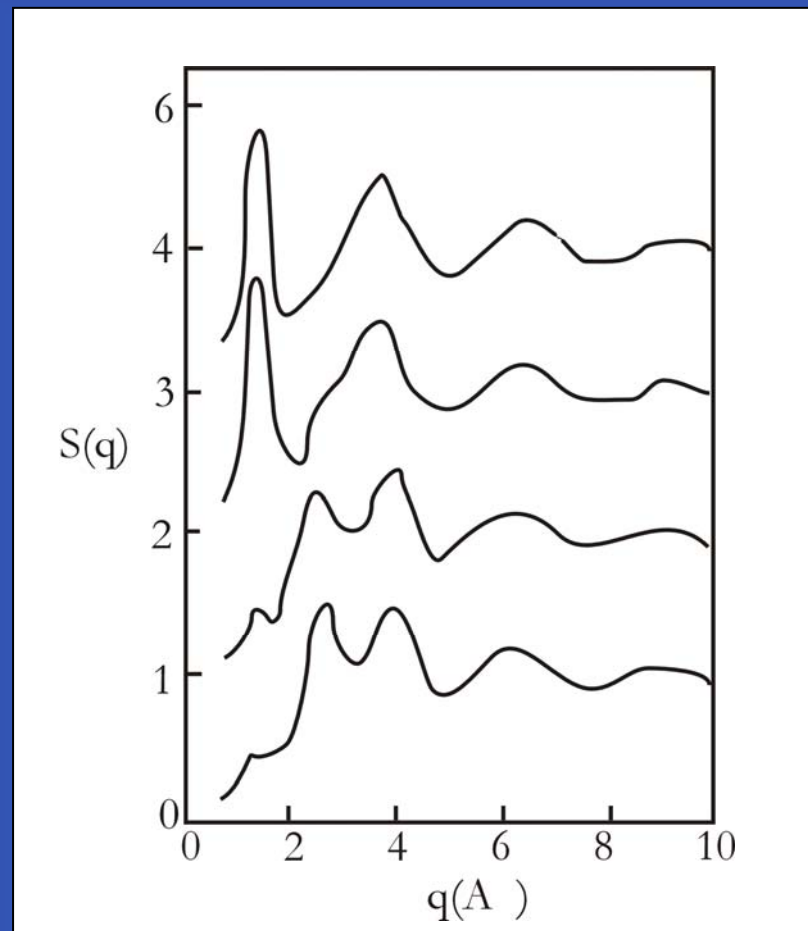


# Diffraction pattern



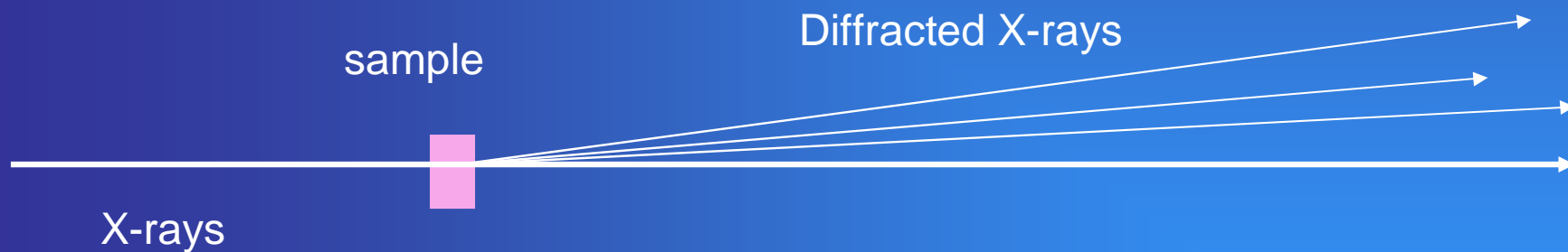
# Scattering from non crystalline materials

- Liquid or amorphous samples



# Small Angle X-ray Scattering

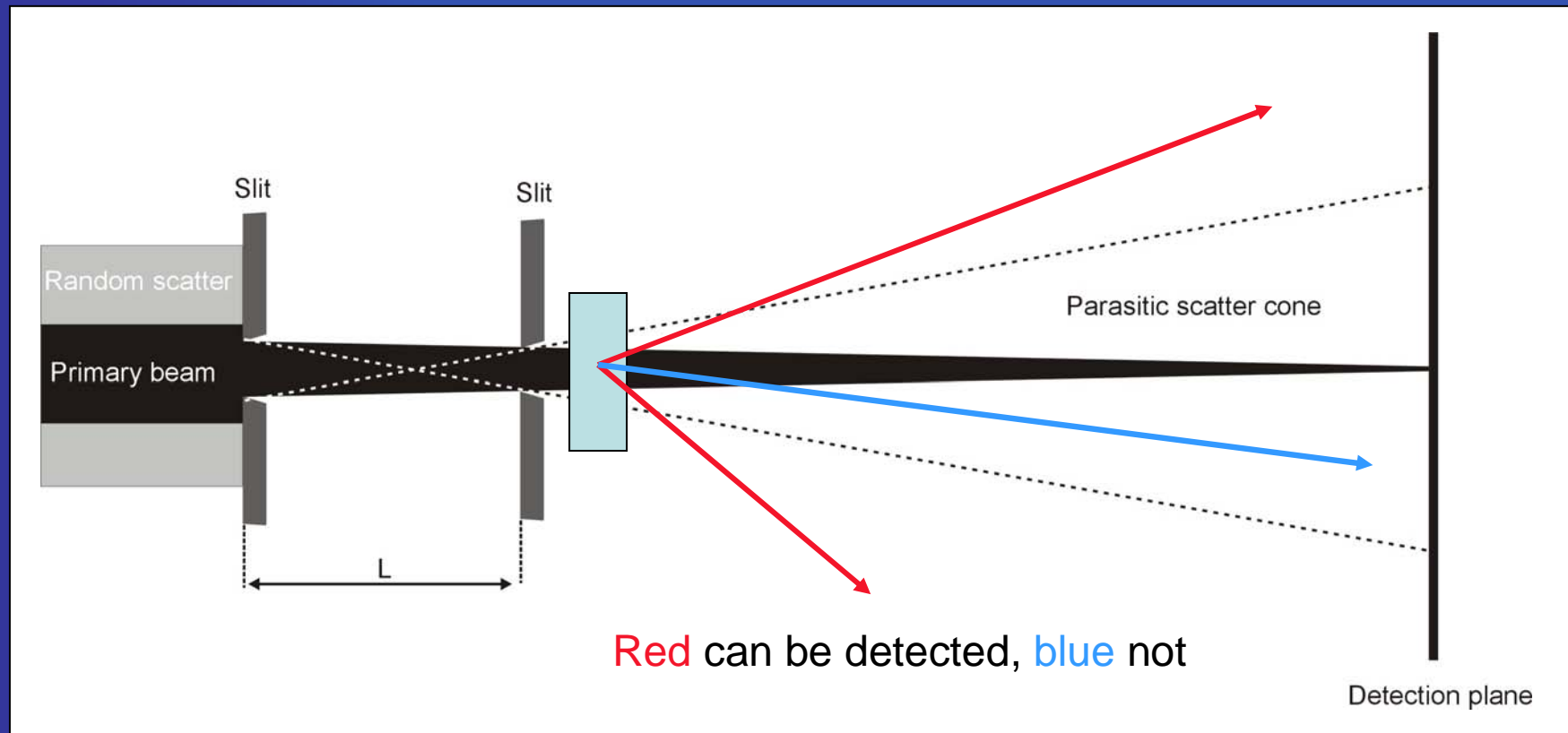
- X-ray scattering under small angles
- Information about larger structural distances



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

$\theta$  small  $\longrightarrow$   $d$  large

# SAXS camera



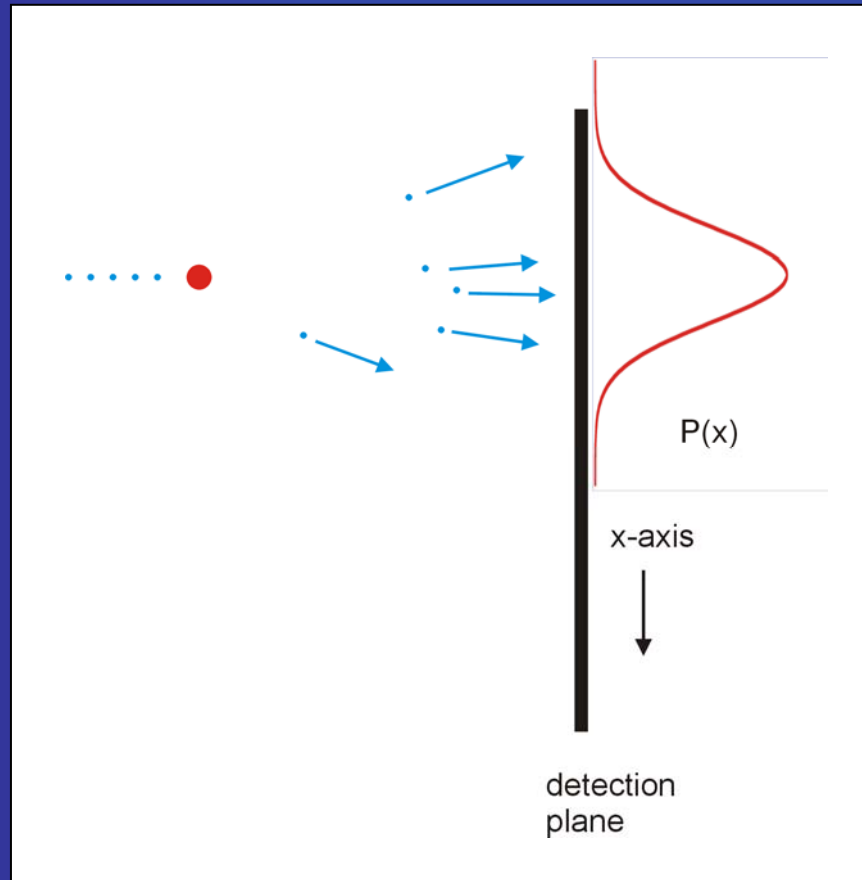
# SAXS beam lines on synchrotrons

- Not difficult to construct
- Simple monochromator and focussing in two planes
- Only have to take care that the parasitic scatter cone is reduced as much as possible

# Small Angle X-ray Scattering

- Often given the same name
  - Small Angle X-ray Scattering
  - Small Angle Diffraction
  - Small Angle Fibre Diffraction
- For me this is all linguistics
- Here is discussed what one can do with a Small Angle Synchrotron beam line

# Scattering from a single scatterer



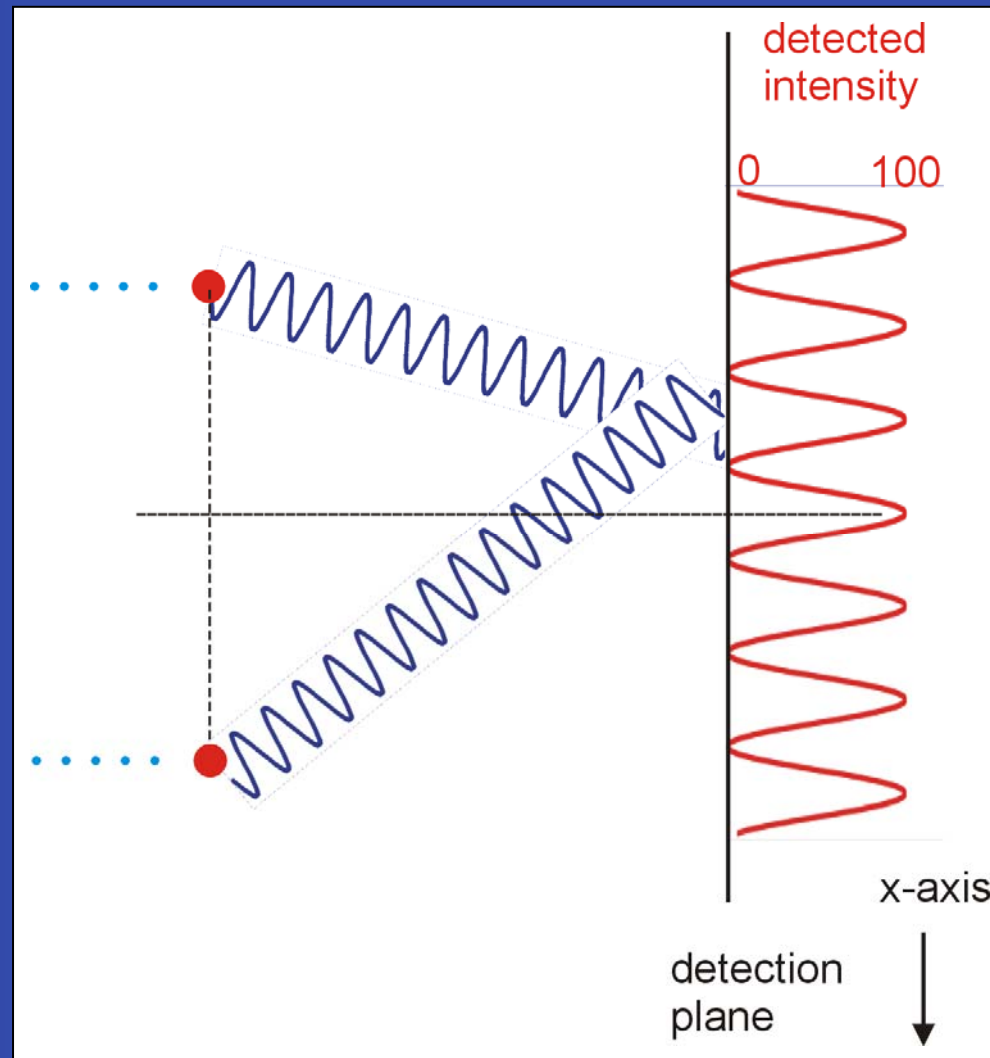
- Red dot is 'something' that scatters
- Blue dots represent waves
- $P(x)$  indicates the probability that a photon/neutron will scatter in that direction



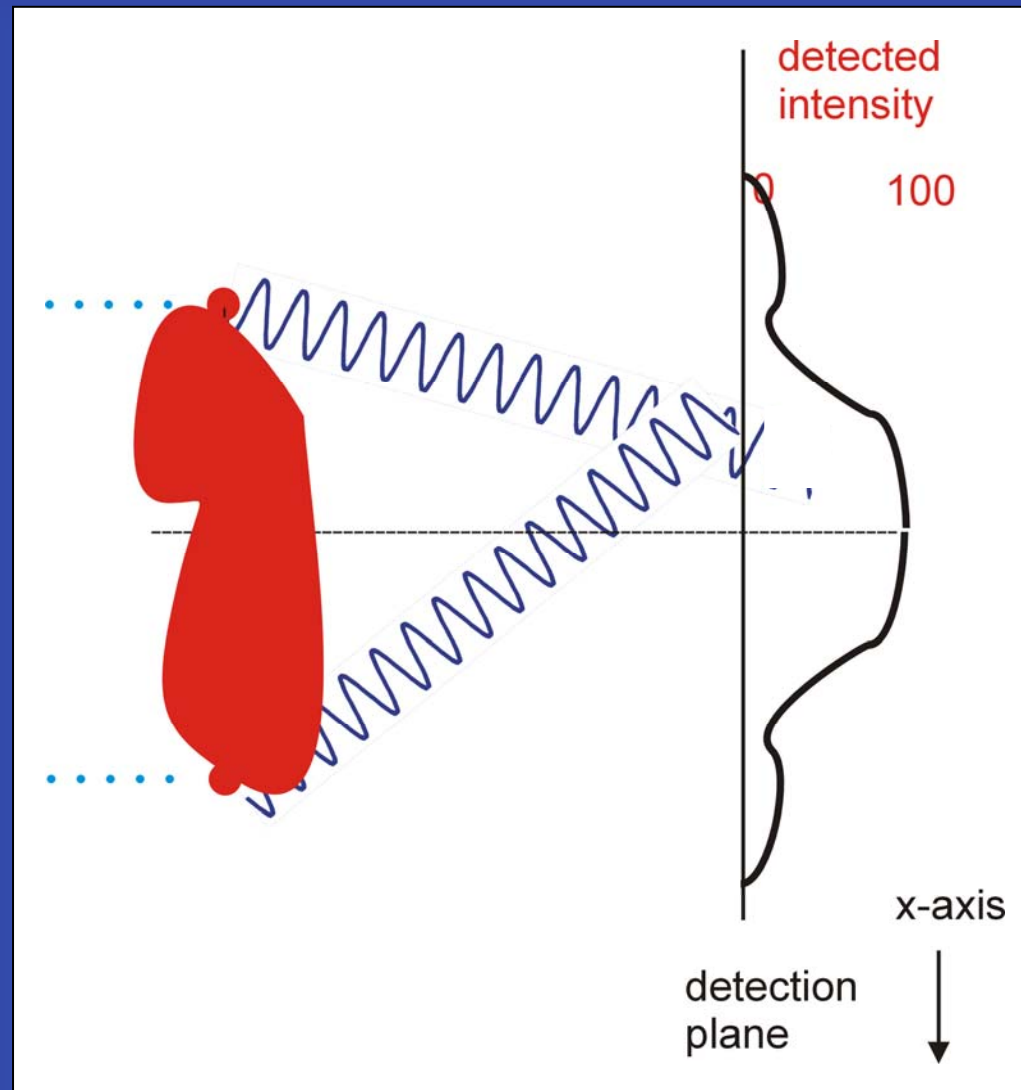
# Scattering

- The scattering from X-ray photons is due to their interaction with electrons
- The larger the number of electrons the larger the probability that a photon will scatter

# Scattering in the detection plane two point sources



# Scattering in the detection plane particle



# Scattered intensity from a 'blob'

$$I(q) = \int_0^{\infty} \rho(r) e^{iqr} dr$$

- The scattered intensity is the Fourier Transform of the electron density of the scattering object
- We have to sum the intensity caused by all the scattering particles
- These particles have to be randomly oriented
- The intensity is strongly dependent on the electron density contrast

# Saxs from isolated particles

- Requirements
  - ‘diluted’
  - Complete random orientation in space
  - Or all the same shape
  - Or all the same size

These conditions are required to be able to do sensible analysis on the data

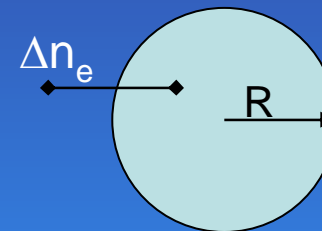
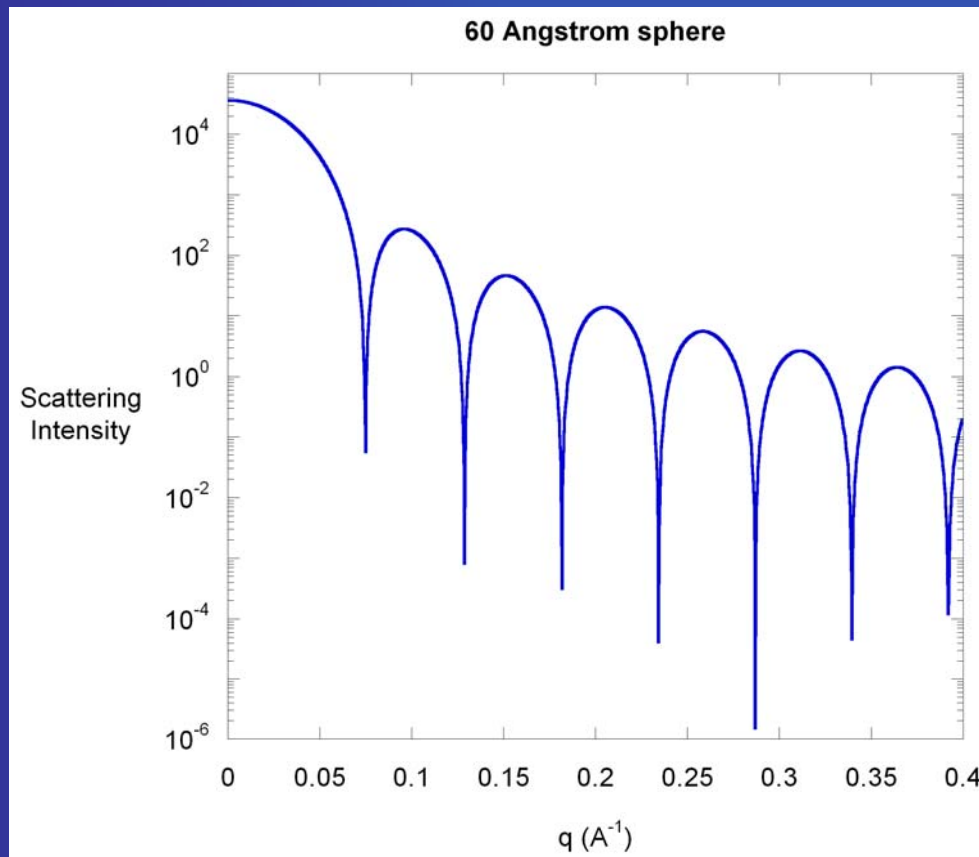
# If these conditions are not satisfied:

- It is still possible to obtain a SAXS spectrum
- Sensible analysis will be very difficult

# SAXS

- SAXS is sensitive to electron density contrast between particles and the surrounding matrix

# SAXS from a homogeneous spherical particle



- Shape: Form factor  $F(q)$
- Size: periodicity
- Electron density difference: scattering intensity

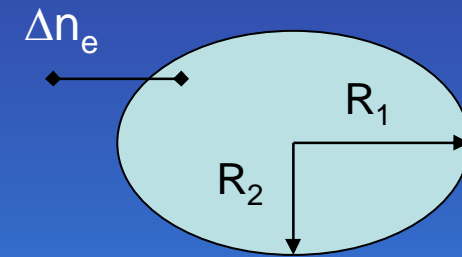
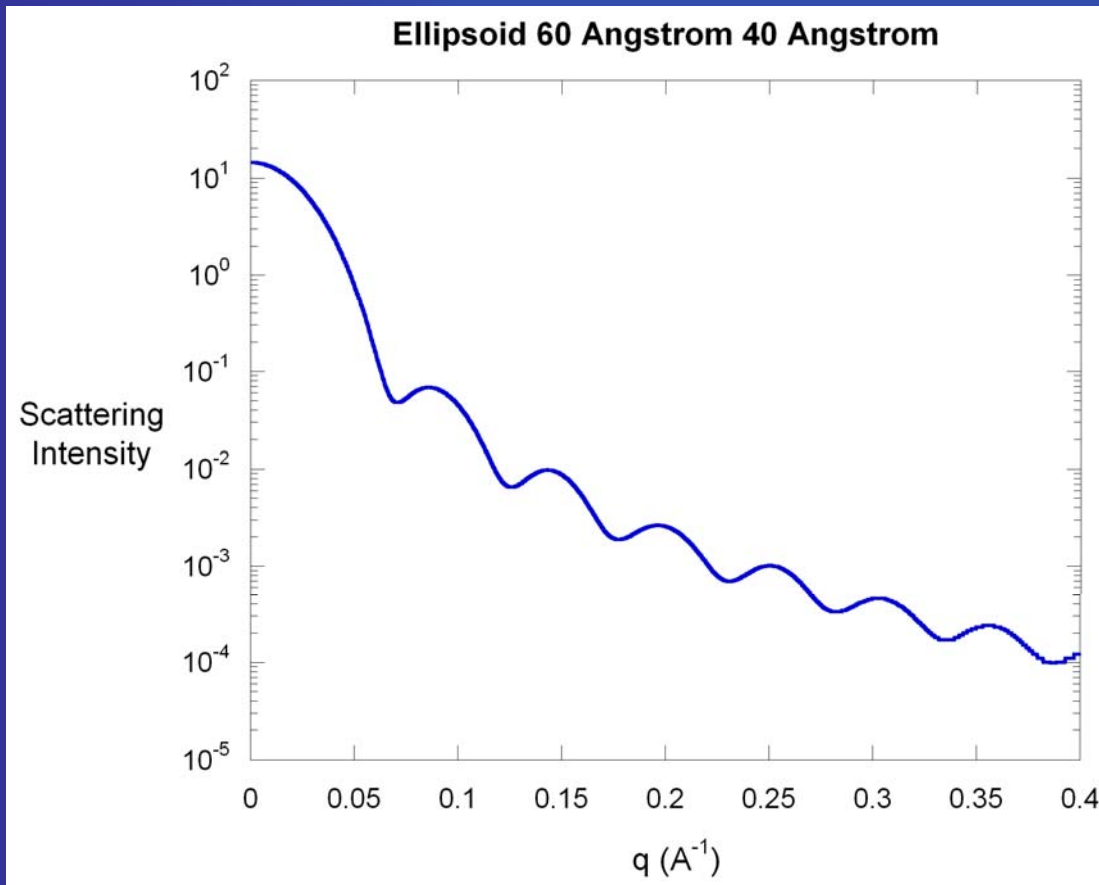


# Analytical expression for sphere

$$I(q) = \left( 3 \frac{\sin qR - qR \cos qR}{(qR)^3} \right)^2$$

- there also exist expressions for other shapes but not many
- most times these have to be calculated numerically

# Different shape

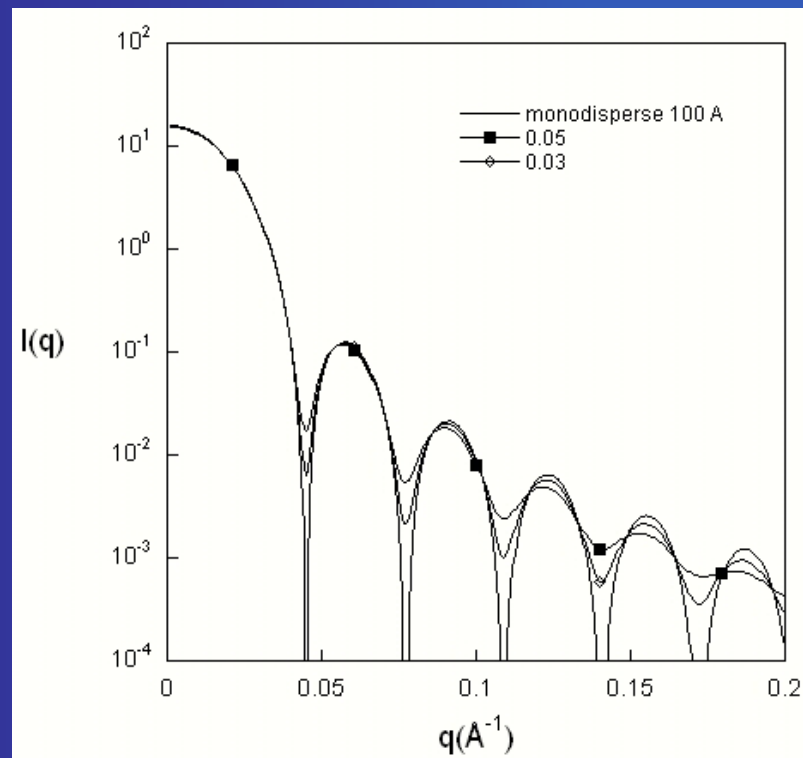


- Shape: Form factor  $F(q)$
- Size: periodicity
- Electron density difference: scattering intensity

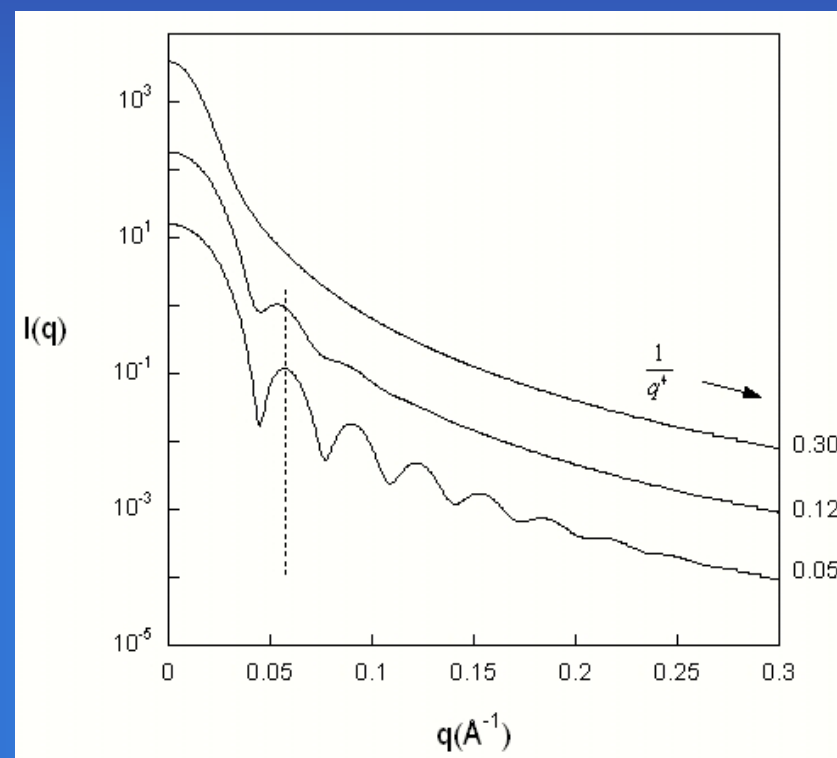
- For some shapes there exists analytical functions.
- Also for inhomogeneous particles
- See review Jan Skov Pedersen

# What happens when the size is not uniform?

$$\frac{\Delta R}{R} < 0.1$$



$$\frac{\Delta R}{R} \geq 0.1$$



# Intensity at very low angles: Guinier approximation

$$I(q) \sim e^{-\frac{(qR_g)^2}{3}}$$

$R_g$  is radius of gyration

(think average distance to center of mass)



# The intensity at wider angles: Porod slope

Conditions:

1 -  $qR \gg 1$

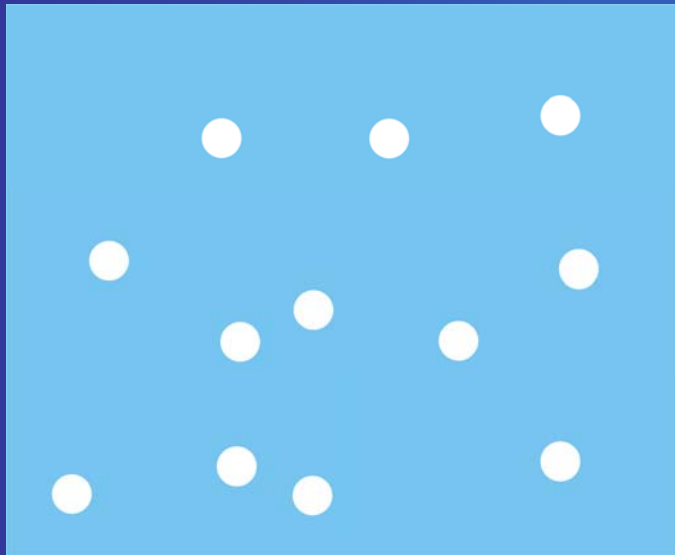
2 - 'smooth surface'

$$\lim_{q \rightarrow \infty} I(q) = K_1 + \frac{K_2}{q^4}$$

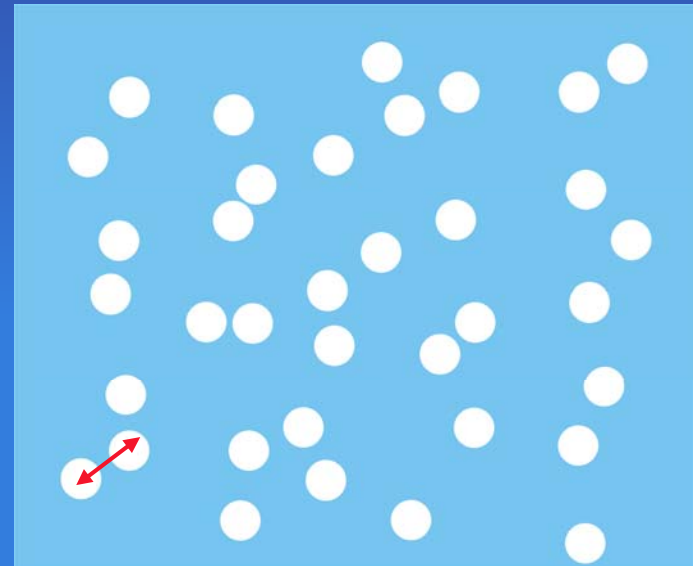
$$K_2 = 2\pi (\Delta\rho)^2 \frac{S}{V}$$

# Structure factor (when samples are not dilute)

dilute



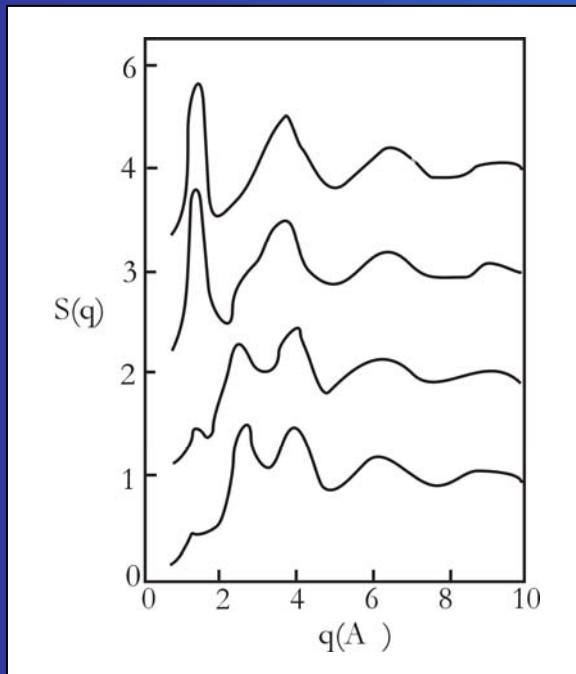
non dilute



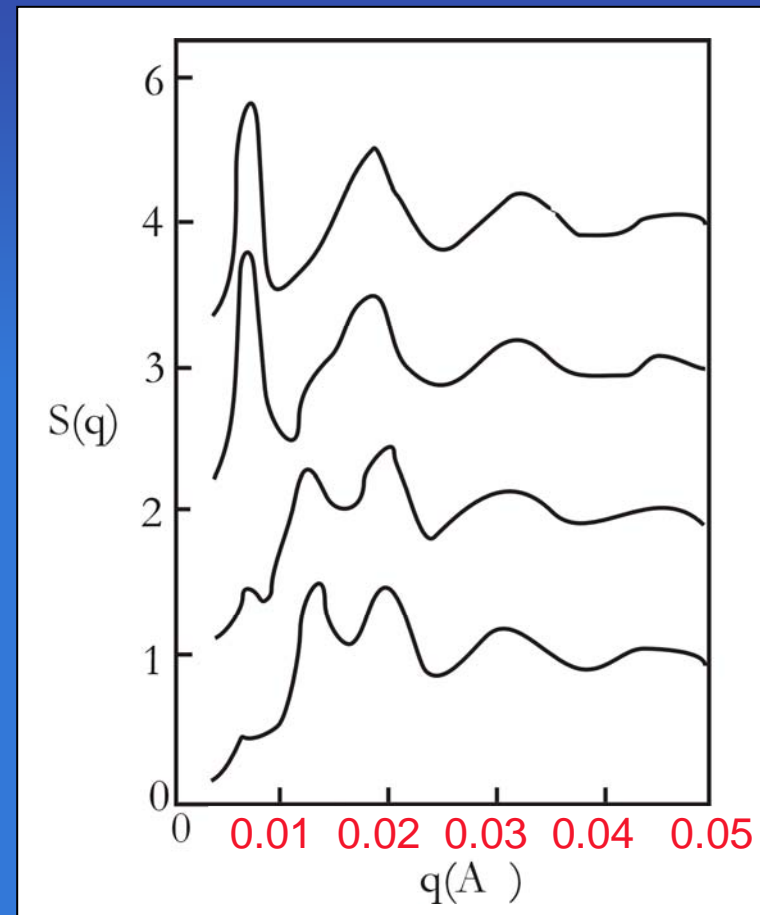
Not only scattering from particles but also scattering 'between' particles

# Structure factor

- Inter-particle scattering



For liquids etc



For SAXS



# Effect:

$$I(q) = S(q) (F(q))^2$$

In general  $S(q)$  decays fairly rapidly

$q$  is scattering vector/angle

$S(q)$  is structure factor: how are the scattering entities arranged in space

$F(q)$  is form factor: what shape do the scattering entities have

# The total scattering: Invariant

$$Q = \int_{\text{Volume}} I(\vec{q}) dV$$

For isotropic scatters this reduces to:

$$Q = \int_0^{\infty} q^2 I(q) dq$$

# Q is useful tool

- In two phase system:

$$Q = \int_0^{\infty} q^2 I(q) dq = \langle n_e \rangle^2 \phi_1 \phi_2 = \langle n_e \rangle^2 \phi_1 (1 - \phi_1)$$

$\phi_{1,2}$  Are the volume fractions of the two phases

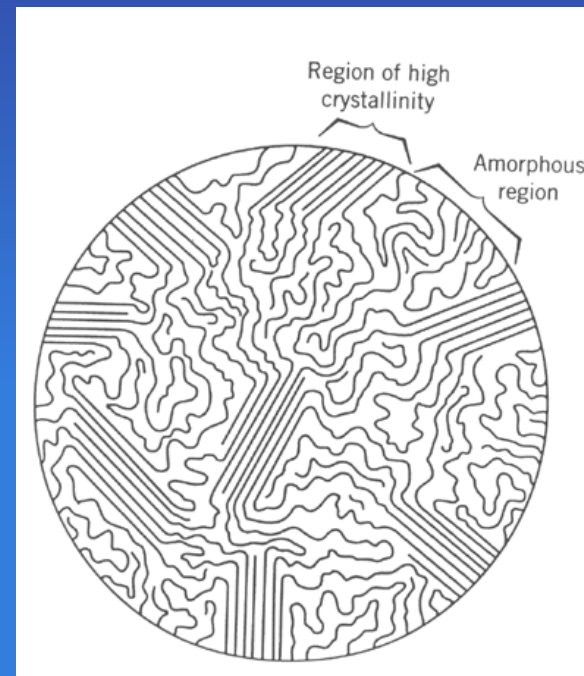
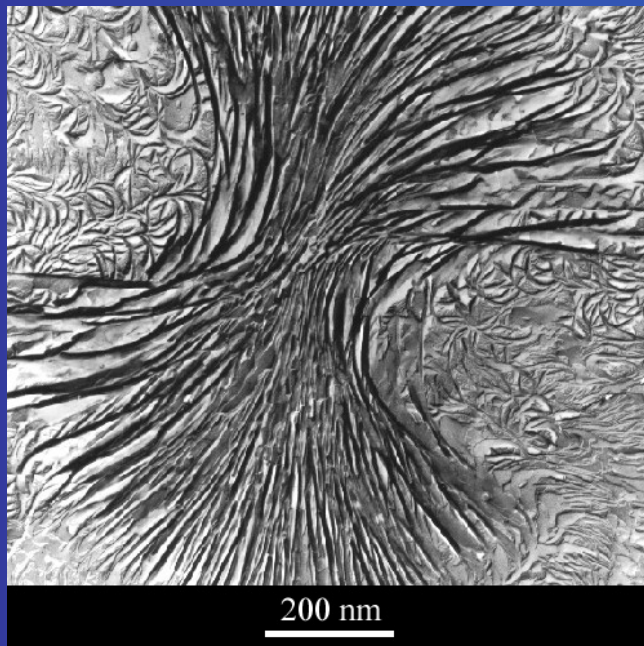
and  $\phi_2 = (1 - \phi_1)$



I'm getting pretty bored with this particle stuff. Don't you have anything else?

# Not only particles give SAXS (1)

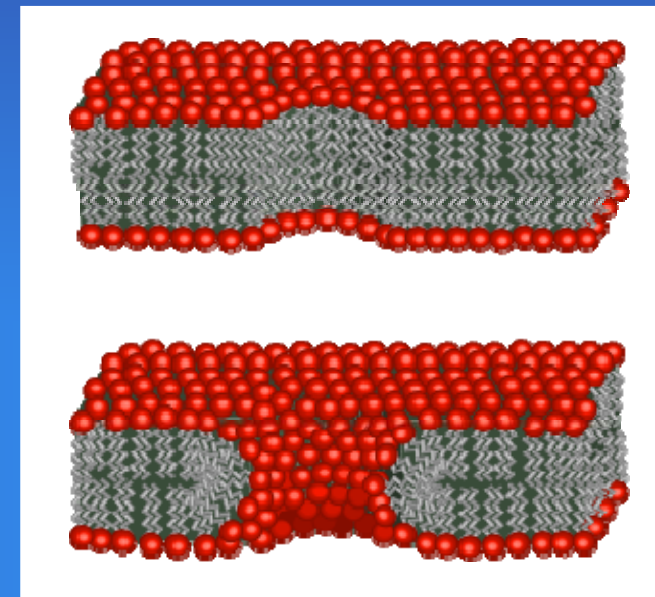
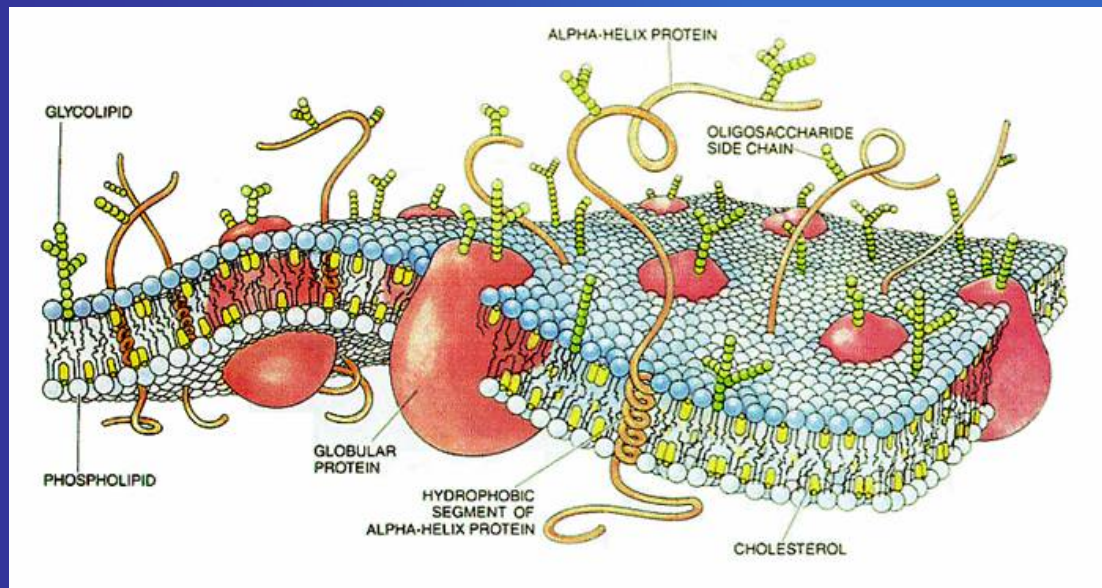
- Lamellae



Polyethylene a semi crystalline polymer

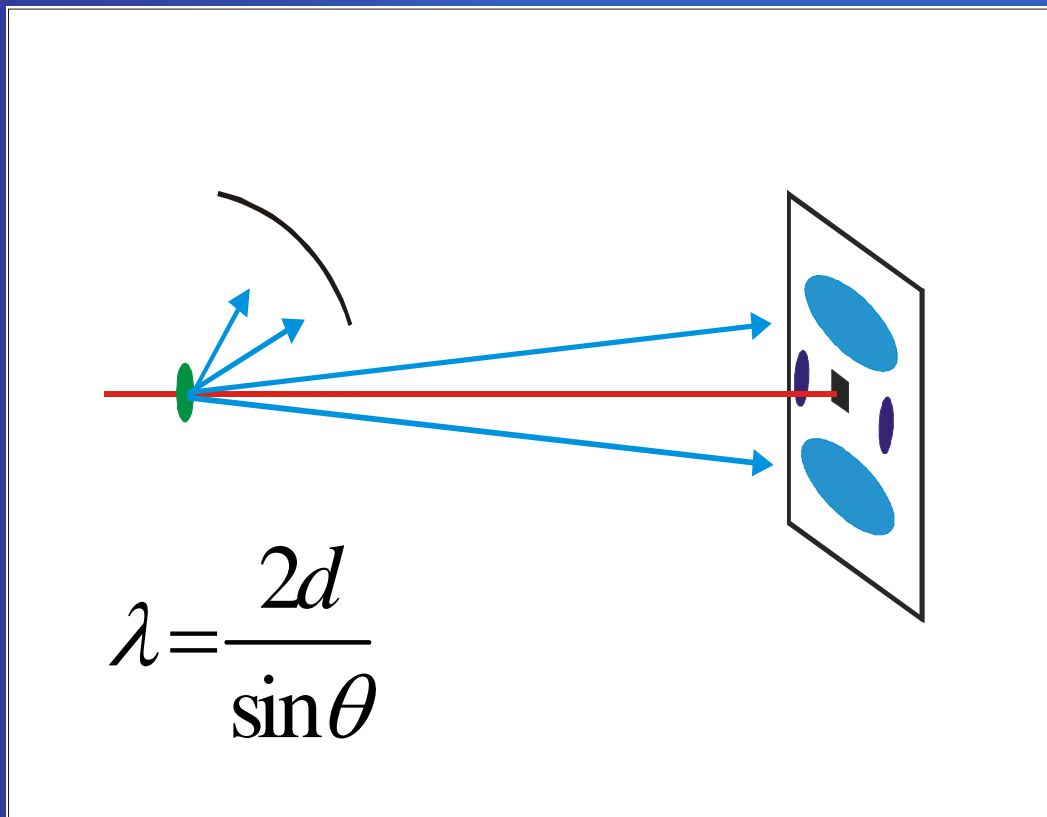
# Not only particles give SAXS (2)

- lipids



# SAXS and WAXS

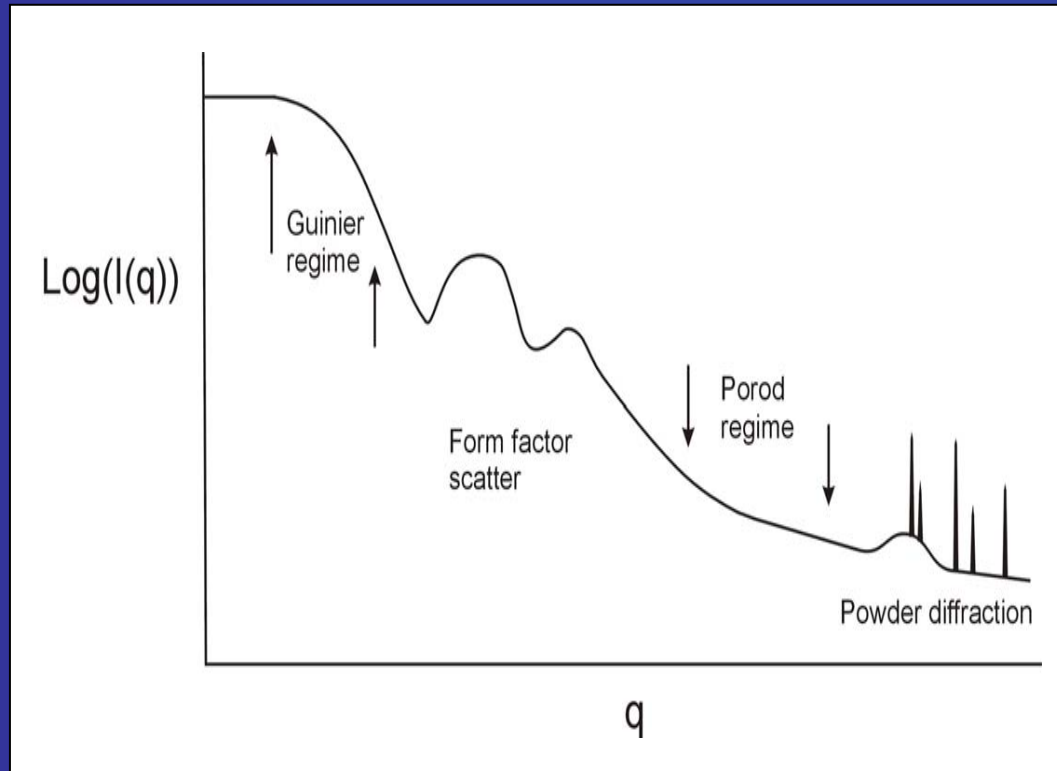
$d$  small,  $\theta$  large



$\theta$  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

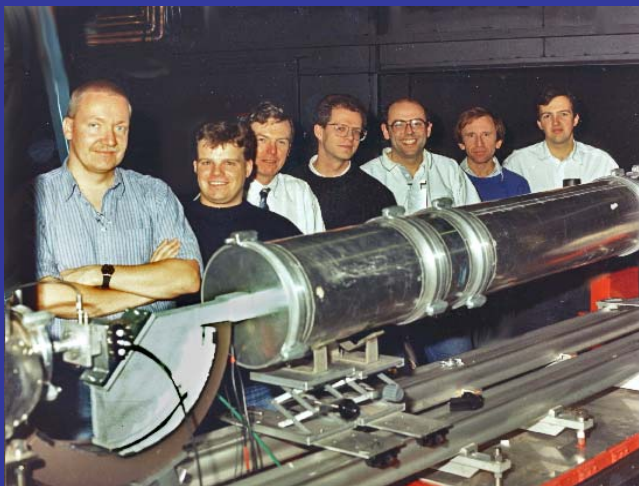
# SAXS and WAXS experiments

- These can be done on a conventional X-ray generator
- Do we really require a synchrotron for this?
- Not always but in some cases you indeed require a synchrotron

# Why synchrotrons for SAXS/WAXS?

- Time-resolved experiments require more flux than generator can produce
  - 1 min/frame possible with generator
- Better collimation of the X-ray beam
- Less divergence of the beam
  - 60 nm low angle resolution in home laboratory

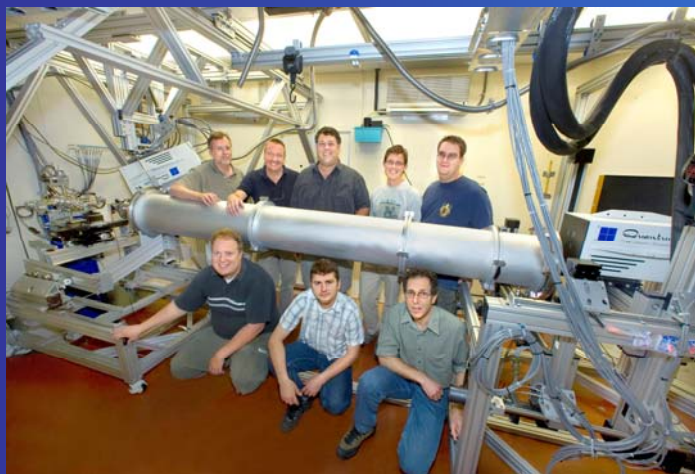
Some SAXS/WAXS beam lines  
I have played with in the last  
20 years



8.2 Daresbury



BM26B ESRF



7.3.3 ALS Berkeley



Daresbury  
2<sup>nd</sup> generation source



ESRF high energy  
3<sup>rd</sup> generation source



ALS low energy  
3<sup>rd</sup> generation source

Storage ring



Control cabin 2

Control cabin 1

Optics hutch



Experiments hutch 2

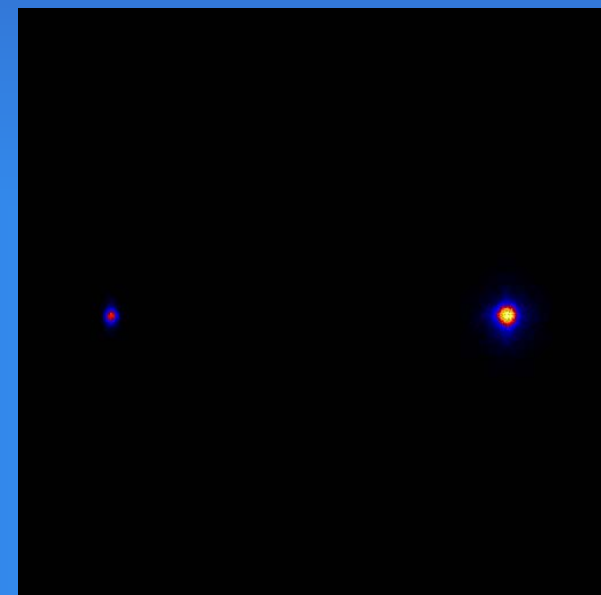
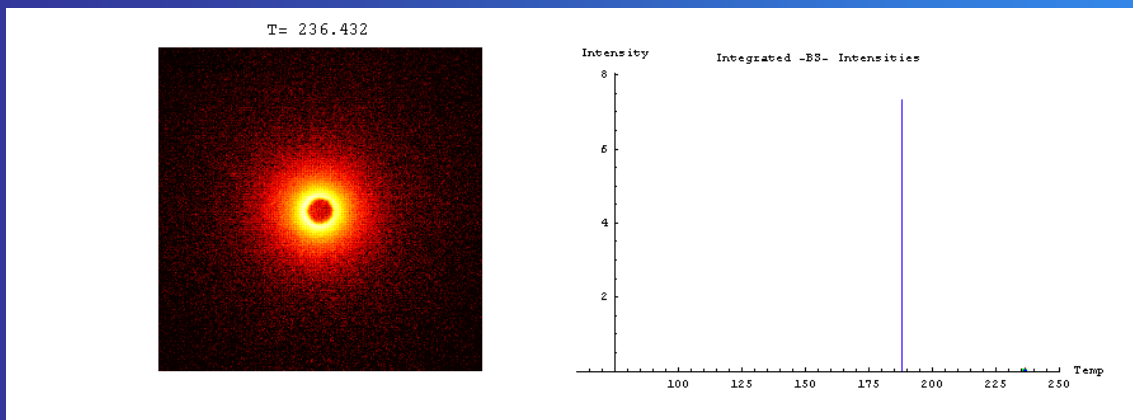
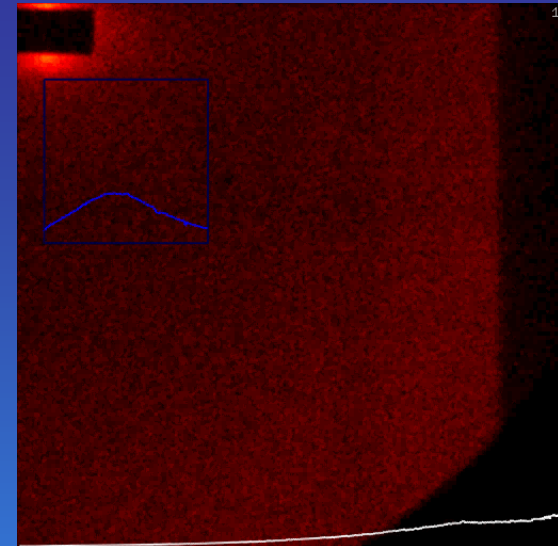
experiments hutch1

# The X-ray beam required for TR SAXS experiments

- $10^{10}$ - $10^{12}$  photons/sec
- $\lambda \sim 0.05 - 0.15$  nm (7 – 15 keV)
- 100 - 300 micron beam size
  
- But also reasonable detectors
  - Preferably photon counting
  - No long dead time between data frames

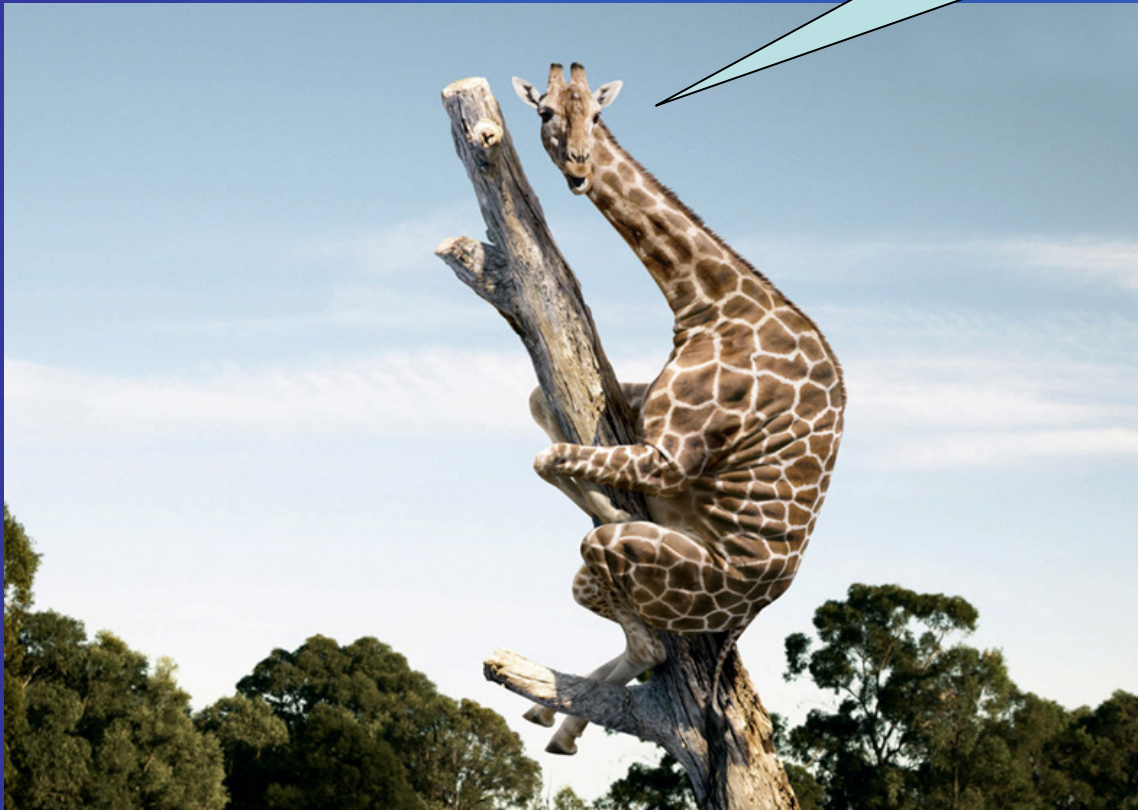
# Applications of SAXS

- Polymers
- Colloids
- Liquid crystals
- Biological macromolecules
- Food stuffs
- Etc.





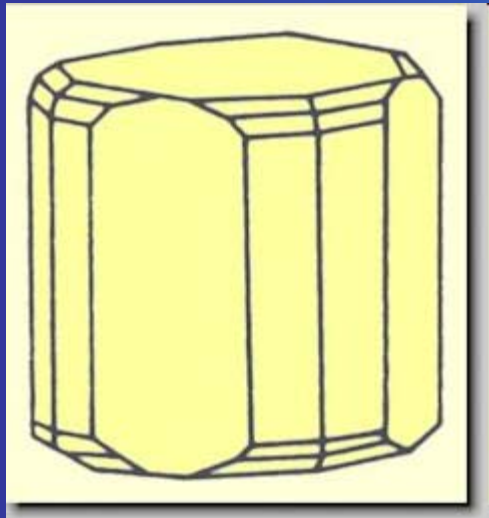
Come on, I want to see some real data.



# Cordierite glass



Mr Cordier



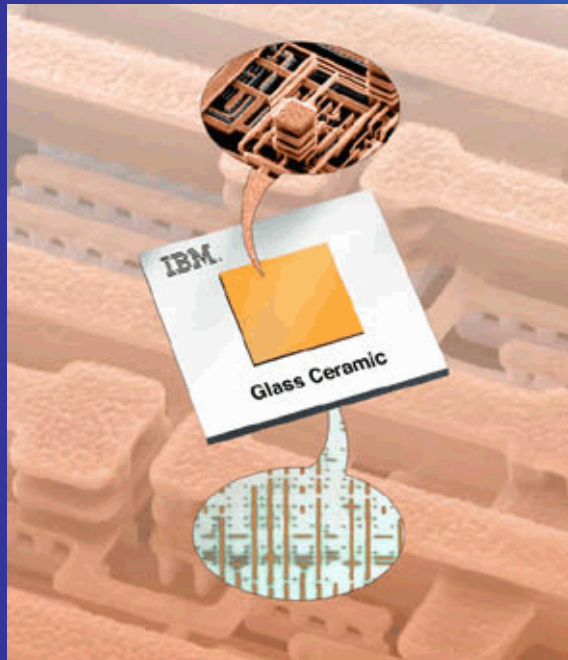
Composition of Cordierite

Mineral:  $Mg_2Al_4Si_5O_{18}$

One can also make a glass with such a composition

# Cordierite based ceramics

## Ceramic chip carriers



Ceramic chip carriers are fabricated with either alumina ( $\text{Al}_2\text{O}_3$ ) dielectric and molybdenum conductors or **Cordierite glass dielectric** with copper conductors. They can be used in high performance applications with I/O exceeding 1,600 pins and chips up to 30mm in size



Heat resistant and low thermal expansion



The ATD is a canister that replaces the muffler. It houses a **Cordierite ceramic substrate** brick called a diesel particulate filter (DPF) and, if required by the engine manufacturer, another substrate brick called a diesel oxidation catalyst (DOC). As exhaust gas passes through the ATD, the DOC oxidizes hydrocarbons and reduces NO<sub>x</sub> and the DPF traps PM.



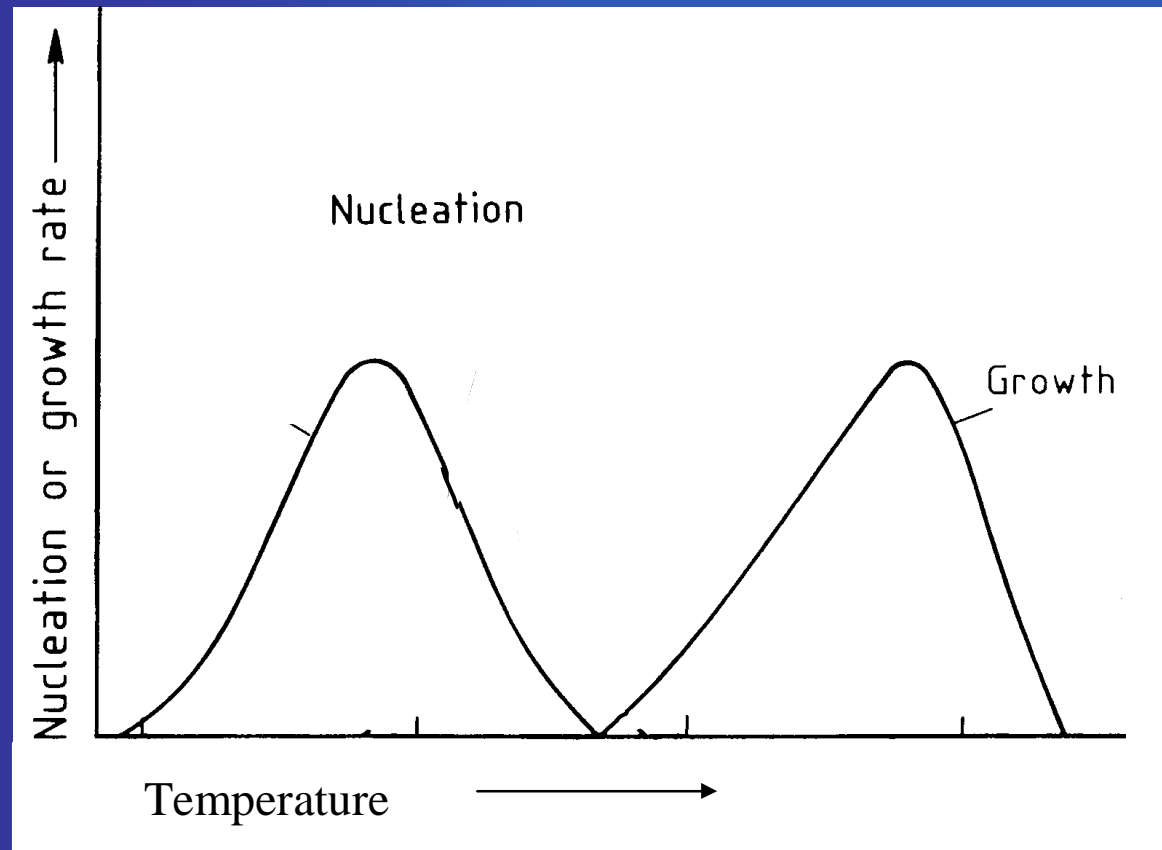
# Why cordierite glass ceramic?

- Shock resistant even at high temperatures
- Glass with very low expansion coefficient

# Why do I tell you this story?

- You might not be interested at all in such boring minerals
- This experiment is one of the most beautiful examples of how much information one can get out of a combined SAXS/WAXS experiment

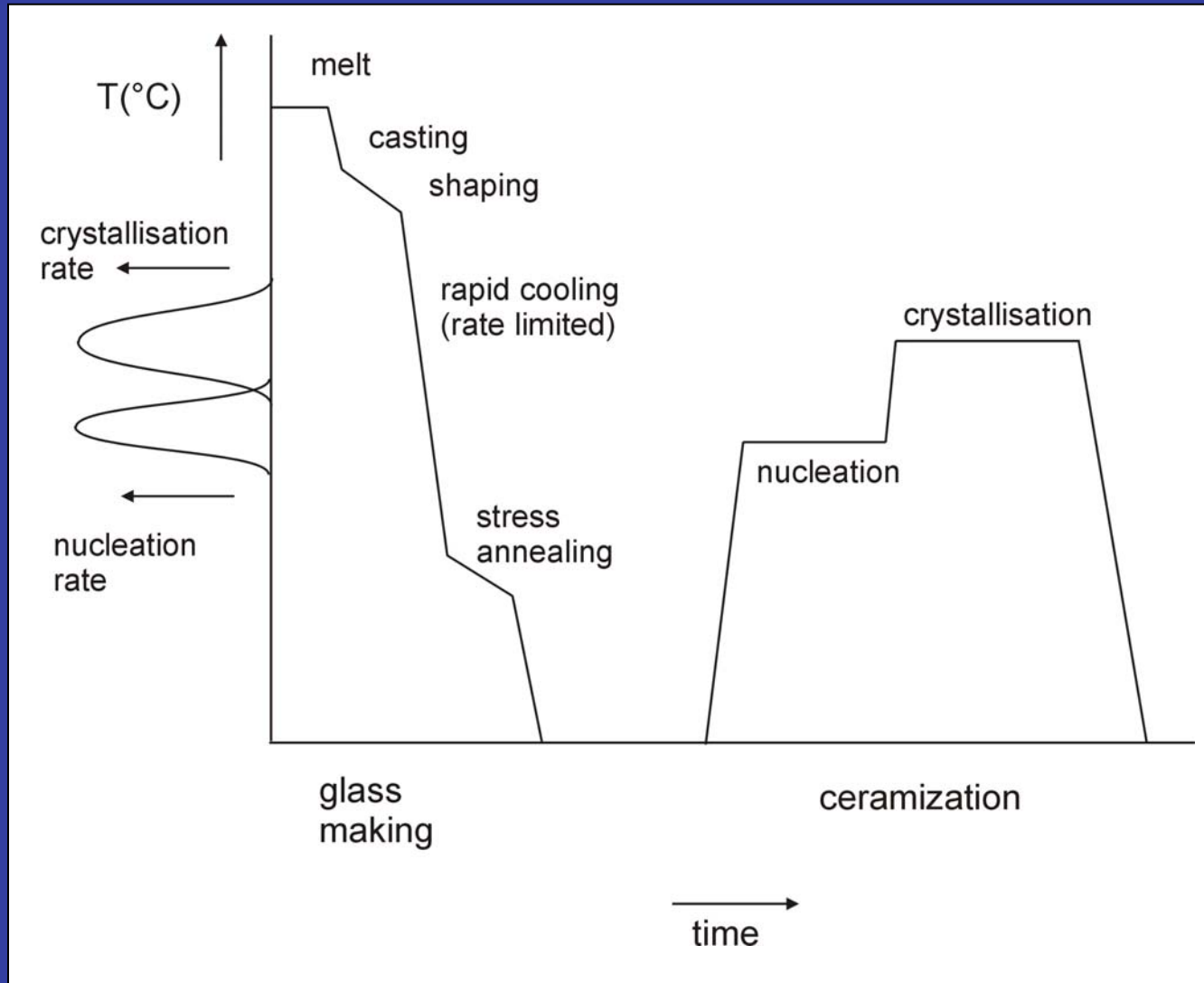
# Cordierite glass devitrification



$\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$   
doped with  
0.34 mol%  $\text{Cr}_2\text{O}_3$   
(crystallization enhancer)

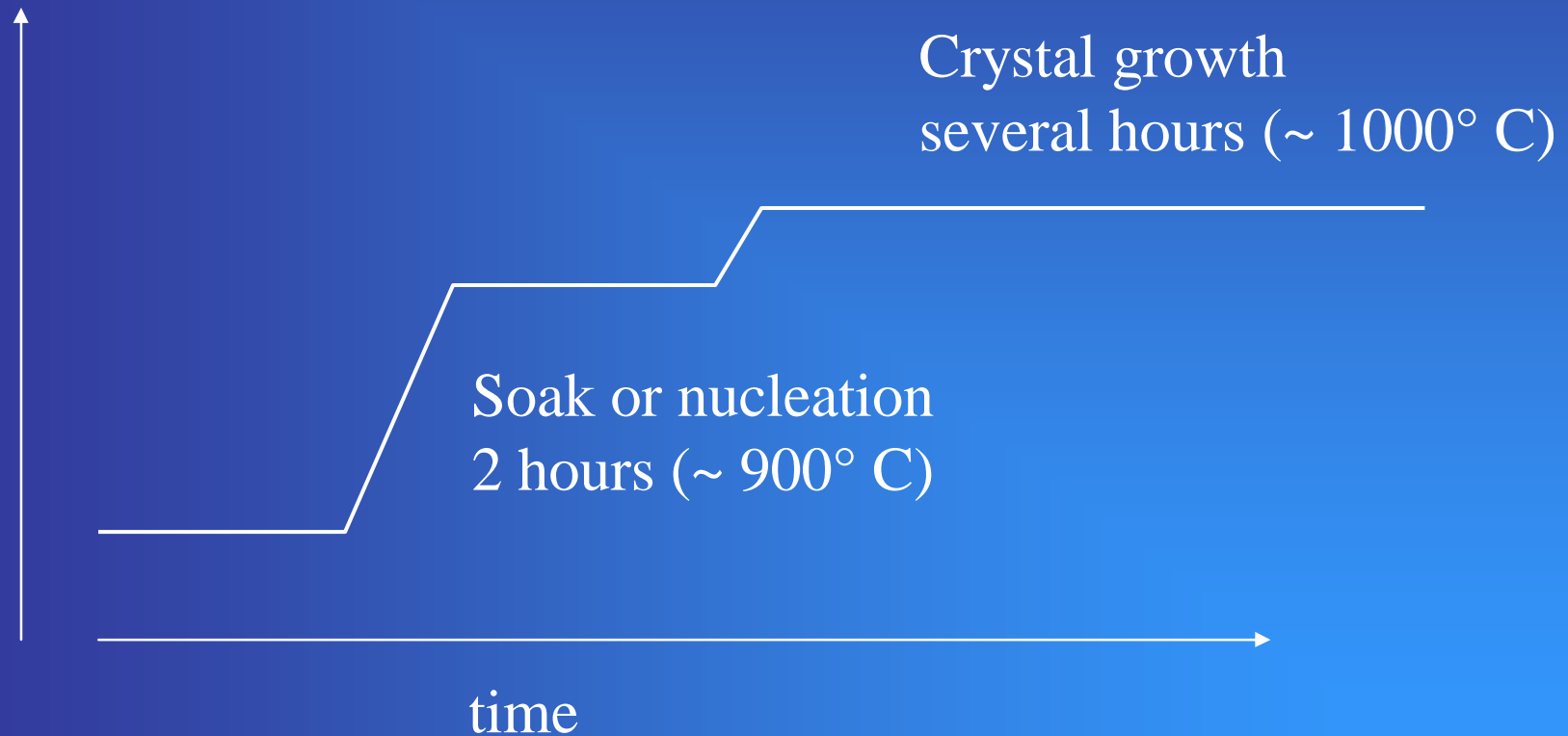


# Normal production process

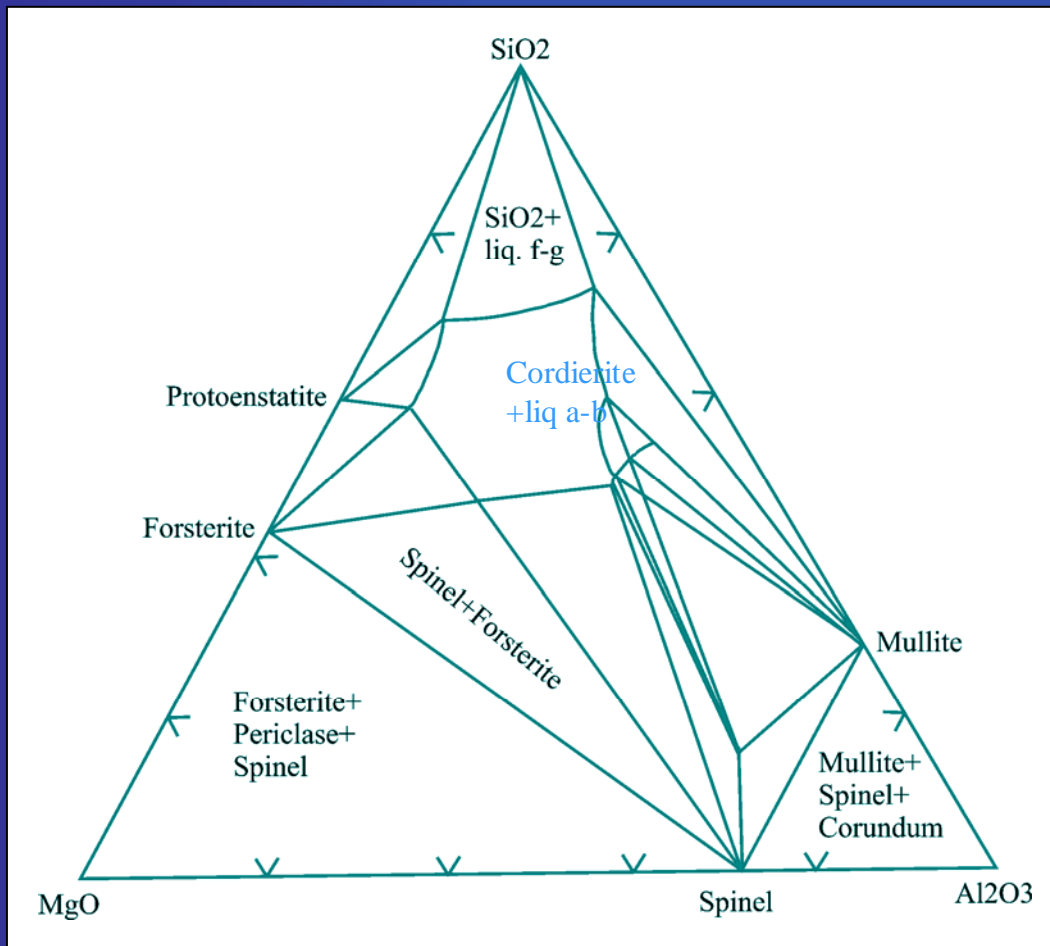


# Experiment on 75 micron thick platelet

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

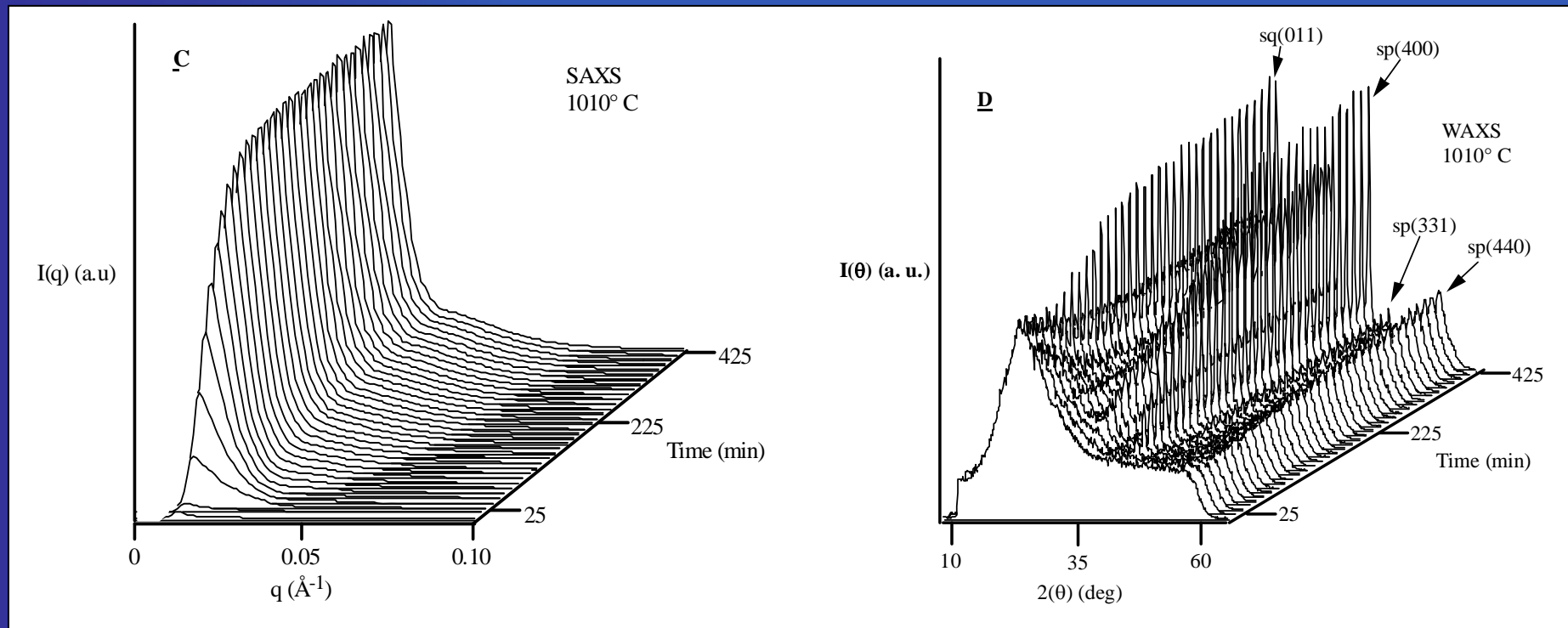
Forsterite  $2\text{MgO} \cdot \text{SiO}_2$

W. Schreyer, J.F. Schairer

J. Petrol., 2, 361, 1961

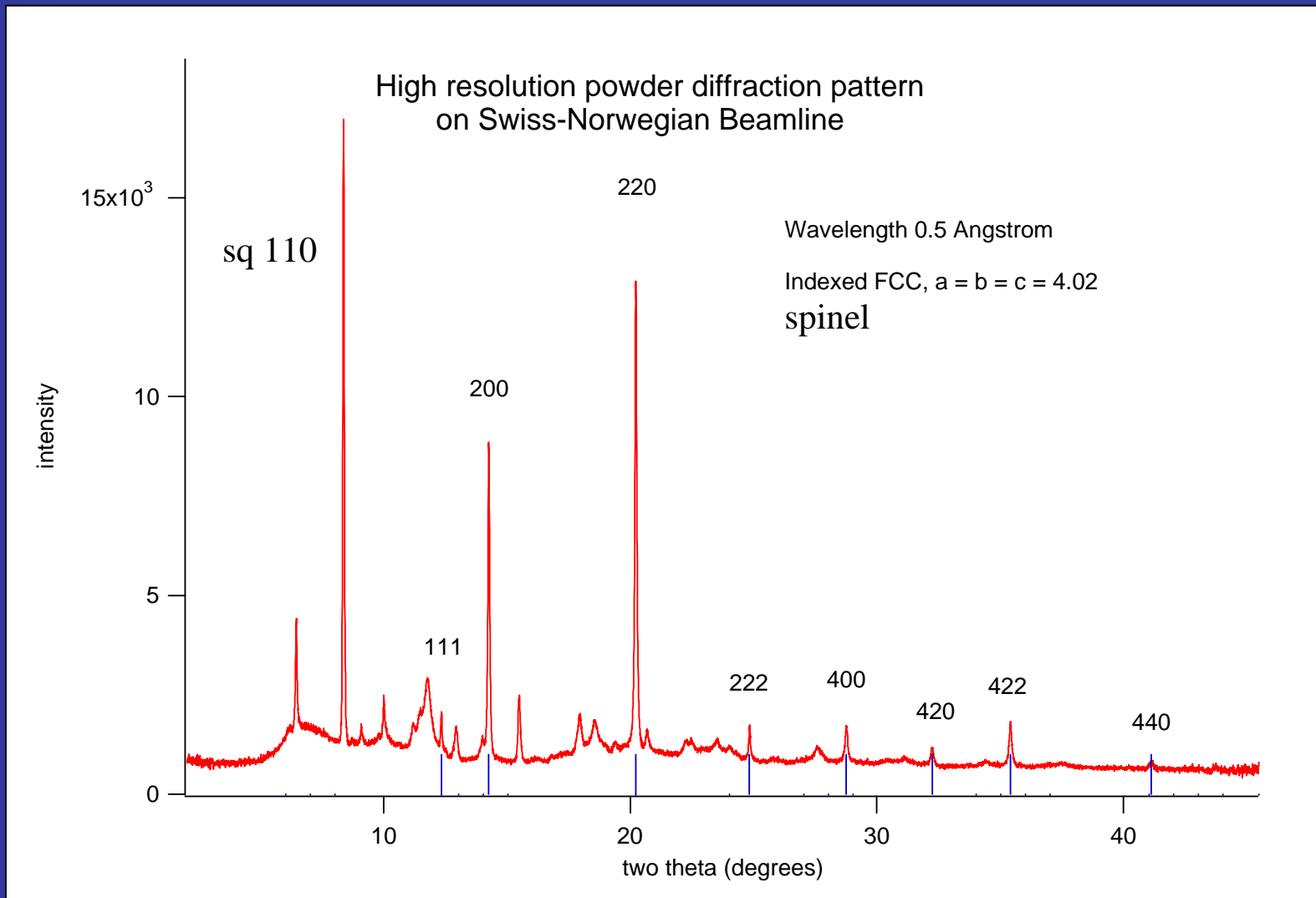
# Structure development

Data taken at 1 minute/frame



SAXS

WAXS



# Post mortem powder diffraction: three different phases



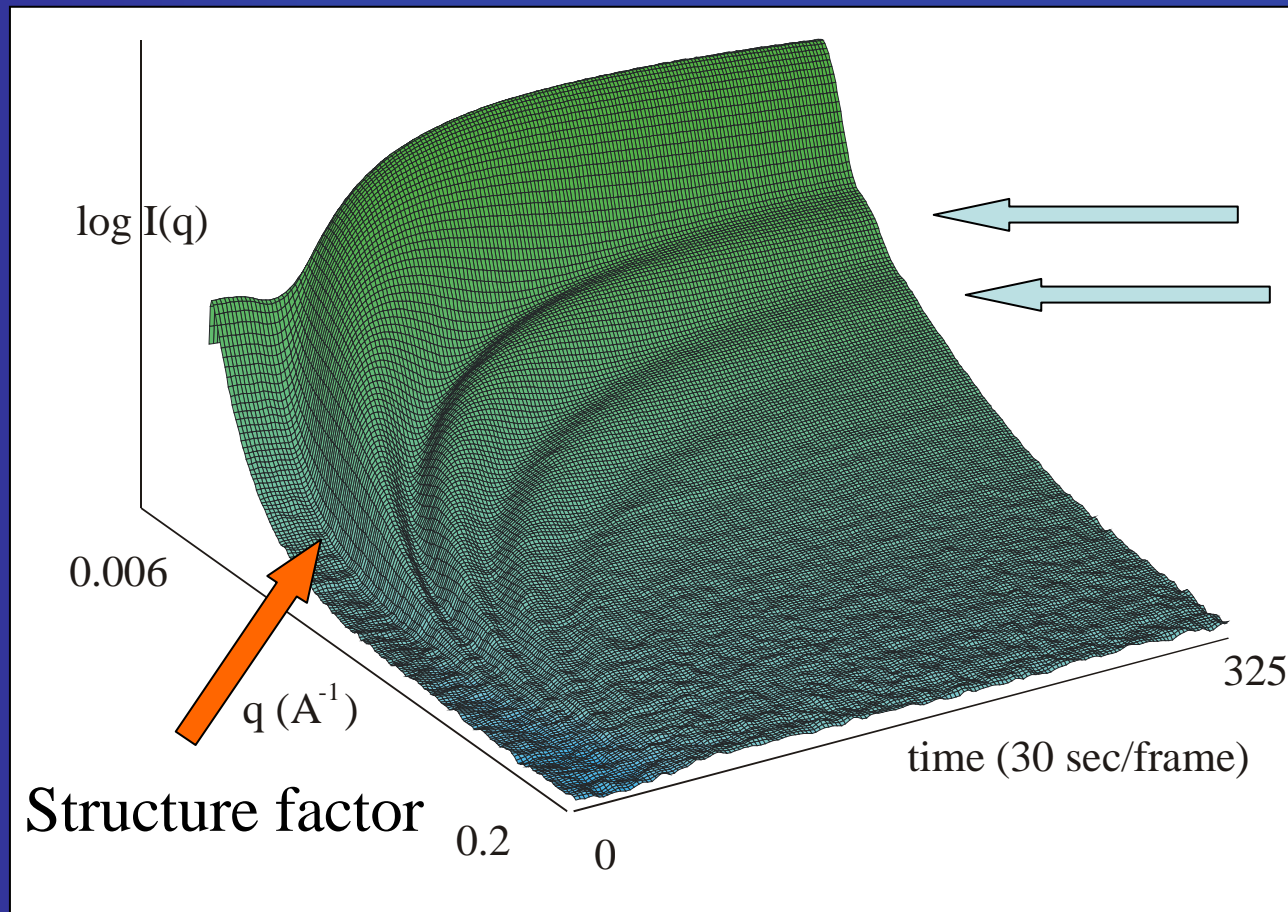
**spinel**



**stuffed quartz**

**+ glass matrix**

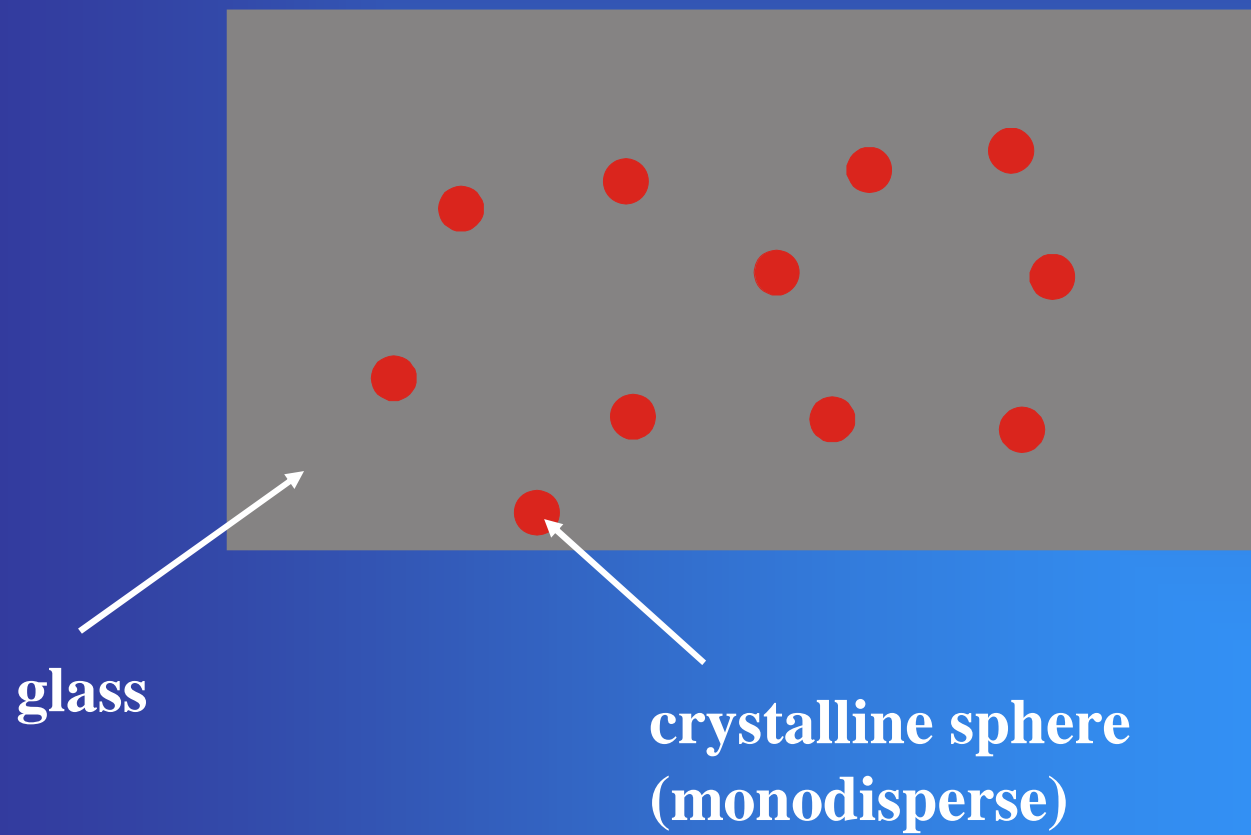
## Time-resolved SAXS



Form factor peaks  
(up to 5<sup>th</sup> order)

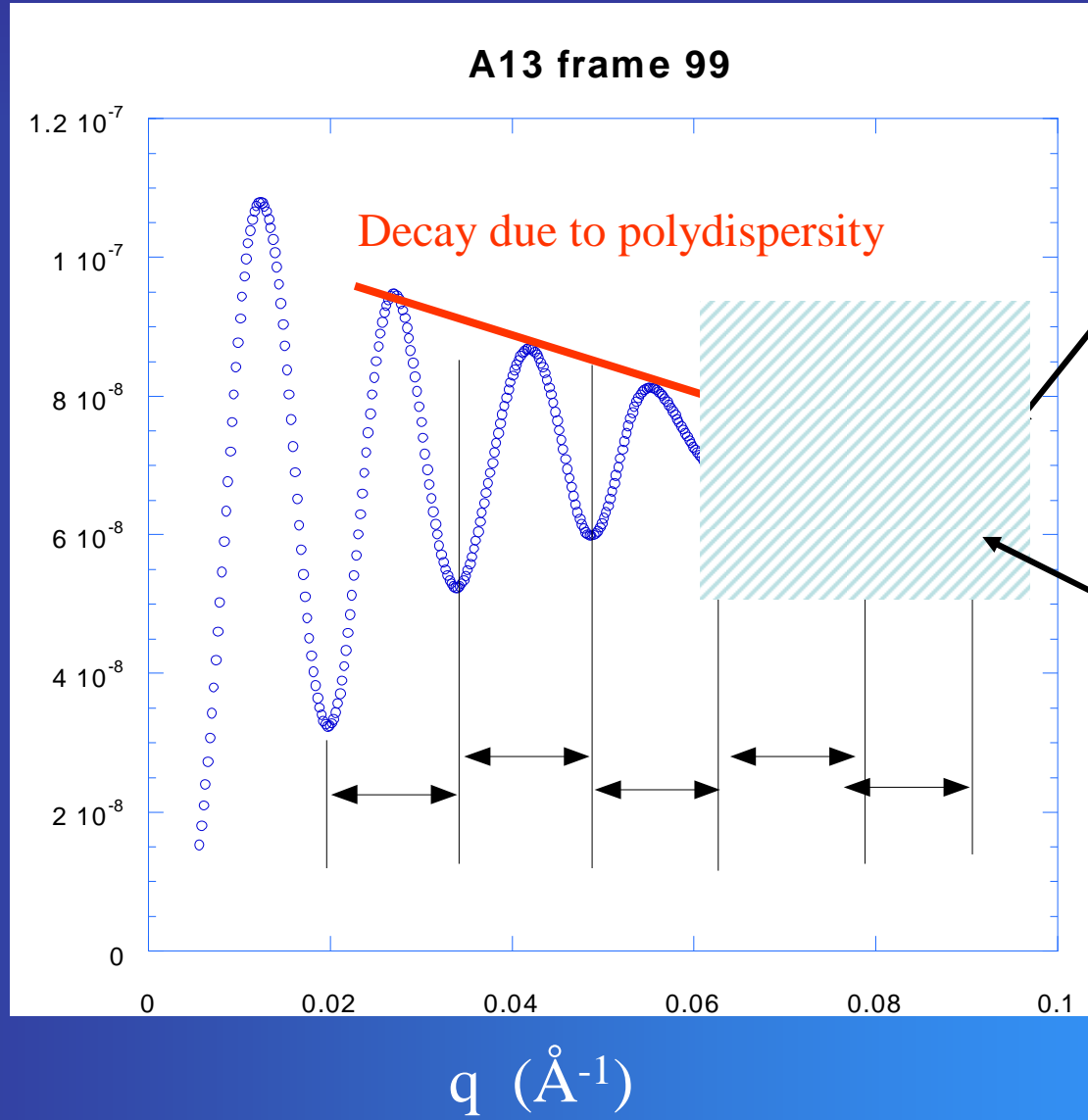
The large number of form factor maxima indicate very monodisperse scattering entities

# Morphology (1)

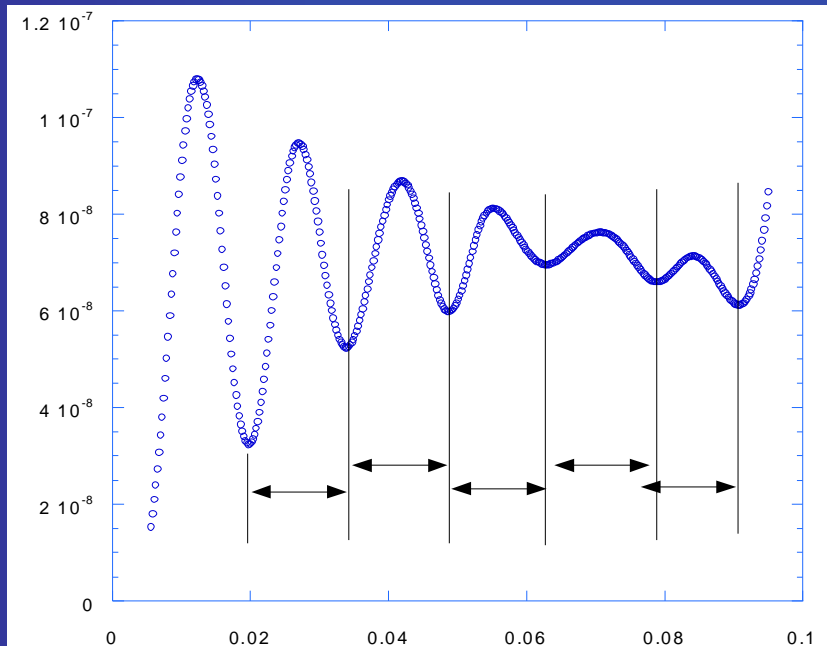




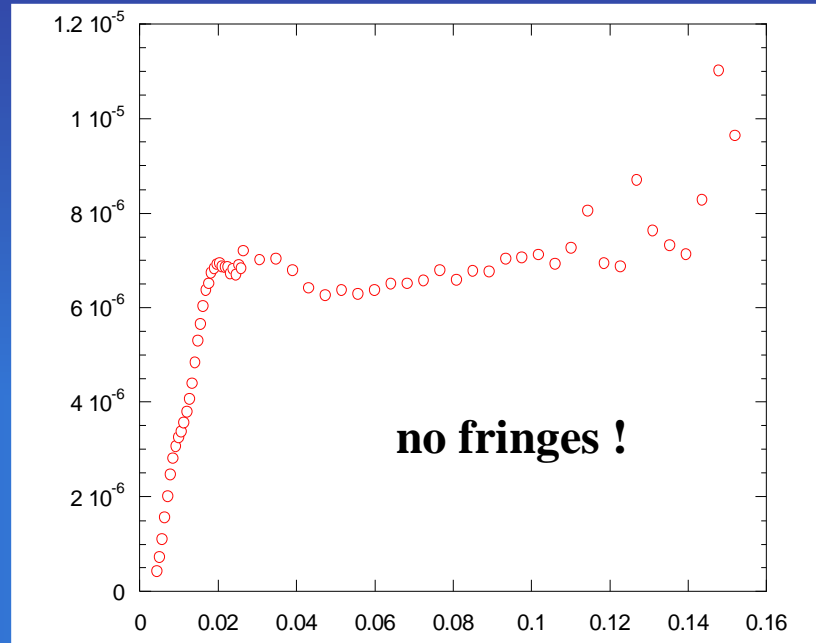
$I(q)q^4$



# Neutron scattering



X-ray

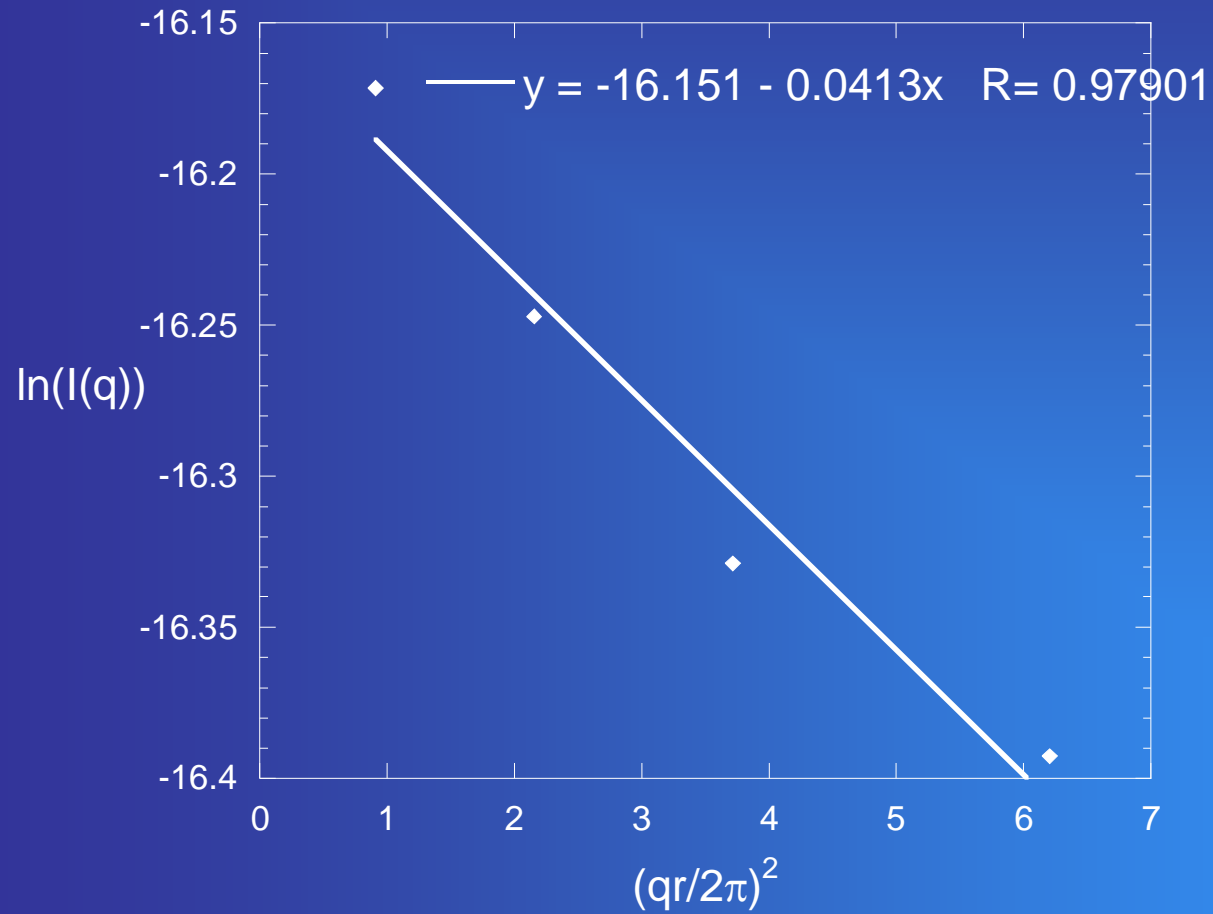


neutron



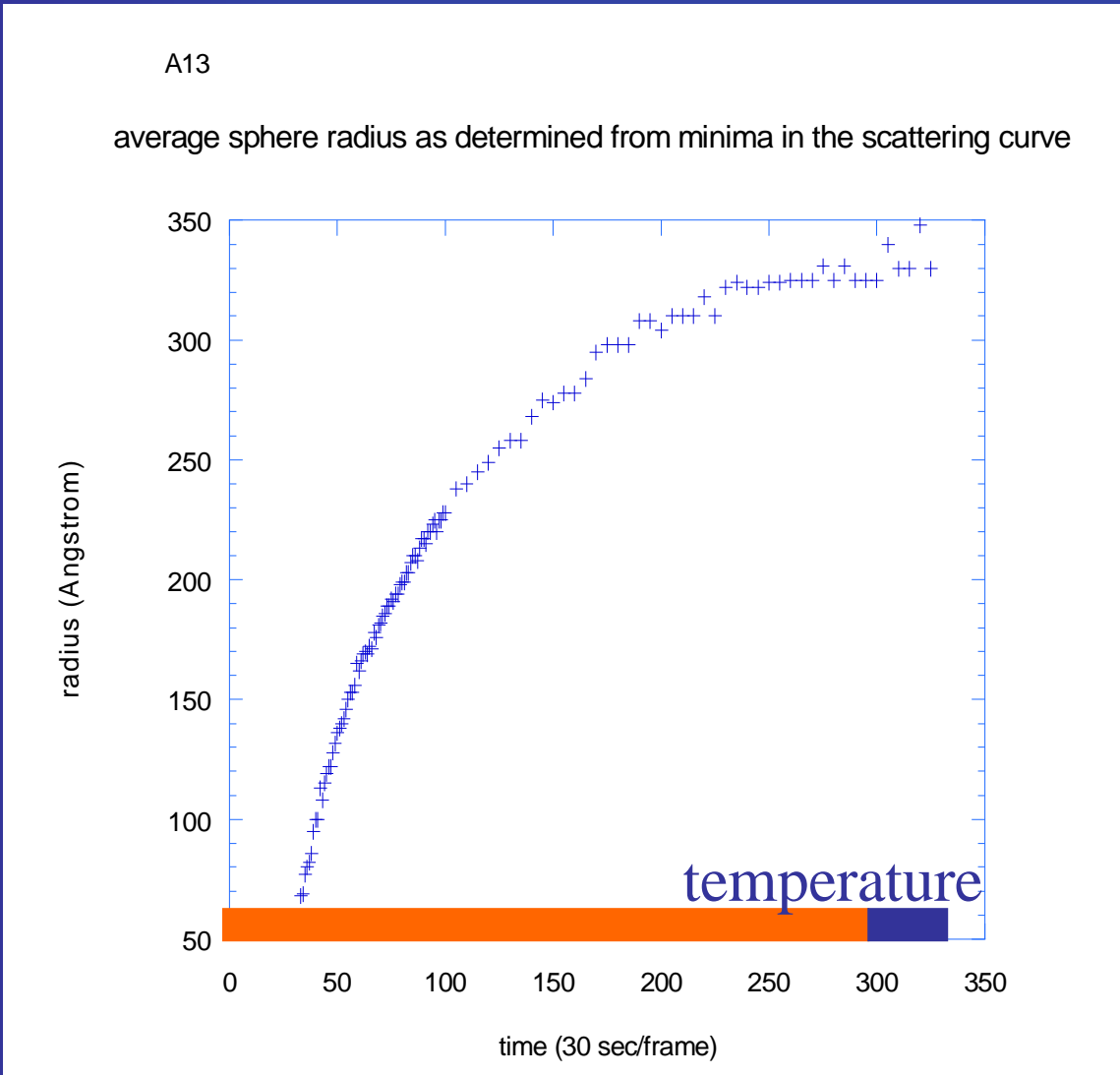
Chromium in crystalline spheres

# polydispersity



$$\Rightarrow \frac{\Delta R}{R} \approx 0.04$$

# Particle size calculated from minima in form factor scatter

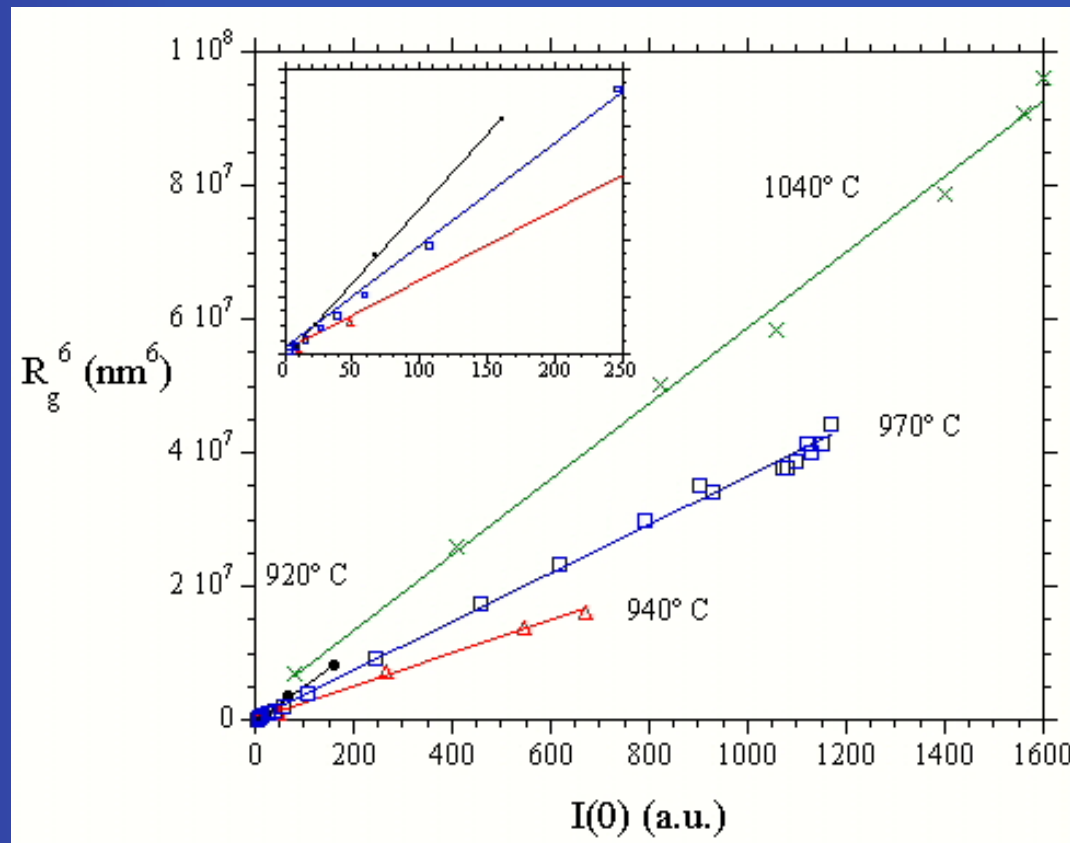


Dimensions of crystallites not influenced by cooling

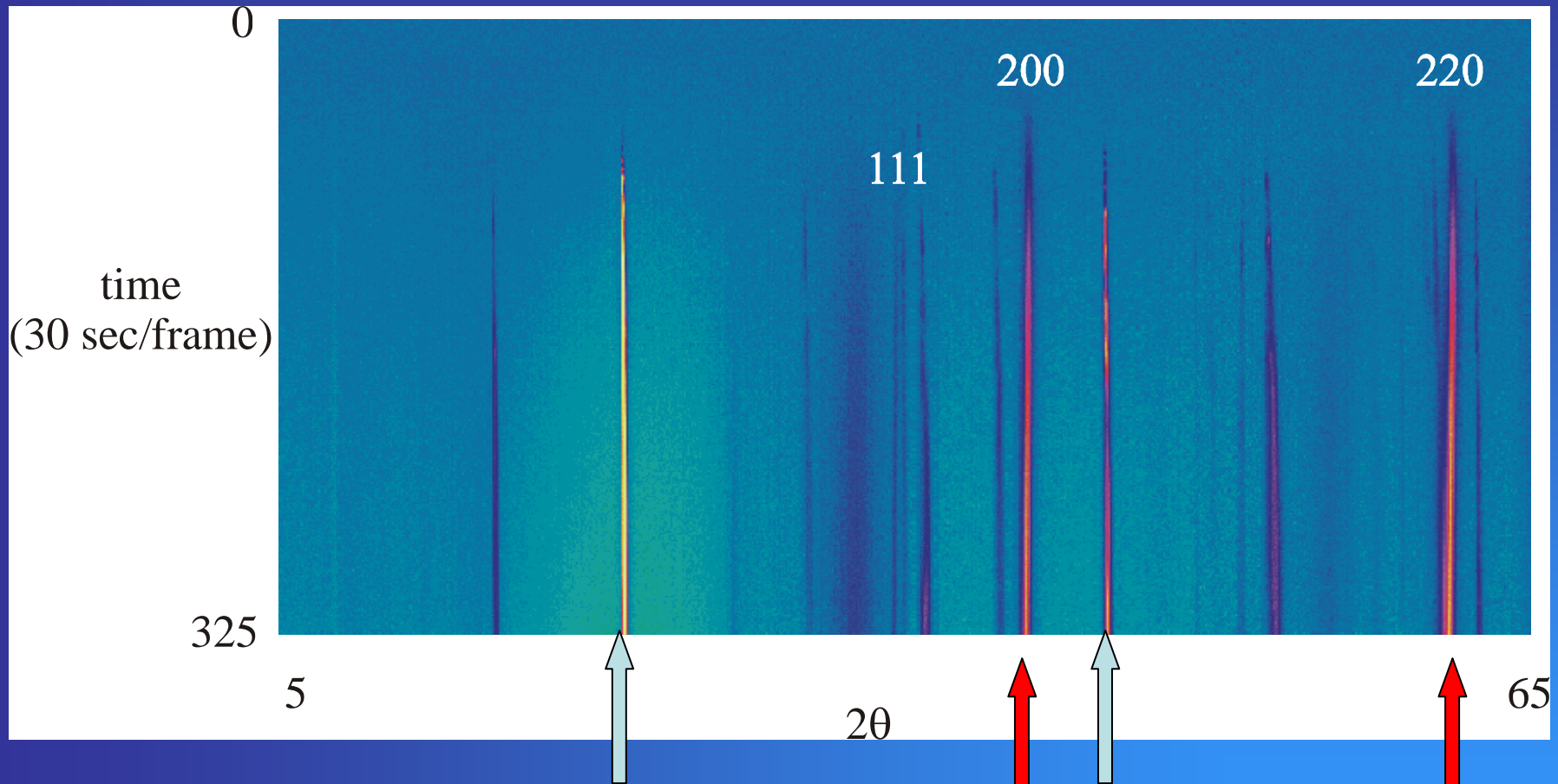


Particles tuneable in size

For fixed number of globular particles  $I(q=0) = CR_g^6$



# WAXS data



Stuffed quartz

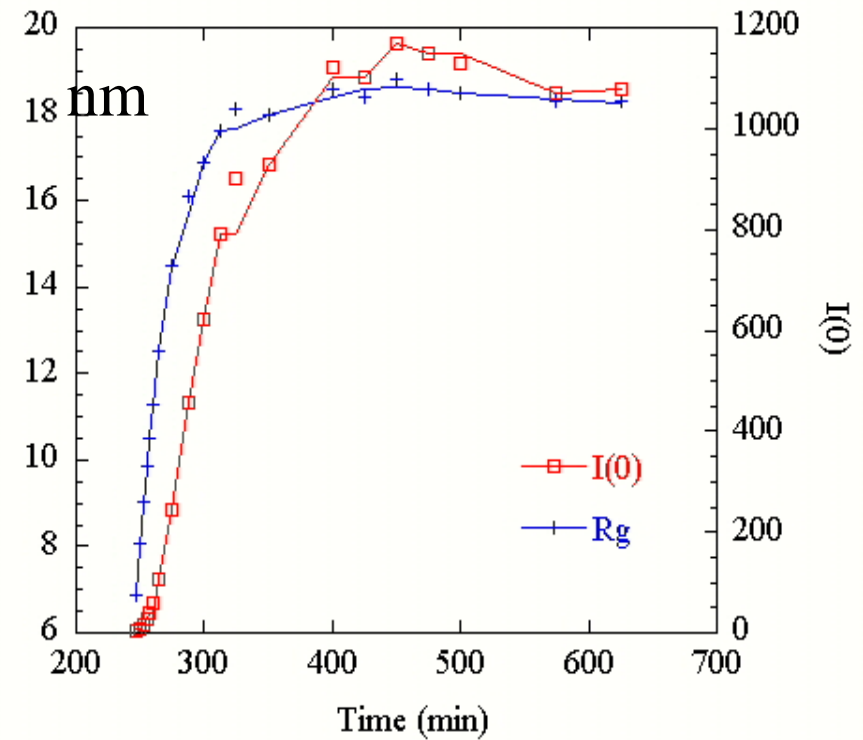
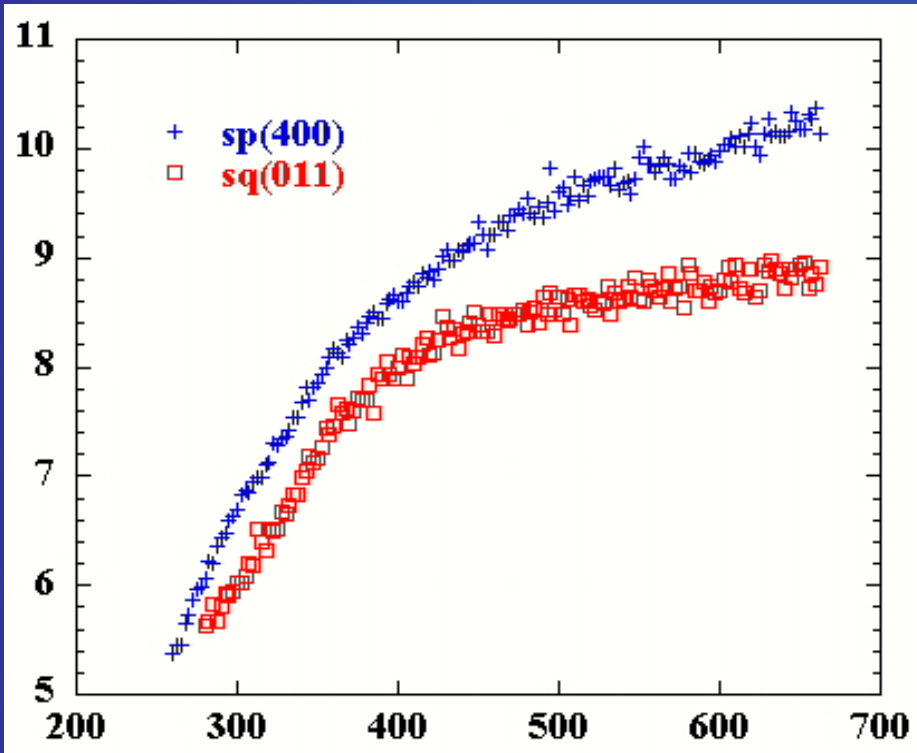
Spinel unit cell increases in time  
 $\text{MgOAl}_2\text{O}_3$  FCC  $a = b = c = 8.06 \text{ \AA}$

Spinel

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

$$X = \int_{q_1}^{q_2} I(q) dq$$

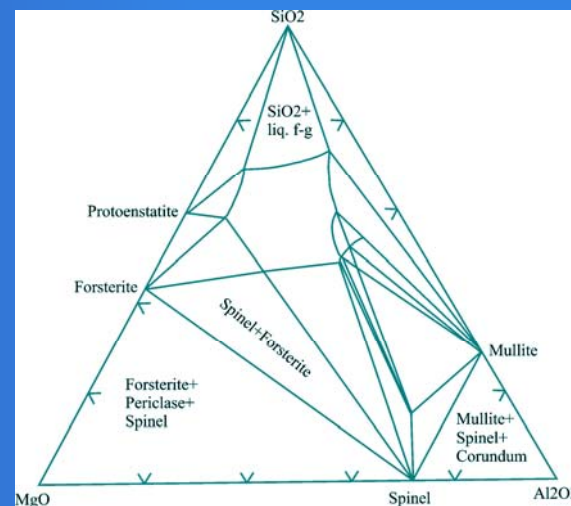
$$I(q \rightarrow 0) = Ce^{\left(\frac{R_g^2 q^2}{3}\right)}$$



Spinel and stuffed quartz  
different time development

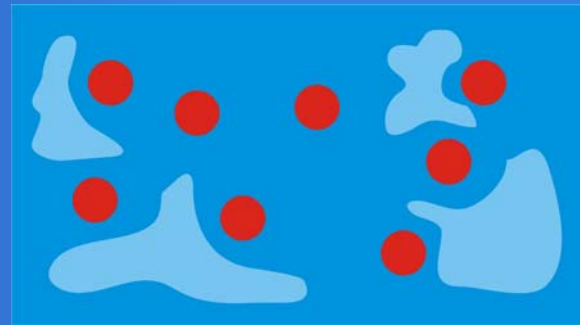
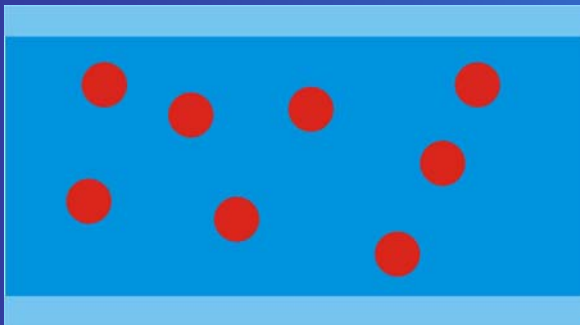
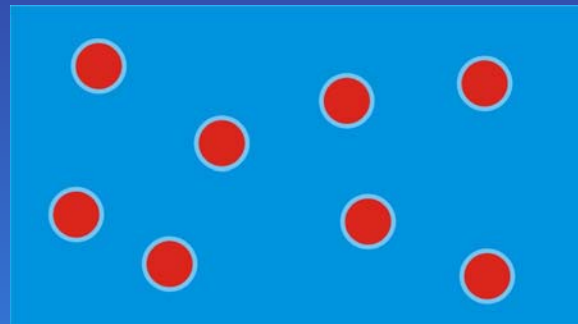
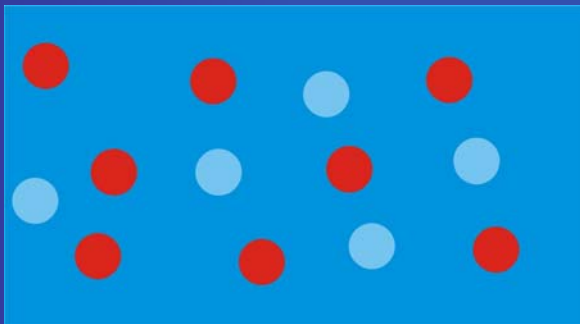
# Question:

- Is one crystalline phase templating the other due to local composition changes? Or are they independent?

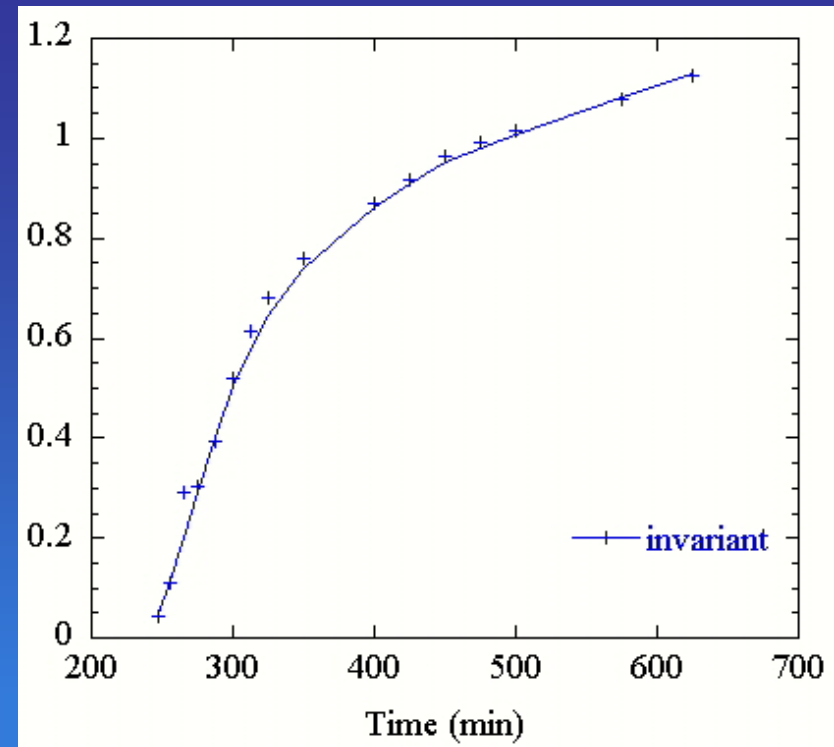
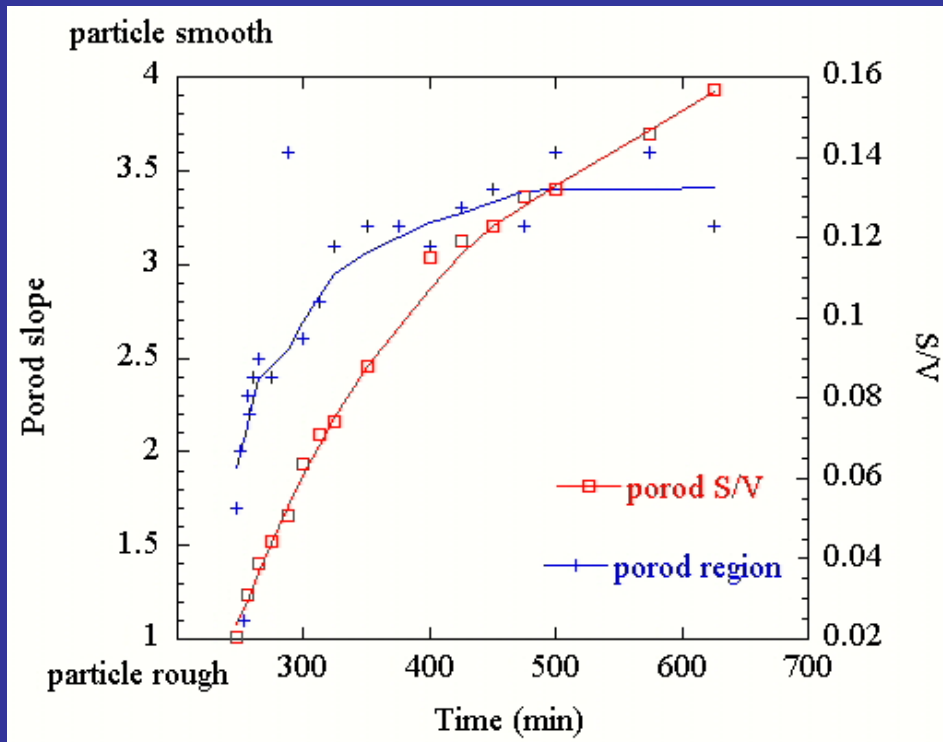




# Morphology (2)



So far all possible



$$I(q) \sim K_1 + \frac{K_2}{q^4}$$

$$Q = \int_0^{\infty} I(q) q^2 dq \sim \langle n_e \rangle^2 \phi(1-\phi)$$

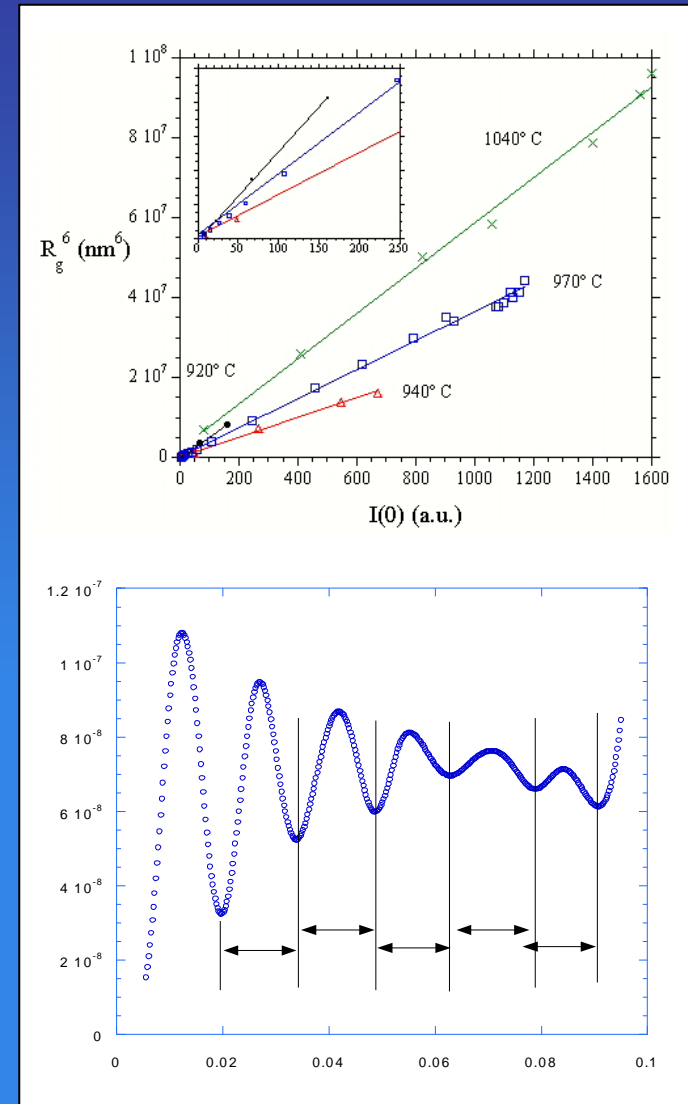
$$\frac{K_2}{Q} = \frac{1}{\pi} \frac{S}{V}$$

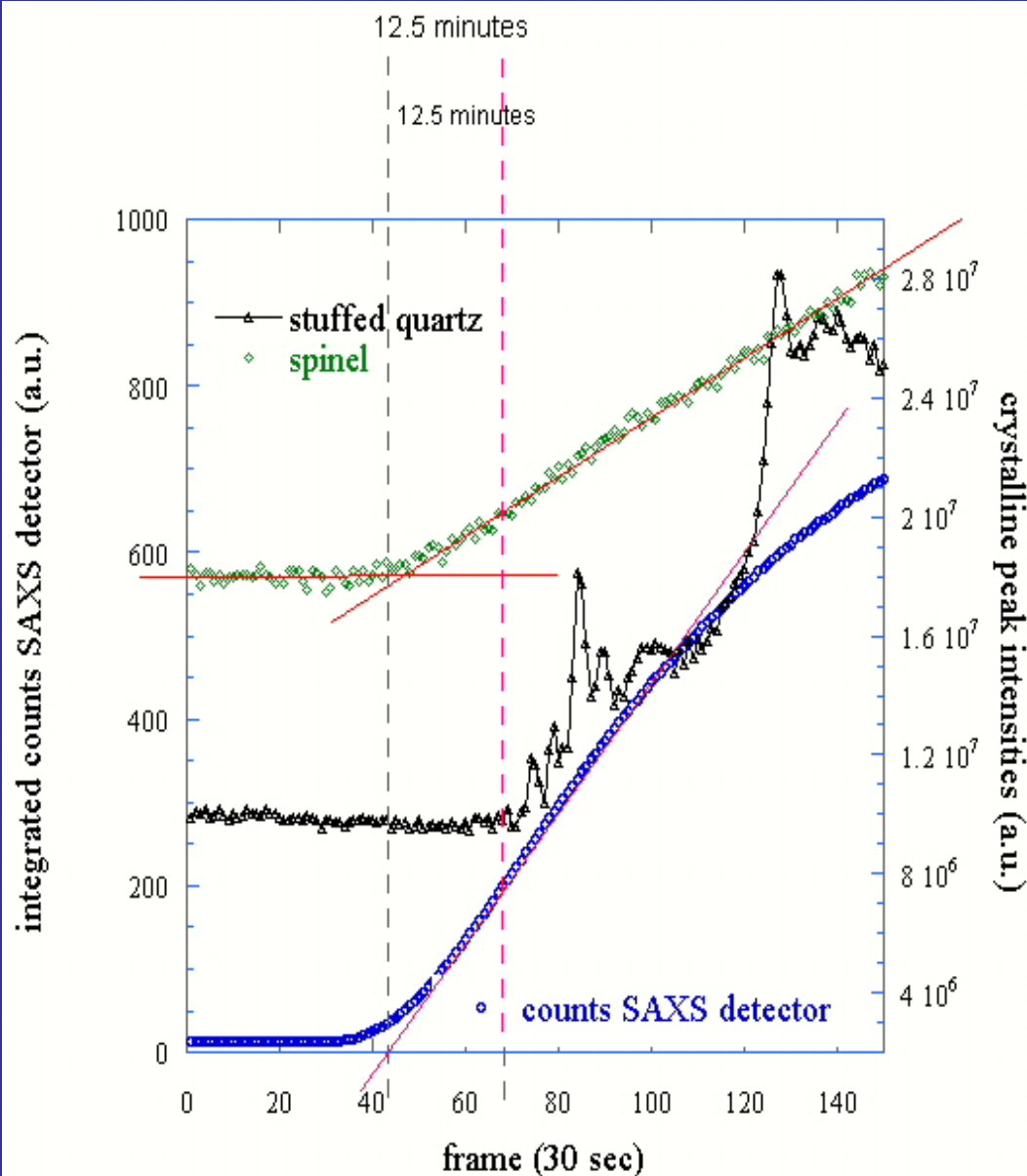
# Can this be correct?

- Radius of particle stops growing
- Surface/Volume ratio of particle keeps increasing
- Maybe new crystallites created ?

# New crystallites can be ruled out:

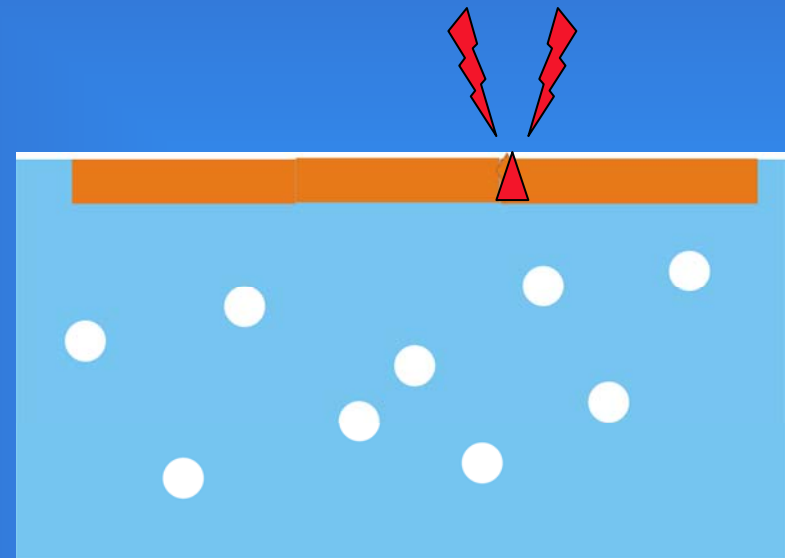
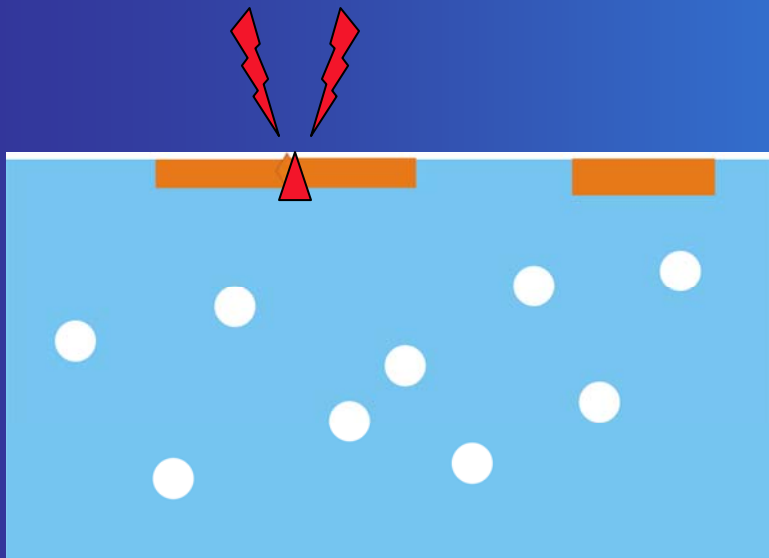
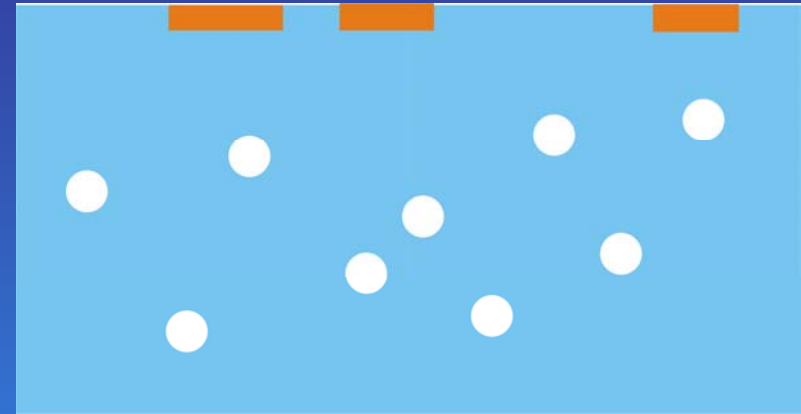
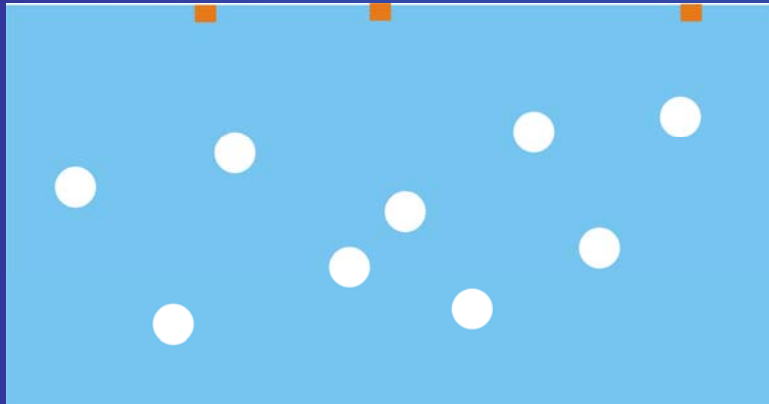
- $I(0) = CR_g^6$   
(only true for constant number of particles)
- We see many form factor maxima
- Polydispersity  $\sim 4\%$

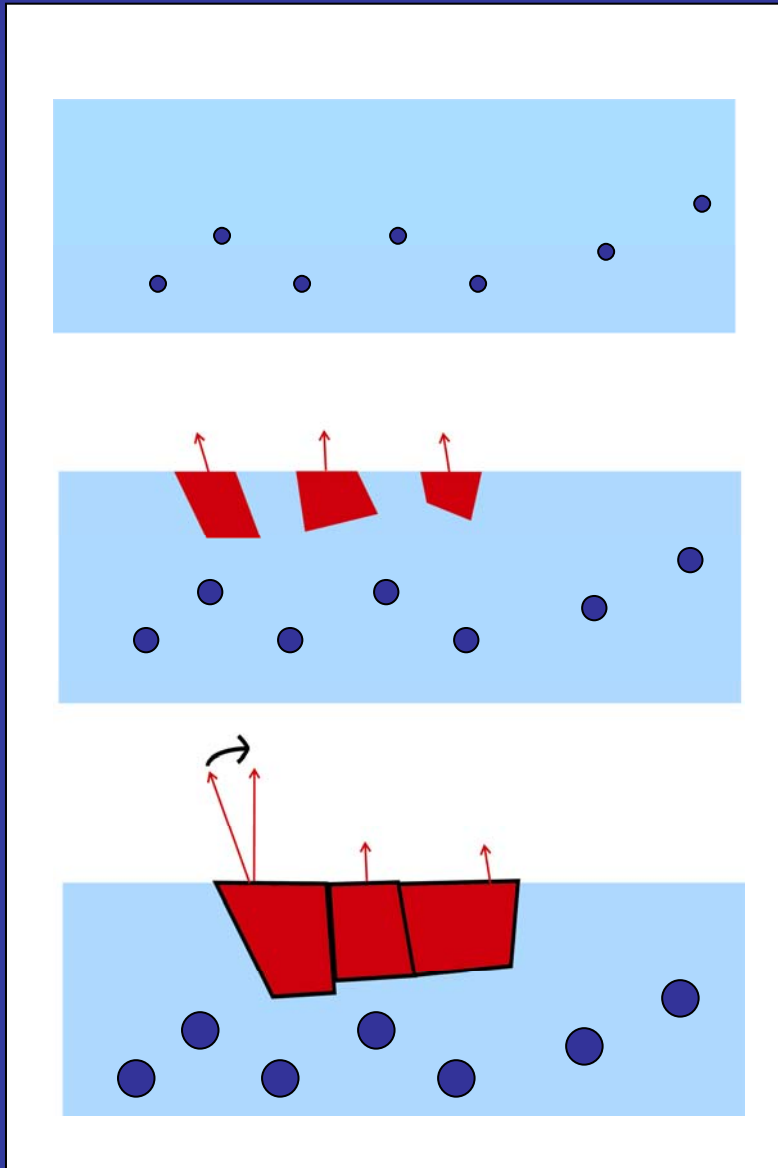




- Spinel increases regularly in time
- Stuffed quartz increases irregular
- Spinel starts at same time as particle growth observable in SAXS

# Why the irregularity in the quartz growth?



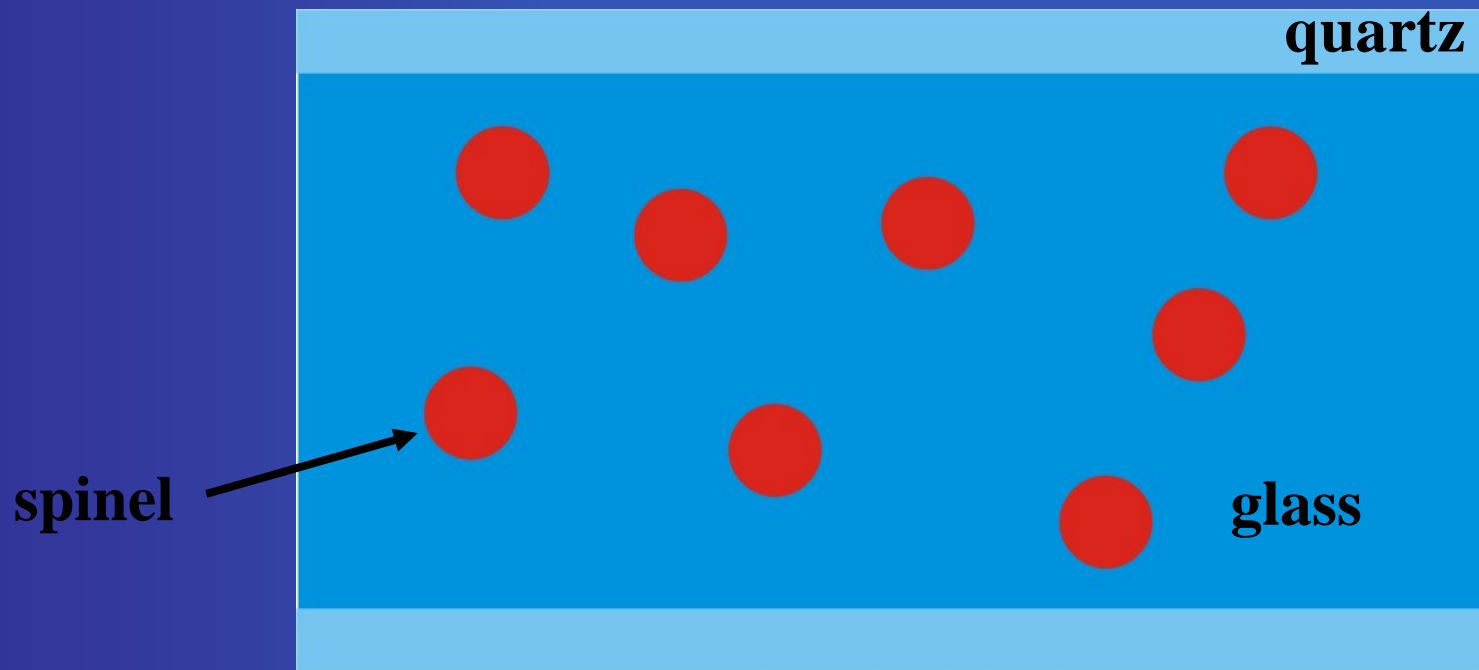


## Growth of stuffed quartz

⇒ texture effects !

Crystals impinge on each other  
⇒ variations in intensity

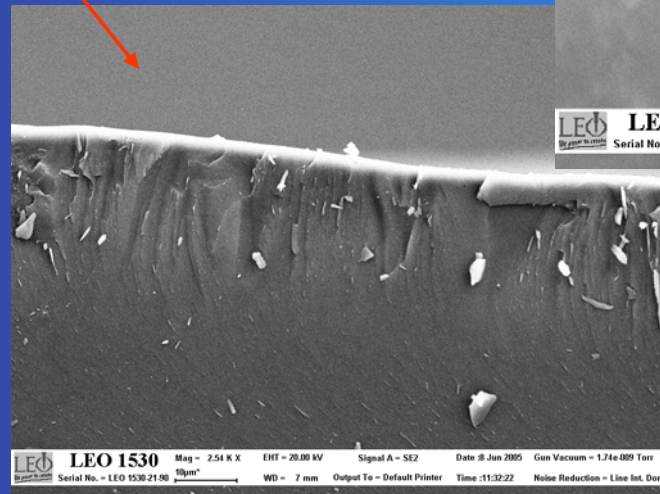
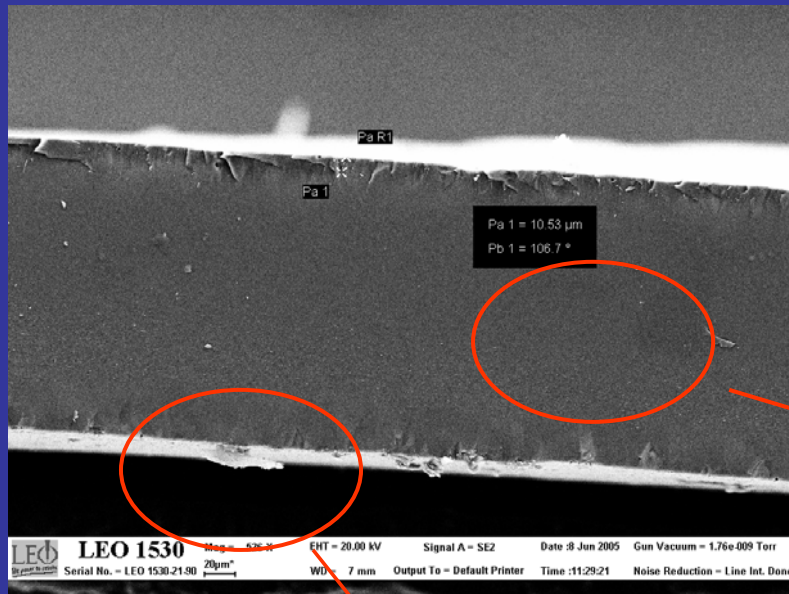
# Prediction Morphology:



This is (so far) the correct morphology



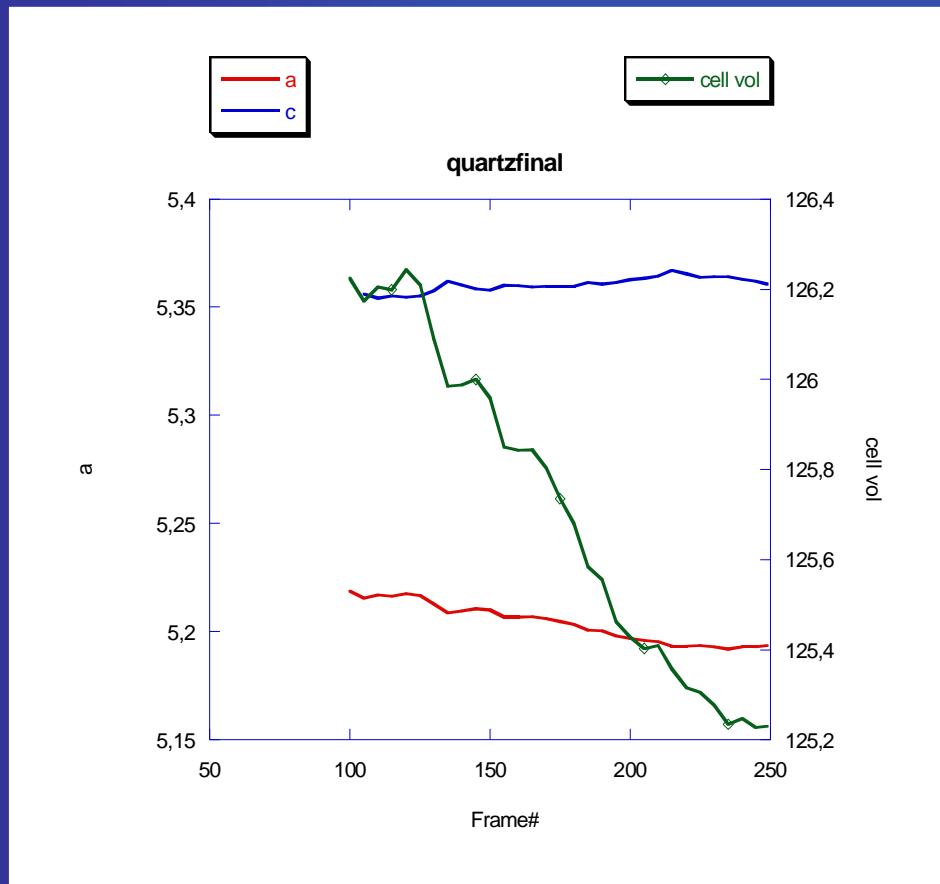
# SEM



# Note:

- This would have been impossible to derive from time-resolved diffraction on powdered samples
- Could possibly have been found with DSC
- Using a platelet sample was lucky choice

# Unit cell (surface) stuffed quartz changes in time



- Unit cell changes in aspect ratio
- Reason not explained yet

# Summarising:

- The irregular growth of the stuffed quartz indicates preferential orientation
- This can only occur at the (slightly polished) surface
- This must mean surface crystallization
- This also explains why the particle radius can stop growing but the S/V ratio keeps increasing

# We can now conclude:

- Spinel grows in bulk
  - Stuffed quartz grows on surface
  - They are uncorrelated
- 
- .....but can we find out more about the system .....?

# 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)

<b>Model</b>		<b>Phase boundary control</b>	<b>Diffusion control</b>
<b>Three dim growth</b>			
<b>Nucleation rate</b>	<b>1 constant</b>	<b>4</b>	<b>2.5</b>
	<b>2 instantaneous</b>	<b>3</b>	<b>1.5</b>
	<b>3 deceleratory</b>	<b>3 – 4</b>	<b>1.5 – 2.5</b>
<b>Two dim growth</b>			
<b>Nucleation rate</b>	<b>1 constant</b>	<b>3</b>	<b>2.0</b>
	<b>2 instantaneous</b>	<b>2</b>	<b>1.0</b>
	<b>3 deceleratory</b>	<b>2 – 3</b>	<b>1.0 – 2.0</b>
<b>One dim growth</b>			
<b>Nucleation rate</b>	<b>1 constant</b>	<b>2</b>	<b>1.5</b>
	<b>2 instantaneous</b>	<b>1</b>	<b>0.5</b>
	<b>3 deceleratory</b>	<b>1 – 2</b>	<b>0.5 – 1.5</b>

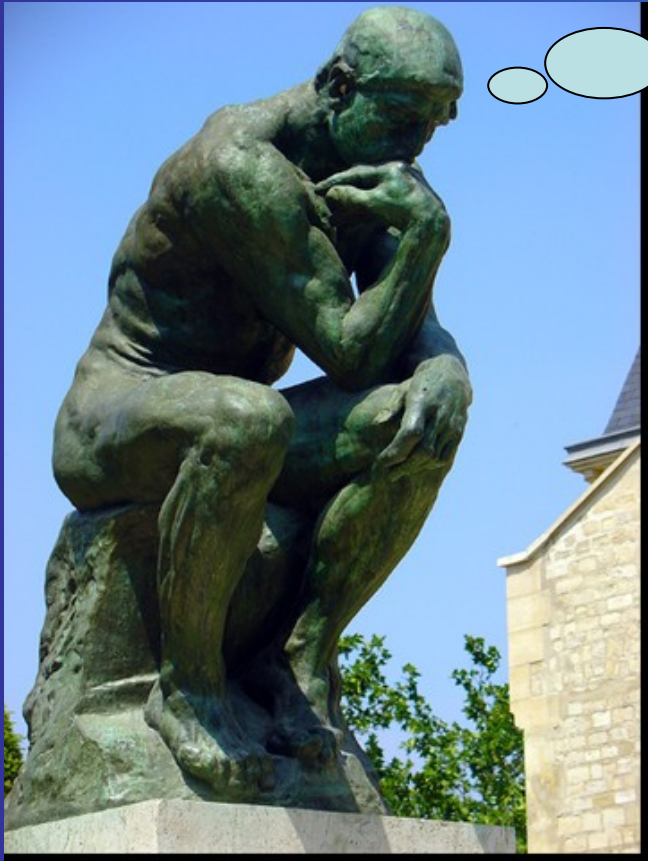
# Avrami analysis

- Named after Milton Avrami
- Well known description of crystallisation kinetics
- Very often used
- Very often misused as well



Dear Wim,  
Are you surprised? To  
such an equation I can  
fit anything.....

Signed: Cynic



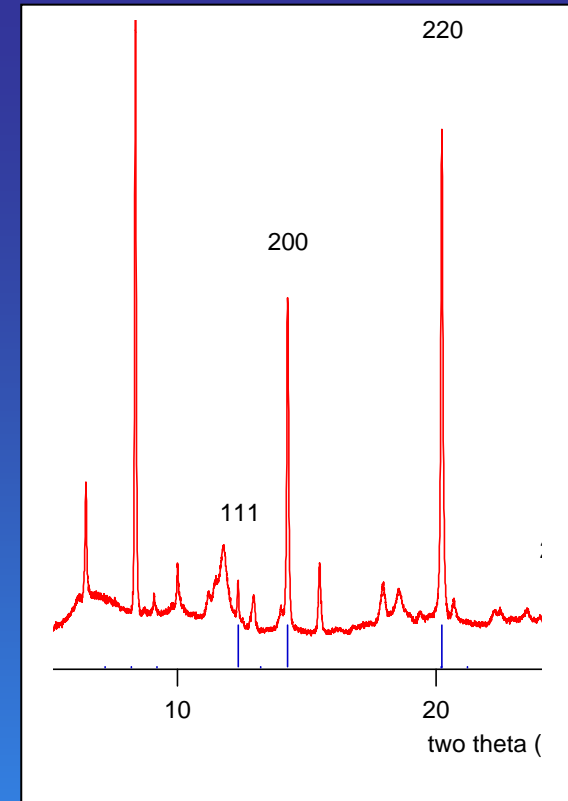
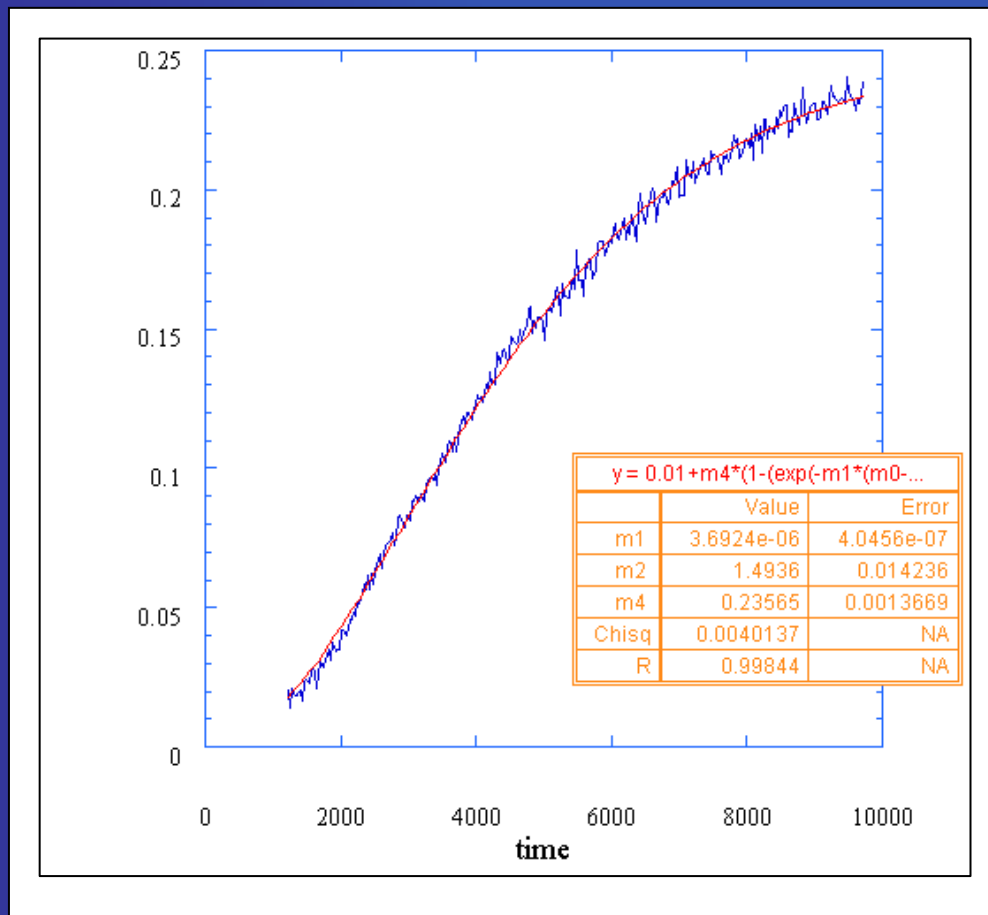
**Dear Cynic,  
Maybe that is true, but  
I'm a careful 'man'.....**

**I double check.....**



**...and I don't like such  
negative questions!**

# WAXS



$$V_c \sim \int_{q_1}^{q_2} I(q) dq$$

Avrami coefficient  
 $1.49 \pm 0.01$

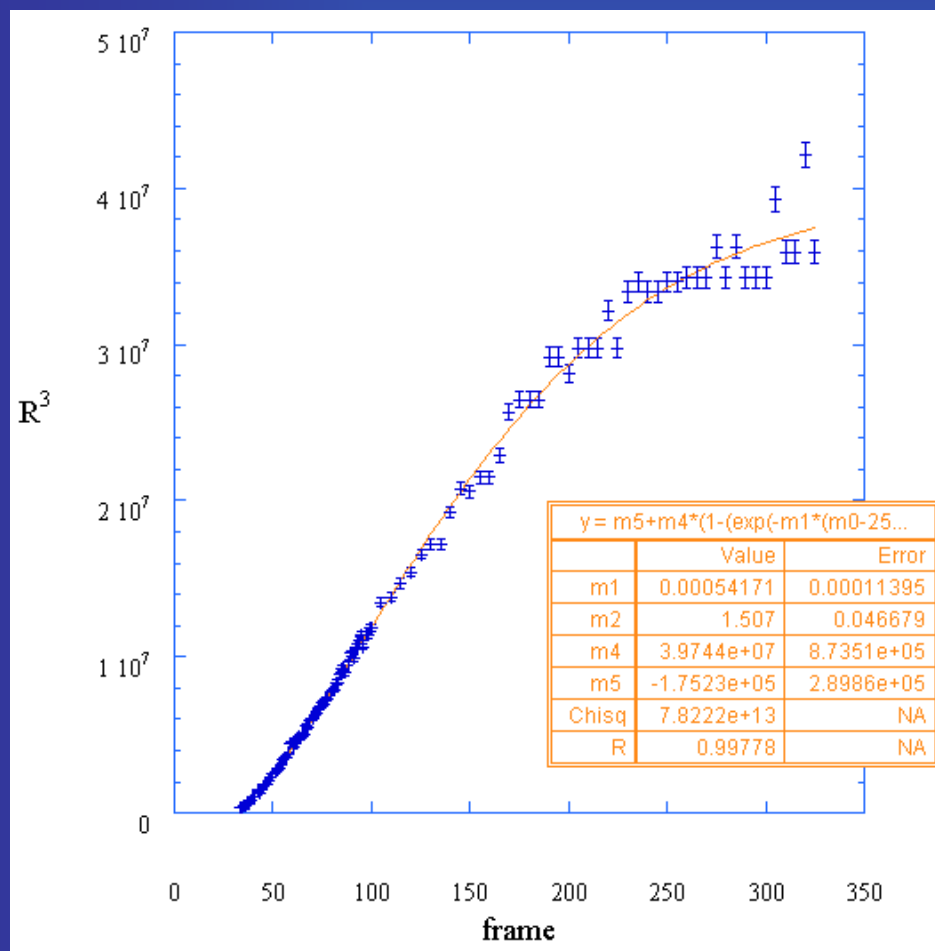
# For SAXS data

- For fixed number of particles  $N$  which are monodisperse with radius  $R$

$$V_c \sim N \frac{4\pi}{3} R^3$$

- $N \times R^3$  is also related to the volume fraction

# SAXS



Avrami coefficient

$$1.51 \pm 0.05$$

For the people with  
poor memories:  
from WAXS  $1.49 \pm 0.01$

# What does this mean according to mr. Avrami?

For a pre-nucleated system

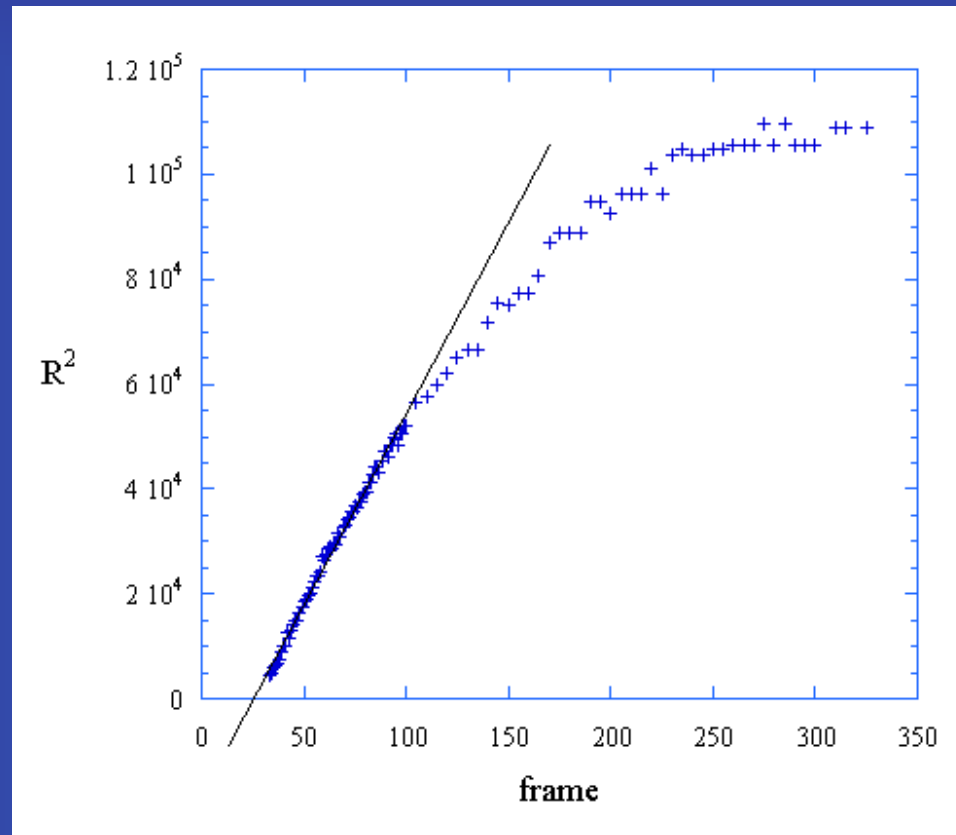
$$V_c = 1 - e^{(-Kt^{1.5})}$$

Means diffusion limited growth

For pre-nucleated, monodisperse spheres  
diffusion limited growth predicts that the particle  
size in the initial stages should behave like:

$$R \sim \sqrt{\text{time}}$$

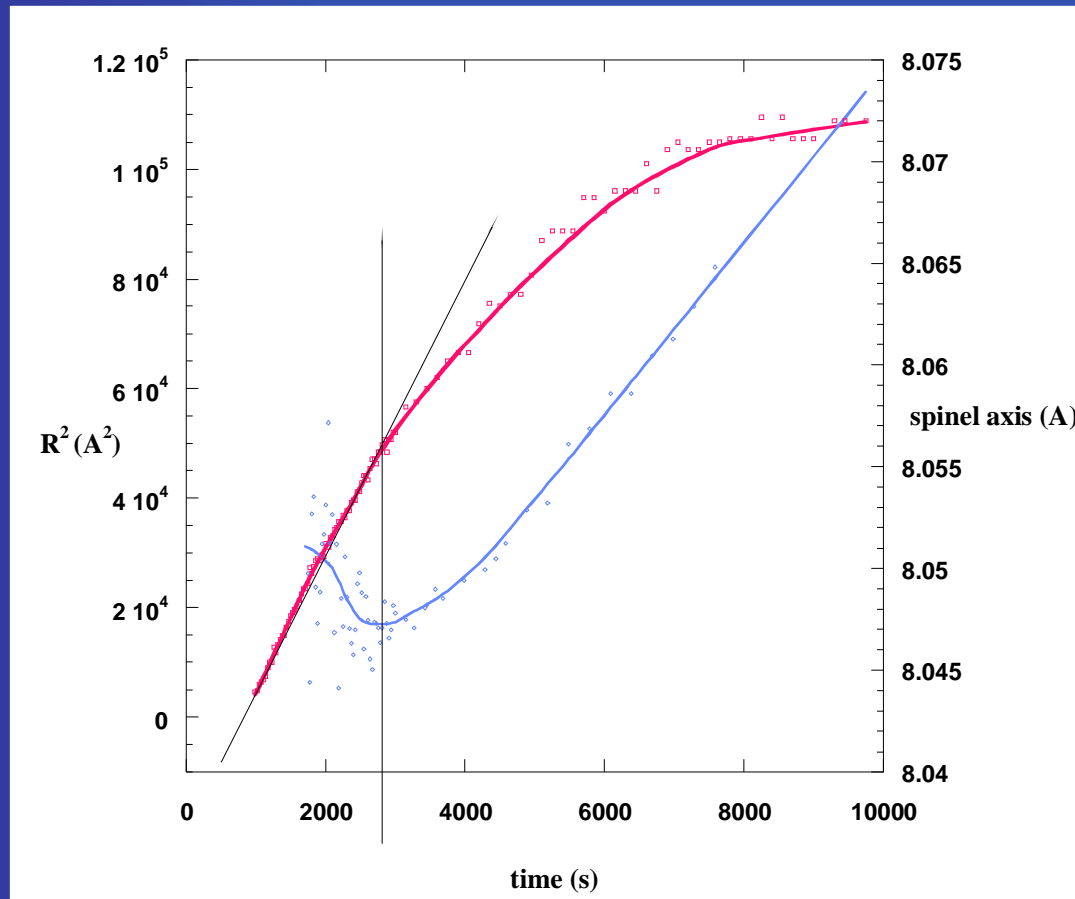
# And so it does !



3 independent ways of checking  
(hope Cynic is happy now)



# Increase in spinel unit cell size



Porod constant approaches 4 when leaving free growth regime

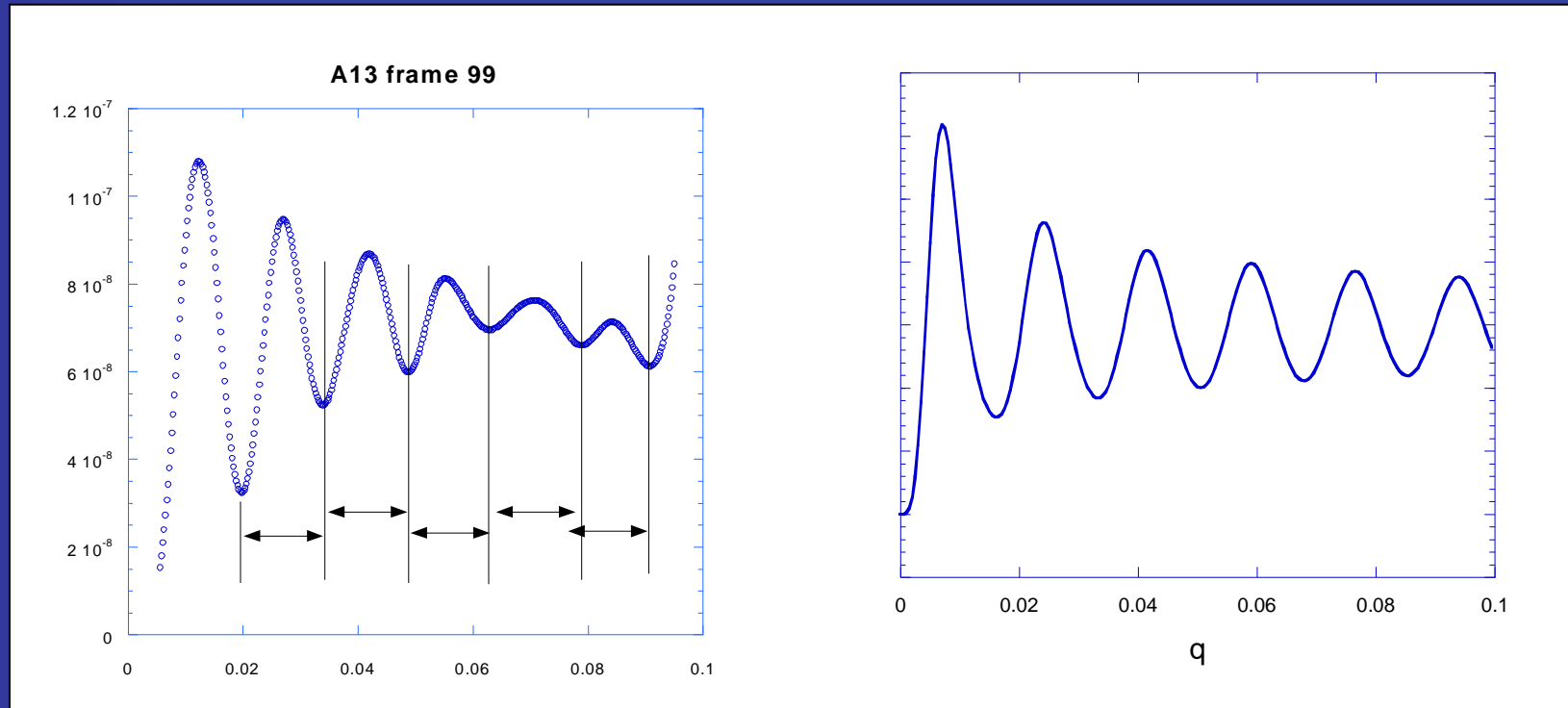
# Change in lattice spacing

- From the change in lattice spacing we can calculate the internal pressure
- Pressure due to mismatch between specific volumes glass matrix versus spinel

$$P = 1.5 \cdot K_{0,1050} \left[ \left( \frac{V_{0,1050}}{V} \right)^{7/3} - \left( \frac{V_{0,1050}}{V} \right)^{5/3} \right]$$

- Pressure changes from 9.5 → 10 → 8.5 GPa

# How well can we trust data?



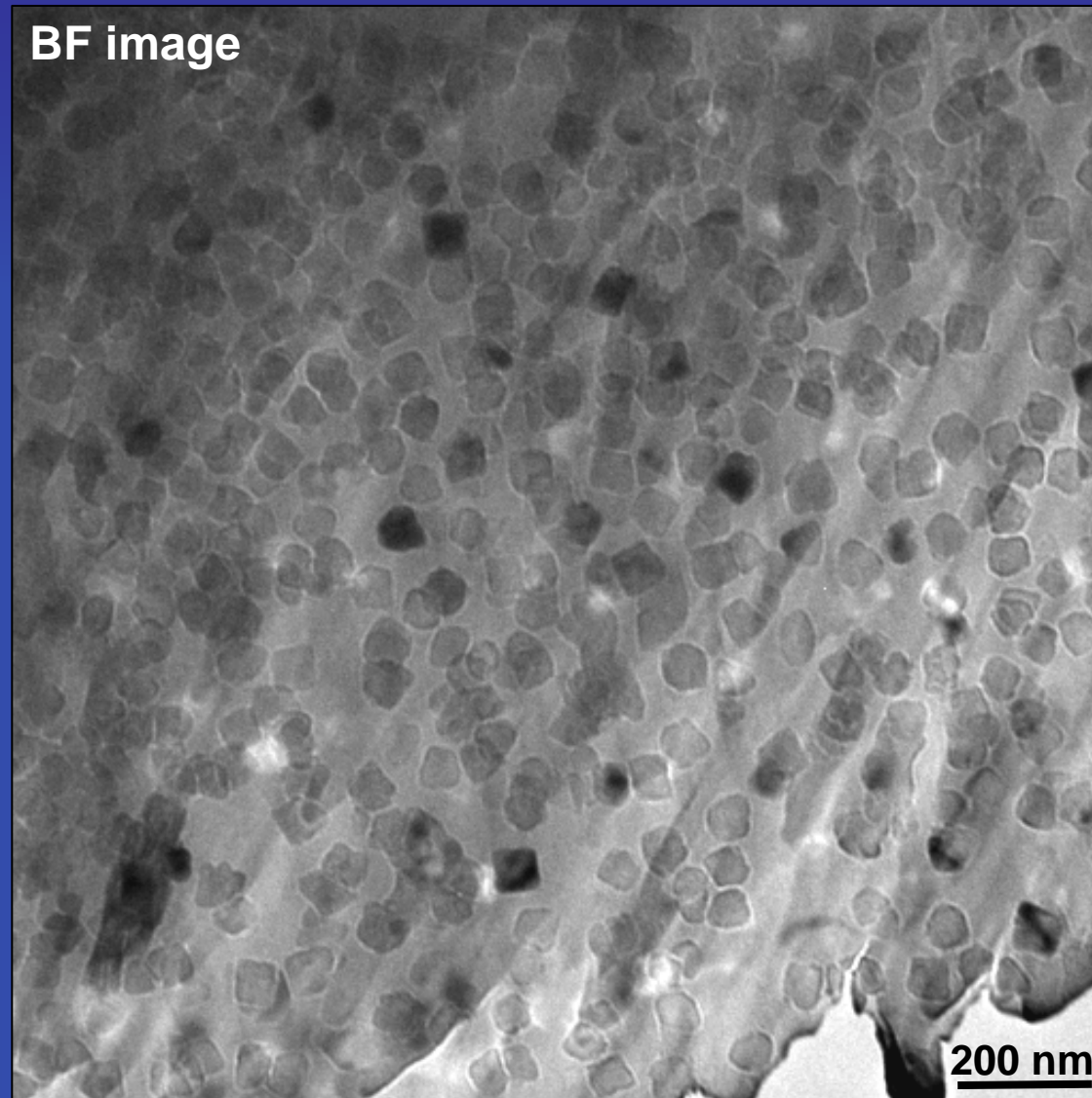
That's a good  
fit!!

# Forget it !!!

The first curve is a polydisperse sphere

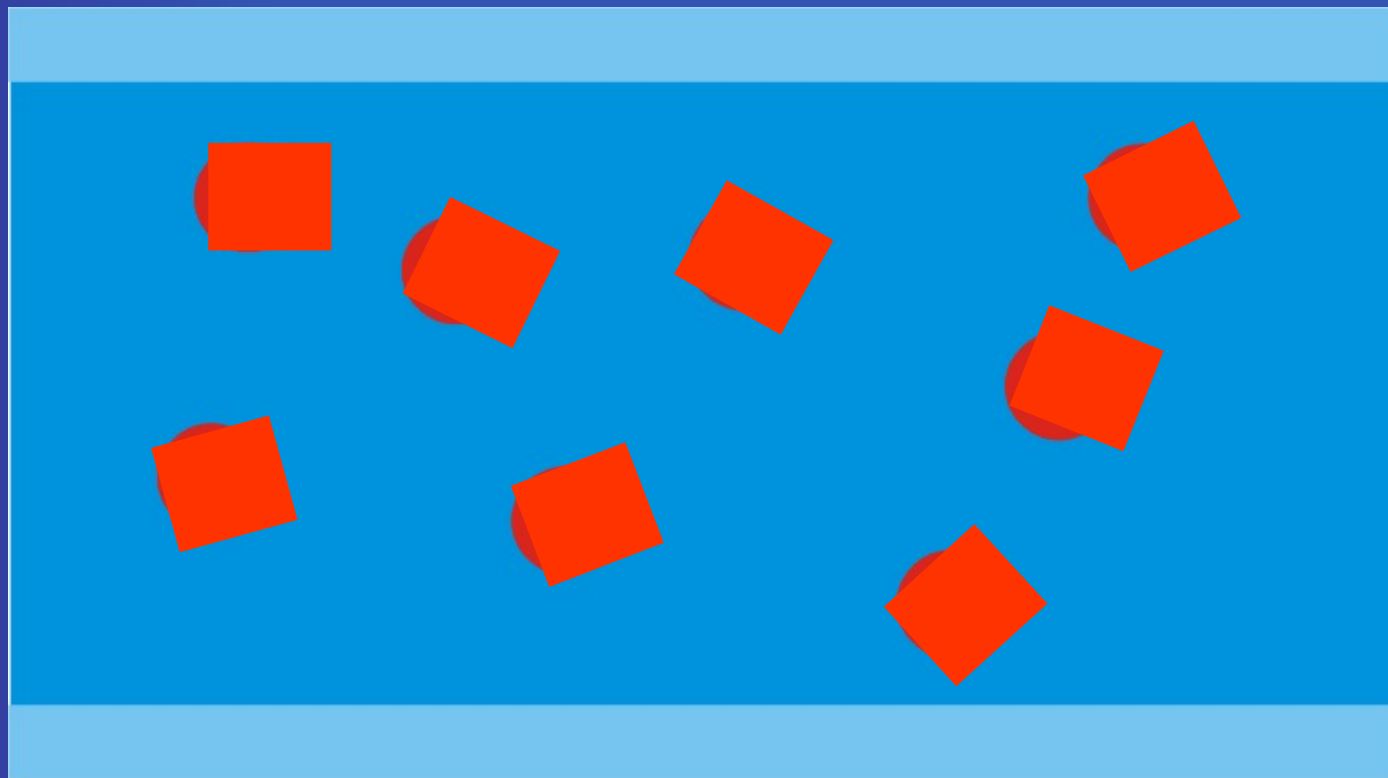
The second is a monodisperse cube

# TEM



The particles are not spherical but cubes.....

# The correct morphology (3)



# Summary:

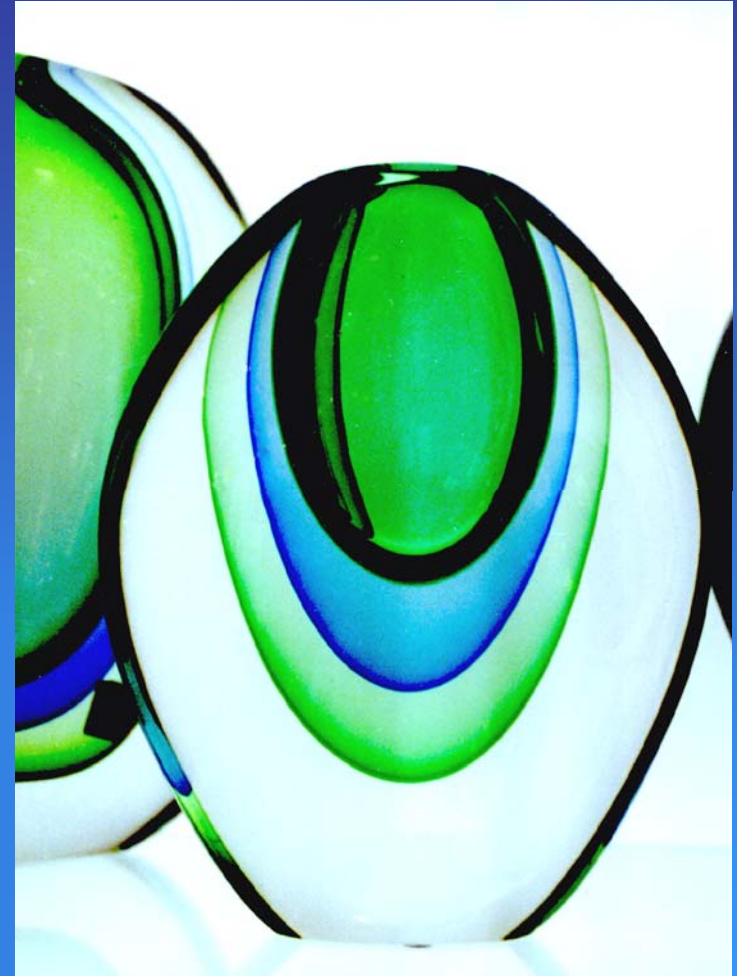
- Spinel grows in bulk of sample
- Stuffed quartz is formed by surface crystallization
- Monodisperse crystallites can be formed by heating sample (uniformly)
- These are formed by a diffusion limited process
- Always try to back up your SAXS results with real space data

# The main message:

- One can obtain a wealth of information with a combined SAXS/WAXS experiment
- Surface/volume ratio, crystallisation energy, surface roughness, volume fractions, morphology, crystallite size etc. etc.

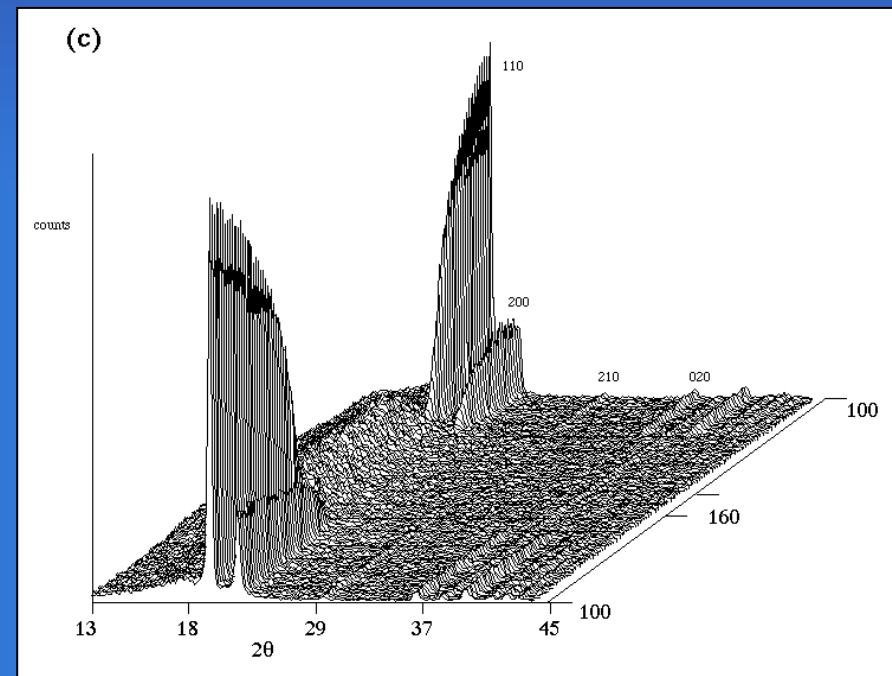
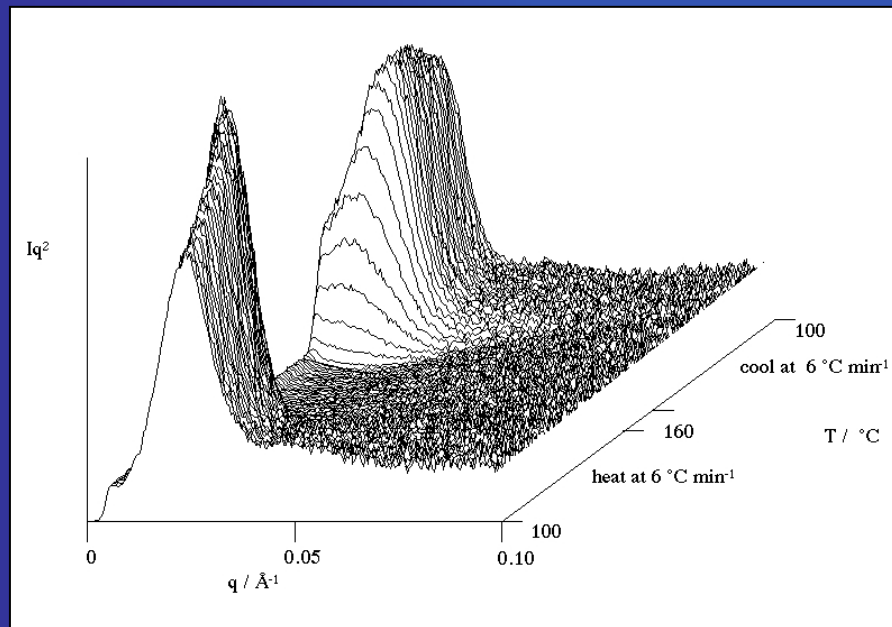


## Venetian glass

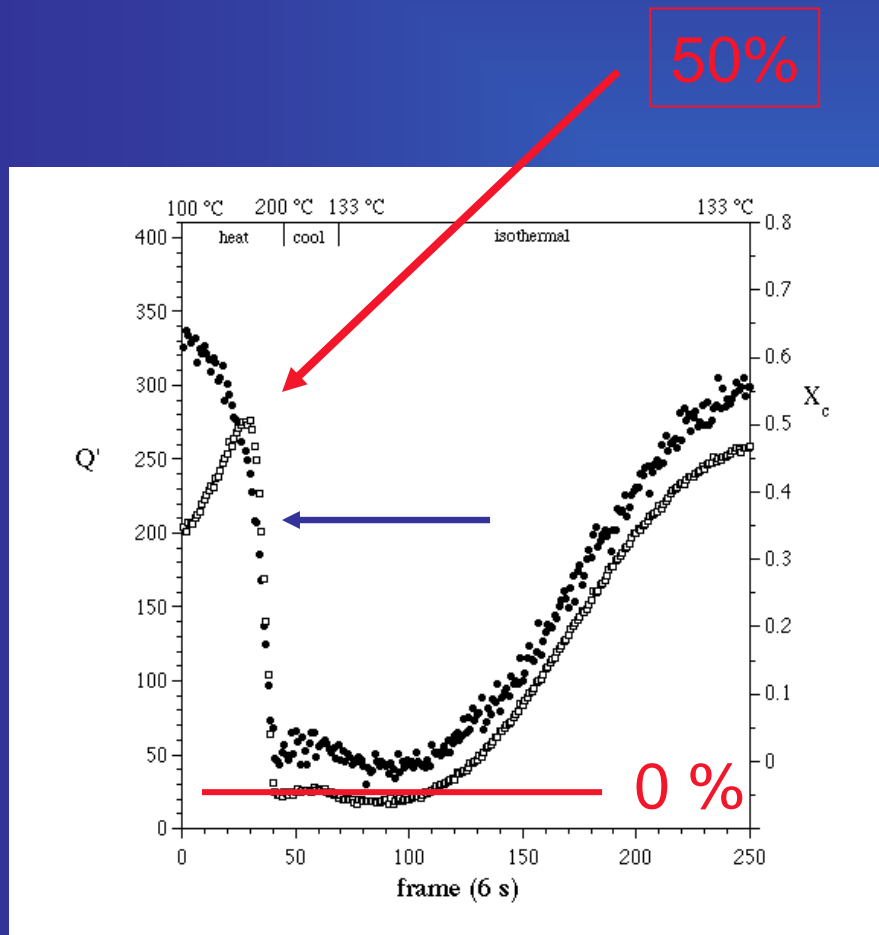


# Optional when time left

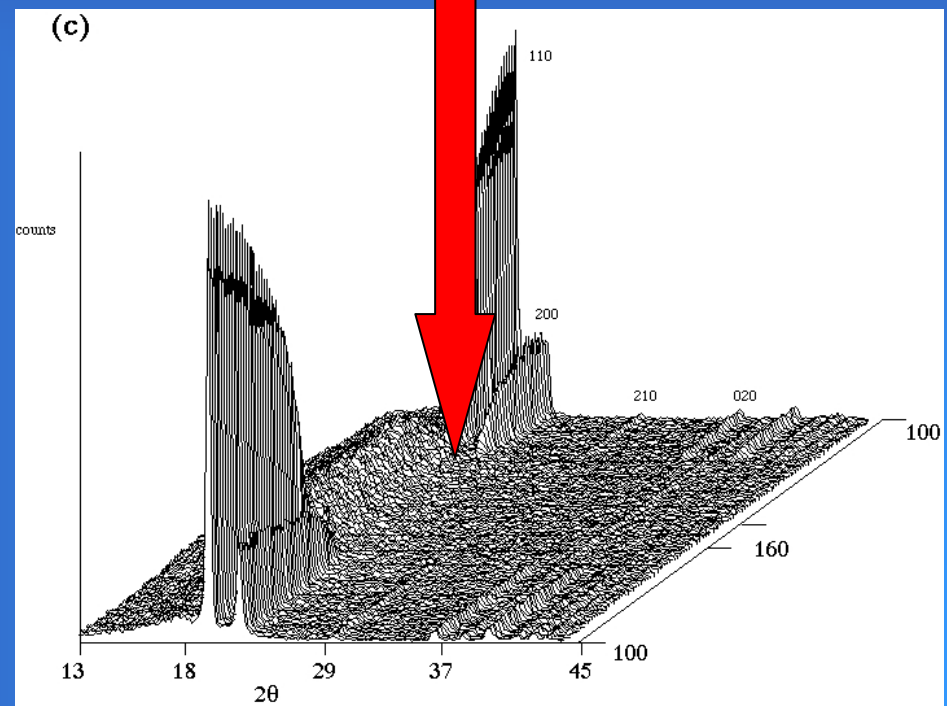
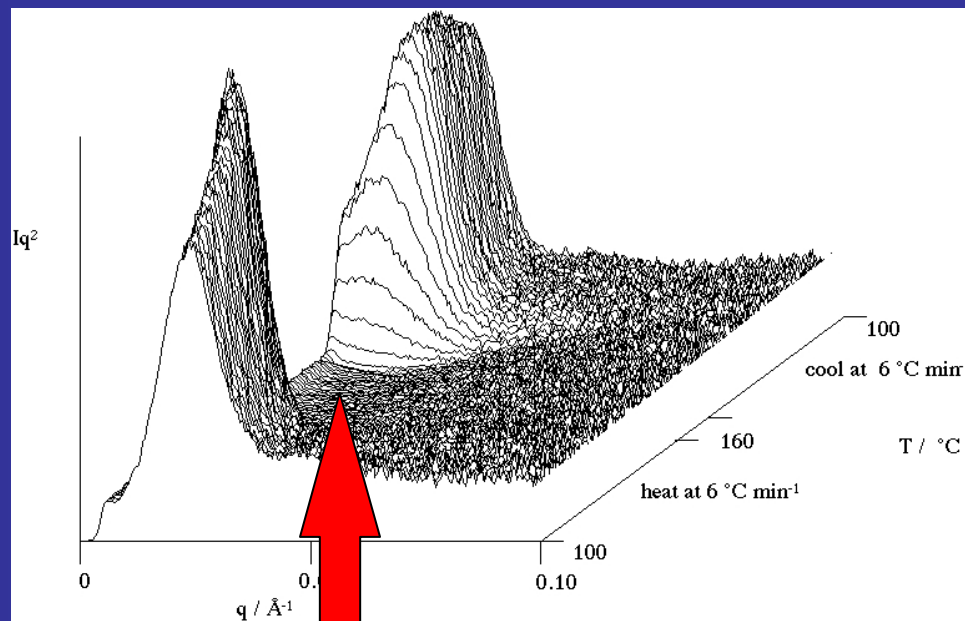
# Heating/cooling cycle on HDPE



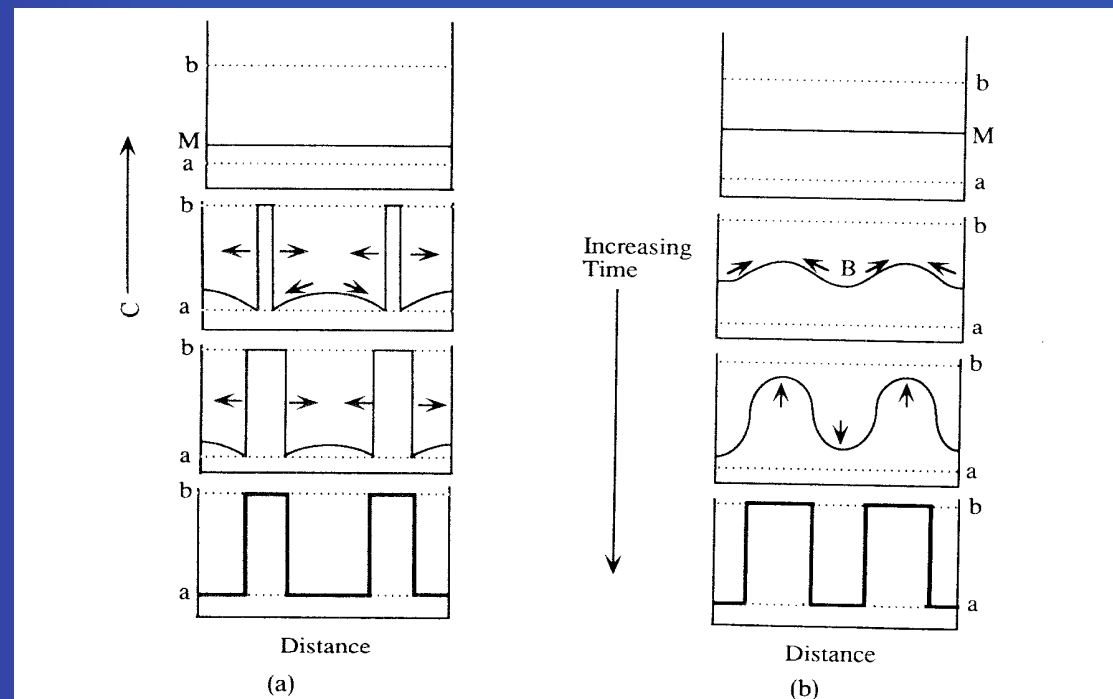
# Routine experiment



- Crystallinity 50% when SAXS invariant has a maximum
- Intensity of crystalline WAXS peaks has linear relation with degree of crystallinity
- Combination of these data sets allow construction of crystallinity scale



# Nucleation and growth or spinodal decomposition?



**Figure 4-7.** Growth of the phase separation for (a) nucleated-type and (b) spinodal-type mechanisms with time at a given temperature. Note that in the nucleated-type mechanism, the droplets have a fixed composition “b” with an interfacial composition “a.” The growth is in the physical size of the droplet. In the spinodal-type mechanism, a small fluctuation in composition gradually grows over a period of time via “uphill” diffusion. The terminal compositions in each case are “a” and “b.” The ratio of the two phases depends upon the starting composition.

# What can the experiment tell us?

If nucleation and growth



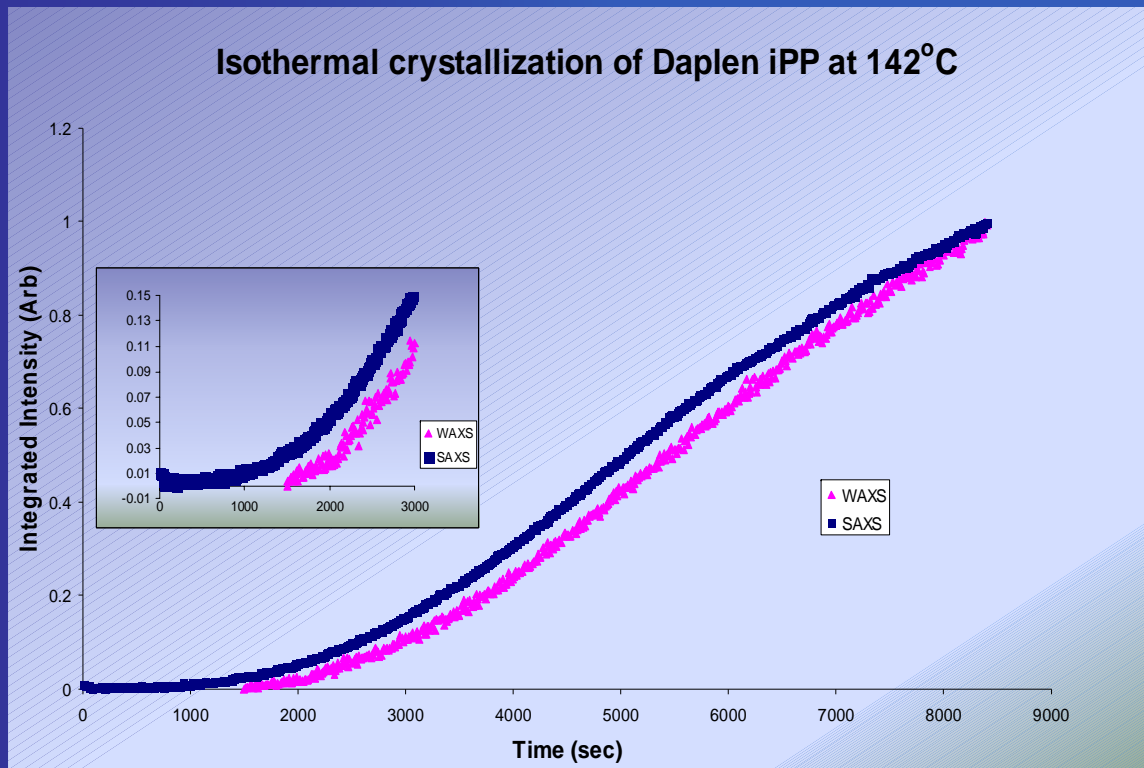
SAXS due to lamellae appear at same time as crystalline WAXS peaks

If spinodal decomposition



SAXS due to density fluctuations appear before WAXS crystalline peaks

# Density fluctuations appear before crystalline peaks



- Better quality than anywhere else due to new WAXS detector



I hope I have given you a taste  
of the possibilities of SR and  
SAXS/WAXS  
experiments



# Some good books for beginners

- Glatter and Kratky
- Feiguin and Svergun
- Lindner and Zemb
- Roe