Combined data sets

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

Why talk after lunch?

Lunch is late…..

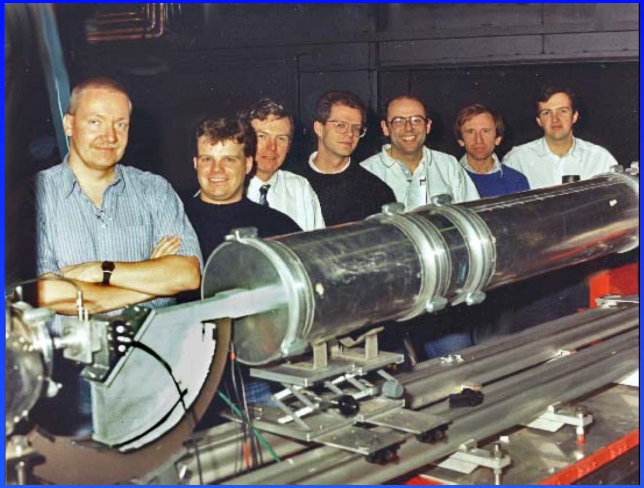
Now we only have to fight the after lunch desire to sleep…..

Outline

- Combined data sets
- Cordierite glass crystallisation kinetics (SAXS/WAXS)
- Polymer phase separation (SAXS/FTIR)

Technique combinations

- Real pioneer Prof H.G. Zachmann from Hamburg University



8.2 Daresbury

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

BM26B ESRF

7.3.3 ALS Berkeley

…. and also with some EAXFS lines……

Why technique combinations?

- In which order do events take place?
- Inhomogeneous samples
- Connection chemical and physical changes
- Connection large and small scale
- Etc.

Why not?

- Time saving?   B*ll*cks

- Optimum data quality for each technique? Forget it!!

What is possible in combination with SAXS?

- X-ray based
  - WAXS/powder diffraction
  - EXAFS
- Non X-ray
  - DSC, FTIR, Raman, UvVis, etc. etc.
  - It depends on the ingenuity of the user

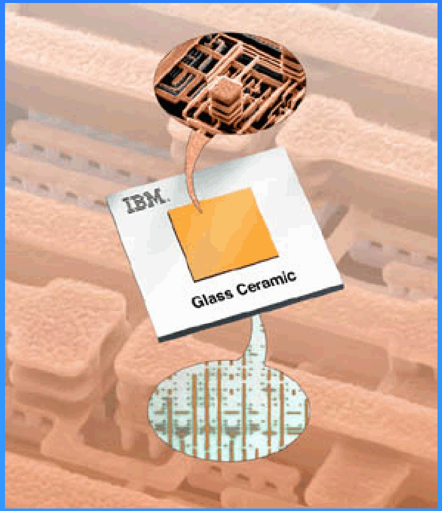
Cordierite based ceramics

Ceramic replacement teeth

Pizza baking stones

Refractory parts

Ceramic chip carriers



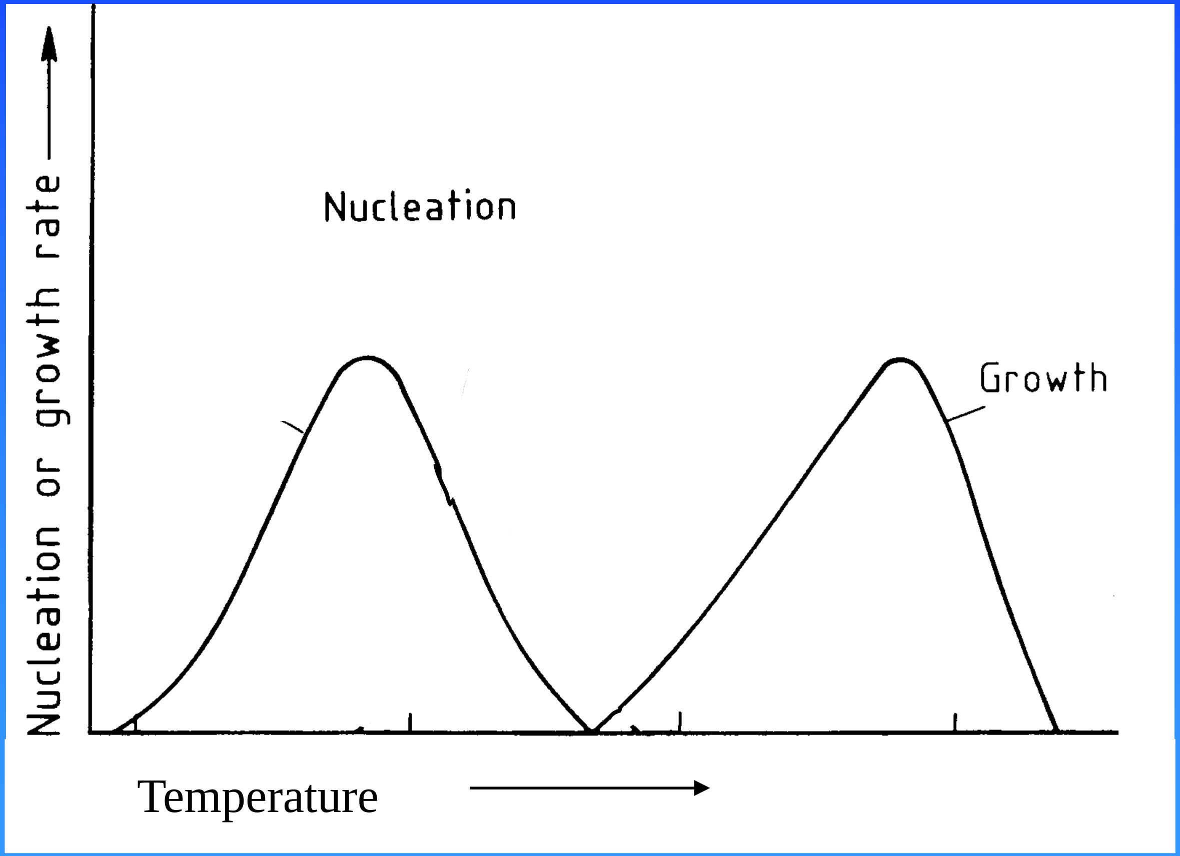
Car exhaust soot filters

Louis Cordier
1777- 1861

Why cordierite glass ceramic?

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

Cordierite glass devitrivication

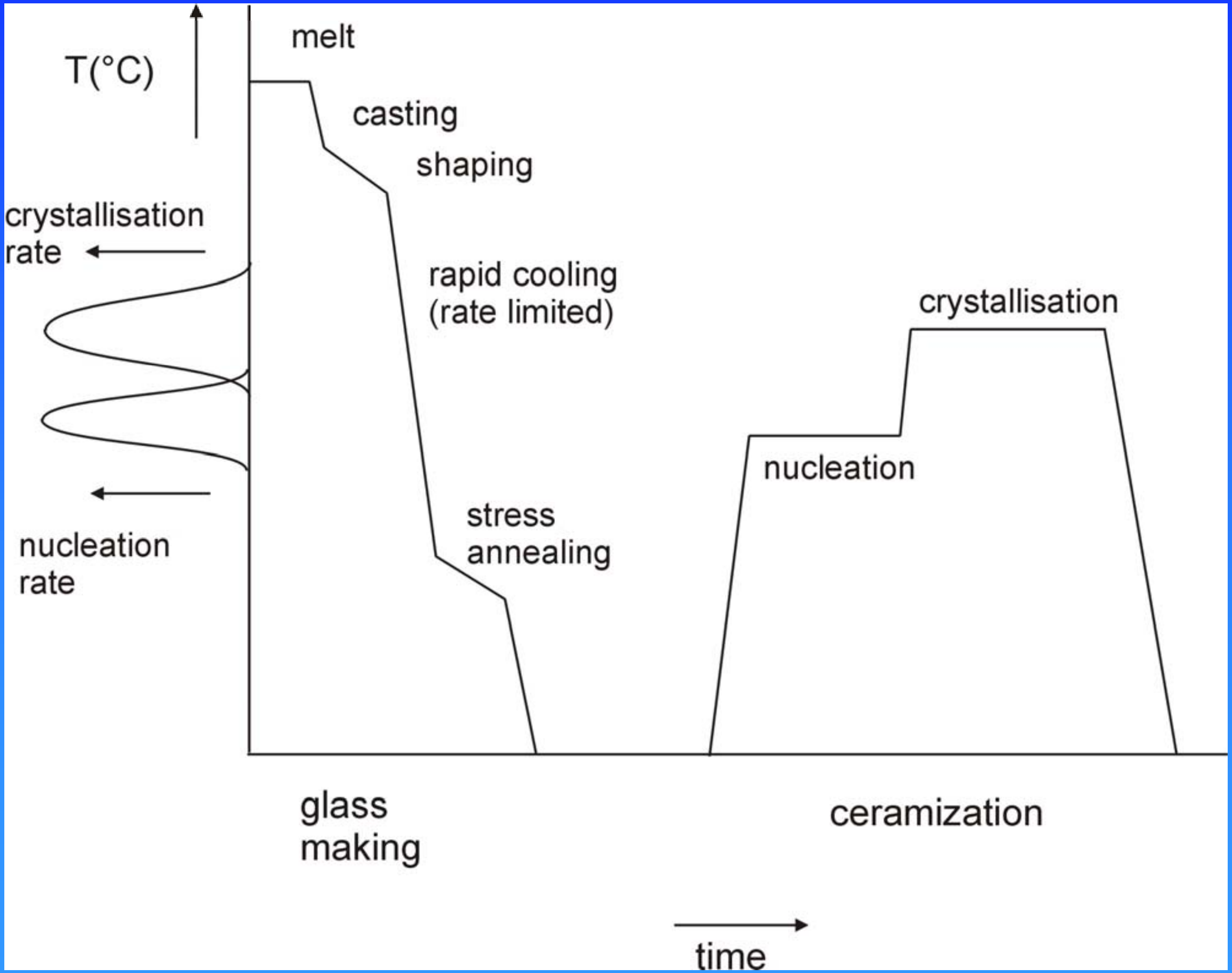


$Mg_2Al_4Si_5O_{18}$
doped with
0.34 mol% Cr_2O_3
(crystallization enhancer)

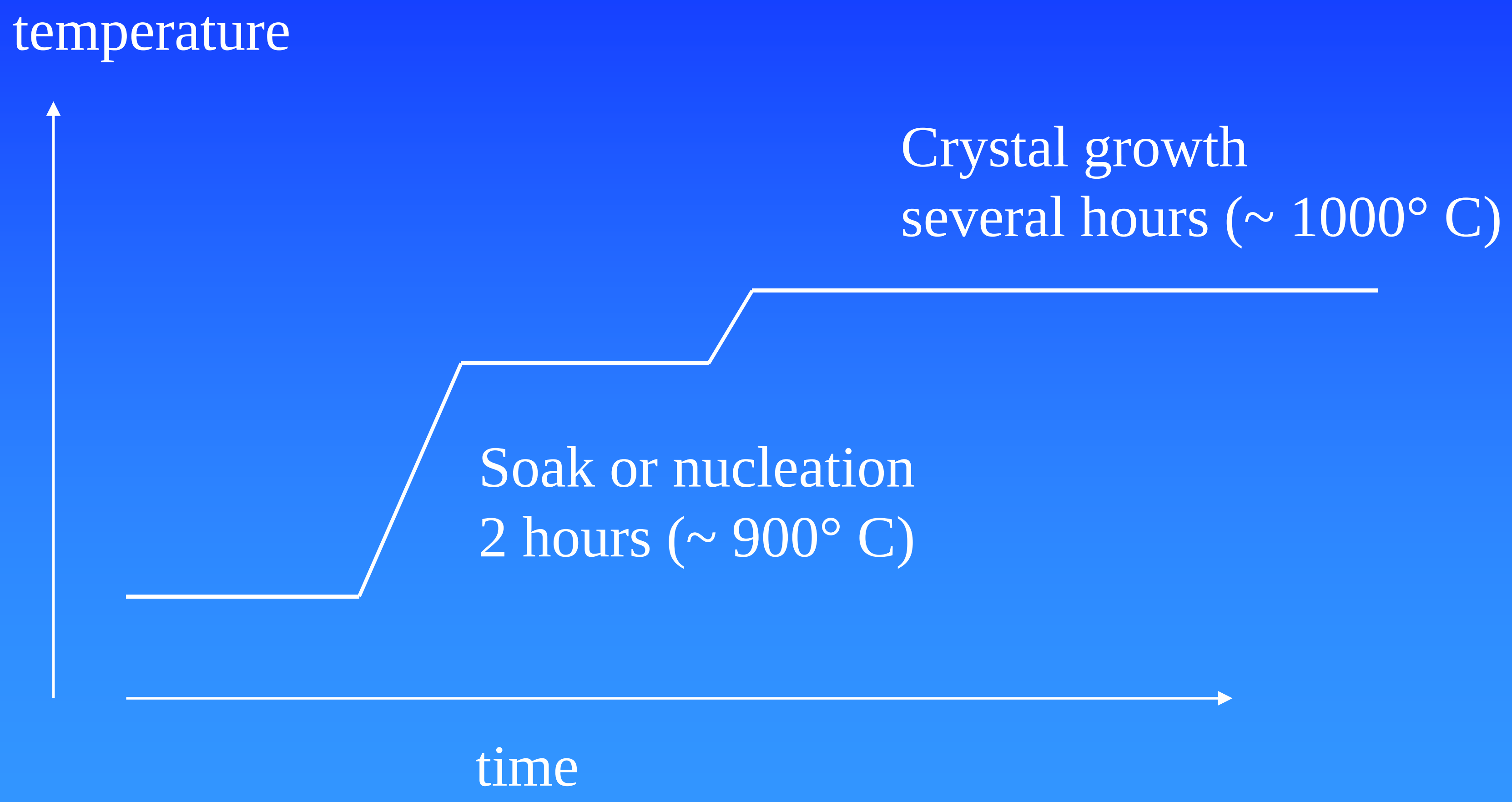
Prifysgol Cymru
Aberystwyth
The University of Wales

DUBBLE

Normal production process



Experiment on 75 micron thick platelet



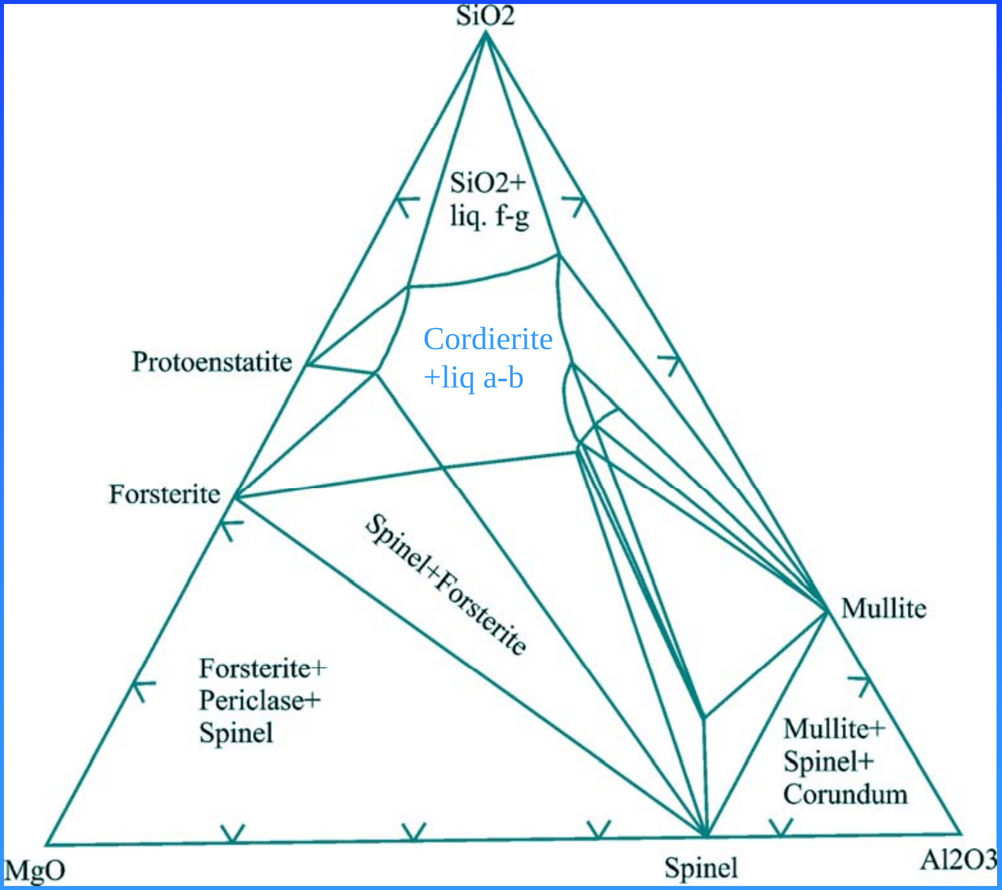
temperature

Crystal growth
several hours (~ 1000° C)

Soak or nucleation
2 hours (~ 900° C)

time

Messy phase diagram

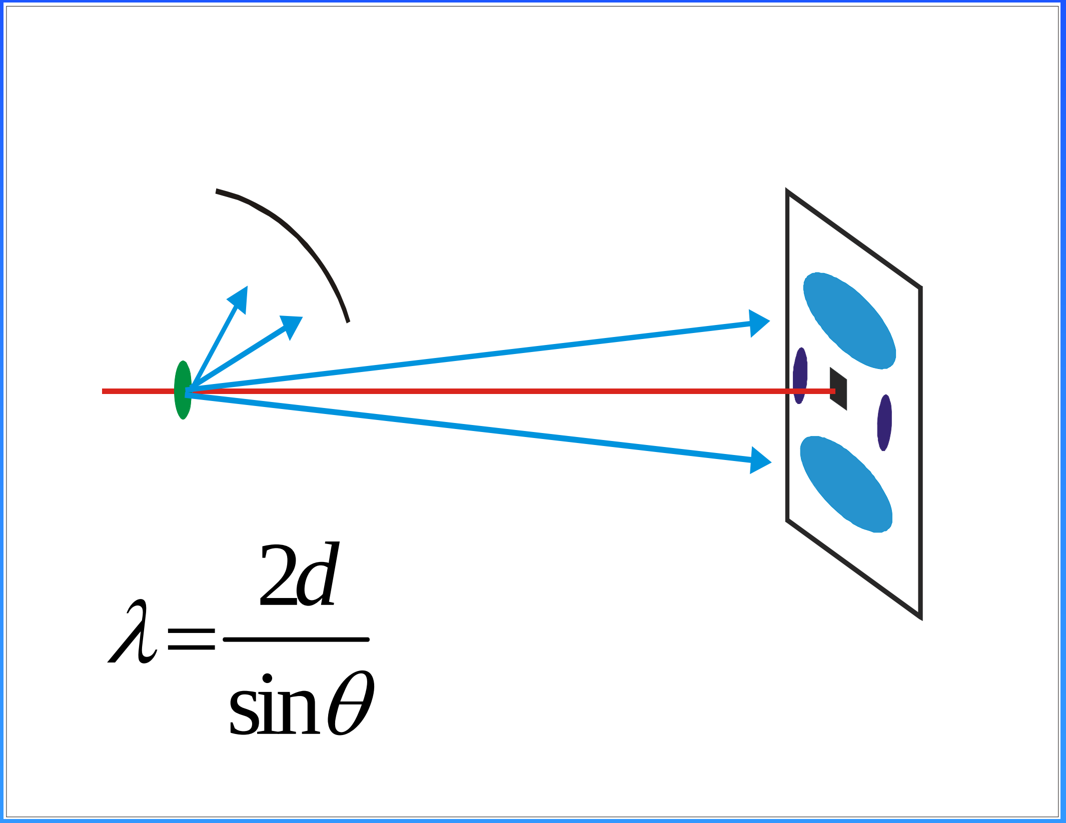


1460° C
Mullite $3Al_2O_32SiO_2$
Protoenstatite $MgOSiO_2$
Spinel $MgO.Al_2O_3$
Forsterite $2MgOSiO_2$

W. Schreyer, J.F.Schairer
J.Petrol., 2, 361,1961

SAXS and WAXS

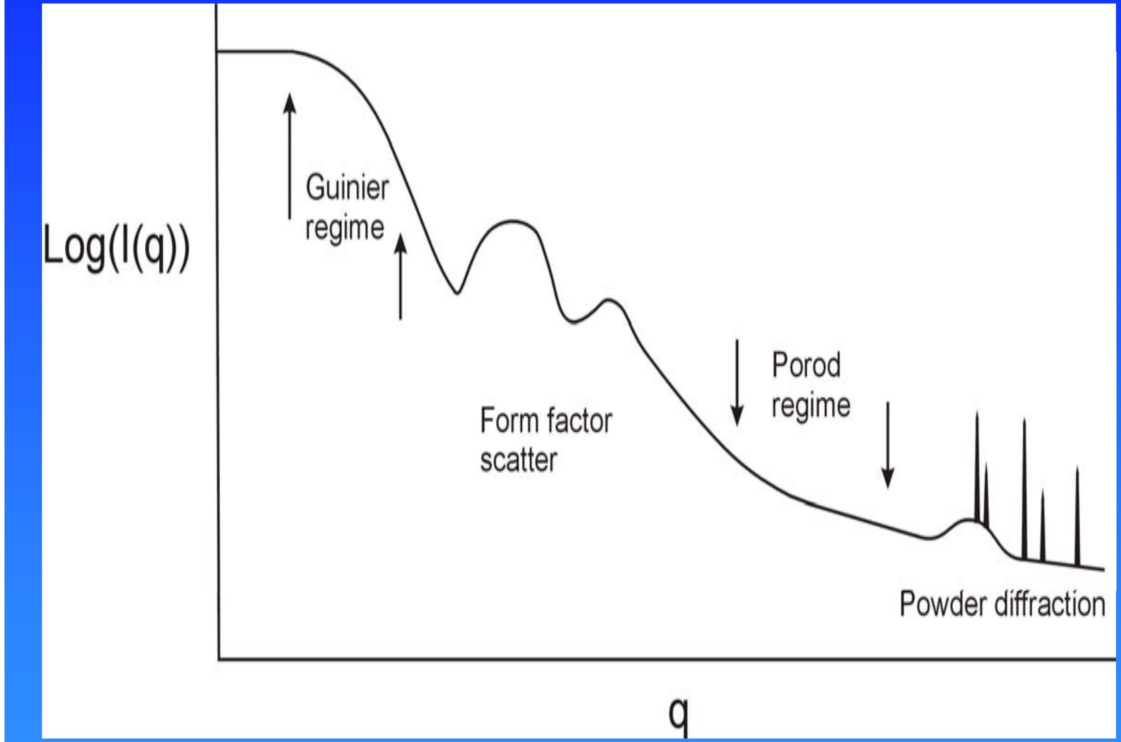
d small, θ large



$$\lambda = \frac{2d}{\sin\theta}$$

θ small, *d* large

SAXS/WAXS



500 nm

0.2 nm

1 limit q → 0
electron density contrast
density fluctuations

2 Guinier range
particle size
interparticle scattering

3 particle shape

4 Porod range
particle surface
Surface/volume

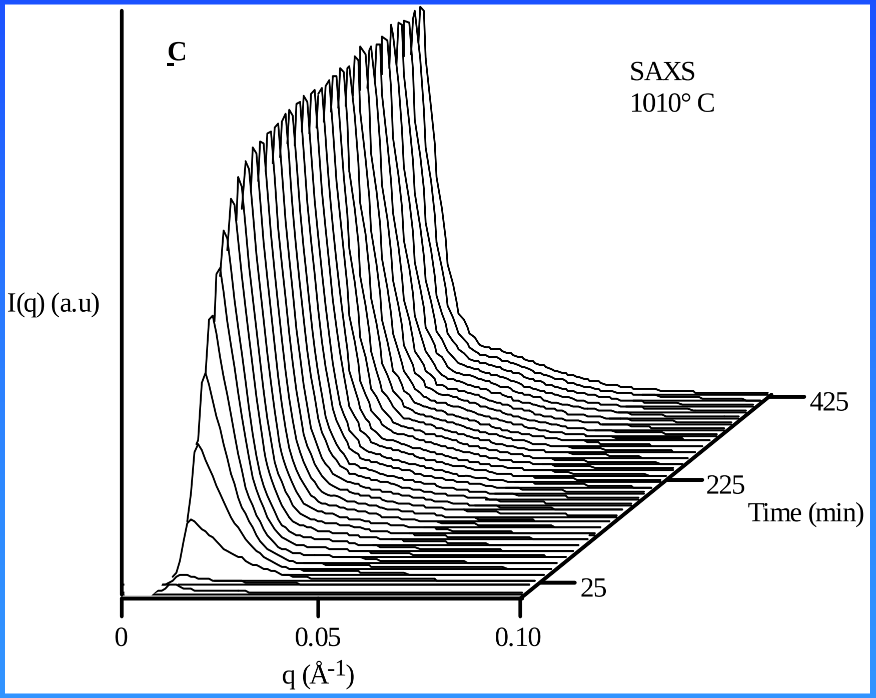
5 Intermolecular/atomic
ordering

The sample is a platelet

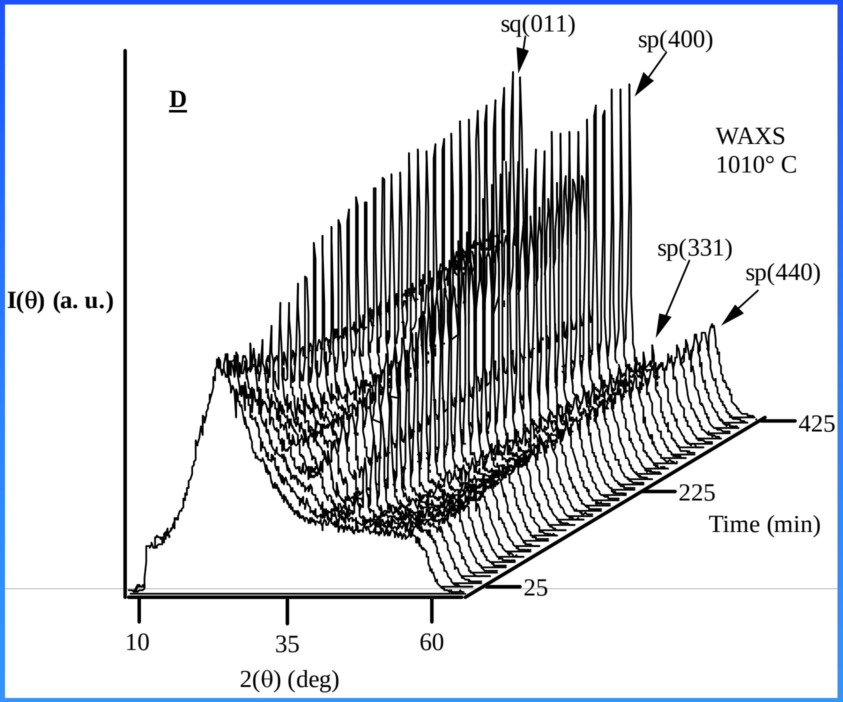
Not a powder

Structure development

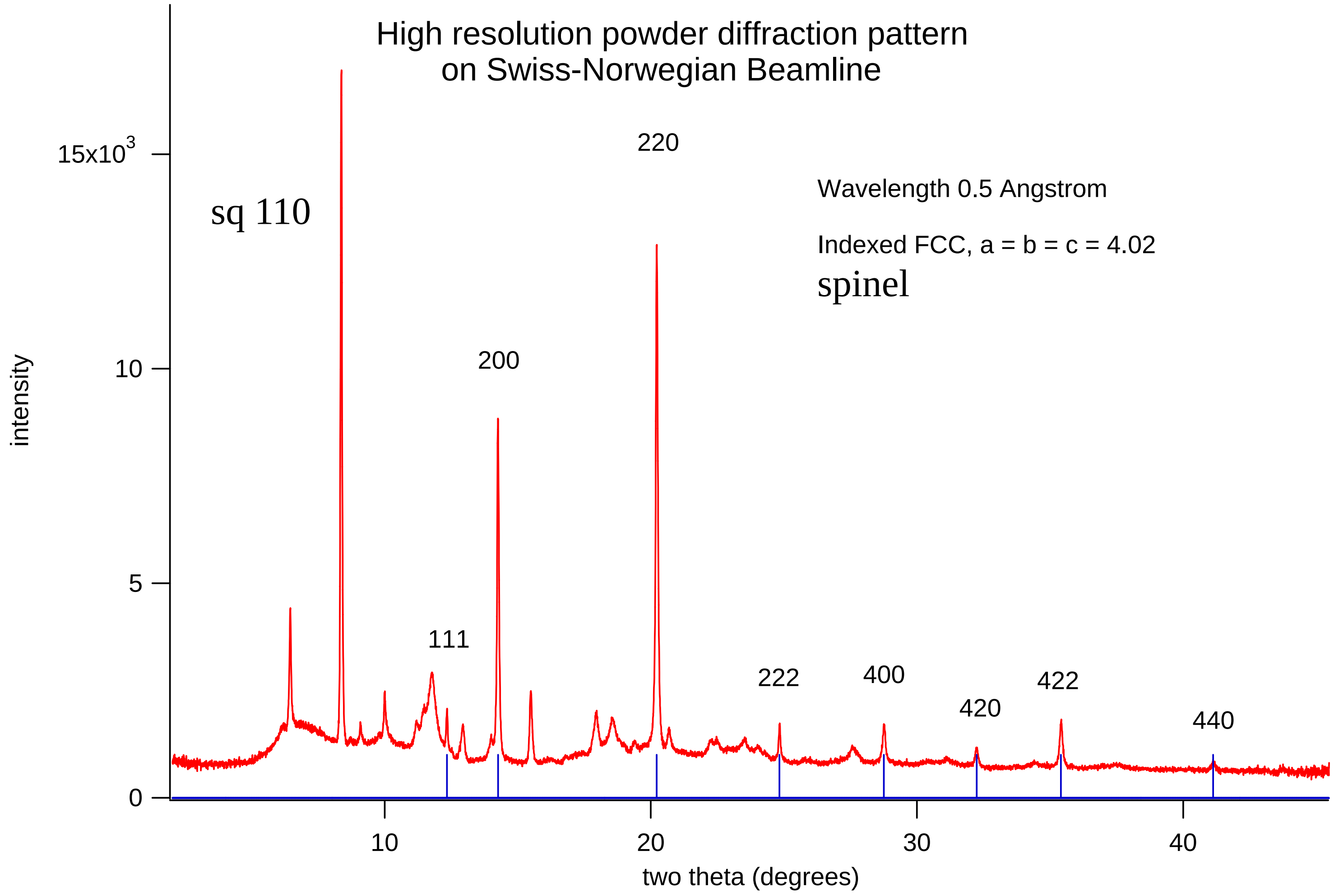
Data taken at 1 minute/frame



SAXS



WAXS



High resolution powder diffraction pattern
on Swiss-Norwegian Beamline

sq 110

Wavelength 0.5 Angstrom

Indexed FCC, a = b = c = 4.02

spinel

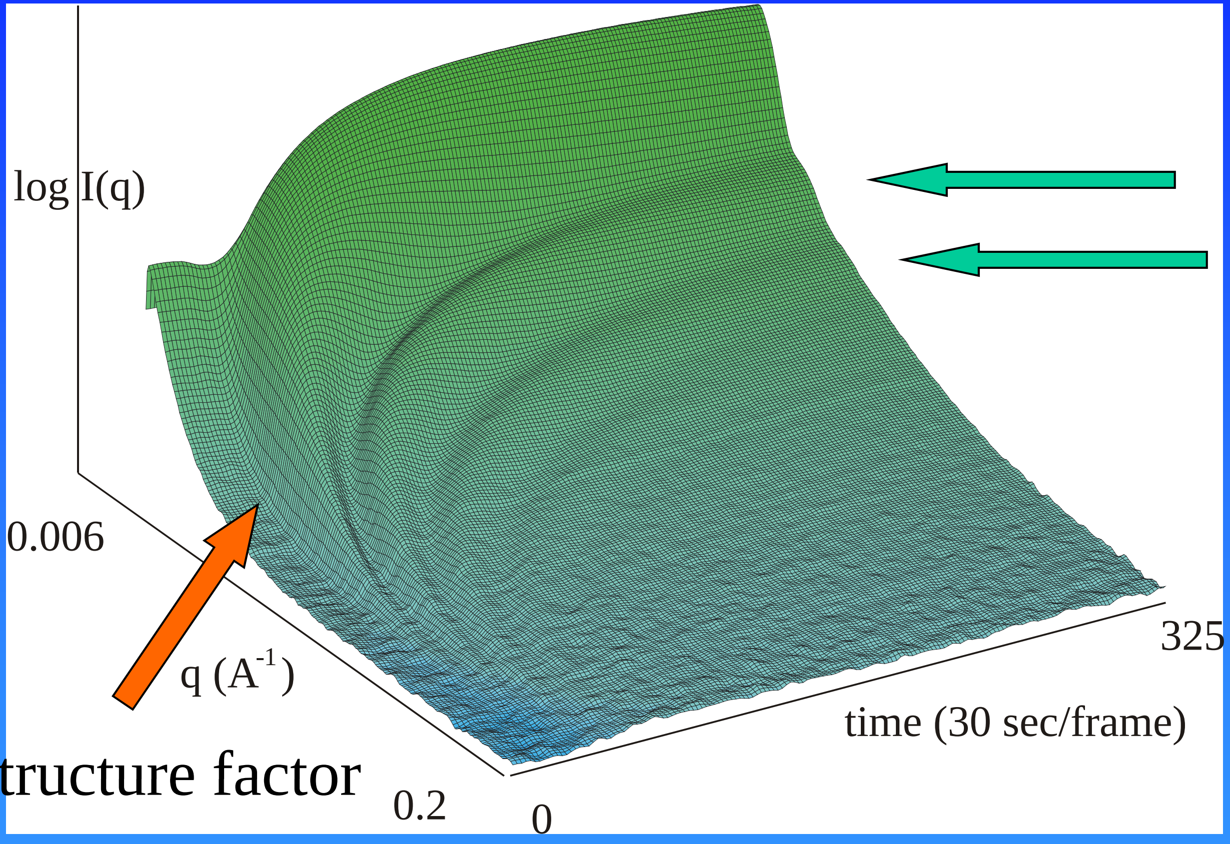
Post mortem powder diffraction: three different phases

spinel

stuffed quartz

+ large amount glass matrix

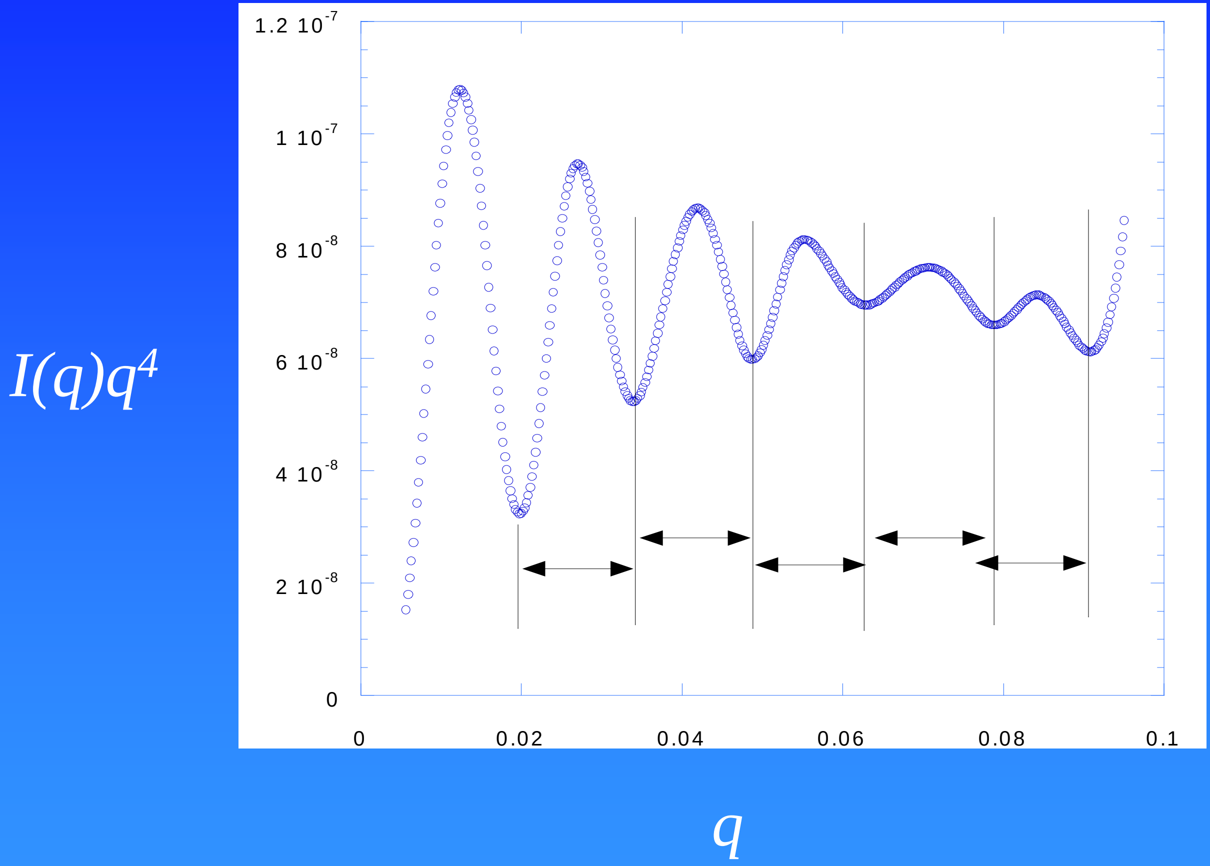
SAXS **$I(q) = S(q)*|F(q)|^2$**



Structure factor

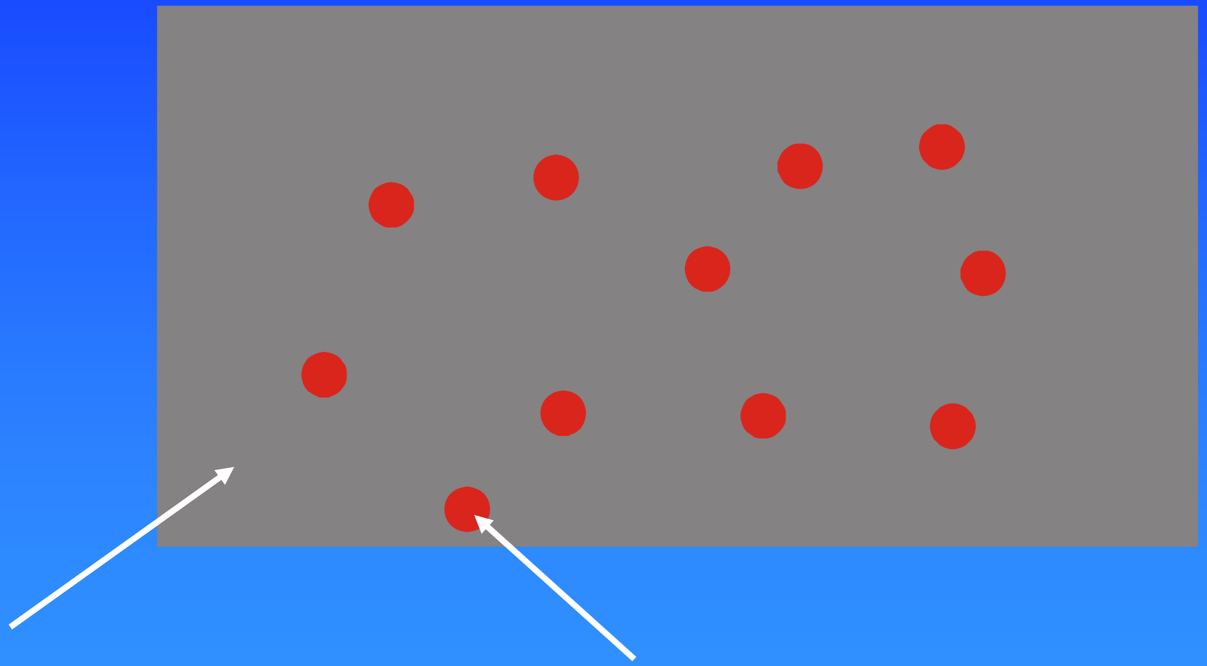
Form factor peaks
(up to 5th order)

$\Delta R/R \sim 0.04$



This can be fitted to a spherical form factor

Morphology (1)



glass

crystalline sphere (monodisperse)

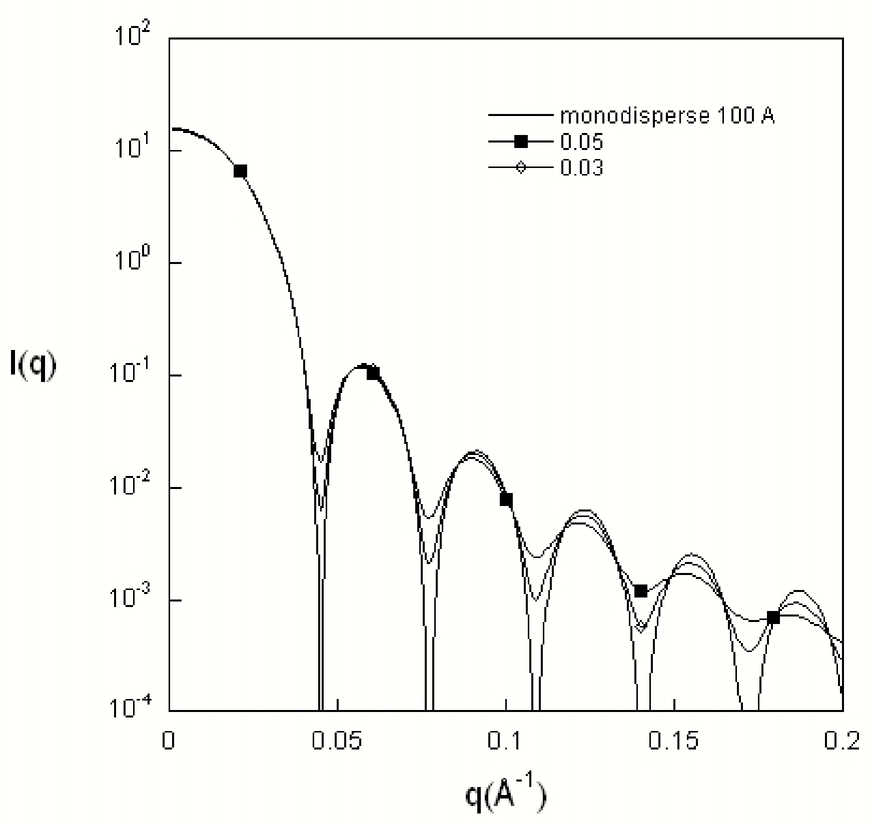
Particle size from SAXS (1)

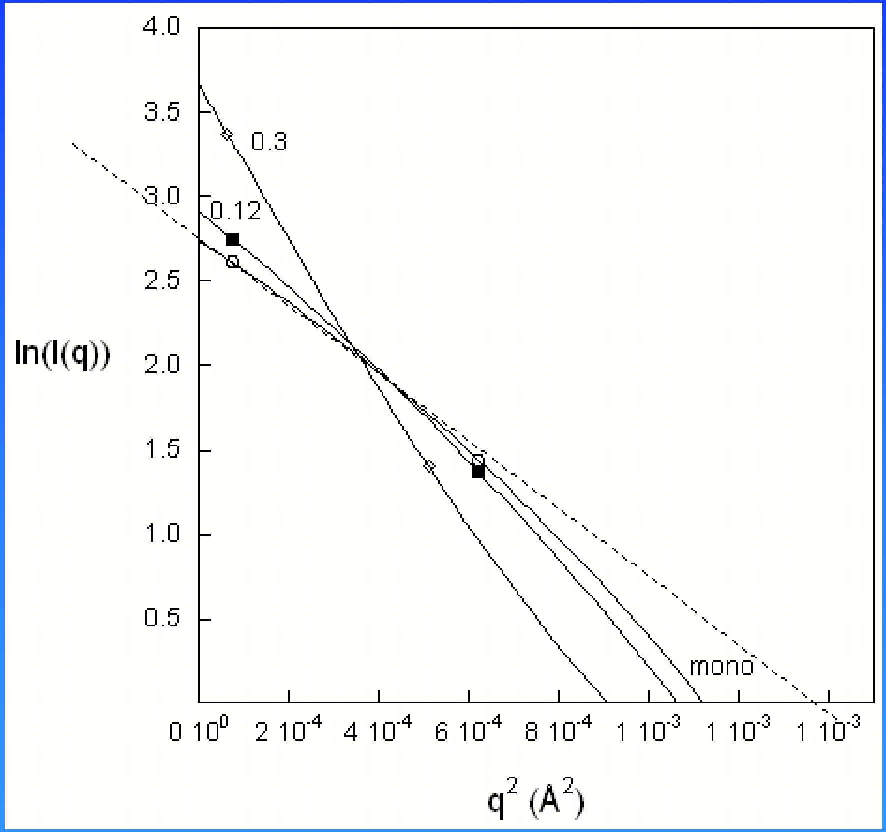
- Guinier approximation

$$I(q)_{q\to 0} = I(0)\exp(-\frac{R_g^2 q^2}{3})$$

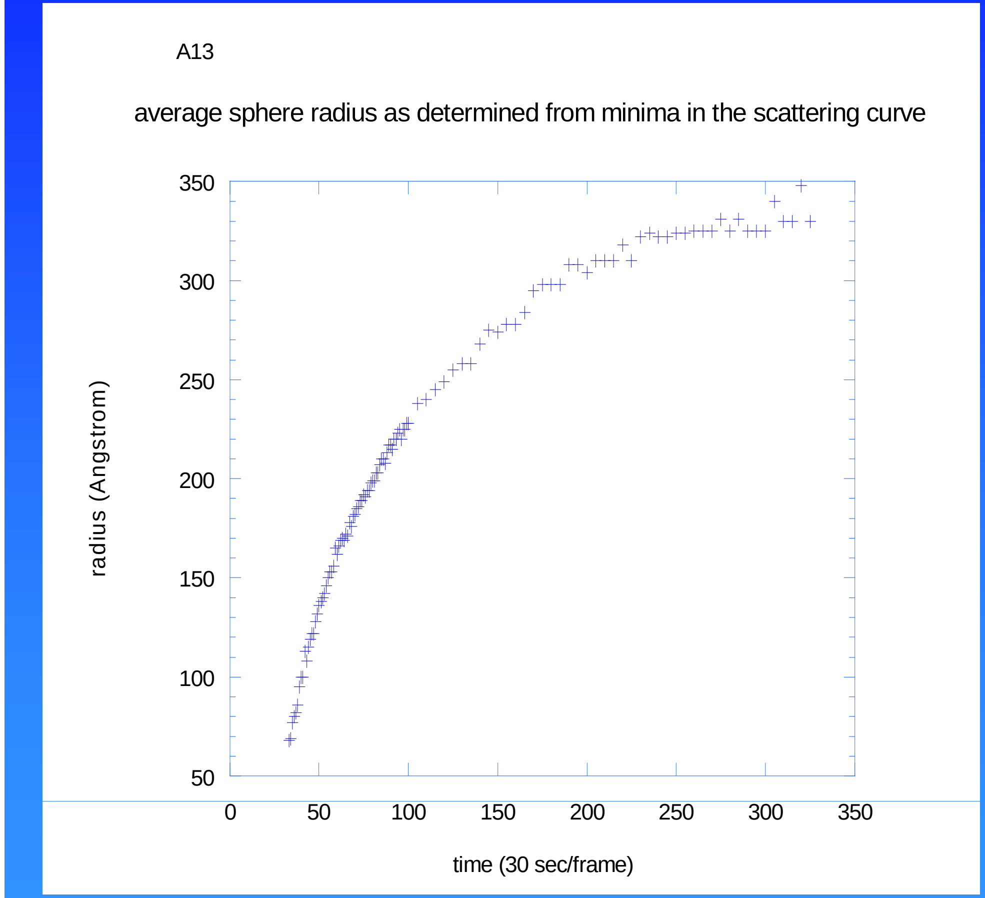
  - Don’t forget this is an approximation! (Taylor expansion)
  - $qR_g < 1$ should hold with q defined as $q = 2\pi / d$
  - for $qR_g = 1.5$ there is an error margin of 20 – 30%

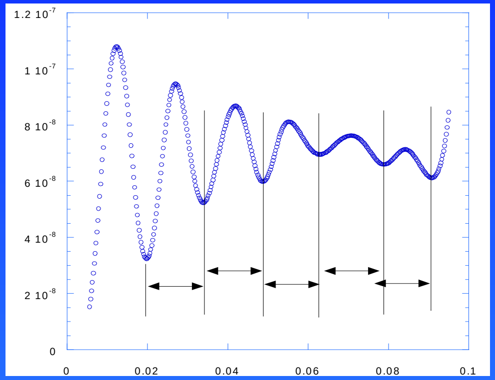
Polydispersity effects on R_g





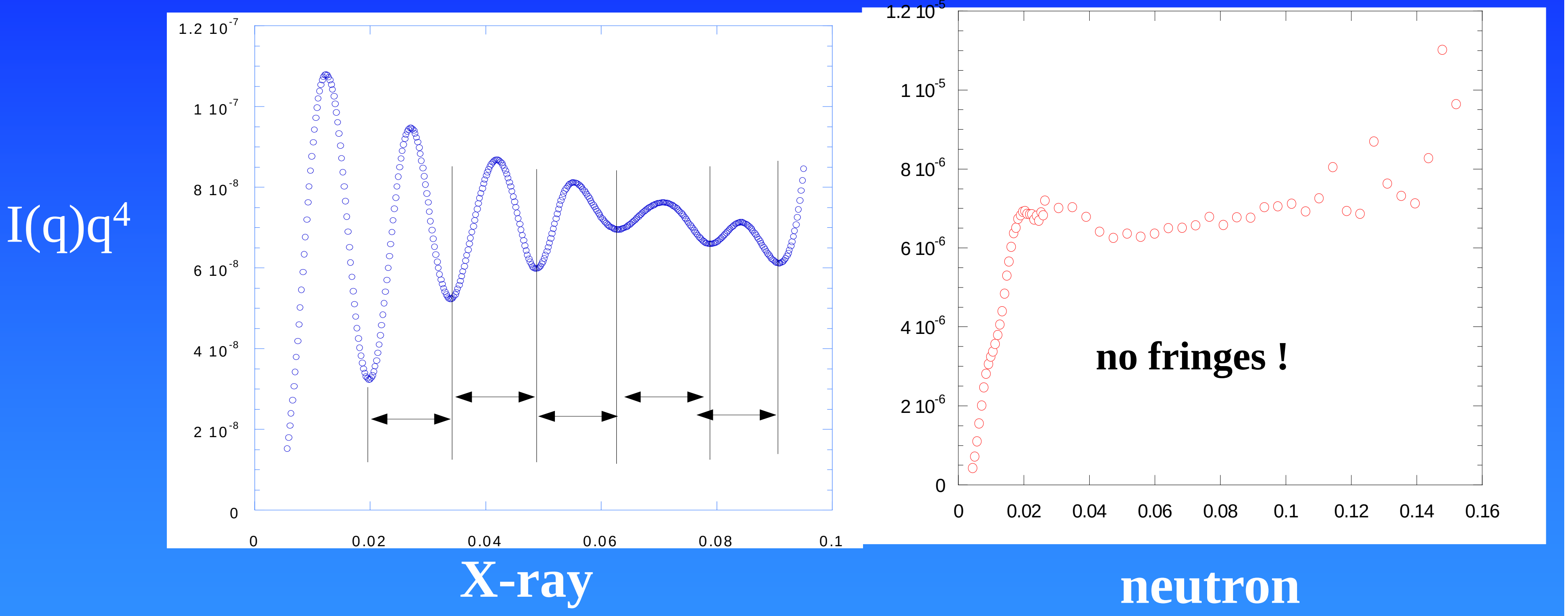
Particle size from SAXS (2)



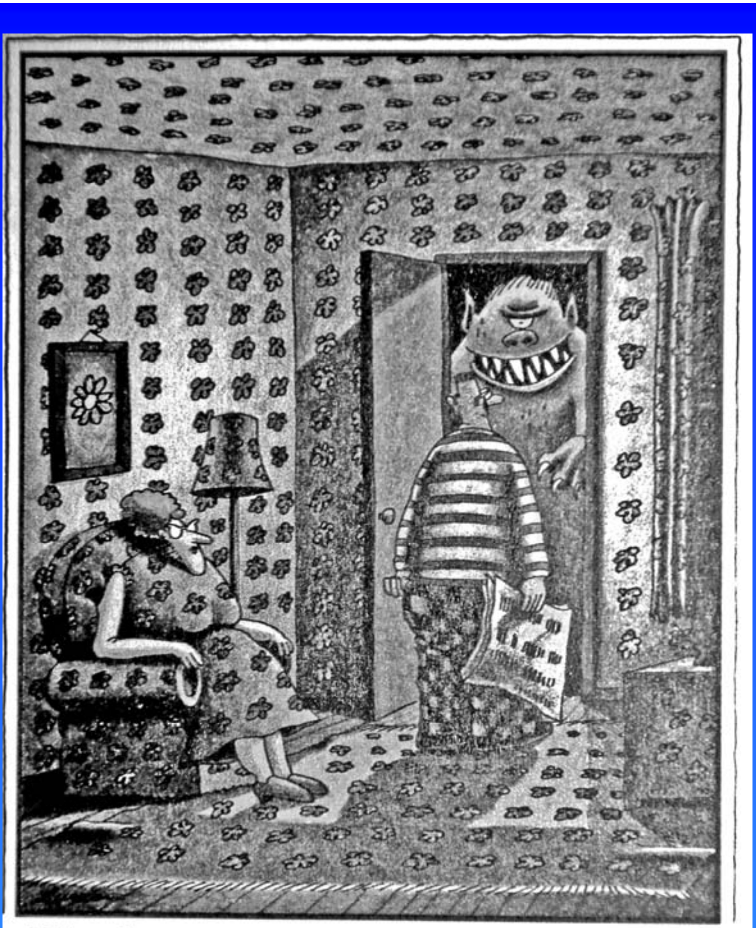


- Particle size
- Minima in form factor
- More accurate than Guinier approximation

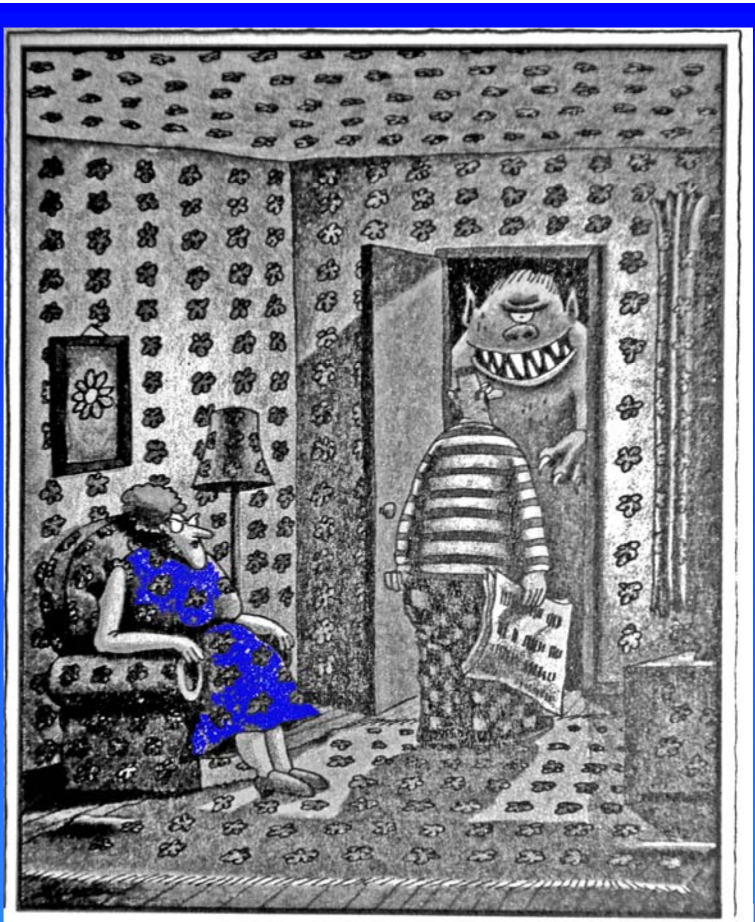
Neutron scattering



Neutron data courtesy Stuart Clarke



When the monster came, Lola, like the peppered moth and the arctic hare, remained motionless and undetected. Harold, of course, was immediately devoured.



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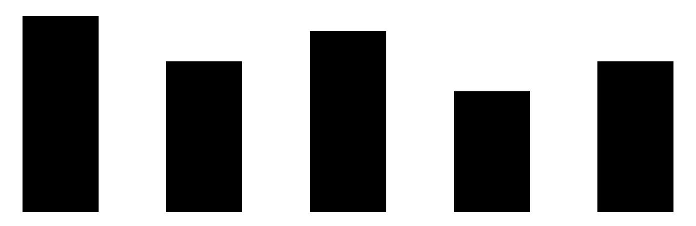
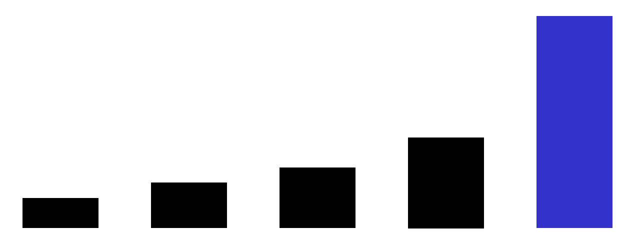
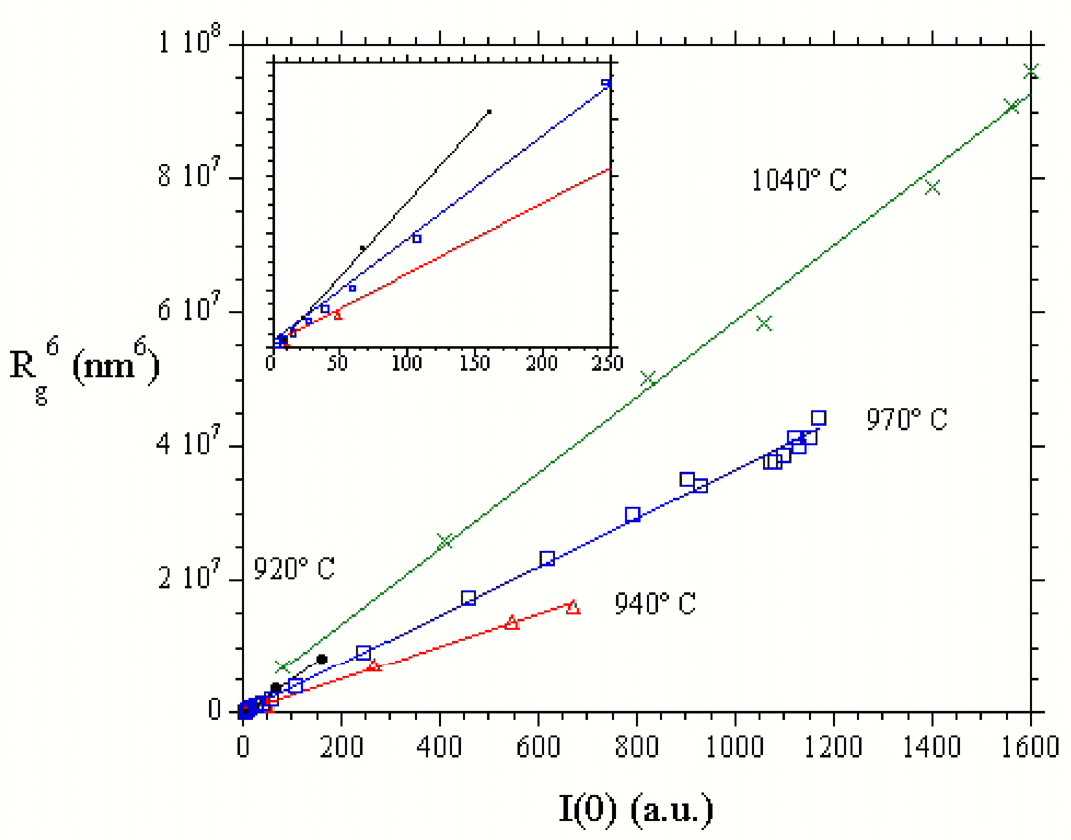




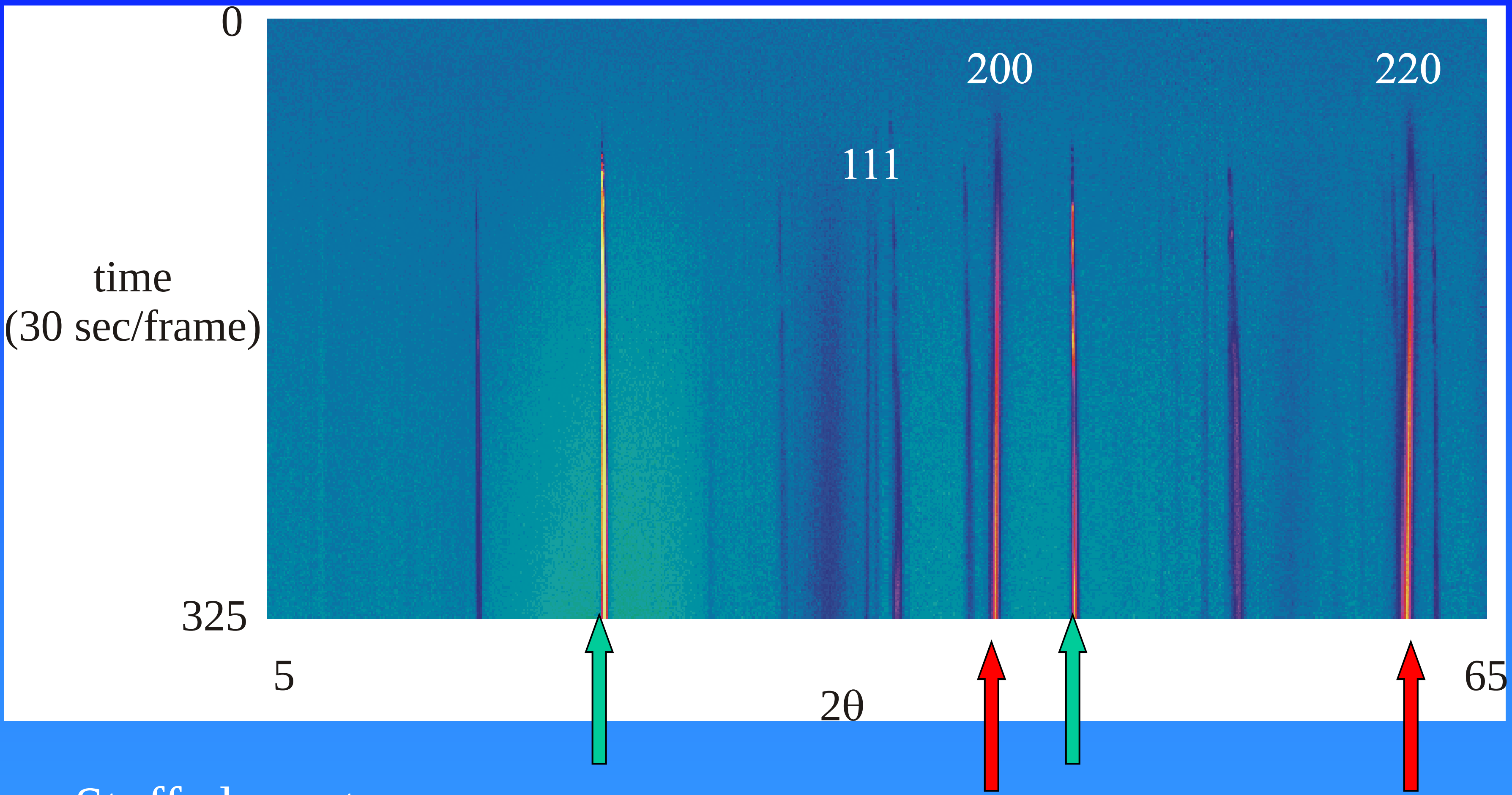
This tells us:

- There is something ‘heavy’ in the scattering entities
- This can only be Chromium, added as crystallisation enhancer

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



WAXS data



Stuffed quartz

Spinel unit cell increases in time

$MgOAl_2O_3$ FCC a = b = c = 8.06 Å

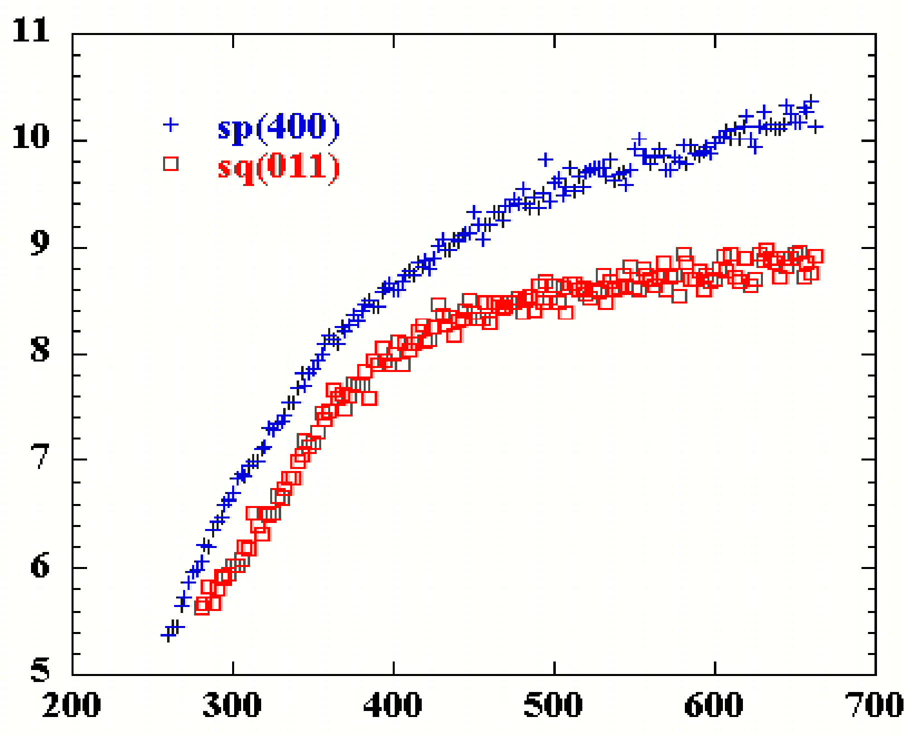
Spinel

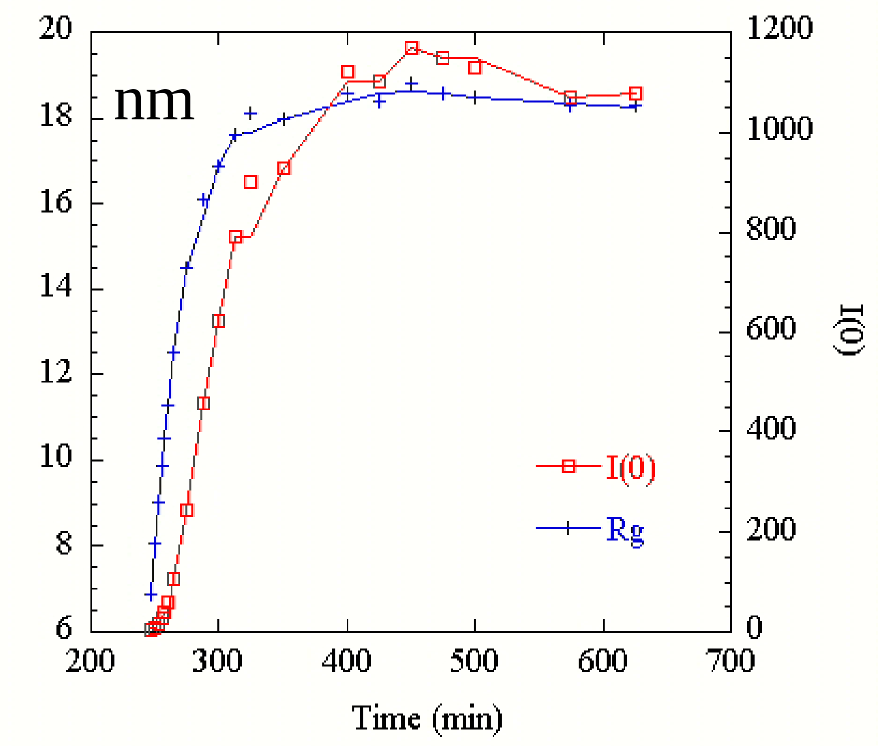
Stuffed quartz unit cell decreases in time

trigonal a = b = 5.13 Å c = 5.37 Å

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

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

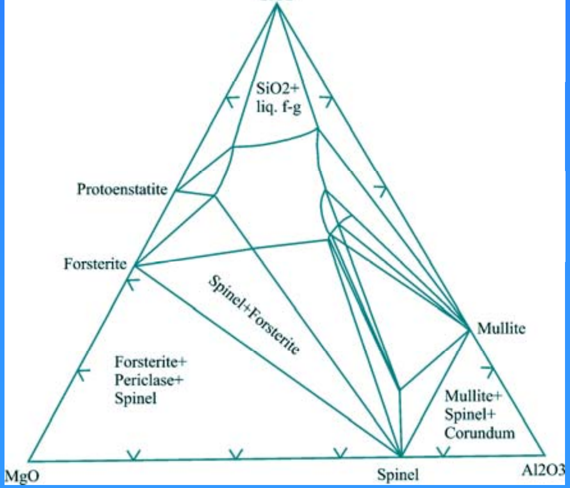




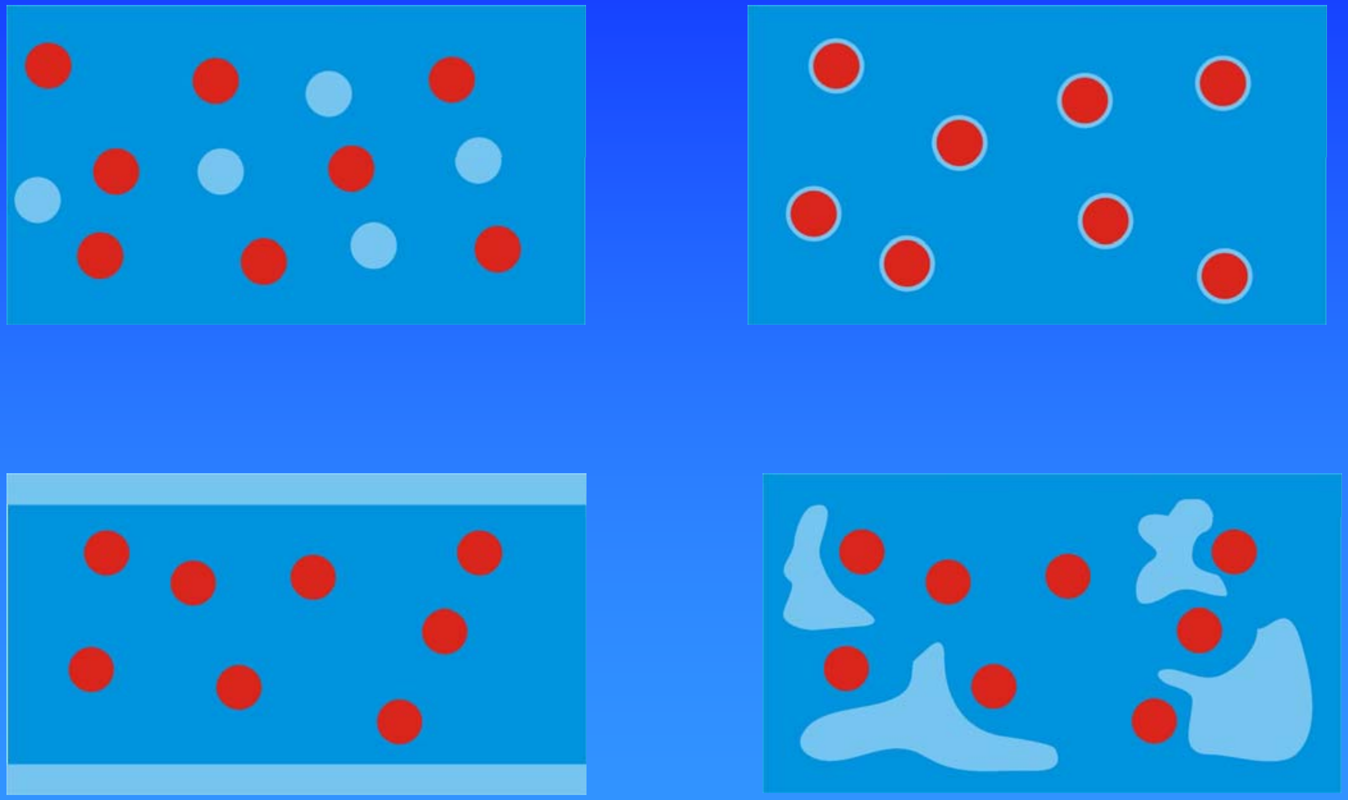
Spinel and stuffed quartz
different time development

Question:

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



Morphology (2)



So far all possible

Surface of particles

- Porod approximation

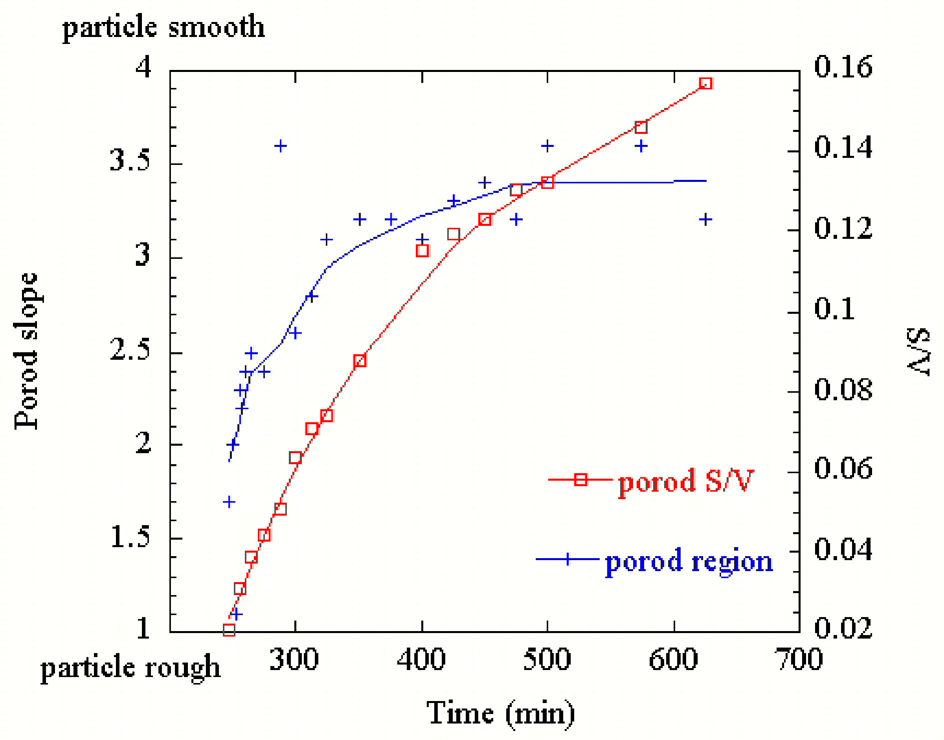
$$I(q)_{q\to\infty} \approx K_1 + \frac{K_2}{q^x}$$

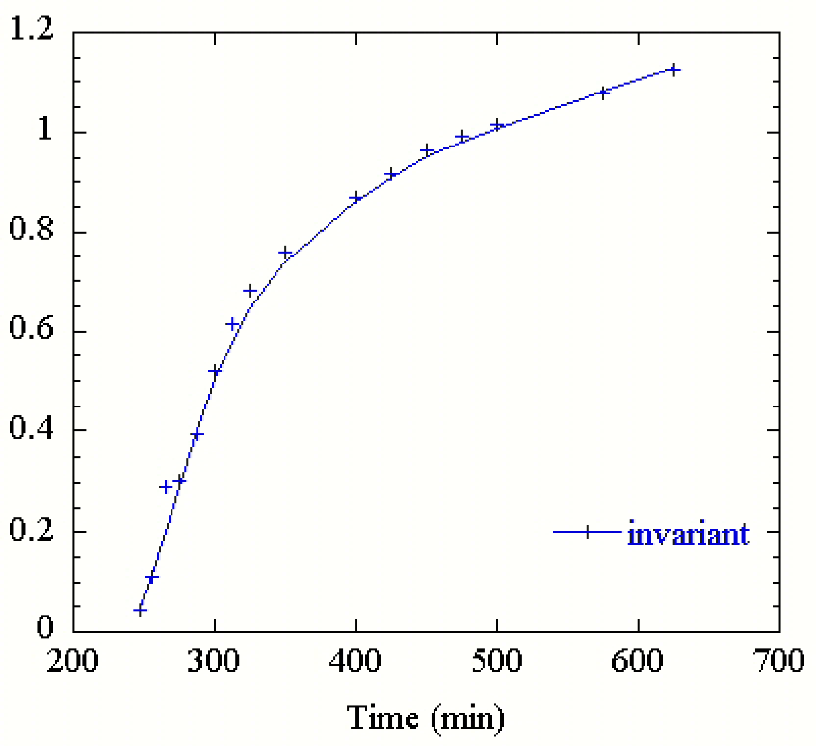
- x = 4, smooth surface; x < 4, ‘rough’ surface
- Again this is an approximation, valid when $qR_g >> 1$
- For particles with density gradient

$$I(q)_{q\to\infty} \approx K_1 + \frac{K_2 e^{-(\sigma q)^2}}{q^x}$$

- K_1 contains information on density fluctuations
- K_2 contains information on internal surface to volume ratio

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





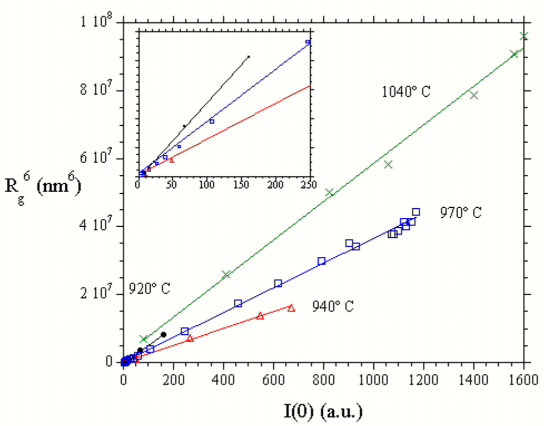
$$\underbrace{I(q) \square K_1 + \frac{K_2}{q^4} \qquad\qquad Q = \int_0^\infty I(q) q^2 dq \square \langle n_e \rangle^2 \phi(1-\phi)}_{\displaystyle \frac{K_2}{Q} = \frac{1}{\pi}\frac{S}{V}}$$

Can this be correct?

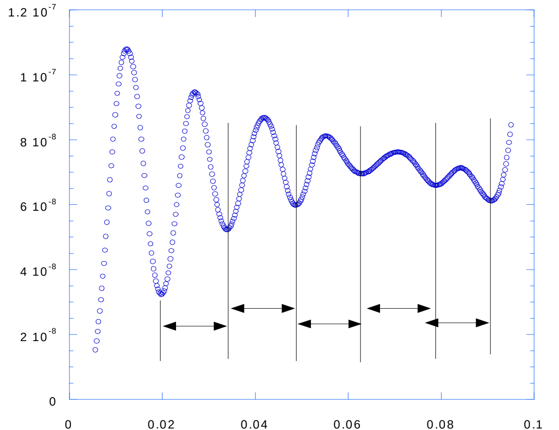
- Radius of particle stops growing
- Surface/Volume ratio of particle keeps increasing
- Maybe new crystallites created ?

New crystallites can be ruled out:

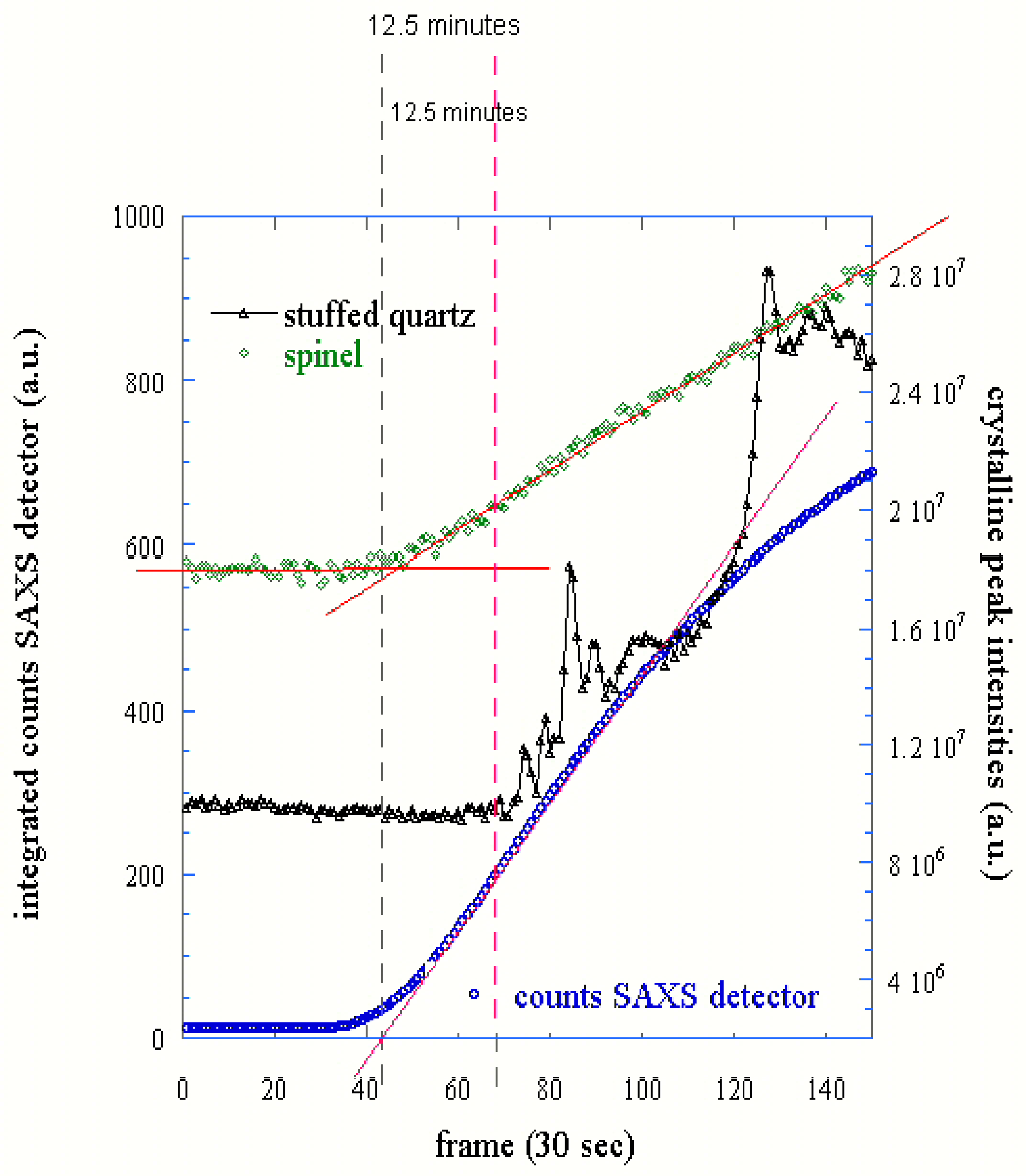
- $I(0) = CR_g^6$
  (only true for constant number of particles)



- We see many form factor maxima



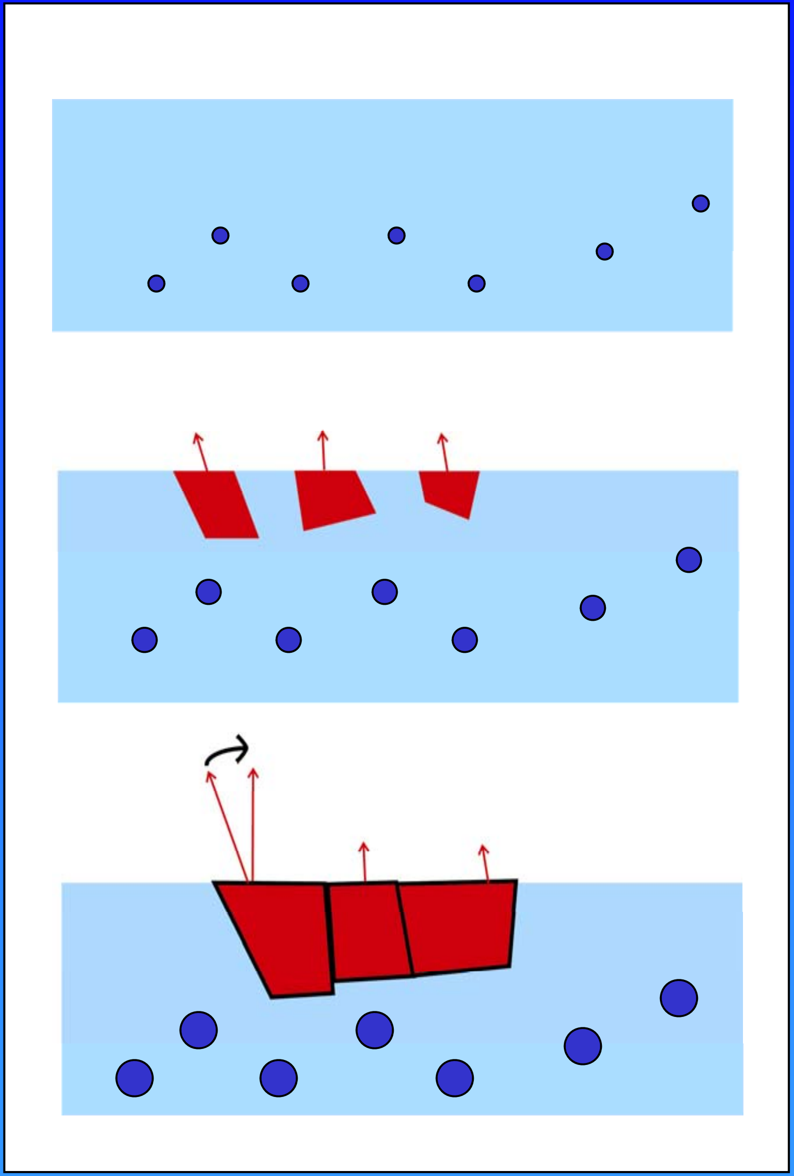
- Polydispersity ~ 4%



-Spinel increases regularly in time

- Stuffed quartz increases irregular

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

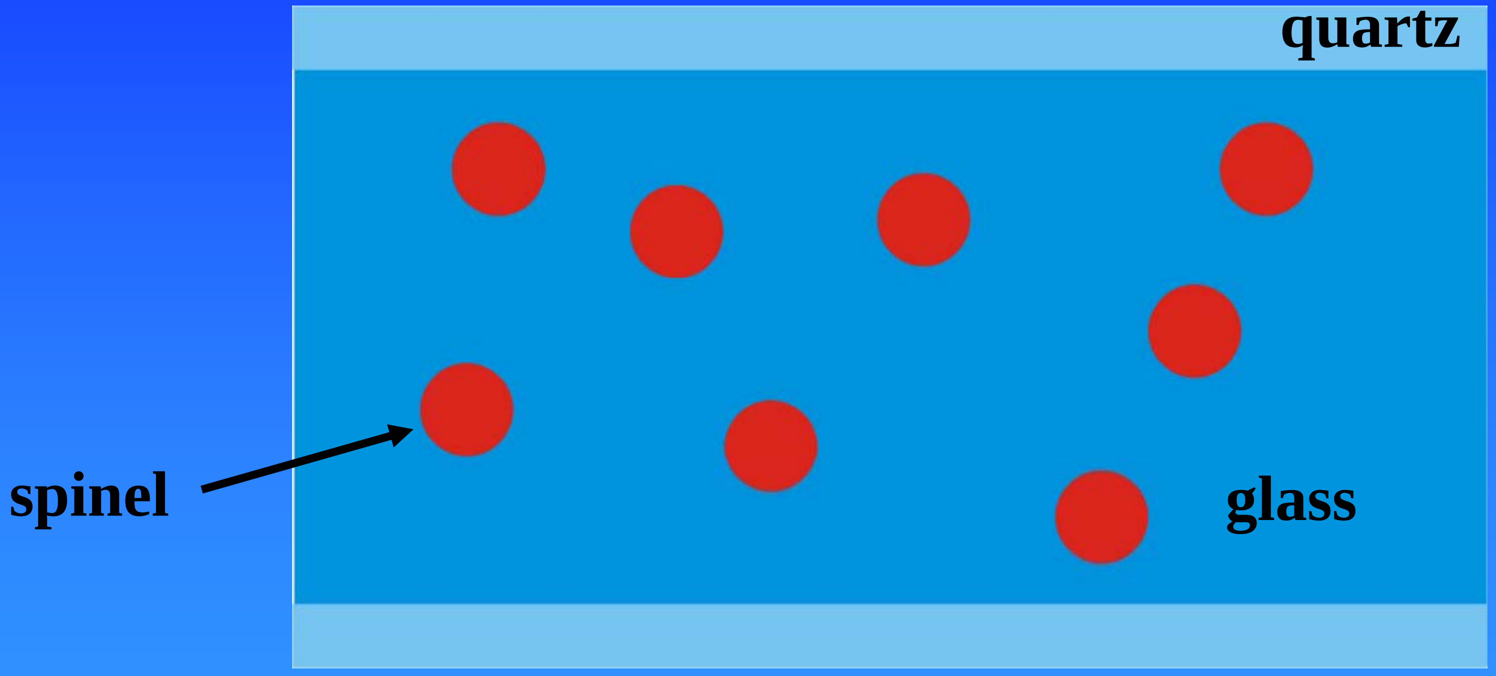


Growth of stuffed quartz

⇒ texture effects !

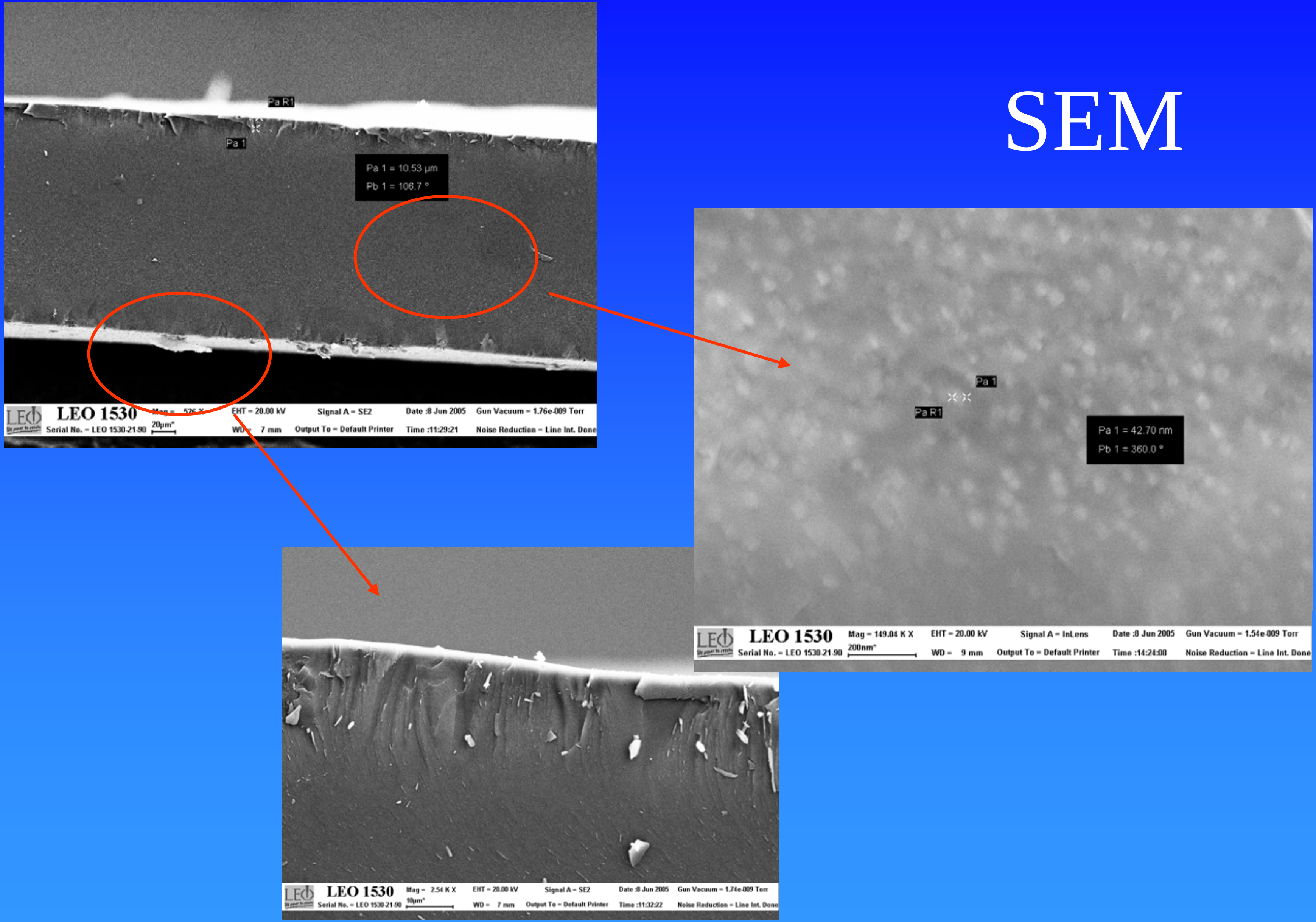
Crystals impinge on each other
⇒ variations in intensity

Prediction Morphology:



This is (so far) the correct morphology

SEM


Pa R1
Pa 1
Pa 1 = 10.53 µm
Pb 1 = 106.7 °
LEO 1530
Mag = 526 X
EHT = 20.00 kV
Signal A = SE2
Date :8 Jun 2005
Gun Vacuum = 1.76e-009 Torr
Serial No. = LEO 1530-21-90
20µm*
WD = 7 mm
Output To = Default Printer
Time :11:29:21
Noise Reduction = Line Int. Done
Pa 1
Pa R1
Pa 1 = 42.70 nm
Pb 1 = 360.0 °
LEO 1530
Mag = 149.04 K X
EHT = 20.00 kV
Signal A = InLens
Date :8 Jun 2005
Gun Vacuum = 1.54e-009 Torr
Serial No. = LEO 1530-21-90
200nm*
WD = 9 mm
Output To = Default Printer
Time :14:24:08
Noise Reduction = Line Int. Done
LEO 1530
Mag = 2.54 K X
EHT = 20.00 kV
Signal A = SE2
Date :8 Jun 2005
Gun Vacuum = 1.74e-009 Torr
Serial No. = LEO 1530-21-90
10µm*
WD = 7 mm
Output To = Default Printer
Time :11:32:22
Noise Reduction = Line Int. Done

Note on bulk/surface crystallisation:

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

Summarising:

- Spinel grows in bulk
- Stuffed quartz grows on surface
- This explains why the particle radius can stop growing but the total S/V ratio keeps increasing

- …..but can we find out more about the system …….?

What's the growth mechanism of the bulk crystallites ?

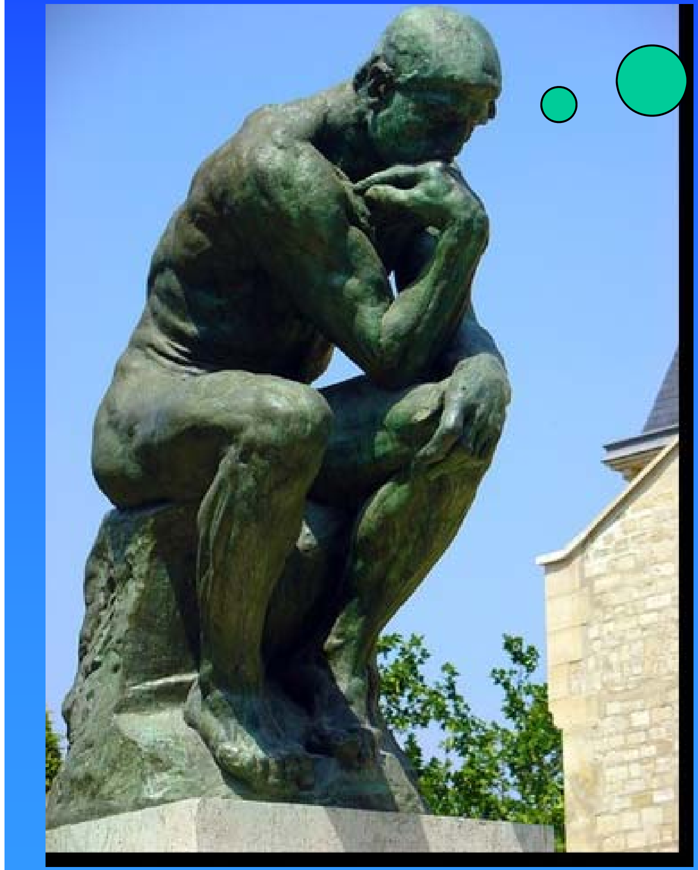
Conventional tool for solid state crystallization is Avrami analysis

(V_c is the crystalline volume fraction)

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

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

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



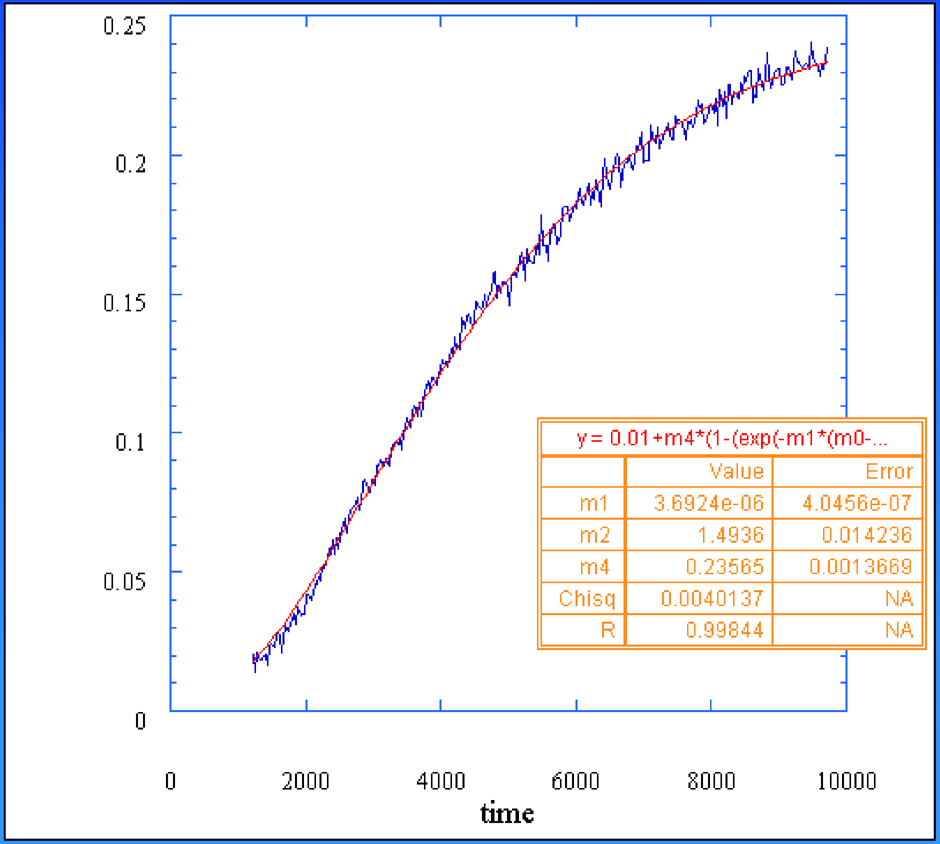
Dear Wim,
Are you serious? To such an equation I can fit anything…….

Signed: Cynic

Dear Cynic,
Maybe that is true, but
I’m a careful ‘man’…..

I double check……

In a WAXS pattern: peak intensity ~ V_c



y = 0.01+m4*(1-(exp(-m1*(m0-...

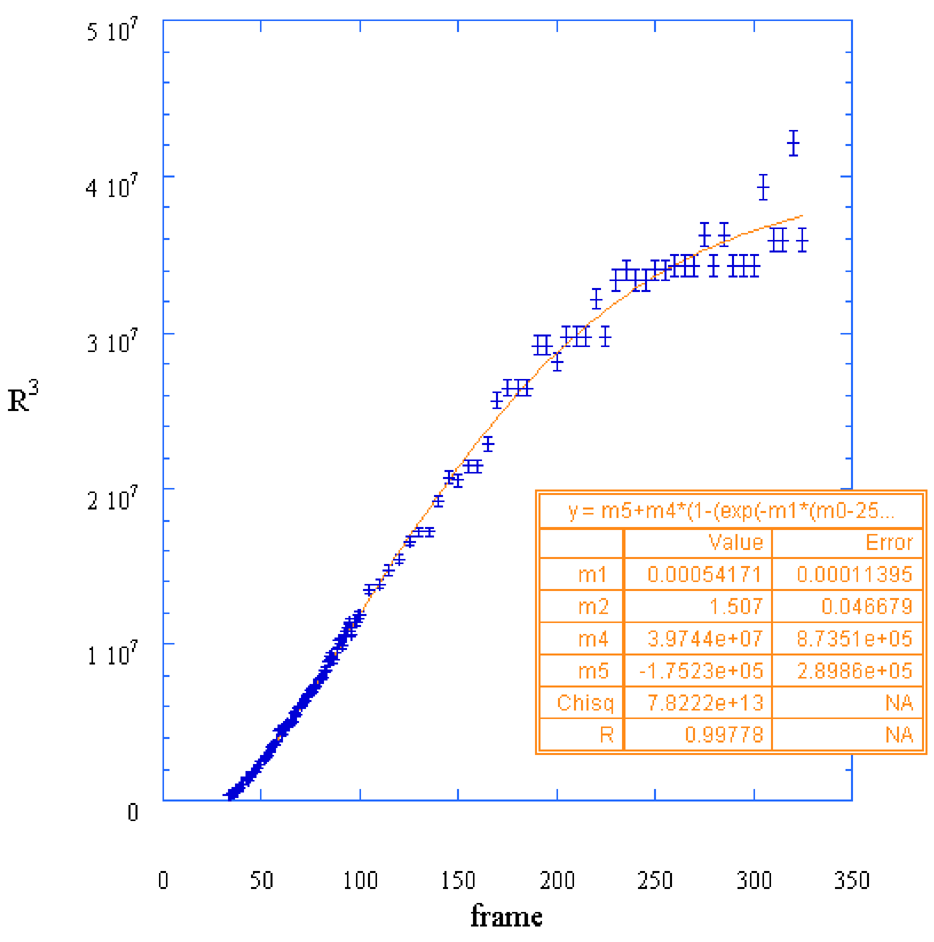
	Value	Error
m1	3.6924e-06	4.0456e-07
m2	1.4936	0.014236
m4	0.23565	0.0013669
Chisq	0.0040137	NA
R	0.99844	NA

Avrami coefficient
1.49 ± 0.01

For SAXS data

- For fixed number of particles N which are monodisperse
- N x R^3 is also related to the V_c

SAXS



y = m5+m4*(1-(exp(-m1*(m0-25...

	Value	Error
m1	0.00054171	0.00011395
m2	1.507	0.046679
m4	3.9744e+07	8.7351e+05
m5	-1.7523e+05	2.8986e+05
Chisq	7.8222e+13	NA
R	0.99778	NA

Avrami coefficient

1.51 ± 0.05

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

What does this mean according to mr. Avrami?

For a pre-nucleated system

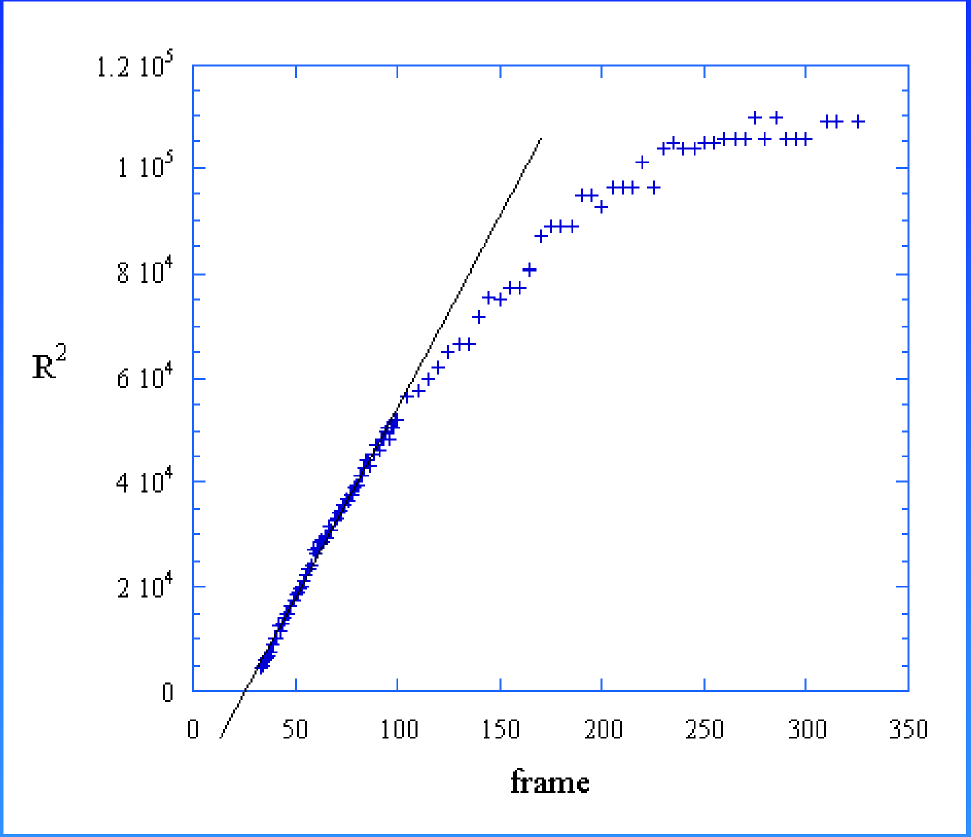
$$V_c = 1 - e^{(-Kt^{1.5})}$$

Means diffusion limited growth

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

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

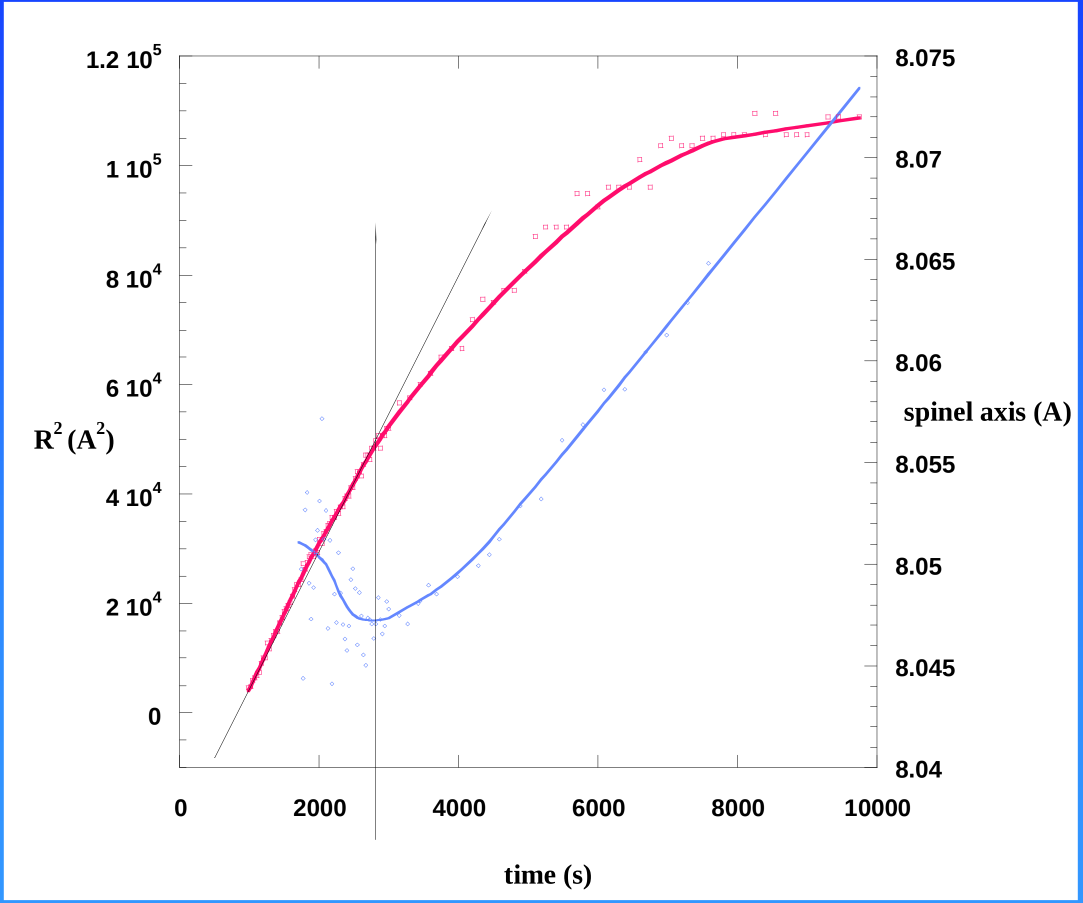
And so it does !



⇨ 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

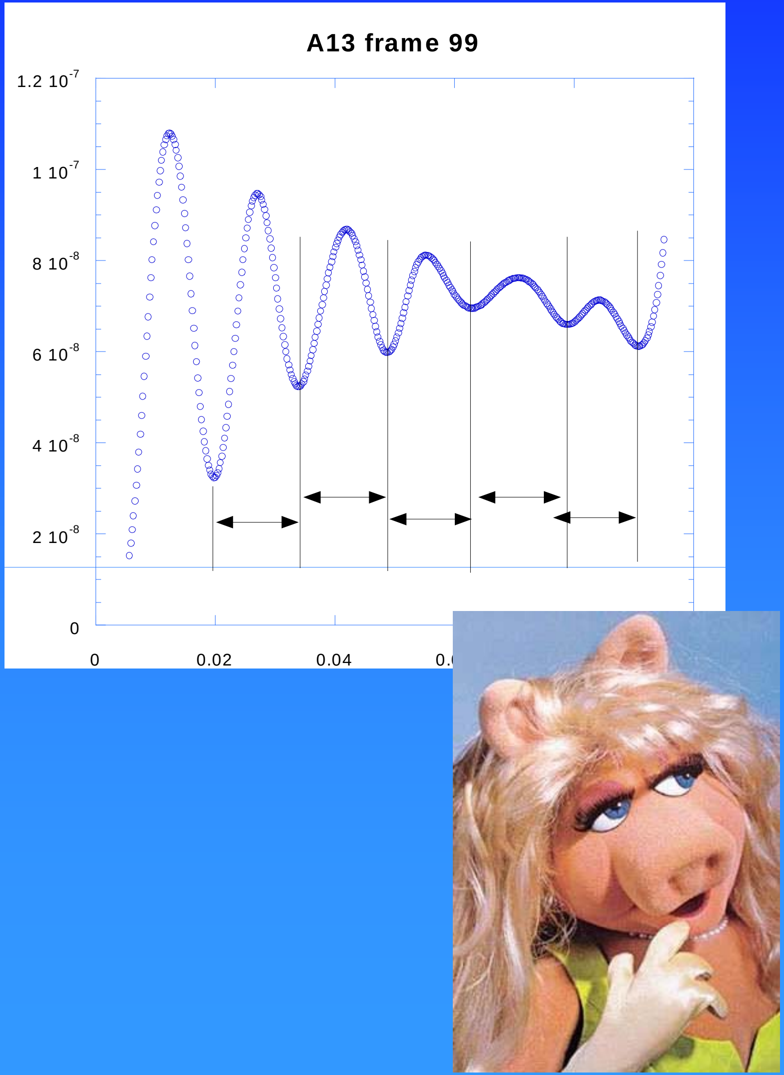
- From the change in lattice spacing we can calculate the internal pressure
- Pressure due to mismatch between specific volumes glass matrix versus spinel

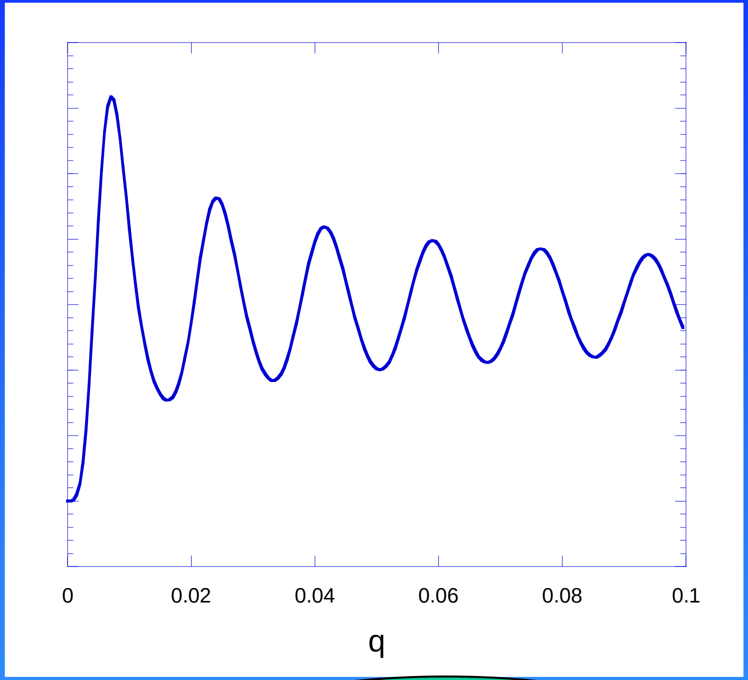
$$P = 1.5 \cdot K_{0,1050} \left[\left(\frac{V_{0,1050}}{V} \right)^{7/3} - \left(\frac{V_{0,1050}}{V} \right)^{5/3} \right]$$

- Pressure changes from 9.5 → 10 → 8.5 GPa

Two little warnings

Warning 1: How well can we trust data?





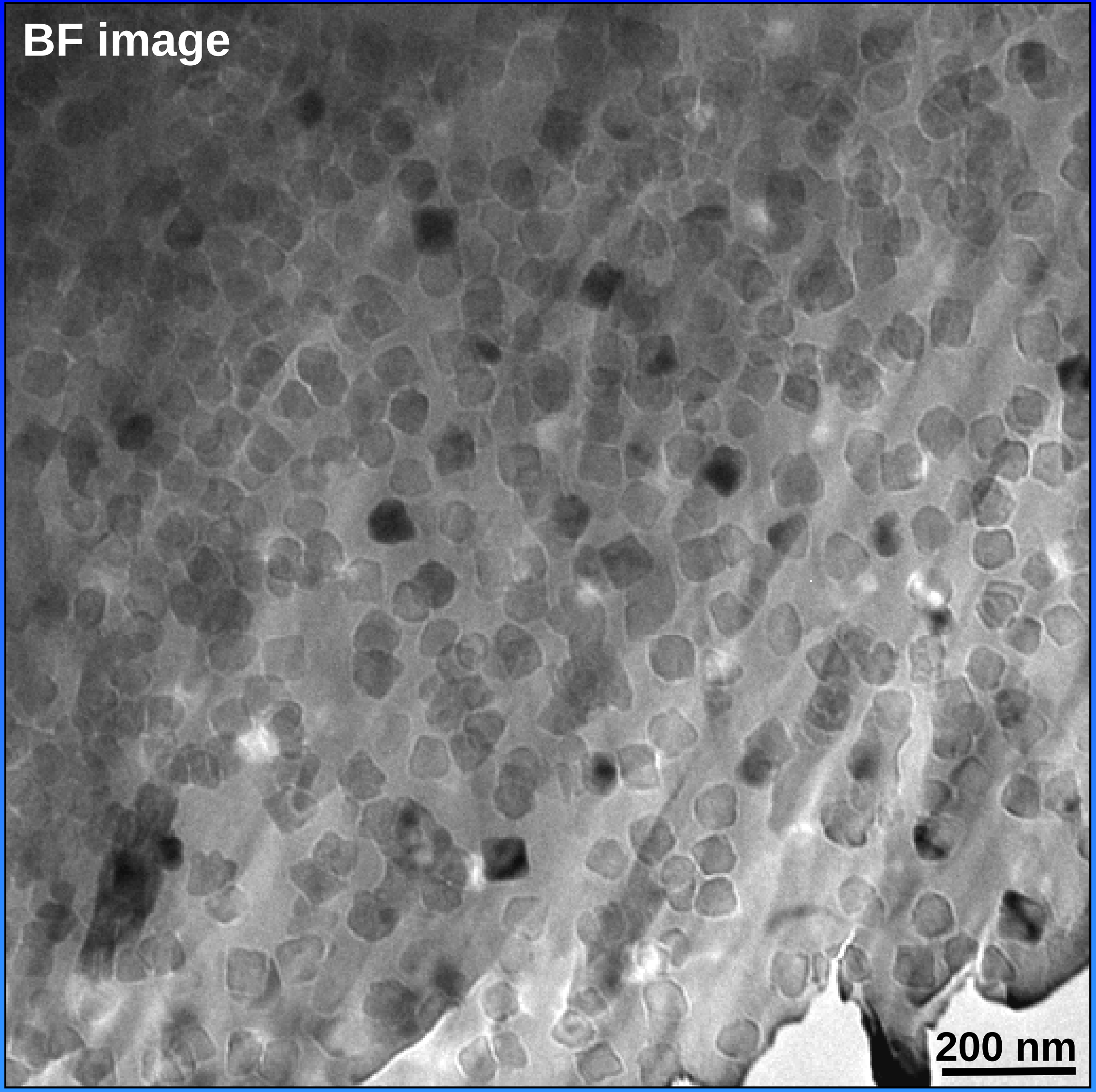
That's a good fit!!

Forget it !!!

The first curve is a polydisperse sphere

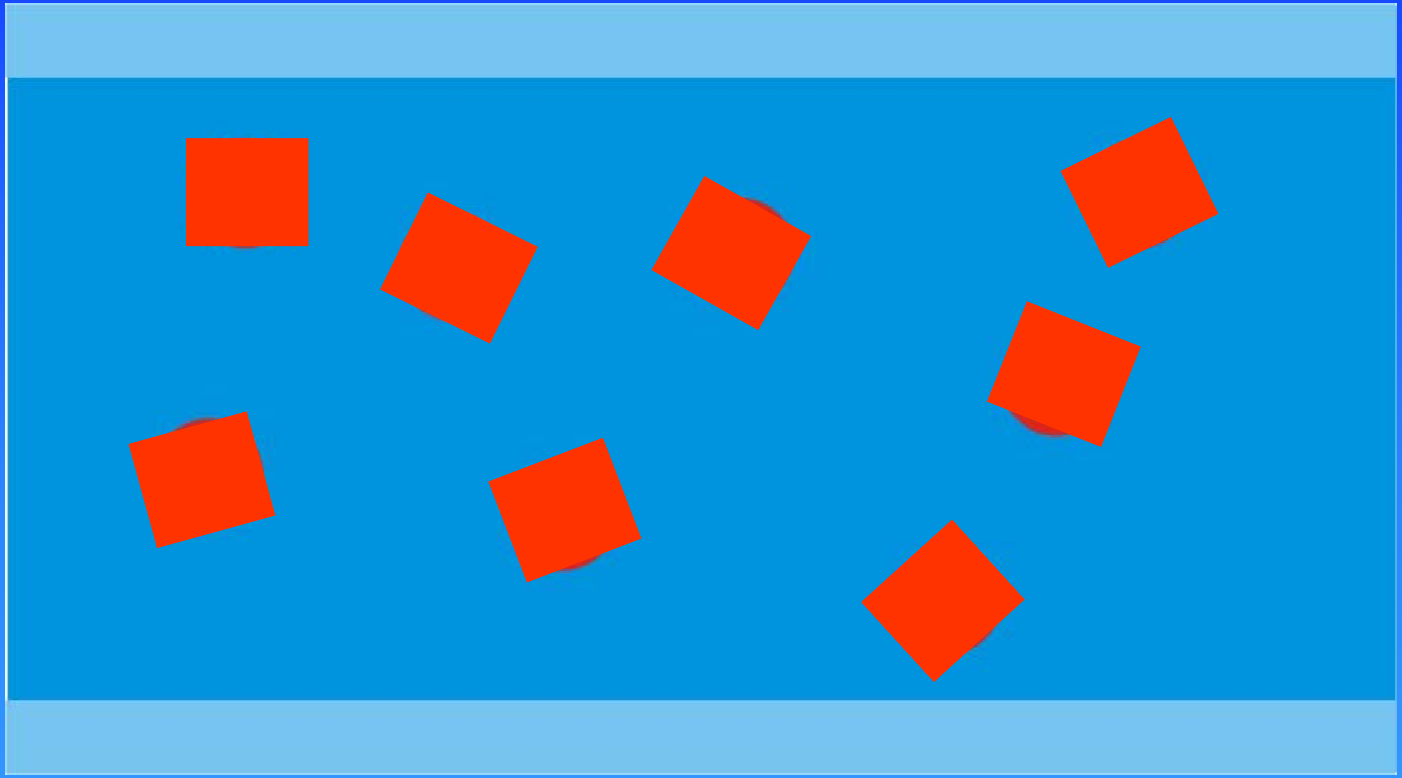
The second is a monodisperse cube

TEM



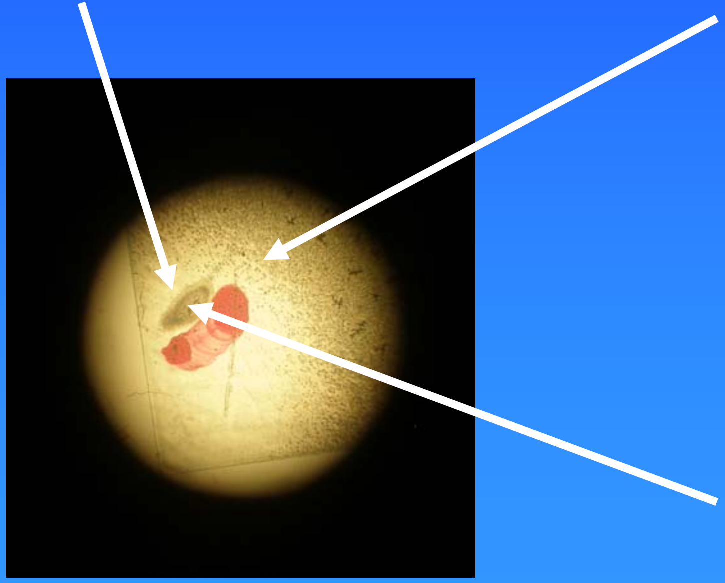
The particles are not spherical but cubes………

The correct morphology (3)



Warning 2: does radiation hurt?

- Lidisilicate glass



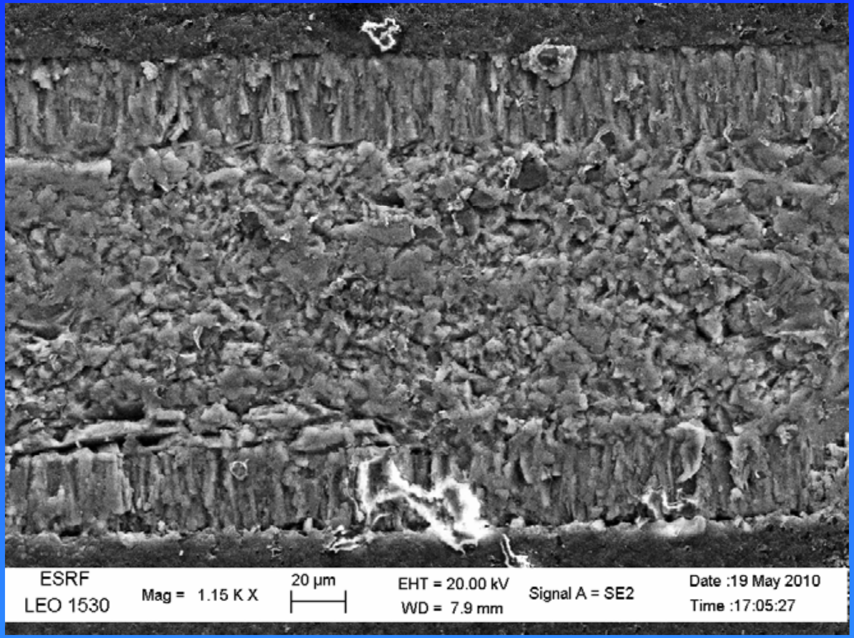
beamspot

XRD pattern heavily textured
Low crystallinity

XRD pattern perfect powder
High crystallinity

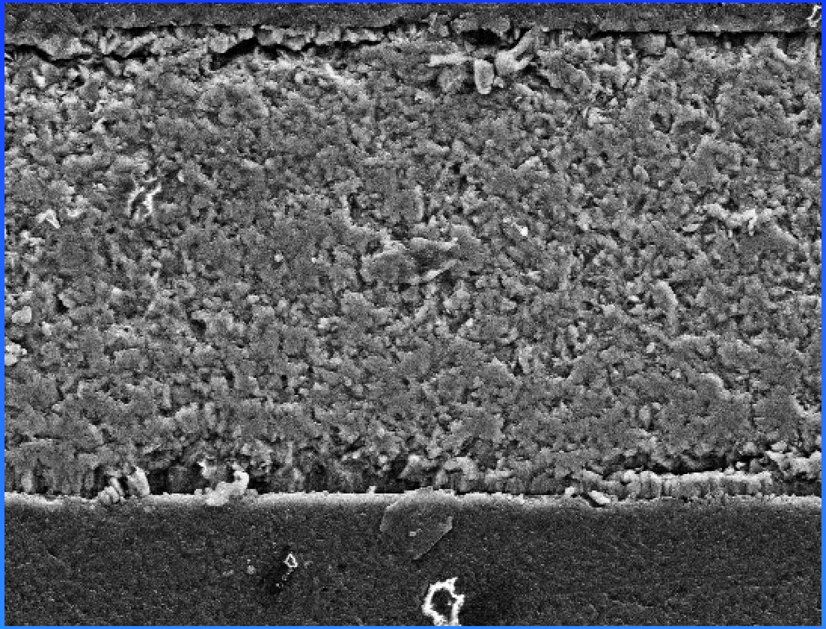
Optical microscopy

SEM



Not irradiated

Coarse grains
Texture on surface



Irradiated

Fine grains
No texture

Effect of X-rays

- More nucleation sites

- Smaller but more crystallites
- Higher chance of random orientation
- Therefore a real powder pattern
- Your kinetics experiment might be ……

And this is only a bending magnet; an undulator has 50-100x more flux

Time resolved SAXS/WAXS derivables

- Particle size/Growth kinetics
- Crystalline phases
- Crystalline volume fraction (not discussed)
- Internal surface/volume ratio
- Growth zone/particle roughness (not discussed)
- Crystallisation energy (not discussed)
- Internal pressure
- Etc.

The main message:

- One can obtain a wealth of information with a combined SAXS/WAXS experiment
- Surface/volume ratio, crystallisation energy, surface roughness, volume factions, morphology, crystallite size etc. etc.
- Over-interpretation of data and underestimate effect of X-rays can lead to false conclusions

Make cross correlations with other techniques

In this example:

SAXS/WAXS
SANS
SEM
TEM

Not shown:

EXAFS
DSC

References:

- W. Bras et al.

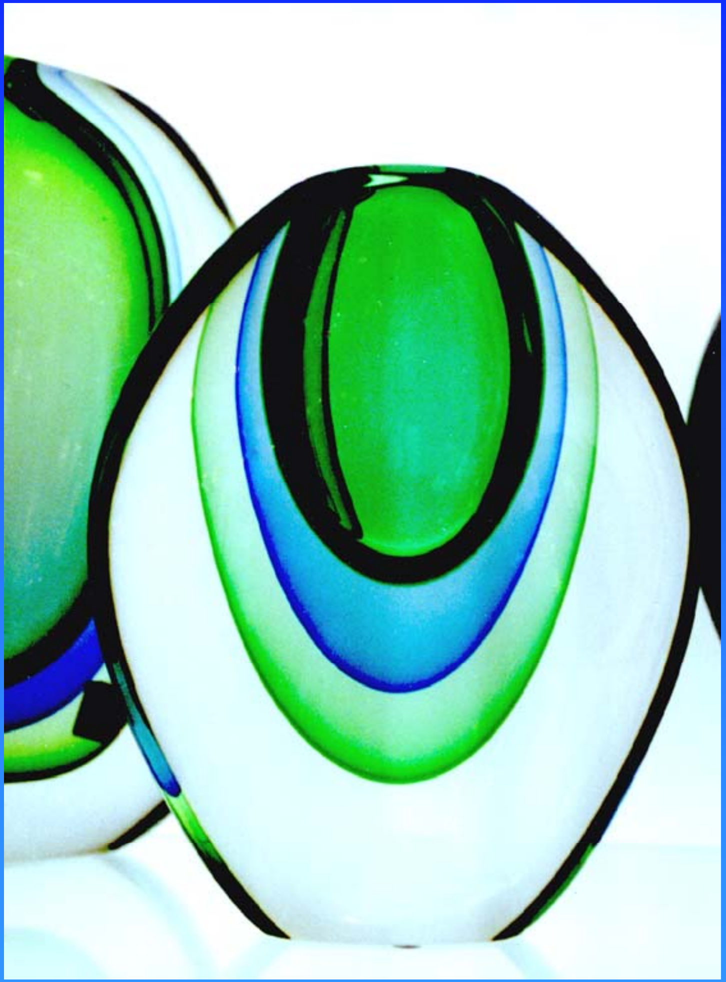
  J. Non Crystalline Solids 351, 2005, 2178-2193
- W. Bras et al.

  Crystal Growth and Design 9(3), 2009, 1297-1305
- W. Bras

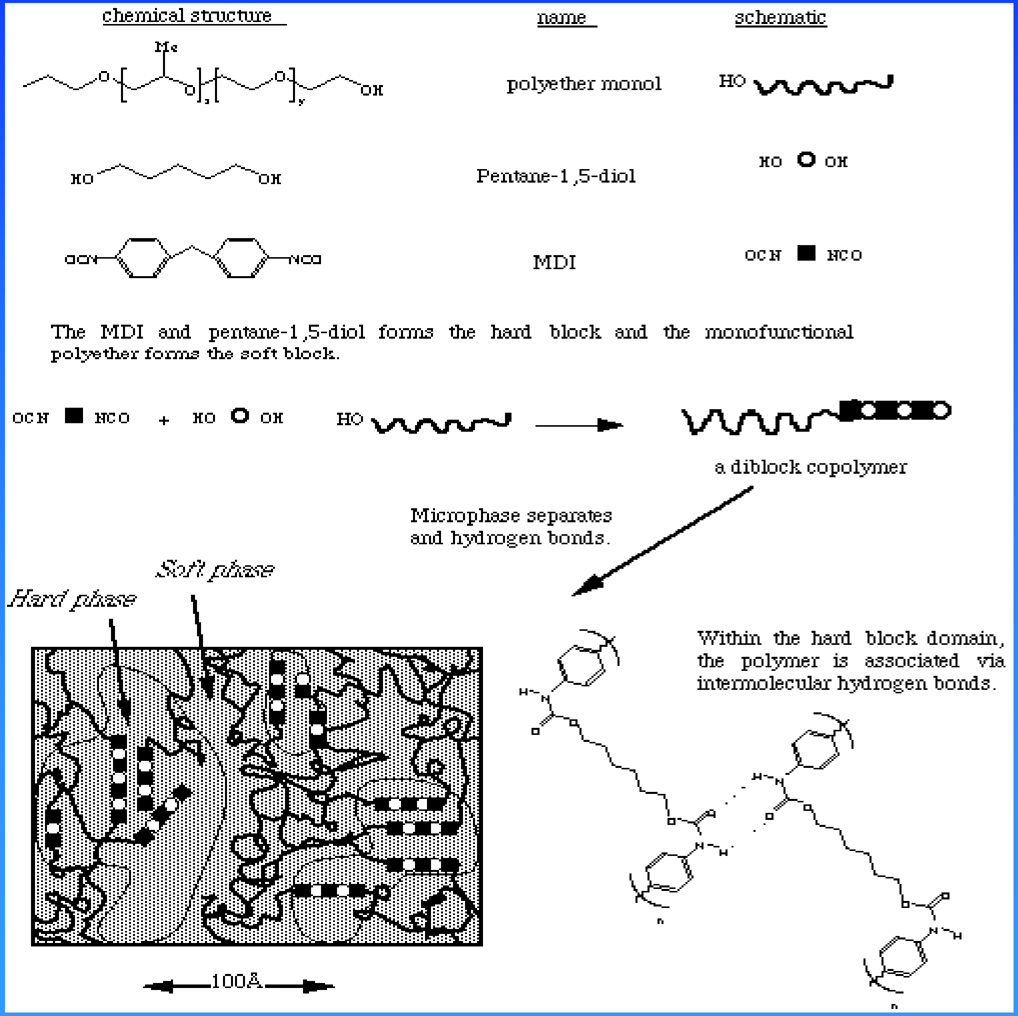
  in Springer Lecture Notes in Physics 776, 2009, 105-132
  Ed. T. Ezquerra

It is not out of vanity that I give these references. It is rare to find so many aspects of scattering theory applicable to a system.

Venitian glass



Example: SAXS and FTIR



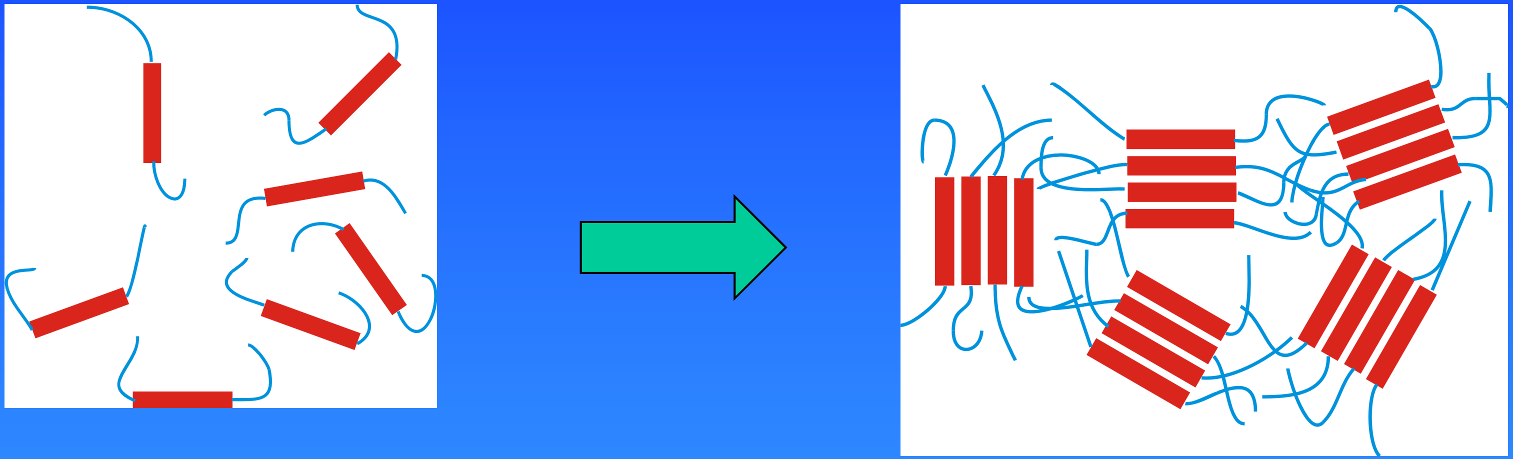
The MDI and pentane-1,5-diol forms the hard block and the monofunctional polyether forms the soft block.

Microphase separates and hydrogen bonds.

Within the hard block domain, the polymer is associated via intermolecular hydrogen bonds.

The question:

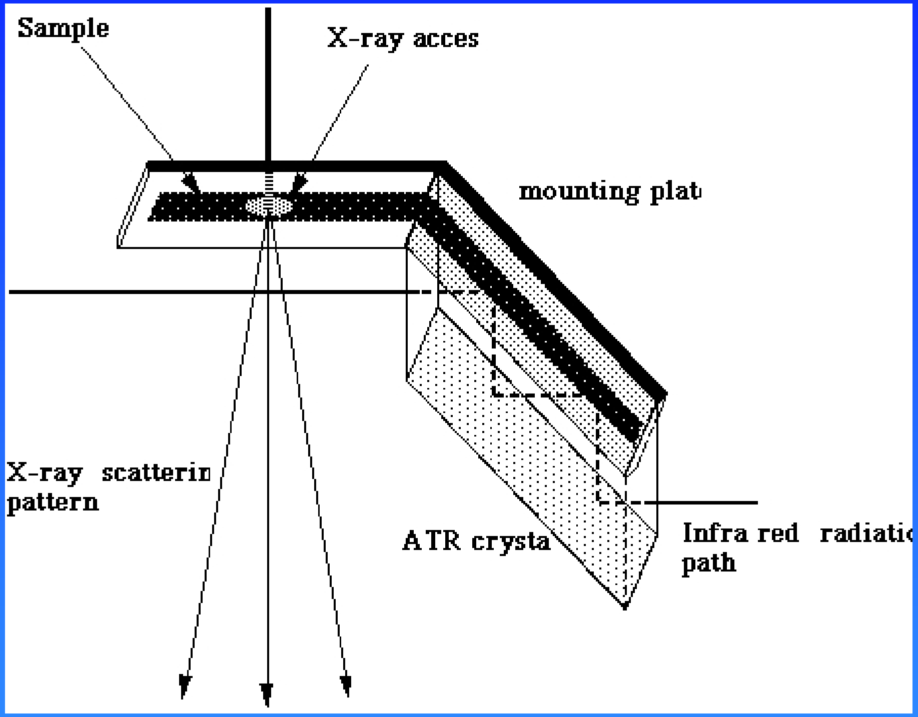
Is hydrogen bond formation the driving force or the consequence of the phase separation?



No SAXS
No FTIR signal

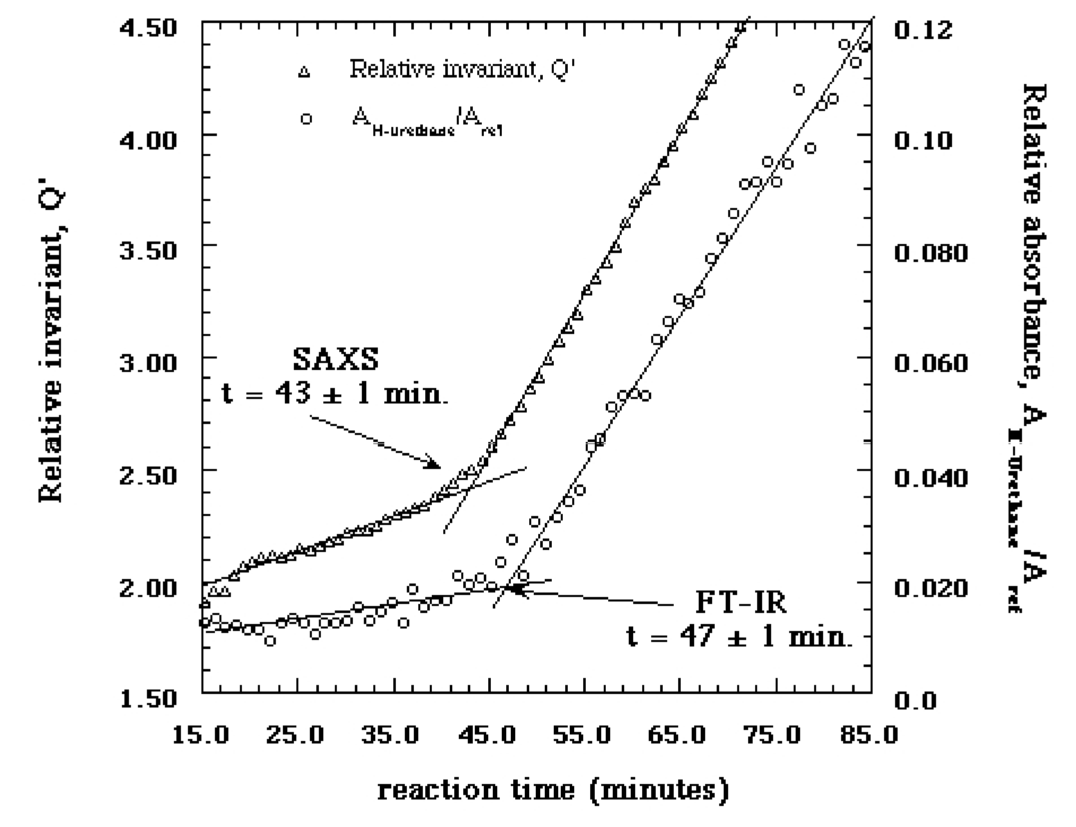
SAXS
FTIR signal

What comes first? The SAXS signal or the FTIR?



- Optimum thickness for transmission only for one technique

SAXS invariant and Hydrogen bond absorption band



Polymer crystallisation

- This is a very interesting subject for combined experiments
- This can easily be treated in another 30 slides
- Main conclusion is that one has to keep an eye on the sensitivity of different techniques before drawing heavy conclusions

But……..

- I’ve bored you long enough now…..

Thanks for your attention