Sample environments and technique combinations for SAS beamlines





Outline

- Very brief synchrotron radiation
- Technique combinations
- Sample environments







ESRF: the Dutch-Belgian National SR facility







DUBBLE

- EXAFS beamline
- SAXS beamline
- free access
- beam time application every6 months



To start with SAXS/SANS



o Vou Can't Ignore fhe 800 Pound Gorilla



Technique combinations



First dedicated SAXS/WAXS set-up 1993



Somewhat more modern SAXS/WAXS





When does one combine techniques?

- Time-resolved experiment
- There must be synergy between the data sets, e.g. what comes first?
- Precious samples
- Inhomogeneous samples
- Etc.

Data should be obtained from the same sample spot



Example: SAXS and FTIR

+10 +20



Note:

- This is old stuff
 Good illustrations don't always have to be done with latest equipment
- Experimental ingenuity has existed through the ages



High tension safety cover



Safety officers



Old FTIR; hacksawed holes to get X-ray beam in.



Example: SAXS and FTIR





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





Result:

- Long range order first
- FTIR signal increase later

 The phase separation induces hydrogen bond formation and not the other way around



Differential Scanning Calorimetry









Timing markers from synchrotron data acquisition system



DSC/SAXS/WAXS on lauric fat







Where is the limitation?

- SAXS/WAXS data will still be good
- DSC maybe less good
- DSC best with full thermal isolation of sample
- This would block X-rays



Differential Scanning Calorimetry

X-ray frame 27



X-ray frame 68



Responsive molecules change shape

- Polyelectrolytes
- Responsive to solvent quality
- ON-OFF response to pH



Macroscopic shape change



The data:





Combinations here:

- Light scattering
- Mechanical
 - Attach a STM tip to the polymer
 - Measure the force it generates
- Is this simple to do?



One has to set up a whole chemical factory on line

The reaction of bromate, sulfite and ferrocyanide ions in a continuously stirred tank reaction vessel exhibits sustained oscillations in pH³. 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 [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 \bigcirc 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.

Cordierite based ceramics Ceramic replacement teeth



Pizza baking stones

Refractory parts





Louis Cordier 1777-1861



Ceramic chip carriers

Car exhaust soot filters





glass ceramic

- Crystalline regions in a glass matrix
- Shock resistant even at high temperatures
- Manufacturing process <u>empirically</u> well understood
- But in fact industries often don't have a clue what they're doing



Cordierite glass devitrivication



Mg₂Al₄Si₅O₁₈ doped with 0.34 mol% Cr₂O₃ (crystallization enhancer)



Experiment on 75 micron thick platelet

temperature

Crystal growth several hours (~ 1000° C) Soak or nucleation 2 hours (~ 900° C)

time





Not a powder



Structure development

Data taken at 1 minute/frame





WAXS







Post mortem powder diffraction: three different phases





stuffed quartz

spinel

+ large amount glass matrix



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



Form factor peaks (up to 5th order)

 $\Delta R/R \sim 0.04$



Morphology (1)





Neutron scattering





Chromium in crystalline spheres

Neutron data courtesy Stuart Clarke



A13

average sphere radius as determined from minima in the scattering curve



 Particle size
 Minima in form factor (no Guinier needed in this case)




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





Fixed number of monodisperse particles



WAXS data



Question:

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





Morphology (2)



So far all possible





K2 = $\frac{1}{S}$ πV



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

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Growth of stuffed quartz

\Rightarrow texture effects !

Crystals impinge on each other \Rightarrow variations in intensity



Prediction Morphology:



This is (so far) the correct morphology







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 (spinel fixed but increase quartz/glass interface)
-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

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

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.....





WAXS: peak intensity ~ V_c



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 V_c







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)



Warning: How well can we trust data?





That's a good fit!!





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)





Muscle diffraction



Arnie (the second most well known Graz native) in better days



Galvani revisited:





Reflection intensity by tropomyosin



Dangerous when using large animals



"Ha! That finishes it! ... I always knew he'd be back one day to get the other one!"









Tom Irving APS Biocat



- Very small sample volume
- Radiation damage
- Moving target





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





Other toys we have played with: on-line film blowing

Rheology on line



Commercial equipment

Or home built Shear machine (built like a German Panzer) According to G. Eeckhaut....



On-line deformation






Deformation/stretching: Not only with an academic little tensile tester



This guy is talking about his hobbies again

And he can go on and on and

on.....



Thanks for your attention

