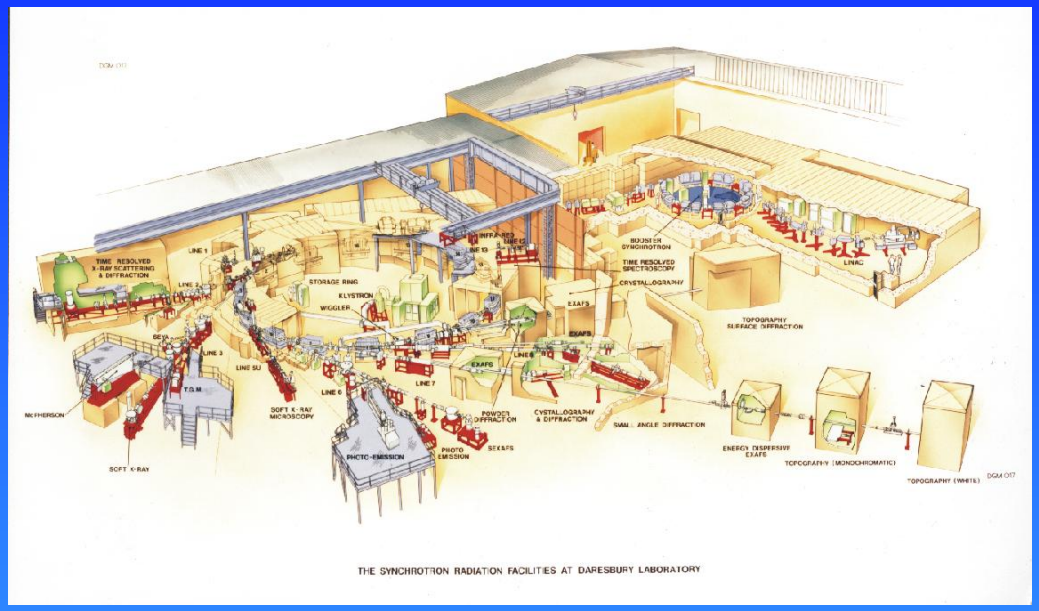
Problems in analysis of time-resolved SAXS/WAXS data

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

The SRS in Daresbury (U.K.)



2 GeV machine

Think fondly about it as the older sister of Diamond

A rather weak machine……

Nothing like the photon hammers we have nowadays……..

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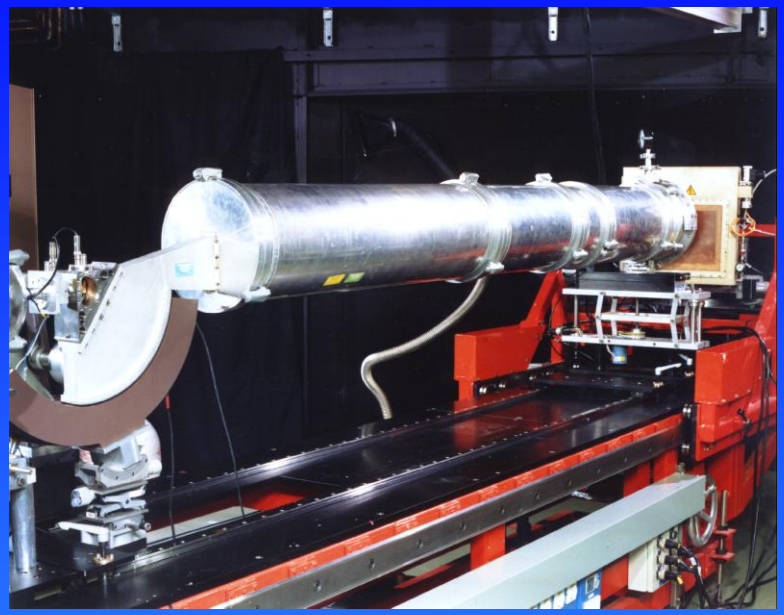

8.2, the ‘weakest’ of the bunch

3 SAXS stations

In order of appearance:
2.1, 8.2 and 16.1
(and much later 6.2)

It’s present state

But, it produced time-resolved SAXS/WAXS data even in single bunch mode …….

Good data…….

1 - 10 second time-resolution……. in single bunch
0.1 - 1 second in multibunch

And a lot of you guys in the audience have un-analysed still in your drawers……

(and this is true for any synchrotron and any beamline)

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Ωιμ, τηατσ ουτραγεουσ!

Oops, Piggy has
been on a holiday
to the Greek Isles

Wim, that's outrageous!

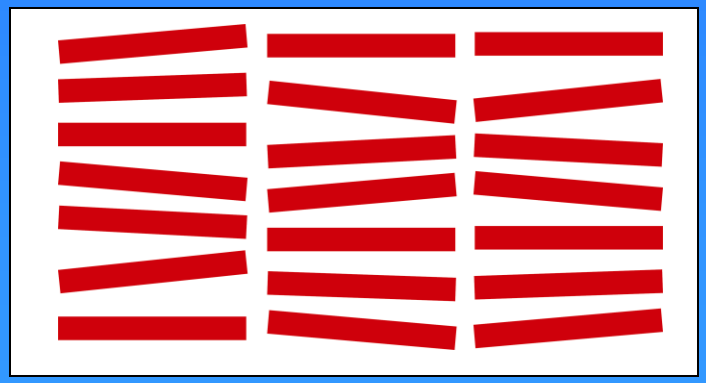
But I do agree with our opinionated porker

- But how do you (and me) get into such a mess?
- Are we just plain lazy?
- Did we go to Daresbury just for the good restaurant?
- Or do we lack the tools that we would like to have?

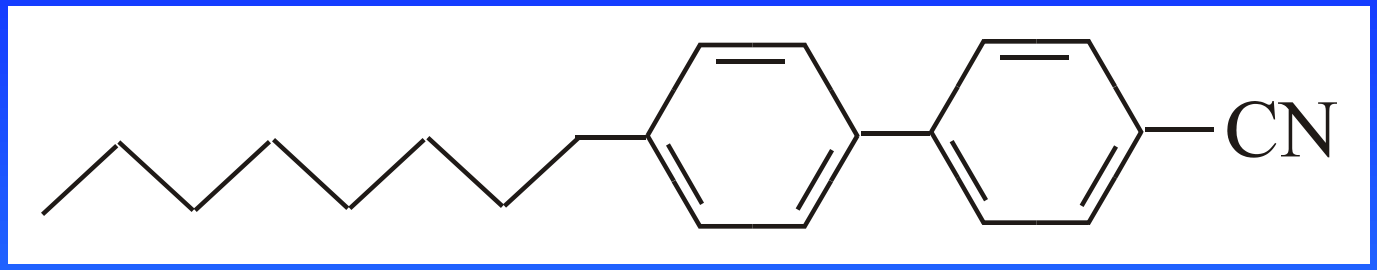
Smectic liquid crystals

- Candidates for fast switching LCD displays since only director movements required and no need of flipping of layers over 90°
- Reorientation mechanism under influence of changing fields not known

- Practical and theoretical interest



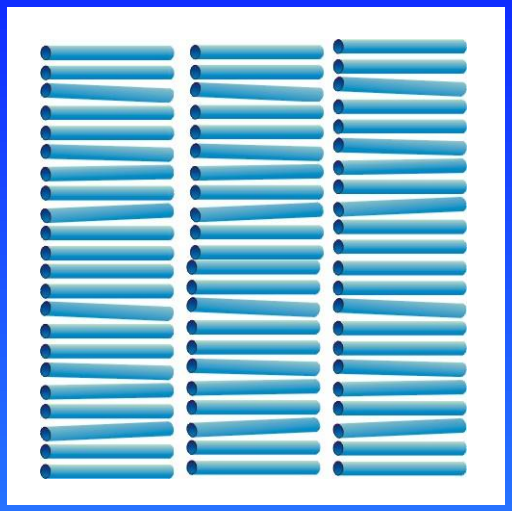
8CB model system



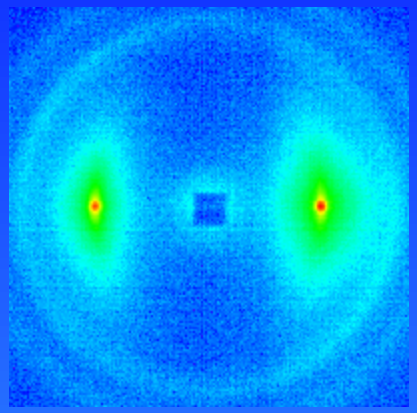
Crystal $-21.5\ ^{\circ}C \longrightarrow$ smectic A $-33.5\ ^{\circ}C \longrightarrow$

$\longrightarrow$ nematic $-40.5\ ^{\circ}C \longrightarrow$ isotropic

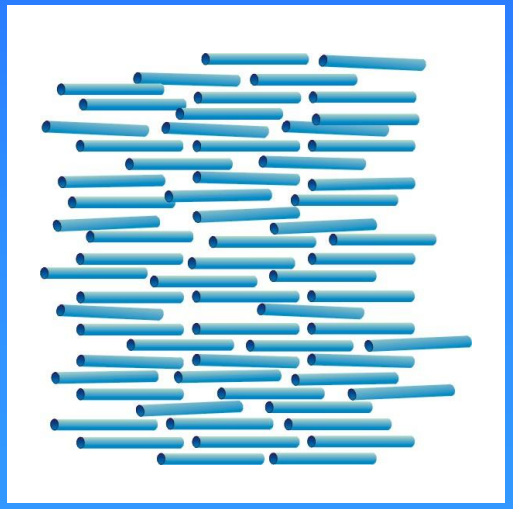
smectic

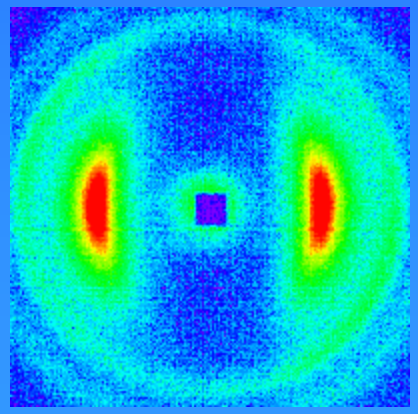


Fourier transform
of electron density



nematic





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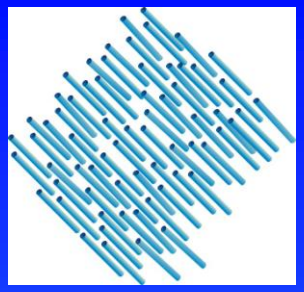
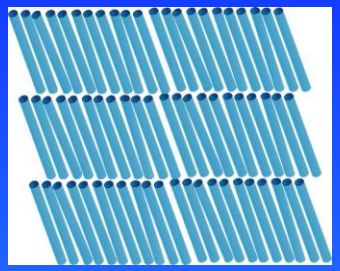
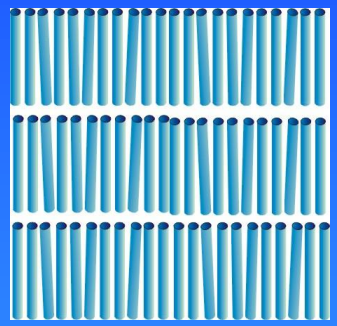
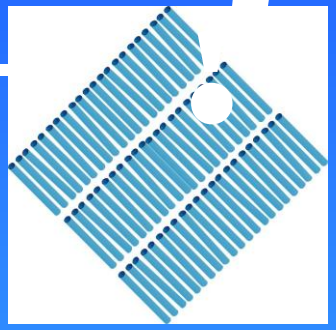
nematic



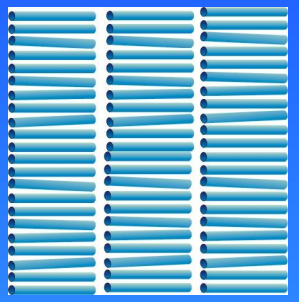


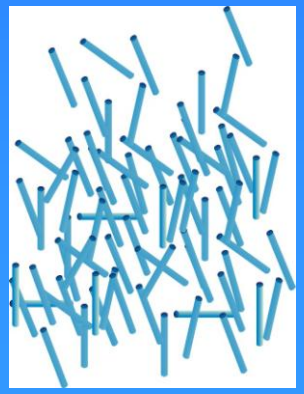
Smectic C





domain





disorder

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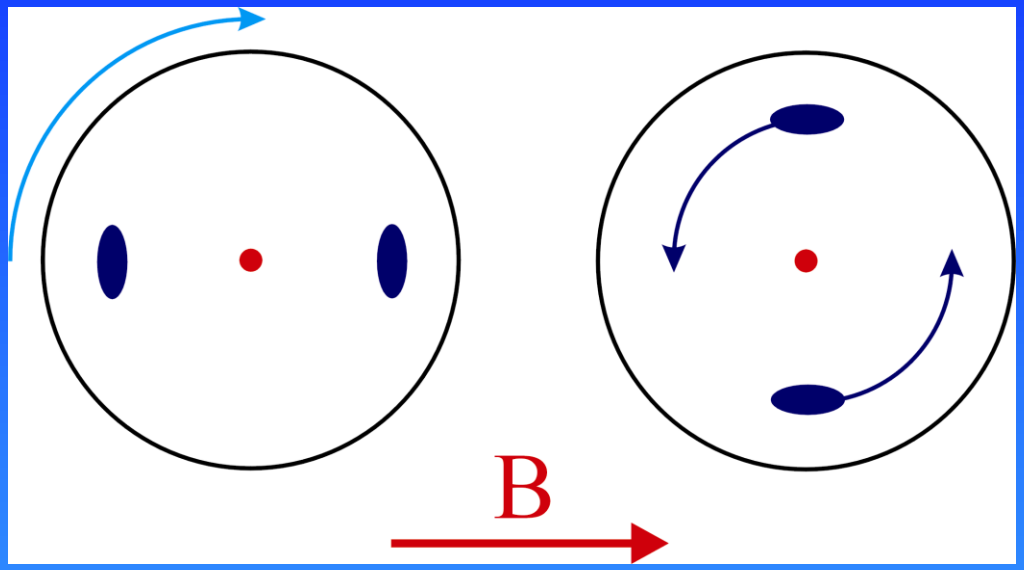
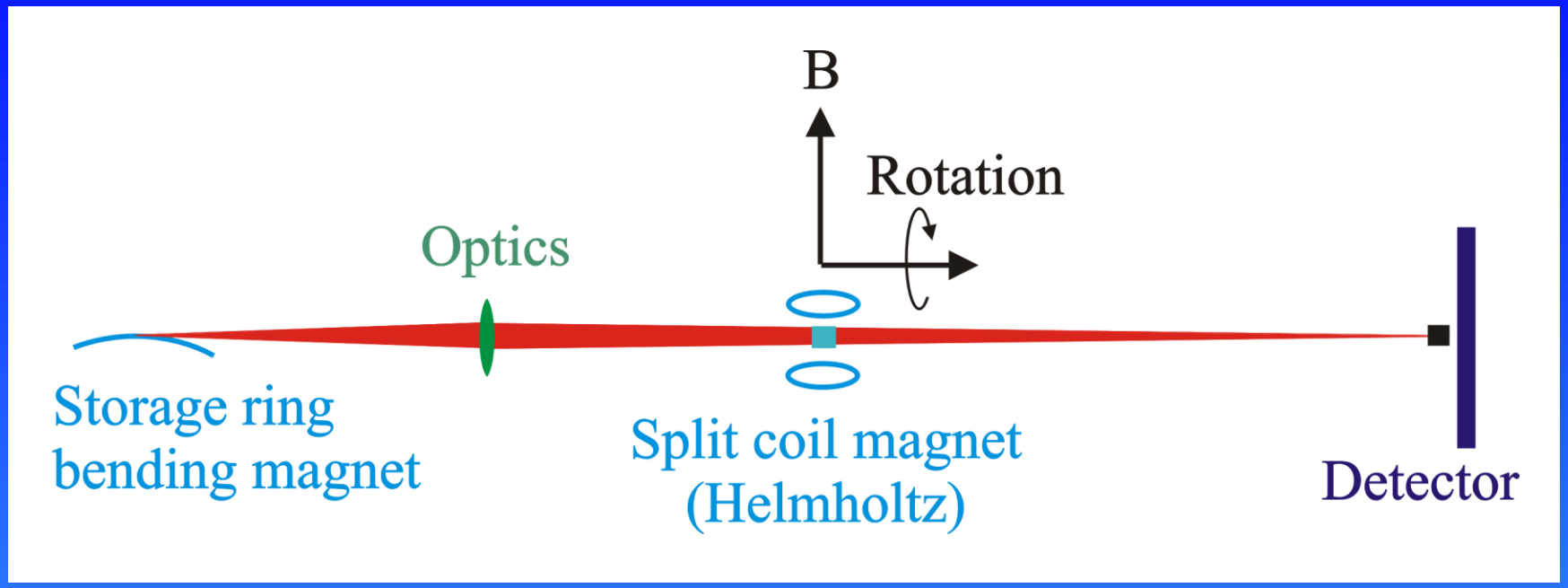
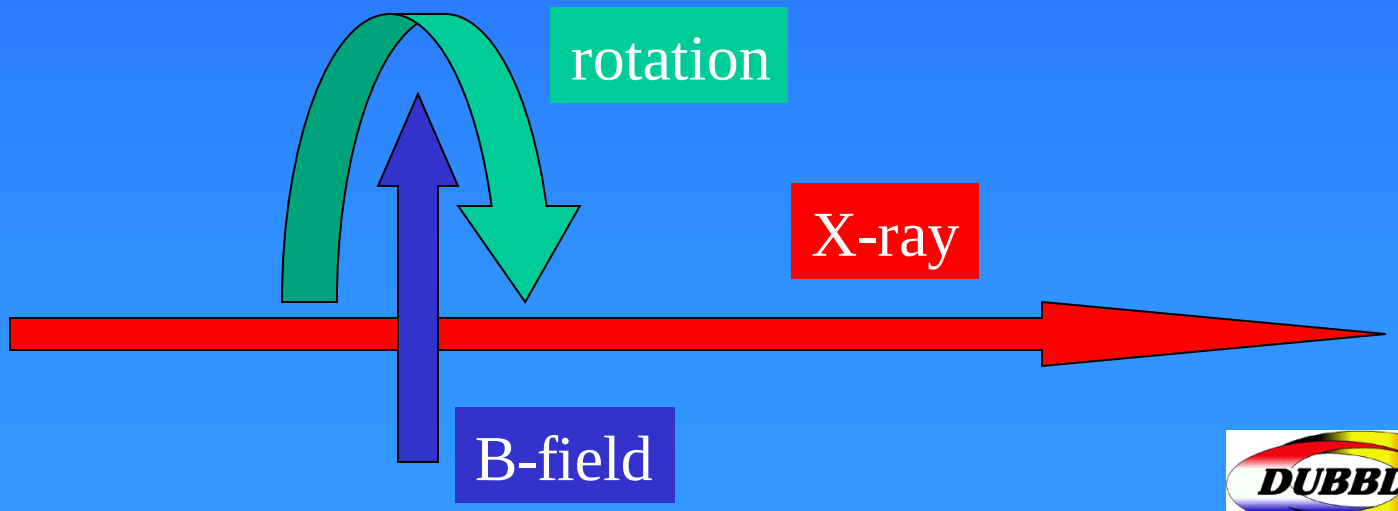
The experiment

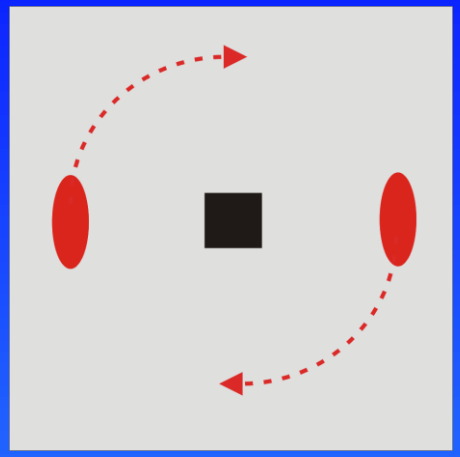


Mechanically rotate the sample around the X-ray beam
Watch it rotate back under the influence of the constant B-field

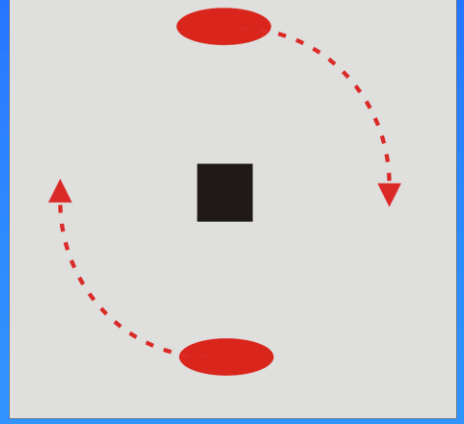

B
Rotation
Optics
Storage ring
bending magnet
Split coil magnet
(Helmholtz)
Detector


rotation
X-ray
B-field

Jump (70 msec)

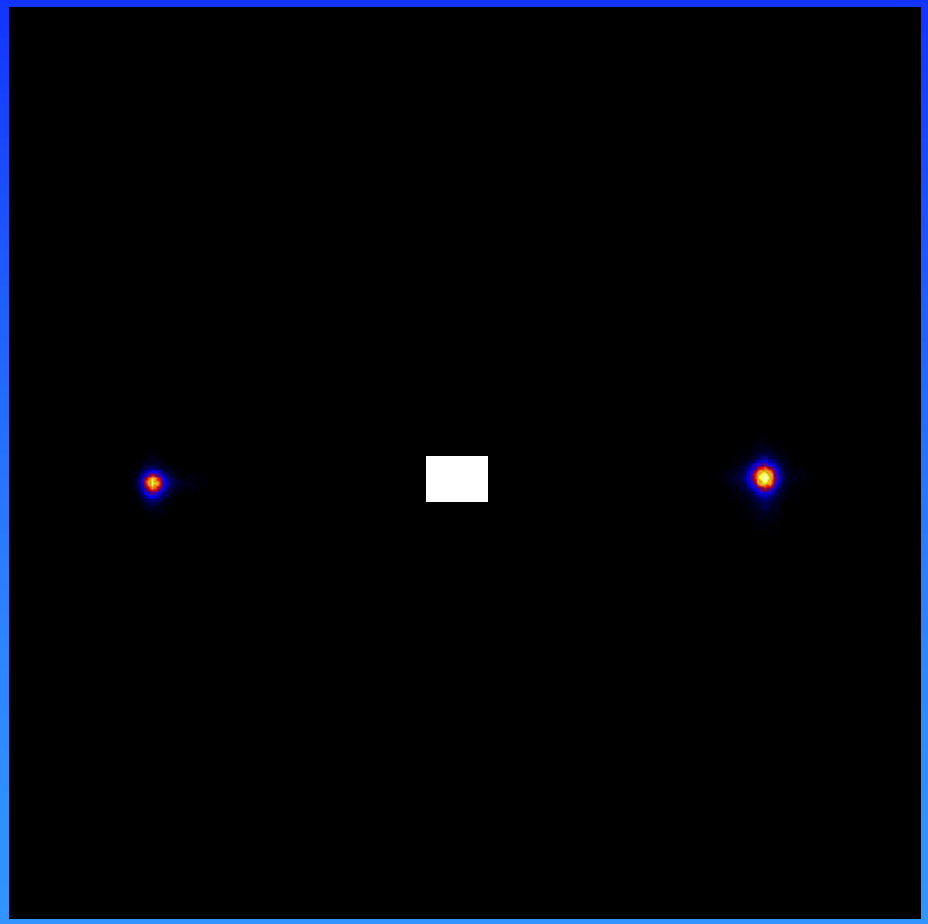


mechanical



Under influence field
(2 sec/frame)

B = 7 Tesla



Jump 45° T = 30 ° C

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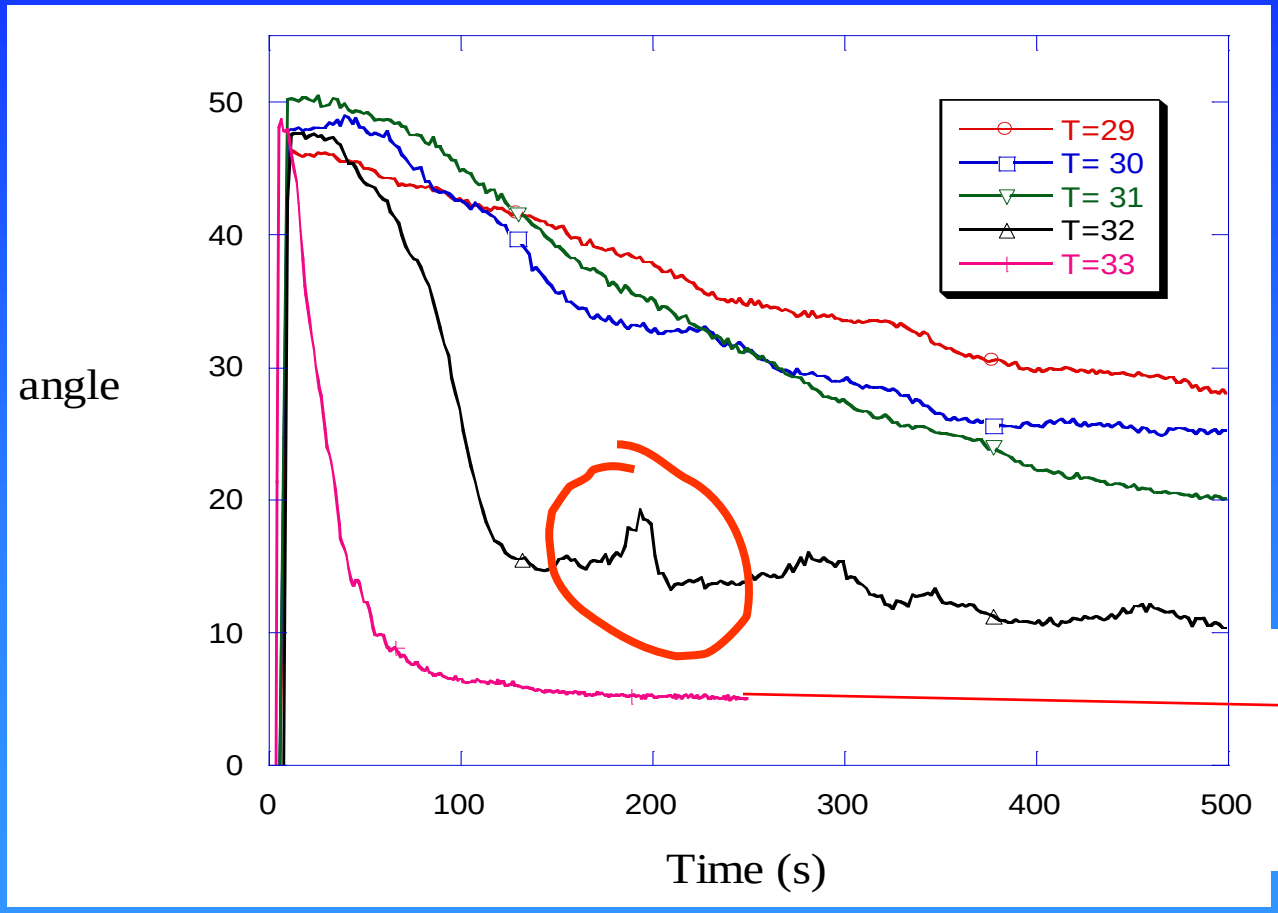
Angular position as function of time



See you tomorrow….

This is fairly simple to do

integrate over sectors

fit peak

plot as function of frame

calculate angular velocity

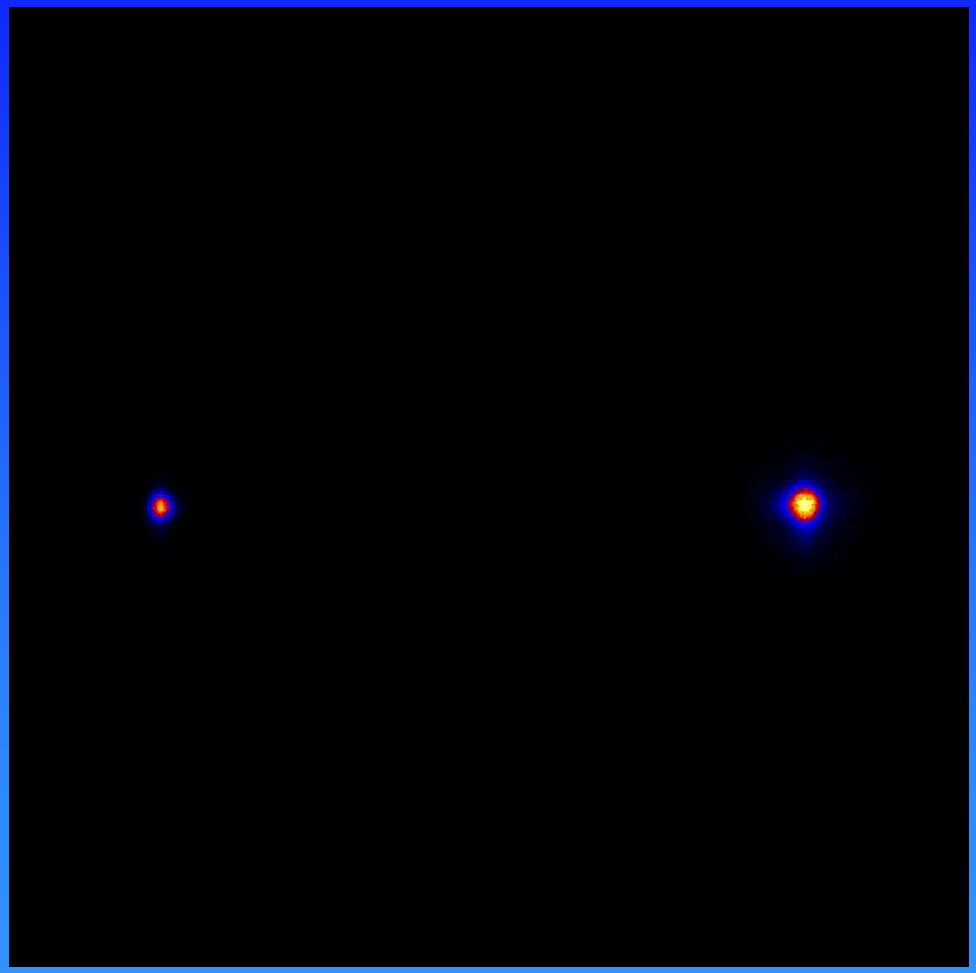
write paper

But…….

B = 7 Tesla

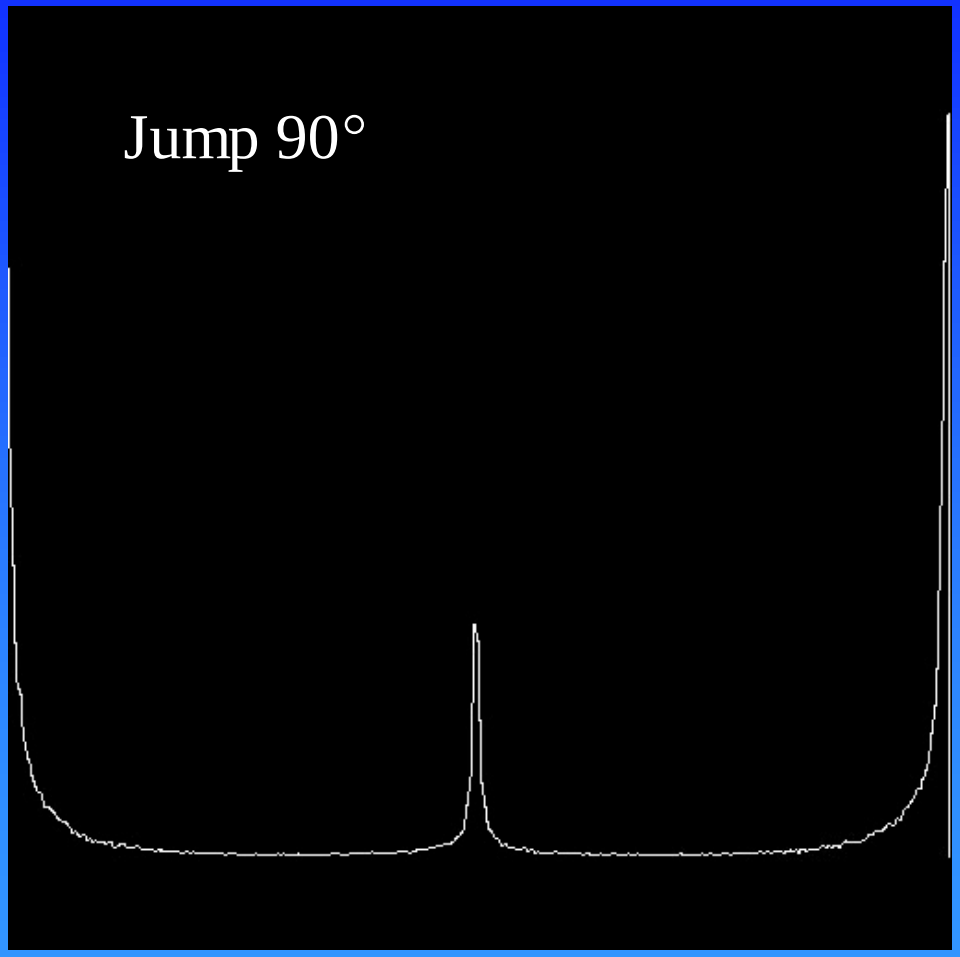
Jump (70 msec)

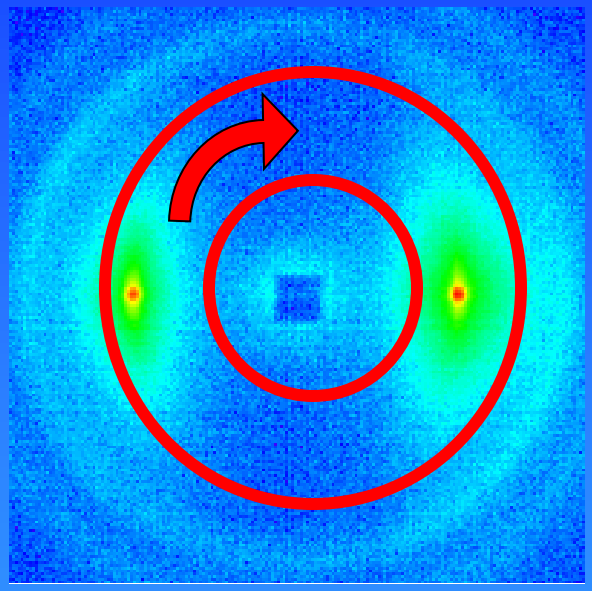
Rotate back
(2 sec/frame)



Jump 66.6° T = 30 ° C

Intensity distribution I(q = c, θ)





0° 90 180 270 360°

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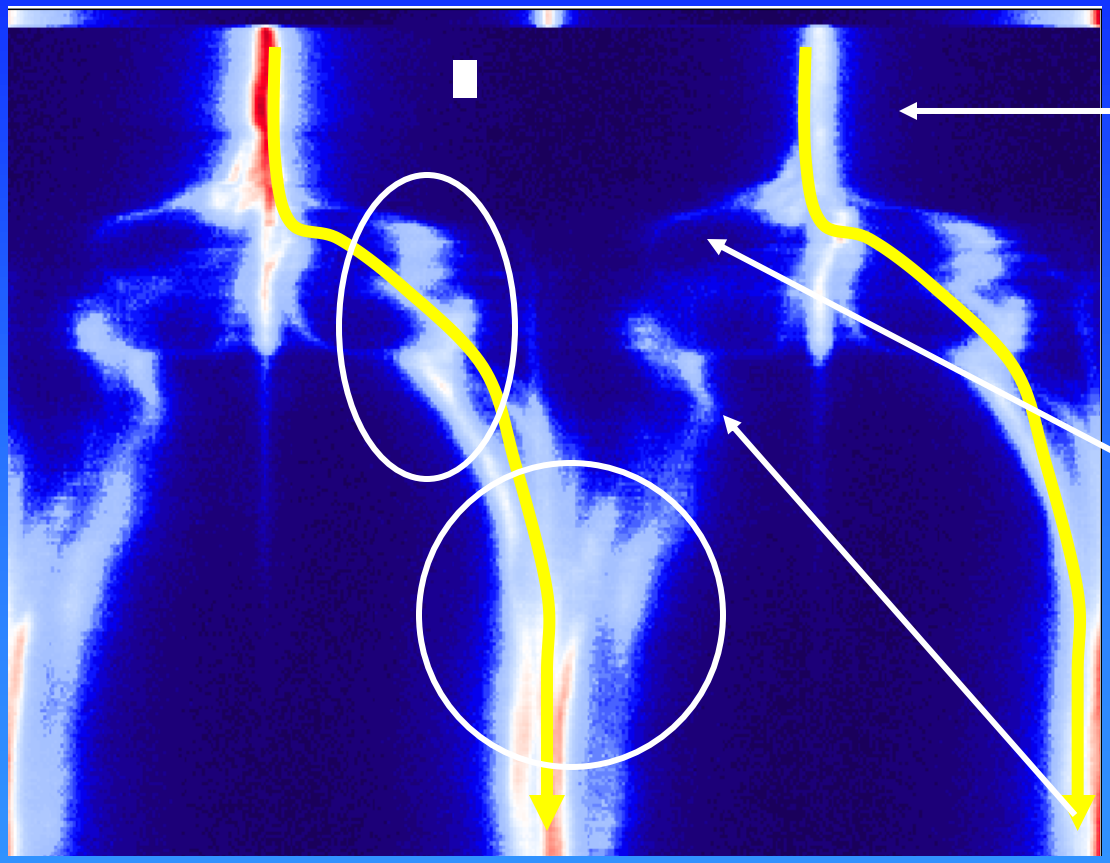
90° rotation
T = 29 ° C
B = 7 Tesla
Time framing
250 x 1.5 sec

360 270 180 90 0

time



Induction period

Hints of rotation but also of counter rotation

This would indicate monodomain rotation

Well, there goes the mono domain hypothesis out of the window !

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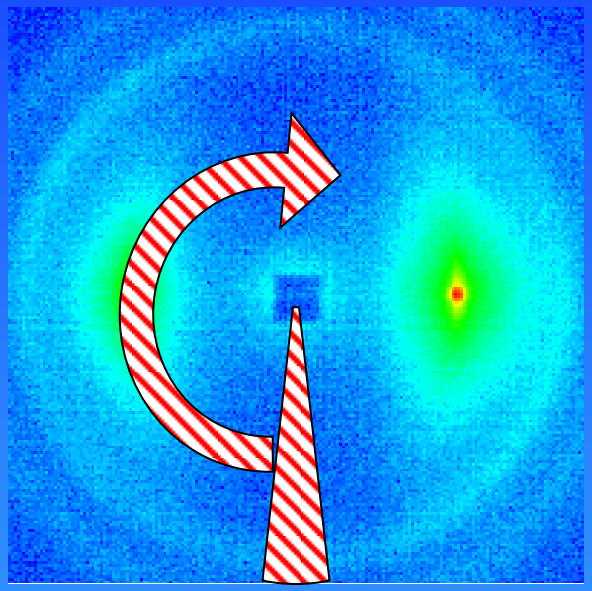
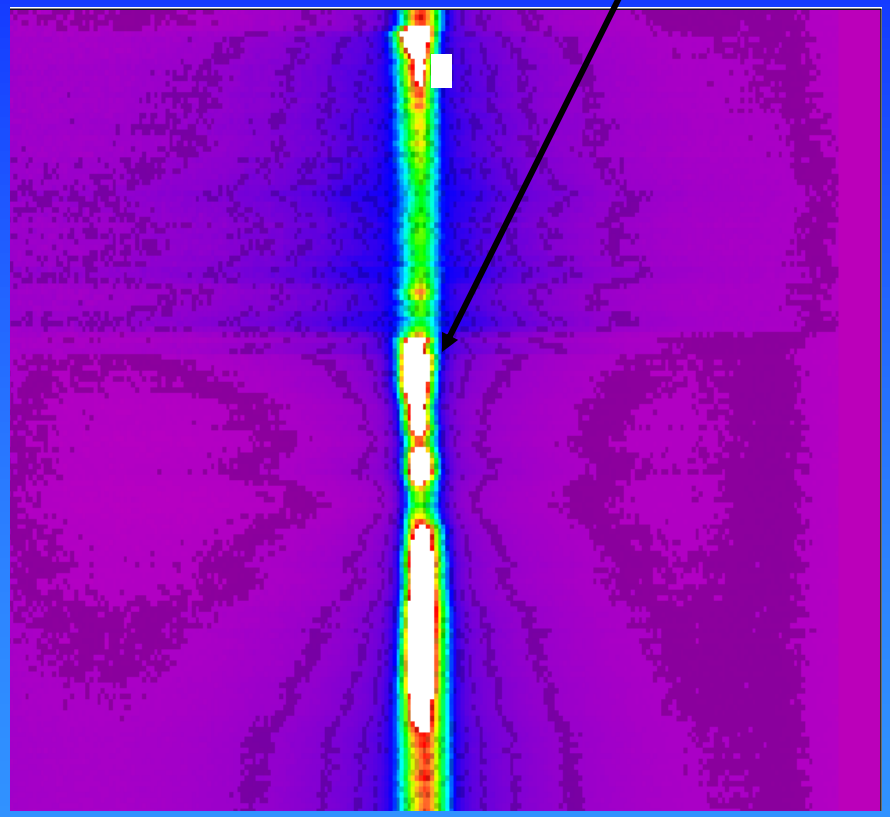
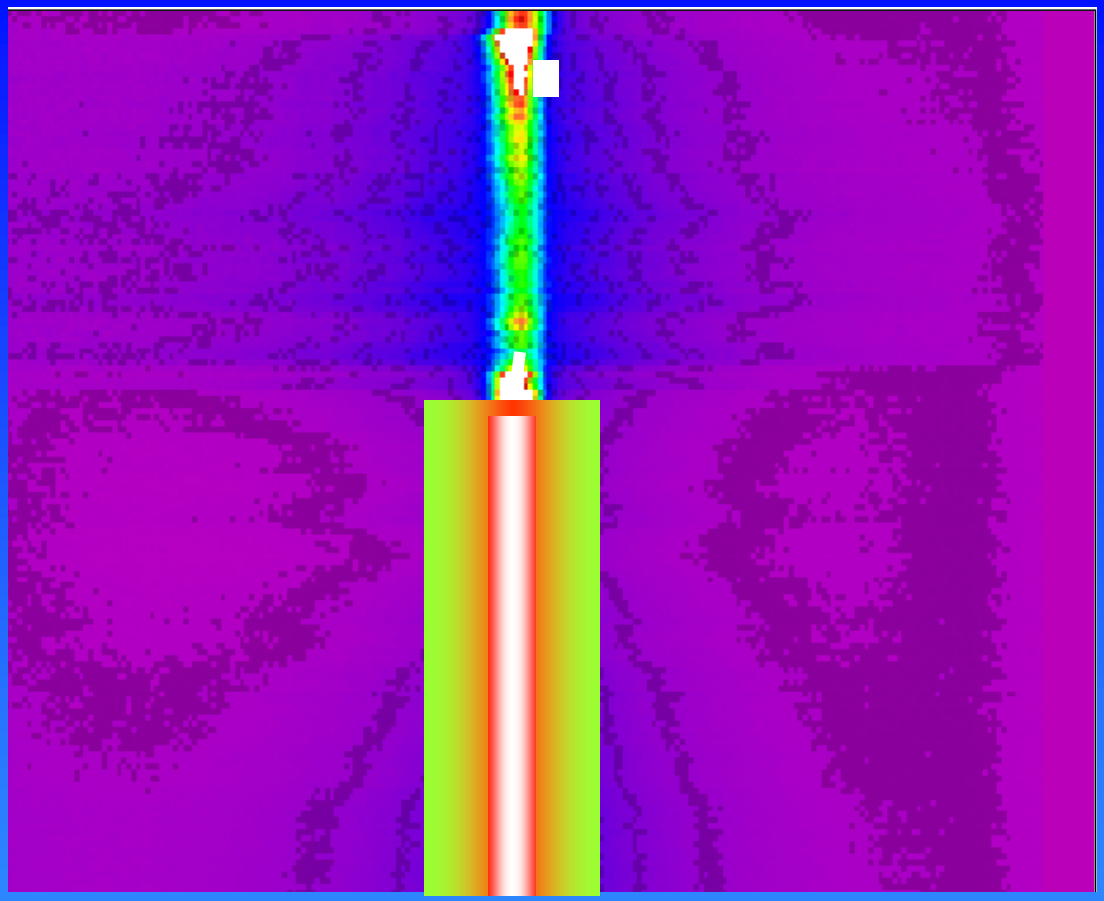
Back to 90°

$$\int_0^{360} I(q,\theta,t)d\theta$$







time

0
beamstop

q (Å^{-1})

0.3
Detector edge

No shift in line spacing $\Rightarrow$ no smectic C intermediate

No broadening $\Rightarrow$ no nematic intermediate

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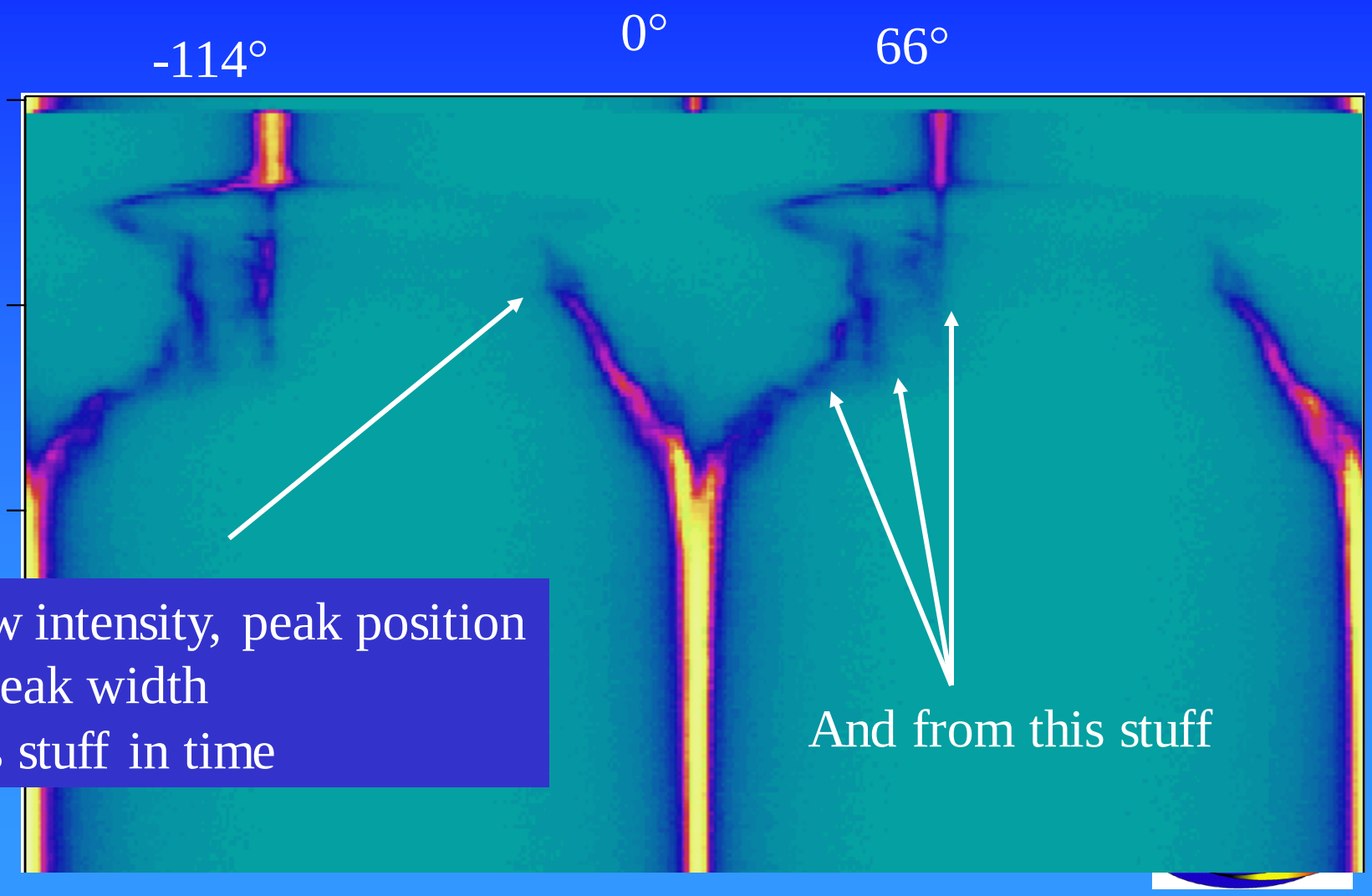
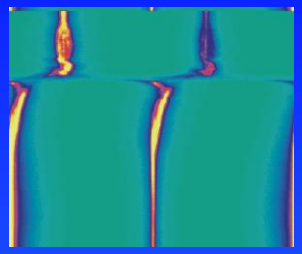
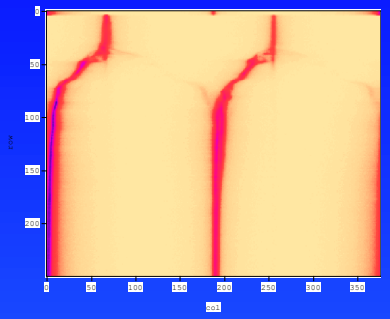
What we want to do:



And further:

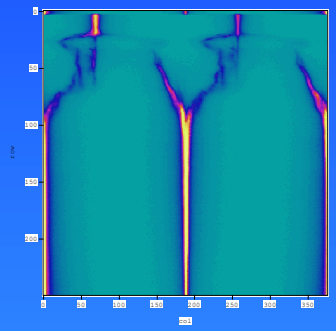
- Correlate the 100 intensity with the –100
- For each domain
- And correlate the domains with each other

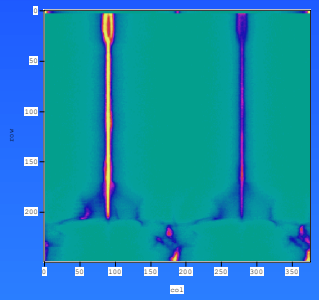


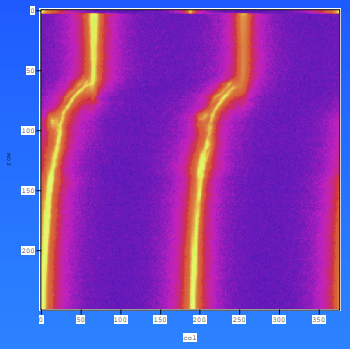


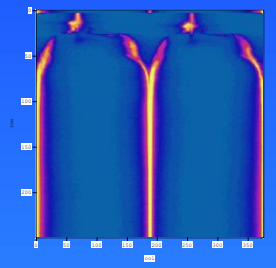
And from the other experiments done in the same session.

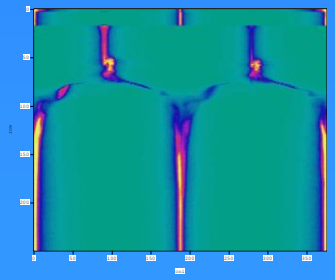
In total > 200 experiments

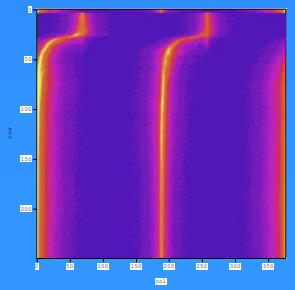


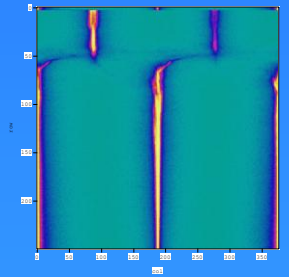


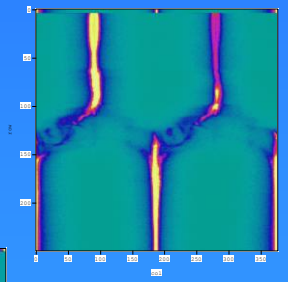


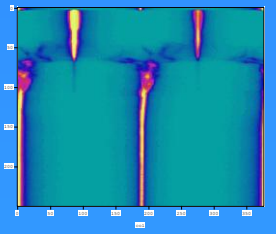




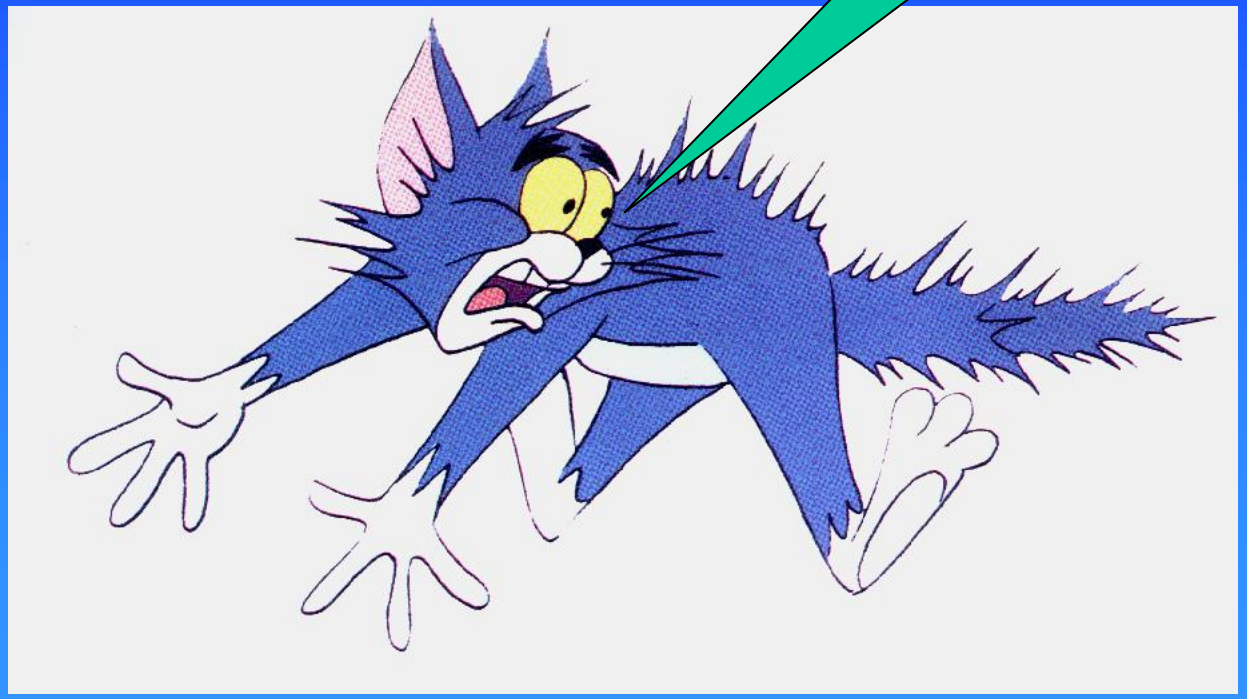






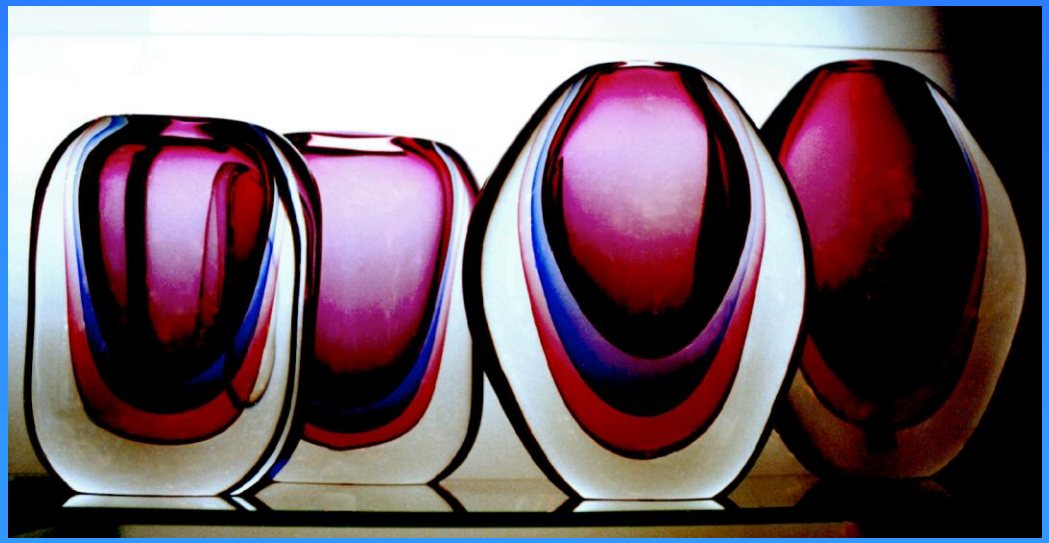


I need an aspirine !

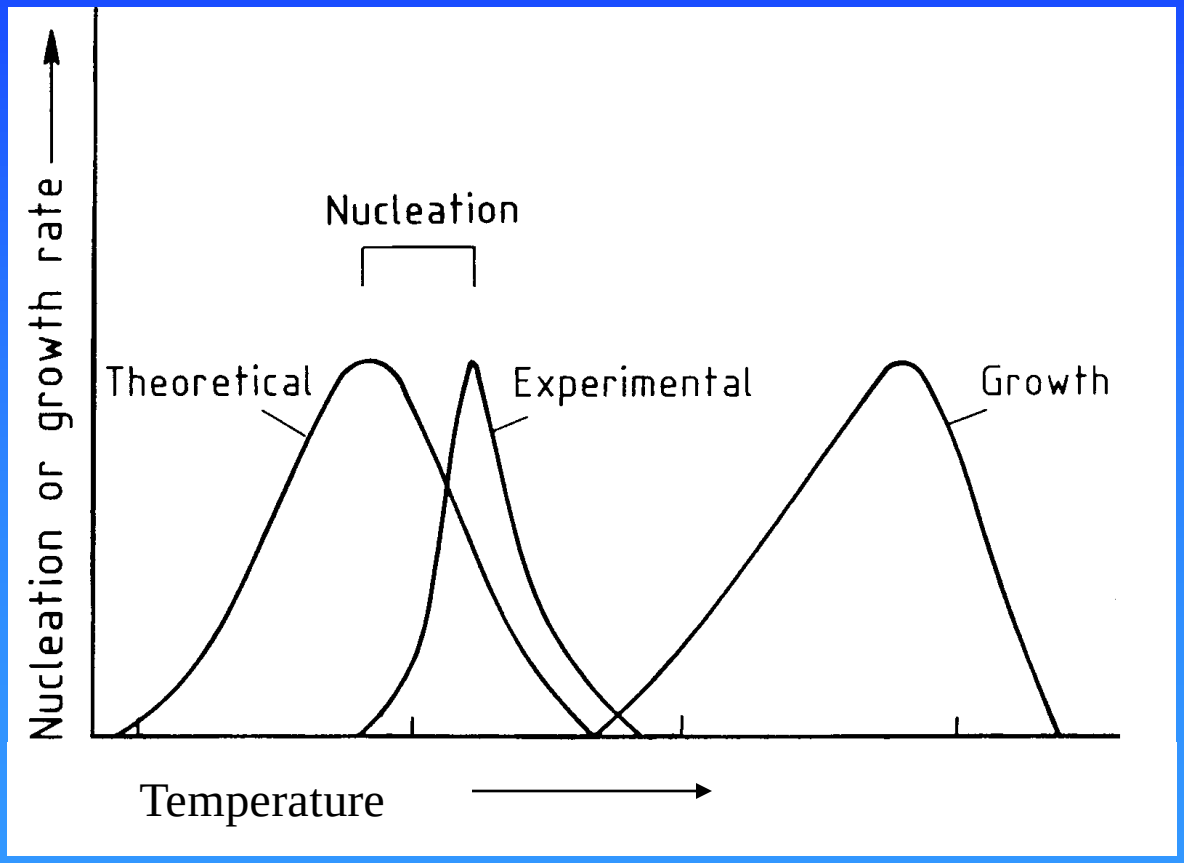


Maybe we should start with something simpler

The 2002 SAS conference in Venice



Cordierite glass devitrivication



Cordierite
Glass with very low expansion coefficient

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

Prifysgol Cymru
Aberystwyth
The University of Wales

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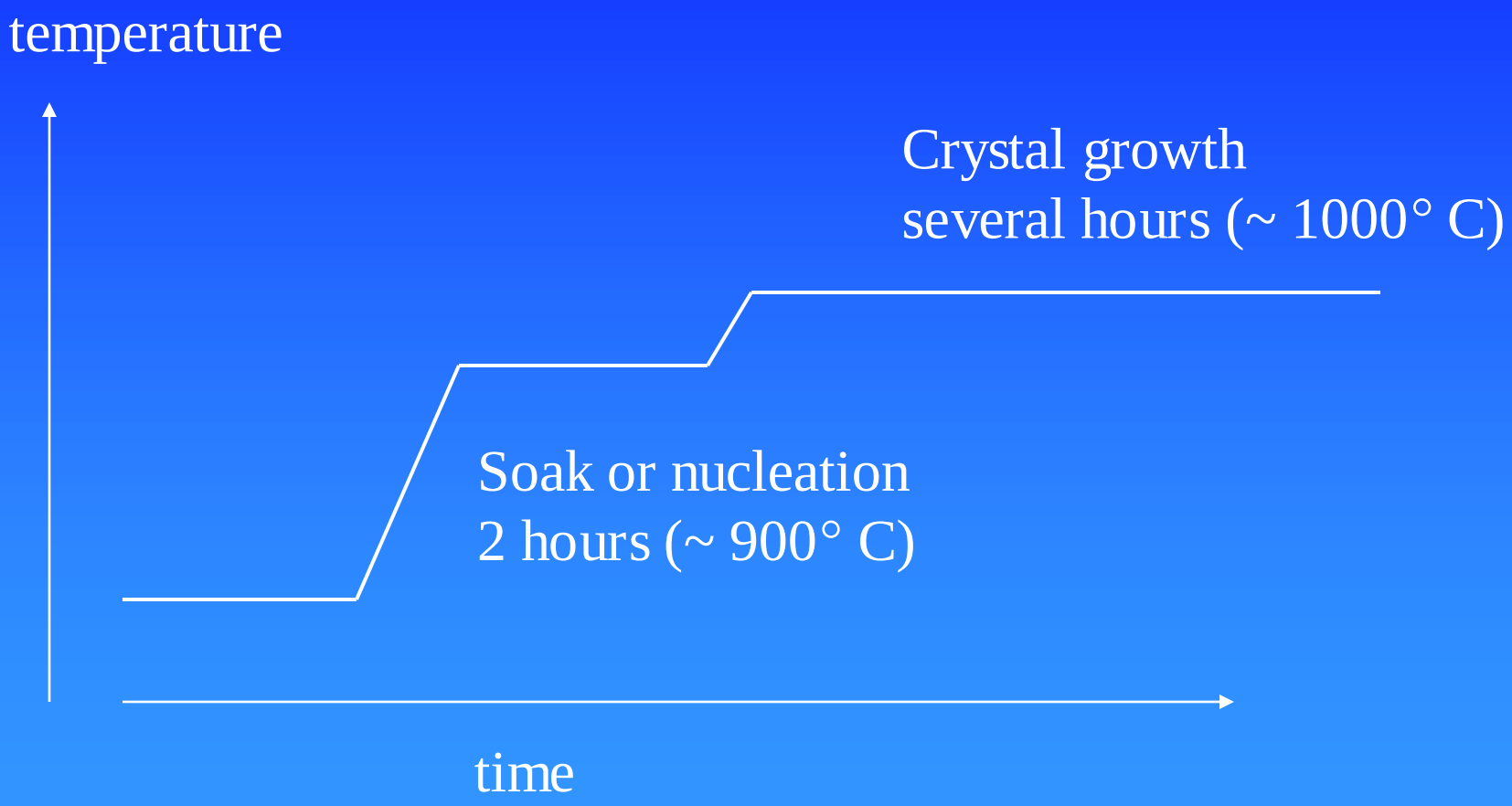
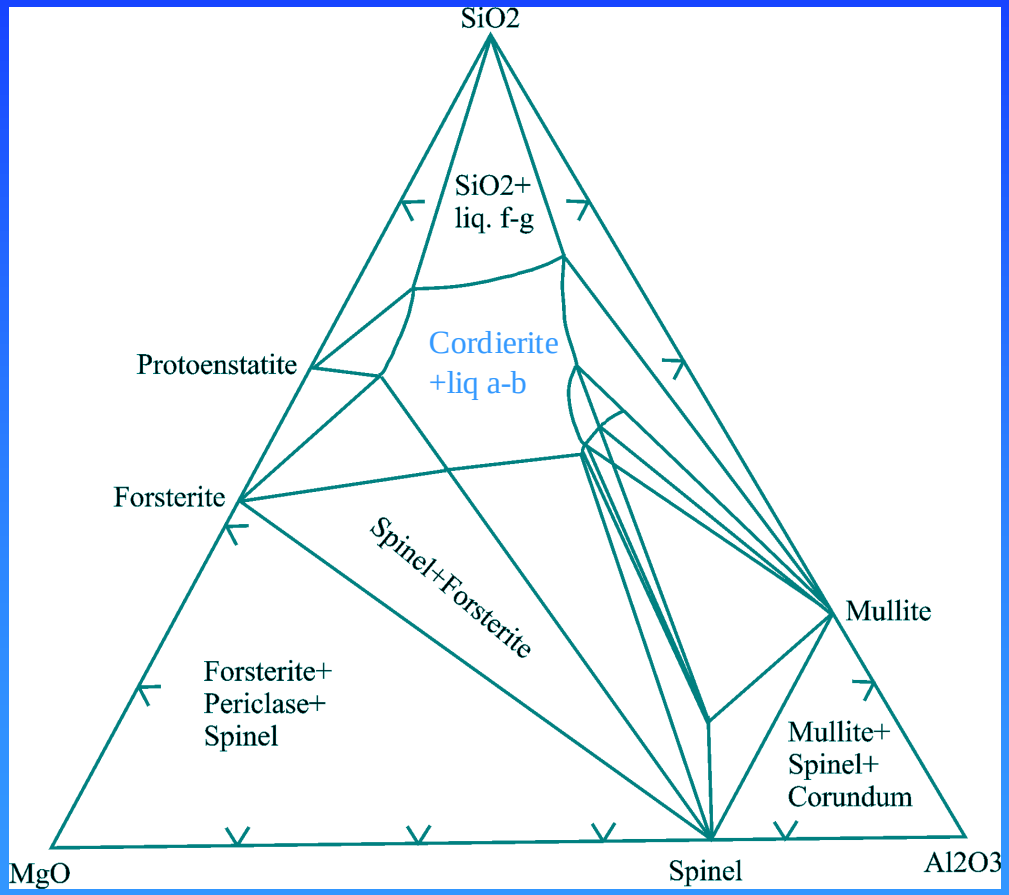
Experiment


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

Messy phase diagram

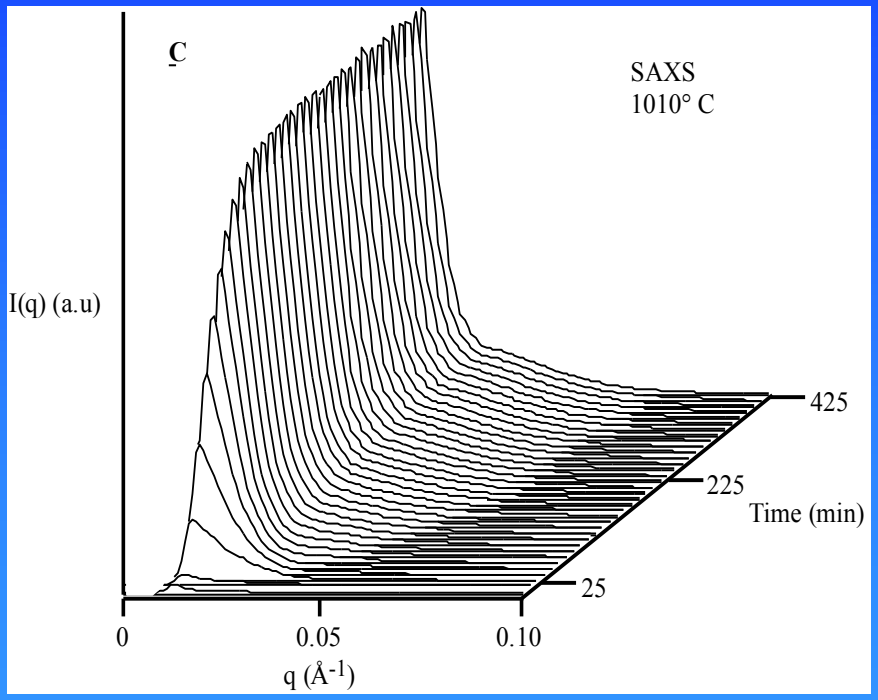


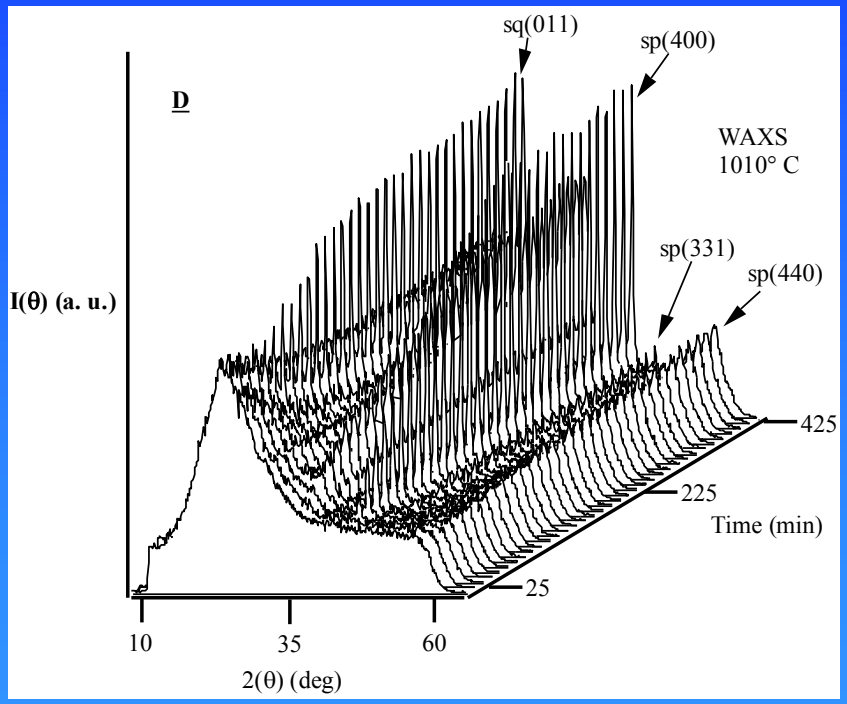
1460° C
Mullite $3Al_2O_32SiO_2$
Protoenstatite $MgOSiO_2$
Spinel $MgO.Al_2O_3$
Forsterite $2MgOSiO_2$

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

Structure development

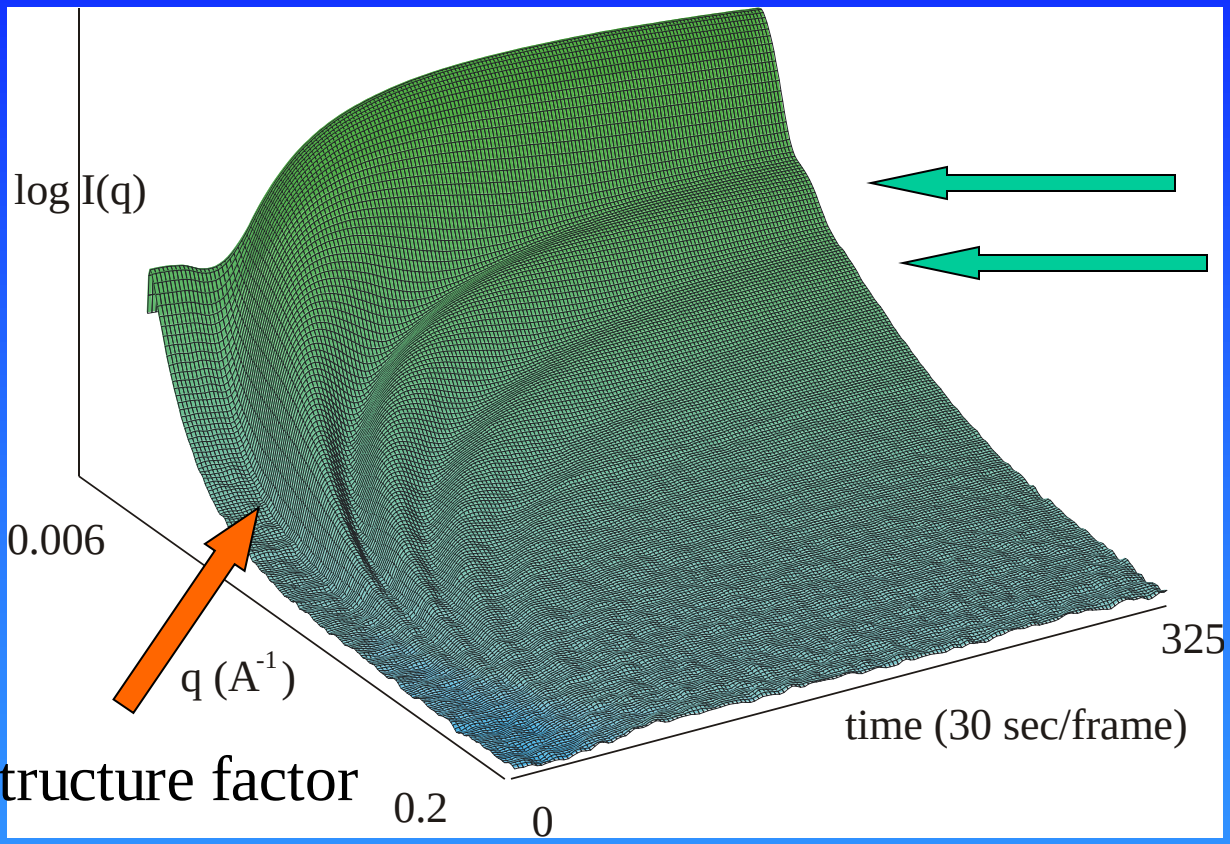
Data taken at 1 minute/frame





SAXS

WAXS



Structure factor

Form factor peaks (up to 5th order)

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

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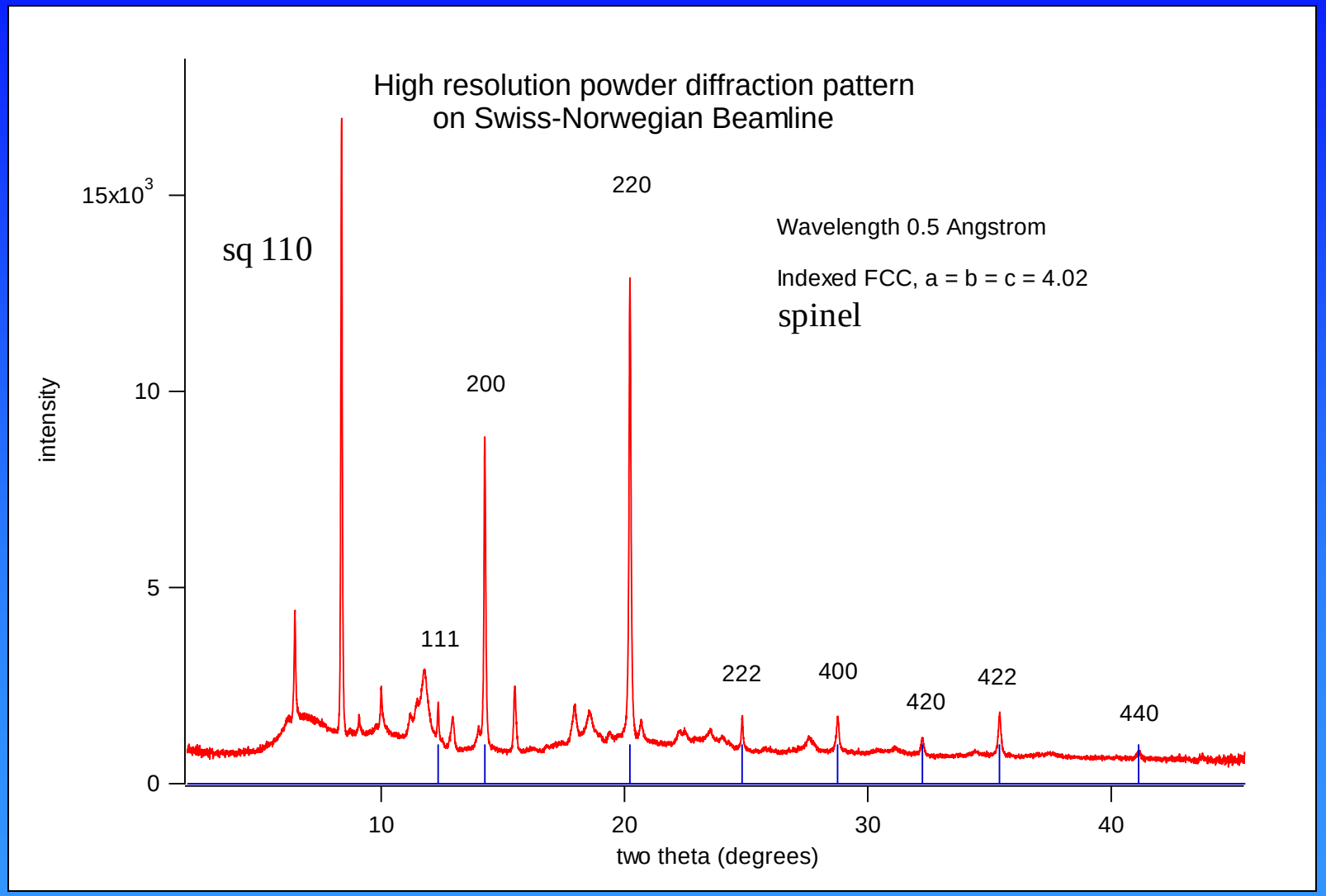
Relatively easy to analyse

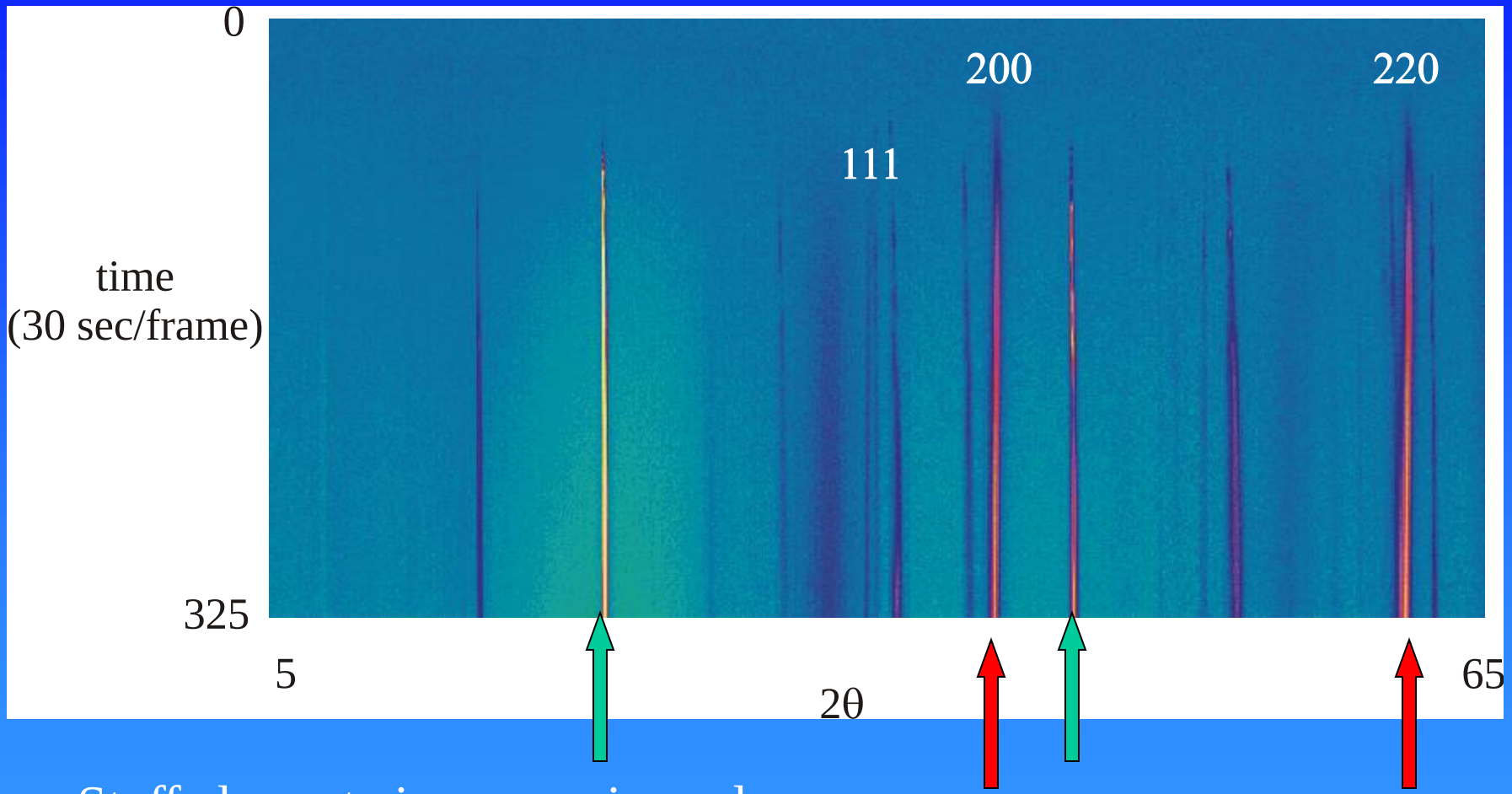
- Find peak structure factor
- Find minima form factor
- Use these to calculate the particle size
- Fit formfactor function

- And repeat 250 times for one data set…..

And we have 40 data sets…..


High resolution powder diffraction pattern
on Swiss-Norwegian Beamline
sq 110
220
Wavelength 0.5 Angstrom
Indexed FCC, a = b = c = 4.02
spinel
200
111
222
400
420
422
440
15x10^3
10
5
0
intensity
10
20
30
40
two theta (degrees)

WAXS data



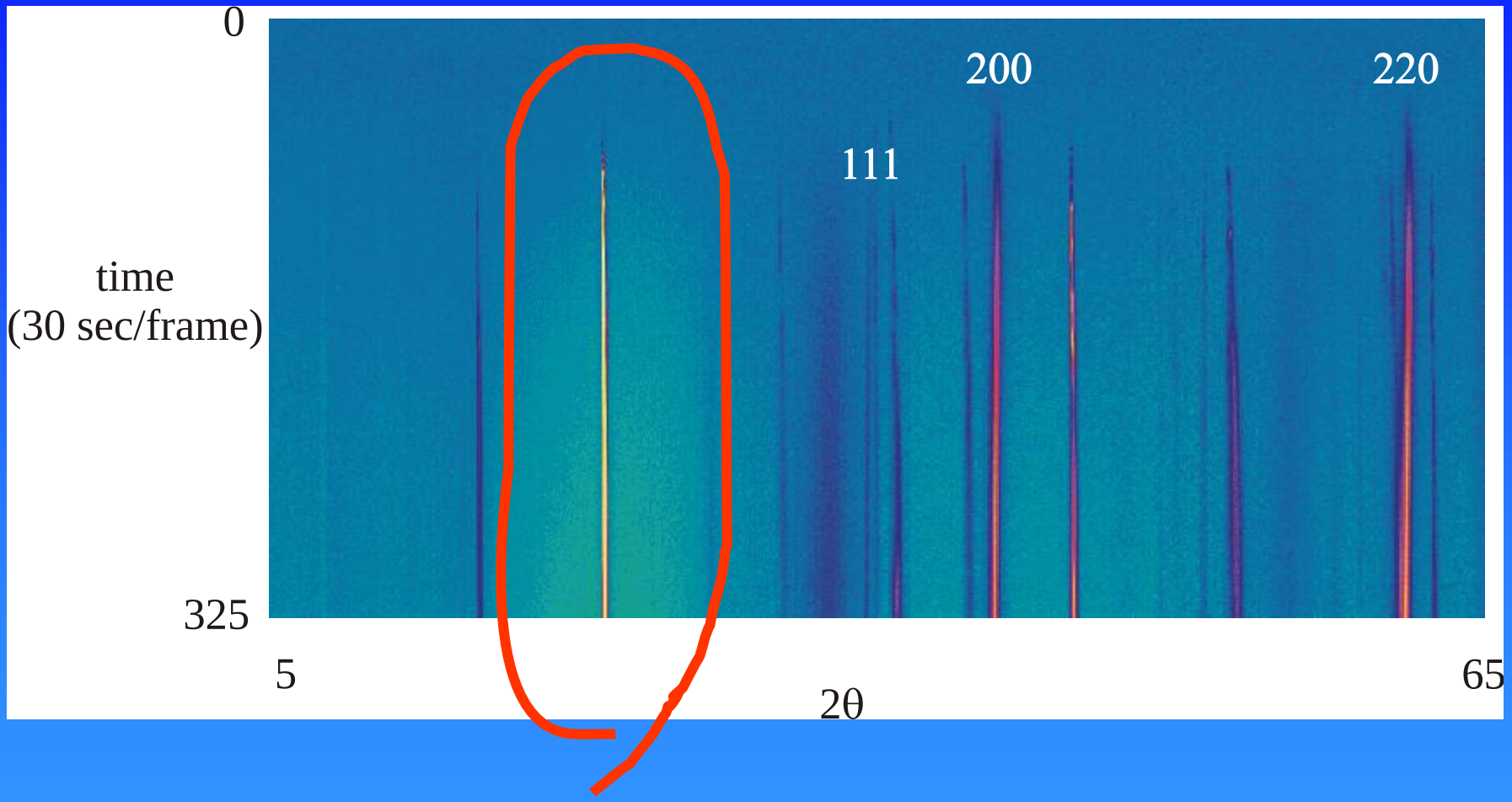
Stuffed quartz increases irregular

Spinel increases regularly

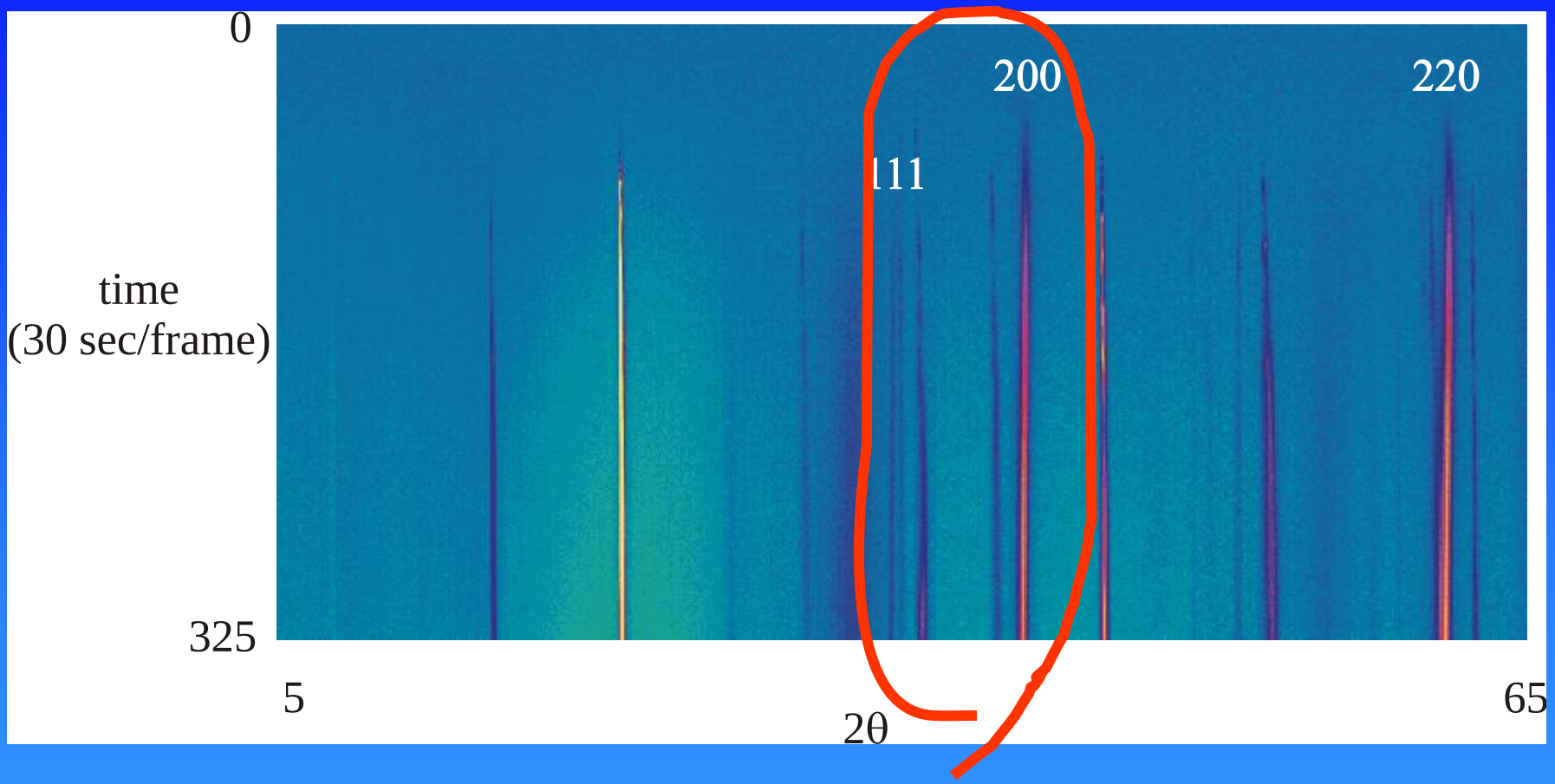
Spinel unit cell increases in time
$MgOAl_2O_3$ FCC a = b = c = 4.03 Å

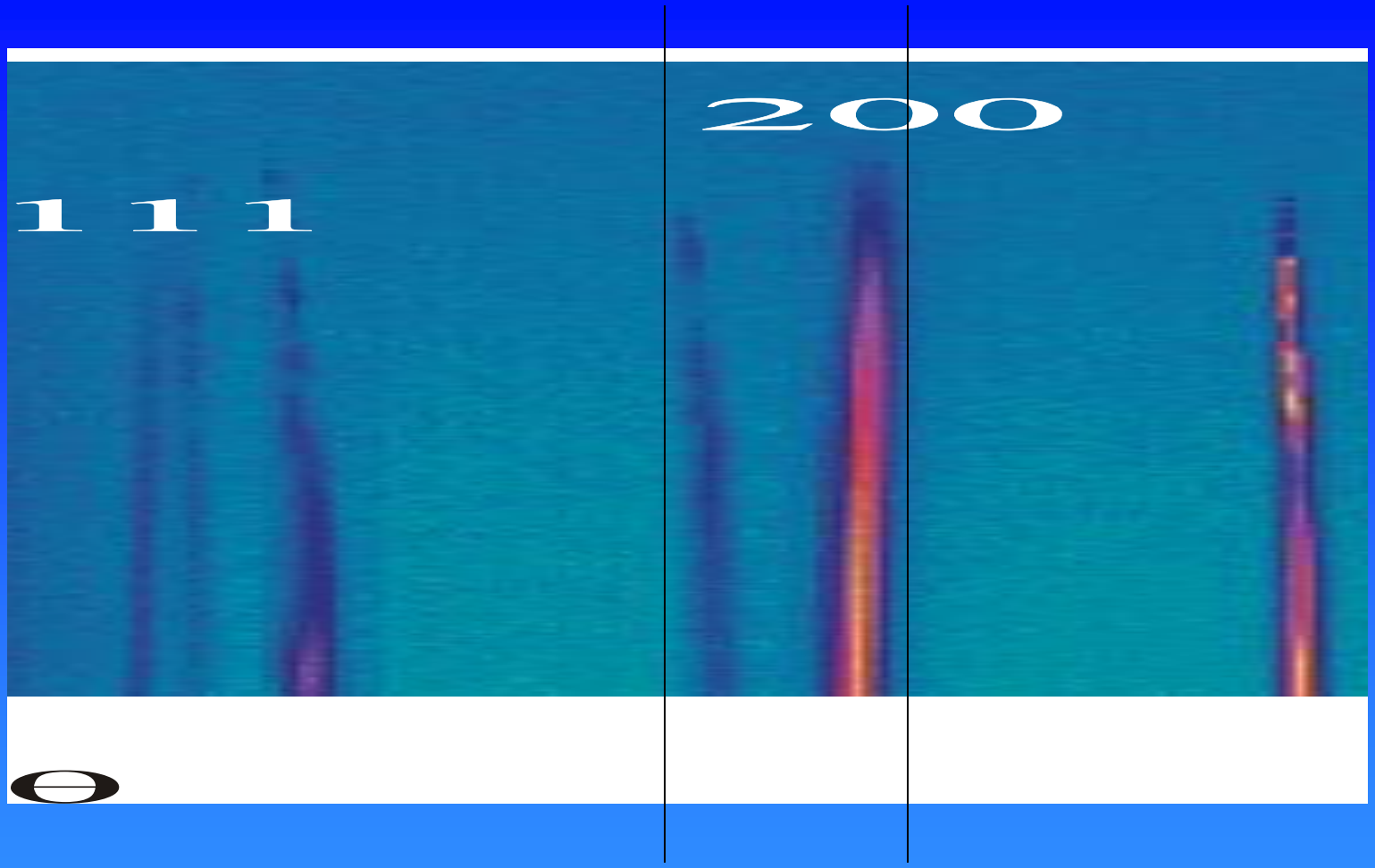
Stuffed quartz unit cell decreases in time
trigonal a = b = 5.13 Å c = 5.37 Å

DUBBLE


0
200
220
111
time
(30 sec/frame)
325
5
65
2θ

Continuously changing background


0
200
220
111
time
(30 sec/frame)
325
5
65
2θ



The spinel peaks move right

The stuffed quartz peaks move left

So:

- Changing background
- Moving peaks
- Varying intensity

- And off course a lot of sh*te of the detector which I will not show you since I, just like any other beamline guy, pretend that my detectors are perfect……..

But:

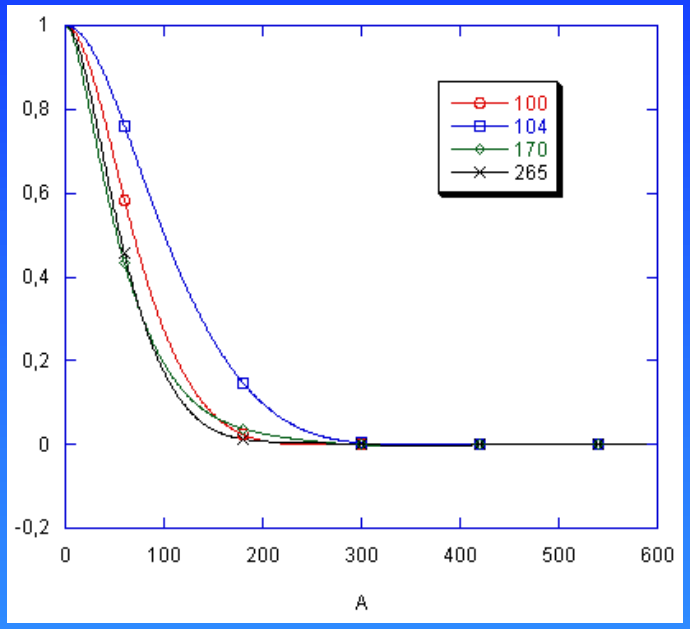
- Some people call this data analysis
- I call it data reduction

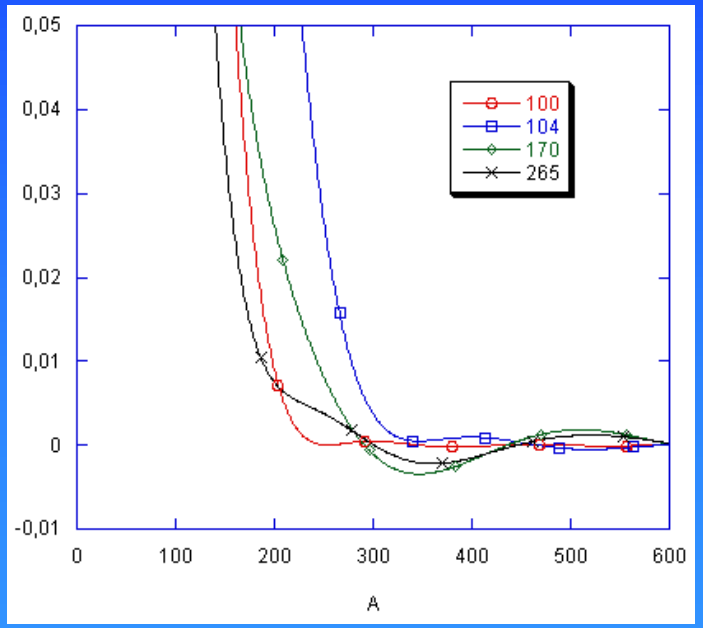
- What about analysis software?

Let’s take a look at the correlation function of this stuff

That’s more like data analysis

(self) correlation function



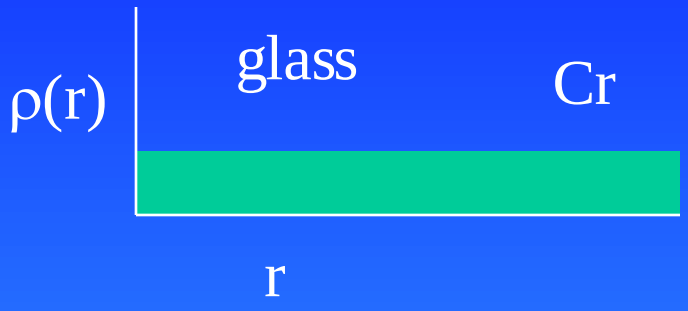


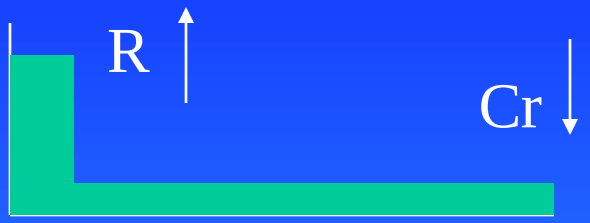
$$\gamma(r) \sim \rho(r)\,\rho(r - r')$$

Courtesy of my mate Guy Eeckhaut

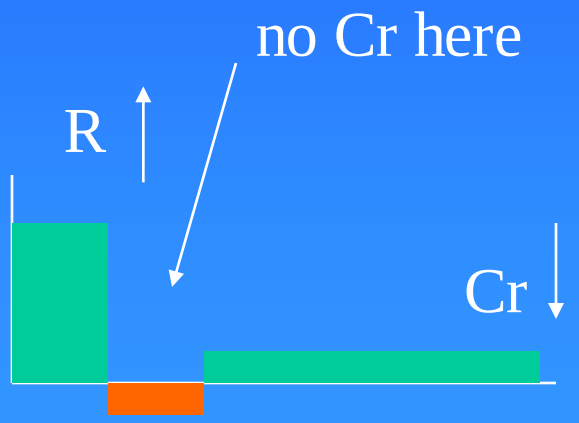
DUBBLE

Development electron density profile

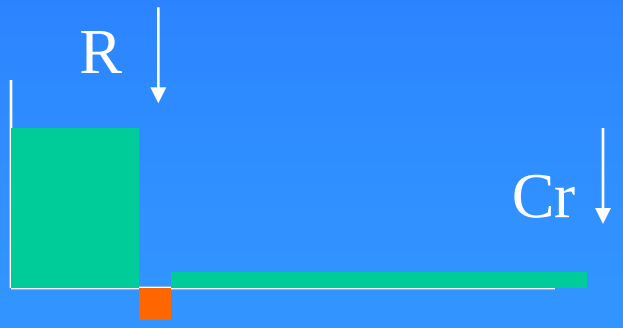




Nucleation and initial growth



Growth and depletion zone



Reduction depletion zone

DUBBLE

But how was this done?

That’s easy

You phone up Otto or Dmitri

Ask for a copy of their programs

Change your data format so that THEY like it

Plug in the curve

Analyse

Go for coffee break

You deserved that coffee break……

The previous step took you about an hour……

Cheer up……

Only 255 to go……

Question:

Is there software that can do this reliably, i.e. no weird results that require extensive human intervention to get it right?

My answer to this is: NO

We can't even do that for a Guinier radius or Porod slope

So:

- I don’t have the answer to how to solve our problems with time resolved data
- We don’t get the full benefits out of our data
- We’re robbing ourselves

- We keep moaning about better beamlines
- Better detectors

- What we reallly need is better software

- What we really need is a strong and focussed effort to achieve this.

And I've heard it all before

I have a little program that…..

I never have problems with background…..

Fit2D does…..

It falls under the remit of CCP13 to…..

A shellscript for OTOKO that does…….

In my laboratory we have solved this problem in…..

Thanks for your attention