Spice up your beam time experience with exciting sample environments

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

- Some old
- Some new
- Some heavy duty
- Some grazing incidence

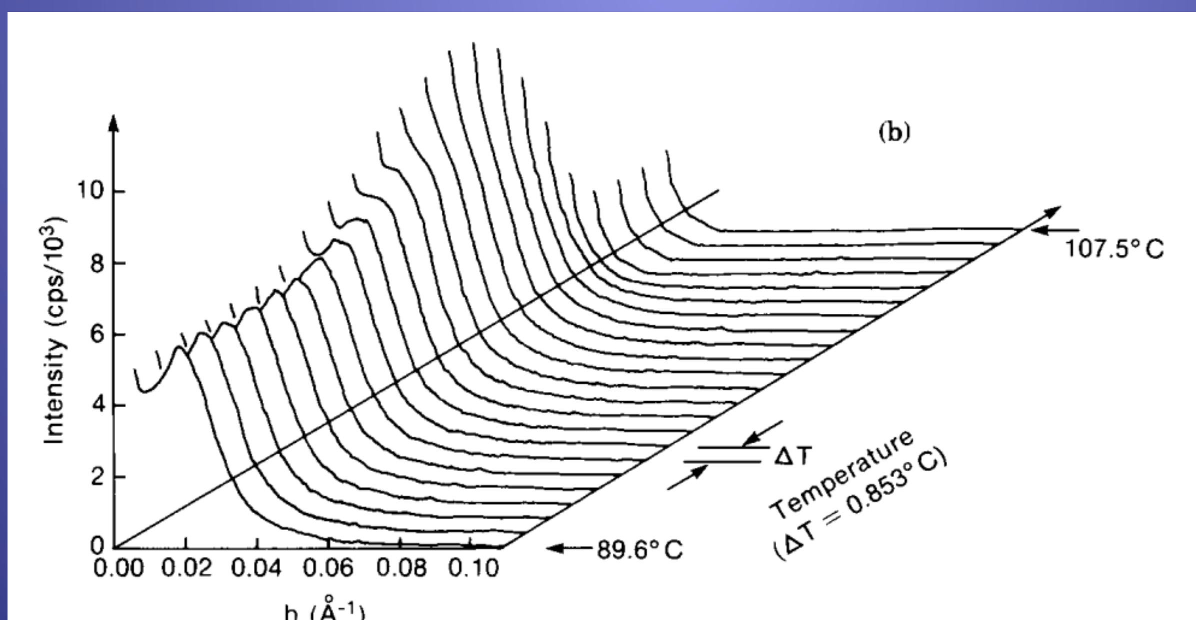
SAXS/WAXS
Daresbury 8.2/2.1
ESRF BM26B/BM16
ALS 7.3.3

Some spectroscopy beamlines

Technique combinations

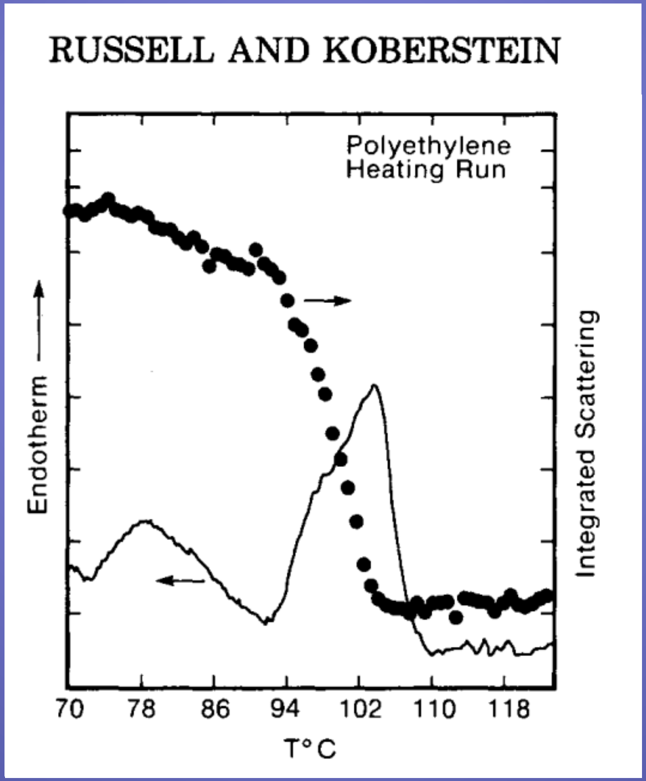
in the days that life was still simple

Mettler DSC stage



1985

DSC and
SAXS invariant



Tom Russell,
the author

1984 Hamburg SAXS/WAXS

1984 ... – Simultanity in Action

An stimulating task: Watch polymer materials crystallize, fail, . . .

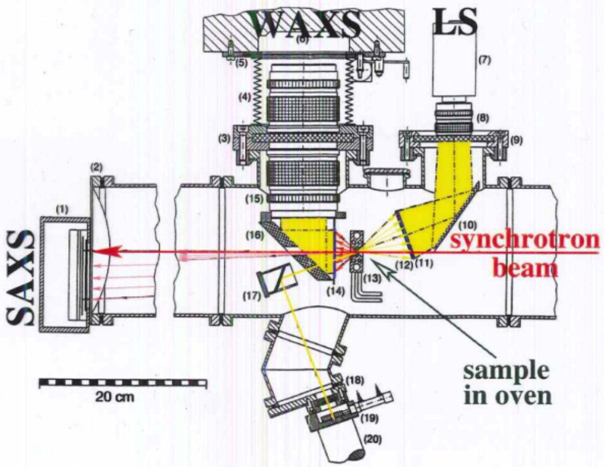


Figure 2: Setup for simultaneous measurement of two–dimensional SAXS, WAXS, and Light Scattering in Hamburg. Blue: Converter screens. Yellow: Visible light.

Simultaneous *in situ* measurements — the most vicious instrument is shown in Figure 2. Problems?

- Synchrotron beam instability
- Poor detectors (Vidicon)
- Interference of intertwined setups

Demonstrate the potential of such experiments (Figure 3).

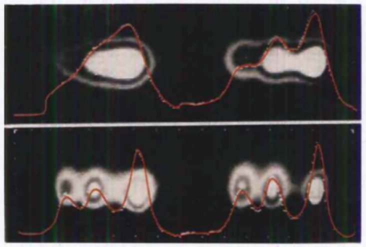
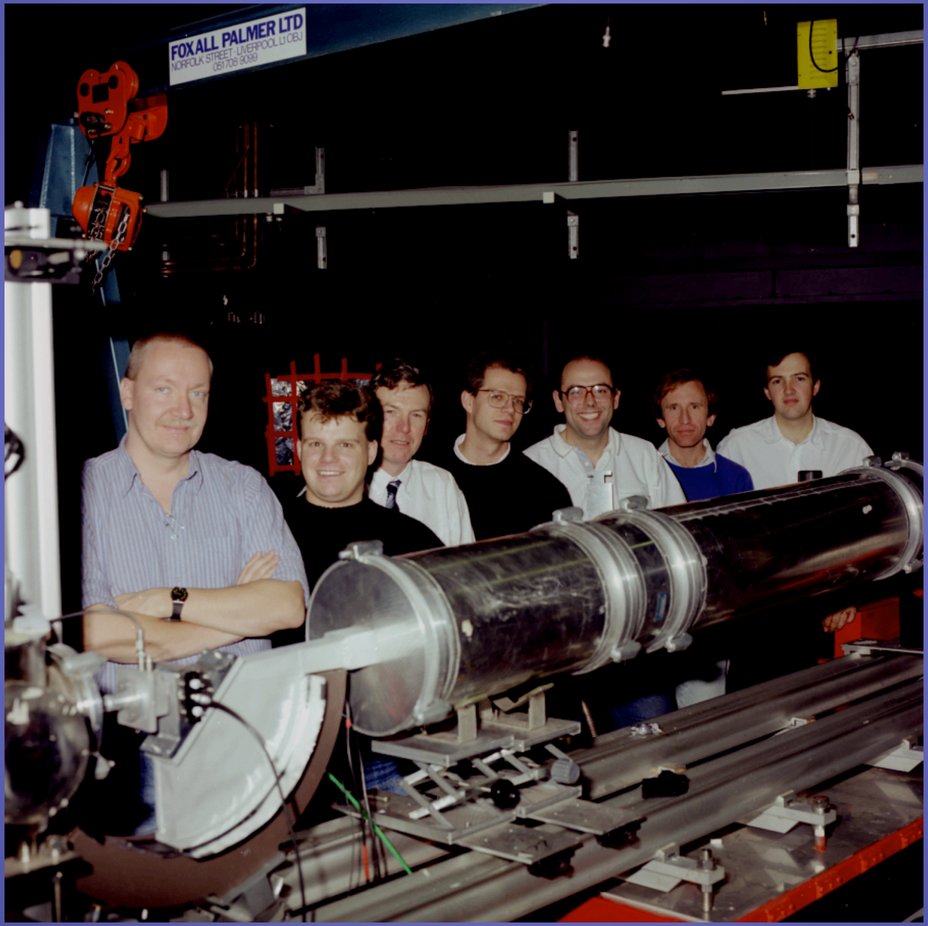


Figure 3: Vidicon image: Transformation of smectic polypropylene into the α-phase

Universität Hamburg

Courtesy Prof Stribeck

Daresbury 1993

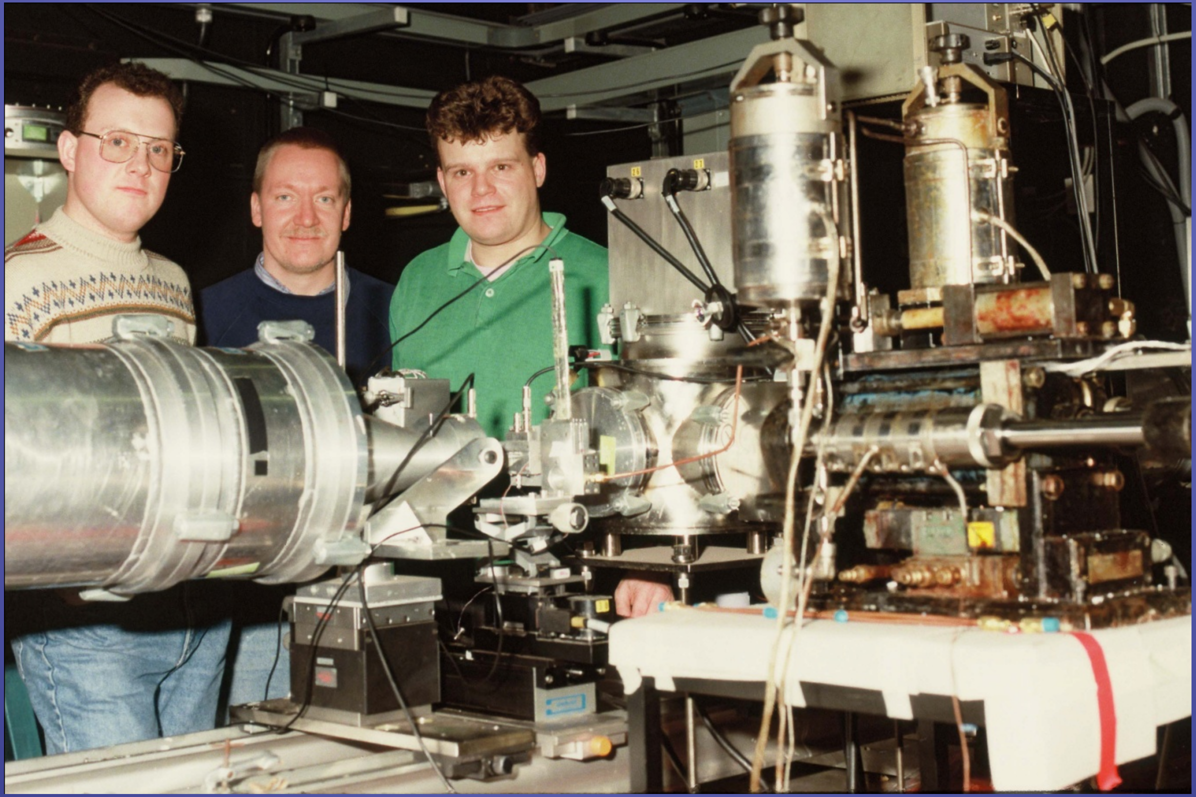


Bras NIM 1993

First dedicated SAXS/WAXS set-up

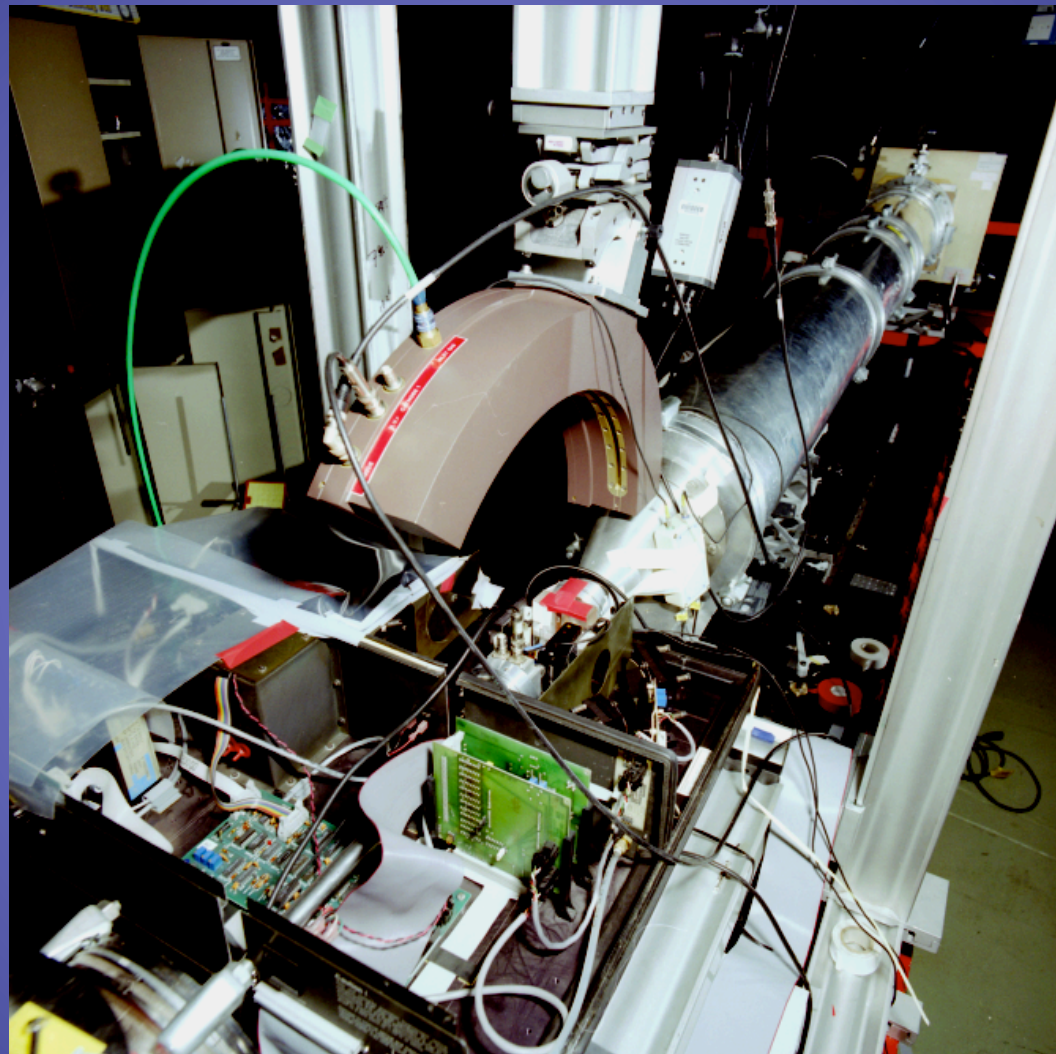
1994 SAXS and RIM

+15 +25



Ellwel, 1995

1995 SAXS and FTIR



High tension safety cover

Safety officers

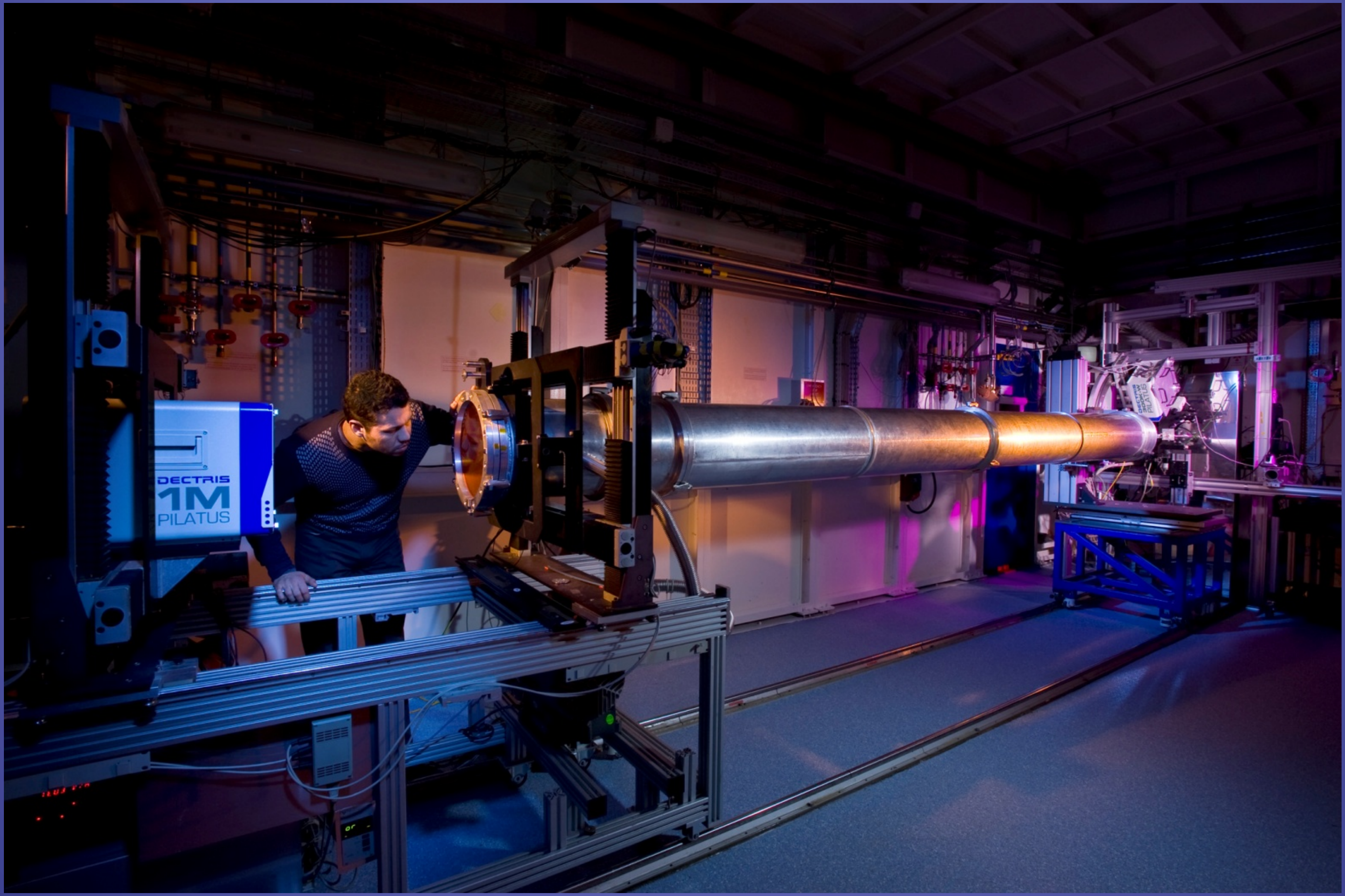
Old FTIR; hacksawed holes to get X-ray beam in.

Bras, Science, 1995

This was some old stuff

- Done on first and second generation SR sources
- Experimental adventure is from all ages
- This makes predictions of the future demands pretty hard

Somewhat more modern SAXS/ WAXS



Diamonds are forever

- New generation of single crystal CVD grown diamonds are beautiful windows
- Strong
- Thermal conduction very good
- Chemically pretty inert

- And not really very expensive

Supercritical CO_2 Cell

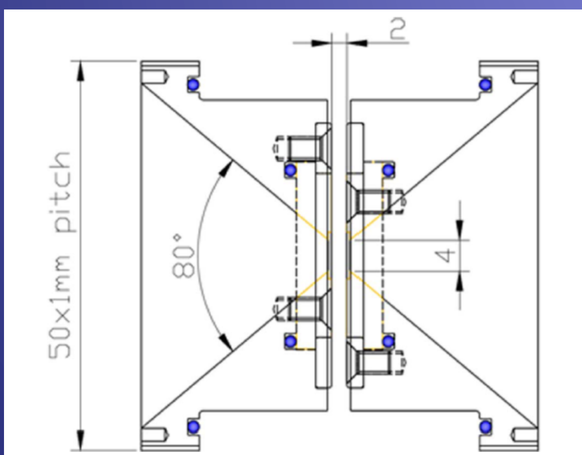
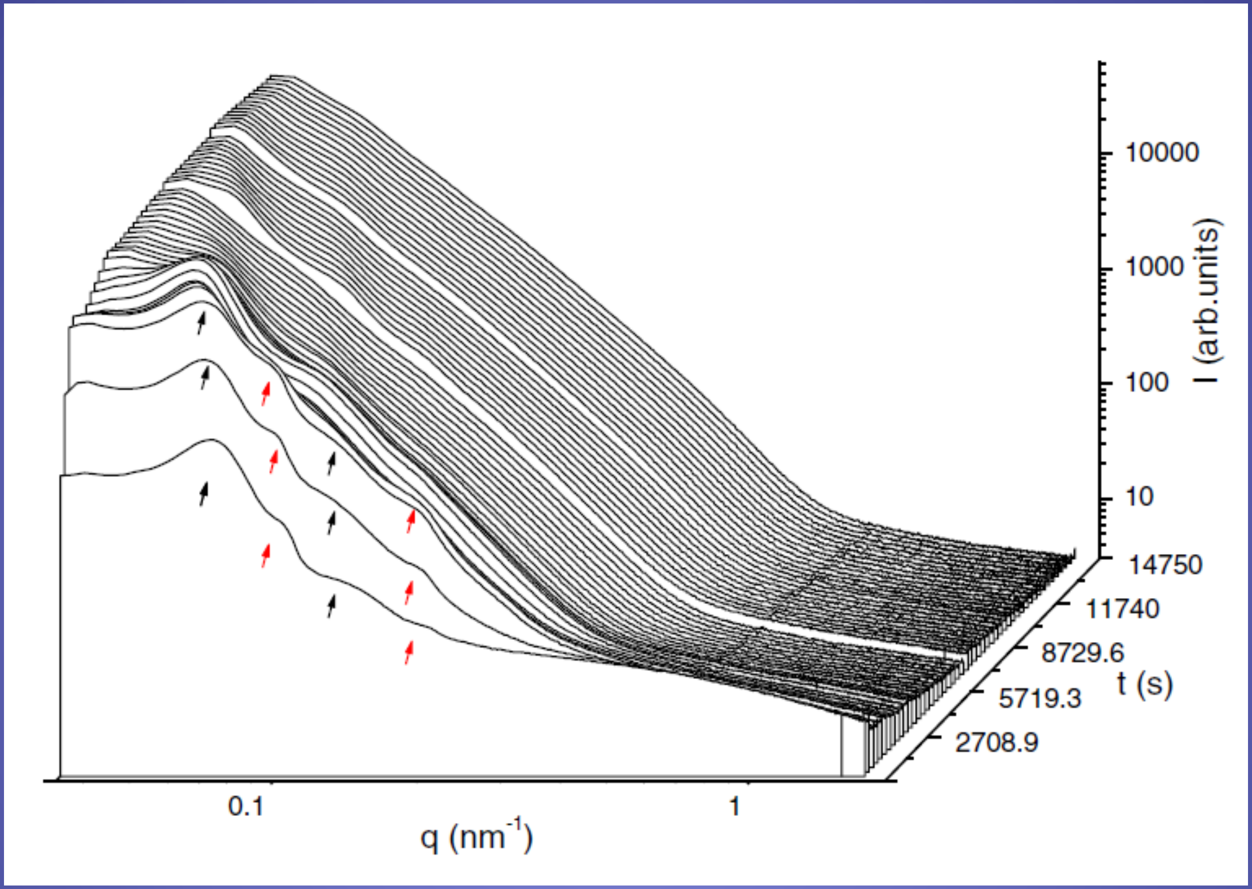


FIG. 4. Diamond window inserts showing the 40° clear optical aperture for collecting simultaneous SAXS-WAXS. The free window diameter is 4 mm and the exit opening angle is 40°. (All values on the diagram are in mm).

- 200 Bar max pressure
- chemical sampling possible
- extra ports for Raman/DSC available
- At 15 keV 95% transmission
- Diamond windows 4 mm clear aperture, 0.4 mm thick

Hermida-Merino Rev Sci Instr 2015



Raft polymerization of PMMA – b – PbzMA

Data rate 1 frame/minute (determined by reaction rate, not by detectors or flux)

200 Bar, 65° C

Main problem:

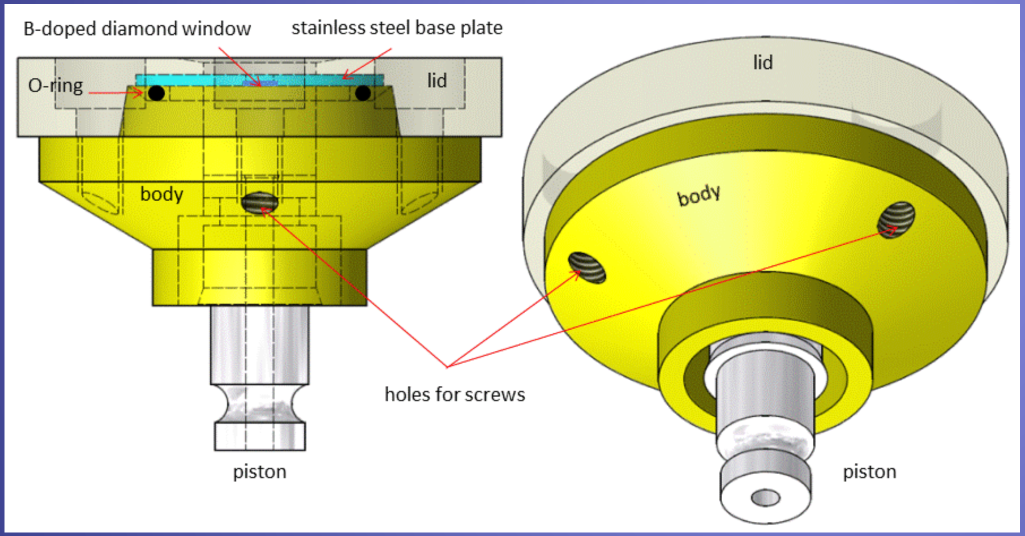
- Not the pressure
- Not the X-ray transmission

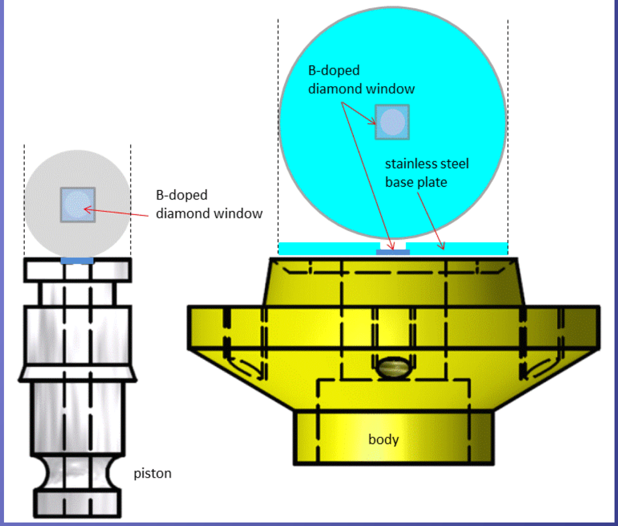
- But the stirring, i.e. homogeneity in the reaction cell
- The reaction volume is large but the X-ray path is only 2 mm

More diamonds: electrochemistry

- Doping with Boron can make diamonds electrically conductive
- Combined window/electrode
- Only small amount of doping required
- Single crystal structure still ok
- Parasitic scatter still pretty low

Li-ion batteries
polymer – silicon basis





Where does the Li go in a charge/discharge cycle?
Why does the capacitance detoriorate as function of the number of charging cycles?

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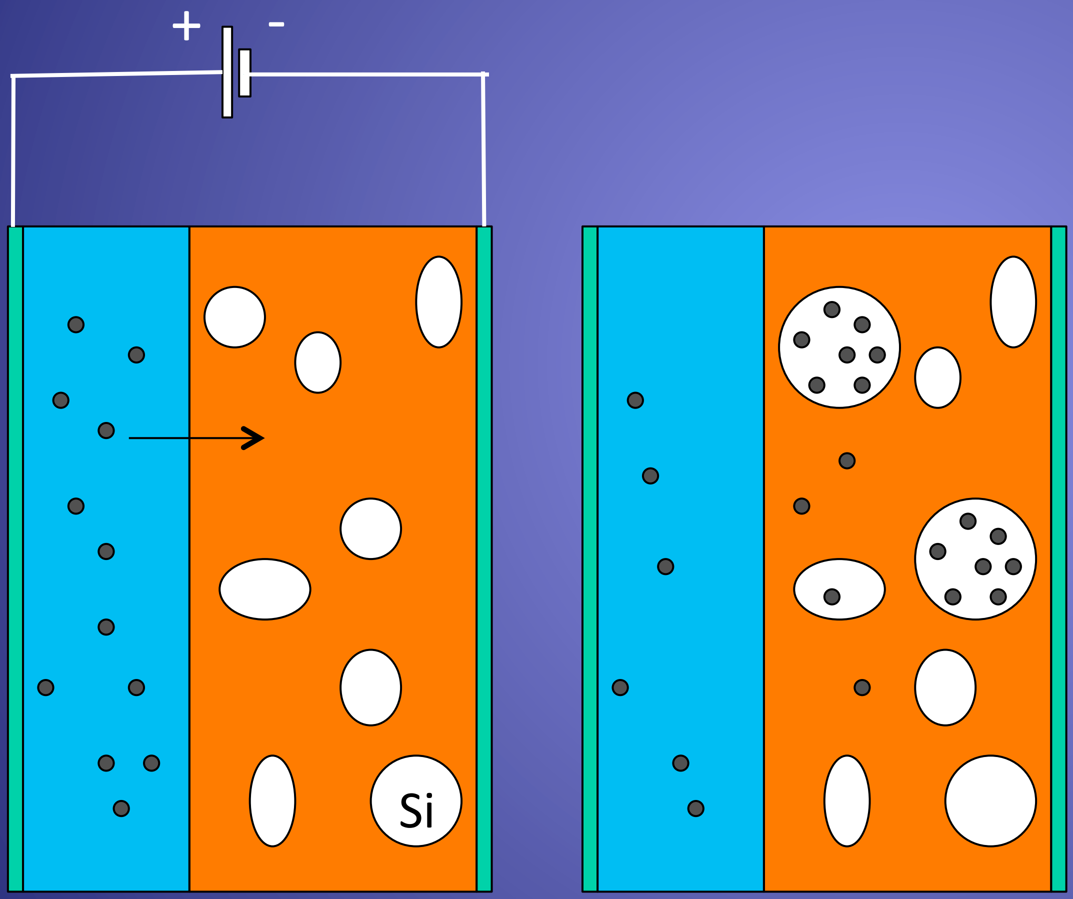
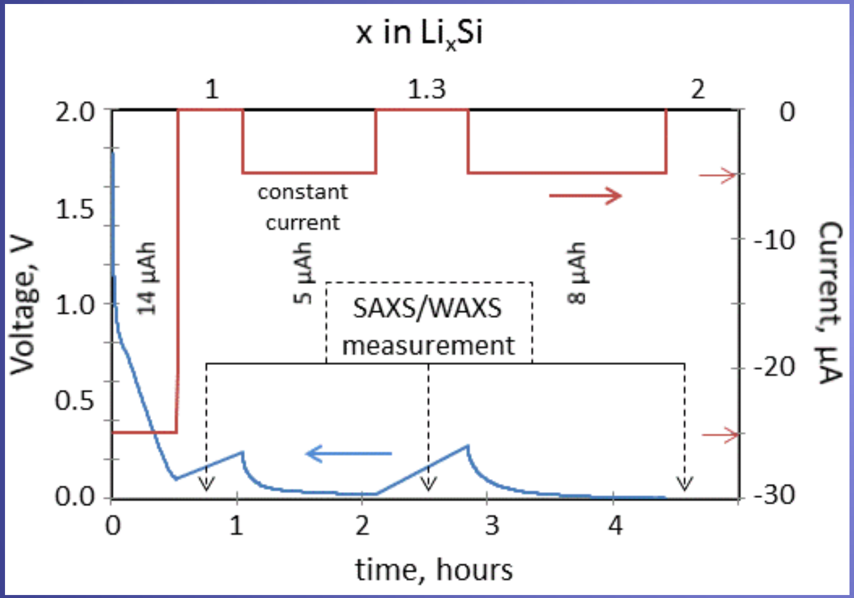
charging

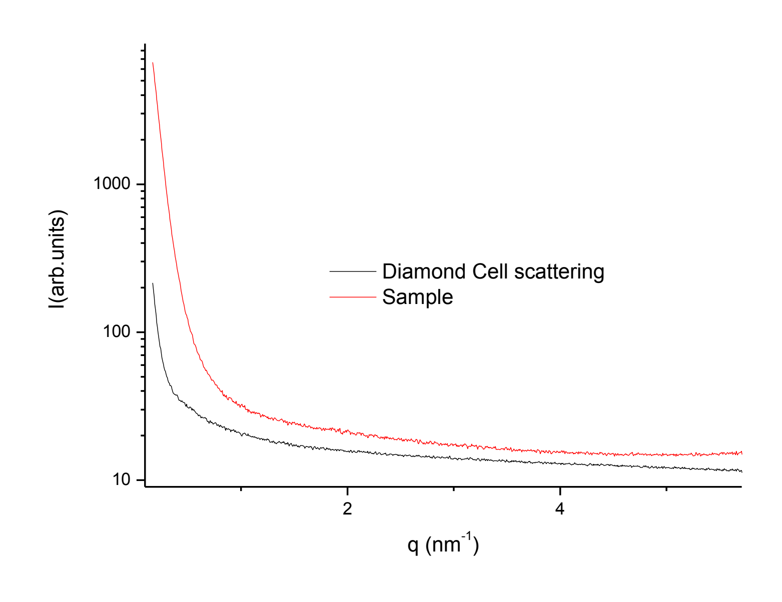


Li ions Polymer binder

Expected:

- Li enters Si particles
- These particles increase in volume (SAXS)
- Crystalline lattice changes (WAXS)



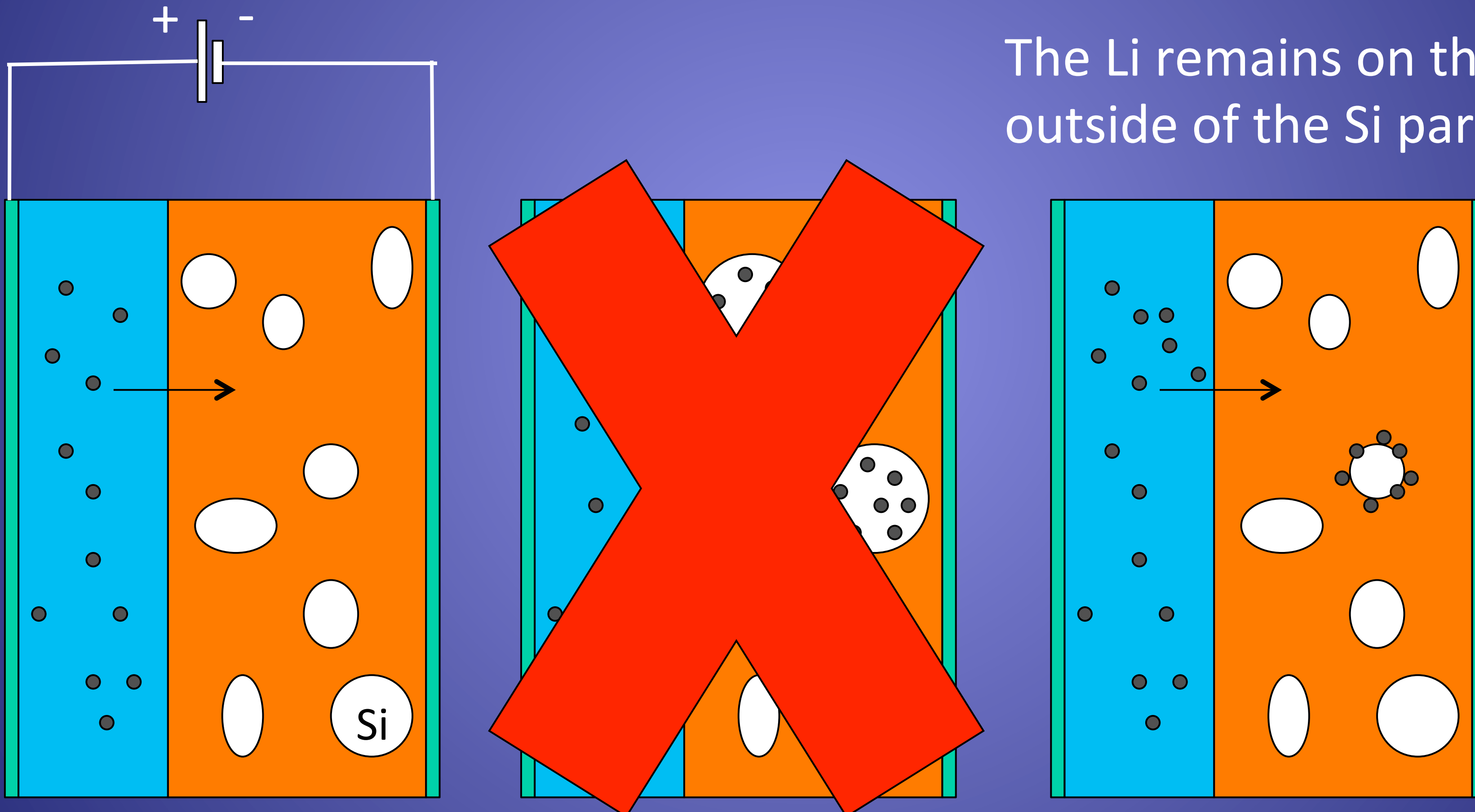


Electrochemistry shows Li enters the Si-polymer matrix

But the bl**dy SAXS and WAXS don't change!!!

charging

The Li remains on the outside of the Si particles



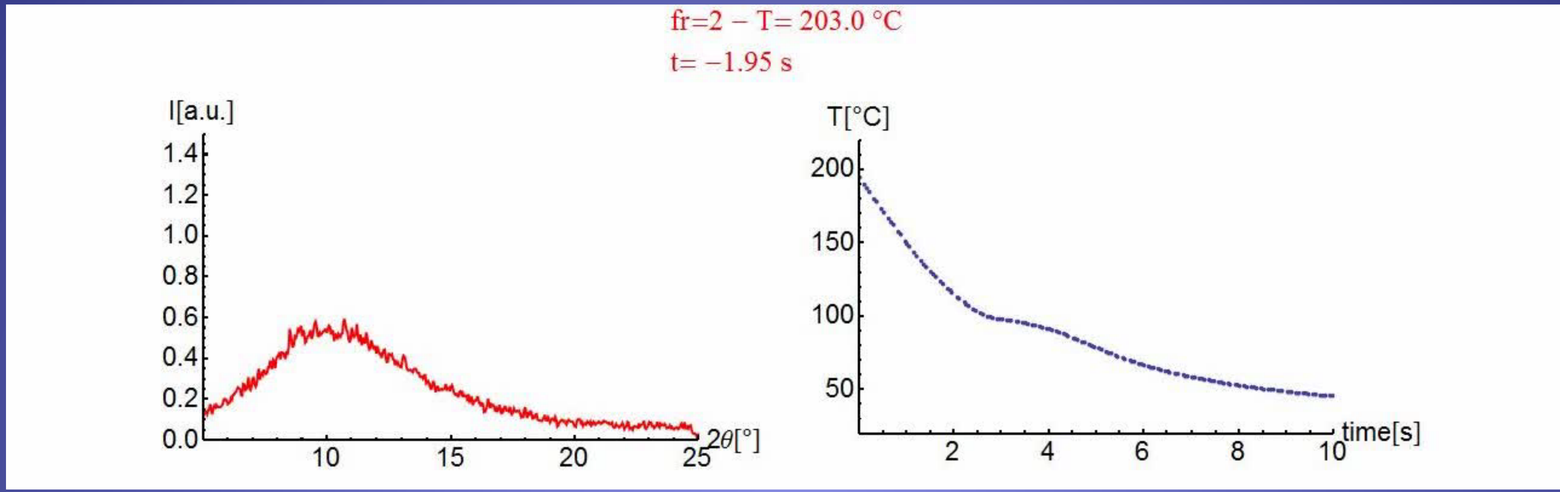
Li ions Polymer binder

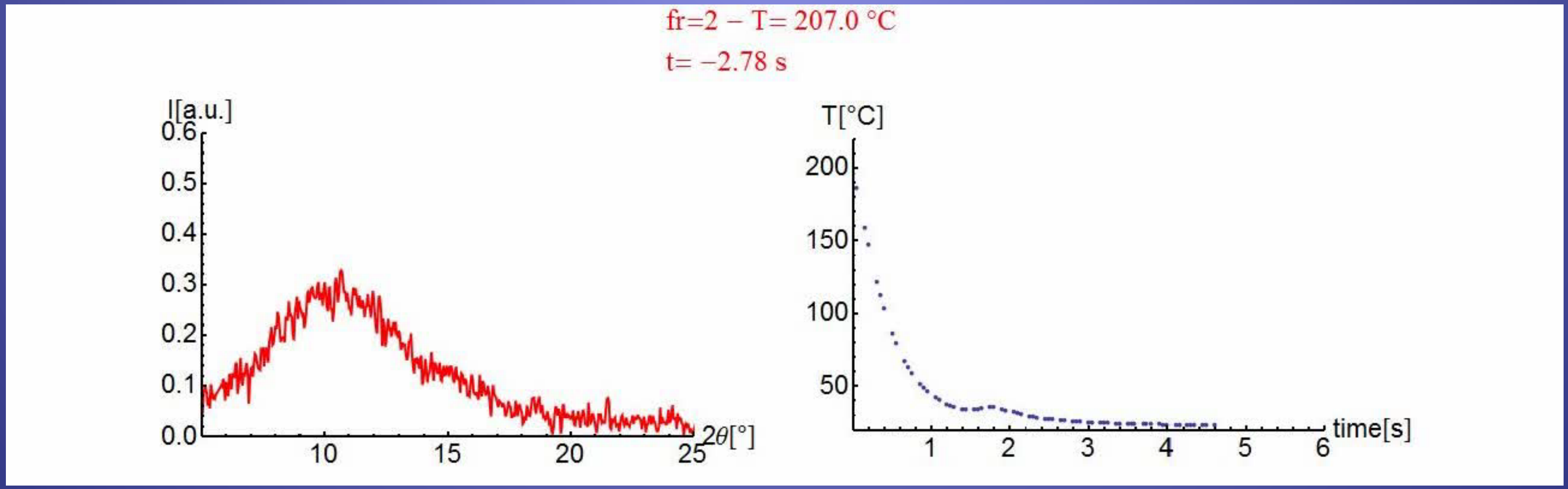
‘similar’ sample environments

- Different shear cells
  - Parrallel plate
  - Couette
  - Cone-plate
  - etc
- Heating/cooling stages
- Small tensile/deformation rigs
- Etc.

Speed: rapid cooling

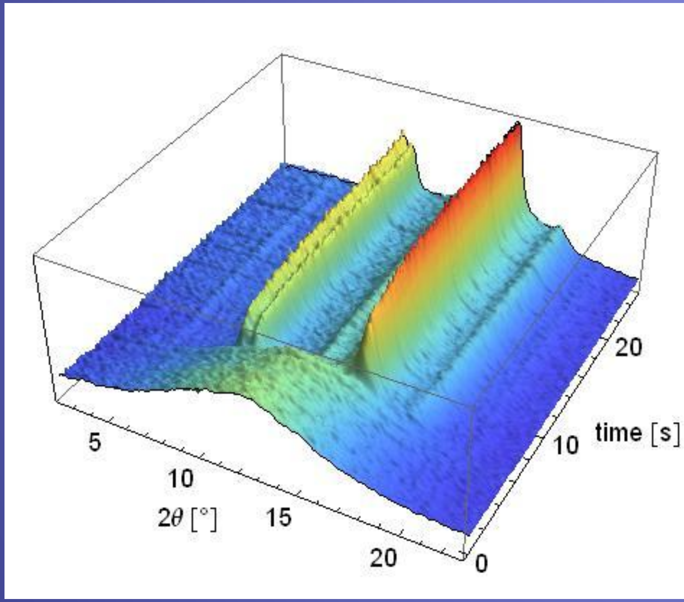
- When just fast: crystallization takes place
- When very fast: crystallisation can not finish before material is frozen
- On-line flash DSC


fr=2 − T= 203.0 °C
t= −1.95 s
I[a.u.]
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
10
15
20
25
2θ[°]
T[°C]
200
150
100
50
2
4
6
8
10
time[s]

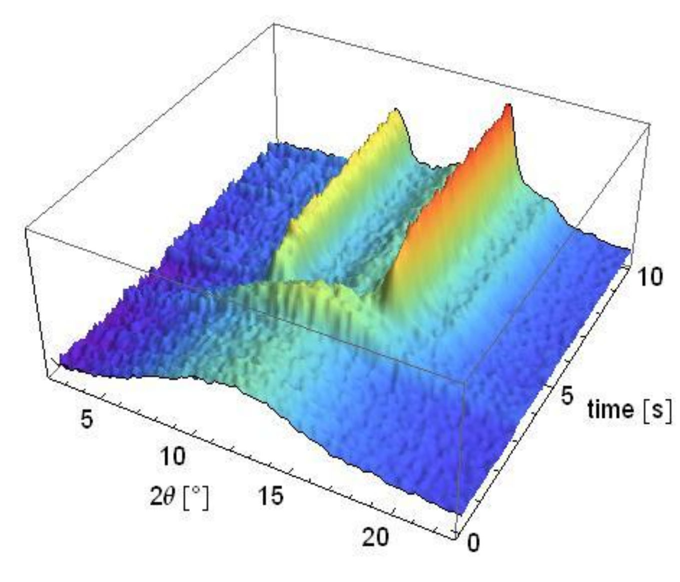

fr=2 − T= 207.0 °C
t= −2.78 s
I[a.u.]
0.6
0.5
0.4
0.3
0.2
0.1
0.0
10
15
20
25
2θ[°]
T[°C]
200
150
100
50
1
2
3
4
5
6
time[s]

PBN – crystallization from a (LC) mesophase

30 °C/s



100 °C/s



(Cavallo, Portale et al. Macromolecules 2010)

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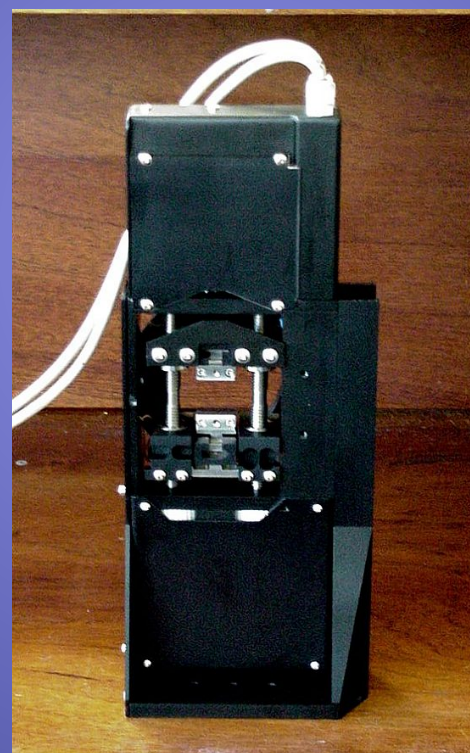
Some other examples that one should be able to accommodate



Linkam DSC, Bras J Appl Cryst 1995

What is required for such experiments?

- ‘small’ equipment
- Mainly isotropic scattering
- Translation stages up to 20-50 kg load capacity
- Sometimes a cradle if there are orientation effects (no diffractometer accuracy required)

Exception:

- Protein solution scattering
- This is a special sport
- Fixed sample-detector distance
- Liquid robots
- Pipe-line data analysis
- Automatic manuscript generation…..

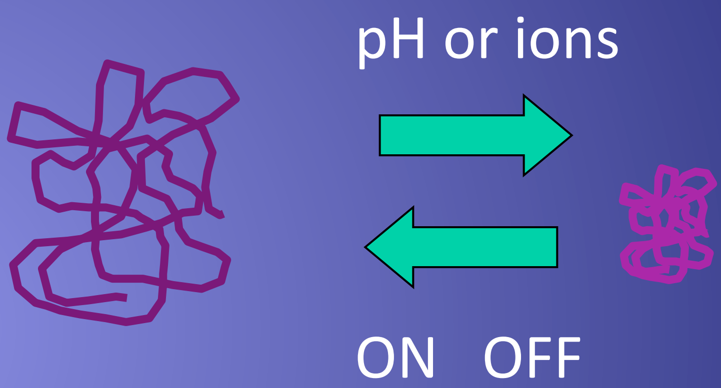
- Preferably dedicated beam line…….

A little more complicated

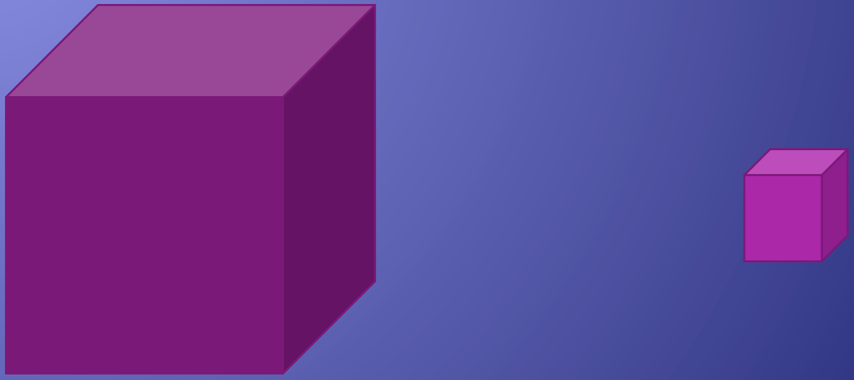
- On-line chemistry
- Biological extruders (spiders, silk worms, etc.)
- Combinations with other techniques (Raman, FTIR, light scattering, radiation damage control methods etc.)

Riekel 2001, Irving 2000, Bras 1995, Bryant 1998, Fernandez-Ballester 2008 etc. etc.
recent 'overview' Bras, Satoshi, Terrill IUCrJ 2014

Responsive molecules change shape



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



Macroscopic shape change

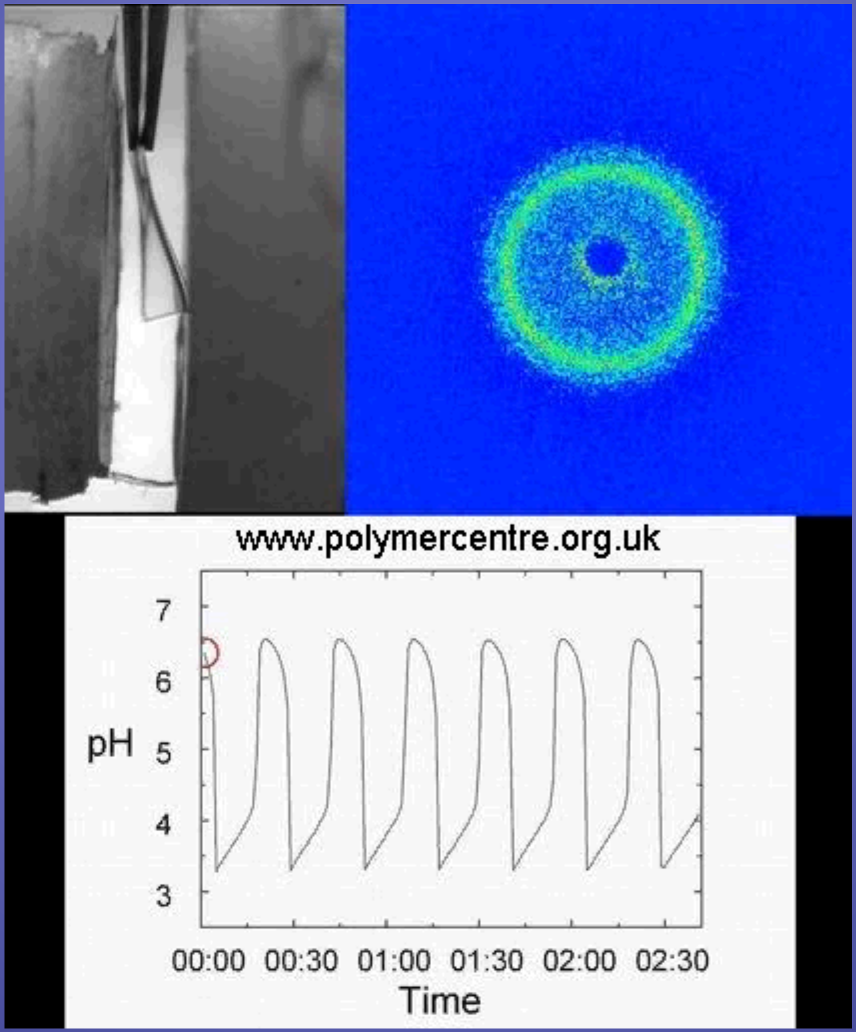
John Howse, Paul Topham, A.J. Ryan and many others; Nanoletters 2006

The challenge:

- Show this is not a one-off actuation
- To be functional it should be possible to reliable cycle between the states

- Build up a chemical pH oscillation factory to achieve this
- Belousov - Zhabotinsky

The data:


www.polymercentre.org.uk
pH
7
6
5
4
3
00:00
00:30
01:00
01:30
02:00
02:30
Time

Information obtained:

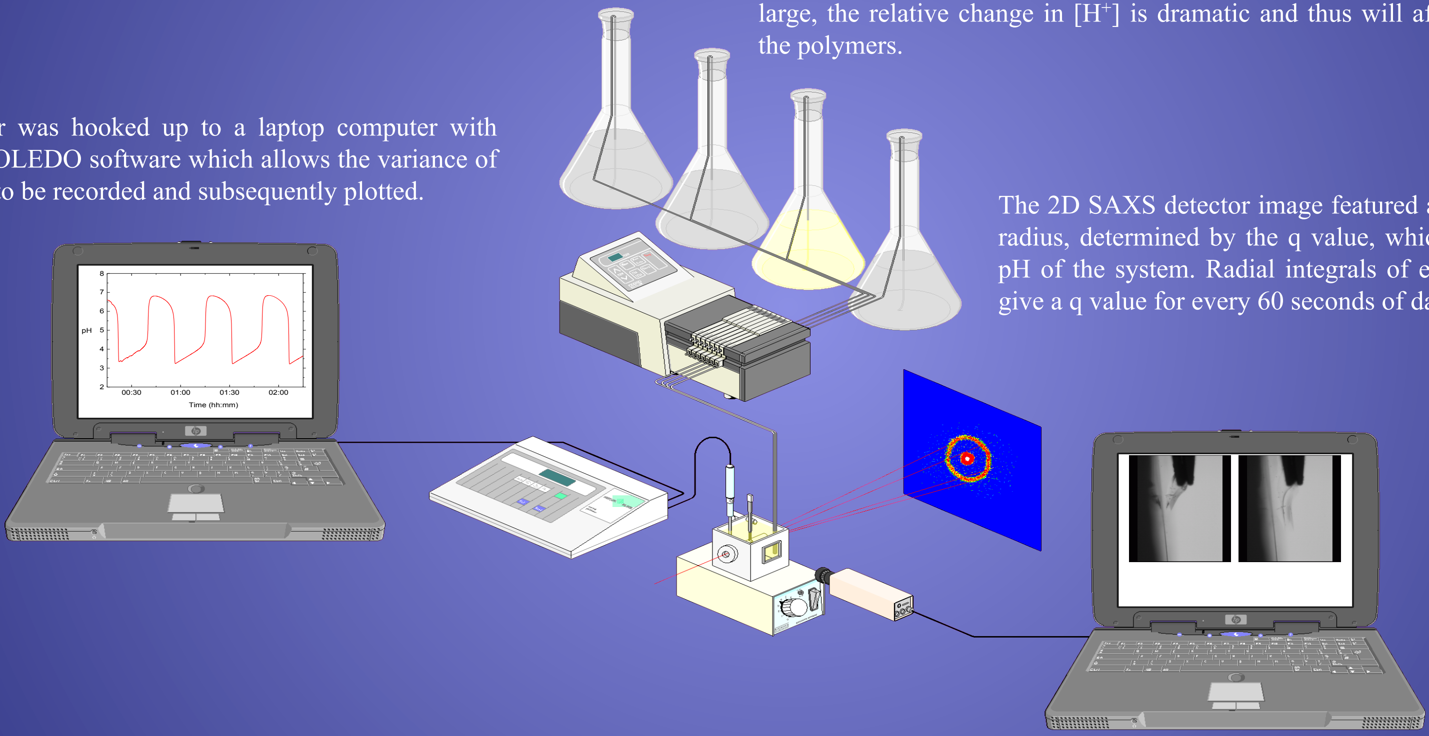
- Changes at molecular level: affine deformation (SAXS)
- Mechanical work
  - Attach a STM tip to the polymer
  - Measure the force it generates
- Macroscopic deformation (laser light, not shown here)

- 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 pH[3]. A low acid input is also required. The pH oscillations display a sustained period. Since the amplitude of the pH change is large, the relative change in $[H^+]$ is dramatic and thus will affect the conformation of the polymers.

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



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

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

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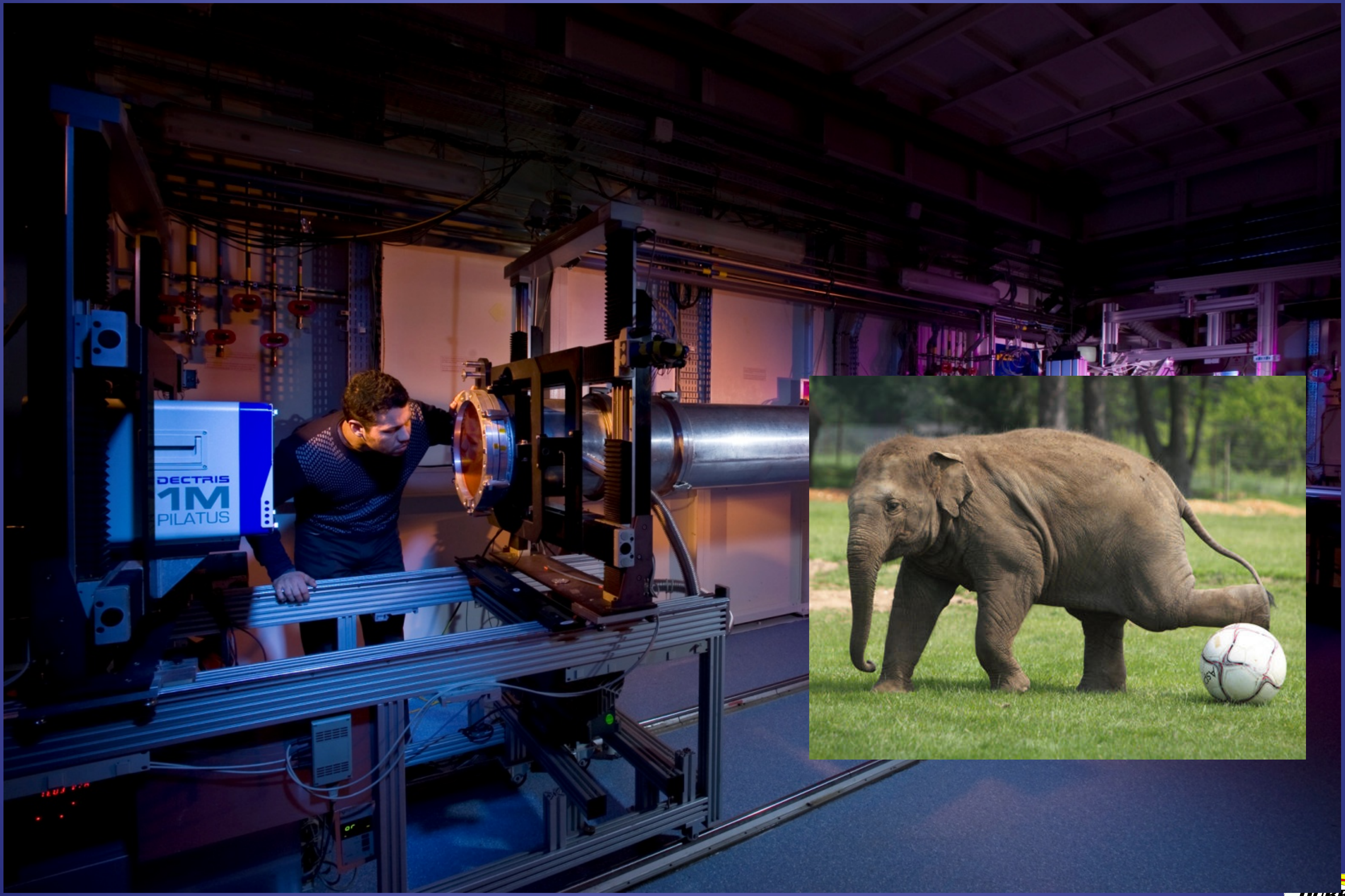
It is indeed not simple to do, but:

- It can be done
- Talk reasonably to safety officers
- Allow for 1-2 unsuccessful attempts
- Don't look for the problems but look for the solutions.....

Practically required

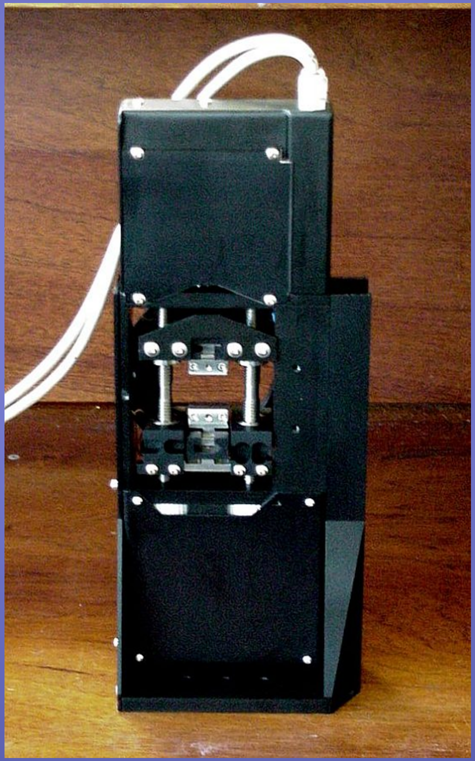
- Infrastructure to place and interface the auxiliary equipment
  - Computer interfaces
  - User dedicated cabling panels
  - Etc……
- Ideally simple interface control that doesn’t require your computer/electronics group for setting up
- Some space around the sample

But enough of this:



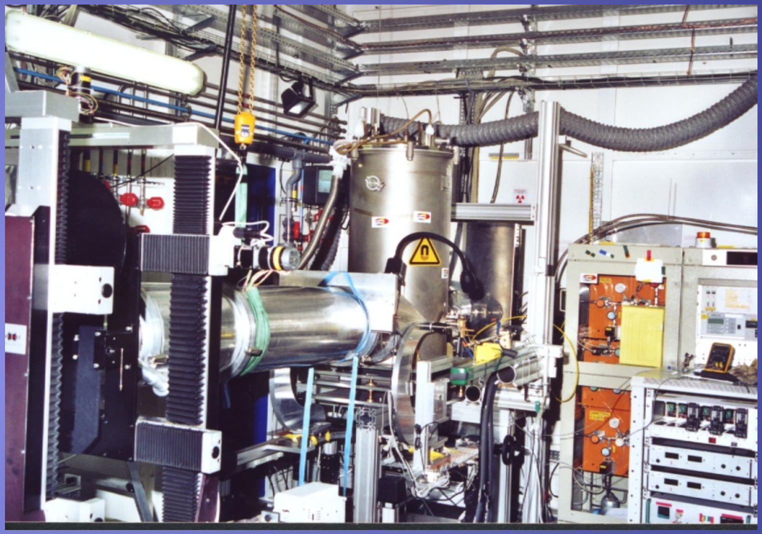
I like experiments which require a hutch spacious enough for elephants to have a football match

This is what we tolerate, but it is not part of the hobby……



I like the sample environments to be shipped in by trucks

Moved in by forklift



Magnet
10 Tesla transverse field, 150 kg, required positioning accuracy
100 micron, 30 years old, definitely French and female

Bras J Chem Phys 2003, McCulloch Macromolecules 2013

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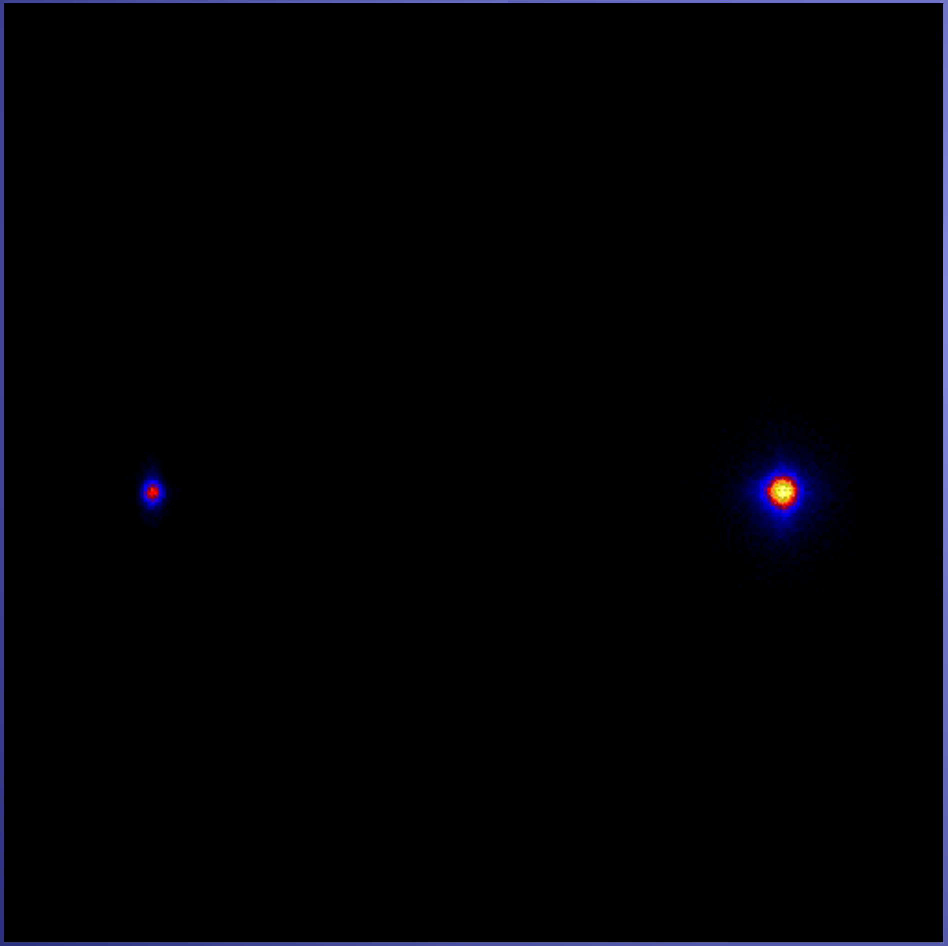
Liquid crystal experiments
static fields for time resolved experiments



Sample mechanically rotated

Watch the field act on the sample

Real time data

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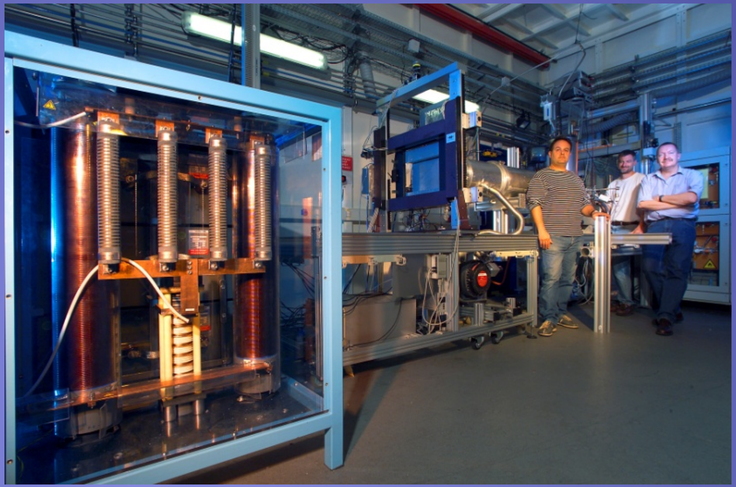
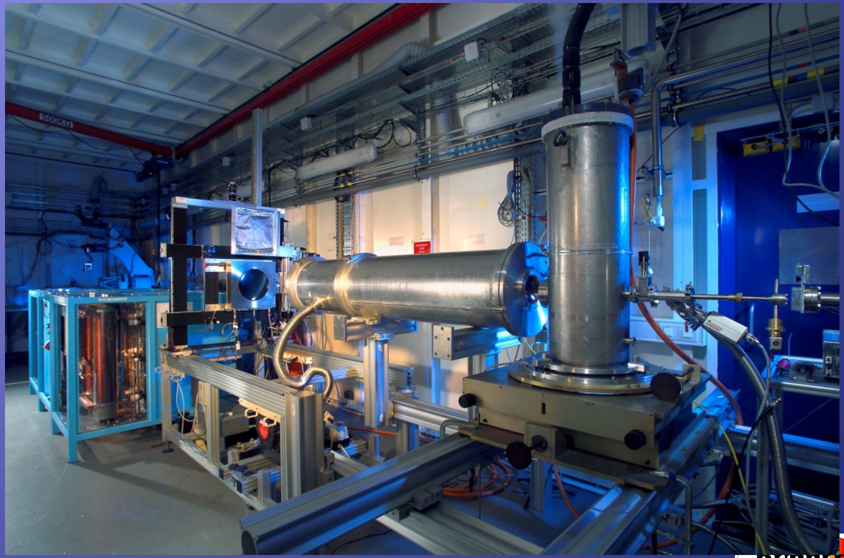
Or lifted in by crane….



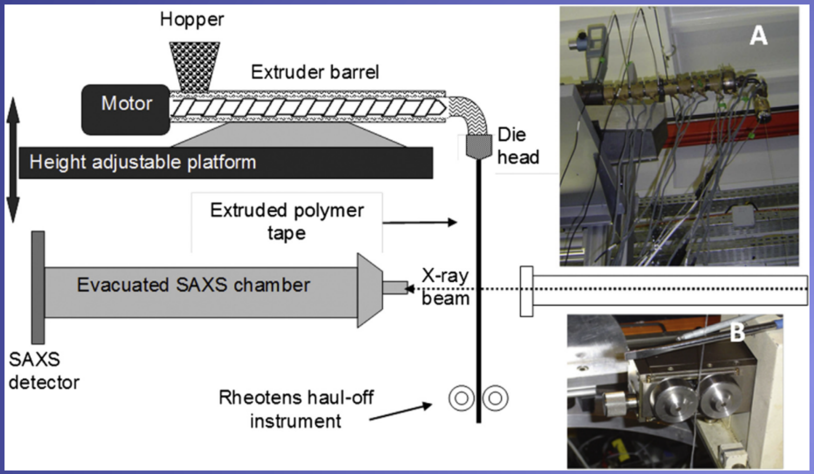


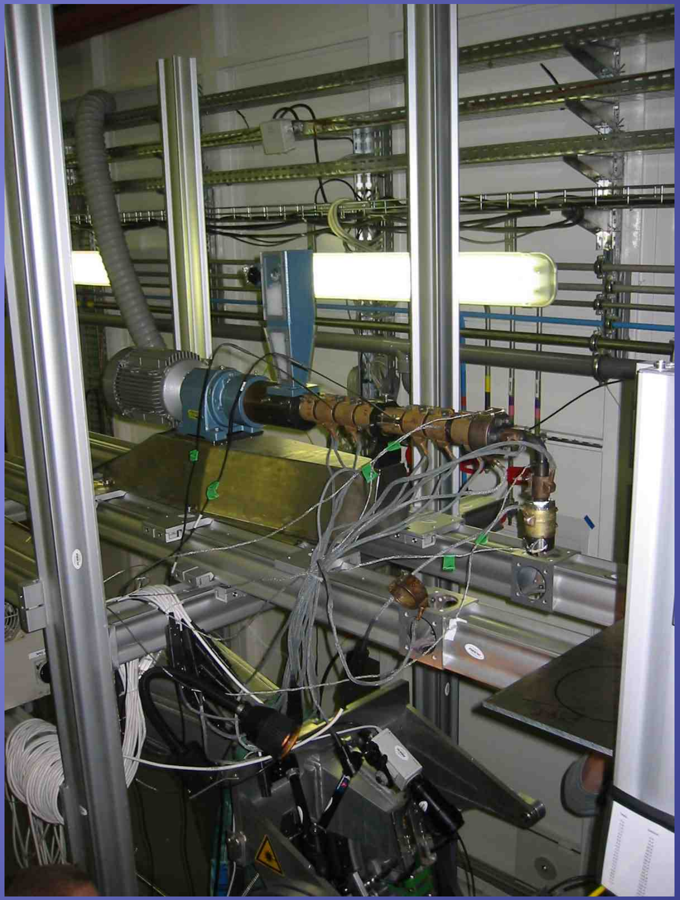
30 Tesla pulsed magnet
Detlefs PRL 2008

Less Wim ego centric argument:

- We get substantial funding of the Dutch Polymer Institute
- Private-public partnership
- Industrialists, and especially their managers, like results from equipment they understand….

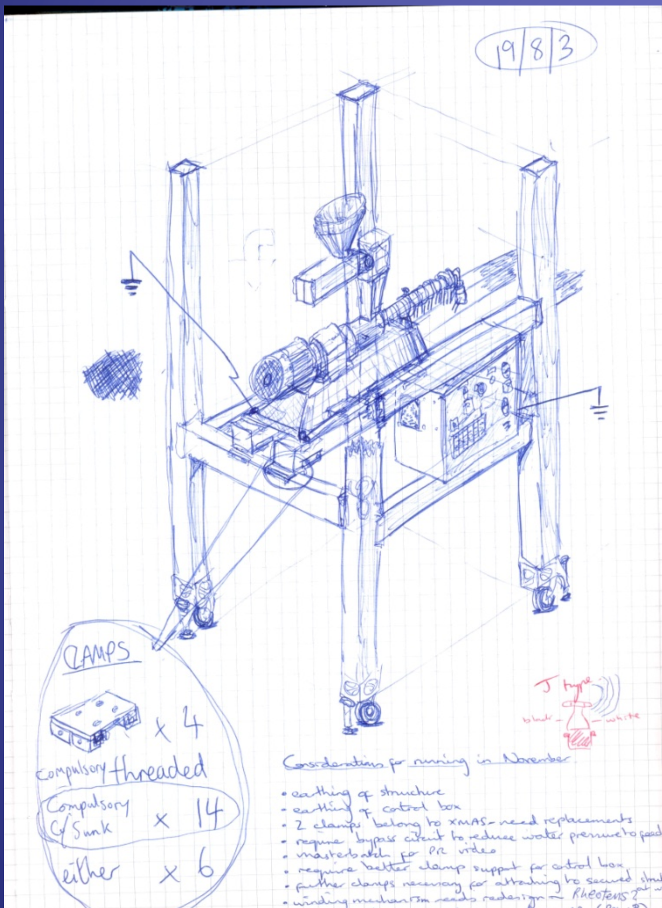
Extruders on beamlines





Heeley, Polymer 2014

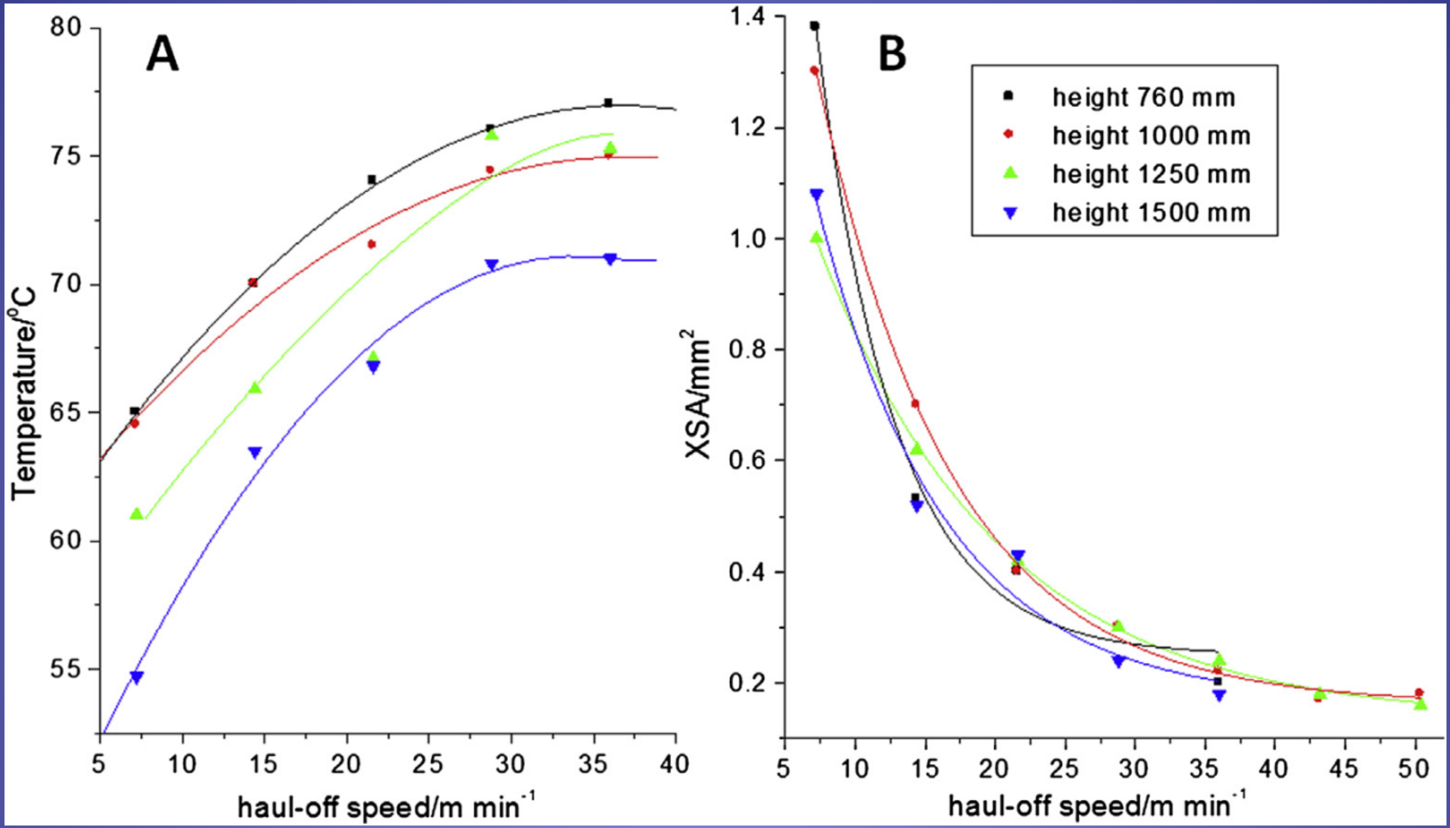
Parameters:



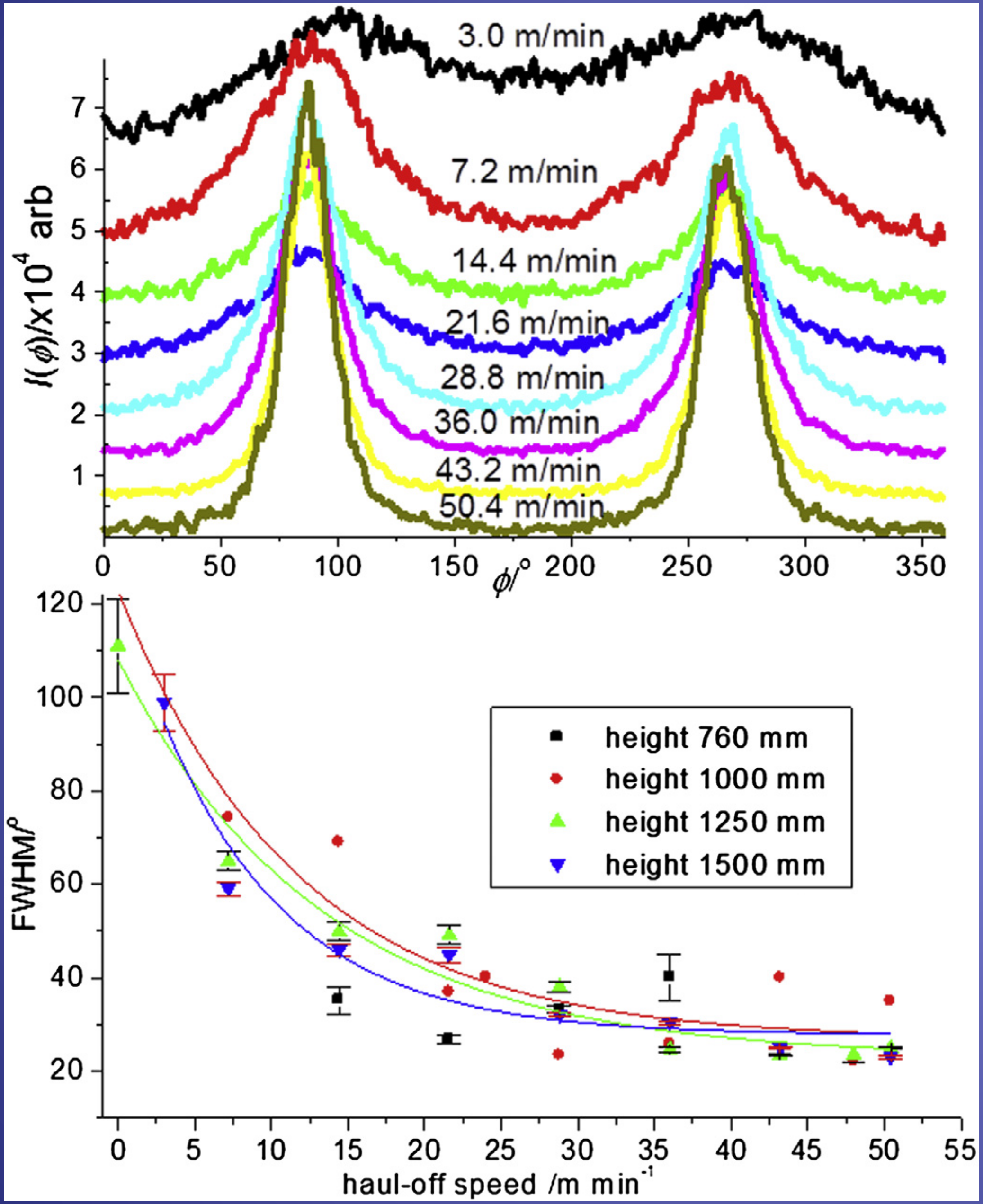
- height 4 meter, 2.6 m extrusion die – beam distance
- Extruder requires translation of about 1.5 m with accuracy of 5 mm
- Extruder equipment up to 200 kg
- Ventilation

- It took us 2 days to build this up
- 2 days in which expensive photons are not used but only heating up a beam stop
- Much too long

- Large doors without doorsteps required
- Accurate heavy duty breadboard flush with hutch floor for mounting would be ideal



For industrially relevant results the sample control is very important, addition of Rheotens was crucial to link orientation and processing parameters



This is roughly the limit of what an industrial manager can understand from X-ray/neutron scattering

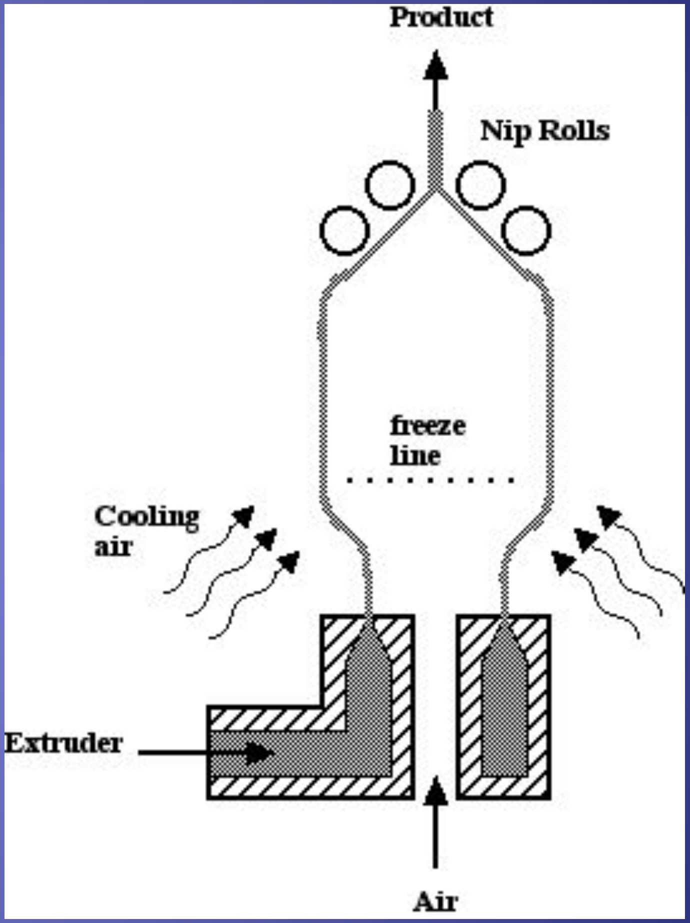
On-line film blowing: Polymer films manufacturing

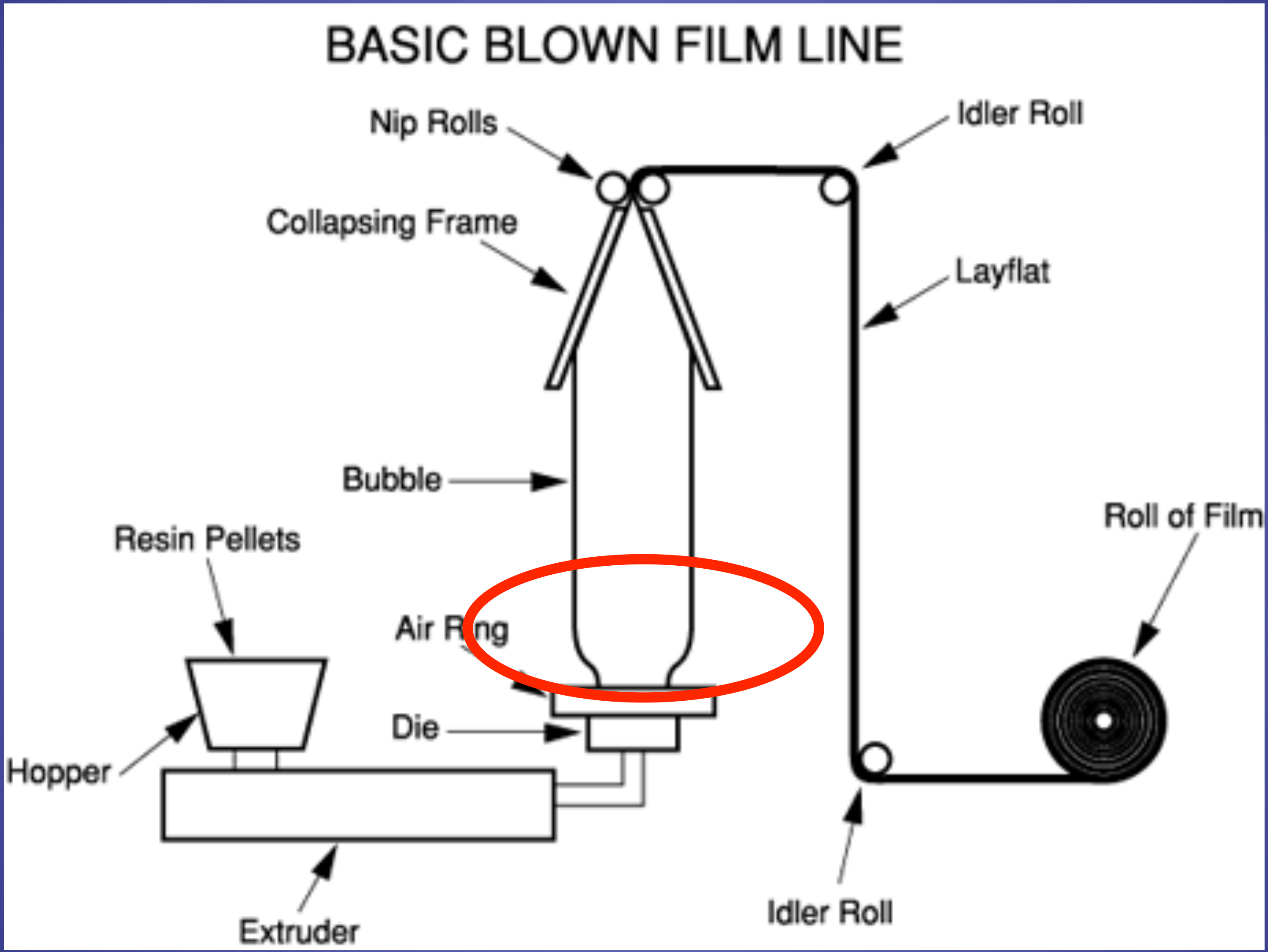
A screw extruder is used to melt the polymer and pump it into a tubular die.

Air is blown into the center of the extruded tube and causes it to expand in the radial direction.

Extension of the melt in both the radial and down-stream direction

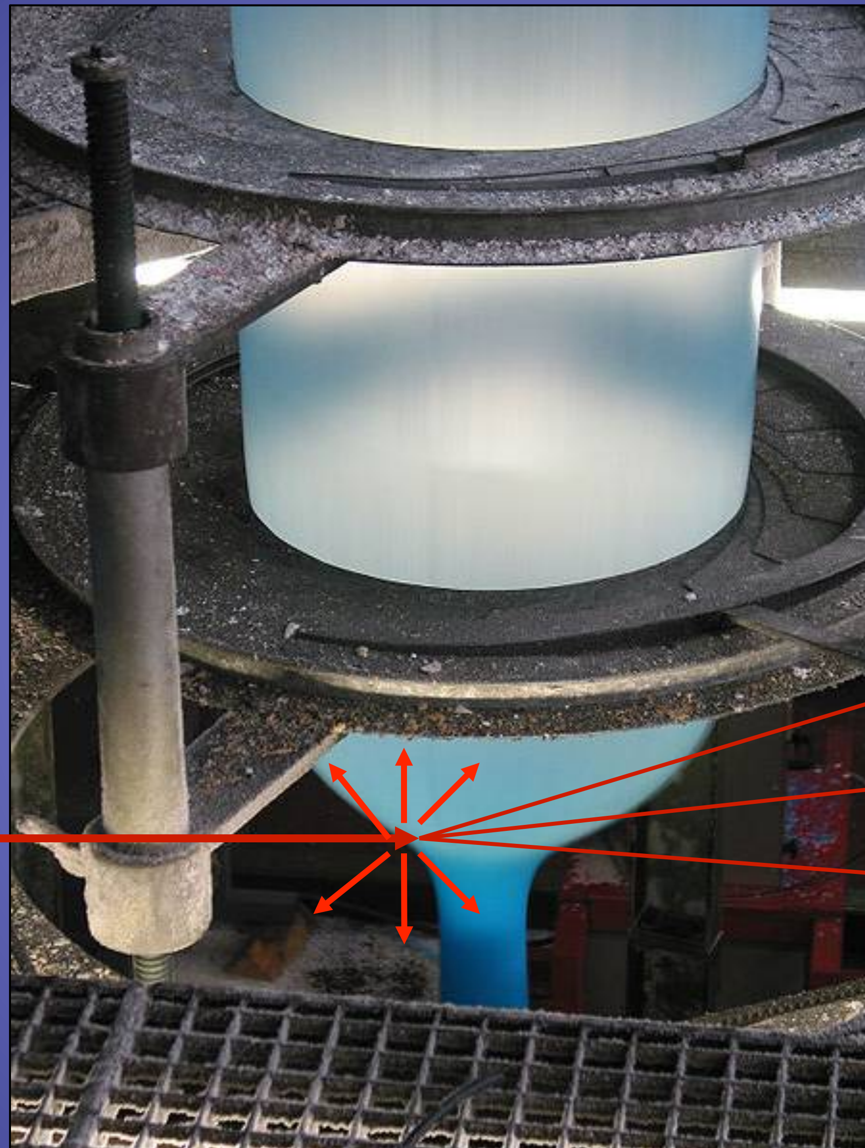
Extensively used for PE and PP.



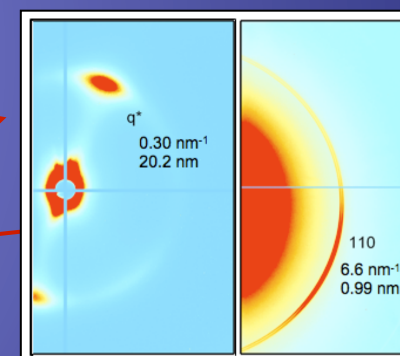


BASIC BLOWN FILM LINE
Nip Rolls
Idler Roll
Collapsing Frame
Layflat
Bubble
Roll of Film
Resin Pellets
Air Ring
Die
Hopper
Extruder
Idler Roll

X-ray beam



SAXS WAXS

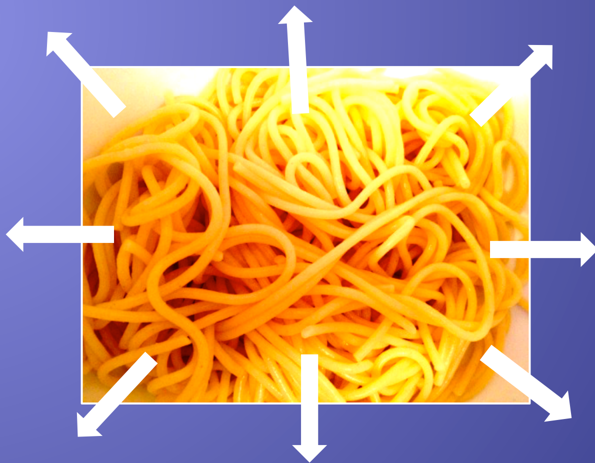


Scattering pattern

elongation multiaxial

Crystallisation easier when molecules are pre aligned

Polymer melt



Where the balloon swages shear forces are multiaxial

Film blowing

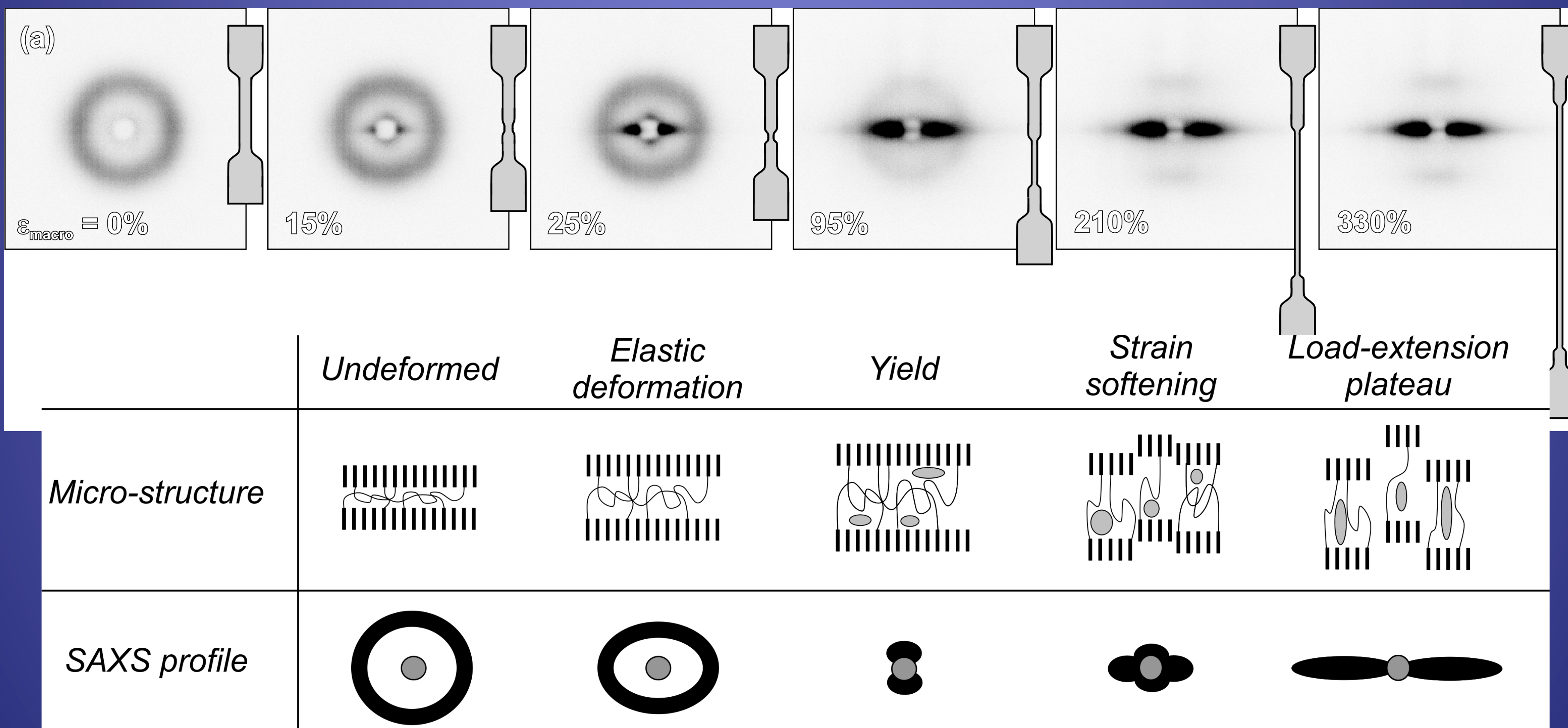
300 kg
Vertical translation
With 10 micron accuracy
Installed in one morning

Young Italian buried in a morning's worth of samples

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

Hermida-Merino

On-line deformation

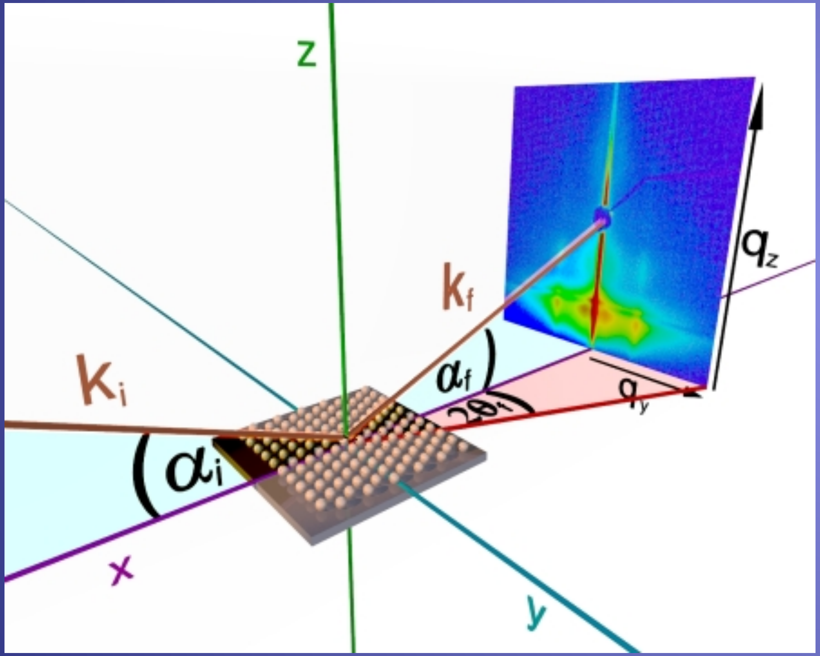


Other heavy duty equipment

- 30 Tesla pulsed magnets
- 10 Tesla static fields
- Ion-beam implanters
- Multi pass rheometer

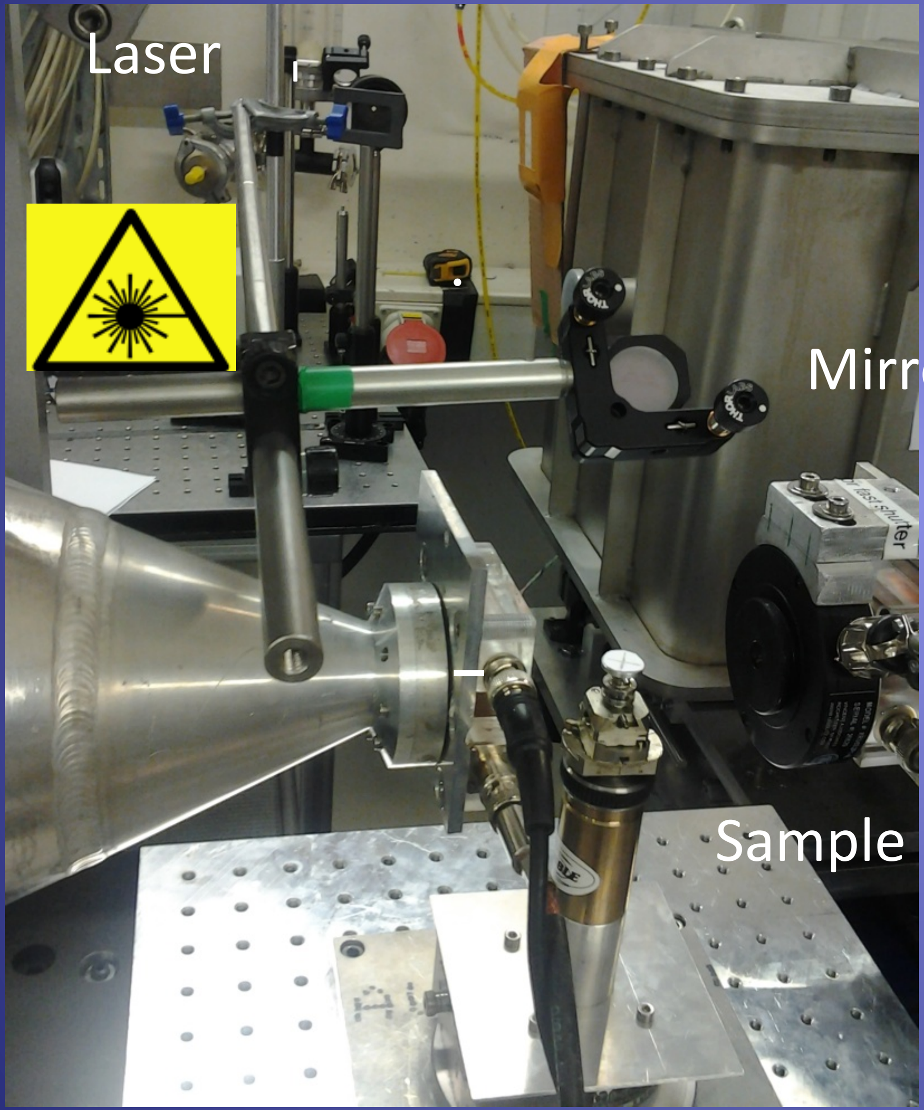
  (for accurate control, p,V and T)
- Etc. etc.

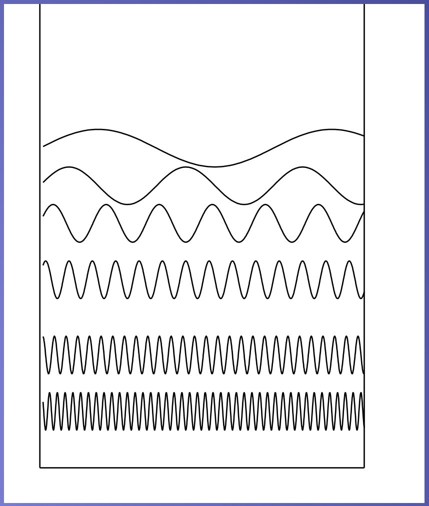
Thin films/coatings



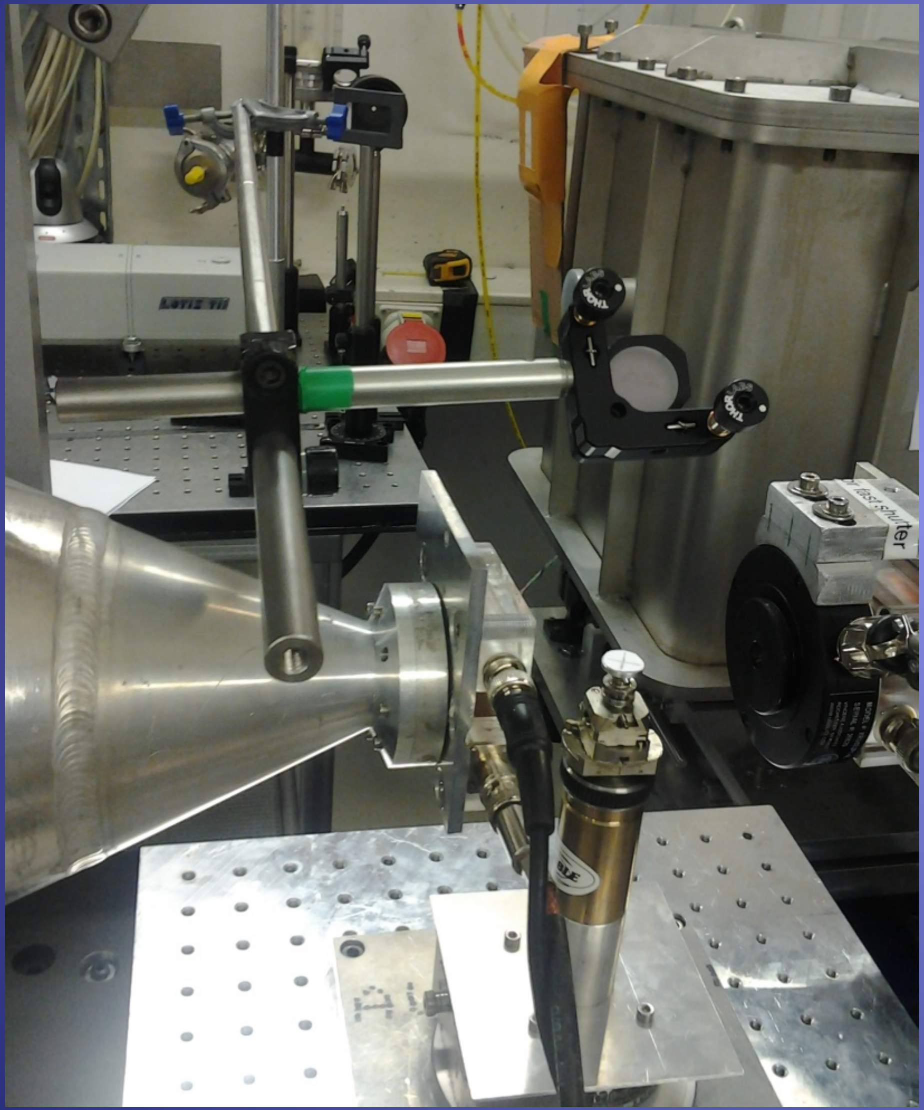
- GISAXS has gained much popularity in recent years
- Sample environments are becoming more complicated

In-situ Laser Induced Periodic Surface Structuring (LIPSS)





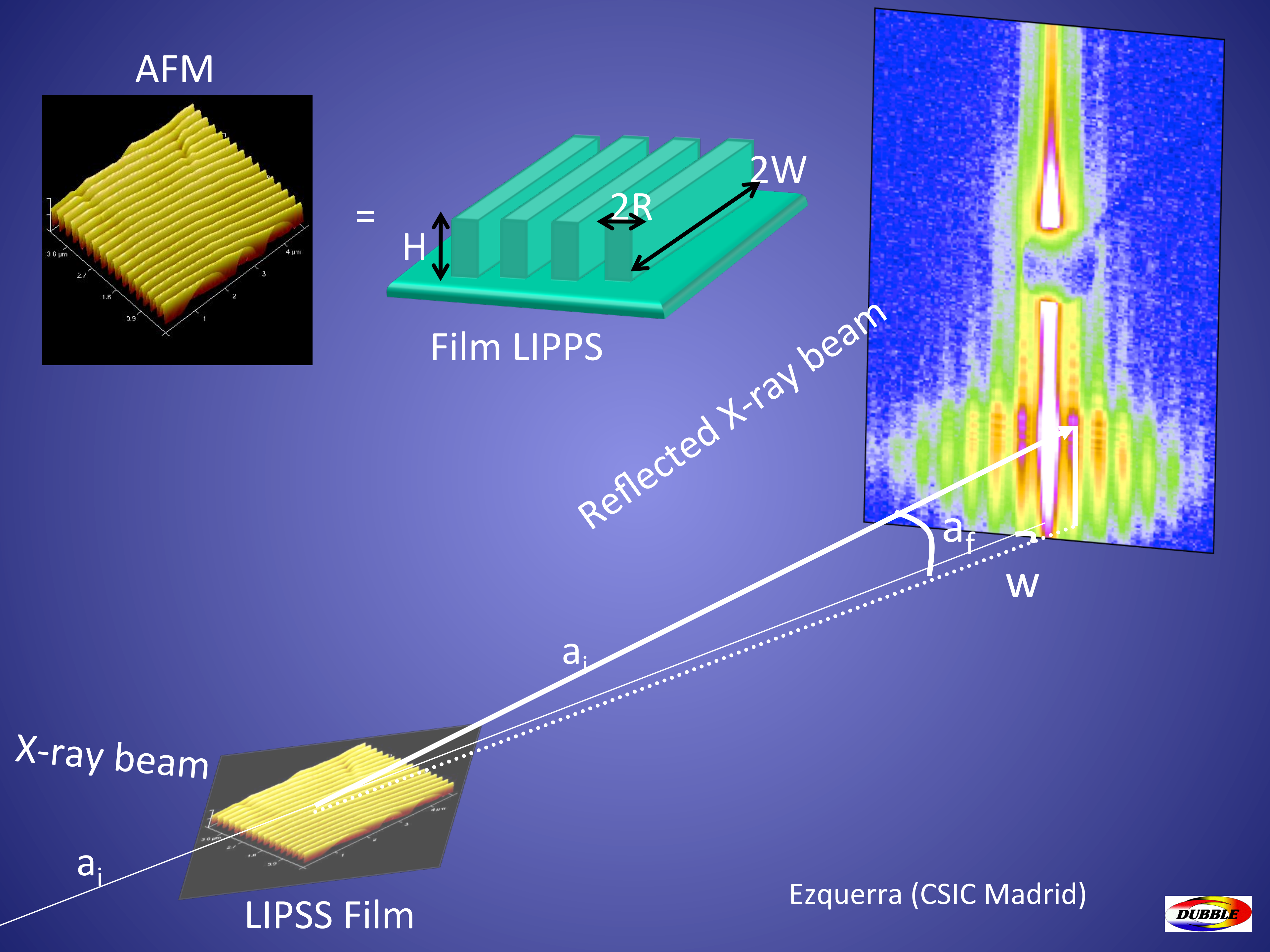
Interference of the incident and reflected light at the interface produces surface ripples

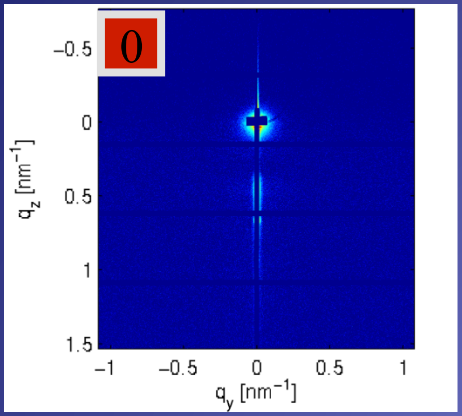


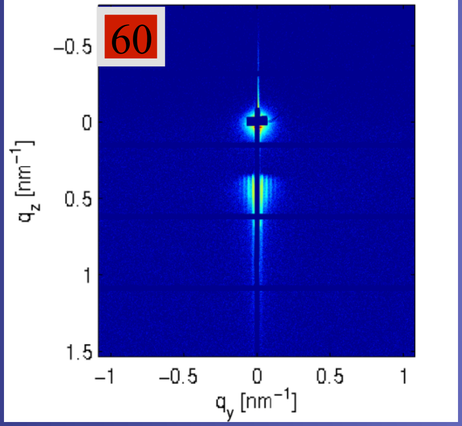
You can’t figure out what is what in this picture?

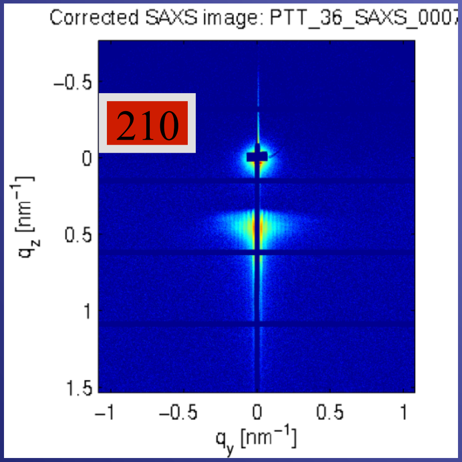
Don’t worry, in real life it is also rather messy

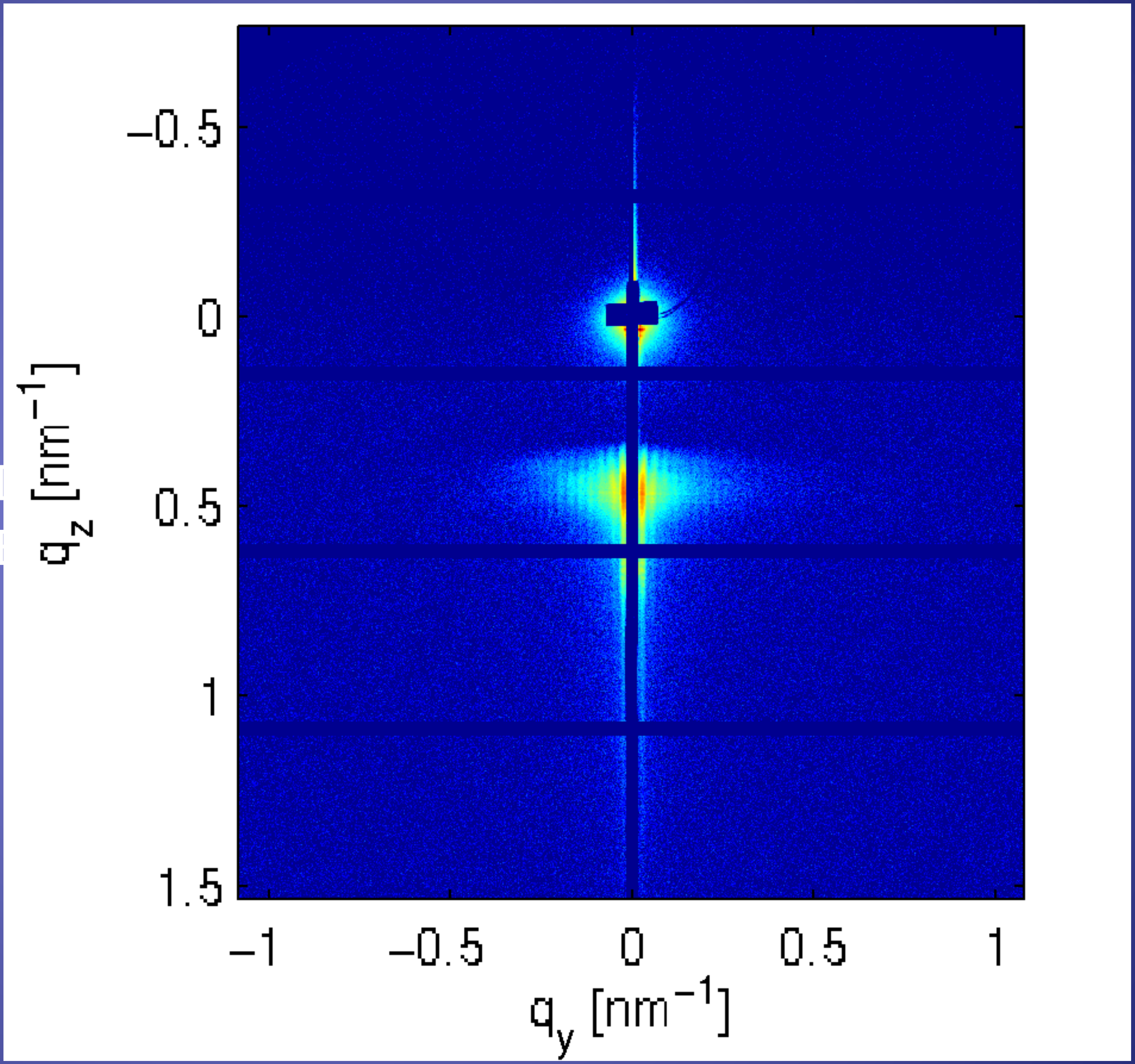
Optical breadboards
Mirrors/diafragms/shutters
Signal/interlock cables
Translation stages/cradles
Etc.


AFM
=
H
2R
2W
Film LIPPS
Reflected X-ray beam
a_f
w
a_i
X-ray beam
a_i
LIPSS Film
Ezquerra (CSIC Madrid)
DUBBLE


0
−0.5
0
0.5
1
1.5
q_z [nm^{-1}]
−1
−0.5
0
0.5
1
q_y [nm^{-1}]

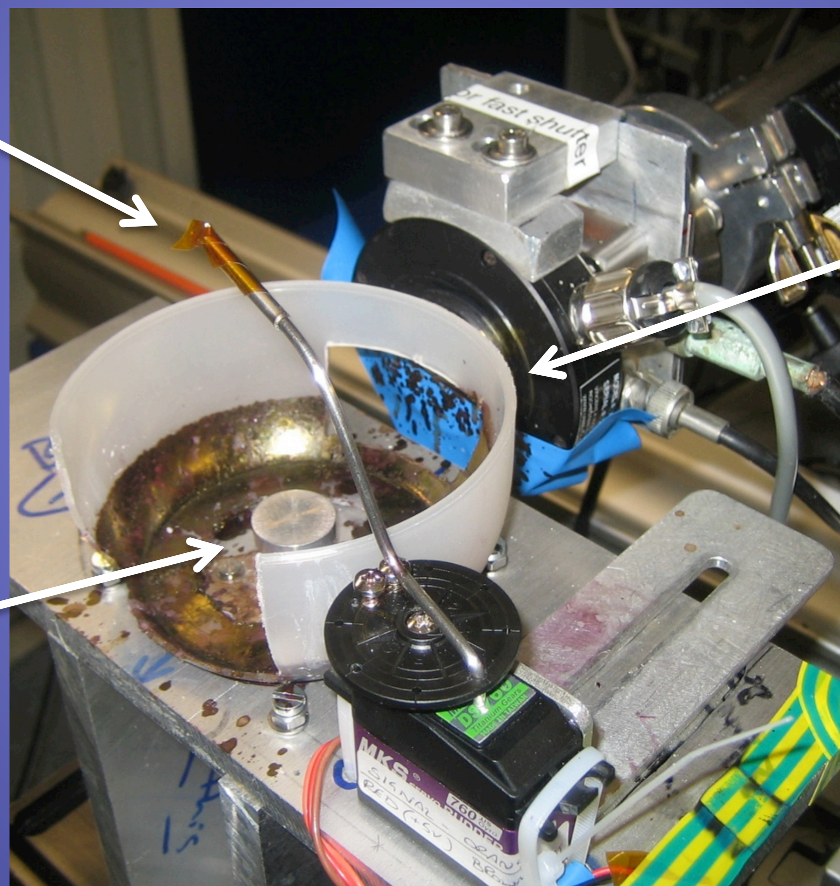

60
−0.5
0
0.5
1
1.5
q_z [nm^{-1}]
−1
−0.5
0
0.5
1
q_y [nm^{-1}]


Corrected SAXS image: PTT_36_SAXS_0007
210
−0.5
0
0.5
1
1.5
q_z [nm^{-1}]
−1
−0.5
0
0.5
1
q_y [nm^{-1}]


−0.5
0
0.5
1
1.5
q_z [nm^{-1}]
−1
−0.5
0
0.5
1
q_y [nm^{-1}]

On-line spin coating

Needle for automatic dispensing



X-ray beam (IN)

Motor to spin the substrate

Howse, Topham Sheffield

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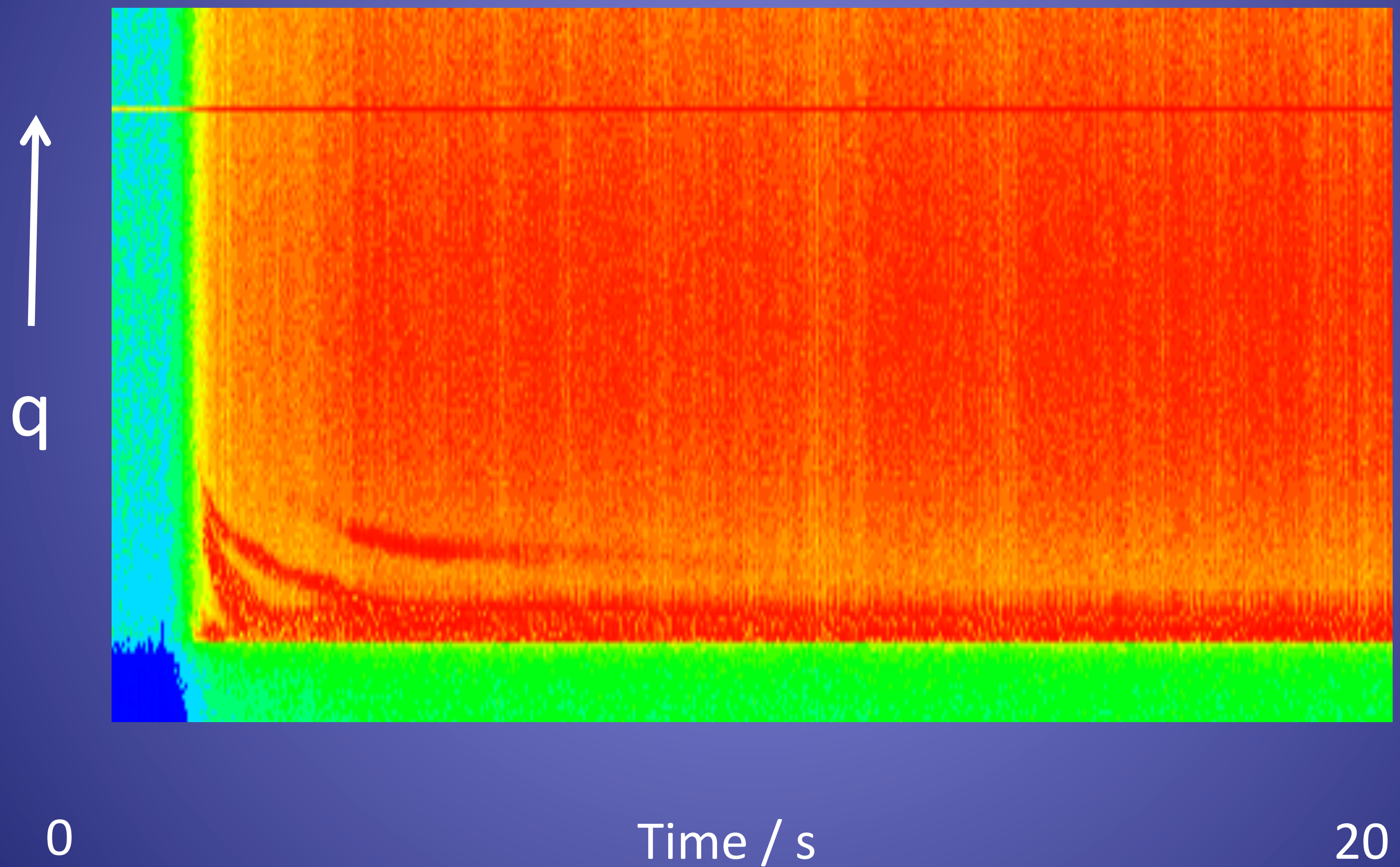
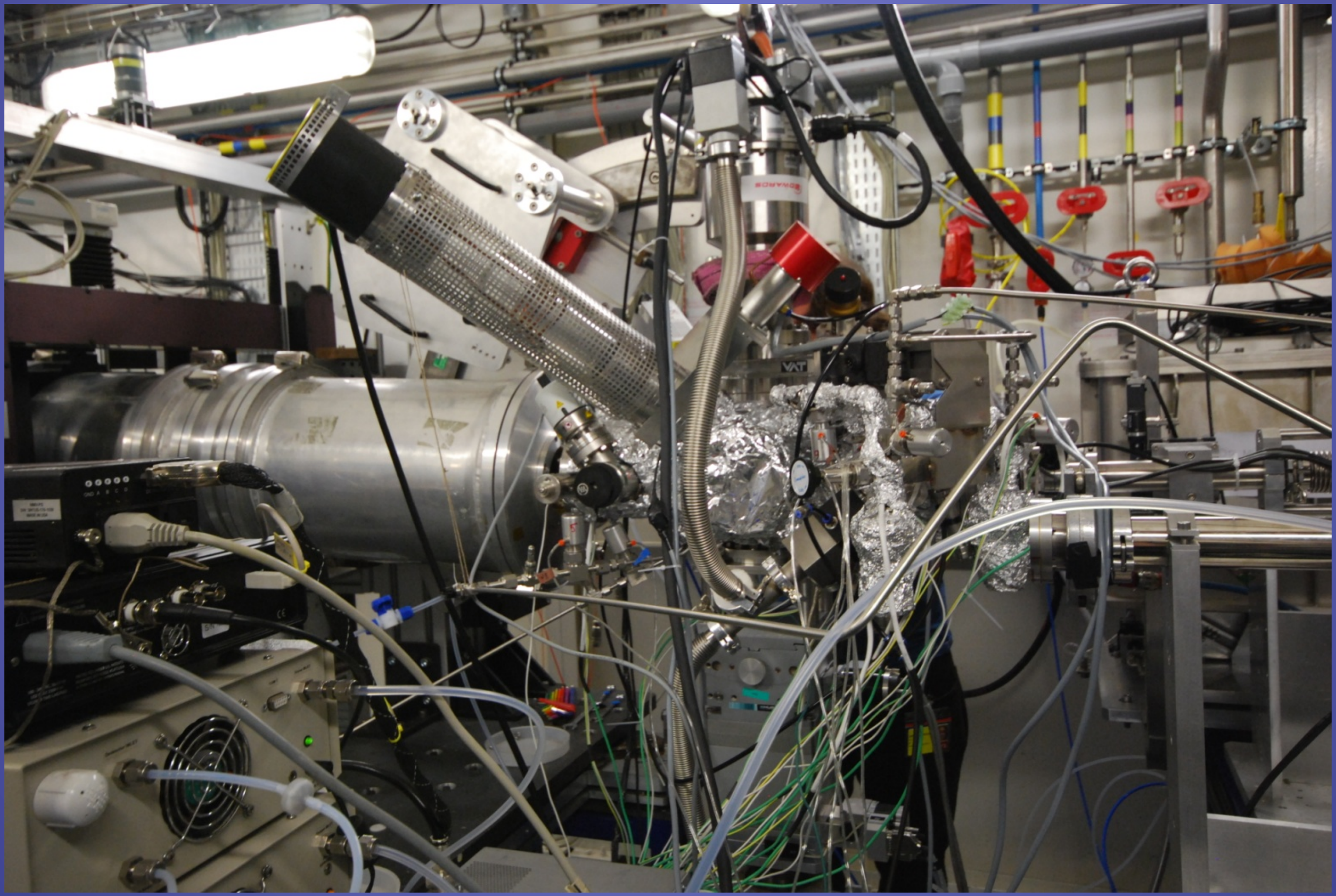
P3HT/PCBM spun cast 2000rpm



Metal coating sputtering
heavy duty vacuum environments



Dendoove (Univ Gent)

Required for these GISAXS things:

- Accurate sample positioning
  - x, y, z, θ, ω
- X-ray reflectivity often required in combination with GISAXS

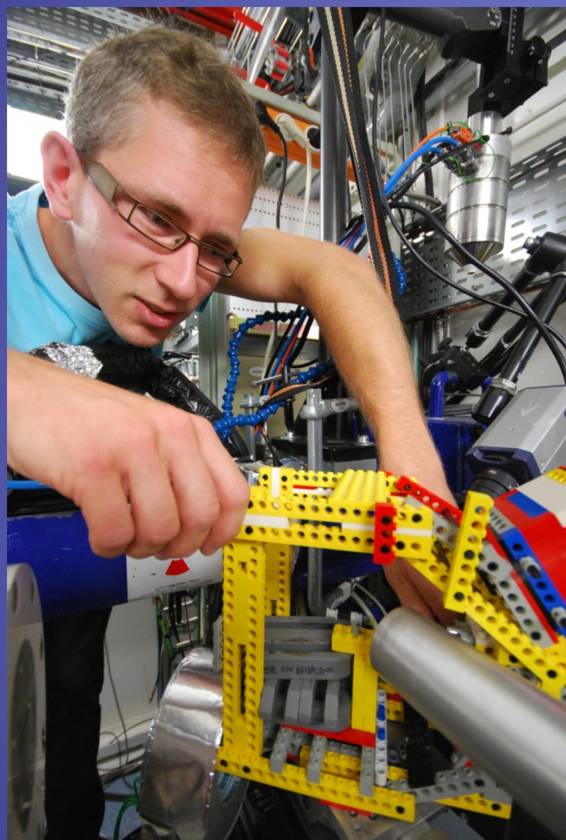
⇨ diffractometer

- Weight up to 50 kg (100 kg exceptional)
- Laser access/safety
  - Ablation, interferometry

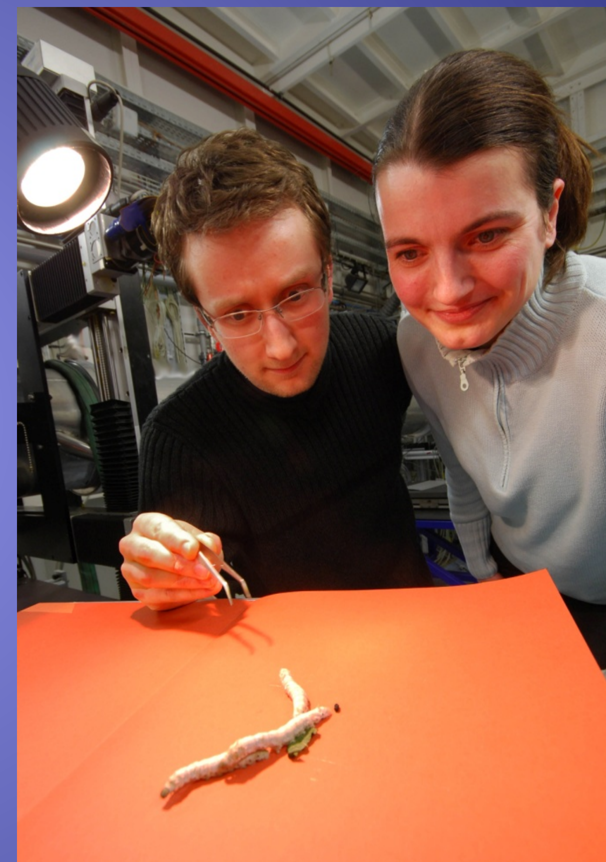
This guy is talking about his hobbies again

And he can go on and on and on……

To finish: In praise of small and ingenious equipment



Two lasers, one X-ray beam, thermal control, all done in Lego



Mini extruder

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Old Chinese proverb:

One stupid user group can think of more problems than ten wise beam line scientist can foresee

Pho Ton

(355 – 302 BCE)

Thanks for your attention

- Examples before 1998
  - Tom Russell, Daresbury beam line 8.2, Tony Ryan + team, Hamburg polymer beam line
- Examples after 1998
  - Liberally stolen from DUBBLE BM26B users

(beautiful examples can be found at many other beamlines as well
recent 'overview' Bras, Satoshi, Terrill IUCrJ Vol1(6) 2014)