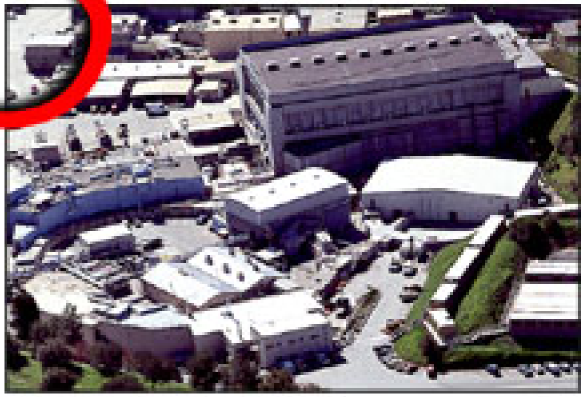
STANFORD SYNCHROTRON RADIATION LABORATORY

SSRL

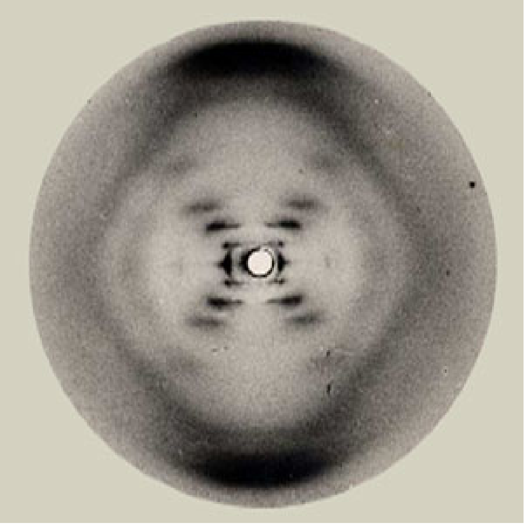


Everything You Ever Wanted to Know About SAXS But Were Afraid to Ask

John A Pople
Stanford Synchrotron Radiation Laboratory,
Stanford Linear Accelerator Center, Stanford CA 94309

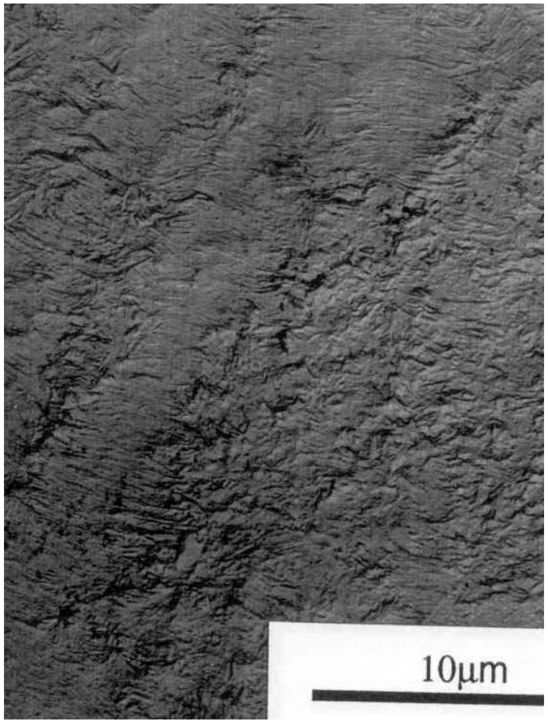
When should I use the Scattering Technique?

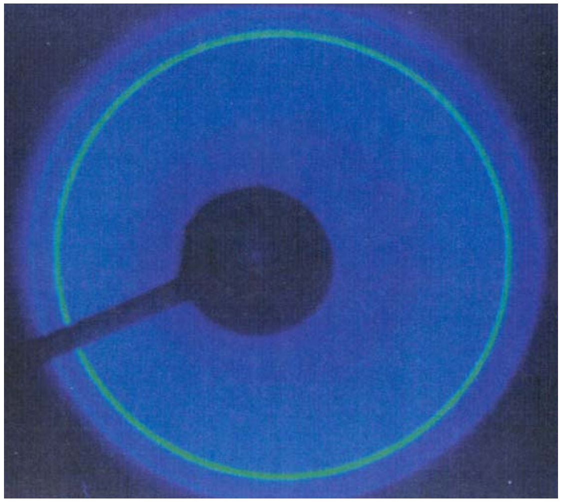
Ideal Studies for Scattering



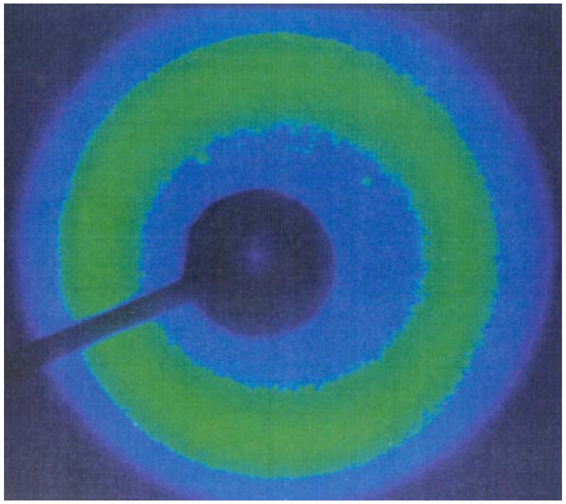
Scattering good for:

- Global parameters, distributions; 1st order
- Different sample states
- In-situ transitional studies
- Non destructive sample preparation

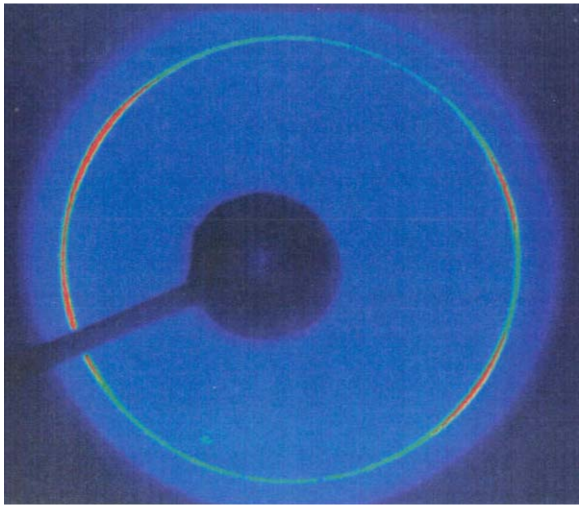




Solid

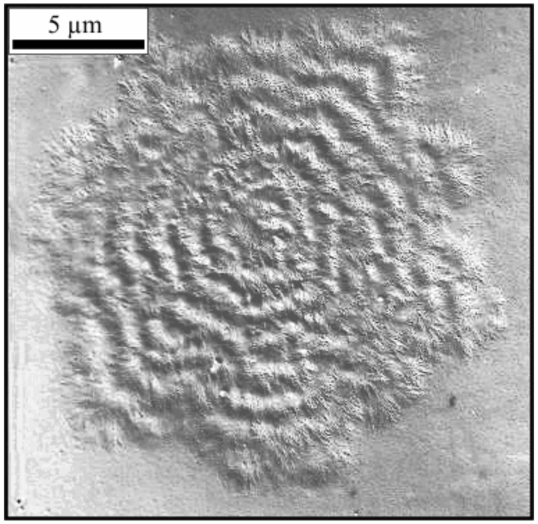


Melted & Sheared



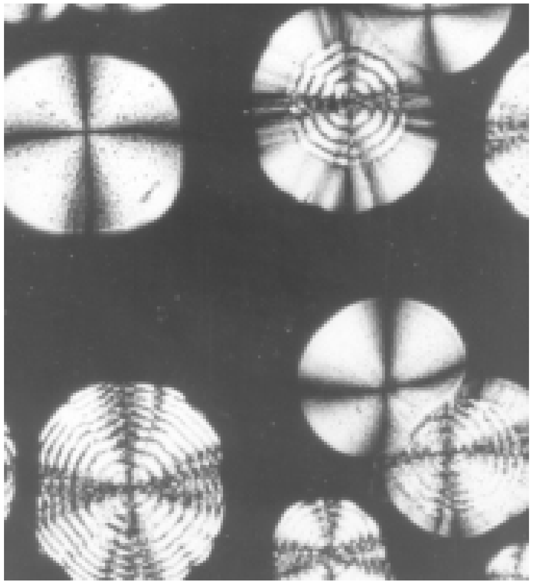
Recrystallized

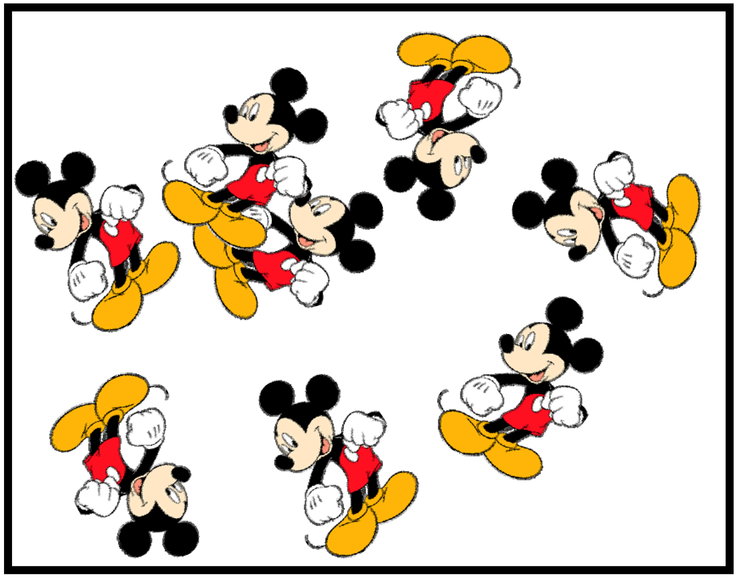
Ideal Studies for Microscopy



Microscopy good for:

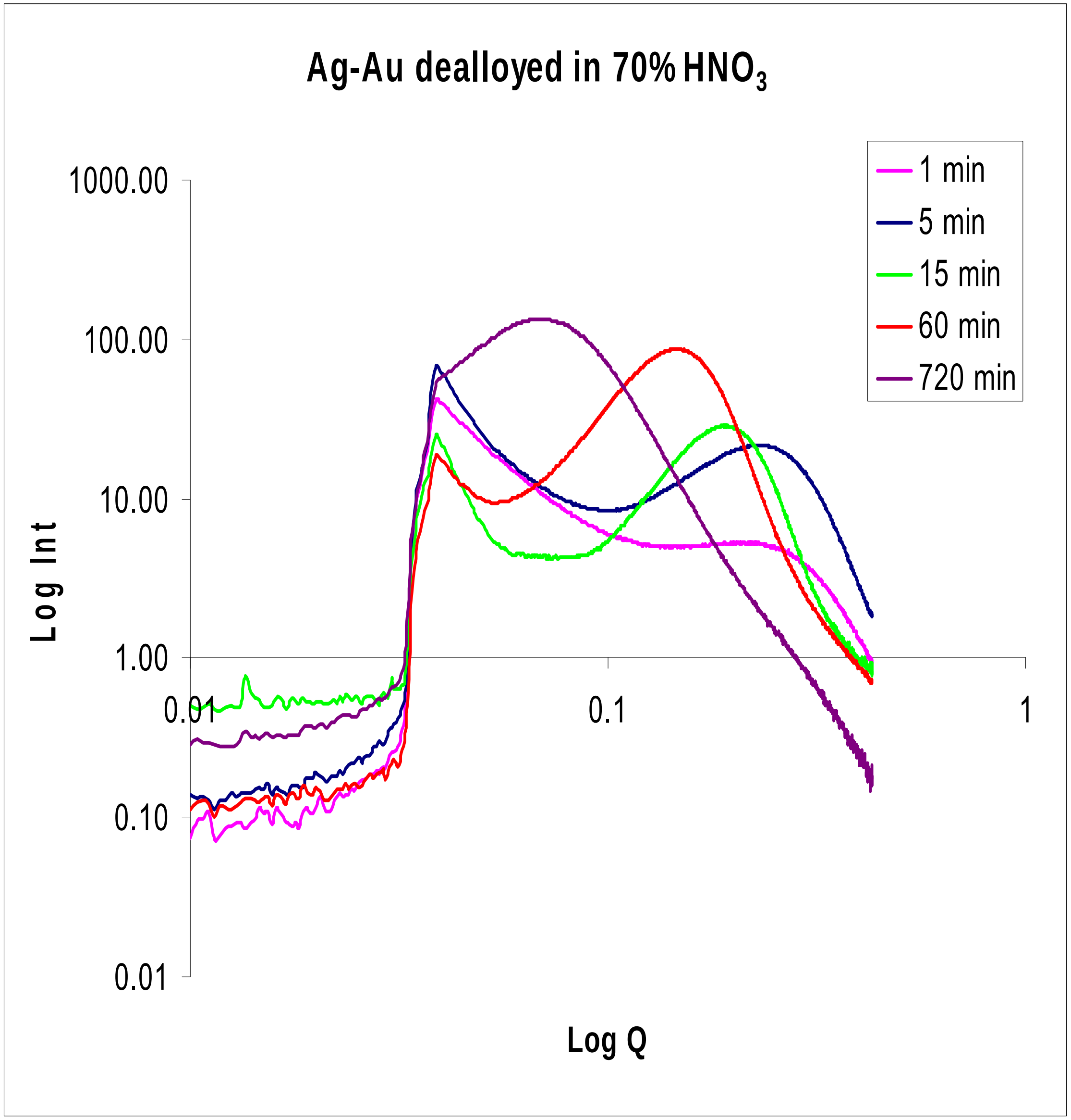
- Local detail
- Surface detail
- Faithfully represents local complexities

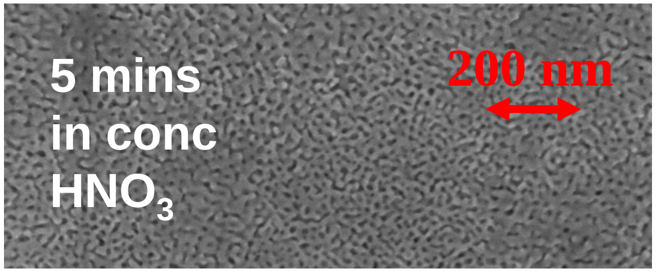


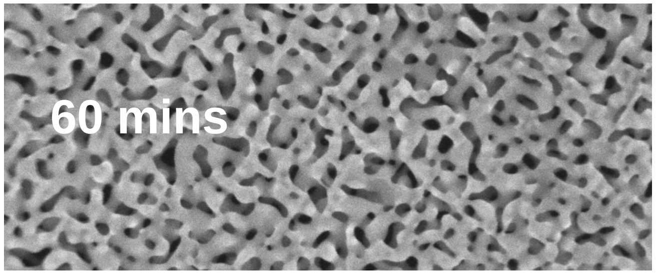


E.g. if objective is to monitor the degree to which Mickey's nose(s) and ears hold to a circular micromorphology… use microscopy not scattering

Complementary Scattering and Microscopy

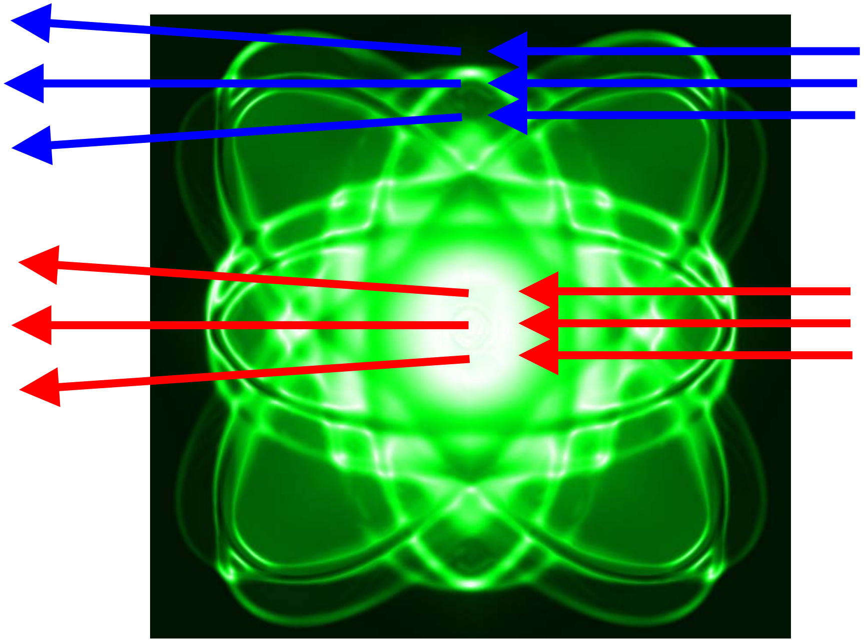






Forming a bi-continuous porous network with ligament width on the nanoscale by removing the less noble element from a binary alloy, in this case Ag-Au

Scattering: Neutrons or Photons?



X-rays

Sensitive to electron density contrast

Neutrons

Sensitive to nuclear scattering length contrast

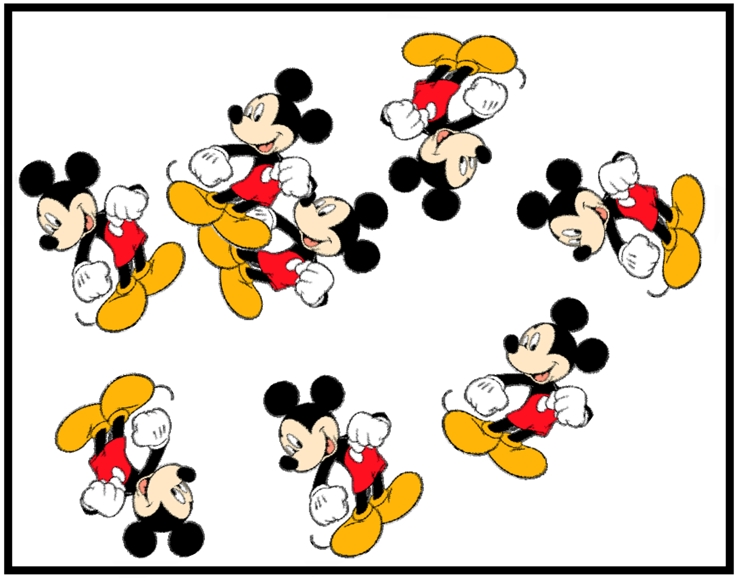
Neutron scattering: Deuteration allows species selection

Advantages of X-ray scattering:

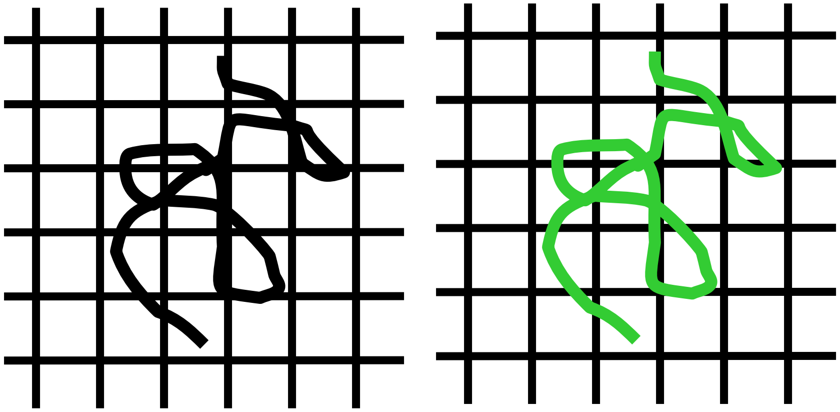
- Relatively small sample quantities required
- Relatively fast data acquisition times - allows time resolved effects to be characterized

Scattering: Neutrons or Photons?

Neutrons: Deuteration allows species selection

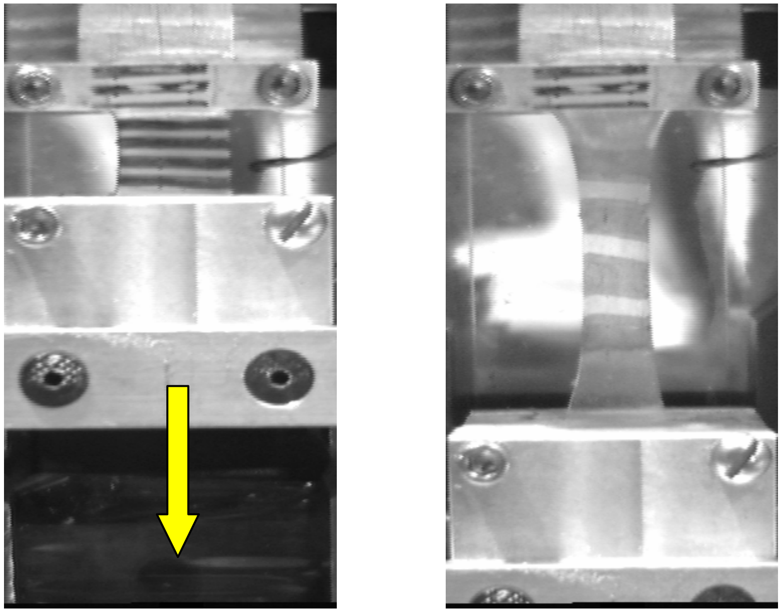


This essentially permits a dramatic alteration to the ‘visibility’ of the tagged elements in terms of their contribution to the reciprocal space scattering pattern

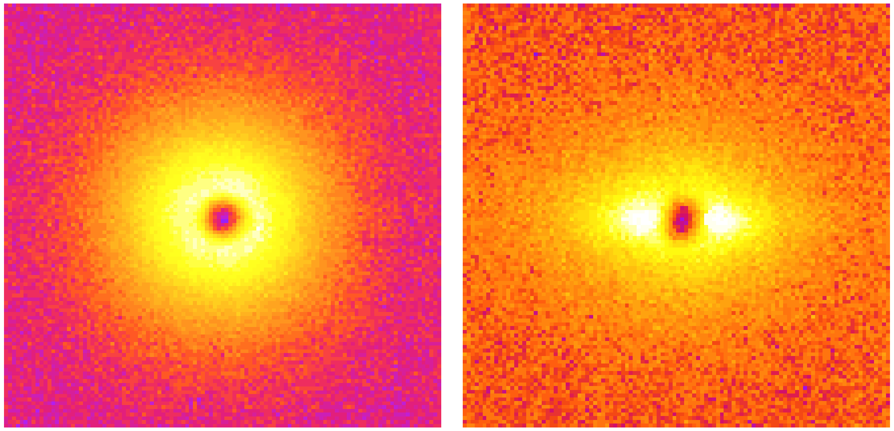


Atom	Scattering length (x 10^{12} cm^2)	Incoherent scattering (x 10^{24} cm^2)
■ ^{1}H	-0.374	80
🟩 ^{2}D	0.667	2

Scattering: Neutrons or Photons?



Photos of deformation

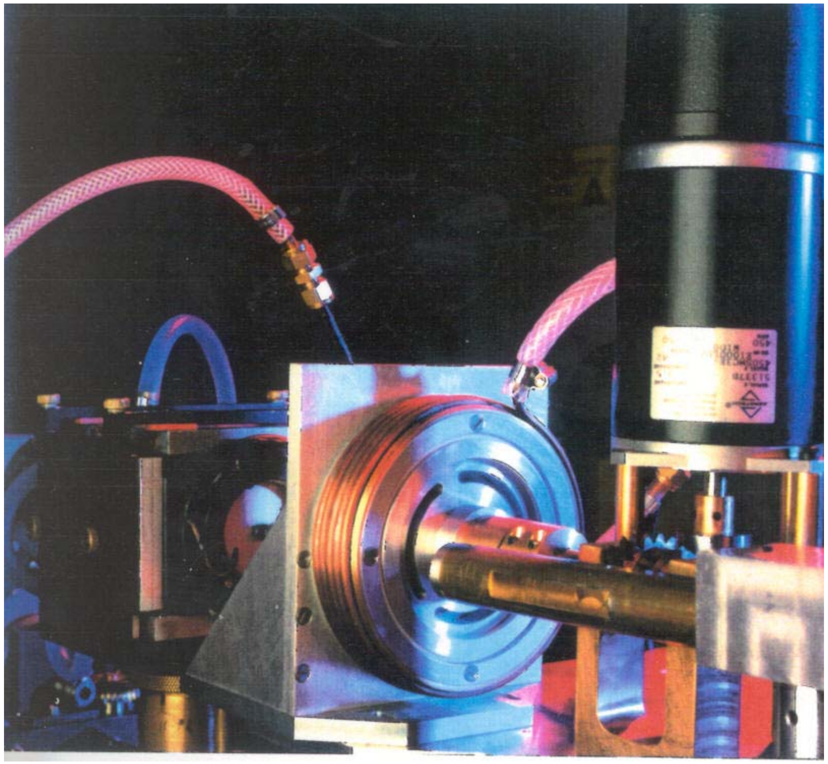


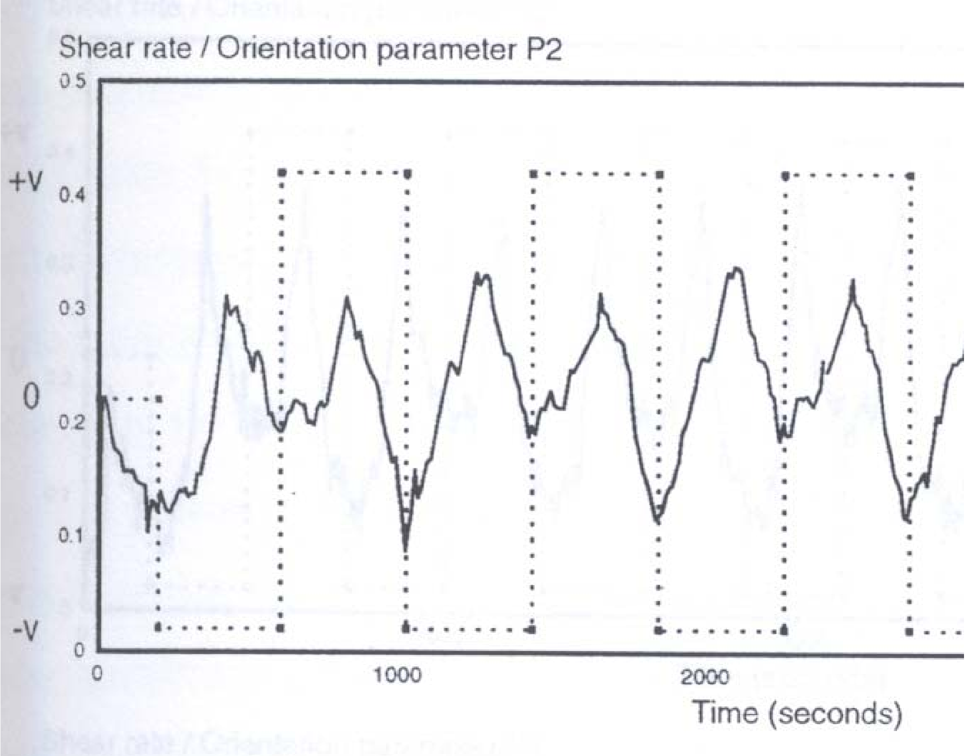
SANS patterns

λ = 0% λ = 300%

Scattering: Neutrons or Photons?

X-rays: Order of magnitude better spatial resolution
Fast data acquisition times for time resolved data



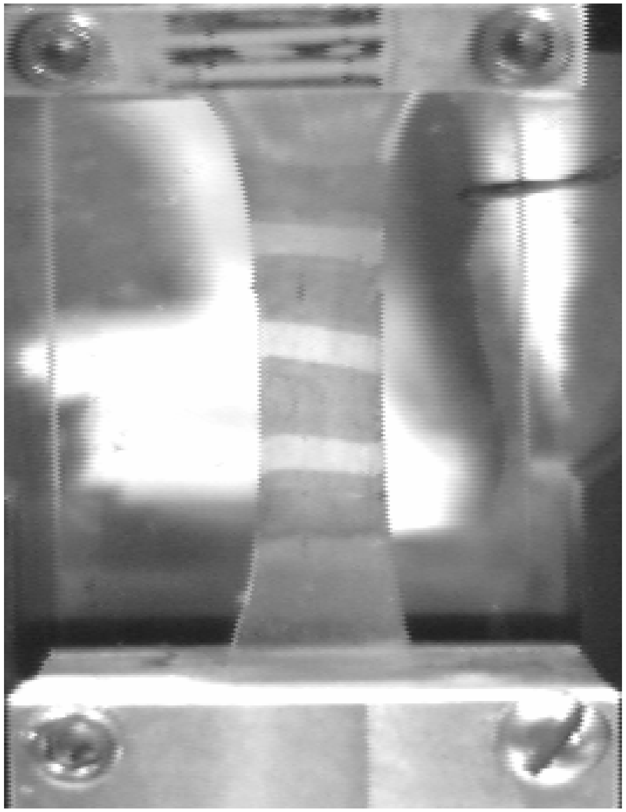


Oscillatory Shearing of lyotropic HPC – a liquid crystal polymer

X-ray Scattering: Transmission or Reflection?

Need to be conscious of:

Constituent elements, i.e. absorption cutoffs
Multiple scattering
Area of interest: surface effect or bulk effect



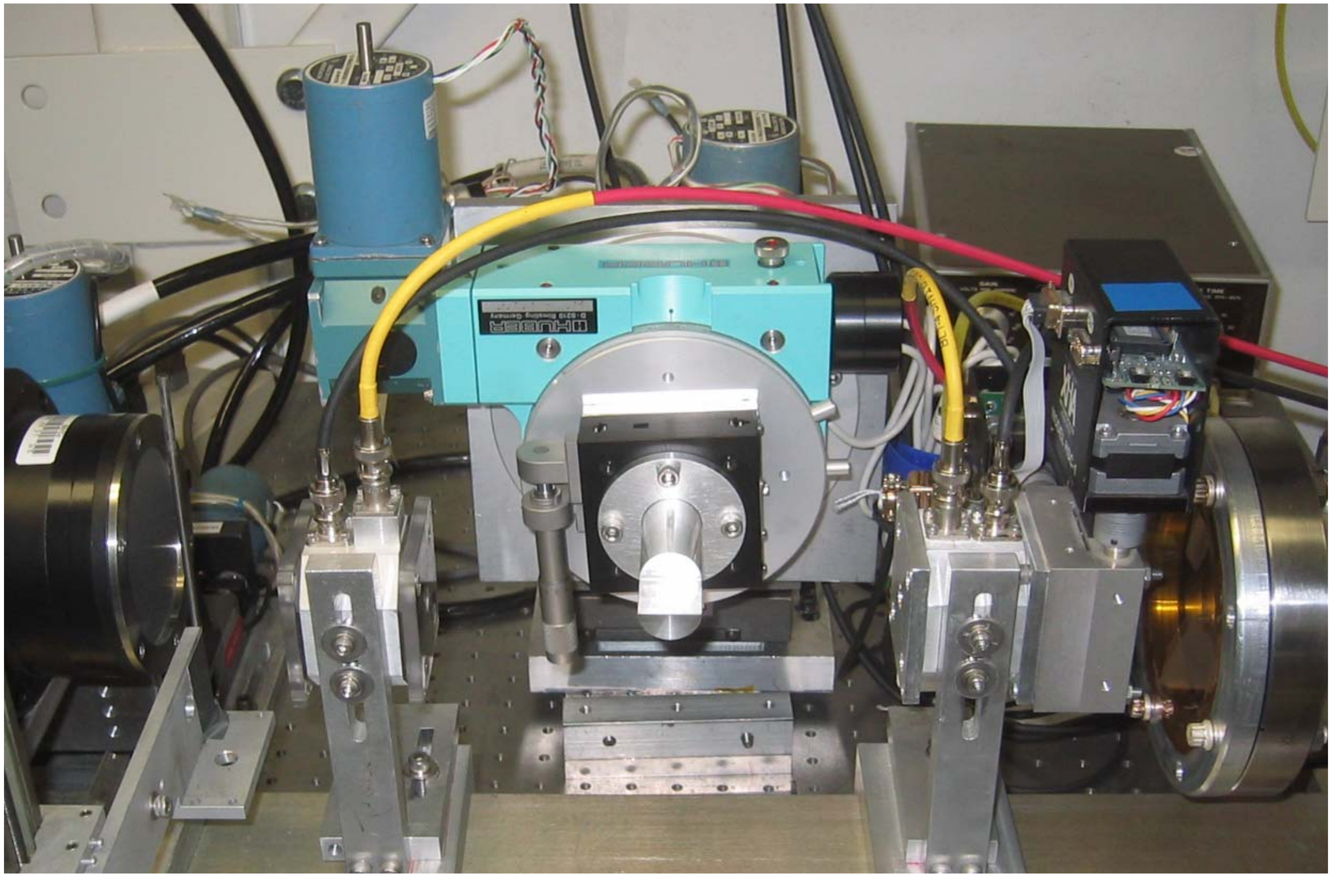
Transmission geometry appropriate for:

- Extracting bulk parameters, especially in deformation
- Weakly scattering samples: can vary path length

X-ray Scattering: Transmission or Reflection?

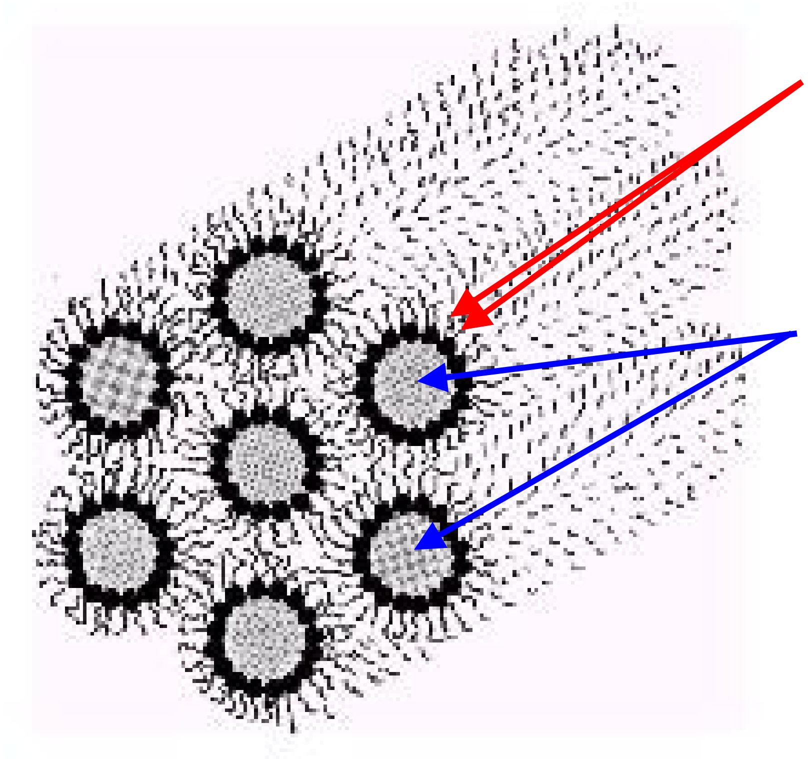
Reflection geometry appropriate for:

- Films on a substrate (whether opaque or not)
- Probing surface interactions



X-ray Scattering: SAXS or WAXS?

No fundamental difference in physics: a consequence of chemistry

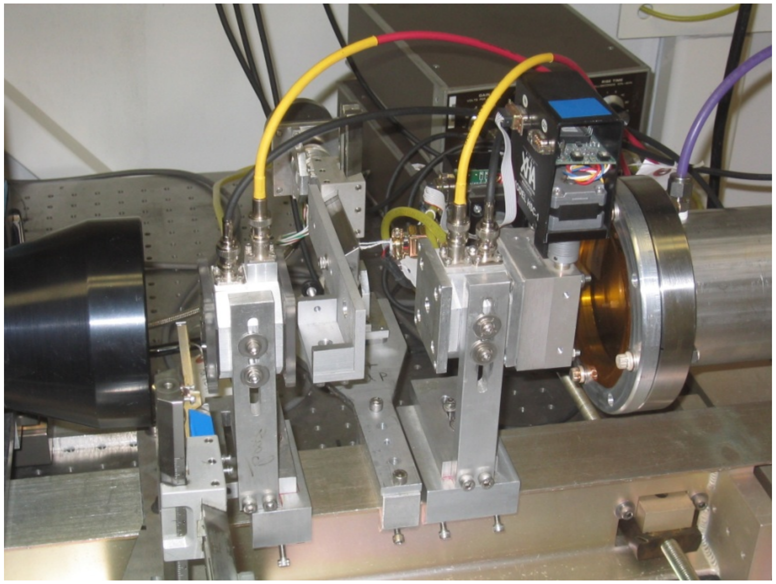


WAXS patterns contain data concerning correlations on an intra-molecular, inter-atomic level (0.1-1 nm)

SAXS patterns contain data concerning correlations on an inter-molecular level: necessarily samples where there is macromolecular or aggregate order (1-100 nm)

As synthesis design/control improves, SAXS becomes more relevant than ever before

X-ray Scattering: SAXS or WAXS?



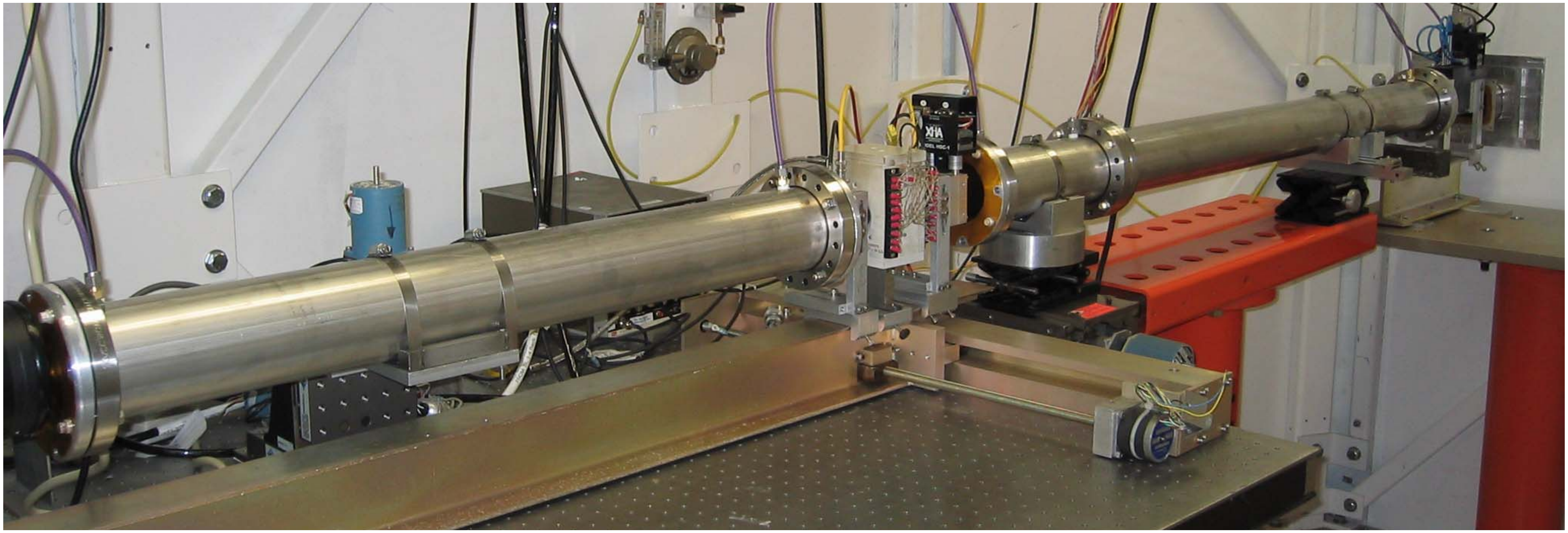
Experimental consequences

WAXS: Detector close to sample, consider:

- Distortion of reciprocal space mapping
- Thermal effects when heating sample
- No ion chamber for absorption

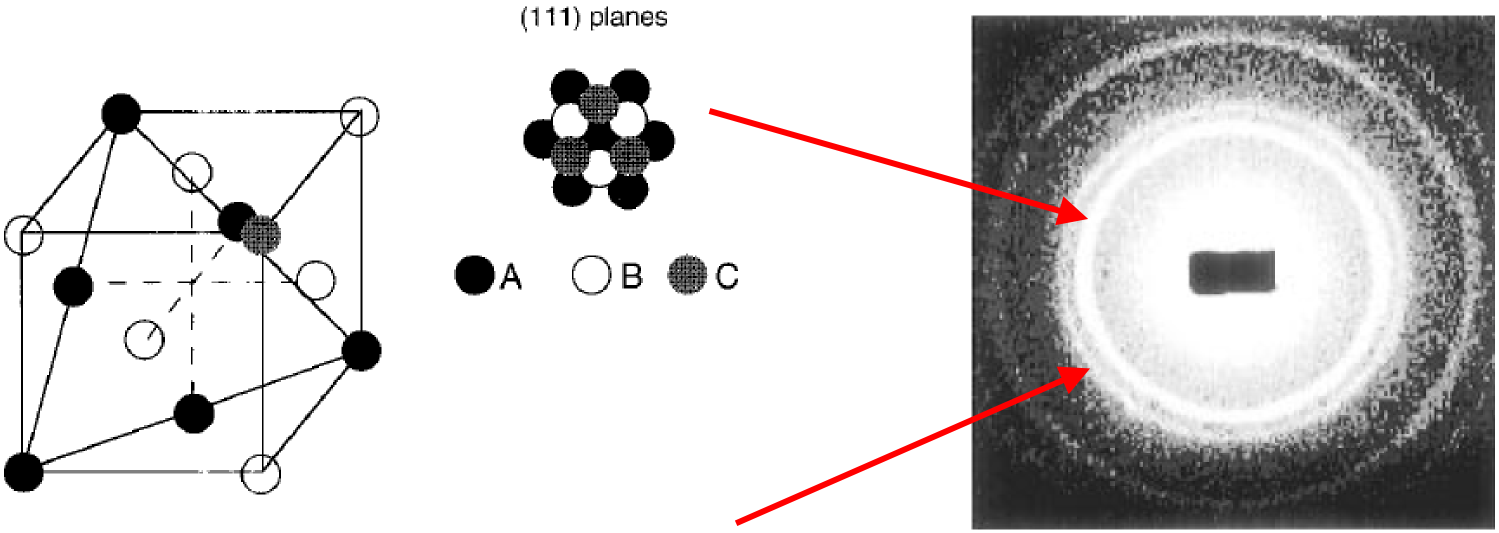
SAXS: Detector far from sample, consider:

- Absorption from intermediate space
- Interception of appropriate q range



What can I Learn from a SAXS Pattern?

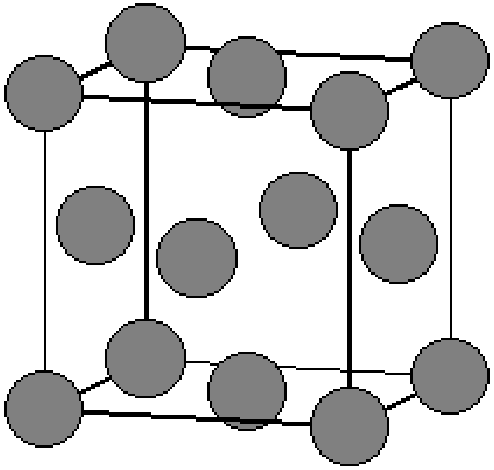
Recognizing Reciprocal Space Patterns: Indexing



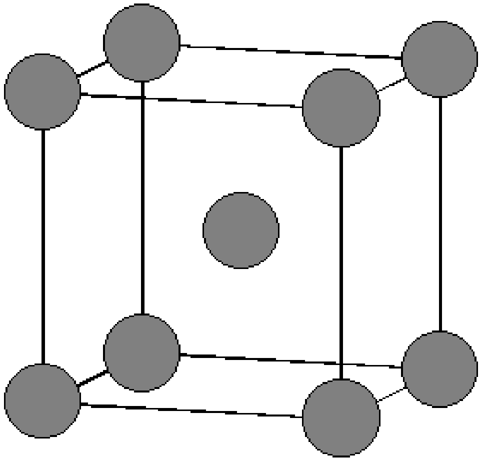
Face centered cubic pattern from diblock copolymer gel

Recognizing Reciprocal Space Patterns: Indexing

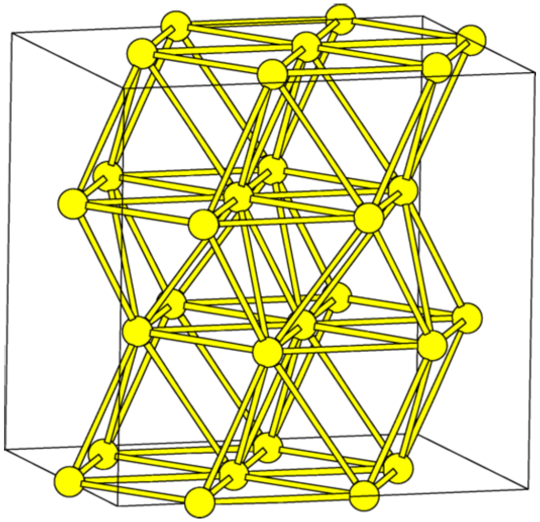
Real space packing



Face centered cubic



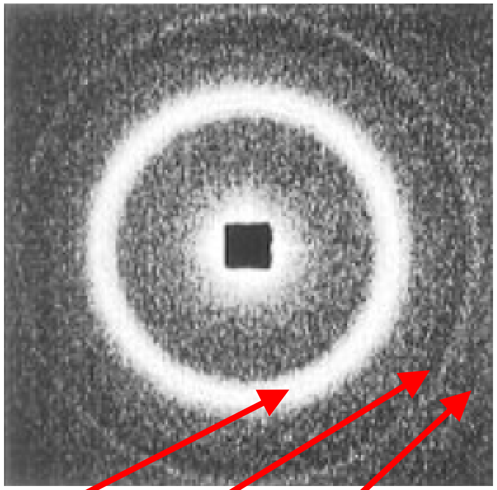
Body centered cubic

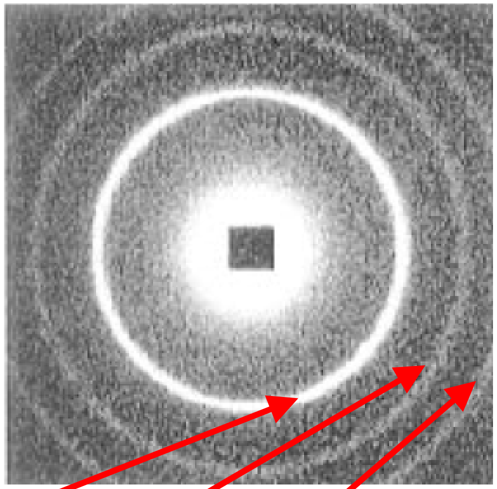


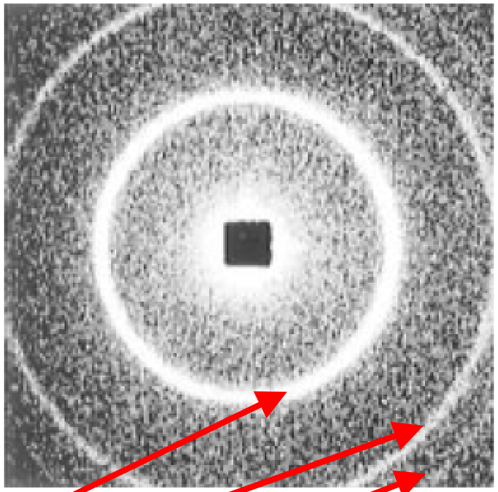
Hexagonal

Reciprocal space image

(unoriented domains)







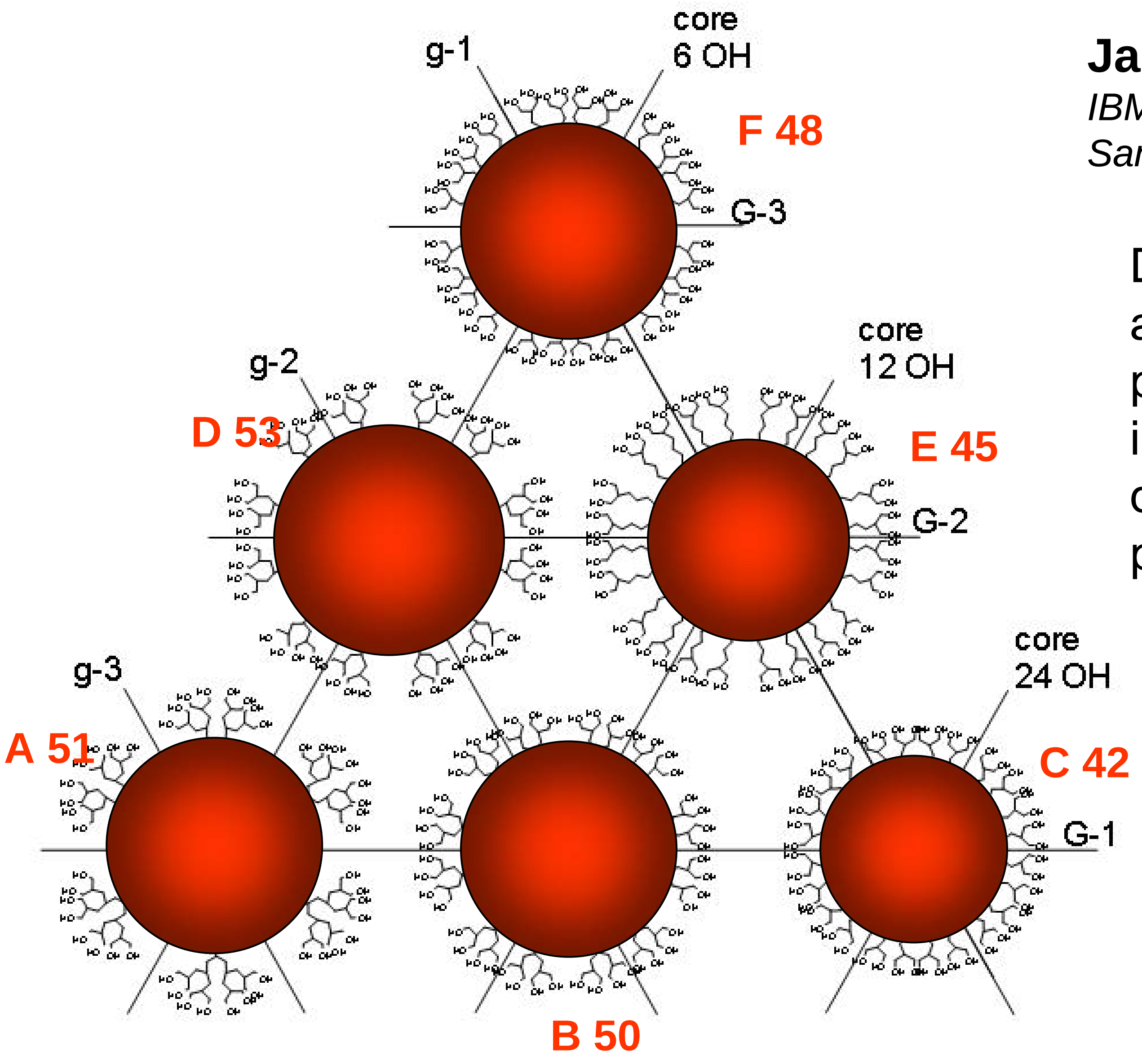
Normalized peak positions

$\equiv 1$; $=\sqrt{4/3}$; $=\sqrt{8/3}$

$\equiv 1$; $=\sqrt{2}$; $=\sqrt{3}$

$\equiv 1$; $=\sqrt{3}$; $=\sqrt{4}$

Recognizing Reciprocal Space Patterns: R_g



James L Hedrick

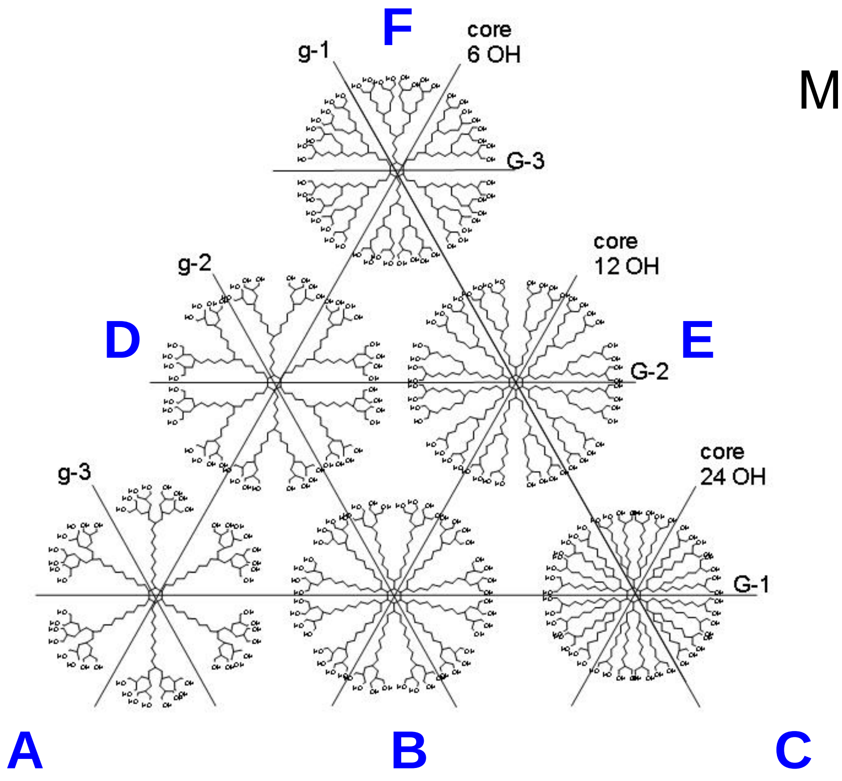
IBM Almaden, 650 Harry Road,
San Jose, CA 95120

Dendrimers designed as poragens for nano-porous media: interest in monodispersity and density distribution per poragen

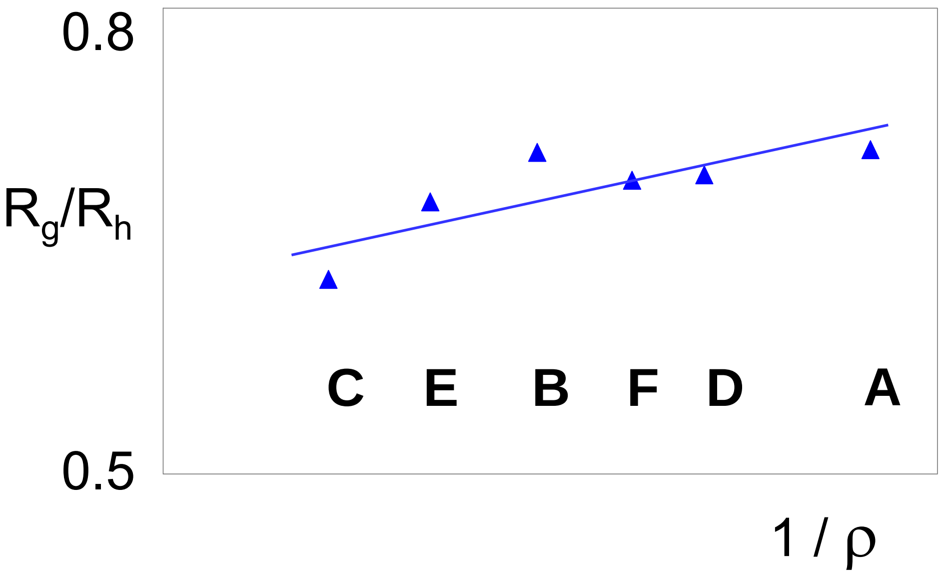
$$R_g^2 \propto \ln I(q) / q^2$$

Modeling Radial Density of Isomer Architectures

Relate the internal density (and thus functionality as nano-electronic application) of dendrimer isomer to the design architecture, modelling as a star with f arms. Can predict size and density of sphere from architectural model.

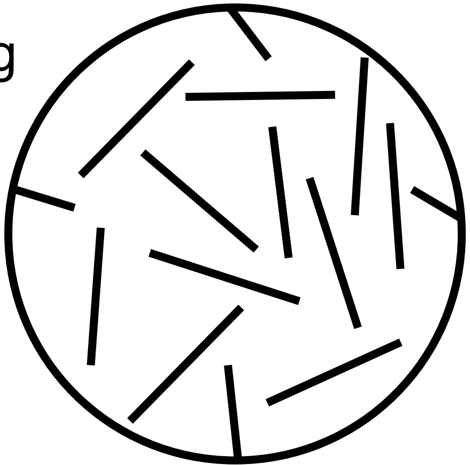


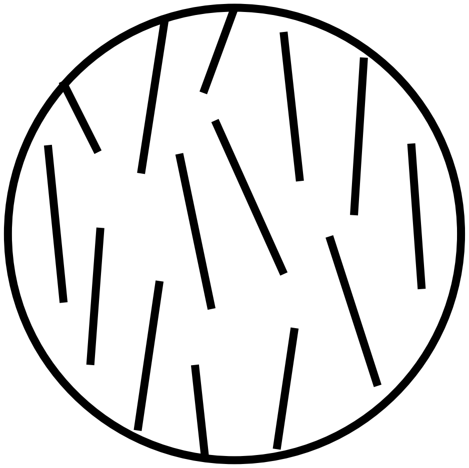
Model: $\rho(r) = \int f^{(3\nu-1)/2\nu} \, r^{(1-3\nu)/\nu} \, dr$



Recognizing Reciprocal Space Patterns: Preferential Orientation

Real
space
packing



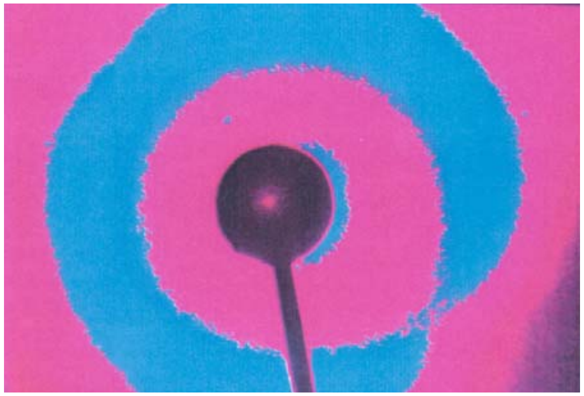


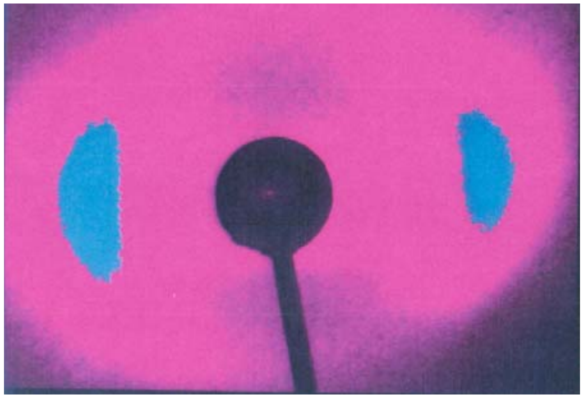
Hydrated DNA

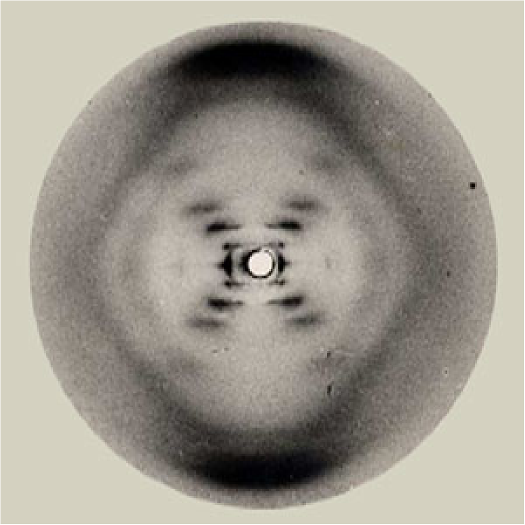
Reciprocal
space
image

Randomly
aligned rods

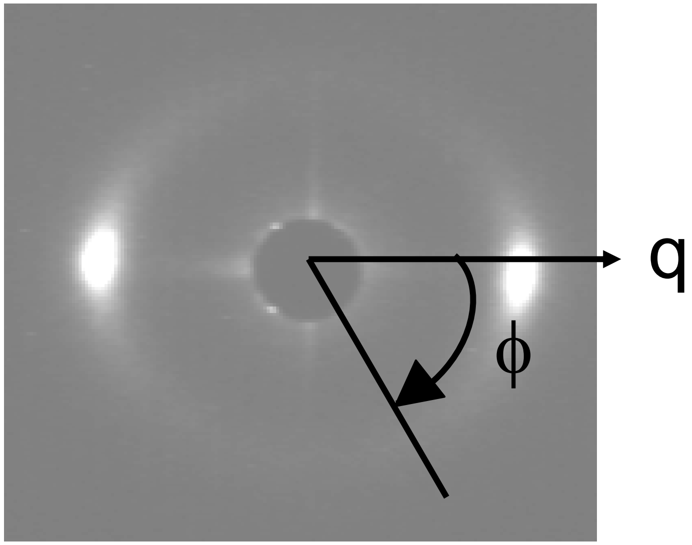
Preferentially
aligned rods

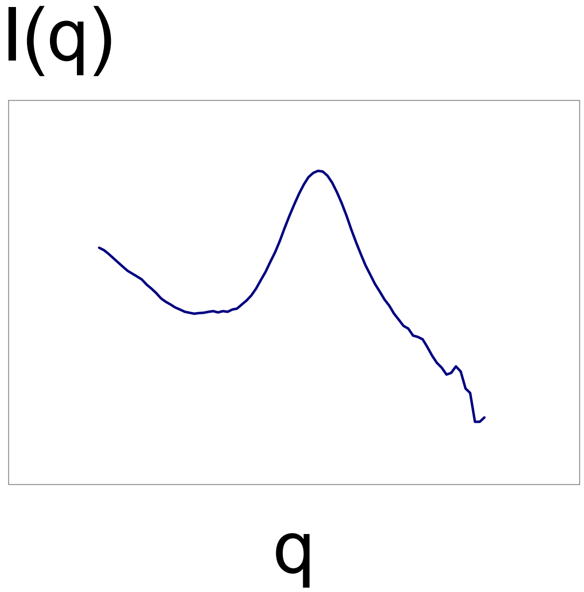


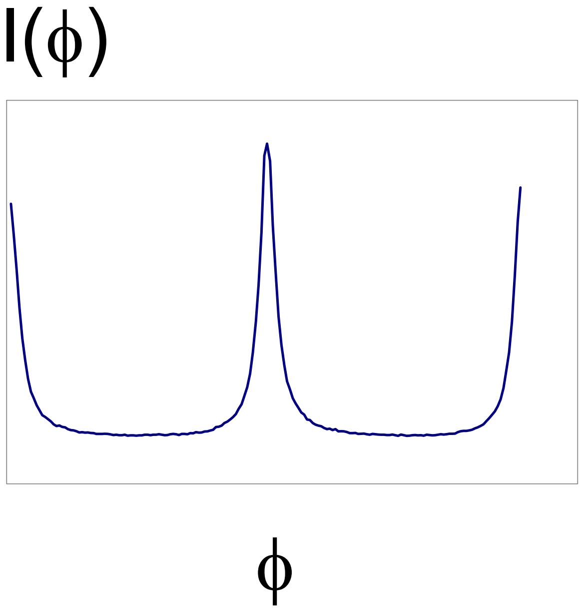




Extracting Physical Parameters from X-ray data

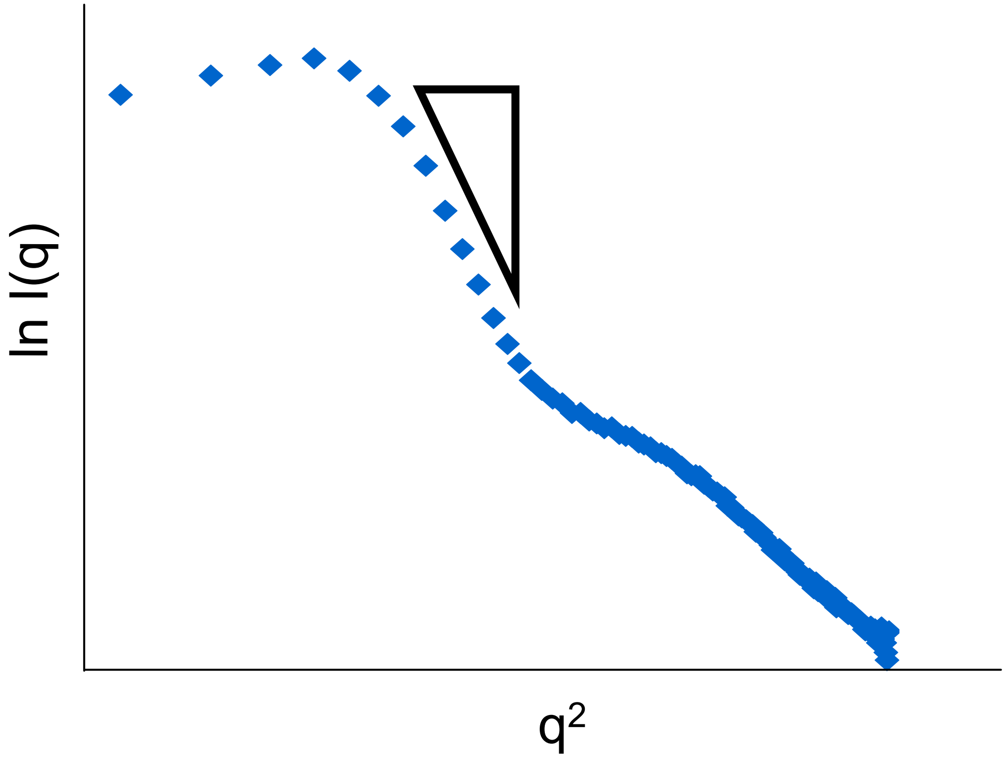




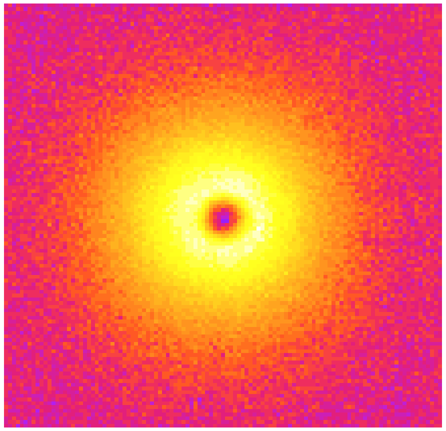


Extracting Physical Parameters from X-ray data

Molecular size: Radius of gyration (R_g)



Guinier plot



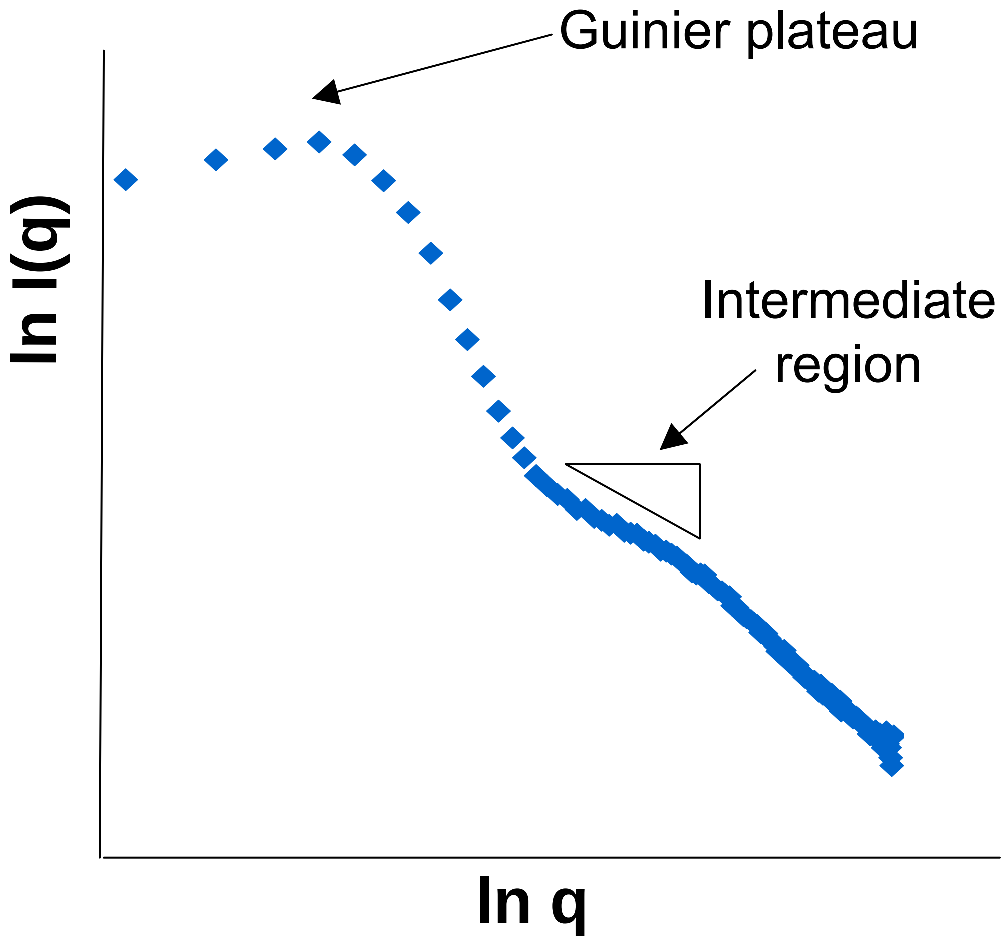
$I(q) = I(0) \exp [-q^2R_g^2 / 3]$

$R_g^2 \propto \ln I(q) / q^2$

Guinier region: $q < 1 / R_g$

Extracting Physical Parameters from X-ray data

Molecular conformation: Scaling exponent

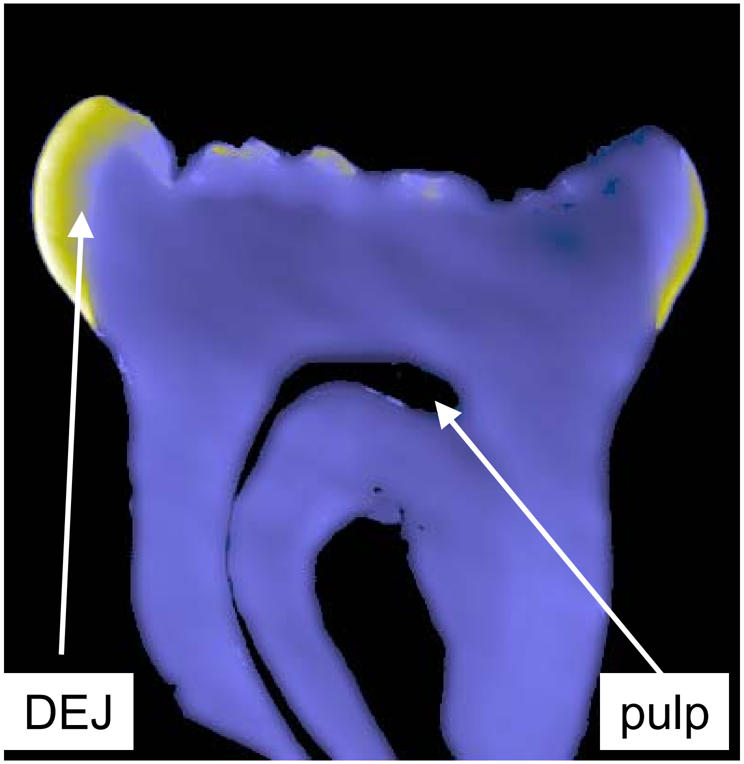


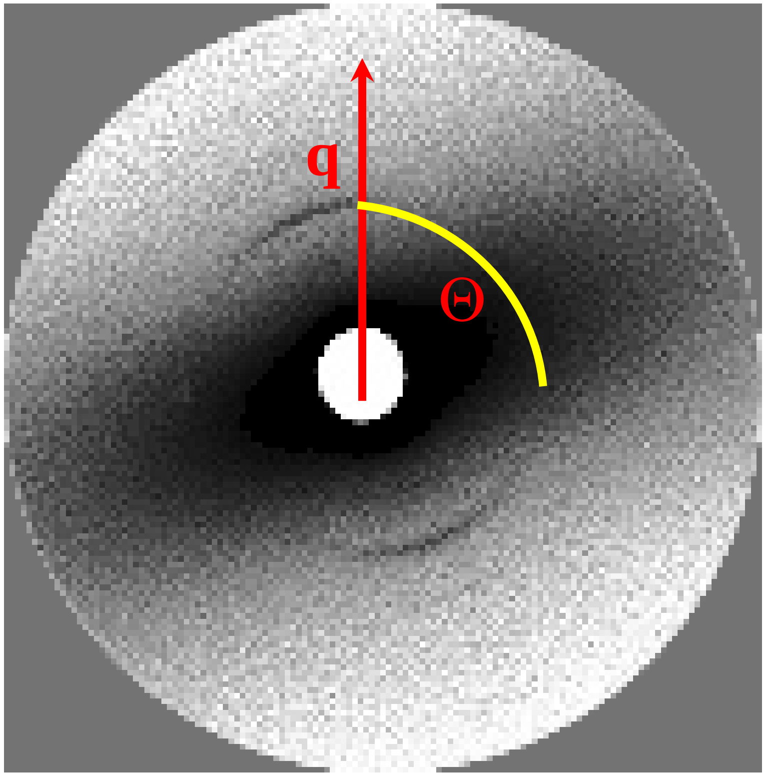
Gradient of profile in intermediate region implies fractal dimension of scattering unit

Rod	q^{-1}
Coil in good solvent	$q^{-5/3}$
Sphere	q^{-4}

Molecular Conformation in Dentin

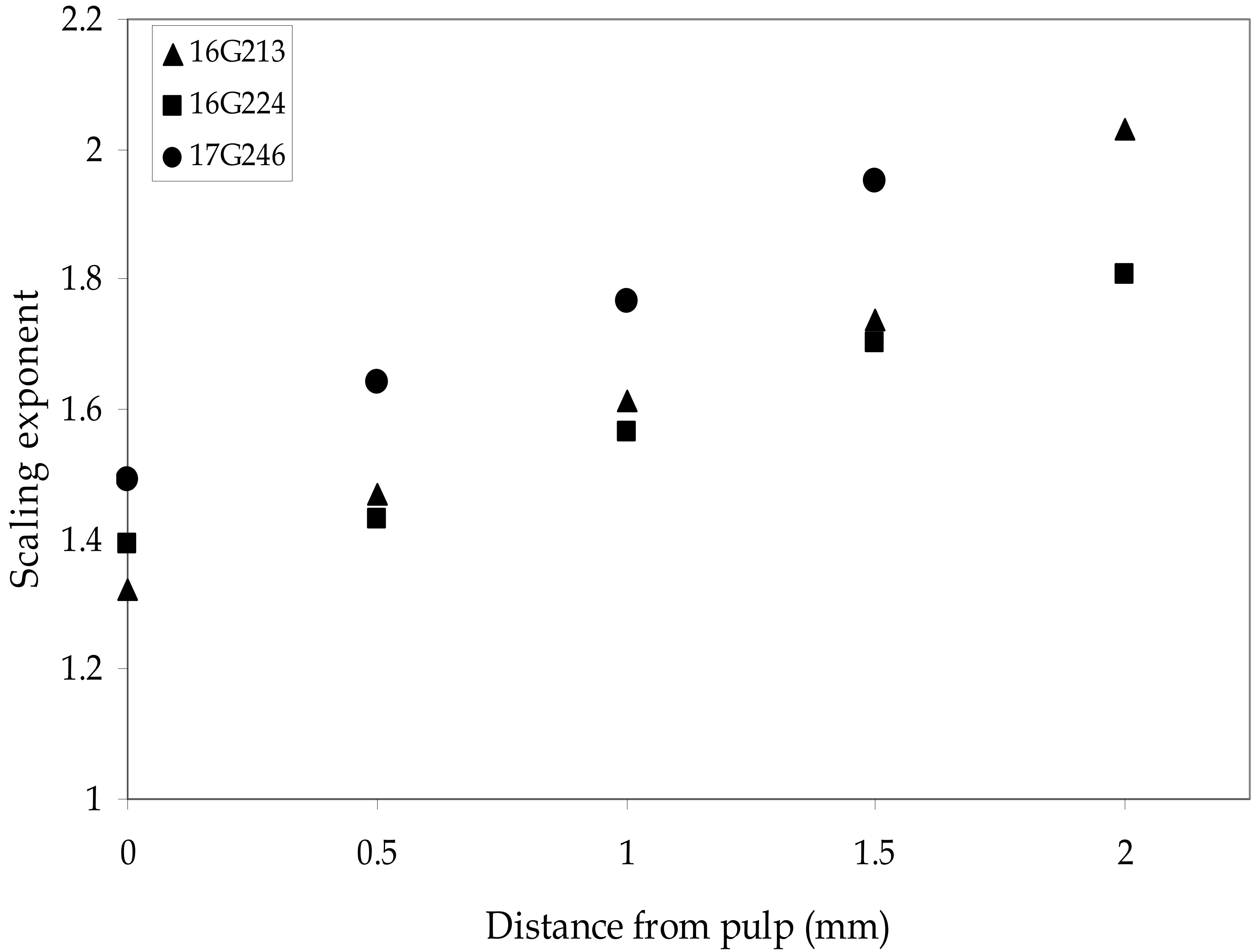
John H Kinney
Department of Preventive and Restorative Dental Sciences,
University of California, San Francisco, CA 94143





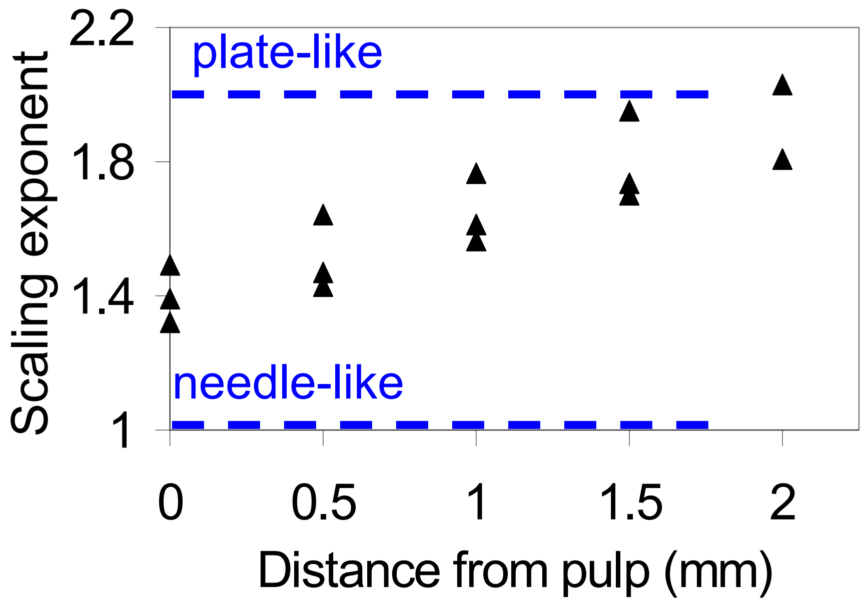
SAXS pattern

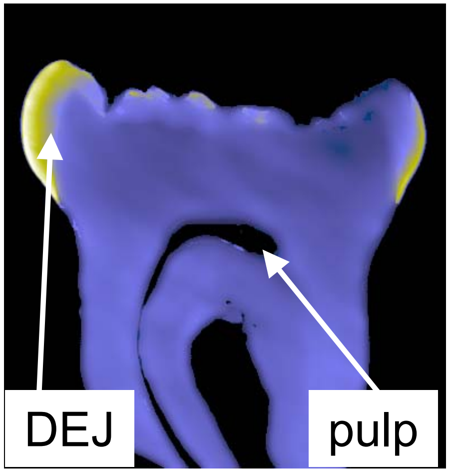
Molecular Conformation in Dentin



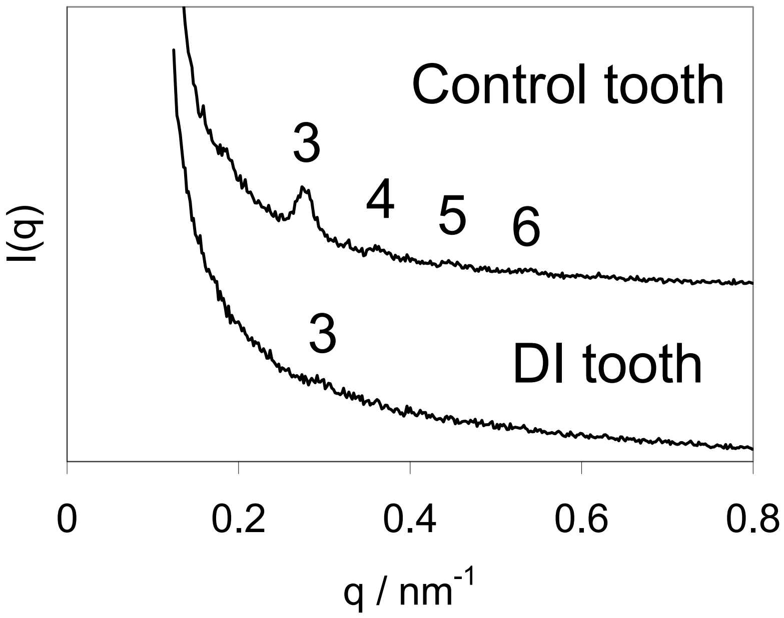
Molecular Conformation in Dentin

Shape change of mineral crystallites from needle-like to plate-like from pulp to dentin-enamel junction (DEJ).



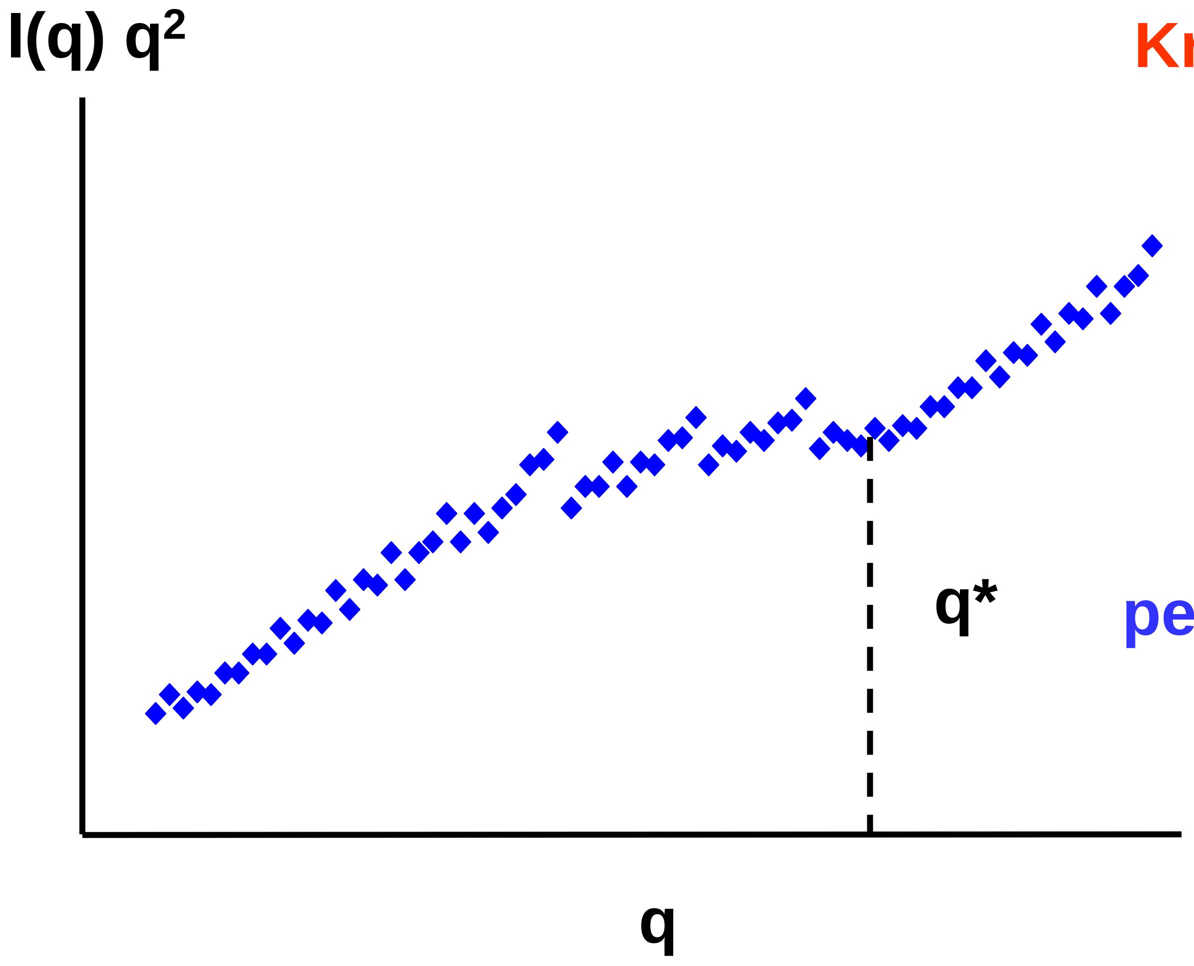


Dentinogenesis imperfecta (DI) teeth shown to exhibit impaired development of intrafibrillar mineral: characteristic scattering peaks are absent from the diseased tooth.



Extracting Physical Parameters from X-ray data

Molecular conformation: Persistence length of coiled chain



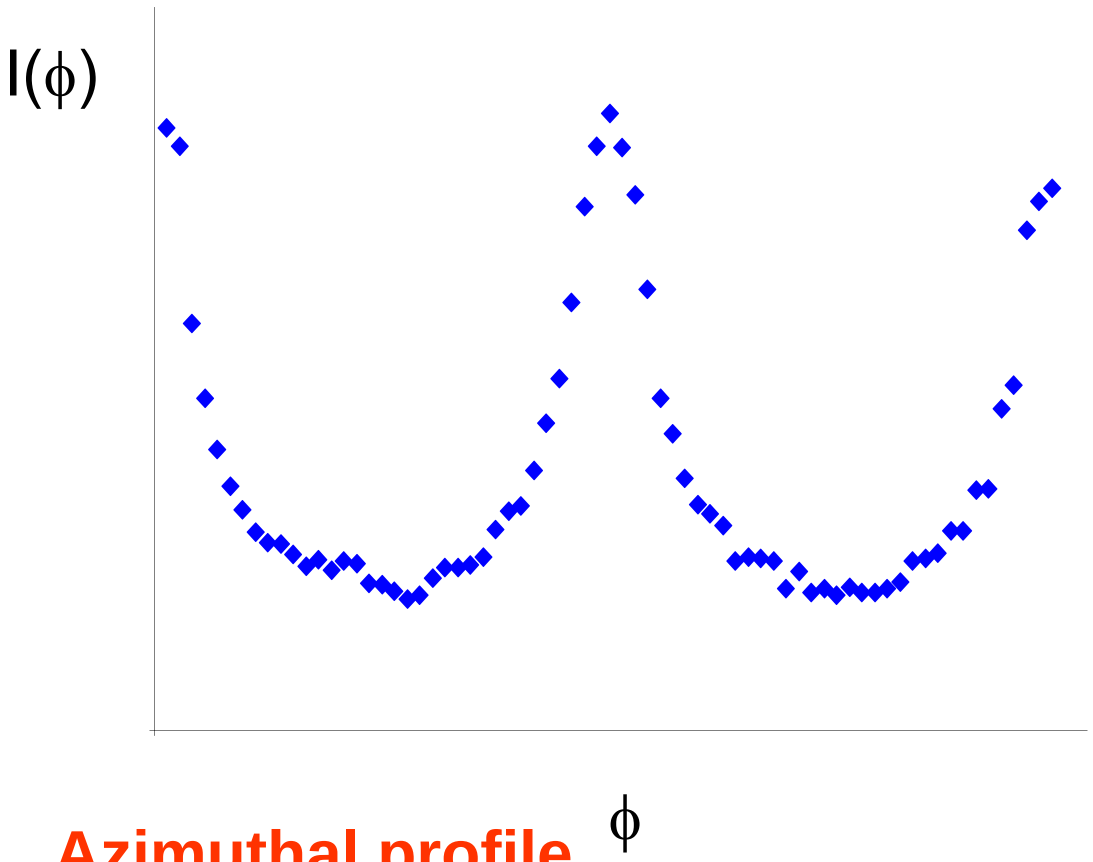
Kratky plot

persistence length
$= 6 / (\pi q^*)$

Extracting Physical Parameters from X-ray data

Molecular orientation: Orientation parameter P_2

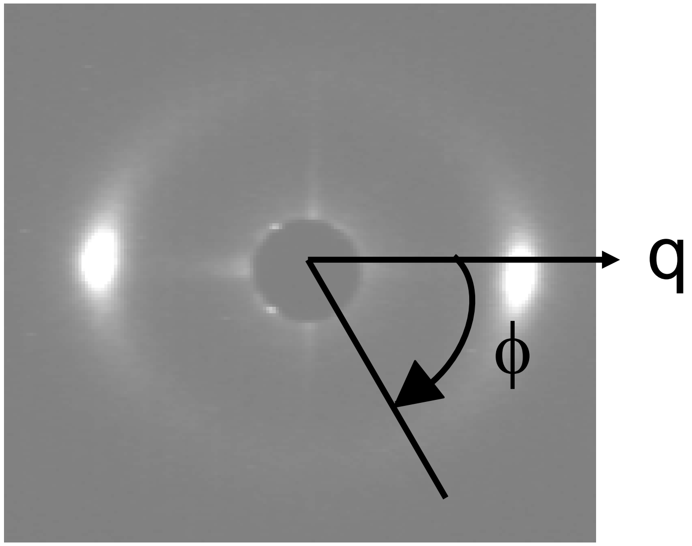
$$\langle P_{2n}(\cos\phi)\rangle = \frac{\int I(s,\phi)\, P_{2n}(\cos\phi)\, \sin\phi\, d\phi}{\int I(s,\phi)\, \sin\phi\, d\phi}$$



Azimuthal profile

Normalized:

$-0.5 < P_2 < 1$

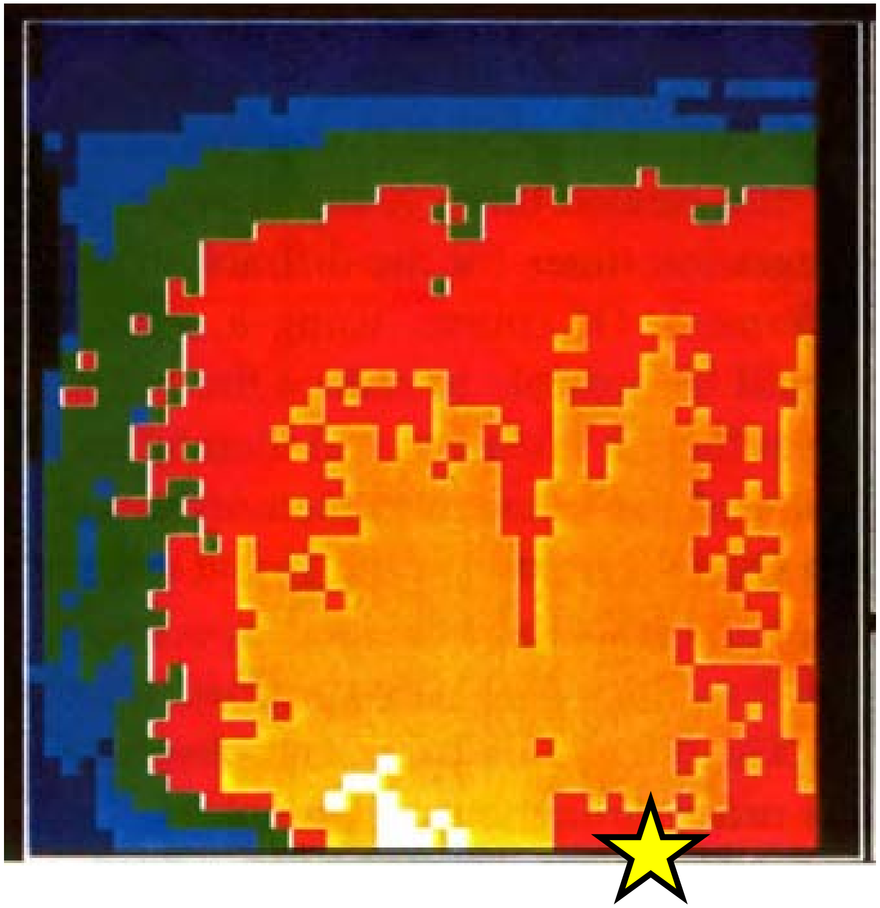


Molecular Orientation in Injection Moldings

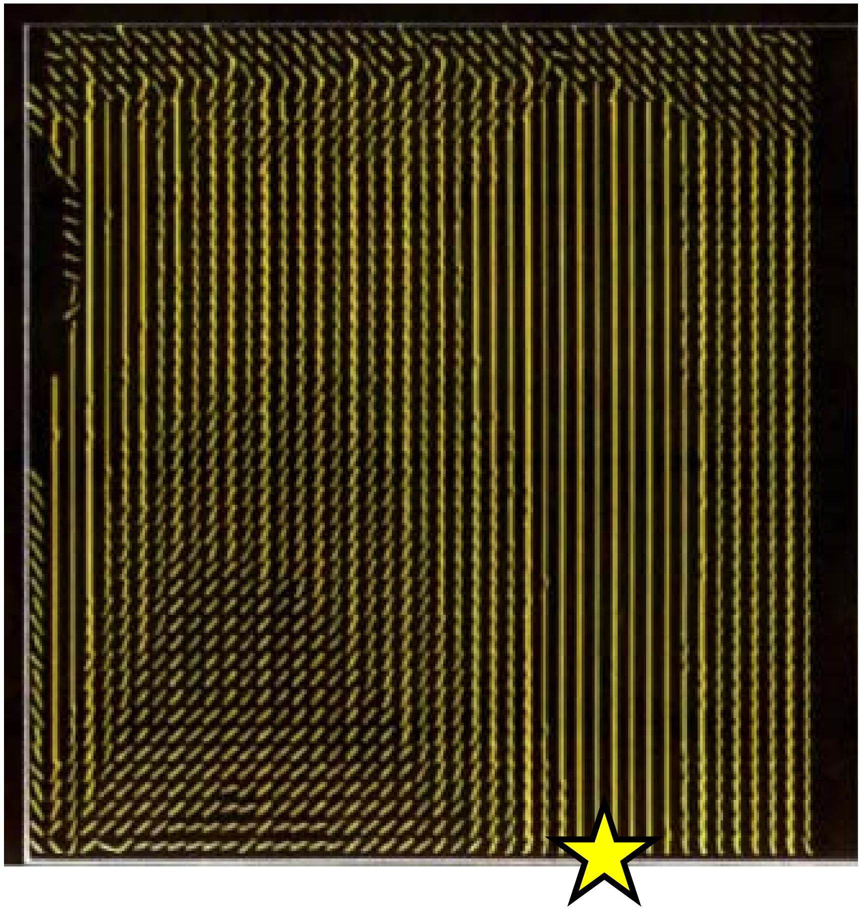
Measuring the degree and inclination of preferential molecular orientation in a piece of injection molded plastic (e.g. hip replacement joints). ~ 1500 WAXS patterns

★ Marks the injection point

Orientation parameters: $0 < P_2 < 0.3$

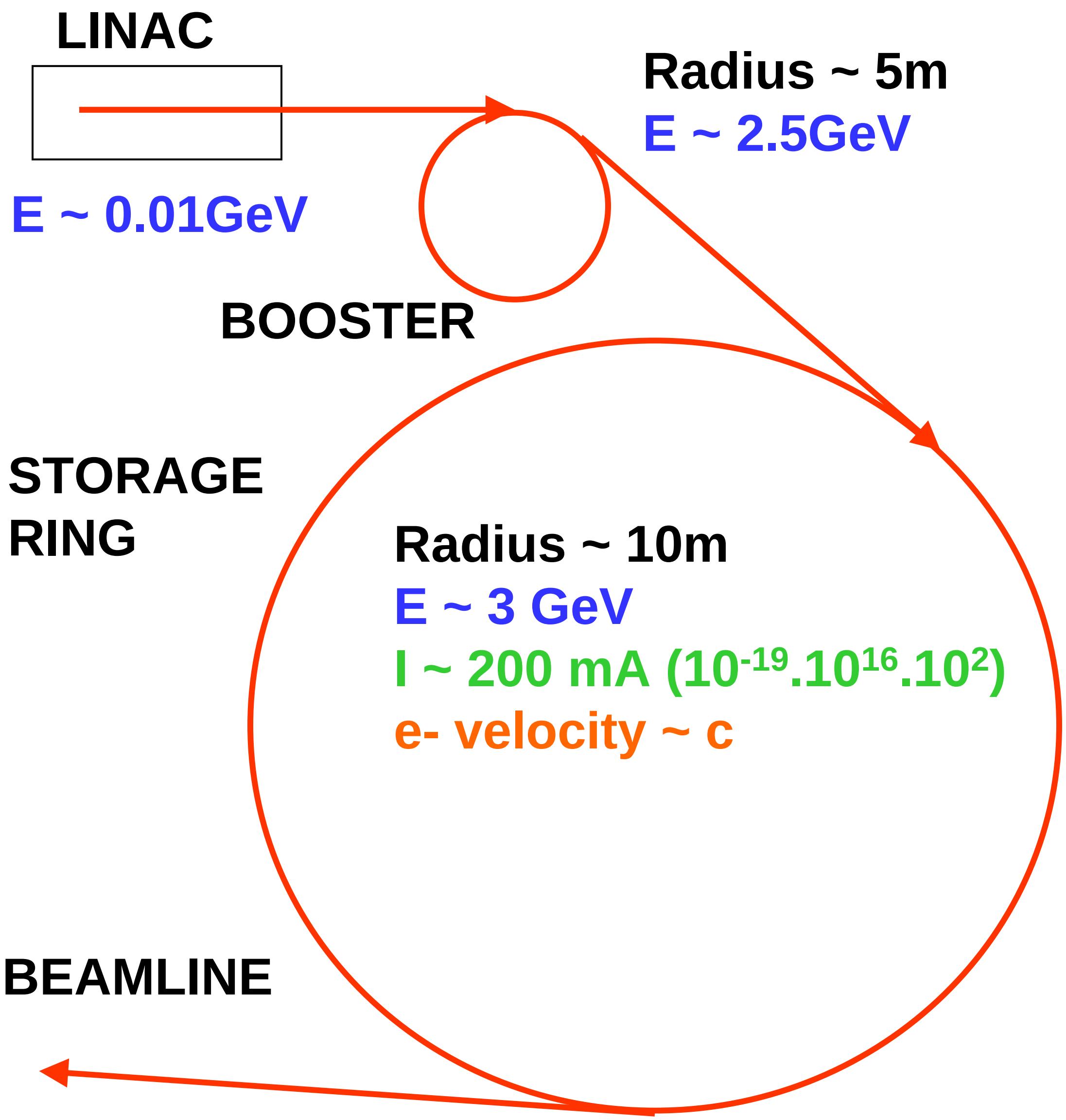


Axis of orientation



What can the SAXS beamline at SSRL do?

GENERIC SYNCHROTRON LAYOUT



LINAC

E ~ 0.01GeV

Radius ~ 5m

E ~ 2.5GeV

BOOSTER

STORAGE RING

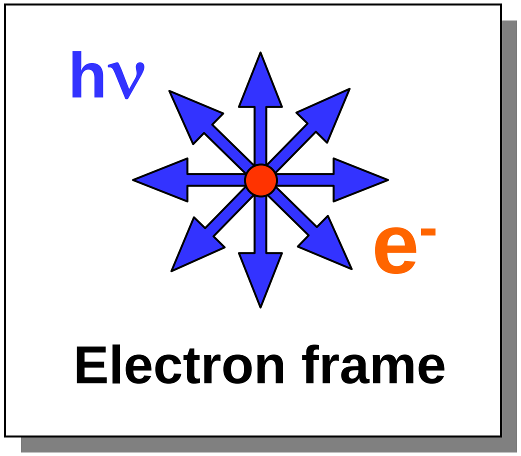
Radius ~ 10m

E ~ 3 GeV

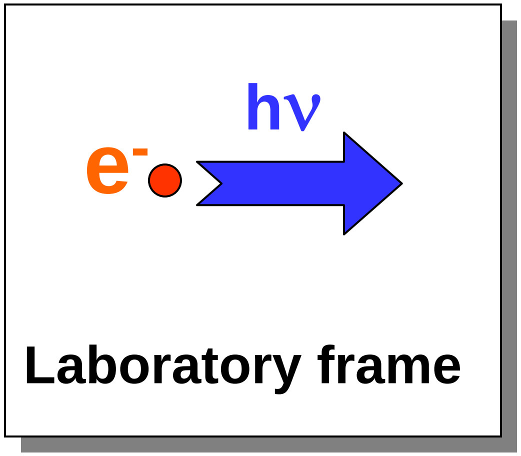
I ~ 200 mA ($10^{-19}.10^{16}.10^{2}$)

e- velocity ~ c

BEAMLINE

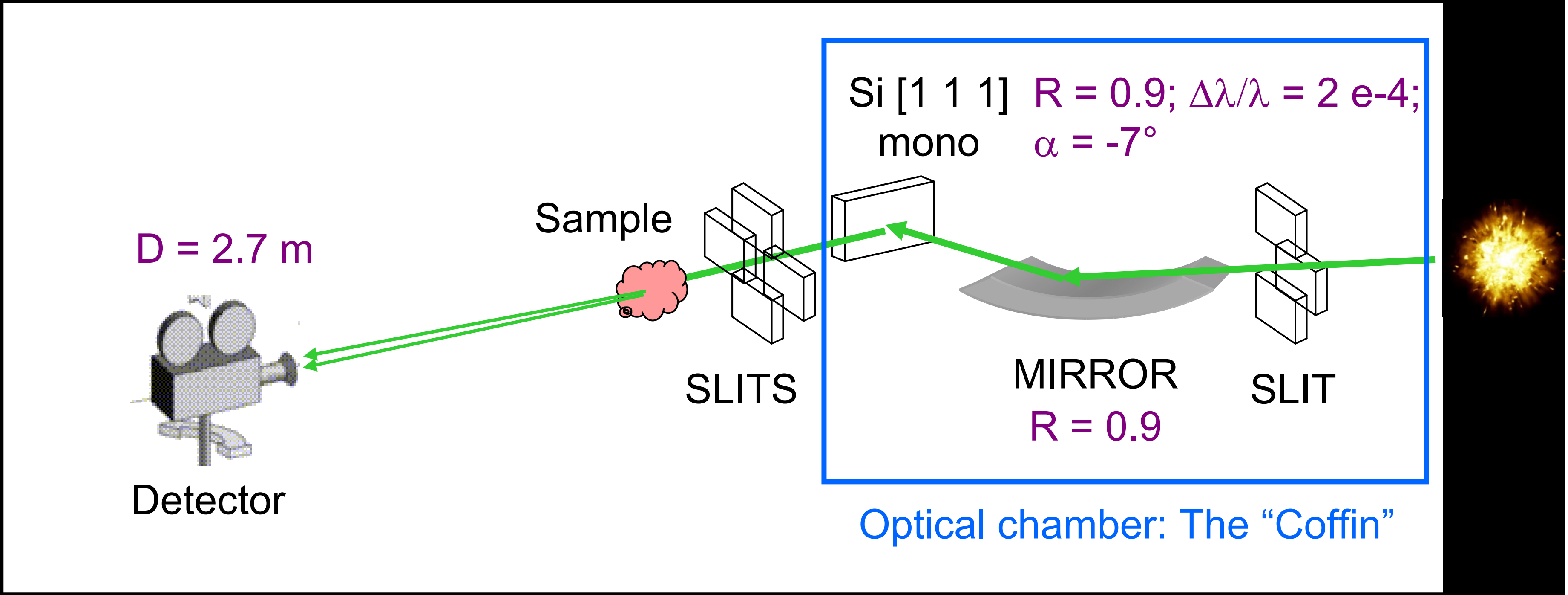


Electron frame



Laboratory frame

Beamline 1-4: Materials Science Scattering



Unfocused ϕ ~ 4e11 hν s^{-1} mA^{-1}

Source size: 8 000 μm^2

Min q ~ 0.015 nm^{-1}

Max d ~ 400 nm

Bent mirror, V focus

Bent, offcut Xtl mono,

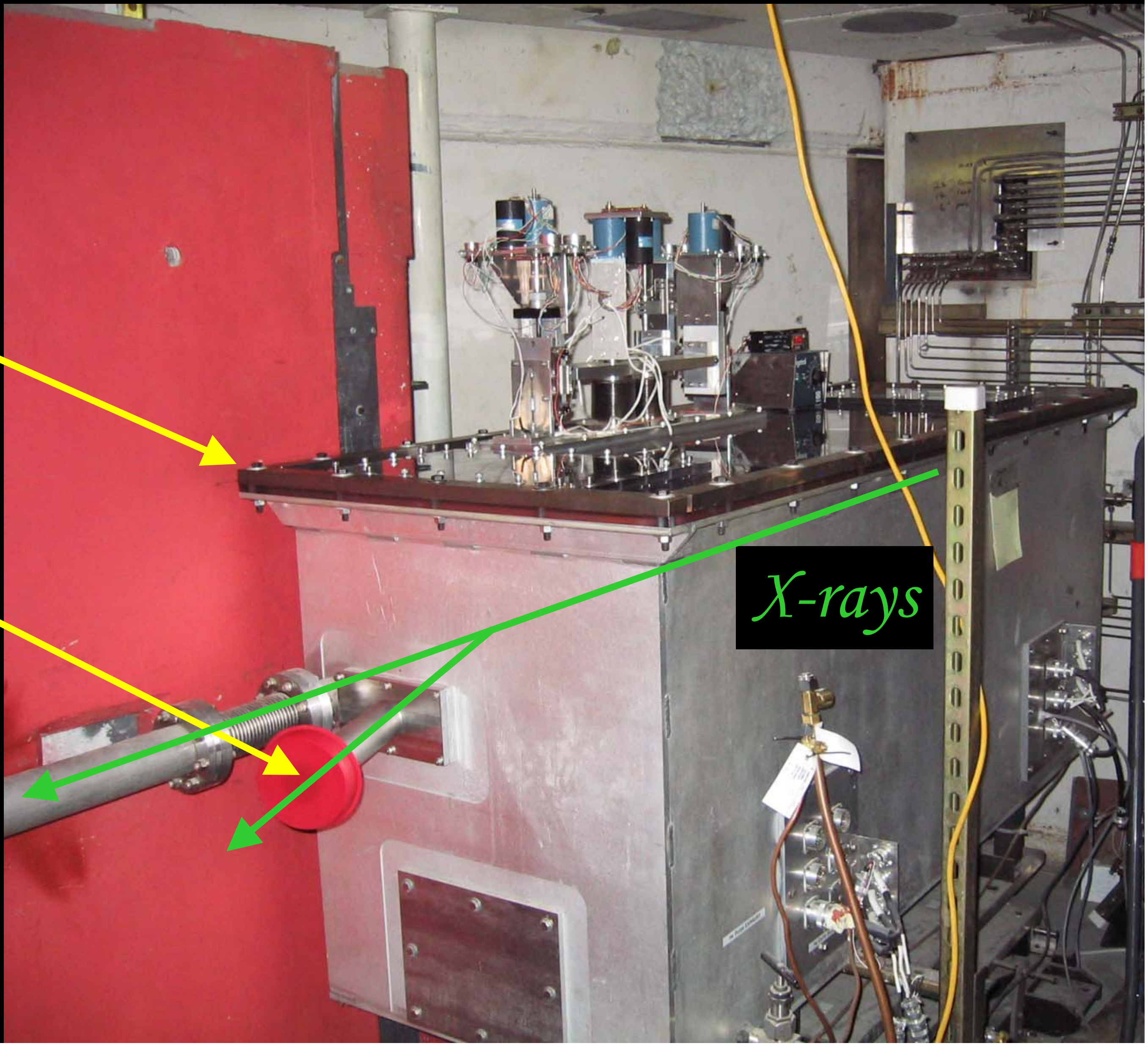
H focus

SPEAR3 bend magnet

I = 500 mA, E = 8333 eV

σ(x), σ(y) 160 x 50 μm

Beamline 1-4 upstream optics: The 'Coffin'

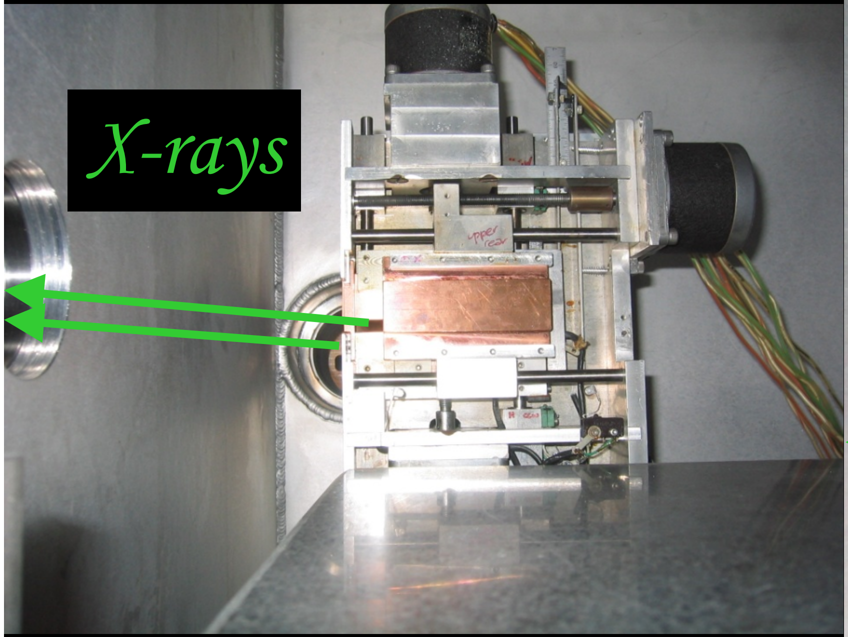


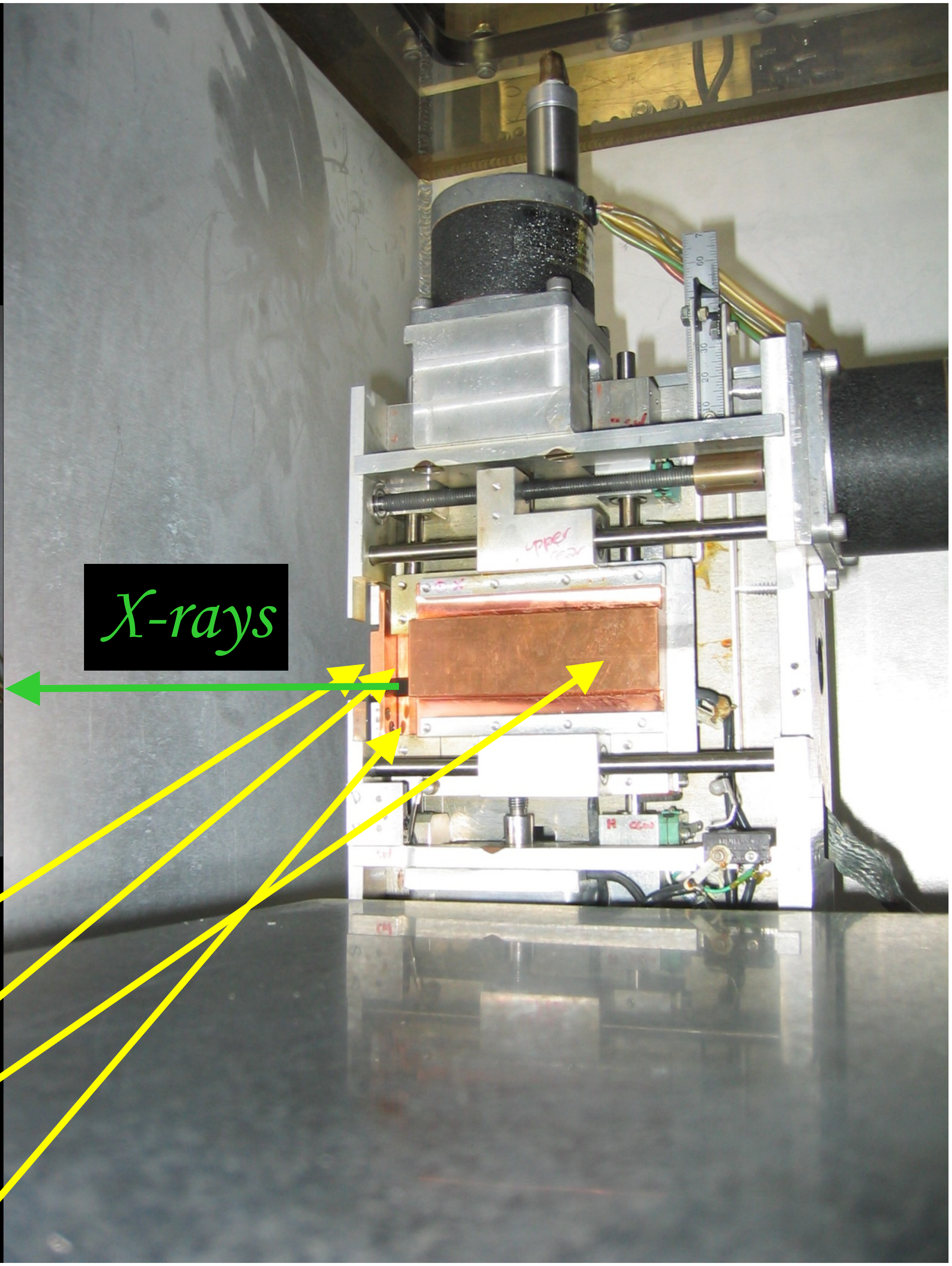
Helium filled drift tank: The 'Coffin'

Beamline 1-4 (early design)

Beamline 1-5

Inside the 'Coffin': Three jaw slit





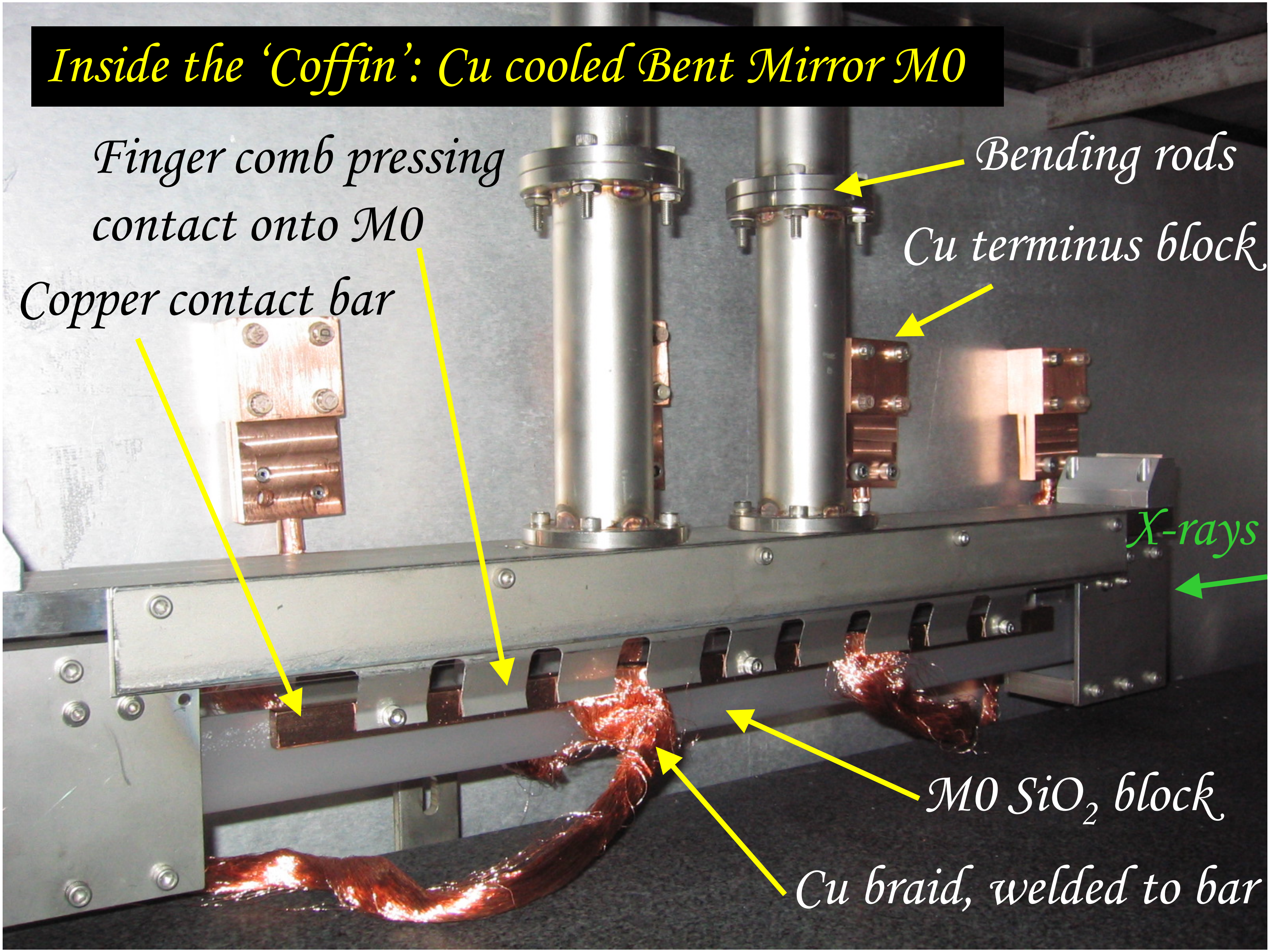
Cu side shielding

Cu Upper slit

Cu Side slit

Cu Lower slit

Inside the 'Coffin': Cu cooled Bent Mirror M0



Finger comb pressing contact onto M0

Copper contact bar

Bending rods

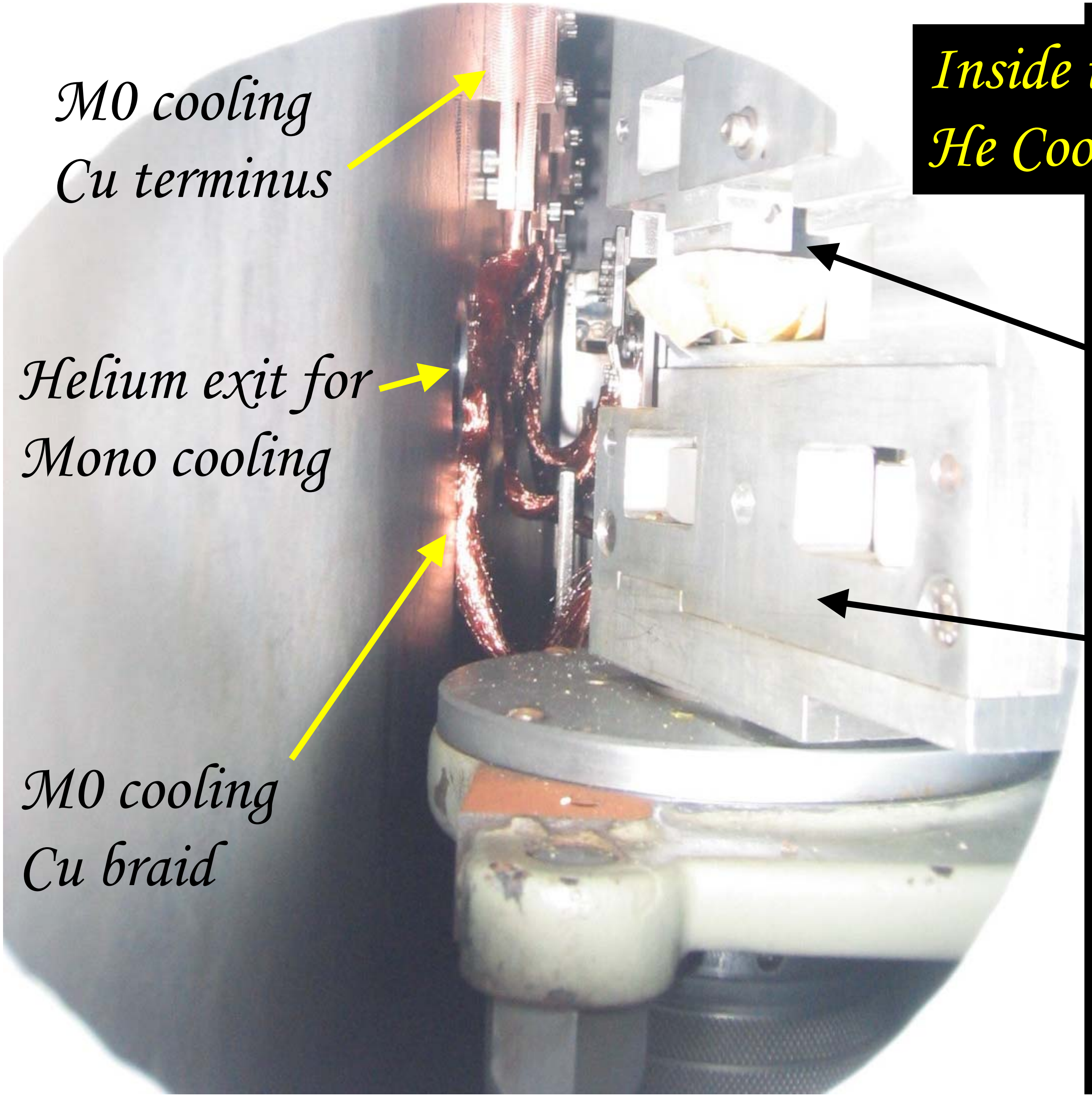
Cu terminus block

X-rays

M0 SiO_2 block

Cu braid, welded to bar

Inside the 'Coffin': He Cooled Si Mono



M0 cooling Cu terminus

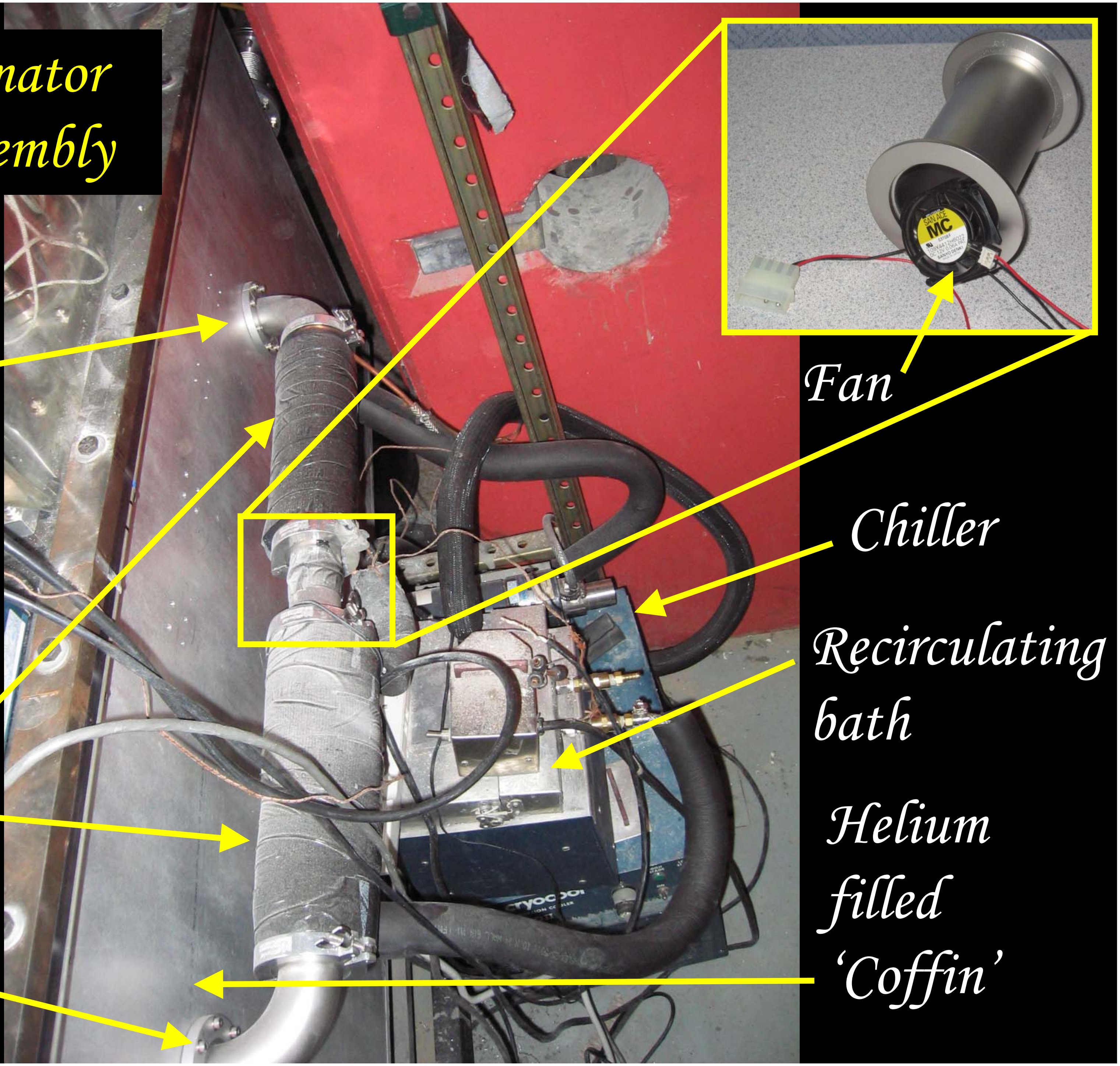
Helium exit for Mono cooling

M0 cooling Cu braid

Si [111] crystal

1-4 mono assembly

Monochromator cooling assembly



He Outlet onto mono

Cu coils around He drift tubes

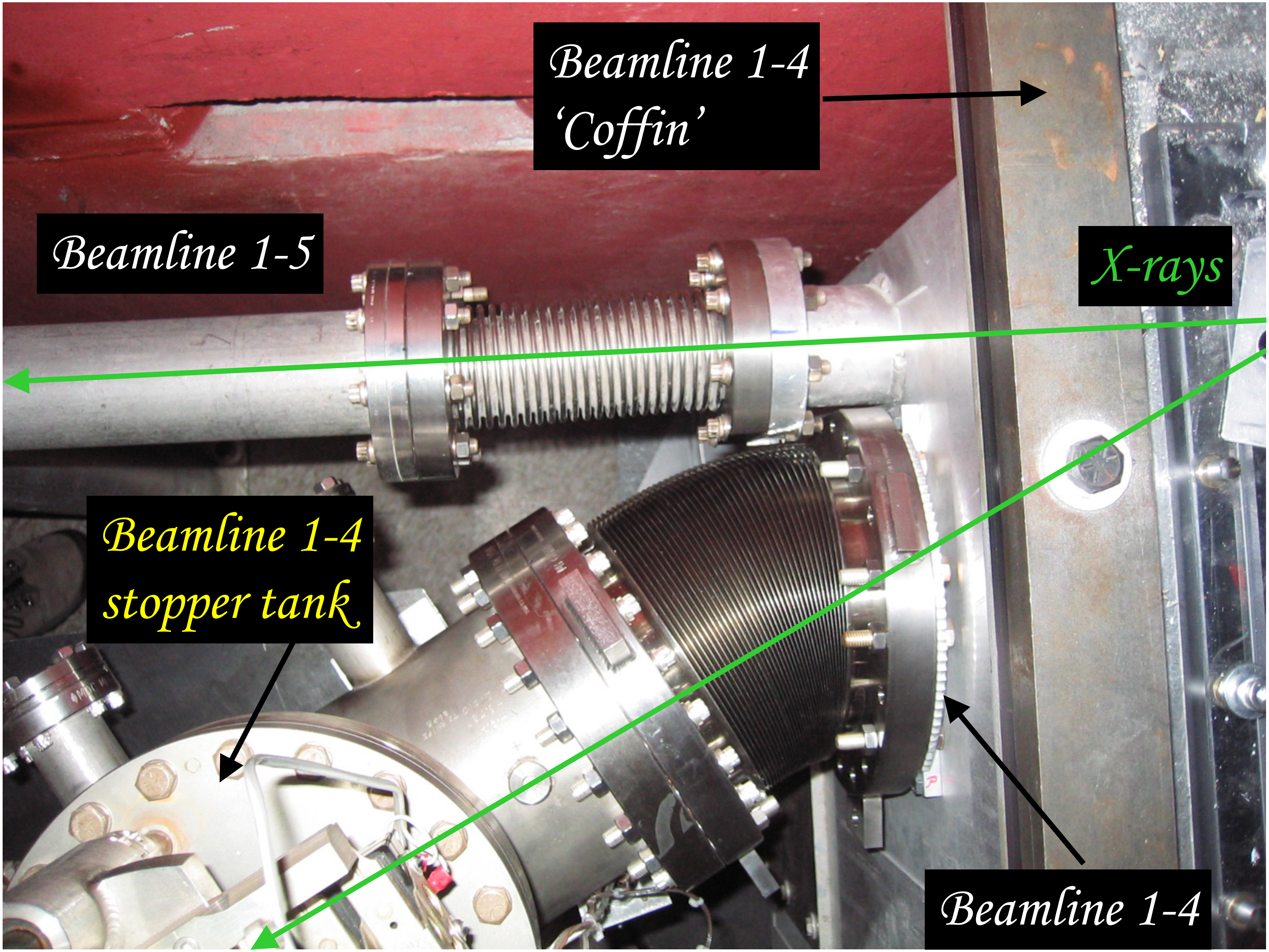
Intake

Fan

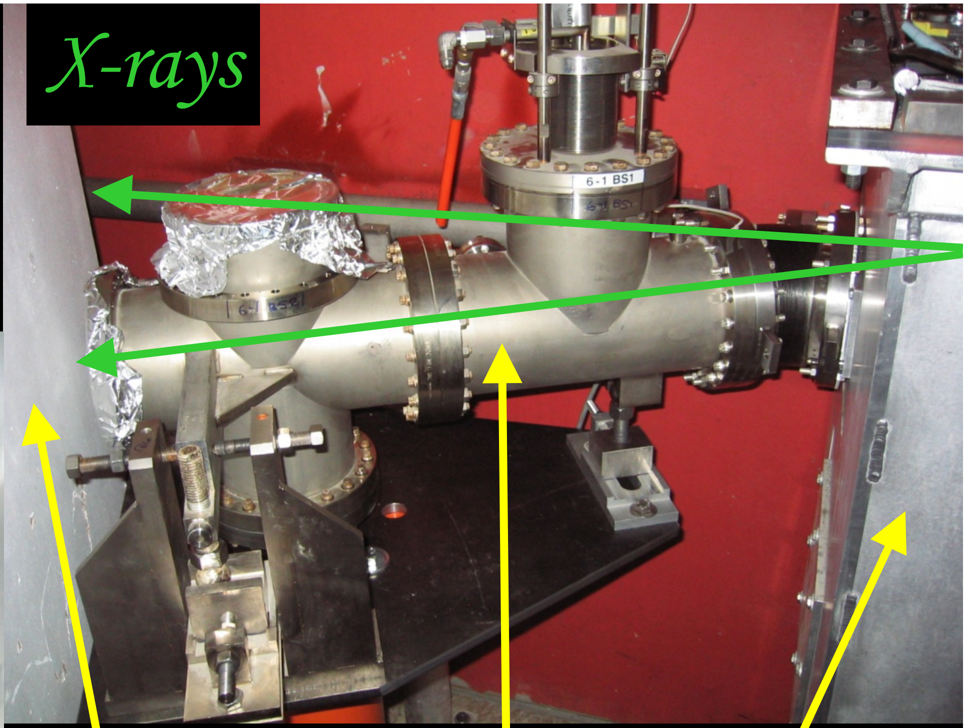
Chiller

Recirculating bath

Helium filled 'Coffin'


Beamline 1-4
'Coffin'
Beamline 1-5
X-rays
Beamline 1-4
stopper tank
Beamline 1-4

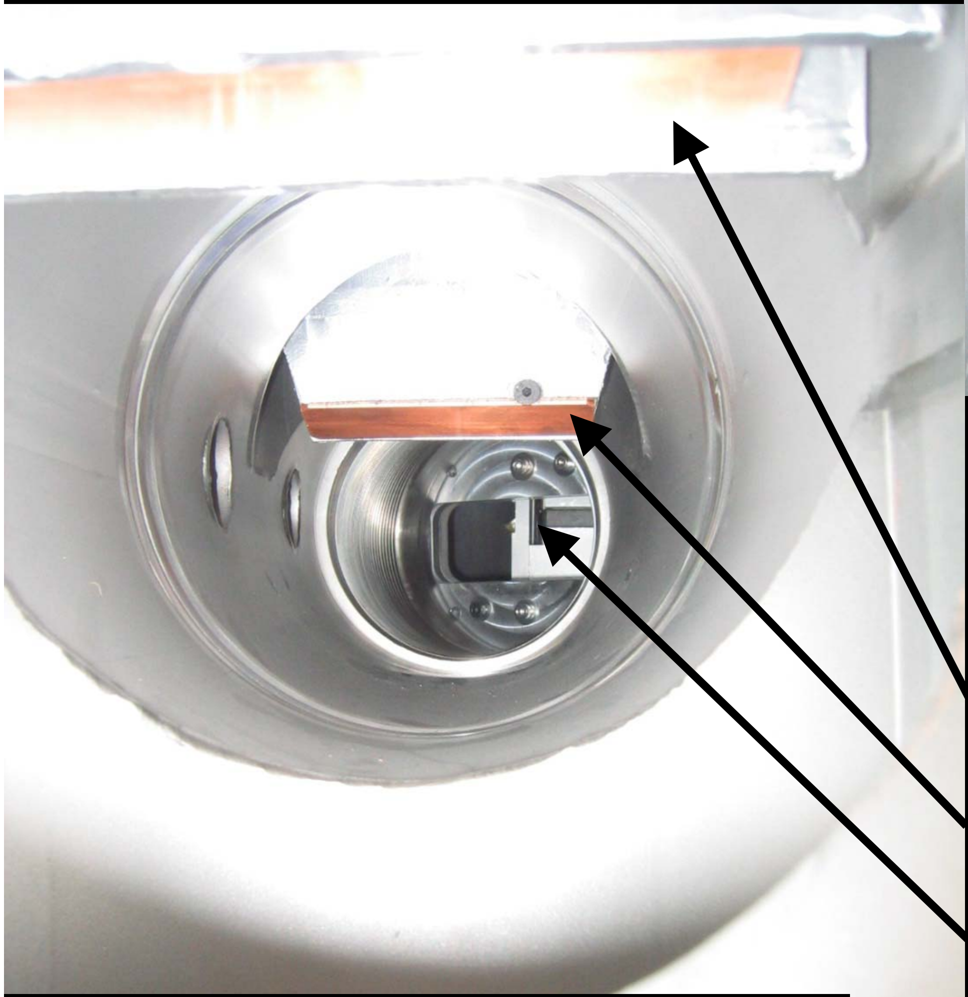
Beamline 1-4 stoppers



Experimental Hutch

Stopper Tank

'Coffin'



Inside 1-4 stopper tank

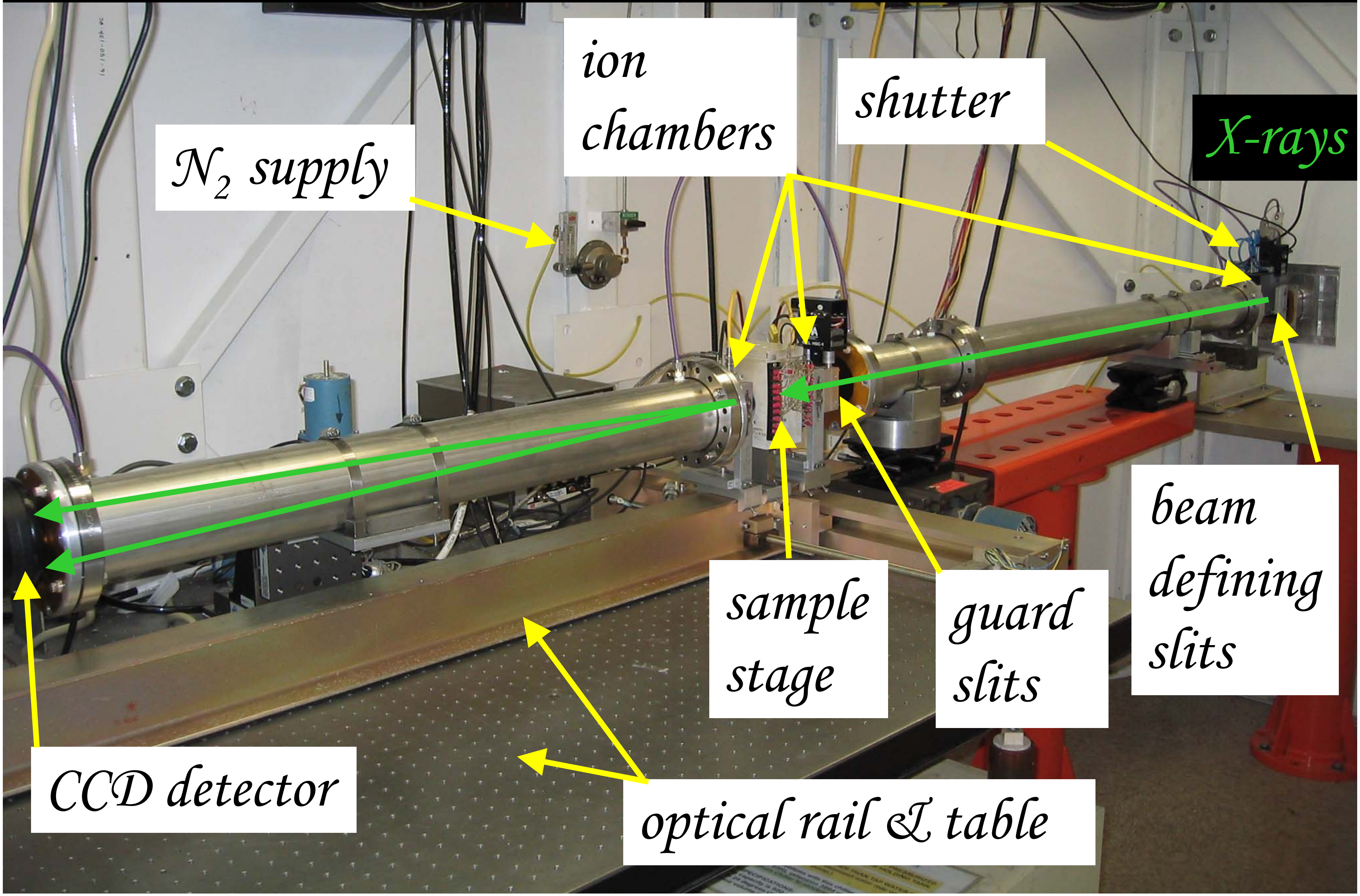
stopper 2

stopper 1

Mono crystal

Each stopper 1.25" Cu + 2 x 3/16" Pb

SSRL Beamline 1-4: SAXS Materials Science



X-rays

ion chambers

shutter

N_2 supply

beam defining slits

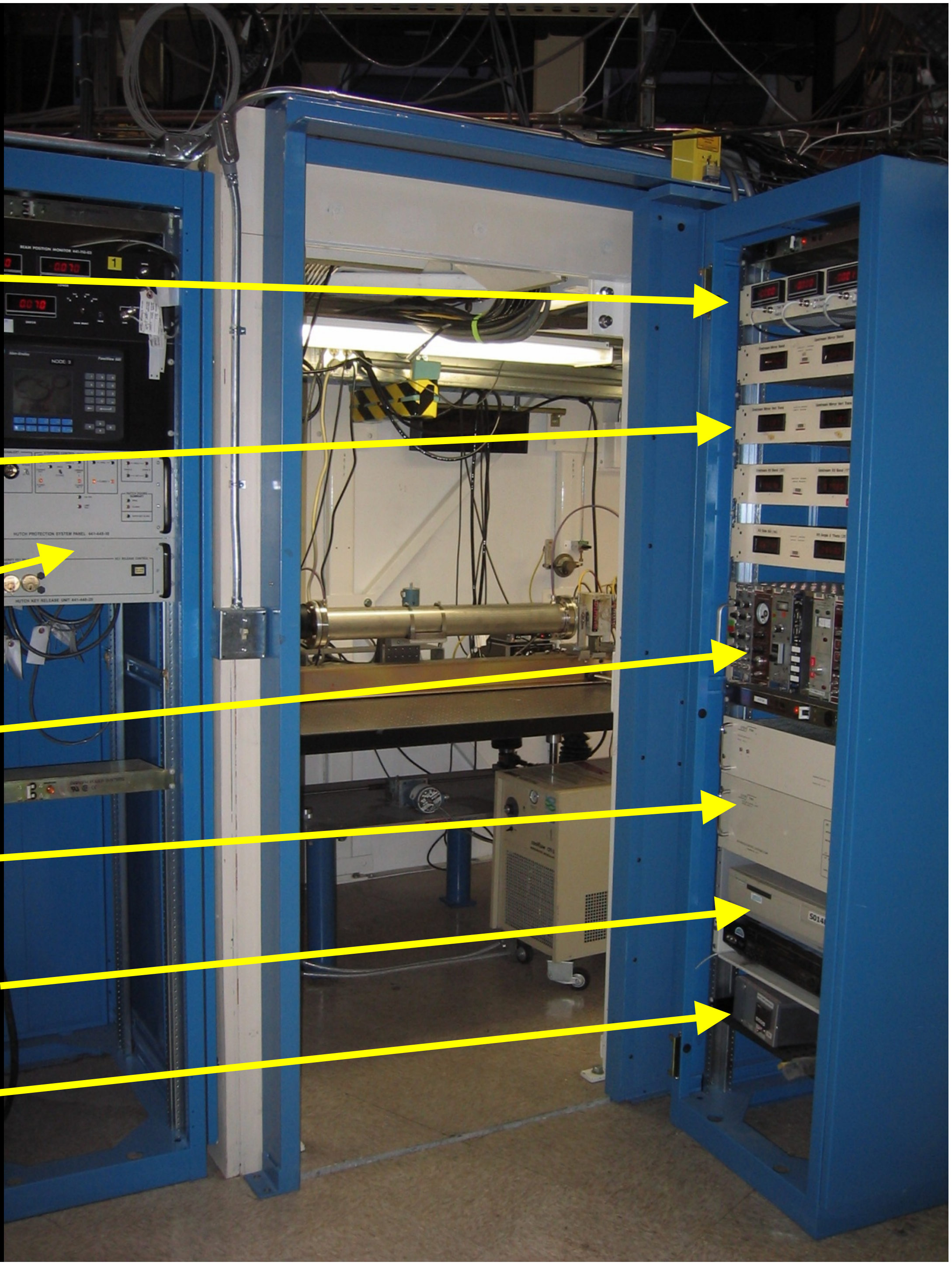
sample stage

guard slits

CCD detector

optical rail & table

Experimental Hutch



Ion chamber readout

Motor position encoders

Hutch stopper control

Electronics control chassis

Motor control chassis

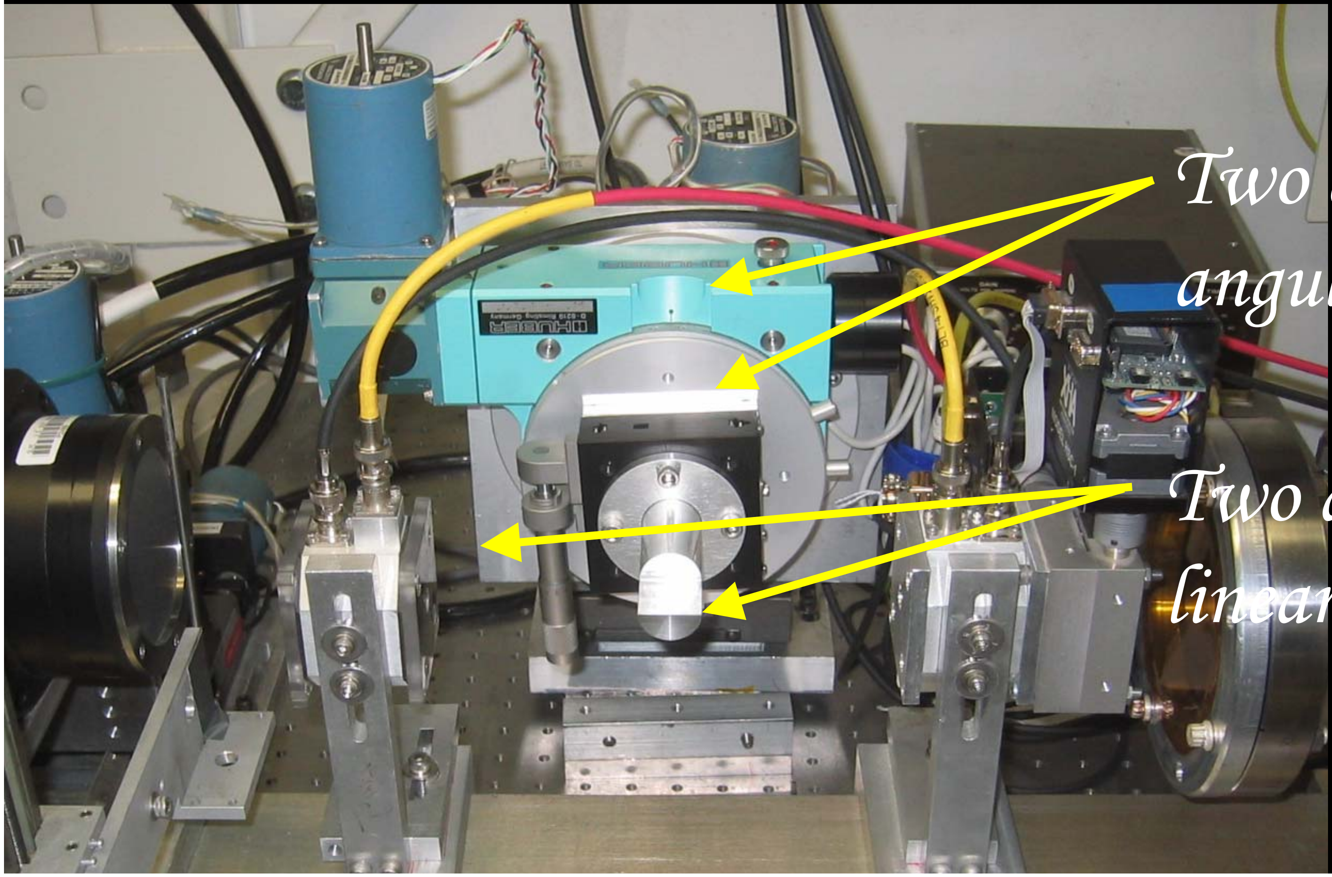
Beamline control computer

Sample temperature control

Sample Environments: Goniometer

Used for Reflection X-ray geometries

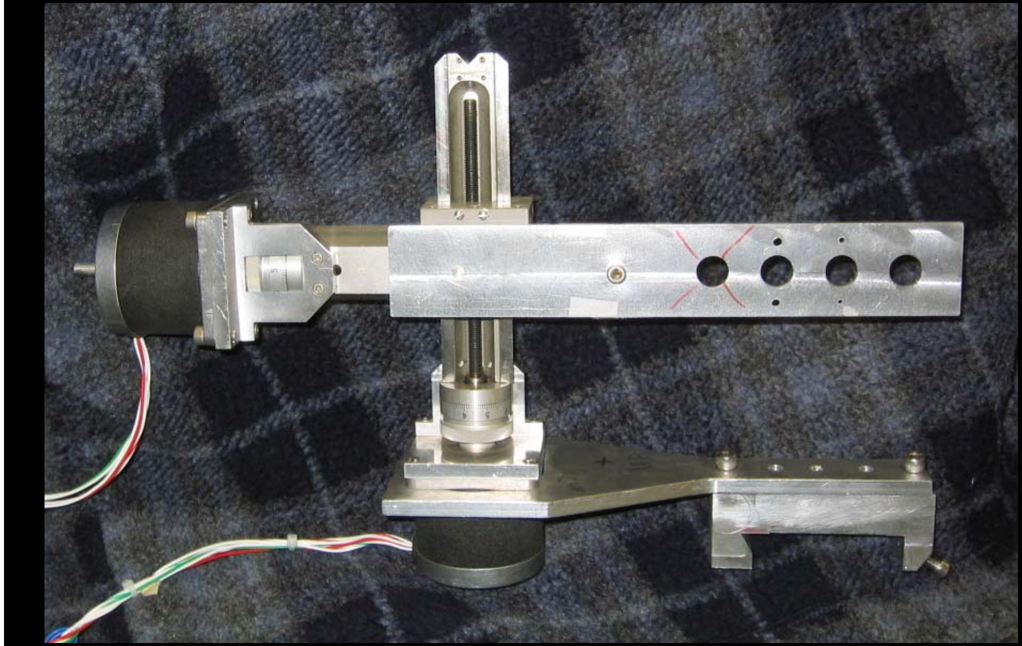
Huber 410 Goniometer



Two axes
angular translation

Two axes
linear translation

Sample Environments: X-Y drivable flat mount



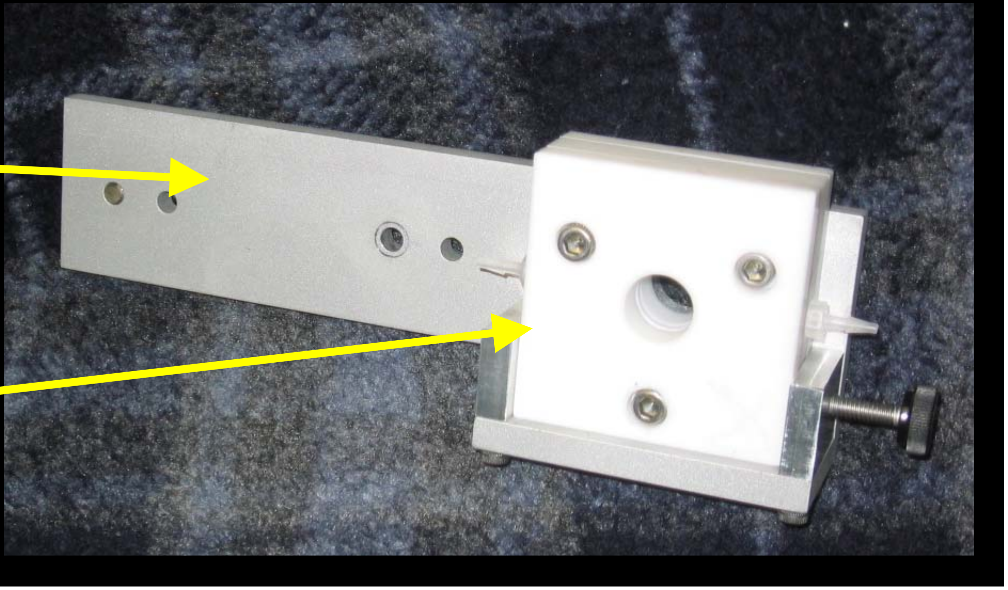
Four sample positions

x and y drives ± 2.25μm

x and y throw ~ 100mm

Adaptor to hold fluid cells

Fluid cell with flow feeds



Sample Environments: Oven

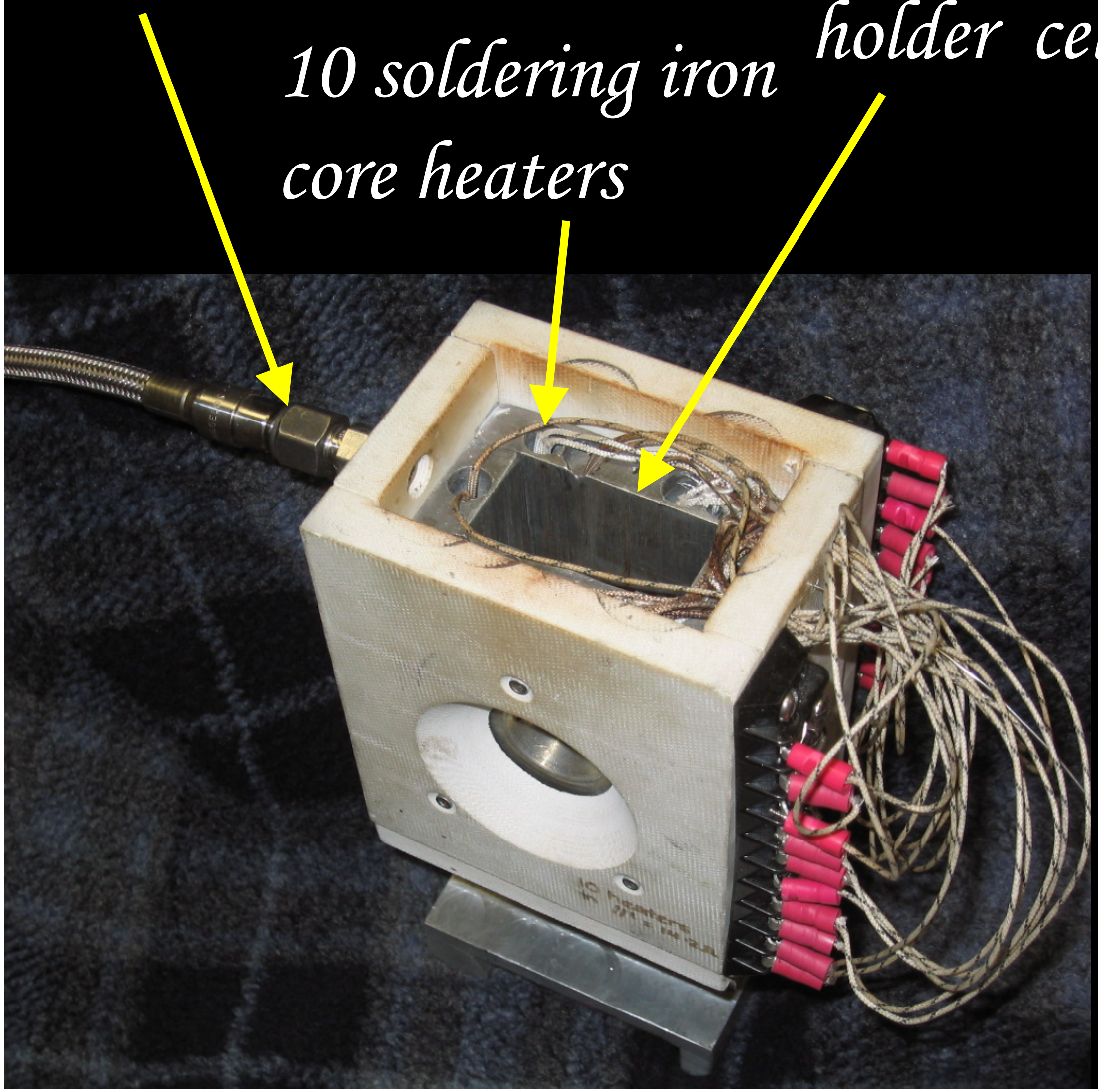
Temp T: 25°C < T < 450°C

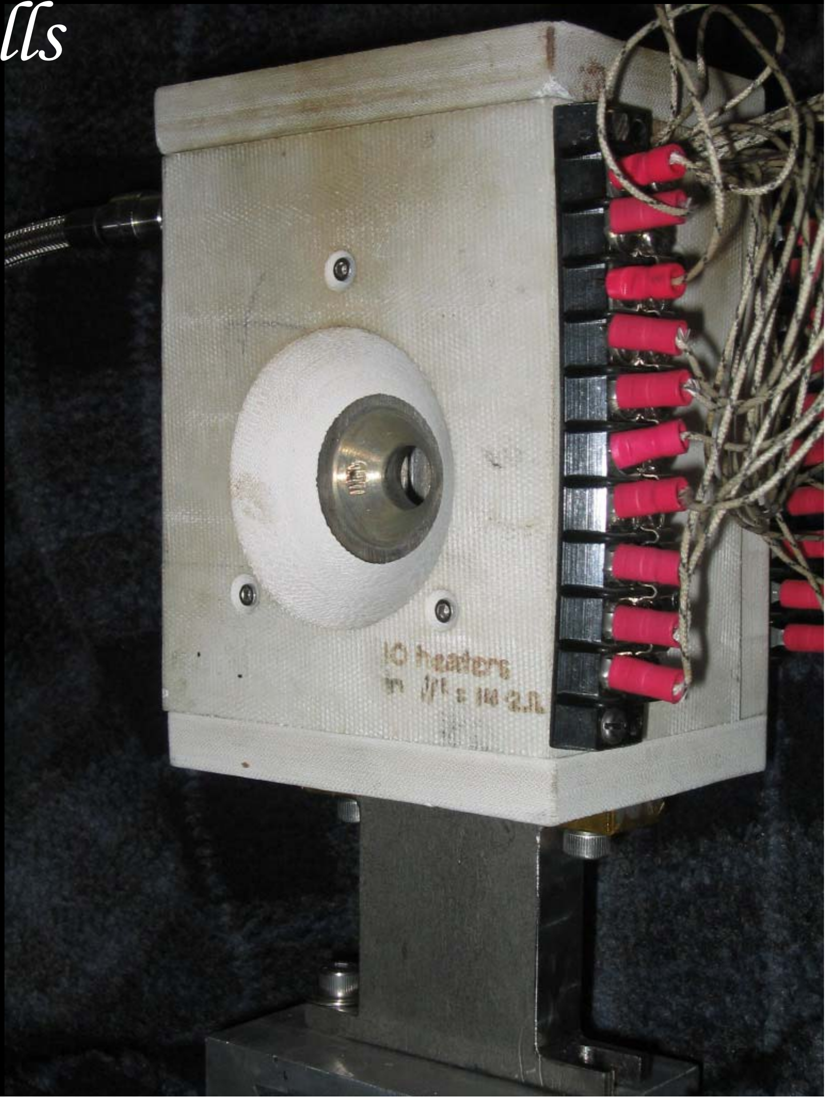
stability ±2°C

Feed for inert gas

10 soldering iron core heaters

Fit for fluid holder cells





Sample Environments: Oven

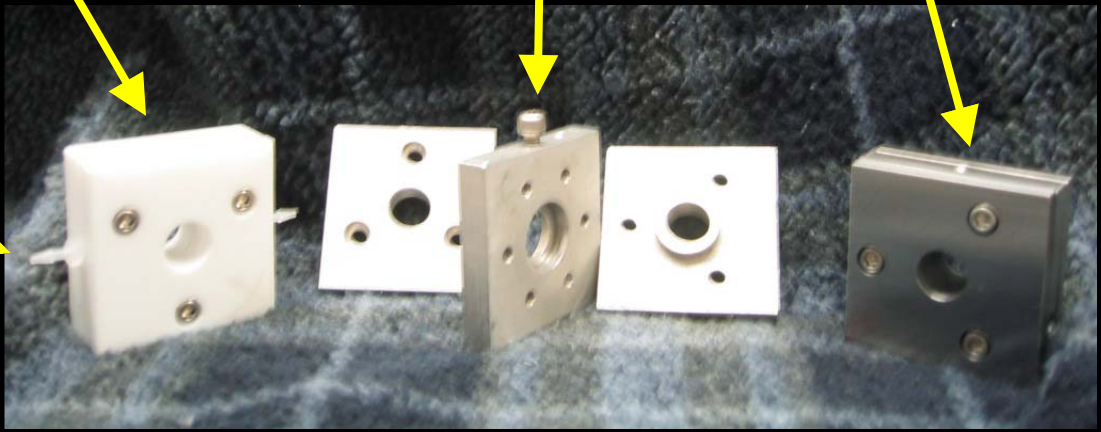
Fluid holder cells: assemble as three parts with windows

Sample volume ~ 2.5 cc

Optical path length = 1 mm

Material: 5 each of

Polytetrafluoroethylene (Teflon); Aluminum & Steel



Teflon cells have flow couplings for in-situ titration

Sample Environments: Tensiometer

Extension rate E:

$0.001\ \mathrm{mm\ s^{-1}} < E < 25\ \mathrm{mm\ s^{-1}}$

Drive motor

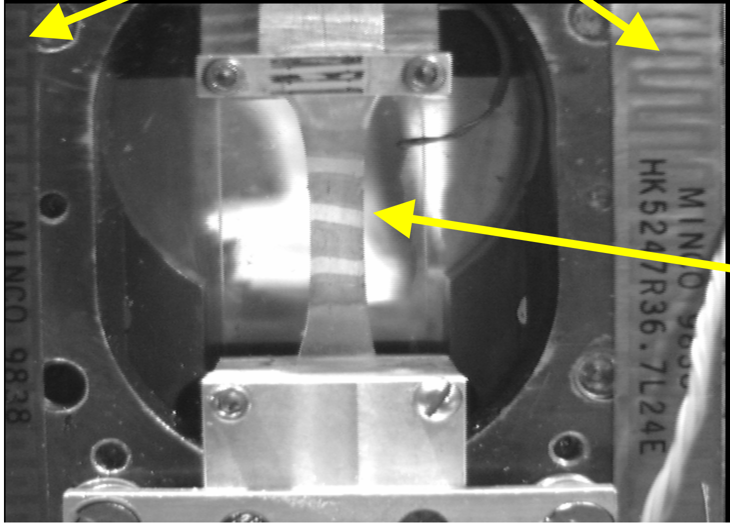
Oven Temp T: $25^\circ\mathrm{C} < T < 100^\circ\mathrm{C}$

Temp stability ±2°C

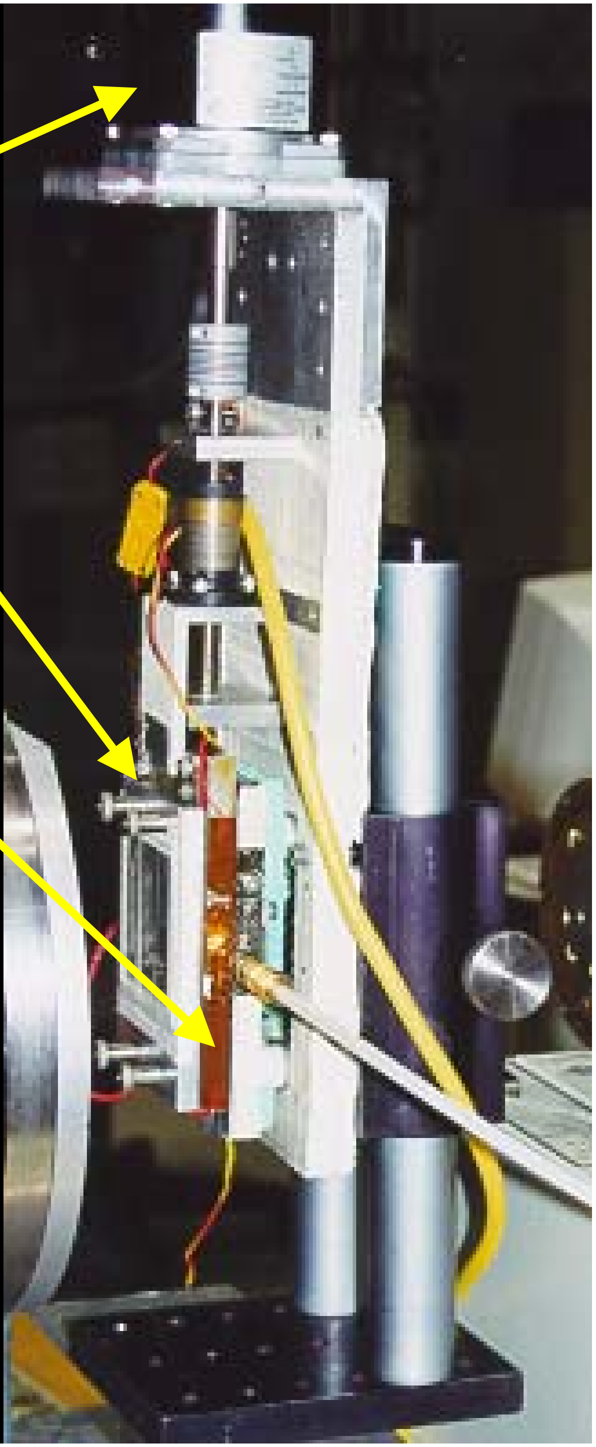
Oven

External heater tape

Internal heater tapes



Elastomeric Polypropylene sample at 300% extension

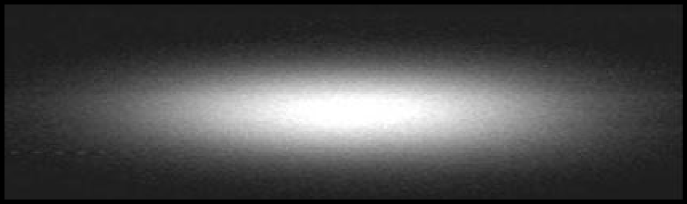


Principal Parameters for Scattering Experiments

q_{min}: 0.03 nm^{-1} (c.f. pre 2004 $q_{min} = 0.07\ nm^{-1}$)

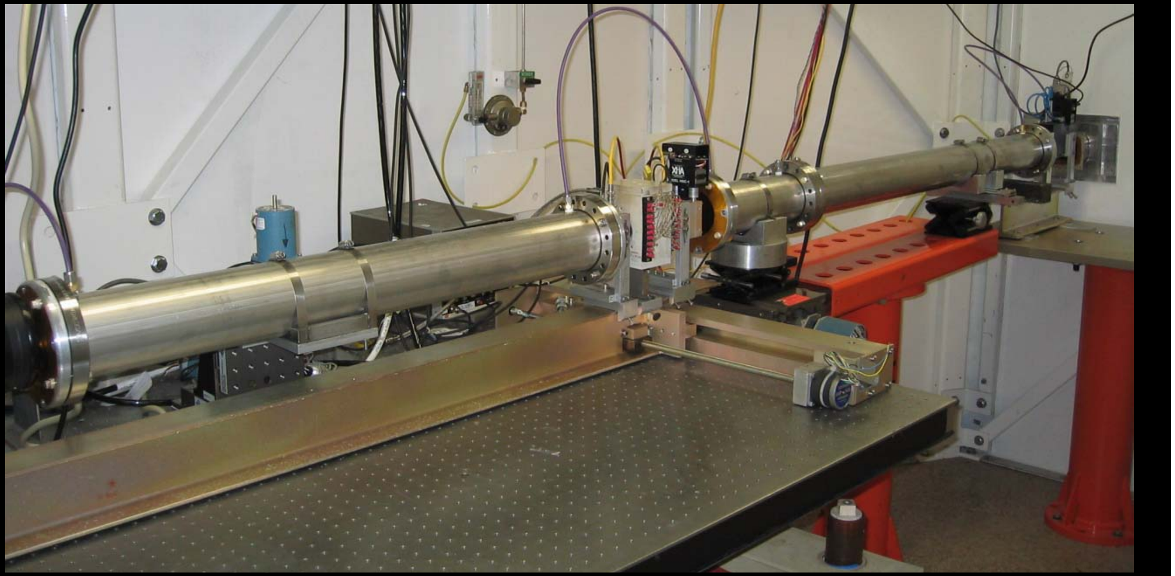
Can observe features d_{max} ~200 nm (c.f. pre-2004 $d_{max} = 90$ nm)

Focused Flux $\Phi \sim 1 \times 10^{10}\ h\nu\ s^{-1}\ mA^{-1}$



pre 2004 source size

Current source size



Source size = 18 nm/rad

(c.f. pre 2004 = 130 nm/rad)

Sample to detector distance

D = 3 m (c.f. pre 2004 D = 1.2m)