STANFORD SYNCHROTRON RADIATION LABORATORY

SSRL

Small-Angle X-ray Scattering (SAXS) at Stanford Synchrotron Radiation Light-Source

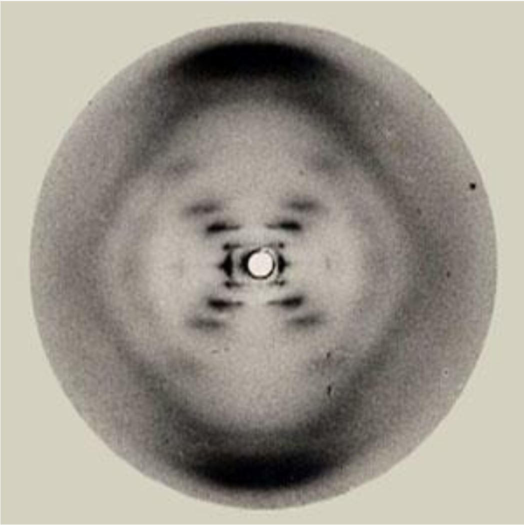
John A Pople

Stanford Synchrotron Radiation Light-Source,

SLAC National Accelerator Laboratory, Menlo Park, CA 94025

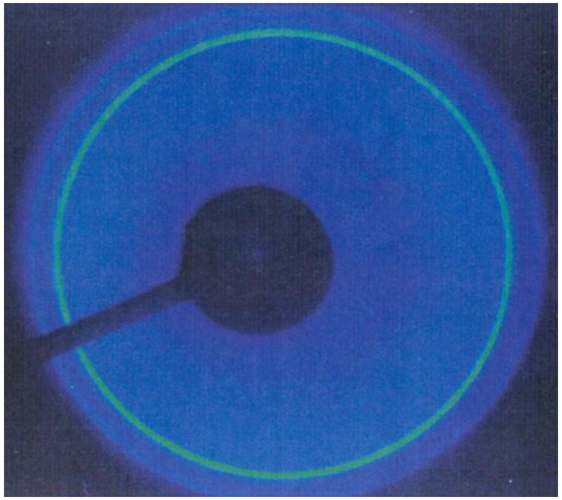
When should I use the Scattering Technique?

Ideal Studies for Scattering

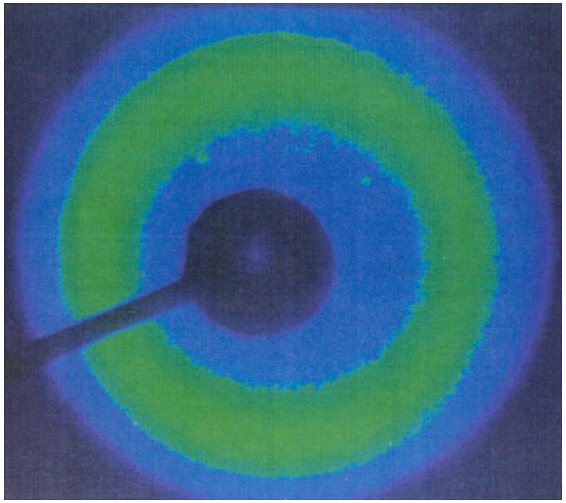


Scattering good for:

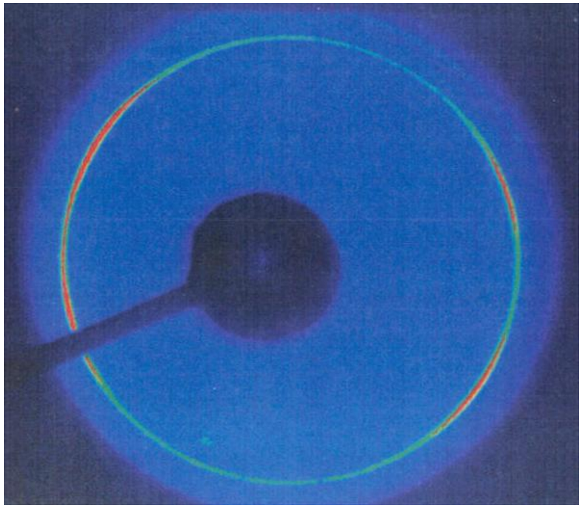
- Global parameters, distributions; 1st order
- Different sample states
- In-situ transitional studies
- Non destructive sample preparation



Solid

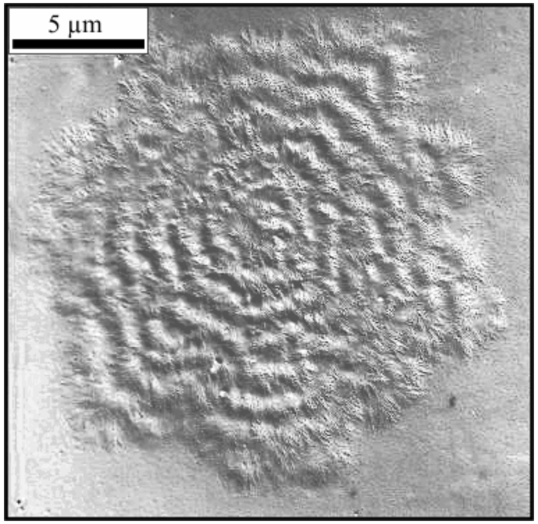


Melted & Sheared



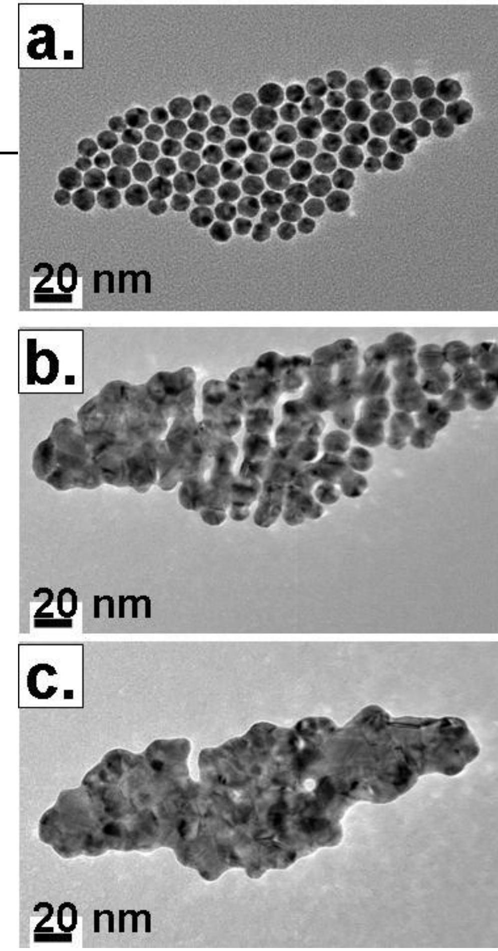
Recrystallized

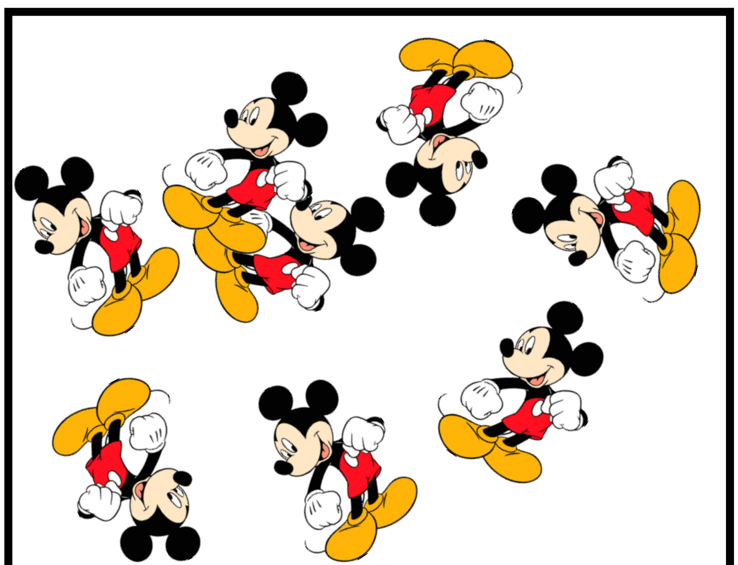
Ideal Studies for Microscopy



Microscopy good for:

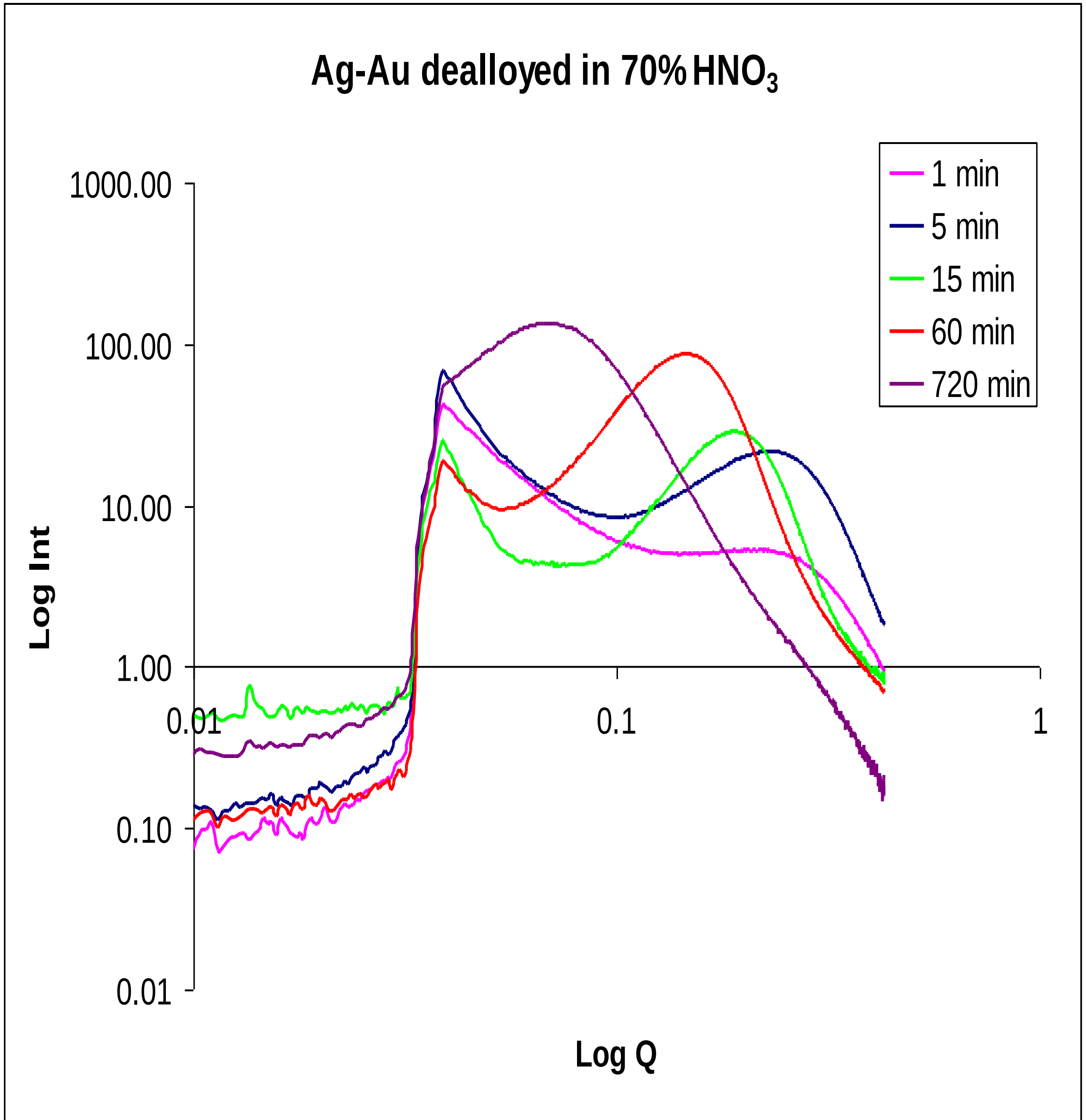
- Local detail
- Surface detail
- Faithfully represents local complexities

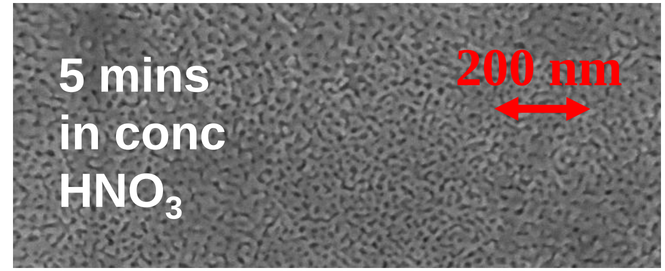


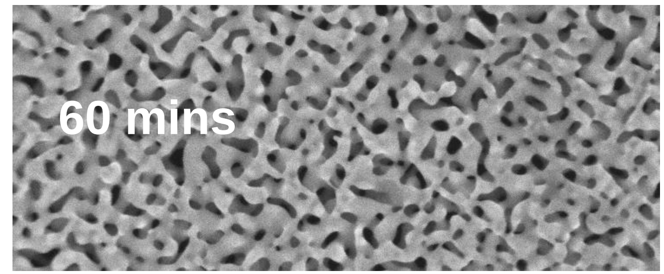


E.g. if the objective is to monitor the degree to which Mickey's nose(s) and ears hold to a circular micromorphology… use microscopy not scattering

Complementary Scattering and Microscopy

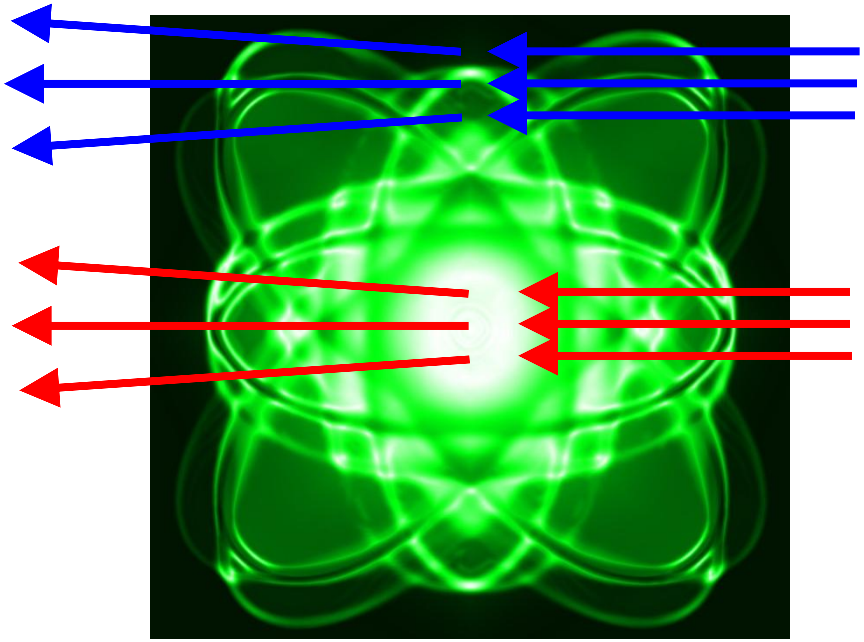






Forming a bi-continuous porous network with ligament width on the nanoscale by removing the less noble element from a binary alloy, in this case Ag-Au

Scattering: Neutrons or Photons?



X-rays

Sensitive to electron density contrast

Neutrons

Sensitive to nuclear scattering length contrast

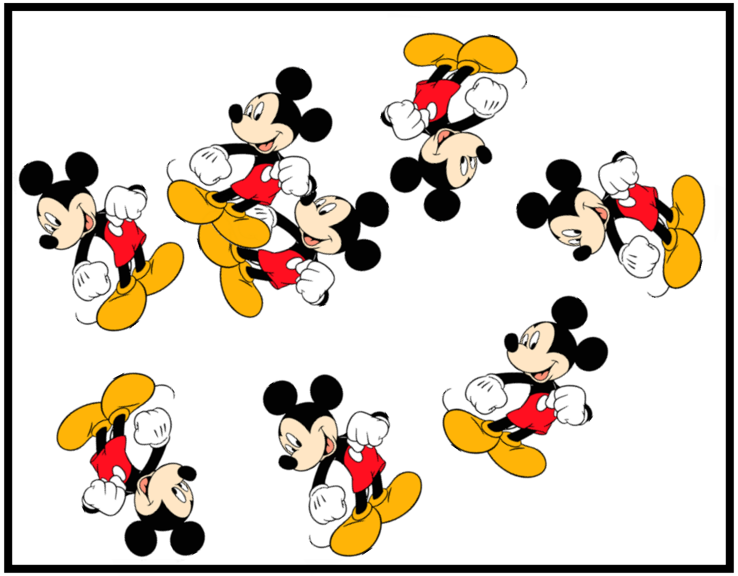
Neutron scattering: Deuteration allows species selection

Advantages of X-ray scattering:

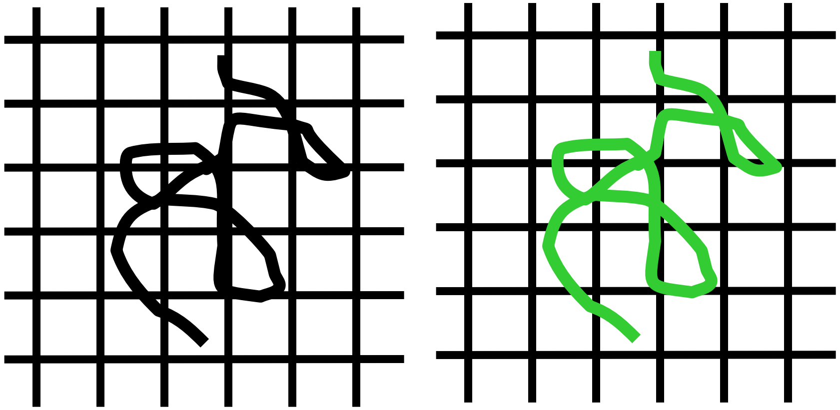
- Relatively small sample quantities required
- Relatively fast data acquisition times - allows time resolved effects to be characterized

Scattering: Neutrons or Photons?

Neutrons: Deuteration allows species selection

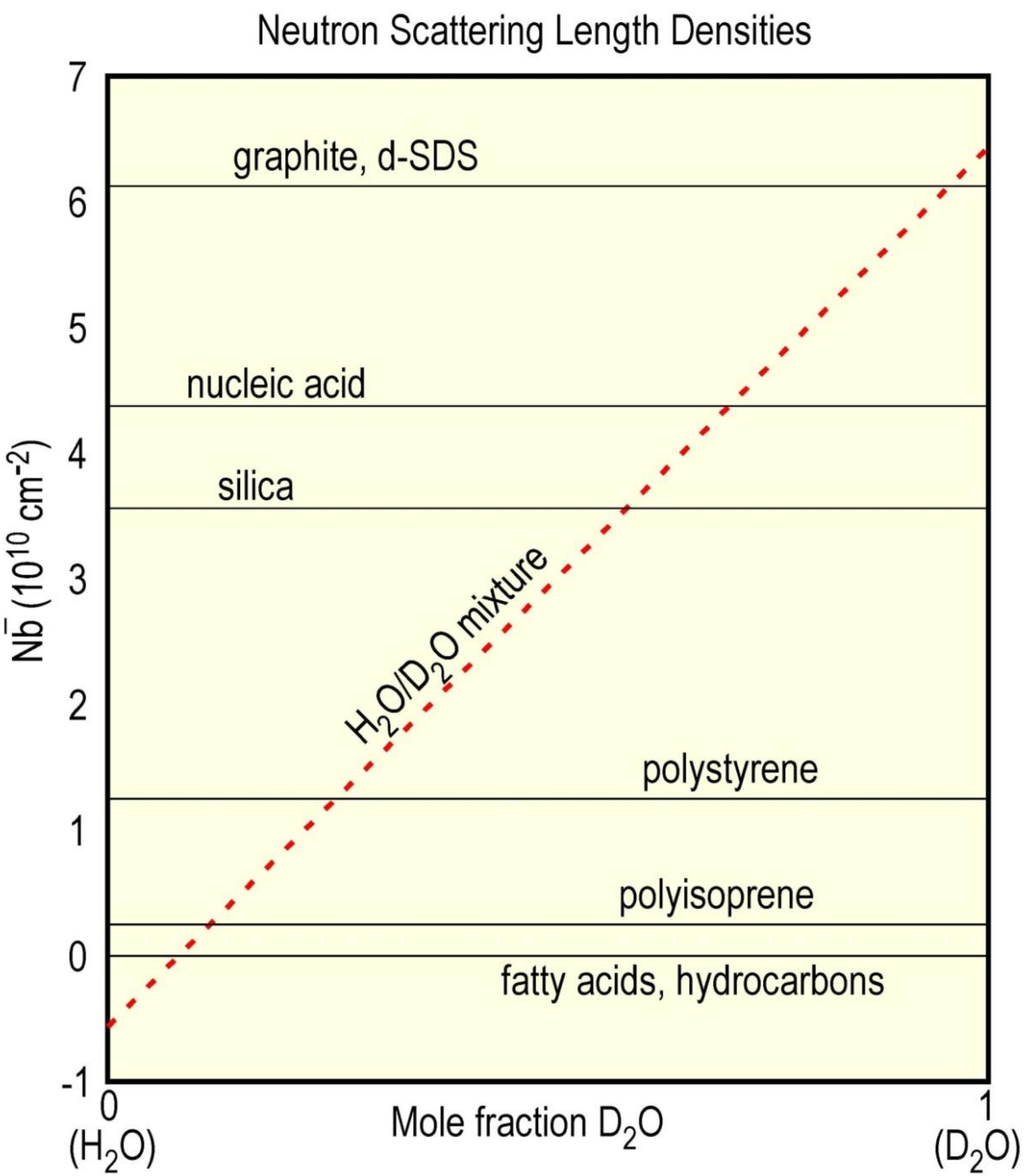


This essentially permits a dramatic alteration to the 'visibility' of the tagged elements in terms of their contribution to the reciprocal space scattering pattern



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

Neutron Scattering: Contrast Matching



Contrast match:

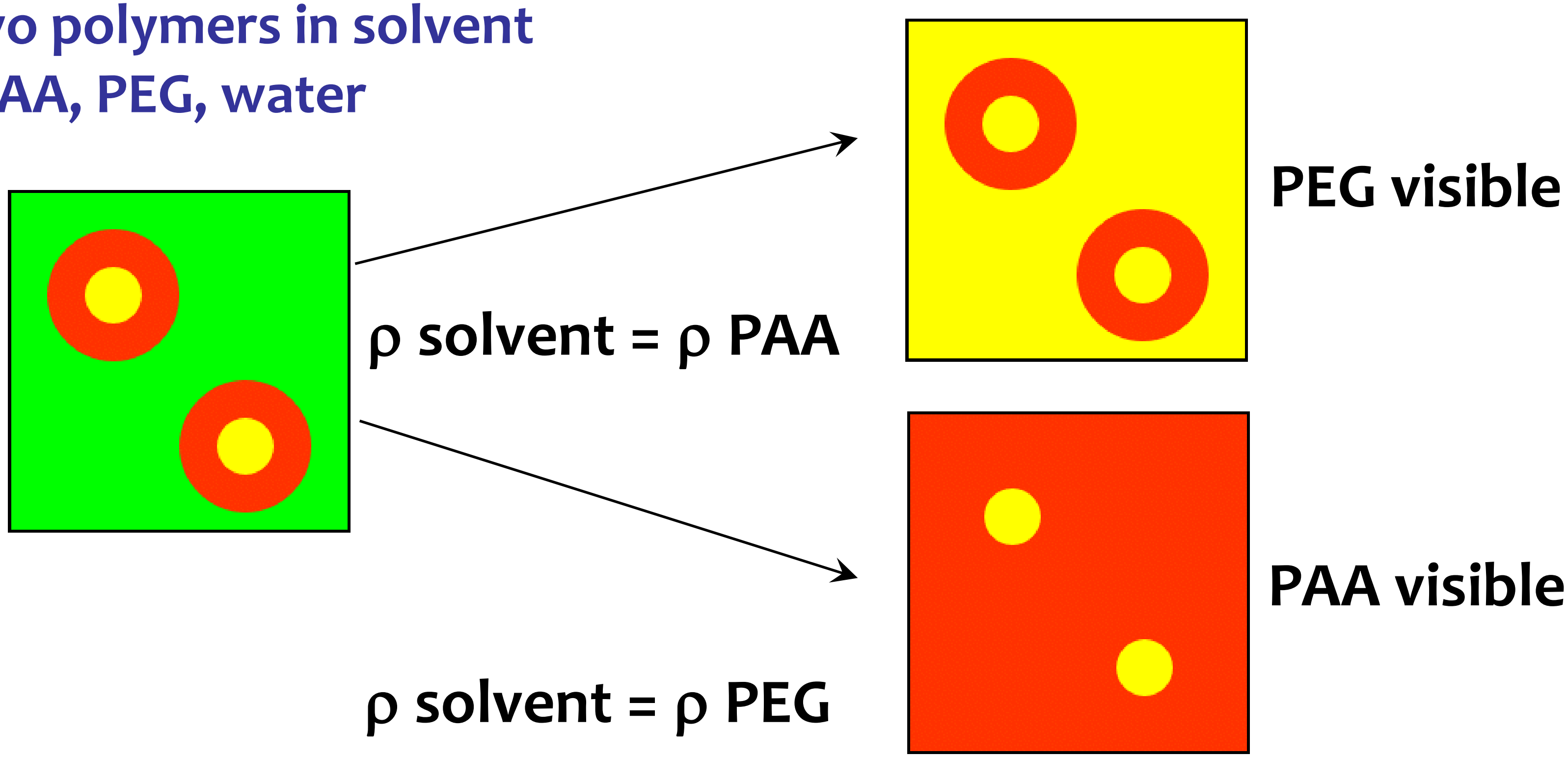
- **Vary H/D ratio to vary scattering strength**
- **can null out one phase (it will not contribute to SANS)**
- **allows different phases to be distinguished**
- **X-rays have similar approach (but not as tunable)**

Scattering: Neutrons or Photons?

Neutrons: Deuteration allows species selection

Two polymers in solvent

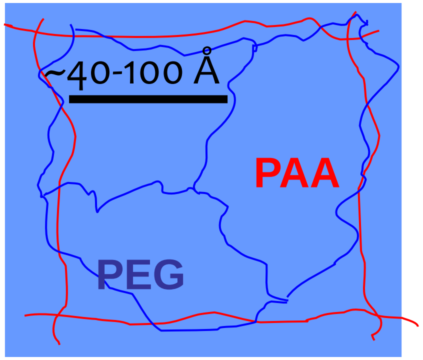
- **PAA, PEG, water**



➢ **Change 3 phase system into 2 simpler 2-phase systems**

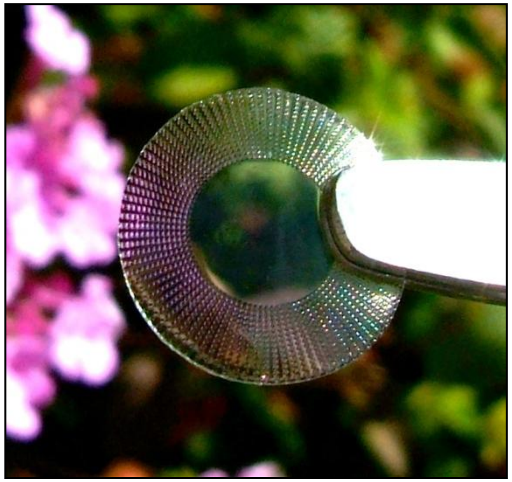
SAXS Characterization of High Strength Interpenetrating Network Hydrogels

Dale Waters, Kristin Engberg, Shira Kelmanovich, Rachel Parke-Houben, Masaki Yanagioka, Curt Frank



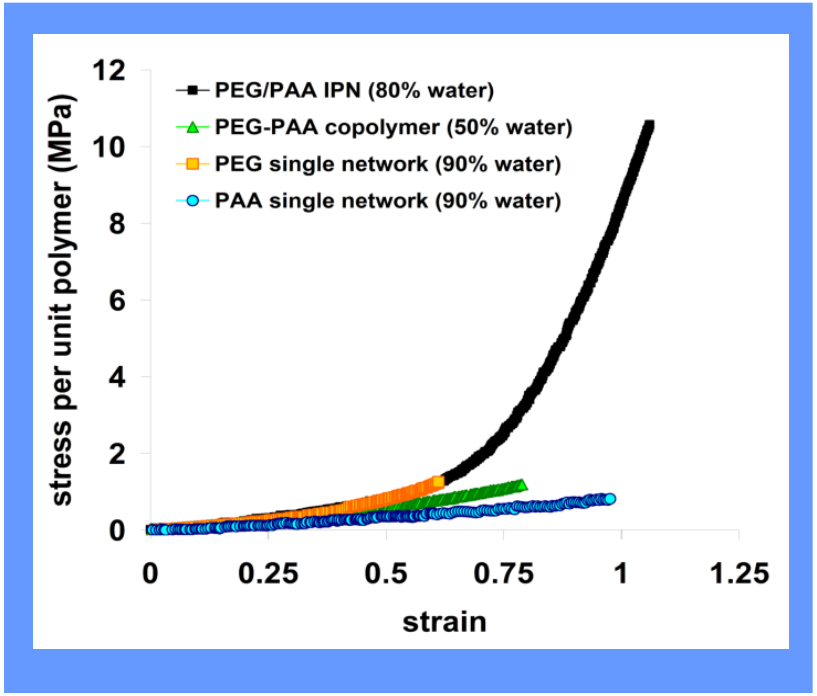
AA monomer is added to polymerized PEG & PAA is polymerized to form an interpenetrating network with the PEG. Result is a viscous gel with much higher elastic modulus and tensile strength than the copolymer PEG-PAA gel. Resulting hydrogel can be employed for medical devices, e.g. artificial cornea or cartilage. Early expts indicate correlation length of interpenetrating gel can be determined at BL 1-4

Goal: To understand structure of hydrogel and perform *in-situ* tensile testing to characterize structure as a function of tensile properties.

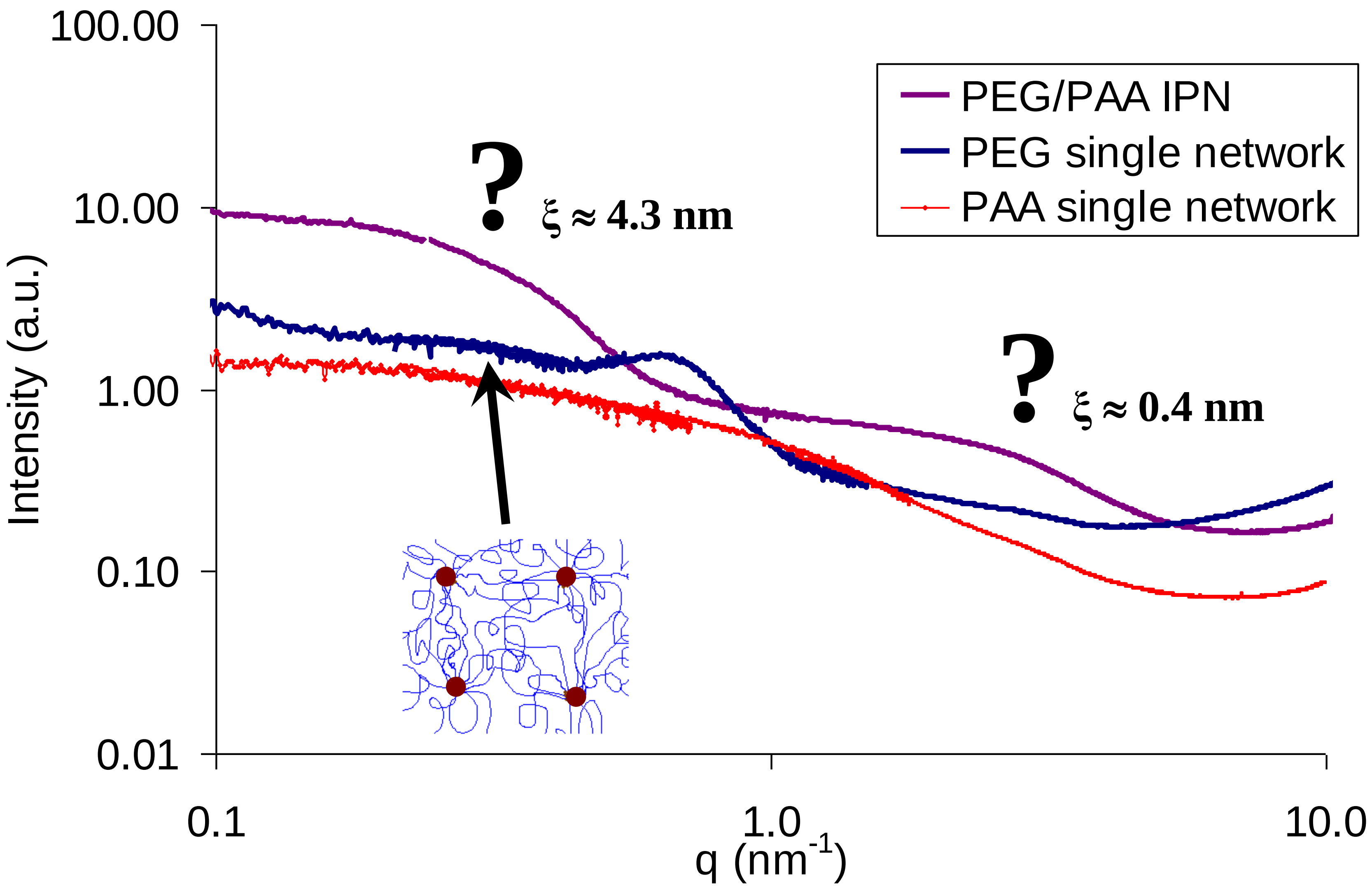


Artificial Cornea

- Core consisting of PEG/PAA with a photo-lithographically patterned skirt.
- Porous skirt designed to allow cell integration into the device

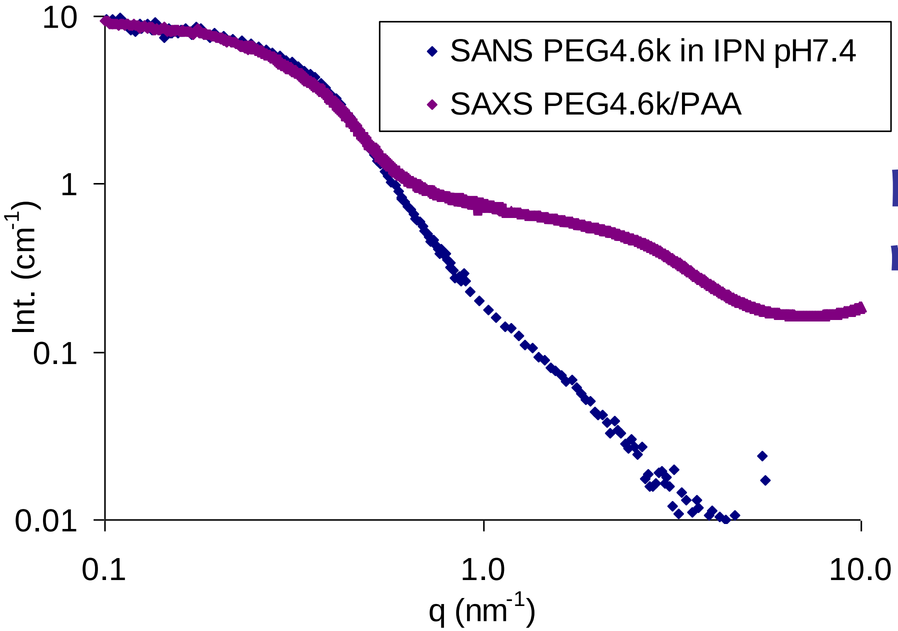


SAXS Data from Network and Components



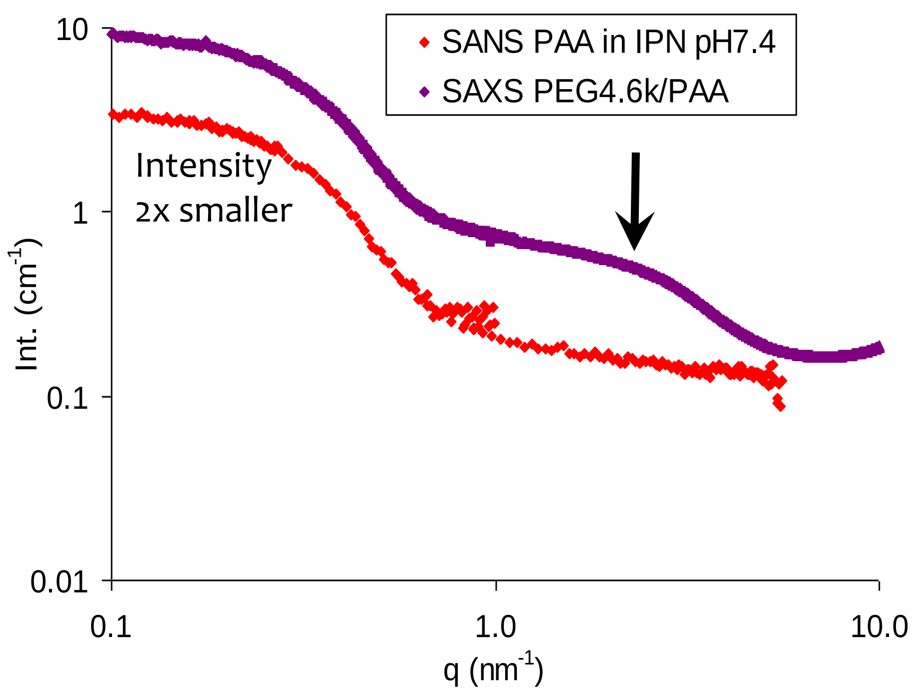
Complementary SAXS / SANS data

Match out PAA



low-q broad shoulder (ξ~ 4 nm) largely due to PEG

Match out PEG



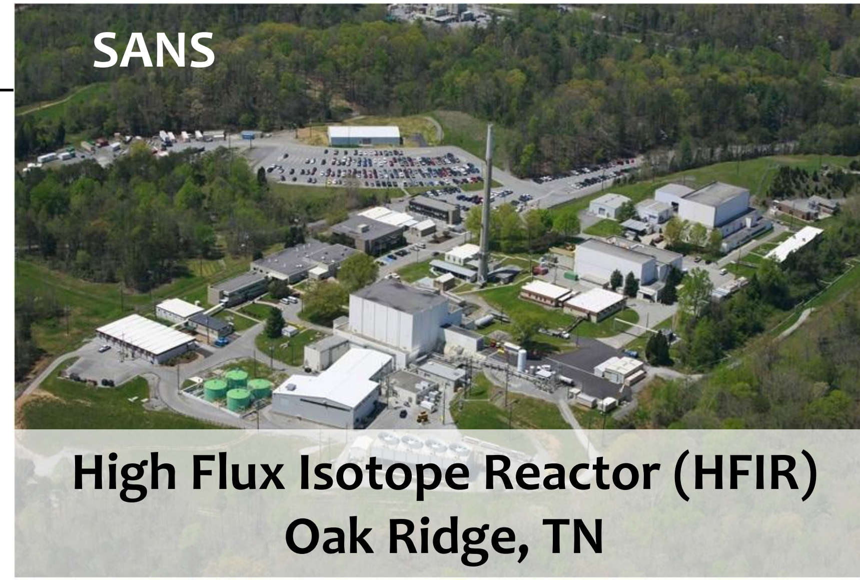
Yet hi-q peak not readily explained by PAA-PAA interactions; could be a solution peak (~4 A)

SAXS / SANS Proposals

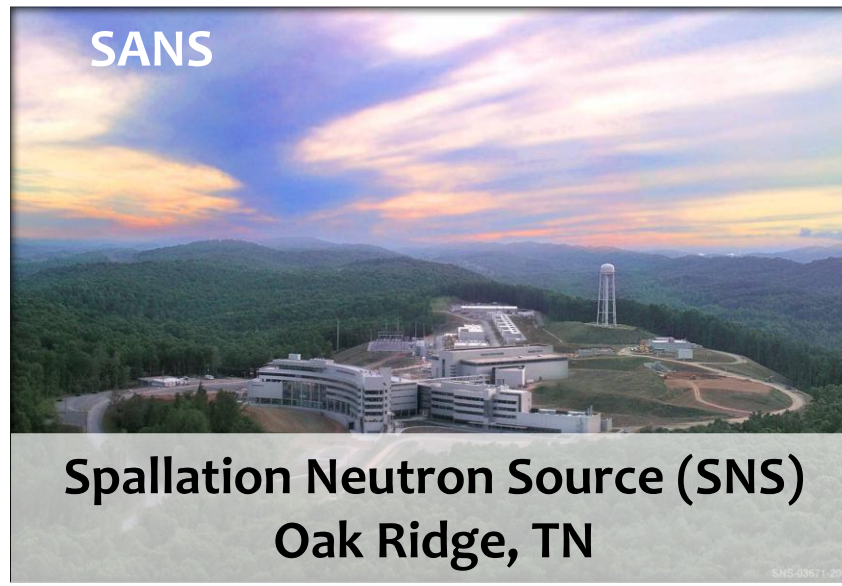
A move to encourage and enable more complementary SAXS/SANS experiments

Stanford Synchrotron Radiation Lightsource (SSRL), Stanford, CA

May 2012: Pilot scheme agreed where an accepted proposal (typically of two year duration) at one facility would enable beam-time requests at all facilities



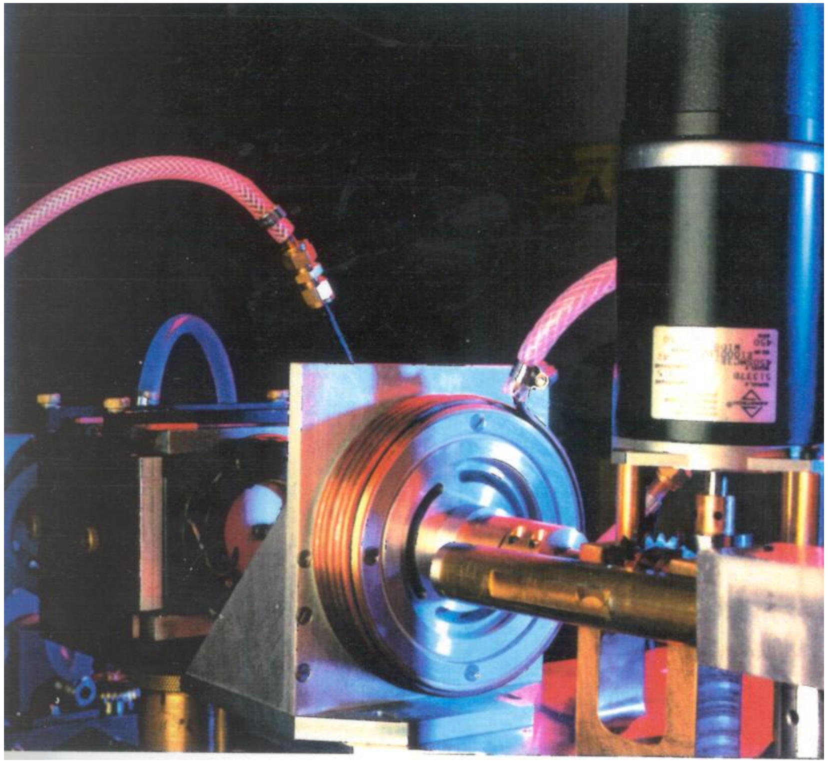
High Flux Isotope Reactor (HFIR)
Oak Ridge, TN

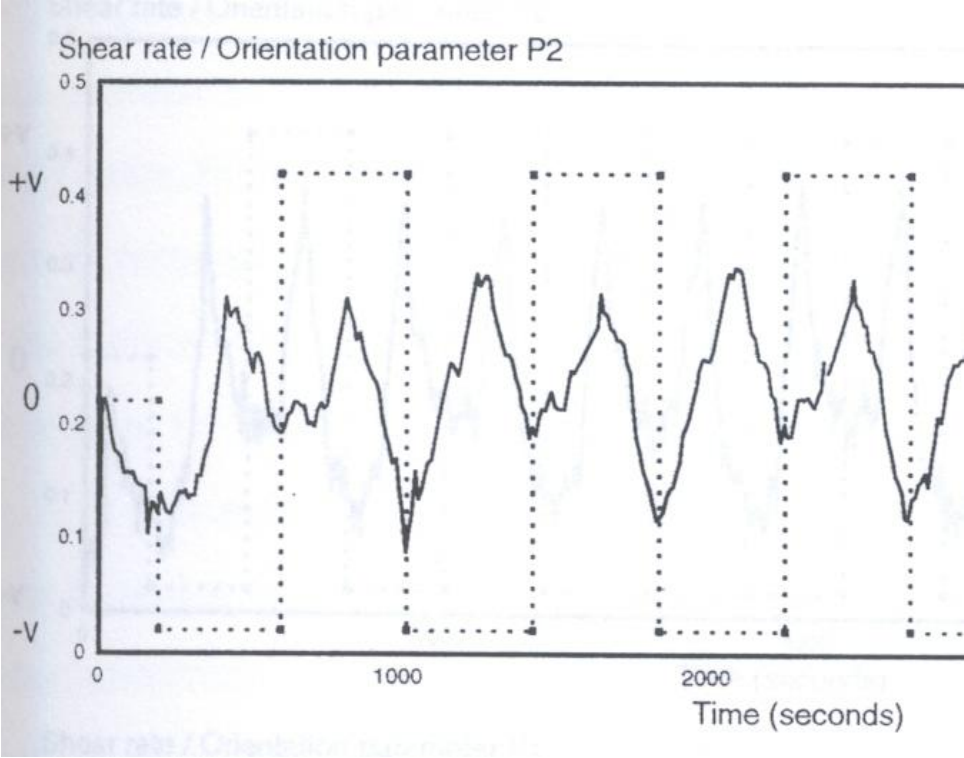


Spallation Neutron Source (SNS)
Oak Ridge, TN

Scattering: Neutrons or Photons?

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



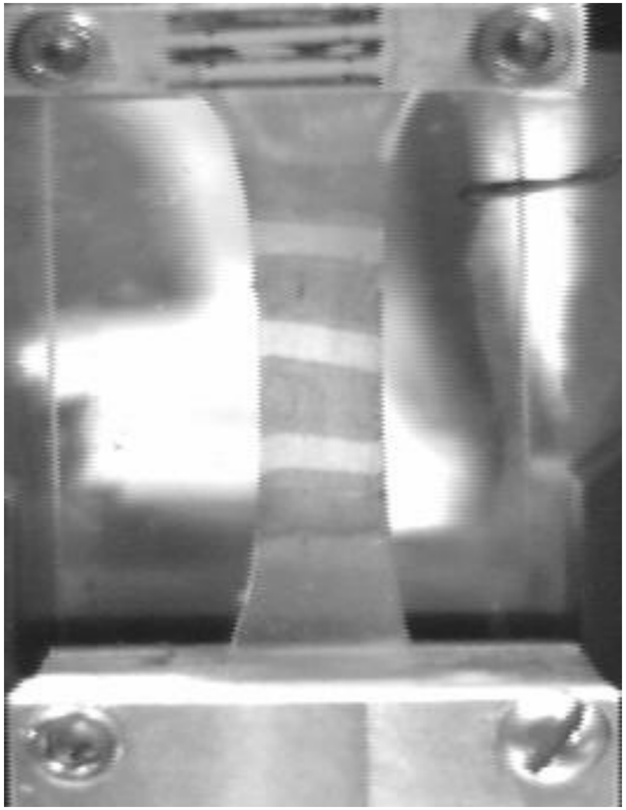


Oscillatory Shearing of lyotropic HPC – a liquid crystal polymer

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



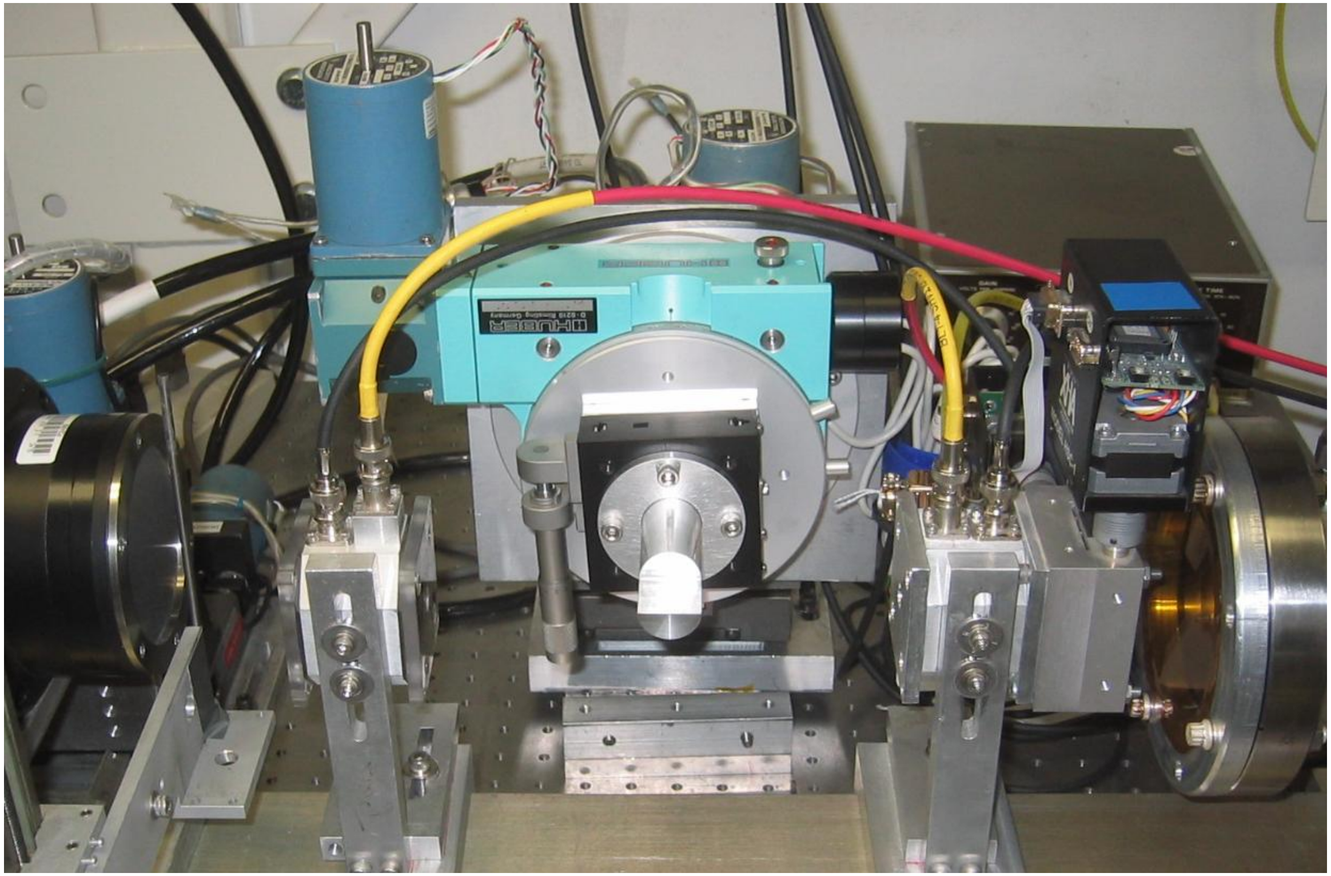
Transmission geometry appropriate for:

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

X-ray Scattering: Transmission or Reflection?

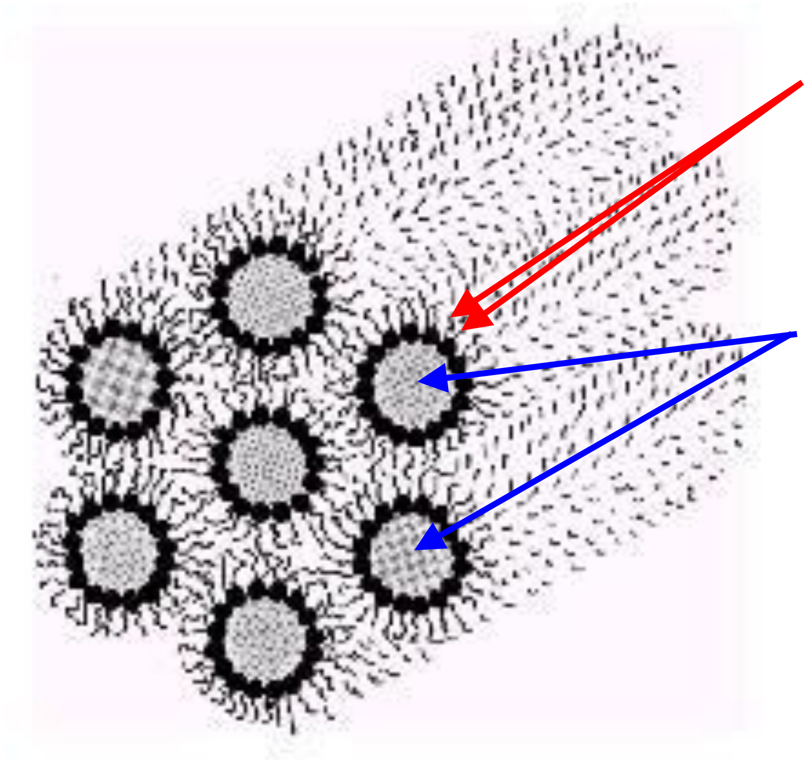
Reflection geometry appropriate for:

- 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



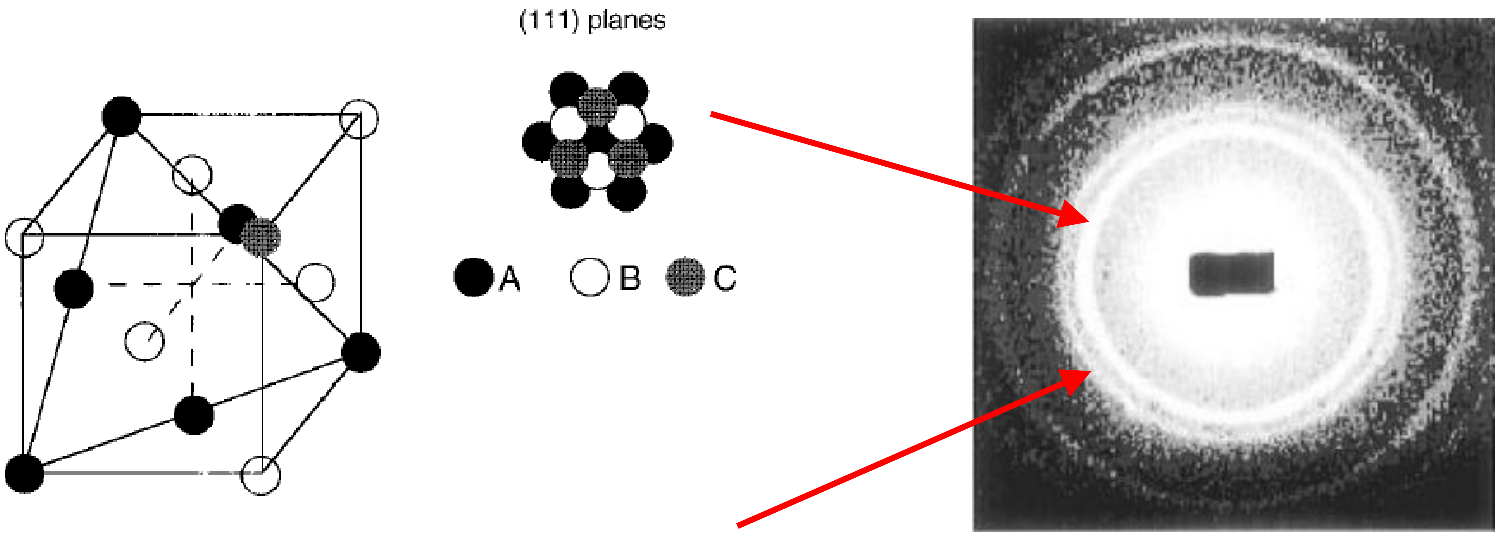
WAXS patterns contain data concerning correlations on an intra-molecular, inter-atomic level (0.1-1 nm)

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

What can I Learn from a SAXS Pattern?

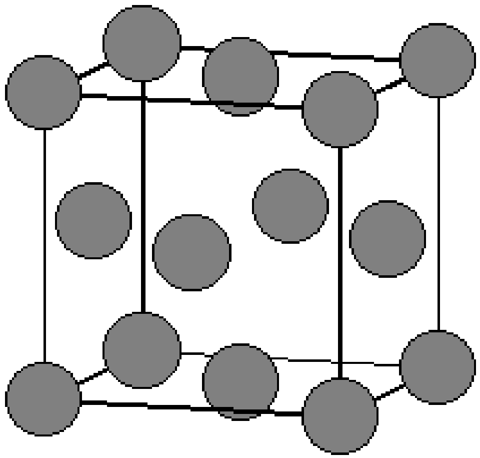
Reciprocal Space Patterns: Indexing



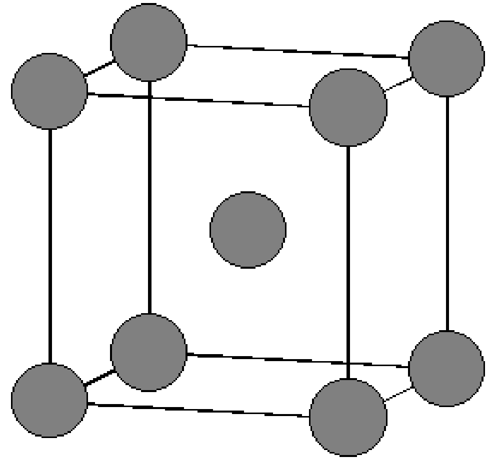
Face centered cubic pattern from diblock copolymer gel

Reciprocal Space Patterns: Indexing

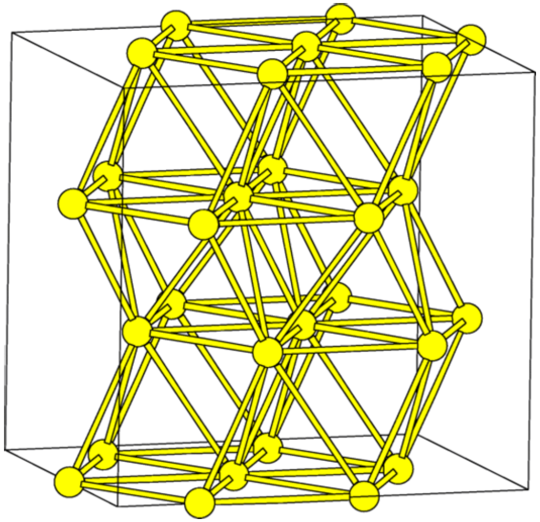
Real space packing



Face centered cubic



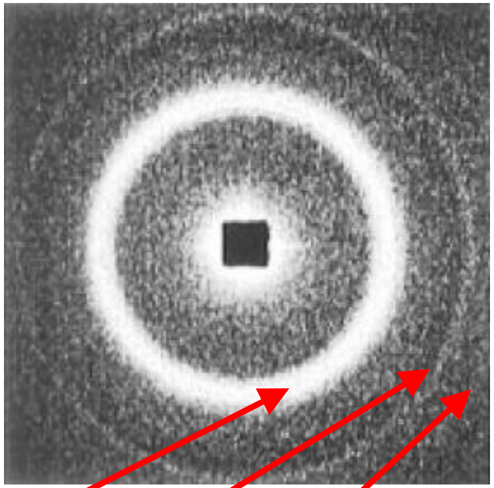
Body centered cubic

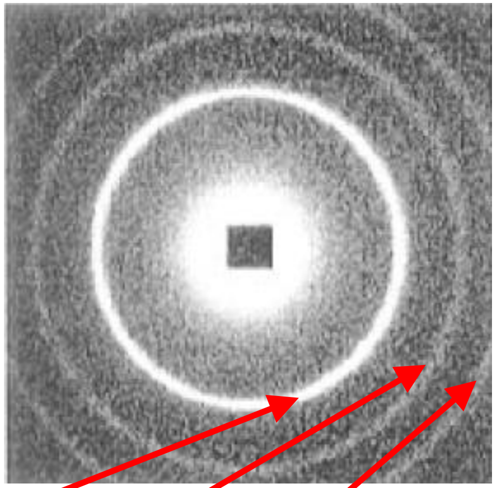


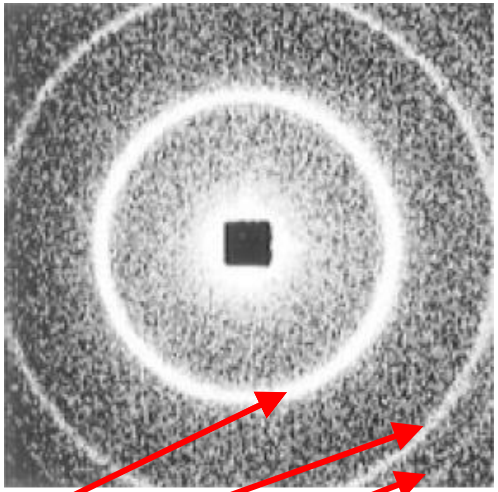
Hexagonal

Reciprocal space image

(unoriented domains)







Normalized peak positions

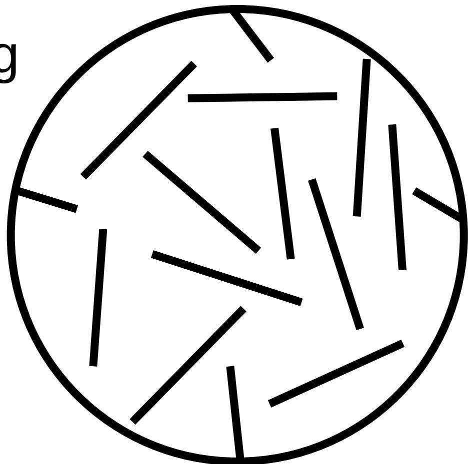
≡1; =√4/3; =√8/3

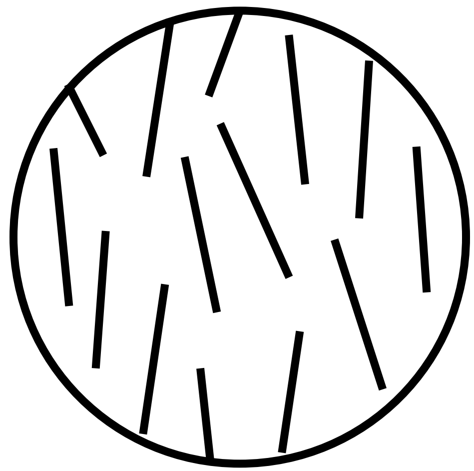
≡1; =√2; =√3

≡1; =√3; =√4

Preferential Orientation

Real space packing

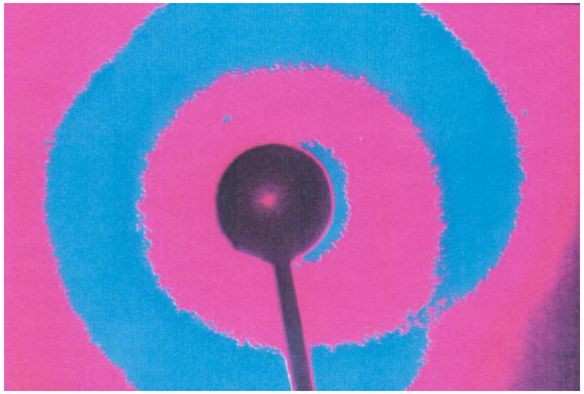




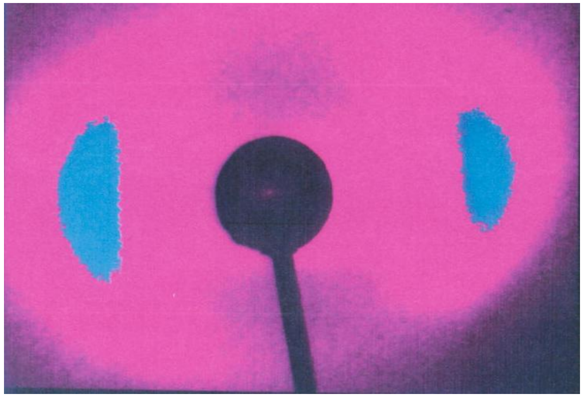
Hydrated DNA

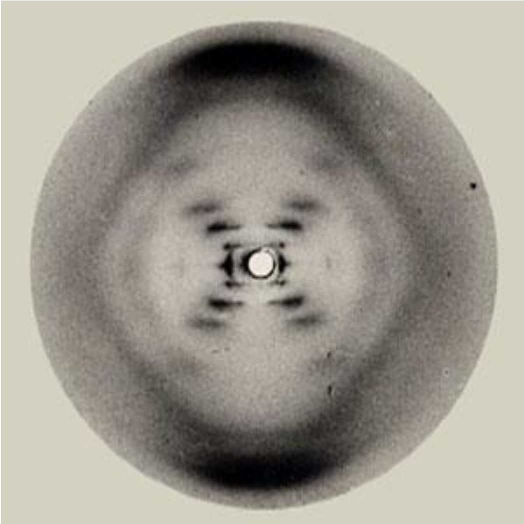
Reciprocal space image

Randomly aligned rods

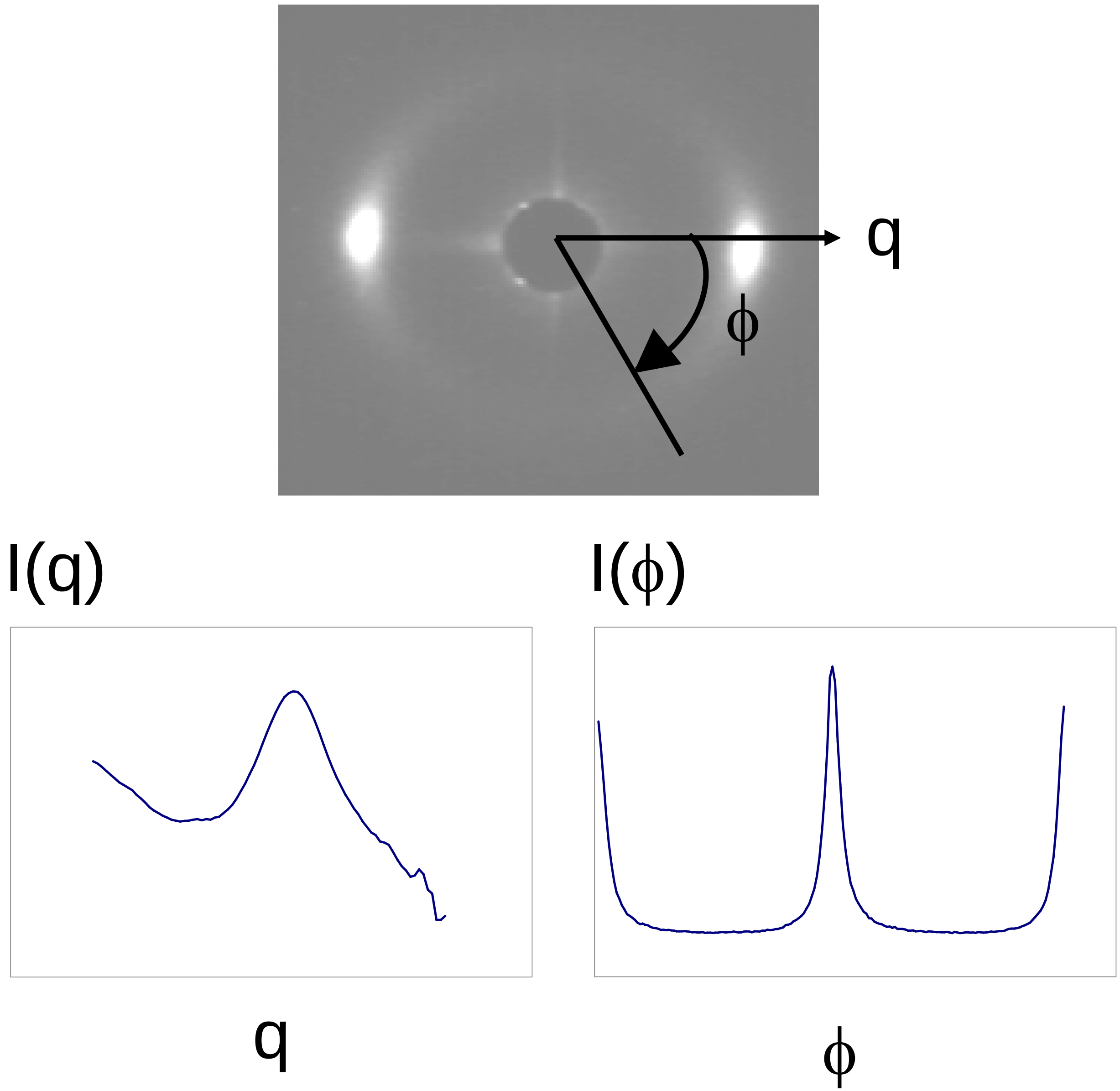


Preferentially aligned rods



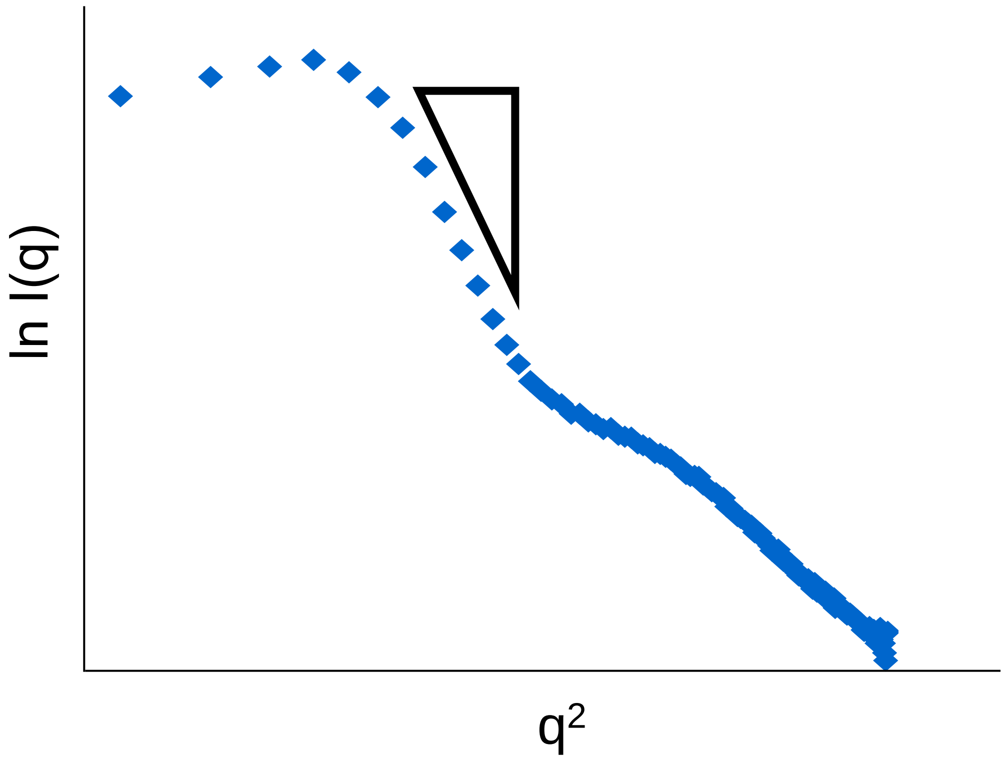


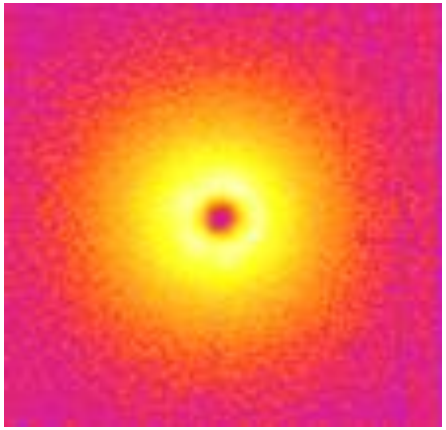
Extracting Physical Parameters



Extracting Physical Parameters

Molecular size: Radius of gyration (R_g)





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

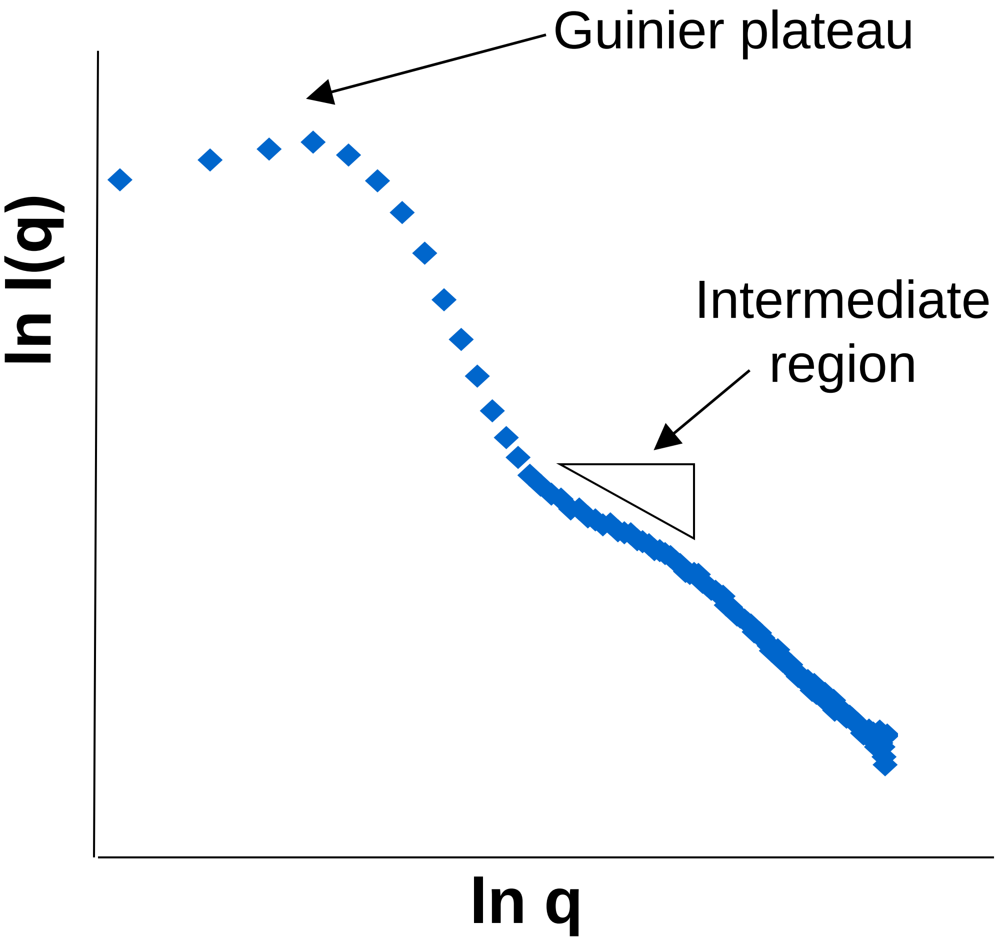
$$R_g^2 \propto \ln I(q) / q^2$$

Guinier plot

Guinier region: $q < 1 / R_g$

Extracting Physical Parameters

Molecular conformation: Scaling exponent

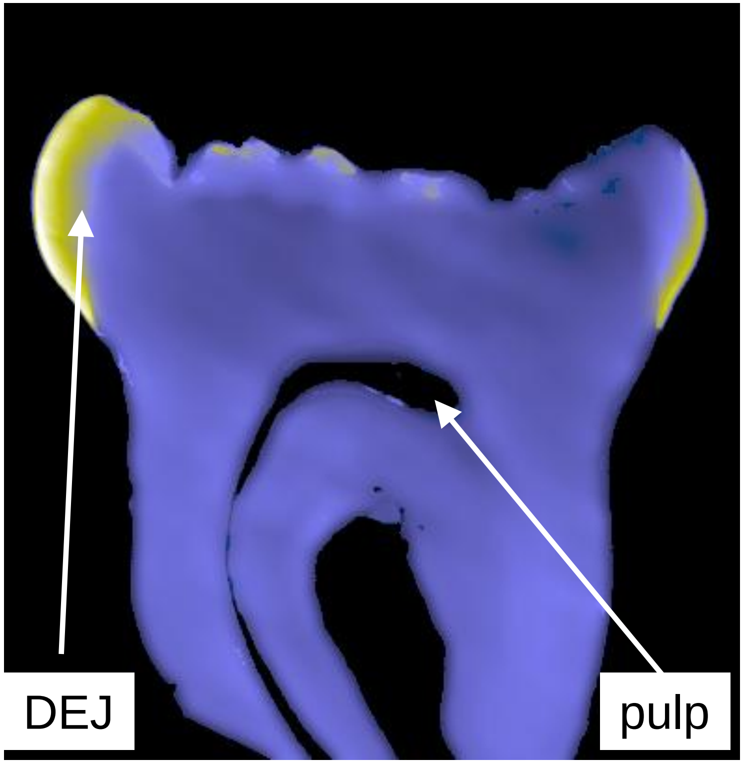


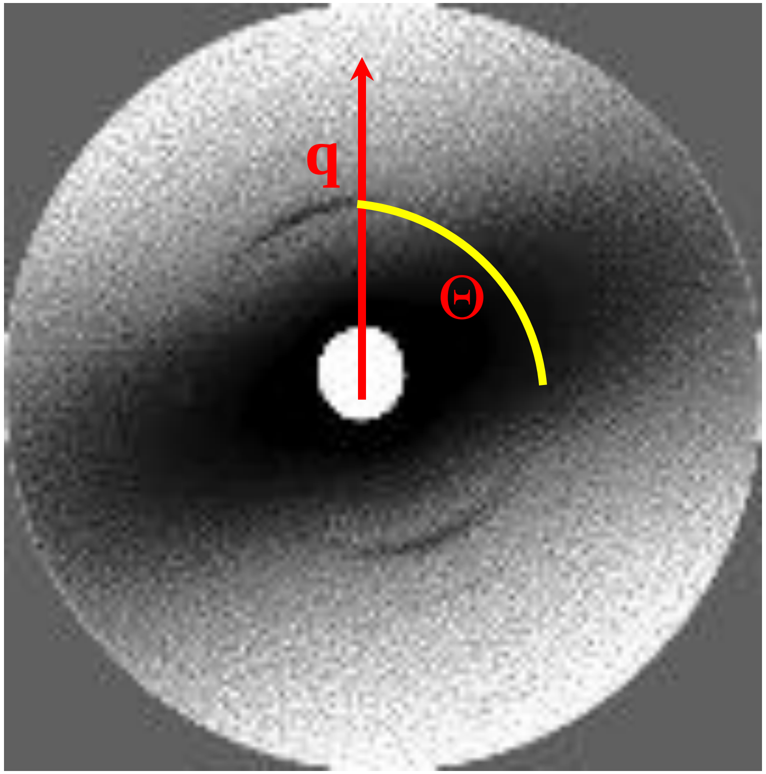
Gradient of profile in intermediate region implies fractal dimension of scattering unit

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

Molecular Conformation in Dentin

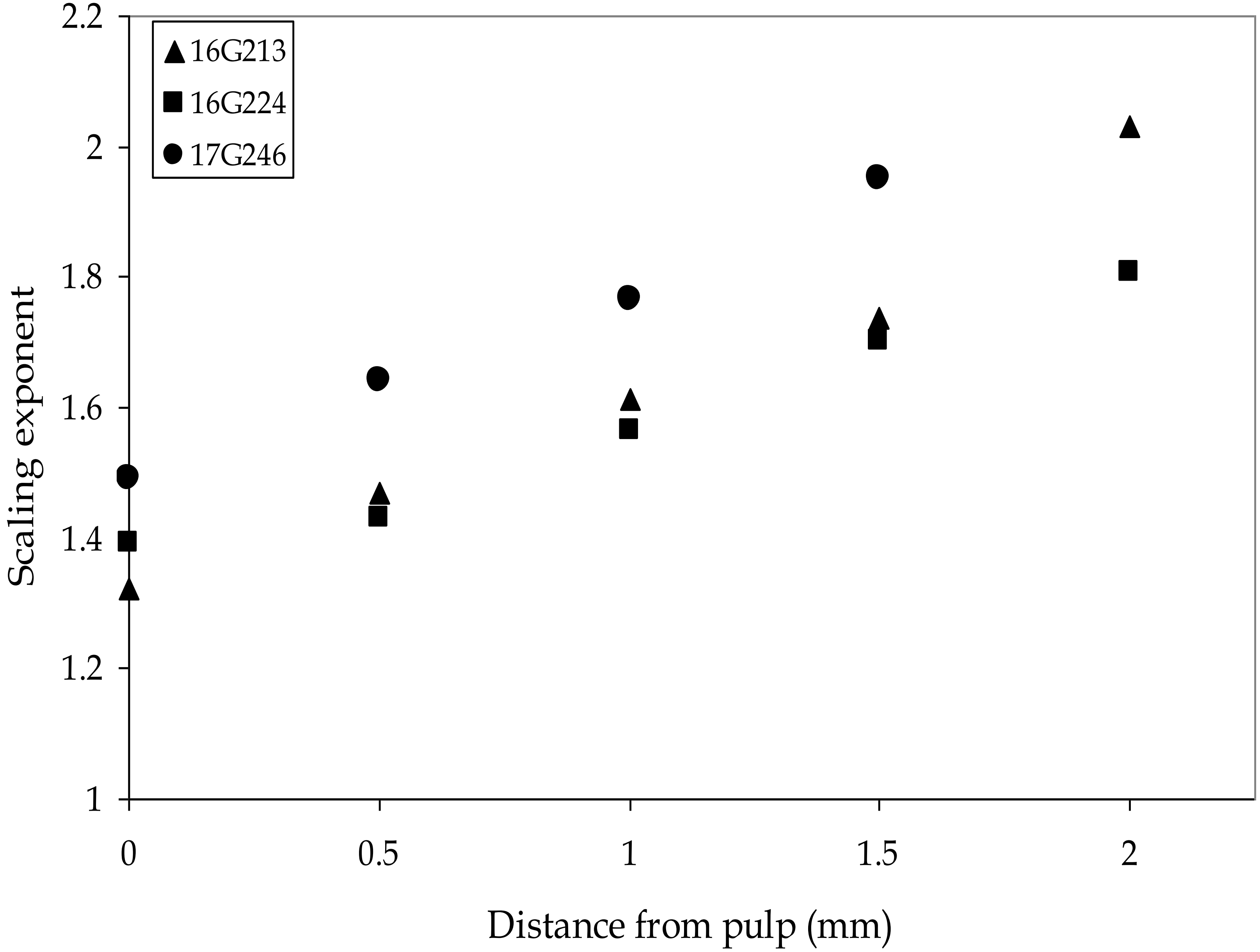
John H Kinney
Department of Preventive and Restorative Dental Sciences,
University of California, San Francisco, CA 94143





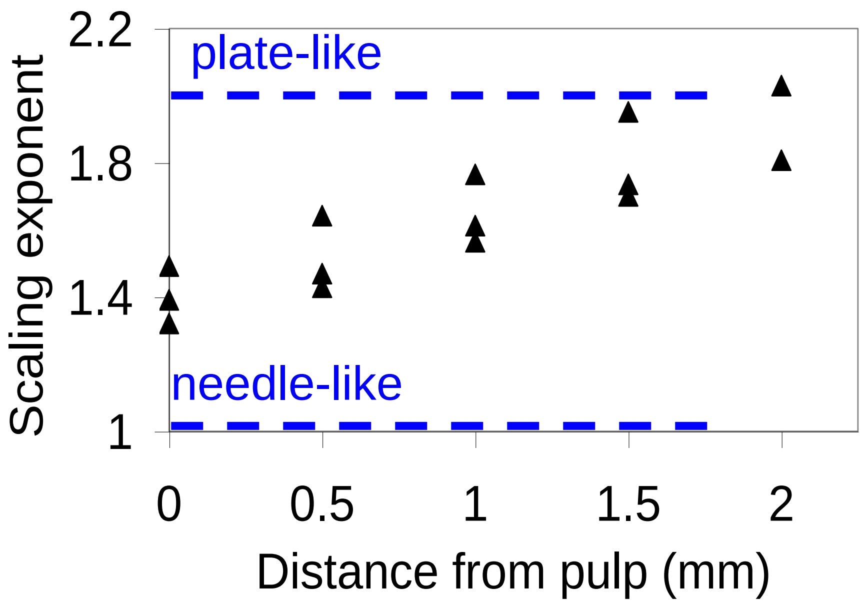
SAXS pattern

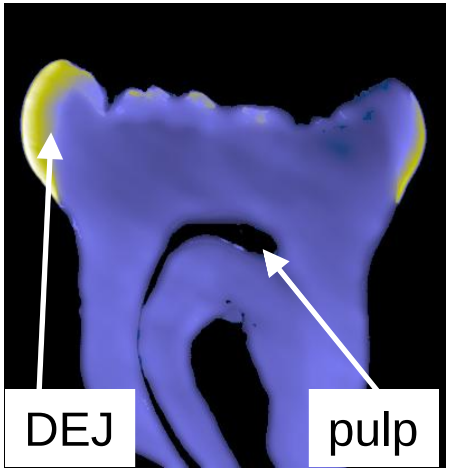
Molecular Conformation in Dentin



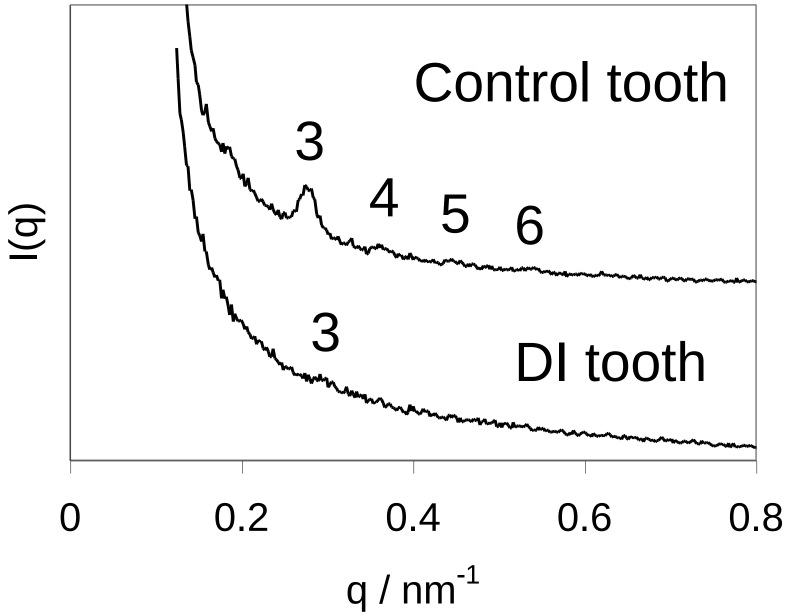
Molecular Conformation in Dentin

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



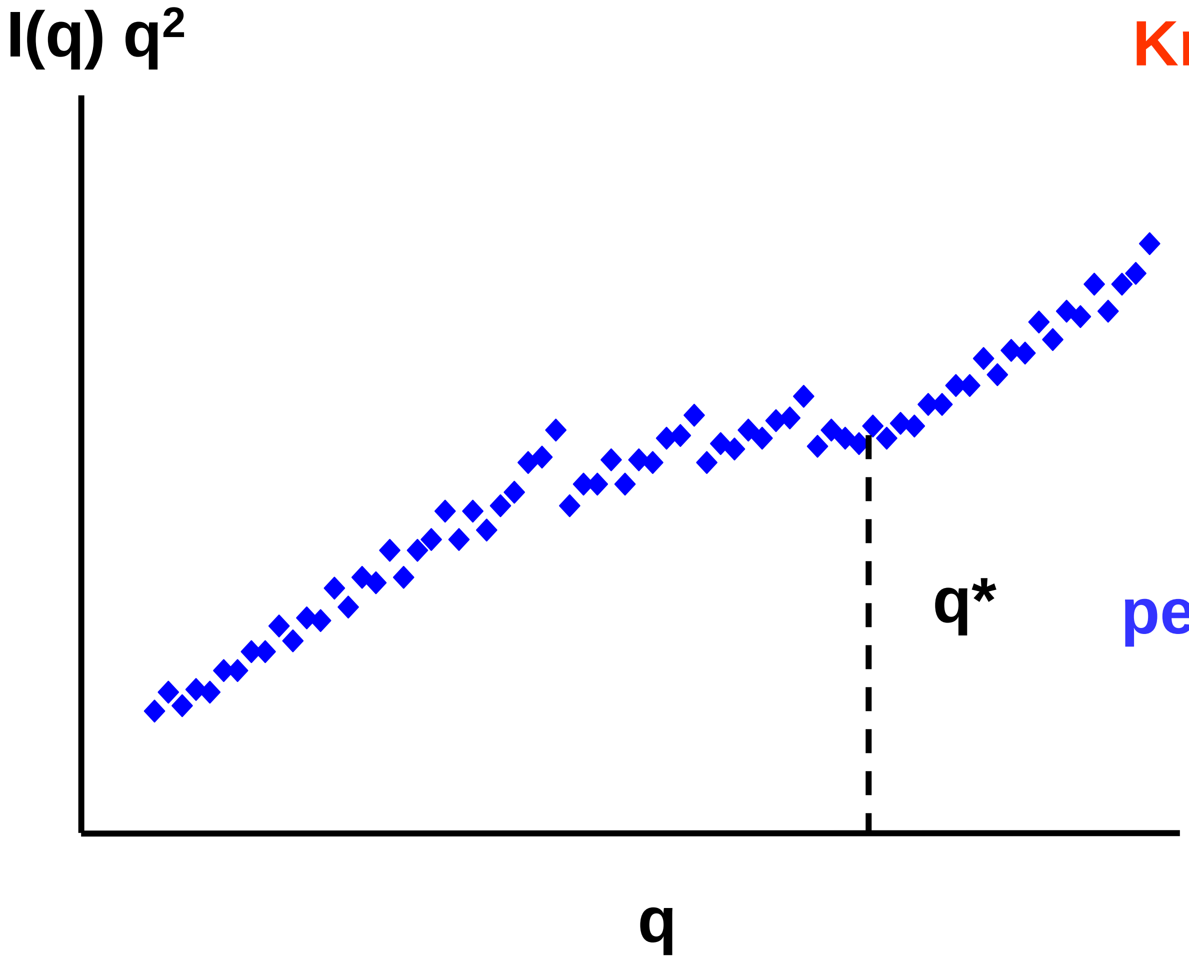


Dentinogenesis imperfecta (DI) teeth shown to exhibit impaired development of intrafibrillar mineral: characteristic scattering peaks are absent from the diseased tooth.



Extracting Physical Parameters

Molecular conformation: Persistence length of coiled chain



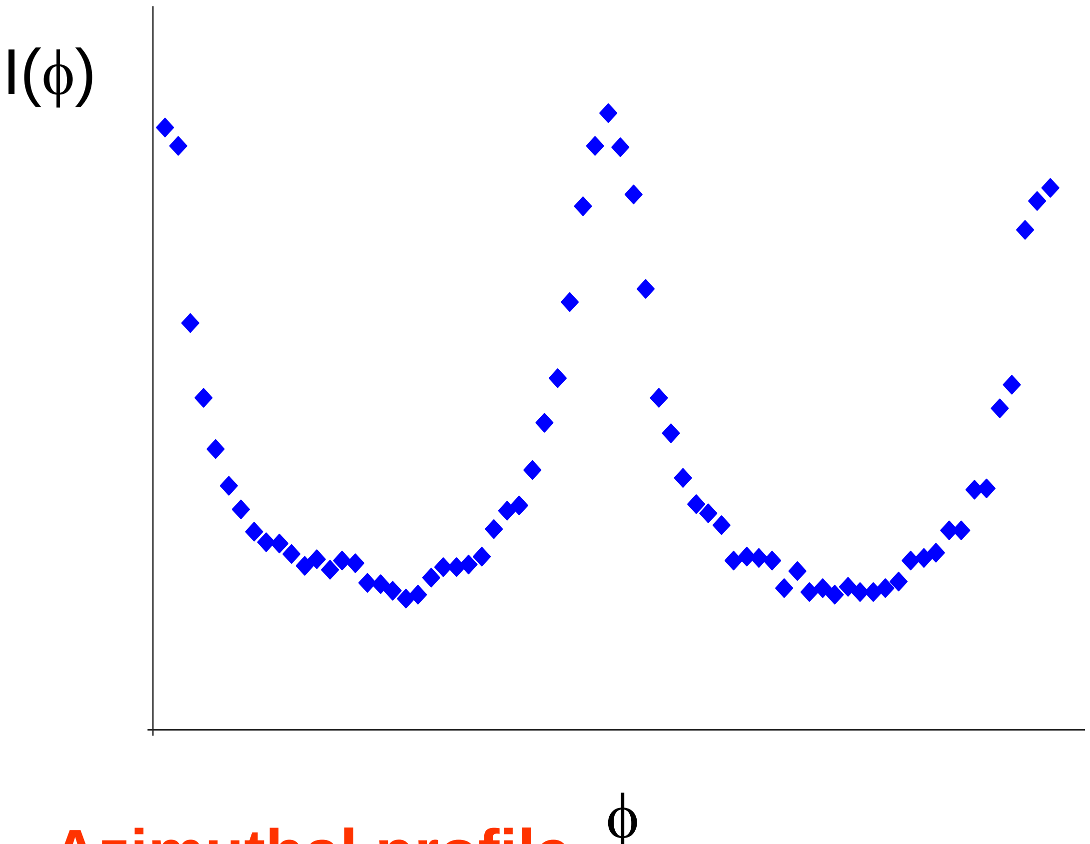
Kratky plot

persistence length
= 6 / (π q*)

Extracting Physical Parameters

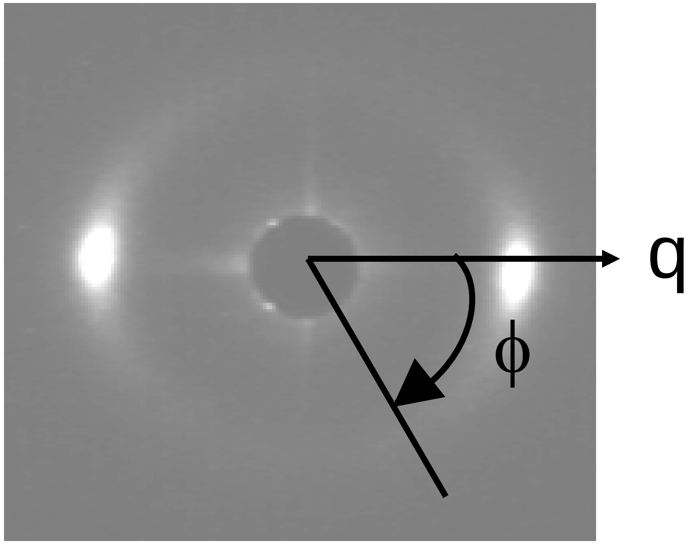
Molecular orientation: Orientation parameter P_2

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



Normalized:

$-0.5 < P_2 < 1$



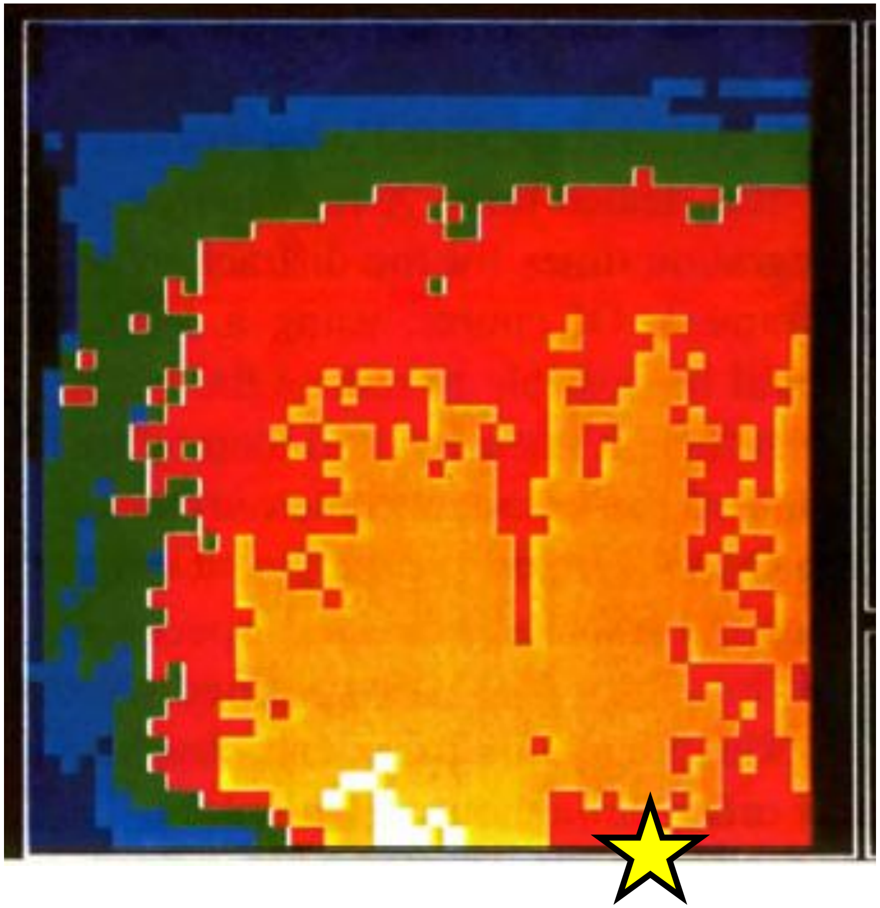
Azimuthal profile

Molecular Orientation in Injection Moldings

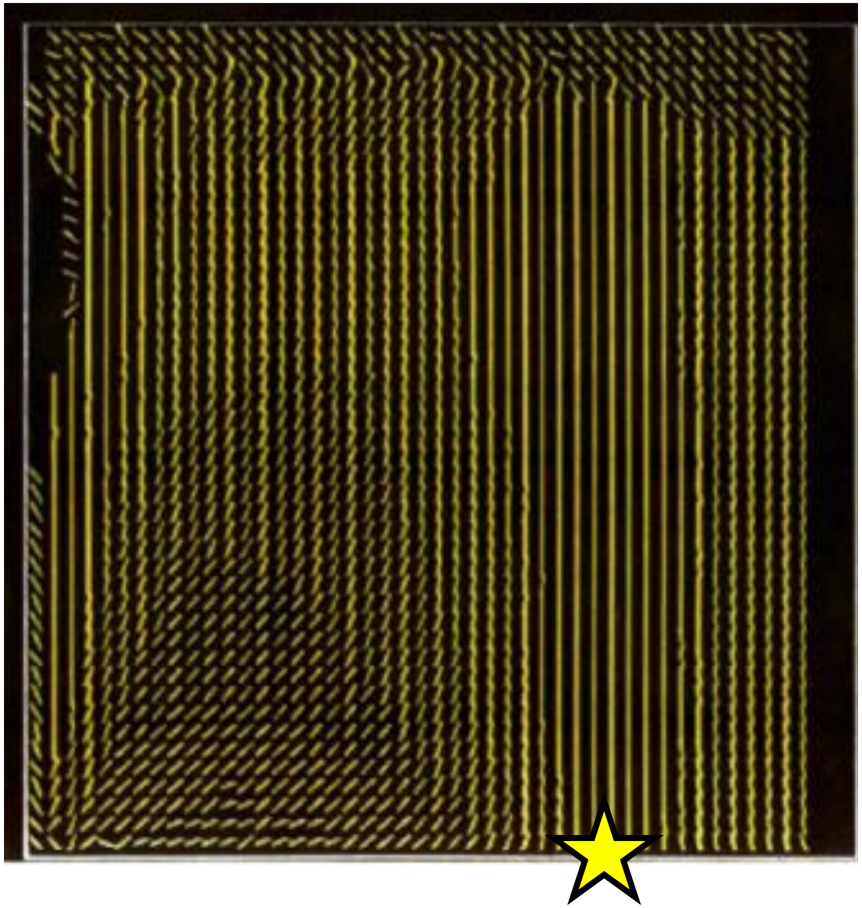
Measuring the degree and inclination of preferential molecular orientation in a piece of injection molded plastic (e.g. hip replacement joints). ~ 1500 WAXS patterns

★ Marks the injection point

Orientation parameters: $0 < P_2 < 0.3$

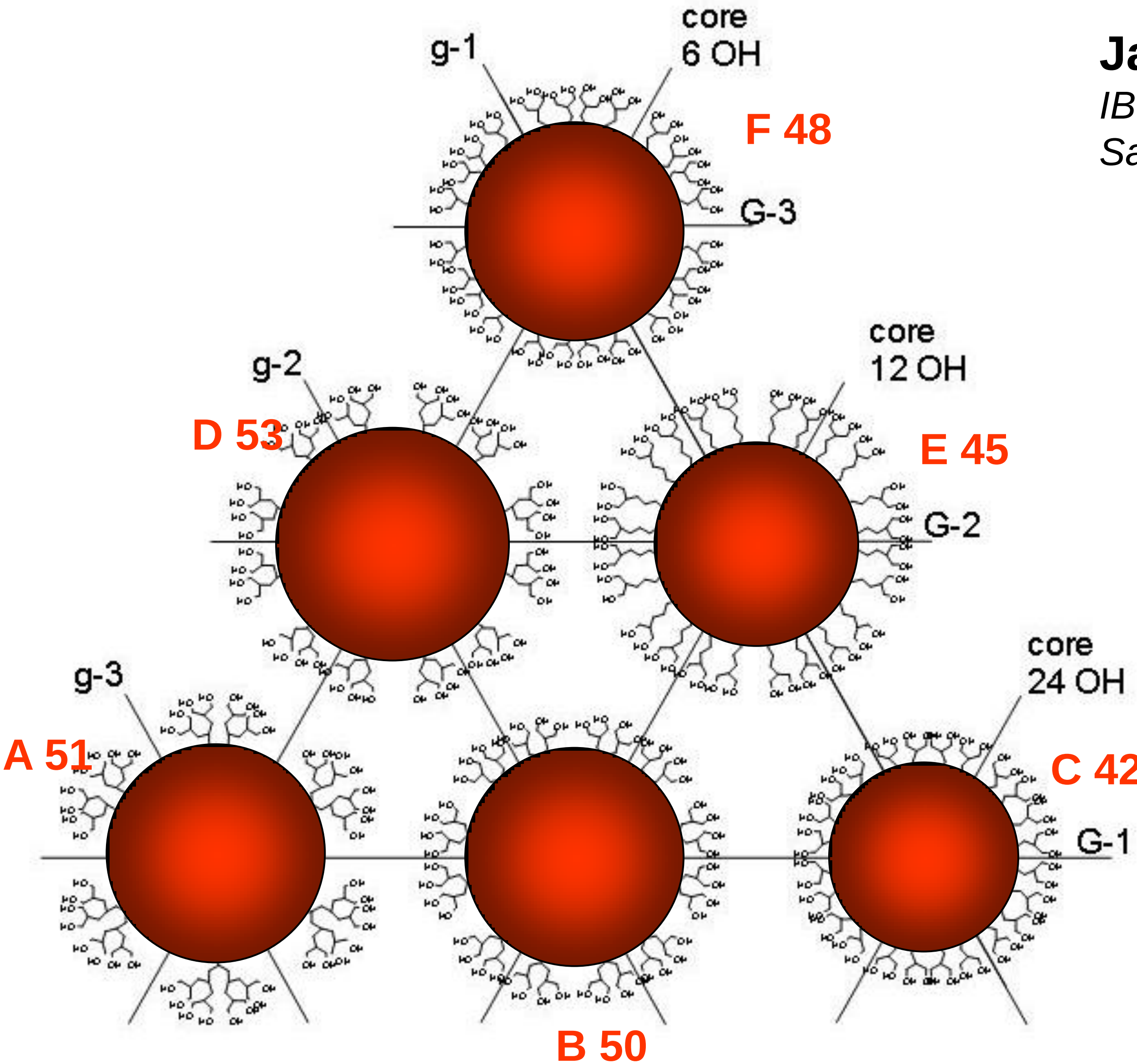


Axis of orientation



Recognizing Reciprocal Space Patterns: R_g

James L Hedrick
IBM Almaden, 650 Harry Road, San Jose, CA 95120

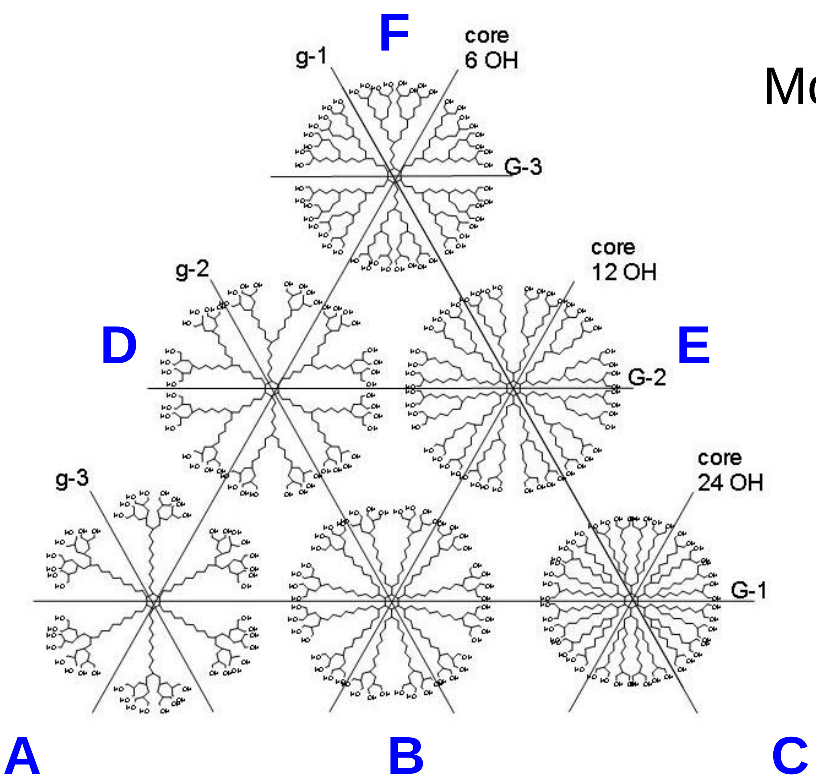


Dendrimers designed as poragens for nano-porous media: interest in monodispersity and density distribution per poragen

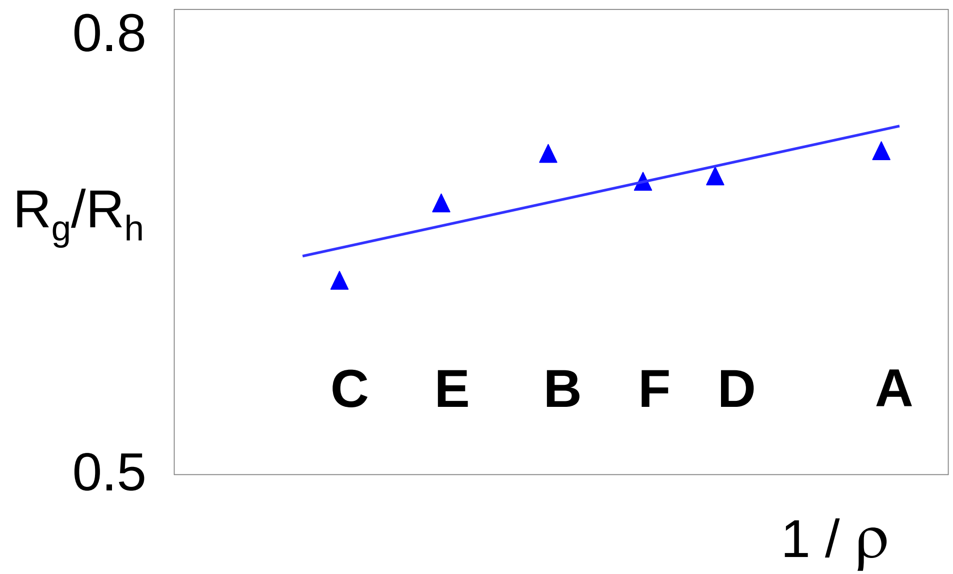
$R_g^2 \propto \ln I(q) / q^2$

Modeling Radial Density of Isomers

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.



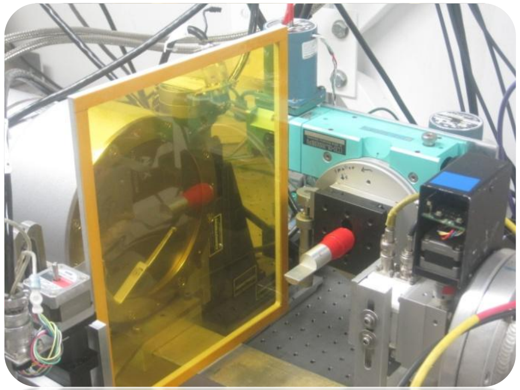
Model: $\rho(r) = \sum f^{(3\nu-1)/2\nu} \, r^{(1-3\nu)/\nu} \, dr$



What SAXS Materials Science Research is ongoing at SSRL?

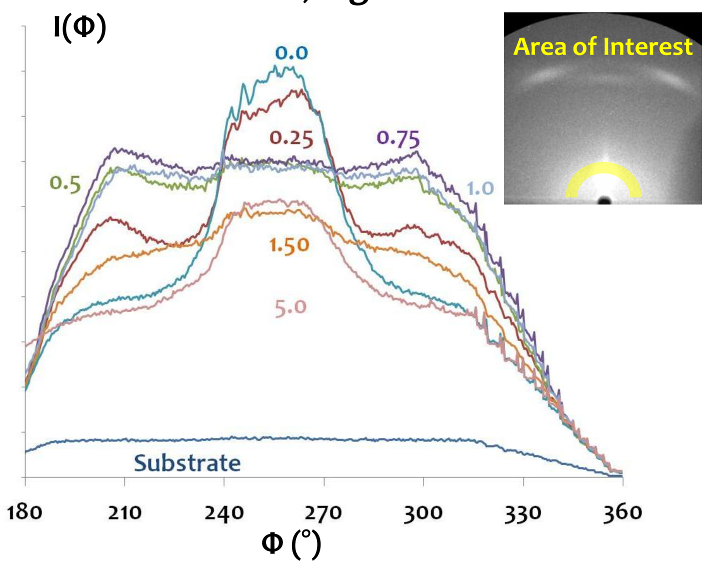
Transition Films for Resistance Switching

B.J. Choi, D. Ohlberg, J.A. Pople, J.P. Strachan

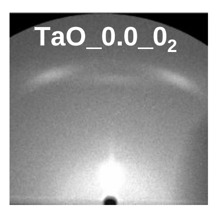


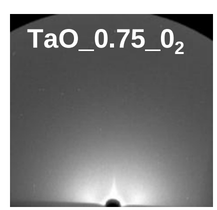
Device: Huber 410 goniometer
Use: Grazing incidence SAXS characterization (GISAXS) of thin films on substrates
Capacity: Drivable in X, Y and Θ. Finest available step size in Θ = 0.09°. Does not have temperature controlled environment at this time

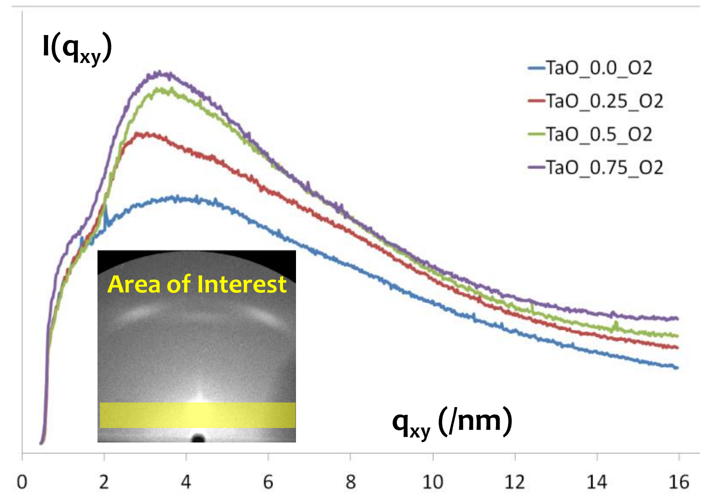
Metal-Oxide-Metal (MOM) thin films are desirable for their resistance switching behavior for computation elements and emulating neural synapses. Oxygen rich/metal poor regions yield high resistance properties and vice versa. Transport may occur by hopping or percolation between charge centers in nanoscale metallic clusters, e.g. TaO$^+$ clusters within insulating Ta_2O_5.



Films with no O_2 treatment uniquely show features at 4.5Å & 5Å, from the metallic lattice.





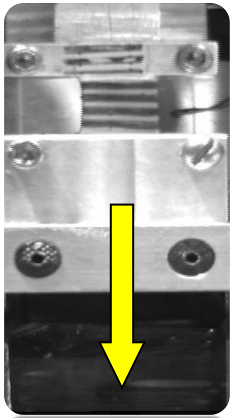


Radial reduction of 2d GISAXS diffraction patterns shows the development of TaO$^+$ features with a correlation length ~2 nm in the films. It also shows that increasing O_2 treatment during development leads to a more pronounced registry of the clusters in the x-y plane.

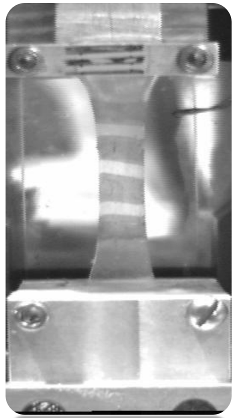
Meridional scattering peak in Φ-dependent GISAXS reduction (left), associated with TaO$^+$, decreases monotonically with increased O_2 treatment. At intermediate levels between pure metal Ta and stable oxide Ta_2O_5 order is preferentially transferred to the x-y plane, as the Ta^{2+} and Ta^{4+} ion clusters form a nanoscale structure throughout the film.

Elastomeric Polypropylene in Dynamic Strain

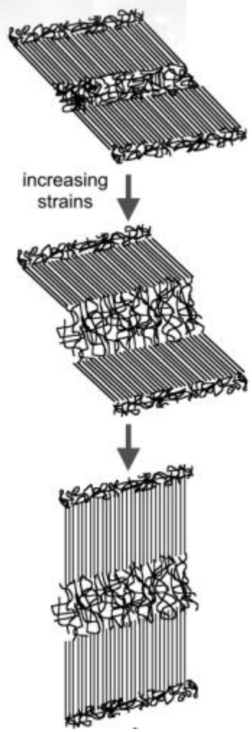
W. Wiyatno, J. A. Pople, A.P. Gast, R.M. Waymouth, G.G. Fuller



λ = 0%



λ = 300%



Device: Tensile Tester

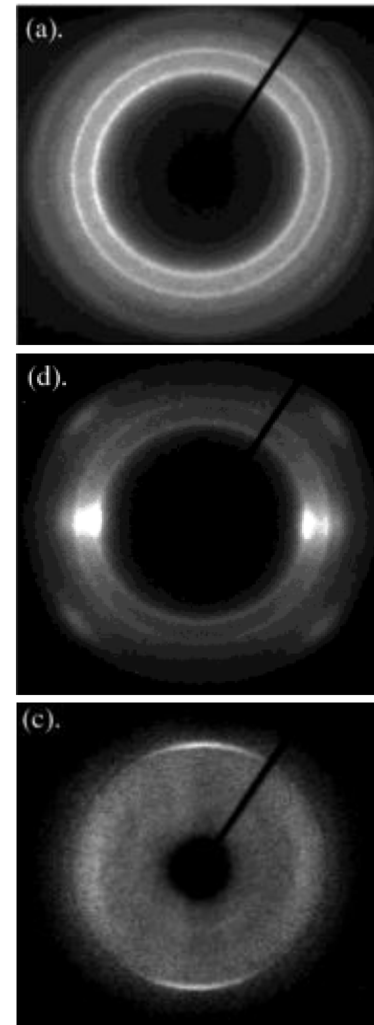
Use: In-situ transmission SAXS studies of polymer networks under dynamic strain

Capacity: Extension rate E:
0.001 mm s^{-1} < E < 25 mm s^{-1};
Strain capability λ:
0 % < λ < 300%
Oven Temp T:
25°C < T < 100°C ±2°C

Unstretched elastomeric polypropylene (ePP) reveals a crystalline phase of the R -form isotactic polypropylene (i-PP). (Right top)

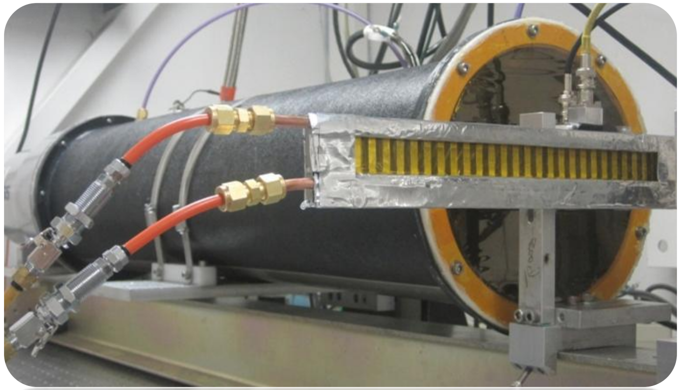
Under tensile stretching, high-tacticity fractions contribute to the equatorial and off-axis diagonal scatterings, revealing molecular-scale orientation parallel to the strain axis and crystalline phase transformation from the R -form to the mesomorphic form. (Right centre) The meridional arc is contributed by the low-tacticity ether-soluble fraction with crystalline chains oriented orthogonally to the strain direction. (Right bottom)

At low strains, most of the strain is accommodated by the inter-lamellar amorphous chains aligning with the strain axis (left), while lamellar ribbons slip rigidly. At higher strain deformation occurs by the slip-tilting of the crystalline lamellae and the crystalline phase changes. At highest strain the lamellae are ruptured by blocks of crystals pulled out of the ribbons.



Structural Effects of Surfactant Proteins on Lipids

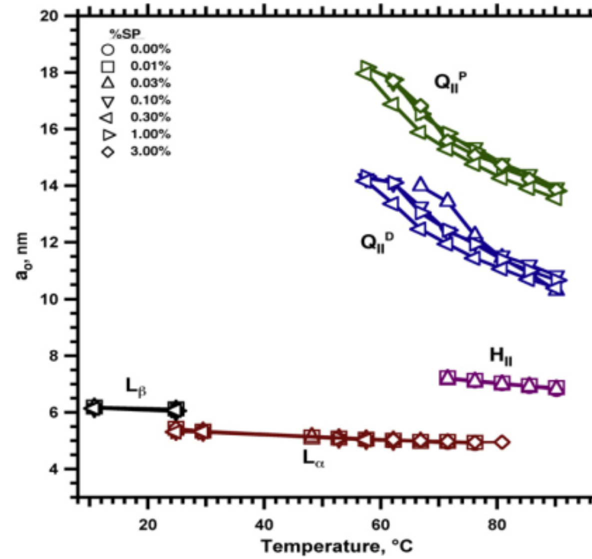
M. Chavarha, L.E. Schulwitz Jr., K. Kumar, R.W. Loney, H. Khoojinian, S.C. Biswas, S.B. Rananavare, S.B. Hall

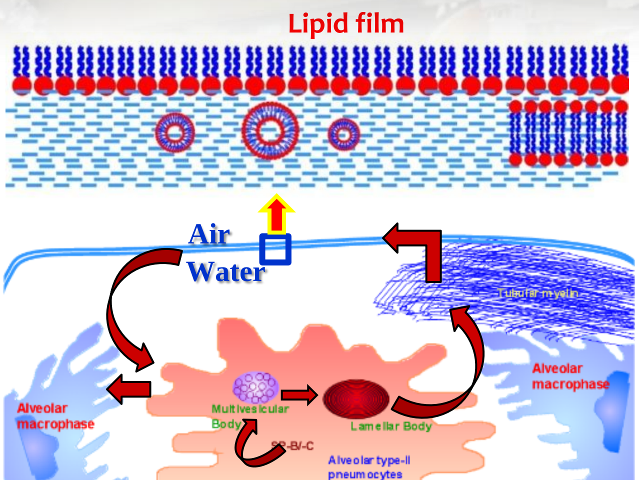


Device: Multi-Capillary Holder

Use: In-situ transmission SAXS studies of fluid, gel, powder samples or colloidal suspensions

Capacity: Drivable in x through 240 mm (24 sample positions) in x and in y through more than a capillary length. Temp control: 10 °C < T < 80 °C ± 1 °C

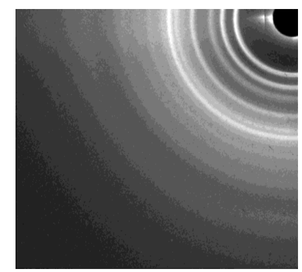


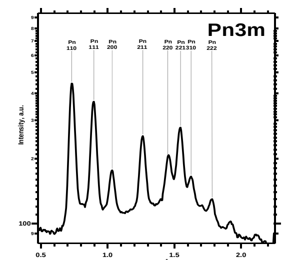


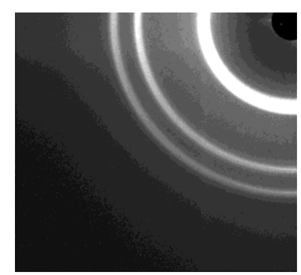
Alveolus in the Lung

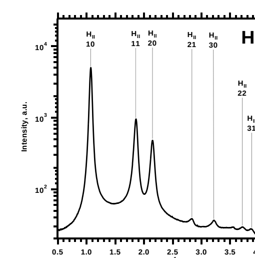
Pulmonary surfactant lowers surface tension in the alveoli of the lungs, preventing alveolar collapse and maintaining bronchial functionality. Two essential hydrophobic proteins, SP-B & SP-C, promote rapid adsorption by the surfactant lipids to the air/water interface.

Small amounts of protein induce lamellar lipids to form curved structures.





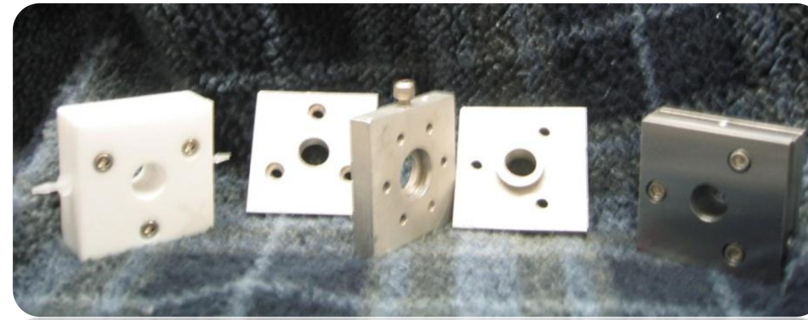




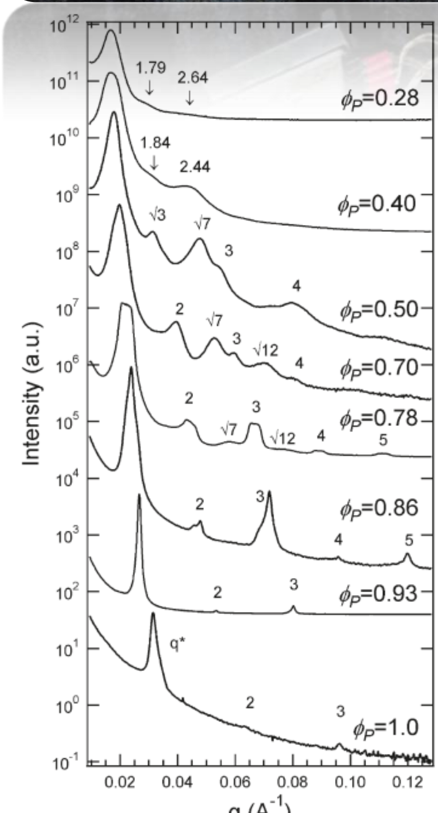
Transport in Nano-structured Media

J.M. Virgili; A. Panday; E.D. Gomez; N.S. Wanakule, S.A. Mullin; N.P. Balsara & J.A. Pople

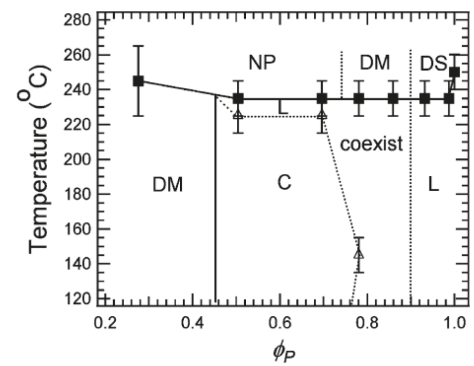
Device: Oven
Use: In-situ transmission SAXS studies of solid, fluid, gel, powder samples or colloidal suspensions in cells designed to provide good thermal contact with oven
Capacity: Temp control: 25 °C < T < 450 °C ± 1 °C. Latest model 25 °C < T < 400 °C also has ability to allow in-situ titration

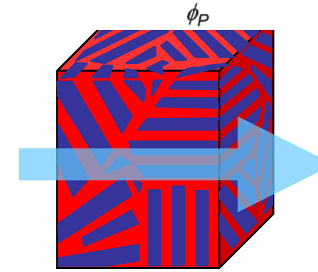


Oven Cell Holders: assemble as three parts with windows & O-ring gaskets. Available in Al, Steel or PTFE (Teflon). Teflon cells have flow couplings for in-situ titration. Volume ~ 2.5 cc; Optical path length = 1 mm



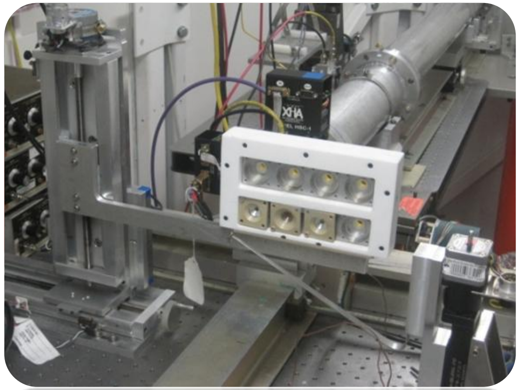
SAXS reveals that the macro-phase of copolymer displays stable coexistent mesophases of lamellar and hexagonally cylindrical morphologies as a function of volume fraction of a selectively solvent ionic liquid. At high block copolymer concentrations, a "salt-like" regime corresponding to an increase in the block copolymer T_g is observed, while at intermediate block copolymer concentrations, a "solvent-like" regime corresponding to a decrease in the block copolymer T_g is observed.





Transport in Nano-structured Media

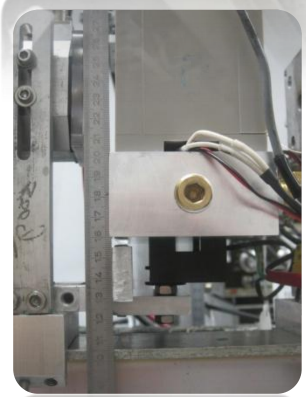
K.M. Beers, D.T. Hallinan, X. Wang, J.B. Kerr; N.P. Balsara & J.A. Pople



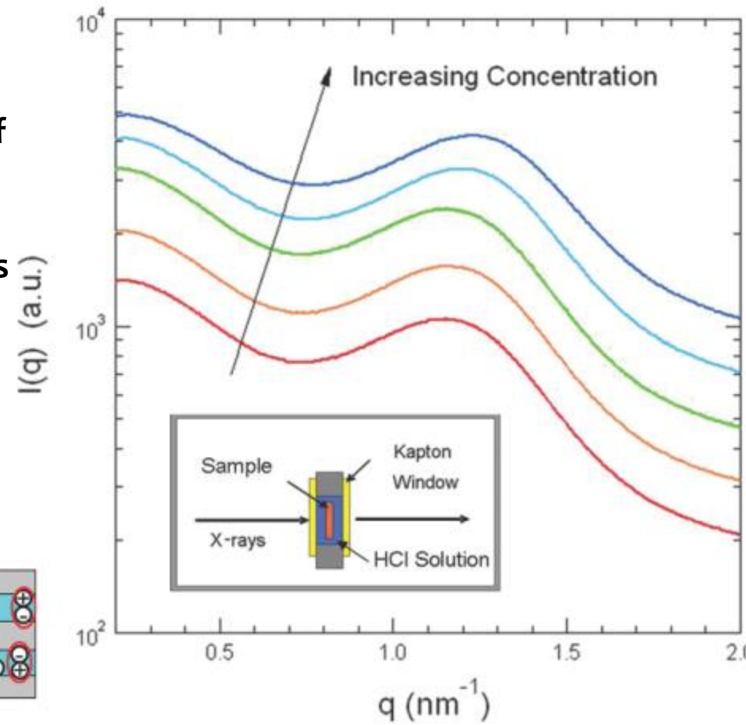
Device: Multi-Purpose X-Y positioner

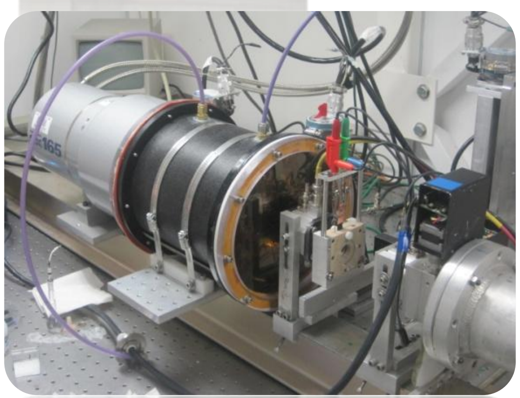
Use: Transmission SAXS studies of solid samples which can be directly attached to the positioner, or as a coupler to a sample environment provided by the experimenter

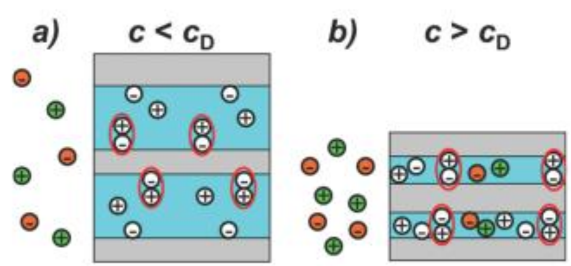
Capacity: 240 mm travel in x; 200 mm travel in y and a multi-purpose adaptor arm which can be modified to hold many different environments; examples below are Balsara group's multi-sample heating stage (left, top) and humidity stage (center) and Strasser group's electrochemical cell (bottom)



Swelling the commercial membrane Nafion in external electrolyte, through use of a humidity chamber, reveals a large fraction of condensed counterions. Extension of this technique to block copolymers and study how this effects performance of nanoporous media is underway.







Mineral Deficiencies in Teeth

J. H. Kinney & J. A. Pople

Previously characterized impaired intrafibrillar mineral growth in Dentinogenesis Imperfecta (DI) teeth

Goal:

To explore mineralization in caries lesions in order to understand caries development, arrest, and treatment. SAXS patterns will reveal presence or absence of gap-zone mineralization within the collagen fibrils, as well as average mineral crystallite size, orientation, and shape