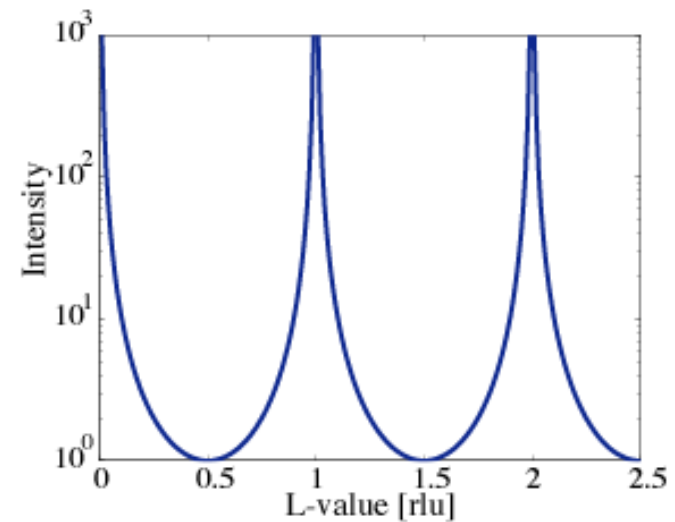
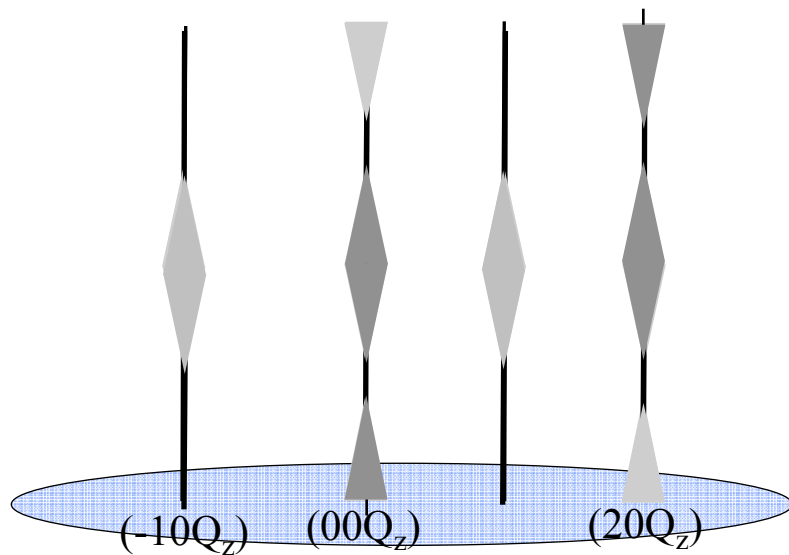


X-ray Scattering

Mike Toney

Stanford Synchrotron Radiation Laboratory



Bibliography



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- M. Tolan, “X-ray Scattering from Soft-Matter: Materials Science and Basic Research”, Springer, 1998.
- RL Snyder, K. Fiala & HJ Bunge, Eds., “Defect and Microstructure Analysis by Diffraction”, Oxford (1999).
- G Renaud, “Oxide Surfaces and Metal/Oxide Interfaces Studied by Grazing Incidence Diffraction”, Surf Sci Repts **32**, 1 (1998)

Outline

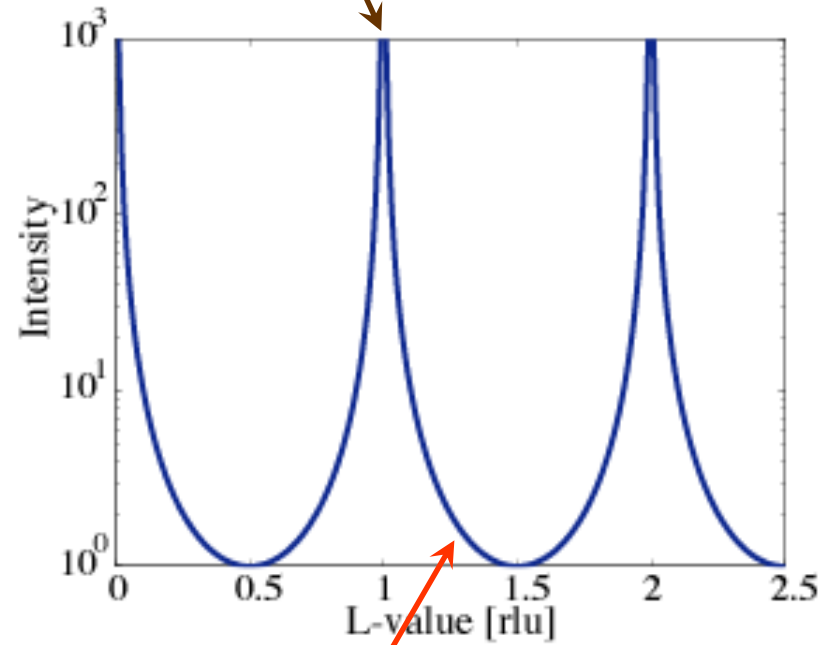
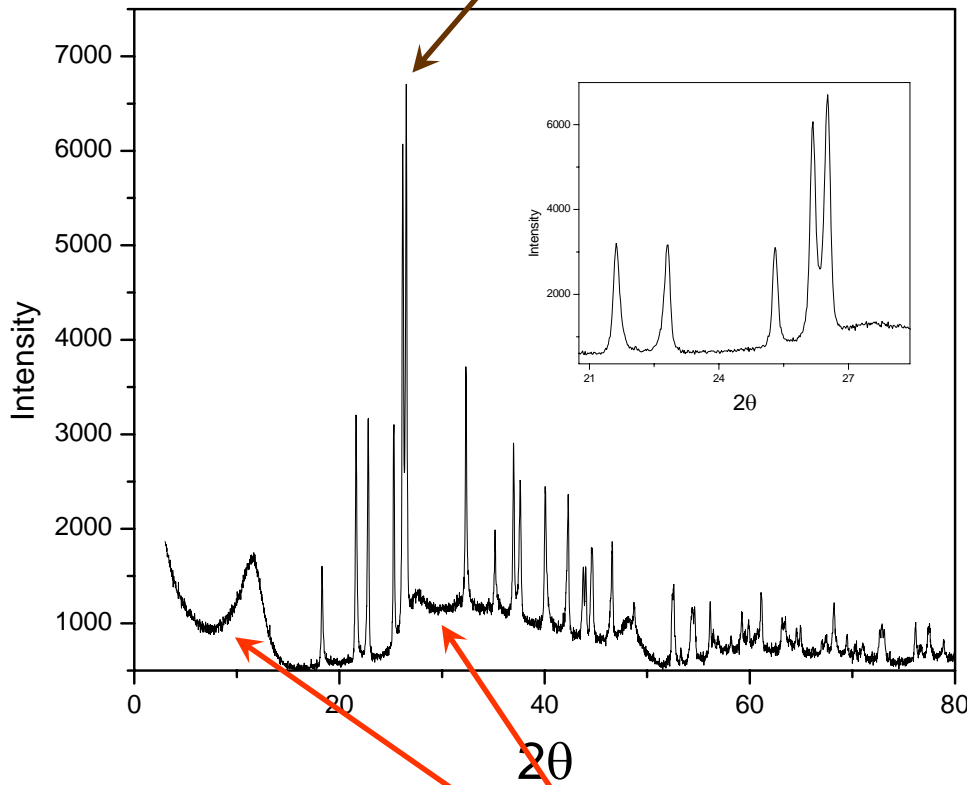


1. Peak Widths & Defects
 - Nanoparticles
2. Monoatomic Layers – Pentacene again
3. Surface Diffraction
 - Oxide Surfaces
 - Interfacial Water
4. Small Angle X-ray Scattering (SAXS)

Diffraction vs Scattering



diffraction: Bragg peaks

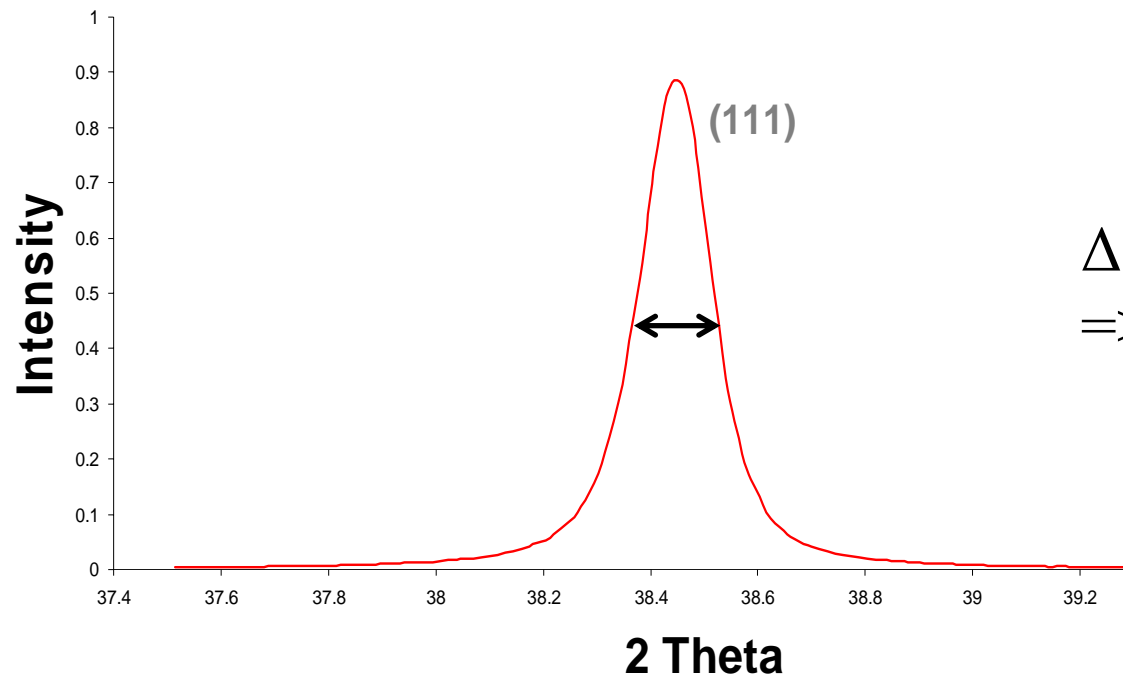


scattering: the rest

Peak Widths

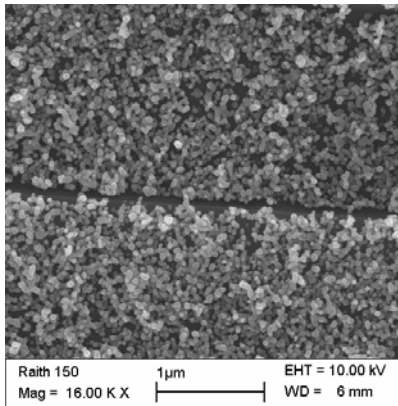


- Widths depend on particle size (D):
 - $\Delta 2\theta = 0.9 \lambda / D \cos \theta$
 - $\Delta Q = \pi/D$

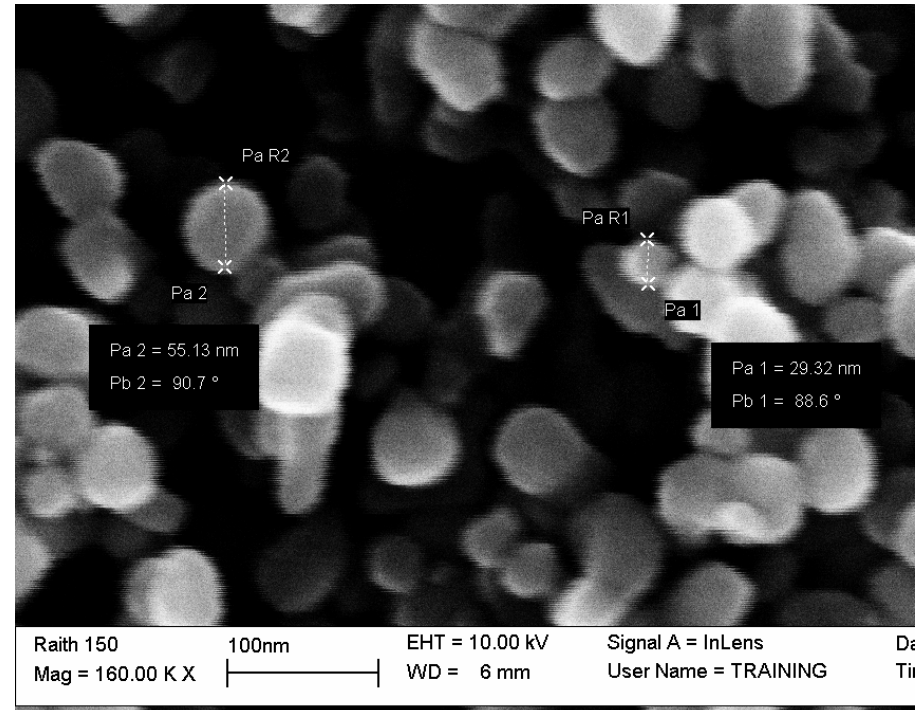


$\Delta 2\theta = 0.15 \text{ deg}$
 $\Rightarrow D = 50 \text{ nm}$

Nanoparticles

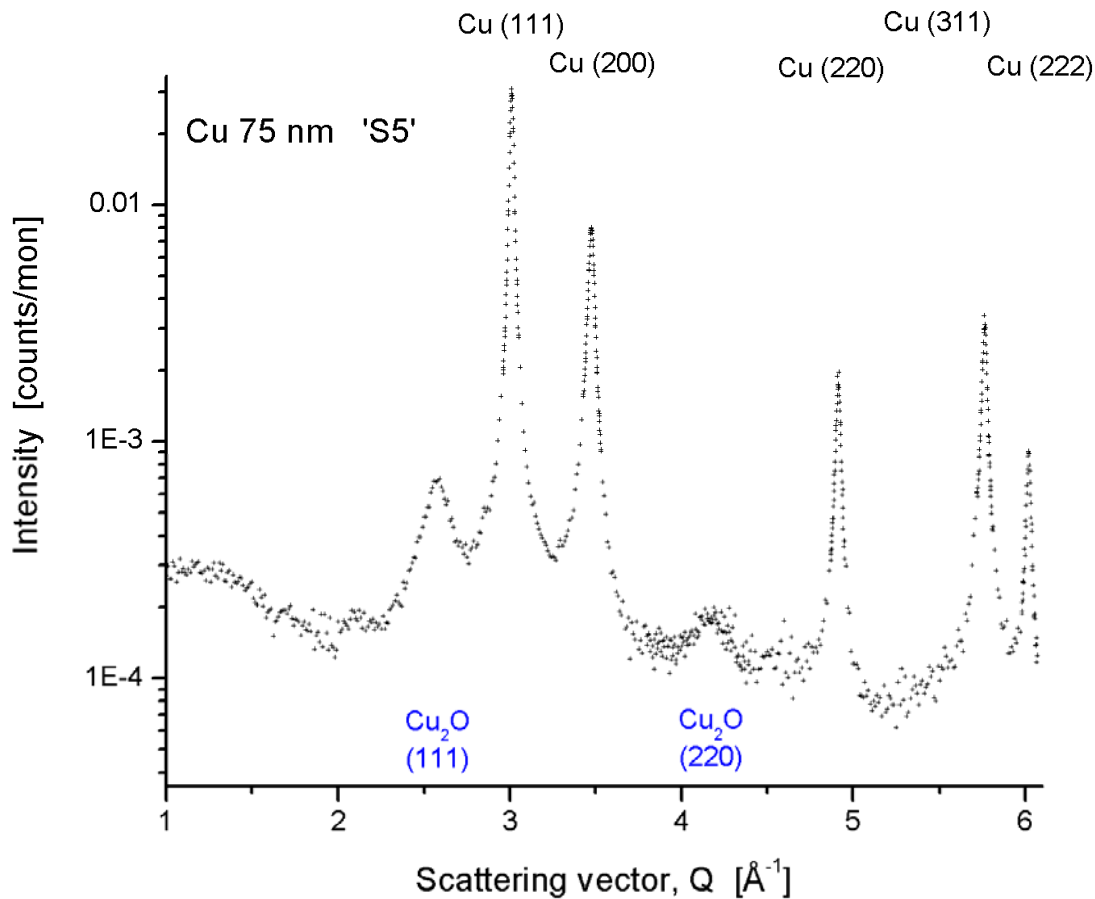


Cu particles nanoscale particles, formed by inert gas aggregation, are deposited from a molecular



Kevin Stevens (MPT Solutions, NZ)
Bridget Ingham (Imperial College, UK)
Simon Brown (U Canterbury, NZ)

Peak Widths



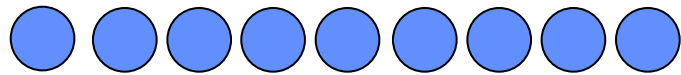
Cu particles:

- $a = 3.6159 \pm 0.0005 \text{ \AA}$
(c.f. bulk 3.6149 \AA)
- $D = 12 \text{ nm}$ compared to $30\text{-}60 \text{ nm}$ from SEM

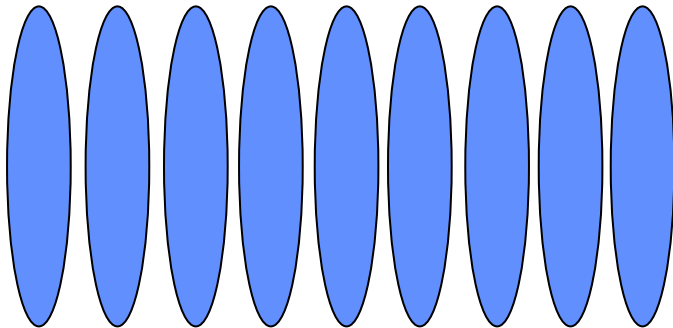
Cu_2O (cuprite):

- ca 5% by volume

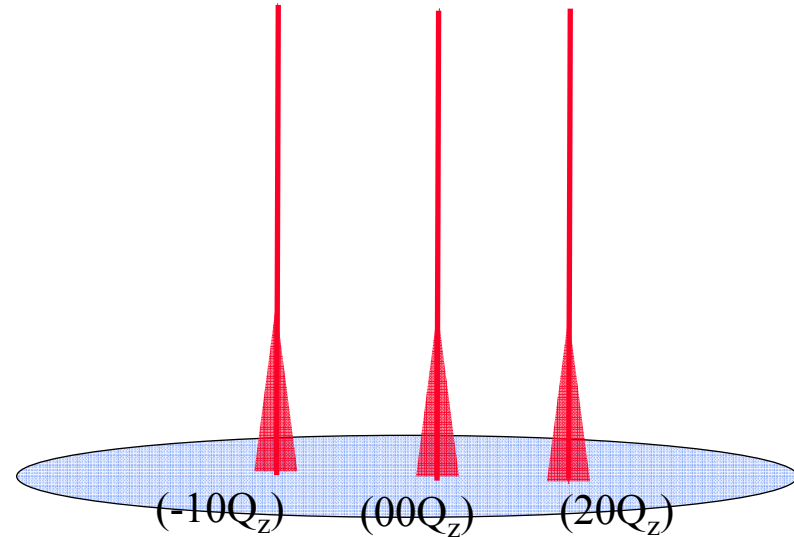
Monolayer Scattering



monoatomic layer of atoms



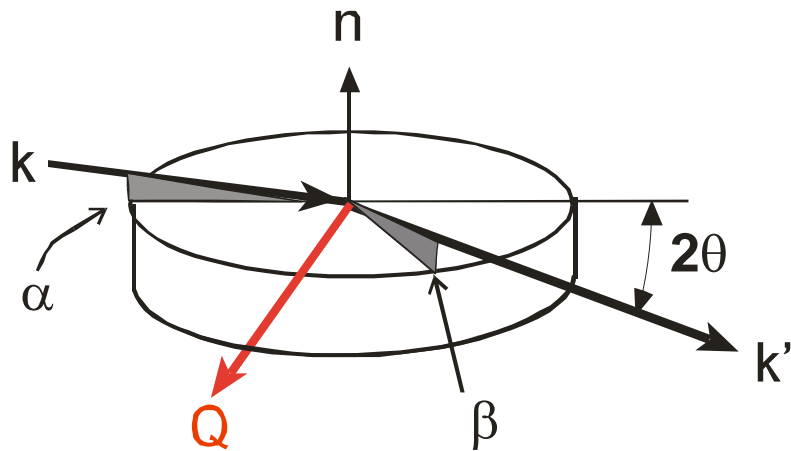
monoatomic layer of molecules



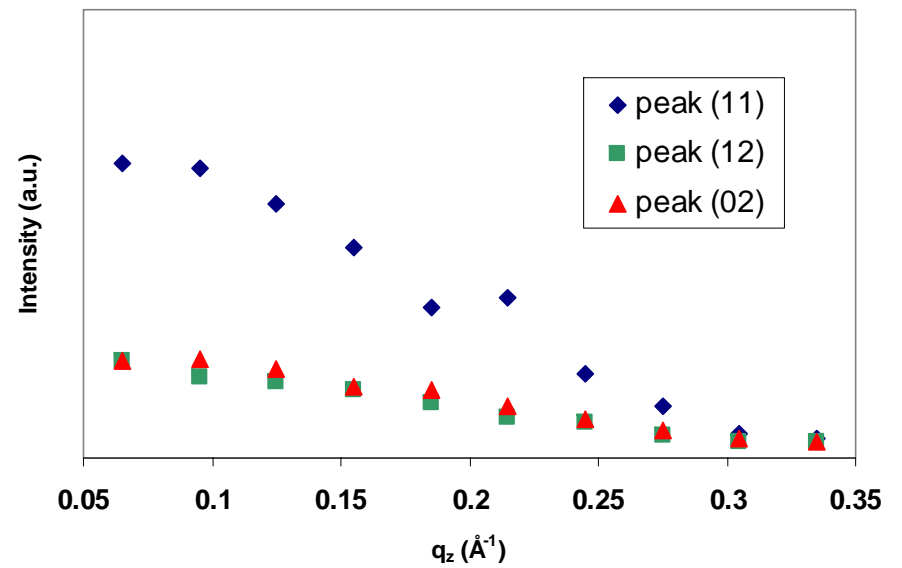
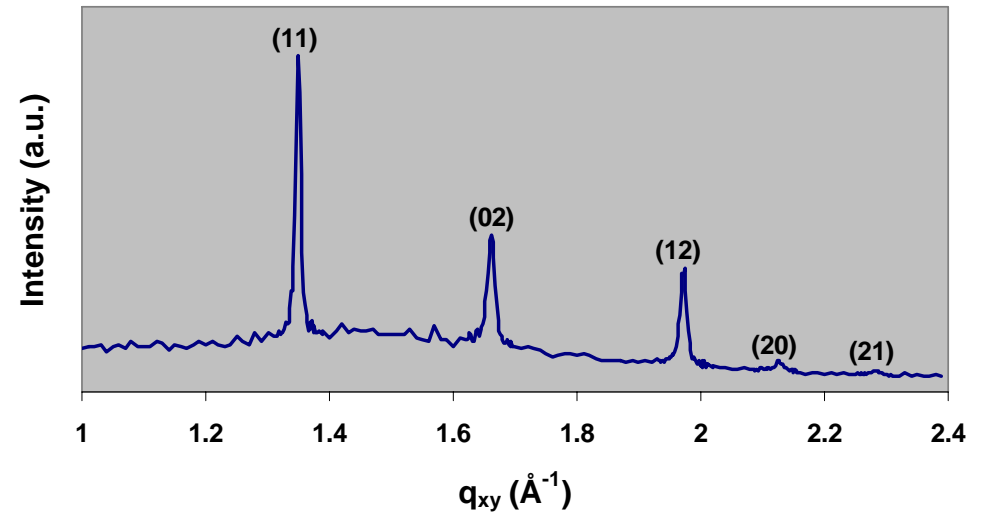
Pentacene Monolayer



Transport in ab plane of crystal structure
Transport in first few layers



Fritz et al., unpublished



Pentacene Monolayer

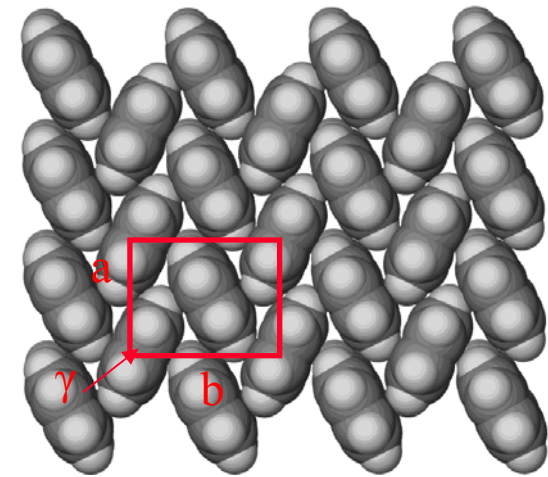


- Monolayer: herringbone motif with molecules untilted
- lattice parameters (monolayer)

$$a = 5.911 (3) \text{ \AA}$$

$$b = 7.566 (3) \text{ \AA}$$

$$\gamma = 90.0 (1)^\circ$$

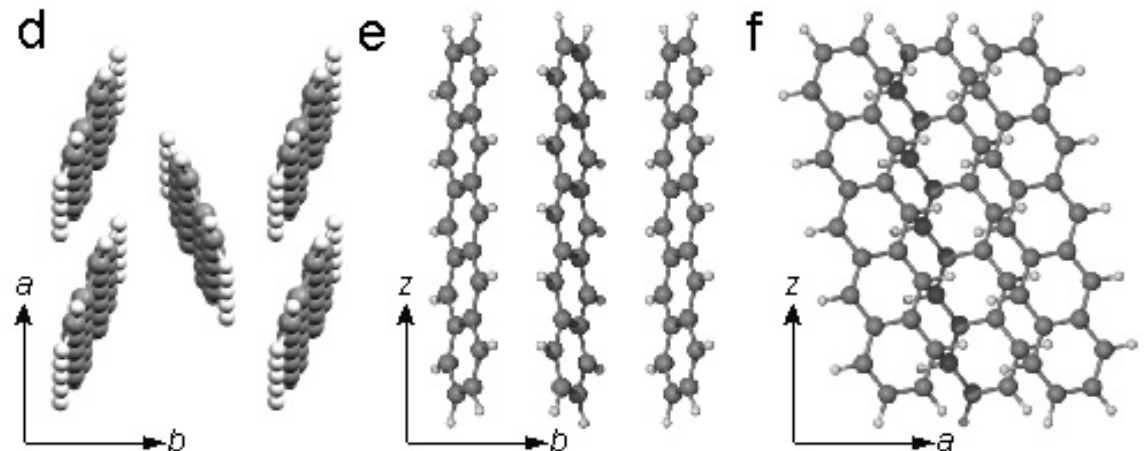


- Thin film:

$$a = 5.933 (3) \text{ \AA}$$

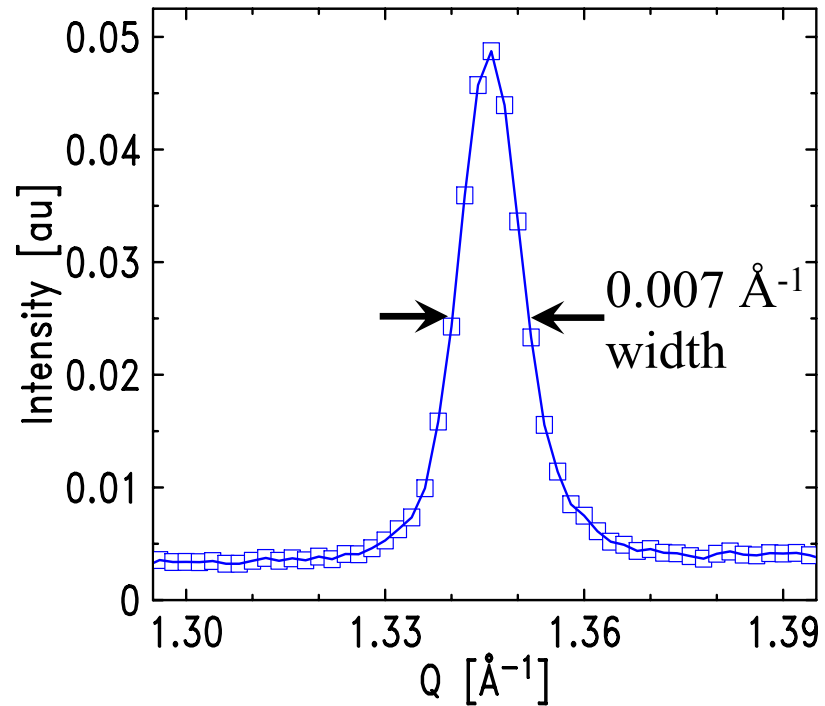
$$b = 7.540 (3) \text{ \AA}$$

$$\gamma = 90 \text{ deg}$$

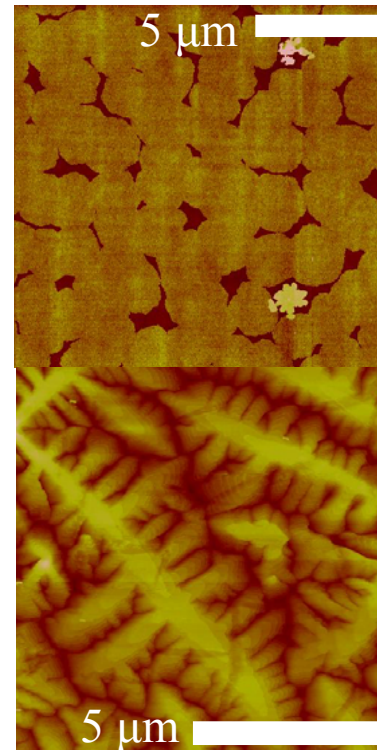


Fritz et al., unpublished

Pentacene revisited



=> Grain size of > 30 nm



1.5 nm - one layer

30 nm - ca 15 layers

Fritz et al., unpublished

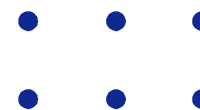
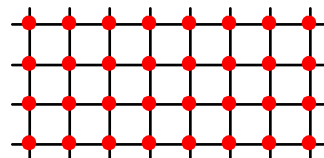
Surface Scattering



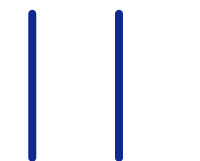
REAL
SPACE

RECIPROCAL
SPACE

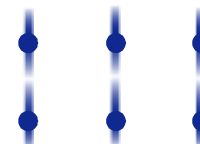
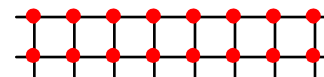
*Infinite lattice results in points
in reciprocal space.*



*A single plane of atoms results
in lines of intensity.*



Surface is combination.



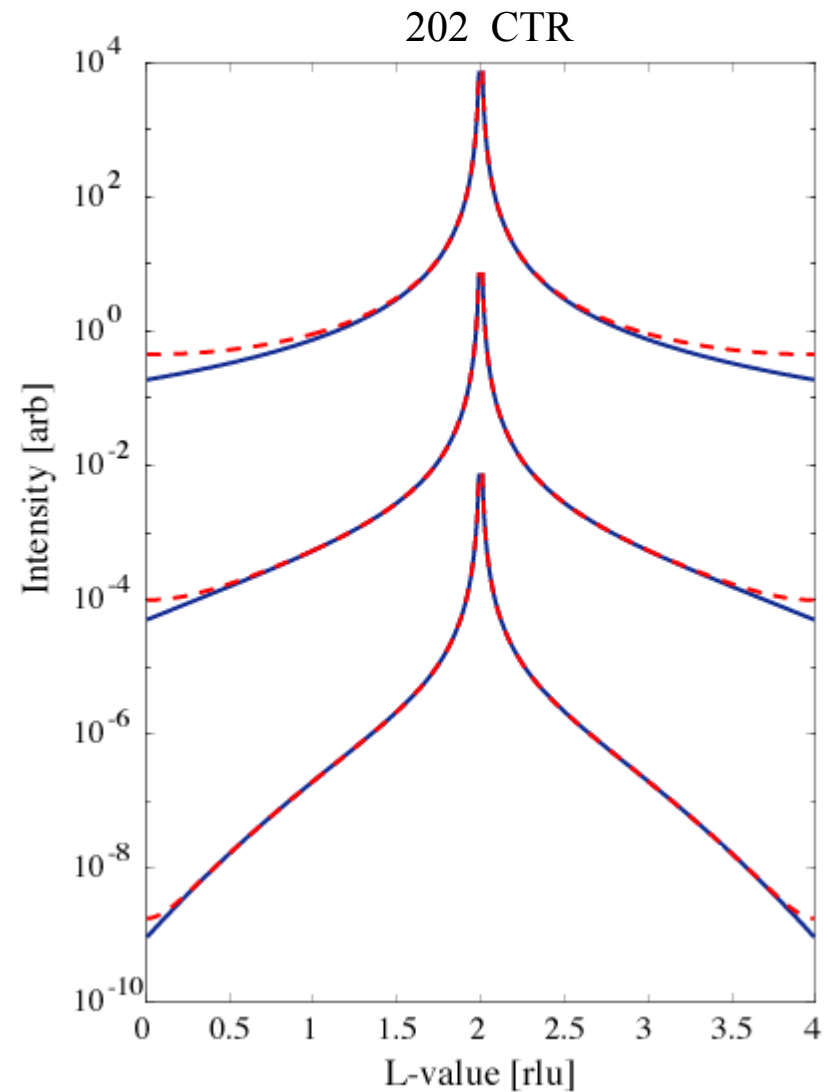
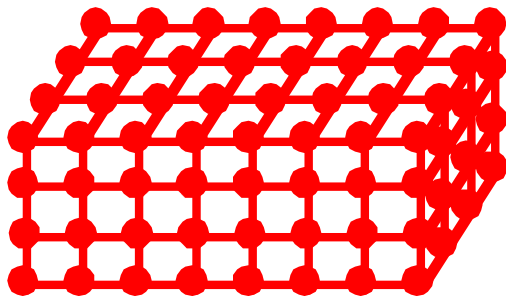
Surface Scattering



CTR: crystal truncation rod

IK Robinson PRB **33**, 3830
(1986).

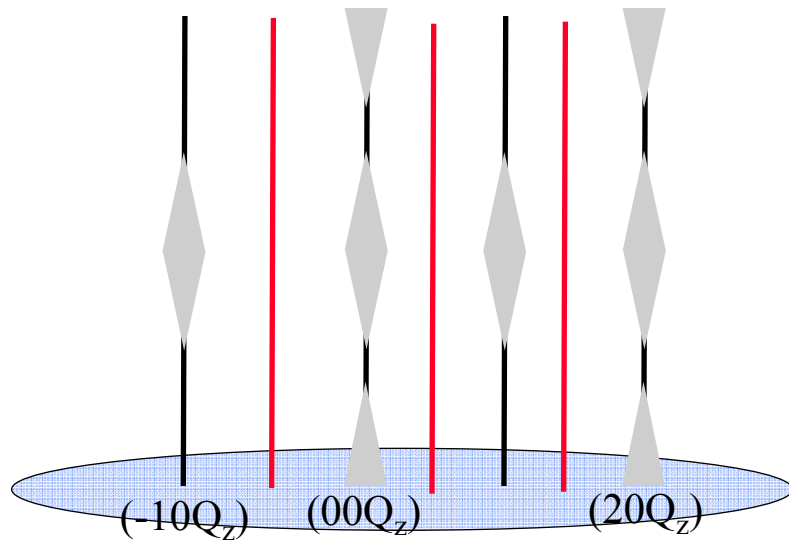
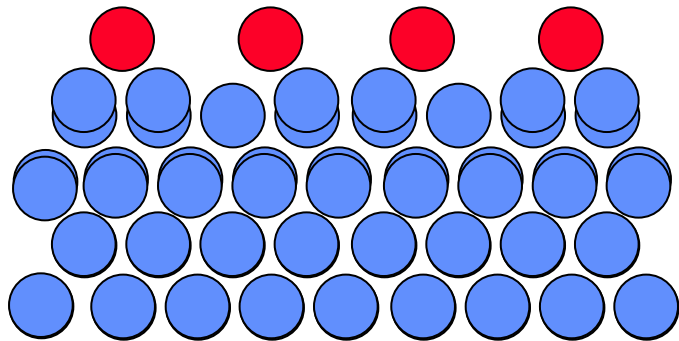
A. Munkholm, S. Brennan
& E.C. Carr, J. Appl. Phys.
82, 2944 (1997).



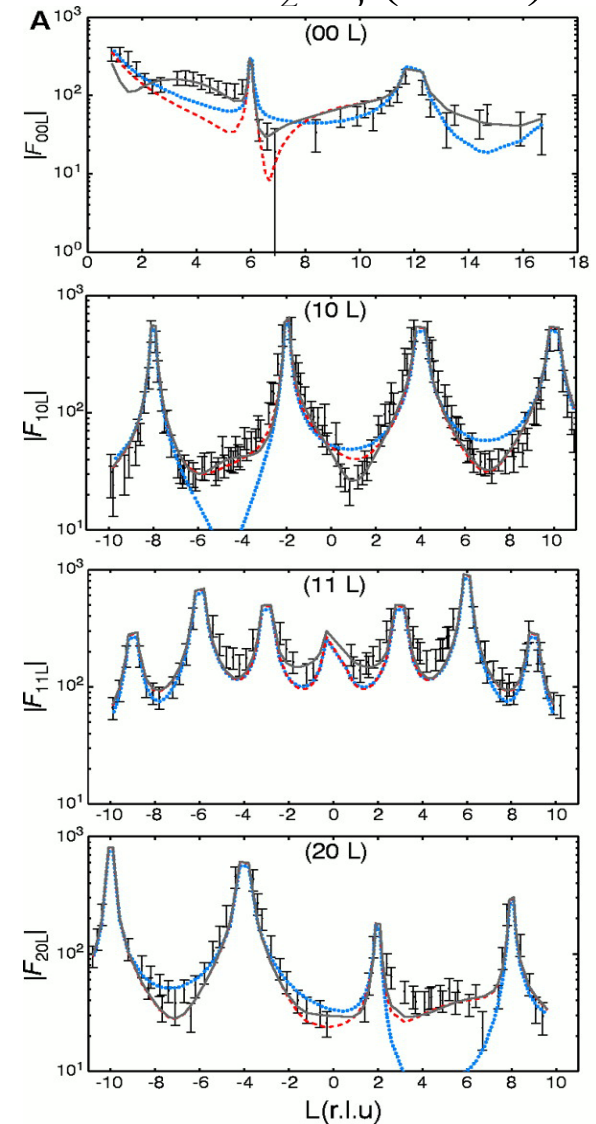
Hydrated Oxide Surface Structure



Surface XRD to probe



α - Al_2O_3 (0001)

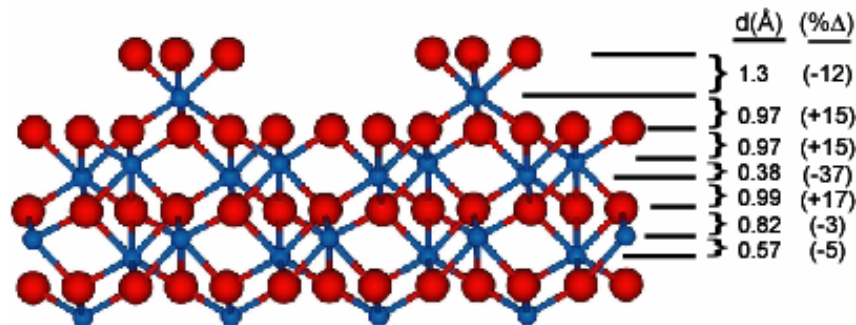


Eng et al., Science **288**, 1029 (2000)

Hydrated Oxide Surface Structure

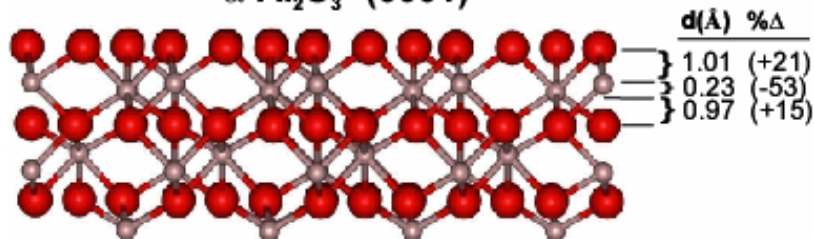


$\alpha\text{-Fe}_2\text{O}_3$ (0001)



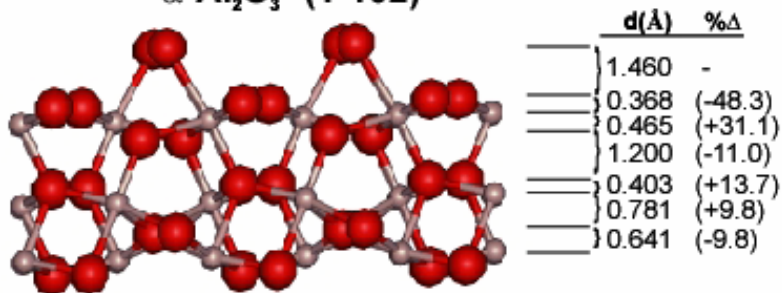
Some hydrated surface structures

$\alpha\text{-Al}_2\text{O}_3$ (0001)



Eng et al., Science **288**, 1029 (2000)
Trainor et al., Surf Sci **496**, 238 (2002)
Trainor et al., Surf Sci (2004)

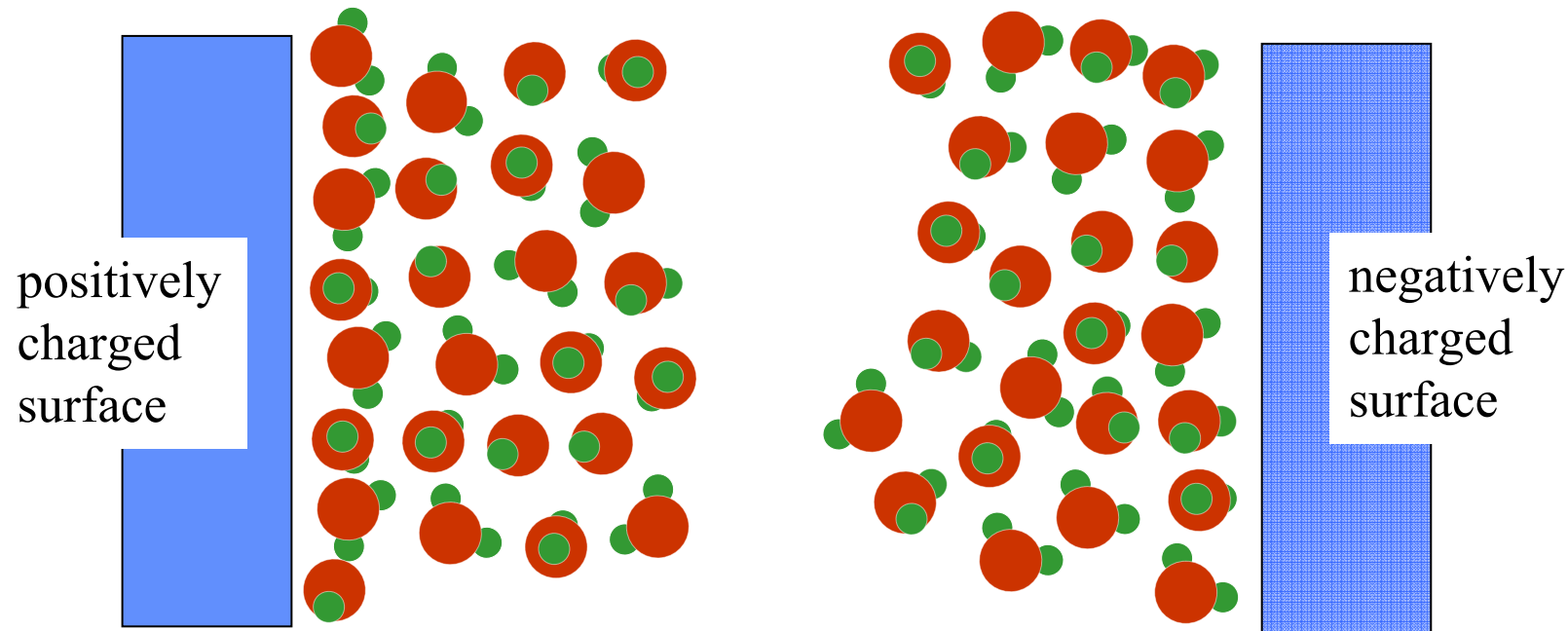
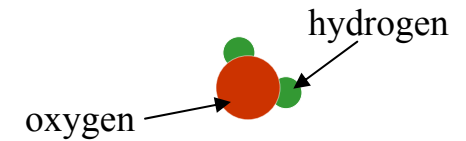
$\alpha\text{-Al}_2\text{O}_3$ (1-102)



Interfacial Water Structure



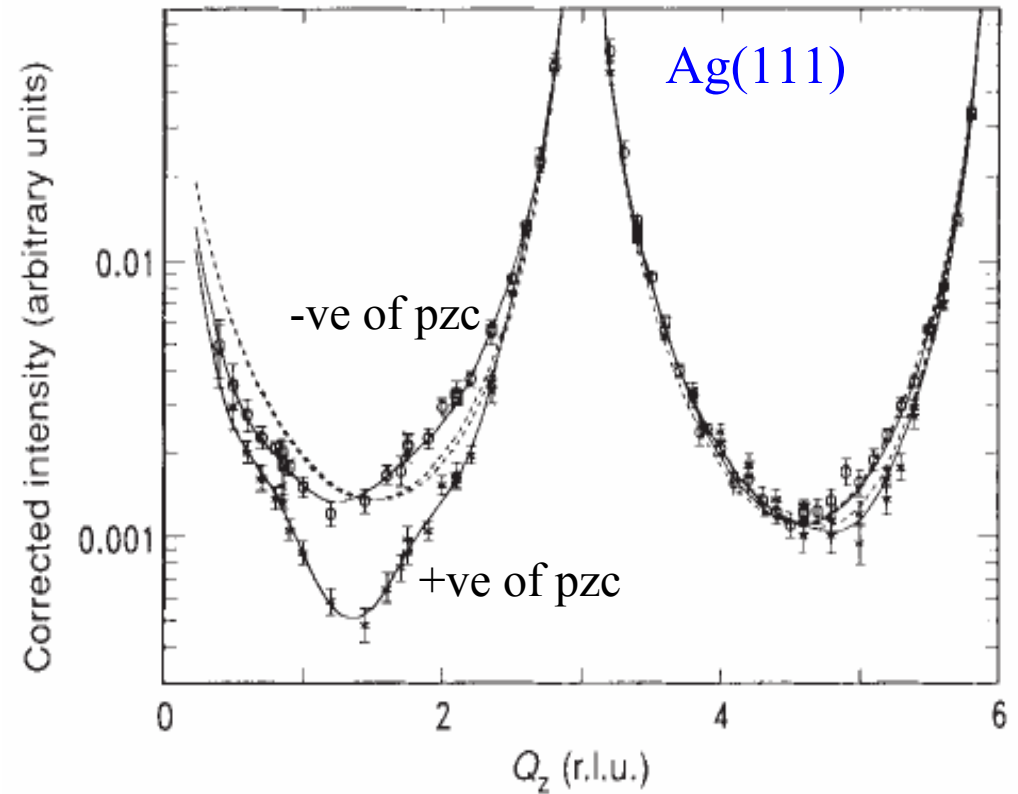
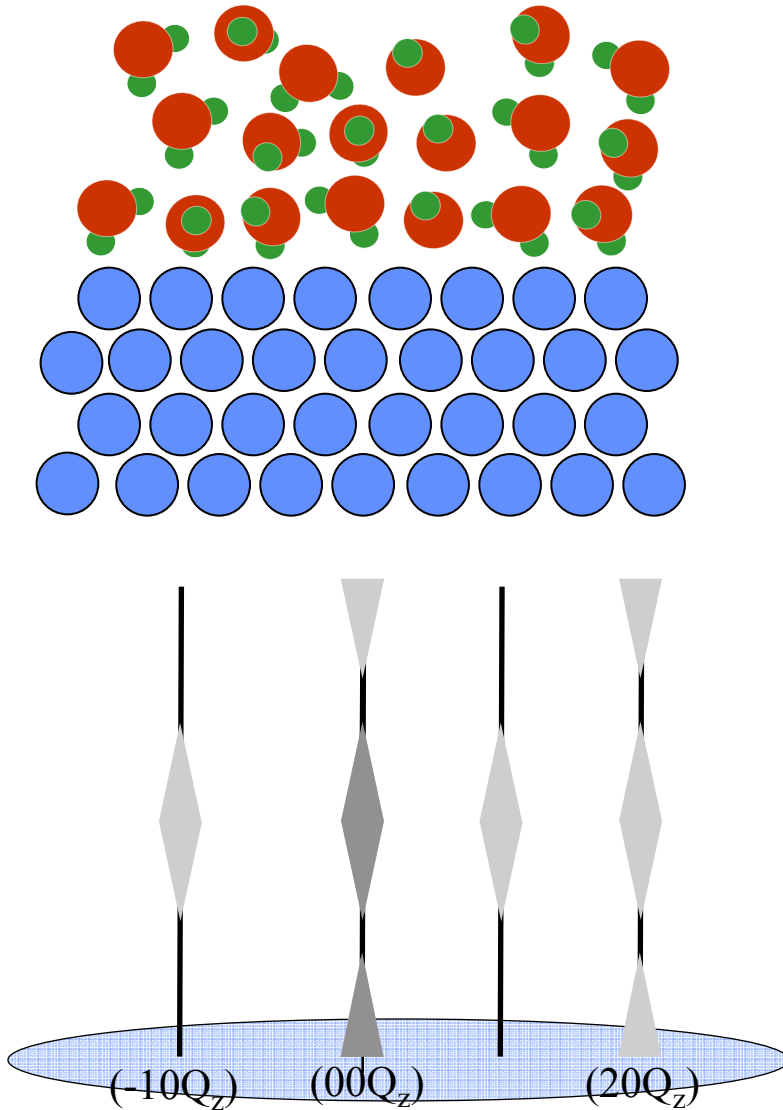
- microscopic picture of the arrangement of water at oxide-aqueous interfaces



Interfacial Water Structure

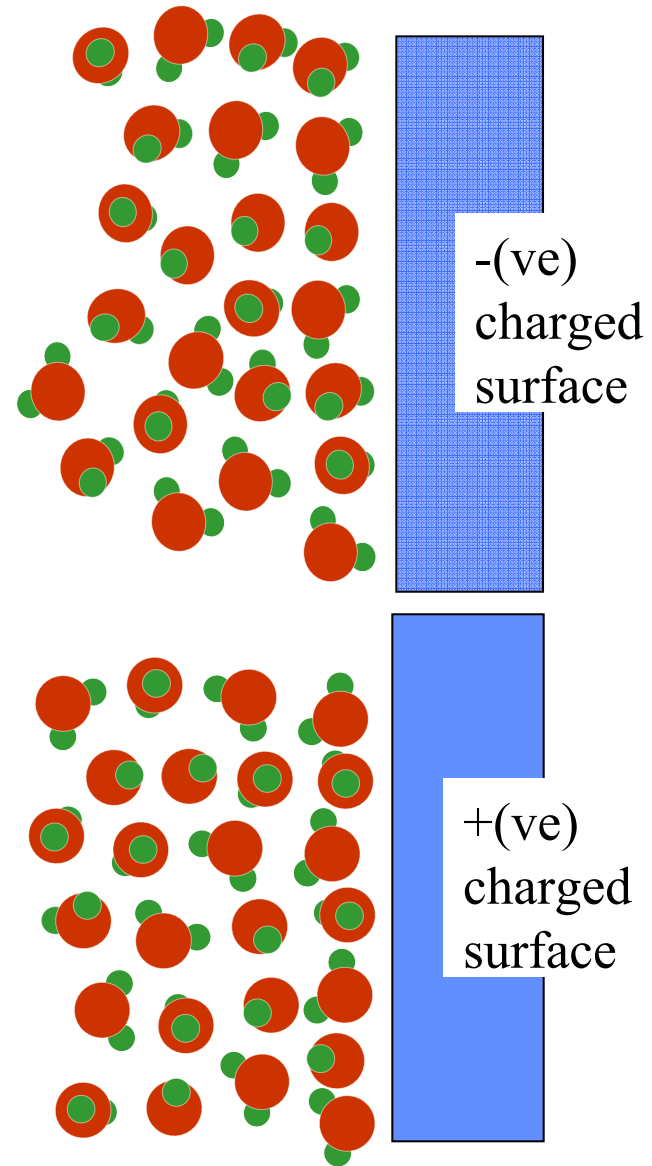
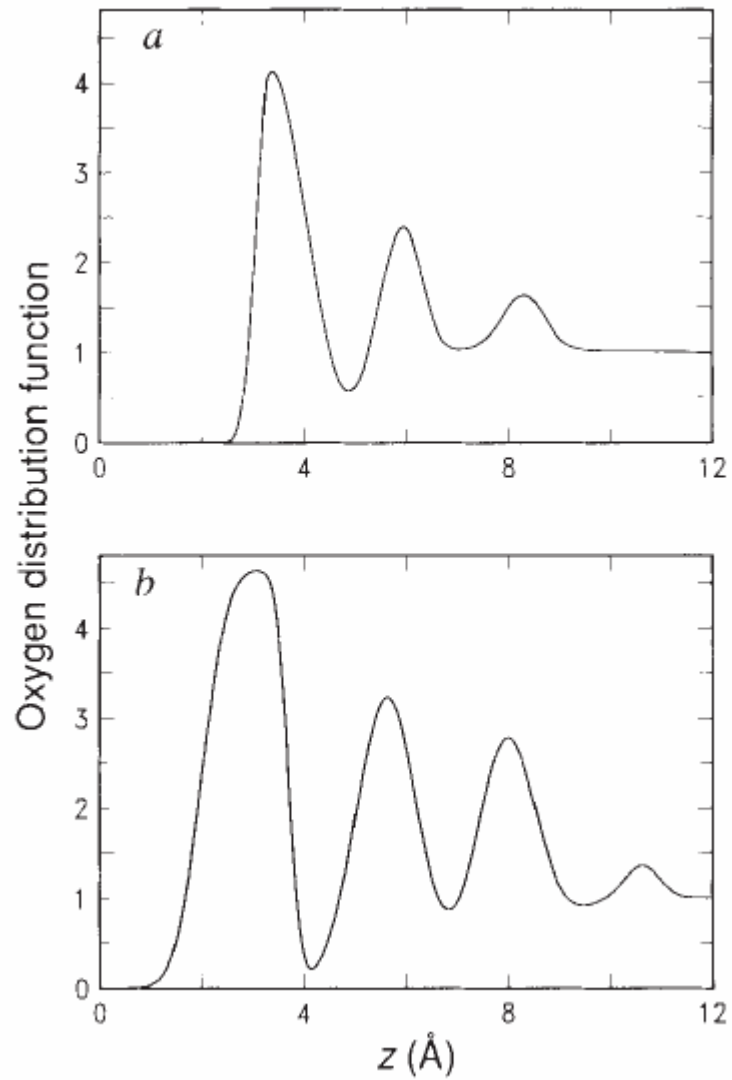


Surface X-ray Diffraction or Crystal Truncation Rods (CTRs)

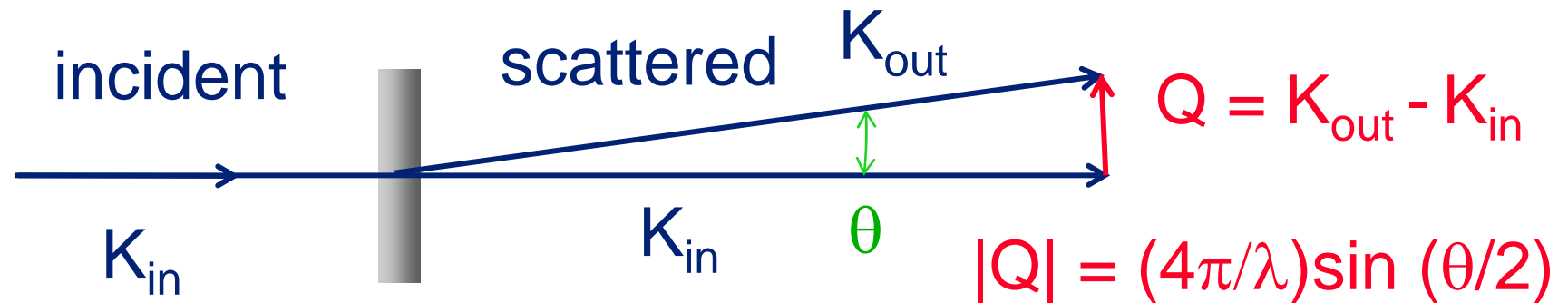


Toney et al., Nature **368**, 444 (1994)

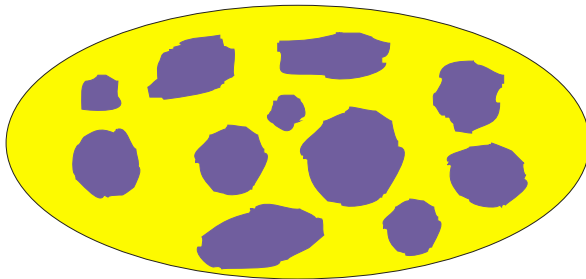
Interfacial Water Structure



Small Angle Scattering



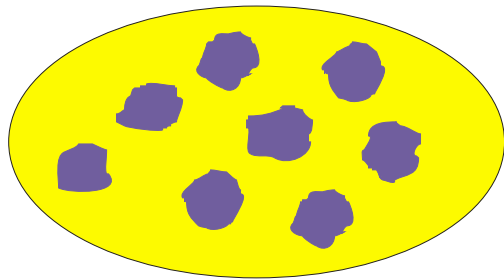
Measure $I(Q)$ with $Q \sim 0.0001 - 1 \text{ \AA}^{-1}$
Scattering from density inhomogeneities
of size $0.5 - 1000 \text{ nm}$



Small X-ray Angle Scattering Intensity



$$I(Q) = \frac{1}{V} \left| \int \rho(\mathbf{r}) e^{i\mathbf{Q} \cdot \mathbf{r}} d^3\mathbf{r} \right|^2 \quad \rho(\mathbf{r}) = \text{electron density}$$



$\rho_{1(2)}$ = electron density
in phase 1(2)

pores = particles

$$I(Q) = \frac{N}{V} (\rho_2 - \rho_1)^2 |F(Q)|^2 S(Q)$$

single particle
SAXS

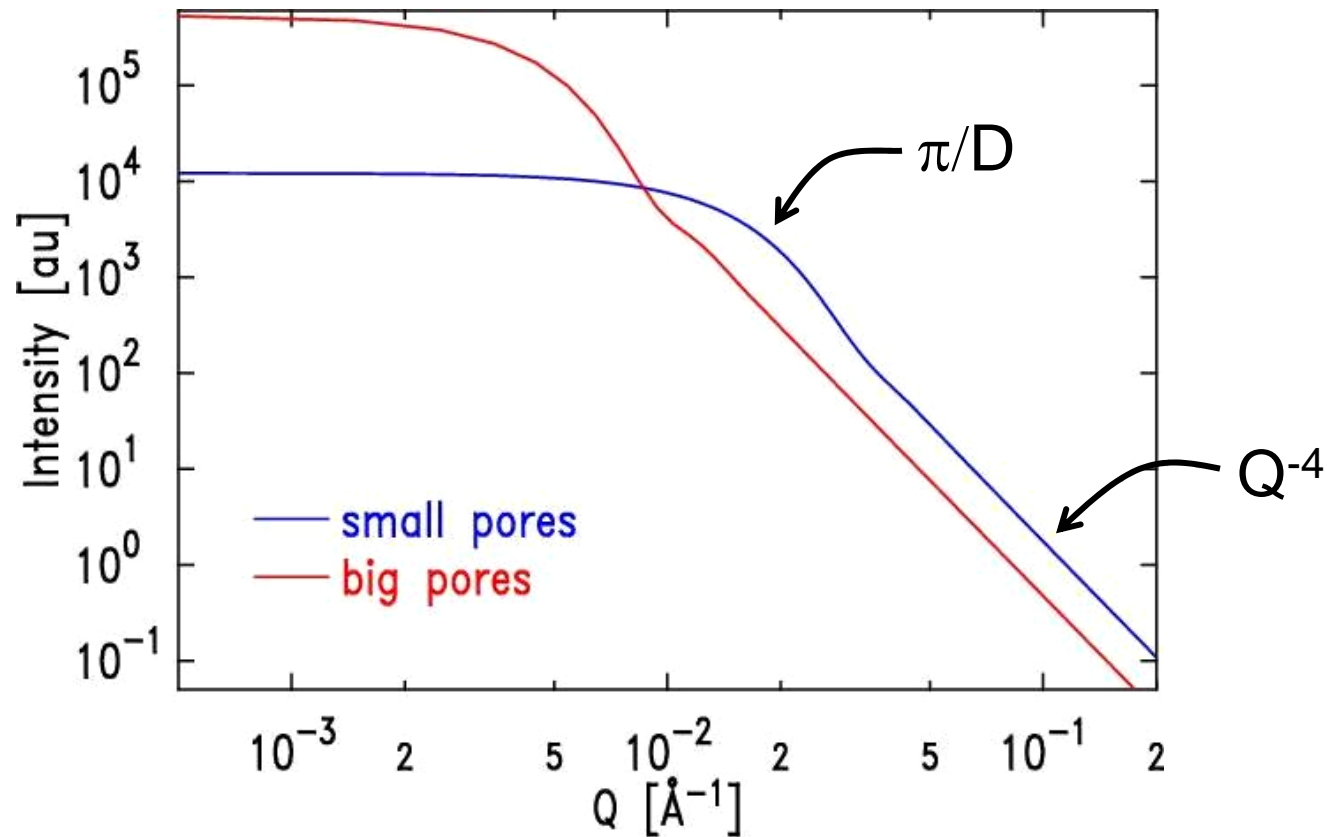
inter particle
scattering

$$\int_{V_1} e^{i\mathbf{Q} \cdot \mathbf{r}} d^3\mathbf{r}$$

Small Angle Scattering

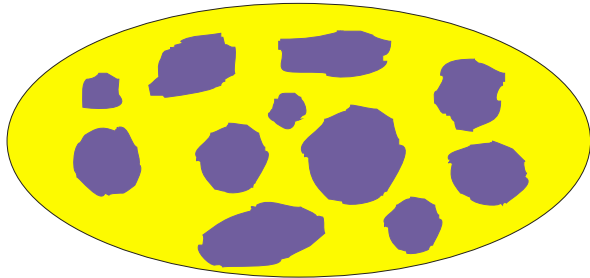


Isolated pores or particles with diameter D



- Experimental Q range gives range of accessible diameters
- Need $1/D \lesssim Q \lesssim 10/D$

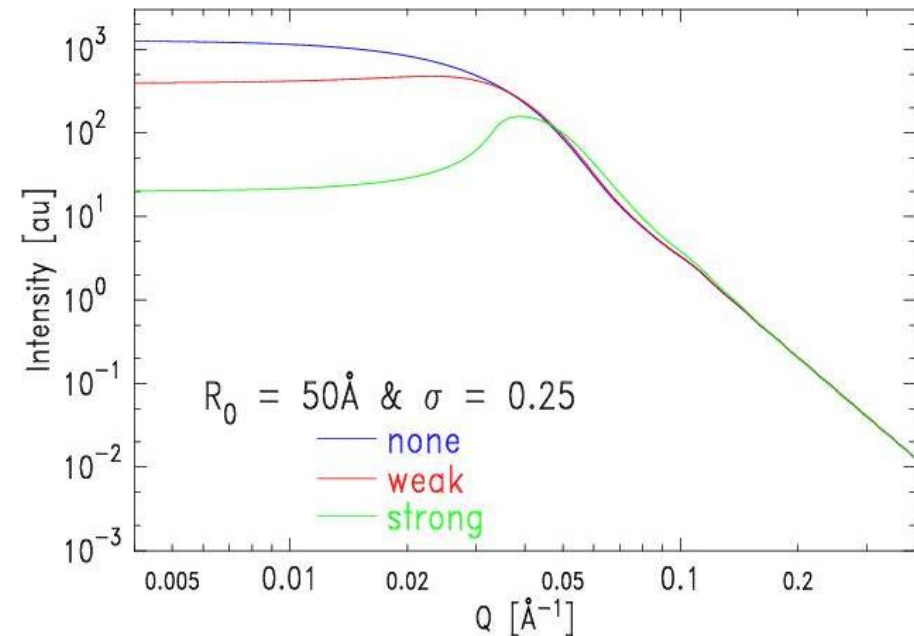
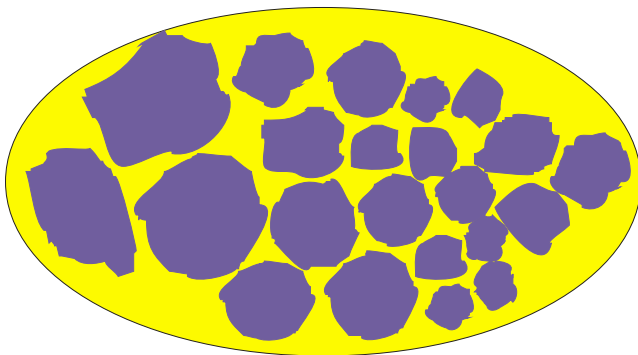
Inter-pore Interference: S(QR)



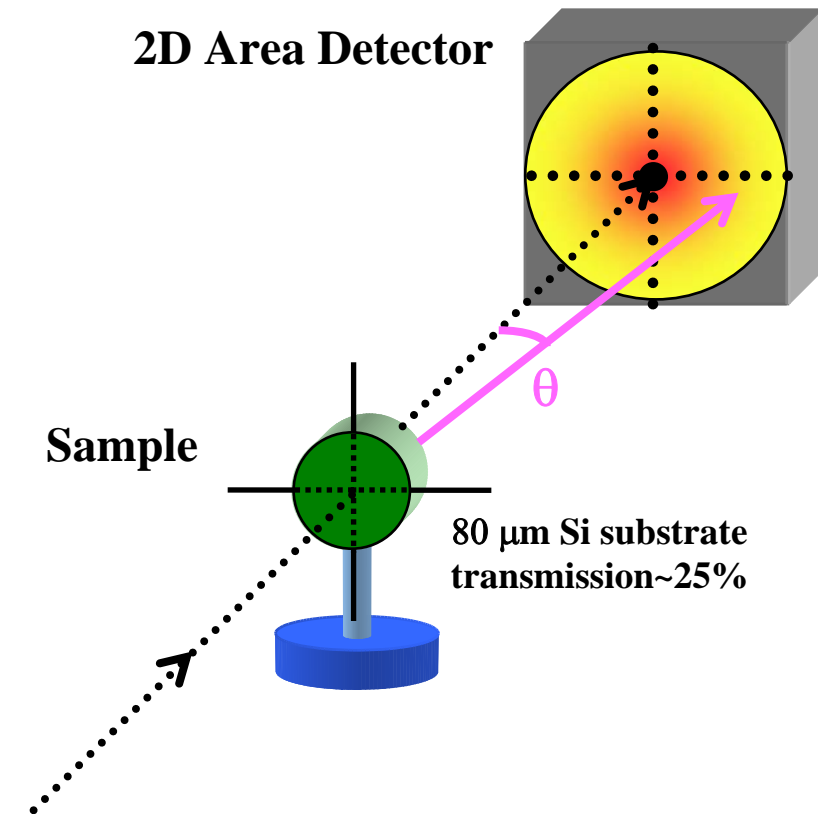
SAXS from nearby pores interfere

$S(QR)$ = interference function using local mono-disperse approximation (positions correlated with size)

JS Pederson, J Appl. Cryst. **27**, 595 (1994)



SAXS Setup



2D Area Detector

Sample

80 μm Si substrate
transmission~25%

Incident X-Ray Beam
Monochromate to $E=7.66$ keV,
Slits: 100 x 100 or 200 x 200 μm

- Sample to detector distance defines Q range (for a given λ)
- $Q = (4\pi/\lambda) \sin(\theta/2)$
- Two or three detector distances (0.1m to 3m) & incident beam sizes
- Gives large Q range
- Performed in transmission
- Window-less environment

**Advanced
Photon
Source**

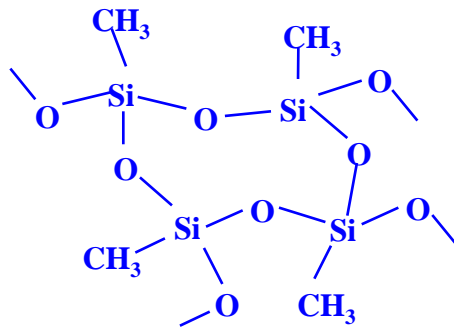


Nanoporous Films



Components

Matrix



**Methyl Silsesquioxane
(MSSQ), CH₃SiO_{1.5}**

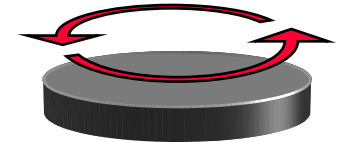
Porogen



**Thermally
Labile Polymer**

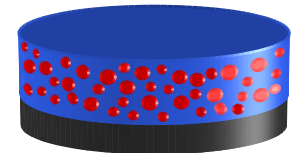
Processing

1. Spin coat MSSQ/Porogen solution



Spin
Coat

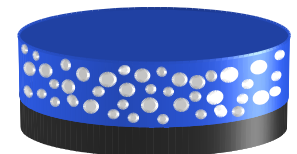
2. Heat to 450°C, at
5°C/min under argon



*MSSQ crosslinks at 200°C
Poragen fully degrades at 400°C*

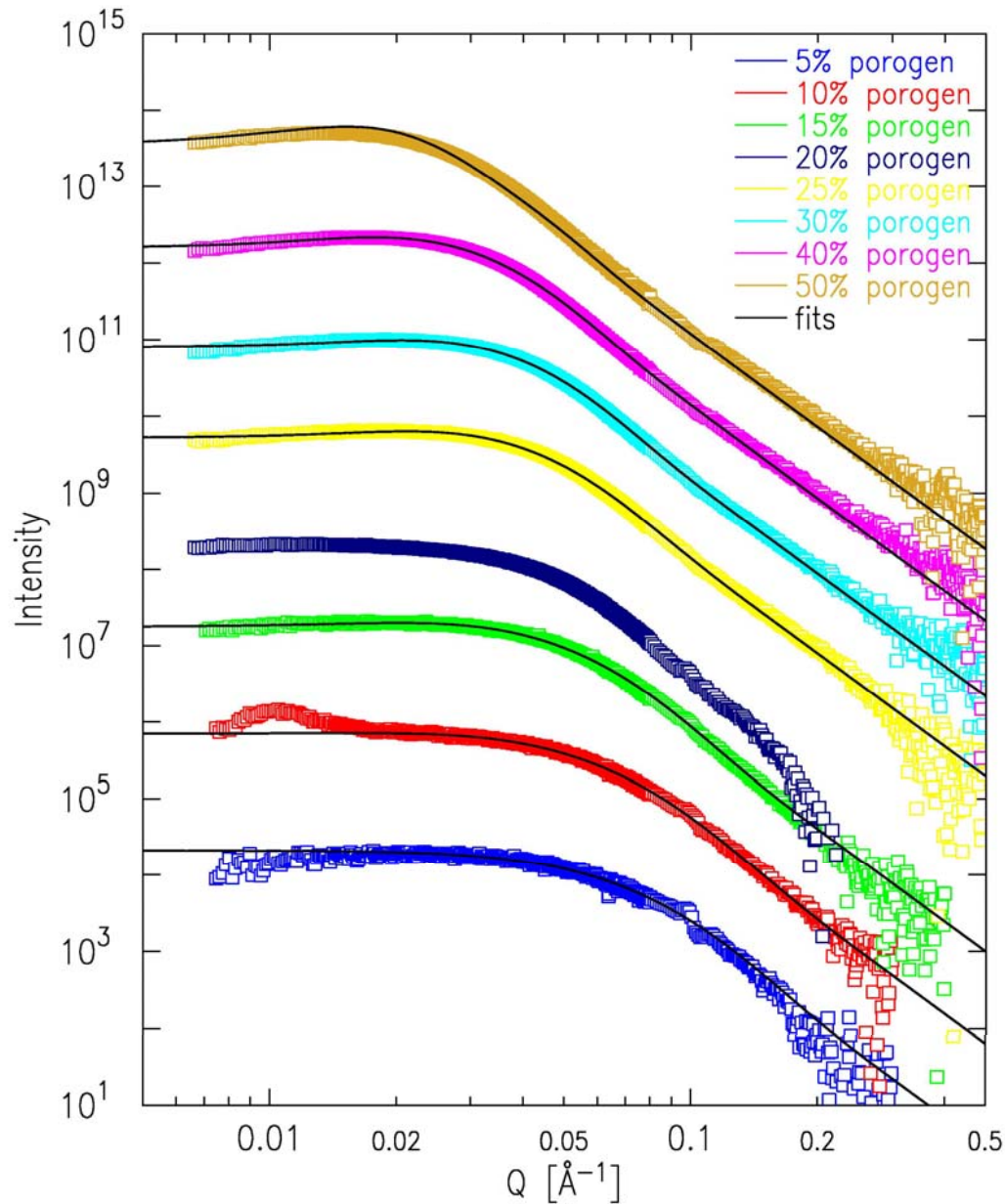
Δ Argon

3. Cool to room temperature



Porogens: copolymer poly(methyl methacrylate-*co*-dimethylaminoethyl methacrylate) or P(MMA-*co*-DMAEMA) & poly(ϵ -caprolactone) or PCL (6-armed star)

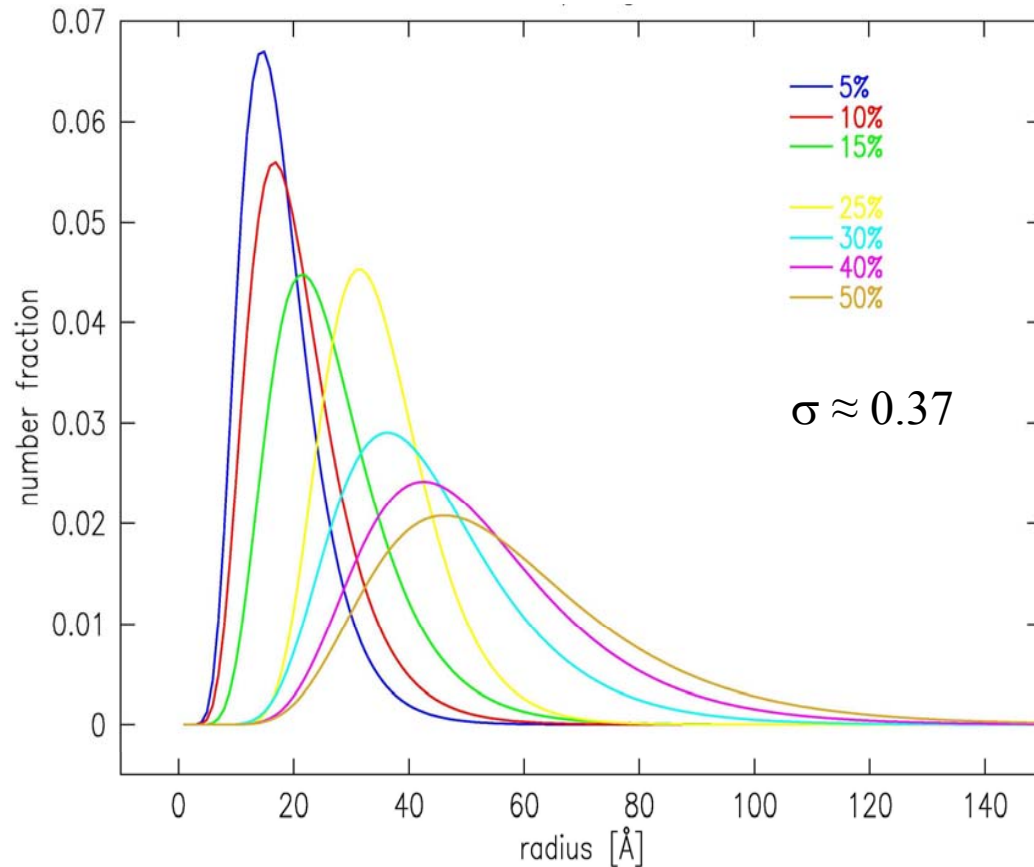
Small Angle X-ray Scattering



- MSSQ matrix
- P(MMA-*co*-DMAEMA) porogen
- Loading = weight percent in initial material
- Porosity is about 90% of loading
- Fits with local monodisperse model and log-normal distribution

Huang et al, Appl. Phys. Lett.
81, 2232 (2002)

Pore Size Distribution

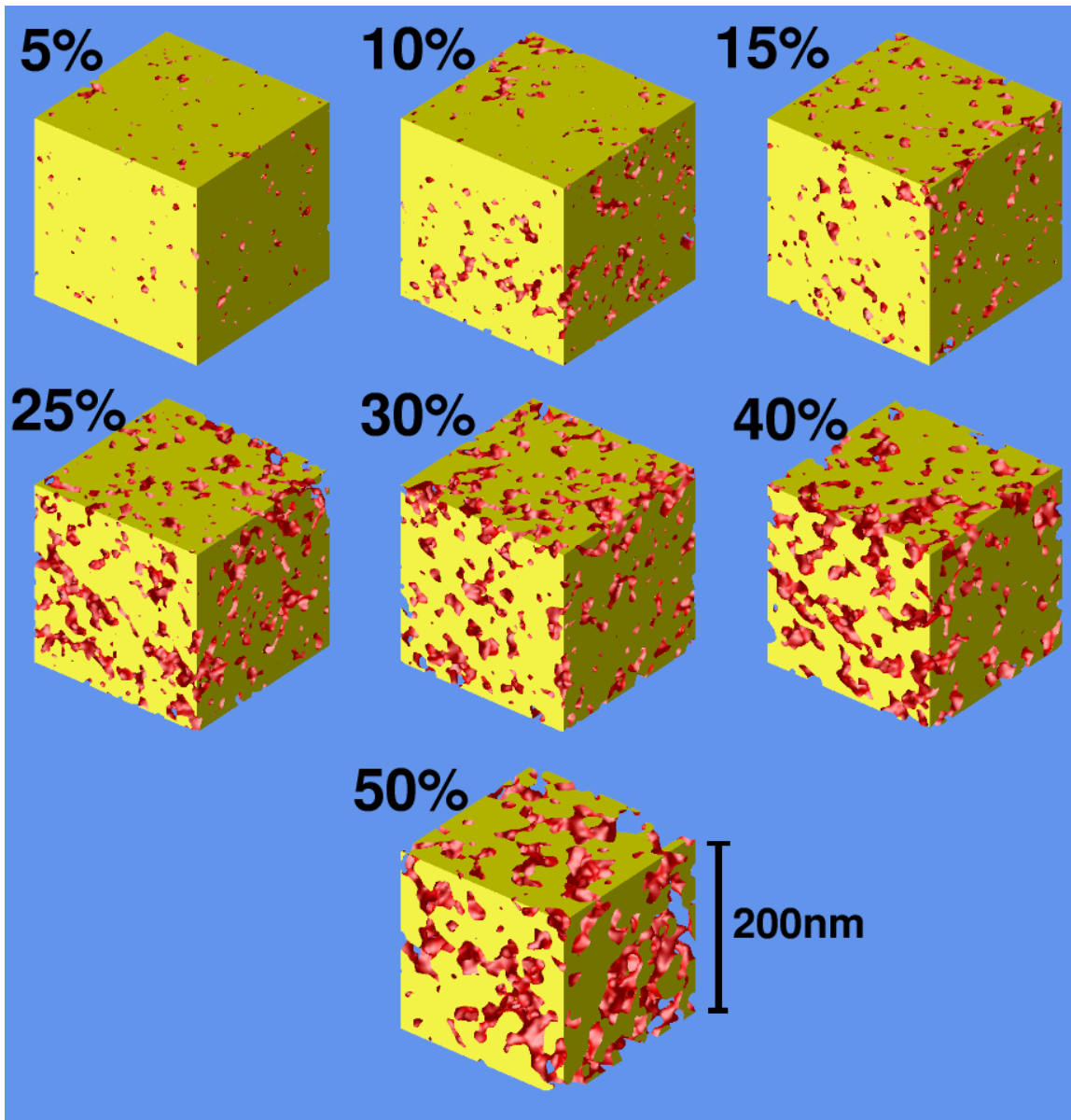


Approximations:

- treat pores as spheres (ignore shape)
- local mono-disperse approximation for inter-pore scattering

loading	$\langle R \rangle$ (nm)	D/2 (nm)
10%	2.1	2.6
15%	2.7	3.1
30%	4.5	4.5
40%	5.3	5.4

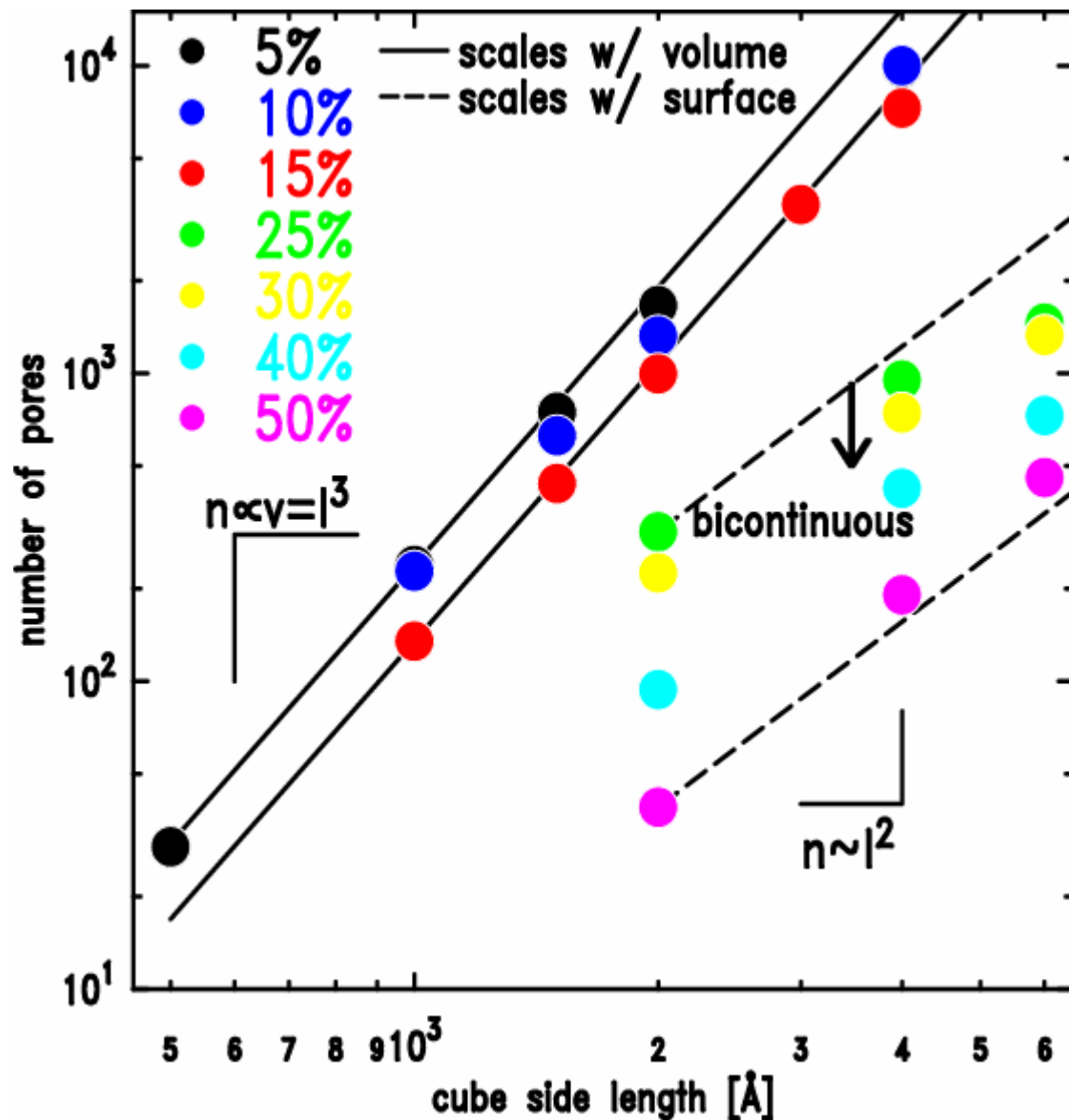
Nanoporous Films



Reconstruction of
Pore Morphology
Allows determination
of transition from
closed pores to
open pores to
bicontinuous
microstructure

*Hedstrom et al, Langmuir
20, 1535 (2004)*

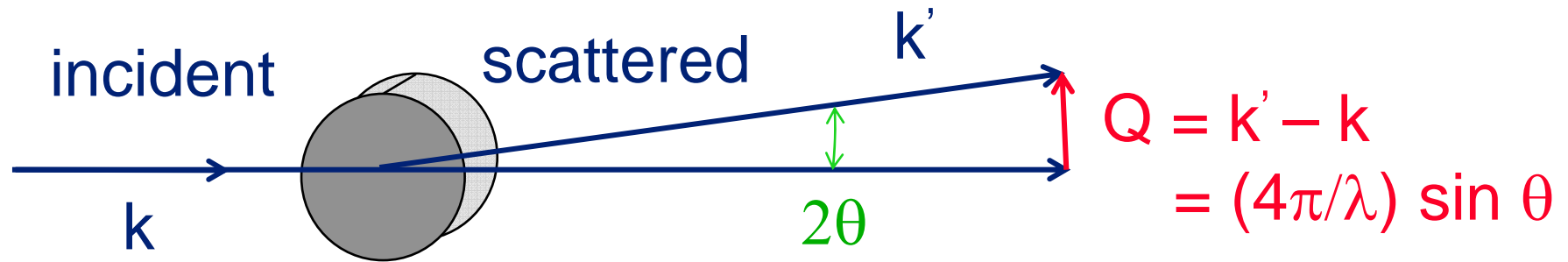
Nanoporous Films



closed and interconnected:
 number \sim length³
 bicontinuous:
 number \sim length²

=> transition to
 bicontinuous
 occurs between
 15 & 25 %

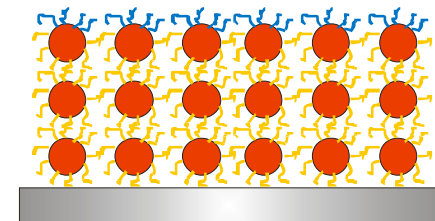
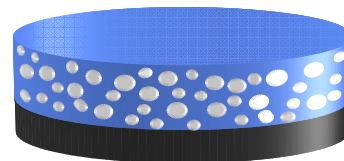
Grazing Incidence SAXS



- Use grazing incidence to limit penetration depth
- Measure $I(Q)$ with $Q \sim 0.01 - 1 \text{ \AA}^{-1}$
- Scattering from density inhomogeneities of size $50 - 100 \text{ \AA}$

Applications:

- Nanoparticles imbedded in thin films
- Nanoparticles on surfaces



Summary



1. Peak Widths & Defects
 - Nanoparticles
2. Monoatomic Layers – Pentacene again
3. Surface Diffraction
 - Oxide Surfaces
 - Interfacial Water
4. SAXS applications to porous and particulate materials