X-ray and Neutron Scattering from Crystalline Surfaces and Interfaces

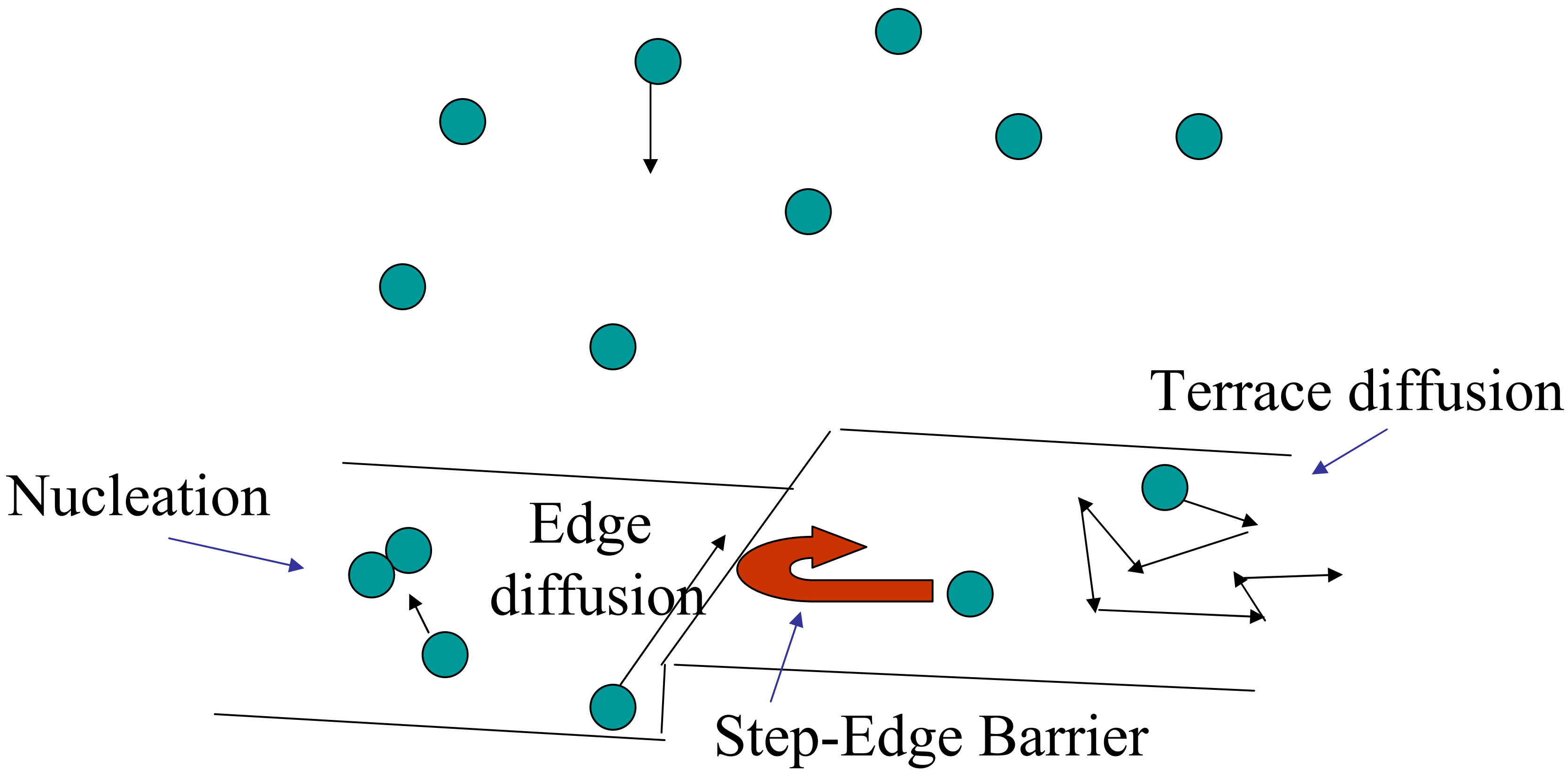
Paul F. Miceli,
Department of Physics and Astronomy
University of Missouri-Columbia

National School for X-ray and Neutron Scattering
Argonne and Oak Ridge National Laboratories

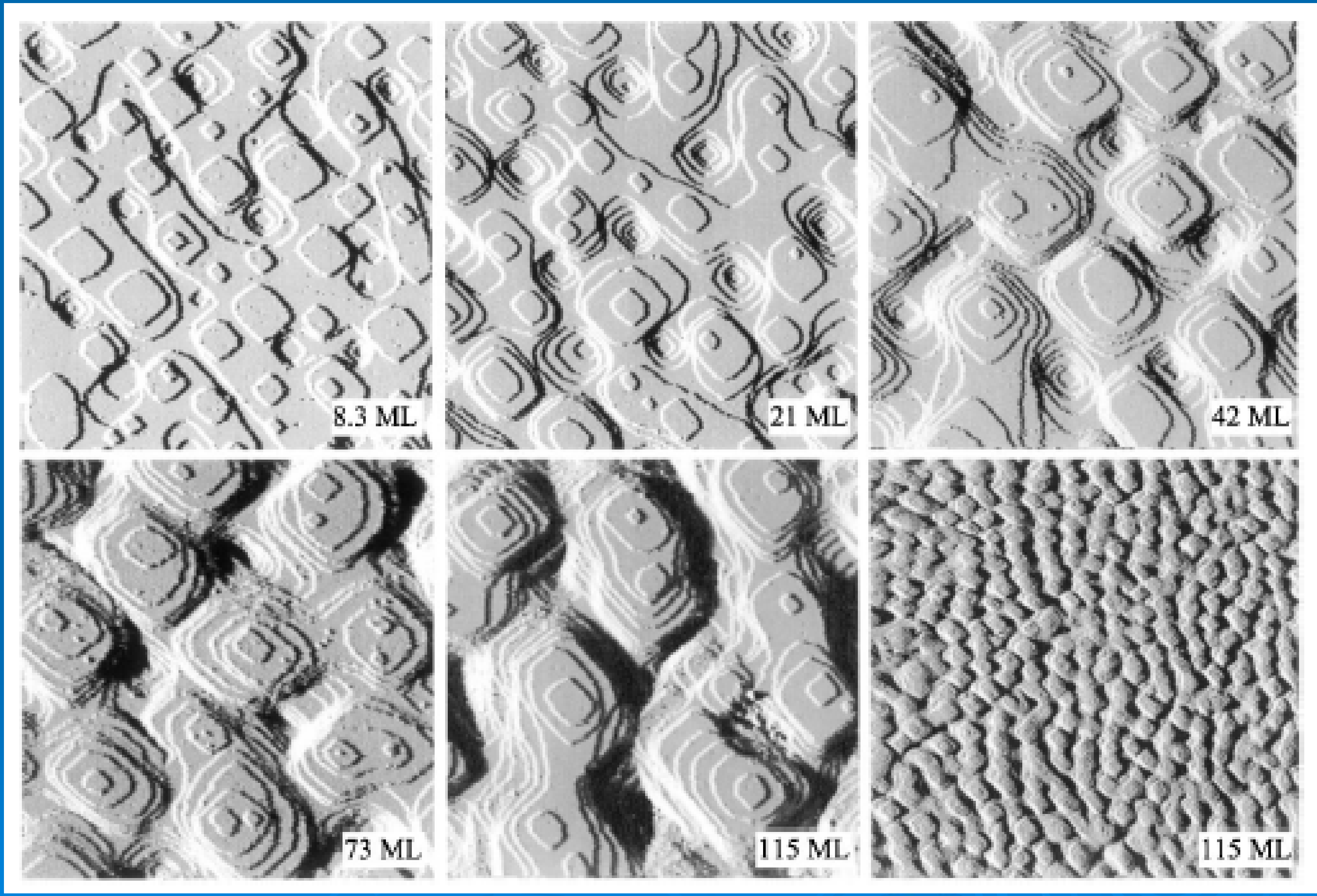
June 23, 2011

Many thanks to students and collaborators:
W. Elliott, C. Botez, S.W. Han, M. Gramlich, S. Hayden, Y. Chen, C. Kim, C. Jeffrey, E. H. Conrad, C.J. Palmstrøm, P.W. Stephens; and to NSF and DOE for funding.

Crystal growth from the vapor

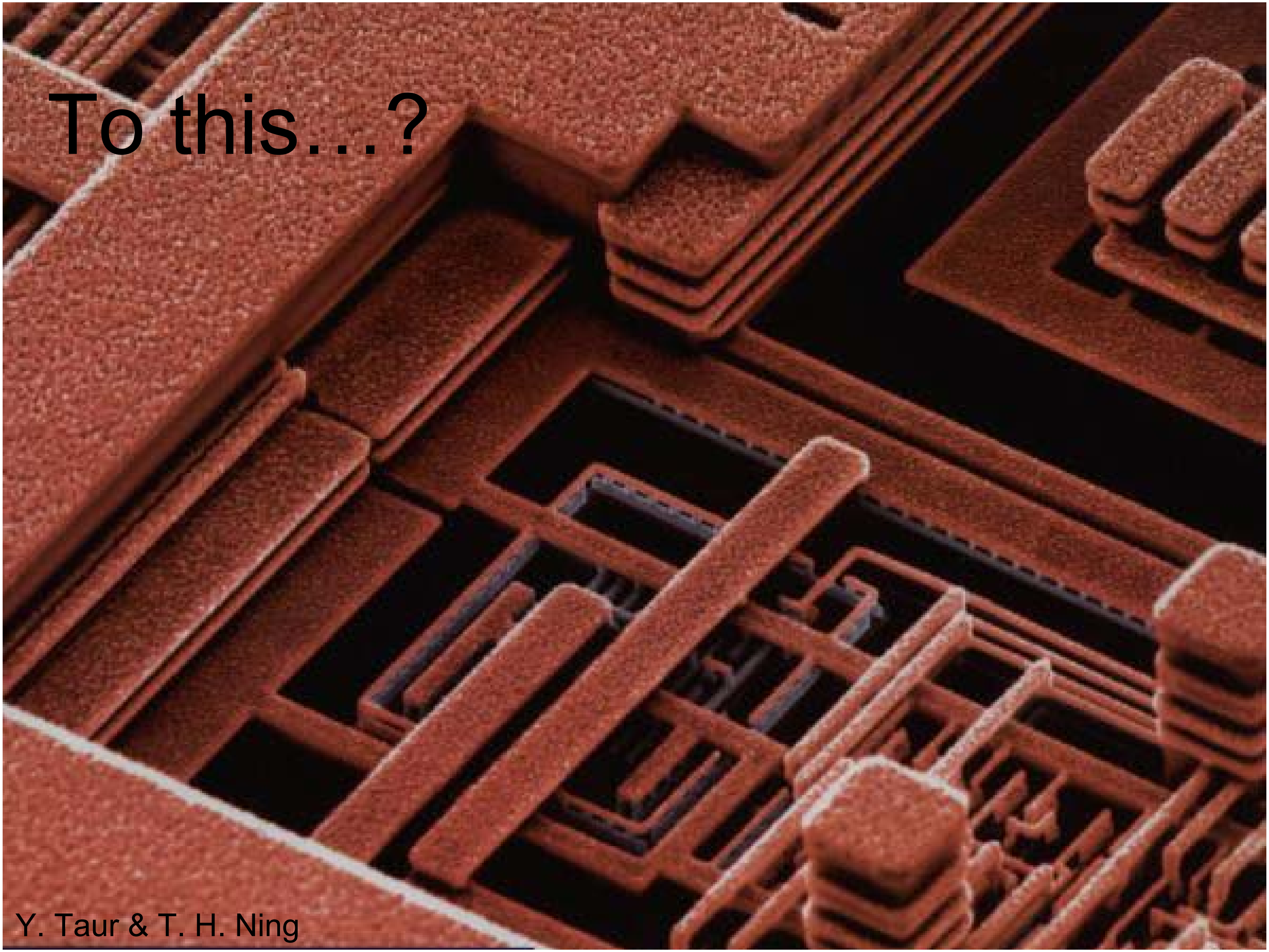


Morphology → atomic scale mechanisms



Cu/Cu(001)

Zuo & Wendelken


To this…?
Y. Taur & T. H. Ning

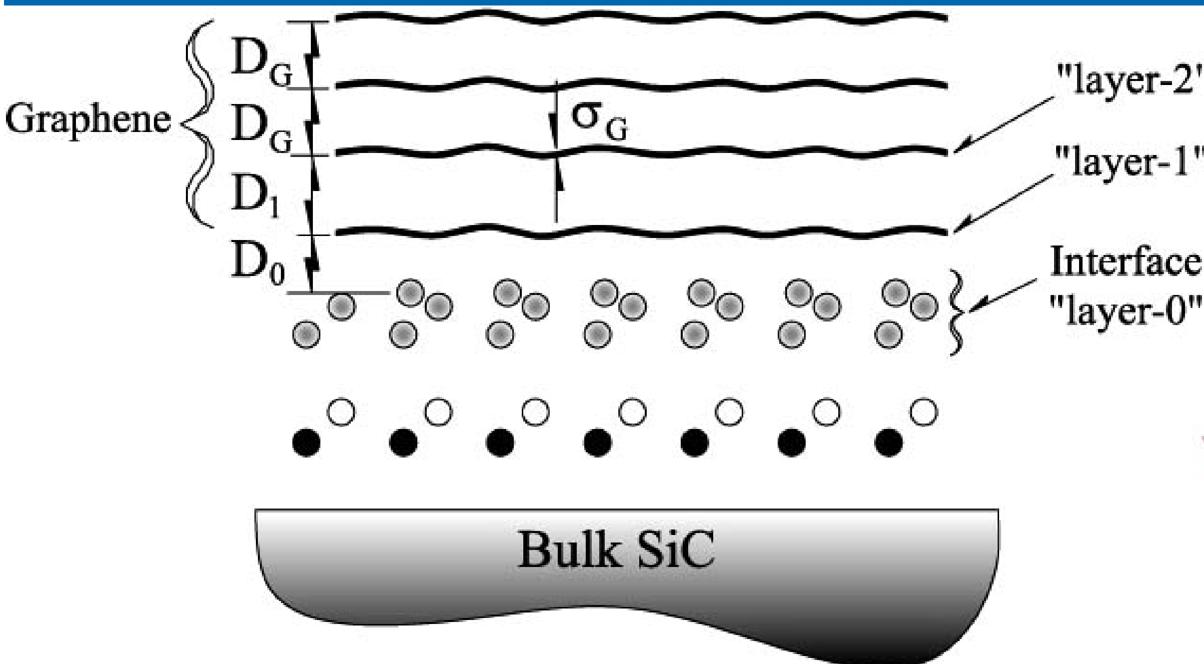
Interplay between two regimes of Length Scales

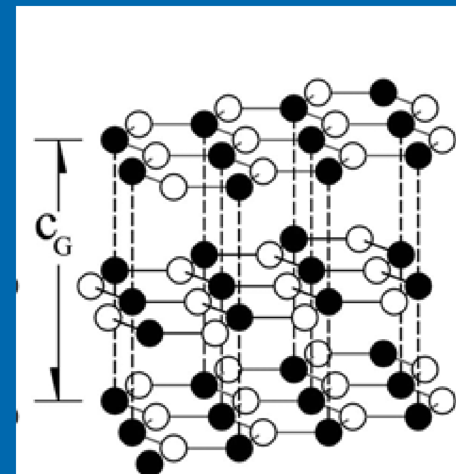
- Interatomic distances
  →Structure, physics, chemistry → Mechanisms

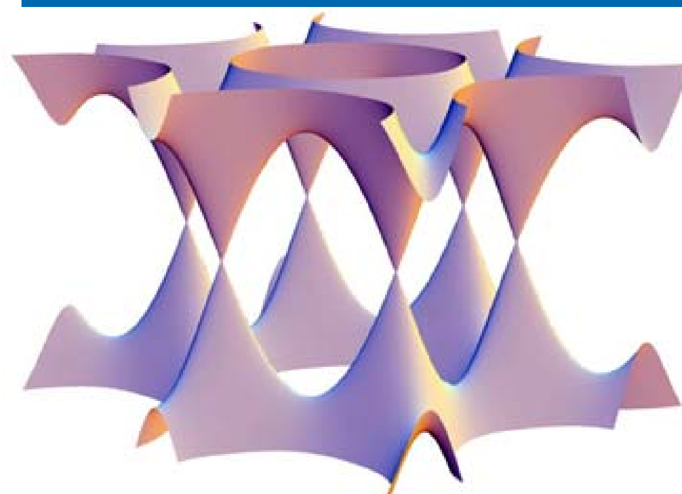
- “Mesoscale” – Nanoscale
  → Morphology → Mechanisms

Example:
Rotation of graphene planes affect electronic properties

Graphene made from SiC



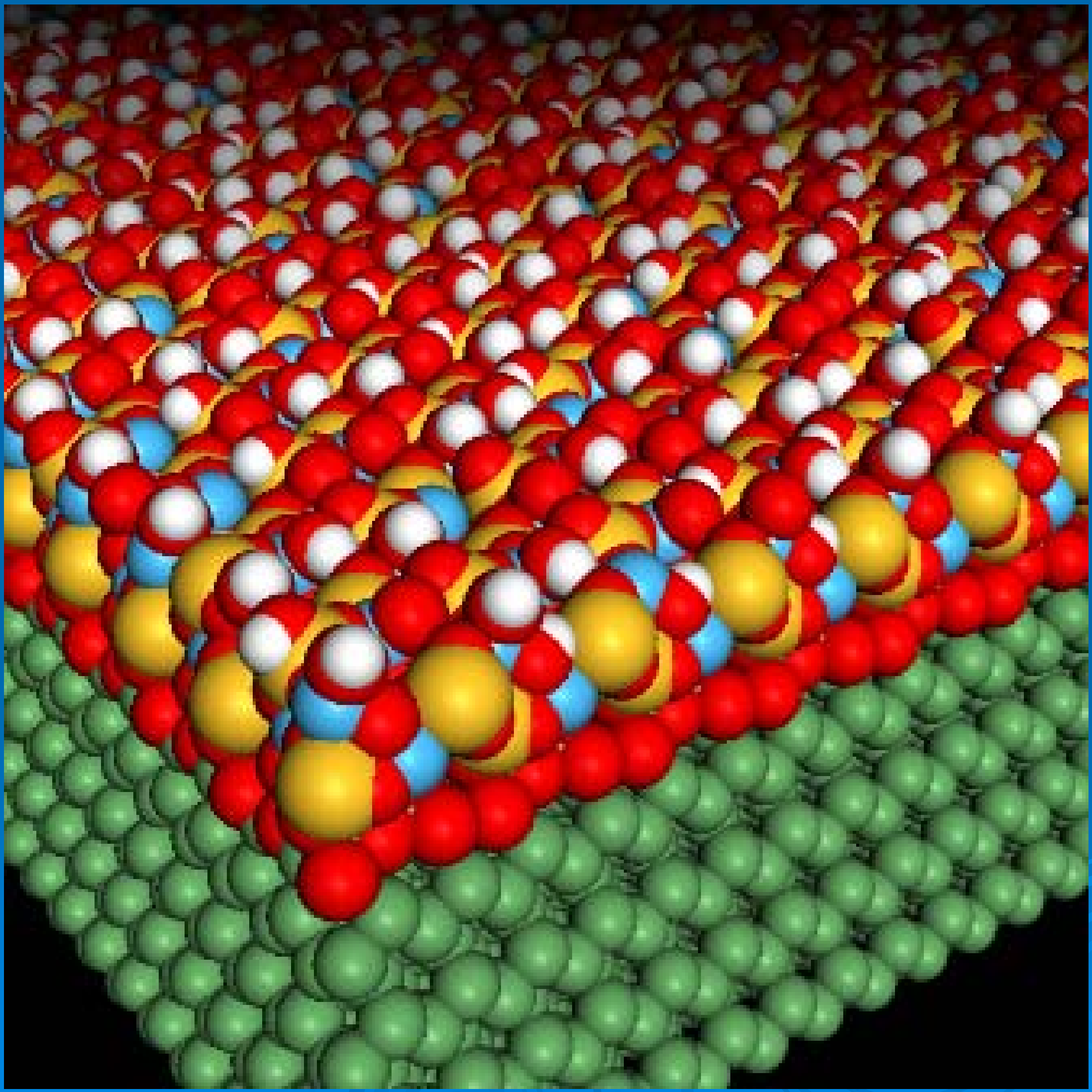




J. Phys.: Condens. Matter **20** (2008) 323202

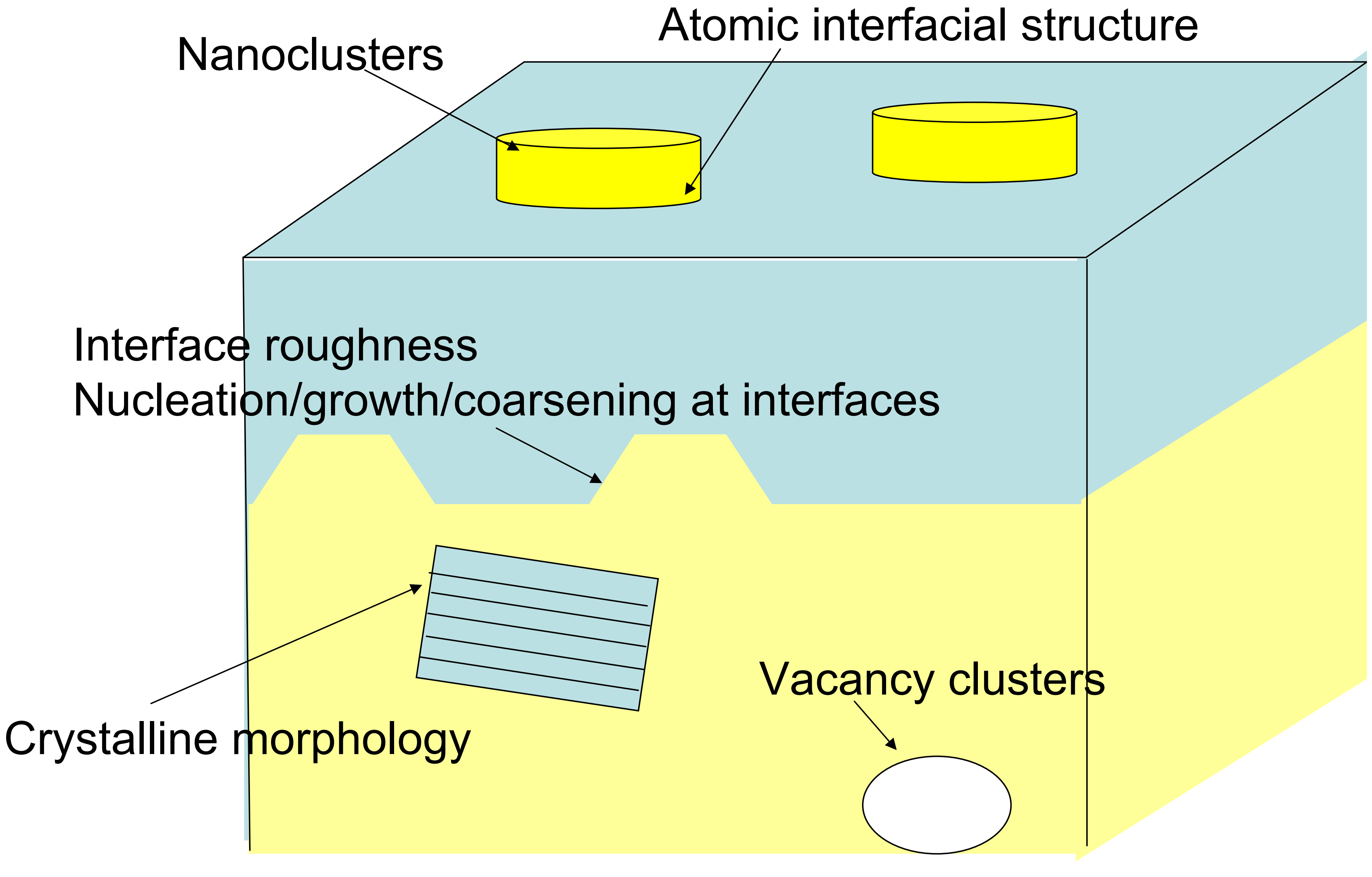
Buried Interface Structure

to understand the growth and function of materials



http://www.tyndall.ie/research/electronic-theory-group/thin_film_simulation.html

Morphology → atomic scale mechanisms



Unique Advantages of X-ray Scattering:

- Atomic-scale structure at a buried interface
- Morphological structure at buried interfaces
- Subsurface phenomena
  Strains and defects near a surface
- Accurate statistics of distributions
  (eg. Island size distributions)

Neutrons: low intensity- limited to reflectivity

- Soft Matter and Bio materials; H_2O & D_2O
- Magnetic materials

Objective

- An introduction to surface scattering techniques
  Build a conceptual framework

- Reciprocal Space is a large place: where do we look?

Scattering of X-rays and Neutrons: Helmholtz Equation

$$k = \frac{2\pi}{\lambda}$$

X-rays

$$\nabla^2 \vec{E} + k^2 n^2(\vec{r})\vec{E} = 0$$

Neutrons

$$\nabla^2 \Psi + \frac{2m}{\hbar^2}\left[E - V(\vec{r})\right]\Psi = 0$$

n(r)=inhomogeneous refractive index

Refractive Index for neutron: $n(\vec{r}) = \sqrt{1 - \frac{2m}{\hbar^2 k^2} V(\vec{r})} = \sqrt{1 - \lambda^2 \rho_b(\vec{r})/\pi}$

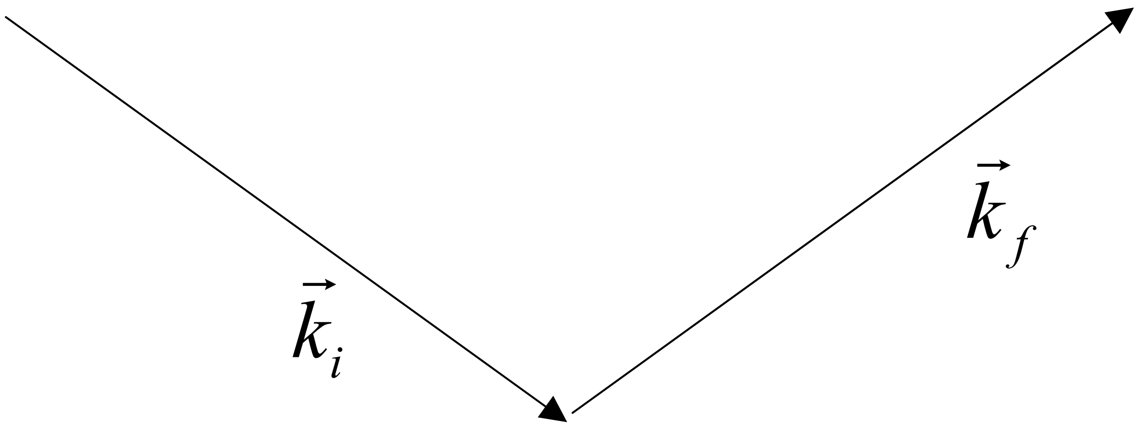
Scattering length density: $\rho_b(\vec{r}) \xrightarrow{monoatomic} \rho_N(\vec{r})\, b$

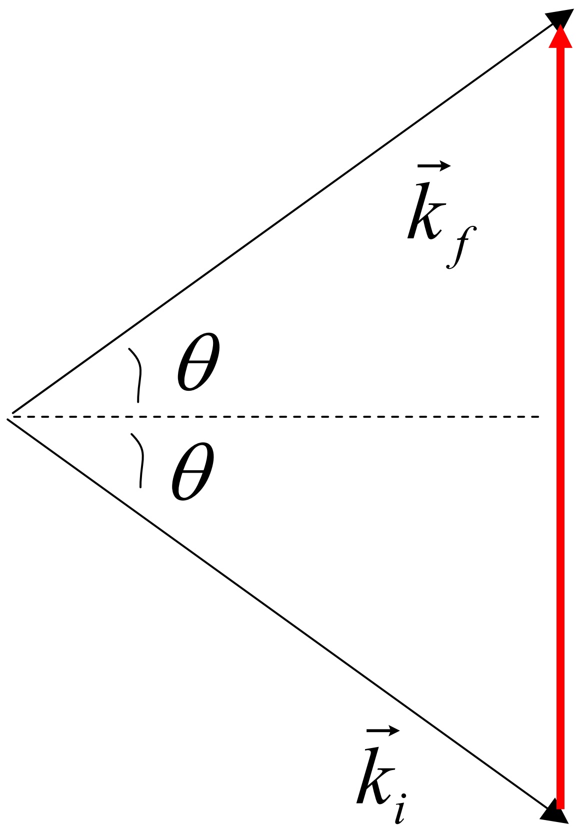
number density

scattering length:

$$b = \begin{cases} r_e f(Q) & x-rays \\ tabulated-neutrons \end{cases}$$

One language for both x-rays and neutrons





Wavevector Transfer:

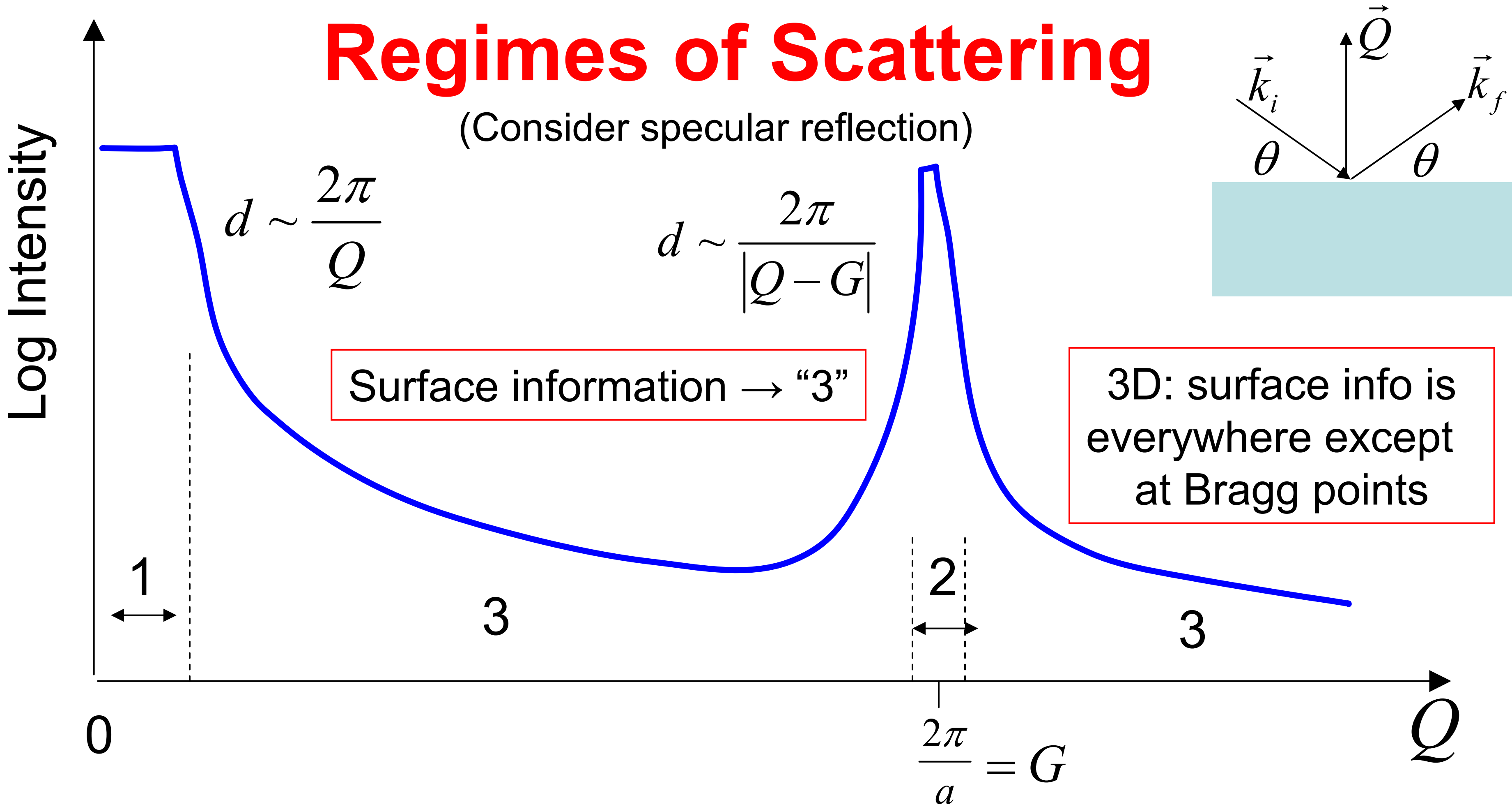
$$\vec{Q} = \vec{k}_f - \vec{k}_i$$

$$\left|\vec{Q}\right| = \frac{4\pi}{\lambda}\sin\theta \sim \frac{2\pi}{d}$$

Probing Length Scale

Regimes of Scattering

(Consider specular reflection)



1. Grazing angle reflectivity: strong scattering d>>interatomic distances
   Exact solution required. Neglect atomic positions: <u>homogeneous medium</u>

2. Bragg region: strong scattering; d~interatomic distances = a
   Exact solution required. Atomic positions needed. Similar to e^- band theory.

3. Everywhere else: weak scattering
   Born approximation →simplification. Atomic positions required.

Grazing Angles: Refraction and Total Reflection

d>>a: consider homogenous medium

Use average refractive index:

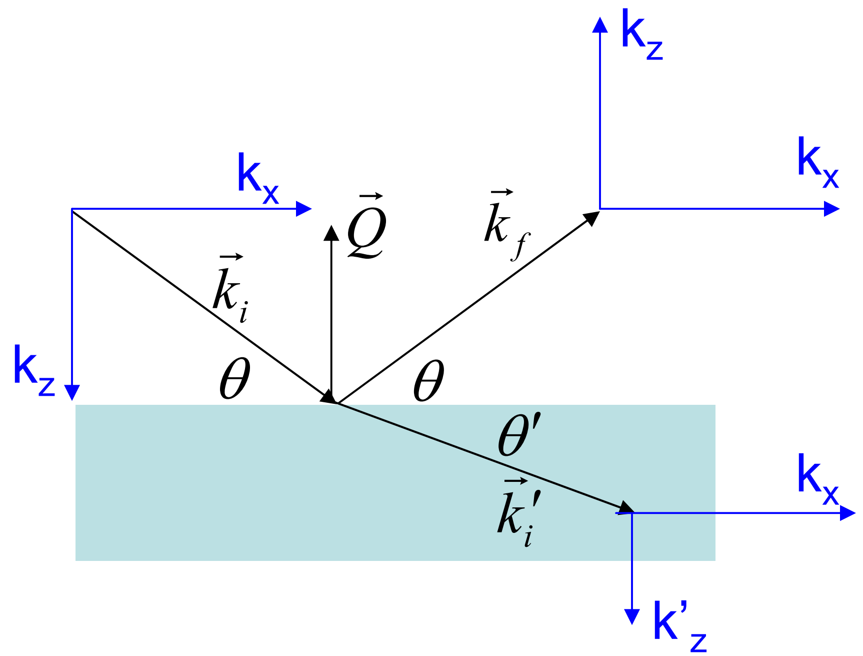
$$n = \sqrt{1 - \lambda^2 \rho_b / \pi} \equiv 1 - \delta \qquad \delta = \frac{\lambda^2 \rho_b}{2\pi} << 1 \quad (\sim 10^{-5})$$

With absorption: $n = 1 - \delta - i\beta$

Snell's Law:

$$\boxed{\sin^2 \theta' = \sin^2 \theta - 2\delta}$$

Critical Angle for Total Reflection: $\boxed{\theta_c = \sqrt{2\delta}}$



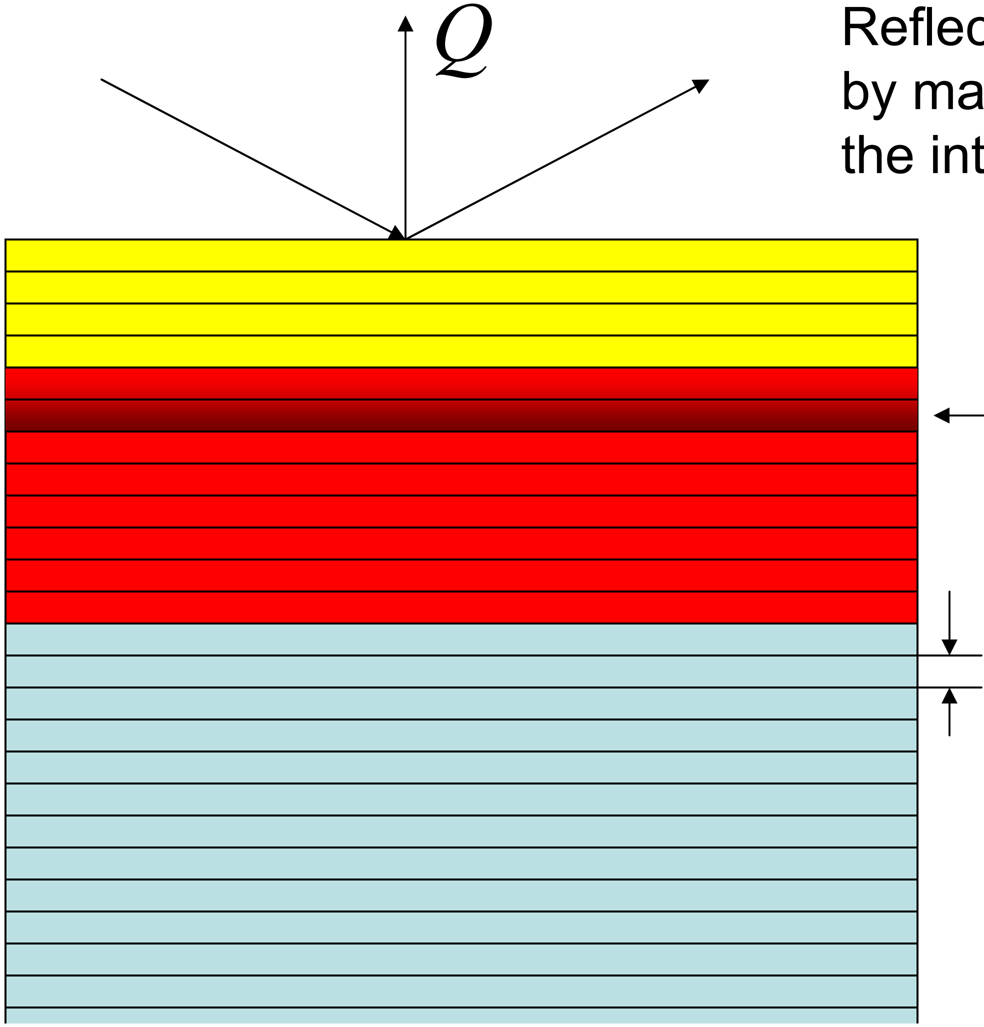
Wavevector transfer:

$$\boxed{Q'^2 = Q^2 - Q_c^2}$$

Only k_z component is affected by the surface.
k_x is unchanged.

$$\boxed{Q_c^2 = 16\pi\rho_b}$$

Calculation of reflectivity



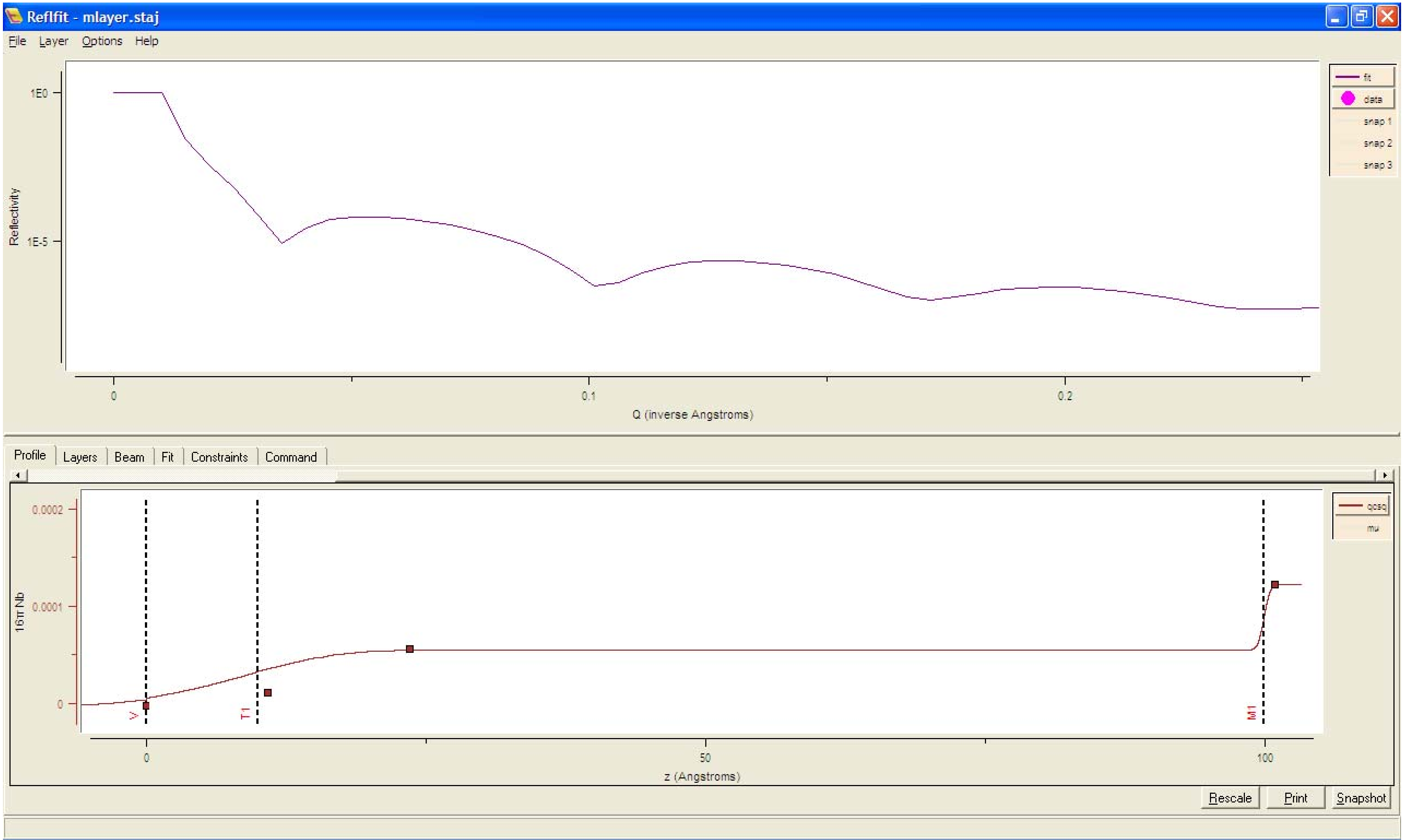
Reflectivity, R, can be calculated, exacty, by matching boundary conditions at the interfaces.

Include an interfacial transition

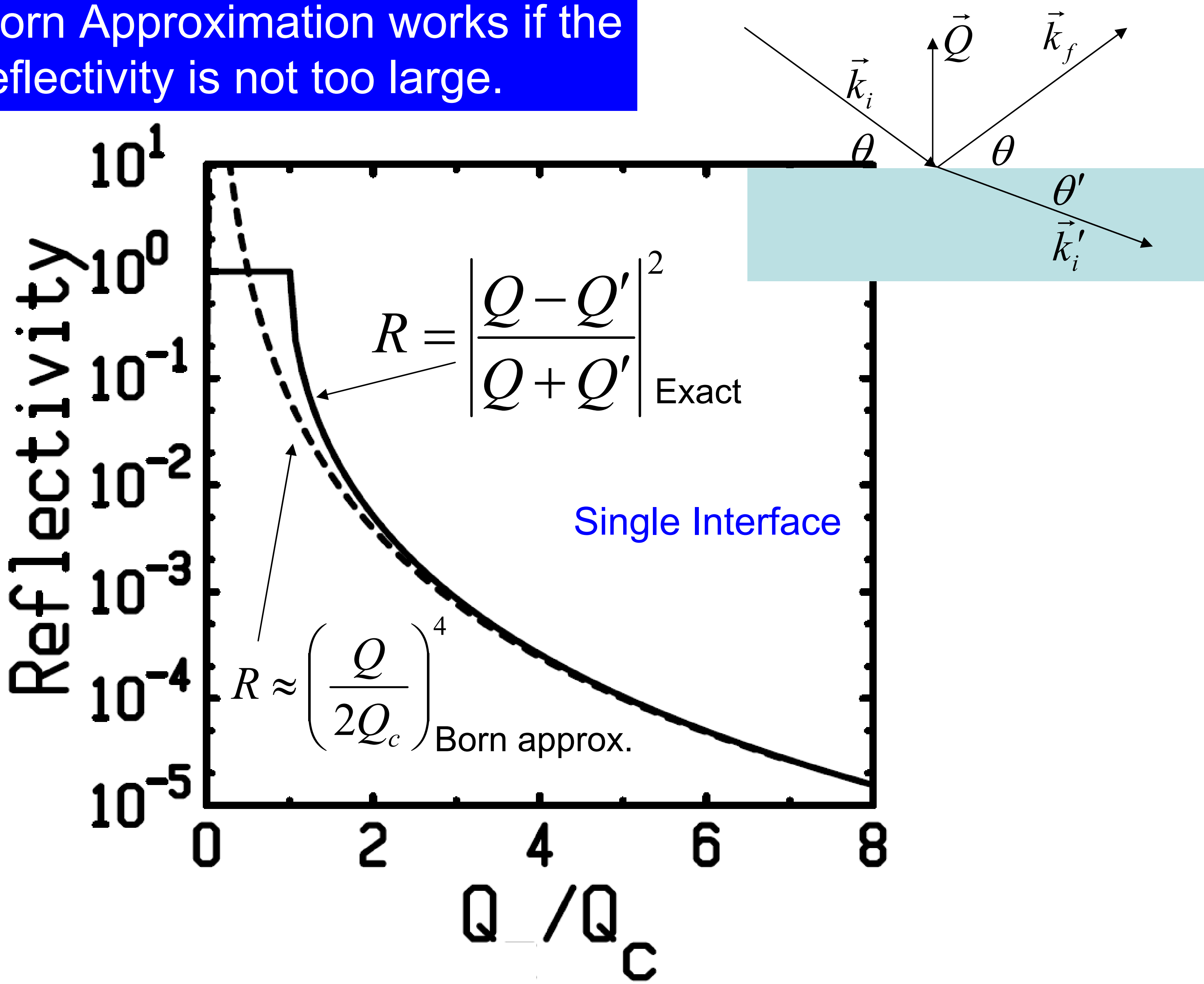
Multi-slice method:
Numerical simulations

M-layer

http://www.ncnr.nist.gov/reflpak/



Born Approximation works if the reflectivity is not too large.



Differential Scattering Cross Section

("Born Approximation" or "Kinematic Approximation")

$$\frac{d\sigma}{d\Omega} = P\,S\left(\vec{Q}\right) = P\left|A\left(\vec{Q}\right)\right|^2$$

Reflectivity:

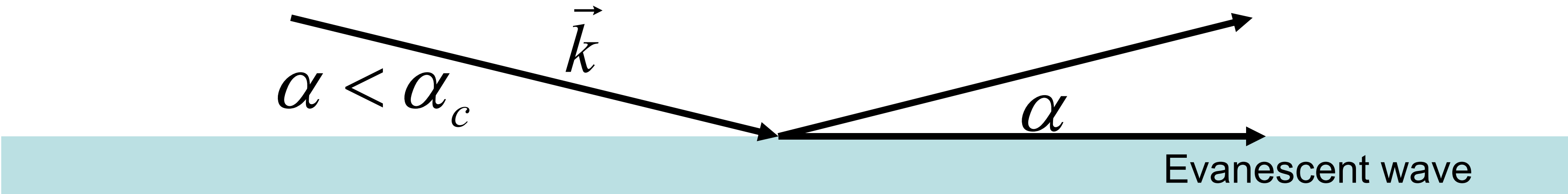
$$R = \frac{1}{A_{inc}}\int d\Omega \frac{d\sigma}{d\Omega}$$

P is the polarization factor (x-ray case)
S(Q) is the structure factor
A(Q) is the scattering amplitude
f(Q) is the atomic form factor
ρ_b is the scattering length density

$$\boxed{A\left(\vec{Q}\right) = \int d^3\vec{r}\,\rho_b\left(\vec{r}\right)e^{i\vec{Q}\cdot\vec{r}} = \sum_{\vec{r}} b_{\vec{r}}\,e^{i\vec{Q}\cdot\vec{r}}}$$

$b = r_e f\left(Q\right)$ for x-rays or tabulated for neutrons

Grazing Incidence Diffraction



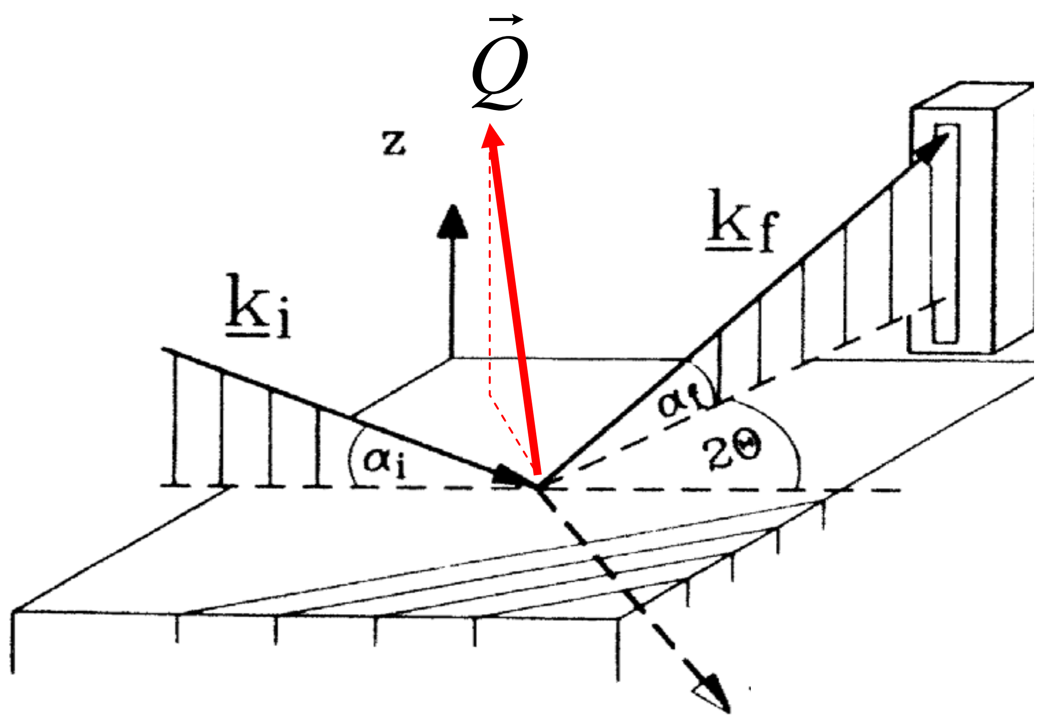
$$\sin^2(\alpha') = \sin^2(\alpha) - 2\delta$$

3D Diffraction

$$\vec{Q} = \vec{k}_f - \vec{k}_i$$

If $\vec{k}_i$ or $\vec{k}_f$ are near grazing:

- refraction α_c
- transmission $T_i\ , T_f$



Perpendicular to Surface: internal **Q'** and external **Q** are different

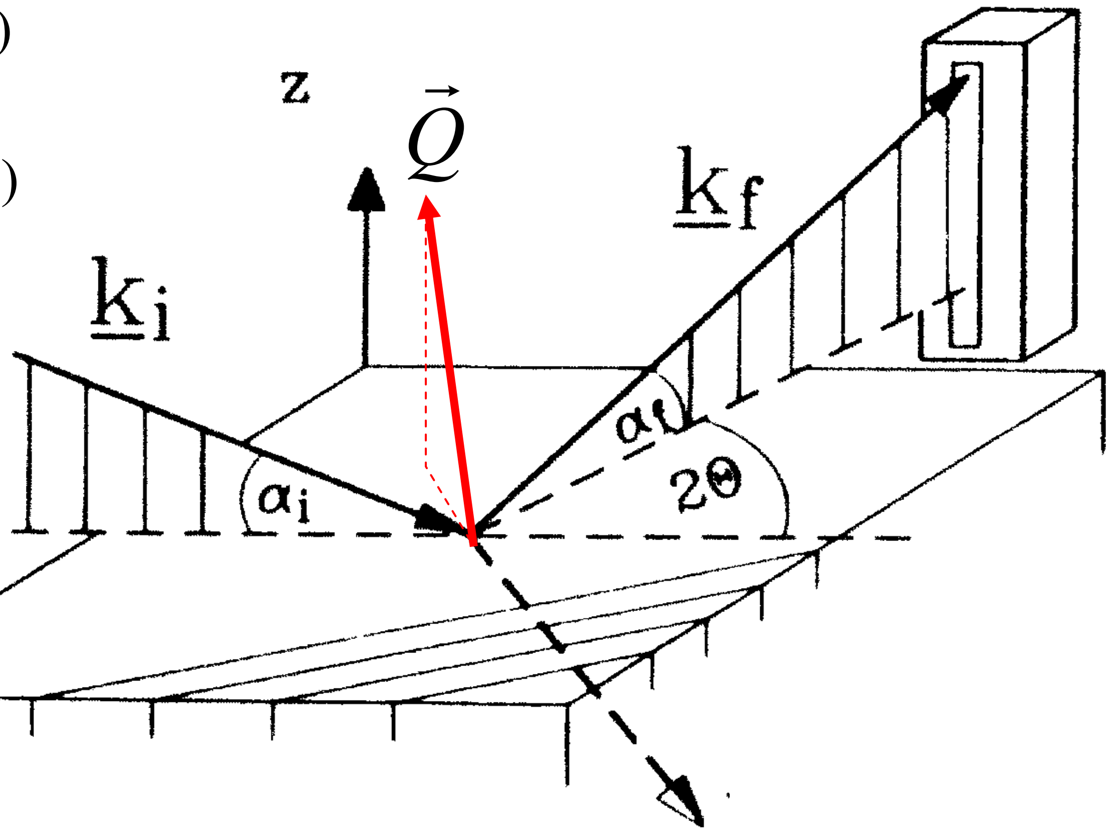
$$Q_z = k_z^{(f)} - k_z^{(i)} = (2\pi/\lambda)[\sin\alpha_f + \sin\alpha_i].$$

$$Q_z' = k_z^{(f)\prime} - k_z^{(i)\prime} = (2\pi/\lambda)[(\sin^2\alpha_f - 2\delta - 2i\beta)^{1/2} + (\sin^2\alpha_i - 2\delta - 2i\beta)^{1/2}].$$

Parallel to Surface: internal **Q'** and external **Q** are same

$$Q_x' = Q_x = k_x^{(f)} - k_x^{(i)}$$

$$Q_y' = Q_y = k_y^{(f)} - k_y^{(i)}$$



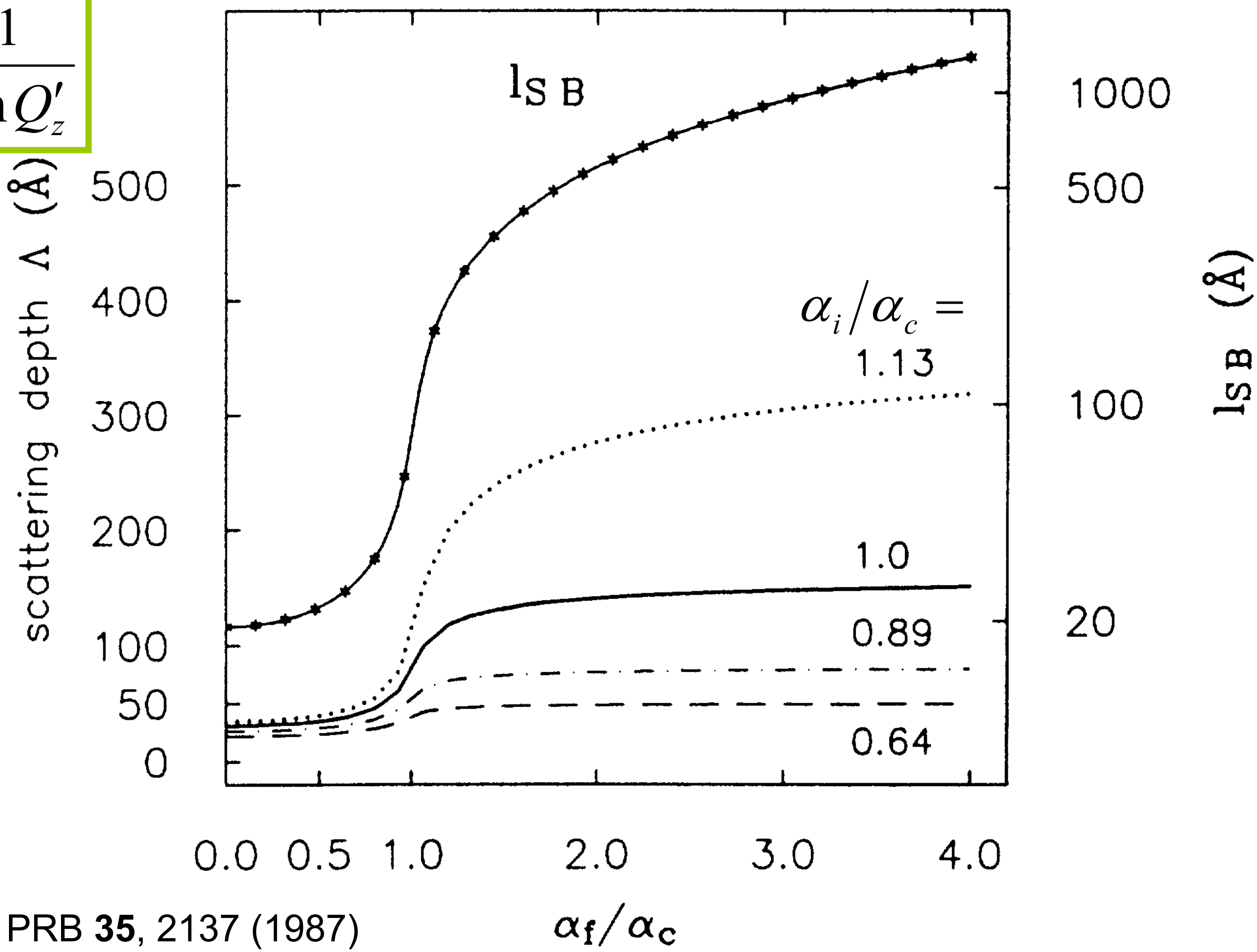
H. Dosch, B.W. Batterman and D. C. Wack, PRL **56**, 1144 (1986)

Penetration Length

$$\Lambda = \lambda / [2\pi(l_i + l_f)]$$

$$l_{i,f} = \frac{1}{2}\sqrt{2}\{(2\delta - \sin^2\alpha_{i,f}) + [(\sin^2\alpha_{i,f} - 2\delta)^2 + (2\beta)^2]^{1/2}\}^{1/2}$$

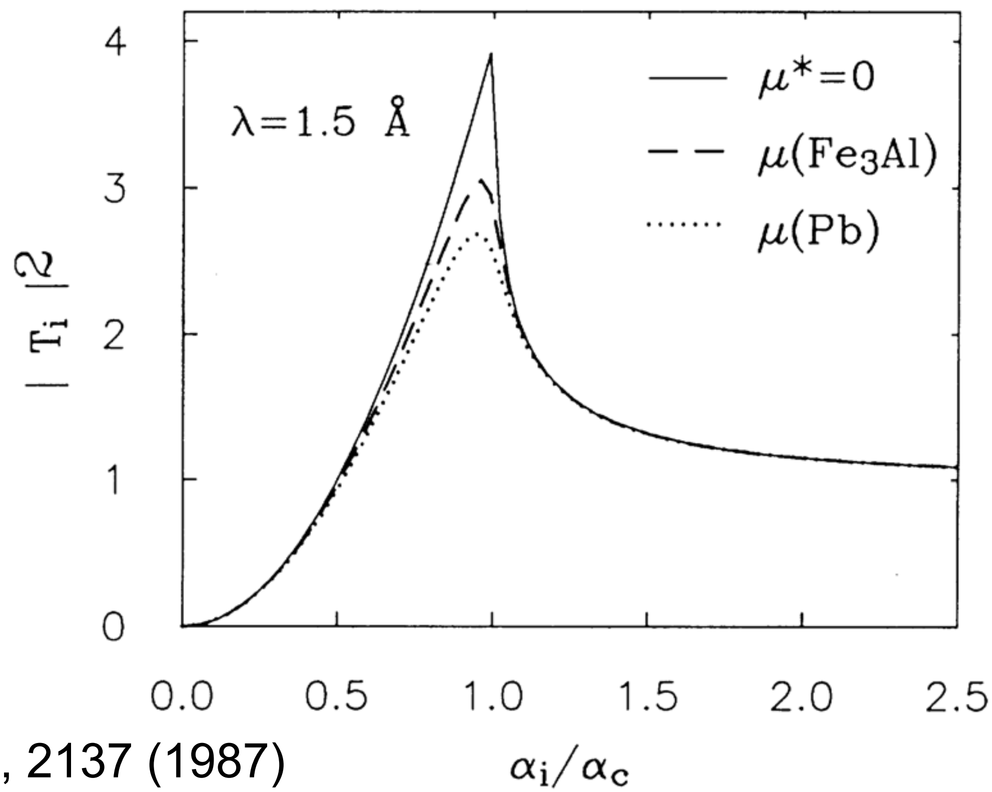
$$\boxed{\Lambda = \frac{1}{\operatorname{Im} Q_z'}}$$



H. Dosch, PRB **35**, 2137 (1987)

Transmitted Beam Amplitude

$$T_i = \frac{2\sin\alpha_i}{\sin\alpha_i + (\sin^2\alpha_i - 2\delta)^{1/2}}$$



H. Dosch, PRB **35**, 2137 (1987)

FIG. 1. Fresnel transmissivity $|T_i|^2$ as a function of α_i/α_c for a transparent medium and the real systems Fe_3Al and Pb.

Fe_3Al

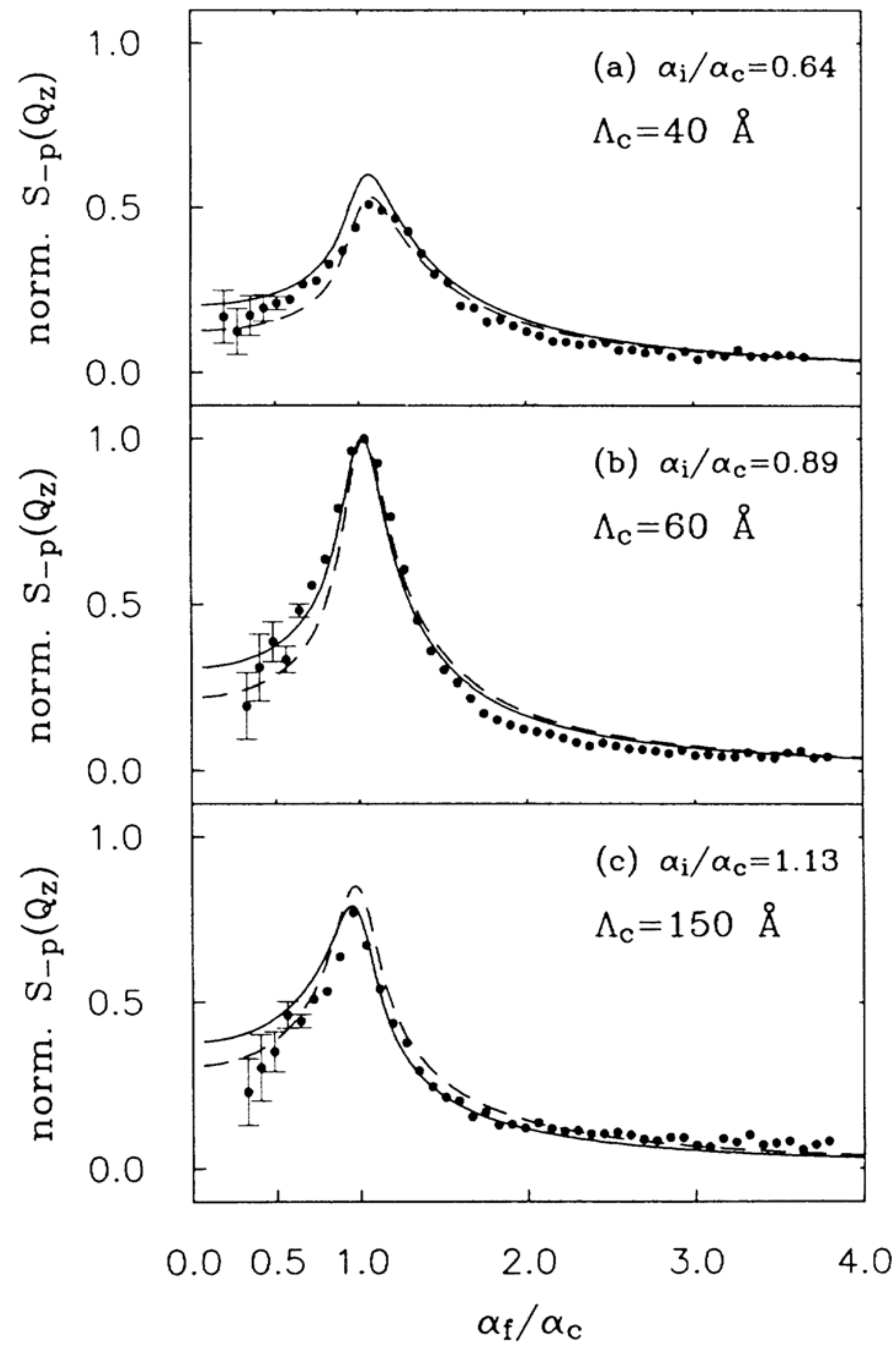
H. Dosch, PRB **35**, 2137 (1987)

Distorted Wave Born Approximation

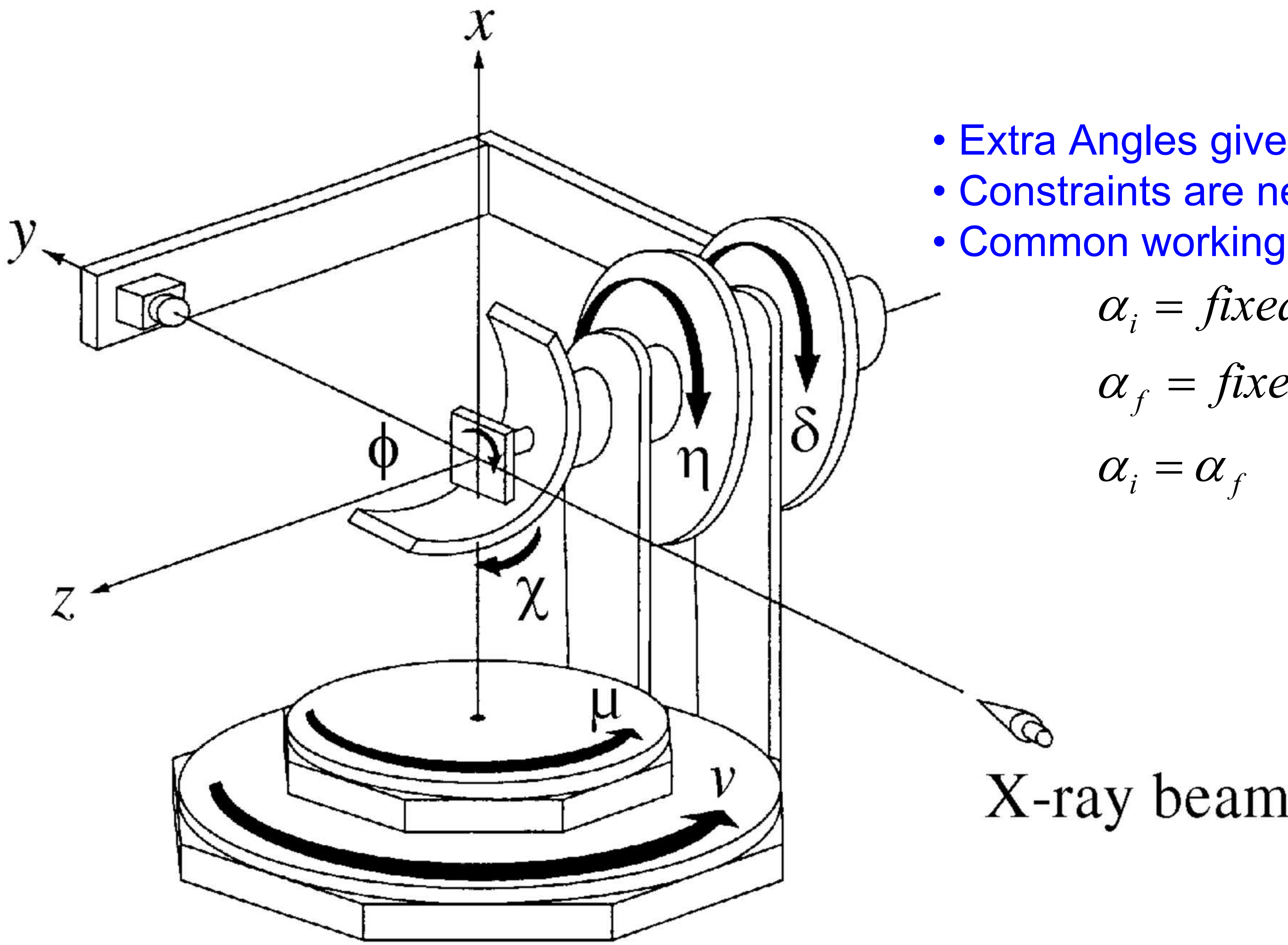
$$I_{GID}(Q') \propto |T_i|^2 S(Q') |T_f|^2$$

- refraction
- transmission

$S(\vec{Q}')$ is the structure factor using the internal wavevector transfer



A Six-Circle Diffractometer



- Extra Angles give flexibility
- Constraints are needed
- Common working modes:

$$\alpha_i = fixed$$

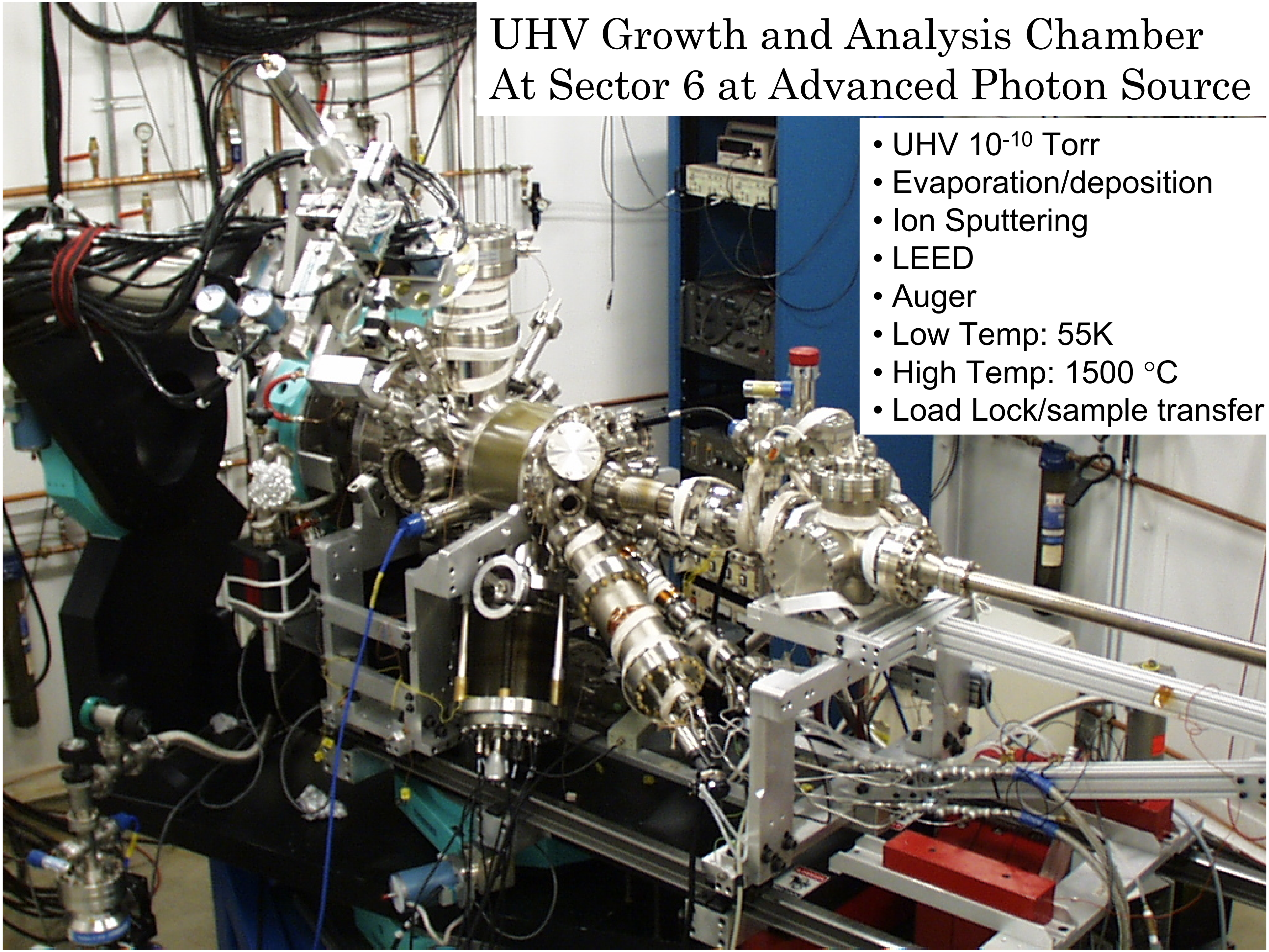
$$\alpha_f = fixed$$

$$\alpha_i = \alpha_f$$

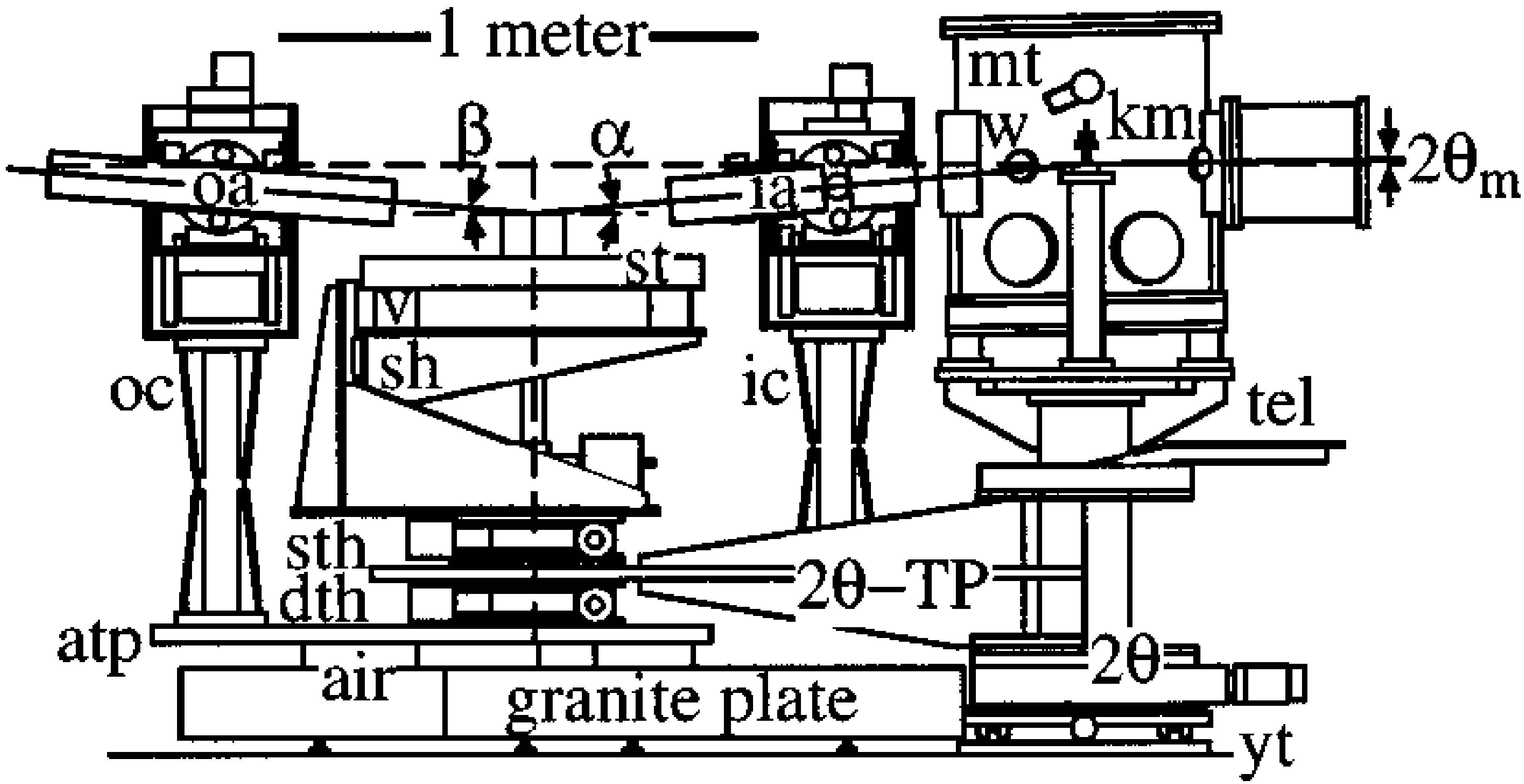
H. You, *J. Appl. Cryst*. **32**, 614-623 (1999)

UHV Growth and Analysis Chamber At Sector 6 at Advanced Photon Source

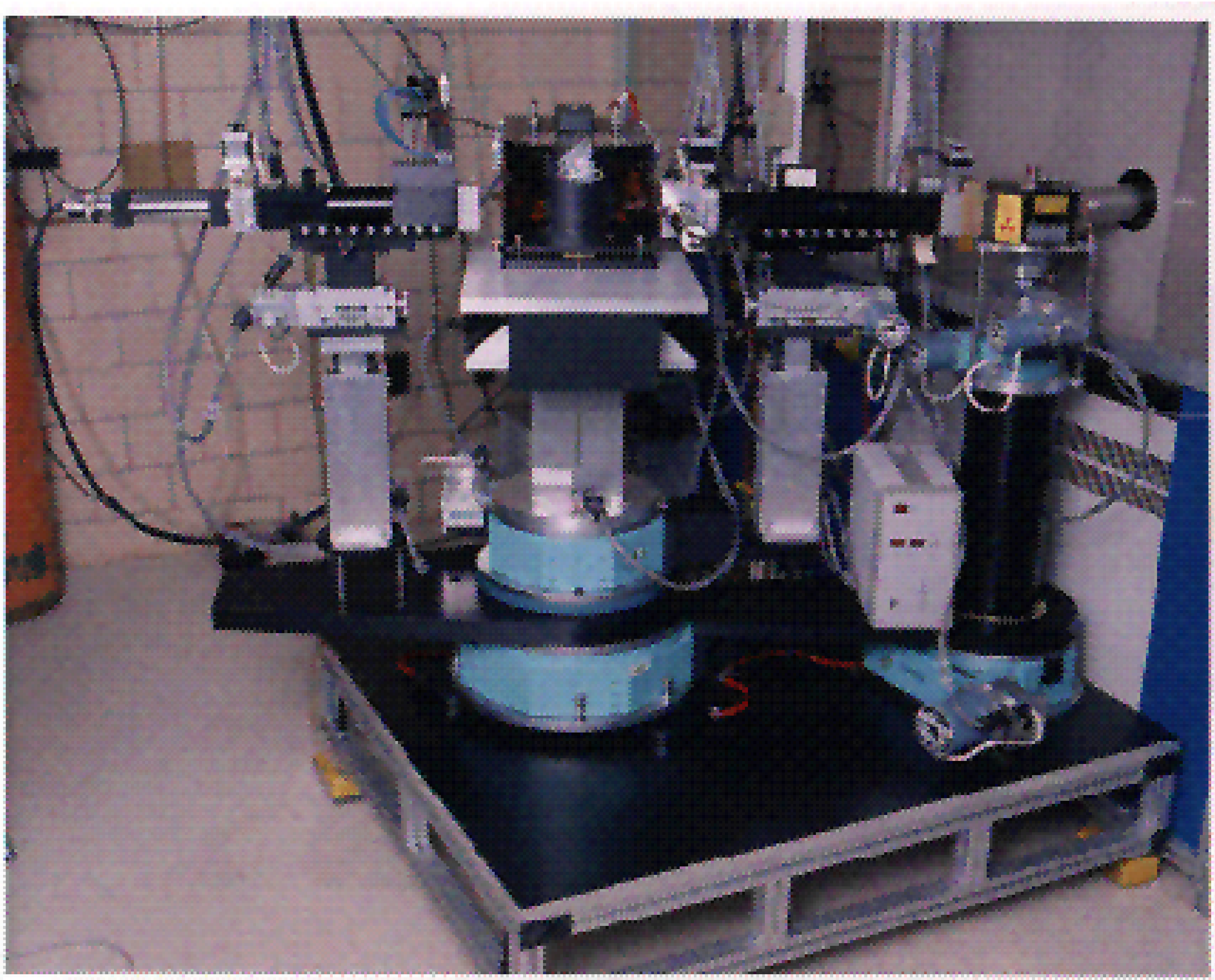
- UHV 10^{-10} Torr
- Evaporation/deposition
- Ion Sputtering
- LEED
- Auger
- Low Temp: 55K
- High Temp: 1500 °C
- Load Lock/sample transfer



Liquid Surface Diffractometer



M. Schlossman et. al., Rev. Sci. Inst. **68**, 4372 (1997)

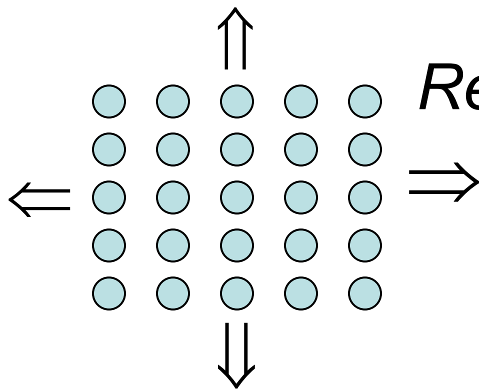


David Vaknin, Ames Lab

What is a crystal truncation rod?

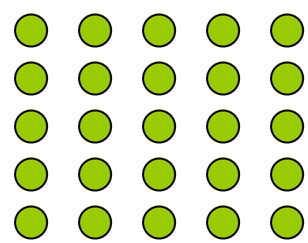
First consider:

- Large crystals; rough and irregular boundaries
- Boundaries neglected

Large crystal  *Real space*

$$S(\vec{Q}) = \left| \sum_{n_x=0}^{N-1} e^{iQ_x a n_x} \sum_{n_y=0}^{N-1} e^{iQ_y b n_y} \sum_{n_z=0}^{N-1} e^{iQ_z c n_z} \right|^2 = \frac{\sin^2\left(\frac{NQ_x a}{2}\right)}{\sin^2\left(\frac{Q_x a}{2}\right)} \frac{\sin^2\left(\frac{NQ_y b}{2}\right)}{\sin^2\left(\frac{Q_y b}{2}\right)} \frac{\sin^2\left(\frac{NQ_z c}{2}\right)}{\sin^2\left(\frac{Q_z c}{2}\right)}$$

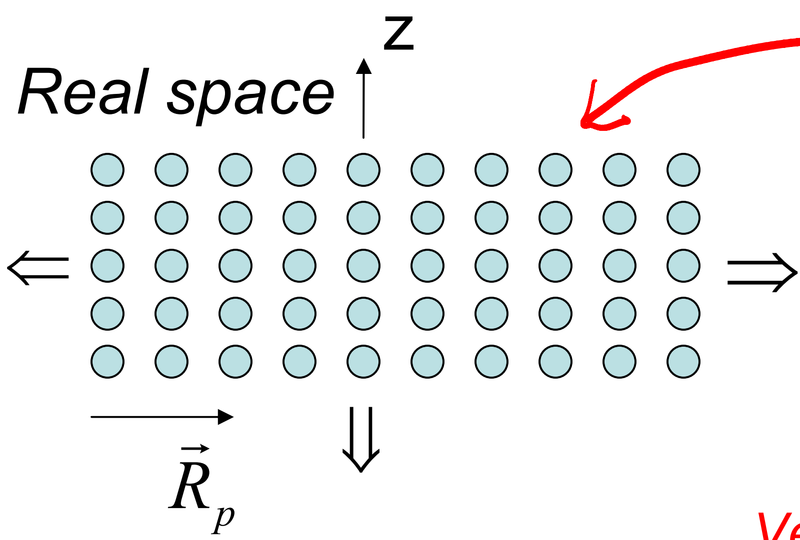
$$\propto \sum_{\vec{G}} \delta\left(\vec{Q} - \vec{G}\right)$$



Reciprocal space
Bragg points

$\vec{G}$ is a reciprocal lattice vector

Now consider a crystal with one atomically flat boundary…



- Large crystal; flat boundary $z = 0$
- Neglect boundary at $z = -\infty$

Very small attenuation $\varepsilon <\sim 1$

$$S(\vec{Q}) = b^2 \left| \sum_{n_z=0}^{N-1} \varepsilon^{n_z} e^{-iQ_z c n_z} \right|^2 \sum_{\vec{R}_p} \sum_{\vec{R}'_p} e^{i\vec{Q}_p \bullet (\vec{R}_p - \vec{R}'_p)}$$

Reflected wave vanishes

Crystal Truncation Rod Factor

$$\lim_{\varepsilon \to 1} \lim_{N \to \infty} \left| \frac{1 - \varepsilon^N e^{-iQ_z cN}}{1 - e^{-iQ_z c}} \right|^2 = \frac{1}{4\sin^2\left(\frac{Q_z c}{2}\right)} \approx \frac{1}{c^2 (Q_z - G_z)^2}$$

By neglecting the lateral boundaries:

$$\sum_{\vec{R}_p}\sum_{\vec{R}'_p} e^{i\vec{Q}_p \bullet \left(\vec{R}_p - \vec{R}'_p\right)} = N_{irr} \sum_{\vec{R}_p} e^{i\vec{Q}_p \bullet \vec{R}_p}$$

and $$\sum_{\vec{R}_p} e^{i\vec{Q}_p \bullet \vec{R}_p} = \frac{(2\pi)^2}{s_c} \sum_{\vec{G}_p} \delta\left(\vec{Q}_p - \vec{G}_p\right)$$

N_{irr} = the number of irradiated atoms at the surface

s_c = area per surface atom

$\vec{G}_p$ = an in-plane reciprocal lattice vector

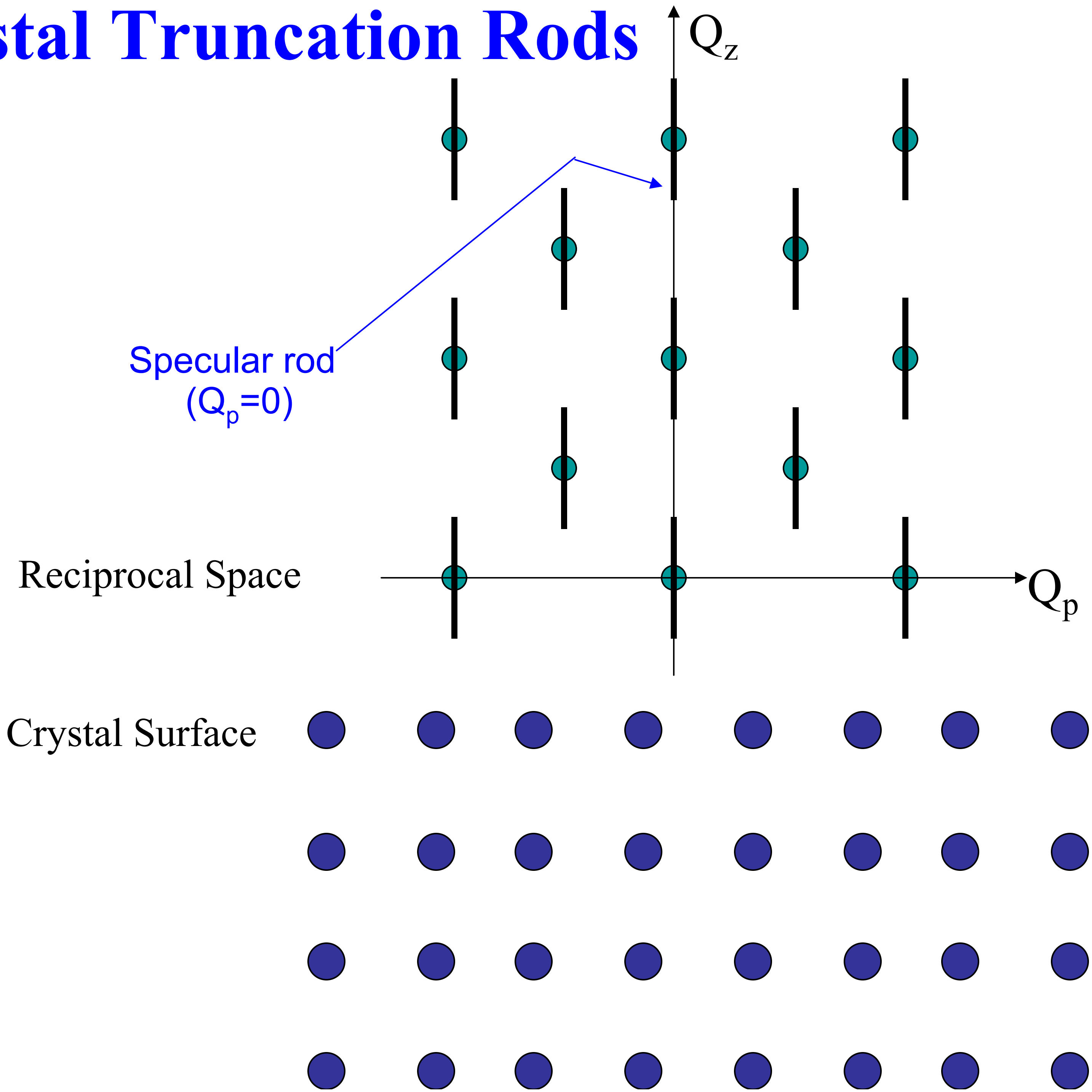
$$\boxed{S\left(\vec{Q}\right) = \frac{(2\pi)^2 N_{irr} b^2}{s_c} \frac{1}{4\sin^2\left(\frac{Q_z c}{2}\right)} \sum_{\vec{G}_p} \delta\left(\vec{Q}_p - \vec{G}_p\right)}$$

CTR

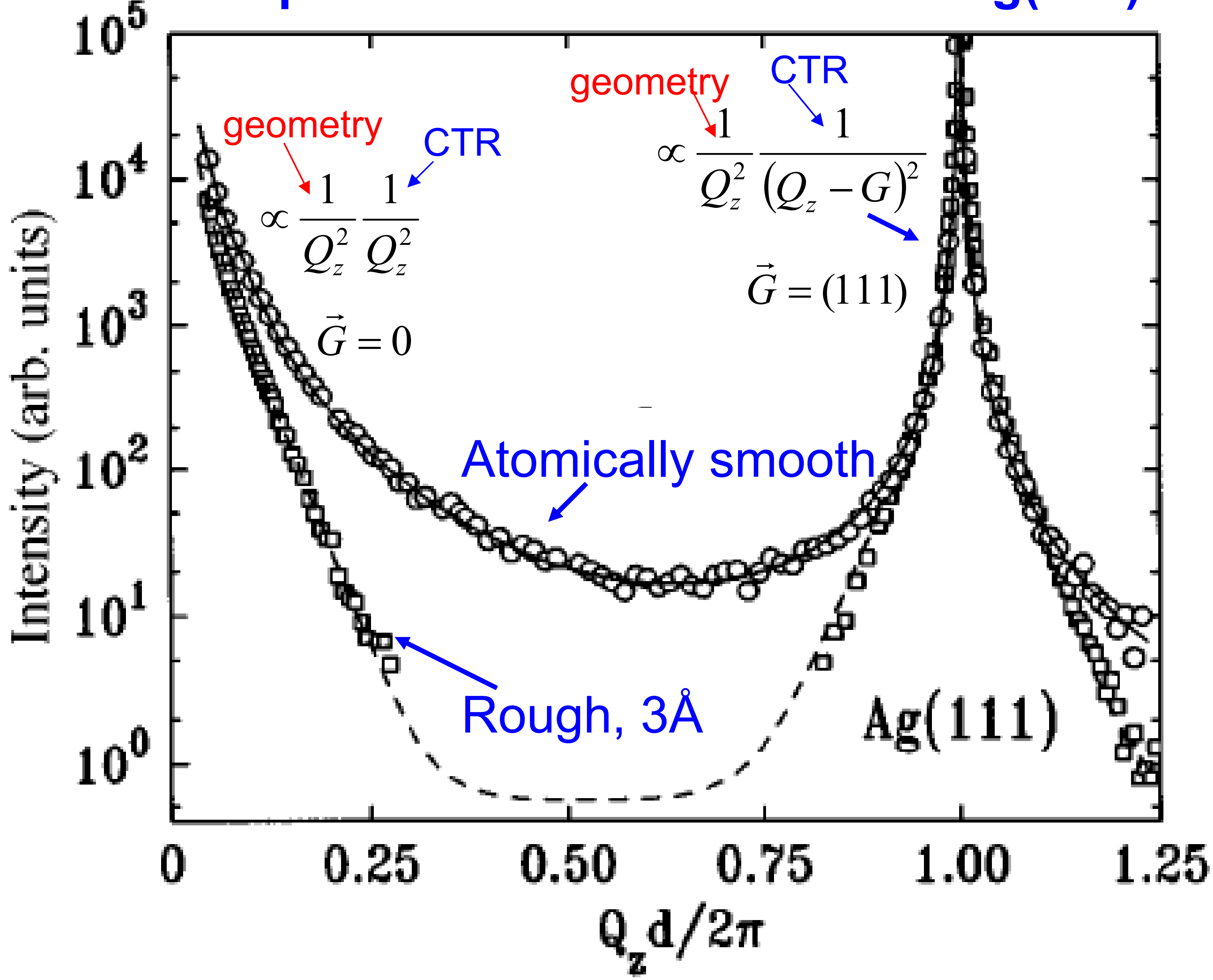
Intensity falls slowly

Narrow reflection in-plane

Crystal Truncation Rods

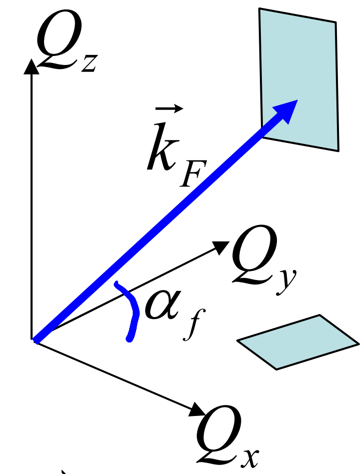


Crystal Truncation Rod Scattering for Specular Reflection from the Ag(111) Surface



Elliott et. al. PRB **54**, 17938 (1996)

Reflectivity: $R = \dfrac{1}{A_{inc}} \int d\Omega\, S(\vec{Q})$



$$d\Omega = \frac{d^2\vec{Q}_p}{k^2 \sin(\alpha_f)}$$

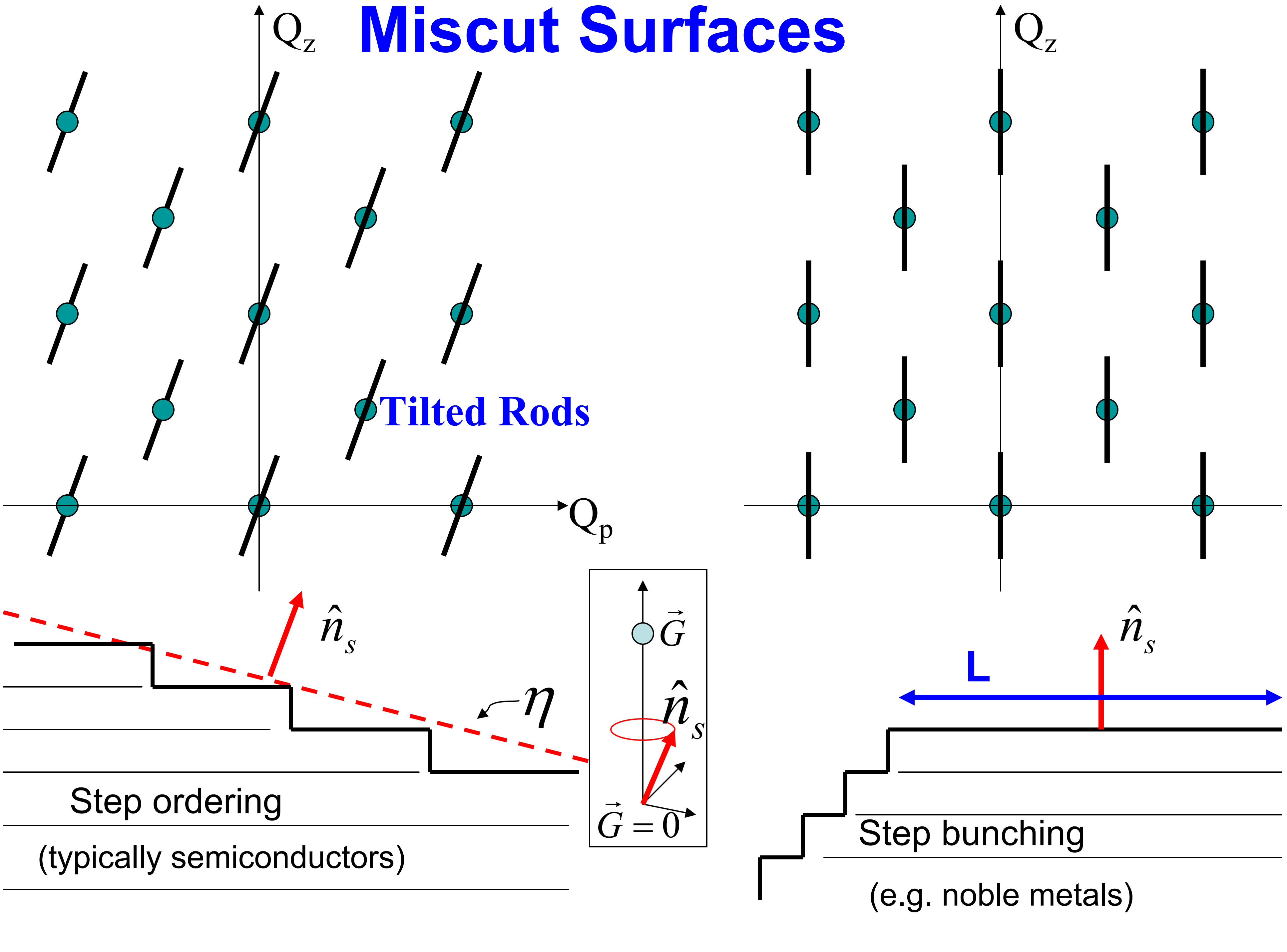
$$R = \int \frac{d^2\vec{Q}_p}{k^2 \sin(\alpha_f)} \frac{A_{irr}}{A_{inc} s_c^2} \frac{\pi^2 b^2}{\sin^2\left(\frac{Q_z c}{2}\right)} \sum_{\vec{G}_p} \delta\left(\vec{Q}_p - \vec{G}_p\right)$$

For specular reflections: $\dfrac{A_{irr}}{kA_{inc}} = \dfrac{2}{Q_z}$ $\qquad \dfrac{1}{k\sin(\alpha_f)} = \dfrac{2}{Q_z}$

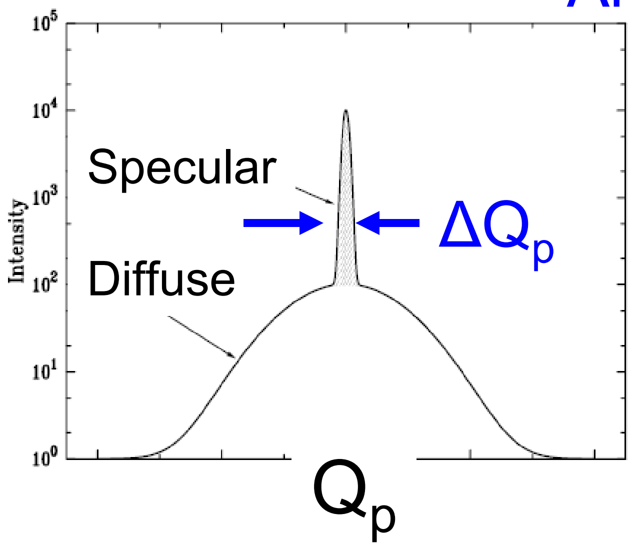
(Two geometric factors of 1/Q)

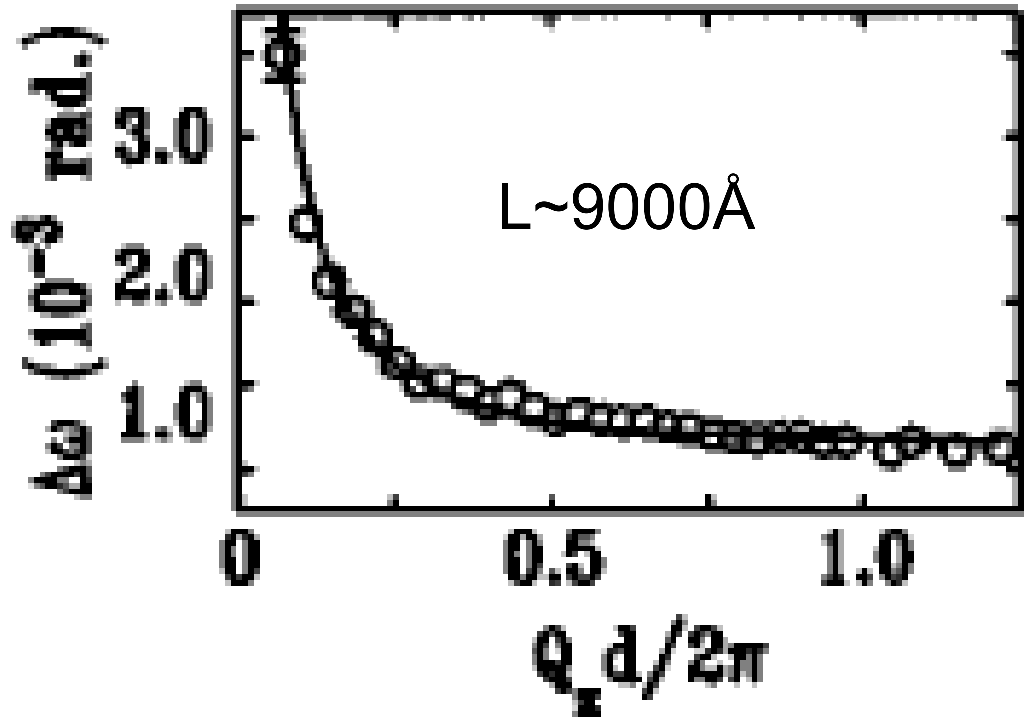
$$\boxed{R_{spec} = \frac{1}{s_c^2} \frac{4\pi^2 b^2}{Q_z^2 \sin^2\left(\frac{Q_z c}{2}\right)} = \frac{(Q_c/2)^4 c^2}{4Q_z^2 \sin^2\left(\frac{Q_z c}{2}\right)}} \approx \frac{(Q_c/2)^4}{Q_z^2 (Q_z - G_z)^2}$$

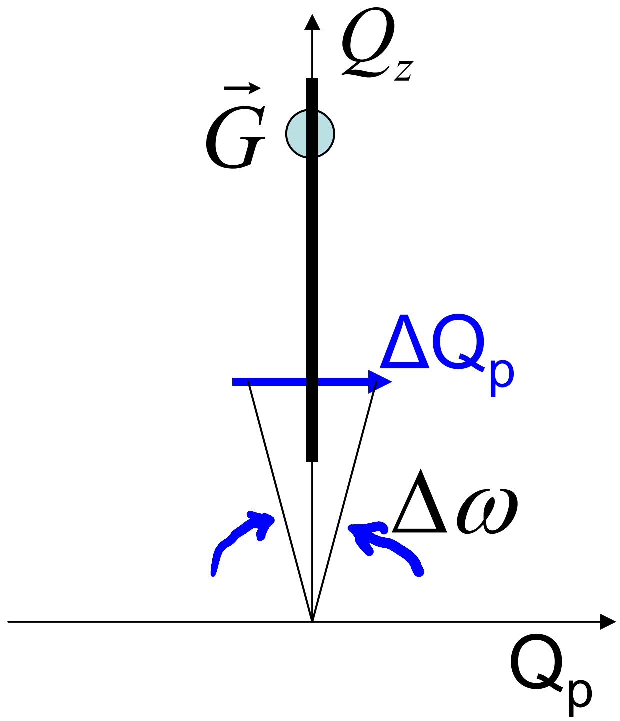
Miscut Surfaces



Angular Width of Specular Decreases with Q_z







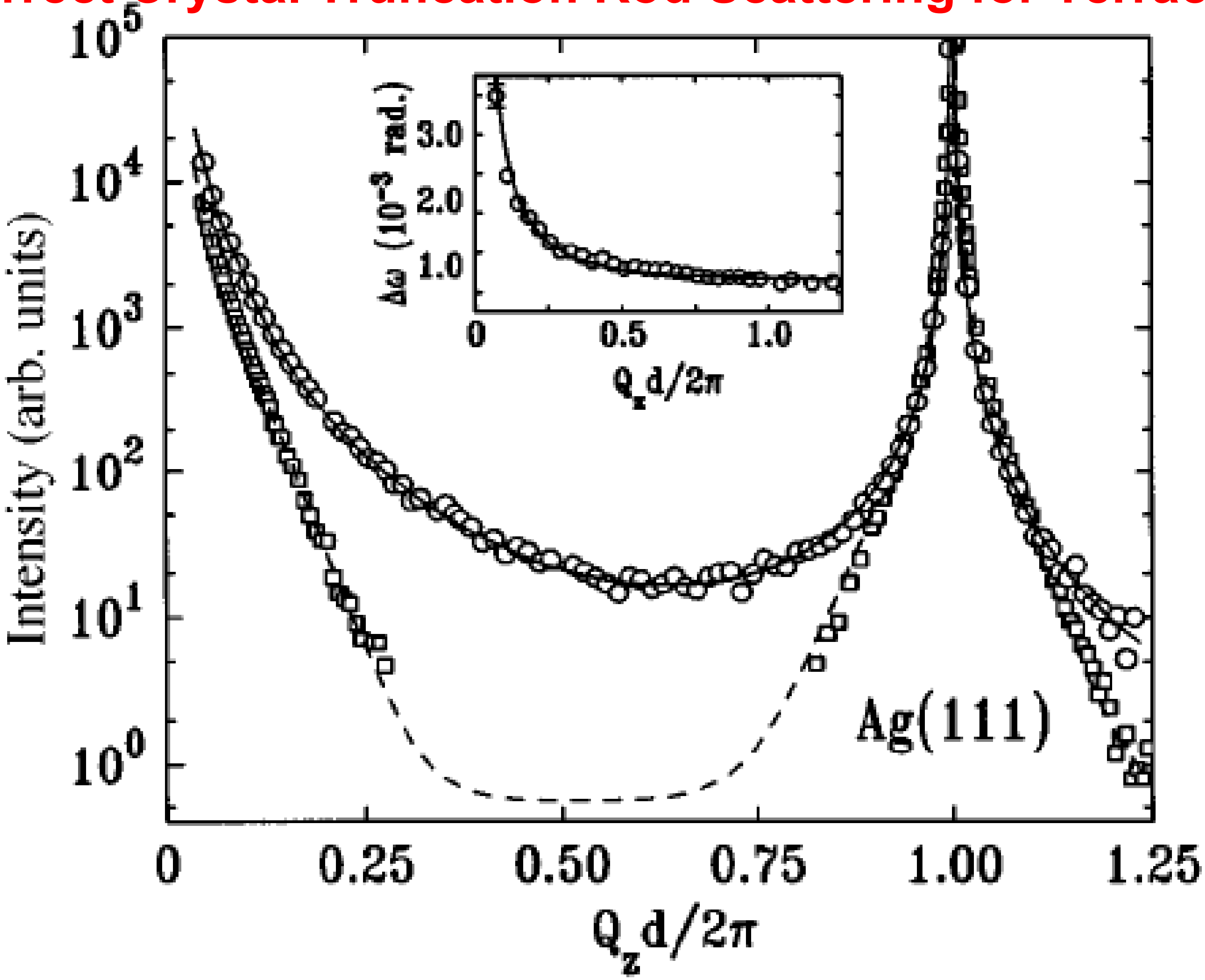
$$\Delta\omega = \frac{\Delta Q_p}{Q_z}$$

Can determine terrace size, L

$$\boxed{\Delta Q_p = \frac{2\pi}{L}}$$

Specular Reflection from the Ag(111) Surface

Correct Crystal Truncation Rod Scattering for Terrace Size



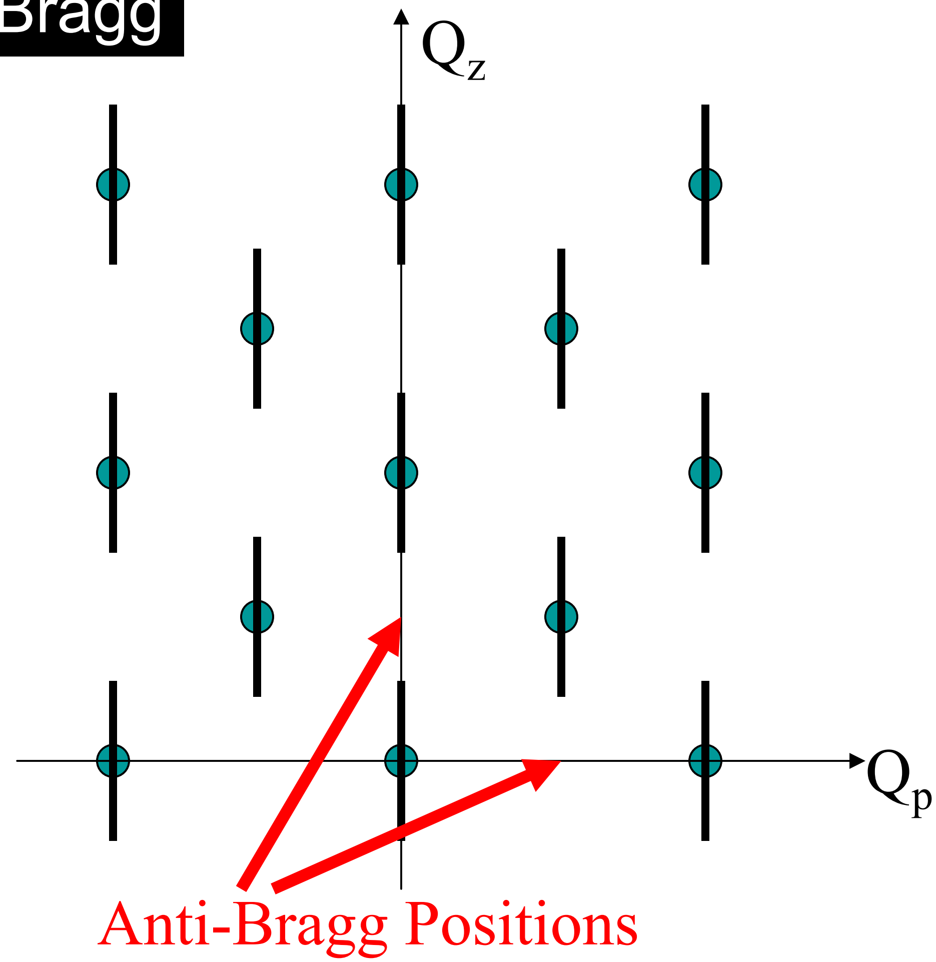
Elliott et. al. PRB **54**, 17938 (1996)

Special location along CTR: anti-Bragg

Bragg Position:

$$Q_z c = 2\pi m$$

$$\left| \sum_{n_z=0}^{N-1} e^{-i2\pi n_z} \right|^2 \to N^2$$

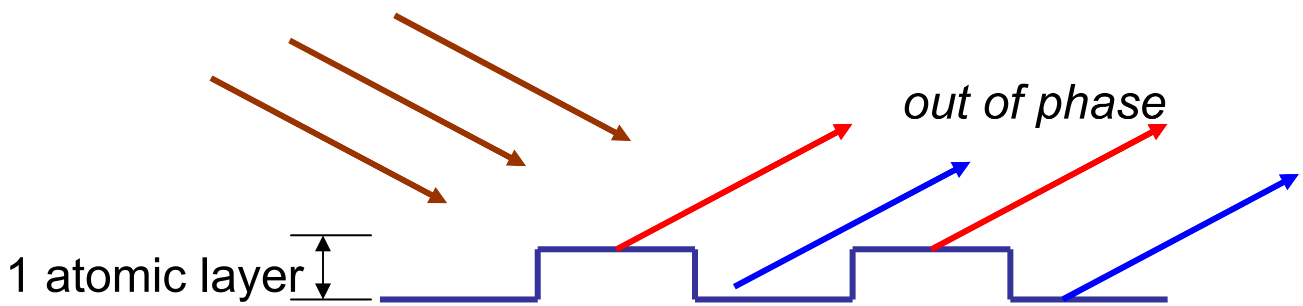


Anti-Bragg Position:

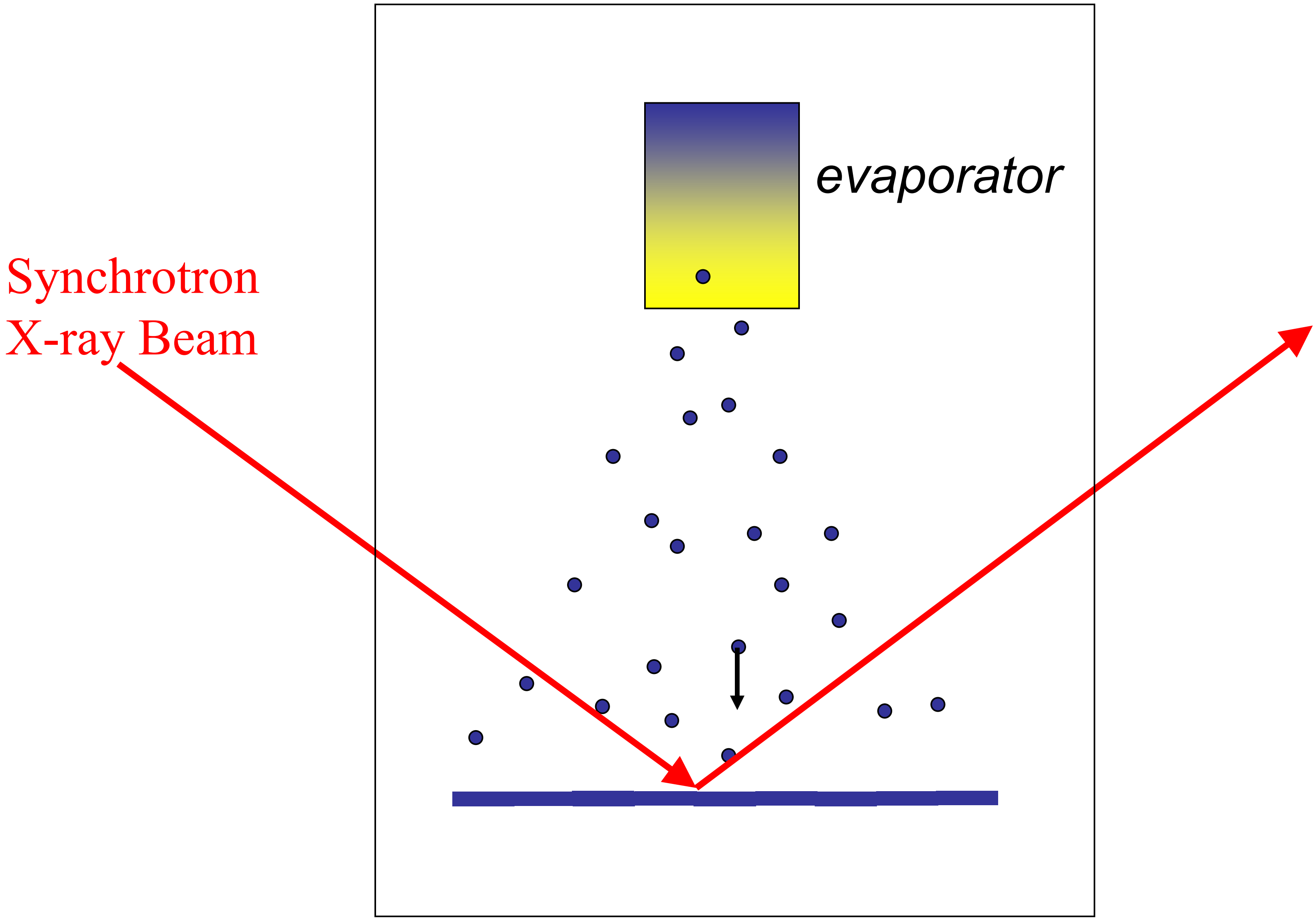
$$Q_z c = \pi m \quad (m \text{ odd})$$

$$\left| \sum_{n_z=0}^{N-1} e^{-i\pi n_z} \right|^2 \to 1$$

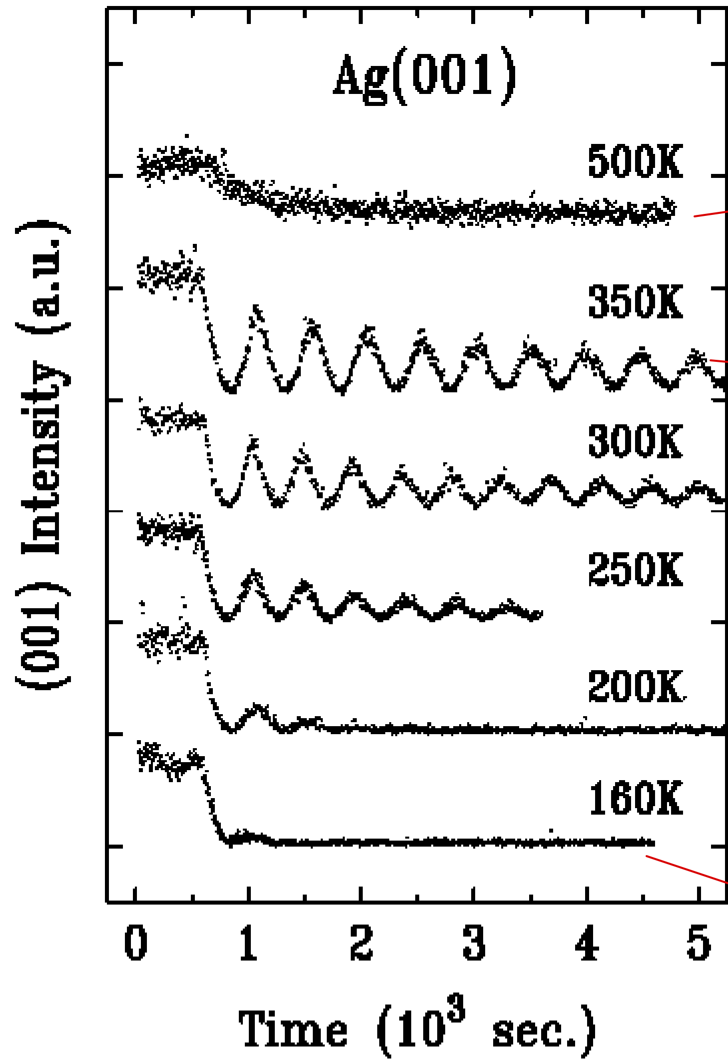
For a smooth surface

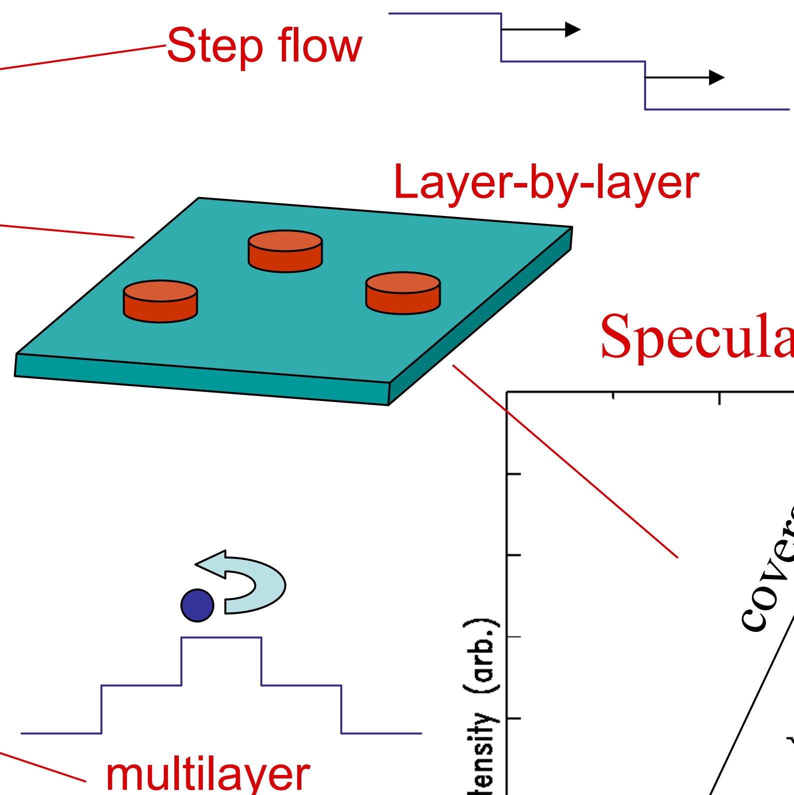


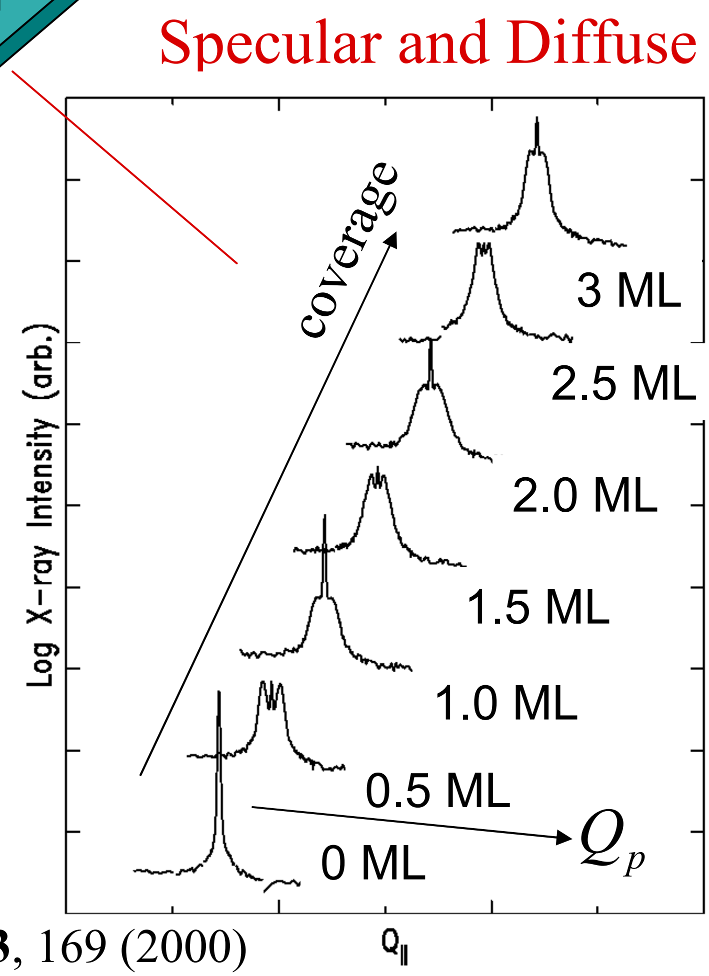
In situ vapor deposition in UHV



Nucleation and Growth





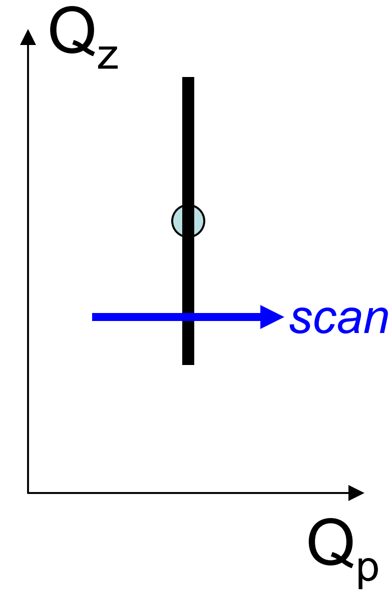


Specular Anti-Bragg Intensity

Elliott et. al. PRB **54**, 17938 (1996) Adv. X-ray Anal. **43**, 169 (2000)

Diffuse Scattering

Caused by lateral structure



$$\left|A(\vec{Q})\right|^2 = \sum_{\vec{r}} \sum_{\vec{r}\,'} b_{\vec{r}}\, b^*_{\vec{r}\,'}\, e^{i\vec{Q}\cdot(\vec{r}-\vec{r}\,')}$$

$$= |b|^2 \sum_{\vec{R}_p} \sum_{\vec{R}'_p} e^{i\vec{Q}_p \bullet (\vec{R}_p - \vec{R}'_p)} \sum_{n=-\infty}^{m(\vec{R}_p)} \sum_{n'=-\infty}^{m(\vec{R}'_p)} e^{iQ_z c(n-n')}$$

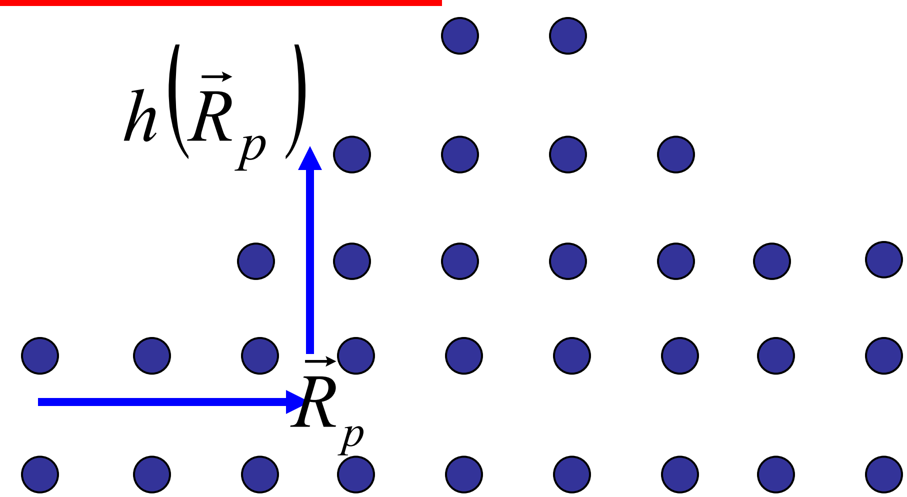
$$= \frac{N_{irr}|b|^2}{\left|1-e^{iQ_z c}\right|^2} \boxed{\sum_{\vec{R}_p} e^{i\vec{Q}_p \bullet \vec{R}_p} \left\langle e^{iQ_z\left(h(\vec{R}_p+\vec{R}'_p)-h(\vec{R}'_p)\right)} \right\rangle_{\vec{R}'_p}}$$

Q_p dependence

$=S_T(Q_p)$

CTR factor

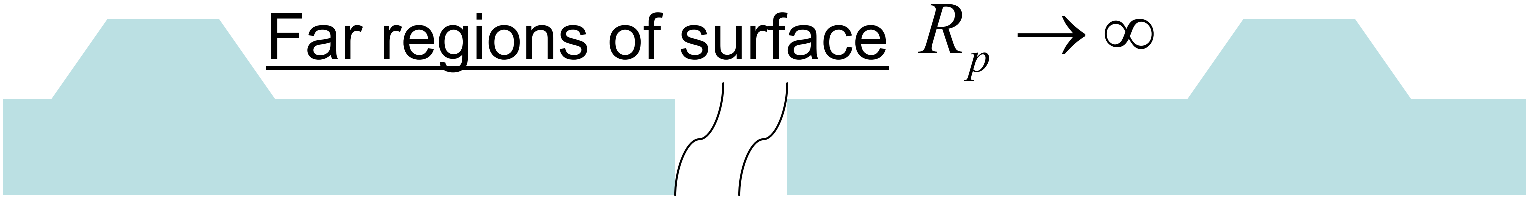
FT of average phase difference due to lateral height-differences



- Neglect lateral boundaries

Transverse Lineshape

Far regions of surface $R_p \to \infty$



Uncorrelated heights

$$\left\langle e^{iQ_z\left(h\left(\vec{R}_p+\vec{R}'_p\right)-h\left(\vec{R}'_p\right)\right)}\right\rangle_{\vec{R}'_p} \to \left|\left\langle e^{iQ_z h}\right\rangle\right|^2$$

Uncorrelated Roughness @ Large Distance Gives Bragg:

$$S_T^{Bragg}\left(\vec{Q}_p\right)=\frac{(2\pi)^2}{s_c}\delta\left(\vec{Q}_p-\vec{G}_p\right)\left|\left\langle e^{iQ_z h}\right\rangle\right|^2$$

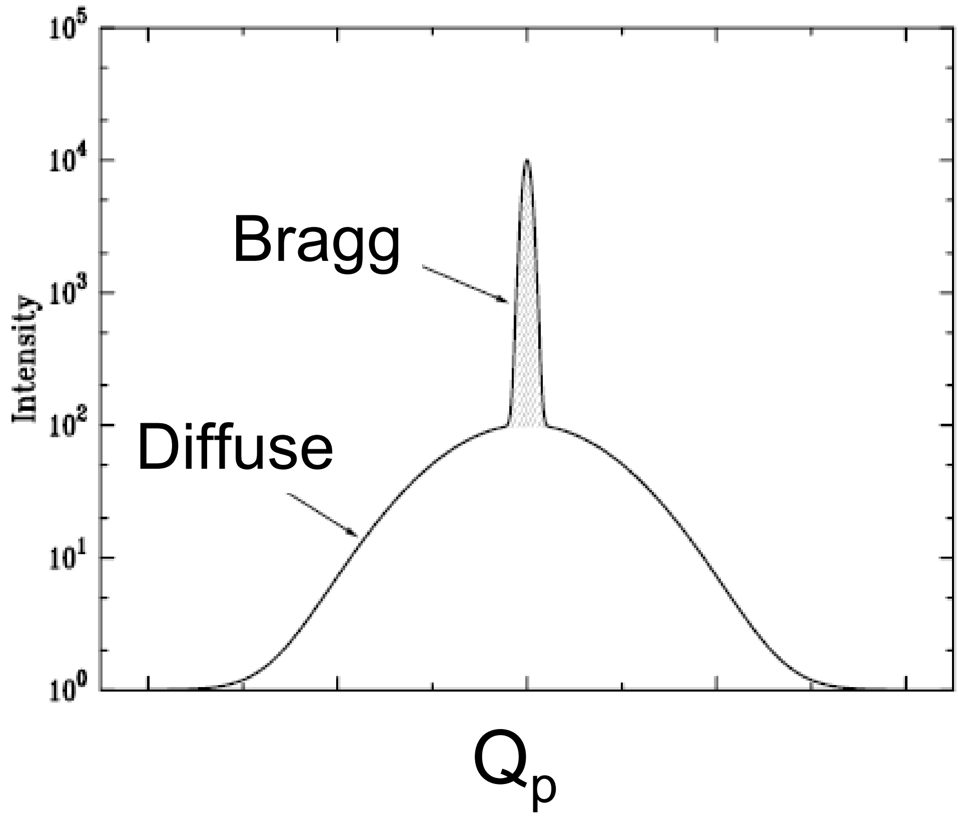
Short-Range Correlations Give Diffuse Scattering:

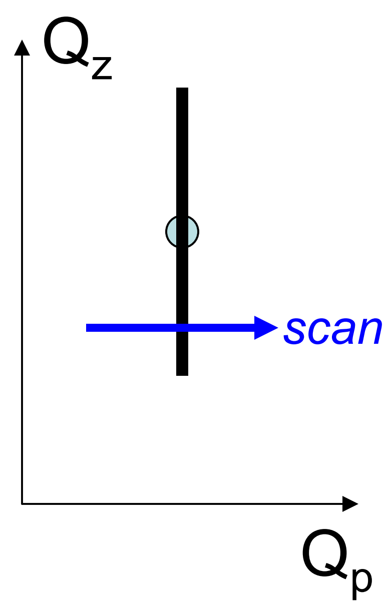
$$S_T^{Diffuse}\left(\vec{Q}_p\right)=\sum_{\vec{R}_p} e^{i\vec{Q}_p\bullet\vec{R}_p}\left\{\left\langle e^{iQ_z\left(h\left(\vec{R}_p+\vec{R}'_p\right)-h\left(\vec{R}'_p\right)\right)}\right\rangle_{\vec{R}'_p}-\left|\left\langle e^{iQ_z h}\right\rangle\right|^2\right\}$$

Two Component Line Shape: Bragg + Diffuse

$$S_T\left(\vec{Q}_p\right) = S_T^{Bragg}\left(\vec{Q}_p\right) + S_T^{Diffuse}\left(\vec{Q}_p\right)$$

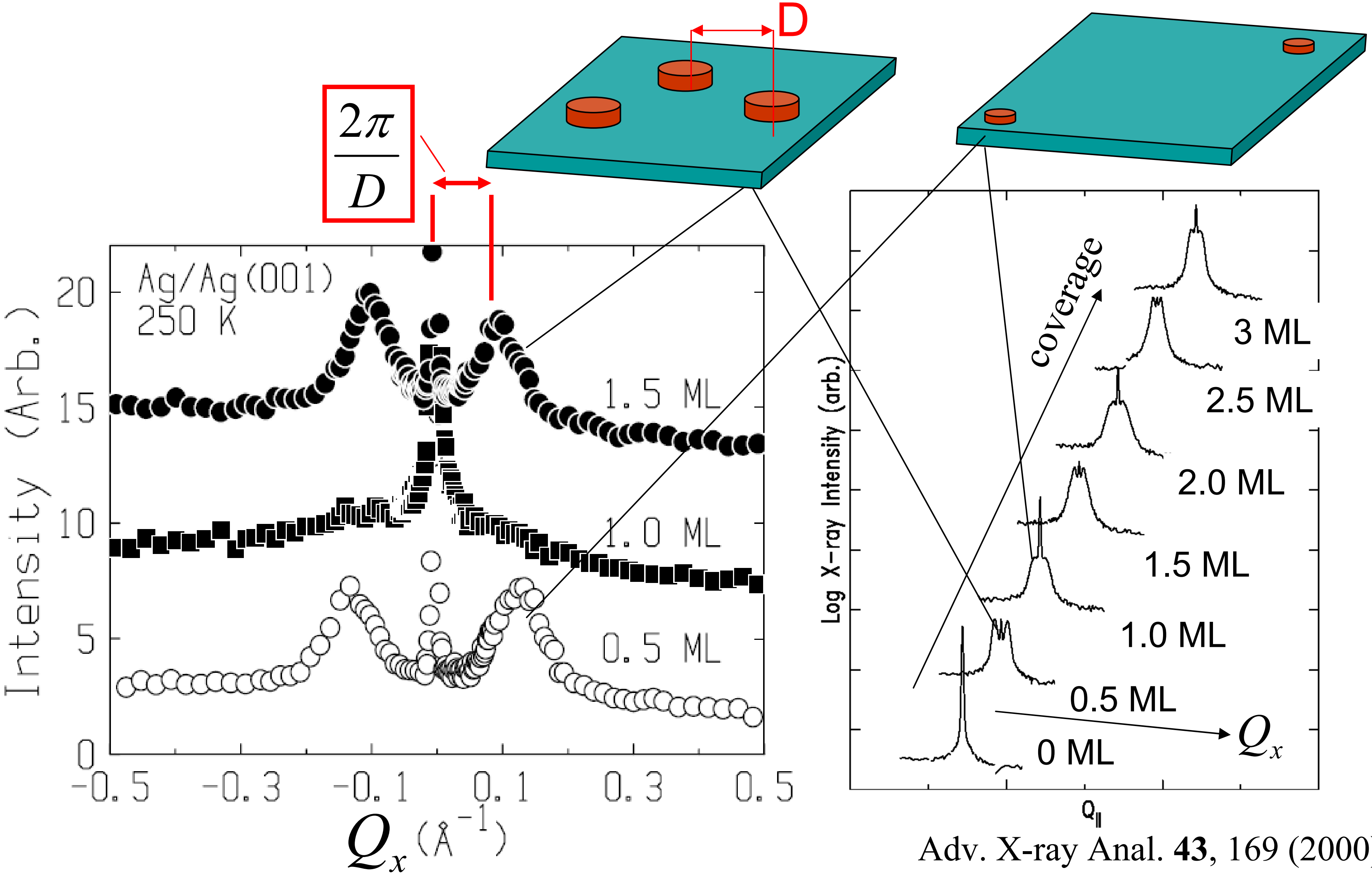
- Bragg due to laterally uncorrelated disorder at long distances
- Diffuse due to short-range correlations





Layer-by-layer growth

- Specular Bragg Rod: intensity changes with roughness
- Strong inter-island correlations seen in the diffuse

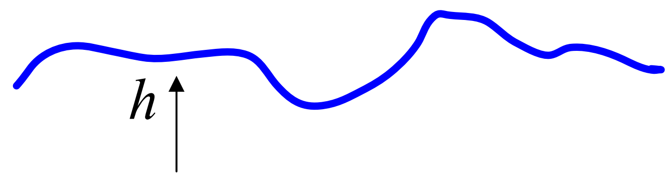


Adv. X-ray Anal. **43**, 169 (2000)

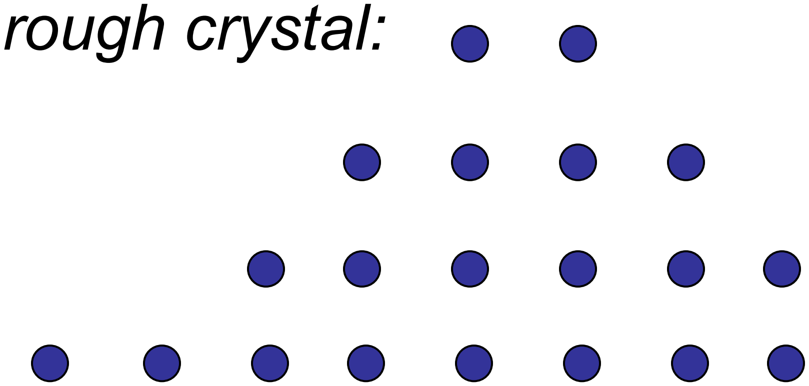
Attenuation of the Bragg Rod and Surface Roughness

If height fluctuations are Gaussian: σ is rms roughness

$$\left|\left\langle e^{iQ_z h}\right\rangle\right|^2 \rightarrow e^{-Q_z^2\sigma^2}$$



But crystal heights are ***discrete*** *for a rough crystal:*



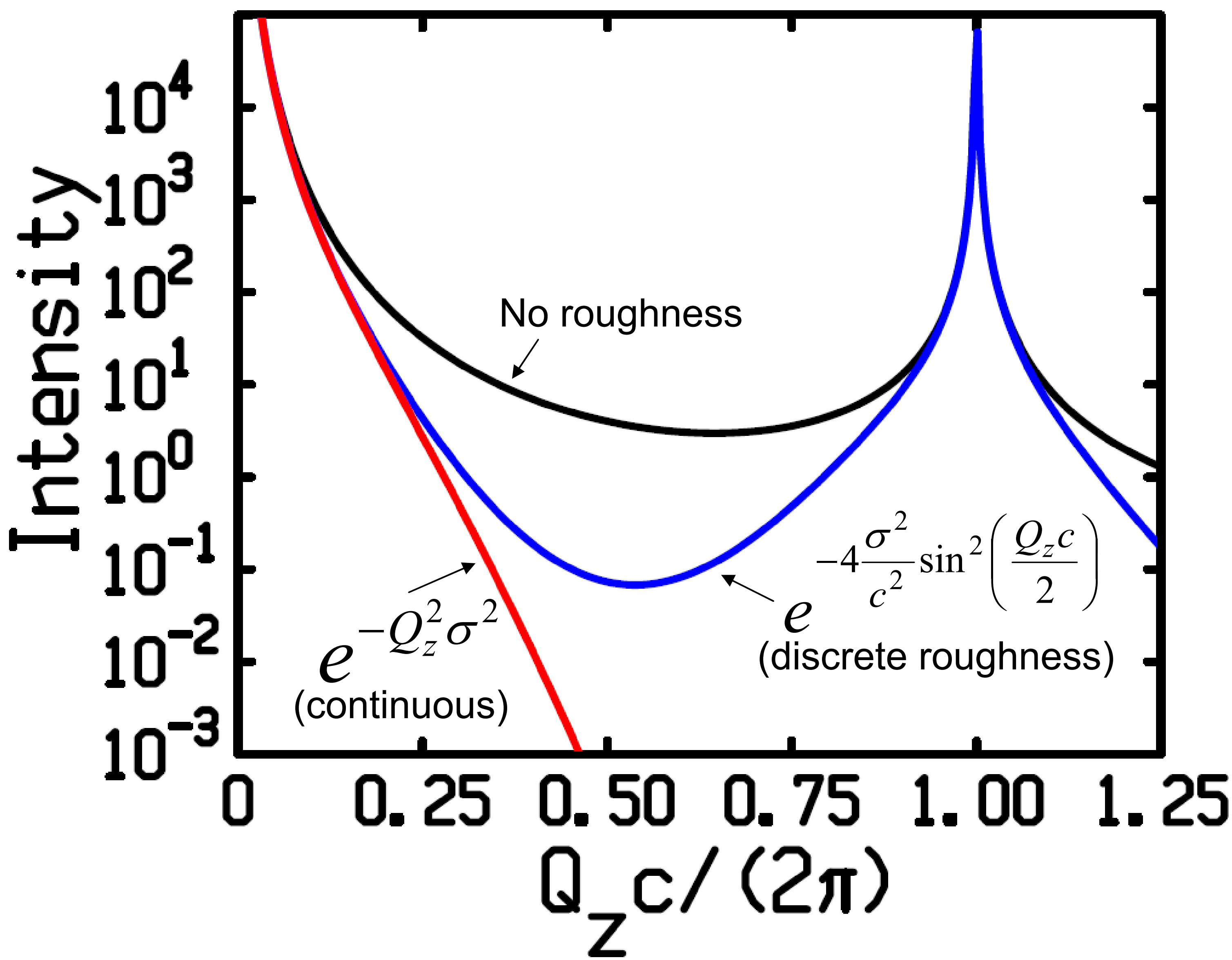
$$\left|\left\langle e^{iQ_z h}\right\rangle\right|^2 \rightarrow e^{-4\frac{\sigma^2}{c^2}\sin^2\left(\frac{Q_z c}{2}\right)}$$

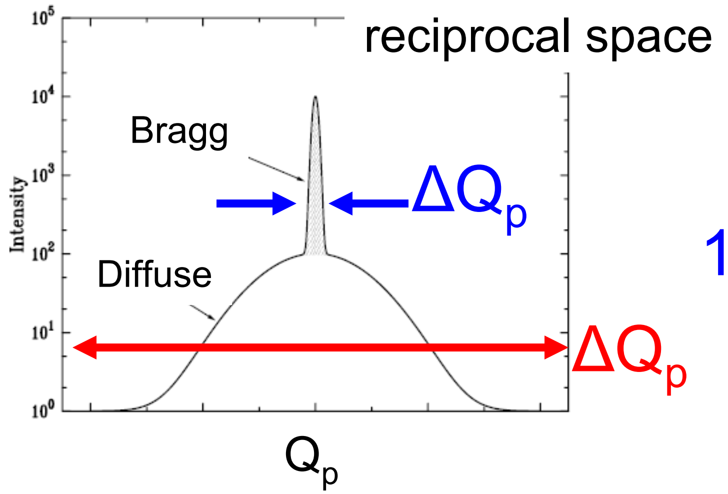
- Binomial distribution (limits to a Gaussian for large roughness)
- Preserves translational symmetry in the roughness

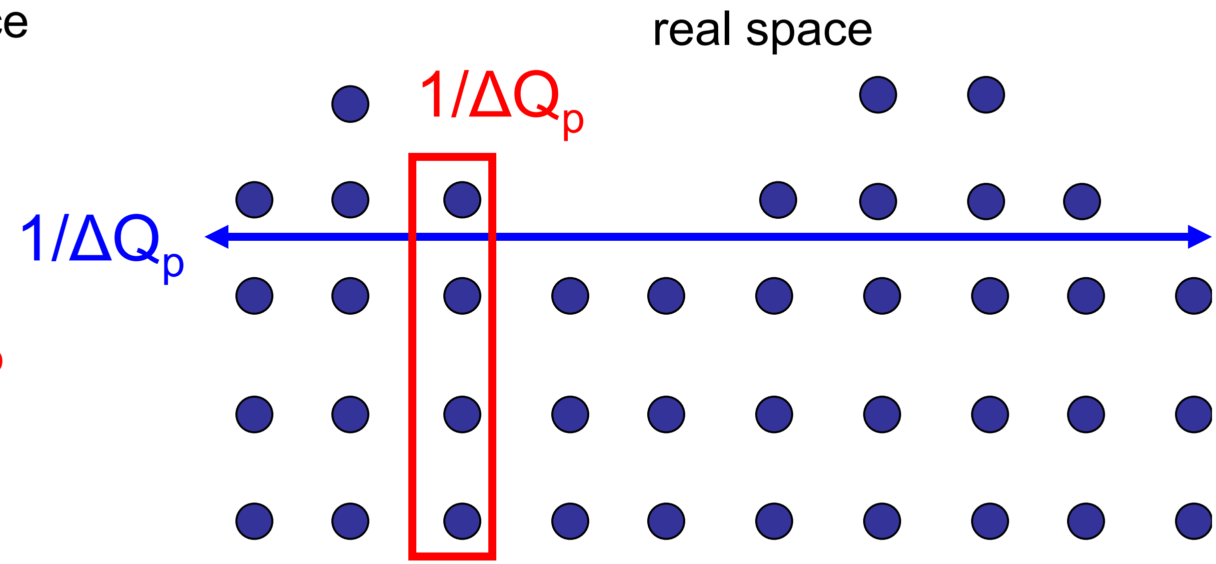
Physica B **221**, 65 (1996)

• Sharper interface (real space) gives broader scattering

• Gaussian roughness does not give translational symmetry







Bragg is narrow:

it samples laterally uncorrelated roughness at long distances

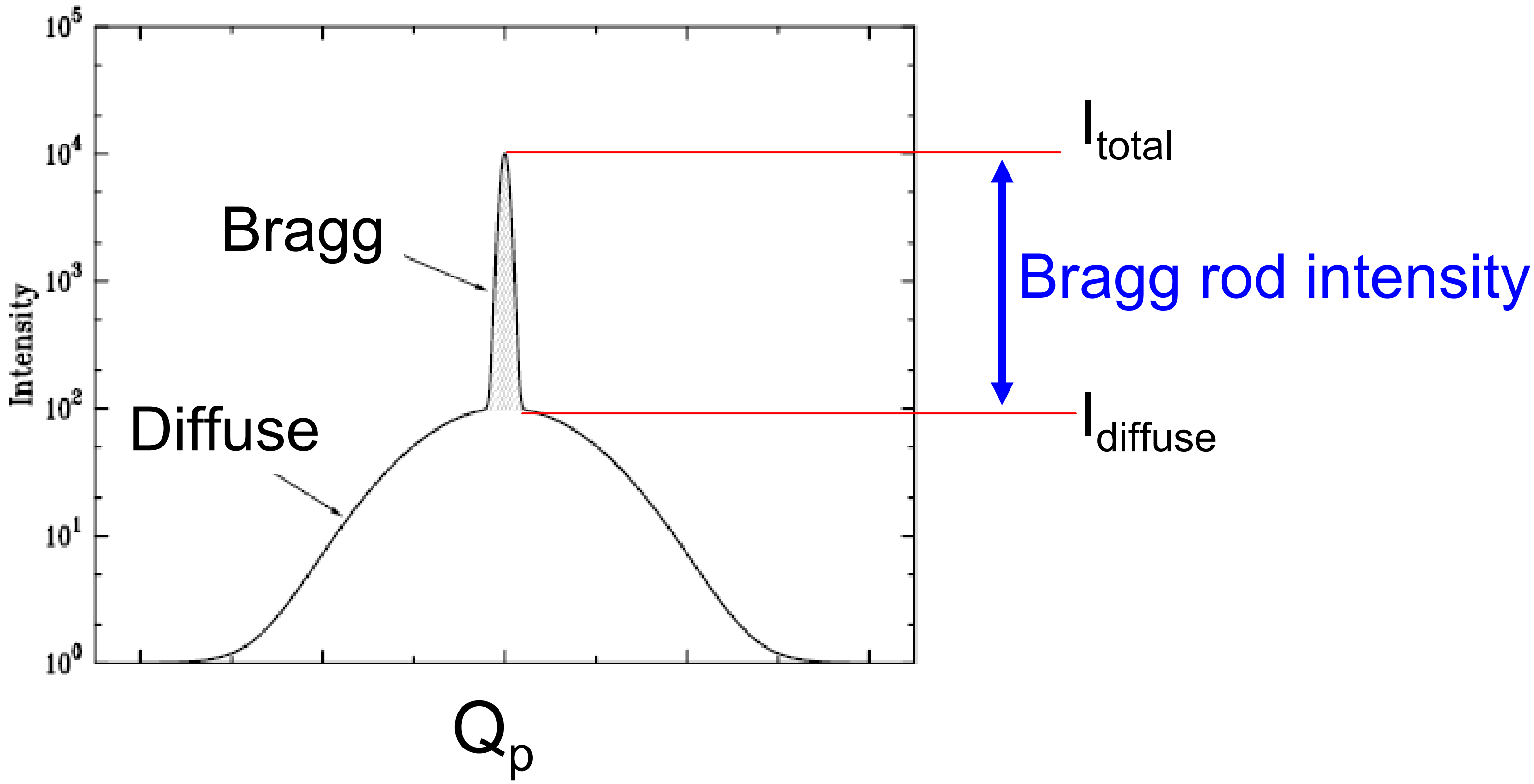
$$S^{Bragg}(\vec{Q}) \propto \frac{|b|^2}{\left|1-e^{iQ_z c}\right|^2} e^{-4\frac{\sigma^2}{c^2}\sin^2\left(\frac{Q_z c}{2}\right)}$$

Transversely-integrated scattering shows no effect of roughness:

(for 1 interface)

$$\iint d^2Q_p \, S(\vec{Q}) \propto \frac{|b|^2}{\left|1-e^{iQ_z c}\right|^2}$$

In practice, at every Q_z the diffuse must be subtracted from the total intensity to get the Bragg rod intensity:



X-ray Reflectivity from Si(111)7x7

Robinson & Vlieg, Surf.Sci **261**, 123 (1992)

- small vertical displacements
- 1st 3 atomic layers
- oscillatory features

$$\sum_{j=-\infty}^{0} e^{-iQ_z dj} + \sum_{j=1}^{3} \rho_j e^{iQ_z z_j}$$

Bulk CTR + layers

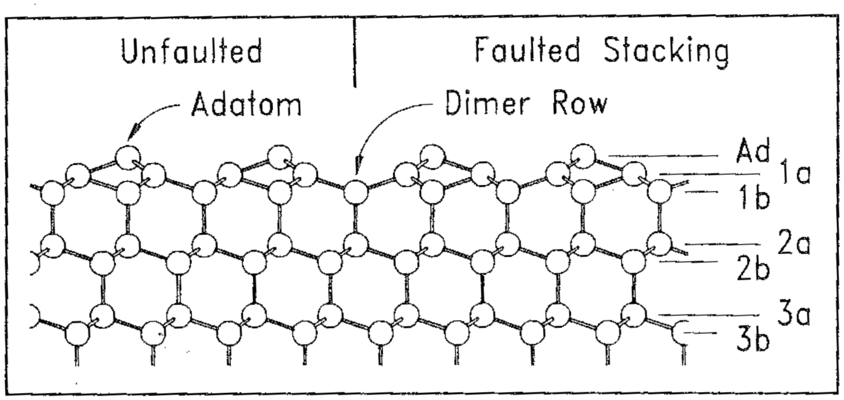
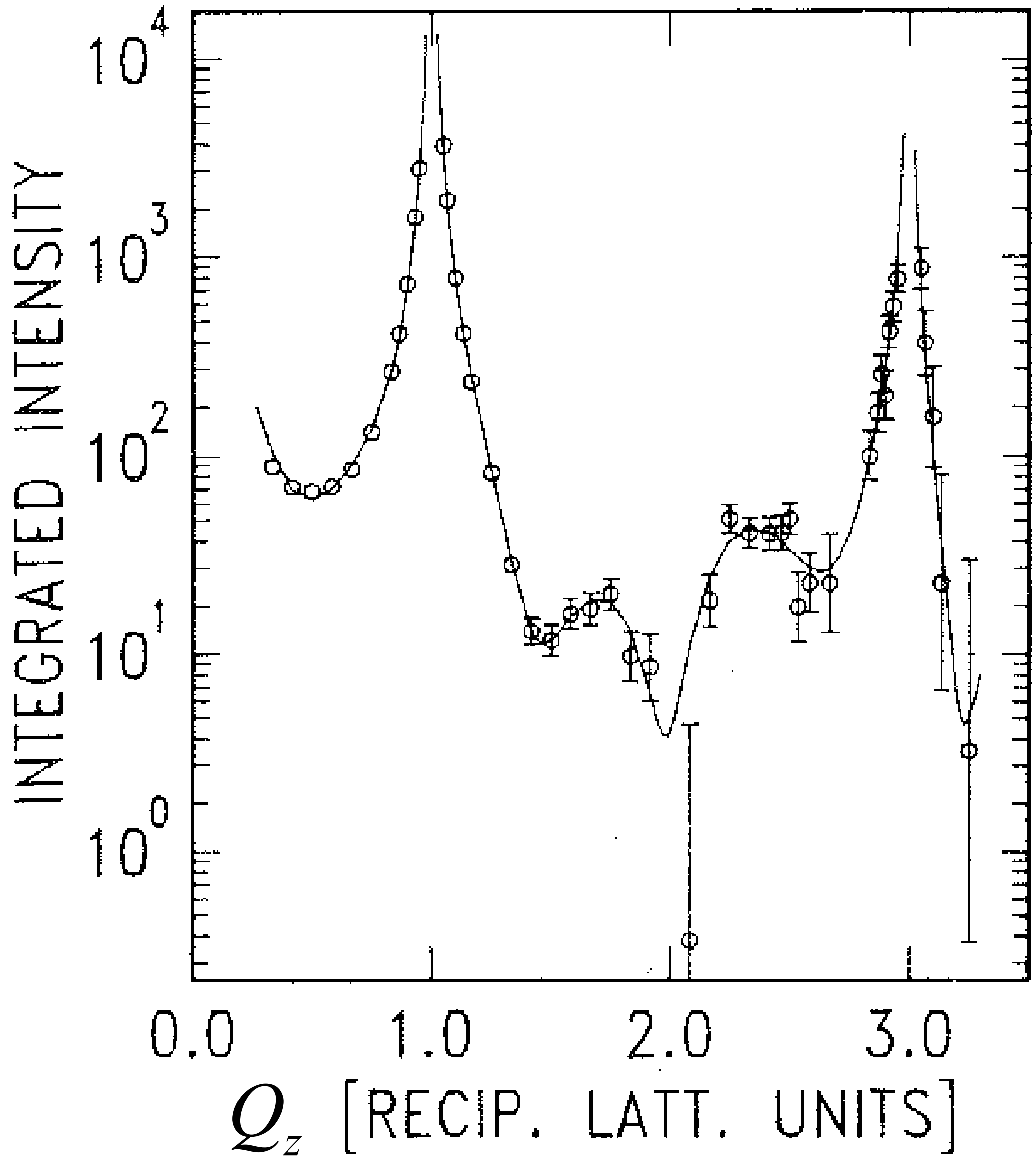


Fig. 3. Ball and stick diagram of the dimer-adatom-stacking fault (DAS) model of the reconstructed Si(111)7×7 surface viewed from the side. All atoms are in unrelaxed "ideal" positions indicated in table 2. The layer notations used in the paper are defined.

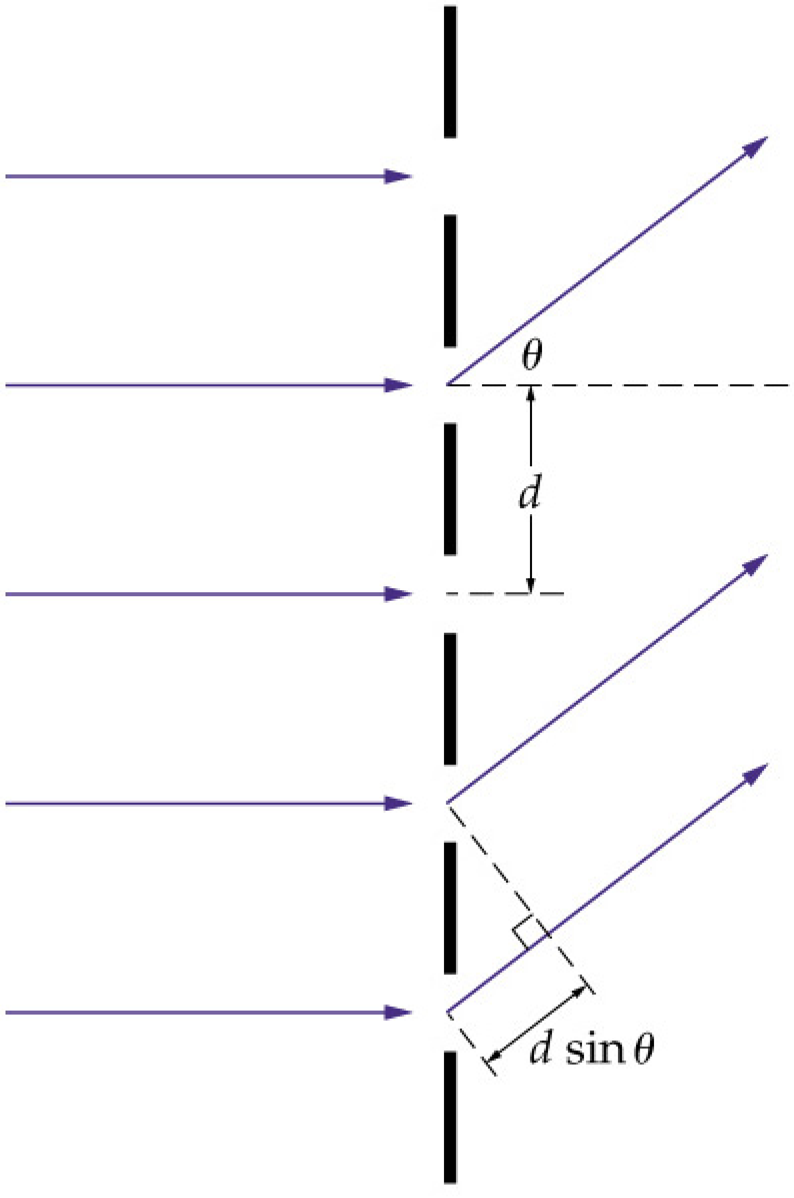


What would we expect from a **thin film**?

1st let's recall Young's slit interference….

Recall…

N-Slit Interference and Diffraction Gratings



Principle maxima

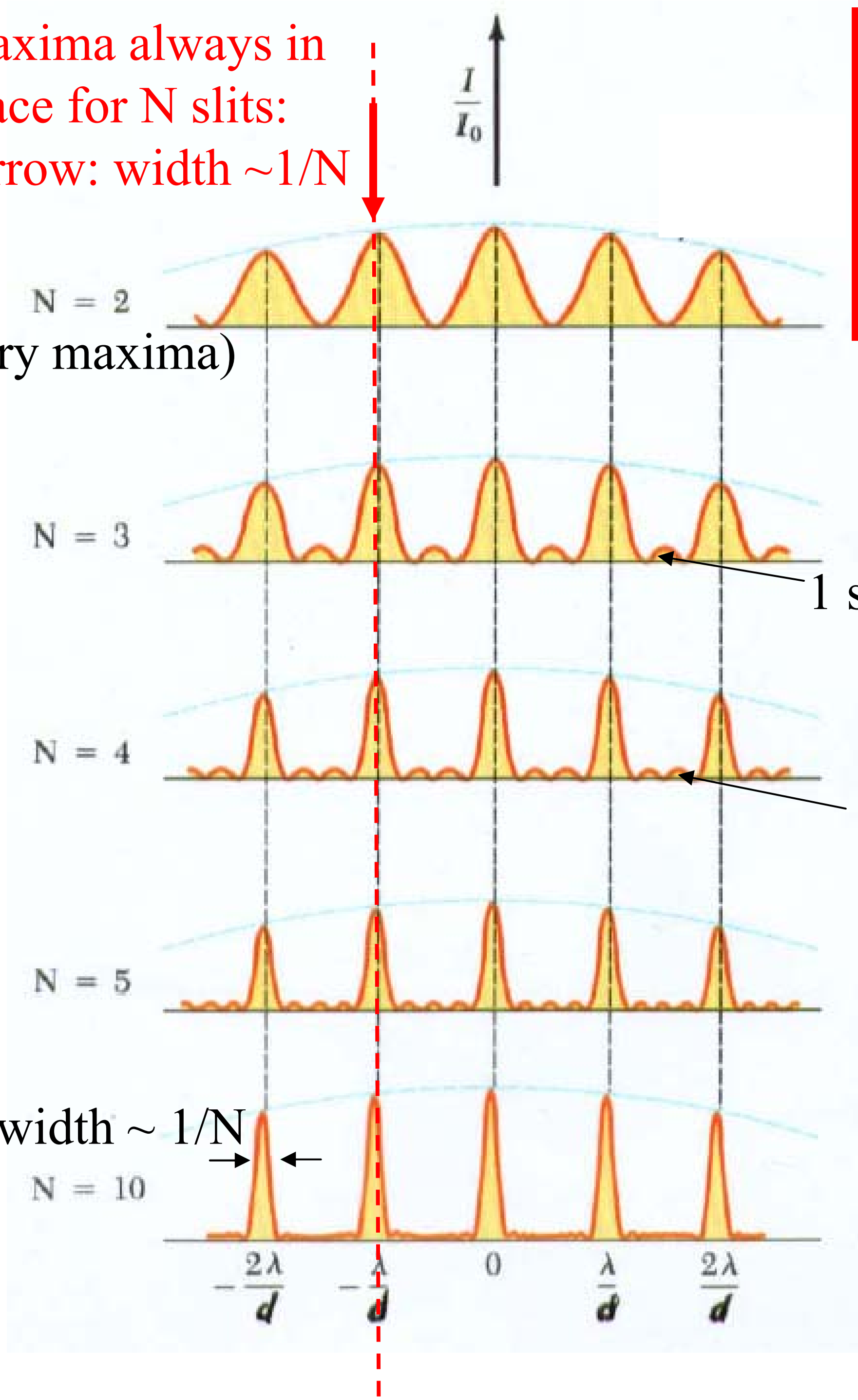
$d \sin \theta = m\lambda$

Principle maxima always in the same place for N slits:
But they narrow: width ~1/N

Principle maxima
$d \sin\theta = m\lambda$

(N-2 subsidiary maxima)

Double Slit
(no subsidiary maxima)



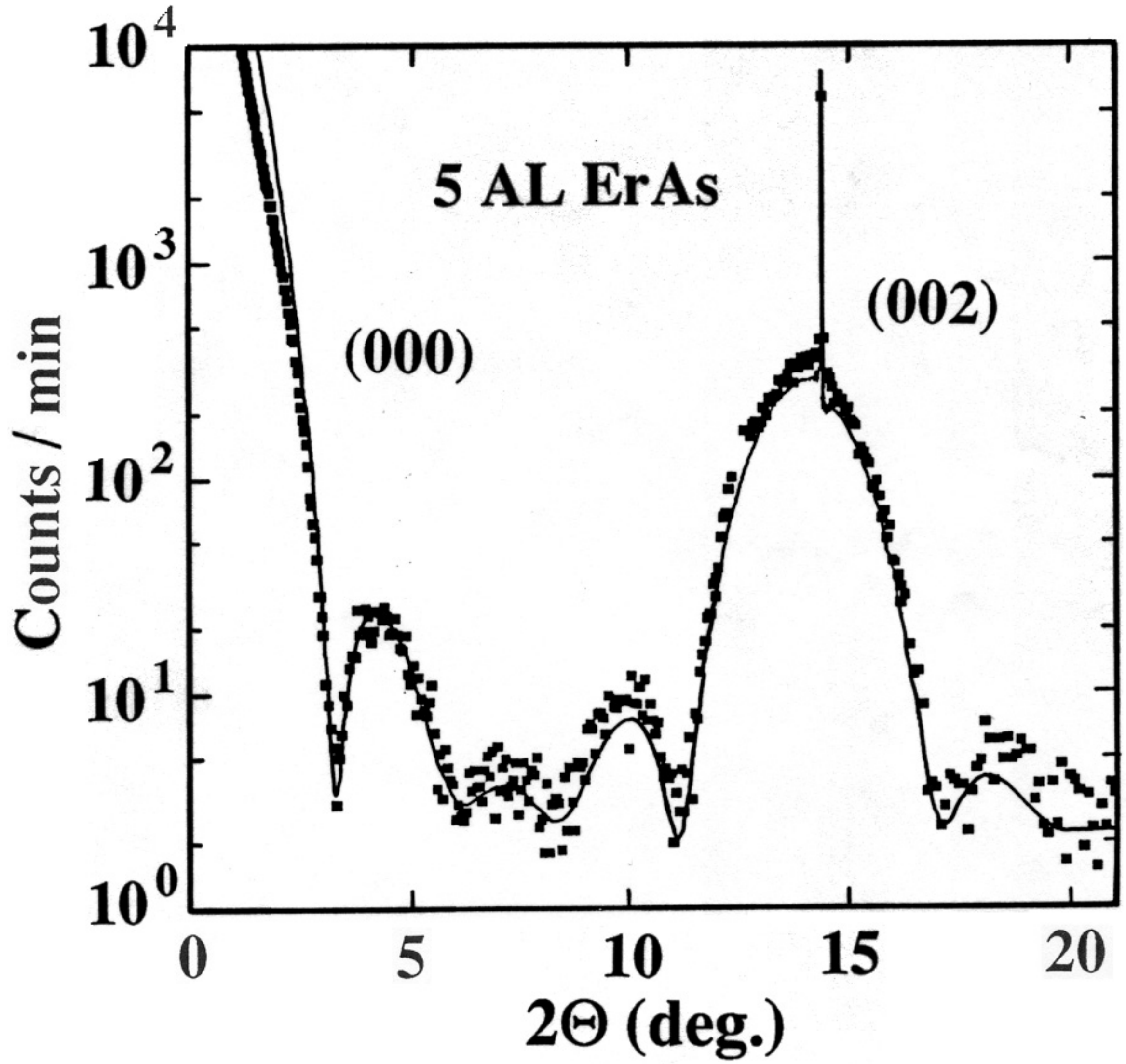
1 subsidiary maximum

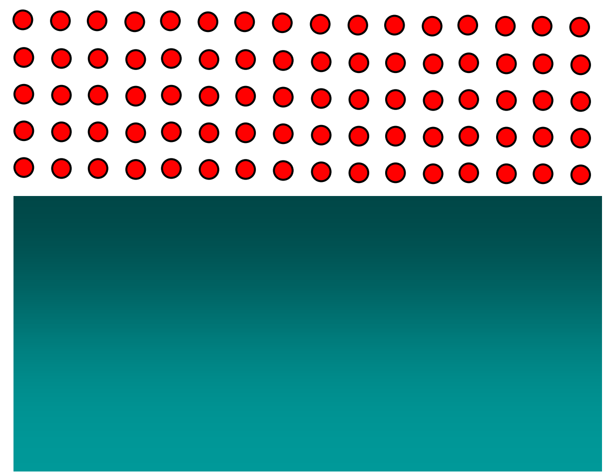
2 subsidiary maximum

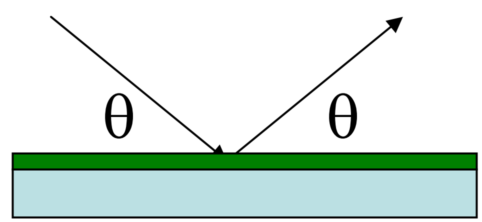
width ~ 1/N

N large:
- Weak subsidiary maxima
- Sharp principle maxima

“5-slit” interference of x-rays from 5 layers of atoms

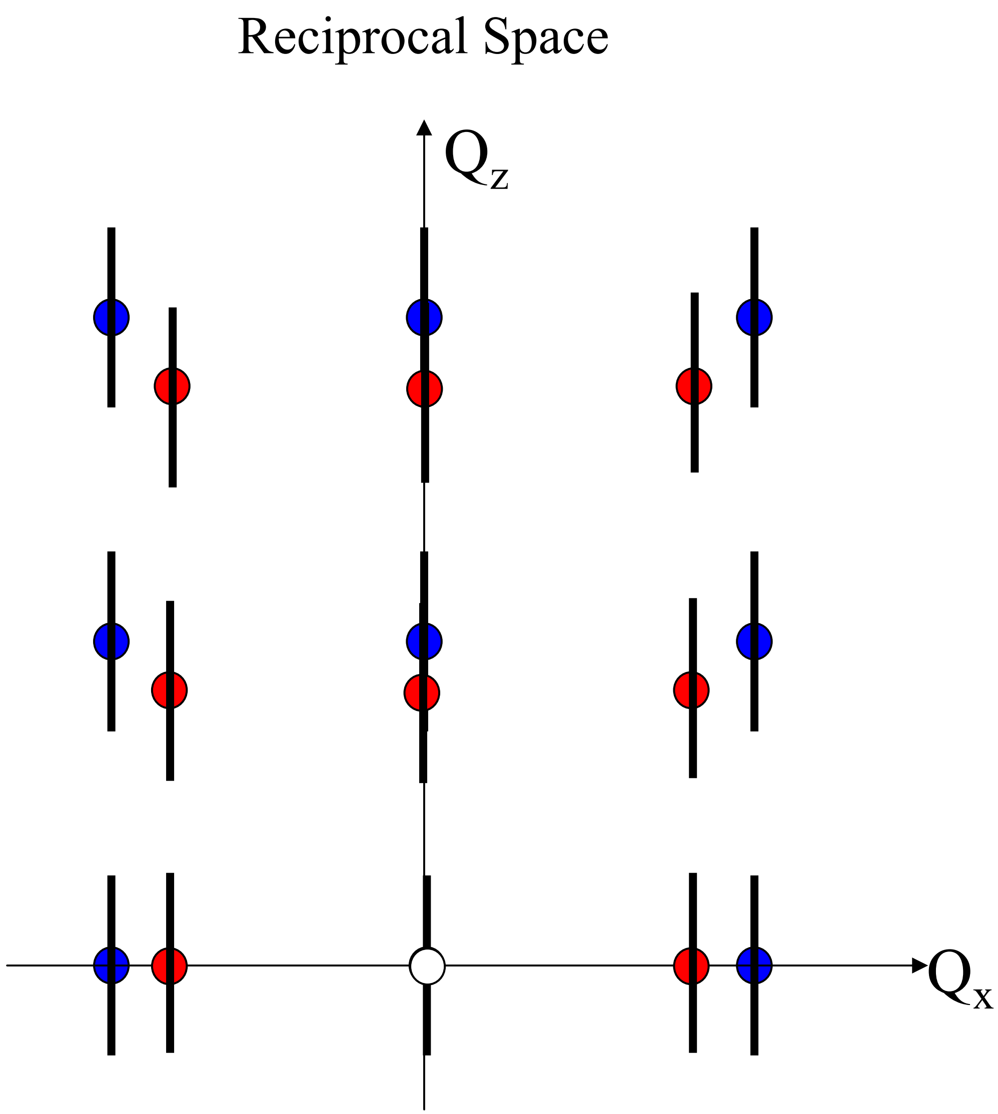


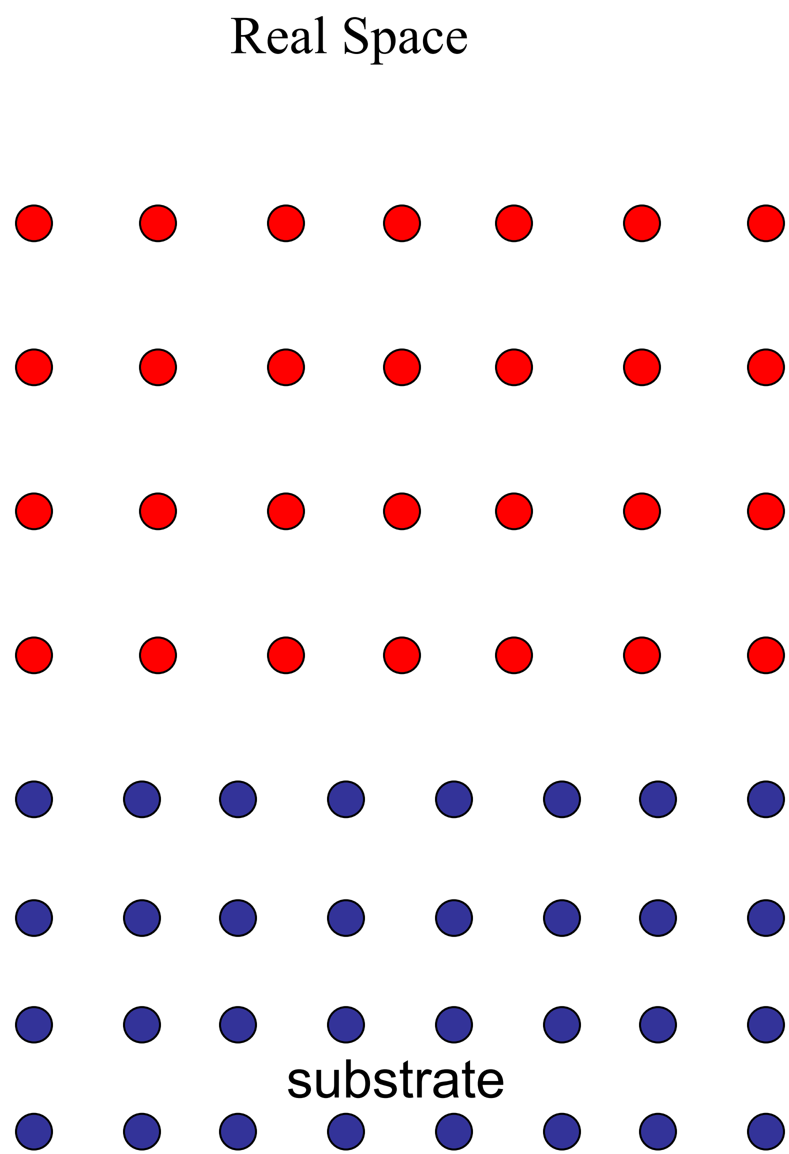




Miceli et al., Appl. Phys. Lett. **62**, 2060 (1992)

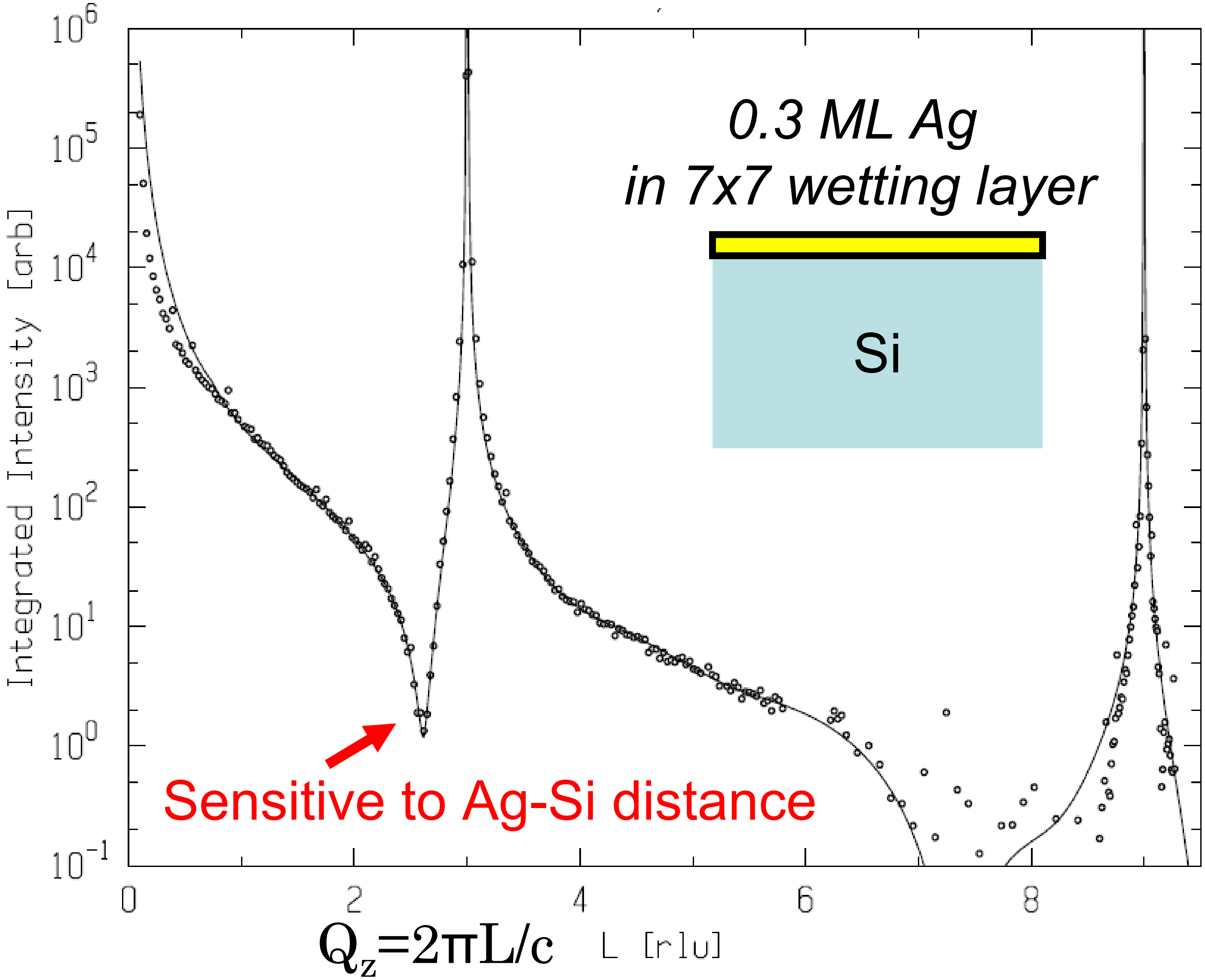
Thin Films

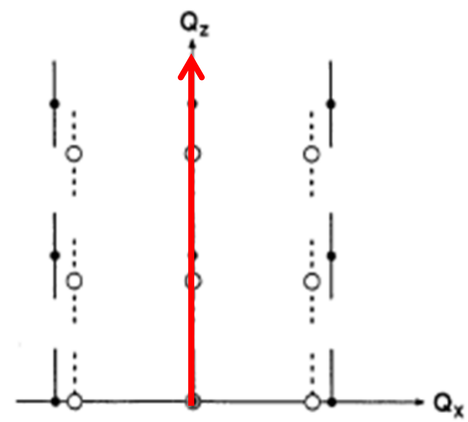




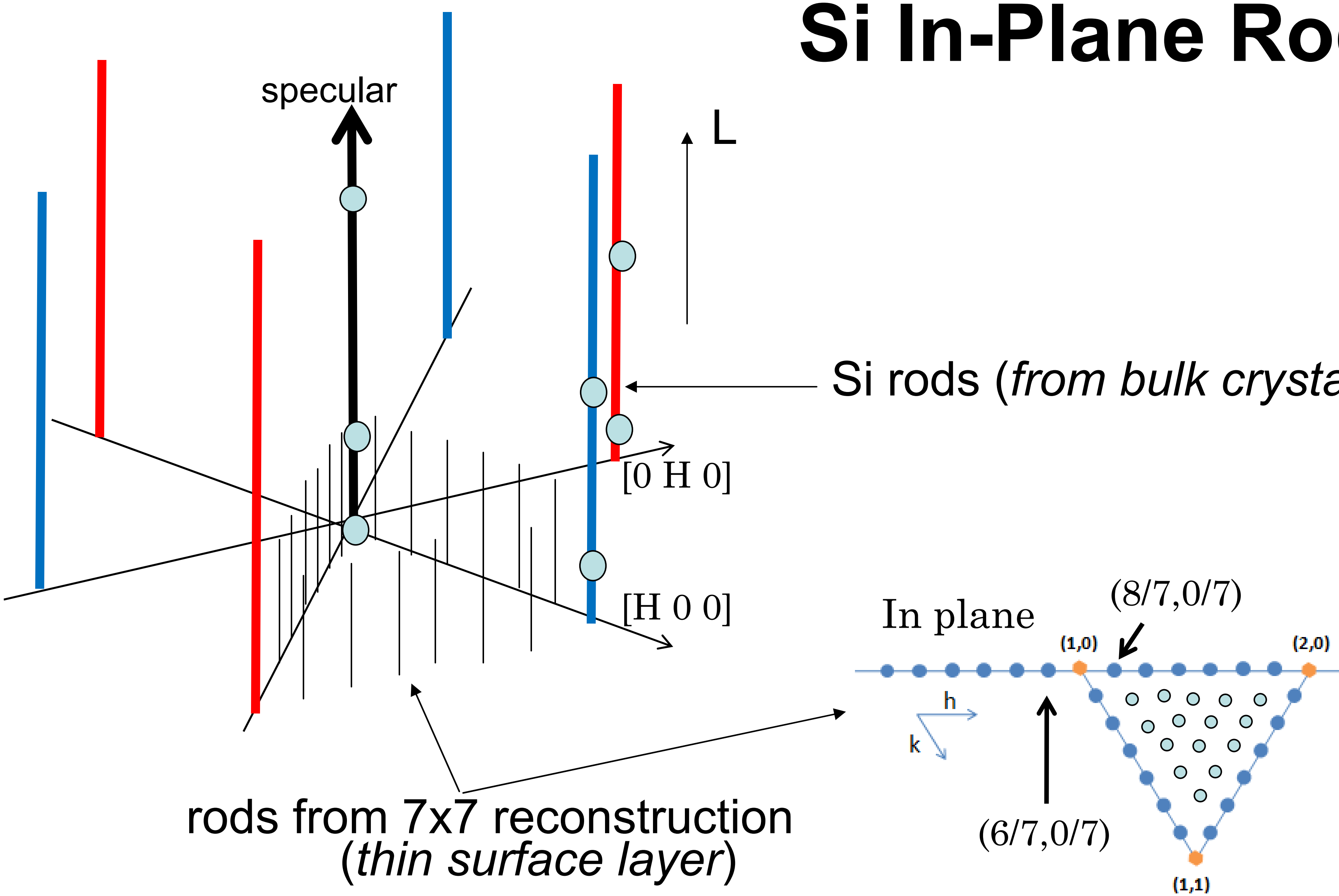
Ag/Si(111)7x7

Specular Reflectivity: 0.3ML Ag/Si(111)7x7



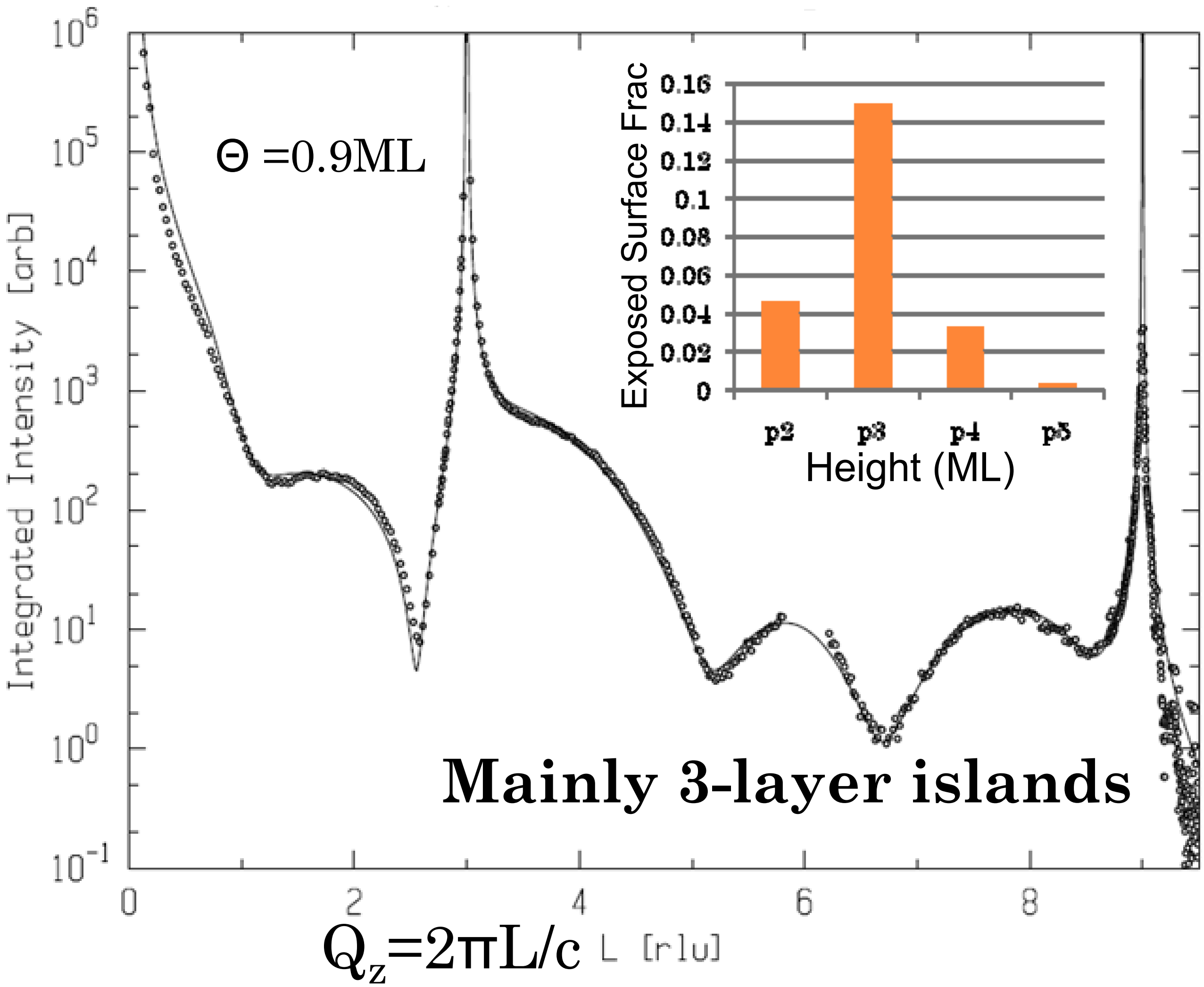


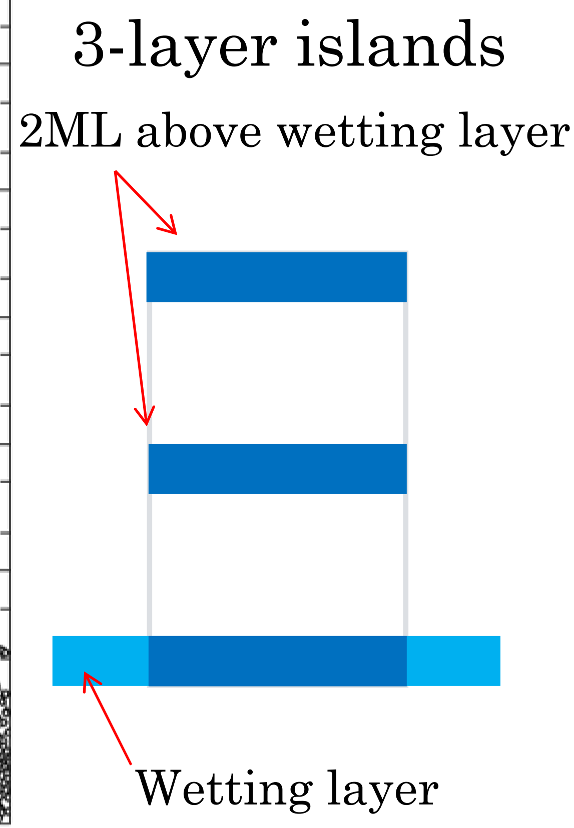
Si In-Plane Rods



Ag/Si(111)7x7

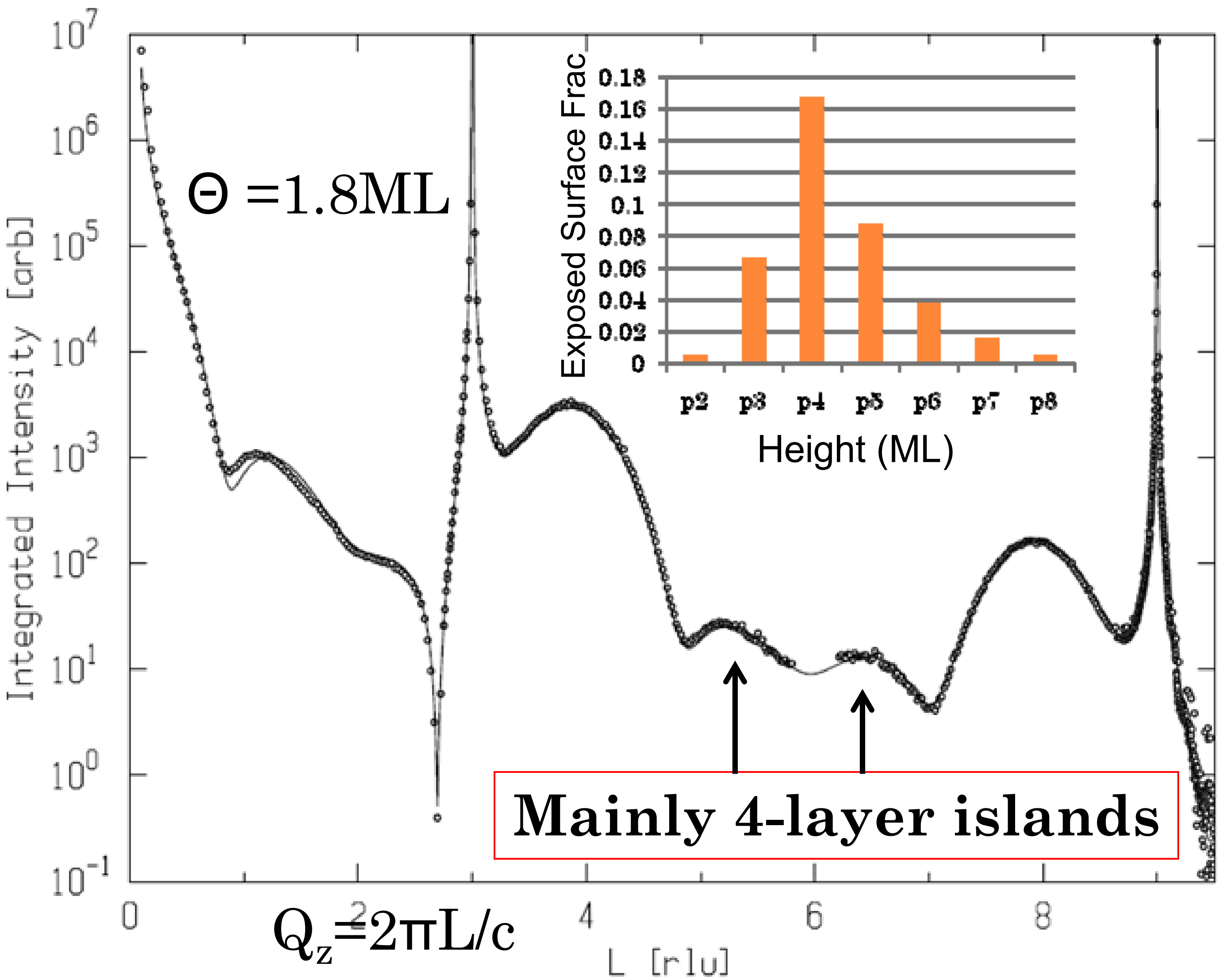
Specular Reflectivity: 0.9ML Ag/Si(111)7x7





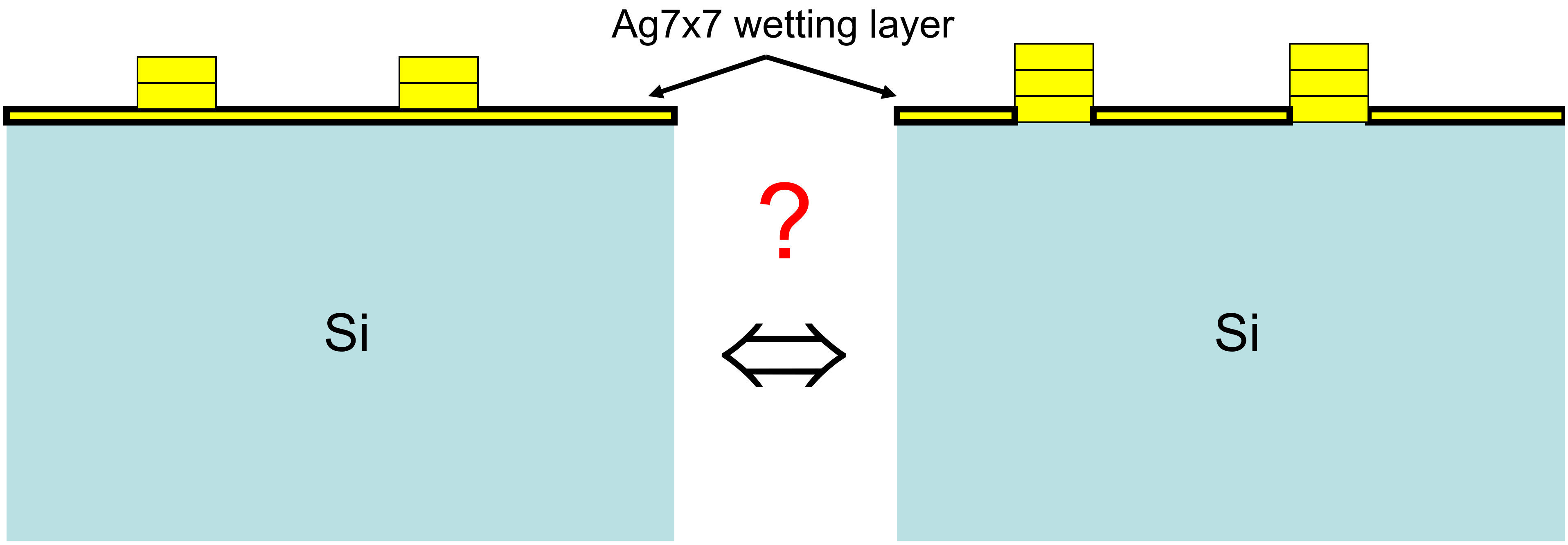
Ag/Si(111)7x7

Specular Reflectivity: 1.8ML Ag/Si(111)7x7

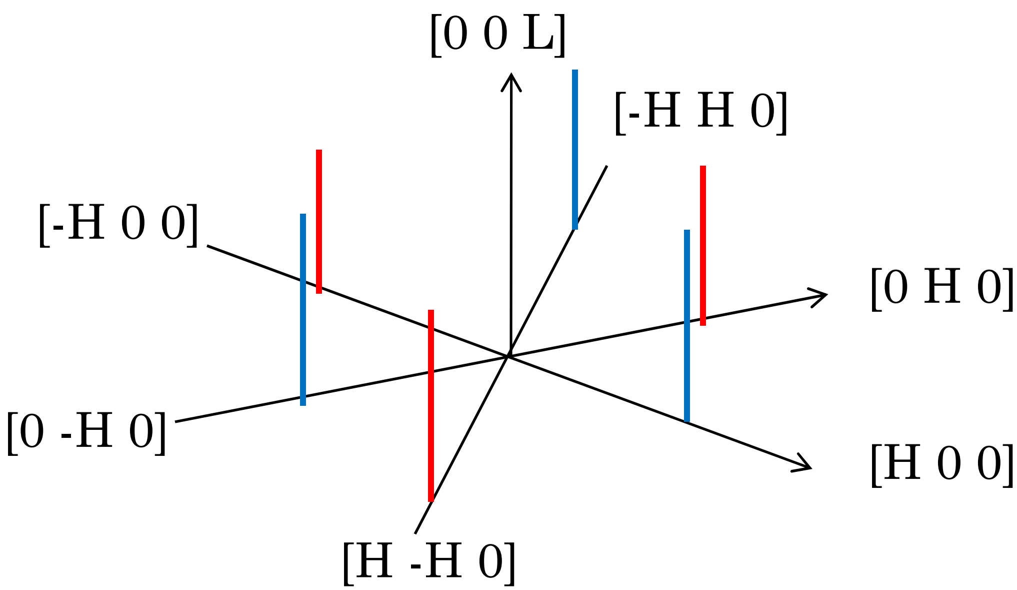


Ag islands <u>on</u> a Ag 7x7 wetting layer: FCC = 2 ML

or… Ag islands all the way to the substrate? FCC = 3 ML



Ag(111) rods

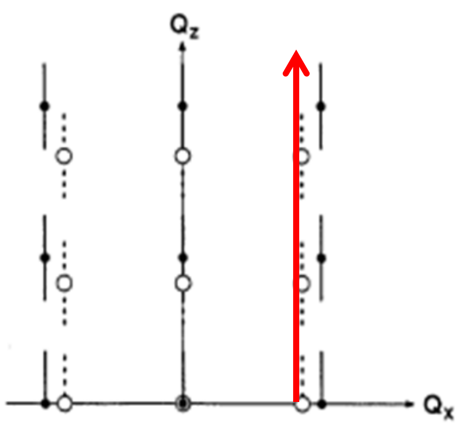


Hex coordinates

$(1\ 0\ 0)_{hex}=1/3*(-4\ 2\ 2)_{cubic}$

$(0\ 1\ 0)_{hex}=1/3*(-2\ -2\ 4)_{cubic}$

$(0\ 0\ 1)_{hex}=1/3*(1\ 1\ 1)_{cubic}$



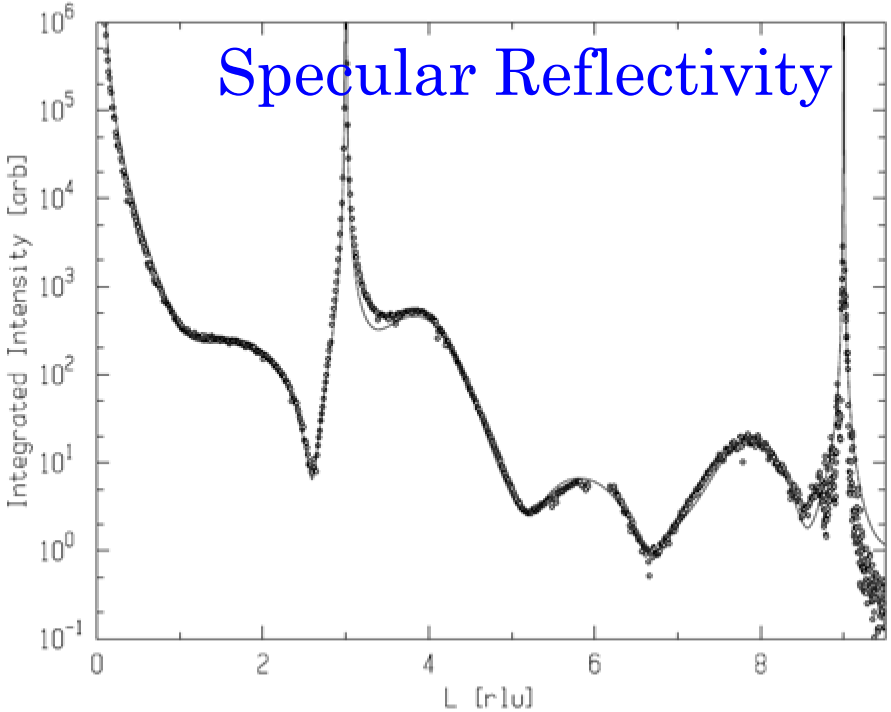
Fcc 3 fold symmetry

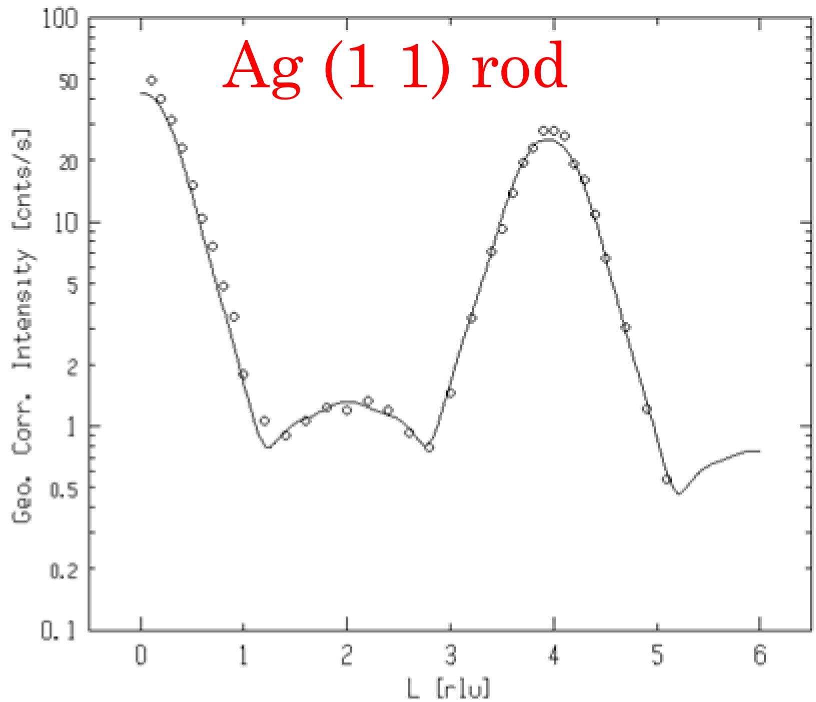
One group: (1 0)rod=(-1 1)rod=(0 -1)rod

Another group: (0 1)rod=(-1 0)rod=(1 -1)rod

Specular reflectivity and rod give same thickness:

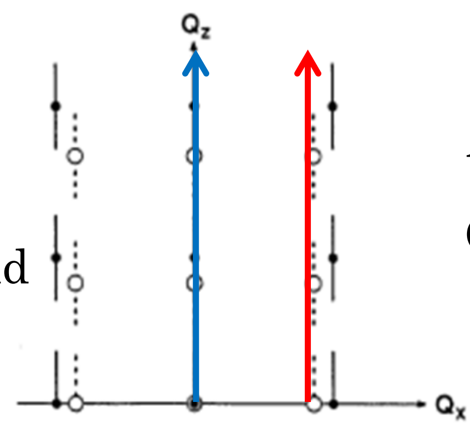
Island is FCC Ag all the way to the substrate





Specular Reflectivity

Probes Si substrate, Ag wetting layer and Ag island



Ag truncation rod

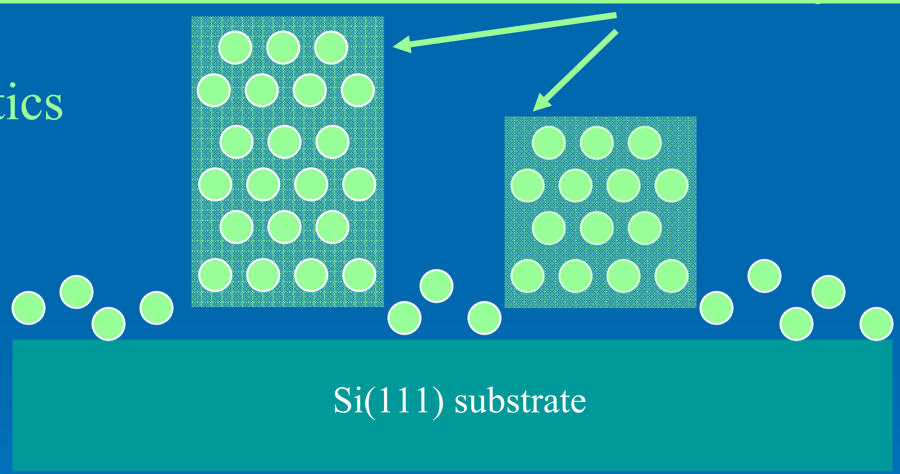
Only probes FCC Ag

Quantum-Size-Effects:
Pb Nanocyrstals on Si(111)7x7

Quantum Mechanics Influences Nanocrystal Growth

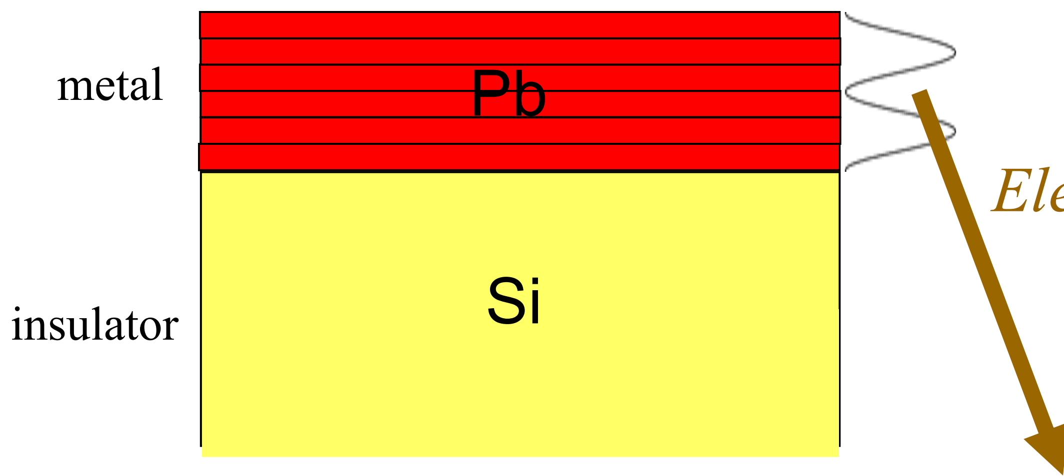
Discoveries:

- anomalously (10^4) fast kinetics
- Non-classical coarsening
- Unusual behavior:
  fast growth => most stable structures

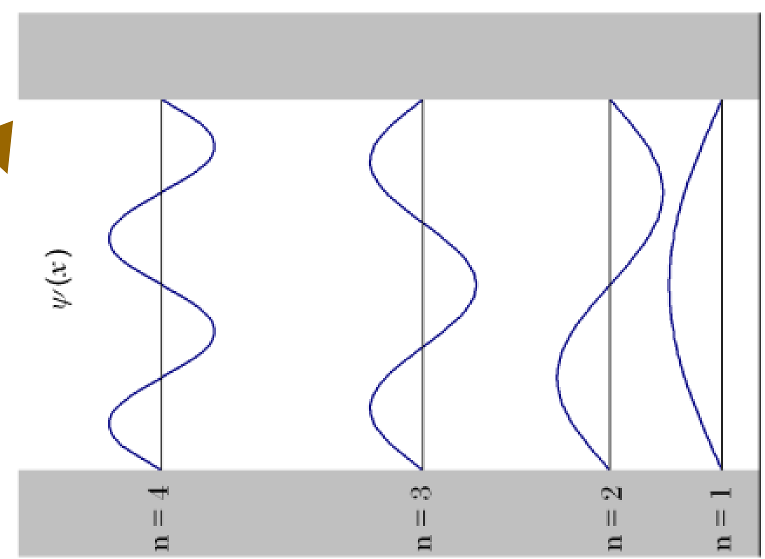


C. A. Jeffrey et al., PRL **96**, 106105 (2006)

Electrons in a “box”



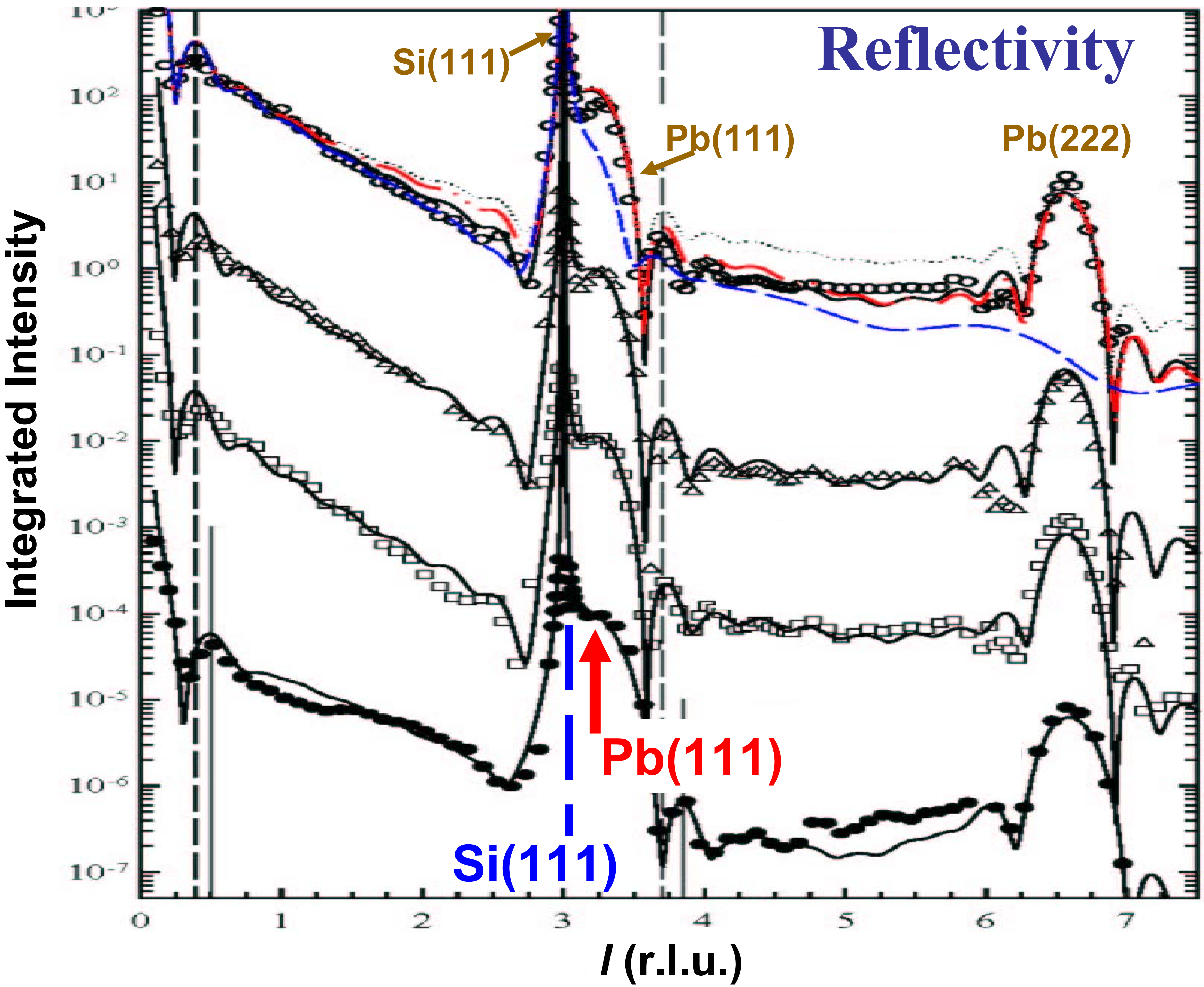
Electrons are confined to the metal



Electrons will Exhibit Discrete Quantum Mechanical Energies

F. K. Schulte, Surf. Sci. **55**, 427 (1976)
P. J. Feibelman, PRB **27**, 1991 (1983)

physchem.ox.ac.uk



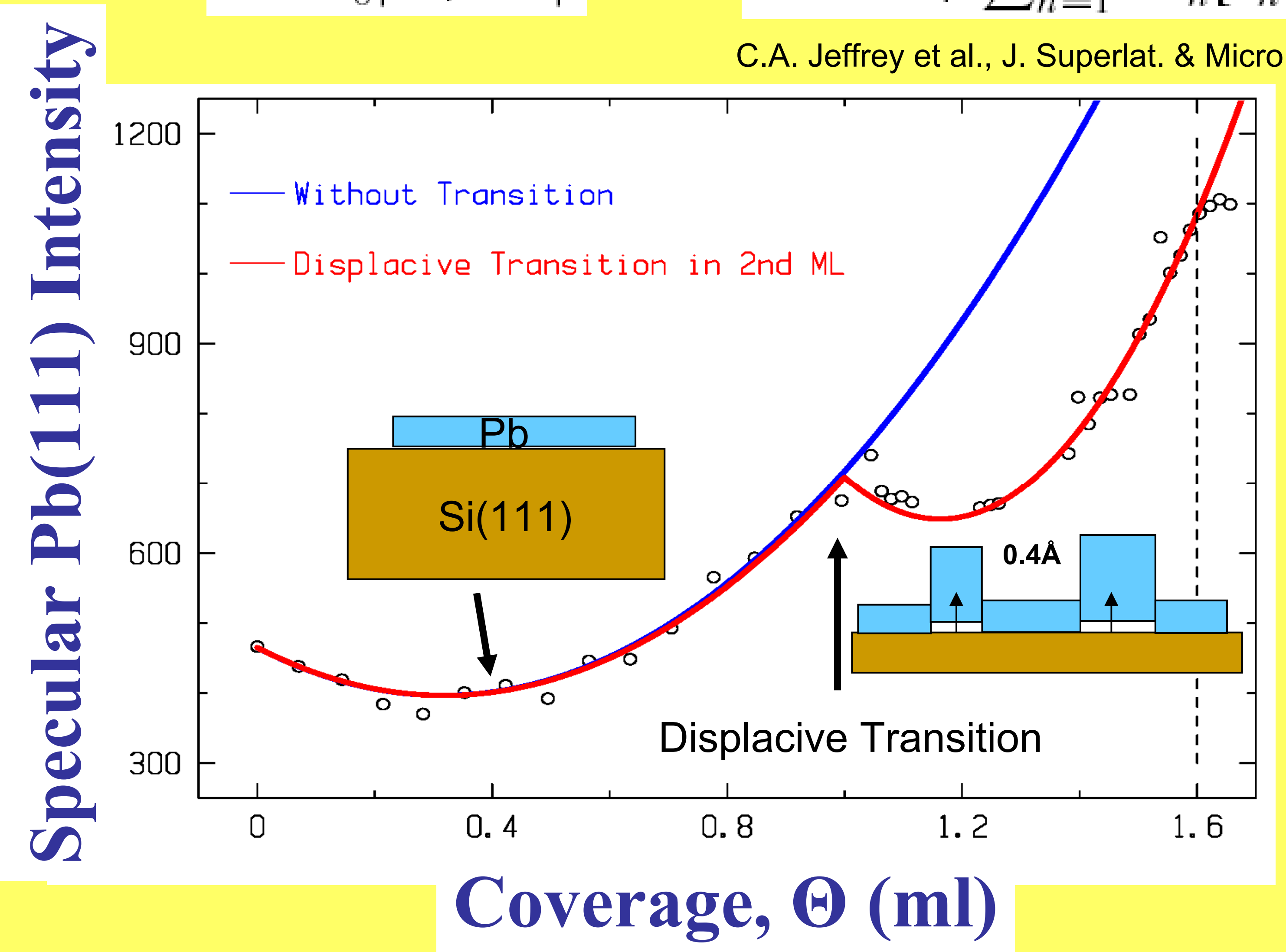
Reflectivity
Si(111)
Pb(111)
Pb(222)
Pb(111)
Si(111)
Integrated Intensity
l (r.l.u.)
10²
10¹
10⁰
10⁻¹
10⁻²
10⁻³
10⁻⁴
10⁻⁵
10⁻⁶
10⁻⁷
0
1
2
3
4
5
6
7

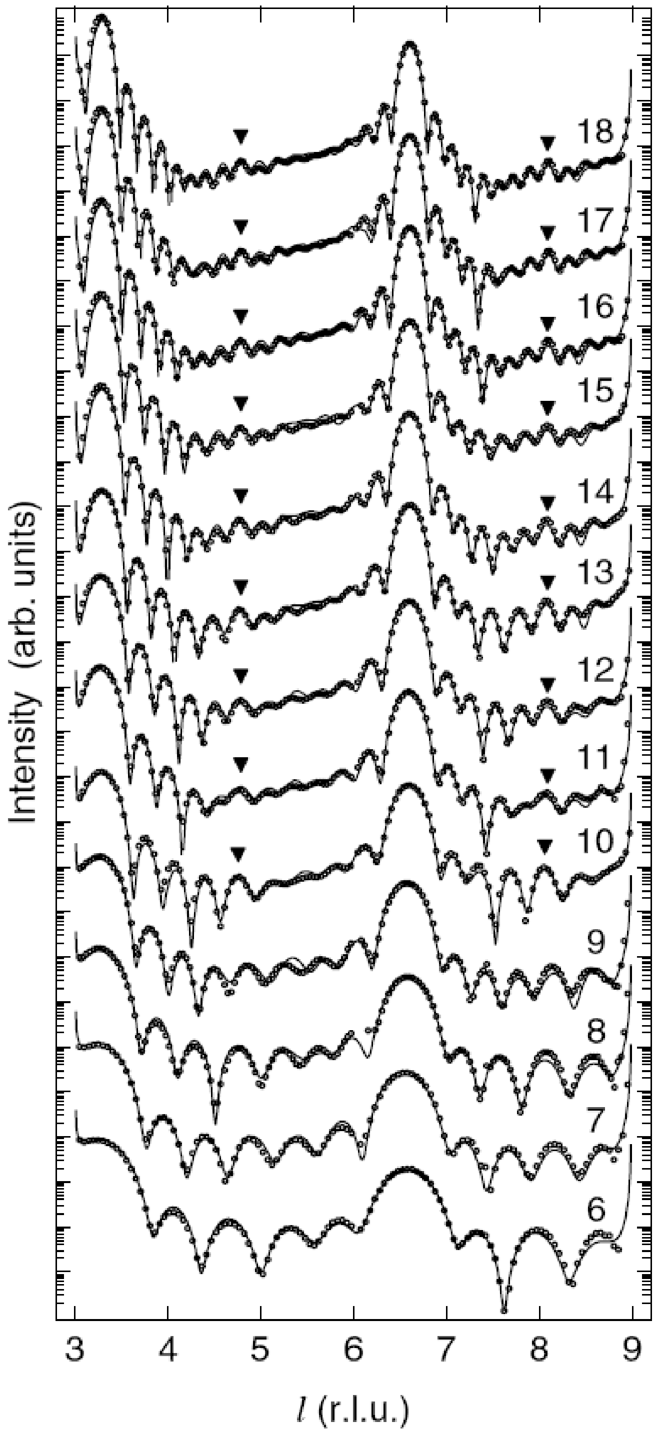
Islands consume the wetting layer & move away from the interface

$$R = R_0 |1 + \tilde{r}\,\tilde{\Theta}|^2$$

$$\tilde{\Theta} = \Theta + \sum_{n=1} n P_n [a_n e^{i\phi_n} - 1]$$

C.A. Jeffrey et al., J. Superlat. & Micro. **41**, 168 (2007)



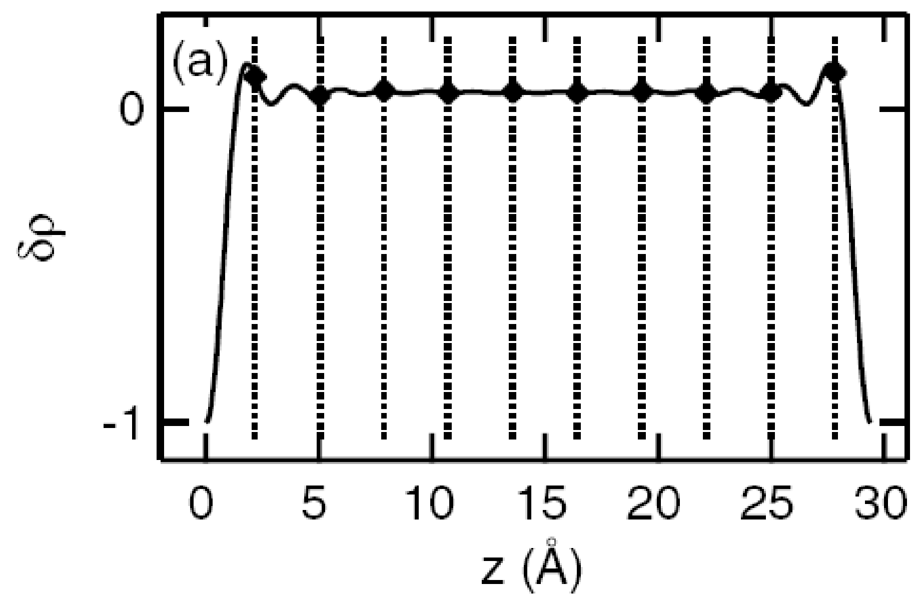


Charge Density Oscillations Due to Quantum Confinement Pb/Si(111)

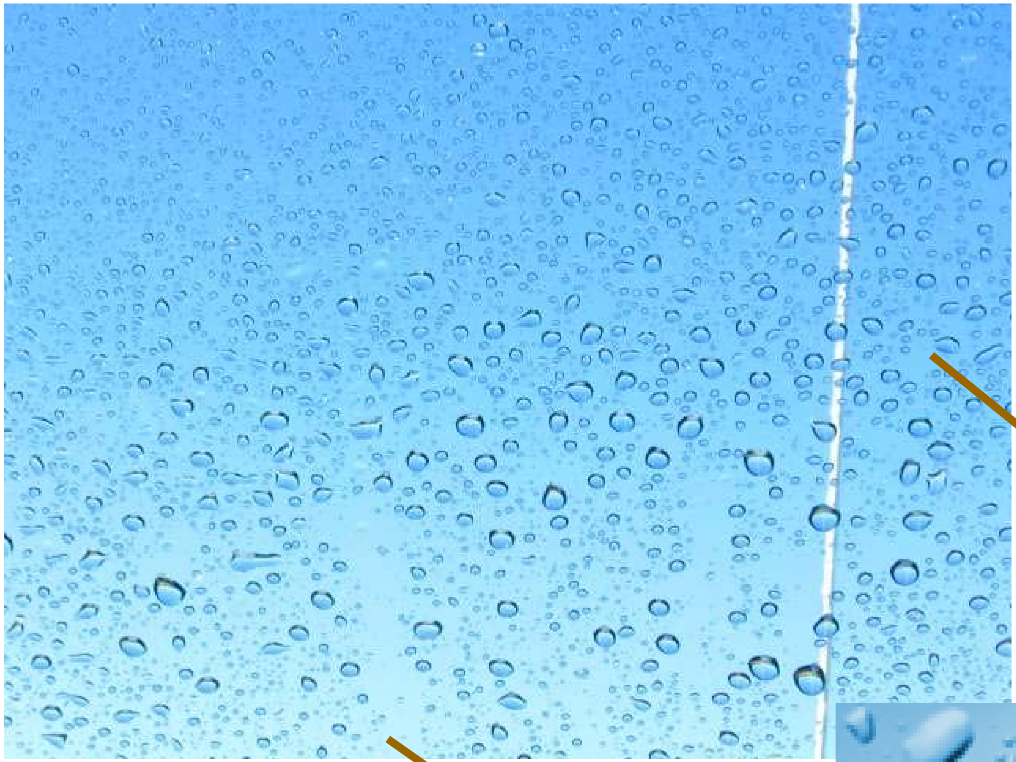
Czoschke et al., PRL **91**, 226801 (2003)

Electron density in Sommerfeld model:

$$\rho(z) \propto \sum_{n=1}^{n_0} (k_F^2 - k_z^2)\sin^2(k_z z)$$



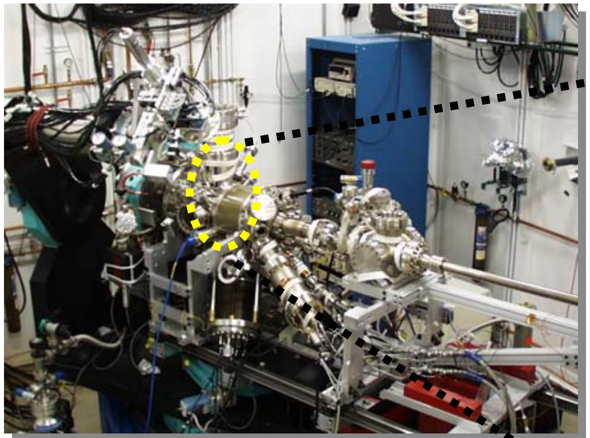
Rain Drops On Your Winshield



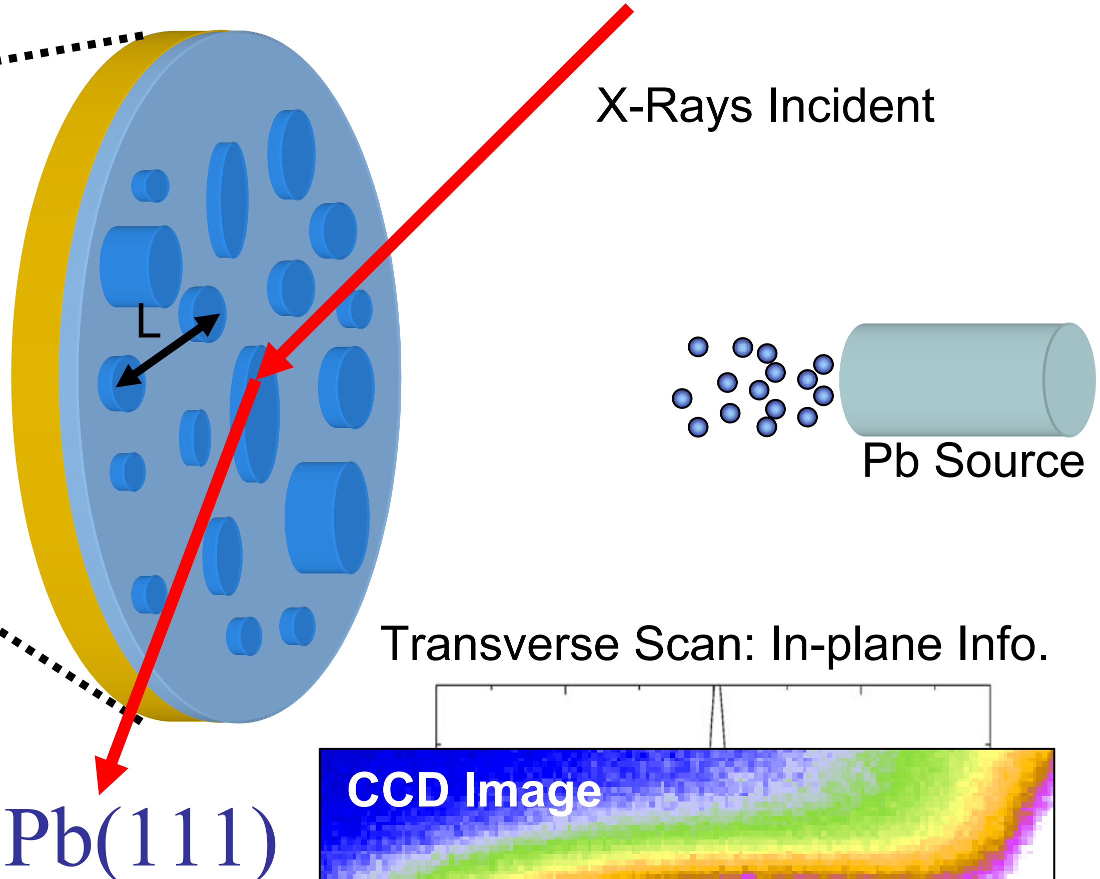
Coarsening

laist.com
greeneurope.org

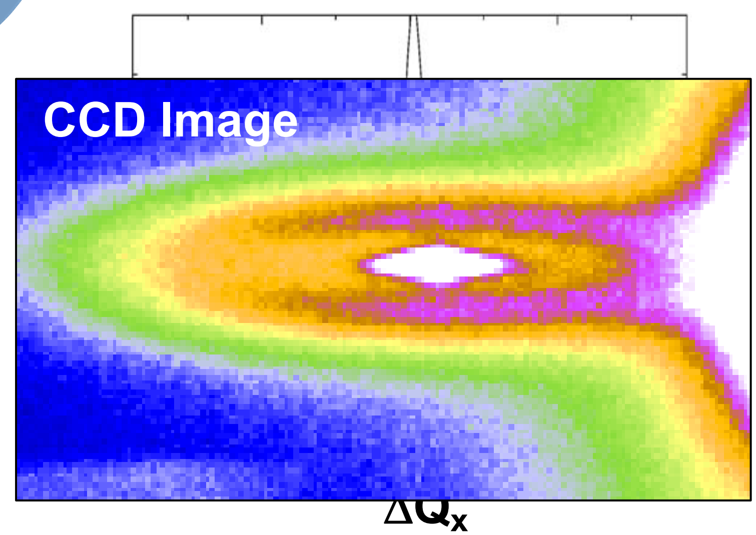
Kinetics: In Situ Surface X-ray Scattering



Surface Chamber
Advanced Photon Source



Transverse Scan: In-plane Info.



Mean island separation, <L>:

$$\Delta\kappa = \frac{2\pi}{\langle L\rangle}$$

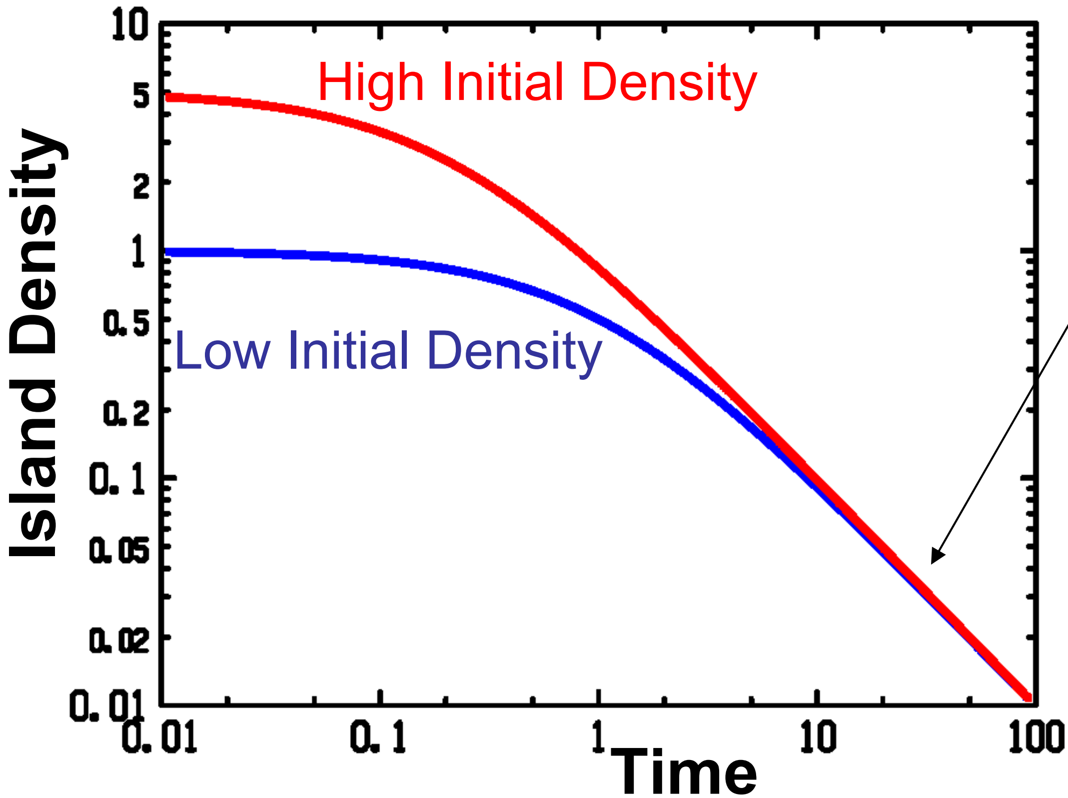
Island Density:

$$n \propto \frac{1}{\langle L\rangle^2}$$

Experiment:
- Deposit Pb (1.2 to 2 ml) at 208K
- Measure the island density vs time (flux off)

Classical Coarsening: Ostwald Ripening

$$n(t) = n_0\left(1+\frac{t}{\tau}\right)^{-\beta} \qquad \beta = \frac{2}{(m+2)}, m = 0,1,2$$



Long time: independent of initial conditions

$$n(t) \Rightarrow \left(n_0\tau^{\beta}\right)t^{-\beta}$$

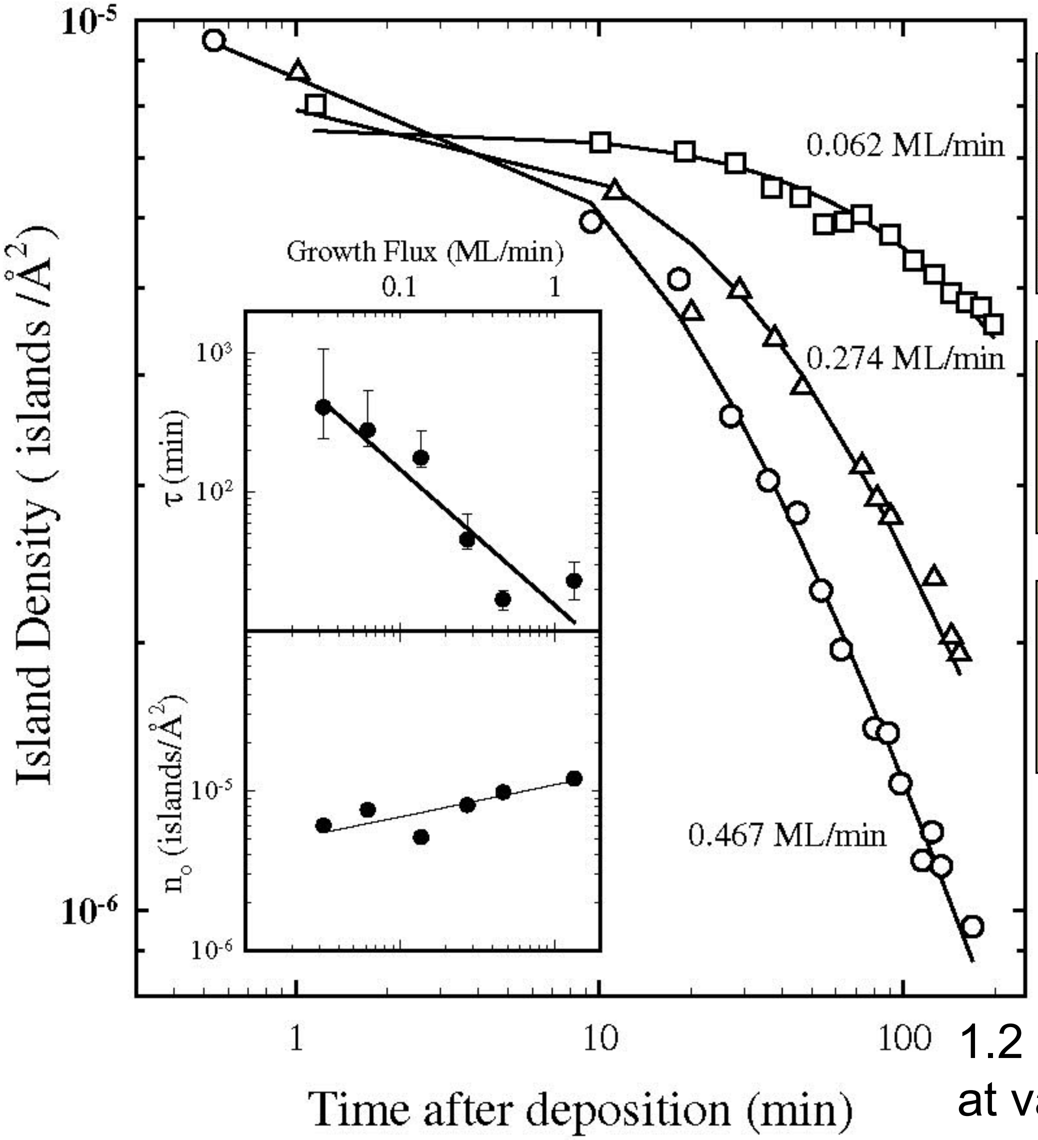
$$\boxed{\tau \propto n_0^{-\frac{1}{\beta}}}$$

Relaxation time depends <u>only</u> on the initial density

Pb Nanocrystal Coarsening

…does ***not*** conform to the classical picture!

C. A. Jeffrey et al., PRL **96**, 106105 (2006)

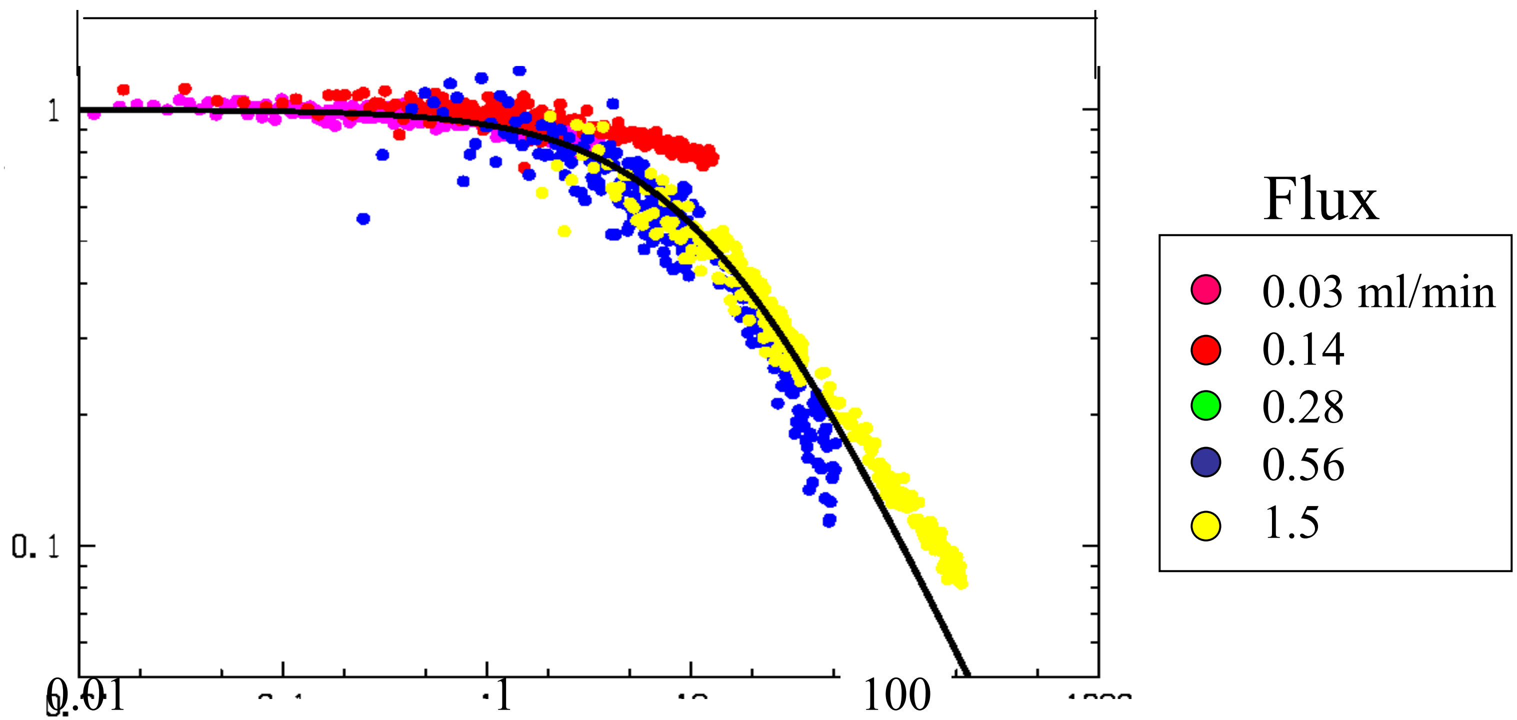


1.2 ML of Pb at 208K
at various flux rates

- Island densities do not approach each other at long times:
  - QSE ⇒ Non-Oswald
  - Breakdown of Classical Coarsening
- Time constant τ **~ 1/Flux**
  - Strong flux dependence!
  - Unexpected!
- Anomalously fast relaxation
  - ~1000x faster than expected!
  - ⇒allows equilibrium!

$$n(t) = \frac{n_0}{\left(1+\frac{t}{\tau}\right)}$$

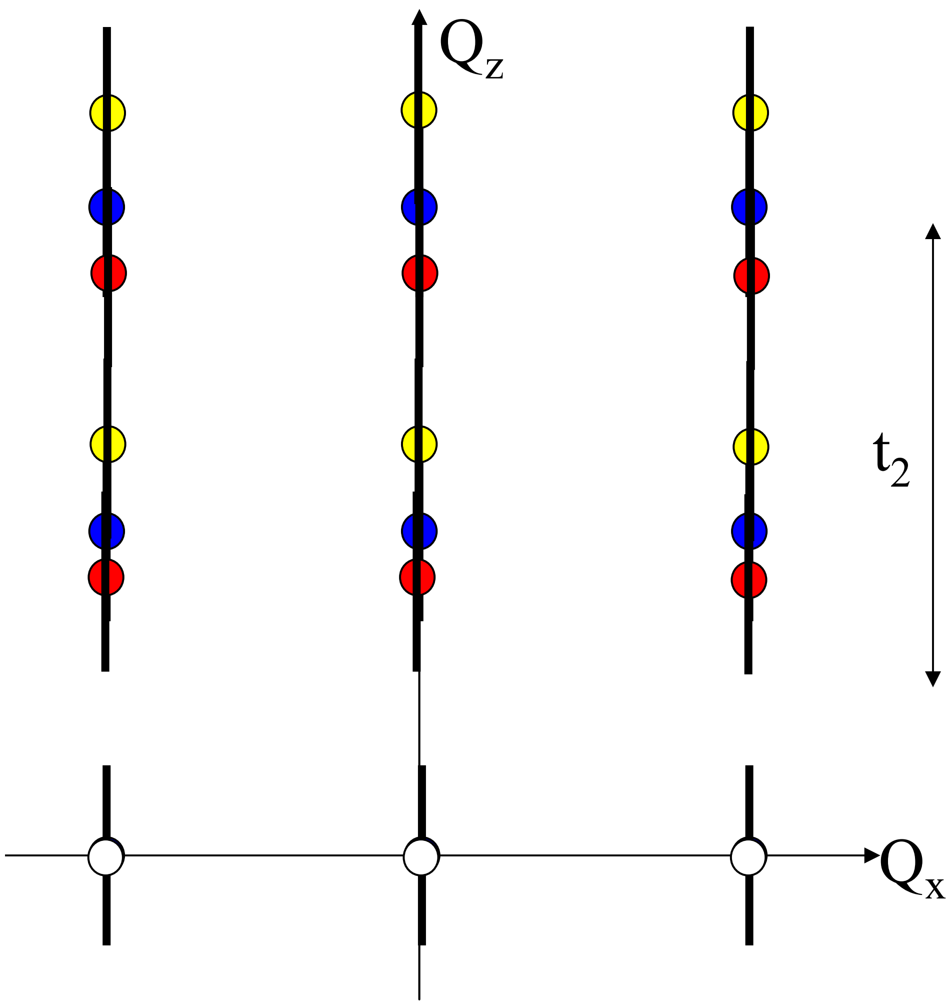
Reciprocal Space is Superb for Obtaining Good Statistics of Distributions

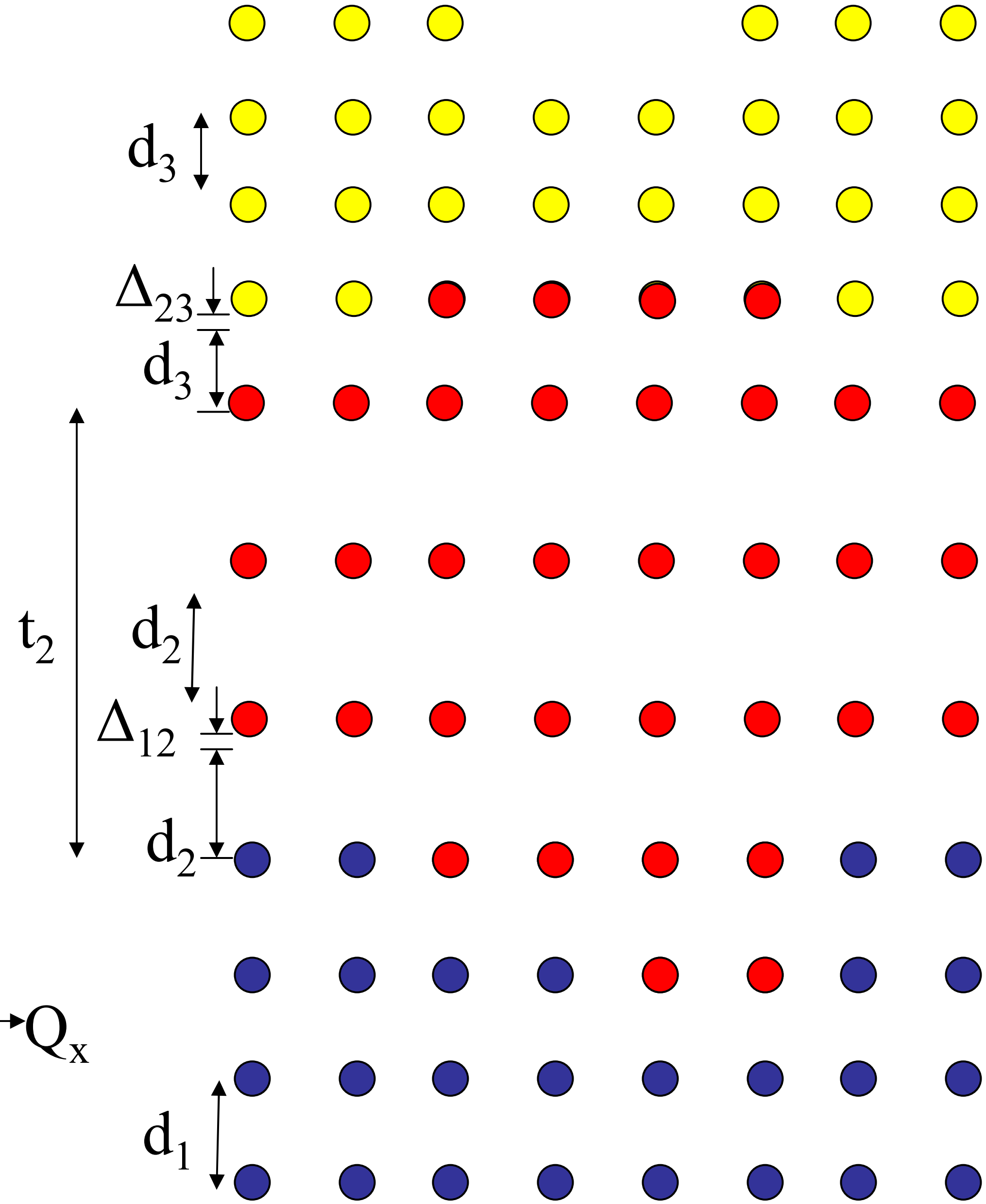


Equivalent ML Time = t*F

Psuedomorphic Laminar Structures

Reciprocal Space

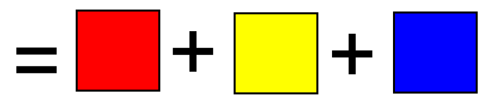




Averaging with Overlapping Rods

Sum 1 column of atoms at R_p:

$$A_c(\vec{R}_p, Q_z) = \sum_{j(\vec{R}_p)} b_j e^{iQ_z z_j}$$



FT all columns:

$$S(\vec{Q}) = \left| \sum_{\vec{R}_p} A_c(\vec{R}_p, Q_z) e^{i\vec{Q}_p \bullet \vec{R}_p} \right|^2 = \sum_{\vec{R}_p} \sum_{\vec{R}'_p} A_c(\vec{R}_p, Q_z) A_c^*(\vec{R}'_p, Q_z) e^{i\vec{Q}_p \bullet (\vec{R}_p - \vec{R}'_p)}$$

$$= N_{irr} \sum_{\vec{R}_p} e^{i\vec{Q}_p \bullet \vec{R}_p} \left\langle A_c(\vec{R}_p + \vec{R}'_p, Q_z)\, A_c^*(\vec{R}'_p, Q_z) \right\rangle_{\vec{R}'_p}$$

= FT of an amplitude-amplitude correlation function

Familiar short-range order diffuse and long-range uncorrelated disorder in the Bragg

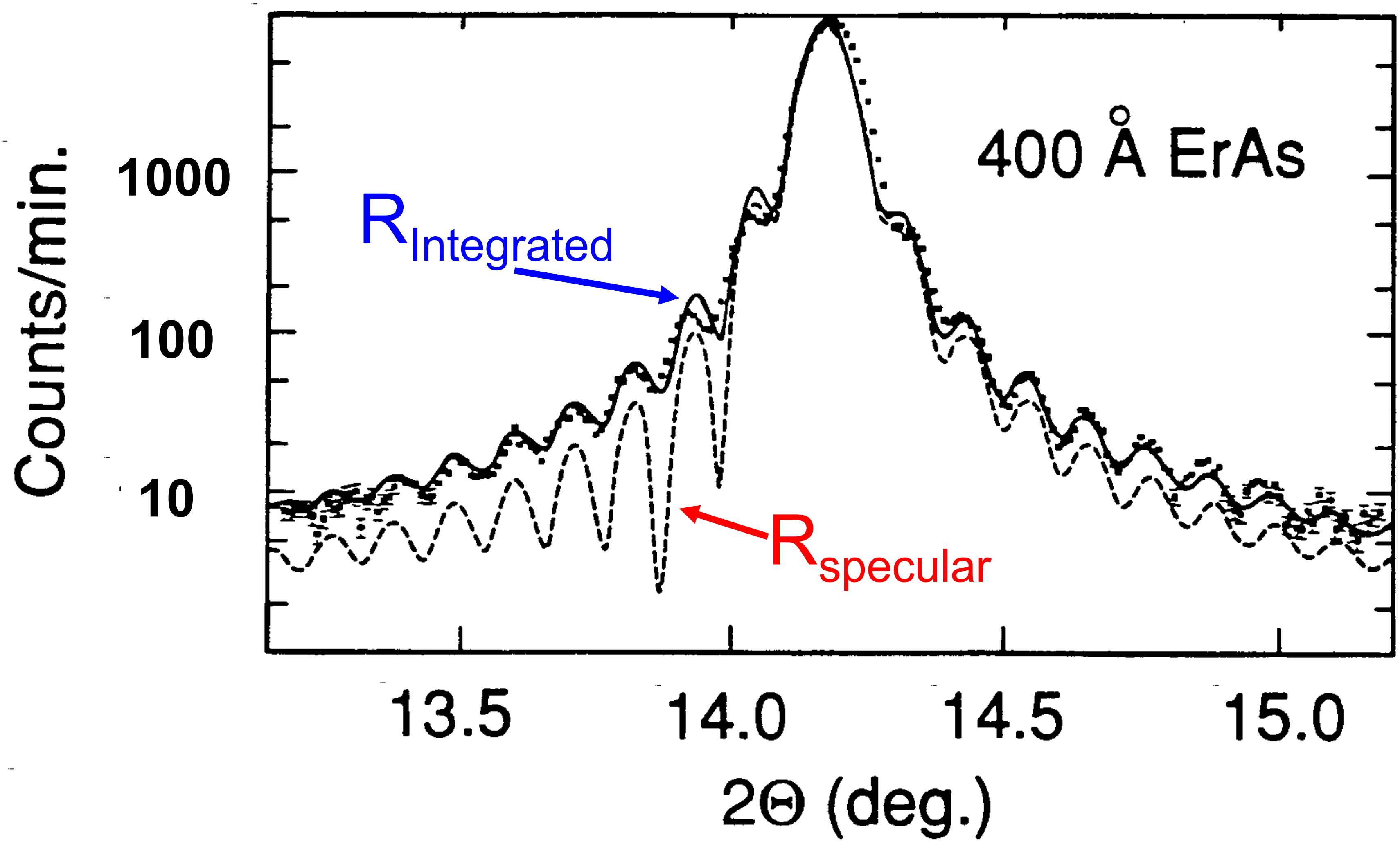
$$S\left(\vec{Q}\right) = N_{irr} \sum_{\vec{R}_p} e^{i\vec{Q}_p \bullet \vec{R}_p} \left\{ \begin{array}{l} \left| \left\langle A_c(\vec{R}'_p, Q_z) \right\rangle_{\vec{R}'_p} \right|^2 + \\ \left\langle A_c(\vec{R}_p + \vec{R}'_p, Q_z)\, A_c^*(\vec{R}'_p, Q_z) \right\rangle_{\vec{R}'_p} - \left| \left\langle A_c(\vec{R}'_p, Q_z) \right\rangle_{\vec{R}'} \right|^2 \end{array} \right\}$$

$$= S^{Bragg}\left(Q_z\right) + S^{Diffuse}\left(\vec{Q}\right)$$

Bragg: $$S^{Bragg}\left(Q_z\right) \propto \left| \left\langle A_c(\vec{R}'_p, Q_z) \right\rangle_{\vec{R}'_p} \right|^2$$

Transversely Integrated: $$\iint d^2 Q_p\, S\left(\vec{Q}\right) \propto \left\langle \left| A_c(\vec{R}'_p, Q_z) \right|^2 \right\rangle_{\vec{R}'_p}$$

Mosaic crystal gave transverse integration: must model with R_{Int}



Miceli,Palmstrom,Moyers, APL **61**, 2060 (1992)

P. Miceli, in *Semiconductor, Interfaces, Microstructures and Devices*.
Ed. Z.C Feng (IOP Publishing, Bristol, 1993) pp. 87-114

Summary

- Scattering from surfaces involves a range of different types of measurements
- Materials research problems require information on a broad range of length scale from atomic to mesoscale
- Unique ability of x-rays: surface and subsurface structure simultaneously

Bibliography

X-ray Diffraction Text Books:

B. E. Warren, *X-ray Diffraction* (Dover Publications, New York, 1990). Originally published by Addison-Wesley (1969).

J. Als-Nielsen and D. McMorrow, *Elements of Modern X-ray Physics* (Wiley, New York, 2001).

U. Pietsch, V. Holy, T. Baumbach, *High Resolution X-ray Diffraction: From Thin Films to Lateral Nanostructures*, (Springer, 2004).

R. W. James, *The Optical Principles of the Diffraction of X-rays* (Cornell University Press, Ithaca, New York, 1965). Now available from Oxbow Press.

A. Guinier, *X-ray Diffraction in Crystals, Imperfect Crystals, and Amorphous Bodies*, (Freeman, San Francisco, 1963).

W. H. Zachariasen, *Theory of X-ray Diffraction in Crystals*, (Wiley, New York, 1945) (and subsequently by Dover in 1967).

J. M. Cowley, *Diffraction Physics*, (North-Holland, Amsterdam, New York, 1981).

Engineering-type books on x-ray diffraction:

B. D. Cullity, *Elements of X-ray Diffraction*, (Addison-Wesley, Reading MA, 1978).

H. P. Klug and L. E. Alexander, *X-ray Diffraction Procedures* (Wiley, New York, 1974).

Useful Reference Books:

International Tables of X-ray Crystallography Vol. 1, 2, 3, 4 and Vol. A (Published for The International Union of Crystallography by Kluwer Academic Publishers, 1989).

P. Villars and L. D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases,* (American Society for Metals, Metals Park, OH, USA, 1986).

Laue Atlas, Ed. Kernforschungsanlage Jülich (Wiley, 1975).

Elementary treatments of crystallography in solid state textbooks, such as

C. Kittel, *Introduction to Solid State Physics, 7th ed.* (Wiley, 2005).

M. P. Marder, *Condensed Matter Physics* (Wiley, 2000) (nice treatment of quasicrystals)

N. W. Aschroft and N. D. Mermin, *Solid State Physics* (Saunders College, 1976).

<u>Excellent (in depth) treatment of scattering from defects</u>:
M. A. Krivoglaz, *Theory of X-ray and Thermal Neutron Scattering by Real Crystals*, (Plenum, New York, 1969).
M. A. Krivoglaz, *X-ray and Thermal Neutron Diffraction in Nonideal Crystals*, (Springer, 1996)
M. A. Krivoglaz, *Diffuse Scattering of X-rays and Neutrons by Fluctuations*, (Springer, 1996)

<u>Neutron Scattering:</u>

G. L. Squires, *Introduction to the Theory of Thermal Neutron Scattering*, (Cambridbge University Press, Cambridge, London, New York, 1978).

G. E. Bacon, *Neutron Diffraction*, (Clarendon Press-Oxford, 1975).

S. W. Lovesey, *Theory of Neutron Scattering from Condensed Matter*, (Clarendon Press-Oxford, 1984). Volumes 1 and 2.

<u>Reviews Articles of Surface Scattering</u>

R. Feidenhans'l, Surf. Sci. Rep. **10**, 105 (1989).

I. K. Robinson and D. J. Tweet, Rep. Prog. Phys. **55**, 599 (1992).

P. F. Miceli, in *Seminconductor Interfaces, Microstructures and Devices: Properties and Applications*, ed. Z. C. Feng, (IOP Publishing, Bristol, 1993) p. 87-116.

H. Dosch, *Critical Phenomena at Surfaces and Interfaces*, (Springer-Verlag, Berlin, 1992).

T. P. Russell, Mat. Sci. Rep. **5**, 171-271 (1990).

I. K. Robinson in *Handbook on Synchrotron Radiation*, Vol.3, ed. G. Brown and D. E. Moncton (Elsevier Science Publishers)

P. H. Fouss and S. Brennan, Annu. Rev. Mater. Sci. **20**, 365 (1990).

J. Als-Nielsen, in *Structure and Dynamics of Surfaces II: Phenomena, Models and Methods*, ed. W. Schommers and P. von Blanckenhagen, Topics in Current Physics, Vol. 43, (Springer-Verlag, Berlin, 1987), p.181