Thin Film Growth:
the Effects of Electronics and Kinetics

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In partial fulfillment of the requirements of the
Preliminary Examination

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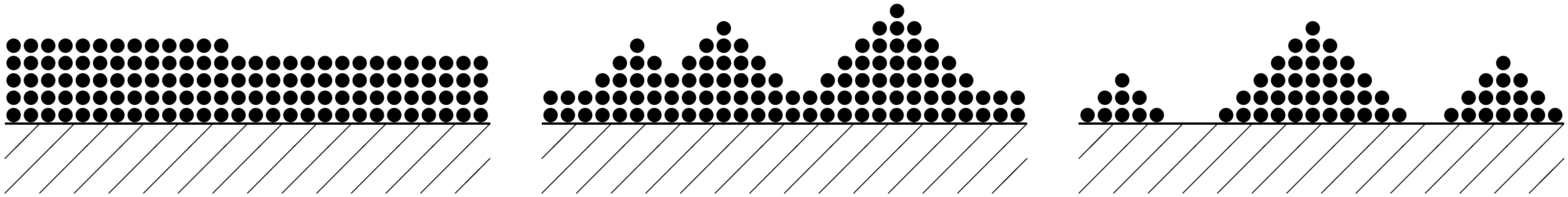
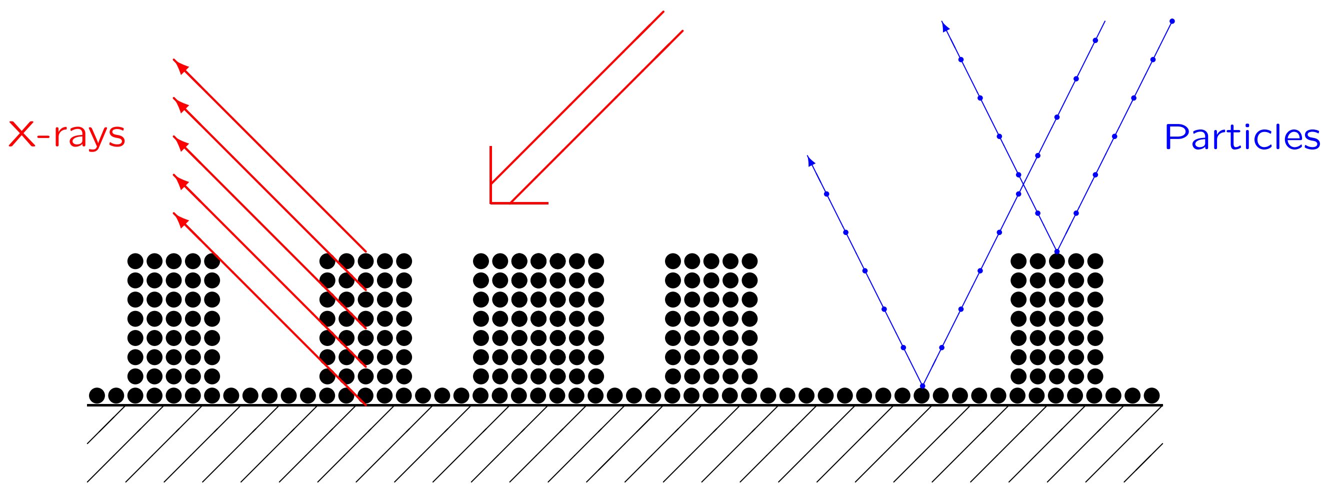
Outline

- Motivation
- Experimental Apparatus
- Surface X-ray Diffraction (SXRD)
- Quantum Size Effects (QSE) and Quantum Confinement
- I. Layer Relaxations in Pb/Si(111)
- II. Temperature-Dependent Growth Studies
- Summary

Thin Film Growth



Layer-by-Layer (van der Merwe) ⟶ Combination (Stranski-Krastanov) ⟵ 3-D island formation (Vollmer-Weber)



?????

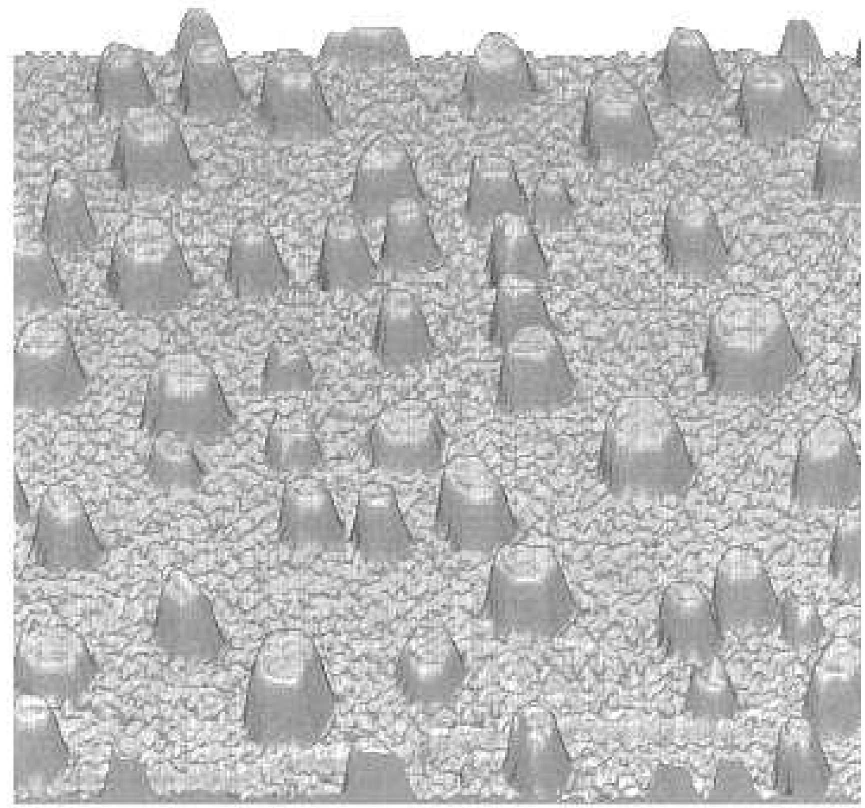
Quantum confinement of electronic states

⇓

Preferred thicknesses

Quantum Size Effects in Pb/Si(111)

- Island heights appear to be highly uniform
  $\Rightarrow$ preferred thicknesses
- Self-organization attributed to QSE
- Morphology depends on:
  $\longrightarrow$ Temperature
  $\longrightarrow$ Pb coverage
  $\longrightarrow$ Pb/Si interface
  $\longrightarrow$ Kinetic pathway

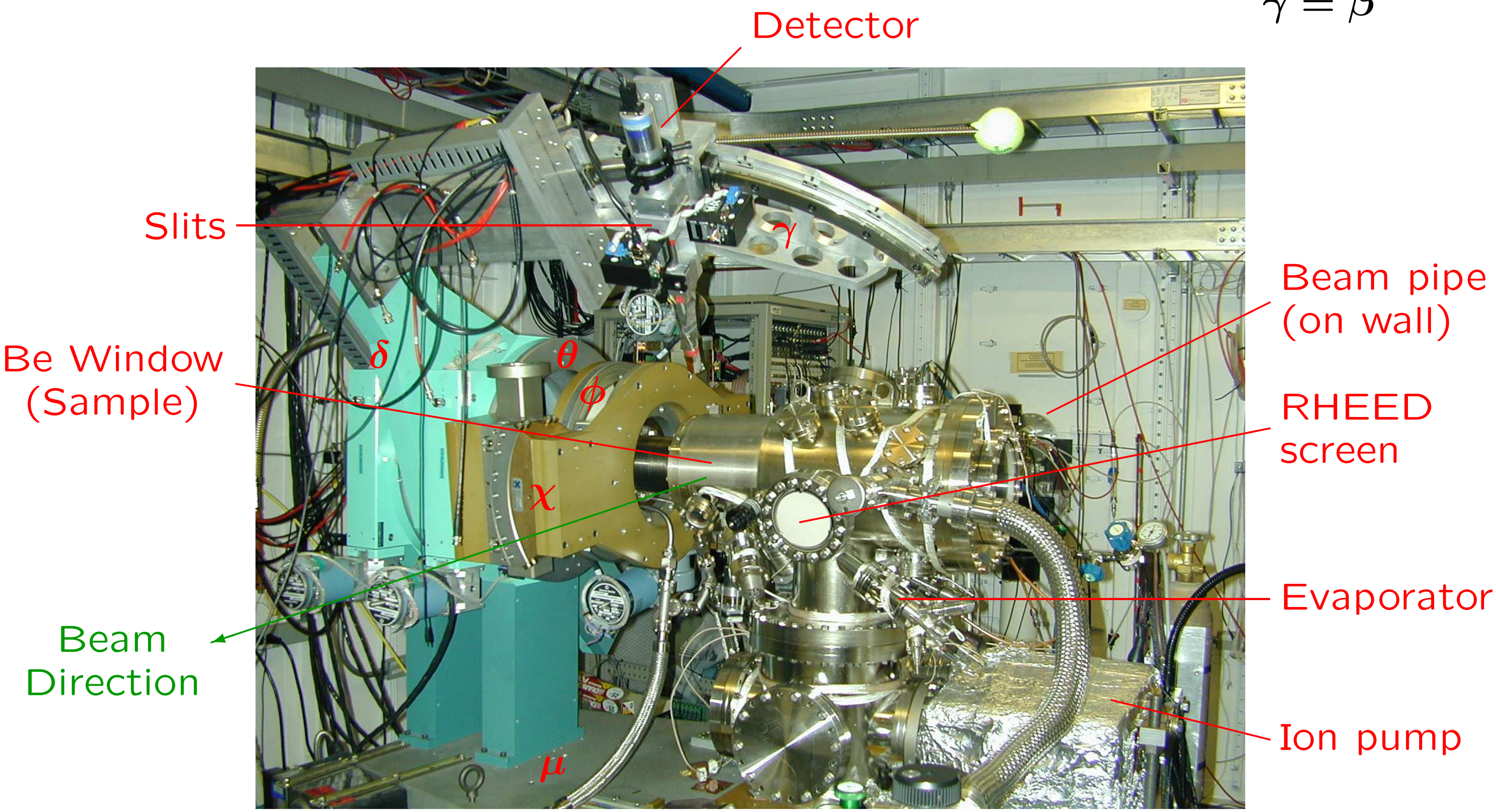


M. Hupalo, et. al., Surf. Sci. 493 (2001) 526

SXRD Chamber at Sector 33ID
UNICAT, Advanced Photon Source

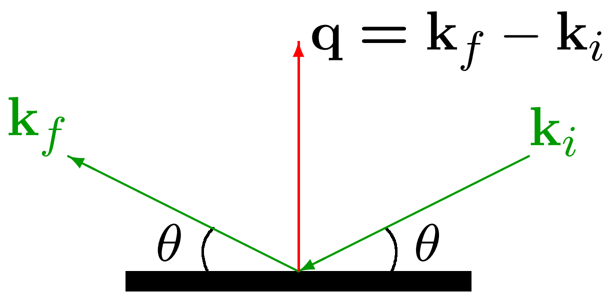
μ (table) $= \alpha$

$\gamma = \beta$



Surface X-ray Diffraction (SXRD)

Specular Reflectivity

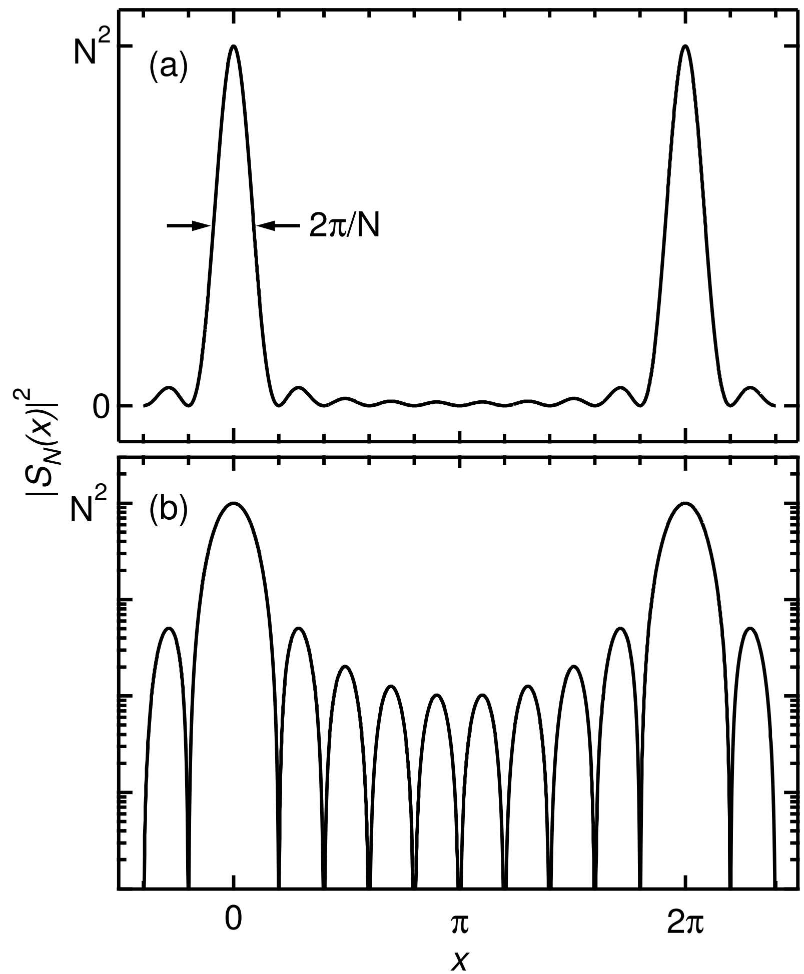


- Since $\mathbf{q} \cdot \mathbf{a}_1 = \mathbf{q} \cdot \mathbf{a}_2 = 0$, the specular rod is insensitive to in-plane order

- Thin film overlayers will contribute an amplitude similar to the N-slit interference function,

$$S_N(x) = \sum_{n=0}^{N-1} e^{i\,nx}$$

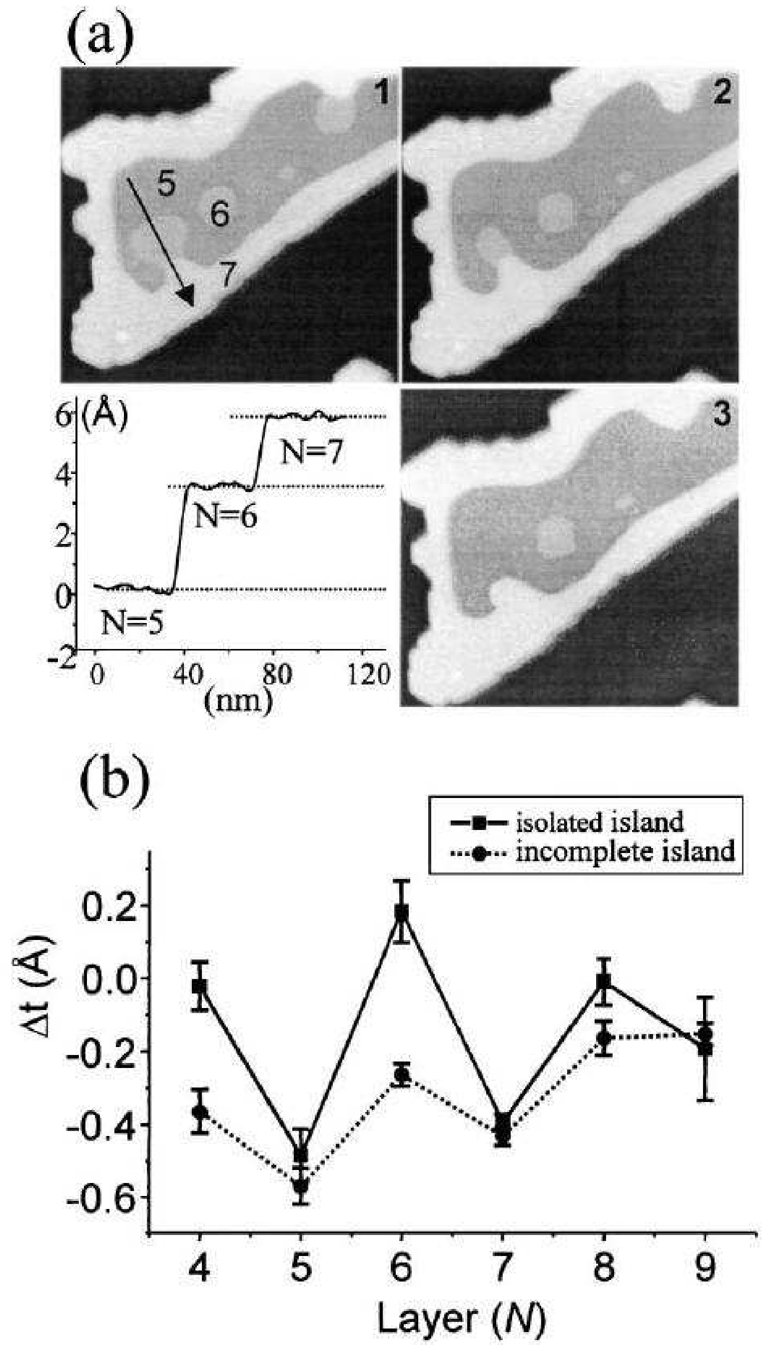
- $x = 0, 2\pi \rightarrow$ Bragg peaks



N-Slit Interference Function

Interlayer Relaxations in Pb/Si(111)

- Previous STM study observed oscillations in step heights
- Step heights correlated with electronic effects
- But: step height $\nRightarrow$ layer thickness
- Magnitude of layer relaxations?
- Penetration into film?
- Follow Friedel oscillations?
- Samples grown on different Pb/Si interfaces exhibit different preferred thicknesses
  $\Rightarrow$ different layer relaxations?



W. B. Su, et. al., PRL 86 (2001) 5116

Electron Confinement and Quantum Size Effects (QSE)

- Conduction electrons in thin metal films take on particle-in-a-box-like states

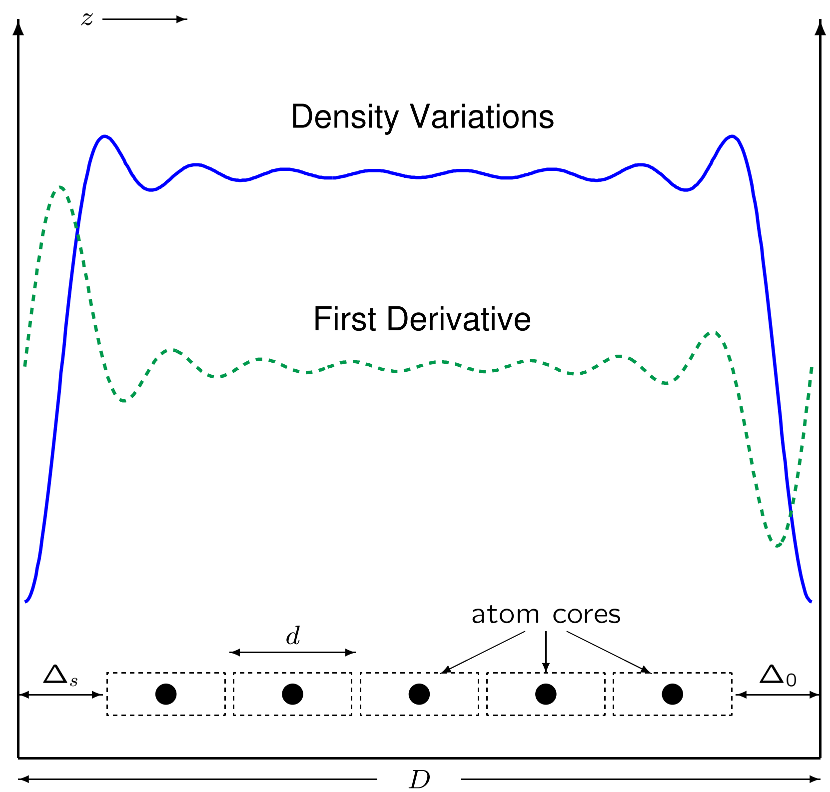
- Free-electron charge density exhibits Friedel oscillations in z-direction

- Oscillations have a wavelength $\approx \pi/k_F = \lambda_F/2$

$$\delta\rho(z) = -\frac{1}{C_D}\left(k_F^2 + \frac{1}{4}\frac{\partial^2}{\partial z^2}\right) S_D$$

$$\Delta s(z) = A\,\frac{\partial}{\partial z}\delta\rho(z)$$

$$S_D = \frac{1}{2}\sin 2k_F z \cot\frac{\pi z}{D} - \sin^2 k_F z$$



SXRD Reflectivity Model for Pb/Si(111)

$$A(l) \propto G(\theta) \Bigg[\underbrace{f_{Si}(l)\, e^{-2M_{Si}} \frac{1 + e^{-2\pi i\, l/12}}{1 - e^{-2\pi i\, l/3}}}_{\text{Si substrate}} + \underbrace{f_{\text{Pb}}(l)\, e^{-M_{Pb}} \sum_{\{N\}} \theta_N \sum_{j=1}^{N} e^{2\pi i\, l z_{j,N}}}_{\text{Pb film}} \Bigg]$$

A range of different island heights $\{N\}$ is used with occupancies θ_N

The atom z-positions are determined via the free-electron model:

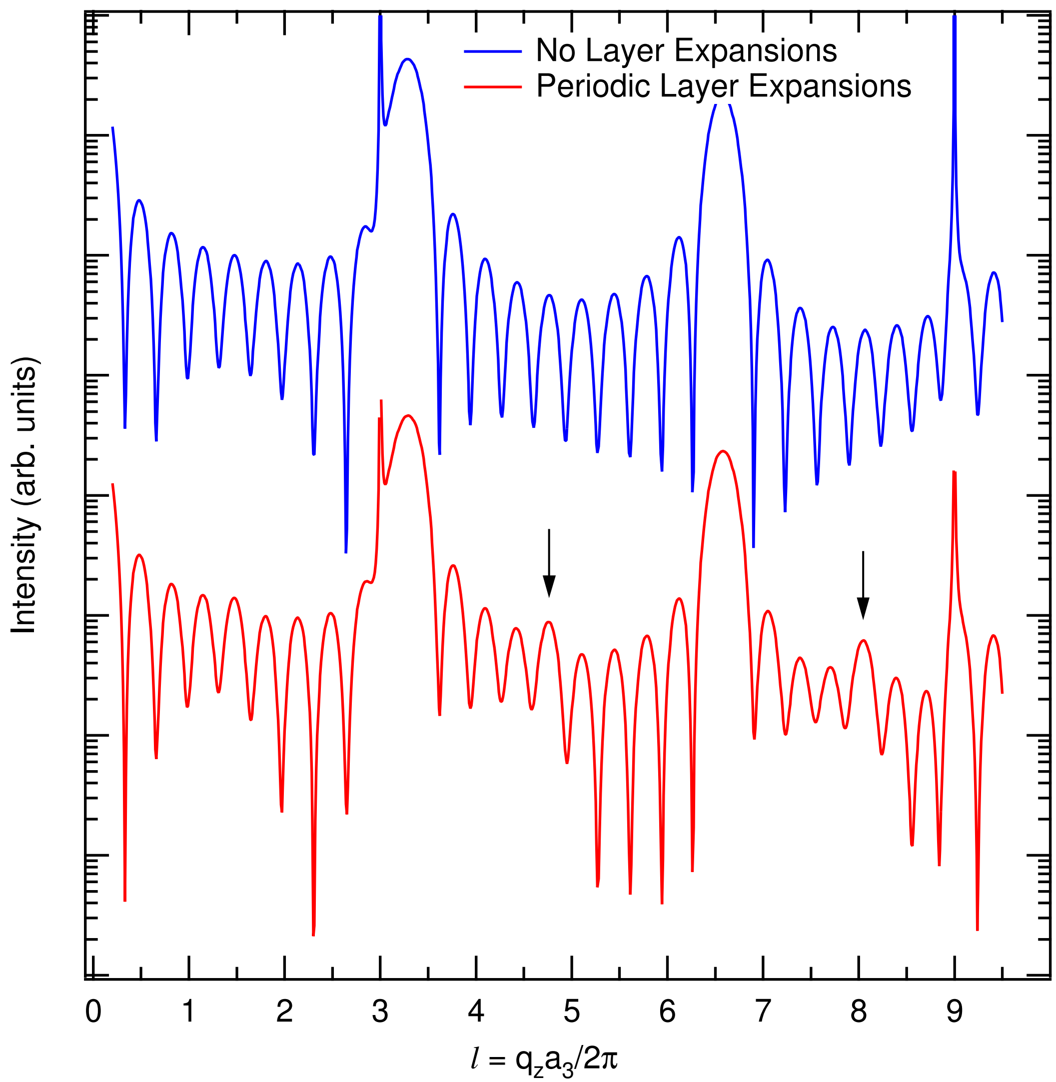
$$z_{j,N} = z_1 + \sum_{n=1}^{j-1} \left[d + \Delta t\big(\Delta_s + (n - \tfrac{1}{2})d\big) \right]$$

where

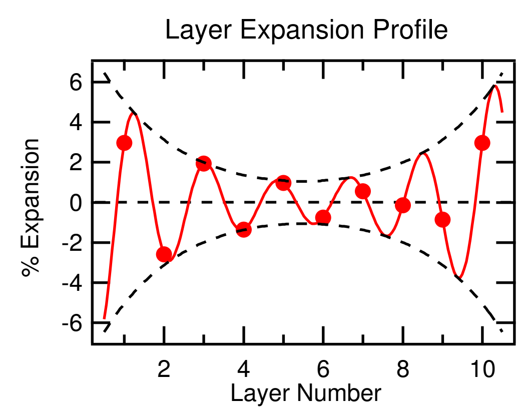
$$\Delta t(z) = \Delta s(z + d) - \Delta s(z)$$

Parameters: scaling factor, A, δd, Δ_0, Δ_s, $\{\theta_N\}$, M_{Pb}

SXRD Reflectivity Simulations



- Simulations are for 10 ML Pb on Si(111)-7x7
- For Pb(111), $\lambda_F/2 \approx 1.8d$
- Used simplistic sinusoidal model for z_j
- Half-order features appear with expansions

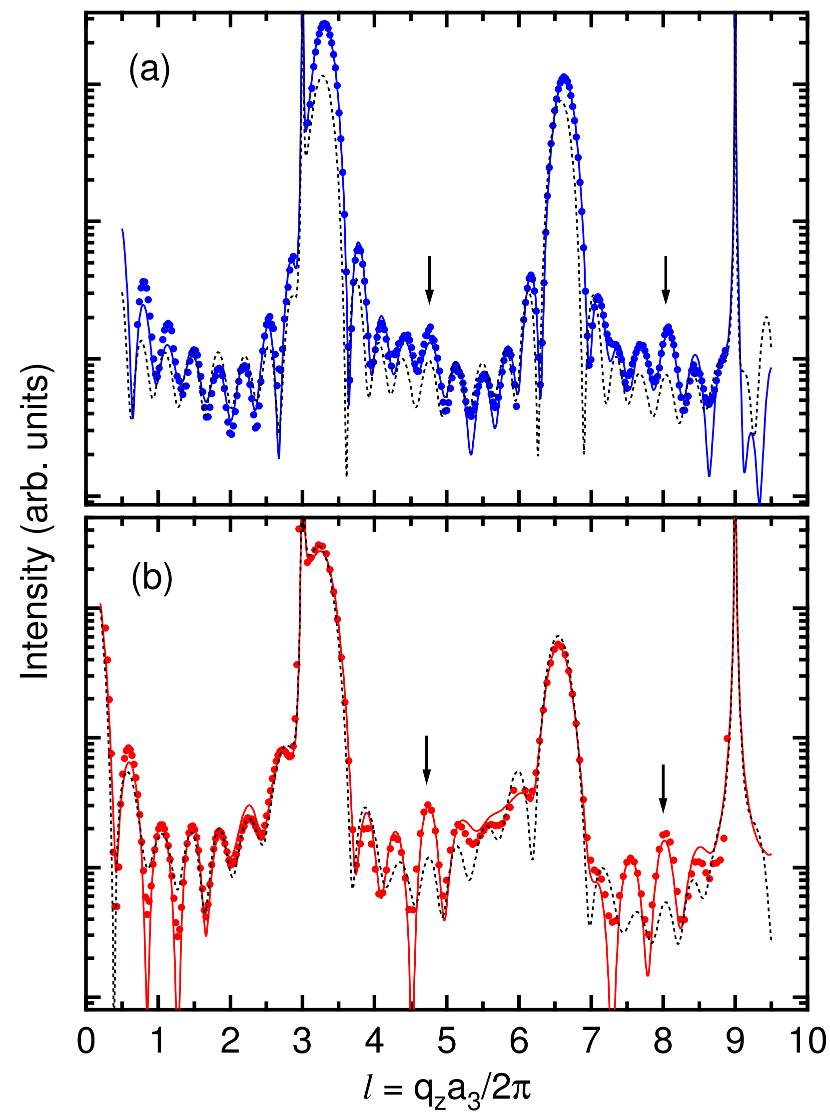


Layer Relaxations in Pb/Si(111)

- Pb was deposited on both the 7×7 and $\sqrt{3}\times\sqrt{3}$-β interfaces
- Profiles were fit with a range of island heights to allow for a non-uniform distribution
- Profiles were fit with and without $(A = 0)$ layer relaxations $\Rightarrow$ half-order features not reproduced without layer relaxations

(a) 8.5 ML Pb on Si(111)-7×7
Deposited at 185 K
$N = 10$ islands

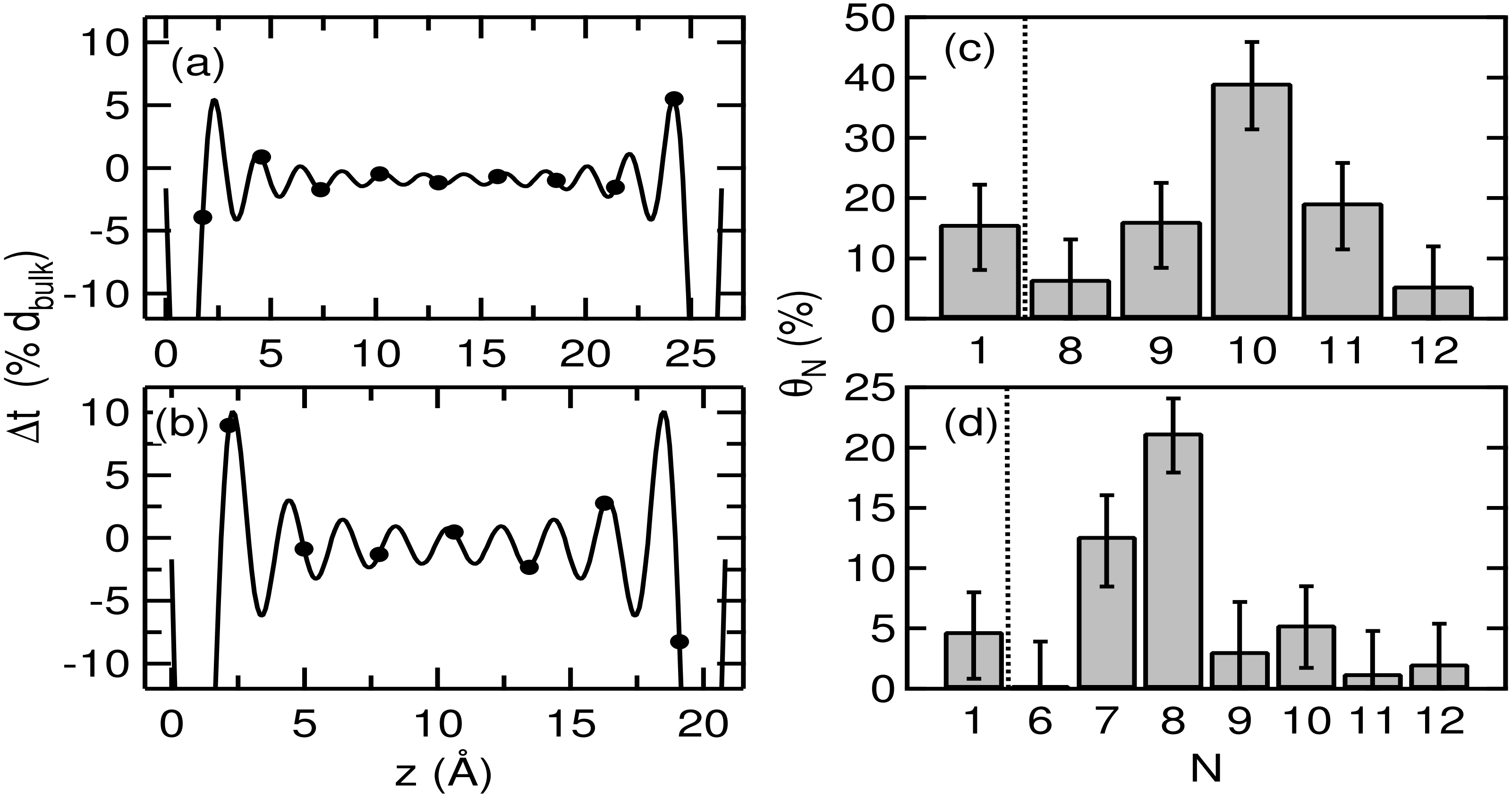
(b) 4.5 ML Pb on Pb/Si(111)-$\sqrt{3}\times\sqrt{3}$-β
Deposited at 115 K
Annealed to 180 K
$N = 8$ islands



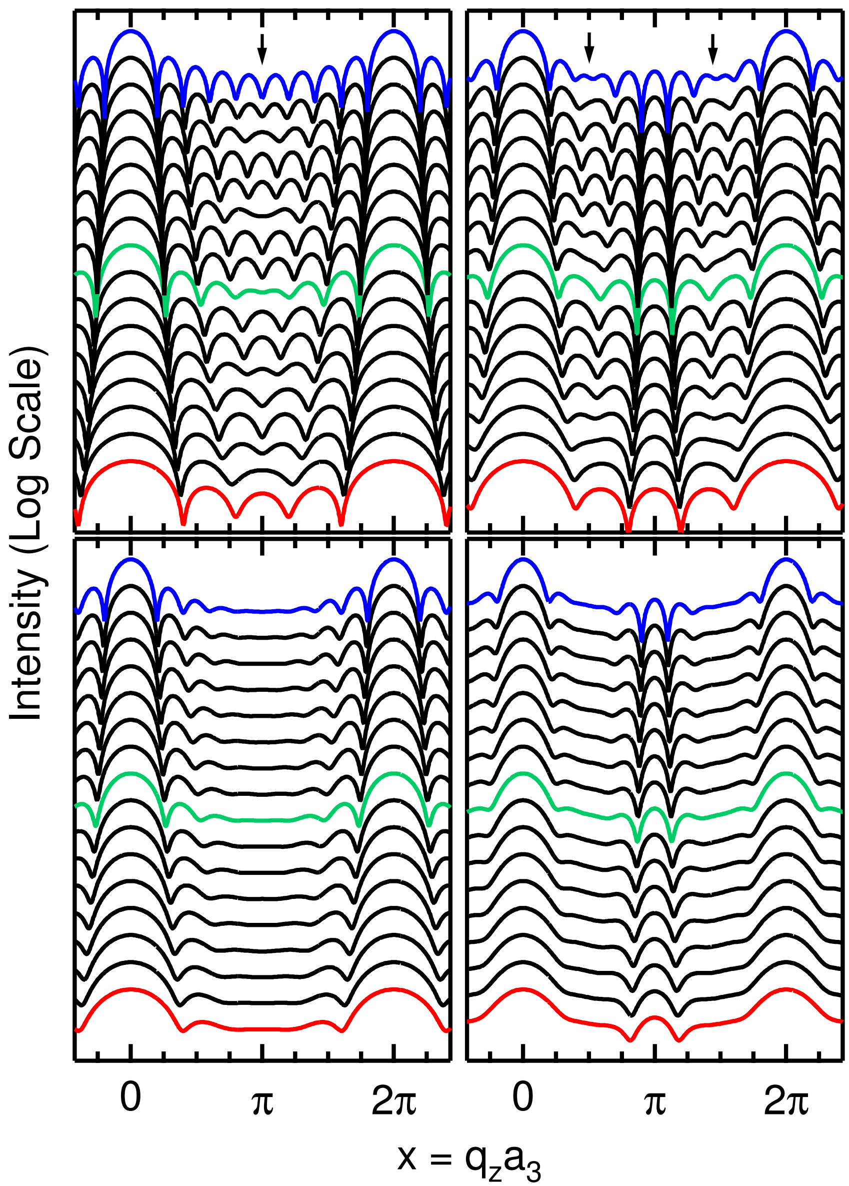
Layer Relaxation Results

Parameter	7×7 N=10	$\sqrt{3} \times \sqrt{3}$-β N=8
A (Å^2)	86±35	135±35
Δ_s (Å)	0.36±0.05	0.76±0.25
Δ_0 (Å)	0.90±0.40	0.31±0.08
δd (%)	-0.90±0.31	-0.77±0.65

- More data needed for trends
- Oscillatory relaxations apparent



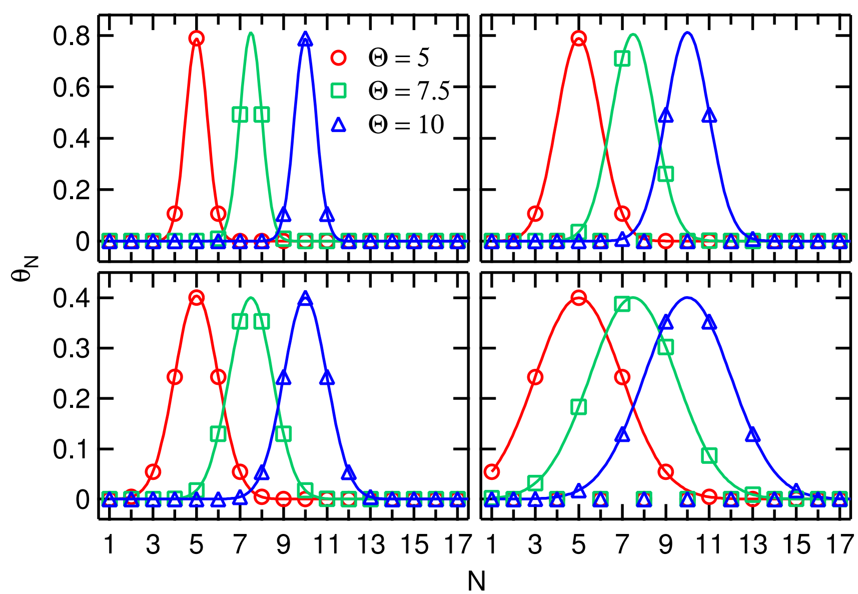
Island Growth



- Growth curve model:
  $A(q_z) = \sum_{\{N\}} \theta_N S_N(q_z a_3)$

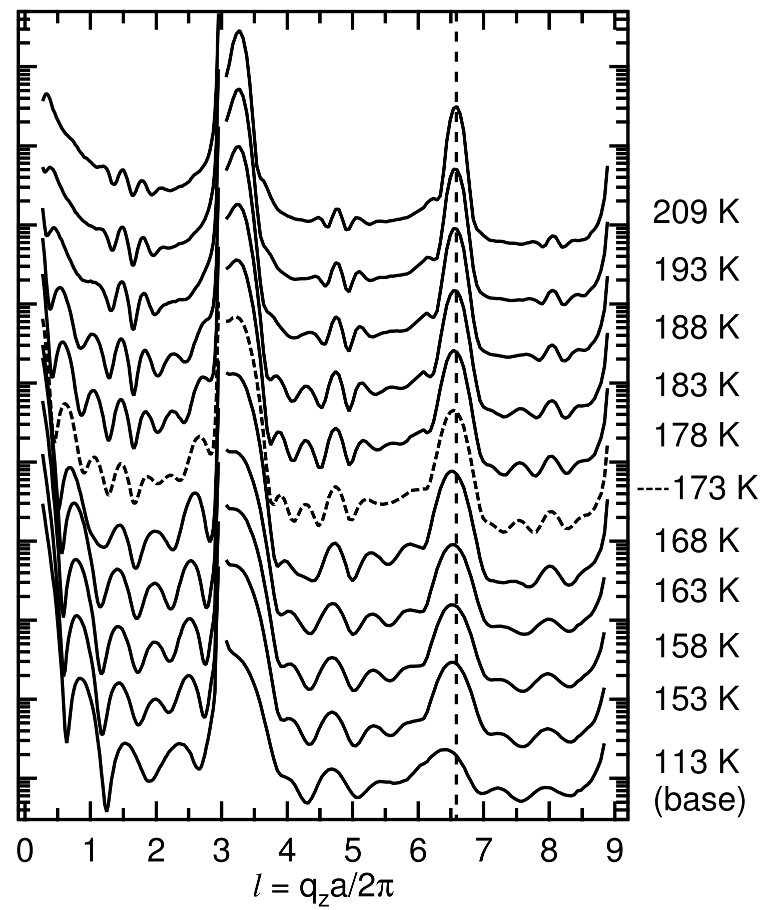
- Monolayer vs Bilayer growth

- Distribution of island heights



Island Growth Example — Pb/Si(111)

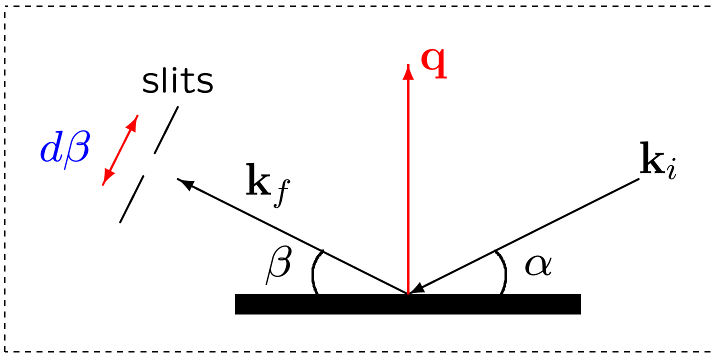
- Started with 4.5 ML Pb on Pb/Si(111)-$\sqrt{3}\times\sqrt{3}$-β
- Primary island height evolves as $T \nearrow$: $N = 5 \rightarrow 6 \rightarrow 8 \rightarrow 10 \rightarrow \cdots$
- Bilayer height selection even as film roughens
- Movement of Pb peak at $l \approx 6.4$ to 6.6 $\Rightarrow$ layer spacing becoming bulk-like
- As $T \nearrow$, islands grow irreversibly $\Rightarrow$ kinetics
- Expect interface dependence
- Application to other systems: Ag/Si, Ag/GaAs, Pb/Ge, Ag/Fe?



Summary

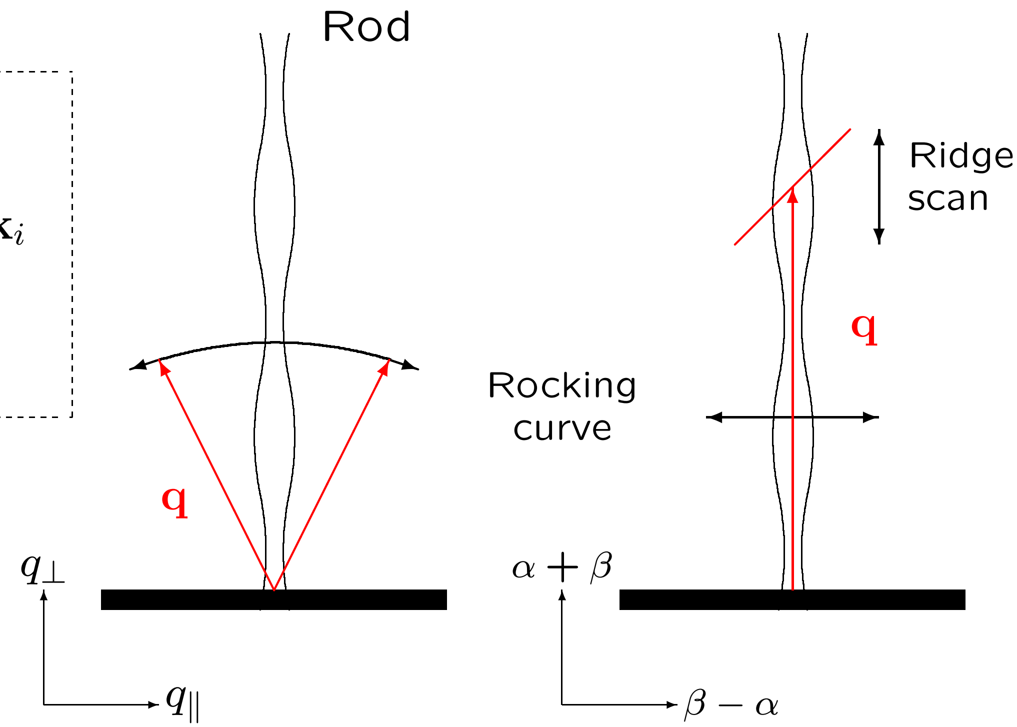
- Unusual growth behavior has been observed in thin metal films $\Rightarrow$ attributed to QSE
- Electronic confinement can lead to preferred thicknesses as well as characteristic structural effects
- Both electronic (thermodynamic) and kinetic effects important
- Proposed experiments:
  1. Layer relaxations in Pb/Si(111)
  2. Studies of island growth with temperature
- Need more data

Measuring Reflectivity



$$\frac{q_\perp}{k} = \sin\alpha + \sin\beta$$
$$\approx \alpha + \beta$$

$$\frac{q_\parallel}{k} = |\cos\alpha - \cos\beta|$$
$$\sim |(\alpha - \beta)(\alpha + \beta)|$$



- Rocking curve takes perpendicular cross-section of rod
- Ridge scan takes diagonal cross-section
- Resolution $= dq_\perp \approx k\, d\beta$

X-ray Integrated Intensity

electron: $A(R,t) = -A_0\, r_0\, \frac{e^{i\,kR}}{R} \cos\phi$ $\qquad r_0 = \frac{e^2}{4\pi\epsilon_0\, mc^2} = 2.82 \times 10^{-5}$ Å

distrib.: $A(\mathbf{q}) = -A_0 \frac{r_0}{R} \sum_{\mathbf{r}_j} e^{i\,\mathbf{q}\cdot\mathbf{r}_j} \quad \rightarrow \quad I(\mathbf{q}) = I_0 \frac{r_0^2}{R^2} |F(\mathbf{q})|^2$

Integrated Intensity (total energy measured by detector)

$$E = \iiint I(\mathbf{q})\, dt\, R^2 d\beta\, d\gamma \qquad \beta, \gamma = \text{angular directions of slits}$$

$$= \iiint I(\mathbf{q})\, \frac{R^2}{\omega} d\alpha\, d\beta\, d\gamma \qquad \text{scan from } \alpha \text{ to } \alpha + d\alpha \text{ in time } t$$

What we really want is the integral in reciprocal space, $\int d\mathbf{q}$

$$= I_0 \frac{r_0^2}{\omega} \iiint |F(\mathbf{q})|^2 J^{-1} dq_x\, dq_y\, dq_z$$

where J is the Jacobian for the transformation $\alpha, \beta, \gamma \rightarrow q_x, q_y, q_z$

J^{-1} = "Lorentz Factor"

Free-Electron Density in a Quantum Well (Expanded)

$$\rho(z) = \frac{2V}{(2\pi)^3} \int_0^{k_F} d^3\mathbf{k}\, |\Psi_{\mathbf{k}}(z)|^2 \sum_n \delta\left(k_z - \tfrac{\pi n}{D}\right) \tag{1}$$

$$= \sum_{n=1}^{n_0} 2\pi \left(k_F^2 - k_z^2\right) \sin^2 k_z z \tag{2}$$

$$\delta\rho(z) \equiv \frac{\rho(z) - \langle \rho(z) \rangle_z}{\langle \rho(z) \rangle_z} \tag{3}$$

$$= -\frac{\sum_{n=1}^{n_0} \left(k_F^2 - k_z^2\right) \cos 2k_z z}{\sum_{n=1}^{n_0} \left(k_F^2 - k_z^2\right)} \tag{4}$$

$$= -\frac{1}{C_D} \sum_{n=1}^{n_0} \left(k_F^2 - \left(\frac{\pi n}{D}\right)^2\right) \cos\left(\frac{2\pi n z}{D}\right) \tag{5}$$

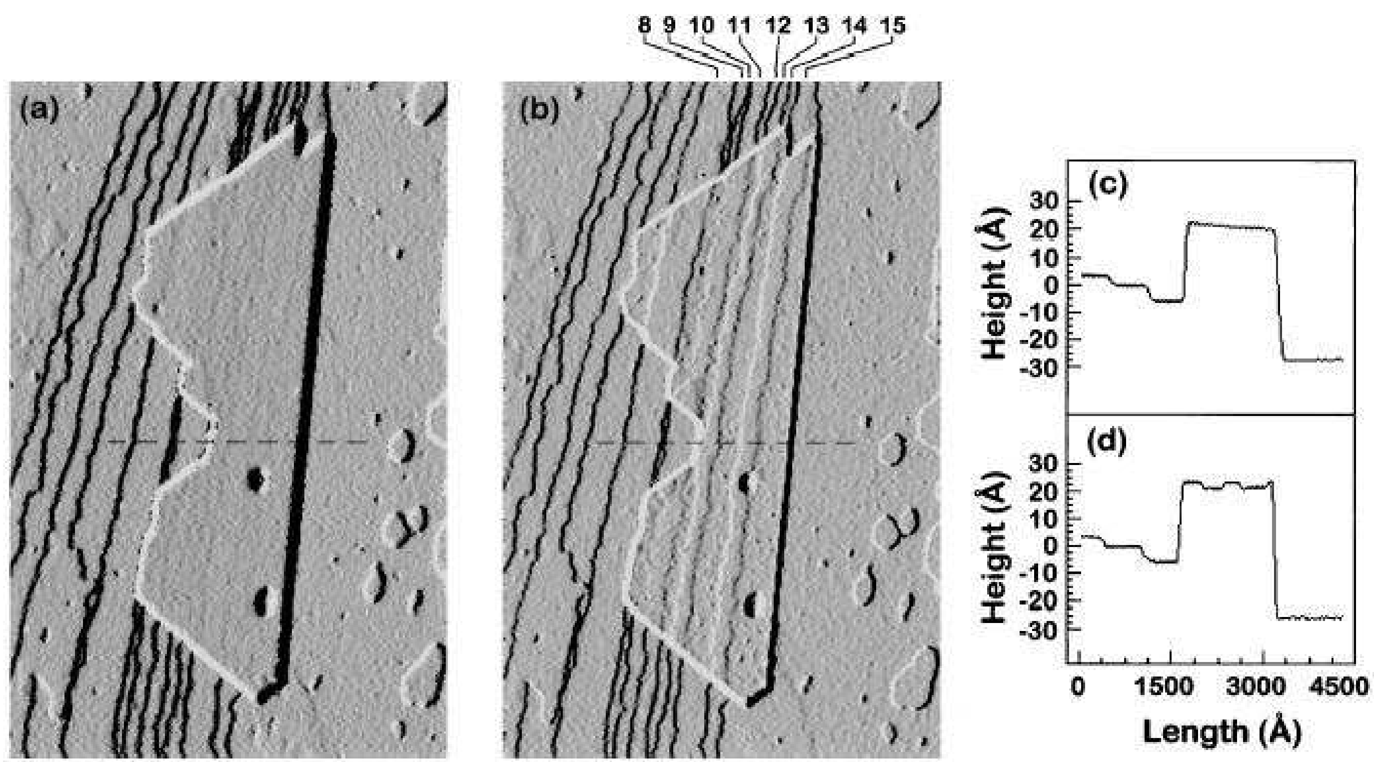
$$= -\frac{1}{C_D} \left(k_F^2 + \frac{1}{4}\frac{\partial^2}{\partial z^2}\right) S_D(2\pi z/D) \tag{6}$$

$$\Delta s(z) = -\frac{A}{C_D} \left(k_F^2 \frac{\partial}{\partial z} + \frac{1}{4}\frac{\partial^3}{\partial z^3}\right) S_D(2\pi z/D) \tag{7}$$

$$\Delta t(z) = -\frac{A}{C_D} \left(k_F^2 \frac{\partial}{\partial z} + \frac{1}{4}\frac{\partial^3}{\partial z^3}\right) \left[S_D\left(\frac{2\pi(z+d)}{D}\right) - S_D\left(\frac{2\pi z}{D}\right)\right] \tag{8}$$

Charge Spillage into Vacuum

- STM images taken with different biases: (a) -5 V (b) +5 V
- (a) ↔ "real" island topology
- (b) ↔ electron fringes showing variable spillage of charge density into the vacuum



I. B. Altfeder, et. al., Phys. Rev. Lett. 78 (1997) 2815

Rocking Curves vs. “Ridge” Scans