Kinematical (weak) Scattering Theory Ignores multiple scattering



Traveling wave scattered by jth pt.

$$A_{j} = f e^{i(kx - \omega t)}$$
$$A_{j} = f e^{i(\beta_{j} - \omega t)}$$

By Superposition the **Total Scattered Amplitude**

$$A_{T} = \sum_{j=0}^{N-1} f e^{i(\beta_{j} - \omega t)} = e^{-i\omega t} f \sum_{j=0}^{N-1} e^{i\beta_{j}}$$

$$A_{T} = f \sum_{j=0}^{N-1} e^{ij\beta} \quad \Rightarrow \text{Since } \beta_{j} = j\beta \text{ and } \beta_{0} = 0 \text{ , can ignore } e^{i\omega t} \text{ .}$$

$$A_{T} = f \frac{\sin(N\beta/2)}{\sin(\beta/2)} e^{i(N-1)\beta/2}$$

$$Geometric Series$$

Geometric Series

N-1

dsmb

R>7d

Total Scattered Intensity:
$$I \propto A_T A_T^* = f^2 \frac{\sin^2(N\beta/2)}{\sin^2(\beta/2)}$$

Normalized 1D Interference Function from N periodic slits



Diffraction peaks when denominator = $0 \rightarrow \beta = n(2\pi) \rightarrow Path-Length$ Diff= $n\lambda$. N-2 secondary peaks due to numerator $\beta = Q d$

Instrument Structure

In reflection geometry $\theta_0 = -\theta$.

The scattering vector or momentum transfer vector.

$$Q = \frac{2\pi}{\lambda} (\sin\theta - \sin\theta_0) = \frac{4\pi\sin\theta}{\lambda}$$

 $\theta = 1/2$ of the scattering angle 2θ .

1D Interference Function
Peak Intensity $\propto N^2$ $I \propto$ Denominator $\rightarrow 0 \rightarrow$ Bragg peaks
Numerator $\rightarrow 0 \rightarrow$ Bragg peak width and
Xtal size (thickness) = Nd = tBragg peak HWFM = Fringe period
= period of numerator
= $\Delta Q = 2\pi/t$ Bragg peak area $\propto N$





The <u>Diffraction Pattern</u> is directly related to the modulus of the <u>Fourier Transform</u> of the set of scattering sources.

$$\mathcal{F}(Q) = \int_{-\infty}^{\infty} f(x) e^{-iQx} dx$$

E.g.: Single Slit w/ width "s"





Relationship between the FT of a single unit f(x) and the FT of a infinite periodic series of that same single unit c(x).

Convolution:
$$c(x) = f(x) \otimes g(x)$$

1D Lattice: $g(x) = \sum_{n=-\infty}^{+\infty} \delta(x - na)$
1D Reciprocal-Space Lattice:
 $G(Q) = \int_{-\infty}^{\infty} g(x) e^{-iQx} dx = \sum_{h=-\infty}^{+\infty} \delta(Q - \frac{2\pi h}{a})$
Convolution Theorem:
 $C(Q) = FT[c(x)]$
 $=FT[f(x) \otimes g(x)]$

 $= F(Q) \bullet G(Q)$



From: [LL] Fig. 3.5. Illustrating the progression from Fourier series to transform.

X-ray Scattering from a free electron

Classical description: electric field of incident x-ray

$$\vec{E}_{\rm in} = \vec{E}_0 \, e^{{\rm i}(\vec{k}\cdot\vec{r}-\omega t)}$$

drives electron oscillation which then re-radiates.

Thomson scattering: 180° phase shift – $\overline{E}_{rad} = \frac{r_e}{R} E_0 \bullet \begin{cases} \cos\psi, & for // polarization \\ 1, & for \perp polarization \end{cases}$

Classical e- radius: $r_e = 2.82 \times 10^{-13} \text{ cm}$



Scattered Intensity from <u>single electron</u>: (for \perp polarization)

$$I_e = \left|\overline{E}_{rad}\right|^2 = \left(\frac{r_e}{R}\right)^2 I_0 \quad \text{at } R = 1 \text{ cm}, \quad I_e = 8x10^{-26} I_0, \text{ very weak}$$

Scattered Intensity from a <u>single atom</u>: $I_a = f^2 I_e$

Atomic form factor: $f^{0}(\overline{Q}) = \int_{atom} \rho(\overline{r}) e^{i\overline{Q}\cdot\overline{r}} d\overline{r}$

Use spherically averaged e- densities $\therefore \rho(\overline{\mathbf{r}}) \rightarrow \rho(r)$ and $f(\overline{\mathbf{Q}}) \rightarrow f(Q)$





X-ray Scattering from a group of N atoms

It's Book Keeping Just add-up the wavelets

$$\mathcal{F}(\overline{Q}) = \sum_{j=0}^{N-1} f_j(\overline{Q}) e^{-i\overline{Q} \cdot \overline{r}_j}$$

$$I(\overline{Q}) = I_e \left| \mathcal{F}(\overline{Q}) \right|^2$$



From: [EI]

Orientational averaging

The instantaneous scattering amplitude from two particles (atoms) is,

$$A(\vec{q}) = f_1 + f_2 e^{i\vec{q}\cdot\vec{r}}$$

The intensity is written as,

$$I(\vec{q}) = f_1^2 + f_2^2 + f_1 f_2 e^{i\vec{q}\cdot\vec{r}} + f_1 f_2 e^{-i\vec{q}\cdot\vec{r}}$$

If the length of r remains fixed but its direction varies,

$$\langle I(\vec{q}) \rangle_{orientation} = f_1^2 + f_2^2 + 2f_1f_2 \langle e^{i\vec{q}\cdot\vec{r}} \rangle_{orientation}$$

$$\left\langle e^{i\vec{q}\cdot\vec{r}}\right\rangle_{orientation} = \frac{\int e^{iqr\cos\theta}\sin\theta d\theta d\phi}{\int\sin\theta d\theta d\phi} = \frac{\sin qr}{qr}$$

From: [EI]

Scattering (diffraction) pattern from two electrons



$$I(\vec{q}) = 2 \operatorname{I}_{e}(1 + \cos(\vec{q} \cdot \vec{r}))$$

$$\langle I(\vec{q}) \rangle = 2 \operatorname{I}_{\mathrm{e}}(1 + \sin qr / qr)$$







Example: CF₄ - Molecule

$$F_{CF_4}(\vec{q}) = f_C(\vec{q}) + f_F(\vec{q}) \left[e^{i\vec{q}\cdot\vec{r}_1} + e^{i\vec{q}\cdot\vec{r}_1} + e^{i\vec{q}\cdot\vec{r}_2} + e^{i\vec{q}\cdot\vec{r}_3} \right]$$

$$= f_{C}(\vec{q}) + f_{F}(\vec{q}) \Big[3e^{-iqR/3} + e^{iqR} \Big]$$

with q parallel to the C-F bond.





X-ray Scattering from a small <u>3D Crystal</u> with M unit cells each with N atoms per unit cell

Use Convolution Theorem: $FT [f(\mathbf{r}) \otimes g(\mathbf{r})] = FT [f(\mathbf{r})] \bullet FT[g(\mathbf{r})]$ From: [ANM]

$$F_{\text{crystal}}(\vec{q}) = \left(\sum_{j=1}^{N} f_j(\vec{q}) e^{i\vec{q}\cdot\vec{r}_j}\right) \cdot \left(\sum_{n=1}^{M} e^{i\vec{q}\cdot\vec{R}_n}\right)$$

Unit Cell Structure Factor $F_{uc}(q)$

Lattice Sum

Kinematical Scattered Intensity from a 3D Crystal

$$I(\overline{Q}) = I_e |F(\overline{Q})|^2 \left| \sum_{m=0}^{M-1} e^{i\overline{Q} \cdot \overline{R}_m} \right|^2$$
Lattice vector: $R_m = m_1 a_1 + m_2 a_2 + m_3 a_3$

$$I(\overline{Q}) = I_e |F(\overline{Q})|^2 \frac{\sin^2 \frac{1}{2} M_1 \overline{Q} \cdot \overline{a}_1}{\sin^2 \frac{1}{2} \overline{Q} \cdot \overline{a}_1} \cdot \frac{\sin^2 \frac{1}{2} M_2 \overline{Q} \cdot \overline{a}_2}{\sin^2 \frac{1}{2} \overline{Q} \cdot \overline{a}_2} \cdot \frac{\sin^2 \frac{1}{2} M_3 \overline{Q} \cdot \overline{a}_3}{\sin^2 \frac{1}{2} \overline{Q} \cdot \overline{a}_3}$$

3D Interference Function
I_{max} Diff. peaks when
all 3 denominators = 0
Laue Condition
 $(2\pi)^{-1} Q \cdot a_1 = h$
 $(2\pi)^{-1} Q \cdot a_2 = k$
 $(2\pi)^{-1} Q \cdot a_2 = k$
 $(2\pi)^{-1} Q \cdot a_3 = l$
 $\overline{Q} = \overline{G}_{hkl} = h\overline{a}_1^* + k\overline{a}_2^* + k\overline{a}_3^*$
hkl Diffract Plane
Miller Indices
Reciprocal-Space Basis Vectors

$$\overline{G}_{hkl} = h\overline{a}_1^* + k\overline{a}_2^* + k\overline{a}_3^*$$

G in recip. space defined by *hkl* diffract planes in real-space. **1. Direction:** *G* perpendicular to *hkl* planes **2. Modulus:** *G* = 2*π*/*d*_{*hkl*}

These 2 conditions define the recip. space basis vectors as:

Vector Rep. in Recip. Space

If incident direction k_0 and λ are fixed. Then:

- 1. Sphere does not move
- 2. k_0 always points from center C to 000
- 3. Rotating xtal in $\theta \Rightarrow$ recip. lat. to rotate about 000
- 4. *k* points from C to any pt. on the sphere.
- 5. Diffraction occurs when an *hkl* rel. pt. coincides with the Ewald sphere surface.

 $Q = k - k_0 = G_{hkl}$

6. For x-ray diffraction multiple reflections are rare.

Real Space ⇔ Reciprocal Space

Xtal Dim	Real- Space Basis	Laue Cond	Recip. Space Periodicity
1D	ā	$h\overline{a}^* = \text{const.}$	// planes $\perp \bar{a}$
2D	$\overline{a_1}, \overline{a_2}$	$h\overline{a}_1^* = const.$ $k\overline{a}_2^* = const.$	// rods $\perp \bar{a_1}\bar{a_2}$ plane
3D	$\overline{a_1}, \overline{a_2}, \overline{a_3}$	$h\overline{a}_{1}^{*} = const.$ $k\overline{a}_{2}^{*} = const.$ $l\overline{a}_{3}^{*} = const.$	points

From: [ANM]

4-Bromostyrene SAM on Si(111) surface. $R(Q_z)$ calculated for 1/2 ML coverage.

Experimental Reflectivity along the (00L) Crystal Truncation Rod (CTR) for ferro-electric PZT thinfilm capacitor heterostructure.

The experimentally measured x-ray reflectivity of the PZT capacitor structure taken at $\lambda =$ 0.914 Å. The inset shows the layers within the heteroepitaxial structure, a SrTiO₃ (001) substrate, a 136-nm-thick SrRuO₃ bottom electrode, a 20-nm-thick PZT film and a 30-nmthick Ag top electrode. The angle positions for the three distinct (001) Bragg peaks mark-off the three distinct *c* lattice constants of SrTiO₃, SrRuO₃, and PZT.

 $d_{001} = 3.905$, 3.970, 4.130 Å

The two patterns of oscillation are due to the thickness of the $SrRuO_3$ and PZT films, the smaller period oscillation belongs to the thicker film. The Ag top electrode has a polycrystalline structure and does not measurably contribute to the scattered intensity in this high-resolution scan.

As predicted by the numerator of the interference function, the widths of the peaks and their Laue fringes are inversely proportional to the film thickness.

$$t = 2\pi/\Delta q = \lambda/(2\Delta\theta)$$

- **Key Examples** to illustrate x-ray characterization of nanomaterials
- A. Br-SAM / Si(111) , self-assembled monolayer on H-Si(111) grown by Hersam Group)
- B. Nanocomposite film self-assembly OPV-silicate / glass (Spin-coat grown by Stupp group)
- C. Poly-DL-lysine single nano- and micro- crystal growth on mica (DPN grown by Mirkin group)
- D. Counterion driven adsorption of polynucleotides to charged surfaces

Self-Assembled Monolayers Br-SAM on H-Si(111) Molecules synthesized by Nguyen group, SAM grown by the Hersam group at NU.

AFM (Hersam) indicates growth mode (chain formation by polymerization process) X-rays used to quantify internal structural details and surface coverage "X-ray studies of self-assembled organic monolayers grown on hydrogen-terminated Si(111)", H. Jin, C.R. Kinser, P. A. Bertin, D.E. Kramer, J.A. Libera, M.C. Hersam, S.T. Nguyen, and M.J. Bedzyk, *Langmuir* **20**, 6252-6258 (2004).

Used Liquid Phase NanoLithography

SAM Grown on H-Si(111)

Questions X-rays can answer:

- 1) What is the <u>monolayer coverage</u> (Θ) ? I.e. What fraction of the Si(111) surface dangling bonds are covalently bonded to styrene molecules? For Si(111), $\Theta = 1$ ML -> 7.83 molecules / nm².
 - 1) XRF -> Θ of Br atoms
 - 2) XRR -> Θ of SAM molecules
- 2) What is the interfacial <u>atomic-scale structure</u>? I.e., How is the molecule geometrically configured relative to the (111) Si surface atoms?
 - XRR -> monolayer thickness of SAM Thickness + molecular length from DFT -> molecular tilt angle
 - 2) XSW -> precise location of Br atom relative to Si lattice.
- 3) What <u>ordered fraction?</u> I.e., Fraction of molecules that are part of the ordered structure?
 - 1) XSW -> Br ordered fraction

Overhead schematic view of 18 KW rotating anode setup in NU X-ray Lab used for XRR, XRF and XSW measurements of SAM - Si(111) samples

LS: Vertical Line Source,

Cu Anode (8.04keV) used for XRR;

Mo anode (17.44 keV) used for XRF and XSW

MM: Parabolic multilayer-mirror

S1-4: slits

SS1&2: solar slit for 1° vertical collimation

PM: Si(111) postmonochromator (only used for XSW)

Sample on stepping motor driven θ -2 θ 2-circle, X-translation, and χ -tilt

NaI: pulse counting x-ray detector for reflected intensity on 2θ arm

SSD: Solid-state XRF detector with pulse-height analysis and multichannel analyzer

Br-SAM Grown on H-Si(111)

Br coverage determined by X-ray Fluorescence (XRF)

Method:

•Used solid-state XRF detector system with pulse-height analysis multichannel analyzer.

•Do side-by-side comparison of XRF yield from unknown sample with known standard.

•We used Arsenic implanted in Si as standard with an effective coverage calibrated by RBS.

•Compared Br K α to As K β at E_y=15 keV

•Collect both XRF spectra with identical incident beam and XRF detector geometry

•Must factor in atomic-physics based XRF cross-sections, if the atom in the standard is not the same as your unknown.

•If the two XRF energies differ significantly, X-ray attenuation and detector efficiency must also be included.

XRF -> $\Theta_{Br} = 0.53 \text{ ML}$

5% uncertainty

С

Total External Reflection of X-rays from a Mirror Surface

Fresnel Theory:

R~1 for Q < $Q_C = 0.031 \text{ Å}^{-1}$ Si mirror TER R_F = $(2Q/Q_C)^{-4}$ for Q>>Q_C. Fourier transform of a step function. Example: SAM / Si(111)

- •At 1st dip, the 2 scattered plane-waves from the top and bottom interfaces have a $\lambda/2$ path-length difference (or π phase difference).
- Modulation period -> film thickness Range: 1 to 100 nm
- Modulation Amplitude -> relative electron density of film
- Modulation damping -> roughness of interface(s) Range: < 2 nm

X-ray Reflectivity of UDAME Monolayer on Si (111) Substrate

• 1st step in DNA covalent attachment

X-Ray Reflectivity Analysis Fundamentals

Kinematical approach:

Q = $4\pi \sin\theta /\lambda$

For 1 slab model

 $R(Q) = R_{F}(Q) |\Phi(Q)|^{2}$

$$\Phi(Q) = \frac{1}{\rho_{\infty}} \int \frac{d\rho}{dz} e^{iQz} dz$$

FT of gradient of e- density profile

$$\frac{R(Q)}{R_F(Q)} = \left[1 - 4b(1 - b)\sin^2(Qt/2)\right]e^{-Q^2\sigma^2}$$

0

b	t (Å)	σ(Å)
0.50	12.2	3.2
0.53	13.3	3.6

 $\rho(z) = e^{-}$ density profile, $b = \rho_F / \rho_{Si}$, $\sigma = \sigma_s = \sigma_I = (rms)$ roughness, t = film thickness

Z

XRR Analysis of C₆₀ attached to Silica surface

Grown by the Mirkin Group at NU