X-ray Scattering at the ALS: An Overview

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Outline

• What is scattering and what does it measure?
• Traditional Elastic Scattering
  • Wide-angle scattering and diffraction
  • Small-angle scattering
  • Reflectivity
• Coherent Scattering Techniques
  • Coherent diffractive imaging (ptychography)
  • X-ray photocorrelation spectroscopy (XPCS)
• Resonant Soft X-ray Scattering
  • Sorting out order in molecular systems
What is X-ray Scattering?

• Photon changes trajectory after hitting electron

• Interferes with other photons at detector

• Intensity vs angle ($\theta$) tells about $r$ (distance) between scatterers

$\Delta \phi$ determines if constructive or destructive interference

E.g. Bragg’s Law:

$2d \sin \theta = m\lambda$
Scattering: Statistics of internal structure

- Crystal atomic spacing, arrangement
  - Strain, defects (faults, disorder)
  - Thin film orientation
  - Grain/crystallite size
  - Macromolecular structure
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- Nanoparticle size & shape
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- Nanophase separation/identification
  - Composition, volume fraction
  - Pore size, volume
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- Thin film stratification
  - Thickness, roughness

All non-destructive measurements!
Size Scale Sensitivity

• Bragg Law: \( 2d \sin \theta = \lambda \)
  • \( d_{\text{min}} \sim \frac{\lambda}{2} \)
  • \( d_{\text{max}} \propto \theta_{\text{min}} \)
  (beam size/divergence)

• SAXS vs WAXS
  • Switch \( \theta \sim 2^\circ \) for hard X-rays (10keV)
  • Accomplished via detector distance
Scattering: An FFT of your sample

**Elastic Scattering**

\[ |k_0| = |k_f| = \frac{2\pi}{\lambda} \]

No energy transfer

Constructive Interference

\[ A_{det}(r) = b_e e^{i\phi} \]

Sum over illuminated sample

\[ A_{det}(q) = \int_V \rho_e(r) e^{-iqr} dr \]

Fourier Transform of the electron density distribution!

*(Just like electron microscopists do, but huge sample)*

\[ r: \text{‘Real Space’} \]
\[ q: \text{‘Reciprocal Space’} \]

Also ‘Spatial frequency’

**Big** \( q = \text{Small } r \)

\[ A(x) = A_0 \cos kx = A e^{ikx} \]

\[ k_f \]

\[ q \equiv \Delta k \]

\[ q = 2k \sin \theta \]

\[ \phi = -(k_f - k_0) \cdot r \]
\[ = -\Delta k \cdot r \]
\[ = -q \cdot r \]

Measure intensity, lose \( e^{-iqr} \)

\[ I(q) = A(q)A^*(q) \]

Can’t take IFT to recover \( \rho_e(r) \)

...except for COSMIC!!!
Experiment

Detectors
• Point Detector: High q-res
  • high crystalline materials
• Area Detector (CCD): speed
  • amorphous, in-situ studies

Sample Geometry
• Transmission: probe mainly in-plane (IP) structure
  • Similar to transmission microscopy (TEM)
• Grazing: Probe both IP and out-of-plane (OOP) structure
  • Analysis might be more qualitative/complicated...
• Reflectivity: Probe only OOP structure

Grazing Incidence: Multi directional scattering
Diffraction modes and their applications

- **Powder**: isotropic crystal orientations
  - See every diffraction peak in one $I(\theta)$ scan
  - Get Bulk Properties

- **Thin film**: isotropic IP, but orient OOP
  - Use grazing sample geometry
  - Confinement/interfacial effects

- **Single crystal**: (point detector)
  - Strain states, defects, atomic effects


R. Steyrleuthner, JACS (2014)

Collins, PRB (2008)
Peak broadening: Grain size & disorder

**Instrument Resolution**
(beam divergence, size, $\Delta\lambda$)

**Nanocrystal Size**

Coherence Length

Scherrer Analysis

$$D \cong \frac{2\pi K_{\text{shape}}}{\Delta q_{\text{FWHM}}}$$

**Debye-Waller Disorder**
(Thermal, random)

RMS fluctuation around equilibrium positions

**Paracrystalline Disorder**
Builds up over unit cells

Warren-Averbach Analysis

J. Rivnay, PRB (2011)
Crystal orientation in a thin film

- Interfaces affect crystal orientation distribution in thin films
- Distribution obtained via “Pole Figure” from GIWAXS
- Relative Degree of Crystallinity from integrating pole figure

Electron Conducting Polymer “N2200”

“Face-On” Substrate

“Edge-On” Substrate

Steyrleuthner, JACS (2014)
Aggregation-crystallinity-charge transport in conjugated polymers

**Absorbance**
- Aggregate I
- Aggregate II

**GI-XRD (7.3.3)**
- Vertical Stacking
- Horizontal Stacking

**Steyerleuthner, JACS (2014)**
Small angle scattering

- Larger scale than atomic/molecular $D > 1 \text{nm}$
  - Have to be careful of direct beam!
- Dilute particulate systems
  - Scattering within particle gives shape and size
  - Incoherent scattering between particles
- Phase separated structures
  - Mean domain size, interphase boundary
  - Larger periodic structures from macromolecules or biomolecules
SAS Data Analysis: Dilute Particles

- Simple particle shapes: Get dimension statistics
  - Spheres, Rods, Disks (distribution of radii and length)
  - Assumption: equal probability for all orientations
- Guinier Law: Get size if you don’t know the shape
  - Particle “Radius of Gyration” $R_g$
  - Assumptions: $q \ll 1/R_g$, dilute ($C < 1\nu.$%), no other scattering

\[ \lim_{q \to 0} I(q) = \rho_e \nu^2 \exp\left(-\frac{1}{3} q^2 R_g^2\right) \]
SAS: Two-phase systems

- Auto/Pair Correlation \( \Gamma(r) = IFFT[I(q)] \)
  - Avg length scale of domains (sizes, distances)
- Porod Invariant \( Q = \int I(q) dq = V \phi_1 \phi_2 |\Delta \rho_e|^2 \)
  - Phase volume fractions
  - Domain ‘contrast’ (RMS fluctuations)
- Porod Law
  - Specific Interfacial Area
  - Interface roughness/diffusivity

\[
\lim_{q \to \infty} \frac{I(q)}{Q} = \frac{2\pi S}{\phi_1 \phi_2 q^4 V}
\]
Data Processing

• **NIKA** – processing tool coded by Jan Ilavsky (ANL)
  • Runs in Wavemetrics’ *Igor Pro*
  • Converts 2D CCD data into $I(q)$
  • Handles most detectors

• **XICAM** – Next generation processing/analysis tool
  • Python based
Data Analysis

- IRENA – by Jan Ilavsky (ANL) Igor Pro
  - Power Diffraction fitting
  - Particle Modeling
  - Guinier Analysis
- NCNR/NIST SANS Analysis
  - Igor Pro
- Fit2D (ESRF)

Always need model for accurate interpretation!
(Good to pair with microscopy)
Reflectivity:

Nondestructive depth profile

- Resolution depends on q-range & “Kiessig” fringes (1-2 nm)
- **Software:** MotoFit; Refl1D (NIST)

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Coherent Scattering

• Every source some coherence
  • Depends on source size, beam length, and spectral bandwidth
  • Make beam fully coherent via a pinhole the size of the coherence length

• When scattering, get ‘speckle patterns’ (complex interference pattern)

• Can use to ‘solve the phase problem’ to invert pattern into spatial image
  • “Coherent Diffractive Imaging” – ptychography

• Can monitor in time to capture dynamics
  • X-ray photocorrelation spectroscopy (XPCS)
Ptychography

- Scattered wave is FFT of density distribution
  \[ A(q) = FFT[\rho(r)] \]
- Measured intensities: Only the amplitudes!
  \[ I(q) = A(q)A^*(q) \]
  - Can’t take an inverse FFT to get \( \rho(r) \) back!
- Coherent Diffractive Imaging recovers phase
  - CAN get \( \rho(r) \) maps or even tomograms!
- Overlap coherent beam over sample
  - Diffraction limited microscopy

Pfeiffer, Nat Photon (2018)


Thibault, Science (2008)
X-ray Photo Correlation Spectroscopy

Time scales of dynamic processes at the nano/atomic scale

Correlation functions at specific q-values for NPs in a polymer melt

Carnis, Sci Rep (2014)
X-ray energy: New dimension in scattering

- Combine spectroscopy and scattering
  - Adds chemical information to structure measurement
- Elemental absorption edge (NEXAFS or XANES)
  - Organics: Carbon/Nitrogen/Oxygen – bond-sensitivity!
  - Metals: Fe/Co/Mn – oxidation & spin state sensitivity!

\[ I(q) = \int \Delta \rho_e^2(r)e^{-irq} \quad \rho_e = \frac{2\pi}{r_\epsilon \lambda} n \]

Refr. Index: \[ n(E) = 1 - \delta(E) + i\beta(E) \]
RSoXS: Bond-Sensitive Scattering

- **Resonance**: 100x better contrast, No Tagging
  - $I(E) \propto |\Delta \tilde{n}(E)|^2$ ($n$ - index of refraction)
- **Contrast variation** (w/out isotopic labeling)
  - Non-resonant: roughness, porosity
  - Resonant: Material domains
- **Domain compositions/purity** from Total Scattering Intensity (TSI)
  \[
  TSI = \int_0^\infty I(q)q^2 dq \propto \langle \Delta x \rangle^2
  \]
Measuring Nonplanar Interfaces

- Block copolymers have known morphologies
  - Thermo properties determines limits of nanostructure (energy cost of mixing)
  - Bottom-Up assembly for sub-10nm devices
  - Need to measure $w$

- Porod Invariant & Spectral Analysis

\[
\int I(q, E)q^2 dq = V |\Delta x_{12}|^2 |\Delta n_{12}(E)|^2 \left( \phi_1 \phi_2 - \frac{1}{\sqrt{2}} \frac{S}{V} w \right)
\]

\[
TSI(E) = \frac{1.1}{\chi^2}
\]

$w = 4.4 \pm 0.7 nm$

1st measurement of non-planar interfaces in thin film!

Ferron *PRL* (2017)
RSoXS Data Processing Tool for 11.0.1.2

- Wrapper on NIKA to incorporate energy series into scattering experiments
- Download at Collins Website [https://labs.wsu.edu/carbon/xray-analysis-tools/]
Polarized RSoXS: *Spatially correlated orientation*

- Angle-dependent NEXAFS Spectroscopy: 
  
  \[ I \sim \mu_{\text{avg}} \cdot E \]

- Can use microscopy and scattering to measure *local orientation*
  
  \[ I_{\text{scatt}} \sim (\mu_1 - \mu_2) \cdot E \]


STXM: P3HT dark phase

Quantifying Scattering Anisotropy

- **Magnitude**: Degree (statistics) of molecular ordering
- **Sign**: Preferred orientation in nanostructure

Anisotropy Ratio

$$A(q) = \frac{I_S(q) - I_P(q)}{I_S(q) + I_P(q)}$$

RSoXS: High-Dimensional SAXS/SANS

Deep characterization of molecular nanostructures

**Chemical Ordering**


What about Solvated Nanostructures?!


Operando Environments

- Liquids, temperatures, electric fields
- TEM flow/electrochem cell by Protochips
  - Testing stage
- New RSoXS instrument designed by David Kilcoyne
  - Assembly and testing starting August

Collab with ALS (Wang & Kilcoyne), Penn State (Gomez), and NCSU (Ade)

X-rays from David Kilcoyne
Summary

• Scattering reveals statistics of ordering
• Atomic $\rightarrow$ nano $\rightarrow$ micron sizescales
• Crystalline $\rightarrow$ amorphous materials
• Inorganic $\rightarrow$ organic $\rightarrow$ biological materials
• Many opportunities at the ALS for scientists of all disciplines
Resources

- X-Ray Diffraction
  - B.E. Warren

- Methods of X-Ray and Neutron Scattering in Polymer Science
  - Ryong-Joon Roe

- X-Ray Scattering of Soft Matter
  - N. Stribeck

10/4/2018
Light Sources 101, ALS User Meeting 2018