What does a diffraction pattern tell us?

- **Peak Shape & Width:**
  - Zero order peak
  - Higher order peaks
    - Crystallite size
    - Strain gradient

- **Peak Positions:**
  - Phase identification
  - Lattice symmetry
  - Lattice strain

- **Peak Intensity:**
  - Structure solution
  - Crystallite orientation

Small Angle Scattering & Reflectivity

Wide Angle Scattering
Lensless Imaging

Sample Space ➔ Angular Space ➔ Image Space

Fourier Transform

Q = 4\pi \sin(\theta) / \lambda

Fourier Transform
Phase Problem

Measurement $\rightarrow (\text{Amplitude})^2$ – no phase.
Phase Problem

\[ A(r) = \text{FT} \{ F_1 + a F_2 e^{i\phi} \} \]

Amplitude unknown

Phase Unknown

\[ F_1 \]

\[ F_2 \]
Solving the Phase Problem

- Holographic
- Guess/Trial+Error

If sufficient coherence
Magnetic x-ray holography

X-rays

Magnetic Sample

Hologram

A lensless image

Intensity

2D Fourier Transform

Fourier Transform Hologram
Solving the Phase Problem

• Holographic

• Guess/ Trial+Error

• X-ray Crystallographic Methods
  – Heavy Atom substitution
  – Patterson Method
  – Multi-wavelength Anomalous Diffraction
  – Reitveld Method
  – Fourier Difference Method

• Iterative Phase Retrival

If sufficient coherence
Solution to Phase Problem

• Phase/Structure must be guessed
  – And then refined.

• How to guess?
  – Heavy atom substitution, SAD or MAD
  – Structure with one strong scatterer – e.g. U in Phosphates matrix –
  – Similarity to homologous compounds, e.g. NaCl $\rightarrow$ KCl

  – Patterson function or pair distribution analysis.

B. Shyam
Structure Solution

• Single Crystal
  – Protein Structure
  – Sample with heavy Z problems Due to
    • Absorption/extinction effects
  – Mostly used in Resonance mode
    • Site specific valence
    • Orbital ordering.

• Powder
  – Due to small crystallite size kinematic equations valid
  – Many materials can not be readily prepared in single-crystal form: their structures obtained via synchrotron powder diffraction
  – Peak overlap a problem – high resolution setup helps
  – Much lower intensity – loss on super lattice peaks from small symmetry breaks. (Fourier difference helps)
Inverse Modeling Method 1

- Reitveld Method
Profile Shape function

• Empirical
  – Voigt function modified for axial divergence (Finger, Jephcoat, Cox)
    • Refinable parameters – for crystallite size, strain gradient, etc...

• From Fundamental Principles
Inverse Modeling Method 1

- Reitveld Method

**Model**

**Background**

**Profile shape**

**Data**

**Refined Structure**
Inverse Modeling Method 2

- Fourier Method

![Diagram showing the process of inverse modeling with Fourier method]

- Subtract Background
- Profile shape
- Integrated Intensities
- Model
- Refined Structure

**Profile shape**

**Integrated Intensities**

**phases**
Inverse Modeling Methods

Linda Lim will say much more....

- Rietveld Method
  - More precise
  - Yields Statistically reliable uncertainties

- Fourier Method
  - Picture of the real space
  - Shows “missing” atoms, broken symmetry, positional disorder

- Should iterate between Rietveld and Fourier.
  - Be skeptical about the Fourier picture if Rietveld refinement does not significantly improve the fit with the “new” model.
Procedure for Refinement/Inverse Modeling

- **Measure peak positions:**
  - Obtain lattice symmetry and point group
    - **Guess the space group.**
      - Use all and compare via F-factor analysis
- **Guess the motif and its placement**
  - Phases for each hkl
- **Measure the peak widths**
  - Use an appropriate profile shape function
- **Construct a full diff. pattern and compare with measurements**
Collect data on Calibrant under the same conditions

- Obtain accurate wavelength and diffractometer misalignment parameters
- Obtain the initial values for the profile function (instrumental only parameters)
- Refine polarization factor
- Tells of other misalignment and problems
Need for High Q

Many more reflections at higher Q.

Therefore, most of the structural information is at higher Q.
Structure Refinement Method

Reitveld Method

Fourier Difference Method

Questions?