Rietveld Refinement

Basics of background and general “recipe” for refinement of powder diffraction data in GSAS-II
Historical development

• **Before 1967**
  - Single peak fits to powder pattern to obtain integrated intensities and structure factors

• **After 1967**
  - Hugo Rietveld implements whole powder pattern fitting to a diffraction data from neutron source.
    - Whole pattern fitting extended to just profile shape constrained by unit cell
      - G. Stuart Pawley, 1981
      - Armel Le Bail, 1986
Historical development

Hugo Rietveld in Australia, late 1960’s

• Develops pull profile fitting with least-squares method

• Applies it to structures of uranium salts $\text{AUO}_4$ for $A = \text{Ca, Sr, Ba}$

• Solve problem of overlapping peaks
  – First patterns were of neutron diffraction data
    • Constant wavelength source
    • Well separated peaks for $\lambda = 2.6 \text{ Å}$ (as opposed to 1.55 Å)
    • Peak profile was a simple Gaussian
    • Decent intensities at high angles

Popularizing the Rietveld method

- Cheetham & Taylor, 1977
- Catalog 172 structures determined with Rietveld methods
- Method extended to pulsed neutron data, X-rays
- Especially important for inorganic materials where obtaining single crystals difficult

Other great contributors:
- R. Young
- R. Von Dreele
- P.W. Wilson
- A. Hewat

Non-linear least squares refinement

Function to minimize

\[ M = \sum w (Y_o - Y_c)^2 \]

- \( Y_o \) = observed intensity at step 2\( \theta \)
- \( Y_c \) = calculated intensity at step 2\( \theta \)
- \( w = 1/Y_o \)

\[ Y_c = K \times |F_{hkl}|^2 \times H(\Delta T_h) \]

- Scale factor and other corrections to intensity
- Structure factor squared, i.e. the crystal structure
- Profile parameter function, information on peak width, shape, and asymmetry
Residuals and goodness-of-fit

**$R$-Bragg factor**

$$R_B = \frac{\sum |I_K(\text{obs}) - I_K(\text{calc})|}{\sum I_K(\text{calc})}$$

**$R$-pattern factor**

$$R_p = \frac{\sum |Y_o - Y_c|}{\sum Y_o}$$

**Weighted $R$-pattern factor**

$$R_{wp} = \sqrt{\frac{\sum w(Y_o - Y_c)^2}{\sum wY_o^2}}$$

**$\chi^2$**

$$\chi^2 = \frac{\sum w(Y_o - Y_c)^2}{N_{\text{obs}} - N_{\text{var}}}$$

**$\chi^2$**

$$\chi^2 = \frac{M}{N_{\text{obs}} - N_{\text{var}}}$$

**Goodness of fit or chi-squared**

$\sim 10\%$
Parameters: To model a crystal structure with Rietveld, we must fit experimental parameters (parameters influenced by the scattering experiment itself) and crystallographic parameters (parameters influenced by the sample itself).

Controls: Controls dictate how the programs operate. These are high-level such as number of refinement cycles, etc.

Constraints: Often, we do not always have enough data to fit all the parameters we wish to refine for a sample. Thus, we use some level of expertise or knowledge of the system to add constraints which ease the refinement into the minimum by lowering degrees of freedom.
Factors which determine peak profile

Common Factors:
1. Instrumental resolution
2. Axial divergence (low angle asymmetric peak shape)
3. Sample displacement
4. Crystallite broadening
5. Strain broadening

Less Common Factors:
1. Stacking faults
2. Compositional inhomogeneity
3. Modulated superstructures

Peaks can be fit by a Gaussian peak shape, Lorentzian peak shape or a combination of the two using a Voigt convolution or pseudo-Voigt peak shape.
Peak shapes

Gaussian peak shape

\[ G(t) = \frac{1}{\sqrt{2\pi \sigma^2}} \exp\left(\frac{-t^2}{2\sigma^2}\right) \]

Lorentzian peak shape

\[ L(t) = \frac{\Gamma}{2\pi} \frac{1}{\left(\Gamma/2\right)^2 + t^2} \]

Pseudo-Voigt peak shape

\[ P(t) = \eta \cdot L(t, \Gamma) + (1 - \eta) \cdot G(t, \sigma) \]
Parameters – Peak width

GSAS-II defaults to using a pseudo-Voigt peak shape which is a weighted sum of Gaussian and Lorentzian.

**Gaussian:**
GU, GV, and GW are Cagliotti terms which are derived as instrumental response function to constant wavelength diffraction for neutrons, not complete for X-rays. *(Instrumental)*

P is a term added for crystallite broadening *(Sample)*

\[ \sigma^2 = U \tan^2 \theta + V \tan \theta + W + \frac{P}{\cos^2 \theta} \]

**Lorentzian:**
X is crystallite broadening
Y is strain broadening *(Both for Sample)*

\[ \Gamma = \frac{X}{\cos \theta} + Y \tan \theta \]
**Instrumental Parameters**

**Axial divergence:**

\[
\Delta 2\theta = -h^2 \left( K_1 \cot(2\theta) + K_2 \csc(2\theta) \right) / 3R^2
\]

\( h = \) axial width of sample, \( K_1/K_2 = \) Soller slit constants, \( R = \) goniometer radius

[Link](http://pd.chem.ucl.ac.uk/pdnn/diff2/kinemat2.htm)
Instrumental Parameters

**Sample displacement:**
Displacement of peak in $2\Theta$ due to non-ideal perfectly flat surface.

**Sample transparency:**
Displacement of peak in $2\Theta$ due to non-negligible x-rays penetrating sample surface.

**Zero error:**
Displacement due to misaligned detector

$$\Delta 2\theta' = \Delta 2\theta + S_s \cos \theta + T_s \sin 2\theta$$

Bragg-Brentano – only refine displacement and transparency.

Parallel beam – only refine zero error.
Sample Parameters - Peak Width/Intensity

Unit cell and space group:
• GSAS-II can support up to 9 phases for each Rietveld refinement. Lattice parameters is one of the first things to be changed.

Atomic coordinates:
• Refine non-special crystallographic positions within the unit cell. Special positions for each space group are fixed and cannot be changed.

Occupancy:
• Refine atomic occupancy at each unique crystallographic site in the space group. Needs to be done very carefully and can be highly correlated to other parameters.

Thermal parameters:
• Intensity shifts due to thermal vibrations of atoms – usually larger for lighter atoms but bonding/structure play a role. Can only be refined with high quality data.

Preferred orientation:
• If crystallites are not aligned randomly in the powder sample some reflections may have too high intensity due to overpopulation of that orientation. Can be problem depending on morphology of the sample (layered samples).
Crystallite Size Broadening

The Fourier transform of an infinite array of periodic objects is an array of delta functions.

• The finite sizes of crystallites will broaden the delta function and all reflections equally in units of Q (∝ 1/d).

• If the crystallite size is not isotropic, then the broadening will not be isotropic.

• The broadening can be modeled as isotropic, uniaxial, or some combination of multiple axes.
Microstrain Broadening

When a material has some internal stress, some crystallites may be compressed or expanded due to local environment.

This leads to a range of lattice constants as the reflections will be broadened in $Q (\propto 1/d)$.

The peak width modulation increases linearly with $Q$ such that $(\Delta Q/Q$ or $\Delta d/d$ are constants) - therefore microstain is unitless in GSAS-II.
Histogram Parameters

Each powder pattern is called a histogram in GSAS-II and some parameters need to be fit for each histogram as a whole.

Background:
- One of the first things that should be determined for a pattern. Chebyshev polynomial is recommended with as many terms as needed. Different background types can be used if known issue appears in pattern.

Scale Factor/Phase Factor:
- Scales the peak intensities of all phases relative to background baseline. Phase fraction of each included phase in histogram multiples the scale factor. Only need to refine phase fraction if multiple phases are present.
Constraints to reduce complexity

Often times the data we receive is not robust enough to match our desired modeling. In these cases, we can often use expertise and knowledge of the system to introduce constraints.

- Occupancy – set doping level maximum based on experimental setup.
- Bond angle and distances – these can be fixed with a priori knowledge of the system. Especially useful for systems with light elements.
- Phase fraction – constrain phase fractions of known amounts of each phase.
- Rigid body – groups of atoms have fixed geometry relative to another – can be useful in very complex systems (macromolecular).
Refinement recipe

In practice, all parameters must be refined slowly and step-wise to ensure low correlation and finding the global minimum.

*For GSAS-II, you need reasonable starting points for unit cell, scale factor, background and instrumental peak profile.

I. Instrumental peak profile can be determined by beamline scientists or by running X-ray standards to determine your instrumental idiosyncrasies.

II. Can use Lebail refinement to determine unit cell parameters, background, and profile initially. Lebail refinement only matches peak position and peak intensity - no complex crystallographic parameters added.

1. Fit unit cell with small # of background terms. (Are reflections in the correct place)

2. Fit 2Θ correction. (are all peaks indexed? If no, change unit cell or add impurity phase) -- Bragg-Brentano (sample displacement + transparency) or Parallel Beam (zero error).

3. Fit peak shape. (if peak shape is way off and you have reasonable instrumental terms, you can refine sample terms)
Refinement recipe

4.) Fit atomic coordinates. (most unit cells have some special positions that
cannot be changed. Allow “big” atoms in non-special positions to change
first and then move onto other atoms. “big” = high multiplicity in the unit
cell or large scattering factor for your experiment.

5.) Refine thermal parameters. (for complex structures with many sites of
the same element - these terms can be constrained to be equal)

6.) Occupancy. (This should be done before thermal parameters if occupancy
is something that you think should/could be changing in your system – for
most systems this is not needed)

7.) Peak profile revisited. (if the initial peak profile was an OK match - the
sample-dependent terms such as GP or LX/LY can be added now to finalize
the refinement.)
Refinement recipe

8.) Evaluate the fit. (this should be done at every step but especially when determining if the refinement has succeeded to your desire.) Residuals are a good metric but difference curves tells more information such as small unfit peaks (impurity?), small peak offset (unit cell off?), individual peaks intensity mismatch (preferred orientation?), etc.

9.) Prepare data for publication. (export data from GSAS to plot in GSAS or your preferred graphic software, prepare CIF if structure is new or want easy visualization using VESTA for publication)

Rietveld refinements are never perfect and are just a model of the data and system you are considering. Laboratory x-ray is often insufficient for very complex structure determination. Advanced diffraction experiments such as synchrotron powder x-ray diffraction or powder neutron diffraction are often needed to determine complex crystal structures with occupancy, minor impurities, thermal parameters, etc.
Rietveld and GSAS-II References


Schools on diffraction:

- https://www.aps.anl.gov/Structural-Science/SRS-Courses
- https://acasmerrcourse.net/