Neutron Rietveld Refinement

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“Rietveld refinement is one of those few fields of intellectual endeavor wherein the more one does it, the less one understands.” (Sue Kesson)
Powder - polycrystalline mass

All orientations of crystallites possible

Sample: 1cc powder of 10\(\mu\)m crystallites - \(10^9\) particles
if 1\(\mu\)m crystallites - \(10^{12}\) particles

Single crystal reciprocal lattice
- smeared into spherical shells
- broadened by instrumental & sample effects
Neutron Diffractometers - Constant Wavelength

Reactor

$\alpha_1$

Monochromator

$2\Theta_M$ - fixed

Sample

$0.8 \leq \lambda \leq 5.0\text{Å}$

$\alpha_3$

Detector (can be many)

Debye Scherrer geometry

$\lambda = 2d\sin\Theta$

Vary $\Theta$
Neutron Diffractometers - Time-of-Flight

9 \leq L_0 \leq 100m

2\Theta - fixed

\lambda = 2dsin\Theta

Vary \lambda (T)

T=Cd+Ad^2+Z

Also Debye Scherrer
Source comparison: CW vs TOF

Typical monochromator cut at 1.54 Å

T = 300K
CW neutron pattern (& Rietveld refinement fit)
TOF neutron pattern (& Rietveld refinement fit)

Mg2Ti04 spinel
Bank 3, 2-Theta 151.1, L-S cycle 56 Obsd. and Diff. Profiles

Hist 1

TOF, msec

Counts/10E-3

-1.0 -0.0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0

X10E-3

-1.0 -0.0 1.0 2.0 3.0

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Rietveld refinement – multiparameter curve fitting

\[ I_c = I_i \left[ \sum_h k_h F_h^2 m_h L_h P(\Delta_h) + I_b \right] \]

Rietveld minimize

\[ M_R = \sum w(I_o - I_c)^2 \]

Exact overlaps
- symmetry

Incomplete overlaps

Residual:

\[ R_{wp} = \sqrt{\frac{\sum w(I_o - I_c)^2}{\sum wI_o^2}} \]
Least Squares Theory - simple

Given a set of observations: $G_o$

and a function: $G_c = g(p_1, p_2, p_3..., p_n)$

then the best estimate of the values $p_i$ is found by minimizing

$$M = \sum w(G_o - G_c)^2$$

This is done by setting the derivative to zero

$$\sum w(G_o - G_c) \frac{\partial G_c}{\partial p_j} = 0$$

Results in n “normal” equations (one for each variable) - solve for $p_i$
Least Squares Theory - continued

Problem - \( g(p_i) \) is nonlinear & transcendental (sin, cos, etc.) for crystallography - so can’t solve directly

Expand \( g(p_i) \) as Taylor series & toss high order terms

\[
I_c(p_i) = I_c(a_i) + \sum_i \frac{\partial I_c}{\partial p_i} \Delta p_i
\]

\( a_i \) - initial values of \( p_i \)

\( \Delta p_i = p_i - a_i \) (shift)

Substitute above

\[
\sum w \left[ \Delta I - \sum_i \frac{\partial I_c}{\partial p_i} \Delta p_i \right] \frac{\partial I_c}{\partial p_j} = 0
\]

\( \Delta I = I_o - I_c(a_i) \)

Normal equations - one for each \( \Delta p_i \); outer sum over observations

Solve for \( \Delta p_i \) - shifts of parameters, **NOT** values
Least Squares Theory - continued

Rearrange

\[ \sum w \frac{\partial l_c}{\partial p_1} \left( \sum_{i=1}^{n} \frac{\partial l_c}{\partial p_i} \Delta p_i \right) = \sum w \Delta l \frac{\partial l_c}{\partial p_1} \]

\[ \vdots \]

\[ \sum w \frac{\partial l_c}{\partial p_n} \left( \sum_{i=1}^{n} \frac{\partial l_c}{\partial p_i} \Delta p_i \right) = \sum w \Delta l \frac{\partial l_c}{\partial p_n} \]

Matrix form: \( Ax = v \)

\[ a_{i,j} = \sum w \frac{\partial l_c}{\partial p_i} \frac{\partial l_c}{\partial p_j} \quad x_j = \Delta p_j \quad v_i = \sum w (\Delta l) \frac{\partial l_c}{\partial p_i} \]
Least Squares Theory - continued

Matrix equation \( Ax = v \)
Solve \( x = A^{-1}v = Bv; \quad B = A^{-1} \)

This gives set of \( \Delta p_i \) to apply to “old” set of \( a_i \)
repeat until all \( x_i \sim 0 \) (i.e. no more shifts)

Rietveld refinement - this process applied to
powder profiles – curve fitting!

**Note:** Starting model **REQUIRED**

- \( I_o \) – observed powder profile (including
  background)
- \( I_c \) - model function for the powder profile
Least Squares Theory - continued

Error estimates (mostly from W.C. Hamilton) Given observations $n > m$ parameters with distributions that have finite 2nd moments (no need to be “normal”) Then LS gives parameter estimates (shifts in our case) with the minimum variance in any linear combination

The error estimates (“esd’s” or “su’s”) are

$$\sigma_i = \frac{b_{ii}^{1/2}}{\chi} \quad \chi^2 = \frac{\sum w(l_o - l_c)^2}{n - m}$$

$b_{ii}$ - diagonal elements of the inverted A matrix

Note: There is little justification for additional scaling of the $\sigma_i$
Rietveld refinement in GSAS - minimization function

\[ M = \sum w_i (I_{oi} - I_{ci})^2 \]

- Powder profiles (Rietveld)

\[ + f_a \sum w_i (a_{oi} - a_{ci})^2 \]

- Bond angles

\[ + f_d \sum w_i (d_{oi} - d_{ci})^2 \]

- Bond distances

\[ + f_t \sum w_i (t_{oi} - t_{ci})^2 \]

- Torsion angles

\[ + f_p \sum w_i (-p_{ci})^2 \]

- Plane RMS displacements

\[ + f_v \sum w_i (v_{oi} - v_{ci})^4 \]

- van der Waals distances

\[ + f_h \sum w_i (h_{oi} - h_{ci})^2 \]

- Hydrogen bonds

\[ + f_x \sum w_i (x_{oi} - x_{ci})^2 \]

- Chiral volumes

\[ + f_R \sum w_i (-R_{ci})^2 \]

- "φ/ψ or χ_1/χ_2" pseudopotential

\[ w_i = 1/\sigma^2 \] weighting factor

\[ f_x - \text{ weight multipliers (typically 0.1-3)} \]
Model - represent each profile intensity

\[ I_c = I_i \left[ \sum_h k_h F_h^2 m_h L_h P(\Delta_h) + l_b \right] \]

\[ I_i - \text{incident intensity - variable for neutron TOF} \]

\[ k_h - \text{scale factor for particular phase} \]

\[ F_h^2 - \text{structure factor for particular reflection} \]

\[ m_h - \text{multiplicity of the reflection} \]

\[ L_h - \text{correction factors on intensity} \]

\[ P(\Delta_h) - \text{peak shape function} \]

Minimize \[ \sum w(I_o - I_c)^2 \] thus need all \[ \frac{\partial I_c}{\partial p_i} \]
Profile Functions - Basics

\[ \Delta T = T_{\text{reflection}} - T_{\text{profile}} \]

Gaussian profile - generally instrumental origin

\[ G(\Delta T, \Gamma) = \sqrt{\frac{4\ln2}{\pi\Gamma^2}} \exp\left[ -\frac{4\ln2(\Delta T)^2}{\Gamma^2} \right] \]

Lorentzian profile - largely sample effect

\[ L(\Delta T, \gamma) = \frac{2}{\pi\gamma} \frac{1}{1 + \left( \frac{2\Delta T}{\gamma} \right)^2} \]
Constant Wavelength Profile Function - GSAS

Thompson, Cox & Hastings (with modifications)

Pseudo-Voigt

\[ F(\Delta T) = \eta L(\Delta T, \Gamma) + (1 - \eta) G(\Delta T, \Gamma) \]

Mixing coefficient

\[ \eta = \sum_{j=1}^{3} k_j \left( \frac{\gamma}{\Gamma} \right)^j \]

FWHM parameter

\[ \Gamma = \sqrt[5]{\sum_{i=1}^{1} c_i \Gamma_g^{5-i} \gamma^i} \]
CW Function Coefficients - GSAS

Asymmetry

Sample shift

Sample transparency

Gaussian profile

Lorentzian profile

\( \Gamma_g = U \tan^2 \Theta + V \tan \Theta + W + \frac{P}{\cos^2 \Theta} \)

\( \gamma = \frac{X}{\cos \Theta} + Y \tan \Theta \)

(plus anisotropic broadening terms)
Microstrain Broadening – simple model

\[ \frac{\Delta d}{d} = \text{cons} \tan t \]

\[ \frac{\Delta d}{d} = \frac{\Delta d^*}{d^*} = \Delta \Theta \cot \Theta \]

\[ \Delta 2\Theta = \frac{2\Delta d}{d} \tan \Theta \]

Lorentzian term - usual effect

Gaussian - Remove instrumental part

\[ S = 100\% \frac{\pi}{180} "LY" \]

\[ S = 100\% \frac{\pi}{180} \sqrt{\Delta "GU"} \]
Crystallite Size Broadening

\[ \Delta d^* = \text{constant} \]

\[ \Delta d^* = \frac{\Delta d}{d^2} = \frac{\Delta \Theta \cot \Theta}{d} \]

\[ = \frac{\Delta 2 \Theta \cot \Theta \sin \Theta}{\lambda} \]

\[ \Delta 2 \Theta = \frac{\lambda \Delta d}{d^2 \cos \Theta} \]

Lorentzian term - usual
K - Scherrer const.

Gaussian term - rare
particles same size?

\[ p = \frac{180K\lambda}{\pi "LX"} \]

\[ p = \frac{180K\lambda}{\pi \sqrt{"GP"}} \]
Neutron TOF Neutron Profile Function

Von Dreele, Jorgenson & Windsor (with modifications)
Convolution of paired exponentials and a Gaussian

\[ H(\Delta T) = N [e^u \text{erfc}(y) + e^v \text{erfc}(z)] \]

where \( u, v, y \) & \( z \) are functions of profile coefficients

\[ \alpha = \alpha_o + \alpha_1/d \quad \text{exponential rise} \]
\[ \beta = \beta_0 + \beta_1/d^4 \quad \text{exponential decay} \]

\[ \sigma^2 = \sigma_0^2 + \sigma_1 d^2 + \sigma_2 d^4 + (\sigma_3 e d^2 + \sigma_4 e d^4) \cos 2\phi \]

Gaussian variance - also anisotropic terms

\[ \Delta T = (T - T_{ph}) \cdot \varepsilon_i d - \varepsilon_a d \cos \phi - \varepsilon_A d \frac{(hk)^2 + (hl)^2 + (kl)^2}{2^2 2^2 2^2} \]

peak displacement - macrostress
Microstrain broadening – physical model

Model – elastic deformation of crystallites


**d-spacing expression**

\[
\frac{1}{d_{hkl}^2} = M_{hkl} = \alpha_1 h^2 + \alpha_2 k^2 + \alpha_3 l^2 + \alpha_4 kl + \alpha_5 hl + \alpha_6 hk
\]

**Broadening – variance in** \(M_{hkl}\)

\[
\sigma^2(M_{hkl}) = \sum_{i,j} C_{ij} \frac{\partial M}{\partial \alpha_i} \frac{\partial M}{\partial \alpha_j}
\]
Microstrain broadening - continued

Terms in variance

\[
\frac{\partial M}{\partial \alpha_1} = h^2, \quad \frac{\partial M}{\partial \alpha_2} = k^2, \quad \frac{\partial M}{\partial \alpha_3} = l^2, \quad \frac{\partial M}{\partial \alpha_4} = kl, \quad \frac{\partial M}{\partial \alpha_5} = hl, \quad \frac{\partial M}{\partial \alpha_6} = hk
\]

Substitute – note similar terms in matrix

\[
\frac{\partial M}{\partial \alpha_i} \frac{\partial M}{\partial \alpha_j} = \begin{bmatrix}
h^4 & h^2k^2 & h^2l^2 & h^2kl & h^3l & h^3k \\
h^2k^2 & k^4 & k^2l^2 & k^3l & hk^2l & hk^3 \\
h^2l^2 & k^2l^2 & l^4 & kl^3 & hl^3 & hkl^2 \\
h^2kl & k^3l & kl^3 & k^2l^2 & hkl^2 & hk^2l \\
h^3l & hk^2l & hl^3 & hkl^2 & h^2l^2 & h^2kl \\
h^3k & hk^3 & hkl^2 & h^2l & h^2kl & h^2k^2
\end{bmatrix}
\]
Microstrain broadening - continued

Broadening – as variance

$$\sigma^2(M_{hkl}) = \sum_{HKL} S_{HKL} h^H k^K l^L, H + K + L = 4$$

General expression – triclinic – 15 terms

$$\sigma^2(M_{hkl}) = S_{400}h^4 + S_{040}k^4 + S_{004}l^4 + 3(S_{220}h^2k^2 + S_{202}h^2l^2 + S_{022}k^2l^2) + 2(S_{310}h^3k + S_{103}hl^3 + S_{031}k^3l + S_{130}hk^3 + S_{301}h^3l + S_{013}kl^3) + 4(S_{211}h^2kl + S_{121}hk^2l + S_{112}hkl^2)$$

Symmetry effects – monoclinic (b unique) – 9 terms

$$\sigma^2(M_{hkl}) = S_{400}h^4 + S_{040}k^4 + S_{004}l^4 + 3S_{202}h^2l^2 + 3(S_{220}h^2k^2 + S_{022}k^2l^2) + 2(S_{301}h^3l + S_{103}hk^3) + 4S_{121}hk^2l$$
Unusual line broadening effects

Seeming inconsistency in line broadening
  - hkl dependent
Na parahydroxybenzoate

Unusual microstrain effects - peak broadening

Directional dependence - Lattice defects?
Exploded view of HIPPO Diffractometer

- Sample chamber: 29.13” opening & 32” from rim to beam center
- 150deg panels
- 90deg panels
- 40 & 20deg panels
- 10deg panels
Neutron TOF Diffractometer - multiple detectors

High to low scattering angles
\[ \lambda = 0.4\text{Å} \text{ to } 10\text{Å}; \ d = 0.2\text{Å} \text{ to } 30\text{Å} \]
\[ \Delta d/d = 0.3\% \text{ to } 5\%(\text{other instr. } <0.1\%) \]

E.g. HIPD & HIPPO at LANSCE;
POWGEN3 at SNS

Fixed $2\Theta$, TOF $\propto \lambda \propto d$
What is texture? “Interesting Preferred Orientation”

Random powder - all crystallite orientations equally probable - flat pole figure

Pole figure - stereographic projection of a crystal axis down some sample direction

Loose powder

(100) random texture  (100) wire texture
Crystallites oriented along wire axis - pole figure peaked in center and at the rim (100’s are 90° apart)

Orientation Distribution Function - probability function for texture
Texture - measurement by diffraction

Non-random crystallite orientations in sample

Debye-Scherrer cones
• uneven intensity due to texture
• also different pattern of unevenness for different hkl’s
• Intensity pattern changes as sample is turned
Texture effect on reflection intensity - Rietveld model

\[ A(h, y) = \sum_{l=0}^{\infty} \frac{4\pi}{2l + 1} \sum_{m=1}^{l} \sum_{n=-1}^{1} C_{l}^{mn} K_{l}^{m}(h)K_{l}^{n}(y) \]

- Projection of orientation distribution function for chosen reflection (h) and sample direction (y)
- \( K \) - symmetrized spherical harmonics - account for sample & crystal symmetry
- “Pole figure” - variation of single reflection intensity as fxn. of sample orientation - fixed h
- “Inverse pole figure” - modification of all reflection intensities by sample texture - fixed y - Ideally suited for neutron TOF diffraction
- Rietveld refinement of coefficients, \( C_{l}^{mn} \), and 3 orientation angles - sample alignment
Example: CaCO₃ calcite - “Standard Round Robin Sample”

- Two patterns from different sample orientations and different detector banks
- Very different reflection intensities from texture
- Any one pattern useless for Rietveld due to texture variation
- But all 52 combined in single LS gives texture and crystal structure
Calcite pole figures - compute from $C_{ij}^{mn}$

006 pole figure for calcite - shows sampling orientations

Other pole figures generated from harmonic coefficients

Match those from neutron measurements given by Wenk
Crystal structure of calcite - refined with texture

Result – matches “best” single crystal X-ray result

1/2 calcite unit cell
A final word

“A Rietveld refinement is never perfected, merely abandoned”

(P. Stephens, 2000)