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GSAS Parameters & Controls

**What to Refine when?
(Refinement Recipes)**


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A U.S. Department of Energy Laboratory managed by The University of Chicago

Outline

- Definitions of terms
- Powder peak shapes
 - Fitting functions
 - Size vs. strain broadening
 - Low angle asymmetry
 - Bragg-Brentano issues
- GSAS control values
- Setting up a refinement
- Profile functions and parameter definitions
- Preferred orientation
- Reducing model complexity (constraints/restraints)
- What to refine when (refinement recipe)




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Parameters/Controls/Constraints

Parameters:
To model a "crystal structure" with Rietveld, we must fit a large number of "experimental" parameters in addition to the "crystallographic" parameters.


Controls:
Controls dictate how the programs operate.

Constraints:
We do not always have enough data to fit all the parameters robustly. If so, we must approach the minimum with care and sometimes introduce constraints to reduce degrees of freedom.



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Profile parameters



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Profile Models

Rietveld refinement requires that the shape of diffraction peaks (profile) as well as their intensity be reproduced.

Intensities: determined by structural parameters

Profile: determined by instrument & by sample

- Instrument response function
- Residual stress
- Crystallite (Scherer) broadening

Approaches to Profile Models

Three different approaches to reproducing peak shapes have been used:

- Empirical functions

Functions are chosen simply because they are computationally simple and fit peaks well. The parameters cannot be interpreted because they have no relationship to the underlying physics of diffraction.

- Physically-based parameters

Functions are based on the physical phenomena. Parameters are usually found empirically, but often have a physical meaning.

- "Fundamental Parameters"

Functions and where possible parameter values are determined from diffraction physics. The only adjustable parameters are those related to sample properties.

The physics that determine peak profiles

Common factors

- Instrumental Resolution
- Axial Divergence (Low Angle Asymmetry)
- Sample placement/transparency
- Crystallite Broadening*
- Strain Broadening*

* Note that these effects can vary for different classes of reflections (anisotropic peak broadening)

Less common factors

- Stacking faults*
- Modulated Structures*
- Coherence differing by atom type*
- Compositional inhomogeneity[†]

* Hard to model

† Sometimes impossible to model

Results of these factors are convoluted to produce the observed peak shape.

Lorentz (Cauchy) and Gaussian Broadening Functions

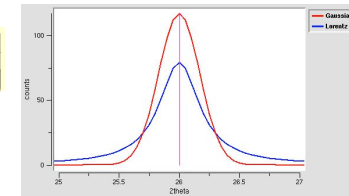
Most instrument & sample broadening contributions are Lorentzian or Gaussian

Normalized Gaussian

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

Normalized Lorentzian

$$L(\Delta T, \gamma_L) = \frac{2}{\pi \gamma_L} \frac{1}{1 + \left(\frac{2 \Delta T}{\gamma_L} \right)^2}$$



Note that peak widths vary so Γ_G and γ_L are both functions of Q

Gaussian & Lorentzian functions compared. Both curves have same FWHM & area, but note the much longer tails for the Lorentzian.

Voigt vs. Pseudo-Voigt

A Gaussian convoluted with a Lorentzian function is a Voigt function, however the Voigt is slow to compute and the derivatives are messy. Few Rietveld programs implement a Voigt.

The "pseudo-Voigt" is the weighted sum of a Gaussian & Lorentzian function – approximation is normally pretty good

Fractions of each function depend on the relative widths of each [see mixing factor (η) in GSAS manual, $\eta=0$ is Gaussian, $\eta=1$ is Lorentzian]

CW: Variation of FWHM with Q

Gaussian

- U, V & W are Cagliotti terms, derived as instrument response function for CW neutron diffraction. Incomplete for x-rays.
- P is a crystallite broadening contribution

Lorentzian

- X is crystallite broadening
- Y is strain broadening

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

N.B. no instrumental broadening term

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

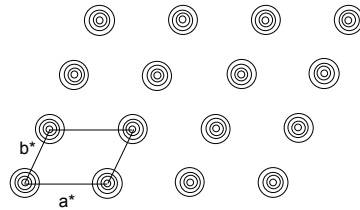
Crystallite Size Broadening

The Fourier transform (FT) from an infinite array of regularly spaced objects is an array of delta functions.

The FT from a finite length array is broadened.

The finite sizes of crystallites will broaden all orders of reflections equally in units of Q ($\propto d^*$)

- differing reciprocal space directions may have differing amounts of broadening, if crystallites dimensions are not isotropic on average



Crystallite Size Broadening can produce Lorentzian peak shapes (common) or Gaussian peak shapes (uncommon) or a combination of both.

Crystallite Size Broadening

$\Delta d^* = \text{constant}$

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

$$= \frac{\Delta 2\Theta \cot \Theta \sin \Theta}{\lambda}$$

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

See GSAS Manual, pp 158-167.

GSAS fits crystallite broadening with two profile terms:

- LX -> Lorentzian
- GP -> Gaussian

Relation between avg. size (p) and GSAS terms:

$$p = \frac{18000K\lambda}{\pi LX} \quad p = \frac{18000K\lambda}{\pi \sqrt{GP}}$$

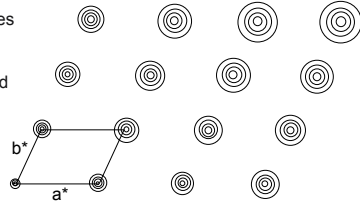
$K \approx 1$ (Scherrer constant, related to crystal shape)

Microstrain Broadening

When a material has residual stresses present, some crystallites are compressed. This must be balanced by other crystallites that are stretched (because $\sum F=ma=0$)

This leads to a range of lattice constants.

The spread between diffraction locations for the maximum and minimum lattice constant increases linearly with Q ($\Delta Q/Q$ or $\Delta d/d = \text{constant}$)



Microstrain Broadening

$$\frac{\Delta d}{d} = \text{constant}$$

$$\frac{\Delta d}{d} = \frac{\Delta d^*}{d^*} = \Delta\theta \cot\theta$$

$$\Delta 2\theta = \frac{2\Delta d}{d} \tan\theta$$

GSAS fits strain broadening with two profile terms:

- LY -> Lorentzian (most common)
- GU -> Gaussian

(note that GU also has an instrumental contribution)

See GSAS Manual, pp 158-167.

Relation between strain (as percentage) and GSAS terms:

$$S = 100\% \frac{\pi}{18000} LY \quad S = 100\% \frac{\pi}{18000} \sqrt{GU - GU_I}$$

where GU_I accounts for the instrumental contribution

Where Strain Differs by Reflection Class: "Anisotropic peak broadening"

Strain may be anisotropic

- think of a layered material where the layers can be pulled apart without much effort, but the layers themselves are quite "hard" (resistant to applied forces).
- Such a material will be "squishy" in the layer direction and rigid in the other two (more broadening in the squishy direction.)

Canonical anisotropic strain model: P. W. Stephens, *Journal of Applied Crystallography* **32**, 281 (1999).

- Restricts strain components in terms of 1st & 2nd-order terms allowed by lattice symmetry

Anisotropic strain broadening terms

Broadening – as variance

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

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

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

Anisotropic strain broadening terms

Symmetry effects – orthorhombic - mmm – 6 terms

$$\sigma^2(M_{hkl}) = S_{400}h^4 + S_{040}k^4 + S_{004}l^4 + 3(S_{220}h^2k^2 + S_{202}h^2l^2 + S_{022}k^2l^2)$$

Tetragonal – 4/mmm – 4 terms

$$\sigma^2(M_{hkl}) = S_{400}(h^4 + k^4) + S_{004}l^4 + 3S_{220}h^2k^2 + 3S_{202}(h^2l^2 + k^2l^2)$$

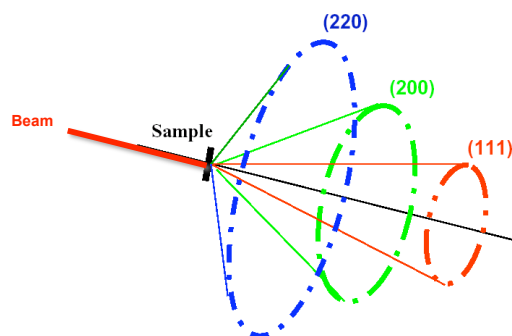
Cubic – m3m – 2 terms

$$\sigma^2(M_{hkl}) = S_{400}(h^4 + k^4 + l^4) + 3S_{220}(h^2k^2 + h^2l^2 + k^2l^2)$$

Trigonal, Rhombohedral & Hexagonal – it depends – 3 or 4 terms

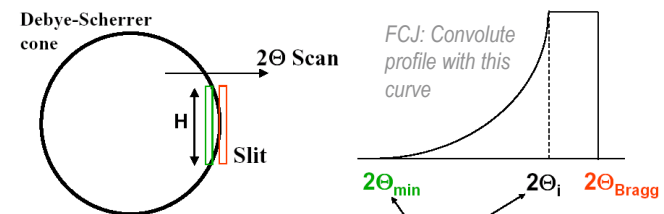
Axial Divergence: Low-angle peak asymmetry

Bragg cones in powder diffraction



Axial Divergence (Low Angle Asymmetry)

Work of Finger, Cox & Jephcoat, based on derivations by van Laar & Yelon

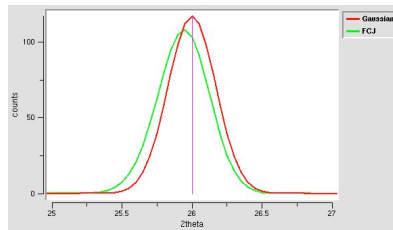


Depend on slit & sample “heights” wrt diffr. radius
H/L & S/L - parameters in function
(typically 0.005 - 0.020)

F-C-J: Example

- The Finger-Cox-Jephcoat correctly models the effective shift of the peak due to axial divergence.

Note: the "competition," the split Pearson VII (empirical), does not model this effect at all!



Other instrumental effects

Sample Displacement & Transparency

In **Bragg-Brentano geometry**, samples are ideally placed exactly at rotation axis and all diffraction occurs from sample surface (highly absorbing sample). Neither is commonly true.

- Peak centers are shifted by
 - Sample Displacement (SHFT), S_s
 - Sample transparency (TRNS), T_s
- $$\Delta T' = \Delta T + S_s \cos \Theta + T_s \sin 2\Theta$$
- $$\text{displacement} = \frac{-\pi R S_s}{36000} \quad \mu_{\text{eff}} = \frac{-9000}{\pi R T_s}$$
- R is diffractometer radius*

These corrections correlate very highly with the zero correction for 2θ , ZERO. **Do not refine this too.**

Parallel-Beam instruments (neutron or synchrotron) are very tolerant of displacement and transparency. Never refine SHFT or TRNS, but do refine ZERO (correction to 2θ).

GSAS Controls

Least Squares Controls

Title	There is an overall title & one for each phase
# of cycles	0 to compute pattern with no refinement, N.B. Le Bail extraction is performed even with 0 cycles
Print options	<i>I recommend always using</i> "summary of shifts"
Convergence Criterion	GSAS considers the refinement to be converged when $\sum(\text{shift}/\sigma)^2$ is less than this. Increase with large numbers of parameters.
Marquardt Damping	Values >1 (1.2 recommended?) decrease the sensitivity of the refinement to correlation, but slows convergence.

Intensity Extraction Controls

These settings determine if and how reflection intensities will be estimated.

Extract Fobs*	Compute F_{obs} values. Needed for Le Bail extraction & Fourier computation (<i>I recommend: always on</i>)
Extraction Method	Normal extraction + two LeBail options: F(calc) → Start LeBail using $F_{\text{obs}} = F_{\text{calc}}$ from structure or Equal Weighted → start LeBail with $F_{\text{calc}} = 1$

* note there is a Extract Fobs flag for each histogram and a extraction methods set for each phase in each histogram

Damping Controls

Damping is available throughout GSAS to decrease the changes made to parameters.

- More damping:
 - smaller changes,
 - more least-squares cycles required for convergence,
 - but divergence is less likely.
- Damping values:
 - 0: apply full shift
 - 1: apply 90% of shift...
 - 9: apply 10% of shift

Setting up GSAS Models

What parameters should be used?

Phase (structural) Parameters

Unit cell & atom parameters

- GSAS allows up to 9 phases
- Occupancy of 1 => fully occupied site, even for special positions (unlike SHELX)
- GENLES constrains cell, atom coordinates, anisotropic displacement parameters according to space group
 - N.B. EXPGUI does not enforce symmetry in site/cell edits

Histogram Parameters

(one set for each histogram)

- Phase flags
 - select which phases are present
 - run POWPREF after changing
 - Background
 - I recommend use of type 1 (Chebyshev polynomial) with as many terms as needed
- CW Diffractometer constants
(note data type & defaults determined by instrument parameter file)
- Wave -- refine if cell is fixed or if multiple histograms of different types are used
- POLA -- don't refine
- Zero -- **refine** for neutron & synchrotron, **never** for flat-plate Bragg-Brentano

Scale Factor

- There is a scale factor for each histogram
- There is a phase fraction for every phase in every histogram.
 - Phase fraction multiplies scale factor
 - Phase fraction $\times Z \times$ Molecular Weight (asym unit) \propto weight fraction of phase (GSAS computes this in .LST file)

Redundant parameters: Don't refine scale and all phase fractions together

Profile functions and profile parameter definitions

CW Profile functions summarized

- #1: Gaussian only (rare except for BT-1 @ NIST)
- #2: Pseudo-Voigt "standard"
- #3: same as #2, but with Finger-Cox-Jephcoat asymmetry. Much slower than #2, but needed with low angle data
- #4: same as #3, but also has Stephens anisotropic strain broadening parameters

CW Profile terms

GU, GV, GW	Gaussian widths as polynomial in $\tan\theta$; referred to as Cagliotti terms (U,V,W)
GP	Gaussian crystallite size (Scherrer) broadening, if GP is refined, fix GU, GV, GW to instrumental values. I recommend leaving GP=0, but refine GU, GV & GW
LX	Lorentzian crystallite size (Scherrer) broadening
LY	Lorentzian strain broadening

- Use care when initially refining terms, correlation is usually high
- GSAS constrains GU, GV, GW, LX & LY > 0 & GV < 0; Bad things happen, if terms will refine out of bounds.

Start with "reasonable" GU, GV, GW, then refine them together. I then fix them & try LX & LY one at a time & retain if >> 0.

See FitWidths in CMPR for a way to find starting UVW values

CW Profile terms (cont.)

GSAS offers two ways to treat low-angle asymmetry

- poor: **asym** (profile functions #1 & #2)
 - works only if small or no low-angle data
 - excellent: Finger-Cox-Jephcoat (profile #3 & #4)
 - two terms: **S/L** & **H/L**
 - *refine with care, if at all (I never do)*
 - *never refine both together*
 - S = sample height
 - H = detector height,
 - L = diffractometer diameter
- (N.B. FCJ use radius & half-heights, equivalent, but messy)*

CW Profile terms (cont.)

Peak cutoff -- where to stop computing peak tails (smaller \Rightarrow GENLES slower)

- set to match experimental signal-to-noise

For use in Flat-plate Bragg-Brentano only:

- shft** -- sample displacement
- trns** -- sample transparency
- prone to correlation. N.B fix histogram **zero**=0 if these are used.

Other CW Profile terms (cont.)

I seldom, if ever, use these:

- stec** – anisotropic strain broadening (profile type 4 does this better)
- ptec** – anisotropic crystallite size broadening
- sfec** – sublattice anisotropic broadening (typically due to stacking faults)
- L11...** – don't use (use type 4 profile instead)

Before using any of these terms, spend a while reading the GSAS Manual (pages 158-167) and make sure you understand how these terms are implemented and the physics behind them (none in the case of L_{xx}).

Profile: Asymmetric Broadening

- # 4 profile function
 - The number of **Sxxx** terms dictated by unit cell symmetry
 - **Eta**: 0 to 1
 - 0 Gaussian; 1 Lorentzian

If you suspect asymmetric broadening, test:

- Change to function #4, fix all other profile terms, refine the **Sxxx** terms and see if they refine away from 1.
- If the fit improves significantly, then refine **Eta**, then relax original terms, a few (or one) at a time.

Preferred Orientation Corrections

Preferred Orientation: March-Dollase

concept:

- define one (or more) *hkl* vectors that are over- or under-represented relative to random distribution
- abundance ratio for that direction
- if 2+ directions, relative amounts for each
- orientation flag (not implemented in EXPGUI)

Note: there is a M-D parameter set for each phase and each histogram

Preferred Orientation: ODF

- Orientational Distribution Function (ODF) aka Spherical Harmonics
- concept: define a shape that defines the relative amounts of crystallites in each direction
 - shape constrained by material (space group) and by specimen symmetry
 - Set of terms per phase (not histogram)
 - easy to use
- Use Cylindrical symmetry, increase order slowly

Reducing Model Complexity

“Hard” Constraints

- Constraints reduce the # of parameters
- Two common uses:
 - where data provide no information
 - model must be simplified to match data
- EXPGUI implement profile & atom parameter constraints
 - (many more constraint types in EXPEDT)
- Note: constraints fix shifts not values
 - Exception: rigid bodies

Hard Constraint Limitation

- A parameter cannot appear in more than one constraint equation
 - Problem: A_2B_3 structure where A is divided between three sites: 1, 2 & 3
- Starting model $Occ_1 = Occ_2 = Occ_3 = 1/3$
 - define two constraints: $\delta_1 = -\delta_2$ & $\delta_1 = -\delta_3$

Does not work! (N.B. no error message in EXPEDT)

Trick solution: define two atoms that share a site, 1A & 1B: Occ_{1A} & Occ_{1B}

- $Occ_{1A} + Occ_{1B} = Occ_2 = Occ_3 = 1/3$
- and the define two constraints:
 - $\delta_{1A} = -\delta_2$
 - $\delta_{1B} = -\delta_3$

This Works!

"Soft" Constraints

- Build a priori knowledge into refinement
- Weighted "cost" function added to total χ^2
 - bond distances & angles
 - unit cell contents
 - misc. geometrical (mostly for macromolecular)
- Can be used to guide a balky refinement
 - relax weight at end to 0 (if possible)
- Not always possible to remove S-C weight
 - be sure to separate derived vs. "driven" results in your paper!

Rigid Body Refinement

- **Rigid Body:** group of atoms have a fixed geometry relative to each other
 - position in cell & orientation can be refined
 - 1 or more "size" parameters can be refined
 - must be defined in EXPEDT (not EXPGUI)
- Two steps in rigid body setup:
 1. Rigid bodies are defined in cartesian coordinates
 2. They are then added into the model (up to 9 times):
 - *Designate the first atom in the group*
 - *Define the location of the origin in fractional coordinates*
 - *Specify the orientation of the body by setting axes & rotations*
- Guides to setting up rigid bodies:
 - http://www.uni-bayreuth.de/departments/crystal/rietveld/rigid_bodies.pdf
 - http://www.ccp14.ac.uk/ccp/web-mirrors/ian-swainson/fireside_fuide_to_rigid_bodies.pdf

Refinement Recipes (Tricks of the trade)

Getting GSAS to give good fits

What to Refine and When?

If all parameters in a refinement were close to the true minima and correlation is minimal, then it would fine to start by optimizing all everything.

Who is that lucky?

In practice parameters must be relaxed slowly, with the order dictated by which parameters are farthest from the correct values

Basic strategy

Need reasonable values for unit cell, scale factor, background and profile before refining structural parameters, locating missing atoms...

- Le Bail fit provides cell, background and profile
- Having reasonable profile terms for instrumental resolution can save you from heartache
 - With this, you only need to fit sample broadening
 - This is a good justification for refining standards

Refinement Recipe (part 1)

No single strategy works in all cases

- Fit unit cell with small # of background terms
 - Think:* Are reflections in ~ the correct places?
- Fit 2theta zero (neutron/synchrotron)
 - Think:* Are all peaks indexed?
 - If not: check cell & rethink space group
 - impurity phases?

Refinement Recipe (part 2)

- Is peak shape in the right ballpark?
 - If possible, postpone profile refinement to later stages
 - If profile is way off due to sample broadening, (you do have reasonable instrumental terms!) refine only sample terms
- Fit atom coordinates
 - release "big" atoms first
 - $big = high\ multiplicity * b\ or\ *f(Q)$

Refinement Recipe (part 3)

- Refine displacement parameters (U_{iso})
 - for complex structures, group U_{iso} terms
 - Think:* Is the structure reasonable in terms of distances & angles?
 - missing atoms? Examine Fourier map
 - Refine occupancies? (x-rays: beware!)
- When fit is pretty good, refine profile terms (damping is often needed).
 - To begin, vary sample-dependent terms like GP, LX and/or LY one at a time.
 - Many terms are "clamped" >0 . Turn off terms that try to refine "out of bounds"

Refinement Recipe (part 4)

Think: Are all lines indexed & reasonably fit?

If not, are some peaks wider than others?

- Consider anisotropic broadening

Are groups of reflections all computing high or low?

- Consider preferred orientation

Think: Is refinement stable and are values chemically plausible?

Wrong space group?

Too few reflections?

- Get better (or more) data, add hard/soft constraints

Refinement Recipe (part 5): Finish up

- Refine background, if fixed from LeBail. Add more background terms, if needed.
- Ungroup U_{iso} 's if data allow.
- Attempt anisotropic refinement of "big" atoms, when data quality permits.

Refinement Recipe (part 6)

Common problem: At high Q, peaks run together so that background cannot be determined.

- Choice of Background determines average U_{iso} . Refining Background and U_{iso} together results in good fits but unreasonable average U_{iso} (<0.001 or >0.025 Å²) values.

Solution: Need to fix the average U_{iso} .

- set all U_{iso} = to something reasonable (say 0.01 to 0.03)
- refine background
- fix background, & refine U_{iso} 's
- Document in your paper that background and displacement parameters had too much correlation for independent refinement & say what was done.

Wrap up

Rietveld fits are almost never perfect since materials and instruments are not perfect. There is almost always something more to try.

Complex problems may stretch the limits of what can be learned from the data. Getting better data is always best, but more frequently one must reduce the complexity of the model (restraints and constraints)

GSAS offers many options to address the above – the GSAS manual is a great place to start learning more about the options.