Le Bail Intensity Extraction

Brian H. Toby

Outline

1. What is the Le Bail method?
2. Other approaches
3. Why use the Le Bail method?
4. Parameter fitting with Le Bail intensity extraction
5. Le Bail refinement strategies
6. Avoiding problems with background fitting: BKGEDIT

Le Bail Background Info: Reflection Intensity Estimation

- Rietveld fit *computes* F_{hkl} from structure model
- We want *observed* F_{hkl} for Fourier maps, etc.
  (can't get it -- life is not fair)

Best we can do: use *computed* F_{hkl} to guess how to apportion intensity between overlapped reflections

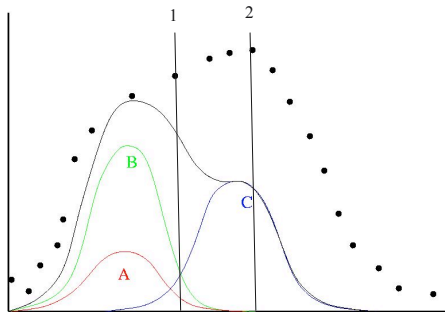Hugo Rietveld's intensity extraction algorithm

- For every point in pattern, we know what % of *computed* intensity comes from each reflection.
- Take that % of *observed* intensity and sum to estimate reflection intensity
  - Accurate without overlap
  - With overlap, only as good as the model is.

Hugo Rietveld's other breakthrough: F_{obs} estimation

- Based on intensities from the model, estimates for F_{hkl} can be made, even when reflections are completely overlapped:

Location 1:
20% to A
40% to B
40% to C

Location 2:
100% to C

Le Bail Intensity Extraction

Armel Le Bail's idea: can the Rietveld extraction method be used to estimate reflection intensities even without a structural model?

- • *Answer: Yes!*
- How: modify Rietveld code to set all F_{hkl}(calc) = 1
  - – Use Rietveld algorithm to extract F_{hkl}(obs)
  - – set F_{hkl}(calc) from extracted F_{hkl}(obs)
  - ↻ Iterate: repeat F_{hkl}(obs) extraction with better now F_{hkl}(calc) values
  - – Unit cell, bkg, peak shape,… can be refined
  - – "Easy" to implement
- Ultimate result of Le Bail fit:
  - – optimal peak intensities (for all indexed peaks)
  - – Completely overlapped reflections: intensity apportioned according to reflection multiplicity (equal F values)
  - – Partially overlapped reflections: intensity will be pushed away from equal F_{hkl} values only as much as needed

A. Le Bail, H. Duroy, and J.L. Fourquet, "Ab Initio Structure Determination of LiSbWO₆ by X-ray Powder Diffraction". Materials Research Bulletin 23(3): p. 447-52 (1988).

The Von Dreele approach to the Le Bail Fit

- Von Dreele's modification of the Le Bail approach:
  - – Start using F_{hkl}(calc) from a starting model -- not 1

- Model should have non-zero F_{hkl} for all reflections

- Also gives optimal intensity fit, however now intensity apportionment is prejudiced toward the starting model
  - – e.g.: completely overlapped reflections have intensity ratios that match the starting model

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GSAS/EXPGUI implementation

Note that each phase/histogram has its own extraction setting

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What does LeBail fitting do?

Le Bail technique is effectively a steepest descent minimization
- – Converges slowly
- – Yields best possible intensity values, equivalent to ideal (∞ parameters) structural model

GSAS implements two Le Bail approaches:

Le Bail (equiweighted) method:
- – For overlapped reflections, intensity is apportioned by reflection multiplicity

Von Dreele (model weighted) approach
- – Overlapped reflections: intensity apportioned by model

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Alternative Approaches for Intensity Fitting

- Fit peaks individually or in small groups
  - Loss of unit cell constraints on reflection positions

- Pawley technique (ALLHKL)
  - Fit full pattern where reflection positions are generated by unit cell, reflection intensities are fit by least-squares.
  - Popularized by Toroya
  - Errors can be propagated correctly (see works by E. Prince or W.I.F. David, et al.)

Why use the Le Bail method?

- Get good experimental parameters (bkg, cell, profile) before fitting structure

- Estimate best possible fit when profiles are irregular, etc.

- Fit an additional phase where structure is not known or where texture is a problem (this phase must be indexed)

- Get reflection intensities for *ab initio* structure solution (see EXPO program)

Parameter fitting with Le Bail Intensity Extraction

- One can combine Le Bail intensity extraction along with refinement of non-structural parameters
  - Least-squares on parameters & steepest descents on intensities
  - If intensities and parameters are changing significantly, refinement is prone to "blow up"
    - *Best to converge intensity extraction before refining parameters*

- Refinement of parameters coupled with Le Bail extraction can provide best possible profile R-factor.

Le Bail Refinement Strategy

Important GSAS trick:

- ***Intensities are extracted & optimized even with 0 refinement cycles***

  - It is best to "converge" intensities by running GENLES many times with 0 cycles, before refining anything.
  - When parameters shift that will have large impact on reflection intensities, GSAS tends to diverge
    - *Use Damping!*

- ***Intensities are reset to Model (or 1) when POWPREF is run***

  - Best to rerun GENLES several times with number of cycles set to zero after running POWPREF

Le Bail Refinement Recipe

1. Run GENLES with 0 cycles x3-5 times
   - get R-factor close to minimum.
2. Fit background with 4-8 Chebyshev terms (#1)
3. Fit lattice constants *(damp if shifts will be large!)*
4. Fit zero *(damp if shifts will be large!)*
   - *Think:* Are all lines indexed?
5. Profile *(damp!)*
   - *Think:* Is the fit good. Why not?
6. More background terms?

Le Bail with complex background shapes

When many peaks lay grouped together, the choice of where to draw the background becomes ambiguous.

- Refining background with Le Bail in these cases is problematic
  - Bad Solution: Use fixed background points

  - Good Solution:
    - *Use BKGEDIT to fit a Chebyschev polynomial to fixed points*
    - *Fit background once a good Le Bail or structural model is obtained*

BKGEDIT

- Input enough points to describe where the background should be drawn
- Increase number of terms a few at a time until a reasonable fit is obtained
- Add/move points where needed to better define desired shape
- Fix background & don't refine
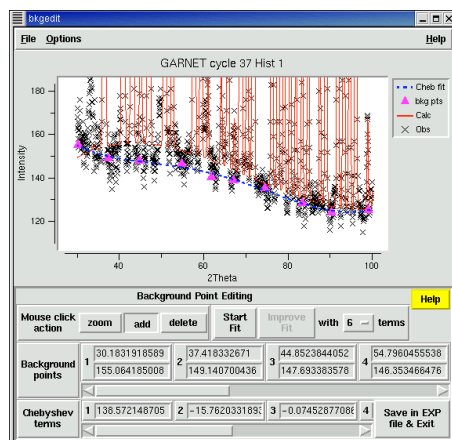
Conclusions

- Understand how the Le Bail algorithm works
- Le Bail fitting is useful for getting started, solving structures, and treating impurities
- For GSAS:
  - Note two different extraction implementations
  - Understand the effect of POWPREF and GENLES with 0 cycles
  - Use BKGEDIT when backgrounds cause a problem