Parametric Rietveld Refinement

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Outline

- What is parametric Rietveld refinement?
  - Should you do it?
  - How do you do it?
  - What can you parameterise?

- Examples
  - Cell parameter parameterisation
  - Subtle structural phase transitions
  - Background & amorphous content
  - Poor/low quality data

- Accuracy in Powder Diffraction
  - Accuracy – getting the answer right
  - Precision – better precision by more appropriate data analysis


X+N refinements

Jean Francois Berar, XND
Diffraction = f(x)

\[ I \propto F_{hk}^2; F_{hk} = \sum_{j=1}^{N} f_j \exp \left[ 2\pi i (h x_j + k y_j + l z_j) \right] \]

\[ 8\pi^2 U_j s \propto \frac{\theta}{\lambda^2} \]

\[ I_{hkl} = f(xyz, occ, adp) \]
$I_{hkl} = f(\text{xyz}(t = 2), \text{occ}(t = 2), \text{adp}(t = 2))$

$time$

$I_{hkl} = f(\text{xyz}(t = 1), \text{occ}(t = 1), \text{adp}(t = 1))$
Diffraction = f(x)

\[ I_{hkl} = f(xyz, occ, adp) \]

- \( adp = f(t) \)
- \( occ = f(t) \)
- \( xyz = f(t) \)

(time)

(2-theta)
Parametric Rietveld Refinement

Observed
Calculated

Difference

Temp
Parametric Rietveld Refinement


Activation Energies

rate constants
\[ k = 3.7(2) \times 10^{-5} \text{ s}^{-1} \]
Things you Might Parameterise….

\[ a(T) = \exp\left(\ln(a_0) + \frac{c_1 \theta_1}{\exp(\theta_1/T) - 1}\right) \]

\[ x(T) = x_0 \left(1 + c_1 T + c_2 T^2 + c_3 T^3\right) \]

\[ \Delta T = c_0 + c_1 T_{\text{set}} + c_2 T_{\text{set}}^2 \]

\[ \text{height}(T) = h_0 \left(1 + c_1 T + c_2 T^2\right) \]

\[ \text{frac}(t) = c_1 \left[1 - \exp(-k_{\text{frac}} t)\right] + c_2 \]

\[ \text{cell}(t) = c_2 \left[1 - \exp(-k_{\text{cell}} t)\right] + c_3 \]
Parametric/Surface vs Sequential

- Parametric fitting is a specialist beast

- Sequential fitting generally much easier, easily automated, fewer assumptions
EPDIC 2012 Software Discussion

• Misquotes from “Profs F/G” EPDIC 2012:
  1. I don’t think we should be doing that.
  2. Why not just take all refined variables and variance-covariance matrices and analyse externally?
  3. What happens if you don’t choose the proper functional form?

• Misquotes in return:
  1. I agree with you 90% of the time.
  2. What piece of software do we have to do that (ANO); what if you’re in completely the wrong minimum.
  3. You learn a lot about your system.
  4. It’s really powerful when the wrong answer gives a better fit than the right answer
Unit Cell Parameterisation

- Refine independently?
- Refine parametrically?

\[ a(T) = \exp \left( \ln(a_0) + \frac{c_1 \theta_1}{\exp(\frac{\theta_1}{T}) - 1} + \frac{c_2 \theta_2}{\exp(\frac{\theta_2}{T}) - 1} + \ldots \right) \]
ZrW$_2$O$_8$ Phonons – Don’t Parameterise

260 relatively quick diffraction patterns

Cell Parameter at 260 temperatures

Complex physics

Bill David
WO_3 Phase Transitions – Do Parameterise

\[ Pm\bar{3}m \xrightarrow{??K} P4 / nmm \xrightarrow{1173K} P4 / ncc \xrightarrow{1073K} P_{21} / c \]

\[ 993K \xrightarrow{} Pbcn \xrightarrow{623K} P_{21} / n \xrightarrow{\sim 230K} P\bar{1} \xrightarrow{\sim 190K} Pc \]
Laboratory VT Data

90 K

T = 300 K

Counts

2θ Degrees

300 K

$P_c \xrightarrow{\sim 170 K} P\bar{1} \xrightarrow{\sim 190 K} P2_1 / n$
VT Lab Diffraction Data

90 K

300 K

\[ \text{Pc} \quad \sim 170 K \quad \rightarrow \quad \text{P1} \quad \sim 190 K \quad \rightarrow \quad \text{P2}_1 / n \]
Peak Overlap/Structural Distortions

90 K

P2$_1$/n (002)/(020)/(200) reflections

300 K
Sequential Phase Fractions

\[ P_c \overset{\sim 170 K}{\rightarrow} P \overset{\sim 190 K}{\rightarrow} P_{21} / n \]
Sequential Cell Volumes

90 K

300 K

$Pc \xrightarrow{\sim 170 K} P\bar{1} \xrightarrow{\sim 190 K} P2_1 / n$
Parametric Assumptions

- Individual phases show smooth variations in $a/b/c$ and $\alpha/\beta/\gamma$ with temperature
- Temperature factors vary smoothly with temperature
- Peak shape for each phase derived from all data
- Einstein/polynomial type expressions

- 1102 parameters not 8100
Overall Refinable Parameters:

- $a_0 = 5.42999$
- $c_1 = 4.86977 \times 10^{-6}$
- $\theta_1 = 570.1$

Refinement info for Temperature = 300 K

$$ T = 300 $$

$$ a(T) = \exp \left( \ln(a_0) + \frac{c_1 \theta_1^*}{\exp(\theta_1/T)} + ... \right) $$

Refinement info for Temperature = 350 K

$$ T = 350 $$

$$ a(T) = \exp \left( \ln(a_0) + \frac{c_1 \theta_1^*}{\exp(\theta_1/T)} + ... \right) $$
Surface Fitting – Smooth ADPs

Overall Refinable Parameters:

\[
\begin{align*}
    a_0 & = 5.42999 \\
    c_1 & = 4.86977 \times 10^{-6} \\
    \theta_1 & = 570.1 \\
    b_0 & = 0.113 \\
    c_2 & = 2.33 \times 10^{-3} \\
    \theta_2 & = 500
\end{align*}
\]

Refinement info for Temperature = 300 K

\[
T = 300
\]

\[
a(T) = \text{Exp}\left( \ln(a_0) + \frac{c_1 \theta_1^*}{\exp(\theta_1^* T)} - 1 \right) + \ldots
\]

\[
b(T) = b_0 + \frac{c_2 \theta_2^*}{\exp(\theta_2^* T)} - 1
\]

Refinement info for Temperature = 350 K

\[
T = 350
\]

\[
a(T) = \text{Exp}\left( \ln(a_0) + \frac{c_1 \theta_1^*}{\exp(\theta_1^* T)} - 1 \right) + \ldots
\]

\[
b(T) = b_0 + \frac{c_2 \theta_2^*}{\exp(\theta_2^* T)} - 1
\]
.inp file format/implementation

- Topas input file

```plaintext
`a bit of the input file
prm zero_ma 7.2900
prm theta_ma 150
prm grad_ma 1.02e-5

str
    phase_name p21n_t0001
#endif param_cell
    prm mlpa_t_0001 = zero_ma + (grad_ma/(Exp(theta_ma/t_0001)-1));:7.30037
    a =mlpa_t_0001;:7.30037`
    ....
#else
    a mlpa_t_0001 7.30735 mlpaminmax
    ....
#endif
```
Sequential Phase Fractions

Phase Fraction

Temperature (K)

$P_c \xrightarrow{\sim 170 K} P1 \xrightarrow{\sim 190 K} P2_1 / n$
Parametric Phase Fractions

$P_c \xrightarrow{\sim 170K} P\bar{1} \xrightarrow{\sim 190K} P2_1/n$
Parametric Cell Volumes

90 K

300 K

$P_c \xrightarrow{\sim 170 K} P \overline{1} \xrightarrow{\sim 190 K} P2_1 / n$
Parametric R-factors

$P_c \xrightarrow{\sim 170 K} P1 \xrightarrow{\sim 190 K} P2_1 / n$
“Best Possible” Independent Fitting?

- Start all refinements at “perfect” cell parameters from parametric fit
- Minimum number of parameters (identical peak shapes etc)
- Perform limited simulated annealing at each T
- “Wrong” answer can have lower R-factor
Wrong Model?

- Different sample
- Equivalent X-ray experiment

![Graph showing phase fraction vs. temperature](image)

- $P_c \xrightarrow{\sim 170\text{K}} P\bar{1} \xrightarrow{\sim 190\text{K}} P2_1/\mathbf{n}$
Cell volumes and R-factor

- Cell volumes with temperature very suspicious
- R-factors very suspicious
- Unusual trends suggest something wrong
Raw data – additional peaks

- Extra low temperature phase
- Without surface fitting these peaks get “mopped up” by P-1 phase
- Phase transitions very dependent on thermal history
Quantitative Analysis – Advantages

- Impose “physically sensible model” on well understood quantities
- Prevent “wrong solutions” fitting data
- Prevent peaks becoming infinitely broad and correlating with background
- Unbiased way to refine data?
Example 2 – Proton Migration

- Subtle structural change in the organic solid state
- 3,5 pyridine dicarboxylic acid (3,5 PDCA)
3,5-PDCA

- 3,5 pyridine dicarboxylic acid
- Unusual difference between cell volumes of H and D isotopologues
Single Crystal neutron diffraction

285 K

15 K

O · · · D – N

O – D · · · N
35-PDCA - Questions

- Smooth effect or sharp phase transition?
- 1\textsuperscript{st} or 2\textsuperscript{nd} order?
- Isosymmetric phase transition
HRPD Observed Powder Data

285 K

15 K
Parametric fitting

- 2 phase Rietveld refinement
- Assume each phase has a smooth evolution of cell parameters away from $T_c$
- Allow a critical excess cell close to $T_c$

$$a(T) = \exp\left[\ln\left(a_0\right) + \frac{c_1 \theta_i}{\exp\left(\theta_i/T\right) - 1}\right] + c_2 \exp\left(-c_3 |T - T_c|^\beta\right)$$
Surface Rietveld

285 K

observed
calculated

15 K
Results - 1

Phase Fractions

Phase Percentage

Temperature /K

285 K

% N–D

% O–D

Cell Volumes

Vol N–D

Vol O–D

655

660

665

670

675

680

685

690

0 50 100 150 200 250 300

Temperature /K

0 50 100 150 200 250 300

vol ND

vol OD

average

(c)

N–D

O–D

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Results - 2

Unit cell param a

Size broadening

(a) Unit cell param a

(b) Size broadening
3,5-PDCA Summary

- 3,5 pyridine carboxylic acid
- Unusual proton migration
- Unusual isotopologue polymorphism

285 K

15 K
Example 3 – in situ synthesis

- Lab data following in situ synthesis
- Short 2-theta range
- Relatively quick data collections
- Several hundred data sets on each of 10 compositions
- Need to quantify several crystalline phases
- Need to quantify amorphous content
Quantify Amorphous Background?

- Separate instrumental and amorphous (sample + diffuse) contributions to background?
Parametric Fitting

observed

calculated
Parametric Fitting

Overall + Individually refined background
Temperature Calibration/Internal Standards

$\Delta T$ fit all data sets
$\Delta T$ individual data sets

X-ray $T_c < 567$ K
DSC $T_c = 565$ K
Individual Fitting
4.75 minutes

Surface Fitting
871*4.75 minutes
(~3 days)
Parameterising sample height offset improves precision
Average esd 0.00028 to 0.00017 Å
When/What Should you Parameterise?

• When should you parameterise?
  • Rarely……5-10% of systems?
  • When you have poor data
  • When you have significant correlations
  • When you know the wrong answer
  • When you want to quickly test a model against 1000s of data sets
  • When you want to test if you’re assumption is right/wrong

• What should you parameterise?
  • Information you’re not particularly interested in
  • Information for which you’re sure of model to apply
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Thank you!