LeBail Fitting - Application To Mantid.

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Chapter 1

Le Bail Fit in Mantid

1.1 Introduction

Le Bail method (fitting) is a profile fitting technique without structural model for powder diffraction data. The method uses a two-step cyclic process. The following parameters are fitted by a standard least-squares methods:

- Unit-cell metric tensor parameters;
- Instrumental zero error and other instrumental parameters including length of neutron flight path and etc.
- Peak width and peak shape parameters;

The intensities of the individual peaks are no longer treated as least-squares parameters and are never refined. Initially, all of the peak intensities are set to an arbitrary value, e.g. 1000.0. These are treated as "calculated" values as if they had been derived from a structural model. The observed values can be used instead of a structural model for the least-squares fitting of the diffraction profile. This leads to an improvement in (a) cell parameters and, consequently, peak positions, (b) resolution function parameters, i.e. peaks widths, and (c) peak shape parameters. The process is now iterated and a fresh set of observed intensities are obtained.

1.2 Implementaion in Mantid

A layered structure is proposed to implement Le Bail fit in Mantid. From the bottom to top, here are the functions in *CurveFitting*.

1. Peak function (inheriting IPeakFunction). It will calculate a single peak by given peak parameters. The peak parameters of this function will not be fitted, because any peak profile is not independent, but a function of some common parameters among all peaks and d-spacing value of this peak.

   For POWGEN, it is a thermal neutron back-to-back exponential psuedo-Voigt peak profile function.

2. 2 Component functions which are in parallel.

3. LeBailFunction (inheriting ILeBailFunction). It will calculate peak profile parameters and intensity for each peak from (1) fittable parameters including lattice constants, instrument zero and geometry parameters, and some common peak profile parameters for all peaks, and (2) non-fittable parameters including a list of peaks' miller indices and unit cell space group.

   For POWGEN, it will be a function named *ThermalNeutronLeBailFunction*.

4. Background function (BackgroundFunction). It will calcualte the background from given background parameters. User will determine which background function to use.

5. LeBailCompositeFunction. This is a *CompositeFunction* containing two and only two functions, i.e., (1) ILeBailFunction and (2) BackgroundFunction.

   LeBailCompositeFunction's *function()* will be overloaded such that

   (a) Calcualte background function;

   (b) Subtract calculated background from observed diffraction data;

   (c) Calculate peaks intensities from the outcome of above step;

   (d) Calculate LeBail function;

   (e) Sum over LeBail function and background function.

6. LeBailFit. This is a wrapping algorithm to set up, execute and process the result of the fit of LeBailCompositeFunction. User will interface Le Bail fit through this algorithm.

Chapter 2

Neutron Peak Profile

2.1 Thermal Neutron Back-to-back Exponential Pseudo-Voigt Peak Profile

Nuetron TOF peak profile is a convolution of a pseudo-Voigt function $pV(t)$ and a pair of back-to-back exponentials $E(t)$.

$$\Omega(x) = \int_{-\infty}^{+\infty} pV(x-t)E(t)dt \tag{2.1}$$

2.1.1 Back-to-back exponentials

$$\begin{aligned} E(d,t) &= 2Ne^{\alpha(d)t}(t \leq 0) & (2.2)\\ &= 2Ne^{-\beta(d)t}(t \geq 0) & (2.3)\\ N(d) &= \frac{\alpha(d)\beta(d)}{2(\alpha(d)+\beta(d))} & (2.4) \end{aligned}$$

where d is the d-spacing (total time of flight)

2.1.2 Pseudo-Voigt Basic

$$pV(x) = \eta L'(x) + (1-\eta)G'(x) \tag{2.5}$$

where

1. $0 \leq \eta \leq 1$;

2. $L'(x)$ is a Lorentzian;

3. $G'(x)$ is a Gaussian;

FWHM H and η can be calculated by numerical approximation:

$$\begin{aligned} H &= H_G^5 + 2.69269H_G^4H_L + 2.42843H_G^3H_L^2 + 4.47163H_G^2H_L^3 + \quad (2.6)\\ &\quad 0.07842H_GH_L^4 + H_L^5 \quad (2.7)\\ \eta &= 1.36603\frac{H_L}{H}0.47719(\frac{H_L}{H})^2 + 0.11116(fracH_LH)^3 \quad (2.8) \end{aligned}$$

2.1.3 Neutron TOF Peak Parameters: Geometry and Back-to-back Exponentials

$$T_h = Z_0 + D_1d_h + D_2d_h^2 \quad (2.9)$$

$$\begin{aligned} \alpha(d) &= \alpha_0 + \frac{\alpha_1}{d_h} \quad (2.10)\\ \beta(d) &= \beta_0 + \frac{\beta_1}{d_h^4} \quad (2.11) \end{aligned}$$

2.1.4 Thermo Neutron TOF Peak Parameters: Geometry and Back-to-back Exponentials

Be noticed that

- superscript **e stands for epithermal neutron;**
- **superscript t stands for thermal nuetorn**

For geometry parameter:

$$\begin{aligned} T_h^e &= Z_0^e + D_1^ed_h \quad (2.12)\\ T_h^t &= Z_0^t + D_1^td_h - \frac{D_2}{d_h} \quad (2.13)\\ n(d) &= \frac{1}{2}erfc\{w_{cross}(T_{cross} - \frac{1}{d_h})\} \quad (2.14)\\ T_h &= nT_h^2 + (1-n)T_h^t \quad (2.15) \end{aligned}$$

where

- w_{cross} is the width of the crossover between thermal and epithermal components;
- T_{cross} is the position of the crossover between thermal and epithermal components;

For back-to-back rising exponential

$$\begin{aligned} \alpha^e(d) &= \alpha_0^e + \alpha_1^e d_h & (2.16)\\ \alpha^t(d) &= \alpha_0^t - \frac{\alpha_1^t}{d_h} & (2.17)\\ \alpha(d) &= \frac{1}{n\alpha^e + (1-n)\alpha^t} & (2.18) \end{aligned}$$

For back-to-back decay exponential

$$\begin{aligned} \beta^e(d) &= \beta_0^e + \beta_1^e d_h & (2.19)\\ \beta^t(d) &= \beta_0^t - \frac{\beta_1^t}{d_h} & (2.20)\\ \beta(d) &= \frac{1}{n\alpha^e + (1-n)\beta^t} & (2.21) \end{aligned}$$

2.1.5 d-dependence Peak Profile Parameters

In this subsection, the formula is applied to both epithermal and thermal neutron peak profile.

For pseudo-Voigt

$$\begin{aligned} \sigma_G^2(d_h) &= \sigma_0^2 + (\sigma_1^2 + DST2(1-\zeta)^2)d_h^2 + (\sigma_2^2 + Gsize)d_h^4 = \frac{H_G^2}{8\ln 2} & (2.22)\\ \gamma_L(d_h) &= \gamma_0 + (\gamma_1 + \zeta\sqrt{8\ln 2 DST2})d_h + (\gamma_2 + F(SZ))d_h^2 = H_L & (2.23) \end{aligned}$$

2.1.6 Analysis Solution of Convolution

The peak profile can be obtained by analysis solution from the formula.

$$\Omega(TOF(d_h)) = (1-\eta(d_h))N\{e^u erfc(y) + e^v erfc(z)\} - \frac{2N\eta}{\pi}\{\Im[e^p E_1(p)] + \Im[e^q E_1(q)]\} \quad (2.24)$$

where

$$erfc(x) = 1 - erf(x) = 1 - \frac{2}{\sqrt{\pi}}\int_0^x e^{-u^2} du$$

$$
\begin{aligned}
&= \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-u^2} du \\
E_1(z) &= \int_z^\infty \frac{e^{-t}}{t} dt
\end{aligned}
$$

$erfc(x)$ and $E_1(z)$ will be calculated numerically.

And

$$
\begin{aligned}
u &= \frac{1}{2}\alpha(d_h)(\alpha(d_h)\sigma^2(d_h) + 2x) \\
y &= \frac{\alpha(d_h)\sigma^2(d_h) + x}{\sqrt{2\sigma^2(d_h)}} \\
p &= \alpha(d_h)x + \frac{i\alpha(d_h)H(d_h)}{2} \\
v &= \frac{1}{2}\beta(d_h)(\beta(d_h)\sigma^2(d_h) - 2x) \\
z &= \frac{\beta(d_h)\sigma^2(d_h) - x}{\sqrt{2\sigma^2(d_h)}} \\
q &= -\beta(d_h)x + \frac{i\beta(d_h)H(d_h)}{2}
\end{aligned}
$$

where $x = TOF$.

Chapter 3

Implementation in Mantid