Refinement parameters

What are the parameters to be determined?

- atom positional parameters
- atom thermal motion parameters
- atom site occupancy parameters
- background function parameters

**peak shape parameters**

- sample displacement, sample transparency, zero-shift errors
- unit cell dimensions
- preferred orientation, absorption, porosity, extinction parameters
- scale factor(s)
Peak shape parameters

What determines peak shape?

Instrumental

source image
flat specimen
axial divergence
specimen transparency
receiving slit
monochromator(s)
Peak shape parameters

What determines peak shape?

Spectral

inherent spectral width

most prominent effect - $K_{\alpha_1} K_{\alpha_2} K_{\alpha_3} K_{\alpha_4}$ overlap
Peak shape parameters

What determines peak shape?

Specimen

mosaicity

crystallite size

microstrain
Peak shape parameters

Historical

Began with neutron diffraction

- peak shapes nearly Gaussian
Peak shape parameters

1st basic peak parameter - FWHM

Caglioti formula: \[ H = (U \tan^2 \theta + V \tan \theta + W)^{1/2} \]

i.e., FWHM varies with \( \theta \) or \( 2\theta \)
Peak shape parameters

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Peak shape parameters

X-ray case more complicated

not usually Gaussian

not usually Lorentzian

usually need to mix the two somehow
Peak shape parameters

Both functions have been normalized to result in identical definite integrals.
Peak shape parameters

4 most common profile fitting fcns

Gauss:
\[ y(x) = G(x) = \frac{C_G^{1/2}}{\sqrt{\pi H}} \exp\left(-C_G x^2\right) \]

Lorentz:
\[ y(x) = L(x) = \frac{C_L^{1/2}}{\pi H} \left(1 + C_L x^2\right)^{-1} \]

Pseudo-Voigt:
\[ y(x) = PV(x) = \eta \frac{C_G^{1/2}}{\sqrt{\pi H}} \exp\left(-C_G x^2\right) + \left(1 - \eta\right) \frac{C_L^{1/2}}{\pi H} \left(1 + C_L x^2\right)^{-1} \]

Pearson-VII:
\[ y(x) = PVII(x) = \frac{\Gamma(\beta)}{\Gamma(\beta - 1/2) \sqrt{\pi H}} \frac{C_p^{1/2}}{(1 + C_p x^2)^{\beta}} \]
Peak shape parameters

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- \( H \) and \( H' \) are the full widths at half maximum (often abbreviated as FWHM).
- \( x = (2\theta_i - 2\theta_k)/H_k \), is essentially the Bragg angle of the \( i^{th} \) point in the powder diffraction pattern with its origin in the position of the \( k^{th} \) peak divided by the peak’s FWHM.
- \( 2\theta_k \), is the Bragg angle of the \( k^{th} \) point of the powder diffraction pattern;
- \( 2\theta_k \), is the calculated (or ideal) Bragg angle of the \( k^{th} \) Bragg reflection.
Peak shape parameters

4 most common profile fitting fcns

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Pearson-VII:

\[ y(x) = PVII(x) = \frac{C_{p}^{1/2}}{\Gamma(\beta - 1/2) \sqrt{\pi H}} \left(1 + C_{p}x^{2}\right)^{\beta} \]

\[ \Gamma(z) = \int_{0}^{\infty} t^{z-1} e^{t} \, dt \]
Peak shape parameters

4 most common profile fitting fcns

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\[ y(x) = PVII(x) = \frac{\Gamma(\beta)}{\Gamma(\beta - 1/2) \sqrt{\pi H}} C_p^{1/2} \left(1 + C_p x^2\right)^{-\beta} \]

- \( H = \left(U \tan^2 \theta + V \tan \theta + W\right)^{1/2} \), which is known as Caglioti formula, is the full width at half maximum as a function of \( \theta \) for Gauss, pseudo-Voigt and Pearson-VII functions, and \( U, V \) and \( W \) are free variables.
- \( H' = U / \cos \theta + V' \tan \theta \), is the full width at half maximum as a function of \( \theta \) for the Lorentz function, and \( U \) and \( V \) are free variables.
- \( \eta = \eta_0 + \eta_1 \theta + \eta_2 \theta^2 \), where \( 0 \leq \eta \leq 1 \), is the pseudo-Voigt function mixing parameter, i.e. the fractional contribution of the Gauss function into the linear combination of Gauss and Lorentz functions, and \( \eta_0, \eta_1 \) and \( \eta_2 \) are free variables.
Peak shape parameters

But peaks are usually asymmetric - even after $\alpha_2$ stripping!
Peak shape parameters

Finally - use NIST std 660 (LaB$_6$) to determine broadening from instrumental and spectral contributions & kept constant (U, V, W)
Scale factors

Constant factor which scales calculated intensities of all reflections in pattern up to the observed intensities

Determined by least squares refinement
Scale factors

Constant factor which scales calculated intensities of all reflections in pattern up to the observed intensities

Determined by least squares refinement

In GSAS, two types of scale factors:

- histogram scale factor
- phase scale factor

\[ I_c = I_b + I_d + S_h \sum_p S_{ph} Y_{ph} \]
Scale factors

Constant factor which scales calculated intensities of all reflections in pattern up to the observed intensities

Determined by least squares refinement

In GSAS, two types of scale factors:

- histogram scale factor
- phase scale factor

\[ I_c = I_b + I_d + S_h \sum_p S_{ph} Y_{ph} \]

At any point in pattern, calc'd I is then obtained as above – then compared with obs'd I
Scale factor

When more than one phase, $S_{ph}$ calculated for each

w/o of each phase present automatically calc'd:

$$W_p = \frac{S_{ph} m_p}{N_p} \sum_{p=1}^{N_p} S_{ph} m_p$$

$$I_c = I_b + I_d + S_h \sum_p S_{ph} Y_{ph}$$
Lattice parameters

In general

\[ \frac{1}{d^2} = \frac{1}{V^2} (S_{11} h^2 + S_{22} k^2 + S_{33} l^2 + 2S_{12} hk + 2S_{13} hl + 2S_{23} kl) \]

\[ S_{11} = b^2 c^2 \sin^2 \alpha \]
\[ S_{22} = a^2 c^2 \sin^2 \beta \]
\[ S_{33} = a^2 b^2 \sin^2 \gamma \]
\[ S_{12} = abc^2 (\cos \alpha \cos \beta - \cos \gamma) \]
\[ S_{13} = ab^2 c (\cos \gamma \cos \alpha - \cos \beta) \]
\[ S_{23} = a^2 bc (\cos \beta \cos \gamma - \cos \alpha) \]
Lattice parameters

\[
\frac{1}{d^2} = \frac{1}{V^2} (S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{13}hl + 2S_{23}kl)
\]

**GSAS:**

Reflection d-spacing and lattice parameters

The d-spacing for a reflection, \( h=(h,k,l) \), is given by the standard expression

\[
\frac{1}{d^2} = hgh = Ah^2 + Bk^2 + Cl^2 + 2Dhk + 2Ehl + 2Fkl
\]

where \( g \) is the reciprocal metric tensor

\[
g = \begin{pmatrix}
    a^*^2 & a^* b^* \cos \gamma^* & a^* c^* \cos \beta^* \\
    a^* b^* \cos \gamma^* & b^2 & b^* c^* \cos \alpha^* \\
    a^* c^* \cos \beta^* & b^* c^* \cos \alpha^* & c^2
\end{pmatrix}
\]

which is the inverse of the metric tensor

\[
G = \begin{pmatrix}
    a^2 & ab \cos \gamma & ac \cos \beta \\
    ab \cos \gamma & b^2 & bc \cos \alpha \\
    ac \cos \beta & bc \cos \alpha & c^2
\end{pmatrix}
\]

The refined coefficients for a powder diffraction pattern are the reciprocal metric tensor elements A-F, as allowed by symmetry.