Profile functions used in Jana2020

The profile functions are used to model the shape of diffraction peaks. It is a function of the argument $x = \theta - \theta_{\mathbf{h}}$, the difference between the actual position and the expected position of the diffraction **h.** There are three possible profile functions in Jana2020.

Gaussian function: $G(x) = a_G \exp\left(-x^2 / 2b_G^2\right)$ (1)

The coefficients a_G b_G can be expressed as a function of FWHM called H_G :

$$a_G = \frac{2}{H_G}\sqrt{\frac{\ln 2}{\pi}} \qquad b_G^2 = \frac{H_G^2}{8\ln 2} \tag{2}$$

Lorentzian function: $L(x) = \dfrac{a_L}{1 + \left(2x/b_L\right)^2}$ **y** (3)

Similarly, as for the Gaussian, the coefficients a_L and b_L can be expressed as a function of H_L :

$$a_L = \frac{2}{\pi H_L} \qquad b_L = H_L \tag{4}$$

Pseudo-Voigt function: $pV(x) = \eta L(x) + (1-\eta)G(x)$ (5)

Both FWHM for Lorentzian and Gaussian parts in the above formula are supposed to be the same, calculated from the equation:

$$H = H_G^5 + 2.69269\, H_G^4 H_L + 2.42843\, H_G^3 H_L^2 + 4.47163\, H_G^2 H_L^3 + 0.07842\, H_G H_L^4 + H_L^5 \tag{6}$$

The second parameter η:

$$\eta = 1.36603\,\frac{H_L}{H} - 0.47719\left(\frac{H_L}{H}\right)^2 + 0.11116\left(\frac{H_L}{H}\right)^3 \tag{7}$$

Angular dependence of FWHM

The FWHM parameters are dependent on the scattering angle. The Gaussian H_G is composed of five terms:

$$b_G^2 = U\tan^2\theta + V\tan\theta + W + \frac{P}{\cos^2\theta} + (1-\zeta)^2\,\Gamma_A^2 \tag{8}$$

The first three terms account for basic broadening due to slits, wavelength dispersion, and the monochromator, as described by Cagliotti, Pauletti & Ricci (1958, Nucl. Instrum., **3**, 223). The fourth term is the Scherrer coefficient for Gaussian broadening. It should be noted that only U and W or P and W or P and U can be refined together to avoid singularity caused by the trigonometric relationship $\tan^2\theta+1=\frac{1}{\cos^2\theta}$. The last term accounting for anisotropic strain will be discussed separately.

The Lorentzian b_L is composed of five terms as well:

$$b_L=\left(X+X_e\cos\phi_X\right)/\cos\theta+\left(Y+Y_e\cos\phi_Y\right)\tan\theta+\zeta\Gamma_A \qquad (9)$$

The *X* terms account for Lorentzian Scherrer particle broadening. X and X_e stands for isotropic and anisotropic parts, respectively. ϕ_X is the angle between the diffraction vector and the broadening direction.
The *Y* terms describe strain broadening, and the meaning of the constants is analogous to that for particle broadening.
The last term represents Stephen's strain anisotropy and cannot be combined with Y_e.

Anisotropic peak broadening as introduced by P.W.Stephens

The phenomenological model is based on a general tensor expression in which a symmetrical 4th order tensor describes the anisotropic strain:

$$\sigma^2(hkl)=D^{ijmn}h_ih_jh_mh_n=\sum_{HKL}S_{HKL}h^Hk^Kl^L$$

The first term is a general tensor expression using the Landau summation convention, allowing a simple derivation of symmetry restrictions similar to those for 4th-order ADP parameters. The second term has the explicit form used by Stephens, in which the summation is restricted to $H+K+L=4$.
Using the Bragg equation, we can finally get the contribution to FWHM :

$$\Gamma_A=\left[\sigma^2(h,k,l)\right]^{1/2}d^2\tan\theta$$

The ratio of the broadening between the Gaussian and Lorenzian parts is $(1-\zeta)/\zeta$.

Jana2000 uses the notation similar to that in GSAS:

$U\rightarrow$ GU, $V\rightarrow$ GV, $W\rightarrow$ GW, $P\rightarrow$ GP

$X,X_e\rightarrow$ LX, LXe, $Y,Y_e\rightarrow$ LY, LYe

The Stephens' parameters are chosen in analogy to his paper - J. *Appl. Cryst.* (1999), **32**, 281-289.

Origin shift parameters

shift – defines the zero shift (units of 0.01 deg).

sycos –in analogy with the Fullprof: $\Delta 2\theta = \mathrm{c.}\cos\theta$ relates to a specimen displacement

sysin – in analogy with the Fullprof: $\Delta 2\theta = \mathrm{s.}\sin 2\theta$ relates to a transparency correction

These three values are added to the theoretical peak position to obtain a position in the experimental profile.

Different R values used in Jana2020

profile R-factor

$$R_p = \frac{\sum_i \left| y_i(obs) - y_i(calc) \right|}{\sum_i y_i(obs)} \cdot 100$$

i run over all points of the profile, $y_i(obs)$ and $y_i(calc)$ are the observed and calculated intensity, respectively.

weighted profile R-factor

$$R_{wp} = \sqrt{\frac{\sum_i w_i (y_i(obs) - y_i(calc))^2}{\sum_i w_i y_i(obs)^2}} \cdot 100$$

where the weights are calculated from standard uncertainties of profile intensities:

$$w_i = \frac{1}{\sigma^2 \left[y_i(obs) \right]}$$

experimental R factor

$$R_{\exp} = \sqrt{\frac{\sum_i w_i y_i(obs)^2}{n - p}} \cdot 100$$

n number of profile points, p number of refined parameters

goodness of fit

$$GOF = \frac{R_{wp}}{R_{\exp}}$$

pure profile R-factor

$$cR_p = \frac{\sum_i \left| y_i'(obs) - y_i'(calc) \right|}{\sum_i y_i'(obs)} \cdot 100$$

weighted profile R-factor $$cR_p = \frac{\sum_i w_i\left(y_i'(obs) - y_i'(calc)\right)^2}{\sum_i w_i y_i'(obs)^2} \cdot 100$$

where $y_i'(obs) = y_i(obs) - b_i$ and $y_i'(calc) = y_i(calc) - b_i$ are intensities corrected for background.

The conventional structural R values are calculated after the le Bail separation. The R values based on F and I are listed for both all and observed reflections. The R factor based on F is $R_F(obs)$, $R_F w(obs)$, $R_F(all)$, $R_F w(all)$. Those based on intensities are $R_B(obs)$, $R_B w(obs)$, $R_B(all)$, $R_B w(all)$.

Extraction of F$_{obs}$ and σ(F$_{obs}$ from powder profile

Powder diffraction: the $F_{hkl}(obs)$ values for the calculation of Fourier maps, structural R values, and MEM are to be derived from the observed and calculated powder profiles and $F_{hkl}(calc)$ as follows from the temporary structural model. From all profile points to which the reflection (*h,k,l*) contributes, we can write:

$$L_i.A_i.R_i.P_i(h,k,l)\Omega_i(h,k,l)F_{hkl}^2(obs) = \frac{y_i'(obs)}{y_i'(calc)}.L_i.A_i.R_i.P_i(h,k,l)\Omega_i(h,k,l)F_{hkl}^2(calc)$$

L_i contains the Lorentz, polarization, and multiplicity factor of the reflection (h,k,l)

A_i is an absorption factor

R_i is a roughness correction

$P_i(h,k,l)$ is the preference orientation function

$\Omega_i(h,k,l)$ is the reflection profile function

It means that for all profile points to which the reflection (h,k,l) makes a non-zero contribution, we have $F_{hkl,i}^2(obs)$:

$$F_{hkl,i}^2(obs) = \frac{y_i'(obs)}{y_i'(calc)}.F_{hkl}^2(calc)$$

Then the final values $F_{hkl}^2(obs)$ and $\sigma\left[F_{hkl}^2(obs)\right]$ can be calculated as an average and standard error.

However, as profile points do not have the same experimental accuracy, two methods to suppress undesired fluctuations:

1. For the calculation of averaged values, only profile points to which the relevant reflection (h,k,l) contributes significantly are used. As a criterion, we are using values of the profile function $\Omega_i(h,k,l)$ which must be at least 10% of its maximal value.

2. In the average procedure, we use weights based on experimental standard uncertainties:

$$F_{hkl}^2(obs)=\frac{\sum_i w_i \frac{y_i'(obs)}{y_i'(calc)} F_{hkl}^2(calc)}{\sum_i w_i}$$

The weights w_i are derived from the estimated values of standard uncertainties of the expression:

$$Y_i=\frac{y_i'(obs)}{y_i'(calc)}=\frac{y_i(obs)-b_i}{y_i(calc)-b_i}$$

Following the propagation rule, we have:

$$\sigma^2(Y_i)=1/w_i=\left[\frac{-1}{y_i(calc)-b_i}\right]^2\sigma^2[y_i(obs)]+\left[\frac{(y_i(obs)-b_i)}{(y_i(calc)-b_i)^2}\right]^2\sigma^2[y_i(calc)]+$$
$$\left[\frac{-y_i(calc)+y_i(obs)}{(y_i(calc)-b_i)^2}\right]^2\sigma^2[b_i]$$

The values $\sigma[y_i(calc)]$ and $\sigma[b_i]$ are estimated from experimental $\sigma[y_i(obs)]$:

$$\sigma[y_i(calc)]=\frac{y_i(calc)}{y_i(obs)}\sigma[y_i(obs)] \qquad \sigma[b_i]=\frac{b_i}{y_i(obs)}\sigma[y_i(obs)]$$

Then for $\sigma^2(Y)$ we have:

$$1/w_i=\sigma^2[y_i(obs)]\left[\frac{1}{(y_i(calc)-b_i)^2}+\left\{\frac{y_i(obs)-b_i}{(y_i(calc)-b_i)^2}\frac{y_i(calc)}{y_i(obs)}\right\}^2+\left\{\frac{y_i(obs)-y_i(calc)}{(y_i(calc)-b_i)^2}\frac{b_i}{y_i(obs)}\right\}^2\right]$$

A similar method is used for the estimation of $\sigma[F_{hkl}^2(obs)]$:

$$\sigma[F_{hkl}^2(obs)]=\sqrt{\frac{\sum_i w_i\left[\frac{y_i'(obs)}{y_i'(calc)}F_{hkl}^2(calc)\right]^2}{\sum_i w_i}-F_{hkl}^4(obs)}$$

This method combines experimental standard uncertainties expressed by weights with a profile fit. In the case that peaks are too sharp, it could be preferable to concentrate only on experimental uncertainties and calculate $\sigma[F_{hkl}^2(obs)]$ using the error propagation formula:

$$\sigma[F_{hkl}^2(obs)]=\frac{\sqrt{\sum_i w_i F_{hkl}^4(calc)}}{\sum_i w_i}$$

This equation follows from the expression for $F_{hkl}^2(obs)$:

$$F_{hkl}^2(obs) = \frac{\sum_i w_i \frac{y_i'(obs)}{y_i'(calc)} F_{hkl}^2(calc)}{\sum_i w_i}$$

and the application of the error propagation theorem under the assumption that the terms in the summation have zero correlations:

$$\sigma\left[F_{hkl}^2(obs)\right] = \sqrt{\frac{1}{\left(\sum_i w_i\right)^2}\left(\sum_i w_i^2 \sigma^2(Y_i) F_{hkl}^4(calc)\right)} = \frac{\sqrt{\sum_i w_i F_{hkl}^4(calc)}}{\sum_i w_i}$$

Particle size and strain parameters as follows from the Jana profile parameters

The particle size and strain parameter are usually expressed as functions of the integral breadth β, which represents the width of a rectangle with the same height and area as the diffraction peak.

Gaussian distribution:

$$G(x) = a_G \exp\left(-x^2 / 2b_G^2\right)$$

$$\Rightarrow \qquad \beta_G = \frac{H_G}{2}\sqrt{\frac{\pi}{\ln 2}} = \sqrt{2\pi} b_G$$

$$a_G = \frac{2}{H_G}\sqrt{\frac{\ln 2}{\pi}} \qquad b_G^2 = \frac{H_G^2}{8 \ln 2}$$

Lorentzian distribution:

$$L(x) = \frac{a_L}{1 + (2x/b_L)^2}$$

$$\Rightarrow \qquad \beta_L = \frac{\pi H_L}{2} = \frac{\pi b_L}{2}$$

$$a_L = \frac{2}{\pi H_L} \qquad b_L = H_L$$

The particle size is generally associated with the line broadening proportional to $\frac{1}{\cos\theta}$. It means that, for the Gaussian distribution, it is related to the parameter P (equation (8)), and for the Lorentzian distribution, to the parameter X (equation (9).

According to the Scherrer formula for D_V the so-called volume weighted crystalline size, we have:

$$D_V = K\lambda/(\beta\cos\theta)$$

K = Scherrer constant, a somewhat arbitrary value that falls in the range 0.87-1.0. I usually assume K = 1.
λ = wavelength of the radiation
β = integral breadth of a reflection (in radians) located at 2θ.

For the Gaussian distribution, we have from equations (8):

$D_V = 180\,K\lambda/\left(\sqrt{2\pi^3 P}\right)$ if P expressed in degs^2 (Fullprof) or
$D_V = 18000\,K\lambda/\left(\sqrt{2\pi^3 P}\right)$ if P expressed in (0.01 degrees)^2 (GSAS, Jana)

For the Lorentzian distribution, we have from equation (9):

$D_V = 360\,K\lambda/\left(\pi^2 X\right)$ if X is expressed in degrees (Fullprof) or
$D_V = 36000\,K\lambda/\left(\pi^2 X\right)$ if X is expressed in 0.01 degrees (GSAS, Jana)

The strain parameter is generally associated with the line broadening proportional to $\tan\theta$

$$\beta = 4\varepsilon_{str}\tan\theta$$

Where β are expressed in radians. For the Gaussian distribution, we have from equations (8):

$\varepsilon_{str,G} = \sqrt{2\pi^3 U}/720$ if U expressed in degrees^2 (Fullprof) or
$\varepsilon_{str,G} = \sqrt{2\pi^3 U}/72000$ if U expressed in (0.01degrees)^2 (GSAS, Jana)

For the Lorentzian distribution, we have from equations (9):

$\varepsilon_{str,L} = \pi^2 Y/1440$ if Y is expressed in degrees (Fullprof) or
$\varepsilon_{str,L} = \pi^2 Y/144000$ if Y is expressed in 0.01degrees (GSAS, Jana)

However, such an interpretation has real meaning only if we are correcting the integral breadth for instrumental broadening.

An alternative, more elegant approach is a fundamental one. In the Jana2020 program, we have used the approach developed by A.Coelho and R.W.Cheary:

J. Appl. Cryst. (1992). **25**, 109-121.
J. Appl. Cryst. (1998). **31**, 851-861.
J. Appl. Cryst. (1998). **31**, 862-868.

Particle size:

Instead of parameters X in equation (9), the so-called apparent crystallite size is used:

$$T_{app} = 18000\,\lambda/(\pi X)$$

in Jana2020, this parameter is expressed in nm, and its relationship to D_V is:

$$D_V = (2K/\pi)T_{app}$$

For the Gaussian distribution, we are using the reduced form of equation (8):

$$b_G^2 = U\tan^2\theta + \frac{P}{\cos^2\theta} + (1-\zeta)^2\Gamma_A^2$$

where instead of the parameter P, we also use the apparent crystallite size:

$$T_{app} = \sqrt{8\ln 2}\,18000\,\lambda/\left(\pi\sqrt{P}\right) \Rightarrow D_V = K\sqrt{\frac{4\ln 2}{\pi}}T_{app}$$

The strain parameters U_{FA} and Y_{FA} (in Jana2020 called StrainG and StrainL) are just transformed to radians/100.

$$Y_{FA} = \pi Y/180$$
$$U_{FA} = \pi\sqrt{8\ln 2U}/180$$

The factor $\sqrt{8\ln 2}$ transforms b_G to H_G according to the equation (2).

Then the parameter $\varepsilon_{str,L}$ and $\varepsilon_{str,G}$ are related to Y_{FA} and U_{FA}:

$$\varepsilon_{str,L} = \pi Y_{FA}/800$$
$$\varepsilon_{str,G} = \sqrt{\frac{\pi}{4\ln 2}}U_{FA}/400$$