Profile functions used in Jana2006

The profile functions are used to model a shape of diffraction peaks. It is a function of the argument $x = \theta - \theta_{\mathbf{h}}$, the difference of the actual position from the expected position of the diffraction **h.** There are three possibilities for the profile function in Jana2006.

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

the coefficients a_G and 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: $L(x) = \dfrac{a_L}{1 + (2x/b_L)^2}$ (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 part in the above formula are supposed to be same calculated from the equation:

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

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 from 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 by slits, wave length dispersion and influence of monochromator as described by Cagliotti, Pauletti & Ricci 1958

(Nucl.Instrum., **3**, 223). The forth 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 trigonometry 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 from 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 accounts for Lorentzian Scherrer particle broadening. X and X_e stands for isotropic and anisotropic part, 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 analogical to those for particle broadening.
The last term stands for the Stephen's stain anisotropy and it could not 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 the anisotropic strain is described by a symmetrical 4th order tensor:

$$\sigma^2(hkl) = D^{ijmn} h_i h_j h_m h_n = \sum_{HKL} S_{HKL} h^H k^K l^L$$

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

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

The ratio in which is the broadening is included to Gaussian and to Lorenzian part 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 of his paper - *J.Appl.Cryst.* (1999), **32**, 281-289.

Different R values used in Jana2006

profile R-factor $$R_p = \frac{\sum_i |y_i(obs) - y_i(calc)|}{\sum_i y_i(obs)} \cdot 100$$

i runs over all points of the profile, $y_i(obs)$ and $y_i(calc)$ are 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:

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

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

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

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 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

are $R_F(obs)$, $R_F w(obs), R_F(all)$, $R_F w(all)$. Those based on intensities are $R_B(obs)$, $R_B w(obs), R_B(all)$, $R_B w(all)$.

Extraction of F_{obs} and $\sigma(F_{obs})$ from powder profile

Powder diffraction the $F_{hkl}(obs)$ values for calculation of Fourier maps, structural R values and for MEM are to be derived from the observed and calculated powder profile 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

This means that for all profile points to which the reflection (h,k,l) makes 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 value $F_{hkl}^2(obs)$ and $\sigma\left[F_{hkl}^2(obs)\right]$ can be calculated as an average and standard error. However, as profile points do not have same experimental accuracy, two methods how to suppress undesired fluctuations:

1. For 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 by at least 10% of its maximal value.

2. In the average procedure uses 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 by 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:

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

Similar method is use for 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 $\sigma[F_{hkl}^2(obs)]$by 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 application the error propagation theorem under assumption that term 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 Jana profile parameters

The particle size and strain parameter are usually expressed as a function of the integral breath β which represent the width of a rectangle with the same height and area as the diffraction peak.

Gaussian distribution:

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

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

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

Lorentzian distribution:

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

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

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

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

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

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

K = Scherrer constant, 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 Gaussian distribution we have from the 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 (0.01degs)^2 (GSAS, Jana)

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

$D_V = 360\,K\lambda/\left(\pi^2 X\right)$ if X expressed in degs (Fullprof) or

$D_V = 36000\,K\lambda/\left(\pi^2 X\right)$ if X expressed in 0.01degs (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 Gaussian distribution we have from the equations (8):

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

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

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

$\varepsilon_{str,L} = \pi^2 Y/1440$ if Y expressed in degs (Fullprof) or

$\varepsilon_{str,L} = \pi^2 Y/144000$ if Y expressed in 0.01degs (GSAS, Jana)

However such an interpretation has real meaning only if the integral breadth is corrected for instrumental broadening.

An alternative more elegant way is a fundamental approach. In Jana2006 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:

The instead of parameters X in the equation (9) the so called apparent crystallite size is used:

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

in Jana2006 this parameter is expressed in nm and its relationship to D_V is:

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

For Gaussian distribution we are using the reduced form of the 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 Jana2006 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 $\sqrt{8\ln 2}$ just 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}:

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