Refinement of time-of-flight Profile Parameters in GSAS

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In order to fit the peaks observed in a time-of-flight diffraction experiment two sets of information are required. The first set, the ***diffractometer constants***, is used to calculate the time-of-flight positions of the Bragg reflections (whose d-spacings can be determined from the unit cell parameters and space group information). The second set, the ***profile parameters***, are used to calculate the widths of each of these Bragg reflections.

Starting values for both these sets of parameters are given in the Instrument Parameter File and are determined by fitting data collected from a standard sample (Silicon powder, NBS SRM 640b). During this instrument calibration procedure the silicon cubic lattice parameter is fixed at its certified value (a = 5.43094Å) and all other profile and instrument parameters are refined freely.

1. Diffractometer constants.

For a time-of-flight neutron diffraction measurement, the three diffractometer constants in GSAS - DIFC, DIFA and ZERO - relate the time of flight, t, of a reflection to its d-spacing, d, as follows:

$$t = \text{DIFC d} + \text{DIFA d}^2 + \text{ZERO}$$

1.1 DIFC DIFC relates the theoretical time-of-flight of a measured Bragg reflection to its d-spacing, and an approximate value can be calculated from a knowledge of the total flight path L and scattering angle, 2θ, of a detector by combining Bragg's Law,

$$\lambda = 2d \sin \theta,$$

with the de Broglie relationship,

$$\lambda = \frac{h}{mv} \quad \left(= \frac{h}{m} \frac{t}{L} \right),$$

to yield the expression

$$t = \left(\frac{2m}{h} \right) L \sin \theta \, d,$$

where h is Planck's constant; m is the neutron mass; t is the total time of flight; L is the total flight path from moderator to sample to detector; d is the interplanar spacing; and θ is half the Bragg scattering angle (2θ).

Substitution for h and m and conversion to appropriate units yields:

$$t = 505.56 L \sin\theta \; d$$

or

$$d = \frac{1.977 \times 10^{-3}}{L \sin\theta} t$$

where t is in μs, L is in m, and *d* is in Å.

Thus it can be seen that DIFC = 505.56 *L* sinθ (assuming that DIFA and ZERO are equal to 0 in the equation at the beginning of this section). Note that, in general, DIFC will vary from one detector bank to another.

Normally, DIFC will remain FIXED during Rietveld refinement. However, during a multi-histogram refinement, where data collected in more than one detector bank are being used to refine a crystal structure, often it is necessary to refine DIFC for the *lower* resolution histograms **provided** that it remains fixed for the *highest* resolution histogram (in order to prevent the refinement becoming unstable due to the very high degree of correlation between DIFC and the lattice parameters). This is to allow for the small differences in sample positioning that occur between the standard used for instrument calibration purposes and users' own samples during their experiments.

1.2 DIFA The neutron absorption cross-section of an atom is wavelength dependent, which means that in a time-of-flight diffraction measurement the short wavelength (low tof) neutrons will experience less absorption than the larger wavelength (longer tof) neutrons. Thus the average penetration into the sample, and hence the apparent total flight path and scattering angle, will vary with neutron wavelength and the observed times-of-flight of reflections may be noticeably different from those expected from the expression involving DIFC alone (above), especially at longer d-spacings (which are measured with longer wavelengths, where absorption is greater).

DIFA introduces small corrections to the expected time-of-flight of a reflection to allow for peak shifts due to absorption in the sample. Empirically, it has been found that a quadratic (i.e. d^2) dependence provides a good fit to observed shifts in reflection positions.

Initially DIFA may be fixed at 0.0, but in latter stages of refinement it can be REFINED.

1.3 ZERO This parameter accounts for small differences between the various timing signals in the ISIS accelerator and the instrument data acquisition system, and also allows for the finite response times in the detector electronics. It is instrument dependent and must remain FIXED.

2. Profile Parameters.

Peak shape function 3 in GSAS, which is used to model the peak shapes observed on Polaris, is a convolution of a pseudo-Voigt function with two back-to-back exponentials. The pseudo-Voigt function models the effects of instrument design and detector geometry on the **width** of reflections, and also any broadening due to sample effects such as strain and particle size. The exponential functions model the physics of neutron production at ISIS, and describe the extremely sharp build-up in intensity when the proton beam strikes the neutron target followed by the slower drop-off in intensity as the neutrons emerge from the moderator.

The Pseudo-Voigt function is a linear combination of Gaussian and Lorentzian functions, whose full widths at half maximum are parameterised in GSAS as follows.

2.1 Gaussian width The width, σ, of the Gaussian part of the pseudo-Voigt function is parameterised as:

$$\sigma^2 = \sigma_0^2 + \sigma_1^2 d^2 + \sigma_2^2 d^4$$

In GSAS these parameters are called sig-0, sig-1 and sig-2 respectively.

2.2 Lorentzian width The width, γ, of the Lorentzian part of the pseudo-Voigt function is parameterised as:

$$\gamma = \gamma_0 + \gamma_1 d + \gamma_2 d^2 \quad \text{(+ other terms associated with strain broadening)}$$

In GSAS these first three terms are called gam-0, gam-1 and gam-2.

Partial differentiation of the equation above (top of p. 2) relating time-of-flight to d-spacing shows that for a fixed detector the resolution approximates closely to $\Delta d / d = \text{constant}$ - the width of a reflection is proportional to its d-spacing, i.e. $\Delta d = kd$. Comparing this expression with the above parameterisations of the Gaussian and Lorentzian widths it can be seen that the terms σ_1 and γ_1 both describe linear relationships between peak width, Δd, and d-spacing.

$$\Delta d^2 = \sigma^2 = \sigma_1^2 d^2 \quad (\sigma_0 \text{ and } \sigma_2 = 0), \text{ therefore } \Delta d / d = \sigma_1 \, ,$$

likewise $\quad \Delta d = \gamma = \gamma_1 d \quad (\gamma_0 \text{ and } \gamma_2 = 0), \text{ therefore } \Delta d / d = \gamma_1 \, .$

Thus, in structure refinement sig-1 and gam-1 may be REFINED.

However, in most samples there is likely to be some degree of particle size or strain broadening. As detailed in the GSAS manual, particle size broadening has a d^2 dependence and thus is fitted by the gam-2 parameter, whereas strain broadening has a linear dependence on d and may be fitted by the gam-1 or sig-1 parameters.

2.3 Exponential parameters

The rise and decay coefficients for the two exponential functions are described by the parameters alp, bet-0 and bet-1. During instrument calibration, these parameters can be refined with care. During structure refinement they must be kept FIXED.

3. Summary of Refinement Parameters

DIFC — is instrument dependent and must remain FIXED. (but may be refined for lower resolution banks during a multi-histogram refinement).

DIFA — is sample dependent and may be REFINED.

ZERO — is instrument dependent and must remain FIXED.

alp, bet-0 and bet-1 — are instrument dependent and must remain FIXED.

sig-0, sig-1, sig-2 — sig-1, sig-2 may be REFINED*.

gam-0, gam-1 and gam-2 — gam-1, gam-2 may be REFINED*.

* Note that although in principle it is possible to refine all four of the parameters sig-1, sig-2, gam-1 and gam-2, in practice it is often found that this results in unstable refinements and that only a subset of these parameters are able to be refined satisfactorily. Frequently this will be different for each detector bank.

Finally, in the case of anisotropic line broadening, where different classes of reflections are broadened to differing degrees, the refinement strategy suggested above for the parameters sig-1, sig-2, gam-1 and gam-2 will fail to provide a satisfactory fit to the observed reflections. In such cases, further parameters are available in the Lorentzian component of the pseudo-Voigt function. These are described briefly in the GSAS Manual (a pdf version of which is included in the GSAS/EXPGUI download package).

For a much fuller description of a comprehensive anisotropic line broadening description which has been incorporated into GSAS see P.W. Stephens, "Phenomenological model of anisotropic peak broadening in powder diffraction", *J. Appl. Cryst.*, **32**, 281-289 (1999).