MCGRtof: Monte Carlo *G*(*r*) with resolution corrections for time-of-flight neutron diffractometers

Matthew G. Tucker, Martin T. Dove and David A. Keen

MCGRtof: Monte Carlo $G(r)$ with resolution corrections for time-of-flight neutron diffractometers

Matthew G. Tucker,[a] Martin T. Dove[a]* and David A. Keen[b]

[a]Mineral Physics Group, Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, UK, and [b]ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, UK. Correspondence e-mail: martin@esc.cam.ac.uk

A new implementation of the program *MCGR* [Pusztai & McGreevy (1997). *Physica B*, **234–236**, 357–358] for the calculation of pair distribution functions from neutron total scattering data using an inverse Monte Carlo algorithm is presented. The new implementation, called *MCGRtof*, incorporates the resolution functions for time-of-flight neutron diffractometers, and is suitable for analysis of data from instruments such as GEM at the ISIS spallation neutron source. The effect of including resolution correctly is to increase the magnitude of the pair distribution function at larger distances. The working program is illustrated with total scattering measurements from crystalline AlPO$_4$.

1. Introduction

The pair distribution function, $G(r)$, contains information about the distribution of instantaneous interatomic distances. It is obtained by Fourier transform of the total scattering, which for crystalline materials will be the sum of the Bragg scattering and the diffuse scattering. Formally we can write (Keen, 2001)

$$S(Q) = \frac{1}{N}\frac{d\sigma}{d\Omega} = i(Q) + \sum_{i=1}^{n} c_i \overline{b_i^2}, \qquad (1)$$

$$i(Q) = \rho_0 \int_0^\infty 4\pi r^2 G(r)(\sin Qr)/Qr\, dr, \qquad (2)$$

$$G(r) = \sum_{i,j=1}^{n} c_i c_j \bar{b}_i \bar{b}_j [g_{ij}(r) - 1], \qquad (3)$$

$$D(r) = 4\pi \rho_0 r G(r). \qquad (4)$$

$S(Q)$ is the basic measurement, after a number of essential corrections have been carried out (Howe *et al.*, 1989). $D(r)$ is an alternative representation of the information contained with $G(r)$, giving a more balanced presentation of the information in the sharp peaks at low r and the broader features over intermediate values of r. Similarly, it is common to plot the function $Qi(Q)$ instead of $i(Q)$ in order to present better both the low Q and high Q together. Moreover, the transformation equations above effectively link $D(r)$ to $Qi(Q)$. The formalism of the analysis of total-scattering experiments can be expressed in many different ways, as reviewed by one of us (Keen, 2001).

$G(r)$ is essentially the Fourier transform of $S(Q)$ after accounting for the isotropic average, namely the average over all relative orientations of **Q** and **r**. One important correction is that due to resolution. Writing $R(Q)$ as the instrument resolution function, the measurement is actually of

$$S^E(Q) = R(Q) \otimes S(Q), \qquad (5)$$

where the superscript E denotes the experimental function. Without accounting for resolution, the Fourier transform of $S^E(Q)$ will be

$$G^E(r) \simeq \mathrm{FT}[R(Q)] \times G(r). \qquad (6)$$

In short, the derived value of $G(r)$ will be the true value modulated by the Fourier transform of $R(Q)$. Technically, this is only exact if the resolution function is equivalent for all points in $S(Q)$, which is not actually the case. The width of $R(Q)$, ΔQ, will vary with Q, and for a time-of-flight diffractometer, the ratio $\Delta Q/Q$ will be roughly constant. This precludes performing a direct deconvolution of $S^E(Q)$ prior to the determination of $G(r)$.

In this note we propose that the best solution to the problem of instrument resolution is the use of an inverse transformation method (Soper, 1990; Pusztai & McGreevy, 1997). We present a version of the *MCGR* program previously developed for inverse transformation, with resolution corrections properly incorporated.

There is increasing interest in measuring $G(r)$ for crystalline materials, particularly for disordered crystalline materials where true instantaneous bond lengths may differ significantly from the distances between the mean atomic positions given by Rietveld refinement. Our own work on the crystalline polymorphs of silica has shown how the instantaneous Si—O bond lengths are much larger than would be given by the distances between the mean Si and O positions, even if care is taken in setting up a crystallographic model for the refinement that takes account of presumed structural disorder (Tucker *et al.*, 2000, 2001).

2. Inverse transformation method with resolution corrections

The inverse transformation method involves generating a numerical form of $G(r)$, and adjusting it point by point until its Fourier transform is in best agreement with the experimental data. Pusztai & McGreevy (1997) argue that there are a number of inherent advantages in this approach, particularly in that it is possible to apply constraints to the form of $G(r)$, such as on its value at low r, and the possibility of performing the transform to $G(r)$ from total-scattering data with a restricted range of Q. Even with the highest quality data, for example from a time-of-flight instrument with data to maximum Q of $Q_{max} \simeq 50\,\text{Å}^{-1}$, the use of the inverse transformation method

ensures that there are no transformation ripples and avoids the need for a smoothing function.

Incorporation of resolution corrections within an inverse transformation method is reasonably straightforward. The model $G(r)$ is computed with a very large value of r to avoid truncation ripples when transformed to produce a model $i(Q)$. The model $i(Q)$ can then be convolved, point by point, with a model $R(Q)$, which can easily vary across the range of Q in the data. The resultant $i(Q) \otimes R(Q)$ can then be compared with the experimental $i(Q)$. The quality of the agreement can be quantified by

$$\chi^2 = \sum_j |i_{\text{model}}(Q) - i_{\text{exp}}(Q)|^2 / \sigma^2, \quad (7)$$

where 'model' and 'exp' indicate the model and experimental functions, respectively. σ is a weighting function, which could be related to the actual experimental errors if these are properly propagated through the data correction and normalization procedures. The Metropolis Monte Carlo algorithm is used to allow the model $G(r)$ to give a better $i(Q)$ by treating χ^2 as an energy function.

The resolution function for time-of-flight instruments is relatively complex but well established. We use the formalism used in the popular *GSAS* Rietveld refinement code, which is described in detail in the *GSAS* manual. We have coded this into the *MCGR* program of Pusztai & McGreevy (1997); our version is called *MCGRtof*.

In operation, the parameters of the time-of-flight line shape are obtained by performing a Rietveld or Le Bail analysis on the diffraction data in normal time-of-flight mode (that is, the flight time is treated as the variable). The fitted line-shape parameters can easily be transformed into the Q domain.

Time-of-flight instruments have several banks of detectors and the spectra from all detectors in a single bank are grouped together. The result of a single measurement will be spectra from each of the banks of detectors. The original *MCGR* program is able to handle several sets of $i(Q)$ spectra and in *MCGRtof* a different set of resolution parameters can be obtained for each spectrum.
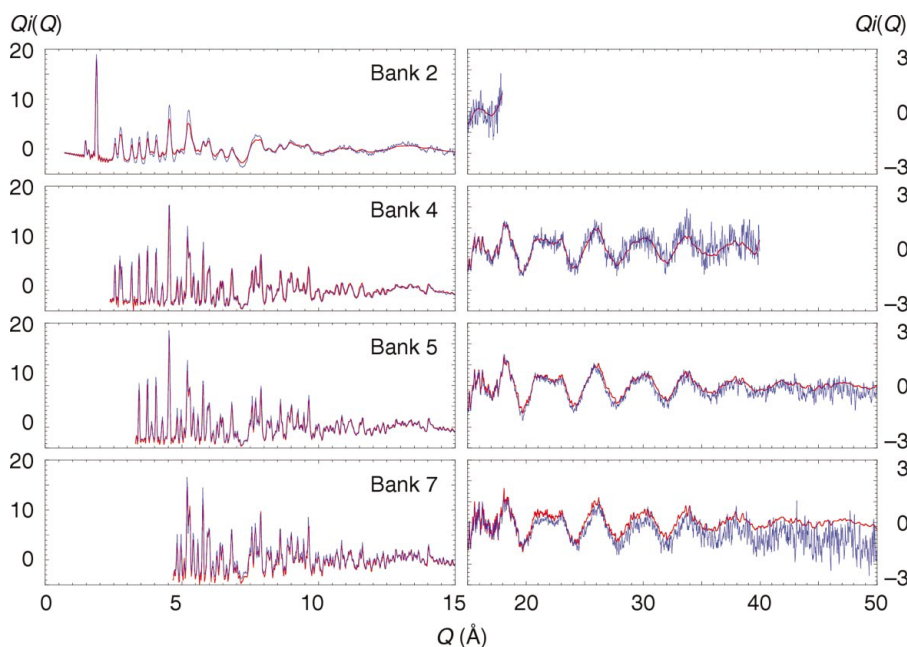
For polycrystalline materials, the parameters of the resolution function can easily be obtained for the sample from the total-scattering measurement. On the other hand, the parameters for non-crystalline materials will need to be obtained from a standard sample. In both cases, it should be noted that the parameterization of the resolution function will only involve fitting to diffraction data over a limited range of Q. Beyond that, we are relying on the theoretical extrapolation of the line-shape function. This is unlikely to lead to significant problems, particularly because the features in $i(Q)$ will be both weak and broad.

3. Example: measurement on crystalline AlPO$_4$

Fig. 1 shows measurements of the total-scattering function $Qi(Q)$ of crystalline AlPO$_4$, obtained on four different banks of detectors on the GEM diffractometer at the ISIS spallation neutron source (Williams *et al.*, 1997). These data are fitted using the *MCGRtof* program using resolution corrections obtained using the procedures outlined above. The data from the different detector banks cover different ranges of Q. The banks at lower scattering angles (mean scattering angles of 17 and 63.5° for banks 2 and 4, respectively) extend the range to lower values of Q, with a reduction in the resolution. The banks at higher scattering angles (mean scattering angles of 91.5 and 159.5° for banks 5 and 7, respectively) extend the range to higher values of Q (without the low-Q data) and give greatly improved resolution at the lower values of Q within the range of data. However, the highest-angle bank (7) also has the worst counting statistics at higher values of Q. There is a slight systematic mismatch between the measured and calculated $Qi(Q)$ at the highest values of Q in the highest-angle bank. This is not seen in the fit of bank 5. We believe that the much poorer statistics of the data in bank 7 have led to difficulties in obtaining a completely accurate correction. However, the much lower statistical accuracy of the high-Q data in bank 7 has meant that its contribution to the fitting procedure in *MCGRtof* is greatly reduced compared with the contribution from the data over the same range of Q from bank 5, which have a much better statistical accuracy.

Fig. 2 shows the $D(r)$ function for AlPO$_4$ obtained using the *MCGRtof* program, with and without the use of resolution corrections in order to highlight the effect they have. The difference between the two sets of results is that the pair correlation functions obtained with the resolution corrections have higher values at larger values of r, exactly as expected from the discussion in §1.

It is interesting to note that the $D(r)$ function in Fig. 2 has sufficient resolution to see separate first-neighbour P–O and Al–O peaks. The positions of these peaks differ by 0.2 Å. The actual resolution of the function, given by $\Delta r = 2\pi/Q_{\text{max}}$, is only 0.13 Å, which is about one half of the peak separation. The peaks corresponding to the O–O distances in both the PO$_4$ and the AlP$_4$ tetrahedra are also separately resolved in Fig. 2. It is interesting to note that the positions of these five first peaks in $D(r)$, namely P–O at 1.52 Å, Al–O at
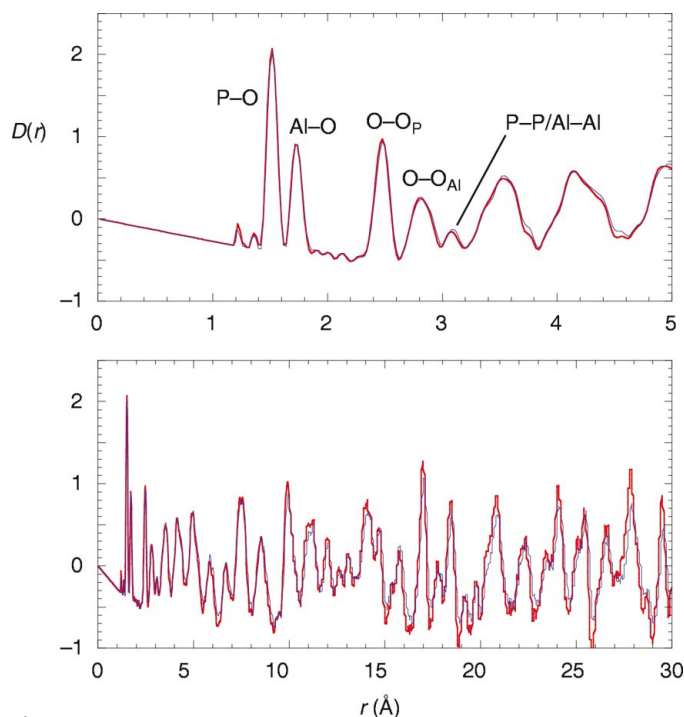

Figure 1
Experimental $Qi(Q)$ functions of AlPO$_4$ for four banks of detectors on the GEM diffractometer, fitted by *MCGRtof*. The mean scattering angles for banks 2, 4, 5 and 7 are 17, 63.5, 91.5 and 159.5°, respectively. The smoother curves are the fitted functions, while the experimental data are the lines with statistical scatter.

Figure 2

$D(r)$ function for AlPO$_4$ obtained from the data shown in Fig. 1 using *MCGRtof*. The data with the thicker curve represent the analysis taking account of instrument resolution, while the data with the thinner curve represent the analysis without taking account of instrument resolution.

1.74 Å, O–O within the PO$_4$ tetrahedra at 2.48 Å, O–O within the AlO$_4$ tetrahedra at 2.83 Å, and P–P and Al–Al at 3.09 Å, all match exactly the mean distances obtained by Rietveld refinement of the

diffraction data (multi-bank) to within one digit of the second decimal.

4. Availability of *MCGRtof*

Like the original *MCGR* program, *MCGRtof* is written in Fortran, and will run under Unix or on a PC. We have linked the output to a graphics display using the *PGPLOT* routines, which allow real-time visualization of the fitting procedure. We anticipate that *MCGRtof* will be of particular value for the new generation of time-of-flight instruments such as GEM at ISIS (Williams *et al.*, 1997). *MCGRtof* is available from the authors. The original *MCGR* program, together with details of the method, can be obtained from http://www.studsvik.uu.se/Software/rmc/mcgr.htm.

References

Howe, M. A., McGreevy, R. L. & Howells, W. S. (1989). *J. Phys. Condens. Matter.* **1**, 3433–3451.
Keen, D. A. (2001). *J. Appl. Cryst.* **34**, 172–177.
Pusztai, L. & McGreevy, R. L. (1997). *Physica B*, **234**–**236**, 357–358.
Soper, A. K. (1990). In *Neutron Scattering Data Analysis*, edited by M. W. Johnson, IOP Conference Series, Vol. 81. Bristol: IOP.
Tucker, M. G., Dove, M. T. & Keen, D. A. (2000). *J. Phys. Condens. Matter*, **12**, L723–L730.
Tucker, M. G., Squires, M. D., Dove, M. T. & Keen, D. A. (2001). *J. Phys. Condens. Matter*, **13**, 403–423.
Williams, W. G., Ibberson, R. M., Day, P. & Enderby, J. E. (1997). *Physica B*, **241**, 234–236.