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A comparison of various commonly used correlation functions for describing total scattering

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Total scattering, an increasingly important crystallographic research area, is defined theoretically in terms of correlation functions. Different researchers use different definitions for these functions, frequently leading to confusion in the literature. Here, a consistent set of equations for total-scattering correlation functions are developed and explicitly compared with other, often encountered, definitions. It is hoped that this will lead to increased transparency for newcomers to the field of total scattering.

1. Introduction

Total scattering is the measurement of the complete diffraction pattern, including both the Bragg and diffuse components. It is a routine scattering technique for liquid and amorphous systems and is becoming increasingly important for powdered crystalline materials which display disorder. Interpretative methods have emerged over the past ten years, notably reverse Monte Carlo modelling (McGreevy & Pusztai, 1988; McGreevy, 1995) and *PDFFIT* (Proffen & Billinge, 1999), leading to important structural studies of a diverse range of crystalline materials including collosal magneto-resitant materials (Billinge *et al.*, 1996), semiconductors (Petkov *et al.*, 1999) and network silicates (Keen & Dove, 1999). In addition, new diffractometers, such as the GEM instrument at ISIS (Williams *et al.*, 1998), are being developed, providing opportunities for improved total-scattering measurements.

However, total-scattering notation often appears confusing. This does not arise from any fundamental difference in theoretical formulation, but rather from the preferences of different workers in different subject areas for different formalisms which emphasize particular physical features of the correlation functions. Most of this confusion arises from different definitions of the same or similar symbols and different additive and/or multiplicative constants within the correlation functions. Problems will arise when these differences are not carefully described, particularly when data are taken from the literature by others for analysis.

It is for these reasons that this paper sets out a self-consistent set of formulae for total scattering. These are then simply re-cast to yield the equations which are most useful for total-scattering work from crystalline systems. The formulae are compared directly with the equations contained in a work by Hannon *et al.* (1990), which describes the *ATLAS* suite of programs (hereafter referred to as HHS), and the relationships between them and other commonly encountered definitions are also defined. This is the first time that the

relationships between the different correlation functions used to describe total scattering have been presented in a coherent manner. This will be of considerable benefit to those entering this emerging field and will provide clear and consistent definitions on which to base future work.

The discussion will be restricted to correlation functions where orientational ('powder') averaging has been assumed, and will also be largely confined to functions which refer to neutron scattering. X-ray weighted scattering functions can be formulated from these expressions (see §5), but the Q-dependent X-ray form factors which replace the neutron scattering lengths result in more complex correlation functions (Warren, 1990; Wagner, 1985; Wright, 1974). Finally, it is emphasized that the functions $F(Q)$ and $S(Q)$ described here are total-scattering structure factors, as distinct from those often associated with Bragg scattering [such as the Bragg structure factor $F_{hkl}(Q)$].

2. Total-scattering nomenclature

2.1. Definitions

We start with the following definition of the double differential neutron cross section per unit solid angle, Ω, and energy interval, $\hbar\omega$, for a multi-component system (*e.g.* Lovesey, 1984):

$$\frac{1}{N}\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}\omega} = \frac{k'}{k}\sum_{i=1}^{n}\overline{b_i^2}S_i^s(\mathbf{Q},\omega) + \frac{k'}{k}\sum_{i,j=1,i\neq j}^{n}\bar{b}_i\bar{b}_jS_{ij}^d(\mathbf{Q},\omega), \quad (1)$$

where there are N atoms in the material which contains n distinct chemical species. k and k' are the initial and final wavevectors of the scattered neutron, respectively, and $\mathbf{Q} = \mathbf{k} - \mathbf{k}'$ is the scattering vector of length $4\pi\sin\theta/\lambda$ for a neutron of wavelength λ scattered at an angle 2θ. $S_i^s(\mathbf{Q},\omega)$ and $S_{ij}^d(\mathbf{Q},\omega)$ are the self and distinct parts of the structure factor, respectively. $\bar{b}_i$ is the coherent bound neutron scattering length of species i, averaged over the different isotopes and

nuclear spin states of i. Hence, for species i, the coherent scattering cross section $\sigma_i^{\mathrm{coh}} = 4\pi \bar{b}_i^2$, the total-scattering cross section $\sigma_i = 4\pi \overline{b_i^2}$ and the incoherent scattering cross section $\sigma_i^{\mathrm{inc}} = \sigma_i - \sigma_i^{\mathrm{coh}}$. By removing the $i = j$ term in the first summation and adding it to the second, we obtain

$$\frac{1}{N}\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}\omega} = \frac{k'}{k}\sum_{i=1}^{n}(\overline{b_i^2} - \bar{b}_i^2)S_i^{\mathrm{s}}(\mathbf{Q}, \omega) + \frac{k'}{k}\sum_{i,j=1}^{n}\bar{b}_i\bar{b}_j S_{ij}(\mathbf{Q}, \omega), \quad (2)$$

with the cross section now separated into an incoherent scattering term in $S_i^{\mathrm{s}}(\mathbf{Q}, \omega)$ and a coherent scattering term in $S_{ij}(\mathbf{Q}, \omega)$. In the static approximation and considering a system whose scattering is only dependent on $|\mathbf{Q}|$ and not on the direction of $\mathbf{Q}$ (*e.g.* a crystalline powder, liquid or amorphous material), we may integrate equation (2) over energy to obtain

$$\frac{1}{N}\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \sum_{i=1}^{n}(\overline{b_i^2} - \bar{b}_i^2)S_i^{\mathrm{s}}(Q) + \sum_{i,j=1}^{n}\bar{b}_i\bar{b}_j S_{ij}(Q). \quad (3)$$

Here $S_i^{\mathrm{s}}(Q) = c_i$, the proportion of species i in the material, and

$$S_{ij}(Q) = c_i c_j[A_{ij}(Q) - 1] + c_i\delta_{ij}, \quad (4)$$

where $A_{ij}(Q)$ are the Faber–Ziman partial structure factors (Faber & Ziman, 1965) and δ_{ij} is a Dirac delta function. This leads to the following, more familiar, re-arrangement:

$$\frac{1}{N}\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \sum_{i,j=1}^{n}c_i c_j\bar{b}_i\bar{b}_j[A_{ij}(Q) - 1] + \sum_{i=1}^{n}c_i\overline{b_i^2}. \quad (5)$$

$4\pi\sum_i c_i\overline{b_i^2}$ is the total-scattering cross section of the material. $A_{ij}(Q)$ are related to the partial radial distribution functions, $g_{ij}(r)$, as follows:

$$A_{ij}(Q) - 1 = \rho_0 \int_0^\infty 4\pi r^2[g_{ij}(r) - 1]\frac{\sin Qr}{Qr}\,\mathrm{d}r \quad (6)$$

and

$$g_{ij}(r) - 1 = \frac{1}{(2\pi)^3\rho_0}\int_0^\infty 4\pi Q^2[A_{ij}(Q) - 1]\frac{\sin Qr}{Qr}\,\mathrm{d}Q, \quad (7)$$

where $\rho_0 = N/V$ is the average number density of the material (in atoms $\mathrm{\mathring{A}}^{-3}$). $g_{ij}(r)$ are defined explicitly as

$$g_{ij}(r) = \frac{n_{ij}(r)}{4\pi r^2\,\mathrm{d}r\,\rho_j}, \quad (8)$$

where $n_{ij}(r)$ are the number of particles of type j between distances r and $r + \mathrm{d}r$ from a particle of type i and $\rho_j = c_j\rho_0$.

If the total-scattering structure factor, $F(Q)$, is defined as the interference term [or 'distinct scattering' (Hannon *et al.*, 1990)] in equation (5), then

$$F(Q) = \sum_{i,j=1}^{n}c_i c_j\bar{b}_i\bar{b}_j[A_{ij}(Q) - 1]. \quad (9)$$

A total radial distribution function, $G(r)$, is defined as

$$G(r) = \sum_{i,j=1}^{n}c_i c_j\bar{b}_i\bar{b}_j[g_{ij}(r) - 1], \quad (10)$$

such that $F(Q)$ and $G(r)$ are related to each other in an identical manner to $A_{ij}(Q)$ and $g_{ij}(r)$, *i.e.*

$$F(Q) = \rho_0 \int_0^\infty 4\pi r^2 G(r)\frac{\sin Qr}{Qr}\,\mathrm{d}r \quad (11)$$

and

$$G(r) = \frac{1}{(2\pi)^3\rho_0}\int_0^\infty 4\pi Q^2 F(Q)\frac{\sin Qr}{Qr}\,\mathrm{d}Q. \quad (12)$$

2.2. Limiting values

Since $A_{ij}(Q \to \infty) = 1$, $F(Q \to \infty) = 0$. For most simple systems, as $Q \to 0$, the values of $A_{ij}(Q)$ tend to

$$A_{ii}(0) - 1 \simeq \rho_0 k_B T\kappa_T - 1/c_i,$$
$$A_{ij}(0) - 1 \simeq \rho_0 k_B T\kappa_T, \quad (13)$$

where κ_T is the isothermal compressibility. However, when there are large chemical concentration fluctuations in the material, such as phase separation or critical behaviour, additional small-angle (low-Q) scattering may also occur. This is discussed in detail by Bhatia & Thornton (1970). For dense materials at modest temperatures, $\rho_0 k_B T\kappa_T$ is relatively small and, neglecting additional low-Q scattering,

$$F(Q \to 0) = -\sum_{i=1}^{n}c_i\bar{b}_i^2 + \eta, \quad (14)$$

where η accounts for the small contribution from the compressibility term. In most practical cases η can be ignored.

The limiting values for $g_{ij}(r)$ are 0 $[g_{ij}(r < r_{ij}^0)]$ and 1 $[g_{ij}(r \to \infty)]$, where r_{ij}^0 is the closest distance that atoms i and j may approach each other. The self-correlation terms, which would produce a delta function at $r = 0$, have been ignored. Following equation (10), the limiting values of $G(r)$ are correspondingly

$$G(r < r^0) = -\left(\sum_{i=1}^{n}c_i\bar{b}_i\right)^2,$$
$$G(r \to \infty) = 0. \quad (15)$$

r^0 is the shortest distance of the different r_{ij}^0.

2.3. Alternative normalizations

Equation (10) is not the only commonly used definition of $G(r)$. Indeed, $G(r)$ is often normalized further to remove the scaling arising from the species concentrations and scattering lengths, *i.e.*

$$G'(r) - 1 = G(r)\Big/\left(\sum_{i=1}^{n}c_i\bar{b}_i\right)^2, \quad (16)$$

which, when rearranged, leads to

$$G'(r) = \left(\sum_{i=1}^{n}c_i\bar{b}_i\right)^{-2}\sum_{i,j=1}^{n}c_i c_j\bar{b}_i\bar{b}_j g_{ij}(r). \quad (17)$$

This function now has the same limiting values as the $g_{ij}(r)$ from which it is composed:

$$G'(r < r^0) = 0,$$
$$G'(r \to \infty) = 1. \quad (18)$$

In addition, a normalized total-scattering structure factor $S(Q)$ is also often quoted,

$$S(Q) - 1 = F(Q) \Big/ \left(\sum_{i=1}^{n} c_i \bar{b}_i \right)^2, \qquad (19)$$

which, when rearranged, leads to

$$S(Q) = \left(\sum_{i=1}^{n} c_i \bar{b}_i \right)^{-2} \sum_{i,j=1}^{n} c_i c_j \bar{b}_i \bar{b}_j A_{ij}(Q). \qquad (20)$$

$S(Q)$ has the limiting values

$$S(Q \to 0) = -\sum_{i=1}^{n} c_i \bar{b}_i^2 \Big/ \left(\sum_{i=1}^{n} c_i \bar{b}_i \right)^2 + \eta',$$

$$S(Q \to \infty) = 1. \qquad (21)$$

Again η' is small. Both $G'(r)$ and $S(Q)$ appear independent of scattering factors and hence independent of the measurement method. However, this is only true for monatomic systems. For all other cases, the total functions are still composed of scattering-factor-weighted sums of the partial functions and are dependent on the measurement method. $S(Q)$ is described in more detail in §4.2.

2.4. Coordination numbers

The number of atoms of type j between distances r_1 and r_2 ($r_1 < r_2$) from an atom of type i is simply determined from the partial radial distribution functions, $g_{ij}(r)$, and inspection of equation (8), *i.e.*

$$\text{coordination} = \int_{r_1}^{r_2} 4\pi r^2 c_j \rho_0 g_{ij}(r)\,\mathrm{d}r. \qquad (22)$$

It is also possible to obtain local coordinations from total radial distribution functions, where individual peaks are known to arise from only one partial radial distribution function, although extra care is required to scale the result with the appropriate scattering factors.

3. HHS nomenclature

The *ATLAS* suite of programs (Soper *et al.*, 1989) is routinely used at ISIS and elsewhere to analyse neutron total-scattering data from liquid and amorphous materials and produce normalized differential neutron cross sections. Following the nomenclature of HHS, the differential cross section is defined as the sum of two terms, *i.e.*

$$\frac{1}{N}\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = I(Q) = I^S(Q) + i(Q), \qquad (23)$$

where

$$I^S(Q) = \sum_{i=1}^{n} c_i \frac{\sigma_i}{4\pi}, \qquad (24)$$

ignoring inelasticity effects. Comparing equation (23) with equations (5) and (9), it is evident that

$$i(Q) = F(Q). \qquad (25)$$

HHS define $D(r)$, the differential correlation function, and $T(r)$, the total correlation function, as

$$D(r) = \frac{2}{\pi} \int_0^\infty Q i(Q) \sin Qr \, \mathrm{d}Q \qquad (26)$$

and

$$T(r) = D(r) + T^0(r), \qquad (27)$$

where

$$T^0(r) = 4\pi r \rho_0 \left(\sum_{i=1}^{n} c_i \bar{b}_i \right)^2. \qquad (28)$$

Hence

$$D(r) = 4\pi r \rho_0 G(r) \qquad (29)$$

and

$$T(r) = 4\pi r \rho_0 \left[G(r) + \left(\sum_{i=1}^{n} c_i \bar{b}_i \right)^2 \right]$$

$$= 4\pi r \rho_0 \left(\sum_{i=1}^{n} c_i \bar{b}_i \right)^2 G'(r). \qquad (30)$$

$D(r)$ and $T(r)$ are defined in terms of their respective partial functions as follows:

$$T(r) = \sum_{i,j=1}^{n} c_i \bar{b}_i \bar{b}_j t_{ij}(r)$$

$$D(r) = \sum_{i,j=1}^{n} c_i \bar{b}_i \bar{b}_j d_{ij}(r) \qquad (31)$$

$$t_{ij}(r) = 4\pi r g_{ij}^{\text{HHS}}(r)$$

$$d_{ij}(r) = t_{ij}(r) - t_j^0(r)$$

where $t_j^0(r) = 4\pi r c_j \rho_0$. Note that $g_{ij}^{\text{HHS}}(r)$, the partial pair distribution functions, have the same r dependence as $g_{ij}(r)$ (partial radial distribution functions), but are distinct from $g_{ij}(r)$ since they tend to $c_j \rho_0$ rather than 1 at high r. This also means that $g_{ij}^{\text{HHS}}(r) \neq g_{ji}^{\text{HHS}}(r)$ and

$$\frac{g_{ji}^{\text{HHS}}(r)}{g_{ij}^{\text{HHS}}(r)} = \frac{c_i}{c_j}. \qquad (32)$$

Hence

$$t_{ij}(r) = 4\pi r c_j \rho_0 g_{ij}(r) \qquad (33)$$

and

$$d_{ij}(r) = 4\pi r c_j \rho_0 [g_{ij}(r) - 1]. \qquad (34)$$

4. Comparison with other formalisms

4.1. ACW formalism

Wright (1974) uses similar labels to those of HHS, but uses a less-common definition of concentration, defining it in terms of 'composition units', a formalism probably first utilized by Warren (1969). Although $t_{ij}(r)$ and $d_{ij}(r)$ have the same form as the HHS notation, the radial distribution function $g_{ij}^{\text{ACW}}(r) = 4\pi r^2 g_{ij}^{\text{HHS}}(r)$ and the radial density $\rho_{ij}^{\text{ACW}}(r) = g_{ij}^{\text{HHS}}(r)$.

In the ACW formulation,

$$I^{\mathrm{ACW}}(Q) = \sum_l \overline{b_l^2} + \sum_l \sum_m \bar{b}_l \bar{b}_m \int\limits_0^\infty 4\pi r^2 \rho_{lm}^{\mathrm{ACW}}(r) \frac{\sin Qr}{Qr}\, dr \quad (35)$$

or

$$I^{\mathrm{ACW}}(Q) = \sum_l \overline{b_l^2} + i^{\mathrm{ACW}}(Q). \quad (36)$$

There are two key differences between this formulation and those described previously, namely the manner in which $I^{\mathrm{ACW}}(Q)$ is normalized and the way in which the summations are carried out. First, $I^{\mathrm{ACW}}(Q) = (1/N_u)\, d\sigma/d\Omega$, where N_u is the number of composition units in the sample, which may be distinct from the number of atoms N. Secondly, the summations are over the l individual atoms in the composition unit and over the m atom types. Comparing equation (35) with equations (5) and (9), we see that

$$\frac{N_u}{N} \sum_l \overline{b_l^2} = \sum_{i=1}^n c_i \overline{b_i^2}, \quad (37)$$

$$F(Q) = \frac{N_u}{N} \sum_l \sum_m \bar{b}_l \bar{b}_m \int\limits_0^\infty 4\pi r^2 \rho_{lm}^{\mathrm{ACW}}(r) \frac{\sin Qr}{Qr}\, dr$$
$$= \frac{1}{Q} \frac{N_u}{N} \sum_l \sum_m \bar{b}_l \bar{b}_m \int\limits_0^\infty d_{ij}(r) \sin Qr\, dr \quad (38)$$

and

$$F(Q) = \frac{N_u}{N} i^{\mathrm{ACW}}(Q). \quad (39)$$

This factor N_u/N between $F(Q)$ and $i^{\mathrm{ACW}}(Q)$ leads to different scaling of the total-scattering structure factor. In the specific case of silica, SiO_2, which has three atoms per formula unit, there is a factor of three difference between $F(Q)$ and $i^{\mathrm{ACW}}(Q)$.

4.2. *PDFFIT* formalism

The *PDFFIT* program (Proffen & Billinge, 1999) is a means of refining local crystalline structures using real-space correlation functions which have been derived from diffraction data. The equations underpinning this program have been described by Billinge & Egami (1993) and Proffen & Billinge (1998). A normalized total-scattering structure factor, $S(Q)$, is defined by

$$\frac{1}{N} I(Q) = \left(\sum_{i=1}^n c_i \bar{b}_i \right)^2 [S(Q) - 1] + \sum_{i=1}^n c_i \overline{b_i^2}. \quad (40)$$

Assuming that $I(Q)$ can be directly equated with $d\sigma/d\Omega$, then, by comparing equation (40) with equation (5), it is clear that $S(Q)$ here also satisfies equations (19) and (20).

The PDF method uses a real-space correlation function, $\rho^{\mathrm{PDF}}(r)$, which tends to ρ_0 at high r and is zero below r^0. Hence

$$\rho^{\mathrm{PDF}}(r) = \rho_0 G'(r) \quad (41)$$

and

$$G(r) = \frac{[\rho^{\mathrm{PDF}}(r) - \rho_0]}{\rho_0} \left(\sum_{i=1}^n c_i \bar{b}_i \right)^2. \quad (42)$$

In addition, *PDFFIT* uses another function

$$G^{\mathrm{PDF}}(r) = 4\pi r[\rho^{\mathrm{PDF}}(r) - \rho_0] \quad (43)$$

such that

$$D(r) = 4\pi r \rho_0 G(r) = G^{\mathrm{PDF}}(r) \left(\sum_{i=1}^n c_i \bar{b}_i \right)^2. \quad (44)$$

By using equations (19) and (42) in equations (11) and (12),

$$S(Q) - 1 = \frac{4\pi}{Q} \int\limits_0^\infty r[\rho^{\mathrm{PDF}}(r) - \rho_0] \sin Qr\, dr \quad (45)$$

and

$$\rho^{\mathrm{PDF}}(r) - \rho_0 = \frac{1}{2\pi^2 r} \int\limits_0^\infty Q[S(Q) - 1] \sin Qr\, dQ. \quad (46)$$

4.3. AL formalism

Another formalism, introduced by Ashcroft & Langreth (1967) (hereafter referred to as the AL formalism) and described by Price & Sköld (1986), Susman *et al.* (1990) and Vashishta *et al.* (1989), is similar to the *PDFFIT* formalism, except that the partial structure factors are described using terms with the square-root of the species concentration. This formalism is not so readily related to the preceding formalisms, but is stated here for completeness.

$$\frac{1}{N} \frac{d\sigma}{d\Omega} = \sum_{i=1}^n c_i (\overline{b_i^2} - \bar{b}_i^2) + \sum_{i,j=1}^n (c_i c_j)^{1/2} \bar{b}_i \bar{b}_j S_{ij}^{\mathrm{AL}}(Q), \quad (47)$$

suggesting that (assuming that 'concentration' is actually 'proportion', c_i, as before)

$$S_{ij}^{\mathrm{AL}}(Q) = (c_i c_j)^{1/2} [A_{ij}(Q) - 1] + \delta_{ij}. \quad (48)$$

$S_{ij}^{\mathrm{AL}}(Q \to \infty)$ is equal to 1 if $i = j$ and to 0 if $i \neq j$.

$S(Q)$ is identical to that defined in equation (19) and

$$S(Q) - 1 = \left(\sum_{i=1}^n c_i \bar{b}_i \right)^{-2} \sum_{i,j=1}^n (c_i c_j)^{1/2} \bar{b}_i \bar{b}_j [S_{ij}^{\mathrm{AL}}(Q) - \delta_{ij}]. \quad (49)$$

The partial structure factors are defined in terms of the partial radial distribution functions, $g_{ij}(r)$,

$$g_{ij}(r) - 1 = \frac{1}{2\pi^2 \rho_0 (c_i c_j)^{1/2}} \int\limits_0^\infty Q^2 [S_{ij}^{\mathrm{AL}}(Q) - \delta_{ij}] \frac{\sin Qr}{Qr}\, dQ \quad (50)$$

or

$$S_{ij}^{\mathrm{AL}}(Q) - \delta_{ij} = 4\pi \rho_0 (c_i c_j)^{1/2} \int\limits_0^\infty r^2 [g_{ij}(r) - 1] \frac{\sin Qr}{Qr}\, dr \quad (51)$$

with a weighted total

$$g^{\mathrm{AL}}(r) = \left(\sum_{i=1}^n c_i \bar{b}_i \right)^{-2} \sum_{i,j=1}^n c_i c_j \bar{b}_i \bar{b}_j g_{ij}(r) \quad (52)$$

and

$$g^{\mathrm{AL}}(r) - 1 = \frac{1}{2\pi^2 \rho_0 r} \int\limits_0^\infty Q[S(Q) - 1] \sin Qr\, dQ. \quad (53)$$

Hence $g^{\mathrm{AL}}(r) = G'(r)$, $g^{\mathrm{AL}}(r \to \infty) = 1$ and $g^{\mathrm{AL}}(r < r^0) = 0$. The total correlation function, $T^{\mathrm{AL}}(r)$, is defined as

$$T^{AL}(r) = 4\pi r \rho_0 g^{AL}(r) = \left(\sum_{i=1}^{n} c_i \bar{b}_i \right)^{-2} T(r). \qquad (54)$$

4.4. Other formalisms

For completeness, note that Bhatia & Thornton (1970) describe one other common definition of partial structure factors, which is mostly used for binary systems. They separate the structure factor into partial structure factors which relate to the global structure of the material and into those which relate to chemical ordering. They have been rarely used for crystalline systems and their relationship with the partial structure factors $A_{ij}(Q)$ and $S_{ij}^{AL}(Q)$ is defined explicitly by Bhatia & Thornton (1970).

5. X-ray scattering nomenclature

In this section, a description of how total-scattering correlation functions may be obtained from X-ray scattering is presented. As alluded to in the introduction, this is not as straightforward as obtaining total-scattering correlation functions from neutron scattering, since the Q-dependent X-ray scattering factors modify some of the function definitions in a non-trivial manner. For this reason, a simple set of equations is developed here, without working through the various comparisons that are described in the previous sections for the neutron-weighted correlation functions. The superscript X is used to describe X-ray functions which are different from the equivalent functions used previously; the functions which do not have this superscript are identical to those already defined.

The extension to X-ray total scattering follows Pings & Waser (1968) and begins by exchanging the coherent bound neutron scattering lengths, $\bar{b}_i$, in equations (5) and (9) for the Q-dependent X-ray scattering factors, $f_i(Q)$,

$$F^X(Q) = \left[\frac{1}{N}\frac{d\sigma}{d\Omega} - \sum_{i=1}^{n} c_i f_i(Q)^2 \right] \Big/ \left[\sum_{i=1}^{n} c_i f_i(Q) \right]^2. \qquad (55)$$

Here we have also introduced a 'sharpening' term similar in form to that used in §2.3, although in this case, because of the nature of $f_i(Q)$, it serves to enhance the scattering at high Q. $F^X(Q)$, the X-ray weighted total-scattering structure factor, may also be written [following the relation in equation (6)] as

$$F^X(Q) = \rho_0 \sum_{i=1}^{n} c_i c_j f_{ij}(Q) \int_0^\infty 4\pi r^2 [g_{ij}(r) - 1] \frac{\sin Qr}{Qr} \, dr, \qquad (56)$$

where

$$f_{ij}(Q) = f_i(Q)f_j(Q) \Big/ \left[\sum_{i=1}^{n} c_i f_i(Q) \right]^2. \qquad (57)$$

The Fourier inverse of $F^X(Q)$ may be defined as [following equation (12)]

$$G^X(r) = \frac{1}{(2\pi)^3 \rho_0} \int_0^\infty 4\pi Q^2 F^X(Q) \frac{\sin Qr}{Qr} \, dQ, \qquad (58)$$

although the $f_i(Q)$ in $F^X(Q)$ mean that $G^X(r)$ will have very different behaviour from that of the neutron weighted $G(r)$. As such it is not always helpful to consider this function, particularly since, without care, it can lead to misconceptions. However, for completeness and in order to understand $G^X(r)$, we define $g_{ij}^X(r)$ such that

$$G^X(r) = \sum_{i,j=1}^{n} c_i c_j g_{ij}^X(r), \qquad (59)$$

where $rg_{ij}^X(r)$ is the convolution of $r[g_{ij}(r) - 1]$ and $j_{ij}(r)$,

$$g_{ij}^X(r) = \frac{1}{r} \int_{-\infty}^{\infty} y[g_{ij}(y) - 1] j_{ij}(r - y) \, dy, \qquad (60)$$

and $j_{ij}(r)$ is the Fourier transform of $f_{ij}(Q)$,

$$j_{ij}(r) = \frac{1}{\pi} \int_0^\infty f_{ij}(Q) \cos Qr \, dQ. \qquad (61)$$

To simplify the convolution above, the scattering factors are frequently approximated to $f_i(Q) = K_i f_e(Q)$, where K_i is the effective number of electrons for species i, approximately equal to the atomic number Z_i and

$$f_e(Q) = \sum_{i=1}^{n} c_i f_i(Q) \Big/ \sum_{i=1}^{n} c_i Z_i \qquad (62)$$

is an average scattering factor per electron for the material. Then

$$f_{ij}(Q) = K_i K_j \Big/ \left(\sum_{i=1}^{n} c_i K_i \right)^2 \qquad (63)$$

and $G^X(r)$ is now proportional to $[g_{ij}(r) - 1]$,

$$G^X(r) = \sum_{i,j=1}^{n} c_i c_j \frac{K_i K_j}{\left(\sum_{i=1}^{n} c_i K_i \right)^2} [g_{ij}(r) - 1]. \qquad (64)$$

6. Recommendations

As noted in the introduction, the various different functions are the result of attempting to highlight specific features. For example, $T(r)$, equation (30), or $D(r)$, equation (29), both scale as r and are often used because in the harmonic approximation the peaks are broadened symmetrically by thermal motions (Hannon *et al.*, 1990). In other cases, different functions are preferred for historical reasons. There are also advantages in using different functions when checking the effectiveness of data correction and others when comparing corrected data to calculated functions. It is therefore not easy to make recommendations for the 'best' functions to use in the general case, although it is hoped that this paper has shown the importance of being very specific when defining the functions used.

For total-scattering structure factors, clearly $F(Q)$ and $i(Q)$ are identical [see equation (25)], so both are acceptable! Although $S(Q)$ is only a simple scaling of $F(Q)$, by tending to unity at high Q, it gives the impression that the function is independent of scattering factors, which is clearly not the case.

$Qi(Q)$ is often plotted, but this does not make it easy to see where the $Q = 0$ limit is, although it may make it easier to plot the low-Q Bragg peaks and high-Q diffuse scattering on the same graph.

For real-space functions there are many options. $T(r)$ is useful for peak fitting. However, $T(r)$ and functions which scale as r^2 are not convenient for plotting, especially for crystalline systems, since the plot area is quickly exceeded and the structural detail at high r is lost. Equally, $G(r)$ may not be ideal because it makes the low-r peaks prominent. $D(r)$ is probably the best compromise. However, $d_{ij}(r)$ are not necessarily the best real-space partial functions since $d_{ij}(r) \neq d_{ji}(r)$ is confusing. Also, since the real-space partial functions are often used to distinguish between low-r features in the structure and because $g_{ij}(r)$ are genuinely scattering-factor independent, these are the recommended functional forms for presenting real-space partial functions.

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