Notes On Scattering/Diffraction Theory And Its Extension To The Pair Distribution Function (PDF) Formulation

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Once we have defined the origin of a lattice system, we can then write down the scattering effect from a single particle j located at $\mathbf{r}_j$ as the corresponding structure factor (for a single atom):

$$F_j(\mathbf{Q}) = exp(i\mathbf{Q} \cdot \mathbf{r}_j) \tag{1}$$

Then for a discrete system where we have a collection of atoms, the scattering effect can be simply written down as the overall structure factor for the system:

$$F(\mathbf{Q}) = \sum_j exp(i\mathbf{Q} \cdot \mathbf{r}_j) \tag{2}$$

As for a continuous system, we can write down the scattering factor corresponding to an infinitely small region as:

$$dF(\mathbf{Q}) = \rho(\mathbf{r})exp(i\mathbf{Q} \cdot \mathbf{r})dV \tag{3}$$

where the $\rho(\mathbf{r})dV$ gives the number of particles within the small region dV, and all particles located within that infinitely small region gives the same scattering factor $exp(i\mathbf{Q} \cdot \mathbf{r})$. Therefore the scattering factor corresponding to the whole distribution becomes:

$$F(\mathbf{Q}) = \int \rho(\mathbf{r})exp(i\mathbf{Q} \cdot \mathbf{r})d\mathbf{r} \tag{4}$$

From equation-4, we know that in general for any distribution of scatters, the corresponding scattering factor is just the Fourier transform of the distribution function. Now, we consider a general type of distribution where we have the scatters (e.g. electrons for X-ray scattering) distributed around a certain position (e.g. the nucleus position). Such a distribution can be mathematically described as:

$$\rho_j(\mathbf{r}) \otimes \delta(\mathbf{r} - \mathbf{r}_j) \tag{5}$$

where $\mathbf{r}_j$ is the nucleus position and $\rho_j(\mathbf{r})$ refers to the corresponding electron density distribution (here it should be noticed the different meaning of $\rho(\mathbf{r})$ in equation-4 and 5. In equation-4, it means general distribution function of the scatters, and in equation-5, it means specifically the distribution of electrons. The whole expression of 5 is actually the $\rho(\mathbf{r})$ in 4). Then according to the principle discussed above, the Fourier transform of 5 will give the scattering factor corresponding to the scatter distribution function specified by 4:

$$\begin{aligned} F_j(\mathbf{Q}) &= \mathcal{F}[\rho_j(\mathbf{r}) \otimes \delta(\mathbf{r} - \mathbf{r}_j)] \\ &= \mathcal{F}[\rho_j(\mathbf{r})] \times \mathcal{F}[\delta(\mathbf{r} - \mathbf{r}_j)] \\ &= f_j(\mathbf{Q})exp(i\mathbf{Q} \cdot \mathbf{r}_j) \end{aligned} \tag{6}$$

where $f_j(\mathbf{Q})$ is just the form factor of atom-j, defined as:

$$f_j(\mathbf{Q}) = \int \rho_j(\mathbf{r})exp(i\mathbf{Q} \cdot \mathbf{r})d\mathbf{r} \tag{7}$$

Again, attention should be paid here about the different meaning of $\rho(\mathbf{r})$ in equation-4 and 7 as already discussed above.
Furthermore, if considering all the atoms in the system, the overall structure factor can be written as:

$$F(\mathbf{Q}) = \sum_j f_j(\mathbf{Q})exp(i\mathbf{Q} \cdot \mathbf{r}_j) \tag{8}$$

Equation-8 gives the expression for the structure factor for a general system where we have a whole bunch of atoms and intuitively we can think of the form factor $f_j(\mathbf{Q})$ as the contribution to the scattering factor from each

single atom-j. From equation-8, the scattering theory then can be extended to the derivation of the pair distribution function, which will be covered next. But before that, it should be pointed out that the equation-8 for the overall structure factor is still not general enough to take into account of the contributors (to the structure factor). In the most general situation, we describe the crystal structure as convoluted by several parts:

$$
\begin{aligned}
&Crystal\ structure \\
&= lattice \otimes unit\ cell \otimes electrons\ in\ atoms \otimes thermal\ motion
\end{aligned} \tag{9}
$$

To put equation-9 in a specific way, let's assume we have three atoms in the unit cell located at $\mathbf{r}_1$, $\mathbf{r}_2$ and $\mathbf{r}_3$, respectively. The electrons (here, assuming we are talking about X-ray scattering, which is actually the scattering from electrons) density for each atom in the unit cell is given as $\rho_1(\mathbf{r})$, $\rho_2(\mathbf{r})$ and $\rho_3(\mathbf{r})$, respectively. Also in real situation, the atoms are not staying at the equilibrium position, and the distribution of atom displacements from the average position can be written as $p_1(\mathbf{r})$, $p_2(\mathbf{r})$ and $p_3(\mathbf{r})$, respectively for the three atoms in the unit cell in current situation. Moreover, the lattice structure can be defined as the sum of a series of δ function:

$$
L(\mathbf{r}) = \frac{1}{V} \sum_j \delta(\mathbf{r} - \mathbf{r}_j) \tag{10}
$$

where $\mathbf{r}_j$ refers to the lattice points and V is the normalization factor. Now for our currently assumed system, equation-9 specifically becomes:

$$
\begin{bmatrix}
\rho_1(\mathbf{r}) \otimes \delta(\mathbf{r} - \mathbf{r}_1) \otimes p_1(\mathbf{r}) \\
+ \\
\rho_2(\mathbf{r}) \otimes \delta(\mathbf{r} - \mathbf{r}_2) \otimes p_2(\mathbf{r}) \\
+ \\
\rho_3(\mathbf{r}) \otimes \delta(\mathbf{r} - \mathbf{r}_3) \otimes p_3(\mathbf{r})
\end{bmatrix} \otimes \frac{1}{V} \sum_j \delta(\mathbf{r} - \mathbf{r}_j) \tag{11}
$$

Then the overall structure factor is just the Fourier transform of the whole expression-11.

Next we will move on to the discussion about the PDF pattern to see how we can go from the basic scattering theory to the establishment of the theoretical description of PDF. Going back to the expression-11, let's first of all consider the thermal vibration part $p(\mathbf{r})$. If we just want to focus on the static structure and the corresponding structure factor, we can ignore the convolution of the $p(\mathbf{r})$ function. This does make sense, for example, for the big-box modeling since the thermal motions of atoms can be represented by the various positions corresponding to different structure configurations obtained from the data-driven simulation. The expression-11 can be further simplified, again, considering the big-box modeling. Taking the first atom in expression-11 in the unit cell as an example, the corresponding Fourier transform can be written as:

$$
\mathcal{F}[\rho_1(\mathbf{r}) \otimes \delta(\mathbf{r} - \mathbf{r}_1) \otimes p_1(\mathbf{r})]
$$

$$
= \mathcal{F}[\rho_1(\mathbf{r})] \times \mathcal{F}[\delta(\mathbf{r} - \mathbf{r}_1)] \times \mathcal{F}[\frac{1}{V} \sum_j \delta(\mathbf{r} - \mathbf{r}_j)]
$$

$$
= \frac{1}{V} \sum_j f_1(\mathbf{Q}) exp(i\mathbf{Q} \cdot \mathbf{r}_1) exp(i\mathbf{Q} \cdot \mathbf{r}_j)
$$

$$
= \frac{1}{V} \sum_j f_1(\mathbf{Q}) exp[i\mathbf{Q} \cdot (\mathbf{r}_j + \mathbf{r}_1)] \tag{12}
$$

Here $\mathbf{r}_j + \mathbf{r}_1$ in expression-12 refers to the actual position in the whole system of atom-1 belonging to unit cell j. Since the index j goes over all the lattice points, the expression-12 therefore goes over all atom-1 in the whole system. Then we know that expression-12 goes back to 8 where we consider all

the scattering atoms independently without even talking about the lattice! This is natural since anyways the lattice structure is just an abstract notion that we introduce to describe the crystal structure. Therefore the structure factor, which is physical quantity, really should not depend on whatever method we use to describe the system. Hereafter, we will then start from expression-8 to derive the PDF formulation – we are going to focus on the big box modeling where we don't have the unit cell. To do this, we should first of all think about what we are measuring experimentally. The structure factor given by 8 is a complex number, which, obviously cannot be measured directly in experiments. What we can measure (and indeed we are measuring) is the module of 8, which can be written as:

$$
|F(\mathbf{Q})|^2 = \left| \sum_j f_j(\mathbf{Q}) exp(i\mathbf{Q} \cdot \mathbf{r}_j) \right|^2
$$
$$
= \sum_{j,k} f_j(\mathbf{Q}) f_k(\mathbf{Q}) exp[i\mathbf{Q} \cdot (\mathbf{r}_j - \mathbf{r}_k)] \tag{13}
$$

Till now, we keep writing the atomic form factor as $f(\mathbf{Q})$ which means it is the function of $\mathbf{Q}$. This is indeed true for X-ray scattering. But for neutron scattering, the neutron beam does not 'see' the electrons and hence we don't have the $\mathbf{Q}$-dependent form factor. What we have instead is a $\mathbf{Q}$-independent **scattering length**, which goes to the same place as $f(\mathbf{Q})$ in equation-8 as a constant modulation for the overall structure factor. At this stage, for simplicity, we focus on the neutron scattering formulation instead of X-ray and we use b to replace $f(\mathbf{Q})$ for clearance.

Also we can notice from 13 that as we are calculating/measuring the module of $F(\mathbf{Q})$, we cannot go back from $|F(\mathbf{Q})|^2$ to obtain the information about the absolute position of atoms. All we can get is the relative position (i.e. PDF, specified by $\mathbf{r}_j - \mathbf{r}_k$). Therefore we are going to start from here to see how we can establish the theoretical description for PDF. Before starting, there is still one thing we haven't considered yet – the concentration of different types of atoms in the system. This should definitely influence the absolute scale of the contribution to the structure factor from certain type of atoms. Putting all of the recipes together we now have the structure factor (the module) for neutron scattering:

$$
|F(\mathbf{Q})|^2 = \sum_{j,k} c_j c_k b_j b_k exp[i\mathbf{Q} \cdot (\mathbf{r}_j - \mathbf{r}_k)] \tag{14}
$$

Now, let's define the function $G(\mathbf{r})$ as:

$$
G(\mathbf{r}) = \sum_{j,k} c_j c_k b_j b_k \left[\frac{1}{V} \Big[\delta[\mathbf{r} - (\mathbf{r}_j - \mathbf{r}_k)] - \delta(\mathbf{r}) \Big] \right] \tag{15}
$$

Currently let's not think about what the defined $G(\mathbf{r})$ function means, just Fourier transforming it to see what we will get:

$$
\mathcal{F}\big[G(\mathbf{r})\big] = \mathcal{F}\left(\sum_{j,k} c_j c_k b_j b_k \left[\frac{1}{V} \Big[\delta[\mathbf{r} - (\mathbf{r}_j - \mathbf{r}_k)] - 1 \Big] \right] \right)
$$
$$
= \sum_{j,k} \frac{c_j c_k b_j b_k}{V} \mathcal{F}\Big[\delta[\mathbf{r} - (\mathbf{r}_j - \mathbf{r}_k)] \Big] - \sum_{j,k} c_j c_k b_j b_k \mathcal{F}\Big[\frac{\delta(\mathbf{r})}{V} \Big]
$$
$$
= \sum_{j,k} c_j c_k b_j b_k exp[i\mathbf{Q} \cdot (\mathbf{r}_j - \mathbf{r}_k)] - \sum_{j,k} c_j c_k b_j b_k \tag{16}
$$

From equation-16 we can see that the Fourier transform of the defined function $G(\mathbf{r})$ is equivalent to the structure factor given by 14 with just an extra constant (the second term in the third line of equation-16). Since

we already know that the Fourier transform of the structure factor is just the distribution function of the scatters, hence now we know that the defined function $G(\mathbf{r})$ just decribes the distribution of the scatters (atoms) – the pair correlation.

In practice for the neutron total scattering measurement, there are actually several different forms for the definition of the pair correlation. Also there may be introduced many symbols and notions to go through the Fourier transform in between real and recipocal space. Detailed introduction about the formulation can be found in D. Keen's review paper: Click Me! Taking two of them as examples here, we can see how the formulation of total scattering theory is correlated to the basic theory talked about in this context. The first one is the so-called Faber-Ziman partial structure factor, which, according to D. Keen's paper, is given as $A_{i,j}(Q)$ in the following expression:

$$F(Q) = \sum_{i,j}^{n} c_i c_j \bar{b}_i \bar{b}_j [A_{ij}(Q) - 1] \tag{17}$$

By comparing 17 to 16 (here, the original form of 17 is taken from D. Keen's paper, where $F(Q)$ and $A(Q)$ actually means the module. Also it should be noticed that the 'F(Q)' in 17 does contain the constant term while the formulation given in 14 does not. In literatures, there exists some confusions in the usage of such symbols to represent different theoreticla notions, and again for details, refer to the review paper by D. Keen: Click Me! Usually, the '$F(Q)$' in 14 (the one without the constant term) is called $S(Q)$) , we could find that the Faber-Ziman partial structure factor is just the expotential part in the first term of the third line in 16. The second example is the practical realization of the δ function in the definition of the pair correlation function $G(\mathbf{r})$. In practice for a given box of atoms, the corresponding $G(r)$ (here the vector is no longer used since we are concerning the powder samples under the neutron beam where the direction does not really matter) function is given as:

$$G(r) = \sum_{i,j}^{n} c_i c_j \bar{b}_i \bar{b}_j [g_{ij}(r) - 1] \tag{18}$$

where g_{ij} is given as:

$$g_{ij}(r) = \frac{n_{ij}(r)}{4\pi r^2 dr\, \rho_j} \tag{19}$$

Here $n_{ij}(r)$ are the number of particles of type j between distances r and $r + dr$ from a particle of type i and $\rho_j = c_j \rho_0$, where c_j is the number concentration of atom j. Also it should be mentioned that the pratical formulation of the Fourier transform in between the real and reciprocal space is given as:

$$F(Q) = \rho_0 \int_0^\infty 4\pi r^2 G(r) \frac{\sin Qr}{Qr} dr \tag{20}$$

and

$$G(r) = \frac{1}{(2\pi)^3} \int_0^\infty 4\pi Q^2 F(Q) \frac{\sin Qr}{Qr} dQ \tag{21}$$

As for how the complex form of the Fourier transform becomes the real form given by 20 and 21, this is owing to the isotropic orientational average, for which we can refer to Appendix-J in Martin Dove's book on general crystallography: Click Me! (here, it should be pointed out that in Martin's book, the symbol used for the Q-space function is consistent with current context, e.g. 14, which is however, as mentioned above, the other way round in D. Keen's review paper)

Now, it's time to go back to the original formulation 13 where the factor $f(\mathbf{Q})$ is not a constant, which is exactly the case for X-ray scattering. Taking

the atom concentration c into consideration, also assuming we have two types of atoms in the system, the equation-13 can be written as:

$$|F(\mathbf{Q})|^2 = [c_1 f_1(\mathbf{Q})]^2 \sum_{j_1, k_1} exp[i\mathbf{Q} \cdot (\mathbf{r}_{j_1} - \mathbf{r}_{k_1})]$$
$$+ [c_1 c_2 f_1(\mathbf{Q}) f_2(\mathbf{Q})]^2 \sum_{j_1, k_2} exp[i\mathbf{Q} \cdot (\mathbf{r}_{j_1} - \mathbf{r}_{k_2})]$$
$$+ [c_2 f_2(\mathbf{Q})]^2 \sum_{j_2, k_2} exp[i\mathbf{Q} \cdot (\mathbf{r}_{j_2} - \mathbf{r}_{k_2})] \tag{22}$$

Here in 22, in each term on the right-hand side, the sum is just the Fourier transform of the sum of a series of δ functions representing the different pair of atoms in the system. The problem for X-ray scattering is that if we want to go from 22 to real space by direct Fourier transform, we find that the **Q**-dependence of the form factor makes it impossible to go directly back to the properly defined real-space pair correlation functions (as a matter of fact, what we get will be the complicated convlution of the atomic position function (the sum of δ functions) and the electron density function of different types of atoms in the system). Ideally, if we can measure the partial scattering corresponding to each different types of pairs (e.g. 1-1, 1-2 and 2-2 pairs for the assumed two-type-of-atoms system), then we can divide each of the three terms on the right-hand side of 22 by the corresponding **Q**-dependent form factor (which can be tabulated) to obtain the pure atomic position concerned structure factor. Then carrying out the Fourier transform will give us the properly defined pair correlation function as that for the neutron scattering. Unfortunately, this is not the case in practice. Currently, the way that RMCProfile uses to deal with such a problem is to divide the Q-space data by a normalized Q-dependent factor to try to get rid of of the Q-dependent part in each term in the right-hand side of 22. However, obviously we can see the problem with such an approximation especially when the difference of the form factors between different types of atoms included in the concerned system is large. Finally, it should be mentioned that since the X-ray experimental scattering data is processed with the approximation mentioned above for RMCProfile to refine, then definitely we should implement the same approximation when calculating the theoretical X-ray scattering r-space pattern (for Q-space refinement, since there is no need for the Fourier transform for the experimental data, therefore there is not the problem of the Q-dependent form factor at all).