The technique of RDF of nanovolumes using electron diffraction

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Abstract. Amorphous materials are not, as the Greek etymology suggests, “without form”. Indeed, as with crystalline materials, their structure determines their properties. The overwhelming number of structural studies of amorphous materials use the diffracted intensity to give the radial distribution function, which can be used as data against which to test, or refine, structural models. Neutron and X-ray diffraction examples abound. However, neutrons and X-rays are of no use when small volumes are involved. This paper reports the current state of RDF analysis of nanovolumes using electron diffraction.

1. The RDF technique
The structure of amorphous materials is widely investigated by using the direct mathematical relationship between \( I(q) \), the scattered intensity as a function of the scattering vector \( q \), and the radial distribution function \( J(r) \). The relationship assumes single scattering. Comparing \( J(r) \) (or its associated parameters \( \phi(q) \) (the reduced intensity) or \( G(r) \) (the reduced density function)) from experiment with the equivalent functions derived from modeled structures gives a test of the model structure, at least in terms of the first order correlation function. The model can be refined against the experimental data using e.g. Reverse Monte Carlo (RMC) or other techniques, and constraints can be applied during the refinement.

This procedure has been widely employed using both neutron and X-ray scattering. It is also used in electron diffraction from gases, where the density of the gas can be such as to ensure single scattering. This paper reviews the current state of the technique using electron diffraction for studying amorphous solids.

2. The electron RDF technique
Grigson [1] and Gragzyk and Moss [2] were the first to use electron \( I(q) \) to give \( J(r) \) from thin samples of solid materials. Difficulties with maintaining calibration and collecting \( I(q) \) to sufficiently high \( q \) resulted in there being no further progress until Cockayne and McKenzie [3] realized that advances in electron optics and data collection overcame some of these difficulties. The key issues in obtaining reliable data are the following.

2.1. Calibration of \( q \)
Since \( G(r) \) is a Fourier transform of a function of \( I(q) \) (see equation below), inaccuracy in the calibration of \( q \) leads directly to errors in the scale of \( r \) (bond lengths). Consequently a major part of
RDF analysis with electrons is determining and maintaining a stable calibration of \( q \) (camera length) throughout an experiment. The optimum approach is to use an internal crystalline standard; using external standards requires a thorough appreciation and minimization of changes in camera length which can result from experimental variables such as sample height and lens hysteresis. With carefully developed protocols, an accuracy of \( \pm 0.5\% \) can be achieved.

To obtain precision in \( G(r) \), \( I(q) \) needs to be collected to large \( q \). We routinely use CCDs with 2048 \( \times 2048 \) pixels (or even larger), which, operating at a small camera length, allows collection to \( q = 220 \) nm\(^{-1}\). Transmission electron microscopes are not optimized for linearity over such a wide range of \( q \), but calibration of the camera length as a function of \( q \) can minimize problems.

2.2 Sample thickness

The conversion of \( I(q) \) to \( G(r) \) assumes single scattering, easily achieved with neutrons and X-rays, but more difficult to achieve with electrons. There are two tests available to determine whether a sample is sufficiently thin. Firstly, multi-slice calculations using a large super-cell of a model amorphous structure can give \( I(q) \) as a function of thickness. Secondly, the goodness of fit of the atomic scattering curve \( Nf^2(q) \) (\( N \) a fitting parameter) to \( I(q) \) throughout the range of \( q \) can be tested (the fit deteriorates with multiple scattering) (See Figure 1). Thirdly, if the ratio of elastic to inelastic mean free paths is known, the latter can be determined from EELS. Finally there is the possibility of recovering single scattering \( I(q) \) from multiple scattering data Chen et al (to be published).

![Figure 1. Comparison of single scattering \( I(q) \) with no correlations and experimental \( I(q) \) from GeSbTe. The inset is the enlargement at high \( q \) up to 25 Å\(^{-1}\).](image)

2.3 Inelastic scattering

The conversion of \( I(q) \) to \( G(r) \) assumes elastic scattering. In early studies, this was thought to be a major problem, and elastic data was collected using energy filters (e.g. [1], [4]). However our recent studies show that, provided one is within the single scattering regime of thickness, the major difference between filtered and unfiltered data arises from dispersion within the energy filter i.e. drift of the energy selecting aperture on the energy loss spectrum with \( q \). Figure 2 demonstrates this effect. When this problem is overcome, we have observed little advantage in using energy filtered data. TDS could in principle be important, but its effects can be reduced by cooling the sample.
3. Electron RDF from nanovolumes
To obtain the RDF from a local volume of amorphous material, three methods are possible:

3.1 Small probe
Modern TEM/STEMs can produce a focused electron beam as small as 0.1nm in width. Such a narrow beam results in a diffraction pattern without sufficient averaging for RDF analysis. A probe of width 1nm can be usefully used, provided it can be made sufficiently parallel not to convolute $I(q)$ with the angular probe function. McBride et al [5] have discussed the possibility of deconvoluting such data, but this is difficult to do routinely. Establishing a protocol which will maintain a calibrated camera length requires care to achieve in practice.

3.2 Selected area diffraction
It is well known that the diffraction data at the scattering angle $q$ arises from the local sample at position $C_c q^3$. If one is investigating the RDF from local regions, this can cause a difficulty. The use of an aberration corrected TEM removes the problem. After that, $C_c$ will be the limiting aberration.

3.3 Exit wave reconstruction
Koch and Garofalini [6] showed that a small local region of the exit wave, reconstructed from a through-focal or through-tilt series, could be used to give the selected area diffraction pattern without the effects of lens aberrations as in 3.2. The shortcoming of this method is that the resultant range of $q$ over which $I(q)$ is obtained is limited to the range of data faithfully passed by the restoration process. This is well below $q = 220 \text{ nm}^{-1}$ achievable by straightforward diffraction, and so limits the achievable precision in $G(r)$.

4. Converting $I(q)$ to $G(r)$
$I(q)$ can be investigated as a function of scattering direction, but generally improved signal to noise is achieved by azimuthally averaging the data. First the centre of the diffraction pattern must be found. Various techniques are available, including a Digital Micrograph plug-in involving drawing circles through points of equal intensity. Tests show that the centre can be determined to a precision of 1 pixel. Averaging data azimuthally (taking into account pixels necessarily masked because of the beam stop) leads to $I(q)$ with good signal to noise even at the highest $q$. For improved signal to noise at high $q$, diffraction patterns with different exposure times can be overlapped, or repeated patterns can be accumulated.
Figure 1 shows the output from a program which compares the experimental \( I(q) \) with the scattering from an amorphous alloy with no correlations, using the parameterised forms of the atomic scattering factors \( f_i(q) \) [e.g. [7]], and which accepts \( N \) and \( c_i \) (the number of atoms and the atomic concentrations of different atomic species) as variables. The \( c_i \) are generally known for a given sample, or can be determined by EDX or EELS, and \( N \) can be chosen to match the two curves at a selected \( q \). It is the difference between these two curves which carries the information about local order, and which, when Fourier transformed, gives \( G(r) \). In this way, \( G(r) \) can be obtained from \( I(q) \) on line at the microscope.

The expression which relates \( G(r) \) to \( I(q) \) is

\[
G(r) = 4\int_0^\infty \phi(q)\sin(qr)dq \quad \text{where} \quad \phi(q) = \frac{I(q) - N \langle f_i(q)^2 \rangle}{N \langle f_i(q)^2 \rangle} \quad \text{is the reduced intensity function.} \quad \phi(q) \text{ can be damped by an expression such as } \exp(-bq^2), \text{ where } b \text{ is the damping factor, to reduce the effects of limited experimental data range and noise at high } q.
\]

5. Using \( G(r) \) to refine models of amorphous structures

There is an extensive literature on the interpretation of \( G(r) \) from X-rays and neutrons in terms of nearest neighbour distances and coordination numbers, and this is directly transferable to electron RDF. There is, however, no technique for experimentally obtaining partial RDFs with electrons, as there is with neutrons and X-rays. For single element materials, nearest neighbour distances can be read directly from the peak positions in \( G(r) \), we find to an accuracy of 0.01\( \text{A} \). For alloys, the interpretation of \( G(r) \) is not necessarily straightforward. \( G(r) \) (or \( \phi(q) \)) can be compared with the equivalent expression derived from a model structure, and the model can be refined, with or without constraints, through a reverse Monte Carlo (RMC) procedure which follows techniques used with X-rays and neutrons (see e.g. [8]). A typical protocol is shown in Figure 3.

**Figure 3.** Protocol (flow diagram) for model refinement

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