Electron Pair-Distribution Function (ePDF) Analysis

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Introduction

A crystal structure can be described by a combination of the unit cell content and the translation vectors of this cell. In this case one can easily calculate which atoms are placed at each point of a crystal. In a disordered or amorphous material, the atomic arrangement does not follow a strict lattice rule; therefore, it is in principle impossible to know exact atomic composition at a specified point. The structure of such material is described by a Pair Distribution Function (PDF) – a probability to find an atom at a certain distance r from a given atom. The first peak in a PDF (having the shortest r-value) corresponds to a direct interatomic distance. The integrated intensity of the peak represents the number of atoms at this distance, therefore describing the coordination of atoms in the structure. For nanocrystalline and amorphous materials a PDF curve will soon go down to zero. A distance, at which the PDF does not have any peaks anymore, is related to a distance in the structure at which atoms know nothing about other atoms – there are no correlations anymore. Other valuable information about defects and atomic arrangement can be obtained from PDFs.

Experimental data for PDFs has special requirements. Typically, PDF experiments are done using synchrotron facilities or neutron spallation sources. These experiments are quite sophisticated and costly. Here an alternative experimental setup using electron radiation is demonstrated. Electron diffraction experiment for PDF can be done using a Transmission Electron Microscope (TEM) – an instrument available in many laboratories across the world.

Models of amorphous materials

Understanding medium-range structural order in amorphous materials is a long-standing problem. In contrast to periodically arranged crystalline materials, in amorphous solids, the positions of atoms cannot be predicted by any equation based on the translation vectors. Analogous to an ideal crystal, one can speak of a ideal amorphous solid¹, for which any straight line of arbitrarily direction that passes through atoms will meet atoms at irregular intervals of a random sequence, which can be represented by a corresponding statistical distribution function. In reality most amorphous materials have a short-range order (SRO), which typically resent in a corresponding crystalline phase. The difference between amorphous and crystal structures must therefore lie at distances outside the first coordination shell, in the medium-range order (MRO) region.

In 1932 Zachariasen proposed a simple method to build a model of an oxide glass based on a few simple rules²: (1) an oxygen atom is linked to not more than two atoms A; (2) the number of oxygen atoms surrounding atoms A must be small; (3) the oxygen polyhedra share corners with each other, not edges or faces; (4) at least three corners in each oxygen polyhedron must be shared. The fourths rule brings the third dimension in the model. Although being a very simple construction, the method retained its actually up to now – most models of oxide glasses, like SiO₂, are created using the continuous random network (CRN) model.

Metallic glasses were first reported in 1960³, opening a new direction in the modeling of amorphous solids - random packing structures (RPS). Metallic glasses are believed not to have directional interactions, and thus, only reflect the size and the nearest coordination of the different metals constituting the sample. Nevertheless, it was shown that some materials can have a hidden order in the MRO region responsible for different packing in crystalline structures⁴. ⁵ As in the case of ice⁶, different amorphous states can realize for metallic glasses⁷, thus we can talk of polyamorphism of these materials.

Many more modelling concepts of homogeneous non-periodic networks can be found in ^{8,9}.

The structure of amorphous Si was long under particular interest due to varying physical properties of the material. Different content of H-terminated bonds has a great effect on the structure¹⁰ and

the effectiveness in solar-cells applications.¹¹ The view on amorphous silicon completely changed recently with a report on a paracrystalline structure with a local ordering on 10 to 20 Angstrom length scale.¹²

In recent years the interest to organic glasses increased significantly.¹³ Hybrid organic-inorganic networks provide even more flexibility in designing physical properties.¹⁴ Despite intensive investigations, it is yet unclear what the true structure of the materials is, though a very recent study showed that molecular compounds can form textured poly-crystalline structures.¹⁵

Especially for molecular materials ¹⁶ Molecular Dynamics (MD) simulations is an essential tool for the structure understanding. In the meantime, MD has become the standard method of producing a model of an amorphous material. In an MD experiment atoms are represented by point particles with more or less realistic interactions, and the equations of motion are integrated numerically.



Figure 1 A model of water (hydrogen-bonds are shown with blue dashed lines) produced by MD using VMD software¹⁷.

The aim of this short section was to demonstrate a variety of different mathematical concepts used to create models for different materials. The most general way to compare the models is to describe them in the terms of (1) atomic density; (2) average coordination number and its variability, and (3) the radial distribution function.

PDF as a structure fingerprint

Different correlation functions can be used in order to describe an atomic distribution. ¹⁸ The common variables used to describe the correlations are:

- f_i scattering power of the atom *i*;
- $f_i(0)$ scattering power of the atom *i* at the scattering angle position 0;
- r_{ij} scalar distance between two atoms *i* and *j*;
- N total number of atoms in a sample;
- ρ_0 number density of atoms

Radial distribution function, R(r) is defined as

$$R(r) = \frac{1}{\langle f(0) \rangle^2} \sum_i \sum_j f_i(0) f_j(0) \delta(r - r_{ij})$$

The atomic scattering factors f(s) for electrons are tabulated¹⁹ and are functions of the scattering vector. Note, that the electron scattering factors are measured in Angstroms, while the electron form-factors (*ff*) are dimensionless and are calculated from the corresponding scattering factors using the equation:

$$f(s)[\text{\AA}] = \frac{m_e e^2}{2\pi\hbar^2 s^2 \mathcal{E}_0} ff(s)$$

Here m_e is the electron mass, e is the electron charge, \hbar is the Planck constant, and \mathcal{E}_0 is the vacuum permittivity.

Figure 2 shows the electron atomic scattering curves for oxygen (blue), hydrogen (black), and the average scattering amplitude for water molecule calculated as

$$\langle f \rangle = \frac{1}{3} f_{oxygen} + \frac{2}{3} f_{hydrogen}$$

The values for the atomic scattering factors at zero-scattering angle position are²⁰ 1.983 for oxygen, 0.529 for hydrogen and 1.499 for water molecule average scattering.

For an MD water model consisting of 3921 water molecules (3921 oxygen and 7842 hydrogen atoms) shown in Figure 1, the radial distribution function is shown in Figure 3. The radial distribution function grows very fast with r, making it difficult to work with medium range distances, therefore another correlation function – the real-space pair density was defined. The value of $\rho(r)$ is the probability density of finding an atom at the distance *r* from a given atom.

$$\rho(r) = \frac{1}{4\pi r^2 N \langle f(0) \rangle^2} \sum_i \sum_j f_i(0) f_j(0) \delta(r - r_{ij})$$

The $\rho(r)$ for the water model is shown in Figure 4. Finally, the atomic pair distribution function (PDF) is given by:

$$g(r) = \frac{1}{rN\langle f(0) \rangle^2} \sum_i \sum_j f_i(0) f_j(0) \delta(r - r_{ij}) - 4\pi r \rho_0 = 4\pi r(\rho(r) - \rho_0)$$

The PDF for the water model is presented in Figure 5.

The PDF concept is general – it can be applied to any arrangement of atoms, also to ideal or nonideal crystals. Figure 6 shows a PDF of an fcc gold cluster consisting of 610 atoms.



Figure 2 Atomic scattering factors for electrons for oxygen (blue), hydrogen (black) and a combined scattering factor or a water molecule.



Figure 3 The radial distribution function for the MD water model.



Figure 4 The real-space pair density distribution for the MD water model.



Figure 5 The calculated PDF (without normalization to 0) for the MD water model.



Figure 6 The PDF (without normalization to 0) of a fcc gold cluster consisting of 610 atoms.

How to "read" a PDF

Peak position

The PDF describes a probability to find a pair of atoms at a certain distance. In Figure 6, no atoms are places at distances closer than 2.9A representing the closest interatomic distance in the fcc structure of gold. The next peak in the PDF appears at 4.1A representing the second coordination shell. In this way, when the structure is known, all peaks in the PDF can be assigned to an interatomic distance existing in the structure.

For the water model (Figure 5), the first sharp peak close to 1A correspond to the O-H covalent distance. The peak at 1.5A comes from the two hydrogen atoms of the same water molecule. The broad peak before 2A corresponds to the oxygen to hydrogen distance of two adjacent molecules connected by a hydrogen bond. The broad peak before 3A is the first oxygen-oxygen coordination

shell. No peaks after 3A can be seen. It is obvious that in this model, each water molecule has one solvation shell only.

Peak intensities

The relative intensities of the peaks represent the coordination number in the shell. For the gold cluster PDF shown in Figure 6, the second peak intensity is roughly the half of the first peak reflecting the ratio of the coordination numbers of the two shells -12:6. Figure 7 shows the first and the second coordination shells of the fcc-gold structure.



Figure 7 The first and the second coordination shells of the fcc gold structure.

Overall peak intensity decay

For an ideal crystal the probability to find atomic pairs at a specified distance will oscillate infinitely. As the result, the peaks in a PDF will be seen up to very large interatomic distances. These peaks will probably overlap. When the crystal size is limited as in the case of the gold cluster, the probability to find as atomic pair at a distance exceeding the size of the cluster will be equal zero. As approaching the size of the cluster, the intercity of the peaks will decay. The form of the crystal-size dumping function depends on the size and the shape of the particle. For the cluster shown in Figure 6, the particle diameter is about 30 A. as the result the intensities are

dumped significantly, as the PDF approaches to 20A. The dumping is already seen in the ratio of the firs and the second peak – in the ideal case this should be 2:1.

The situation is somewhat different for an amorphous model – in the PDF of water (Figure 5), the probability to find atomic pairs at high distances remain more of less the same, as a signature of a totally random structure.

Peak width

The peak width is related to the experimental parameter Q_{max} , not relevant in the calculating presented above, and the spread of atomic distances for a given structure, related to the crystallographic thermal factor. For the case of gold cluster, a certain constant thermal factor was assigned to all atoms, resulting in a peak broadening in the PDF:

In the case of water, it is evident that the first two peaks are rather sharp compared to the following. The first two peaks describe the interatomic distances within a single molecule. The following peaks correspond to intramolecular distances. In the model, the molecule has a rigid geometry, thus the distances within the molecule are well defined. The intermolecular distances have a broader variety, which is reflected in the width of the peaks corresponding to the intermolecular distances.

A similar effect has been observed for molecular crystals. The thermal vibration of atoms belonging to one molecule have usually a smaller amplitude then the thermal vibration between different molecules, and is better described with a smaller effective thermal factor.²¹

Experimental PDF

The PDF concept introduced so far was rather abstract. The attractive size of the PDF business is that the PDF can be obtained experimentally using a relatively easy experimental setup. The data for PDF calculation is collected through a powder diffraction experiment.

In the PDF analysis the scattering vector is usually measured in Q, which is related to the reciprocal distance and the scattering vector s as follows:

$$Q[Å^{-1}] = \frac{4\pi \sin\theta}{\lambda} = \frac{2\pi}{d}$$
$$s[Å^{-1}] = \frac{\sin\theta}{\lambda} = \frac{1}{2d}$$

Azimuthal integration of a powder diffraction pattern results in scattering intensity profile I(Q). The intensity profile is first normalized to the average scattering factor of the sample f(Q), and eventually background-subtracted in order to obtain the total scattering structure function S(Q)



Figure 8 Azimuthally integrated experimental scattering intensity (blue) and the corresponding average atomic scattering factor (red) used for the normalization.



Figure 9 Normalized scattering intensity (blue) and the final S(Q) obtained from it by background subtraction.

The PDF is obtained from the structure function through a sine Fourier transformation as follows:²²

$$g(r) = \frac{2}{\pi} \int_0^\infty Q[S(Q) - 1] \sin(Qr) \, dQ$$

Practical issues associated with electrons

Data acquisition

For electrons, a powder diffraction pattern must be collected. The diffraction pattern should be collected up to relatively high scattering angles, i.e. using a relatively short camera length. Good X-ray PDFs are usually done using the Q_{max} of 30 A⁻¹ (d=0.2 A), which is rather challenging for a TEM. Usually, electron diffraction data until Q_{max} of 20 A⁻¹ (d=0.3 A) is collected.

The diffracted intensity at high scattering angles is very weak, therefore high exposures may be needed to record the data of sufficient quality. All uneven features of the background with initially weak intensity can be enhanced during the data collection. Stray scattering often present in SAED data makes SAED patterns less attractive for PDF analysis as the data collected in nano-beam diffraction mode.²³

Mosaic diffraction data acquisition can be used; in this case the centering routines must include the calibration for the diffraction pattern shift.

All disturbing features in the pattern as beam stop, blooming effects, shatter shadows must be masked out prior to the integration. The diffraction patterns may need to be corrected for elliptical distortion.

The center of the diffraction pattern must be found as accurate as possible. There are different algorithms for data centering realized in different programs. Most of them rely on the radial symmetry of the pattern.



Figure 10 A mosaic diffraction pattern of nanocrystalline anatase, recorded using calibrated diffraction shift.

Integration

Once the disturbing features are masked out, and the center of the pattern is found, the 2D diffraction pattern can be integrated into a one-dimensional I(Q) scattering profile. There are several programs available for this procedure – DiffTool, a plugin for GMS (Digital Micrograph Suite, GATAN, USA), developed by Dave Mitchell has a number of scripts allowing diffraction data processing and integration into a one-dimensional profile²⁴; ELD - a part of CRISP (CALIDRIS, Sweden);²⁵ FIT2D²⁶ is the software used for the X-ray diffraction integration.

Normalization and background subtraction

The average electron scattering factors are calculated as a weighted sum of individual atomic scattering factors (as explained above). Then, the experimental scattering curve is normalized by the obtained f(Q). In most cases, if the whole scattering profile is normalized, no proper S(Q) asymptotically oscillating around a straight line can be obtained. A part of the scattering profile must be omitted during the normalization. Usually the very low-Q region is excluded as it includes

the primary unscattered beam. Even then, for most samples, the S(Q) contains low-frequency oscillations, appearing as the curve bending (Figure 9), so that additional background subtraction is necessary. The redistribution of the scattering intensity is believed to be a result of multiple scattering and appears for both amorphous and crystalline materials. The empirical background correction can either be done at this stage using a polynomial function, or at earlier stage – before the normalization using a 1/Q dependence.

Fourier

A Fourier transformation is done to obtain the PDF from S(Q) using the formula shown above. At high scattering angles the noise in the experimental data increases, the amount of the structural information decreases. The usual practice is to clip the scattering data at a certain Q_{max} to eliminate possible artefacts in the PDF due to the noise. The width of the peak in the PDF is directly related to the value of Q_{max} used for the calculation, the smaller the Q_{max} is, the broader are the peaks.

The clipping of the experimental data unavoidably produces ripples around the peaks with the frequency related to Q_{max} . These ripples can be very strong around strong peaks and be easily misinterpreted as extra structural features. In order to check, if the peaks are "real" it is recommended to calculate several PDFs with different values of Q_{max} . The positions of the peaks related to the structure will not be affected by that.

Towards quantitative interpretation

The experimental PDF contains the structural information mixed with the instrumental parameters of the TEM. Some of these parameters are correlated and are difficult to separate.

The electron diffraction peak width is related to the crystal size in the sample – the structural parameters. On the other hand, it is related to the focusing of the diffraction pattern and amount of astigmatism in the projector lens. Finally, it is related to the Modulation Transfer Function (MTF) of the recording medium. The effect of the instrumental broadening in electron diffraction should be underestimated – the width of peaks in electron diffraction in relative scattering angles values is much larger than that of X-rays. As the result, in the PDF, the decay of the peak intensities is related to the size of the correlation domains and the instrumental influence.

The same holds for the width of the peaks in the PDF. This is related to the structural parameters as the static disorder in the sample, and the thermal factor. The peak width is also influenced by the Q_{max} clipping of the reciprocal space, and, finally by the transfer of high spatial frequencies in an electron diffraction pattern, which may be non-homogeneous.

The slope in the low-r region of the PDF contains the information about the number density ρ_0 of the material. The red linear fit shown in Figure 11 follows -0.8r.

$$-4\pi r \rho_0 = -0.8r$$
$$\rho_0 = \frac{0.8}{4\pi} = 0.0637$$

On the other side, the number density for a given structure can be calculated as follows:

$$\rho_{0} = \frac{\rho N_{A}}{M} = \frac{19.32 [\frac{g}{cm^{3}}] \cdot 6.022 \cdot 10^{23} [\frac{atoms}{mol}]}{196.97 [\frac{g}{mol}]} = 0.05907 \cdot 10^{24} \left[\frac{atoms}{cm^{3}}\right] = 0.05907 \left[\frac{atoms}{A^{3}}\right]$$



Figure 11 A simulated PDF (DISCUS) from crystalline gold (black), a linear fit used to determine the number density (red).

Software for ePDF calculation

There are several different software packages available to the processing of electron diffraction data in order to obtain the PDF.

Name	Diffraction data integration	Distribution
ProcessDiffraction ²⁷	yes	free
SUePDF ²⁸	no	free
eRDF Analyser ²⁹	yes	free
ePDF suite ³⁰	yes	commercial

Other relevant programs include those, which calculate PDF for a known structural model: DISCUS³¹ and PDF GUI³².

Outlook

Electron PDF is a relatively new and fast growing field of research. Many questions are relationships are yet to be disclosed as the effect of electron energy filter and multiple scattering. The influence of the instrumental parameters is not yet fully understood. Despite all these unresolved issues, electron PDF remains a unique method to study the signatures of MRO in poorly crystalline and amorphous materials.

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