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Introduction to Pair Distribution Function Analysis

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What is a Pair Distribution Function (PDF)?

A PDF is a weighted histogram showing the distribution of inter-atomic distances in a material.

This makes it an excellent probe of the local structure of a material.

r is the distance between pairs of atoms in the material.

The intensity of a point in $G(r)$ is proportional to the number of pairs of atoms at that r value weighted by products of the scattering powers of the pairs.

Basic Description of a Pair Distribution Function

A PDF is a radial distribution function. To generate one take a sphere around an atom and expand it, whenever you encounter another atom you make a peak. The peaks are not sharp delta functions because of the thermal motion of the atoms. PDFs can be obtained equally well for amorphous or crystalline materials, or anything in between.

Example of an X-ray PDF

X-ray PDFs will have stronger sensitivity to heavy elements.

Notice how the strongest features are those for distances between metal atoms while oxygen-oxygen distances make only a small contribution.

An X-ray PDF and fit of the perovskite NaLaFeTaO_6 over an r -range of just beyond one unit cell.

Example of a Neutron PDF

With neutrons light atoms such as O can make a much more significant contribution.

Some elements, such as Ti and Mn, have negative neutron scattering lengths. Notice how the Ti-O and Ti-Sr distances create negative peaks.

A neutron PDF of SrTiO_3 to just beyond one unit cell.

Crystal Structure of SrTiO_3

Neutron Scattering Lengths:
Ti = -3.44, Sr = 7.02, O = 5.81

Obtaining an Experimental PDF

A PDF is the sine Fourier transform of the total scattering pattern.

The total scattering pattern shows how the sample scatters at all values of Q . This includes both Bragg and diffuse scattering.

In crystallography only the Bragg peaks which arise from the long range periodicity are analyzed. The diffuse scattering is subtracted along with the background. This type of analysis only gives information on the long-range average structure.

When there are deviations from the crystal structure this gives rise to diffuse scattering, which appears between the Bragg peaks and is not strongly localized in Q . In amorphous materials all the scattering is diffuse. In many mostly-crystalline materials there is both Bragg and diffuse scattering.

In a total scattering experiment we use all the structural information contained in both the Bragg and diffuse scattering to generate a PDF. In other words, we make use of more information than in traditional crystallography.

The PDF as the Fourier Transform of S(Q)

To obtain a pair distribution function:

- 1) Collect a total scattering pattern (X-ray or neutron) to high Q values. This raw data is referred to as I(Q).
- 2) Apply a number of corrections to the data and normalize so that S(Q) goes to 1 at high Q. This normalized function is called S(Q).
- 3) Take the sine Fourier transform of the function F(Q). F(Q) is just Q[S(Q)-1]. The Fourier transform converts the data from reciprocal space to real space giving the pair distribution function G(r).

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

Features of the Function $G(r)$

Termination ripples: Since the Fourier transform is an integral from $0 \rightarrow \infty$, and we can't possibly collect data to $Q = \infty$, the truncation convolute $G(r)$ with the function $\sin(Q_{\max}r)/r$. This is the origin of the small periodic features at r -values below inter-atomic distances.

In $G(r)$ a value of 0 represents the average pair density.
 $G(r) < 0$, less than random chance of finding two atoms separated by distance r .

$G(r) > 0$, greater than random chance of finding two atoms separated by distance r .

$G(r) \rightarrow 1$ at high r for amorphous materials.

The baseline of a PDF (the value representing no atom-atom pairs) is a straight line determined by the average pair density, ρ_0 : baseline = $-4\pi r \rho_0$

Some Related Functions

There are a number of related PDF functions that you may encounter.

$$G(r) = \frac{2}{\pi} \int_0^{\infty} Q[S(Q) - 1] \sin(Qr) dQ \quad = \quad G(r) = 4\pi r [\rho(r) - \rho_0]$$

Experimental PDF from diffraction data.
(Fourier Transform of S(Q))

PDF written according to pair density.
(ρ_0 is the average pair density and $\rho(r)$ is the actual pair density at a given r , must be weighted by scattering power for non-monoatomic systems)

coherent sample scattering

Scattering power, b_i , scaled by fraction of species i , c_i

$$S(Q) = \frac{I_{coh}(Q) - \sum c_i |b_i|^2}{\left(\sum c_i |b_i|^2 \right)^2} + 1$$

Normalized by average sample scattering power

S(Q) according to sample scattering.

$$G(r) = \sum_{ij} \left[\frac{b_i b_j}{\langle b \rangle^2} \delta(r - r_{ij}) \right] - 4\pi r \rho_0$$

PDF according to structure.
(how to calculate from a structural model)

Some other PDF functions:

Pair distribution function: $g(r)$, $\rightarrow 1$ at high r

Pair density function: $\rho(r) = \rho_0 g(r)$, $\rightarrow \rho_0$ at high r

Reduced PDF, $G(r) = 4\pi r \rho_0 (g(r) - 1)$, $\rightarrow 0$ at high r

Radial distribution function, $R(r) = r[G(r) + 4\pi r^2 \rho_0]$, not normalized so it grows exponentially

Experimental Considerations: $Q_{\max}$

Higher $Q_{\max}$ = Better r -spacing resolution

A finite $Q_{\max}$ broadens the peaks in $G(r)$. The larger the $Q_{\max}$ the more this effect is minimized. The high energy X-ray beams at synchrotrons and the energy spectrums at time-of-flight spallation neutron sources give the highest $Q_{\max}$ data, which is why most total scattering experiments are done at such facilities.

Typical $Q_{\max}$ values for different sources:

Cu X-ray tube $\sim 8 \text{ \AA}^{-1}$

Mo X-ray tube $\sim 17 \text{ \AA}^{-1}$

Ag X-ray tube $\sim 22 \text{ \AA}^{-1}$ *

Constant wavelength neutron $\sim 6\text{-}12 \text{ \AA}^{-1}$ *

TOF neutron or spallation $\sim 24\text{-}40 \text{ \AA}^{-1}$

* Silver tubes have very low fluxes, requiring very long counting times. Hot neutron sources can give $Q_{\max}$ values up to $\sim 35 \text{ \AA}^{-1}$, but with poor resolution, making them only appropriate for liquids and amorphous materials.

PDFs of $\text{Sr}_2\text{FeMnO}_5$ created with 2 different $Q_{\max}$ values.

Experimental Considerations: Resolution

Better resolution = Less intensity dampening at high r

- The intensity of $G(r)$ is dampened by: $\exp(-(r\Delta Q)^2/2)$
- Matters little if only the nearest neighbor distances are of interest, but can matter a lot if the higher r data is of interest.
- The $G(r)$ of amorphous materials goes to 0 quickly anyway, so resolution is not very important, while for crystalline materials it can be.
- Limited resolution also results in a r -dependent broadening of the peaks in a PDF. Generally only significant at high r .

Experimental Considerations: Statistics

Low noise needed, especially at high Q

Since it is $Q(S(Q)-1)$ that is Fourier transformed, the noise at high Q gets amplified, making the quality of the data at high Q particularly important.

Choice of $Q_{\max}$ a trade off:

Value chosen is often the point where the extra r -space resolution no longer outweighs the extra noise. $S(Q)$ often available up to $\sim 40\text{-}50 \text{ \AA}^{-1}$, but only used up to $30\text{-}35 \text{ \AA}^{-1}$.

Experimental Considerations: Background

A reproducible background is essential

The data must be corrected for non-sample scattering. This involves making calibration measurements so that signal from sources other than sample scattering can be subtracted out.

Calibrations:

1. Empty instrument measurement.
2. Empty sample container (for neutrons usually a vanadium can and for X-rays usually a capillary tube). Any other equipment that is in the beam should also be included so its scattering can be subtracted.

For this to be successful the background must remain the same between measurements.

Data Processing

Background subtraction (empty instrument and empty sample container)

Corrections for absorption, multiple scattering, detector deadtime, and sometimes inelastic scattering (Placzek correction) applied.

$S(Q)$ normalized so that it goes to 1 at high Q . $S(Q)$ is an absolute function where the scattering intensity normalized by the average sample scattering power. In practice the sample density is adjusted to make $S(Q)$ go to 1.

Fourier transform of $F(Q)$ to get $G(r)$

Software:
Neutrons – PDFgetN
X-rays – PDFgetX3

Incoherent Scattering

Only elastic coherent scattering desired.

Incoherent scattering produces a background that interferes with the generation of a PDF.

Hydrogen is the most problematic element as it has a huge incoherent scattering cross section.

No analytical method to remove it. Can be dealt with by fitting with a smooth function, subtracting it, and then adding the Debye-Waller contribution back in.

Differential PDFs

Normally the partial PDFs (the PDF for just one type of atom-atom pair) are obtained through modeling. However, there are some experimental methods that can be used to directly obtain the partial PDFs. By varying the scattering power of an element and taking the differential, then repeating this for several elements, the individual partials can be extracted.

For X-rays: Make two measurements near the absorption edge of an element. The scattering power for the one element will vary greater while the others remain essentially the same.

For neutrons a similar approach can be used by making the same material with different isotopes and taking the differential of these total scattering patterns.

PDF as a Mesoscale Probe

A pair distribution function is an excellent probe of local structure, but also of intermediate length scales which are not accessible by many techniques.

- Local structure probes such as EXAFS, XANES, and NMR mainly probe just the first coordination sphere, and maybe the second or third to a lesser extent.
- X-ray and neutron crystallography probe the average structure over length scales of hundreds of Angstroms or more.
- PDF can cover length scales of ~ 1 -200 Å, sometime even larger, providing structural information not available from most other techniques.

For crystalline materials PDFs can be generated up to 200+ Å with high resolution data.

Facilities: Neutrons

USA:

Lujan Center: (no user program)

NPDF: high resolution, low background

HIPD: medium resolution, high intensity

Oak Ridge SNS: (open user program)

NOMAD: medium resolution, high intensity

non-USA:

- GEM, ISIS, UK: high resolution, high intensity
- Nimrod, ISIS, UK: uses longer wavelengths
- D4, ILL, France, hot CW for liquids and amorphous materials
- Nova, JPARC, Japan, specializing in non-crystalline materials

NPDF

HIPD

Facilities: X-rays

Image plate detector at 11-ID-B

USA

Advanced Photon Source, Argonne National Laboratory

11-ID-B: dedicated PDF beamline

NSLS II at Brookhaven National Laboratory:

XPD: brand new and about to start operation

non-USA (not comprehensive)

- ID11 and ID22, ESRF, France
- I12 and I15, Diamond, UK
- Powder, Australian Synchrotron
- BL14B1, Spring-8, Japan

Methods to Model PDF Data

Small Box Method:

Uses a unit cell like model where the position of each atom serves as the peak of a Gaussian curve which takes into account thermal vibrations.

Pros:

Computationally cheap.

Easy to interpret results.

Cons:

Cannot model all systems.

Needs a good starting model.

Different r -ranges often require different models.

Large Box Reverse Monte Carlo (RMC) method:

Uses a supercell containing 10,000-20,000 atoms to model the PDF. There is no broadening function, the PDF is modeled by the actual distribution of atom pairs.

Pros:

Starting model easy to construct.

Can handle systems with many
different local environments.

Short, medium, and long range
structure accounted for in a single model.

Cons:

Computationally expensive.

Results can be difficult to interpret.

“Small Box” Modeling

Uses a crystallographic unit-cell-like description.

- Input includes unit cell parameters and atomic positions.
- Must include all atomic positions, symmetry related ones can be created from space groups.
- Peak broadening is determined by atomic displacement parameters. Includes corrections for correlated motion of neighboring atoms, which sharpens the first peak or peaks.
- Can model instrumental corrections such as dampening from finite resolution, peak broadening, and termination ripples (based on the $Q_{\max}$ used to generate the data).
- Often local distortions do not correlate very far, so one model is needed to fit the low- r region of the PDF and the average structure is needed to fit the high- r region. Good for determining the correlation length of structural features but also means large r -ranges often cannot be fit by a single model.

A PDF fit with a *Pnma* average structure model over three r -ranges. Notice how the average structure does not fit the low- r region well but does fit the high- r regions well.

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“Large Box” RMC Modeling

Reverse Monte Carlo modeling uses a large supercell of 10,000-20,000 atoms.

- No broadening function, there are enough atoms to generate the actual peak widths.
- Creates the most random configuration which is still consistent with the data, could be more order that the fit is insensitive to.
- Solution is not unique.
- In many cases able to model complex systems and give more detail than small box fitting.

The Reverse Monte Carlo Method

How it Works:

Step 1) An atom is moved.

Step 2) The program determines if this improves the fit or worsens it.

Step 3) If it improves the fit the move is accepted. If worsened, it is accepted or rejected with a probability proportional how much worse it makes it.

Step 4) Repeat millions of times.

- A typical run takes 12-36 hours on a standard desktop.
- Initial configurations are usually just expansions of the average crystal structure.
- Most time is spent analyzing the data.
- Some constraints are usually needed.

Example of an 8 x 8 x 8 RMC supercell of $\text{SrRu}_{0.5}\text{Mn}_{0.5}\text{O}_3$ containing 10,240 atoms. Dimensions of 43.6 Å x 43.6 Å x 63.3 Å.

RMC as a Multi-Scale Modeling Method

By fitting $G(r)$, $S(Q)$, and the Bragg peaks an atomic configuration is obtained which is simultaneously consistent with the short, medium, and long range structural features of the material. A complete structural description.

Recently RMCPProfile has been updated so that it can also fit EXAFS data as an additional constraint. It is expected that in the near future additional data types such as NMR, Raman, TEM, etc. will be added in.

RMC Outputs

- Inter-atomic distance distributions for all types of atom-atom pairs.
- Bond angles distributions
- Shapes of atom distribution “clouds”

Example for the “cubic” HT form of perovskite K_3AlF_6

Distribution of distances is very different from the single Gaussian expected from the average structure.

The final RMC configuration folded back into a single unit cell to show “clouds” of atom distributions.

Bond angles differ significantly from the 180° expected from the average structure.

Liquids and Amorphous Materials

- Data collection is often different as high Q space resolution is not needed since there are no sharp Bragg peaks
- Modeling is often more difficult and different, but there are RMC methods to handle it.
- Often coordination numbers are extracted without modeling by integrating the area under a peak in the $D(r)$ function.

Neutron PDF of amorphous SiO_2 , one of the most abundant glasses, and the RMC fit.

Example: Orbital Ordering in LaMnO_3

At RT the MnO_6 octahedra in LaMnO_3 are Jahn-Teller (JT) distorted, but at high temperature these distortions disappear in the average structure. PDF was used to show that the JT distortions are always present, they just lose long range correlation.

Nearest neighbor behavior shows local atomic arrangements change little with temperature.

Higher r -range gives information about the correlation of the JT distortions.

The diameter of orbitally ordered domains is found to be ~ 16 Å above T_{JT} .

Example: Multiple Cations on One Site

$\text{Sr}_2\text{FeMnO}_5$ and $\text{Sr}_2\text{FeMnO}_{5.5}$

On average they appear to be oxygen deficient cubic perovskites with equal Fe-O and Mn-O bonds. Locally they look more like brownmillerites and Fe and Mn are not equal.

Neutron scattering lengths of Fe (9.45) and Mn (-3.73) give strong contrast.

Using RMC modeling the local Fe and Mn coordination environments were determined.

Conclusions: Oxygen vacancies concentrate between Fe pairs such that Fe tends to have a lower coordination number compared to Mn. Mn tend to be Jahn-Teller distorted locally when +3 in $\text{Sr}_2\text{FeMnO}_5$ but not when +4 in $\text{Sr}_2\text{FeMnO}_{5.5}$.

G. King, et al., *J. Solid State Chem.* (2013) 198, 407-415.

Example: Nanoparticles

PDF can be used to learn about the structures of particles which are too small to produce Bragg peaks.

- Particle size determined by observing when $G(r) \rightarrow 0$. Can give shape information.
- Models often specify the position of every atom in the particle.
- Information on capping ligands can sometimes also be obtained
- Information on core-shell structures.

See: K. Page, et al., *J. Appl. Cryst.* (2011) 44, 327-336.

Example: Pore Structure of Activated Carbon

Synchrotron XRD used to reveal atomic and pore structure in activated carbon.

4 nanometer sized pores identified from oscillations.

$G(r)$ over a short length scale gives information on carbon-carbon bonding.

$G(r)$ over an intermediate length scales gives information about pore sizes.

L. Temleitner, et al., *Mater. Res. Bull.* (2012) 47, 4409-4413.

Emerging Topics in PDF

- Dynamic PDF: make energy resolved measurements to determine the dynamic of motion of atoms (use inelastic scattering to gain information about time correlation).
- Magnetic PDF: determination of short range magnetic correlations (useful for studying spin ices and such).

Summary

- By collecting a total scattering pattern, subtracting the non-sample background, applying corrections, and taking the Fourier transform, the real space pair distribution function can be obtained.
- A PDF gives the distribution of inter-atomic distances in a material and is an excellent probe of short and intermediate range structure.
- RMC refinements using multiple data types are an excellent method for multi-scale modeling, including the mesoscale range.