

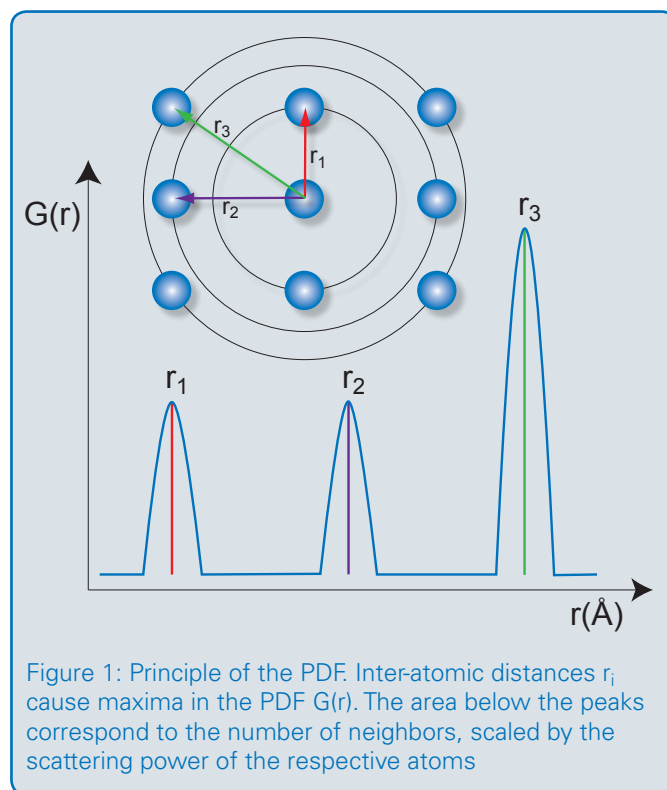
## Determination of Pair Distribution Functions (PDF)

The Pair Distribution Function (PDF) can be determined from laboratory or synchrotron X-ray or neutron diffraction data. The PDF is the key to investigate short, medium or long-range order of materials. The method can be applied to crystalline and amorphous solid material as well as to liquids. For crystalline materials, PDF is a powerful tool to determine the deviation of the short range order from the average crystal structure. The examples of nano-anatase and  $C_{60}$  measured with Ag-radiation show the great potential of the D8 ADVANCE for such investigations.

### What is a PDF ?

The PDF analysis is a principally well understood method that was already described in the classical 1969 textbook of Warren on X-ray diffraction (Addison Wesley; New-York, Dover). It describes a probability of finding any two atoms at given inter-atomic distances  $r$  (Fig. 1). The primary application of PDF was the study of materials that do not show a long-range lattice periodicity, i.e. liquids or glasses. Their PDFs show broad features and do not extend over the short-range of the first few coordination spheres.

A PDF from crystalline material is much more structured and gives information on a medium-range of inter-atomic distances. This is complimentary to the Rietveld method (TOPAS), which models the average crystal structure from the intensities of the Bragg reflections in a diffraction pattern. Dynamic thermal vibrations that are always present in crystals disturb the ideal atomic arrangement. They are considered in the Rietveld method by the thermal



displacement parameters and treated as random deviations. Other deviations from the ideal symmetry, e.g. short-range order do not contribute to the Bragg reflections but to the diffuse scattering.

The PDF is calculated from the Bragg as well as the diffuse scattering intensities. Therefore, a PDF can discriminate between short range order (represented by finite non-random displacements from the ideal crystal structure) and random displacements of the atoms. Systematic deviations from the ideal structure are frequently observed in very small particles. Therefore, the determination of PDF has seen a renaissance with the present interest in nano-scaled materials.

### How to calculate a PDF ?

The experimental PDF  $G(r)$  or the radial distribution function  $4\pi r^2 G(r)$  are directly obtained from the diffraction data by Fourier transforming the normalized total structure factor  $S(Q)$  with  $Q=4\pi(\sin \theta)/\lambda$ .  $S(Q)$  is the measured intensity corrected for background, Compton and multiple scattering, absorption, geometric and other factors. For the calculation of  $S(Q)$  and  $G(r)$  academic software (e.g. PDFgetX2, RAD) is available from the internet, [www.totalscattering.org](http://www.totalscattering.org).

Note: The software licenses only allow using the software for research or educational purposes. Commercial users need to obtain permission to use this software from the respective license holders. Thus, the software comes without support from Bruker AXS.

The interpretation of experimental PDFs is very similar to the Rietveld method. A structural model of the atomic arrangement is the origin to calculate a PDF. Best agreement with the experimental PDF is obtained by optimizing the model parameters using e.g. PDFfit, a program for the full profile structural least squares refinement of the atomic pair distribution function. The same support and license issues as described above also apply to PDFfit.

### Experimental aspects

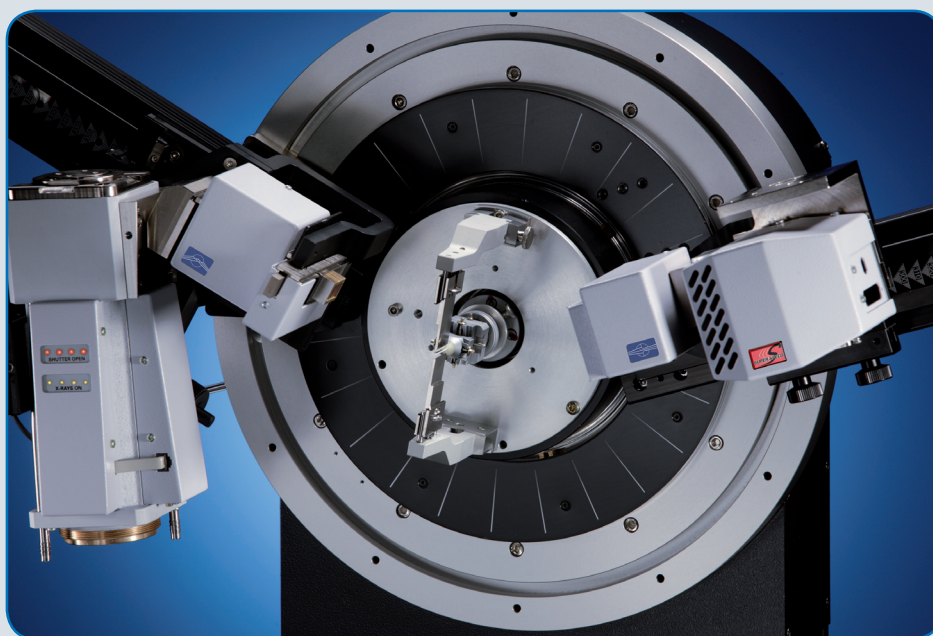
Three factors mainly influence the quality of the experimental PDF: Fourier termination errors, resolution and counting statistics. Termination errors are minimized by measuring to largest values of  $Q$ . The maximum value of  $Q$  is limited by the instrument setting for the highest diffraction angle (typically up to  $160^\circ 2\theta$ ) and the wavelength of the X-ray source.

For an assumed largest angle of  $160^\circ 2\theta$  the maximum  $Q$  value for Cu-radiation is  $8 \text{ \AA}^{-1}$ . The use of Mo-radiation more than doubles this value to  $17.4 \text{ \AA}^{-1}$ . Additional extension is obtained when using Ag-radiation. It enlarges the accessible  $Q$ -range to  $24 \text{ \AA}^{-1}$  (compare Fig. 2). Consequently, the lowest termination effects can be expected for Ag-radiation.

Bruker AXS offers a complete and unique solution for high energy X-ray powder diffraction. This solution consists of either a Mo or Ag sealed tube, a primary focusing monochromator for Mo or a focusing Goebel mirror for Mo or Ag radiation, and the LYNXEYE detector.

An example setup of the new D8 ADVANCE diffractometer, which is perfectly suited for structure research is shown aside. The system is equipped with a primary focusing Johansson monochromator for Mo-radiation and a LYNXEYE detector optimized for hard X-rays, and air scatter screens to reduce the background. The instrument delivers very high-resolution data at optimum flux to sufficiently high  $Q$  values.

This new and innovative instrument is unique to Bruker AXS. It combines a high flux of hard X-rays and fast data collection with the superior resolution of the focusing incident monochromator. Besides outstanding capabilities for crystal structure determination and refinement with TOPAS such an instrument is also optimally equipped for



Goniometer with primary focusing Johansson monochromator and LYNXEYE detector

PDF analysis. Hence, it is the perfect choice for structure research in general.

If the scattering properties of the sample should justify the use of Ag-radiation and an application should require the use of very high- $Q$  data the combination of Ag sealed tube and focusing Goebel mirror provides the highest conceivable data quality.

However, the benefit of an extended  $Q$ -range needs to be traded off for the unavoidable loss of intensity while using Ag-radiation. The flux of X-rays from an Ag-tube is low compared to Mo, and the detector efficiency is lower for Ag-radiation as well. Furthermore, the decrease of the X-ray scattering power of the atoms with increasing  $Q$  frequently contributes no additional information from very high  $Q$  data.

The penetration depth of X-rays into the sample is larger for higher energies, or smaller wavelengths, respectively. In reflection geometry this causes a loss of resolution due to the related peak broadening. Therefore, the use of transmission geometry together with either capillary or flat-sample stages is required for PDF experiments.

The measurement time needed to collect data of sufficient counting statistics to high- $Q$  values is long. For a very basic instrumental set-up for PDF investigations using Ag-radiation, capillary sample, and scintillation counter the measurement time easily exceeds one day per scan. Such long measurement time clearly calls for a modern linear detector – as the unique LYNXEYE with the sensor optimized for higher energies – that drastically reduces the counting time.

A superior counting statistics is particularly important for the collection of high- $Q$  data. Together with the use of a one-dimensional detector (LYNXEYE) the data quality mostly benefits from using the Variable Counting Time (VCT) measurement strategy. VCT is a standard Bruker AXS solution that became available in DIFFRAC<sup>plus</sup> with version 2.6 of the WIZARD already. Of course, VCT is also contained in the new DIFFRAC.SUITE.

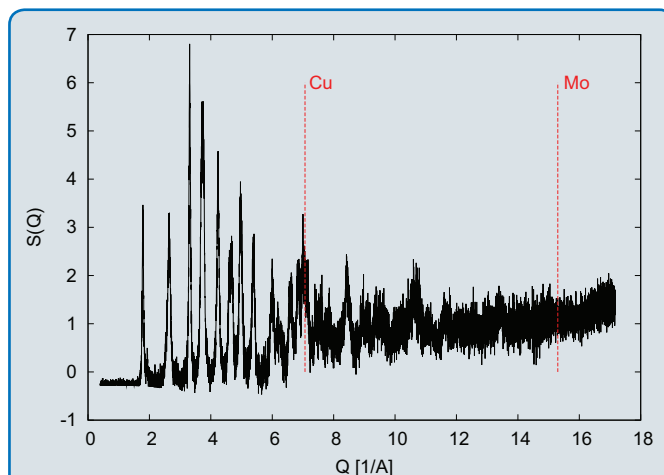


Figure 2: Total experimental structure factor  $S(Q)$  of nano-Anatase measured with Ag-radiation. The respective cut-off for Cu- and Mo-radiation for  $2\theta$  max  $120^\circ$  is indicated.

### Sample applications

Powder samples of nano-anatase ( $\text{TiO}_2$ ) and of  $\text{C}_{60}$  were prepared in low background Kapton® capillaries and measured on a D8 ADVANCE with Ag radiation, a focusing Goebel mirror, sample spinner and LYNXEYE detector (optimized for high energy radiation) applying the VCT strategy. The measurement range was 2 to  $160^\circ 2\theta$  in steps of  $0.01^\circ$ . A rotating empty capillary was measured with the same parameters for background correction.

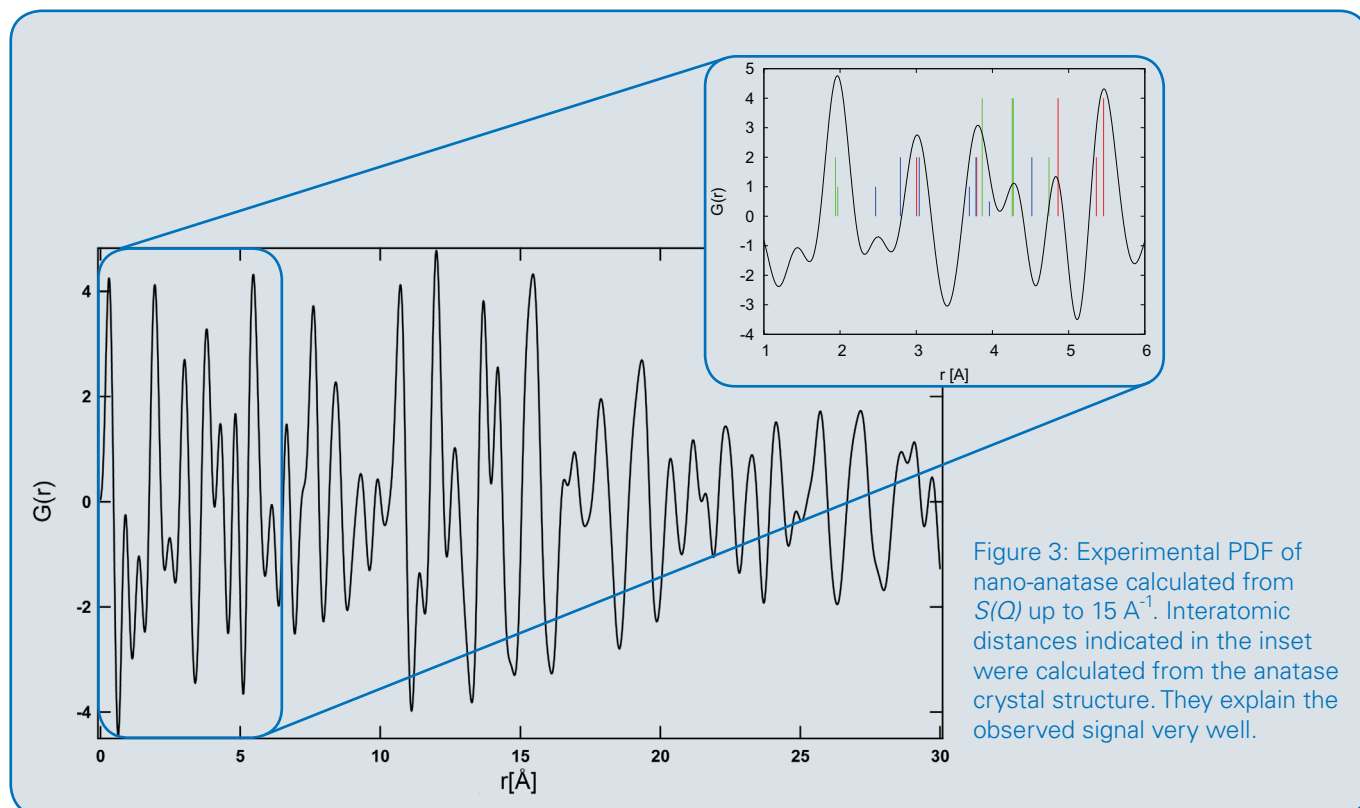


Figure 3: Experimental PDF of nano-anatase calculated from  $S(Q)$  up to  $15 \text{ \AA}^{-1}$ . Interatomic distances indicated in the inset were calculated from the anatase crystal structure. They explain the observed signal very well.

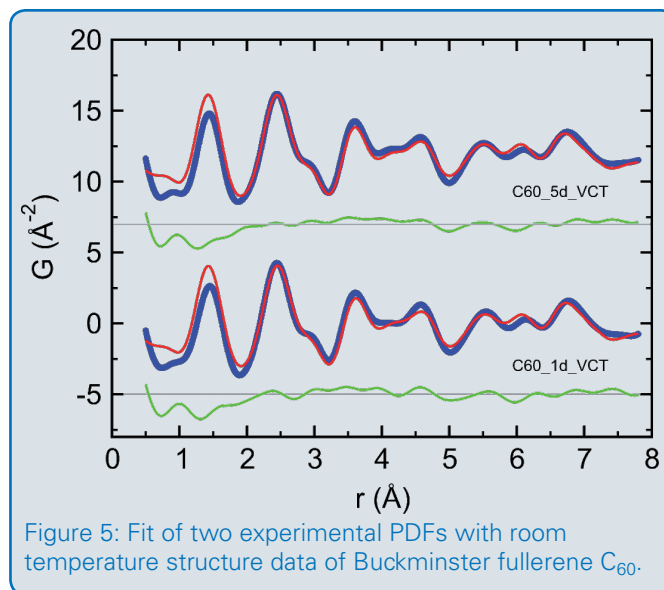
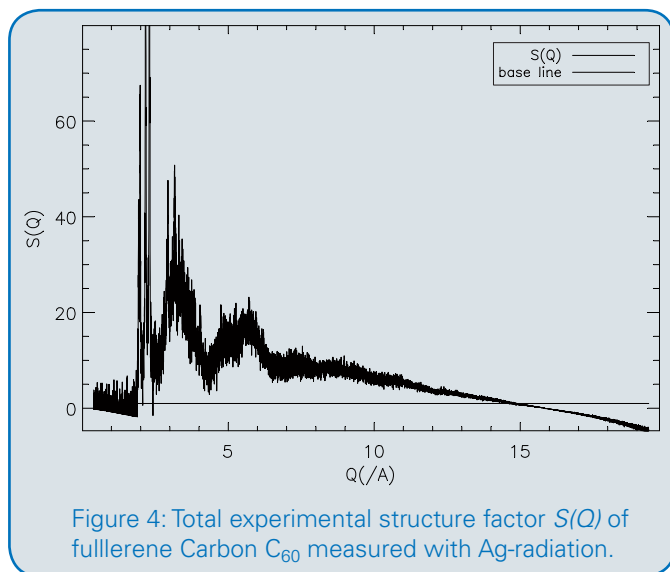
## Nano-Anatase

Figure 2 shows the normalized total scattering structure function  $S(Q)$  measured with Ag-radiation. The corresponding maximal  $S(Q)$  ranges for Cu- and Mo-radiation are indicated. Beyond  $Q = 15 \text{ \AA}^{-1}$  the  $S(Q)$  function contains only little information. The reason for this is mainly the decrease of the X-ray scattering power with increasing  $Q$ . Clearly, the same information obtained from the Ag-data could have been get from Mo-data as well.

The pair distribution function  $G(r)$  calculated for a maximum  $Q$  of  $15 \text{ \AA}^{-1}$  shows well resolved correlations (Fig. 3). The positions of the maxima correspond to the interatomic distances in anatase, while the area below the signals corresponds to the number of the respective distances. This is depicted in the inset, which shows a detail from the PDF together with stick markers, representing length and relative frequency of interatomic distances between Ti-Ti (red), Ti-O (green) and O-O (blue) atoms in anatase

## C<sub>60</sub> Buckyballs

The example of a quantitative evaluation of an experimental PDF is shown below. There is only negligible scattering signal from the specimen observed for  $Q > 14 \text{ \AA}^{-1}$  in the experimental structure factor curve (Fig. 4). Therefore, this maximum  $Q$  cut-off value is taken for the calculation of the experimental PDF, shown in Fig. 5.



PDFfit results are given in Figure 5. The experimental data (collected with different measurement times, blue curves) are modelled (red curves) based on the known structure of the high-temperature form of  $C_{60}$ . The difference curves (green) show a good agreement between experiment and theory.

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