

Supporting Information for Manuscript:

Characterisation of amorphous and nanocrystalline molecular materials by total scattering

Simon J. L. Billinge,* Timur Dykhne, Pavol Juhás, Emil Božin, Ryan Taylor, Alastair Florence and Kenneth Shankland

1. Sample Preparation

Data were collected from samples of CBZ and IND prepared by a melt-quenching method whereby molten compound was rapidly cooled in liquid N₂, lightly ground, sieved and filled into a 1mm diameter Kapton capillary. The laboratory data shown in Figure 1 of the manuscript were collected on a Bruker-AXS D8 diffractometer using capillary transmission geometry, primary monochromated CuKα₁ radiation (λ = 1.54056 Å) in the range 2-40 °2θ, 0.016 °2θ step size, 10s per step at 100 K. Total scattering data were collected using the Rapid Acquisition PDF method [1]. A 2D image plate detector was placed perpendicular to the high energy X-ray beam, 198 mm behind the sample. Data were collected for 300s and this was repeated between 5 and 8 times for a total collection time of 30 minutes for each data-set.

1. Data Processing and PDF Analysis

The PDF is linked to the scattering intensity through the sine Fourier transform

$$G(r) = \int_{Q_{\min}}^{\infty} F(Q) \sin QrdQ, \quad \text{Eq 1}$$

where

$$F(Q) = Q \left[\frac{I_c(Q) + \langle f \rangle^2 - \langle f^2 \rangle}{\langle f \rangle^2} - 1 \right]. \quad \text{Eq 2}$$

Here Q_{\min} is a Q value that excludes any small angle scattering intensity but includes all the wide-angle scattering [2]. $I_c(Q)$ is the powder diffraction intensity that has been properly corrected by removing experimental artefacts, such as fluorescence, multiple scattering and Compton scattering, corrected for such effects as sample self-absorption, and normalized by the incident intensity and the number of scatterers in the sample. The quantity $f=Z$ is the atomic scattering factor evaluated at $Q=0$, where Z is the atomic number. The $\langle \dots \rangle$ indicate compositionally weighted averages over the atomic species in

the sample.

Data from the 2D detector were first reduced to a 1D intensity vs. Q by integrating around the Debye-Scherrer rings using the program Fit2D [3]. The other data-corrections to obtain $F(Q)$ and $G(r)$ were carried out using the program PDFgetX2 [4].

2. PolySnap comparison of TSPDFs

TSPDF data were converted to comma separated variable (csv) format and full-profile comparisons carried out using PolySNAP v.1.7.2 [5] over the range $r = 3 - 20 \text{ \AA}$. The correlation co-efficients for the profile comparisons for the carbamazepine and indomethacin samples are shown in Tables SI1 and SI2 respectively.

2.1 Carbamazepine

Table SI1. Correlation coefficients for the comparisons of CBZ TSPDF data in PolySNAP.

100K APS data	CBZ-III	CBZ-I	CBZ-melt quenched
CBZ-III	1	0.3245	0.8389
CBZ-I		1	0.5164
CBZ-melt quenched			1

The highest correlation coefficient was returned for the melt-quenched CBZ sample and CBZ III [0.8389]. Overlays are shown below for each Polysnap comparison in Figures ES1-3.

Figure ES1. CBZ melt-quenched vs CBZ III [0.8389]

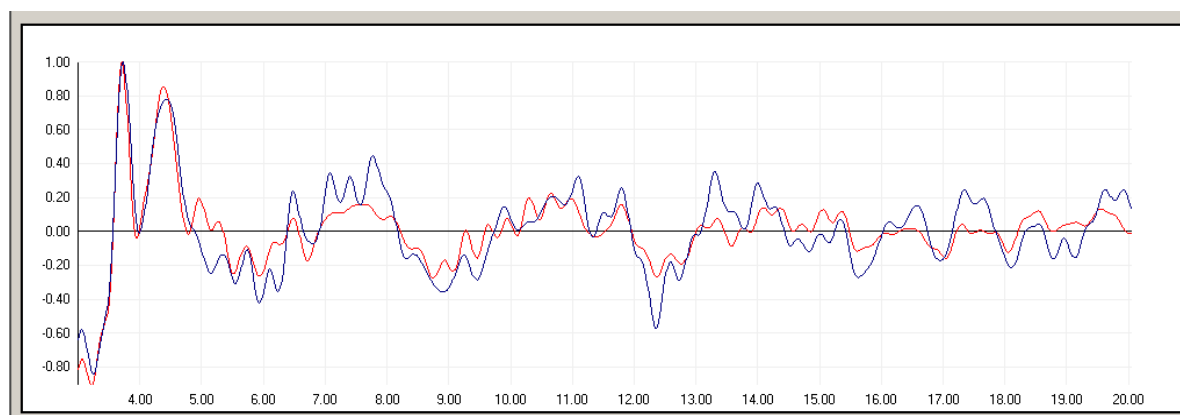


Figure ES2. CBZ melt-quenched vs CBZ I [0.5164]

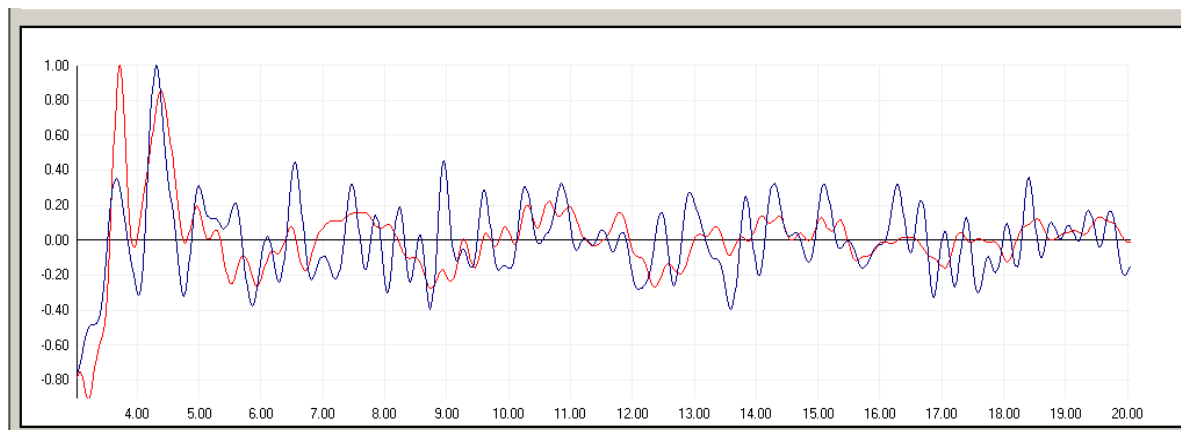
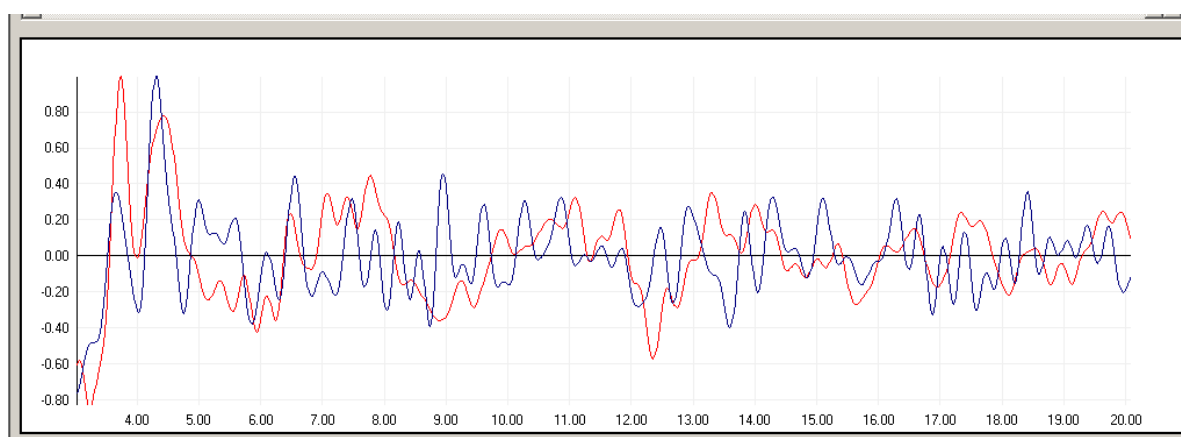


Figure ES3. CBZ III vs CBZ I [0.5828]



2.2 Indomethacin

TSPDF data were converted to csv format and full-profile comparisons carried out using PolySNAP v.1.7.2 [5] over the range $r = 3 - 20 \text{ \AA}$. Table SI2 below shows the correlation coefficients for the profile comparisons.

Table SI2. Correlation coefficients for the comparisons of IND TSPDF data in PolySNAP.

100K APS data	IND-melt quenched	IND α	IND γ
IND-melt quenched	1	0.6770	0.4886
IND α		1	0.4057

IND γ			1
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The highest correlation coefficient was returned for the melt-quenched IND sample and IND α , but the value 0.6770 is low and does not indicate a strong correlation in this case.

Overlays are shown below for each Polysnap comparison in figures ES4-6.

Figure ES4. IND melt-quenched vs IND α [0.6770]

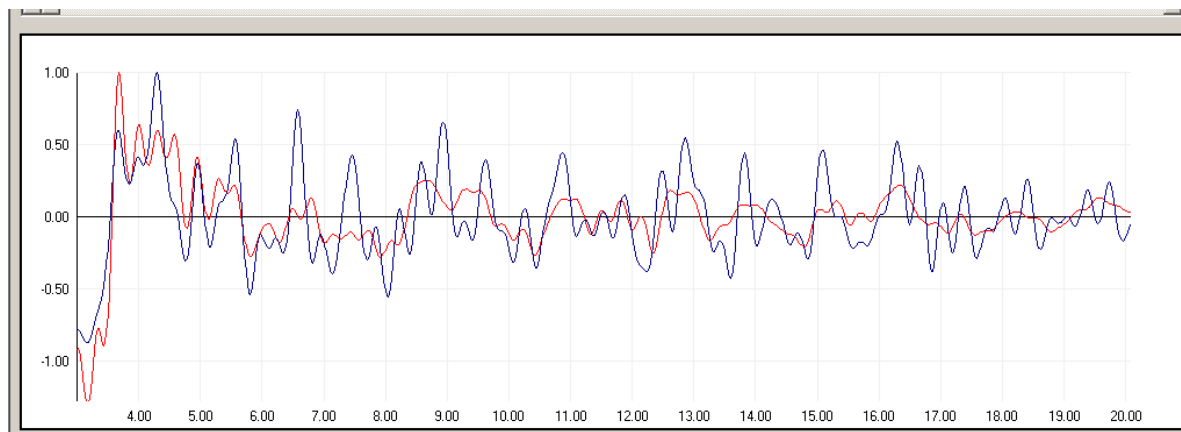


Figure ES5. IND melt-quenched vs IND γ [0.4886]

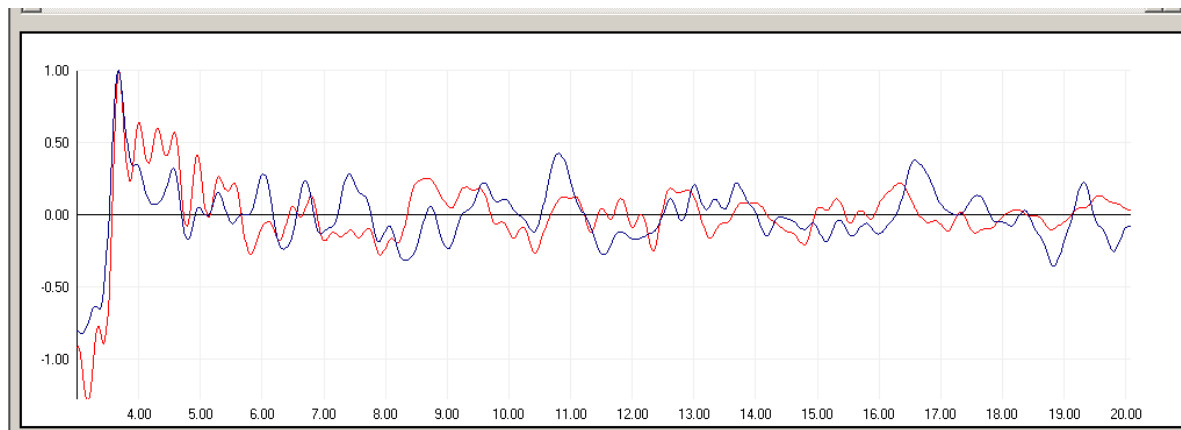
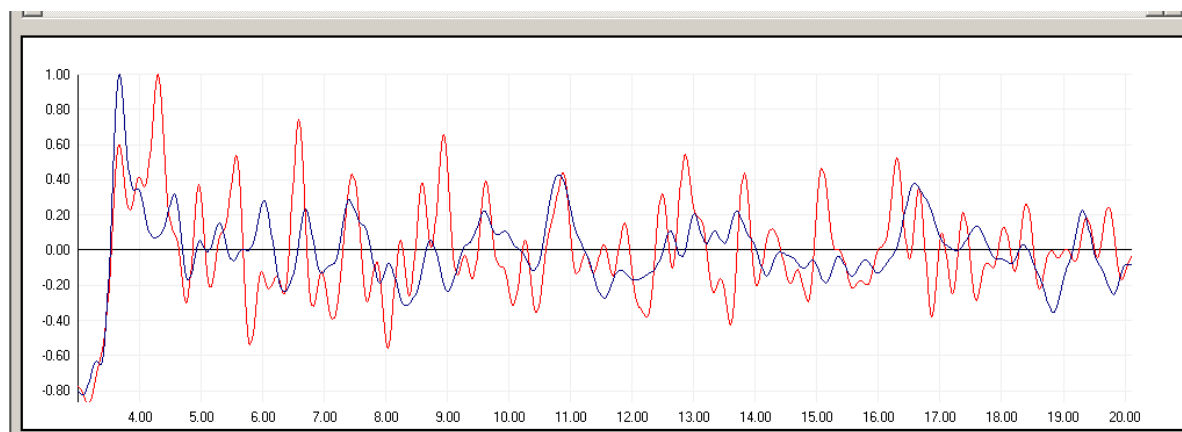


Figure ES6. IND γ vs IND α [0.4057]



3. Modelling of TSPDF for particle size

The shape function defines the shape of the nanoparticle and has value 1 inside the surface and value 0 outside the surface of the particle. For spherical particles the form of the autocorrelation function, or PDF characteristic function, is

$$f(r; d) = \left[1 - \frac{3r}{2d} + \frac{1}{2} \left(\frac{r}{d} \right)^3 \right] \Phi(d - r), \quad \text{Eq 3}$$

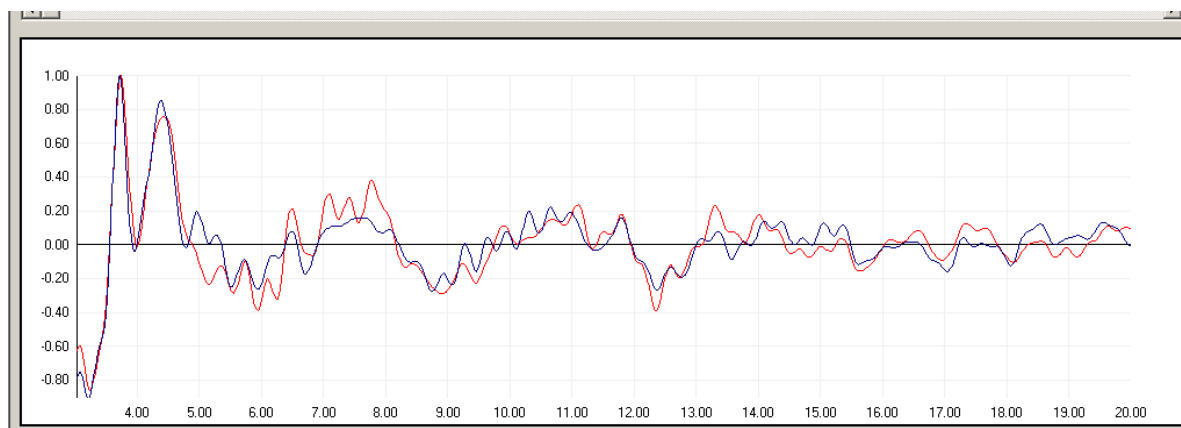
where d is the diameter of the spherical particle.

To obtain Figure 3 in the manuscript, the measured TSPDF of bulk crystalline CBZ III was multiplied by Eq 3, where d , the nanoparticle diameter, was varied by hand until reasonable agreement was obtained over the whole range of r as shown.

Table SI3. Correlation coefficients for the comparisons of CBZ TSPDF data for the melt-quenched sample and particle size adjusted CBZ-III TSPDF in PolySNAP.

100K APS data	CBZ-III (form factor)	CBZ-melt quenched
CBZ-III (form factor)	1	0.8601
CBZ-melt quenched		1

Figure ES7. CBZ melt-quenched vs CBZ III (form factor) [0.8601]



References

- [1] P. J. Cupas, X. Qiu, J. C. Hanson, P. L. Lee, C. P. Grey and S. J. L. Billinge, *J. Appl. Cryst.*, 2003, 36, 1342-1347.
- [2] C. L. Farrow and S. J. L. Billinge, *Acta Crystallogr. A* 65, 232 (2009).
- [3] Computer code FIT2D, in A. P. Hammersley, European Synchrotron Radiation Facility, Grenoble, France, Internal Report No. ESRF98HA01T, 1998 (unpublished); see web site for details at <http://www.esrf.fr/computing/scientific/FIT2D/>
- [4] X. Qiu, J. W. Thompson and S. J. L. Billinge, *J. Appl. Cryst.*, 2004, 37, 678.
- [5] G. Barr, W. Dong and C. J. Gilmore, *J. Appl. Cryst.*, 2004, 37, 658-664.

Electronic Supporting Information for Manuscript:

Erratum: Characterisation of amorphous and nanocrystalline molecular materials by total scattering

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Table SII. Correlation coefficients for the comparisons of CBZ TSPDF data in PolySNAP.

100K APS data	CBZ-III	CBZ-I	CBZ-melt quenched
CBZ-III	1	0.4467	0.8389
CBZ-I		1	0.6124
CBZ-melt quenched			1

Figure ES2. CBZ melt-quenched vs CBZ I [0.6124]

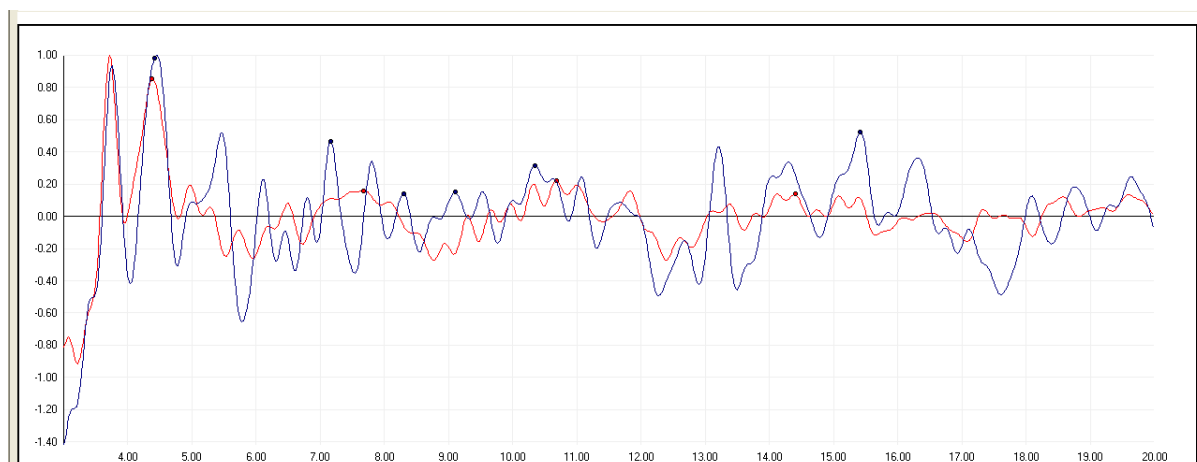


Figure ES3. CBZ III vs CBZ I [0.4467]

