Multidimensional nanostructure retrieval from anisotropic Small-Angle Scattering pattern analysis

Abstract

Your material is beautiful on every level; practically, macro- and microscopically. For systematic materials development, however, reliable numbers are needed which are often very difficult to get for the nanostructure.
Small-angle scattering (SAS) has been seen as a solution for about a century, promising to deliver statistically significant structural parameters easily measured over non-negligible quantities of material. Now, a complete methodology has been developed capable of determining (with the highest possible accuracy) all available nanostructural information complete with uncertainties from isotropic as well as anisotropic scattering patterns.

Generally applicable methods for analysis of small-angle scattering patterns may offer a good supplement to classical forms of analysis. These general methods try to find a form-free solution to the pair-distance distribution function or particle size distribution in real space, whose transformation would result in a matching scattering pattern. One such method for full information retrieval from isotropic scattering systems has recently been implemented using a Monte-Carlo (MC) approach (Pauw *et al*, J. Appl. Cryst., 2013)

Given the additional dimension of information present in anisotropic scattering patterns (carrying information on aspect ratio as well as orientation distribution), a similar method for these anisotropic patterns is desirable alongside more classical approaches (Pauw *et al*, 2010, 2011).
Such a method is here shown, where an anisotropic scattering pattern from PPTA fibre is analyzed using an MC approach (c.f. Figure 1). Each MC result is fit until it describes the data to within the data uncertainty.

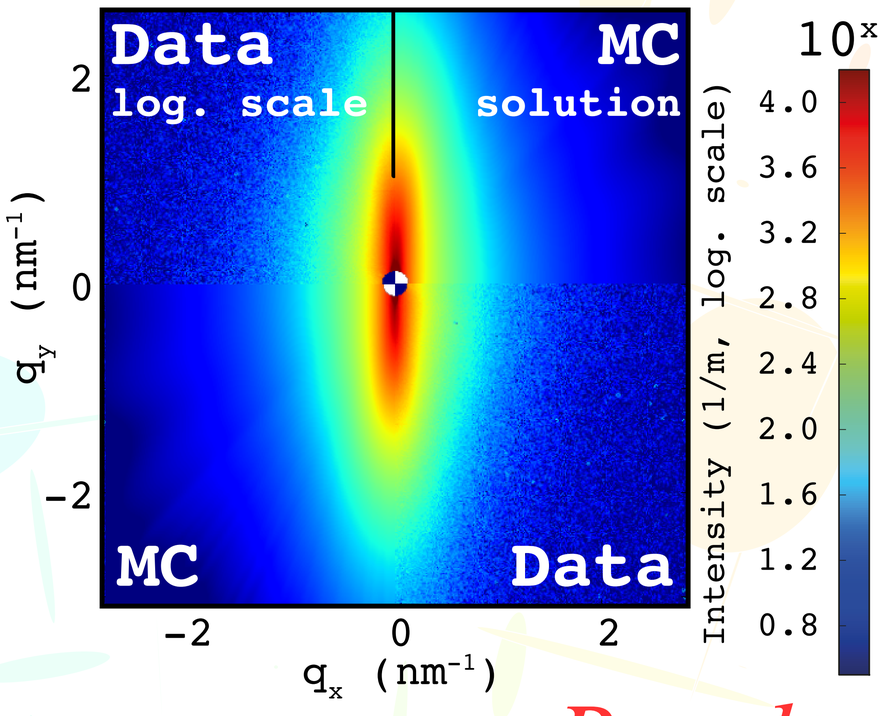

Figure 1 *- Scattered intensity (top left and bottom right quadrants) of a PPTA fibre with the fibre axis horizontal. This is compared to the Monte-Carlo fitted results for prolate ellipsoids (top right and bottom left quadrants).*

Results and Discussion

Information extracted from the MC solutions are visualized in Figure 2. The two major assumptions made are: 1. the scatterers are mainly ellipsoidal in shape, 2. their equatorial axes are within 45 degrees to either side of the fibre axis (leading to a solution consisting mainly of prolate ellipsoids).
From the MC solutions, other information can be extracted besides those shown in Figure 2. These include aspect ratio versus particle volume, or radius distribution versus orientation angle in order to check for correlations between these parameters. The size distributions in Figure 2 (left) show a multimodal distribution in equatorial radii of the voids, though due to information limitations, information of equatorial radii around 10 nanometer carry a high degree of uncertainty (this will be investigated in more detail in the near future). There is also a large volume of ellipsoidal voids aligned parallel to the fibre axis.

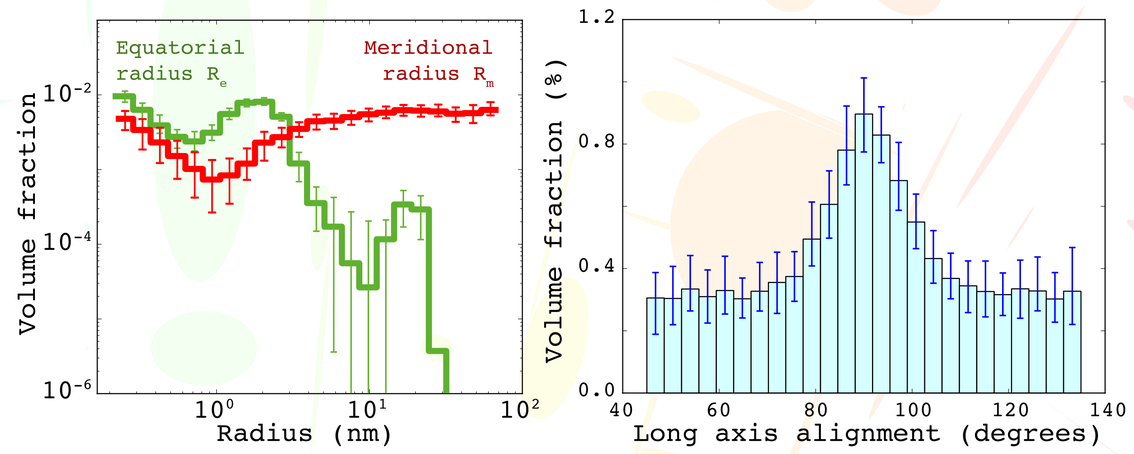

Figure 2 *-Basic information extracted from the MC result, showing the ellipsoid radius distributions (left) and axis alignment (right). Error bars indicate +/- 1 SD.*

A sample of PPTA fibre was measured on a laboratory SAXS machine consisting of a Rigaku SAXS instrument coupled with a motorized Pilatus 100K detector. A Twaron 1000 fibre sample was measured for 14 hours (50400 s) per frame, with an entire 2D image consisting of three frames. The background was measured for 6.7 hours (24000 s) immediately following the Twaron 1000 measurement. The data was corrected for background, transmission, polarization, sample self-absorption, spherical correction and Rigaku's uncommon 16th bit, and scaled to absolute units.

Poisson statistics were used as error estimates, propagated, and where necessary superseded by a lower limit of 1%.
The MC method starts with a random set of ellipsoids (Figure 3, left), calculating its theoretical scattering intensity (model). If a random replacement of one of the ellipsoids improves the agreement between the model intensity and measured scattering pattern, the replacement ellipsoid is kept. Through repetition of this trial-and-error replacement procedure, the model intensity is brought to agreement with the data. The optimization is stopped when the model intensity describes the data *on average* to within the data uncertainty (c.f. Figures 1, Figure 3, right). Accuracy of the result is estimated by repeating this entire MC process a multitude of times. Checks for overfitting and uncertainty can then be made by correlating these results.

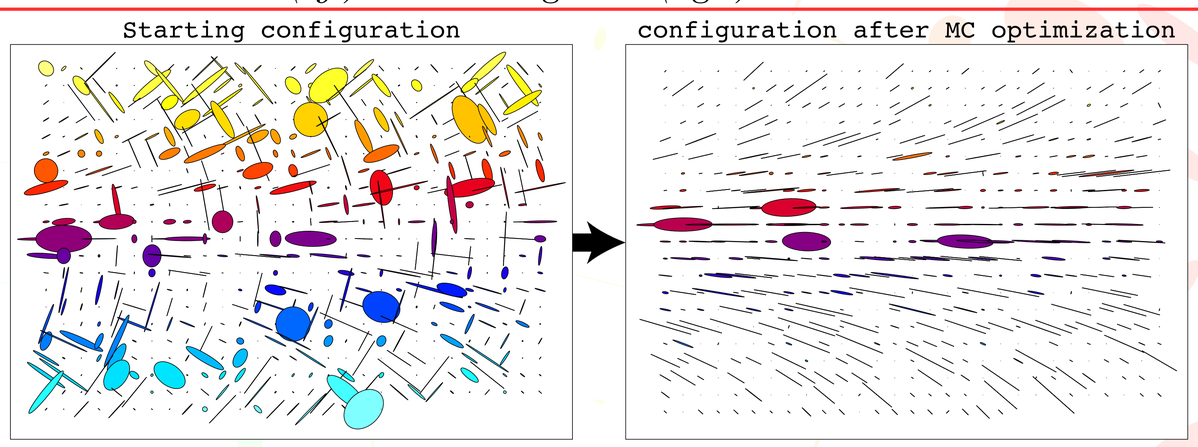

Figure 3 *- The ellipsoids before and after MC iterations (here shown sorted by meridional axis orientation)*

Experimental

Conclusion

The applicability of MC methods to anisotropic scattering patterns is shown, allowing the extraction of all available information. A wide range of morphological questions can be answered through careful interpretation of the MC result. Uncertainties on the MC solution can be estimated by testing the reproducibility of the solution to within the limits of the scattering pattern uncertainty.

Interested?
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