

SasView Tutorials

Correlation Function Analysis in SasView Version 5

www.sasview.org

Preamble

SasView was originally developed by the University of Tennessee as part of the Distributed Data Analysis of Neutron Scattering Experiments (DANSE) project funded by the US National Science Foundation (NSF), but is currently being developed as an Open Source project hosted on GitHub and managed by a consortium of scattering facilities. Participating facilities include (in alphabetical order): the Australian National Science & Technology Centre for Neutron Scattering, the Diamond Light Source, the European Spallation Source, the Federal Institute for Materials Research and Testing, the Institut Laue Langevin, the ISIS Pulsed Neutron & Muon Source, the National Institute of Standards & Technology Center for Neutron Research, the Oak Ridge National Laboratory Neutron Sciences Directorate, and the Technical University Delft Reactor Institute.

SasView is distributed under a 'Three-clause' BSD licence which you may read here: <https://github.com/SasView/sasview/blob/master/LICENSE.TXT>

SasView is free to download and use, including for commercial purposes.

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If you make use of SasView

If you use SasView to do productive scientific research that leads to a publication, we ask that you acknowledge use of the program with the following text:

This work benefited from the use of the SasView application, originally developed under NSF Award DMR-0520547. SasView also contains code developed with funding from the EU Horizon 2020 programme under the SINE2020 project Grant No 654000.

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Acknowledgements

The correlation function analysis used in SasView was originally coded by Adam Washington and released on GitHub under an MIT License (<https://github.com/rprospero/corfunc-py>). It was incorporated into SasView by ISIS Summer Student Lewis O'Driscoll in 2016. However, the inspiration for the code lie in a much earlier piece of software, *CORFUNC*, developed by Tom Nye (then an undergraduate mathematician at Cambridge, UK in 1994) at the request of Tony Ryan (then at the Daresbury SRS). *CORFUNC* was later released as part of the CCP13 software suite for Fibre & Polymer Diffraction.

Learning Objective

This tutorial will demonstrate how to perform correlation function analysis on 1D ('intensity' versus Q) datasets in SasView. But please note that this analysis is not available before Version 4.1.0.

It is assumed that the reader has some familiarity with the purpose and principles of correlation function analysis. If not, these references provide an overview:

- Ruland, W. *Coll. Polym. Sci.* (1977), 255, 417-427
- Strobl, G.R.; Schneider, M. *J. Polym. Sci.* (1980), 18, 1343-1359
- Koberstein, J.; Stein R. *J. Polym. Sci. Phys. Ed.* (1983), 21, 2181-2200
- Baltá Calleja, F.J.; Vonk, C.G. *X-ray Scattering of Synthetic Polymers*, Elsevier. Amsterdam (1989), 247-270
- Göschel, U.; Urban, G. *Polymer* (1995), 36, 3633-3639
- Stribeck, N. *X-ray Scattering of Soft Matter*, Springer-Verlag. Berlin Heidelberg (2007), Section 8.5
- <http://www.sasview.org/docs/user/sasgui/perspectives/corfunc/fdr-pdfs.html#fdr>

Also note that the integrals applied by the correlation function analysis in SasView (see page 11) assume that the data being transformed was either collected on a pinhole-collimated instrument or, if it was instead collected on a slit-collimated instrument, that it has been suitably Lorentz-corrected. Transforming slit-smearred data directly will generate invalid output.

The program interface shown in this tutorial is SasView Version 4.2 running on a Windows platform but, apart from a few small differences in look and functionality, this tutorial is generally applicable to SasView 4.1.x running on any platform. However, there is a separate tutorial for using the new program interface released with SasView 5.0.

Glossary

<i>a priori</i> information	Known facts about the system whose datasets are being analysed.
Correlation function	A real-space function that describes spatial relations in the system whose datasets are being analysed. The greater the degree of structural order in the system, the more periodicity the correlation function will display. In essence, the correlation function is a density probability function.
Correlation length	A measure of the periodicity of a correlation function.
Extrapolation	A mathematical process for inferring unknown values, or extending a function beyond known limits, using trends in known data or established dependencies.
Fourier Transform	A mathematical 'tool' that decomposes a measured signal into a sum of sine or cosine functions.

Invariant	Also called the Porod Invariant, the Scattering Invariant, and the Total Scattering: $Invariant = \int_0^{\infty} I(Q) Q^2 dQ$
Inverse-space	See reciprocal-space
Long Period	In a lamellar system, the distance from one face of a lamellae to <u>the same face</u> of the adjacent lamellae.
Real-space	Real world coordinates. The opposite of inverse-space or reciprocal space.
Reciprocal-space	The Fourier Transform of real world coordinates. The opposite of real-space. In scattering measurements, Q is the reciprocal-space equivalent of a real world length scale.
SLD	Abbreviation for Scattering Length Density, a measure of the ability of a molecule to scatter. Strictly speaking, SLD is a SANS quantity, so if fitting SAXS data use electron density values in their place. SLD values (neutron and X-ray) can be calculated with the SLD Calculator Tool in SasView.
Total Scattering	See Invariant
Transformation	A mathematical process for converting between real-space and inverse-space.
Uncertainties	Every experimental measurement, including the measurement of $I(Q)$, is subject to some degree of error (which will, ideally, be included in the dataset). Similarly, the parameters returned by any analysis will have some associated range of uncertainty. Parameters with uncertainties that are more than 95% of the parameter value should be viewed with deep suspicion.

Running SasView

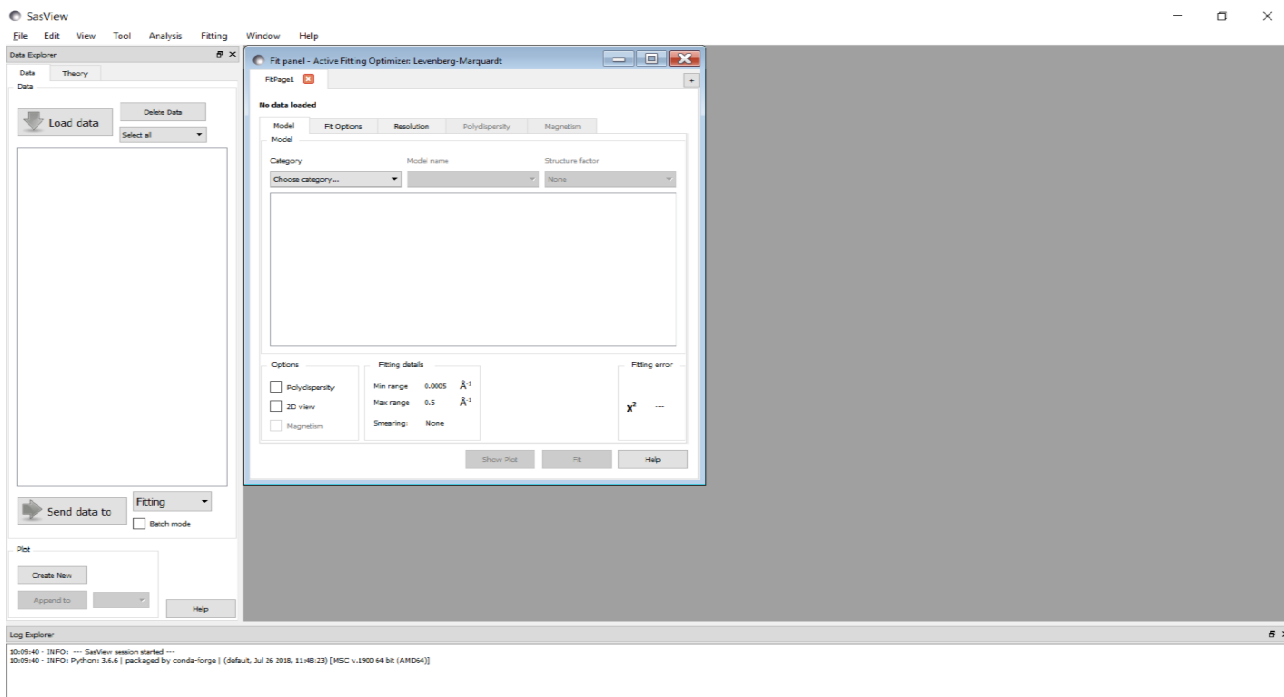
Windows

Either select SasView from 'Start' > 'All Programs' or, if you asked the installer to create one, double-click on the SasView desktop icon.



Mac OS

Go in to your 'Applications' folder and select SasView.

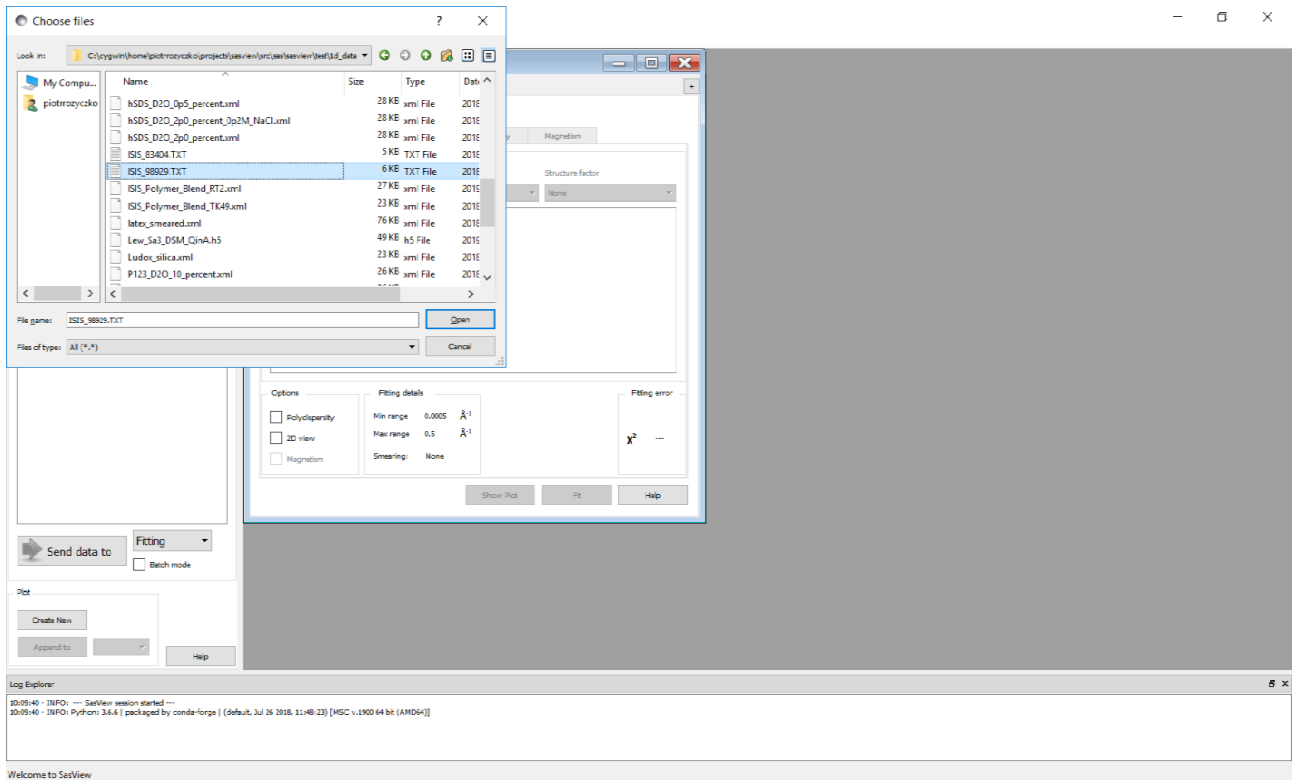


Example 1

This computes the correlation function from a quasi-lamellar system and then interprets that correlation function to extract parameters characterising the underlying nanostructure. This is a typical use case.

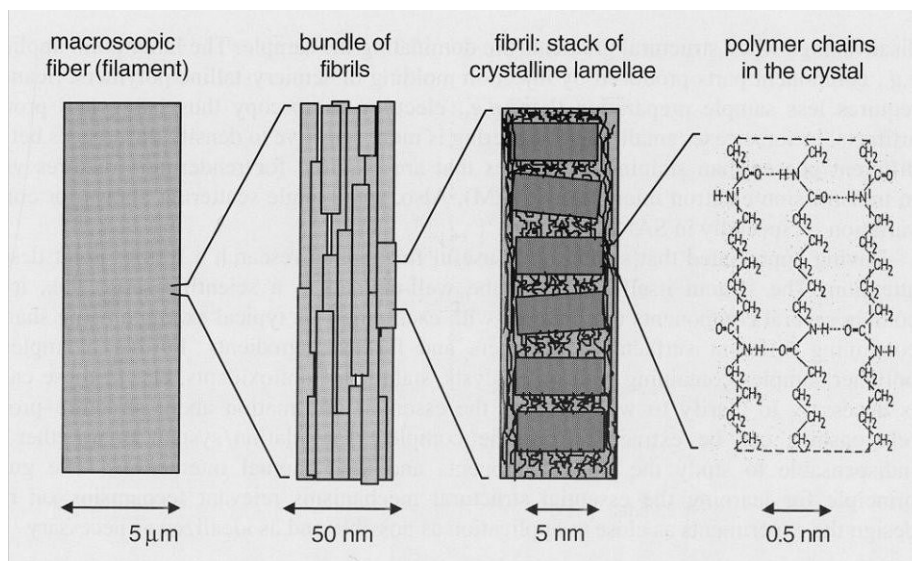
In the Data Explorer panel, click the **Load Data** button, and navigate to the `test1d_data` folder in the SasView installation directory.

Select the **ISIS_98929.txt** dataset and click the **Open** button.



This dataset is the SANS from fibres of nylon-6 (polyamide-6) hydrated with heavy water. The fibres are aligned perpendicular to the neutron beam and parallel to the detector meridian.

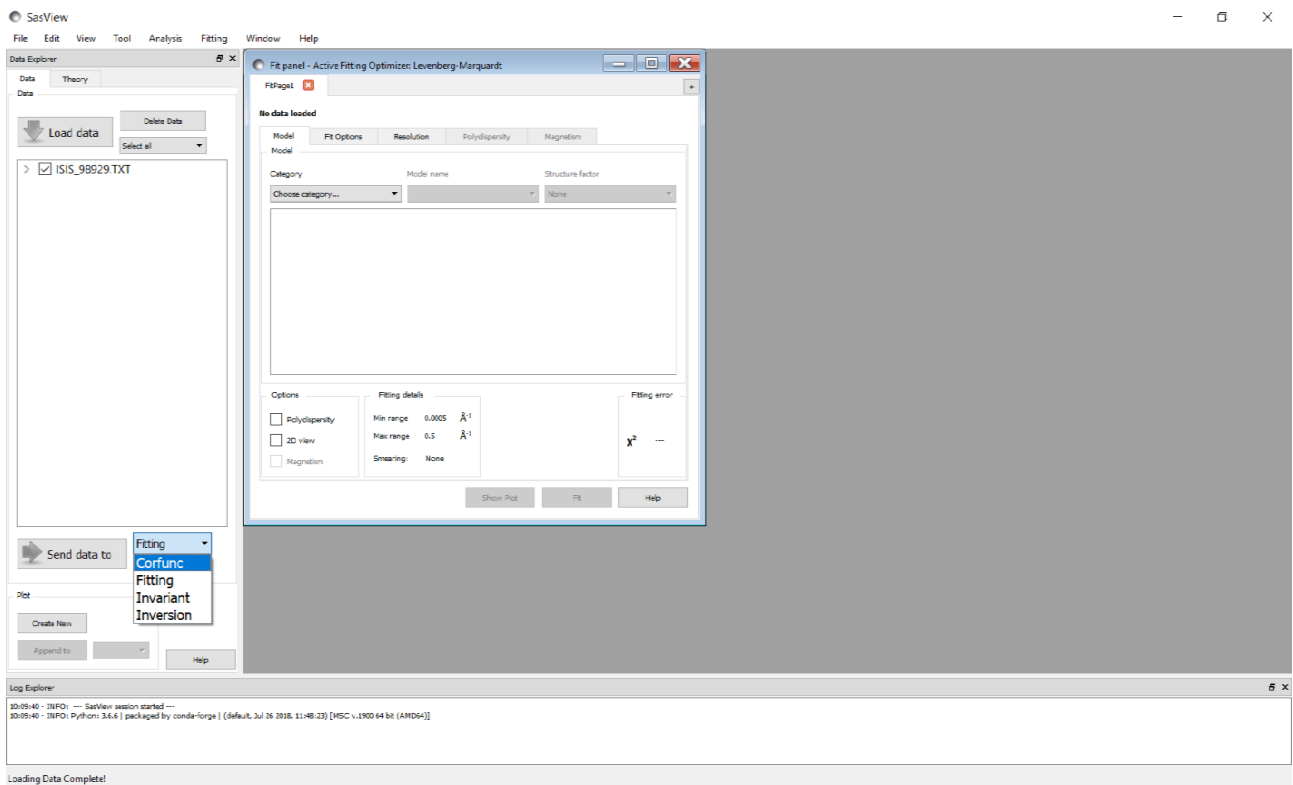
Nylon is a semi-crystalline polymer, meaning it is composed of alternating regions of crystalline (more dense) and amorphous (less dense) polymer. When hydrated, water molecules preferentially locate to the amorphous regions. If heavy water is used the SLD of the amorphous regions is enhanced relative to the SLD of the crystalline regions.



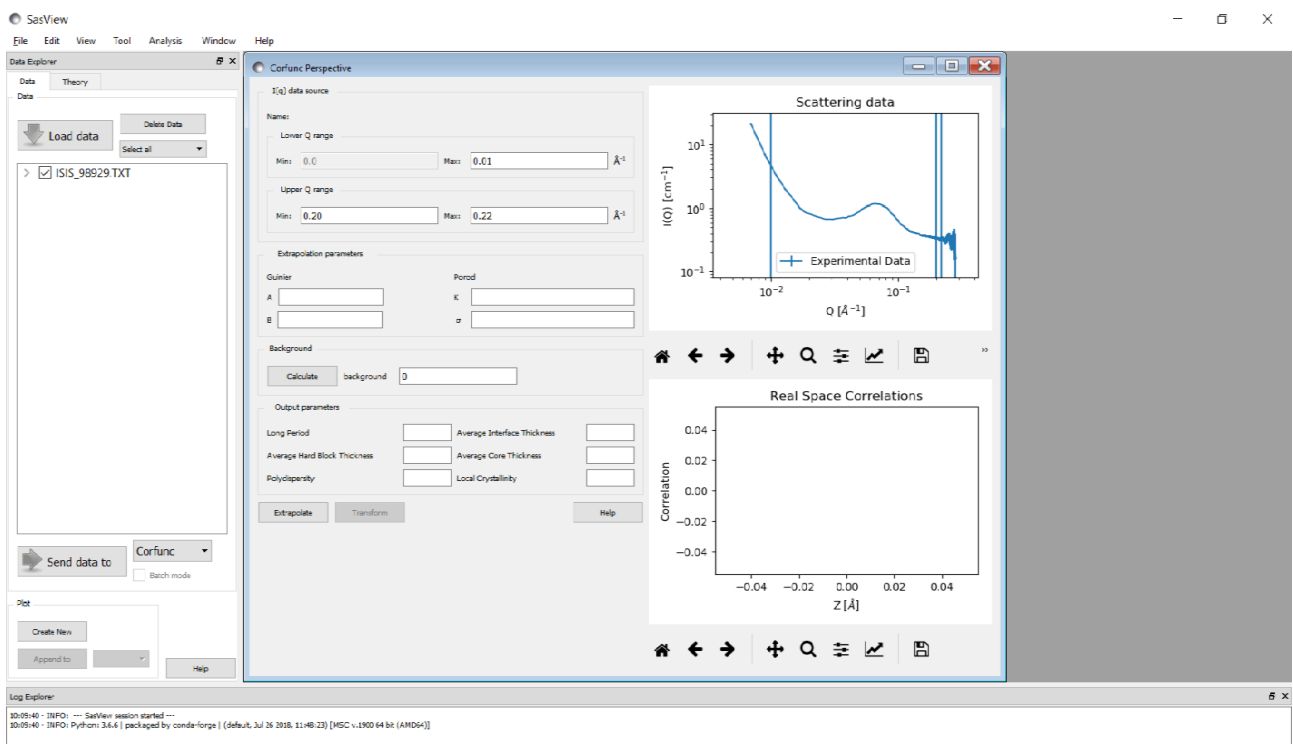
The hierarchical structure of nylon fibres. Figure reprinted from "Use of scattering methods in chemical industry - SAXS and SANS from fibers and films". Chapter 21, in "Neutrons, X-rays and Light: Scattering Methods Applied to Soft Condensed Matter". Lindner & Zemb (editors), North-Holland. 2002.

This periodicity in the nanostructure manifests itself as a peak in the scattering data.

At the bottom of the Data Explorer panel, click the drop-down that currently says 'Fitting' and select **Corrfunc**. Then click the **Send To** button.



The FitPage transforms into a Correlation Function analysis page and the measured data is displayed along with three vertical bars.



Tip: If you want to change the axis scales to alter the appearance of the plot, right-click on the graph and select Change Scale.

The correlation function is computed by taking the (cosine) Fourier Transform of the scattering data. However, this requires performing an integration between $Q=0$ and $Q=\infty$, and quite clearly the measured data do not extend to those limits (and nor could they)! The prerequisite, therefore, is to extrapolate the measured data towards those limits.

The three bars represent the limits of the measured data that will be used to construct the extrapolation functions. In the case of the low-Q extrapolation, all data to the left of the red vertical bar is used. In the case of the high-Q extrapolation, data between the two purple vertical bars is used.

Tip: You can change the default extrapolation ranges by typing appropriate Q-values in the “Q Range” boxes in the Correlation Function analysis page.

Aside: At the present time, SasView extrapolates the measured data with the following functions:

Low-Q

Guinier function

$$I(Q) = A \cdot e^{(B \cdot Q^2)}$$

High-Q

Porod function

$$I(Q) = K \cdot Q^{-4} \cdot e^{(-\sigma^2 \cdot Q^2)} + Bg$$

where B is proportional to a radius-of-gyration, σ is a measure of how abruptly the SLD changes between the quasi-lamellar regions ($\sigma \geq 0$; 0 represents a step function), and Bg is a Q-independent background level. A and K are just scale factors.

Though the *Guinier function* may be a dubious description of the low-angle scattering from some systems, because of the transformation from reciprocal-space to real-space any artefacts that the use of this function introduces only manifest themselves in the region of the correlation function where the density probability is close to zero anyhow.

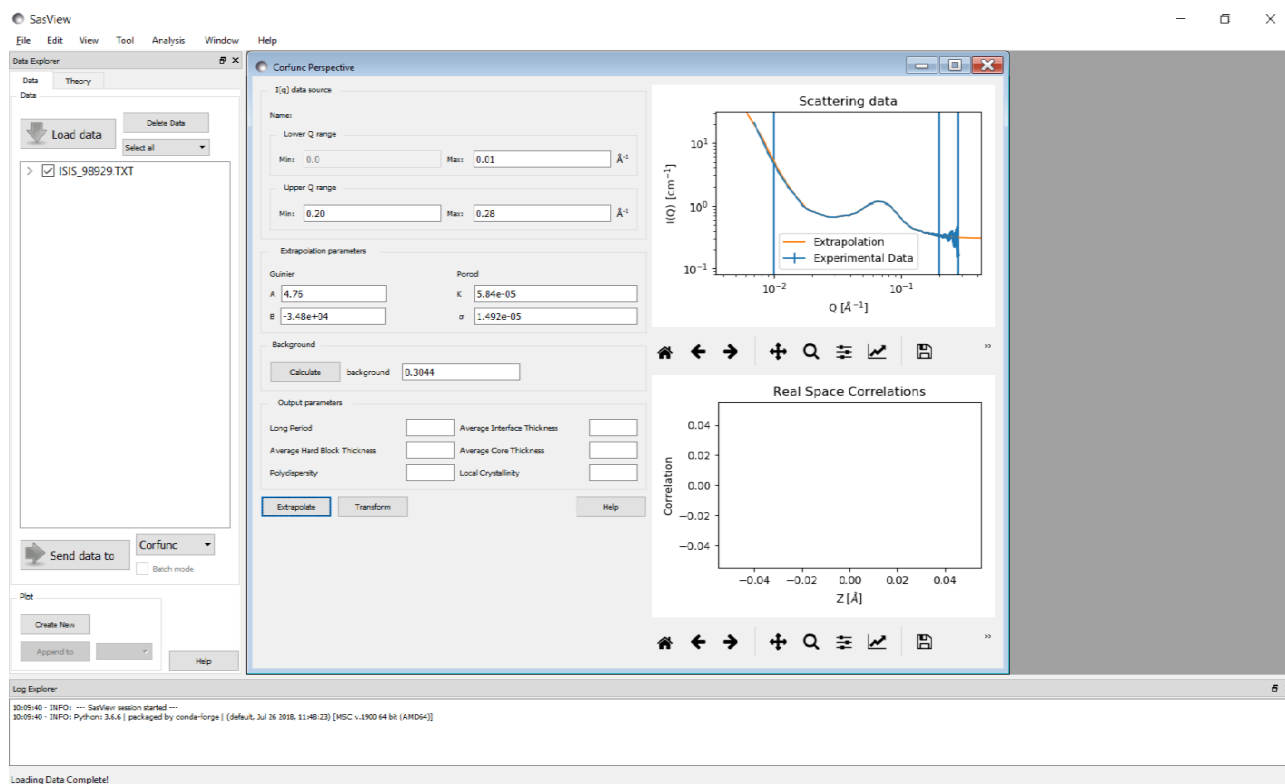
Conversely, the quality of the high-Q extrapolation is much more important, so consider carefully which datapoints to include between the purple bars. Do not include any datapoints within the peak itself. *In lieu* of infinity, SasView computes the high-Q extrapolation out to 100 times the largest Q value in the measured dataset.

In this example, the low-Q extrapolation range looks ok. However, close inspection reveals that the last three datapoints have gone negative after background subtraction, so set the upper limit for the high-Q extrapolation to $Q=0.28$.

Tip: If the limit bar does not update when a limit is changed, move the mouse pointer over the graph window.

Now recalculate the background level by clicking the **Calculate** button in the *Background* section of the Correlation Function analysis page. The value displayed will change slightly.

Next, click the **Extrapolate** button at the bottom of the page.



Several things happen:

- SasView computes the low-Q and high-Q extrapolation functions; the values of A , B , K , σ , and B_g are returned in the middle of the Correlation Function analysis page.
- The B_g value is shown. The background level is subtracted from the measured dataset but some datapoints still have negative intensities.
- The graph window updates to show an orange line; this is a smoothed concatenation of the low-Q extrapolation (from $0 \leq Q < Q_{\min}$), the measured dataset (from $Q_{\min} \leq Q \leq Q_{\max}$), and the high-Q extrapolation (from $Q_{\max} < Q \leq 100 \times Q_{\max}$). Note that the full Q-range of the extrapolated data is not displayed for clarity!

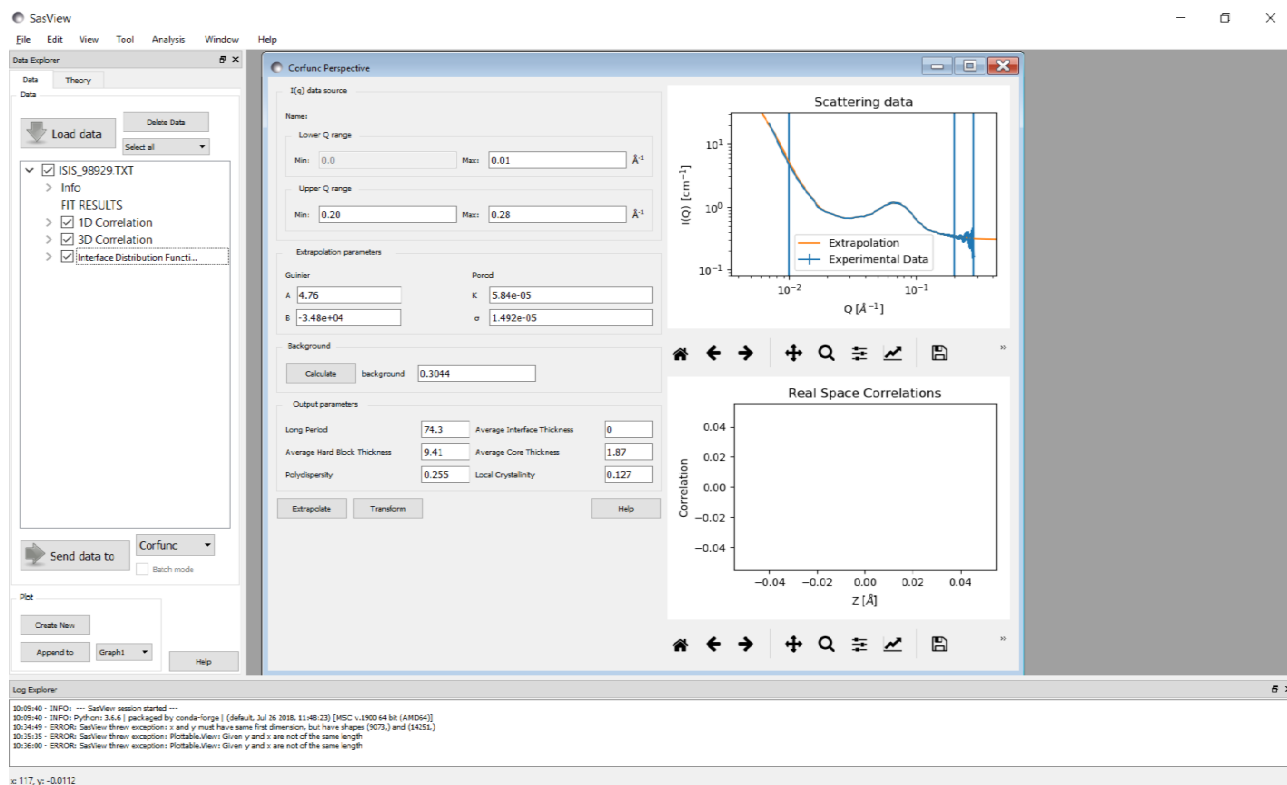
Aside: The smoothing is applied to prevent the joins between the extrapolations and the measured dataset generating 'ripples' in the correlation function. At the same time it provides a means of giving the concatenated dataset equally spaced Q points which facilitates the Fourier Transform.

The algorithm used is described in more detail in the SasView documentation at: http://www.sasview.org/docs/user/sasgui/perspectives/corfunc/corfunc_help.html

*Although the value of B_g calculated by SasView is over-subtracting the background on some datapoints, so long as B_g is not too large compared with the peak height, this should not be a problem. **The essential requirement is that $I(Q) - B_g$ is zero at high Q***

values. If necessary, manually adjust Bg and re-extrapolate.

We are now ready to compute the correlation function. So click the **Transform** button.



Three new graphs appear in the Data Explorer:

- $\Gamma_1(x)$ & $\Gamma_3(x)$ - these are the 1D and 3D-averaged (or 'radial') Correlation Functions
- $g_1(x)$ - this is the Interface Distribution Function (IDF)

The IDF is a superposition of thickness distributions from all the contributing lamellae.

Aside: The transforms that SasView computes are:

1D Correlation Function:
$$\Gamma_1(x) = \frac{1}{\text{Invariant}} \int_0^{\infty} I(Q) Q^2 \cos(Qx) dQ$$

3D Correlation Function:
$$\Gamma_3 = \frac{1}{r} \int_0^r \Gamma_1(x) dz$$

which is equivalent to computing:
$$\Gamma_3(x) = \frac{1}{\text{Invariant}} \int_0^{\infty} I(Q) Q^2 \frac{\sin(Qx)}{Qx} dQ$$

Interface Distribution Function:
$$g_1(x) = \frac{1}{\text{Invariant}} \int_0^{\infty} I(Q) Q^4 \cos(Qx) dx$$

where $\Gamma_1(0) = \Gamma_3(0) = 1$, and $g_1(0) \geq 0$.

The integral breadth of a correlation function is the correlation length:

$$\text{correlation length} = 2 \int_0^{\infty} \Gamma(x) dx$$

Having obtained the correlation functions it is always advisable to inspect them for artefacts from the Fourier Transform procedure:

- Do $\Gamma_1(x)$ & $\Gamma_3(x)$ smoothly curve into the ordinate at $x=0$? (sometimes overly small values of σ can cause the functions to meet the ordinate at a sharp angle)
 - This example: Yes
- Does $\Gamma_1(0) = \Gamma_3(0) = 1$?
 - This example: Yes
- Do $\Gamma_1(x)$ & $\Gamma_3(x)$ tend to 0 as x tends to ∞ ?
 - This example: Yes
- Are there 'ripples' in $\Gamma_1(x)$ & $\Gamma_3(x)$ with a period of $2\pi/(100Q_{\max})$? (ie, corresponding to the truncation point of the Fourier Transform)
 - This example: No (Q_{\max} for this dataset was 0.285 \AA so the period of these ripples would be $\sim 0.2 \text{ \AA}$)
- Are there 'ripples' in $\Gamma_1(x)$ & $\Gamma_3(x)$ with a period of $2\pi/Q_{\max}$? (ie, corresponding to the point at which the measured dataset was extrapolated to high-Q)
 - This example: Not obviously (Q_{\max} for this dataset was 0.285 \AA so the period of these ripples would be $\sim 20 \text{ \AA}$)
- Are there 'ripples' in $\Gamma_1(x)$ & $\Gamma_3(x)$ with a period of $2\pi/Q_{\min}$? (ie, corresponding to the point at which the measured dataset was extrapolated to low-Q)
 - This example: No (Q_{\min} for this dataset was 0.007 \AA so the period of these ripples would be $\sim 900 \text{ \AA}$)

and lastly:

- Do the principle peaks in $\Gamma_1(x)$ & $\Gamma_3(x)$ seem to correspond to expectations?!!!
 - This example: It is well-established that the quasi-lamellar repeat distance between the crystalline regions in hydrated nylon-6 is about $84 \pm 4 \text{ \AA}$ (see for example, King, S.M.; Bucknall, D.G. *Polymer* (2005), 46, 11424-11434). As can be seen the first prominent maximum in $\Gamma_1(x)$ is around 74 \AA , but the fact that it is not a sharp or symmetrical peak bears testament to an underlying distribution of imperfectly ordered spacings. So in general $\Gamma_1(x)$ does seem believable. The maximum in $\Gamma_3(x)$ is around 103 \AA .

Notice that less structure is evident in $\Gamma_3(x)$ because of the orientational averaging.

Tip: To obtain the datapoints for either $\Gamma_1(x)$ & $\Gamma_3(x)$, right-click on the graph, select $\Gamma_1(x)$ or $\Gamma_3(x)$, and then DataInfo or Save Points as a File.

As we have the *a priori* information that this sample possesses a quasi-lamellar structure the final part of the analysis is to look at extracted physical parameters from $\Gamma_1(x)$.

Values will appear in the Output Parameters section.

Corfunc Perspective

I(q) data source

Name:

Lower Q range

Min: 0,0 Max: 0.01 Å⁻¹

Upper Q range

Min: 0,20 Max: 0.28 Å⁻¹

Extrapolation parameters

Guinier

A 4.76

B -3.48e+04

Porod

K 5.84e-05

σ 1.492e-05

Background

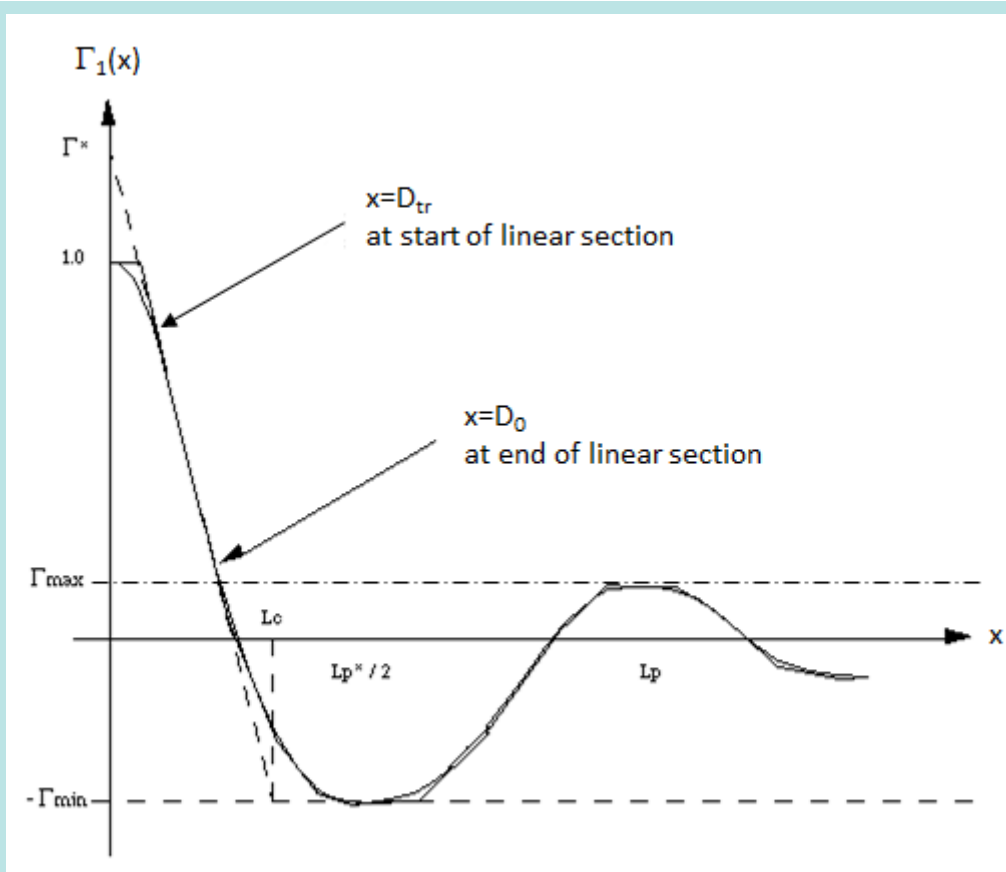
Calculate background 0,3044

Output parameters

Long Period	74.3	Average Interface Thickness	0
Average Hard Block Thickness	9.41	Average Core Thickness	1.87
Polydispersity	0,255	Local Crystallinity	0,127

Extrapolate Transform Help

Aside: Various procedures have been proposed to extract structural parameters from $\Gamma_1(x)$. SasView uses the positions of the first local minima (with $\Gamma_1(x) < 0$) and local maxima (with $\Gamma_1(x) > 0$), along with the extrapolated intercept and gradient of the linear section between the ordinate at $x=0$ and the first local minima, as shown below.



Schematic explanation of the extraction of ideal lamellar structural parameters from $\Gamma_1(x)$.
 Figure reprinted from "SAXS Correlation Function Analysis: Notes on the Software at Daresbury". Nye. 1994.

From which:

Polydispersity	$\Gamma_{\min} / \Gamma_{\max}$
Average Hard Block Thickness [†]	L_c
Long Period	L_p
Average Interface Thickness	D_{tr}
Average Core Thickness	D_0
Local Crystallinity	$L_c / L_p = \Phi_c$

and:

Average Soft Block Thickness [†]	$L_p - L_c = L_a$
Average Chord Length	$((1/L_c) + (1/L_a))^{-1}$
Average Crystalline Chord Length	$((1/L_c) + (1/L_a))^{-1} / \Phi_c$
Non-Ideality	$(L_p - L_p^*)^2 / L_p^2$

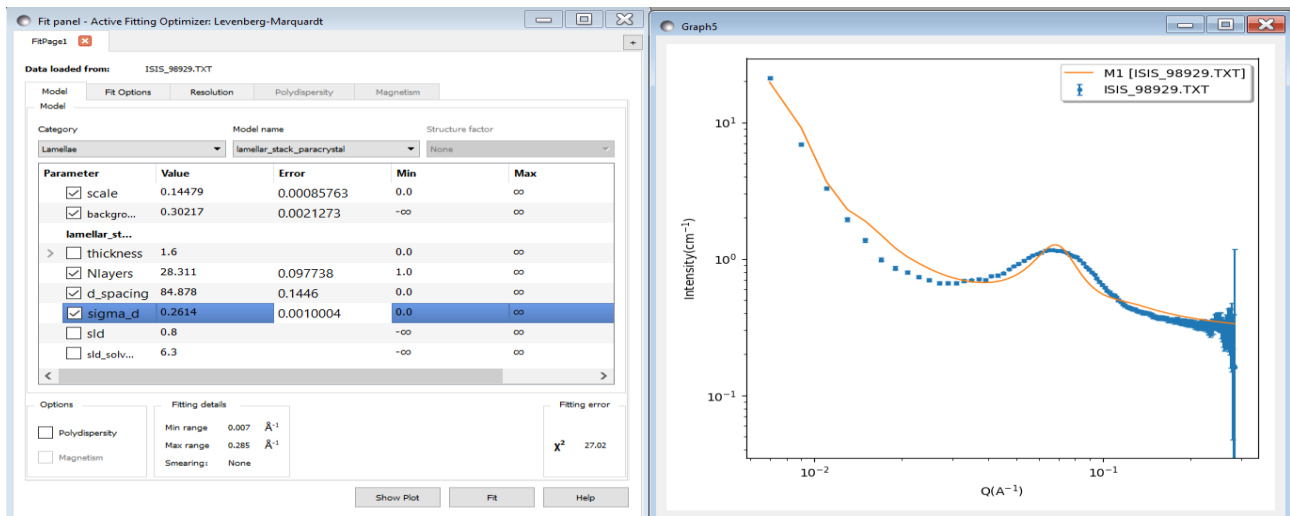
[†] "hard block" = crystalline, "soft block" = amorphous

From this we can see that the analysis suggests that most of the quasi-lamellar nanostructure in the nylon fibres is actually amorphous polymer (10% crystallinity, soft block thickness of 66 Å). And certainly the fibres are highly flexible and extensible.

WARNING!

Compute Parameters will return garbage output unless it is known that the scattering is from a lamellar or quasi-lamellar nanostructure! So use with caution!

For comparison, here is a SasView model-fit to the same dataset. The model used describes a stack of repeating lamellar structures of *infinite* lateral dimensions where the lamellar repeat distance is subject to Gaussian polydispersity.



In this fit the SLD of the hard blocks has been fixed at the SLD for nylon, whilst the SLD of the matrix has been fixed at the SLD of heavy water. The thickness of the lamellae has also been fixed at that deduced from the correlation function analysis.

Although the fit is not very good, it nonetheless returns a repeat distance of 84 Å with 26% polydispersity (one standard deviation), and estimates the volume fraction of the hard blocks (~local crystallinity) as 14%. Both parameters are consistent with those returned by the correlation function analysis. The one additional piece of information the fit returns, that is not accessible by correlation function analysis, is the number of lamellae in each stack; *Nlayers*: ~28.

Optional

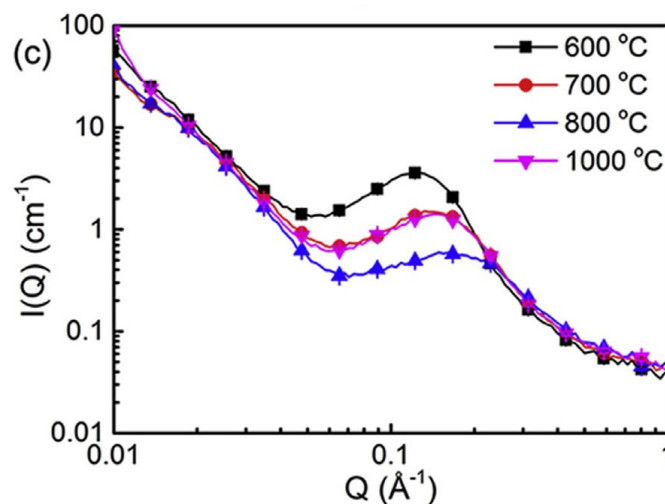
The dataset `test1d_data\ISIS_83404.txt` is SANS from the same fibres but after exposure to sulphuric acid, a reagent known to degrade the amide linkage. If you wish, use correlation function analysis to examine how this changes the nanostructure.

Example 2

This example is actually a demonstration of correlation function analysis from a nanostructure that does not exhibit lamellar order. It is included here to highlight the potential applications of correlation function analysis in other fields.

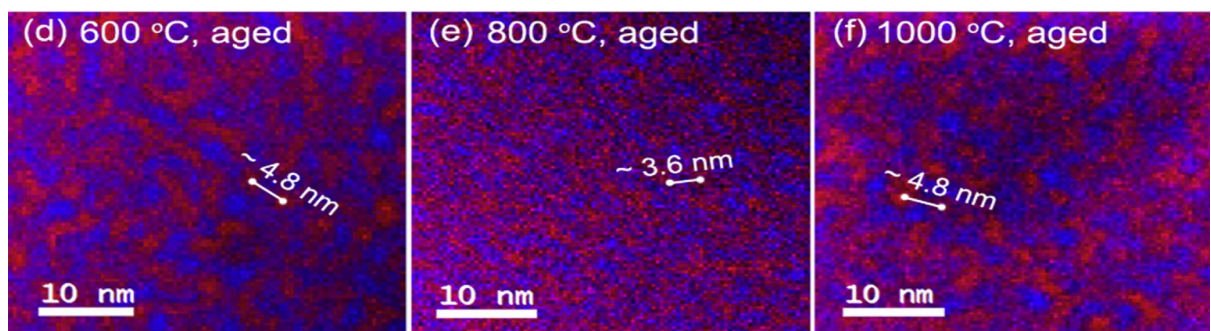
The data in question is from a parametric survey, using a variety of techniques but including SANS, of how different heat treatments affect the nanostructure of Fe-Cr binary alloys. The work is described in Xu *et al*, *Acta Mat.*, (2017) available at <https://doi.org/10.1016/j.actamat.2017.12.008>.

This material undergoes spinodal decomposition on thermal ageing, resulting in Fe-rich and Cr-rich domains and a characteristic 'spinodal peak' in the SANS.



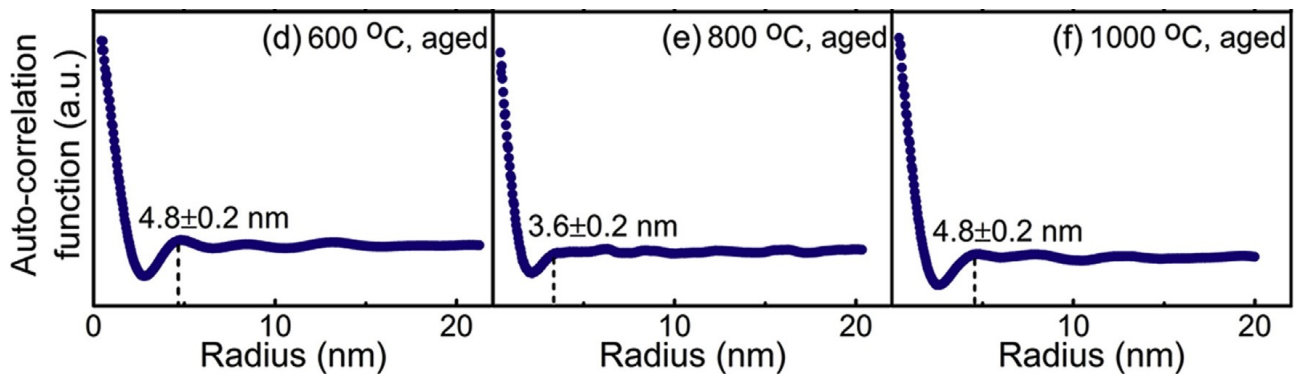
SANS data of alloy specimens treated at different temperatures and subsequently aged at 475 C for 100 hours. Figure reproduced from Fig 6 in Xu *et al*, *Acta Mat.*, (2017).

Thin sections of the alloy specimens were examined by STEM-EELS and the resulting images processed to generate 2D auto-correlation maps of the Fe/Cr distribution.



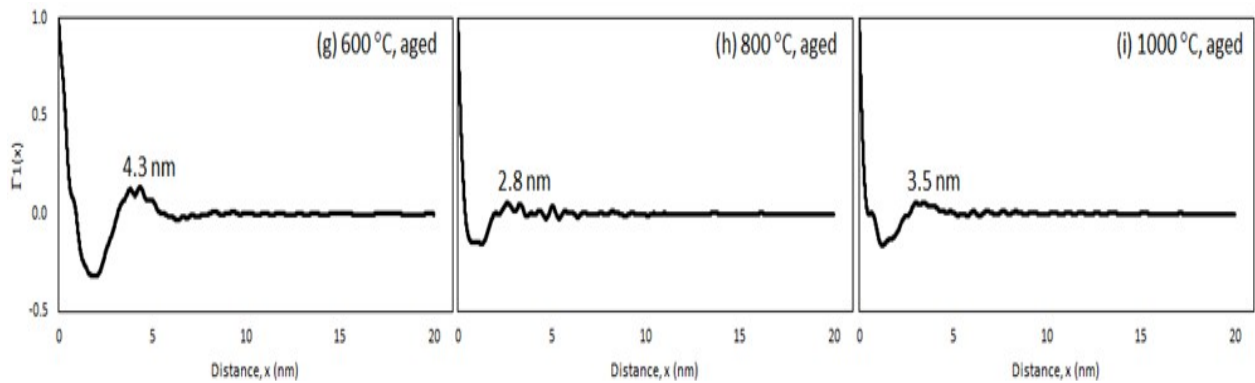
Ratio maps of the intensity of the Cr L3-edge (red) and Fe L3-edge (blue) from alloy specimens treated at different temperatures and aged at 475 C for 100 hours. Figure reproduced from Fig 9 in Xu *et al*, *Acta Mat.*, (2017).

These maps were in turn radially-integrated to yield an averaged (auto)correlation function as shown below.



Azimuthally integrated and averaged profiles of the Cr/Fe L3-edge ratio maps from alloy specimens aged at 475 C for 100 hours. Figure reproduced from Fig 10 in Xu et al, Acta Mat., (2017).

For comparison, here are the correlation functions computed using SasView:



As can be seen, the agreement is actually quite good! But the important point here is that the SANS-derived correlation functions are averaged over a far larger gauge volume (mm^3) compared to that from the STEM-EELS measurements (nm^3).

Further Information

For further information, please consult the

SasView Tutorial Series

or

<http://www.sasview.org>

or email

help@sasview.org