

discerning weak peaks in a high background as the high gain can be offset to the required background level.

The instrument has been developed to take advantage of station 16.1 at the SRS, with the optimum detector quantum efficiency (DQE) in the higher energy 16 keV range (see Figure 2). The tapers for the WAXS detectors are 3.88:1 and for the SAXS it is 2:1. This results in a slightly higher efficiency for the SAXS detector (90%) than the WAXS detector (80%) at 16keV and  $2 \times 10^4$  photons per pixel.

The SAXS detector can be moved from 0.27m to 3m from the sample position. As the hole in the WAXS mosaic is offset from the centre, the full quadrant from the beam stop to  $45^\circ$  can be collected at the 0.27m position. A transparent beam stop will be mounted before the SAXS detector for the collection of normalisation data. The detector is designed to fit seamlessly into the existing Daresbury instrumentation. This will allow the SAXS detector to be replaced by the RAPID SAXS detector, if required.

In normal operation, data will be written to a 20Gb RAID ultra wide SCSI array allowing 2000 frames of data to be collected, before downloading the NCD file server. At slow frame rates, the full image of the data can be sequentially displayed on the console. At high frame rates, an area can be selected for integration and the integrated count can be displayed. For compatibility with the existing Daresbury set-up, the detector will provide the cycle and group functions as standard.

The data will be presented and saved with dark and white-field corrections but without geometrical corrections, allowing the user to select the preferred geometrical corrections during data reduction. These may be a transformation to reciprocal space or a flat plate. The data correlating each pixel to angular position, to allow these transformations to be performed, will be stored separately from the data set as is currently the case on existing equipment.

This detector is scheduled for delivery for January 2000 and should be available as a scheduled instrument shortly afterwards.

## CCP13 Software Development

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*There has been an upgrade of the existing CCP13 program, corfunc (T.M.W. Nye 1994), which can be used to perform correlation function analysis of one-dimensional small-angle scattering (SAXS) data. corfunc is now driven by a Java-based graphical user interface (GUI) and incorporates more robust non-linear least-squares fitting. The GUI greatly enhances the user-friendliness of the program and also allows it to be run with greater efficiency and flexibility. New interactive graphics allow corfunc to be run independently of other programs such as XOTOKO. The program is provided to run on NT/Windows, LINUX and various UNIX operating systems.*

### 1 Introduction

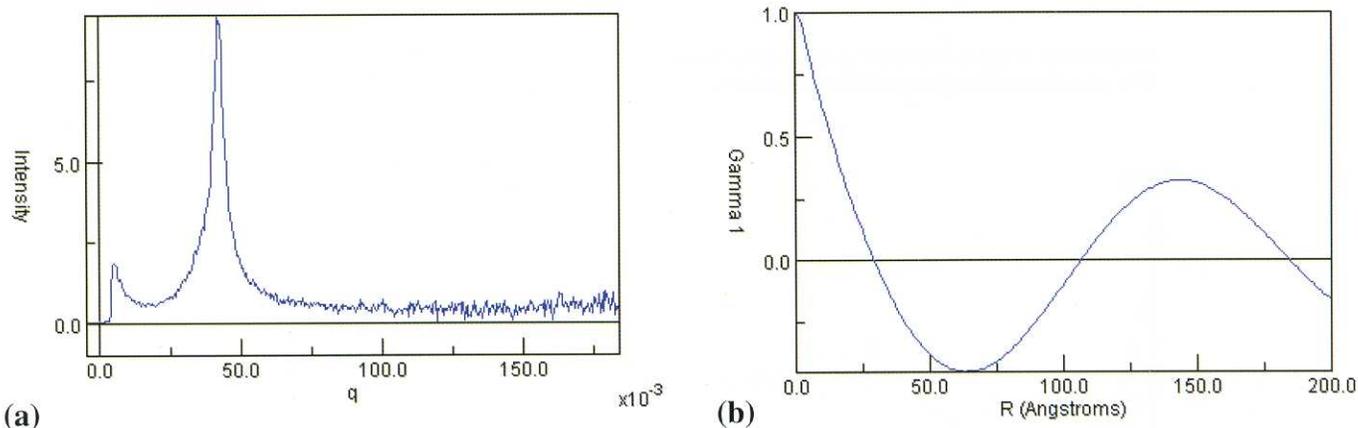
SAXS data can be subjected to correlation function analysis in order to derive structural parameters corresponding to the sample [1-2]. The correlation

function is simply the Fourier Transform of the SAXS curve as shown in Figure 1.1. It is related to the electron density distribution within the sample as shown in Figure 1.2.

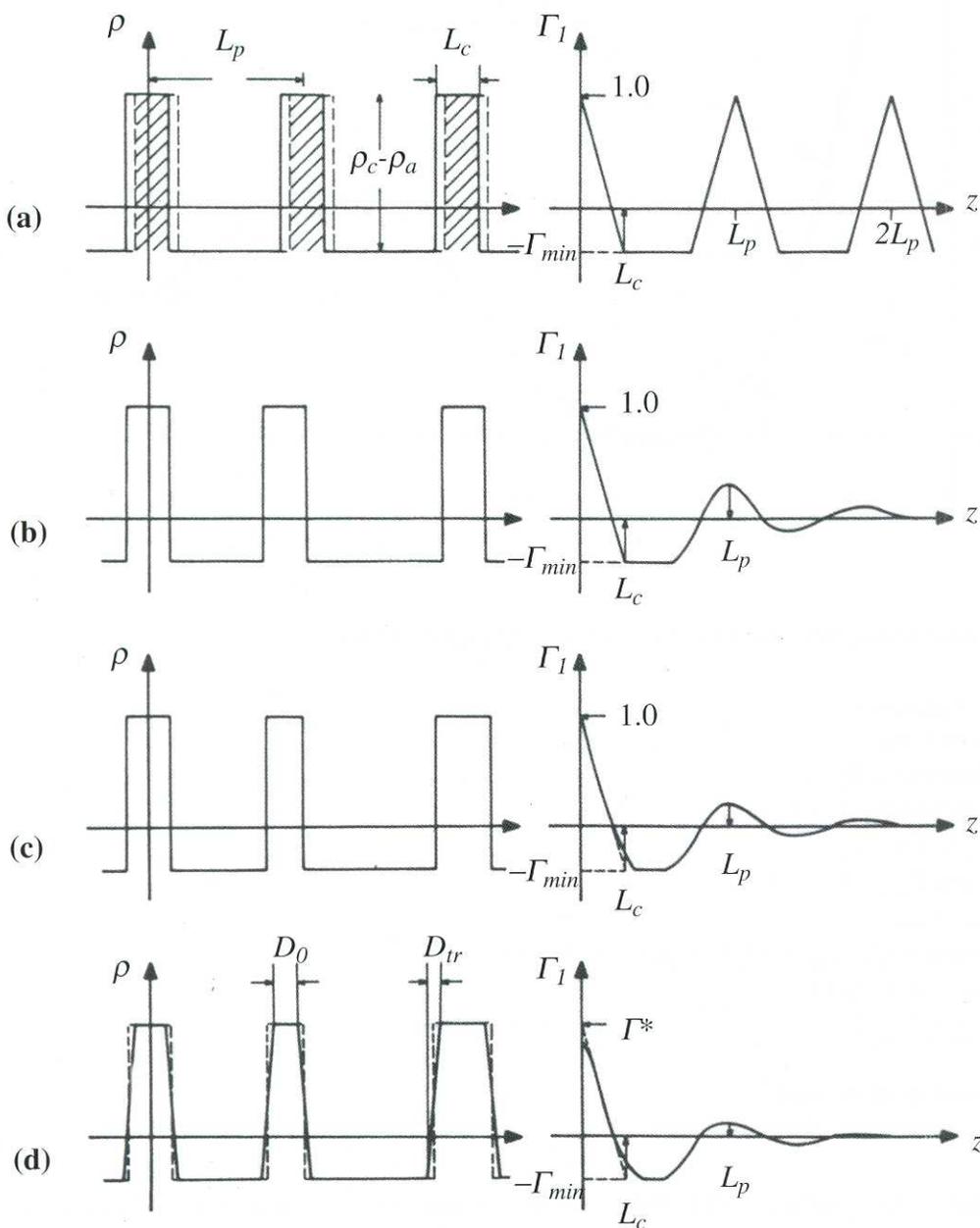
Figure 1.3 shows the structural parameters that can be obtained by interpretation of the 1-D correlation function. This interpretation assumes that the sample has an ideal lamellar morphology, *i.e.* it assumes that the sample consists of an ensemble of isotropically distributed stacks of alternating crystalline and amorphous lamellae. The stacks are assumed to be of dimensions that are large enough not to affect the small angle scattering.

### 2 The corfunc GUI

The Java-based GUI that drives the *corfunc* program (see Figure 2.1) can be run on any Java 1.2 platform or above (see <http://www.javasoft.com>). SAXS data

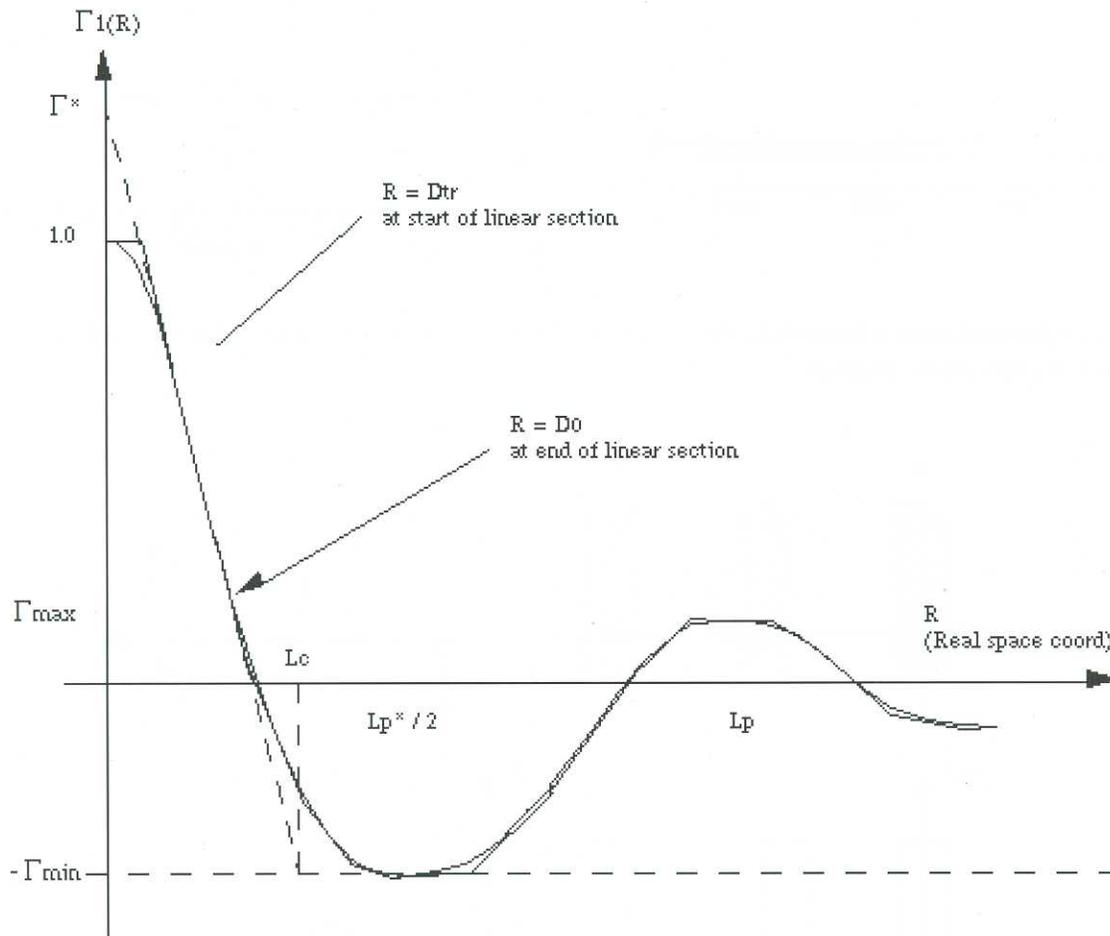


**Figure 1.1:** (a) One-dimensional SAXS data, (b) One-dimensional correlation function calculated as the Fourier Transform of the SAXS data using the *corfunc* program.



**Figure 1.2:** Electron density distribution  $\rho(z)$  and its related correlation function  $\Gamma_1(z)$  for lamellar systems of different regularity [1]. (a) Periodic two-phase system. (b) The effect of long-spacing variations on (a). (c) The effect of thickness fluctuations on (b). (d) The effect of introducing diffuse phase boundaries to (c). Symbols are described in the caption to Figure 1.3.

**Extraction of ideal lamellar parameters from the one dimensional correlation function.**



**Figure 1.3:** One-dimensional correlation function analysis. Parameters obtained:

Long period =  $L_p$

Average hard block thickness =  $L_c$

Average core thickness =  $D_0$

Average interface thickness =  $D_{tr}$

Average soft block thickness =  $L_a = L_p - L_c$

Local crystallinity =  $\phi_l = L_c / L_p$

Bulk crystallinity =  $\phi = \Gamma_{min} / (\Gamma_{min} + \Gamma^*)$

Polydispersity =  $\Gamma_{min} / \Gamma_{max}$

Electron density contrast =  $(\rho_c - \rho_a)^2 = (\Delta\rho)^2 = Q\Gamma^* / (\phi(1 - \phi))$

Specific inner surface =  $O_s = 2\phi / L_c$

Non-ideality =  $(L_p - L_p^*)^2 / L_p^2$

where  $Q$  = second moment or invariant

can be loaded in either OTOKO (see <http://www.srs.dl.ac.uk/NCD/computing/manual.otoko.html>) or ASCII format and are displayed as shown in Figure 1.1. By editing the various input parameters (see Figure 2.2) and then selecting items from the *Actions* menu, the user can perform

consecutively the three stages involved in the correlation function analysis:

- (i) extrapolation of the data to  $q = 0$  and  $q = \infty$
- (ii) calculation of the Fourier transform of the extrapolated data

(iii) interpretation of the correlation function obtained in (ii)

The results of the analysis are displayed graphically in pop-up windows or as scrolling text in the message window. Graphs can be saved in several common image formats. All results are also output to OTOKO and/or ASCII format files. Help pages are displayed in a platform-independent way using the JavaHelp system.

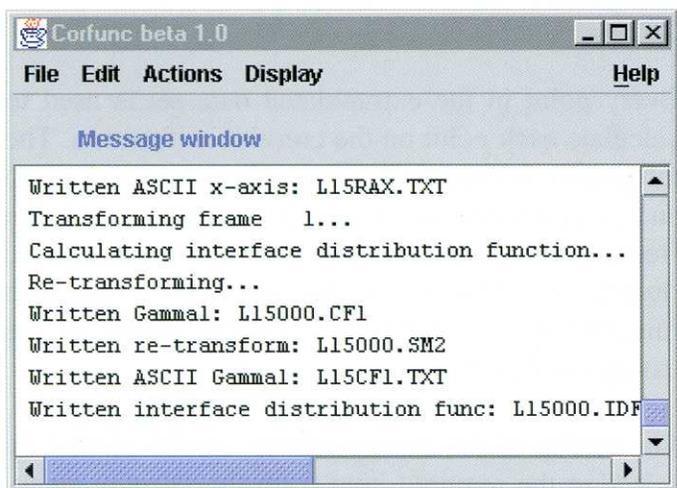


Figure 2.1: The *corfunc* GUI

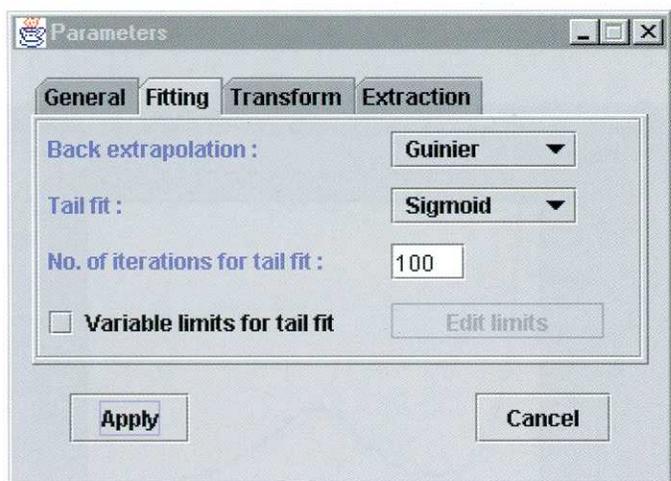


Figure 2.2: Input parameters

### 3 Data processing

#### 3.1 Extrapolation of SAXS data

Prior to calculating the Fourier Transform of the SAXS data, the data must first be extrapolated to  $q = 0$  and  $q = \infty$  to avoid the introduction of series termination errors in the transform.

#### 3.1.1 Extrapolation to $q = \infty$

Extrapolation to  $q = \infty$  is performed by fitting either a Porod [3] or sigmoid [4] function to the tail of the SAXS data. In *corfunc*, the “tail” of the data is taken as those data lying between the two red limit markers on the right of the SAXS data graph as shown in Figure 3.1. These can be positioned interactively by dragging them with the right-hand mouse button. If these limits vary from frame to frame, in the case of real-time data, variable tail limits can also be chosen

Tail-fitting functions:

$$I(q) = B + \frac{K}{q^4} e^{-q^2 \sigma^2} \quad \text{Sigmoid}$$

$$I(q) = B + \frac{K}{q^4} \quad \text{Porod}$$

where  $B$  = Bonart thermal background

$K$  = Porod constant

$\sigma$  describes the electron density profile at the interface between crystalline and amorphous regions.

The tail-fit affects the correlation function in the most important region for the extraction of ideal lamellar morphology parameters. Hence it is vital to obtain a good fit to this tail.

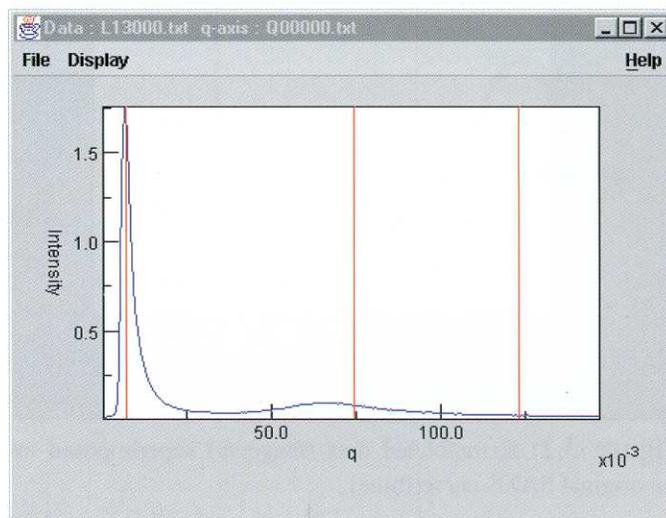


Figure 3.1: Selecting the fitting regions

#### 3.1.2 Extrapolation to $q = 0$

The data are extrapolated to  $q = 0$  by fitting a Guinier or Vonk model to the first few genuine data points after the beamstop. If the experimental data do not increase in intensity as the beamstop is approached, back extrapolation may fail. The first genuine data

point is indicated by the red limit marker on the left of the SAXS data graph as shown in Figure 3.1. This limit marker can be moved by dragging it with the right-hand mouse button. The *corfunc* program will attempt to set a sensible initial value for this limit.

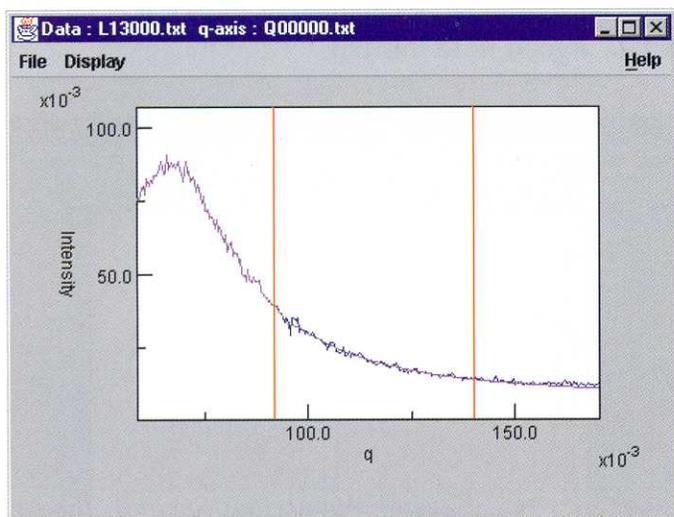
Fitting functions for back-extrapolation:

$$I(q) = Ae^{Bq^2} \quad \text{Guinier}$$

$$I(q) = H_1 - H_2q^2 \quad \text{Vonk}$$

### 3.1.3 Smoothing

The extrapolated data set consists of the Guinier or Vonk back extrapolation up to the first genuine data point, the original SAXS data up to the first tail-fitting limit and the sigmoid or Porod tail beyond this. It is shown as the magenta-coloured line in Figure 3.2. The join between the original SAXS data and tail-fit is smoothed using a Savitzky-Golay [5] smoothing algorithm that smooths the data without greatly altering higher moments. This avoids the formation of ripples in the correlation function that would occur with a period matching the d-spacing of the join. No smoothing is used at the join of the back-extrapolation to the SAXS data.



**Figure 3.2:** Extrapolated data (magenta) superimposed on the original SAXS curve (blue).

## 4 Calculating the correlation function

By selecting the *Transform* option from the *Actions* menu, the user may calculate the one-dimensional correlation function,  $\Gamma_1$  [2] (see Figure 1.1), the second moment of the data [2], the interface distribution function [7], and may re-transform  $\Gamma_1$  back into a scattering curve for comparison with the original data.

$\Gamma_1$  is given by:

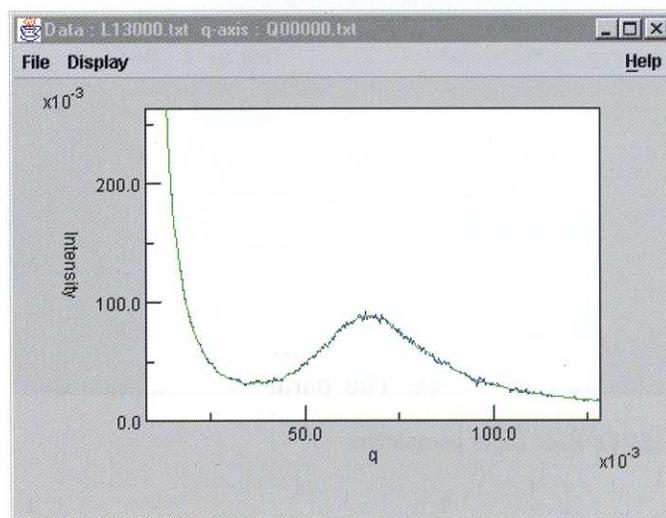
$$\Gamma_1(x) = \frac{\int_0^{\infty} j(q)q^2 \cos(qx) dq}{Q}$$

where  $j(q)$  is the scattering intensity and  $Q$  is the second moment or invariant of  $j(q)$  given by:

$$Q = \int_0^{\infty} j(q)q^2 dq$$

Every point in the extrapolated data set is used to calculate each point on the correlation function. The integration is numerical (a trapezium approximation) and is performed up to  $q = 0.6$ . Together with the fluctuations introduced by this truncation, fluctuations are also introduced into the correlation function by the finite gap between points in the extrapolated data set.

The results of the transformation can be plotted by selecting the required item from the *Display* menu. In the case of the re-transformed correlation function, it will be added to the background found during the extrapolation process and superimposed on the original SAXS data for comparison (see Figure 4.1).



**Figure 4.1:** The re-transformed 1-D correlation function (green) superimposed on the original SAXS data (blue).

## 5 Interpretation of the correlation function

The user may interpret the correlation function by selecting the *Extract parameters* item from the

Actions menu. The correlation function is interpreted in terms of an ideal lamellar morphology [7] and structural parameters are obtained as shown in Figure 1.3. It should be noted that a small beamsize is assumed; no de-smearing is performed.

It is important to note that, according to Babinet's principle, in a two-phase structure such as the ideal lamellar morphology, the electron densities of the two phases (crystalline and amorphous) may be interchanged without affecting the scattering curve or correlation function [6]. Therefore, from correlation function analysis alone, we cannot distinguish between:

$L_c$  and  $L_a$   
 $\phi$  and  $(1 - \phi)$   
 $\rho_c$  and  $\rho_a$

and these parameters may be interchanged, also affecting the other parameters derived from them.

It is also important to check that a horizontal section exists in the first minimum of the 1-D correlation function ( $-\Gamma_{min}$ ) as shown in Figure 5.1. This horizontal region is usually present when the sample crystallinity is  $< 30\%$  or  $> 70\%$ . In the intermediate region between  $30\%$  and  $70\%$  crystallinity, there may be no horizontal section, and in this case, the equation for the bulk crystallinity

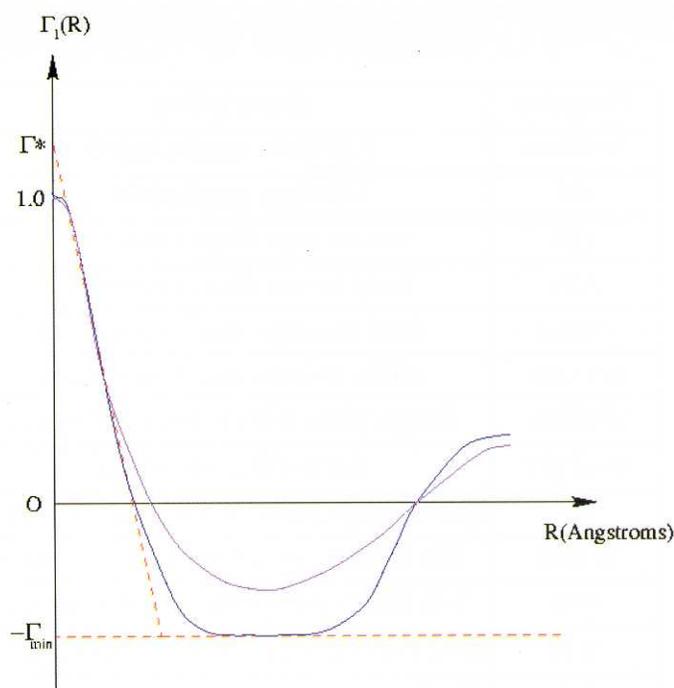
$$\text{Bulk crystallinity} = \phi = \Gamma_{min} / (\Gamma_{min} + \Gamma^*)$$

no longer applies. In order to obtain reliable results for this intermediate crystallinity, other data are needed to complement the correlation function analysis [6].

If a Porod profile was used for tail-fitting, Porod analysis is performed after extraction of the lamellar structure parameters. The parameters calculated by the Porod analysis are given below:

Porod constant  $K$   
 Surface to volume ratio  $= \pi K \phi (1 - \phi) / Q$   
 Characteristic chord length  $l_p = 4Q / \pi K$   
 Crystalline chord length  $= l_p / (1 - \phi)$   
 Amorphous chord length  $= l_p / \phi$

where  $Q$  = second moment or invariant.



**Figure 5.1:** The 1-D correlation function shown in blue has a horizontal section in the first minimum, yielding the bulk crystallinity from the base line  $-\Gamma_{min}$ . The first minimum of the 1-D correlation function shown in magenta has no horizontal section and the equation for bulk crystallinity given above no longer applies.

## References

- [1] Strobl, G. R. and Schneider, M. J., *Polym. Sci.* (1980) **18**, 1343-1359.
- [2] Balta Calleja, F. J. and Vonk, C. G., *X-ray Scattering of Synthetic Polymers*, Elsevier Amsterdam 1989, 247-257.
- [3] Balta Calleja, F. J. and Vonk, C. G., *X-ray Scattering of Synthetic Polymers*, Elsevier Amsterdam 1989, 257-261.
- [4] Koberstein, J. and Stein R. J., *Polym. Sci. Phys. Ed.* (1983) **21**, 2181-2200.
- [5] Press, W. H. *et al.*, *Numerical Recipes: the Art of Scientific Computing*, Cambridge University Press 1986.
- [6] Balta Calleja, F. J. and Vonk, C. G., *X-ray Scattering of Synthetic Polymers*, Elsevier Amsterdam 1989, 261-288.
- [7] Glatter, O. and Kratky, O., *Small Angle X-ray Scattering*, Academic Press Inc. London Ltd. 1982, 433-466.