

## Akima Interpolation: a Tool used in Direct Slit-Length Desmearing Procedures of Non-Frequency-Limited X-ray Scattering Curves

BY JÜRGEN J. MÜLLER,\* EVA-CHRISTINA MÜLLER, CHRISTINE GERNAT AND REINHARD KRÖBER

*Max Delbrück Centre for Molecular Medicine, Robert Rössle Strasse 10, D-13122 Berlin, Germany*

(Received 10 August 1993; accepted 15 July 1994)

### Abstract

X-ray small- and medium-angle scattering of partially ordered or semicrystalline materials is composed of background scattering from the form scattering of the components and from the amorphous phase and of peaks from the scattering of the crystallites. By the slit geometry of X-ray diffractometers constructed for registration of small- and medium-angle X-ray scattering, the diffuse scattering and the peaks are distorted and the peak positions and half-widths are changed. A program module based on the Akima interpolation [Akima (1970), *J. Assoc. Comput. Mach.* **17**, 589–602] is proposed for calculation of the first derivative of the complete smeared scattering curve, which is then explicitly used in direct collimation-correction procedures. The desmearing of scattering curves from semicrystalline starch samples proves the convenience of the method for low-noise conditions and exhibits a significant gain of measuring time in comparison with data of comparable accuracy but measured with Soller-slit collimation systems or desmeared with direct methods using frequency filtering.

### 1. Introduction

In small-angle X-ray scattering experiments, for reasons of intensity, slit-collimation systems are often used instead of pinholes. The slit geometry provides higher intensity but the measured scattered intensity is distorted (smeared). To correct the smearing, a large number of direct and indirect algorithms have been developed (for a review, see Glatter & Kratky, 1982).

In general, band-limited scattering curves with a defined upper-limit frequency or correlation length  $L$  in the sample (Damaschun, Müller & Pürschel, 1968; Luzzati & Taupin, 1986) can be corrected with sufficient accuracy despite the quantum noise overlaid on the smeared scattering data (Glatter, 1977; Gerber, Walter & Schmidt, 1991; Müller & Hansen, 1994). In principle, the small- and wide-angle scattering curves of partially ordered systems are also band limited and can be handled with direct and indirect

methods for desmearing. If the maximum diameter of the ordered regions is roughly known, the scattered intensity has to be measured at least at the sampling points  $s_i = i\pi/L$  to avoid loss of information (Goldman, 1954). For tightly packed systems, such as powders, or other partially ordered materials,  $L$  is unknown but the band width of the diffractometer transfer channel  $L_D$  (Damaschun, 1968) restricts the spatial frequencies contained in the scattering curve. The direct smoothing and desmearing method of Gerber, Walter & Schmidt (1991) is based on that sampling theorem of the information theory and is a powerful direct method. It works without any stability problems for scattering curves measured with relatively large redundancy [that is, measured at points  $s_i = i\pi/(5L)$ ]. Only in the special case of a strongly scattering material can a scattering curve up to  $s \approx 40 \text{ nm}^{-1}$  be measured with such a step width in a finite convenient time. For ordered regions with an approximate diameter  $L$  of 20 nm, the sampling-point distance would be  $0.157 \text{ nm}^{-1}$  and 1300 measuring points would result therefrom.

The required measuring time is unacceptably long. For the special handling of small-angle scattering curves from semicrystalline substances, some efforts have been made up to now that use an iterative numerical procedure (Strobl, 1970) as well as hardware (Hendricks, 1972). But, of course, the hardware solution, which uses Soller slits to reduce the width of the effective slit-length weighting function to avoid numerical desmearing, reduces the detected intensity remarkably. The reduction factor depends on the quality of the Soller slits and on the geometrical data of the collimation equipment and is usually of the order of 0.2 (Hendricks, 1972). The measuring time is correspondingly prolonged.

Here, we present a program module that has been introduced in the direct-desmearing program of Gerber, Walter & Schmidt (1991), called here the GWS method, and that can be inserted in all programs that need an explicit first derivative of the smeared scattered intensity, especially in algorithms using so-called slit functions for slit-length corrections. In the test examples, the step width used for the measuring points was of the order of the sampling-point distance.

\* To whom correspondence should be addressed.

## 2. Theory

The slit-length-corrected scattering curve is calculated by solution of the integral equation

$$I(s) = (-1/\pi) \int_0^{\infty} [J'(s^2 + t^2)^{1/2}/(s^2 + t^2)^{1/2}] H(t) dt \quad (1)$$

with  $H(t)$  being the slit function calculated by a Laplace inversion (Kratky, Porod & Kahovec, 1951; Deutsch & Luban, 1978; Schmidt & Fedorov, 1978). The length of the scattering vector  $s$  is given by  $s = 4\pi \sin \theta/\lambda$ , where  $2\theta$  is the scattering angle and  $\lambda$  is the wavelength.  $J'$  is the first derivative of the slit-smear experimental scattering curve.

The first derivative of the experimental scattered intensity has to be calculated for arguments different from the experimental measured points. In direct methods and for frequency-limited scattering curves, the differentiation has been performed by a Fourier representation (GWS method). For flat scattering curves without strong features, spline functions have been used (Walter, Kranold, Müller & Damaschun, 1976). These methods are in general not applicable to small- and medium-angle scattering curves containing maxima caused by ordered regions or microcrystals of dimensions larger than 10 nm because of the high spatial frequencies needed or because of the unflexibility of the splines. In this case, the scattering curve must be represented and possibly smoothed by local very restricted functions and the first derivative has to be calculated with high precision in the limited region of a peak. This can be done by using the Akima polynomials (Akima, 1970):

$$J_i^*(s) = a_i + b_i(s - s_i) + c_i(s - s_i)^2 + d_i(s - s_i)^3. \quad (2)$$

The coefficients of the cubic polynomial are defined in the interval  $(s_i, s_{i+1})$  by the conditions

$$J_i^*(s_i) = J(s_i) \quad (3)$$

$$J_i^*(s_{i+1}) = J(s_{i+1}). \quad (4)$$

With this definition, the polynomial fits the scattering data exactly at the experimental data points. The gradient of  $J^*(s)$  is defined by

$$J_i^{*\prime}(s_i) = (|m_{i+1} - m_i| |m_{i-1} + |m_{i-1} - m_{i-2}| m_i) \times (|m_{i+1} - m_i| + |m_{i-1} - m_{i-2}|)^{-1} \quad (5)$$

$$J_i^{*\prime}(s_{i+1}) = (|m_{i+2} - m_{i+1}| |m_i + |m_i - m_{i-1}| m_{i+1}) \times (|m_{i+2} - m_{i+1}| + |m_i - m_{i-1}|)^{-1} \quad (6)$$

at the scattering points. In these equations,

$$m_i = [J(s_{i+1}) - J(s_i)]/(s_{i+1} - s_i). \quad (7)$$

From (2)–(7), with the Hermite interpolation, the coefficients of the cubic polynomial in the  $i$ th interval

$(s_i, s_{i+1})$  are

$$a_i = J(s_i), \quad (8)$$

$$b_i = J^{*\prime}(s_i), \quad (9)$$

$$c_i = [m_i - 2J^{*\prime}(s_i) - J^{*\prime}(s_{i+1})]/(s_{i+1} - s_i), \quad (10)$$

$$d_i = [J^{*\prime}(s_i) + J^{*\prime}(s_{i+1}) - 2m_i]/(s_{i+1} - s_i)^2. \quad (11)$$

An automatic smoothing procedure included before the differentiation presented here is very modest and locally restricted. Three points on both sides of a sampling point are included and are weighted by a parabolic declining function (Hilberg, 1989). The weighting factor for the intensities in the surroundings of the point  $i$  is

$$G_j = 1 - [2(s_j - s_i)/(s_{i+3} - s_{i-3})]^2. \quad (12)$$

$j$  runs between  $i-3$  and  $i+3$ . The smoothed scattered intensity is then

$$J^*(s_i) = \sum_{j=i-3}^{i+3} G_j J^*(s_j) / \sum_{j=i-3}^{i+3} G_j. \quad (13)$$

A stronger smoothing deforms the peaks if the smoothing goes from the small-angle peak wing over the top to the large-angle wing, but additional local smoothing of the curve between the maxima can be done (*e.g.* with spline functions) before the calculation of the first derivative  $J^{*\prime}(s)$ .

Because (1) is solved by semi-analytical integration containing an automatic convergence criterion that regulates a step width  $\Delta t$ , the theoretically calculated slit function  $H(t)$  also has to be interpolated. For smooth slit-length profiles (for an overview see Gerber, Walter & Schmidt, 1991) of Gaussian type, the function  $H(t)$  also is smooth and has been approximated by bell splines (Bok, 1978) with high precision. To interpolate the step-slit function  $H(t)$  for a rectangular function  $P(t)$ , the Akima polynomials are used with no smoothing procedure.

## 3. Results

The Akima interpolation has been used in connection with the GWS desmearing method originally developed for frequency-limited scattering curves. It is integrated in the Fortran program package SAXS for a PC (Müller, 1992). Fig. 1 shows a test scattering curve. A Gaussian peak at the position  $s_0 = 3.5 \text{ nm}^{-1}$  and of half-width  $s_{1/2} = 0.5 \text{ nm}^{-1}$  has been smeared by a Gaussian slit-length profile

$$P(t) = c \exp(-c^2 t^2)/\pi, \quad (14)$$

with  $c = 0.25 \text{ nm}$  for values  $s_i = i \times 0.1 \times s_{1/2}$ . The position of the peak is shifted by the smearing operation to  $2.53 \text{ nm}^{-1}$  and the half-width is enlarged to  $0.82 \text{ nm}^{-1}$ . Without an overlaid random noise, the peak can be desmeared exactly. The peak position after the correction procedure is  $s_0 = 3.51 \text{ nm}^{-1}$ , the

half-width  $s_{1/2} = 0.5 \pm 0.005 \text{ nm}^{-1}$  (not shown here). For the same model with a 2% random noise added to the smeared intensity values, the error propagation by the desmearing procedure has been demonstrated in Fig. 1. 2% random noise has been added to the theoretical Gaussian peak for point collimation. The result of the desmearing procedure lies within these error limits, the numerical differentiation has not enhanced the error level remarkably. The peak position after desmearing was calculated to be  $s_0 = 3.49 \text{ nm}^{-1}$  and the half-width  $s_{1/2} = 0.499 (5) \text{ nm}^{-1}$ . Nearly the same result has been obtained when using a doubled step width for data points  $\Delta s = 0.2 \times s_{1/2}$ . The peak position is now deter-

mined to be  $3.52 \text{ nm}^{-1}$  and the half-width is  $0.525 (5) \text{ nm}^{-1}$ .

Experimental scattering curves were measured with an URD65 diffractometer (Seifert & Co. GmbH Freiburger Präzisionsmechanik, Freiberg, Germany), using a slit-collimation system as shown in Fig. 2. Only the slits that are essential for slit-length (slit-height) collimation are depicted. Two effective slit-length profiles have been calculated for the diffractometer with and without a Soller-slit system (SS) by using an algorithm originally developed by Hendricks & Schmidt (1967) and Hendricks (1972).

The first sample is an amylose maize starch gel that contains crystallites (Gidley, 1989) of about 10 nm diameter. In Fig. 3, the small-angle part of the smeared

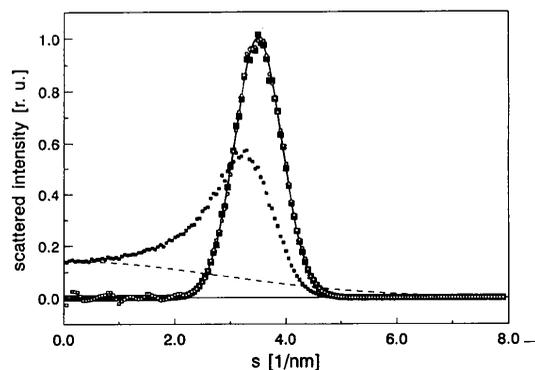


Fig. 1. Slit-length smearing and desmearing of a Gaussian peak at  $s_0 = 3.5 \text{ nm}^{-1}$  with added random noise of 2%. — Pin-hole-collimated scattering of the peak, half-width  $s_{1/2} = 0.5 \text{ nm}^{-1}$ , without random noise. ■ ■ ■ Pin-hole-collimated scattering of the peak; 2% constant relative noise added. ■ ■ ■ Slit-length-smearing scattering data; 2% constant relative noise added. □ □ □ Numerically desmeared intensities obtained using Akima interpolation. - - - Gaussian slit-length profile  $P(t)$ ;  $c = 0.25 \text{ nm}$ . r.u. = relative units.

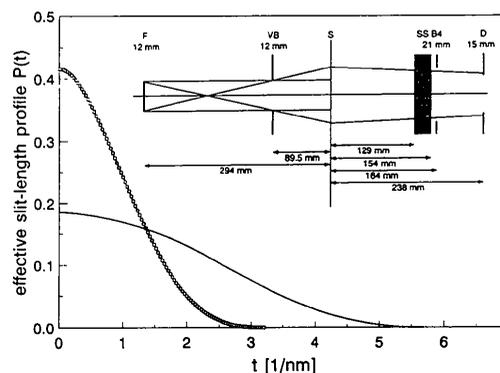


Fig. 2. Effective slit-length profiles  $P(t)$  and diffractometer slit configuration for the slit-length collimation.  $F$  focal spot.  $VB$  collimation slit on the focal side.  $S$  sample plane.  $SS$  Soller slit system: 32 slits; thickness of the lamellas 0.06 mm; distances between lamellas 0.5 mm.  $B4$  collimation slit on the detector side.  $D$  detector slit. — Effective slit-length profile for the collimation system without Soller slits. -□-□-□- Effective slit-length profile for the collimation system with Soller slits in the position shown.

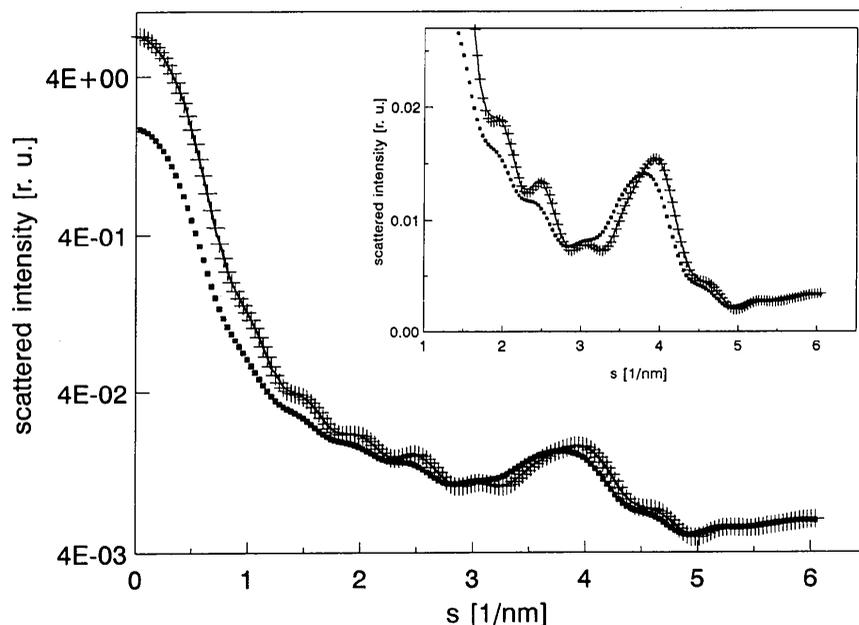


Fig. 3. Experimental and slit-length-corrected scattering curves of an amylose maize starch gel measured without the Soller-slit system. ■ ■ ■ Smeared experimental curve. For clarity only each second point is shown. — Slit-length-corrected data when using Akima polynomials. Only every second point of the smeared data shown is used in the desmearing procedure. + + + Slit-length-corrected data when the GWS method is used. Insert: enlarged region around the 100 reflection of the amylose B-form crystallites.

scattering curve is depicted. The slit-length profile of the primary beam used for these measurements corresponds to the profile shown in Fig. 2 for collimation without Soller slits. It was possible to measure the sample scattering at scattering vectors a quarter of the sampling-point distance. The original GWS method could then be used for comparison with the result reached when using the Akima polynomials in the desmearing procedure. The two methods provide equivalent results in the small-angle region as well as in the region of the 100 reflection of the starch *B*-form crystallites at  $s = 3.9 \text{ nm}^{-1}$  (Imberty & Perez, 1988). The advantage of the Akima interpolation is that it requires only a quarter of the measured points necessary for the corrections with the GWS method without spurious oscillations.

The second sample was a starch powder from potatoes prepared as described by Gernat, Radosta, Damaschun & Schierbaum (1990) that contains semicrystalline starch granules of the *B* form. The upper limit frequency of about  $50 \text{ nm}^{-1}$  is set by the diffractometer transfer function for this sample. For this limit, the measuring time would be unreasonably long for the original GWS method. In Fig. 4 (upper squares), the experimental scattering curve is drawn. This curve was measured in the  $2\theta$  angular region from  $0.3$  to  $56^\circ$  with the collimation system using the Soller slits in front of the detector for smearing reduction as shown in Fig. 2. The noise level is less than 2%. Neither additional interactive smoothing nor an extrapolation to zero scattering angle was done

before the desmearing procedure was carried out. By comparison of the experimental scattering curve with the result of the desmearing procedure, a significant shift to larger scattering angles can be detected for all features with  $s \leq 20 \text{ nm}^{-1}$ . This result proves the necessity for a desmearing also for use of the Soller slits shown in Fig. 2. No instabilities or numerical difficulties disturbed the desmearing process for low noise levels. That has been proven for theoretical scattering curves that were calculated for *B*-form amylose nanocrystallites with an overlaid relative noise of 1–3%. The errors in the desmeared curve, caused by the noise, are then not larger than the experimental noise level. An additional smoothing in the regions between the reflections is necessary for higher quantum noise. After removal of the Soller-slit system, the half-width of the effective slit-length profile is enlarged by the factor 2.4 (Fig. 2) and the integral scattered intensity increases by a factor of about 3.5. The measuring time can then be reduced to maintain the same statistical exactness as before. In Fig. 4, both smeared experimental curves (middle two curves) are also depicted. The stronger distorted curve (full squares) was measured without the Soller slits with the same statistical error but in a quarter of the time. After numerical desmearing using the corresponding slit functions and the Akima polynomials for calculation of the first derivative of the scattering curve, the two collimation-corrected curves are identical within the experimental error limit of 2% (Fig. 4, lower two curves). Peak positions, half-widths and the integral intensities are identical in the two cases. The only precondition for calculation of a correct first derivative under low-noise conditions is that the step width between measured points should be chosen in such a way that at least ten points are positioned at very narrow peaks (e.g. the peaks at  $s = 3.9$  and  $12 \text{ nm}^{-1}$  in Fig. 4).

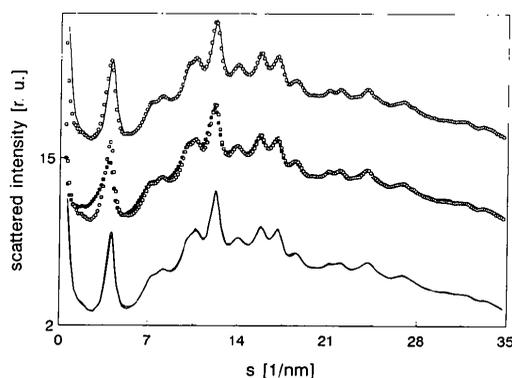


Fig. 4. Experimental and slit-length-corrected scattering curves of a potato starch powder measured with and without the Soller-slit system. Upper two curves:  $\square\square\square$  Experimental data measured with Soller slit system that is shown in Fig. 2;  $\text{---}$  slit-length-corrected data when Akima polynomials are used. Middle two curves:  $\square\square\square$  measured with Soller slit system in the position shown in Fig. 2;  $\blacksquare\blacksquare\blacksquare$  measured without Soller slits. Both curves are fitted by a least-squares routine for  $s > 20 \text{ nm}^{-1}$ . Lower two curves:  $\text{---}$  Slit-length-corrected curve for data measured without the Soller-slit system,  $\text{---}$  slit-length-corrected curve for data measured with the Soller-slit system. Both curves are fitted by a least-squares routine for  $s > 20 \text{ nm}^{-1}$ . All groups of curves are shifted vertically by an arbitrary value for clarity.

#### 4. Concluding remarks

When the Akima interpolation is adapted to small- and wide-angle scattering curves from semi-crystalline substances, there is a new simple but suitable tool for differentiation. In comparison with frequency-filtering methods, a quarter of the measuring points are needed and no equidistant measured points and extrapolation to zero angle are necessary. Instead of a divergence and intensity reduction by Soller slits for reduction of smearing effects in the scattering curves, now the high intensity of a primary beam with a large height can be used when measuring scattering curves from partially ordered systems that contain sharp maxima. The direct numerical desmearing procedure does not enhance statistical errors if the noise level is below 2% in the experimental scattering curve, and it can be used by itself or for comparison

with results from indirect methods. For the collimation geometry used, the elimination of the Soller slits resulted in an effective reduction in the measuring time by a factor of about four or five.

We thank C. Görgens, Technical University, Dresden, for suggestions about the Akima polynomials and P. W. Schmidt, University of Missouri, for helpful discussions. The work was supported by grants from Deutsche Forschungsgemeinschaft (Mu 989/1-1), from Seifert & Co. GmbH Freiburger Präzisionsmechanik and from the Bundesministerium für Forschung und Technologie (0319549 B).

*Note added in proof.* Glatter & Gruber (1993) have recently published a new indirect transformation in reciprocal space (ITS) for handling data from partially ordered systems. Their algorithm is completely different from that proposed above.

#### References

- AKIMA, H. (1970). *J. Assoc. Comput. Mach.* **17**, 589–602.  
 BOK, J. (1978). *Comput. Phys. Commun.* **16**, 113–118.  
 DAMASCHUN, G. (1968). *Exp. Tech. Phys.* **16**, 311–315.  
 DAMASCHUN, G., MÜLLER, J. J. & PÜRSCHEL, H.-V. (1968). *Monatsh. Chem.* **99**, 2343–2348.  
 DEUTSCH, M. & LUBAN, M. (1978). *J. Appl. Cryst.* **11**, 87–101.  
 GERBER, T., WALTER, G. & SCHMIDT, P. W. (1991). *J. Appl. Cryst.* **24**, 278–285.  
 GERNAT, C., RADOSTA, S., DAMASCHUN, G. & SCHIERBAUM, F. (1990). *Starch/Stärke*, **42**, 175–178.  
 GIDLEY, M. J. (1989). *Macromolecules*, **22**, 351–358.  
 GLATTER, O. (1977). *J. Appl. Cryst.* **10**, 415–421.  
 GLATTER, O. & GRUBER, K. (1993). *J. Appl. Cryst.* **26**, 512–518.  
 GLATTER, O. & KRATKY, O. (1982). *Small-Angle X-ray Scattering*. London: Academic Press.  
 GOLDMAN, S. (1954). *Information Theory*. New York: Prentice Hall.  
 HENDRICKS, R. W. (1972). *J. Appl. Cryst.* **5**, 302–304.  
 HENDRICKS, R. W. & SCHMIDT, P. W. (1967). *Acta Phys. Austriaca*, **26**, 97–122.  
 HILBERG, D. (1989). *c't Mag. Computertech.* **6**, 206–215.  
 IMBERTY, A. & PEREZ, S. (1988). *Biopolymers*, **27**, 1205–1212.  
 KRATKY, O., POROD, G. & KAHOVEC, L. (1951). *Z. Elektrochem.* **55**, 53–59.  
 LUZZATI, V. & TAUPIN, D. (1986). *J. Appl. Cryst.* **19**, 39–50.  
 MÜLLER, J. J. (1992). *Programmpaket APX 63, Small-Angle X-ray Scattering*. Seifert & Co. GmbH Freiburger Präzisionsmechanik, Freiberg, Germany.  
 MÜLLER, J. J. & HANSEN, S. (1994). *J. Appl. Cryst.* **27**, 257–270.  
 SCHMIDT, P. W. & FEDOROV, B. A. (1978). *J. Appl. Cryst.* **11**, 411–416.  
 STROBL, G. R. (1970). *Acta Cryst.* **A26**, 367–375.  
 WALTER, G., KRANOLD, R., MÜLLER, J. J. & DAMASCHUN, G. (1976). *Crystallographic Computing Techniques*, edited by F. R. AHMED, pp. 383–388. Copenhagen: Munksgaard.