A Method for Correcting Slowly Varying Small-Angle Scattering Curves for Collimation Effects*

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Abstract
A technique has been developed for correcting slowly varying small-angle X-ray scattering curves for the distortions produced by the length of the collimating slits when, as is very often true, slit-width effects are negligible. The method, which is useful with measured scattering curves which decay so slowly with increasing scattering angle that the usual correction procedures do not converge, is based on approximating the measured curve by a polynomial in $h^2$, where $h=4\pi \lambda^{-1} \sin \theta$; $\lambda$ is the scattering wavelength; and $2\theta$ is the scattering angle. The order $j$ of the polynomial is selected to give the best fit to the measured curve over the entire interval of angles for which data are available. The corrected curve is also a polynomial in $h^2$ of order $j$, and the coefficients of this polynomial can be easily evaluated. Tests of the method on a theoretical scattering curve and two experimental curves are described.

Introduction
When diffuse X-ray scattering is used to study fluctuation structures of liquids and glasses, the scattering must be measured at both large and small scattering angles. For the measurements at small angles, special collimation systems, which in most cases use slit geometry, have been developed. With slit collimation, the measured scattering curves must be corrected (unsmear) to remove the distortion produced by the collimating slits.

Frequently, the width of the slits is so small that its effect is negligible, and only the changes resulting from the length of the slits must be considered. The relation between the measured intensity $I(h)$ and the intensity $I(h)$ for perfect collimation then is given by (Hendricks & Schmidt, 1967)

$$ I(h) = \int_0^\infty P(t) I[(h^2 + t^2)^{1/2}] dt, \quad (1) $$

where $h=4\pi \lambda^{-1} \sin \theta$ is the magnitude of the reciprocal-lattice vector; $\lambda$ is the scattering wavelength; and $2\theta$ is the scattering angle. The function $P(t)$, which is often called the slit-length weighting function, is the convolution of the length of the detector slit and the primary beam profile at the detector plane. If the scattered intensity is measured in absolute, rather than relative, units, the weighting function and the scattered intensity must be correctly normalized (Hendricks, 1972; Kratky, Porod & Skala, 1960). Since scattering curves for fluctuation structures almost always vary slowly throughout the entire small-angle region - that is, for $2\theta$ not greater than a few degrees - the infinite-slit approximation, in which $P(t)$ is considered to be a constant, does not apply, since the use of this approximation would require, as is not true for slowly-varying scattering curves, that for large $t$ the convergence of the integral in (1) is guaranteed by the decay of $I[(h^2 + t^2)^{1/2}]$.

Schmidt (1976) has reviewed many of the existing procedures for solving the integral equation (1). All these methods break down when the measured scattering curve does not decay sufficiently rapidly in the measured interval of scattering angles, either because it is not possible to make a correct extrapolation to angles outside the measured region, as is necessary in many collimation correction procedures, such as those developed by Fedorov (1968), Lake (1967) and Lin, Von Bastian & Schmidt (1974), or because, as with Glatter’s (1977) technique, no correlation range can be given. To avoid this difficulty, special approximations (Weinberg, 1963; Bates, Hendricks & Shaffer, 1974) have been developed for correcting the small-angle scattering curves from SiO$_2$ glasses.

Below, a general procedure is described for correcting slowly varying small-angle X-ray scattering curves for an arbitrary primary-beam profile (weighting function) $P(t)$.

Theory
The perfect-collimation scattering curve $I(h)$ will be considered to vary so slowly that throughout the entire interval of $t$ in which the integral in (1) is not negligible, $I(h)$ can be approximated by the polynomial

$$ I(h) = \sum_{i=0}^{j} \frac{1}{i!} h^{2i}, \quad (2) $$

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where the $I_i$ are constant. Techniques for selecting the optimum value of the degree $j$ of the polynomial are discussed in the following sections. [For isotropic samples, $I(h)$ is an even function of $h$. The scattered intensity is thus approximated by a polynomial in $h^2$, rather than in $h$.]

By substitution of (2) in (1), the measured intensity $\tilde{I}(h)$ can be expressed

$$\tilde{I}(h) = P_{00} \sum_{k=0}^{j} \frac{A_k}{k!} h^{2k},$$

where

$$A_k = \sum_{i=0}^{j-k} P_i I_{i+k},$$

$$P_i = \frac{1}{(i!) P_{00}} \int_{0}^{\infty} t^{2i} P(t) dt$$

and

$$P_{00} = \int_{0}^{\infty} P(t) dt.$$

Note that (3), (4) and (5) are obtained from (1) and (2) without the use of any approximations and that $I(h)$, like $I(h)$, is a polynomial of order $j$ in $h^2$. Also, from (5), $P_0 = 1$.

For $j = k$, (4) gives

$$I_j = A_j.$$  

(6)

When $0 \leq k < j$, from (4),

$$I_k = A_k - \sum_{i=0}^{j-k-1} P_{i+1} I_{i+1+k}. $$

(7)

As (7) expresses each $I_k$ in terms of the $I_i$ for $k + 1 \leq i \leq j$, the $I_k$ can be evaluated successively from (6) and (7), beginning with $I_j$. Equations (6) and (7) are convenient for direct numerical calculation of the $I_k$ with a desk calculator or computer.

For $k = j - 1$, (6) and (7) give

$$I_{j-1} = A_{j-1} - P_1 A_j.$$  

(8)

Similarly, from (6)-(8),

$$I_{j-2} = A_{j-2} - P_1 A_{j-1} - [P_2 - (P_1)^2] A_j.$$  

(9)

If an expression for $P(t)$ is available, the moments $P_i$ can be calculated exactly. They can also be evaluated numerically from a table of the values of $P(t)$.

Equations (6) and (7) provide a convenient way to calculate the $I_k$ on a computer after the $P_i$ and the $A_k$ have been determined.

Rol'bin, Feigin & Shchedrin (1977) have employed a similar polynomial approximation for correcting small-angle scattering curves for slit-width effects. Their technique, however, cannot be directly used for slit-length corrections, since the integral equation which must be solved for width corrections is different from (1), and also because the approximating polynomial in the width correction technique is a polynomial in $h$, rather than in $h^2$.

### Numerical calculations

A computer program which uses the method described in the preceding section has been written for a Hewlett-Packard 9825A programmable desk calculator. This program works in the following steps:

1. A least-squares fit of the measured $I(h)$ curve is made to determine the coefficients $A_k$. The order $j$ of the polynomial (3) is varied, and the sum-of-squares error in the fit is plotted as a function of $j$. The value of $j$ is chosen to minimize this sum-of-squares error.
2. The moments $P_i$ of the weighting function (primary-beam distribution) are computed from (5). The calculation can be done either numerically or analytically. In the numerical calculations, a convergence control is introduced – that is, the integration is done with a prescribed degree of precision.
3. With (6) and (7), the coefficients $I_i$ of the corrected curve are computed for the optimum order $j$ found in step 1. The corrected $I(h)$ curve is obtained by substitution of the $I_i$ in (2).
4. The $I(h)$ curve is then tested by using it to evaluate $\tilde{I}(h)$ numerically with (1), and this $\tilde{I}(h)$ curve is compared with the experimental curve. The integration, as in step 2, includes a convergence control.

A time of 5 to 10 min is necessary with the Hewlett-Packard 9825A for complete collimation correction of a scattering curve. The exact computing time depends on the order $j$ of the polynomial. It should be noted that the moments $P_i$ must be evaluated only once for collimation corrections on all scattering curves recorded for the same collimation conditions.

### Numerical results

The procedure just described was first tested with theoretical scattering curves similar to those expected to be obtained in experimental investigations. The function

$$\tilde{I}(h) = 1 + 10h^2 + 5h^4$$

was chosen and was tested in the interval $h = 0(0.01)0.6$ Å⁻¹ (Fig. 1). (That is, $h$ varied in steps of 0.01 Å⁻¹ from 0 to 0.6 Å⁻¹.) For all calculations, an HP 9825A computer was used. The statistical fluctuations of the theoretical test curves were introduced with the random-number generator of the computer. The nature of these fluctuations depends on the choice of the initial value for the random-number generator. In Fig. 1(a), the points represent values of the test function after a 10% statistical error has been introduced. The curve determined by a least-squares fit (solid line) for a polynomial of order $j = 2$ agrees with the initial test function within the width of the line on the figure. The per cent deviation of the least-squares $\tilde{I}(h)$ curve from the fit to the initial $\tilde{I}(h)$ test function (10) is also plotted in Fig. 1(a). The magnitude of the deviation for a given least-squares fit of course depends on the average size of the statistical fluctuations. (For scattering curves with
no statistical error, the deviation did not exceed the precision of the computer.)

With the coefficients $A_k$ from the least-squares fit, the test function $\hat{A}(h)$ was corrected for a rectangular primary-beam profile $P(t)$ (Fig. 1b). The distribution (weighting function) $P(t)$ was normalized so that $P_{oo} = 1$. The per cent deviation of the corrected scattering curve $I(h)$ from the curve

$$I(h) = 0.7009 + 9.7h^2 + 5h^4$$

from an exact calculation of $I(h)$ is also plotted in Fig. 1(b). It is clear that the deviation remaining after the least-squares fit to the initial $\hat{A}(h)$ curve is magnified by the correction process, especially at smaller scattering angles, where the effect of the finite dimensions of the primary beam are most appreciable.

The results for correcting the test function (10) with different weighting functions (primary beam profiles) are shown in Fig. 2. Each of the three weighting functions is normalized so that $P_{oo} = 1$. While there is hardly any difference between the corrected $I(h)$ curves for a Gaussian profile (standard width $\sigma = 0.1 \text{ Å}^{-1}$) and for a trapezoidal function, particularly at the larger scattering angles, for a rectangular weighting function the form of the corrected curve was quite different from that of the other two curves.

The $I(h)$ curves 1, 2 and 3 in Fig. 2 are the corrected curves that would be obtained if samples, all of which gave the same measured $\hat{A}(h)$ curve, were examined on three different instruments, each of which had one of the three weighting functions in Fig. 2. The differences between the three corrected $I(h)$ curves in Fig. 2 give a rough estimate of the sensitivity of the scattering curves to the form of the weighting function and thus show how much the corrected scattering curves are affected by a weighting function which is not the correct function for the collimation system on which the $\hat{A}(h)$ curve was recorded.

The use of the collimation correction method will now be demonstrated on two experimental small-angle X-ray scattering curves. Fig. 3 shows the measured scattering curve $\hat{A}(h)$ for a tempered SiO$_2$ glass, recorded with a Kratky camera, Cu $K\alpha$ radiation, and counter detection in the interval $m = 1 \ (0.5) \ 30 \text{ mm}$, where $m = h\lambda a/(2\pi)$, for a distance $a = 204 \text{ mm}$ between the sample and the detector plane.

The measured $\hat{A}(h)$ curve can be approximated very well by a relatively low order $j$ of the polynomial in (3). The scattering curves from least-squares fits for $j = 1$ and $j = 2$ are shown as solid lines in Fig. 3. For polynomials of order $j$ higher than 2, the sum-of-squares error does not decrease appreciably, as Fig. 4 indicates. However, it is clear that a first-order polynomial ($j = 1$), such as Weinberg (1963) used for an approximation for...
a Gaussian function for correcting scattering curves from SiO$_2$ glasses, does not give a very good fit. Since the smoothing effect decreases for polynomials of order greater than 2, the scattering curve was corrected with the polynomial for $j=2$. The weighting function used for the experimental collimation system and shown in Fig. 3 was normalized so that $P_{00}=1$.

The small-angle X-ray scattering curve from a solvent (Fig. 5) is also slowly varying, like the curve in Fig. 3, but the former curve has a more pronounced structure. The scattering pattern was measured with a Kratky camera for an interval $m = 3(0.1) 23$ mm and a distance $a=218$ mm with Cu K$_\alpha$ radiation and a proportional counter.

A very satisfactory approximation for the measured points could be obtained with a polynomial of order $j=7$. To select the order $j$ for correcting the scattering curve, the sum-of-squares error again was minimized (Fig. 6). The good agreement between the curve from the least-squares fit and the scattering curve obtained previously (Walter, Kranold, Müller & Damaschun, 1977) by smoothing with spline functions should be noted.

The curve from the least-squares fits was corrected both with the directly measured weighting function $P(t)$ (Fig. 5, crosses) and also with an approximating trapezoid. The average deviation of the scattering curves corrected with the two profiles was of the order of 0.03%. The weighting function $P(t)$ was again given the normalization $P_{00}=1$.

From our experience, as the curves in Fig. 5 illustrate, differences in the form of the weighting function produce greater deviations in the corrected curve than result from statistical fluctuations of the measured weighting function $P(t)$.

**Discussion**

As the examples in Figs. 3 and 5 show, slowly varying scattering curves can often be approximated by a polynomial of relatively low order $j$ in $h^2$ throughout the entire interval of scattering angles in which the curve is recorded. If the effect of the width of the collimating slits can be neglected, collimation effects change only the coefficients of the polynomial. Equations (6) and (7) provide a method by which the coefficients $I_i$ of the polynomial representing the corrected curve $I(h)$ can be uniquely determined if the coefficients $A_k$ of the measured polynomial approximating the measured curve $I(h)$ and the moments $P_i$ of the weighting function have been evaluated. The $A_k$ are computed by a least-squares fit. The precision with which the corrected $I(h)$ curve can be obtained depends only on how exactly the polynomial of order $j$ in $h^2$ approximates the measured scattering curve.

Numerical tests have shown that the method is easy to use. It can be employed with any weighting function (beam profile) and does not require a large computer.

The method does contain the subjective element that the experimenter must choose which order $j$ gives the best approximation for the polynomial in $h^2$. But, as application of this method to experimental scattering...
curves suggests, in practice this choice does not present any difficulties.

It should be noted that for a weighting function which is different from zero only in the finite interval $0 \leq t \leq t_{\text{max}}$, experimental scattering curves can be corrected by this method only at nominal scattering angles $h_{\text{nom}}$ which do not exceed the value $\left(\frac{(h_{\text{max}})^2 - (t_{\text{max}})^2}{2}\right)^{1/2}$, where $h_{\text{max}}$ is the largest $h$ value at which $I(h)$ is measured. This restriction, as can be seen from (1), is a result of the fact that, at a nominal scattering angle $h_{\text{nom}}$, the measured intensity is an average of perfect-collimation intensities over the interval

$$h_{\text{nom}} \leq h \leq \left[(h_{\text{nom}})^2 + (t_{\text{max}})^2\right]^{1/2}.$$

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**References**


