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Slit Height Corrections in Small Angle X-ray Scattering*

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A method of correcting experimental small angle X-ray scattering curves for the effects of the height of the collimating slits is developed. The method has the advantage of eliminating the need for numerical differentiation of the experimental curve. An expression suitable for numerical calculation is given, and an analysis is made of the error in the numerical approximation. The results of some applications of these slit correction techniques are discussed.

Introduction

Small angle X-ray scattering collimation systems ordinarily use slits instead of pinholes in order to give sufficient scattered intensity. With slit collimation, at a particular angular setting of the collimation system, the detector records the scattering from a range of angles, rather than from a single angle. This imperfect collimation leads to a distortion of the curve of the scattered intensity as a function of scattering angle.

The process of correcting experimental scattering curves for collimation errors, which will be referred to as 'unsmearing', has been considered by several authors. Guinier & Fournet (1947*a*, *b*) and Du Mond (1947) gave a rigorous solution for the case of rectangular slits of infinite height and negligible width. Their method was adapted by Kratky, Porod & Kahovec (1951) for use with many collimation systems of finite slit height.

These unsmearing methods have the disadvantage that they require a numerical differentiation of the experimental curve. Numerical differentiation can be quite inexact, especially when applied to an experimental curve which is known only approximately. Although with care good results can be obtained using the above-mentioned unsmearing equations, as was shown by the numerical calculations of Fournet & Guinier (1947*b*) and Anderegg and co-workers (1958) and by the modified planimeter of Gerold (1957), a way of unsmearing the experimental data without differentiating the experimental curve would improve the accuracy of the unsmeared curve and also could simplify the numerical calculations.

In the next section, the unsmearing equation of Kratky, Porod & Kahovec (1951) is modified to eliminate the need for numerical differentiation. The last section describes numerical calculations and some applications of the unsmearing process.

Theory of the unsmearing process

For slits of negligible width, the experimental scattered intensity $F(h)$ for a scattering angle h is related to the perfect collimation scattered intensity $I(h)$ by the equation (Guinier *et al.*, 1955)

$$F(h) = \int_0^\infty W(\varphi) I[(h^2+\varphi^2)^{\frac{1}{2}}]d\varphi \,,$$

where $W(\varphi)$ is a weighting function, the form of which depends on the collimation system. For slits of negligible width and infinite height, $W(\varphi)=1$. Guinier & Fournet (1947*a*) and Du Mond showed that in this case $I(h)$ could be found from the relation

$$I(h) = -\frac{2}{\pi}\int_0^\infty \frac{dt}{(h^2+t^2)^{\frac{1}{2}}} F'[(h^2+t^2)^{\frac{1}{2}}] \,. \tag{1}$$

Kratky, Porod & Kahovec (1951) used similar methods to treat the case of a Gaussian weighting function

$$W(\varphi) = 2p(\pi)^{-\frac{1}{2}} \exp(-p^2\varphi^2) \,,$$

where p is a constant determined by the slit height. A small p corresponds to high slits, and a large p to small slits. Kratky, Porod & Kahovec showed that for this weighting function one can obtain $I(h)$ from

$$I(h) = -\frac{\exp(p^2h^2)}{p(\pi)^{\frac{1}{2}}}\int_0^\infty \frac{dt}{(t^2+h^2)^{\frac{1}{2}}} N'[(t^2+h^2)^{\frac{1}{2}}] \,, \tag{2}$$

where

$$N(h) = F(h)\exp(-p^2h^2) \,.$$

Both (1) and (2) require numerical differentiation of the experimental curve. This differentiation can lead to errors when applied to an experimental curve which is known ordinarily only to a few per cent. In addition, an unsmearing equation which does not involve numerical differentiation can simplify the numerical calculations. Equation (2) will now be modified to eliminate the need for differentiating the experimental curve.

Changing variables in (2) gives

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$$I(h)=-\frac{\exp(p^2h^2)}{p(\pi)^{\frac{1}{2}}}\int_h^\infty \frac{ds}{(s^2-h^2)^{\frac{1}{2}}}N'(s)$$

$$=-\frac{\exp(p^2h^2)}{p(\pi)^{\frac{1}{2}}}\int_h^\infty \frac{ds}{(s^2-h^2)^{\frac{1}{2}}}\left[N'(s)+\frac{hN(h)}{s^2}-\frac{hN(h)}{s^2}\right]$$

$$=\frac{1}{p(\pi)^{\frac{1}{2}}}\left[\frac{F(h)}{h}-\exp(p^2h^2)\right.$$

$$\left.\times\int_h^\infty \frac{ds}{(s^2-h^2)^{\frac{1}{2}}}\left(\frac{hN(h)}{s^2}+N'(s)\right)\right].$$

Integration by parts yields

$$I(h)=\frac{1}{p(\pi)^{1/2}}\left\{\frac{F(h)}{h}\right.$$

$$\left.+\int_h^\infty \frac{ds}{(s^2-h^2)^{3/2}}\left[hF(h)-sF(s)\exp\left[-p^2(s^2-h^2)\right]\right]\right\}. \quad (3)$$

In (3) the perfect collimation scattered intensity is expressed not in terms of the first derivative of the experimental curve, but in terms of the experimental curve itself. As (3) is a rearrangement of (2), it contains no more and no less information than (2). A numerical computation of $I(h)$ from (2) in which the experimental values of $F(s)$ were fed into the computer and then differentiated would represent a rearrangement of the calculation of $I(h)$ from (3), and so the two methods could be expected to give similar results. When $F(s)$ is differentiated before being used in (2), there is a possibility of obtaining a larger error from (2) than from (3). The greatest advantage of (3), however, is that it simplifies the numerical calculations.

Numerical methods

For numerical evaluation, the integral in (3) was broken up into integrals over intervals of length Δh small enough that

$$G(s)=hF(h)-sF(s)\exp-(p^2s^2-p^2h^2)$$

could be approximated by a linear function which equaled $G(s)$ at the end points of the intervals. This particular method of linear approximation was used to permit numerical evaluation of the improper integral. After two partial integrations over each subinterval, the numerical approximation can be expressed

$$\int_h^\infty \frac{G(s)\,ds}{(s^2-h^2)^{3/2}}=\frac{1}{j^2(\Delta h)^3}\sum_{i=0}^{\infty}\Delta_{ij}^2 G(h_i)$$

where

$$h=j\Delta h$$

$$h_i=(i+j)\Delta h$$

$$\Delta_{ij}^2=-R_{i+1}+2R_i-R_{i-1}$$

$$R_i=\Delta h(i^2+2ij)^{\frac{1}{2}}\,.$$

As

$$\sum_{i=1}^{\infty}\Delta_{ij}^2=R_1-\Delta h\,.$$

(3) becomes

$$I(h)=\frac{1}{j^2p(\pi)^{\frac{1}{2}}(\Delta h)}$$

$$\left[j(2j+1)^{\frac{1}{2}}F(j\Delta h)-\sum_{i=1}^{\infty}T_{ij}F[(i+j)\Delta h]\right], \quad (4)$$

where

$$T_{ij}=(\Delta h)^{-1}(j+i)(\Delta_{ij}^2)\exp\left[-(p\Delta h)^2(2ij+i^2)\right]\,.$$

Equation (4) is in a form suitable for numerical evaluation.

Investigation shows that the error in the numerical approximation (4) can be made as small as desired, provided Δh is sufficiently small. Because of the singularity of the integrand at the lower limit in (3), the sub-integral over the interval $h \le s \le h+\Delta h$ gives the largest contribution to the integral. Therefore, for a given accuracy, this sub-integral requires a smaller Δh than do the other sub-integrals. To simplify the numerical calculations, Δh was chosen to provide sufficient accuracy in the other sub-integrals. Correction terms then were calculated to improve the accuracy of the calculation of the first sub-integral.

The corrections express the change in (4) that is caused by breaking the sub-integral over the interval $h \le s \le h+\Delta h$ into 2, 4, and 8 equal parts and using a linear approximation for $G(s)$ in each part. The term $C_{\frac{1}{2}}$ gives the correction found by dividing the sub-integral in two parts. Of these two parts, only the integral over $h \le s \le h+(\Delta h)/2$ was appreciable, and the other part was neglected. Similarly, $C_{\frac{1}{4}}$ and $C_{\frac{1}{8}}$ express the additional correction which comes from dividing the sub-integral over $h \le s \le h+(\Delta h)/2$ into two and four parts, respectively, and considering only the parts nearest the lower limit h. The other parts are found not to be appreciable. The correction terms C_k are given by

$$C_k = D_k[F_o-2E_kF_k+E_{2k}F_{2k}]$$

where

$$F_k = F(h+k\Delta h)$$

$$D_k = (jp\Delta h)^{-1}\pi^{-\frac{1}{2}}[(2j/k+1)^{\frac{1}{2}}-(j/k+1)^{\frac{1}{2}}]$$

$$E_k = (1+k/j)\exp\left[-(p\Delta h)^2(2kj+k^2)\right]\,.$$

If $I_0(h)$ is the value of $I(h)$ found from (4), the corrected value $I_c(h)$ is obtained from

$$I_c(h)=I_0(h)+C_{\frac{1}{2}}+C_{\frac{1}{4}}+C_{\frac{1}{8}}+\dots\,.$$

Calculation of the C_k can give an estimate of the accuracy of the numerical approximation (4). If Δh is small enough to give a good approximation, the C_k should be small, and one should find that $C_{\frac{1}{2}}>C_{\frac{1}{4}}>C_{\frac{1}{8}}$. As the C_k are expressed as small differences of larger terms, the relative error in the C_k will be greater than the relative error in the F_k. The values of the C_k should be compared with the absolute errors in the F_k. If these errors are of the same order of magnitude as the calculated C_k, the corrections are not meaningful, and (4) gives the best approximation that can be found from the experimental data. The error in (4) then can be expected to be of the same order of magnitude as the size of the terms in $C_{\frac{1}{2}}$. The relative error is ordinarily less than twice the relative error in the experimental curves.

The unsmearing process was tested by applying it to experimental curves for which the unsmearing integral could also be evaluated numerically. The results are plotted in Fig. 1. Before calculating curve *A*, the slit smearing was found for a perfect collimation intensity proportional to the inverse fourth power of the angle. This slit-smeared intensity, which can be expressed in terms of tabulated functions, was then used as the experimental intensity for calculating curve *A*. For curve *B* a similar procedure was used with a perfect collimation intensity proportional to the inverse second power of the angle. Curve *C* gives the effect of the unsmearing process on a constant experimental scattered intensity. Substitution of a constant $F(s)$ in (3) shows that the unsmeared intensity is also constant and that the magnitude of the constant is unchanged in the unsmearing process. Curves *A* and *B* in Fig. 1 are curves proportional respectively to the inverse 4th and 2nd powers of the scattering angle. A constant intensity is drawn for curve *C*. The points in Fig. 1 were calculated from (4) and so show the degree of accuracy given by the unsmearing process. To make the unsmearing calculations for curves *A* and *B*, the slit-smeared intensities were plotted, and the values of $F(s)$ used in (4) were read from these graphs. As this same process would be used in applying (4) to experimental data, the results of Fig. 1 can give an idea of the accuracy of the unsmearing procedure. In curve *C*, $F(s)$ was taken to be exactly constant, and so no graph-reading errors would appear.

The errors in Fig. 1 are almost all less than a few per cent. Because of the errors inherent in graph reading, greater precision would be difficult from experimental data. For the larger errors, which occur

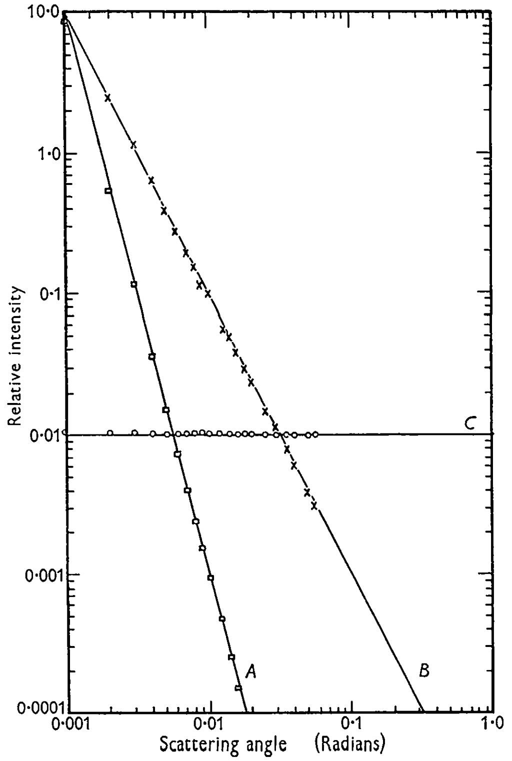

Fig. 1. *A*. The solid line gives the perfect collimation scattering proportional to the inverse fourth power of the angle. The points show the results of applying the unsmearing process to the slit-smeared intensity calculated for perfect collimation scattering proportional to the inverse fourth power of the angle. *B*. The solid line gives the perfect collimation scattering proportional to the inverse second power of the angle. The points show the results of applying the unsmearing process to the slit-smeared intensity calculated for a perfect collimation scattering proportional to the inverse second power of the angle. *C*. The points give the unsmeared intensity calculated for the constant scattered intensity shown by the horizontal line.

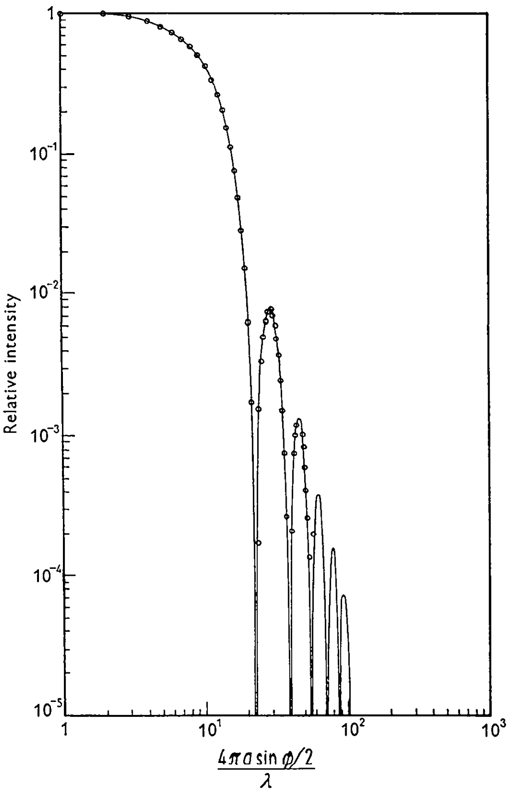

Fig. 2. The effect of the unsmearing process on a curve containing a series of maxima. The scattering curve calculated for infinitely high collimating slits and spherical particles was used for the experimental curve. The curve in Fig. 2 is the theoretical intensity for perfect collimation and spherical particles, for which

$$I(h) = 9\,[(\sin x - x \cos x)/x^3]^2,$$

where

$$x = 4\pi a \lambda^{-1} \sin(\varphi/2)$$

a is the sphere radius, λ is the X-ray wavelength, and φ is the scattering angle. The circles are the points calculated by the unsmearing process, using (4).

at small angles in curve A, use of the correction terms C_k will eliminate most of the error.

The unsmearing process was tested in practice by applying it to some experimental scattering curves obtained in a study of aluminum hydroxide gel (Bale, 1959). The results indicate that the unsmearing process can be used routinely in analysis of scattering data. For the curves considered, the accuracy of the data did not justify calculation of the C_k.

Equation (4) is in a form which allows relatively easy programming for a digital computer. As the T_{kj} are the same for all experimental curves using the same equipment, a point on the unsmeared curves can be calculated in a few minutes with a desk computer when tables of the T_{kj} are available. The authors can supply tables of the T_{kj} and C_k for $\Delta h = 0{\cdot}001$ rad. and

$$p = \tfrac{1}{8}225(\pi)^{\frac{1}{2}}.$$

Although a smooth curve may often be used instead of the actual data points in numerical calculation from (3) or (4), there is nothing in the collimation correction method that requires the use of a smooth curve. There may be occasions when it is preferable to use the actual data points in (3) or (4).

Fig. 2 shows the effect of the unsmearing process on a curve containing a series of maxima. The scattering curve calculated for infinitely high collimating slits and spherical particles (Schmidt, 1955) was used for the experimental curve. The unsmearing procedure sharpens the maxima of the experimental curve, and the unsmeared curve agrees well with the spherical scattering curve for perfect collimation.

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Temperature Variation of the Lattice Constant and the Coefficient of Thermal Expansion of Sodium Chlorate

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Using a back-reflection, flat-film camera and an extrapolation technique, precision determination of the lattice constant of sodium chlorate has been made at different temperatures between the range 30–232 °C. From these, by a graphical treatment, the coefficients of thermal expansion at various temperatures have been evaluated. An equation is also given for evaluating the coefficient of expansion at any temperature.

These coefficients of expansion show a temperature rate of variation higher than the one reported by Sharma (1950*a*) from macroscopic measurements. An explanation for this difference is attempted in terms of imperfections in a single crystal.

Introduction

Sodium chlorate has been the subject of numerous studies because of its simple structure and many of its interesting properties. Zachariasen (1929) gave the length of the unit cell as 6·570 ± 0·006 kX. (6·583 Å). Hüber (1940) studied the mixed crystals of sodium chlorate and sodium bromate and gave the lattice constant of sodium chlorate as 6·568* ± 0·001 Å. Solheim, Konrad & Vegard (1947) report a value of 6·5722* (converted from kX. to Å units). In view of the discrepancies in these values an accurate redetermination of the lattice constant was thought to be worthwhile.

Data on the thermal expansion of this salt have been reported by Mason (1946) and Sharma (1950*a*). Mason quotes the mean values obtained by Miss Armstrong

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* These values are taken from *Structure Reports*.