Reliable values of the B factor for simple crystals can be calculated from an accurate set of dispersion relations at a particular temperature, provided due care is exercised in fitting these dispersion curves, and an adequate frequency sampling is taken.

Present knowledge of interatomic forces does not allow a direct calculation of the anharmonic contributions to the Debye–Waller factor; it may be possible to derive information concerning these forces from the measured high temperature behaviour of B in certain cases.

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An Iterative Method of Slit-Correcting Small Angle X-ray Data

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An iterative method has been developed for correcting experimental small-angle X-ray data simultaneously for the effects of height and width smearing. The advantages of the method are that it does not require the differentiation of an experimental curve, that the height and width weighting functions are completely arbitrary, that the corrected curve remains well defined at small values of the scattering angle, and that the method is designed for use with digital computers. The method may also be applied to the solution of other similar integral equations.

Introduction

In order to obtain sufficient scattered intensity in a small-angle X-ray experiment one normally uses a slit collimation system. The observed intensity in this case is not that obtained with a pinhole collimator, but is the pinhole intensity averaged (smeared) over an angular range which is defined by the slit geometry.

Guinier & Fournet (1947) and DuMond (1947) solved the smearing equation for the case of infinitely high and negligibly narrow slits. Their method was modified by Kratky, Porod & Kahovec (1951) for use

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with certain types of finite slit height geometries. Schmidt & Hight (1960), Heine & Roppert (1962), Kent & Brumberger (1964), Chu & TanCreti (1964) and Schmidt (1965) have used, with modifications, the equations of Guinier & Fournet, DuMond, and Kratky, Porod & Kahovec to program digital computers. Recently, Mazur & Wims (1967) have developed a correction theory for slit systems having negligibly narrow widths and arbitrary height geometries; however, no practical tests of the theory have yet been made. None of these methods corrects for arbitrary slit height and width geometries.

We discuss in the next section a new and general approach to slit corrections.

Theory

By small-angle X-ray scattering we mean the scattering in that region where we can approximate $\sin\theta$ with θ. θ is the angle between the central rays of the incident and scattered beams. If the angular range of X-rays passed by the slits when the detecting aperture is at a fixed position is also small in this same sense then the relationship between the slit-smeared experimental curve, $I_{0S}(h)$, and the pinhole curve, $I_0(h)$ is given by

$$I_{0S}(h)=\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} W_z(z)W_y(y)I_0[((h-y)^2+z^2)^{\frac{1}{2}}]dydz\,, \quad (1)$$

where $h=(4\pi/\lambda)\,.\,\sin(\theta/2)$. W_z and W_y are the slit height and slit width weighting functions respectively, the forms of which depend upon the collimating system, and which are normalized so that

$$\int_{-\infty}^{+\infty} W_z(z)dz=\int_{-\infty}^{+\infty} W_y(y)dy=1.$$

Equation (1) is tractable to iterative approximation methods. Assuming, as an approximation to I_0, an initial trial curve, I_{0T}, it is possible to smear I_{0T} and compare this smeared trial curve, called I_{0TS}, with I_{0S}. The mutual relationships of I_{0TS}, I_{0S}, and I_{0T} may be examined in order to generate a better approximation to I_0. In Fig. 1 are drawn a 'typical' set of I_0, I_{NT}, I_{0S} and I_{NTS}, where I_{NT} is the $(N+1)$th approximation to I_0 and I_{NTS} is the smear of I_{NT}. If I_0 is larger than I_{NT} at some point and if I_0 and I_{NT} do not decrease more rapidly than either the z or the y weighting functions, then since the effect of (1) is to average I_0 over some region of h, it seems we must have that I_{0S} is larger than I_{NTS}. Thus it is reasonable that

$$I_0-I_{NT}\simeq I_{0S}-I_{NTS}$$

or

$$I_0\simeq I_{(N+1)T}=I_{NT}+(I_{0S}-I_{NTS})\,. \quad (2)$$

Equation (2) is the type of equation we have been searching for and works quite well; however, it has a serious drawback. If the 'breadth' of the height weighting function is larger than, or comparable to, the 'breadth' of the central maximum of I_0, then the successive iterations of (2) converge slowly to I_0.

To obtain faster convergence in the region of the central peak an appropriate equation is

$$I_0-I_{NT}\simeq A\,.\,(I_{0S}-I_{NTS}) \quad (3)$$

where A is a positive function of h greater than 1 in the central peak region and is approximately equal to one in the regions in which the corrections are smaller. An A with these properties is $A=I_{NT}/I_{NTS}$. For this choice of A, (3) reduces to

$$I_0\simeq I_{(N+1)T}=(I_{NT}/I_{NTS})\,.\,I_{0S}\,. \quad (4)$$

Equation (4) has all of the virtues of (2) and converges faster. In addition, the $I_{NT}(h)$ are positive for all h provided $I_{0S}(h)$ is positive and provided $I_{0T}(h)$ is chosen positive.

So far we have ignored the selection of an appropriate first trial function. When one examines smeared curves and the corresponding pinhole curves it is noticed that they have roughly the same shape; they have peaks at similar locations and they have minima at about the same positions. Thus a likely candidate for the first trial function is the experimental curve I_{0S} itself. One might be tempted to use a constant curve as the first trial curve. If this is done and one uses equation (4) to predict the next trial curve, it is found that the second trial curve is the experimental curve. For these reasons we will use a first trial curve which is the experimental curve.

Numerical methods

Two Fortran 63 programs were written in order to use this method to obtain solutions to equation (1). The first employed equation (2) and the second used equa-

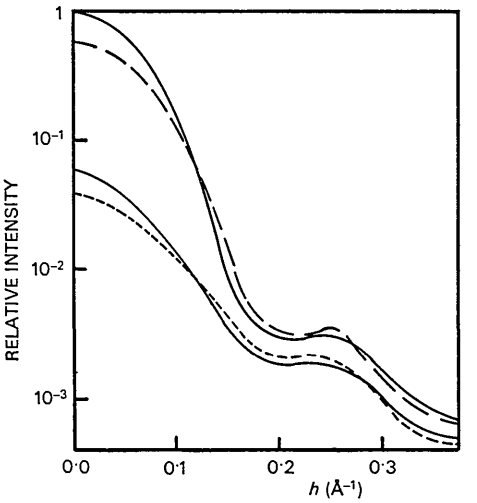

Fig. 1. The upper solid line is the curve which would be seen with pinhole collimation. The lower solid curve is the smear of the pinhole collimation curve. The curve drawn with long dashes is a hypothetical trial function and the curve drawn with shorter dashes is the smear of the hypothetical trial function. These curves are quite representative of the relationships which exist between I_0, I_{0S}, I_{NT} and I_{NTS}.

tion (4) to desmear I_{0S}, *i.e.* to solve equation (1) for I_0. In both programs the smears of the successive approximations to I_0 were printed and by comparison with I_{0S} afforded a check on the convergence of the successive trial functions. Since the width corrections are in general small, the width integrations were done by the method of Gaussian quadratures using a two point integration. The height integration was done by Simpson's rule. All calculations were done on a CDC 1604 computer. Desmearing for both height and width corrections required about twelve seconds for each iteration using an experimental curve extending from 0 to 1 Å^{-1} in one hundred and twenty-five 0·008 Å^{-1} intervals and a height weighting function which vanished at $\pm 0{\cdot}120$ Å^{-1}.

Discussion

Equation (4) was found to be more applicable to small-angle X-ray scattering slit corrections than equation (2) and therefore this discussion is limited to it.

For a number of curves equation (4) converges completely after only one iteration. If the width corrections are negligible and one uses infinitely high slits to smear a curve of the form $I_{0S}=I_{0T}\propto 1/h^3$ one obtains $I_{0TS}\propto 1/h^2$ and equation (4) predicts the correct angular dependence after one iteration. Perhaps the most important case is that in which the width corrections are negligible and the height weighting function is a Gaussian of the form $\exp(-a^2z^2)$. The smear of the Gaussian $I_0=\exp(-b^2h^2)$ is $I_{0S}=I_{0T}=[a^2/(a^2+b^2)]^{\frac{1}{2}}\,.\,I_0$ and likewise $I_{0TS}=[a^2/(a^2+b^2)]\,.\,I_0$. Thus equation (4) predicts $I_{1T}=I_0$ and is exact after the first iteration. The importance of this case lies in the fact that in small-angle X-ray scattering the experimental intensities behave as Gaussians in the region of the origin and one is frequently interested in the exact constant which appears in the exponential. The fast convergence of Gaussian curves allows one to use the results of only a few iterations and to be confident that the corrected curve in the Gaussian region is valid.

In order to investigate the behavior of (4) it is illuminating to see what happens when the first trial curve agrees with the pinhole curve everywhere except in some small region. In Fig. 2, I_0 is a constant everywhere and I_{0T} is the same constant everywhere except for a Gaussian blip centered about 0·20 Å^{-1}. For this test the width corrections were neglected and the height weighting function was a Gaussian which was eight times as wide as the Gaussian blip. As Fig. 2 shows, the successive trial functions converge to I_0 quite rapidly. Furthermore, since any curve can be constructed from a sum of blips, provided the blips are narrow enough, and since equation (1) is linear in I_0 the behavior shown in Fig. 2 demonstrates in a general sense the convergence of the successive I_{NT} to I_0.

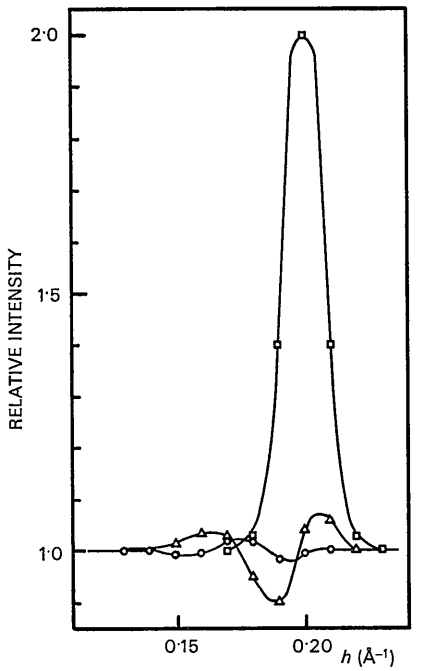

Fig. 2. The curve denoted by the squares is the initial trial function, I_{0T}, which was used in conjunction with a smeared curve, I_{0S}, which had a constant value everywhere. After two iterations the third approximation to I_0, I_{2T}, is shown by the triangles. After four iterations the convergence is almost complete as seen by the fifth approximation, I_{4T}, (circles).

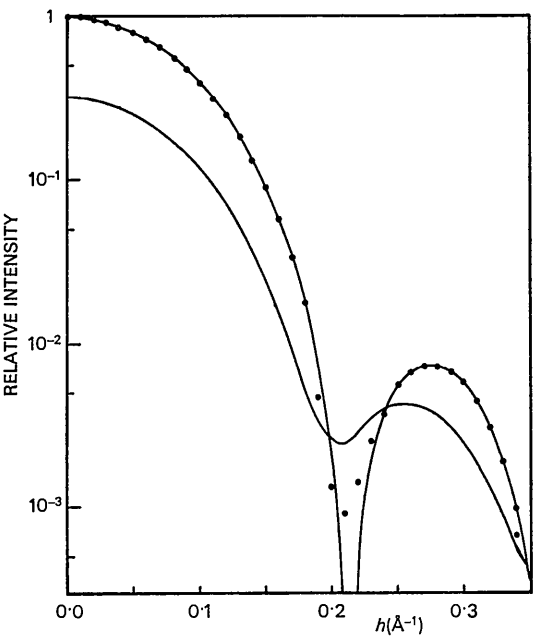

Fig. 3. The upper (in the region of the origin) curve is the scattered intensity from a sphere of uniform density as observed with perfect collimation. The lower (in the region of the origin) curve is the smear of the upper curve using very high, but narrow, slits. The solid points represent the corrected intensity as calculated by (4) after four iterations. After twelve iterations the differences between the perfect collimation curve and the desmeared curve were not visible on this scale. It also should be noted that a graph such as this magnifies small absolute errors.

Perhaps the most difficult curve to desmear is the curve generated by a sphere of uniform electron density. The curve consists of a series of maxima and minima with the intensity rising and falling by many factors of ten in small intervals of h. The curve shown in Fig. 3 was smeared, and later desmeared, using a Gaussian height weighting function which fell to $1/e$ at $\pm 0{\cdot}30$ Å^{-1} and neglecting the width corrections. Since $0{\cdot}30$ Å^{-1} encompassed two secondary peaks this was felt to correspond as closely as was practical to infinite slit height smearing. The results are shown in Fig. 3. The differences between I_0 and I_{4T} are less than one per cent at the points near the peaks but still almost five hundred per cent at the calculated points near the local minima. Nevertheless, the differences would be barely observable experimentally, if at all. If we smeared and desmeared this same sphere scattering function using a height weighting function which fell to $1/e$ at $\pm 0{\cdot}075$ Å^{-1} then the errors at all calculated points, including the local minima, were less than one per cent after four iterations.

It should be noted that this method is not limited to solving the small-angle X-ray collimation equation. The author first derived it in order to correct the X-ray scattering curves for the effect of non-monochromaticity of the incident beam. Ergun (1966) has independently used equation (2) to unfold the convolution equation. Provided that a unique solution exists, it seems that the method can be applied to the solution of any integral equation of the form

$$I_{0S}(x)=\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\cdots\int_{-\infty}^{+\infty} W(y_1,y_2,\ldots,y_n)\, I_0[f(y_1,y_2,\ldots,y_n,x)]dy_1dy_2\ldots dy_n$$

where W is the appropriate weighting function and f is a function of $y_1,y_2,\ldots,y_n$ and x. One such equation which might be of interest is the general (*i.e.* $\sin\theta$ is not necessarily equal to θ) X-ray slit-smearing equation.

Programs can be made available on request by writing to Dr W. W. Beeman, Biophysics Laboratory, University of Wisconsin, Madison, Wisconsin.

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Design Principles of X-ray Diffraction Cameras Linear in $f(\theta)$

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The problem of designing an X-ray diffraction camera linear in an arbitrary function $f(\theta)$ of the Bragg angle is considered. While a general solution determining the shape has not been found, the complete solution for $f=k\theta$ is known, and particular solutions for $f=k\sin\theta$ and $f=k\sin^2\theta$ are given. The shape of a camera linear, along the equatorial plane, in $\sin\theta$ is an upright cardioid cylinder with the specimen at the cusp. For $f=k\sin^2\theta$ no analytic solution has been found, but perturbation and numerical methods have yielded one particular shape satisfying the condition. The practical feasibility of the cameras is discussed.

In conventional X-ray powder diffraction cameras the specimen is situated at the centre or on the circumference of a circular cylinder formed by the film. The primary beam strikes the specimen at a right angle to the cylinder axis or to a line parallel with it. The rectified length of an arc in the equatorial plane is proportional to 2θ when the specimen is at the centre (Debye–Scherrer geometry), or to 4θ when the specimen is on