

the same order as the experimental errors, the effect of many branches is not included in this paper.

The author is grateful to Mr M. Kogiso for critical discussion. Thanks are due to Messrs T. Suzuki and T. Gotō for assistance and the Computation Center of Nagoya University for numerical calculations.

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Acta Cryst. (1981). **A37**, 488–490

Eliminating the Small-Angle Component of the Scattering Calculated for Models

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(Received 2 December 1980; accepted 13 January 1981)

Abstract

A straightforward procedure (assuming spherical symmetry) is described, which enables the unwanted small-angle component of the scattering for a finite model to be calculated. The method may be applied to models of any shape or size. It is illustrated by means of a single polymer chain.

The use of X-ray scattering to elucidate the local structure of non-crystalline materials is well established. This analysis is facilitated by comparison of the experimental scattering with that calculated from models (Wright, 1974; Adams, Balyuzi & Burge, 1976; Lovell, Mitchell & Windle, 1980). For practical as well as structural reasons the size of these models is limited and consequently the calculated scattering contains an unwanted small-angle component, which is only de-

pendent upon the shape and size of the model. This scattering will be dominant at low angles and may swamp relevant structural detail. To make valid comparisons with experimental data in this region, it is vital to eliminate or at least considerably reduce this scattering.

A method of calculating the small-angle scattering (assuming spherical symmetry) is presented for a model of arbitrary shape and size.

In general, comparisons of experimental and model scattering are made with the *s*-weighted reduced intensity function $si(s)$

$$i(s) = kI_{\text{corr}}(s) - \sum_i^n f_i^2(s)/n, \quad (1)$$

where $I_{\text{corr}}(s)$ is the fully corrected data, k a scaling factor, $\sum_i^n f_i^2(s)$ the independent scattering from one

repeat unit of n atoms, and $s = 4\pi \sin \theta/\lambda$. The corresponding model scattering is calculated from the atomic coordinates by the Debye formula (Warren, 1969). For a model of N atoms

$$Ni_m(s) = \sum_{j \neq k}^N \sum_{k=1}^N f_j(s) f_k(s) \sin r_{jk} s / r_{jk} s, \quad (2)$$

where r_{jk} is the distance between the j th and k th atoms.

The simplest method of reducing the effect of the small-angle scattering is to increase the size of the model (Adams, Balyuzi & Burge, 1976) and so move the influence of the scattering to even smaller angles. This is only really effective if it is possible to increase the dimensions of the model in all directions. Furthermore, unless the enlargement of the model contains a disorder component, the correlation length or volume of the model will be increased, and this may well represent a parameter which is to be determined within the framework of the structural investigation.

The small-angle scattering $i'_m(s)$ may be calculated by considering a volume of the same shape and size as the model, but with no internal structure, *i.e.* with constant electron density (based on Guinier & Fournet, 1955)

$$si'_m(s) = \left| \frac{1}{n} \sum_i^n f_i(s) \right|^2 4\pi\rho_0 \int_0^\infty r\gamma_0(r) \sin rs \, dr, \quad (3)$$

where ρ_0 is the average atomic density, and $\gamma_0(r)$ is a shape function. $\gamma_0(r)$ has the value of unity at $r = 0$ and decreases to zero at an r value corresponding to the line of maximum length through the model volume. It is the self-convolution of the shape $\Phi(r)$,

$$\gamma_0(r) = \Phi(r) * \Phi(r), \quad (4)$$

where $\Phi(r) = 1$ within the volume and 0 outside it.

For simple shapes such as spheres (Mason, 1968), rectangular parallelepipeds (Bell, 1968; Goodisman, 1980) and cylinders (Guinier & Fournet, 1955), analytical expressions have been derived for either $\gamma_0(r)$ or its Fourier transform. For models which may be assumed to have one of these smooth envelopes, the small-angle scattering may be readily calculated and subtracted from the total scattering (Wright, 1974), although the 'surface roughness' of a small model may introduce significant aberrations.

Adams, Balyuzi & Burge (1976) and Lovell, Mitchell & Windle (1980) have compared the experimental scattering from non-crystalline polymers with that calculated for a single isolated polymer chain. This type of model is generally neither spherical nor cylindrical. For a chain of irregular trajectory, $\gamma_0(r)$ will be of Gaussian form (Flory, 1969) with a standard deviation related to the second moment of the end-to-end length distribution $\langle r^2 \rangle$. Since if $\gamma_0(r)$ is Gaussian, $si'_m(s)$ will also be Gaussian, the small-angle scattering can be calculated by fitting a Gaussian

function to the low-angle region of the model scattering; this avoids the need to calculate $\langle r^2 \rangle$.

For models of an arbitrary shape, (4) cannot be simply evaluated. However, in calculating the scattering $i'_m(s)$ from (2), the self-convolution of the model has been derived in the form of a set of interatomic distances $\{r_{jk}\}$. These can be sorted into a histogram which represents the self-convolution of a volume with its density concentrated at the atom centres, that is, the atomic radial density function $H(r)$:

$$H(r) = 4\pi r^2 \rho(r), \quad (5)$$

where $\rho(r)$ is the atomic density. To calculate the RDF of a similar but uniform volume, $H'(r)$, the density concentrated at each atom centre must be smeared over a volume representing the average space between atoms. Strictly, this smearing about each atom should be made before convoluting the model with itself and spherically averaging to obtain $H'(r)$. However, if spherical symmetry is assumed about each atom centre then the simple one-dimensional smearing of $H(r)$ may be made

$$H'(r) = 4\pi r^2 \rho_0 \gamma_0(r) = H(r) * V(r), \quad (6)$$

where $V(r)$ is the self-convolution of the average volume about an atom.

To illustrate this average spacing, a simple model of a monatomic fluid (for this example liquid Pb) has been used. The model is an assemblage of random but close-packed spheres whose centres lie within a

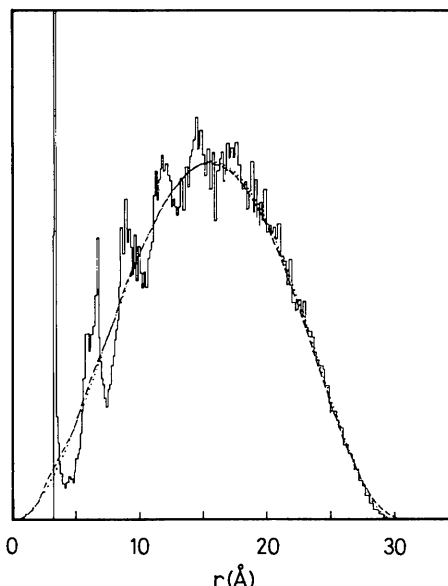


Fig. 1 (a) — The atomic RDF $H(r)$ for an assemblage of randomly close-packed Pb atoms in a spherical envelope of radius 15 Å. (b) — $H'(r)$, the result of smearing $H(r)$ with a Gaussian of standard deviation 1.6 Å. (c) The RDF for a sphere of radius 15 Å with a uniform atomic density.

spherical envelope of radius 15 Å. The atomic RDF, $H(r)$, for this model is shown in Fig. 1 (curve *a*).

If the density at each atom centre is smeared uniformly throughout a sphere of the appropriate van der Waals radius (for Pb $r_v = 1.72$ Å), then all the space will be occupied apart from the interstices of the sphere structure. It is evident that a larger or different smearing shape is required to generate a uniform density throughout the model volume. As the order of operations of smearing, self-convolution and spherical averaging has been altered, the choice of smearing shape, or more exactly the spherical average of its self-convolution, is to some extent arbitrary. Gaussian functions as well as the self-convolution of a sphere have been found to be adequate. The function $H'(r)$, obtained by applying (6) with $V(r)$ a Gaussian of standard deviation 1.6 Å, is shown in Fig. 1 (curve *b*). For comparison, $H'(r)$ for a sphere of radius 15 Å, with the same average density as the model obtained by application of the expression given by Mason (1968), is shown in Fig. 1 (curve *c*). The two curves (*b* and *c*) are very similar, although as they represent slightly different models there is no necessity for a closer agreement.

The smearing of the atomic RDF could of course be carried out in reciprocal space by the equivalent multiplication of the Fourier transforms of the real-

space functions, giving $i'_m(s)$ directly. Equation (3) becomes

$$i'_m(s) = \left| \frac{1}{n} \sum_i f_i(s) \right|^2 v(s) \sum_{j \neq k}^N \sum_{j \neq k}^N \sin r_{jk} s / r_{jk} s, \quad (7)$$

where $v(s)$ is the Fourier transform of $V(r)$. This equation is much simpler to apply as similar components are calculated for (2). Where a Gaussian function is used for $V(r)$, $v(s)$ will also be a Gaussian and an analytical expression for $v(s)$ has been given by Guinier & Fournet (1955) for a sphere.

The versatility of the procedure embodied in (7) will be illustrated by its application to a model of arbitrary shape. The model is a section of a poly(bisphenol A carbonate) chain in zig-zag conformation of overall length 40 Å. The experimental scattering pattern from this material exhibits a temperature-sensitive peak at ~ 0.5 Å⁻¹ (Saffell & Windle, 1980), which is thought to arise from interferences within a chain. The small cross section of the model chain means that the scattering calculated from (2) (Fig. 2 curve *a*) has a small-angle component which swamps all detail from $s = 0$ to 1.5 Å⁻¹. This small-angle component $i'_m(s)$ was calculated from (7) with $v(s)$ for a sphere of radius 1.7 Å. The corrected form of $i'_m(s)$ (Fig. 2 curve *b*), although unchanged for s values > 2 Å⁻¹, reveals a peak at 1.0 Å⁻¹ and a shoulder at 0.5 Å⁻¹.

The application of (7) is easily carried out. It involves little extra computation, and in principle could be extended to the calculation of two-dimensional patterns relevant to oriented material from models with cylindrical symmetry. It is most useful for models with irregular shape or of limited size.

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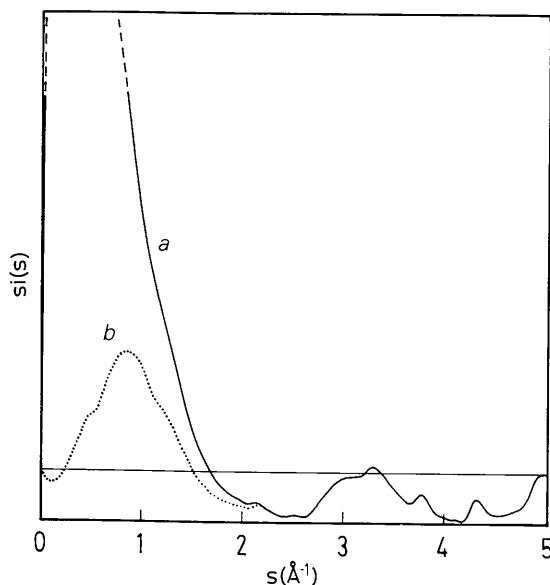


Fig. 2. (*a*) — The s -weighted reduced intensity $si_m(s)$ for a section of a poly(bisphenol A carbonate) chain 40 Å in length. (*b*) $si_m(s)$ with the small-angle scattering $si'_m(s)$ due to the finite model size removed by using (7) with $v(s)$ set to the self-convolution of a sphere of radius 1.7 Å.