X-ray Scattering in Two Dimensions from Shapes with an Inclusion

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The method of molecular shape determination by analysis of small-angle X-ray scattering from dilute monodispersive macromolecular solutions is extended to include the effects of a hole and is applied to scattering in two dimensions.

1. Introduction

In a recent series of papers Stuhrmann (1970*a,b,c*; see also Wu & Schmidt, 1970) has proposed and applied a method for the determination of the surface shape of large molecules by the analysis of small-angle X-ray scattering data obtained from dilute monodispersive macromolecular solutions. The method uses the possibility of varying the mean charge density of the solvent to isolate that fraction of the scattered intensity which is due to the shape of the solute molecules. By expanding the surface shape in terms of spherical harmonics, the spherical symmetry of orientation of the molecules, which is obtained on extrapolating to infinitely dilute concentrations, permits the expansion coefficients of the shape to be successively fitted to the data.

Two questions arise from the analysis. Firstly, how can data from molecules with inclusions be analysed? By an inclusion we mean an internal region of the molecule where the electron density varies with, and is equal to, that of the solvent. Of course, for real molecules this is only a first approximation, but it will be possible to extend the technique to include realistic cases. The original analysis breaks down, since the shape function becomes multivalued and hence cannot be represented by a straight-forward expansion in terms of spherical harmonics. Secondly, is the shape determined uniquely? It is not clear that different shapes must yield different scattering data.

We have considered the case of scattering in two dimensions. Questions of multivaluedness and uniqueness are conceptually the same in two and three dimensions, while, since the corresponding spherical-harmonic expansion is simply a Fourier series, the two-dimensional analysis is considerably simpler. We show how to analyse the shape of a molecule with a single inclusion which encloses the centre of charge of the molecule. In principle, the method should extend to any number of inclusions; however, it may be prohibitively difficult in practice for more than one or two. We intend to consider the problem of uniqueness and to extend the analysis to three dimensions in a future publication.

The theory of shape scattering in two dimensions is developed in § 2. The effects of a hole are considered in § 3. § 4 contains the expansion of some simple shapes, together with the effects of reflexion symmetries and, finally, a test case consisting of an ellipse with a concentric circular hole is analysed in § 5.

It should be noted that as two-dimensional scattering is not equivalent to the scattering by a two-dimensional slice of a three-dimensional object the problem analysed is non-physical. However the technique may be generalized to three dimensions.

2. X-ray shape scattering in two dimensions

If we consider X-ray scattering in two dimensions from a charge cloud having density, $\varrho(\mathbf{r})$, then the relative scattered intensity, $I(\mathbf{s})$, is given by

$$I(\mathbf{s}) = |A(\mathbf{s})|^2 \qquad (2.1)$$

where the scattered amplitude, $A(\mathbf{s})$, is related to the charge density by

$$A(\mathbf{s}) = \int d^2r \exp(i\,\mathbf{s}\cdot\mathbf{r})\varrho(\mathbf{r}) \qquad (2.2)$$

and $\mathbf{s} = 2\pi\lambda^{-1}(\mathbf{M}-\mathbf{M_0})$, where $\mathbf{M_0}$ and $\mathbf{M}$ are the incident and scattered beam directions, while λ is the X-ray wavelength. Since $\varrho(\mathbf{r})$ is real

$$A^*(\mathbf{s}) = A(-\mathbf{s})\,. \qquad (2.3)$$

At infinite solute dilution all angles of incidence are equally likely, and hence the observed scattered intensity is

$$I(\mathbf{s}) = (2\pi)^{-1}\int_0^{2\pi} d\alpha\, I(\mathbf{s}) \qquad (2.4)$$

where

$$\mathbf{S} = s\cos\alpha\,\hat{\mathbf{i}} + s\sin\alpha\hat{\mathbf{j}}\,,$$
$$0\leq s<\infty,\quad 0\leq\alpha<2\pi\,. \qquad (2.5)$$

If the charge cloud has constant density, ϱ, then the charge distribution is

$$\varrho(\mathbf{r}) = \bar{\varrho}\theta[f(\varphi)-r] \qquad (2.6)$$

where $\theta(r)$ is a step-function

$$\mathbf{r} = r\cos\varphi\hat{\mathbf{x}} + r\sin\varphi\hat{\mathbf{y}}\,,$$
$$0\leq r<\infty,\quad 0\leq\varphi<2\pi\,. \qquad (2.7)$$

$f(\varphi)$ is the radial shape function of the molecule. If it is single-valued, *i.e.* the molecule has no inclusions and no surface folds, then it may be expanded as the Fourier series

$$f(\varphi) = \sum_{l=-\infty}^{\infty} f_l \exp\,(il\varphi) \qquad (2.8)$$

where, since $f(\varphi)$ is real,

$$f_l^* = f_{-l}\,. \qquad (2.9)$$

The reason for introducing this expansion is that the angular averaging which occurs in equation (2.4), due to the symmetry of molecular orientation at infinite dilution, allows the mean scattered intensity, $I(s)$, to be expressed directly in terms of the f_l's, and hence enables the shape, $f(\varphi)$, to be determined. The connexion is most easily established by first expanding $A(\mathbf{s})$ as a Fourier series and then expressing the $A(\mathbf{s})$ expansion coefficients in terms of the f_l. We expand

$$A(\mathbf{s}) = \sum_{l=-\infty}^{\infty} A_l(s) \exp\,(il\alpha) \qquad (2.10)$$

where, from equation (2.3),

$$A_l^*(s) = \exp\,(il\pi)\,A_{-l}(s) \qquad (2.11)$$

and consequently the mean intensity, equation (2.4), becomes

$$I(\mathbf{s}) = A_0^2(s) + 2\sum_{l=1}^{\infty} |A_l(s)|^2. \qquad (2.12)$$

The expansion coefficients are defined by

$$A_l(s) = (2\pi)^{-1}\int_0^{2\pi} \mathrm{d}\alpha\,\exp\,(il\alpha)A(\mathbf{s}) \qquad (2.13)$$

$$= (2\pi)^{-1}\int_0^{2\pi} \mathrm{d}\alpha\,\exp\,(il\alpha)\int \mathrm{d}^2r\,\exp\,(i\mathbf{r}\cdot\mathbf{s})\varrho(\mathbf{r})\,. \qquad (2.14)$$

However we may expand (Gradshteyn & Ryzhik, 1965)

$$\exp\,(i\mathbf{r}\cdot\mathbf{s}) = \sum_{n=-\infty}^{\infty} \exp\left(in\frac{3\pi}{2}\right) J_n(\mathbf{r}\cdot\mathbf{s})\,\exp\,\{in(\varphi-\alpha)\} \qquad (2.15)$$

and hence

$$A_l(s) = \varrho\,\exp\left(il\frac{3\pi}{2}\right)\int_0^{2\pi}\mathrm{d}\varphi\,\exp\,(il\varphi)\int_0^{f(\varphi)}\mathrm{d}r\,rJ_l(rs)\,. \qquad (2.16)$$

By employing the series representation of the Bessel function (Gradshteyn & Ryzhik, 1965)

$$J_l(rs) = \sum_{m=0}^{\infty} (-1)^m[2^{l+2m}m!(m+l+1)!]^{-1}(rs)^{l+2m} \qquad (2.17)$$

the r integration of equation (2.16) may be performed allowing the $A(\mathbf{s})$ and $f(\varphi)$ Fourier coefficients to be

related by

$$A_l(s) = 2\pi\bar\varrho\,\sum_{m=0}^{\infty} g(l,m)f_l^{(l+2m+2)}(-rs)^{l+2m} \qquad (2.18)$$

where

$$[g(l,m)]^{-1} = 2^{l+2m}(l+2m+2)m!(m+l+1)! \qquad (2.19)$$

and $f_l^{(N)}$ is the lth coefficient in the Fourier expansion of $[f(\varphi)]^N$.

Using the above relation, the mean intensity, equation (2.12), becomes

$$I(s) = (2\pi)^2\bar\varrho^2 \sum_{n_1,n_2=0}^{\infty} g(0,n_1)g(0,n_2)$$
$$\times f_0^{(2n_1+2)}f_0^{(2n_2+2)}(-s^2)^{(n_1+n_2)}$$
$$+ 8\pi^2\bar\varrho^2 \sum_{l=1}^{\infty}\sum_{n_1,n_2=1}^{\infty} g(l,n_1)g(l,n_2)$$
$$\times f_l^{(2n_1+2)}f_l^{(2n_2+2)*}(-s^2)^{(l+n_1+n_2)} \qquad (2.20)$$

while by comparing the expansions of $f(\varphi)$ and $[f(\varphi)]^N$ it may easily be seen that

$$f_l^{(N)} = \sum_{l_1=-\infty}^{\infty}\cdots\sum_{l_N=-\infty}^{\infty} f_{l_1}\cdots f_{l_N}\delta_{l\,\,l_1+l_2+\,\cdots\,+l_N}\,. \qquad (2.21)$$

The shape of the molecule, which is determined by the f_l, may now be obtained by expanding the intensity $I(s)$ as a power series in s^2 and then fitting a finite subset of the f_l by calculating the coefficients of the powers and then minimizing the differences between the observed and calculated values using simplex routines (Nelder & Mead, 1965). The explicit procedure will be clearer from the example considered in § 5.

3. The effect of an inclusion

If the charge cloud contains a hole which encloses the centre of charge then the shape function, $f(\varphi)$, becomes double valued. It consequently cannot be expanded as a Fourier series. However we may convert it into a single-valued function by mapping the outer shape, $f_O(\varphi)$, onto the range $0 \le \varphi < \pi$, and the inner shape, $f_I(\varphi)$, onto the range $\pi \le \varphi < 2\pi$. We define

$$\begin{aligned} F(\varphi) &= f_O(2\varphi) & 0 \le \varphi < \pi \\ &= f_I(2\varphi - 2\pi) & \pi \le \varphi < 2\pi \end{aligned} \qquad (3.1)$$

with inverse

$$\begin{aligned} f_O(\varphi) &= F(\tfrac{1}{2}\varphi) & 0 \le \varphi < 2\pi \\ f_I(\varphi) &= F(\pi + \tfrac{1}{2}\varphi) & 0 \le \varphi < 2\pi\,. \end{aligned} \qquad (3.2)$$

The composite function, $F(\varphi)$, may now be expanded as a Fourier series

$$F(\varphi) = \sum_{l=-\infty}^{\infty} F_l \exp\,(-il\varphi)\,, \qquad \varphi \ne n\pi\,. \qquad (3.3)$$

Since the charge density is now

$$\varrho(\mathbf{r}) = \bar{\varrho}[\theta(f_o(\varphi) - r) - \theta(r - f_i(\varphi))] \, ,$$

the expression for the l'th Fourier coefficient, $A_l(s)$ of the scattering amplitude, equation (2.19), becomes

$$A_l(s) = \sum_{n=0}^{\infty} g(l,n) \, (-is)^{l+2n} \int_0^{2\pi} \mathrm{d}\varphi \exp(il\varphi)$$

$$\times [\{f_o(\varphi)\}^{l+2n+2} - \{f_i(\varphi)\}^{l+2n+2}]$$

$$= -8\pi i \sum_{n=0}^{\infty} \sum_{m=-\infty}^{\infty} (2l - 2m - 1)^{-1} g(l,n)$$

$$\times F_{2m+1}^{(l+2n+2)}(-is)^{l+2n} \qquad (3.4)$$

and hence the relative intensity is given by

$$I(s) = 64 \sum_{n_1, n_2=0}^{\infty} \sum_{m_1, m_2=-\infty}^{\infty} \frac{(2m_1 + 1)(2m_2 + 1)}{g(0, n_1) g(0, n_2)}$$

$$\times F_{2m_1+1}^{(2n_1+2)} F_{2m_2+1}^{(2n_2+2)*} \, (-s^2)^{n_1+n_2}$$

$$+ 128 \sum_{l=1}^{\infty} \sum_{n_1, n_2=0}^{\infty} \sum_{m_1, m_2=-\infty}^{\infty}$$

$$\times \frac{g(l, n_1) g(l, n_2)}{(2l - 2m_1 - 1)(2l - 2m_2 - 1)}$$

$$\times F_{2m_1+1}^{(l+2n_1+2)} F_{2m_2+1}^{(l+2n_2+2)*} \, (-s^2)^{n_1+n_2} \qquad (3.5)$$

where

$$g(l,n)^{-1} = 2^{l+2n}(l + 2n + 2)n!(n + l + 1)! \, . \qquad (3.6)$$

As in the case of a charge cloud without an inclusion we may fit the F_l to the scattering data and thus determine $F(\varphi)$. However we may now use the inversion formulae, equation (3.2), to obtain both the inner and outer surface shapes.

In order to optimize the information available, the range $0 \le \varphi < 2\pi$ should be split into two parts, whose relative lengths are proportional to the areas of the inclusion and the outer annulus. However, this would further complicate equation (3.5) and would probably not yield significant benefits unless the hole was either small or comparable in size to the total charge cloud.

It should be noticed that the rate at which the F_l tend to zero as $|l|$ increases will be much slower than that of the f_l. Since $f(\varphi)$ is a continuous function of φ, the $|f_l|$ will tend to zero asymptotically, faster than any power of l. $|F_l|$ behaves similarly as $l \to \infty$ through even values, while for odd values $|F_l| \simeq l^{-1}$, owing to the discontinuity of $F(\varphi)$ at $\varphi = \pi$.

4. The effects of reflexion symmetries

We begin with some general considerations: that we are free to fix the angle of orientation of the shape function, that the centre of charge of the molecule must be at the origin of coordinates and that reflexion symmetries impose certain constraints upon the expansion coefficients of the shape. We then calculate the

expansion coefficients for some simple shapes. The general arguments are then applied to the case of a molecule with a hole.

The direction of orientation of the shape function, $f(\varphi)$, is arbitrary. Hence the scattered intensity is unaffected by the transformation $\varphi \to \varphi + \beta$ where β is an arbitrary constant angle (the derivation of equation (2.4) shows that $I(s)$ is invariant under this transformation). This degree of freedom may be partially removed, however, by requiring that f_1 be real, for under the above transformation

$$\mathscr{I}m f_1 \to (2\pi)^{-1} \int_0^{2\pi} \mathrm{d}\varphi \sin(\varphi - \beta) f(\varphi) \, . \qquad (4.1)$$

Therefore, by choosing β such that

$$\tan \beta \int_0^{2\pi} \mathrm{d}\varphi \cos \varphi f(\varphi) = \int_0^{2\pi} \mathrm{d}\varphi \sin \varphi f(\varphi) \qquad (4.2)$$

we may ensure that f_1 is real. Notice that from the reality of $\varrho(\mathbf{r})$ it follows, via equation (2.9), that f_1 is real also.

Similar conditions follow from the requirement that the origin be at the centre of charge

$$\int \mathrm{d}^2r \, \mathbf{r} \, \varrho(\mathbf{r}) = 0 \qquad (4.3)$$

which implies

$$f_1^{(3)} = (2\pi)^{-1} \int_0^{2\pi} \mathrm{d}\varphi f^3(\varphi) \exp(i\varphi) = 0 \, . \qquad (4.4)$$

If the charge cloud has a plane of symmetry, and we choose it such that

$$f(\varphi) = f(2\pi - \varphi) \qquad (4.5)$$

then

$$\int_0^{2\pi} \sin l\varphi f(\varphi) \mathrm{d}\varphi = 0 \qquad (4.6)$$

and consequently all of the f_l are real. If the charge cloud has two perpendicular planes of symmetry, then in addition we may require that

$$f(\varphi) = f(\pi - \varphi) \qquad (4.7)$$

from which it follows that all of the odd partial waves are zero, and incidentally that equation (4.4) is satisfied automatically.

For an ellipse having major and minor axes a and b,

$$f(\varphi) = ab\{b^2 + (a^2 - b^2) \sin^2 \varphi\}^{-1/2} \qquad (4.8)$$

from which it follows that

$$f_{2m} = 4a \sum_{n=m}^{\infty} (-1)^{n+m}(n + 1)^2$$

$$\times \{B(n + 1, n + 1)B(n + m + 1, n + m + 1)\}^{-1}$$

$$\times (a^2 - b^2)^n (4b)^{-2n}$$

$$f_{2m+1} = 0 \quad m = 0, 1, 2, \ldots \, . \qquad (4.9)$$

where $B(n, m)$ is the beta function.

The shape function of a dimer is

$$f(\varphi) = 2R\cos\varphi \quad 0 \le \varphi \le \frac{\pi}{2} \; ; \frac{3\pi}{2} \le \varphi < 2\pi$$

$$= -2R\cos\varphi \quad \frac{\pi}{2} \le \varphi \le \frac{3\pi}{2} \quad (4.10)$$

and the corresponding expansion coefficients are

$$f_{2m} = (-1)^{m+1} 4R\pi^{-1}(4m^2-1)^{-1}$$
$$f_{2m+1} = 0. \quad (4.11)$$

The shape function of an equilateral triangle of side $2\sqrt{3}\,a$ is

$$f(\varphi) = a(\cos\varphi)^{-1} \quad 0 \le \varphi \le \frac{\pi}{3}, \quad \tfrac{5}{3}\pi \le \varphi < 2\pi$$

$$= a\left[\cos\left(\frac{2\pi}{3}-\varphi\right)\right]^{-1} \quad \frac{\pi}{3} \le \varphi \le \pi$$

$$= a\left[\cos\left(\frac{2\pi}{3}+\varphi\right)\right]^{-1} \quad \pi \le \varphi \le \tfrac{5}{3}\pi \quad (4.12)$$

and, correspondingly,

$$f_{2m} = (2\pi)^{-1}a\left(1+2\cos\frac{4\pi m}{3}\right)\left\{(-1)^m \log\left(\frac{2+\sqrt{3}}{2-\sqrt{3}}\right)\right.$$
$$\left. +4\sum_{r=1}^{m}\frac{(-1)^{m+r}}{(2r-1)}\sin(2r-1)\frac{\pi}{3}\right\}$$

$$f_{2m+1} = (2\pi)^{-1}a\left[1+2\cos(2m+1)\frac{2\pi}{3}\right]$$

$$\times\left\{(-1)^m\frac{2\pi}{3}+2\sum_{r=1}^{m}\frac{(-1)^{m+r}}{r}\sin\frac{2r\pi}{3}\right\}, \quad m \ge 2$$

$$(4.13)$$

with

$$f_0 = (2\pi)^{-1}3a\log\left(\frac{2+\sqrt{3}}{2-\sqrt{3}}\right)$$

$$f_1 = \tfrac{1}{3}a(1-\sqrt{3}). \quad (4.14)$$

In general, if the shape is invariant under an mth order rotation group, then only the expansion coefficients, f_l, for which l is a multiple of m will be non-zero.

We now consider the general behaviour of the expansion coefficients, F_l, of a shape function, $F(\varphi)$, corresponding to a molecule with a hole. It follows from the definition

$$F_l = (2\pi)^{-1}\int_0^{2\pi} d\varphi\, \exp(il\varphi)f_0(2\varphi)$$

$$+(2\pi)^{-1}\int_\pi^{2\pi} d\varphi\, \exp(il\varphi)f_I(2\varphi-2\pi) \quad (4.15)$$

that, since f_0 and f_I are both real,

$$F_l^* = F_{-l} \quad (4.16)$$

this being the analogue of equation (4.9).

Upon rotating the axis of coordinates through an angle β

$$\mathscr{R}e(F_1) \to (2\pi)^{-1}\int_\beta^{\pi+\beta} d\varphi\, \cos(\varphi+\beta)f_0(2\varphi)$$

$$+(2\pi)^{-1}\int_{\pi+\beta}^{2\pi+\beta} d\varphi\, \cos(\varphi+\beta)f_I(2\varphi-2\pi). \quad (4.17)$$

Hence, if we may choose β such that the above quantity is zero,

$$\mathscr{R}e(F_1) = 0, \quad (4.18)$$

the requirement that the centre of charge be at the origin becomes

$$\int_0^{2\pi} d\varphi\, \exp(i\varphi)[f_0^3(\varphi)-f_I^3(\varphi)] = 0 \quad (4.19)$$

and leads to the condition

$$F_l^{(3)} = -F_{-l}^{(3)}, \quad l \text{ odd}. \quad (4.20)$$

If the molecule has a plane of symmetry and the axis of coordinates is chosen so that

$$f_0(\varphi) = f_0(2\pi-\varphi); \quad f_I(\varphi) = f_I(2\pi-\varphi) \quad (4.21)$$

then it follows that

$$F_l = (-1)^l F_{-l}. \quad (4.22)$$

Notice that equations (4.16) and (4.22) together imply that F_l is real if l is even and imaginary if l is odd. In addition, equation (4.22) is sufficient to guarantee the centre of charge condition, equation (4.20).

5. A test calculation

In order to test the preceding analysis we have considered the scattering from the shape shown in Fig. 1.
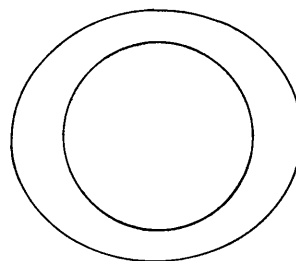
Fig. 1. Ellipse with concentric circular hole.

This is an ellipse having major and minor axes 1·2 and 1·0, with a concentric circular hole of radius 0·75. The corresponding charge density is

$$\varrho(\mathbf{r}) = \theta(f(\varphi)-r) - \theta(h(\varphi)-r) \quad (5.1)$$

where

$$f(\varphi) = \{1-0\cdot306\sin^2\varphi\}^{-1/2} \quad (5.2)$$

and

$$h(\varphi) = 0\cdot75 \quad (5.3)$$

are the outer and inner shape functions respectively.

The scattered intensity, $I(\mathbf{s})$, was determined from equation (2.20), suitably modified to take account of the double-valuedness of the shape.

$$I(s) = \sum_{N=0}^{\infty} C(N)s^{2N} \qquad (5.4)$$

where

$$C(N) = (-1)^N (2\pi)^2 \sum_{n=0}^{N} g(0,n)g(0,N-m)$$

$$\times \{f_0^{(2n+2)} - h_0^{(2n+2)}\} \{f_0^{(2N-2n+2)} - h_0^{(2N-2n+2)}\}$$

$$+ (-1)^N 8\pi^2 \sum_{l=1}^{N} \sum_{n=0}^{N-l} g(l,n)g(l,N-l-n)$$

$$\times \{f_l^{(2n+2)} - h_l^{(2n+2)}\}^*$$

$$\times \{f_l^{(2N-2l-2n+2)} - h_l^{(2N-2l-2n+2)}\} . \qquad (5.5)$$

f_l and h_l are the Fourier expansion coefficients of $f(\varphi)$ and $h(\varphi)$ respectively. The values of $C(N)$ are shown in Table 1. These provide the basic input data from which the shape was determined using equation (3.5).

In order to fit the data to a shape without a hole, equation (2.20) was employed to calculate coefficients, $\bar{C}(N)$ from a shape with Fourier coefficients, f_l, $0 \le l \le 3$. A simplex routine was then employed to vary these until the quantity $\sum_{N=0}^{5} \{C(N) - \bar{C}(N)\}^2 / C^2(N)$ was minimized. The results of this fit are shown in the third column of Table 1. The data were then fitted using equation (3.5), which assumes the existence of a hole, together with the above simplex procedure (Nelder & Mead, 1965). The results are shown in the fourth column of Table 1.

Comparison of the two sets of results, in particular the relative magnitudes of $\sum_{N=0}^{5} \{C(N) - \bar{C}(N)\}^2 / C^2(N)$, shows quite clearly that the second analysis provided a much better fit to the data. This difference would still be observable even when the effects of errors in a notional experiment are taken into account. (Assuming that the scattered intensity is determined by counting techniques under the best conditions as used in real three-dimensional cases, the error per intensity value probably lies in the range 1 to 5%.)

The exact values of the Fourier coefficients, f_l, are shown in Table 2. They are compared with those obtained by the second fitting procedure in Table 3. The differences between the coefficients are due to the finite number of l values used in the fit, since it may be seen from Table 2 that the exact F_l's decrease rather

slowly as l increases. Comparison of the $C(N)$ with the $(\bar{C}N)$ in the second and fourth columns of Table 1 however, shows that experimentally the difference would be unobservable, while the number of $C(N)$'s is limited to about five by the experimental techniques which are available at present.

Table 2. *Fourier coefficients determined directly from shape, $F(\varphi)$*

l	$\mathscr{R}e(F_l)$	$\mathscr{I}m(F_l)$
0	$9 \cdot 215871 \times 10^{-1}$	$0 \cdot 0$
1	$0 \cdot 0$	$1 \cdot 113137 \times 10^{-1}$
2	$0 \cdot 0$	$0 \cdot 0$
3	$0 \cdot 0$	$4 \cdot 986946 \times 10^{-2}$
4	$-2 \cdot 487228 \times 10^{-2}$	$0 \cdot 0$
5	$0 \cdot 0$	$3 \cdot 982444 \times 10^{-3}$
6	$0 \cdot 0$	$0 \cdot 0$
7	$0 \cdot 0$	$7 \cdot 883293 \times 10^{-3}$
8	$1 \cdot 716657 \times 10^{-3}$	$0 \cdot 0$
9	$0 \cdot 0$	$8 \cdot 918888 \times 10^{-3}$
10	$0 \cdot 0$	$0 \cdot 0$
11	$0 \cdot 0$	$7 \cdot 107132 \times 10^{-3}$
12	$-1 \cdot 285163 \times 10^{-4}$	$0 \cdot 0$

Table 3. *Results of the fitting procedure for an ellipse with a hole*

	Exact values	Fitted values, shape with hole
$\mathscr{R}e(F_0)$	$9 \cdot 2159 \times 10^{-1}$	$9 \cdot 2727 \times 10^{-1}$
$\mathscr{I}m(F_0)$	$0 \cdot 0$	$0 \cdot 0$
$\mathscr{R}e(F_1)$	$0 \cdot 0$	$0 \cdot 0$
$\mathscr{I}m(F_1)$	$1 \cdot 1131 \times 10^{-1}$	$1 \cdot 3517 \times 10^{-1}$
$\mathscr{R}e(F_2)$	$0 \cdot 0$	$6 \cdot 7920 \times 10^{-4}$
$\mathscr{I}m(F_2)$	$0 \cdot 0$	$-1 \cdot 5293 \times 10^{-3}$
$\mathscr{R}e(F_3)$	$0 \cdot 0$	$9 \cdot 0502 \times 10^{-3}$
$\mathscr{I}m(F_3)$	$4 \cdot 9870 \times 10^{-2}$	$-3 \cdot 0344 \times 10^{-3}$

Conclusions

The determination of the shape of molecules having an inclusion from an analysis of X-ray scattering data has been formulated in two dimensions. A test case, an ellipse with a concentric circular inclusion, has been analysed. The results show that the existence and approximate dimensions of the hole can be established even when the effects of experimental errors are taken into account. This appears to justify the basic idea of the analysis, which was to map the inner surface onto one half of a circle, the outer surface onto the

Table 1. *Comparison of the exact, C (N), and fitted, $\bar{C}(N)$, values of the data*

N	$C(N)$	Shape $\bar{C}(N)$ without hole	Shape $\bar{C}(N)$ with hole
0	$4 \cdot 011069$	$4 \cdot 759575$	$3 \cdot 958255$
1	$-1 \cdot 805128$	$-1 \cdot 521697$	$-1 \cdot 816531$
2	$3 \cdot 157663 \times 10^{-1}$	$2 \cdot 505975 \times 10^{-1}$	$3 \cdot 170141 \times 10^{-1}$
3	$-2 \cdot 822063 \times 10^{-2}$	$-2 \cdot 413498 \times 10^{-2}$	$-2 \cdot 824941 \times 10^{-2}$
4	$1 \cdot 535482 \times 10^{-3}$	$1 \cdot 506340 \times 10^{-3}$	$1 \cdot 533078 \times 10^{-3}$
5	$-5 \cdot 658913 \times 10^{-5}$	$-6 \cdot 591187 \times 10^{-5}$	$-5 \cdot 632429 \times 10^{-5}$
$\sum_{N} \dfrac{\{(CN) - \bar{C}(N)\}^2}{C(N)^2}$		$1 \cdot 50 \times 10^{-1}$	$2 \cdot 54 \times 10^{-4}$

other half, and then expand the composite function as a Fourier series. The principal difficulty caused by the inclusion is that the expansion coefficients do not decrease as rapidly as in the case without an inclusion. The method will be applied to a physical three-dimensional case in a future publication.

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Limits of Phase Expansion in Direct Methods

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Phase expansion starting from a few initial phases is investigated with reference to the size of the starting set, phase errors in the starting set, the lower limit of the E value in expansion and the different phase-determining formulae. The results stress the need for a sufficient size of the initial phase set with small phase errors for subsequent application of a phase-expanding procedure. The common basis of phase-expansion procedures is shown to consist of a cyclic modification of the preliminary structure and explains the impossibility of correcting substantial errors in already known phases associated with larger E values by subsequent phase determination for smaller E values. The phenomenon of losing structure information by careless application of the tangent formula and consequently the appearance of partial structures is pointed out. This information-destroying phase expansion is shown not to exist in the 'phase-correction' procedure.

Introduction

Several direct methods of crystal structure analysis, differing in their theoretical foundation and practical application, have been developed. The most widely used approaches are the symbolic addition procedure and the multisolution method, several different versions of which have been programmed. Whereas the symbolic addition requires some manual intervention, the multisolution method may be done automatically. (Karle & Karle, 1966; Germain & Woolfson, 1968).

Although many structures have been determined by direct methods, in some cases, for no obvious reasons, there occur difficulties in finding a structure. Sometimes a different initial phase set is successful. In other examples only partial structures have evolved. This investigation has been set up to find reasons for this behaviour of direct methods. As test examples we have chosen structures solved by the symbolic addition procedure, multisolution and structure invariant method (Hauptman, Fisher, Hancock & Norton, 1969).

Theoretical considerations

Apart from the initial stages of phase determination in the above-mentioned methods, the addition of new

phases is done by the tangent formula (Cochran 1955; Karle & Hauptman, 1956). A general form of this formula is

$$U_h = \langle E_k E_{h-k} \rangle_k ,\qquad (1)$$

where U = unitary structure factor, and E = normalized structure factor.

The index k indicates a summation over reflexions. Considering a single contribution with large $E_k E_{h-k}$ this leads to the triple product relation for phases

$$\varphi_h = \varphi_k + \varphi_{h-k} .\qquad (1a)$$

The summation taken over the largest products $E_k E_{h-k}$ leads to the tangent formula

$$\varphi_h = \text{phase of } \langle E_k . E_{h-k} \rangle_k,$$
$$\text{where } k = \text{limited set of reflexions} .\quad (1b)$$

If the summation in equation (1) is taken over all reflexions this is called the Hughes formula and is equivalent to squaring the electron density in direct space (Sayre, 1952).

The initial situation for the addition of new phases in direct methods is as follows. A restricted number of phases associated with large E values has been determined. These phases, together with their observed E values constitute an 'electron density' ϱ_m of a 'prelimi-