Interpretation of Small-Angle Scattering Functions of Dilute Solutions and Gases. A Representation of the Structures Related to a One-Particle-Scattering Function

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Small-angle scattering gives a much poorer resolution of the structure than does diffraction by perfect crystals, *i.e.* the loss of information due to the random orientations of the scattering molecules is far greater than that known from the phase problem. For a quantitative comparison the scalar field functions in physical and reciprocal space are expressed as a series of spherical harmonics Y_{lm}. From the rotational properties of spherical tensors it is deduced that the orientation of the partial structures described by the sum of the multipole components belonging to the same l has no influence on small angle scattering. There are no interference terms between these partial structures, *i.e.* the partial small angle scattering functions arising from the partial structures superimpose independently. Structures giving the same small angle scattering can be generated by displacing the coordinate system and rotating the partial structures in an arbitrary manner and sequence.

The calculations are greatly facilitated by the properties of the 3-*j* and 6-*j* coefficients widely used in nuclear physics. The Hankel transformations of the multipole components are reduced to an algebraic problem by the introduction of Laguerre polynomials.

Introduction

The problem of uniqueness in crystallographic research has been discussed in detail by many authors (Hosemann & Bagchi, 1962). Several techniques have been developed in order to solve the well known phase problem. No comparable investigations have been made in the field of X-ray small angle scattering.

As small angle scattering arises from highly disordered systems, it is likely that the experimentally obtainable information about the structure of individual scatterers is diminished drastically. Therefore a great variety of structures far exceeding the manifold structures due to the loss of phase will give the same small angle scattering.

For the sake of simplicity monodisperse systems at infinite dilution are considered here, *i.e.* all irradiated molecules should have the same configuration and interparticular interference should be eliminated by extrapolation of the normalized scattering to infinite dilution. These conditions reduce the scattering of the whole system to the scattering of one particle.

The small angle scattering function

As the small angle scattering function does not depend on the orientation of the scattering particle, it is convenient to use a mathematical representation of the scatterer which includes the rotational properties of spherical tensors (Brink & Satchler, 1968), and for a bounded scalar field $\varrho(\mathbf{r})$ of the scatterer this is achieved by an expansion as a series of spherical harmonics:

$$\varrho(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \varrho_{lm}(r) Y_{lm}(\theta,\varphi) \qquad (1)$$

where

$$r^l q_{lm}(\mathbf{r}) \equiv \varrho_{lm}(\mathbf{r}) = \int Y_{lm}^*(\omega)\varrho(\mathbf{r})\mathrm{d}\omega \, . \ \mathrm{d}\omega = \sin\theta\mathrm{d}\theta\mathrm{d}\varphi \, .$$

The coefficients $\varrho_{lm}(r)$ are the multipole components of the field $\varrho(\mathbf{r})$. In reciprocal space the scattering amplitude $A(\mathbf{s})$ of $\varrho(\mathbf{r})$ can be described in the same way:

$$A(\mathbf{s}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} A_{lm}(s) Y_{lm}(\Omega) \qquad (2)$$

where

$$s^l p_{lm}(s) \equiv A_{lm}(s) = \int Y_{lm}^*(\Omega)A(\mathbf{s})\mathrm{d}\Omega \, ;$$

$\mathbf{s}$ is the change of momentum of the incident photons induced by the scatterer in $\mathbf{r}$. Assuming only elastic scattering $s = |\mathbf{s}|$ equals $(4\pi/\lambda)\sin\theta$; θ is half the scattering angle. The transition from physical space to reciprocal space is achieved by a Fourier transformation (Sneddon, 1956):

$$A(\mathbf{s}) = (2\pi)^{-3/2} \int \varrho(\mathbf{r}) \exp(i\mathbf{s} \cdot \mathbf{r})\mathrm{d}^3r \, . \qquad (3)$$

The corresponding multipole components are connected by Hankel transformations (Sneddon, 1956) (see Appendix A)

$$\varrho_{lm}(r) = \sqrt{\frac{2}{\pi}}(-i)^l \int A_{lm}(s)j_l(sr)s^2\mathrm{d}s \, ,$$

$$A_{lm}(s) = \sqrt{\frac{2}{\pi}}i^l \int \varrho_{lm}(r)j_l(sr)r^2\mathrm{d}r \, ; \qquad (4)$$

$j_l(sr)$ are the spherical Bessel functions.

The scattering intensity $I(\mathbf{s})$ of $\varrho(\mathbf{r})$ is given by the absolute square of $A(\mathbf{s})$ (see Appendix A)

$$I(s) = A(s)A^*(s)$$

$$= \sum_{l=0}^{\infty} \sum_{m=-l}^{l} I_{lm}(s)Y_{lm}(\Omega) , \qquad (5)$$

where

$$I_{lm}(s) = \sum_{l_1 l_2 m_1 m_2} (-1)^{m_1-m} \sqrt{\frac{(2l_1+1)(2l_2+1)(2l+1)}{4\pi}}$$

$$\times \begin{pmatrix} l_1 l_2 l \\ 000 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l \\ m_1 & -m_2 & -m \end{pmatrix} A_{l_1 m_1}(s)A^*_{l_2 m_2}(s) .$$

The Wigner coefficient $\begin{pmatrix} l_1 l_2 l \\ 000 \end{pmatrix}$ vanishes unless l_1+l_2+l is an even number (Brink & Satchler, 1968; Massot, El-Baz & Lafoucrière, 1967). The phase problem can be characterized by the loss of the multipole components $I_{lm}(s)$ with odd l.

If all orientations of $\varrho(\mathbf{r})$ are equally probable and interference between the particles is negligible, the small angle function of such a monodisperse system can be calculated by integrating $I(s)$ with respect to all orientations of $\varrho(\mathbf{r})$. It is convenient to introduce the Euler angles into $I(s)$ as rotation parameters. A rotation of the field $\varrho(r,\theta,\varphi)$ specified by the Euler angles (α,β,γ) is given by transforming $Y_{lm}(\omega)$ according to the following equation:

$$Y_{lm}(\overline{\omega}) = \sum_{m'=-l}^{l} \mathscr{D}^l_{m'm}(\alpha,\beta,\gamma) Y_{lm'}(\omega) \qquad (6)$$

where $\mathscr{D}^l_{m'm}(\alpha,\beta,\gamma)$ are the matrix elements of the rotation operator (Brink & Satchler, 1968). Integration over (α,β,γ) yields the small angle scattering function $J(s)$.

$$J(s) = \frac{1}{\sqrt{4\pi}} I_{00}(s) = \frac{1}{4\pi} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} A_{lm}(s)A^*_{lm}(s) . \qquad (7)$$

A similar equation has been derived by Debye (1915):

$$J(s) = (2\pi)^{-3} \int \int \varrho(\mathbf{r})\varrho(\mathbf{r}') \frac{\sin s|\mathbf{r}-\mathbf{r}'|}{s|\mathbf{r}-\mathbf{r}'|} d^3r d^3r' .$$

Introducing the multipole expansion of $\sin(s|\mathbf{r}-\mathbf{r}'|)/(s|\mathbf{r}-\mathbf{r}'|)$ equation (7) is obtained. Small angle scattering provides only the zero component of the multipole expansion of $I(s)$.

The small angle correlation function

Every function considered in reciprocal space has its counterpart in physical space. The relation between $\varrho(\mathbf{r})$ and $A(s)$ is given by equation (3).

The Fourier transform of the scattering intensity $I(s)$ is known as the Patterson function $Q(\mathbf{u})$. $\mathbf{u}$ is a vector connecting the points $\mathbf{r}$ and $\mathbf{r}'$ in physical space. $Q(\mathbf{u})$ is the convolution square of $\varrho(\mathbf{r})$.

$$Q(\mathbf{u}) = \int \varrho(\mathbf{r})\varrho(\mathbf{u}+\mathbf{r})d^3r . \qquad (8)$$

According to a proposition of El-Baz & Lafoucrière (1965) $\varrho(\mathbf{u}+\mathbf{r})$ can be expanded as a series of spherical harmonics in the directions of $\mathbf{u}(=\omega_u)$ and $\mathbf{r}(=\omega)$

$$\varrho(\mathbf{u}+\mathbf{r}) = \sum_{\substack{l_1 l_2 L L_1 L_2 \\ m M_1 M_2}} C u^{l_1} r^{l_2} g^{(L)}_{lm}(u,r) Y^*_{L_1 M_1}(\omega_u) Y^*_{L_2 M_2}(\omega) \qquad (9)$$

where

$$g^{(L)}_{lm}(u,r) = \frac{\hat{L}^2}{2} (-1)^L \int_{-1}^{1} q_{lm}(\sqrt{u^2+r^2+2urz}) P_L(z)dz ,$$

$$C = \sqrt{4\pi}\, \hat{l}\hat{l}_1\hat{l}_2\hat{L}_1\hat{L}_2\delta_{l_1+l_2,l} \begin{pmatrix} L_2 L_1 l \\ M_2 M_1 m \end{pmatrix} \begin{pmatrix} l_2 L_2 L \\ 000 \end{pmatrix}$$

$$\times \begin{pmatrix} l_1 L_1 L \\ 000 \end{pmatrix} \begin{Bmatrix} l_1 l_2 l \\ L_2 L_1 L \end{Bmatrix} ,$$

$$\hat{l} = \sqrt{2l+1} ;$$

$P_l(z)$ is the Legendre polynomial.

The range of the summation indices is determined by the properties of the Wigner 3-j and 6-j coefficients defining C. Introducing equation (9) and (1) into equation (8) the multipole expansion of the Patterson function is obtained.

$$Q(\mathbf{u}) = \sum_{L_1=0}^{\infty} \sum_{M_1=-L_1}^{L_1} Q_{L_1 M_1}(u) Y_{L_1 M_1}(\omega_u) , \qquad (10)$$

where

$$Q_{L_1 M_1}(u) = \sum_{\substack{l_1 l_2 l L L_2 \\ m M_2}} C u^{l_1} \int_{r=0}^{\infty} r^{l_2} \varrho_{L_2 M_2}(r) g^{(L)}_{lm}(u,r) r^2 dr .$$

On transition to dilute solution or gases all orientations of the Patterson functions associated with the molecules become equally probable. Such an isotropic system is described by a function $H(u)$ depending only on the absolute value of $\mathbf{u}$. $H(u)$ is obtained by integration of $Q(\mathbf{u})$ with respect to all orientations ω_u (see Appendix B).

$$H(u) = \frac{1}{4\pi} \int Q(\mathbf{u})d\omega$$

$$= \frac{1}{\sqrt{4\pi}} Q_{00}(u) \qquad (11)$$

$$= \sum_{l=0}^{\infty} \sum_{L=0}^{l} \frac{\hat{(l)}}{2\sqrt{2L+1}} u^{l-L} \sum_{m=-l}^{l} \int_{r=0}^{\infty} r^{l+L} q^*_{lm}(r)$$

$$\times \int_{-1}^{1} q_{lm}(\sqrt{u^2+r^2+2urz}) P_L(z)dz r^2 dr .$$

$H(u)$ is the small angle correlation function or characteristic defined independently by Debye & Büche (1949) and Porod (1951). $H(u)$ is related to its counterpart in reciprocal space by a Hankel transformation:

$$H(u) = \pi \int s^2 J(s) \frac{\sin su}{su} ds ,$$

$$J(s) = (2\pi)^{-3} \int 4\pi u^2 H(u) \frac{\sin su}{su} du . \qquad (12)$$

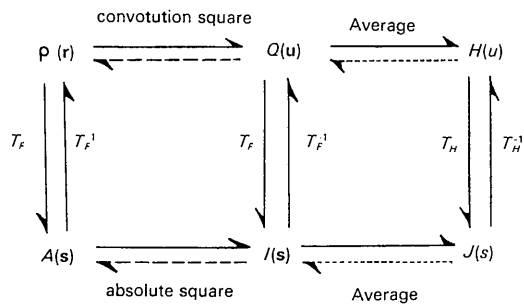Another important function closely connected with the

Fig. 1. Schematic diagram of the steps to be performed in the structure analysis. The dotted lines show ambiguous steps. T_F = Fourier transformation; T_H = Hankel transformation; T^{-1} = inverse transformation.

correlation function is the distance distribution $D(u)$,

$$D(u) = 4\pi u^2 H(u). \tag{13}$$

Fig. 1 shows the relation between these functions in physical and reciprocal space.

Representation of the structures $\varrho(r)$ associated with a small-angle function $J(s)$

The manifold structures giving the same scattering function $J(s)$ can be divided into two classes which are specified by the summation indices l and m of equations (7) and (11).
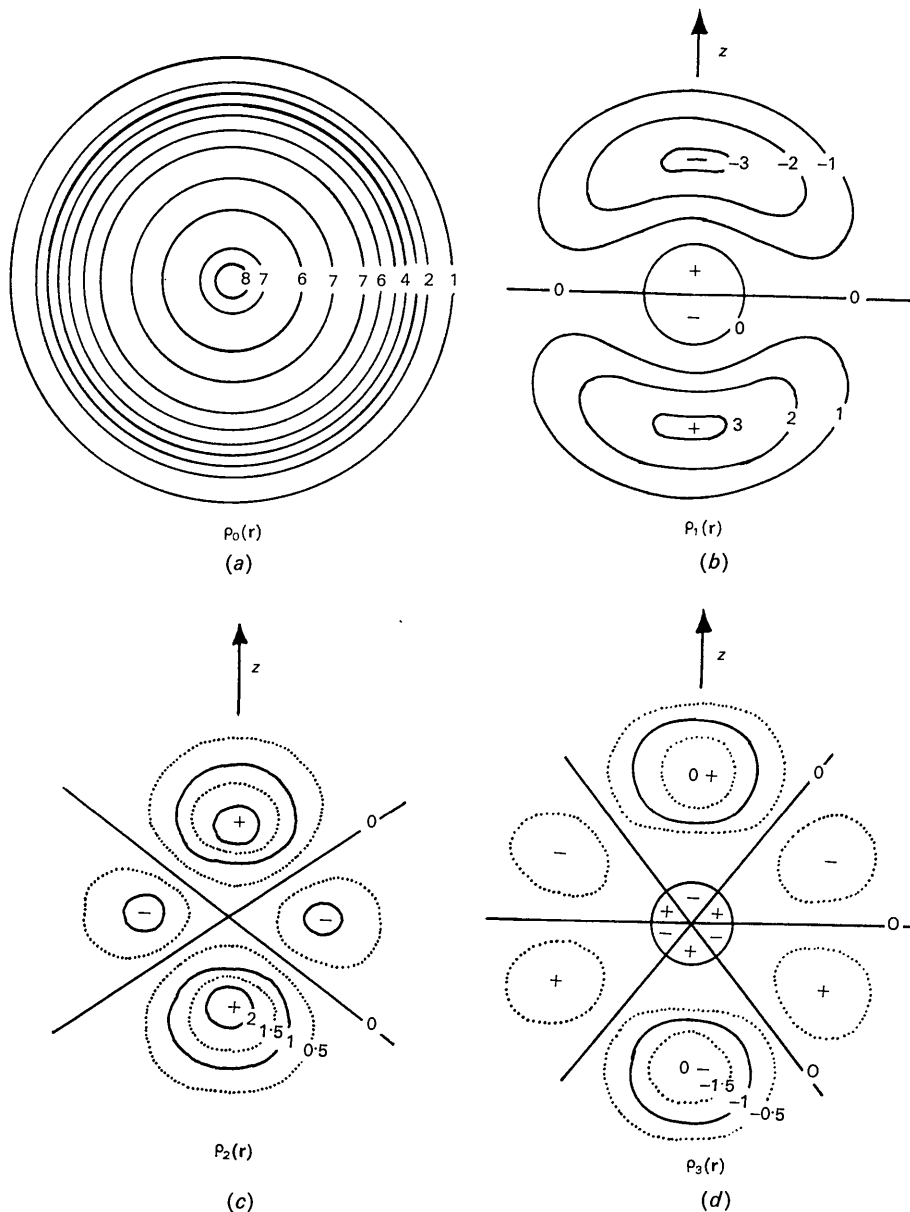

Fig. 2. Partial structures of the model.

(1) From the transformation properties of the Y_{lm} in equation (6) it can be deduced that the lth partial scattering function

$$J_l(s) = \sum_{m=-l}^{l} A_{lm}(s) A_{lm}^*(s) \tag{14}$$

is conserved under rotation of the lth partial structure:

$$\varrho_l(\mathbf{r}) = \sum_{m=-l}^{l} \varrho_{lm}(r) Y_{lm}(\omega) . \tag{15}$$

Thus one class of structures giving the same $J(s)$ is generated by arbitrary independent rotations of the partial structures $\varrho_l(\mathbf{r})$. On rotation the scalar product is conserved:

$$\sum_{m=-l}^{l} \varrho_{lm}(r)\varrho_{lm}^*(r) = \sum_{m=-l}^{l} \overline{\varrho}_{lm}(r)\overline{\varrho}_{lm}^*(r) . \tag{16}$$

The phases of the partial structures can be chosen in such a way that $\varrho(\mathbf{r})$ has rotational symmetry with respect to the z axis. $(\varrho_{lm}(r) = 0$ if $m \neq 0)$.

(2) The analysis of the sum of the partial scattering functions $J_l(s)$ yields another family of solutions.

$$J(s) = \frac{1}{4\pi} \sum_{l=0}^{\infty} J_l(s) = \frac{1}{4\pi} \sum_{l=0}^{\infty} [A_{l0}(s)]^2$$

$$= \frac{1}{4\pi} \sum_{l=0}^{\infty} s^{2l}[p_{l0}(s)]^2 . \tag{17}$$

Different decompositions of $J(s)$ into $J_l(s)$ can be achieved by displacing $\varrho(\mathbf{r})$ according to equation (9). This operation affects neither $I(\mathbf{s})$ nor $J(s)$. $\varrho(\mathbf{r})$ remains congruent under this operation, but the changed multipole components offer a new starting point for the construction of other $\varrho(\mathbf{r})$ by rotation of $\varrho_l(\mathbf{r})$.
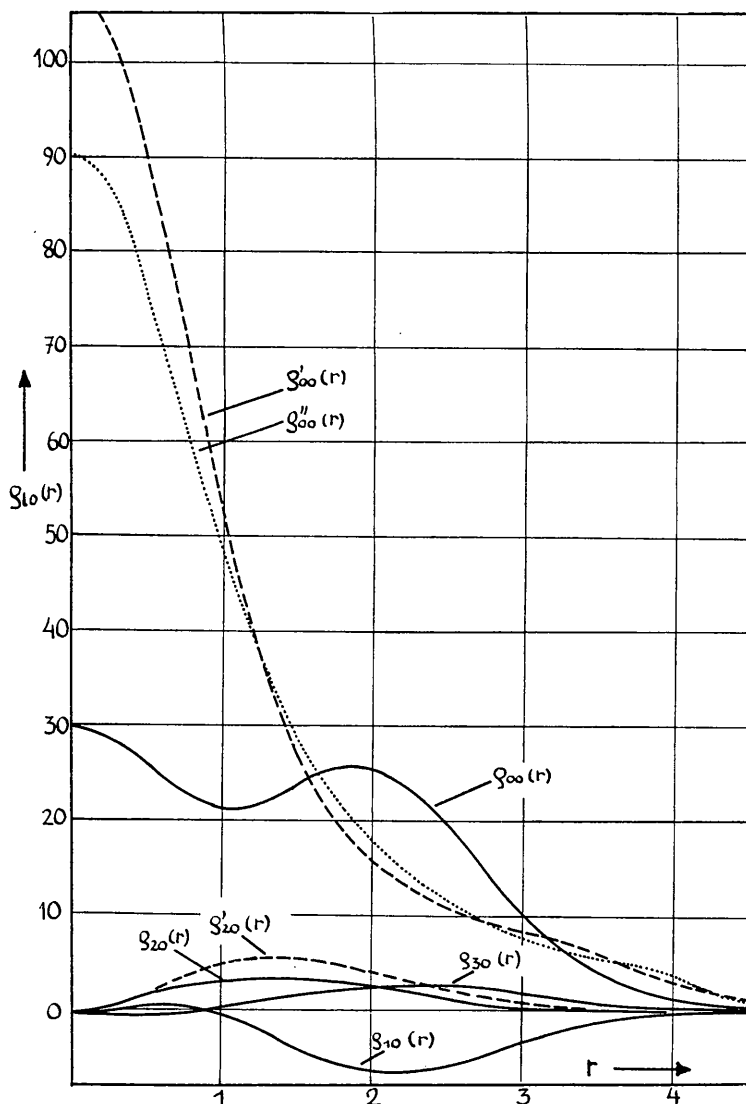

Fig. 3. Radial functions of the partial structures.

We shall assume that rotation of the partial structures $\varrho_l(\mathbf{r})$ and displacement of $\varrho(\mathbf{r})$ in an arbitrary manner and sequence do not change the small-angle scattering.

Small angle scattering is most easily discussed in terms of an $A_{00}(s)$ or $\varrho_{00}(r)$

$$J(s) = J_0(s) = \frac{1}{4\pi} A_{00}^2(s) = \frac{1}{2\pi^2} \int \varrho_{00}(r) \frac{\sin sr}{sr} r^2 dr \ . \ (18)$$

There are as many possible spherically symmetric structures $\varrho_0(r)$ giving the same $J(s)$ as there are roots of $J(s)$. The corresponding formula in physical space is

$$D(u) = u^2 \int_{r=0}^{\infty} q_{00}(r) \int_{-1}^{1} q_{00}(\sqrt{u^2 + r^2 + 2urz})dz r^2 dr \ . \ (19)$$

The distance distribution $D(u)$ of a homogenous sphere is proportional to the common volume of two spheres with centre of mass distance u.

Examples

The calculation of the scattering function $J(s)$ is greatly facilitated by the introduction of Laguerre polynom-

ials (Tricomi, 1955). If $p_{lm}(s)$ and $q_{lm}(r)$ are expanded as a series of Laguerre polynomials of the order $-\frac{1}{2}$,

$$q_{lm}(r) = \sum_{n=0}^{\infty} q_n^{(l,m)} [\exp(-r^2/2)] L_n^{(-1/2)}(r^2)$$

$$p_{lm}(s) = \sum_{n=0}^{\infty} p_n^{(l,m)} [\exp(-s^2/2)] L_n^{(-1/2)}(s^2) \ , \ (20)$$

it can be shown that the vectors

$$\mathbf{q}^{(l,m)} = \{q_0^{(l,m)}, q_1^{(l,m)}, q_2^{(l,m)}, \ \cdot \}$$
$$\mathbf{p}^{(l,m)} = \{p_0^{(l,m)}, p_1^{(l,m)}, p_2^{(l,m)}, \ldots\} \ (21)$$

are related by a linear transformation

$$\mathbf{p}^{(l,m)} = (i)^l \mathbf{H}^{(l)} \mathbf{q}^{(l,m)}$$
$$\mathbf{q}^{(l,m)} = (-i)^l \mathbf{H}^{(l)} \mathbf{p}^{(l,m)} \ . \ (22)$$

$\mathbf{H}^{(l)}$ is a triangular matrix equalling its inverse. The properties of the matrix elements of $H_{ij}^{(l)}$ are discussed in Appendix C. Equation (22) represents the Hankel transformation of order l in an algebraic form. The
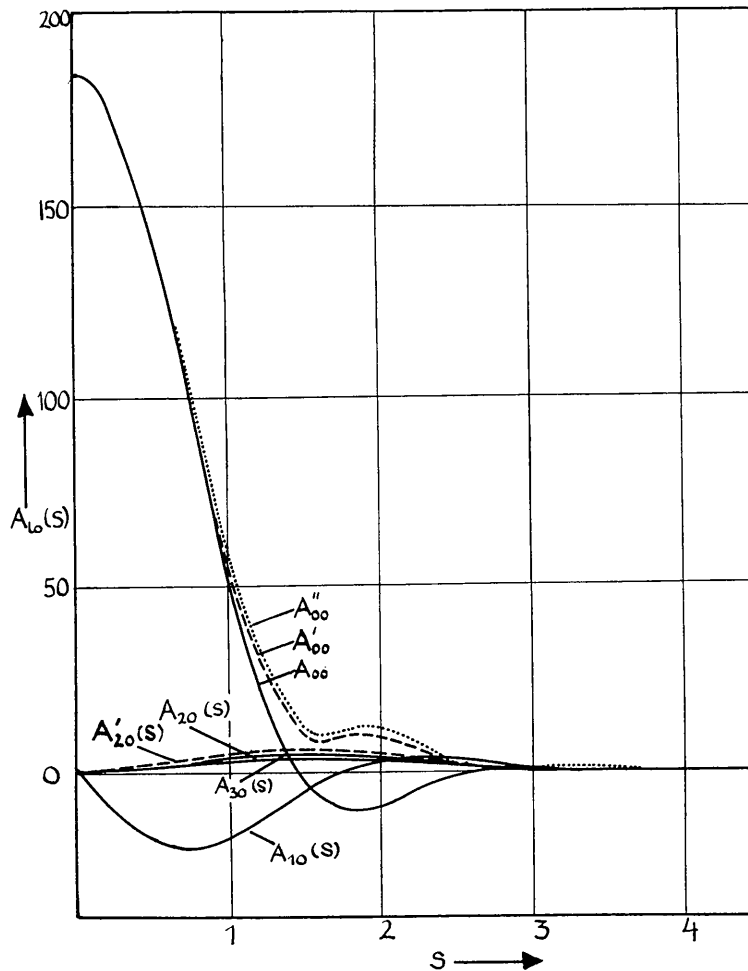

Fig. 4. Multipole components of the scattering amplitude of the model.

advantage of this calculation technique will be demonstrated by the following example:

$$\varrho(\mathbf{r}) = \varrho_0(\mathbf{r}) + \varrho_1(\mathbf{r}) + \varrho_2(\mathbf{r}) + \varrho_3(\mathbf{r})$$

with

$$\varrho_0(\mathbf{r}) = [35 \cdot 5 L_0(r^2) - 28 \cdot 4 L_1(r^2) + 22 \cdot 8 L_2(r^2)]$$
$$\times [\exp(-r^2/2)] Y_{00}(\omega)$$

$$\varrho_1(\mathbf{r}) = [5 \cdot 2 L_1(r^2) - 2 \cdot 06 L_2(r^2)] r [\exp(-r^2/2)] Y_{10}(\omega)$$

$$\varrho_2(\mathbf{r}) = [4 \cdot 8 L_0(r^2)] r^2 [\exp(-r^2/2)] Y_{20}(\omega)$$

$$\varrho_3(\mathbf{r}) = [-0 \cdot 67 L_1(r^2)] r^3 [\exp(-r^2/2)] Y_{30}(\omega) .$$

Fig.2(a)–(d) shows the partial structures $\varrho_l(\mathbf{r})$ all having rotational symmetry with respect to the z axis. The r-dependent functions $\varrho_{l0}(r)$ are given as full lines in Fig.3. The complete structure $\varrho(\mathbf{r})$ is shown in Fig.6(a).* The expansion coefficients of the $p_{l0}(s)$ are connected with those of $q_{l0}(r)$ by the matrix $\mathbf{H}^{(l)}$. In the case $l=0$ the transformation works as follows:

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* Fig.6(a)–(d) resembles rough resolutions of the structures of globular proteins.

$$\begin{pmatrix} p_0^{(00)} \\ p_1^{(00)} \\ p_2^{(00)} \end{pmatrix} = \begin{pmatrix} 1 & -2 & 2 \\ 0 & -1 & 2 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 35 \cdot 5 \\ -28 \cdot 4 \\ 22 \cdot 8 \end{pmatrix}$$

$$p_0^{00} = 35 \cdot 5 + 56 \cdot 8 + 45 \cdot 6 = 137 \cdot 9$$
$$p_1^{00} = \qquad 28 \cdot 4 + 45 \cdot 6 = 74 \cdot 4$$
$$p_2^{00} = \qquad\qquad 22 \cdot 8 = 22 \cdot 8 .$$

Thus we obtain $A_{00}(s)$. The other $A_{l0}(s)$ can be calculated in a similar way according to equation (22).

$$A_{00}(s) = \exp(-s^2/2) [137 \cdot 9 L_0(s^2) + 74 \cdot 5 L_1(s^2) + 22 \cdot 8 L_2(s^2)]$$

$$A_{10}(s) = is \exp(-s^2/2) [-37 \cdot 3 L_0(s^2) - 13 \cdot 4 L_1(s^2) - 2 \cdot 1 L_2(s^2)]$$

$$A_{20}(s) = -s^2 \exp(-s^2/2) 4 \cdot 8 L_0(s^2)$$

$$A_{30}(s) = -is^3 \exp(-s^2/2) [5 \cdot 36 L_0(s^2) + 0 \cdot 67 L_1(s^2)] .$$

The $A_{10}(s)$ are shown in Fig.4 (full lines). The scattering function $J(s)$ is the sum of the absolute squares of $A_{l0}(s)$. The factor $1/4\pi$ has been omitted. The partial
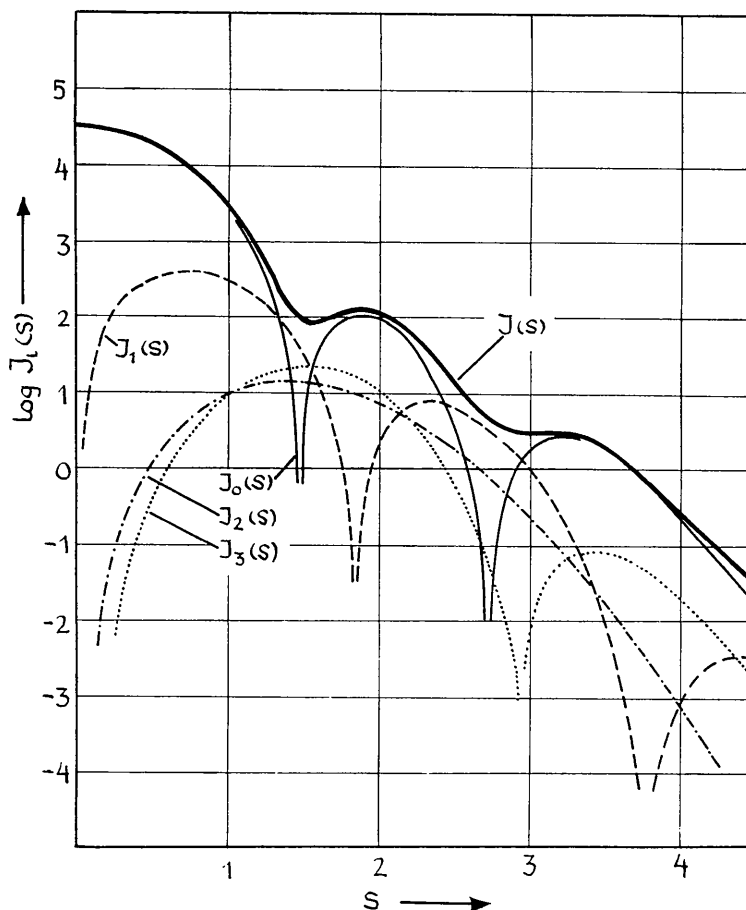

Fig.5. Partial scattering functions $J_l(s)$ and the total scattering function of the model.

scattering functions $J_l(s)$ (Fig. 5) are:

$$J_0(s) = [A_{00}(s)]^2 = \exp(-s^2)[183 \cdot 7 - 108 \cdot 8s^2 + 11 \cdot 4s^4]^2$$

$$J_1(s) = [A_{10}(s)]^2 = s^2 \exp(-s^2)[-44 \cdot 1 + 16 \cdot 6s^2 - s^4]^2$$

$$J_2(s) = [A_{20}(s)]^2 = s^4 \exp(-s^2)23$$

$$J_3(s) = [A_{30}(s)]^2 = s^6 \exp(-s^2)[31 \cdot 5 - 7 \cdot 7s^2 + 0 \cdot 45s^4]^2.$$

The total scattering function $J(s)$ (Fig. 5) is

$$J(s) \simeq J_0(s) + J_2(s) + J_2(s) + J_3(s)$$
$$= \exp(-s^2)[33700 - 37490s^2 + 14533s^4$$
$$- 2090s^6 + 89s^8 + 1 \cdot 5s^{10}].\qquad(23)$$

We have seen that rotation of some partial structures $\varrho_i(\mathbf{r})$ does not change the partial scattering functions $J_i(s)$. The generation of new structures based on this principle was achieved in the following way:

$$\varrho^{(n)}(\mathbf{r}) = \varrho_0(r) + \varrho_1\left(r, \theta + \frac{n\pi}{6}\right)$$
$$+ \varrho_2(r, \theta) + \varrho_3\left(r, \theta - \frac{n\pi}{6}\right), \quad n = 0, 1, 2, 3.\qquad(24)$$

The functions $\varrho^{(n)}(\mathbf{r})$ ($n = 0, 1, 2, 3$) in the xz plane are shown in Fig. 6(a)–(d). The structures $\varrho^{(n)}(\mathbf{r})$ with $n = 1, 2, 3$ have no rotational symmetry.
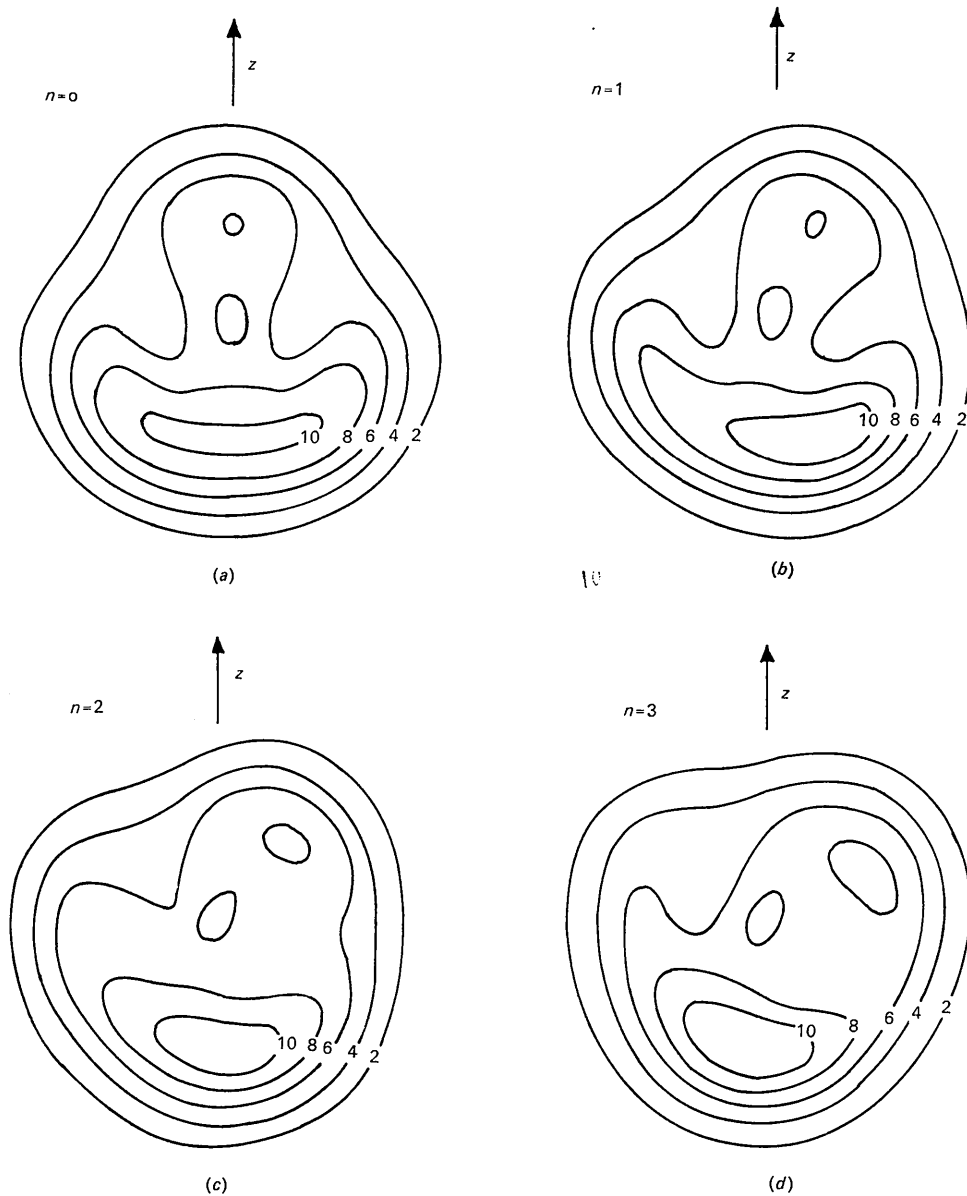

Fig. 6. Different superpositions of the partial structures according to equation (24).

Another class of structures giving the same scattering function $J(s)$ is obtained by different decompositions of $J(s)$ into $J_l(s)$. We interpreted the sums $J_0(s) + J_1(s)$ and $J_2(s) + J_3(s)$ in terms of $\varrho_0(r)$ and $\varrho_2(r)$ respectively:

$$J_0'(s) = J_0(s) + J_1(s) , \qquad J_2'(s) = J_2(s) + J_3(s) ,$$

$$p_{00}'(s) \equiv A_{00}'(s) = \sqrt{J_0'(s)} , \quad s^4 p_{20}'(s) \equiv A_{20}'(s) = \sqrt{J_2'(s)} . \quad (25)$$

$A_{00}'(s)$ and $A_{20}'(s)$ are shown in Fig.4 (broken lines). $p_{00}'(s)$ and $p_{20}'(s)$ can be approximated fairly well by a finite series of Laguerre polynomials $L_n^{-1/2}(s^2)$. The corresponding $\varrho_{00}'(r)$ and $\varrho_{20}'(r)$ (broken lines in Fig.3) are calculated according to equation (22). Thus another structure $\varrho'(\mathbf{r}) = \varrho_0'(\mathbf{r}) + \varrho_2'(\mathbf{r})$, shown in Fig.7, is obtained. $\varrho'(\mathbf{r})$ has rotational symmetry with respect to the z axis.

A model with spherical symmetry can be found by defining $J_0(s) = J_0'(s) + J_2'(s)$. $A_{00}(s)$ (dotted line in Fig.3) is the square root of $J_0(s)$. $\varrho_{00}(r)$ (dotted lines in Fig.2) is the Hankel transform of $A_{00}(s)$. $\varrho''(\mathbf{r})$ is shown in Fig.8.

These are some typical structures belonging to the same small-angle function $J(s)$ defined by equation (23).

APPENDIX

A. Expansions and other formulae

$$\exp (i\mathbf{s} . \mathbf{r}) = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l} i^l j_l(sr) Y_{lm}^*(\Omega) Y_{lm}(\omega)$$

$$\frac{\sin s|\mathbf{r} - \mathbf{r}'|}{s|\mathbf{r} - \mathbf{r}'|} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} j_l(sr) j_l(sr') Y_{lm}^*(\omega) Y_{lm}(\omega') .$$

$j_l(sr)$ are the spherical Bessel functions. The spherical harmonics are denoted by Y_{lm}. ω is a unit vector.

$$Y_{lm}^*(\omega) = (-1)^m Y_{lm}(\omega)$$

$$Y_{l_1 m_1}(\omega) Y_{l_2 m_2}^*(\omega) = (-1)^{m_2} \sum_{\substack{l = l_1 - l_2 \\ m_1 + m_2 + m = 0}}^{l_1 + l_2}$$

$$\times \sqrt{\frac{(2l_1 + 1)(2l_2 + 1)(2l + 1)}{4\pi}} \begin{pmatrix} l_1 l_2 l \\ 0 0 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l \\ m_1 & -m_2 & m \end{pmatrix} Y_{lm}^*(\omega)$$

$$\int_{\alpha=0}^{2\pi} \int_{\beta=0}^{\pi} \int_{\gamma=0}^{2\pi} [\mathscr{D}_{m_1' m_1}^{l_1}(\alpha, \beta, \gamma)]^* \mathscr{D}_{m_2' m_2}^{l_2}(\alpha, \beta, \gamma) d\alpha \sin \beta d\beta d\gamma$$

$$= \delta_{m_1 m_2} \delta_{m_1' m_2'} \delta_{l_1 l_2} \frac{8\pi^2}{2l_1 + 1} .$$

$\mathscr{D}_{m'm}^l(\alpha, \beta, \gamma)$ is the matrix element of the rotation operator.

Further useful formulae are given in modern treatments of the theory of angular momentum (Brink & Satchler, 1968; Massot, El-Baz & Lafoucrière, 1967).

B. The multipole expansion of the small-angle correlation function

Integrating the Patterson function $Q(\mathbf{u})$ with respect to the unit vector ω_u only $Q_{00}(u)$ contributes to $H(u)$.

$$H(u) = \frac{1}{4\pi} \int Q(\mathbf{u}) d\omega_u = \frac{1}{\sqrt{4\pi}} Q_{00}(u) .$$

As $L_1 = 0$ and $M_1 = 0$ the range of the summation indices in equation (10) is greatly reduced because of the albegraic properties of the 3-j coefficients.

$$C \simeq \begin{pmatrix} l_1 L_1 L \\ 0 0 0 \end{pmatrix} \begin{pmatrix} l_2 L_2 L \\ 0 0 0 \end{pmatrix} \begin{Bmatrix} l_1 & l_2 & l \\ L_2 L_1 L \end{Bmatrix} \begin{pmatrix} L_2 & L_1 & l \\ M_2 M_1 m \end{pmatrix} .$$

The triangular conditions of the 3-j coefficients give

$$\left. \begin{array}{l} |l_1 - L_1| \le L \le l_1 + L_1 \to l_1 = L \\ |L_2 - L_1| \le L \le L_2 + L_1 \to L_2 = l \end{array} \right\} \text{ because } L_1 = 0 .$$

As the sum $M_2 + M_1 + m = 0$ and $M_1 = 0$, M_2 equals $-m$.

The 6-j coefficient $\begin{Bmatrix} l_1 & l_2 & l \\ L_2 L_1 L \end{Bmatrix}$ provides no further triangular conditions. Replacing the Kronecker delta function in C [equation (9)] by the substitution $l_2 = l - l_1 = l - L$, we obtain

$$C = \sqrt{4\pi} \ \hat{l} \widehat{\hat{L}l - L\hat{l}} \left[\frac{(2l + 1)!}{(2L + 1)! \ (2(l - L) + 1)!} \right]^{1/2}$$

$$\times \begin{pmatrix} L0L \\ 000 \end{pmatrix} \begin{pmatrix} l - L l L \\ 0 \ 00 \end{pmatrix} \begin{Bmatrix} Ll - Ll \\ l \ 0 \ L \end{Bmatrix} \begin{pmatrix} l & 0 & l \\ -m0m \end{pmatrix} ,$$
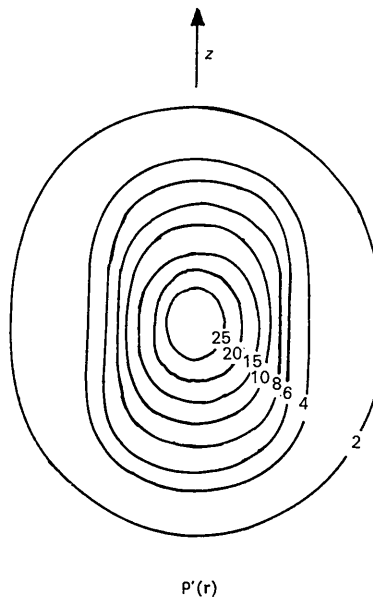
where

$$\hat{l} = \sqrt{2l + 1} .$$

Fig.7. Interpretation of the scattering function in terms of $\varrho_0(\mathbf{r})$ and $\varrho_2(\mathbf{r})$ according to equation (25).

With the explicit expressions of the 3-j and 6-j coefficients

$$\begin{pmatrix} l & 0 & l \\ -m & 0 & m \end{pmatrix} = (-1)^{l-m} \hat{l}^{-1}$$

$$\begin{pmatrix} l-L & l & L \\ 0 & 0 & 0 \end{pmatrix} = \left[\frac{[2(l-L)]! \,(2L)!}{(2l+1)!} \right]^{1/2} \frac{L!}{L! \,(l-L)!}$$

$$\begin{Bmatrix} L & l-L & l \\ l & 0 & L \end{Bmatrix} = \hat{L}^{-1} \hat{l}^{-1}$$

we have

$$C = \frac{\sqrt{4\pi}}{2L+1} (-1)^{L-m} \begin{pmatrix} l \\ L \end{pmatrix}.$$

By introduction of C into equation (10), $Q_{00}(u)$ is obtained.

C. The matrix elements of $H^{(l)}$

As the Laguerre polynomials $L_n^{(\alpha)}(x)$ form a complete system of orthogonal functions with respect to the density function $x^\alpha (\exp - x)$ in the interval $(0, \infty)$, $p_{lm}(s)$ and $q_{lm}(r)$ can be approximated by a series of these polynomials (Tricomi, 1955). In $p_{lm}(s)$ and $q_{lm}(r)$ only even powers of s and r respectively are encountered. Choosing $\alpha = -\frac{1}{2}$ the $L_n^{(\alpha)}(x^2)$ are proportional to the even Hermite polynomials $H_{2n}(x)$

$$q_{lm}(r) = \sum_{n=0}^{\infty} q_n^{(l,m)} [\exp (-r^2/2)] L_n^{(-1/2)}(r^2)$$

$$p_{lm}(s) = \sum_{n=0}^{\infty} p_n^{(l,m)} [\exp (-s^2/2)] L_n^{(-1/2)}(s^2). \quad (20)$$

The coefficients $q_n^{(l,m)}$ and $p_n^{(l,m)}$ are calculated by means of the orthogonality relation of the $L_n^{(-1/2)}(r^2)$.
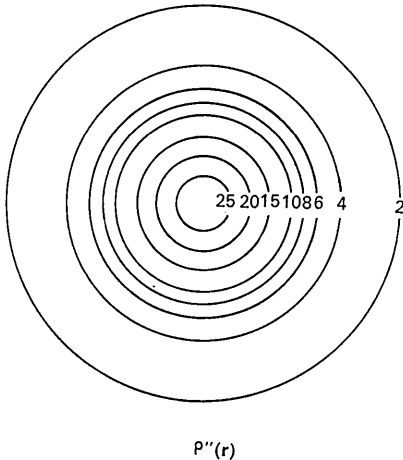

$\rho''(r)$

Fig. 8. Interpretation of the scattering function in terms of a model with spherical symmetry.

$$\int_{r=0}^{\infty} \exp (-r^2) L_n^{(-1/2)}(r^2) L_m^{(-1/2)}(r^2) dr = \frac{\Gamma(n+\frac{3}{2})}{2n!} \delta_{nm}. (26)$$

The choice of the Laguerre polynomials as expansion functions is motivated by their simple transformation properties.

$$\sqrt{\frac{2}{\pi}} \int_{r=0}^{\infty} r^l [\exp (-r^2/2)] L_n^{(l+1/2)}(r^2) j_l(sr) r^2 dr$$

$$= (-1)^n s^l [\exp (-s^2/2)] L_n^{(l+1/2)}(s^2). \quad (27)$$

Expressing $L_n^{(-1/2)}(r^2)$ by linear combinations of $L_n^{(l+1/2)}(r^2)$ we find

$$q_{lm}(r) = \exp (-r^2/2) \sum_{n=0}^{\infty} \sum_{v=0}^{l+1} (-1)^v \binom{l+1}{v} q_{n+v}^{(l,m)} L_n^{(l+1/2)}(r^2) \,(28a)$$

$$p_{lm}(s) = \exp (-s^2/2) \sum_{n=0}^{\infty} \sum_{v=0}^{l+1} (-1)^v \binom{l+1}{v} p_{n+v}^{(l,m)} L_n^{(l+1/2)}(s^2). (28b)$$

Transforming equation (28a) term by term according to equation (27) and equating coefficients we obtain

$$\sum_{v=0}^{l+1} (-1)^v \binom{l+1}{v} p_{n+v}^{(l,m)} = i^{l+2n} \sum_{v=0}^{l+1} (-1)^v \binom{l+1}{v} q_{n+v}^{(l,m)}. \quad (29)$$

From this system of implicit linear equations the matrix elements of $H^{(l)}$ can be calculated. They obey a simple recursion formula.

$$H_{i+1,j+1}^{(l)} = -H_{i,j}. \quad (30)$$

We cite as an example $H^{(2)}$

$$H^{(2)} = \begin{pmatrix} 1 & -6 & 18 & -38 & 66 & -102 & \cdots \\ 0 & -1 & 6 & -18 & 38 & -66 & \cdots \\ 0 & 0 & 1 & -6 & 18 & -38 & \cdots \\ 0 & 0 & 0 & -1 & 6 & -18 & \cdots \\ 0 & 0 & 0 & 0 & 1 & -6 & \cdots \\ 0 & 0 & 0 & 0 & 0 & -1 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

All matrix elements of $H^{(l)}$ can be deduced from the first row of the matrix, Table 1 shows the first matrix elements $H_{0j}^{(l)}$ of $H^{(l)}$.

Table 1. The elements of the first row $H_{0j}^{(l)}$ of $H^{(l)}$

l	j	0	1	2	3	4	5
0	1		-2	2	-2	2	-2
1	1		-4	8	-12	16	-20
2	1		-6	18	-38	66	-102
3	1		-8	32	-88	192	-360
4	1		-10	50	-170	450	-1002
5	1		-12	72	-292	912	-2364

The analysis of the sequence of the $H_{0j}^{(l)}$ by means of higher differences leads to the following formulae:

$$H_{0j}^{(l)} = (-1)^j \sum_{k=0}^{j} \binom{l}{k} B_{jk}. \quad (31)$$

The properties of the B_{jk} are

$$B_{jk}=0, \ k>j \ ; \quad B_{jj}=2^j \ ; \quad B_{j0}=2, j\neq 0 \ ;$$

$$B_{j,j-n}= \sum_{t=0}^{j-n} \binom{j-n}{t} \sum_{n=0}^{u} \binom{t}{u}B_{nu} \ . \quad (32)$$

Table 2 shows some B_{jk}.

Table 2. The elements B_{jk}

j \ k	0	1	2	3	4	5	6
0	1						
1	2	2					
2	2	6	4				
3	2	10	16	8			
4	2	14	36	40	16		
5	2	18	64	112	96	32	
6	2	22	100	240	320	224	64

Equation (32) permits a recursive calculation of further B_{jk}.

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The Structure of Short-Range Ordered Alloys. I. Clustering of Ordered Cells*

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A statistical theory for the X-ray diffuse scattering from disordered binary alloys is developed. It conveys the probability of finding ordered cells as a function of the distance from a given cell. These probabilities are related to the Warren short-range-order parameters. It is also shown that if part of the volume of the crystal is completely disordered, then its size can be calculated from the usual diffuse-scattering measurements. Comparison with experiment shows clustering of ordered cells in disordered CuAu. For alloys which obey the Ornstein–Zernike pair correlation function just above T_c, such as β-brass, there is a clustering of ordered cells, but not an anti-phase domain structure.

Introduction

Binary alloys which undergo an order-disorder transition exhibit short-range order above the transition temperature. The actual substructures of such alloys influence many of their physical properties. Consequently the exact atomic correlation of short-range-ordered alloys has been a subject for many investigations (Gehlen & Cohen, 1965), but the situation is far from being clear.

X-ray diffuse scattering studies from short-range-ordered alloys convey the probabilities for the existence of a given type of atom in each shell of neigh-

bours (Warren & Averbach, 1953). These are statistical results and may be compatible with different models of solid solution, e.g. with a liquid-like character of the distribution of each kind of neighbour or with a model of nucleation of the long-range-ordered phase, i.e. on the assumption that the alloy contains ordered nuclei in an otherwise disordered matrix.

On the other hand, in the parallel case of clustering in pre-precipitation alloys, it has been known for some time that these alloys contain zones of one kind of atom, such as the well-known Guinier–Preston zones in Al–Zn, etc. (Guinier, 1959).

We develop here a new diffraction theory for the diffuse scattering of X-rays from short-range-ordered alloys. This theory converts the treatment of short-range order between atoms to a treatment of 'local