be put into the form

$$H(x',t') = G(t'-x')G(t'+x')/G(t-x)G(t+x)$$

with a nonvanishing μ. If the partial derivative of H with respect to x' is computed, and then x' and t' are set equal to zero, the result is, when (A15) is used,

$$H_{x'}(0,0) = -2[G'(0)/G(0)]t_{x'}(0,0) = 0\,, \quad \text{(A30)}$$

where G' is the derivative of G with respect to its argument. When due account is taken of (7.2), it is easily seen that the condition (A30), applied to $H = D^2/\mu^2$, cannot be satisfied unless μ vanishes.

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Fourier Analysis of X-Ray Diffraction Data from Liquids

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CONTENTS

1. INTRODUCTION

THAT structural information about the liquid state can be obtained by application of x-ray diffraction techniques, has been known since Debye (1915) and Ehrenfest (1915) showed that the periodicity of a crystal structure is not required for the production of diffraction effects. Early experimental diffraction work was done by Debye and Scherrer (1916) on benzene and by Keesom and de Smedt (1923) on liquid argon. This was followed by the introduction by Debye (1927) of the concept of a probability function for the distribution of intermolecular distances. The relation of this function to the production of the diffraction pattern was discussed by Zernike and Prins (1927). These authors also showed how to apply the Fourier integral theorem to the determination of the probability function from diffraction patterns. Debye and Menke (1930, 1931) made the first quantitative application when they treated the case of liquid mercury.

X-ray diffraction measurements were made in a large number of liquids during the first half of this century. In a few instances experimental work was done over a range of pressure and temperature. The results for liquids are summarized in reviews by Gingrich (1943), Furukawa (1962), and Kruh (1962).

The techniques of data treatment by a number of authors were summarized in a book by Randall (1934). The method most commonly used at the present time is that of Warren and Gingrich (1934). A more general approach which treats subtle mathematical points with considerably more elegance is that of Filipovich (1955a, 1955b, 1956a, 1956b). This author rigorously presented the diffraction formulas in terms of both the radial atomic density and the radial electron density. He related these two functions and quantitatively treated the "diffraction error" caused by truncating the formal infinite integral required for the Fourier transformation of the intensity data. Filipovich also wrote expressions for the effect of improper normalization of experimental data. In a treatment applicable to the truncation error as a special case, Waser and Schomaker (1953) discussed the use of intensity data weighting

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functions when the experimental data that are available are incomplete.

The analysis of the radial density functions to identify spurious features resulting from systematic errors was treated by Finbak (1949a, 1949b). In a summary paper (1954), he discussed errors occurring in the work reviewed by Gingrich (1943). These errors in the radial distribution curves generally consist of nonzero density at subatomic radial values and also of ripples of varying severity superposed on the true distribution at higher radii.

The subtleties of the errors arising in the Fourier transform have pointed to the need for caution in the treatment of the experimental data, and, particularly, in the assigning of physical significance to some of the results. The importance of a clear understanding of these problems has become more apparent as attempts have been made to extract progressively more information about distances and configurations from the fine structure of the radial distribution curves. The present authors Pings and Paalman (1962) have recently commented on the difficulties of a critical test of the presence of O_3, O_4, N_4, etc., in a condensed phase in view of the fact that the characteristic interatomic distances of such species correspond to the wavelength of error features that are frequently superimposed on the true distribution functions.

Because of its historical evolution, much of the early literature on experimental determination of liquid structure is couched in the terminology and concepts of solid-state diffraction. There also appear to exist contradictions and ambiguities in several reports on the problems of errors associated with the Fourier integral. For these reasons, and for the reason that the various pertinent contributions are scattered through diverse literature, the present paper presents a coherent treatment of the application of the Fourier integral to liquid x-ray diffraction data, including a systematic analysis of several important sources of error. In view of the recent appearance of the two excellent review articles by Furukawa (1962) and Kruh (1962), we will not comment here on data from actual systems, except as this serves to directly illustrate points associated with the Fourier transform.

2. ELECTRONIC DENSITY

A. General

The phenomenon of diffraction arises when incident x rays cause the excitation of a set of electrons with subsequent radiation from the electrons as secondary sources. When all such scattered rays have the same photon energy, interference effects occur between wavelets from the various scattering points. Several origins of scattering may exist in any given system. The collection of electrons into groups to form atoms gives rise to the diffraction effects typical of a monatomic gas at low density. When a monatomic liquid is irradiated, an additional contribution to the interference pattern is derived from the relative distribution of the individual atoms. Molecular liquids exhibit a third type of influence; together with the effect of atomic structure and relative molecular distribution, the diffraction pattern is affected by the relatively fixed orientation of atoms in the molecule.

The following derivations are qualified by three conditions: First, the primary x-ray beam is composed of radiation with frequency large compared with any natural absorption frequency of the scattering medium; second, each scattered wavelet passes through the sample without rescattering; and third, no absorption of incident or scattered radiation takes place in the medium. The first condition is met by choosing a target material for the x-ray source with an atomic number suitably higher than that of the sample. The necessity for this restriction is twofold. It avoids serious departure of the index of refraction from unity and the attendant difficulties in defining the optics of interference phenomena; it also obviates the laborious recomputation of atomic scattering factors, since tabulated values presuppose this condition. The second qualification is an assumption justified by the relatively small scattering cross sections of most sample materials. The third condition is a theoretical idealization that is never strictly true and requires that mathematical absorption corrections be applied to experimental data before analysis is possible.

The basic problem in an x-ray structural analysis is finding the solution to the integral equation (Filipovich 1955, 1956)

$$\langle I(\mathbf{s},t)\rangle = \left|\int_V \langle \rho(\mathbf{r},t)e^{i\mathbf{s}\cdot\mathbf{r}}dv\rangle\right|^2$$

$$= \int_V\int_V \langle \rho(\mathbf{r}_1,t)\rho(\mathbf{r}_2,t)\rangle e^{i\mathbf{s}\cdot(\mathbf{r}_1-\mathbf{r}_2)}dv_1dv_2\,. \quad (1)$$

In this expression, $\mathbf{s} = (2\pi/\lambda)\,(\mathbf{s}_1 - \mathbf{s}_0)$, where $\mathbf{s}_0$ and $\mathbf{s}_1$ are unit vectors in the direction of the incident and scattered radiation, respectively, λ is the wavelength of the monochromatic radiation used, and $|s| = (4\pi/\lambda)\sin\theta$. In the last relation, θ is just half the scattering angle, i.e., half the angle between $\mathbf{s}_1$ and $\mathbf{s}_0$. The quantity $\rho(\mathbf{r}_i,t)$ is the time-dependent electron density at a point defined by the position vector $\mathbf{r}_i$, included in the volume element dv_i. $\langle I(s,t)\rangle$ is the time-averaged intensity of coherently scattered radiation relative to that which would be scattered by an isolated classical electron under identical conditions (Compton and Allison 1935). A derivation of this relation is given in Appendix I.

Equation (1) can be simplified by a change of variables. Let $\mathbf{r}_2 = \mathbf{r}'$ and $\mathbf{r}_1 - \mathbf{r}_2 = \mathbf{r}$; then rewrite the equation as

$$\langle I(\mathbf{s},t)\rangle = \int_V \left[\int_V \langle \rho(\mathbf{r}',t)\rho(\mathbf{r}' + \mathbf{r},t)\rangle dv' \right] e^{i\mathbf{s}\cdot\mathbf{r}} dv \,. \quad (2)$$

For a system of N spherically symmetrical atoms with atomic number Z, the bracketed term defines a geometrically averaged radial density $\rho(r)$:

$$NZ\rho(r) = \int_V \langle \rho(\mathbf{r}',t)\rho(\mathbf{r}' + \mathbf{r},t)\rangle dv' \,. \quad (3)$$

Although the density function $\rho(\mathbf{r},t)$ characterizes the instantaneous electronic structure of a given point of the scattering material at a given time, the function $\rho(r)$ is, by definition, a time and space average which describes the body as a whole. In the following manipulations on the diffraction equation, explicit expression of functional time dependence and of time averaging is dropped.

When (3) is combined with (1), there results the relation

$$\frac{I(\mathbf{s})}{NZ} = \int_V \rho(r) e^{i\mathbf{s}\cdot\mathbf{r}} dv \,. \quad (4)$$

This may be expressed in scalar form as

$$\frac{I(s)}{NZ} = \int_0^\infty \int_0^{2\pi} \int_0^\pi \rho(r) e^{isr\cos\theta} r^2 \sin\theta d\theta d\phi dr \,. \quad (5)$$

Integrating,

$$\frac{I(s)}{NZ} = \int_0^\infty 4\pi r^2 \rho(r) \frac{\sin sr}{sr} dr \,. \quad (6)$$

The upper limit for integration with respect to r is replaced by infinity with the condition that $\rho(r) = 0$ outside the sample cell. According to James (1954), (6) may be formally transformed by the use of the Fourier integral into

$$4\pi r^2 \rho(r) = \frac{2r}{\pi} \int_0^\infty s \frac{I(s)}{NZ} \sin srds \,. \quad (7)$$

Application of this general expression to the analysis of experimental information is not convenient, because it presupposes a complete knowledge of the intensity $I(s)$, which is never achieved in practice. The following sections tell how this difficulty is partially overcome.

B. Zero-Angle Scattering

The radial density defined earlier may be decomposed into two terms; first, the average density of the system and second, a fluctuating component which describes departures from this average value. This may be written

$$\rho(r) = \bar{\rho} + \Delta\rho(r) \,. \quad (8)$$

It will be of value to discuss at this point the diffraction from a sample composed of a homogeneous electronic medium with density everywhere equal to the average electronic density $\bar{\rho}$. For this system, (2) may be written

$$I_o(s) = \int_V \left[\int_V \bar{\rho}(\mathbf{r}')\bar{\rho}(\mathbf{r}' + r)dv' \right] e^{i\mathbf{s}\cdot\mathbf{r}} dv \,. \quad (9)$$

When a spherical sample is considered, the bracketed integral is restricted to a volume such that the heads of vectors $\mathbf{r}$ and $\mathbf{r}'$ always lie within the sphere. For a sphere of radius R_o, this condition is uniquely met by the volume $\frac{4}{3}\pi R_o^3\alpha(r)$, where $\alpha(r) = 1 - \frac{3}{4}(r/R_o) + \frac{1}{16}(r/R_o)^3$. To retain future infinite integral limits in r, let $\alpha(r) = 0$ for $r > 2R_o$. As observed by Urnes (1960), $\alpha(r)$ takes into account that large separations between atoms are discriminated against by a finite sample size.

Using the defined function $\alpha(r)$, (9) is written

$$I_o(s) = \int_0^\infty 4\pi r^2 [\tfrac{4}{3}\pi R_o^3 \alpha(r) \bar{\rho}^2] \frac{\sin sr}{sr} dr \,, \quad (10)$$

which reduces to

$$\frac{I_o(s)}{NZ} = \int_0^\infty 4\pi r^2 \bar{\rho}\alpha(r) \frac{\sin sr}{sr} dr \,. \quad (11)$$

When the integral (11) is evaluated for the function $\alpha(r)$ proper to a spherical sample, the expression for the intensity becomes

$$I_o(s)/NZ = \tfrac{9}{2} NZ (sR_o)^{-6}[(s^2R_o^2 - 1)\cos 2sR_o - 2sR_o \sin 2sR_o + (s^2R_o^2 + 1)] \,. \quad (12)$$

As s goes to zero, $I_o(s)$ approaches a limit of $(NZ)^2$. It is apparent from (12) that, for experiments carried out in even small laboratory equipment (1 mm $= 10^7$Å), the diffraction effects from such a structureless system are concentrated at very low values of s. Guinier and Fournet (1955) estimate that $I_o(s)$ is significantly different from zero only for values of $s < \pi/R_o$. Furthermore, by inspecting (6) and (12), it is possible to demonstrate that

$$\lim_{s\to 0} [I(s) - I_o(s)] = 0 \,. \quad (13)$$

Because of the masking effect of the main x-ray beam emerging from the sample area, $I(s)$ data cannot easily be obtained experimentally for the region in s about zero. To correct for the inaccessibility of this "zero scattering," it is convenient to substract out the intensity at the origin using (13) and the fact that $I_o(s)$ differs significantly from zero only near the origin. In view of the linear additivity of the Fourier transforms, (6) and (11) may be combined as follows:

$$\frac{I(s) - I_o(s)}{NZ} = \int_0^\infty 4\pi r^2[\rho(r) - \bar{\rho}\alpha(r)] \frac{\sin sr}{sr} dr \quad (14)$$

and

$$4\pi r^2[\rho(r) - \bar{\rho}\alpha(r)] = \frac{2r}{\pi} \int_0^\infty s \frac{[I(s) - I_o(s)]}{NZ} \sin srds\,. \quad (15)$$

For practical analysis of experiments involving studies of distances small compared to the sample size, it is possible to exploit the fact that $\alpha(r)$ is essentially unity yielding in place of (15):

$$4\pi r^2[\rho(r) - \bar{\rho}] = 4\pi r^2 \Delta\rho(r) = \frac{2r}{\pi} \int_0^\infty s \frac{[I(s) - I_o(s)] \sin srds}{NZ}\,, [r \ll R_o]\,. \quad (16)$$

In view of the approximations, (16) would obviously be inapplicable for analysis of low-angle scattering data or for treatment of data where the characteristic sample size R_o is very small.

C. Transform Convergence

In the preceding manipulation of the diffraction integral the infinite limits for r were retained by the artifice of defining $\rho(r)$ and $\alpha(r)$ to be zero outside the sample. This was done to achieve an explicit expression for $\rho(r)$ through the Fourier integral theorem, which requires the infinite limit. The resulting expression for $\rho(r)$ is then obtained at the expense of demanding an infinite integral of the intensity kernel in (15) or (16). By experiment, however, intensity data are accessible only to $s = 4\pi/\lambda$ because of the obvious geometric restriction. Although some advantage obviously can be gained by executing the experiment with radiation of shorter wavelength, this will never eliminate the problem. Most current data are being reported for $s_{\max} < 12$ Å^{-1} and the authors are unaware of any experiment to date involving accurate intensity measurements for values of s greater than 20 Å^{-1}.

Experimentally, it can be shown that the intensity per atom of scattering from a monatomic liquid, coherent and incoherent, approaches the intensity per atom from the material as a dilute gas with increasing s. At large s, the liquid intensity oscillates about that of an isolated atom with ever diminishing amplitude. Indeed, this phenomenon has, until recently, been the sole criterion for normalization of intensity data from arbitrary units to the classical electron basis delineated above. (This aspect will be further discussed in a following section.) Another use can be made of this fact, however. Since Fourier integral analysis of diffraction patterns must inherently be concerned with the effects of integral truncation, it is important to choose an efficient manner of treating the incomplete data. A criterion for this choice may be expressed by the equation

$$\left| \int_0^\infty sI^*(s) \sin srds - \int_0^{s_o} sI^*(s) \sin srds \right| < \left| \int_0^\infty sI(s) \sin srds - \int_0^{s_o} sI(s) \sin srds \right|\,, \quad (17)$$

where $I^*(s)$ is the desired function of the intensity $I(s)$ and s_o is the upper limit in s. This may be written as

$$\left| \int_{s_o}^\infty sI(s) \sin srds \right| > \left| \int_{s_o}^\infty sI^*(s) \sin srds \right| \quad (18)$$

or as the sufficient condition

$$\left| sI(s) \sin sr \right| > \left| sI^*(s) \sin sr \right|\,. \quad (19)$$

In view of the damped oscillations of $I(s)$ about $f^2(s)$, the atomic scattering intensity, a likely choice for $I^*(s)$ is just $I(s) - f^2(s)$. As discussed by James (1954), the atomic form factor $f(s)$ can be defined in terms of the electronic density

$$f(s) = \int \rho(\mathbf{r}) e^{is\cdot\mathbf{r}} dv\,. \quad (20)$$

From experience, the relation

$$\left| I(s) \right| > \left| I(s) - f^2(s) \right| \quad (21)$$

obtains for $s > 5$ Å^{-1}, and in itself is a sufficient condition to satisfy (19). Therefore, the inversion of a truncated portion of $[I(s) - f^2(s)]$ will approximate the true answer better than an inversion of a similar portion of $sI(s)$. It remains to assess the effect of the linear term in $f^2(s)$ upon the desired density function $\rho(r)$.

From (20) it follows that

$$f^2(s) = \int_{V_{\text{at}}} \left[\int_{V_{\text{at}}} \rho(\mathbf{r})' \rho(\mathbf{r}' + r) dv' \right] e^{is\cdot\mathbf{r}} dv\,, \quad (22)$$

where the integrals extend over the nominal volume of one atom. Analogous to (3), an averaged radial density is defined for a spherically symmetrical atom

$$Z\rho_0(r) = \int_{V_{\mathrm{at}}} \rho(\mathbf{r}')\rho(\mathbf{r}' + \mathbf{r})dv' . \tag{23}$$

Thus, (22) may be inverted to

$$4\pi r^2 \rho_0(r) = \frac{2r}{\pi}\int_0^\infty s\,\frac{f^2(s)}{Z}\sin srds . \tag{24}$$

A linear combination of (15) and (24) gives

$$\begin{aligned} &4\pi r^2[\rho(r) - \bar{\rho}\alpha(r) - \rho_0(r)] \\ &\quad = \frac{2r}{\pi}\int_0^\infty s\,\frac{(I(s) - I_o(s) - Nf^2(s))}{NZ}\sin srds . \end{aligned} \tag{25}$$

With the same assumptions leading to (16), the preceding may be simplified to

$$\begin{aligned} &4\pi r^2[\rho(r) - \bar{\rho} - \rho_0(r)] \\ &\quad = \frac{2r}{\pi}\int_0^\infty s\,\frac{(I(s) - I_o(s) - Nf^2(s))}{NZ}\sin srds , \\ &\qquad\qquad\qquad\qquad [r \ll R_0] . \end{aligned} \tag{26}$$

The influence of $\rho_o(r)$ is confined to radii less than a nominal atomic radius. The relationship between the density function evaluated by truncating the infinite integral and the theoretical function is discussed in Sec. 5.

3. ATOMIC DENSITY

Historically, the density function that has been of interest in structural analysis is the atomic density $\rho_a(\mathbf{r}_1)$. This quantity may be defined as

$$\rho_a(\mathbf{r}) = \sum_i^N \frac{\delta|\mathbf{r} - \mathbf{r}_i|}{4\pi|\mathbf{r} - \mathbf{r}_i|^2} , \tag{27}$$

where $\mathbf{r}_i$ is a vector to the center of the ith atom. From this definition, the relation follows that:

$$\int_V \rho_a(\mathbf{r})dv = N . \tag{28}$$

It is necessary to express the basic diffraction equation in terms of this atomic density. Thus, assuming no interpenetration of atomic electron clouds,

$$\begin{aligned} I(\mathbf{s}) &= \left|\int_V \rho(\mathbf{r})e^{i\mathbf{s}\cdot\mathbf{r}}dv\right|^2 \\ &= \left|\sum_i^N \int_{V_i} \rho_i(\mathbf{r} - \mathbf{r}_i)e^{i\mathbf{s}\cdot(\mathbf{r}-\mathbf{r}_i)}e^{i\mathbf{s}\cdot\mathbf{r}_i}dv\right|^2 . \end{aligned} \tag{29}$$

Implicit in (20) is the relation

$$f_i(\mathbf{s}) = \int_{V_{\mathrm{at}}} \rho_i(\mathbf{r} - \mathbf{r}_i)e^{i\mathbf{s}\cdot\mathbf{r}_i}dv . \tag{30}$$

Combining these two equations gives

$$I(\mathbf{s}) = \left|\sum_i^N f_i(s)e^{i\mathbf{s}\cdot\mathbf{r}_i}\right|^2 . \tag{31}$$

This may be written in terms of the atomic density since

$$\begin{aligned} \sum_{i=1}^N f_i(s)e^{i\mathbf{s}\cdot\mathbf{r}_i} &= \int \sum_{i=1}^N \frac{\delta(|\mathbf{r} - \mathbf{r}_i|)}{4\pi|\mathbf{r} - \mathbf{r}_i|^2} f(\mathbf{s})e^{i\mathbf{s}\cdot\mathbf{r}}dv \\ &= \int \rho_a(\mathbf{r})f(s)e^{i\mathbf{s}\cdot\mathbf{r}}dv . \end{aligned} \tag{32}$$

With the usual change of variables, upon expansion an equation analogous to (2) gives

$$I(\mathbf{s}) = \int_V \left[\int_V \rho_a(\mathbf{r}')\rho_a(\mathbf{r}' + \mathbf{r})dv'\right] f^2(s)e^{i\mathbf{s}\cdot\mathbf{r}}dv . \tag{33}$$

Again the bracketed term is used to define a spatially averaged density function. A measure of caution must be exercised at this point, however. From the definition of $\rho_a(r)$, the bracketed term will consist of a set of singularities. There is one isolated singular point at $\mathbf{r} = 0$ because of the limited atomic packing density. The other singularities are not isolated. In fact, the function

$$\psi(\mathbf{r}) = \frac{1}{\delta V}\int_{\delta V}\left[\int_V \rho_a(\mathbf{r}')\rho_a(\mathbf{r}' + r + \mathbf{r}_\delta)dv'\right]dv_\delta \tag{34}$$

for the small element δV is a continuous function of $\mathbf{r}$. This follows since the singular points for $\mathbf{r} \neq 0$ are distributed quite thickly, so that $\psi(\mathbf{r})$ changes infinitesimally for an infinitesimal change in $\mathbf{r}$. In practice, the analysis deals with the time-averaged value of $\psi(\mathbf{r},t)$, the continuous nature of this function being even more plausible.

The radial atomic density is now defined as

$$\begin{aligned} N\rho_a(r) &= \langle\psi(\mathbf{r},t)\rangle \\ &= \frac{1}{\delta V}\int_{\delta V}\left[\int \rho_a(\mathbf{r}')\rho_a(\mathbf{r}' + \mathbf{r} + \mathbf{r}_\delta)dv'\right]dv_\delta , \\ &\qquad |\mathbf{r}| > \text{one atomic diameter} . \end{aligned} \tag{35}$$

The singularity at the origin is isolated and defined as

$$\rho_a(0) = 1/\delta V , \quad \mathbf{r} = 0 , \tag{36}$$

where $\rho_a(0)$ exists only in a small δV about $r = 0$. Therefore, (33) can now be written

$$I(\mathbf{s}) = \int_V N[\rho_a(r) + \rho_a(0)]f^2(\mathbf{s})e^{i\mathbf{s}\cdot\mathbf{r}}dv , \tag{37}$$

or analogous to (6),

$$\frac{I(s)}{N} = \int_0^\infty 4\pi r^2[\rho_a(r) + \rho_a(0)]f^2(s)\,\frac{\sin sr}{sr}\,dr . \tag{38}$$

The atomic scattering intensity $f^2(s)$ may be factored out of the integral and the integration performed for the term in $\rho_a(0)$ to yield

$$\frac{I(s)}{Nf^2(s)} - 1 = \int_0^\infty 4\pi r^2 \rho_a(r) \frac{\sin sr}{sr}\, dr\,. \qquad (39)$$

Fourier transformation of this equation leads to the explicit expression for $\rho_a(r)$:

$$4\pi r^2 \rho_a(r) = \frac{2r}{\pi} \int_0^\infty s\left(\frac{I(s) - Nf^2(s)}{Nf^2(s)}\right) \sin srds\,. \quad (40)$$

The necessary adjustment for the exclusion of the inaccessible "zero scattering" is effected as previously:

$$4\pi r^2[\rho_a(r) - \bar{\rho}_a\alpha(r)] = \frac{2r}{\pi}\int_0^\infty s\left(\frac{I(s) - Nf^2(s) - f^2(s)I_o(s)/Z^2}{Nf^2(s)}\right) \times \sin srds\,. \quad (41)$$

With the same assumptions leading to (16), the preceding may be simplified to

$$4\pi r^2[\rho_a(r) - \bar{\rho}_a] = \frac{2r}{\pi}\int_0^\infty s\left(\frac{I(s) - Nf^2(s) - f^2(s)I_o(s)/Z^2}{Nf^2(s)}\right) \times \sin srds\,. \quad (42)$$

In this relation, the $f^2(s)$ in the numerator of the intensity term arises through the necessity for disposing of the density singularity at the origin. In (25), the same term arbitrarily was added in an attempt to strengthen the convergence of the transform. The reason for this distinction is the presence of $f^2(s)$ in the denominator of (40). This function causes the intensity kernel to tend toward a limit of unity with increasing s if the numerator term in $f^2(s)$ is absent. Such a situation would formally invalidate the integral transform.

The relationships derived above pertain to a system of N atoms of the same kind. No attempt is made here to present corresponding expressions for a system of different atoms. A weighted atomic density function was derived by both Filipovich (1955) and Warren, Krutter, and Morningstar (1936) for the case of a system composed of different types of atoms.

The treatment of this section has led to an expression for the radial atomic density function. In Appendix II this function is related to conventional distribution function $n^{(2)}(r_{12})$ used in liquid-state theory. Equation (41) can thus be restated:

$$n^{(2)}(r_{12}) = \bar{\rho}_a^2\alpha(r_{12}) + \frac{\rho_a}{2\pi^2 r_{12}} \times \int_0^\infty s\left(\frac{I(s) - Nf^2(s) - f^2(s)I_o(s)/Z^2}{Nf^2(s)}\right)\sin sr_{12}ds, \quad (43)$$

where the function $\alpha(r_{12})$ is unity for radii not approaching sample dimensions.

Manipulation of the Fourier integrals enables the electron density to be related to atomic density by a method presented in general form by Waser and Schomaker (1953). Equations (7), (24), and (40) can be rewritten as

$$r[\rho(r) - \rho_0(r)] = \frac{1}{2\pi^2}\int_0^\infty si(s)\frac{f^2(s)}{Z}\sin srds\,, \quad (44)$$

$$r\rho_a(r) = \frac{1}{2\pi^2}\int_0^\infty si(s)\sin srds\,, \quad (45)$$

where $i(s)$ has been introduced as follows:

$$i(s) = (I(s) - Nf^2(s))/Nf^2(s)\,. \quad (46)$$

Define, by means of the Fourier cosine integral, the function $T(r)$ as follows:

$$\frac{f^2(s)}{Z} = \int_0^\infty T(r)\cos srdr\,, \quad (47)$$

$$T(r) = \frac{2}{\pi}\int_0^\infty \frac{f^2(s)}{Z}\cos srds\,. \quad (48)$$

When (47) is inserted into (44) for the function $f^2(s)/Z$, one integration may be carried out to give

$$r[\rho(r) - \rho_0(r)] = \frac{1}{2}\int_{-\infty}^\infty (r - t)\rho_a(r - t)T(r)dt\,. \quad (49)$$

4. MOLECULAR DENSITY

For the sake of presenting a complete theoretical base for the use of x-ray diffraction in liquid structure studies, the pertinent equations are developed for the molecular radial density function for a system of identical molecules. The treatment is essentially that of Menke (1932).

By the use of (31), the intensity for an isolated molecule μ may be written

$$I_m(s) = \left|\sum_p^n f_p(\mathbf{s})e^{i\mathbf{s}\cdot\mathbf{v}_{\mu p}}\right|^2, \quad (50)$$

where $\mathbf{v}_{\mu p}$ is the vector from the molecular center to atom p, $f_p(\mathbf{s})$ is the atomic scattering factor for atom p, and n is the total number of atoms in the molecule. Considering an assembly of molecules, the total intensity becomes

$$I(\mathbf{s}) = \left| \sum_{\mu}^{N_m} \sum_{p}^{n} f_p(\mathbf{s}) e^{i\mathbf{s}\cdot\mathbf{r}_{\mu p}} \right|^2 , \qquad (51)$$

where $\mathbf{r}_{\mu p}$ is the vector from the origin to atom p in molecule μ. Equation (51) can be expanded to

$$I(\mathbf{s}) = \sum_{\mu}^{N_m} \sum_{\nu}^{N_m} \sum_{p}^{n} \sum_{q}^{n} f_p(\mathbf{s}) f_q(\mathbf{s}) e^{i\mathbf{s}\cdot(\mathbf{r}_{\mu p} - \mathbf{r}_{\nu q})} . \qquad (52)$$

Letting $\mathbf{r}_\mu$ be a vector to the center of molecule μ,

$$I(\mathbf{s}) = \sum_{\mu}^{N_m} \sum_{\nu}^{N_m} \sum_{p}^{n} \sum_{q}^{n} f_p(\mathbf{s}) f_q(\mathbf{s}) e^{i\mathbf{s}\cdot(\mathbf{r}_\mu - \mathbf{r}_\nu)} e^{i\mathbf{s}\cdot(\mathbf{v}_{\mu p} - \mathbf{v}_{\nu q})} . \qquad (53)$$

The molecular summations may be replaced by integrals through the use of a molecular density function, in a step similar to (32).

$$I(\mathbf{s}) = \int_V \int_V \sum_{p}^{n} \sum_{q}^{n} f_p(\mathbf{s}) f_q(\mathbf{s}) e^{i\mathbf{s}\cdot(\mathbf{v}_{\mu p} - \mathbf{v}_{\nu q})} \times e^{i\mathbf{s}\cdot\mathbf{R}} \rho_m(\mathbf{r}_\mu) \rho_m(\mathbf{r}_\mu + \mathbf{R}) dv_r dv_R , \qquad (54)$$

where $\mathbf{R} = \mathbf{r}_\mu - \mathbf{r}_\nu$.

By a treatment completely analogous to that for the atomic density case, there results the relation

$$I(\mathbf{s}) = \int_V \sum_{p}^{n} \sum_{q}^{n} f_p(\mathbf{s}) f_q(\mathbf{s}) e^{i\mathbf{s}\cdot(\mathbf{v}_{\mu p} - \mathbf{v}_{\nu q})} \times e^{i\mathbf{s}\cdot\mathbf{R}} [\rho_m(\mathbf{R}) + \rho_m(0)] dv_R . \qquad (55)$$

The above expression relates to one instantaneous spatial configuration of all the N_m molecules. Because of the configurational dependence of the nondensity term in the integrand, it must be spatially averaged to account for the equal probability of all molecular orientations.

Integrating the $\rho_m(0)$ term,

$$\frac{I(\mathbf{s})}{N_m} - \sum_{p}^{n} \sum_{q}^{n} f_p(\mathbf{s}) f_q(\mathbf{s}) e^{i\mathbf{s}\cdot(\mathbf{v}_{\mu p} - \mathbf{v}_{\nu q})} = \int_V \sum_{p}^{n} \sum_{q}^{n} f_p(\mathbf{s}) f_q(\mathbf{s}) e^{i\mathbf{s}\cdot(\mathbf{v}_{\mu p} - \mathbf{v}_{\nu q})} e^{i\mathbf{s}\cdot\mathbf{R}} \rho_m(\mathbf{R}) dv_R . \qquad (56)$$

The summed term on the left-hand side of (56) is just the scattered intensity for an isolated molecule

$$I_m(s) = \sum_{p}^{n} \sum_{q}^{n} f_p(s) f_q(s) \sin \frac{sK_{pq}}{sK_{pq}} , \qquad (57)$$

where $K_{pg} = |\mathbf{v}_{\mu p} - \mathbf{v}_{\mu q}|$. The function

$$\sum_{p}^{n} \sum_{q}^{n} f_p(\mathbf{s}) f_q(\mathbf{s}) e^{i\mathbf{s}\cdot(\mathbf{v}_{\mu p} - \mathbf{v}_{\nu q})}$$

in the integral is independent of $\mathbf{R}$ and may be removed from the integrand. In fact, $\mathbf{v}_{\mu p}$ and $\mathbf{v}_{\nu q}$ are not related and the corresponding exponential terms must be separately averaged. Applying the definition

$$F(s) = \sum_{p}^{n} \sum_{q}^{n} f_p(s) f_q(s) \frac{\sin sl_p}{sl_p} \frac{\sin sl_q}{sl_q} , \qquad (58)$$

where l_p is the distance from the molecular center to atom p, (56) is written

$$\frac{I(s)}{N_m} - I_m(s) = F(s) \int_0^\infty 4\pi R^2 \rho_m(R) \frac{\sin sR}{sR} dR . \qquad (59)$$

Once again invoking the Fourier integral,

$$4\pi R^2 \rho_m(R) = \frac{2R}{\pi} \int_0^\infty s \left(\frac{I(s) - N_m I_m(s)}{N_m F(s)} \right) \sin sRds . \qquad (60)$$

The adjustment for "zero scattering" gives

$$4\pi R^2 [\rho_m(R) - \bar{\rho}_m \alpha(R)] = \frac{2R}{\pi} \times \int_0^\infty s \left(\frac{I(s) - N_m I_m(s) - F(s) I_o(s) / (\sum_p n_p Z_p)^2}{N_m F(s)} \right) \times \sin sRds . \qquad (61)$$

This may be expressed in terms of the pair-distribution function (see Appendix II)

$$n^{(2)}(R_{12}) = \bar{\rho}_m^2 \alpha(R_{12}) + \frac{\rho_m}{2\pi^2 R_{12}} \times \int_0^\infty s \left(\frac{I(s) - N_m I_m(s) - F(s) I_o(s) / (\sum_p n_p Z_p)^2}{N_m F(s)} \right) \times \sin sR_{12} ds . \qquad (62)$$

The above analysis is such that the choice for the molecular center influences the form of the molecular density function. This is apparent from (59), where the function $F(s)$ is dependent upon the molecular coordinate system, but the average intensity must quite obviously be invariant. Furthermore, the origin of the molecular coordinate system must be at an atomic center so that $F(s)$ will not exhibit a zero which would invalidate the transform of (60). The molecular density apparently cannot be simply related to the atomic density or to the electronic density due to gross differences in the intensity kernels.

5. NORMALIZATION AND ERROR ANALYSIS

The analysis of the preceding paragraphs has all been based on intensities expressed in absolute units. These are seldom if ever actually measured directly, the usual procedure being to determine a total experimental intensity $I_t^E(s)$, which is in units that are relatively consistent, but are arbitrary. It is necessary to normalize such data before using it in the formulas for the distribution functions. It is convenient to consider a function $[I_t(s) - I_o(s)]^E$ which is constructed from $I_t(s)^E$ by merely extrapolating the latter function to zero at the origin of s. This observed intensity consists of the coherent plus the incoherent scattering. One thus requires a normalization constant c, such that

$$[I(s) - I_o(s) + NI_{\text{inc}}(s)] = c[I_t(s) - I_o(s)]^E, \quad (63)$$

where $I_{\text{inc}}(s)$ is the incoherent scattering per atom. Allusion was made in a prior section to the fact that frequently in the past normalization was effected by fitting the experimental data to the independent atomic scattering $f^2(s)$ at large values of s

$$\lim_{\text{large } s}\{c[I_t(s) - I_o(s)]\} = \lim_{\text{large } s}\{N[f^2(s) + I_{\text{inc}}(s)]\} . \quad (64)$$

This procedure is subject to error since the scaling constant is rather arbitrarily chosen to center the diminishing oscillations of $I(s)$ about $f^2(s)$. The uncertainty is aggravated because for a given expected error in intensity measurement, the relative error in $I(s)$ is greater by nearly an order of magnitude in the large s region than in the neighborhood of prominent structural features. Thus, an error in normalization is magnified at intensity maxima.

Another criterion for normalization suggested by Krough-Moe (1956), Norman (1957), Vainshtein (1957), and Mendel (1962) is obtained from a form of (25) applicable for r approaching zero. When suitable limiting values are inserted, the expression becomes

$$-2\pi^2\bar{\rho} = \int_0^\infty s^2\left(\frac{I(s) - I_o(s) - Nf^2(s)}{NZ}\right) ds . \quad (65)$$

Upon substituting (63) into this integral, the following relation is obtained for the normalization constant:

$$\frac{c}{NZ} = \frac{\dfrac{1}{Z}\displaystyle\int_0^\infty s^2[f^2(s) + I_{\text{inc}}(s)]ds - 2\pi^2\bar{\rho}}{\displaystyle\int_0^\infty s^2[I_t(s) - I_o(s)]^E ds} . \quad (66)$$

Strictly, the expression is true only when the infinite limit is used in the integrals. However, for a reasonable range of data, c is found to be relatively insensitive to s_o, the upper limit in s. The older normalization criterion of (64) may still be used as a check for consistency.

In general, exact normalization is not achieved and it becomes important to examine the nature of the error from inversion of such data. Consider then the result of using not the correct value of c, but instead $(1 + \epsilon)c$ where ϵ will represent the error. The function involved in the Fourier integral for the electronic case is then:

$$\{(1 + \epsilon)c[I_t(s) - I_o(s)]^E - NI_{\text{inc}}(s) - Nf^2(s)\}(NZ)^{-1} . \quad (67)$$

When this is inserted in (25), the result is:

$$[\rho(r) - \bar{\rho}\alpha(r) - \rho_o(r)]_e = (1 + \epsilon) \times [\rho(r) - \bar{\rho}\alpha(r) - \rho_o(r)] + \frac{\epsilon}{2\pi^2 r} \times \int_0^\infty s\left(\frac{f^2(s) + I_{\text{inc}}(s)}{Z}\right)\sin srds , \quad (68)$$

where the term on the left-hand side is the erroneous value. For the electronic density, normalization error thus leads to a linear perturbation plus a small correction that has the general properties of the transform of the independent scattering plus incoherent intensity.

A corresponding treatment applied to the atomic-density function leads to an analogous equation

$$[\rho_a(r) - \bar{\rho}_a\alpha(r)]_e = (1 + \epsilon)[\rho_a(r) - \bar{\rho}_a\alpha(r)] + \frac{\epsilon}{2\pi^2 r}\int_0^\infty s\left(\frac{f^2(s) + I_{\text{inc}}(s)}{f^2(s)}\right)\sin srds . \quad (69)$$

Thus, for the atomic density, normalization error leads to a linear perturbation plus a correction proportional to the transform of the ratio of the total to the coherent atomic scattering. Because of the particularly involved nature of the molecular density intensity kernel, the normalization error for this case is not presented.

The most important type of error is the "diffraction error" resulting from the truncation of the formal infinite integral of the Fourier transform. Denoting the spurious functions with primed symbols and drawing upon the excellent presentation of Waser and Schomaker (1953), the relations connecting accessible and true functions may be written

$$r[\rho'(r) - \rho_o'(r)] = \frac{1}{\pi}\int_{-\infty}^{\infty}\mu[\rho(\mu) - \rho_o(\mu)]\frac{\sin(r - \mu)s_o}{(r - \mu)}d\mu \quad (70)$$

and

$$r\rho_a'(r) = \frac{1}{\pi}\int_{-\infty}^{\infty}\mu\rho_a(\mu)\frac{\sin(r - \mu)s_o}{(r - \mu)}d\mu . \quad (71)$$

These equations relate the approximate density functions to the true values by means of a convolution with the function ($\sin x/x$). This procedure corresponds to a unit weighting of the measured intensity for arguments zero to s_o in the variable s.

In general, any convenient even-weighting function may be used, the convolution being carried out with the cosine transform of this function.

The effect of the convolutions in (70) and (71) may be assessed by assuming that in the neighborhood of a maximum in $r\rho(r)$ at r_1 this function is given by

$$r\rho(r) = \delta(r - r_1) \,. \tag{72}$$

Then,

$$\begin{aligned} r\rho'(r) &= \frac{1}{\pi}\int_{-\infty}^{\infty} \delta(\mu - r_1)\,\frac{\sin\,(r-\mu)s_o}{(r-\mu)}\,d\mu \\ &= [\sin\,(r - r_1)s_o]/\pi(r - r_1) \,. \end{aligned} \tag{73}$$

The spurious function $r\rho'(r)$ will exhibit a broadened maximum at r_1 of height s_o/π, minima at $r_1 \pm 4.50/s_o$ of height $-0.22\ s_o/\pi$, maxima at $r_1 \pm 7.72/s_o$ of height $0.135\ s_o/\pi$, and so on. Such development of subsidiary features to a density maximum has resulted in much confusion in the theoretical interpretation of past diffraction work, as discussed by Kanda and Sugarawa (1951). Pings and Paalman (1962) have recently commented on the problems of identification of true details of structure in the presence of these spurious ripples arising from transform errors. As suggested by Waser and Schomaker (1953), there is sometimes an advantage to modifying the experimental intensity data with a weighting function of the form exp $(-as^2)$. The resulting convolution involves a similar exponential in r^2, which decreases monatomically, but causes 30% more broadening of the involved peak.

Another general type of error is caused by an erroneous matching of intensity data from experiments involving different x-ray energies. The most serious effect is an amplification of the error at the main intensity peak. This leads in general to a wedge-shaped error, centered at the main peak position in s. A similar difficulty may also be forthcoming from improper correction for absorption in the sample. An elementary understanding of the phenomenon may be gained by characterizing the error at s_ϵ by $\delta(s - s_\epsilon)$. The transform of this function is proportional to $\sin s_\epsilon r$. This leads to a rough method for locating the position of an intensity error causing a ripple in the density function, since $s_\epsilon \approx 2\pi/_{\Delta r}$, where Δr is the ripple period.

Bastiansen and Finbak (1944) treated this problem more elegantly for a simplified hard-sphere system. Their results showed that for a positive error at the intensity peak, spurious maxima will occur at 0.26 r', 1.83 r', and 2.67 r', where r' is the main-peak location in the density function. Similarly, for a negative error at the intensity peak, spurious maxima will occur at 0.60 r', 1.43 r', and 2.23 r'. Obviously, this quantitative description does not exactly describe a system departing from the hypothesized one, but departure should not seriously change the qualitative picture.

In summary, the interpretation of experimental diffraction data is beset with the problem of identifying the aberrations caused by truncating the formal infinite Fourier integral. This difficulty is compounded by the obscuring of systematic errors in the transform integral. The general result of these spurious effects is to superpose oscillations upon the desired density function and to broaden its structural features. Several methods have been described to identify the presence of false information, although correction of the difficulties generally requires, at best, a reprocessing of the data. It may indeed be necessary to repeat experimental work with an emphasis suggested by the error analysis. As a minimum requirement for judging the veracity of an experimental result, the atomic density must essentially equal zero for all radii less than an atomic diameter and both the atomic and electronic densities must be limited to nonnegative values.

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APPENDIX I. DERIVATION OF THE BASIC DIFFRACTION EQUATION (James 1954)

The phenomenon of diffraction results from interference effects among wave trains originating from various points in a medium. The description of such interference involves quantitative evaluation of the phase differences resulting from variation of path length between wavelets. Consider an incident wave specified geometrically by the unit vector $\mathbf{s}_o$, and the scattered wave traveling in the direction $\mathbf{s}$. This wave is scattered from the origin and from the point P, which is located at a vector $\mathbf{r}$ from the origin (see Fig. 1). Erecting perpendiculars to $\mathbf{s}_o$ and $\mathbf{s}_1$ at O and P, it is evident that the difference in path length for waves scattered by these points is just $\mathbf{r}\cdot\mathbf{s}_1 - \mathbf{r}\cdot\mathbf{s}_o$.

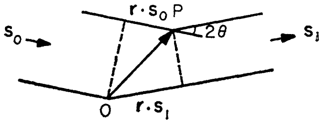

FIG. 1. Scattering geometry.

The corresponding phase angle in terms of the wavelength λ is

$$(2\pi/\lambda)\mathbf{r}\cdot(\mathbf{s}_1 - \mathbf{s}_o). \tag{74}$$

If for a given set of geometrical parameters the displacement of a wave scattered from O is $A_o e^{i\omega t}$, then the displacement of the wave from P is just

$$A_o e^{i\omega t + i(2\pi/\lambda)\mathbf{r}\cdot(\mathbf{s}_1 - \mathbf{s}_o)}\,.$$

The resultant displacement for a system of points is

$$A_o e^{i\omega t} \textstyle\sum_j e^{i(2\pi/\lambda)\mathbf{r}_j\cdot(\mathbf{s}_1 - \mathbf{s}_o)}\,.$$

This may be expressed for a continuum in terms of the scattering point density, where the resultant displacement becomes

$$A_o e^{i\omega t} \int_V \rho(\mathbf{r}) e^{i(2\pi/\lambda)\mathbf{r}\cdot(\mathbf{s}_1 - \mathbf{s}_o)} dv\,. \tag{75}$$

The corresponding intensity may be written

$$A_o^2 \left| \int_V \rho(\mathbf{r}) e^{i(2\pi/\lambda)\mathbf{r}\cdot(\mathbf{s}_1 - \mathbf{s}_o)} dv \right|^2, \tag{76}$$

or stated as the intensity relative to that of an isolated scattering point

$$\left| \int_V \rho(\mathbf{r}) e^{i(2\pi/\lambda)\mathbf{r}\cdot(\mathbf{s}_1 - \mathbf{s}_o)} dv \right|^2. \tag{77}$$

APPENDIX II. THE RELATIONSHIP BETWEEN RADIAL DENSITY AND PAIR DISTRIBUTION

(Hill 1956)

The probability that a particular molecule is in $d\mathbf{r}$ at $\mathbf{r}_1$ while any molecule is in $d\mathbf{r}_2$ at $\mathbf{r}_2$ may be written

$$(N-1)P^{(2)}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 = (1/N)n^{(2)}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2\,. \tag{78}$$

since $N - 1$ choices exist for occupancy of $d\mathbf{r}_2$. This relation implies that the probability that a particular molecule is fixed at $\mathbf{r}_1$ while any second molecule is in $d\mathbf{r}_2$ at $\mathbf{r}_2$ is proportional to $n^{(2)}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_2$. Integrating this expression over the volume of the system V to determine the proportionality constant,

$$\text{const} \times \int_V n^{(2)}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_2 = N - 1\,, \tag{79}$$

the summed probabilities for the total number of molecular pairs considered.

But the recurrence relation

$$\int n^{(h+1)}(\mathbf{r}_1,\cdots\mathbf{r}_{h+1})d\mathbf{r}_{n+1} = (N-h)n^{(h)}(\mathbf{r}_1\cdots\mathbf{r}_n) \tag{80}$$

gives, upon integration,

$$\iint n^{(2)}(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 = (N-1)\int n^{(1)}(\mathbf{r}_1)d\mathbf{r}_1 = N(N-1)\,. \tag{81}$$

For an isotropic fluid, $n^2(\mathbf{r}_1,\mathbf{r}_2)$ can only be a function of $|\mathbf{r}_1 - \mathbf{r}_2|$, which may be expressed by writing $n^2(r_{12})$. Thus,

$$\iint n^{(2)}(r_{12})d\mathbf{r}_1 d\mathbf{r}_2 = V\int n^{(2)}(r_{12})d\mathbf{r}_2\,. \tag{82}$$

Combining (81) and (82),

$$\frac{V}{N}\int n^{(2)}(r_{12})d\mathbf{r}_2 = (N-1)\,. \tag{83}$$

Thus, the constant in (79) is just V/N or $1/\bar{\rho}_m$.

Observing that the right-hand side of (79) or (83) is essentially equal to the total number of molecules in the volume, V, the function $n^{(2)}(\mathbf{r}_1,\mathbf{r}_2)/\bar{\rho}_m$ or $n^{(2)}(r_{12})/\bar{\rho}_m$, expresses the radial density. Therefore, the number of molecules between r and $r + dr$ from a specified molecule is

$$4\pi r^2[n^{(2)}(r_{12})/\bar{\rho}_m]dr\,.$$

Since x-ray diffraction intensity measurements comprise the time-averaged data for an assemblage, Fourier inversion of the intensity function gives access to the average number of molecules in a spherical shell about an average molecule.

APPENDIX III. NOTATION

c	Normalization constant
dv_i	Differential volume element about the point defined by $\mathbf{r}_i$
$f(s)$	Atomic scattering factor
$F(s)$	Interaction term between atoms from different molecules
$i(s)$	Intensity kernel for the Fourier transform
$I(s)$	Theoretical intensity of diffracted coherent radiation
$I_{\text{inc}}(s)$	Incoherent intensity from an independent atom
$I_m(s)$	Scattered intensity for an isolated molecule
$I_o(s)$	"Zero-scattering" intensity
$I_t(s)^E$	Total intensity of radiation observed experimentally
$I^*(s)$	Unknown function of intensity
K_{pq}	$\lvert\mathbf{v}_{\mu p} - \mathbf{v}_{\nu q}\rvert$
l_p	Distance from molecular center to atom
N	Number of atoms in system
N_m	Number of molecules in system
n	Pair-distribution function
n_p	Number of p atoms in a molecule
r	Radial argument of electronic or atomic density, Å
r_{12}	Distance between atoms 1 and 2
$\mathbf{r}_i$	Position vector of ith particle
R	Radial argument of molecular density, Å
R_{12}	Distance between molecules 1 and 2
$\mathbf{R}$	Vector between molecular centers
R_o	Radius of spherical sample

s	Scattering angle parameter, $(4\pi/\lambda)\sin\theta$, Å^{-1}
s_ϵ	Location of erroneous intensity feature, Å^{-1}
s_o	Upper limit for s in truncated Fourier integral transform, A^{-1}
t	Dummy variable; time
$T(r)$	Fourier cosine transform of $f^2(s)$
V	Volume
$\mathbf{v}_{\mu p}$	Vector from center of molecule $_\mu$ to atom p
Z, Z_p	Atomic number
$\alpha(r)$	Geometrical factor for "zero scattering"
$\delta(\mathbf{r} - \mathbf{r}_i)$	Delta function
δV	Finite increment of volume
Δr	Ripple of density error, Å
Δs	Increment in s, Å^{-1}
$\Delta\rho(r)$	Density fluctuation about $\bar{\rho}$
θ	Half-angle of diffraction
λ	Radiation wavelength, Å
$\rho(r)$	Electron density, electrons / Å^3
$\bar{\rho}$	Average electron density
$\rho'(r)$	Value of density from truncated Fourier transform
$\rho_o(r)$	Electron density within one isolated atom
$\rho_a(r)$	Atomic density
$\rho_m(r)$	Molecular density
ϕ	Angular coordinate
ω	Frequency
ϵ	Error in normalization constant

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