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NITROGEN, OXYGEN, AND THEIR MIXTURES

Dissertation
Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

by
Horace Wataru Furumoto, B.S.

*****
The Ohio State University
1963

Approved by

[Signature]
Adviser
Department of Physics
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I. INTRODUCTION

The first person to notice x-ray diffraction patterns in liquids was Friedrich (1); Debye (2) later showed that a regular crystalline array was not necessary in order to give diffraction effects. Debye and Scherrer's (3) intra-atomic scattering theory, Keesom and De Smedt's (4) intermolecular interference model, and Smoluchowski (5) and Einstein's (6) density fluctuations in a continuous medium theory were proposed to explain the diffraction patterns. Stewart (7) claimed that the size and shape of the atoms contributed to local orientation associated with the dense packing in a liquid.

Progress in organizing the concepts on a logical basis was made by Debye (8,9), who suggested the utility of the probability distribution function. Following this line, Zernike and Prins (10) created several hypothetical distribution functions and calculated the intensity patterns expected from these distribution functions. These functions were mainly hard sphere distribution functions. More important, however, was their suggestion that the inverse was also possible. The calculation of the
distribution function was possible through the use of the Fourier integral theorem on the known intensity function. Debye and Menke (11) were the first to use this concept to derive the radial distribution curve.

Gingrich's (12) comprehensive review of the liquid elements covers work in the field up to that time quite thoroughly. Warren, Krutter, and Morningstar (13) extended the theory to non-crystalline materials containing more than one element.

Prins and Prins (14) have all but given up trying to glean more information about asymmetry of the scattering centers from x-ray diffraction patterns of liquids; they consider optical scattering experiments promising. In trying to distinguish the effects of the shape of the atoms or molecules in a liquid, the best distribution function they could derive was the rather simple one in which elongated scattering centers are either aligned or not aligned with respect to a reference scattering center. Following this historical introduction to the investigation of x-ray diffraction by non-crystalline substances, the study of liquid structure by means of x-ray diffraction will be considered.

Liquids produce x-ray diffraction patterns from a time averaged distribution of scatterers; whatever distribution function the pattern reveals is not a function of
time. The analysis of liquid diffraction patterns will give an over-all distribution function which is correlated to some theoretical distribution function. The simplest distribution function conceivable, other than the macroscopic mean density, is the distribution function resulting from two body interaction and is called the pair distribution or pair correlation function, \( g^{(2)}(12) \), between elements 1 and 2. The notation follows Hill (15). Higher order interactions can be approximated by a superposition of pair distribution functions. For example, the three body correlation function, \( g^{(3)}(123) \), can be approximated by a set of pair distribution functions,

\[
g^{(3)}(123) = g^{(2)}(12)g^{(2)}(13)g^{(2)}(23). \tag{1.1}
\]

In principle, x-ray data can be used to calculate the equation of state by means of the pair distribution function and the superposition approximation. However, in practice the limitations are:

1) Extremely accurate experimental measurements are required.

2) Measurements over a wide range of temperature and density are needed.

3) Atomic scattering factors must be known accurately.

4) Interference effects by different types of atoms both bound and unbound must be understood.
The first limitation is imposed by time considerations. Quantum detectors can give accurate measurements; an accuracy of 1%, i.e., a fractional standard deviation per point of 0.01, can be obtained by taking over 10,000 counts per point. A minimum counting rate expected from a liquid diffraction experiment runs about 100 counts/minute; therefore, 1% accuracy per point is not unreasonable. With a higher intensity x-ray source, the accuracy of the over-all curve can be improved by taking more data at the portions of the diffraction curve which are weighted more heavily during the Fourier inversion process. The Fourier inversion process produces the radial distribution function from the x-ray diffraction curve. Unfortunately, for x rays the portion of the experimental curve weighted most heavily in the Fourier inversion has the lowest counting rate.

Measurements over a wide range of temperature and density have been made for argon (16, 17), xenon (18), krypton (19), and neon (20). Henshaw (17) and Clayton and Heaton (19) used neutrons while the others (16, 18, 20) used x rays. The argon study (16) has been extremely useful in correlating theoretical distribution functions to the experimentally obtained distribution functions (15, 21). There is a close similarity in the distribution functions of neon, krypton, and argon when the functions are plotted in reduced variables (22).
James and Brindley (38) compiled the first useful table of coherent and incoherent scattering factors. In the last decade renewed interest (23-37) in atomic scattering factors has produced improved values for both the coherent and incoherent scattering factors. Freeman's (30-37) works are the most comprehensive and include most of the coherent and incoherent scattering factors for the lighter elements. Freeman used the latest Hartree-Fock self consistent field wave functions in his calculations. These wave functions include exchange terms which enable the last term, the exchange term, of the equation (39)

\[ I_{\text{inc}} = \sum_{k} \left( 1 - |f_k|^2 \right) - \sum_{j \neq k} |f_j|^2 \]  

(1.2)
to be calculated. \( I_{\text{inc}} \) is the incoherent scattered intensity from a free atom while \( f_k \) is the scattering factor for the \( k \)th electron in the atom. The exchange term appears only when two electrons associated with the wave functions have the same spin.

James and Brindley (38) used wave functions that did not include exchange effects. The neglect of exchange effects not only affects the values of the atomic scattering factors, through the exchange term \( \sum \sum |f_{jk}|^2 \) of equation (1.2), but also affects any value of \( f \) used in both the coherent and incoherent atomic scattering factor calculations. Freeman used antisymmetrized wave functions (29, 31); his values for the scattering factors differ from those
of James and Brindley. Freeman also considers the effect of aspherical charge distributions in his calculations.

For the elements with high atomic numbers, \( Z \geq 25 \), Thomas Fermi wave functions can be used to calculate the atomic scattering factors. Thomas and Umeda (28) have tabulated data for the elements in this region.

The problems associated with limitation four have been considered by Warren, Krutter, and Morningstar (13). For samples containing more than one element they use the approximation of an average scattering factor per electron. This is a good approximation if the constituent elements do not differ greatly in atomic number. This process is readily applicable only to samples of fixed concentration as determined by molecular structure, in other words, the method of Warren, Krutter, and Morningstar is not applicable to mixtures.

Finbak (40, 41) and Mendel (42) derive electronic distribution functions to describe the electronic configuration of non-crystalline substances. The approximation of an average electron scattering factor is not necessary, nor is the method limited by the restriction of a fixed concentration as determined by the molecules in the samples. However, the distribution so derived is an electronic distribution and, therefore, lacks the resolution of a distribution of atomic centers.
With the four limitations in mind, the present study of nitrogen and oxygen liquids was begun. Experiments were conducted on the pure liquids at two different temperatures and on mixtures of the liquids of three different compositions at a single temperature. The data on the pure liquids were compared with the data from an earlier work by Gingrich (12), who used x rays, and with the data of Henshaw (43, 44), who used neutrons. The temperatures at which the present experiments were conducted differed from those of the earlier experiments, but comparisons could be made by interpolation.

The presence of $O_4$ molecules in liquid oxygen has been suggested by the measurement of the magnetic susceptibility of liquid oxygen (45, 46). Henshaw's neutron diffraction data on liquid oxygen (44) is ambiguous on this point, but a concentration of up to 25% $O_4$ at 62 degrees K is suggested from his data. A more precise determination should clarify this point. Knaap, Knoester, and Beenakker (47) have measured directly the volume contraction resulting from the mixing of nitrogen and oxygen liquids. The contraction is in the order of a few tenths of a per cent. X-ray diffraction analysis does not directly yield macroscopic densities of liquids; however, some information may be gained about the nearest neighbor configuration when unlike molecules are present.
The equipment and techniques which make up the bulk of this study and which are necessary to give precise data are described in Chapter III. Finally, the computer program which was used to process and analyze the data is reproduced in Appendix D.
II. X-RAY DIFFRACTION ANALYSIS OF LIQUIDS

2.1 The Atomic and Electronic Radial Distribution Functions

A summary of the derivation of the atomic radial distribution function is given by Gingrich (12). He derives the x-ray intensity scattered by an aggregate of scattering centers as,

\[ I_{\text{eu}}(s) = \sum_{m} \sum_{n} f_m f_n \sin(s r_{mn}) / s r_{mn}. \]  \hspace{1cm} (2.1)

\( I_{\text{eu}}(s) \) = the scattered intensity in electron units
\( N \) = the number of atoms in the sample volume
\( f_m, f_n \) = the atomic scattering factors for the \( m^{th} \) atom and the \( n^{th} \) atom respectively
\( r_{mn} \) = the distance between atom \( m \) and atom \( n \)
\( s = 4 \pi \sin \theta / \lambda \), where \( \lambda \) is the wavelength of the scattered radiation and \( \theta \) is half the scattering angle \( \varnothing \).

The double summation is over all the atoms in the scattering volume. The \( N \) terms where \( m = n \) can be taken outside the summation since \( r_{mn} = 0 \) and \( \sin(r_{mn}s) / r_{mn}s = 1 \). If the sample is composed of a single element, \( f \) can be taken outside the summation to give

\[ I_{\text{eu}}(s) = N f^2 (1 + \sum \sin(s r_{nm}) / s r_{nm}) \]  \hspace{1cm} (2.2)
where the prime denotes exclusion of intra-atomic scattering. To be useful the sum must be converted to an integral. The density of distributed atoms will be called $\rho(r)$.

Gingrich converts the sum to an integral to give

$$I_{eu}(s) = Nf^2(1 + \int_0^\infty 4\pi r^2 \frac{(\rho(r) - \rho_o)\sin sr}{sr} dr)$$

$$\quad + Nf^2 \int_0^\infty 4\pi r^2 \rho_o \sin sr \frac{dr}{sr}$$

(2.3)

where $r$ is a radial distance and $\rho_o$ is the mean atomic density. This procedure is not valid for the second term on the right is not validly derived. Gingrich ignores this term by assuming it to be small, but when the term is evaluated, it is not small compared to the other terms in the equation. Klug and Alexander (48) also follow Gingrich's example. James (49) derives this term properly, and when this term is evaluated, it is, indeed, small compared to the other terms in equation (2.3).

The equation (2.3) can then be Fourier inverted to give the equation defining the atomic radial distribution function,

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_o + \frac{2r}{\pi} i(s) \sin rs ds$$

(2.4)

Now, $i(s) = (I_{eu}(s)/Nf^2 - 1)$.

Another type of distribution function that may prove to be useful is the electronic distribution function.

Finbak (40, 41) and later Mendel (42) have derived the electronic distribution function. The electronic
distribution function $\sigma(r)$ is defined by the equation,

$$\sigma(r) = \int \int \int \delta(p + r) \rho(p) \rho'(p + r) dA dV \quad (2.5)$$

where $\int dA$ is the integration with respect to the components of $r$ over the surface of the spherical shell $(r)$ with origin at $p$. $\int dV$ is the volume integral of the whole scattering volume over the components of $p$. $\rho'(p)$ is the electron density at $p$ and $\rho'(p + r)$ is the electron density at $(p + r)$. The derivation (40, 41, 42) of the electronic distribution function from x-ray diffraction data is analogous to the derivation of equation (2.3). The scattered intensity is divided into two groups: the scattered intensity from intra-atomic electrons and the scattered intensity from interatomic electrons. The Fourier inversion of the scattered intensity is

$$G(r) = 4\pi r^2 \rho^2 \bar{z}^2 + \int (2r/\pi) s i'(s) sin rs ds \quad (2.6)$$

where,

$$i'(s) = (I_{eu}(s) - f^2) = i(s)f^2$$

and where $\bar{z}$ is the mean charge per atom. The only essential difference between (2.6) and (2.3) is the factor $f^2$ modifying $I_{eu}(s)$ in $i(s)$ in equation (2.4).

Otvos and Mendel (50) have derived a third type of distribution which is called the intermolecular electron distribution function. This distribution function describes the distribution of electrons belonging to molecules
other than the reference molecule. In other words, this distribution is the electron density distribution for intermolecular vectors only. The intermolecular electron distribution function has the same form as equation (2.6) except that the intramolecular scattering is subtracted from $i'(s)$. Therefore, the intermolecular electron distribution function $\mathcal{O}_L(r)$ is,

$$\mathcal{O}_L(r) = 4\pi r^2 \left( c^2 + (2r/\pi) \int i''(s) \sin rs \, ds \right)$$

(2.7)

where,

$$i''(s) = i'(s) - \sum_{m,n} f_m f_n (\sin r_{mn}s)/r_{mn}s.$$  

The double sum is over all the pairs of different atoms in the molecule and $r_{mn}$ is the bond distance between the atoms.

The computation of the radial distribution functions from the diffraction patterns requires the use of the Fourier integral theorem (51). The Fourier integral theorem is valid when the limits of integration are minus to plus infinity and in the special case here, where $1(s) = 0$ for $s < 0$, from zero to infinity. The independent variable for the Fourier inversion process is $s = 4\pi \sin \theta / \lambda$ where $2\theta$ is the scattering angle. Since $\lambda$, the wavelength of the radiation used, is never zero, the upper limit $s_m$ of the Fourier integral is always finite. The finite termination introduces undesirable effects called truncation effects in the inverted curve. Waser and
Shomaker (52) investigated these effects and suggest using the transform of the modification function $g(s)$ which modifies the observed intensity to correct for the truncation effects. The modification function is defined in the following manner,

$$
g(s) = \begin{cases} 
1 & 0 \leq s \leq s_m \\
0 & s_m < s
\end{cases}
$$

The transform is multiplied to some hypothetical "true" distribution function that is similar to the experimental distribution function but has the objectionable effects removed. If the product of the hypothetical curve and the transform of the modification function agrees with the experimental distribution curve, then the hypothetical curve can be assumed to be the true distribution curve. In reality, the process is rather involved for a large number of integrals must be evaluated numerically. Waser and Shomaker (52) give proofs of the validity of their method for different types of modification functions. Stirpe and Thompson (2) have applied this method in their study of neon, and they give a description of the use of the step function as a modification function.

Klug and Alexander (53) can be consulted for a comprehensive list of errors that can be expected from the Fourier inversion process. Finbak (41) describes the source of spurious peaks in the radial distribution
function at $0.3 \leq r \leq 1.0$ angstroms, the effect of poor normalization, and the effect of a sharp peak in the intensity curve. Sugawara (54) claims ghost peaks flanking real peaks at small $r$ values are caused by a finite limit of integration.

2.2 Small Angle Scattering

If $D(r_{nm})$ is the probability that an atom $n$ will be in an element of volume $dV_n$ at $r_n$ when atom $m$ is in an element of volume $dV_m$ at $r_m$, then Hill (55) shows that the number fluctuation $(N^2 - \bar{N})$ in the volume $V$ is,

$$(N/V)^2 \iint D(r_{nm})dV_n dV_m = \bar{N}^2 - \bar{N} \quad (2.8)$$

where $\bar{N}$ is the mean number of particles in $V$, therefore, $\bar{N}/V$ is the mean density $\rho_0$. For independent particles equation (2.8) reduces to,

$$(\bar{N}/V)^2 \iint D(r_n)D(r_m)dV_n dV_m = \bar{N}^2 \quad (2.9)$$

Hill (56) shows that the isothermal compressibility $\chi$ and the temperature $T$ are related to the number fluctuation by,

$$
(N - \bar{N})^2 = (\bar{N}/V)/kT \chi \quad (2.10)
$$

where $k$ is the Boltzmann constant. The difference of equations (2.8) and (2.9) divided by $\bar{N}$ is,

$$
(\bar{N}/V^2) \iint (D(r_{nm}) - D(r_n)D(r_m))dV_n dV_m
= (\bar{N}^2 - \bar{N})/\bar{N} - 1
= (\bar{N}/V)kT \chi - 1 \quad (2.11)
$$
$D(r_n) = D(r_m)$ is the probability of finding any atom in volume $dV_n$ or $dV_m$ and $D(r_{nm})$ is the probability of finding an atom $m$ in $dV_m$ when an atom in is in $dV_n$, therefore,

$$\int (N/V^2)D(r_m)D(r_n)dV_m = \bar{N}/V = \bar{\rho}$$

(2.12)

and,

$$\int (\bar{N}/V^2)D(r_{nm})dV_m = \rho(r)$$

(2.13)

$\rho(r)$ is the atomic radial distribution function of section 2.1. Equation (2.11) becomes,

$$(\bar{N}/V)kT \chi = 1 + \int (\rho(r) - \bar{\rho})4\pi r^2dr$$

The second term of equation (2.3) is negligible so the liquid structure factor $L(s)$ is,

$$L(s) = I_{eu}(s)/N r^2 = 1 + \int 4\pi r^2(\rho(r) - \bar{\rho})\sin sr dr$$

(2.14)

In the limit $s = 0$, $\sin sr/sr = 1$, therefore,

$$L(0) \approx 1 + \int 4\pi r^2(\rho(r) - \bar{\rho})dr$$

$$= (N/V)kT \chi$$

(2.15)

There is a direct relation between the liquid structure factor and the isothermal compressibility at zero scattering angle. Therefore, the intensity at small angles which cannot be observed by the detector because of interference from the main beam can be extrapolated to a value proportional to the isothermal compressibility. This is a good first approximation for small angle scattering. Fournet (57) mentions other factors that must be considered especially when the sample is close to the critical point.
Equation (2.14) ignores the term contributed by all the scatterers acting as a unit. Indeed, a simple calculation shows that the ignored term is appreciable only when \( s < 0.2^\circ \) for liquids. However, for \( s \) smaller than this value, the contribution from the ignored term rises sharply (58). Since the ignored term is reintroduced into the radial distribution function through the term \( 4\pi r^2 \rho_0 \), equation (2.4), small angle observation should exclude the region where there is contribution from all the scatterers acting as a unit.

2.3 Distribution Functions and the Structure of Liquids

The analysis of x-ray diffraction patterns does not lead directly to any one model of fluids such as the lattice, hole, or free volume theory. Recent investigators, Rowlinson (59) and Hildebrand and Scott (60), prefer the view that liquids exhibit "maximum randomness." Hill (61) using statistical mechanical principles derives various types of distribution functions one of which corresponds to the atomic radial distribution function used in x-ray diffraction analysis.

Hill lets \( \rho_1 (r_1) \) be the probability that one of the molecules of the system will be found in the element of volume \( dV_1 \) at \( r_1 \). For a crystal \( \rho_1 (r_1) \) is a periodic function of \( r_1 \) with sharp maxima at lattice points, but in
a fluid all points \( x_1 \) inside of \( V \) are equivalent, therefore, for a fluid,

\[
\frac{1}{V} \int (\rho^{(1)}(x_1) \text{d}V_1 = \rho^{(1)} = \frac{\mathcal{N}}{V} = \rho_0
\]

where \( \rho_0 \) is the macroscopic density.

\( \rho^{(2)}(x_1, x_2) \text{d}V_1 \text{d}V_2 \) is the probability that one molecule of the system will be found in \( \text{d}V_1 \) at \( x_1 \) and another in \( \text{d}V_2 \) at \( x_2 \) if the configuration of the system is observed. In a crystal \( \rho^{(2)} \) depends, in general, on both \( x_1 \) and \( x_2 \) even if \( |x_{12}| = |x_1 - x_2| \) is very large. In a fluid \( \rho^{(2)} \) can depend only on \( x_{12} \). For fluids,

\[
\rho^{(2)}(x_1, x_2) = \rho^{(2)}(x_{12})
\]

and,

\[
\int \int \rho^{(2)}(x_{12}) \text{d}V_1 \text{d}V_2 = V \int \rho^{(2)}(x_{12}) \text{d}V = \mathcal{N}(\mathcal{N}-1)
\]

Similarly, higher order distribution functions can be built. The distribution functions above can be separated into two components, the product of an independent distribution and a correlation function. Therefore,

\[
\rho^{(n)}(x_1, x_2, \ldots, x_n) = \rho^{(1)}(x_1) \rho^{(1)}(x_2) \ldots
\]

\[
\rho^{(1)}(x_n) g^{(n)}(x_1, x_2, \ldots, x_n)
\]

The correlation function is \( g^{(n)} \). There are several ways of describing the correlation function; the above is a description by Kirkwood (62, 63). For a fluid \( \rho^{(1)} \) is not a function of the individual coordinates \( x_j \), therefore,
The normalization condition is,
\[ \langle n \rangle(r_1, \ldots, r_n) = \rho^n g^n(r_1, \ldots, r_n) \]  
(2.20)
Finally, the pair correlation function \( g(2) \) that is of interest in the discussion of x-ray diffraction analysis has the properties,
\[ g(2)(r_1, r_2) = g(2)(r_{12}) \]  
(2.22)
\[ (1/V) \int g(2)(r_{12})dV = 1 - 1/N \]  
(2.23)
In a fluid, the \( g(2) \) in equation (2.23) is identical to the radial distribution function \( C(r_{12}) \) described in section 2.1 aside from a multiplicative constant \( N/V \).

Examination of distribution functions aids in solving some of the problems involving intermolecular forces. Before beginning a discussion on intermolecular forces necessary basic assumptions must be considered. They are (1) the assumption that the potentials are additive, i.e., the total potential energy of the assembly of molecules can be written as the sum of pair potentials between all of the \( N(N-1)/2 \) possible pairs, and (2) that these pair potentials can be in turn separated into attractive and repulsive terms.

The positive or repulsive term arises from the overlap of the electron clouds of the two molecules. The
exact form of this term is not known, but theoretical considerations give it the form \( F(r) \exp(-Br) \), where \( F(r) \) is a polynomial and \( B \) a positive parameter. For simplicity in calculations this potential form is usually replaced by the exponential alone or by an inverse power function \( r^{-n} \), where \( n \) is an integer. The exact form of the repulsive term is not too critical, especially at low temperatures, where overlap of the molecules is not appreciable.

One of the more useful potentials used to describe the properties of fluids is the Lennard-Jones potential \( (64) \). This potential has a bi-reciprocal relation,

\[
 u(r) = \lambda r^{-n} - \gamma r^{-m} \quad n > m
\]

(2.24)

where \( \lambda \) and \( \gamma \) are parameters characteristic of the interaction, and \( n \) and \( m \) are assumed to be the same for all chemical species. The choice of \( 6 \) for \( m \) is justified by a consideration of London forces \( (65) \), but the choice of \( n \) is quite arbitrary. Predictions of experimental results using this potential are not critically dependent on the choice of \( n \) as long as it is in the region of 10 to 14. The conventional choice of 12 is admittedly based on the fact that it is twice 6. Two convenient ways of writing the Lennard-Jones potential \( u(r) \) are,

\[
 u(r) = 4 \varepsilon \left( \sigma^2/r^6 \right) - \left( \sigma^2/r^6 \right) \quad (2.25)
\]

\[
 u(r) = \varepsilon \left( \sigma^{*2}/r^6 \right) - \left( \sigma^{*2}/r^6 \right) \quad (2.26)
\]

where \( \sigma \) is the collision diameter or intermolecular
distance of closest approach without overlap, $r^*$ is the equilibrium separation of a pair of molecules or the position of the potential minimum, and $\epsilon$ is the maximum depth of the potential, see Figure 1. If a 12-6 potential is assumed, the relation between $\sigma$ and $r^*$ is,

$$\sigma = r^*/2^6 = 0.8909 \, r^*$$

This potential, though simple, is suitable for all inert gases and for the simpler non-polar molecules like nitrogen, oxygen, and methane.

For pure liquids the parameters $\lambda$, $v$, and $n$ in equation (2.24) can be evaluated by assuming the Lennard-Jones potential is a good approximation of the intermolecular potential. The total energy can then be computed,

$$E = \sum \frac{N}{4} \pi \rho^2 r^2 g(r)u(r)dr$$

$$= (N/2) \rho^2 \sum \frac{4}{4} \pi r^2 g(r)u(r)dr$$  \hspace{1cm} (2.27)

where $g(r)$ is the pair correlation function and the sum is over the pairs of molecules. Setting $E = -\Delta E^v$, the energy of vaporization, and using the Lennard-Jones potential for $u(r)$, one obtains for the heat of vaporization per mole the equation

$$-(\Delta E^v/N) = 2\pi \int (\lambda g(r)/r^{n-2} - \nu g(r)/r^4)dr$$

$$= 2\pi (\lambda \int (r)/r^{n-2} - \nu \int (r)/r^4)dr$$  \hspace{1cm} (2.28)

By finding the values of $-(\Delta E^v/N)$ from published data, and by calculating $\rho(T)$ from experimental data at
Fig. 1 Lennard-Jones Pair Potential
several temperatures, the parameters $\lambda$, $J$, and $n$ can be found by evaluating a set of simultaneous equations.

In examining the parameters mentioned in (2.25) for the case of mixtures, questions arise as to how these parameters for the mixtures are related to those for pure liquids. By examining how the London forces are modified by a mixture of two species, one can justify the use of the geometric mean of $\xi_{11}$ and $\xi_{22}$ for $\xi_{12}$. The theoretical relations between $\sigma_{12}$ and $\sigma_{11}$ and $\sigma_{22}$ is unknown. However, from empirical evidence the parameter $\sigma_{12}$ can be assumed to be the hard sphere distance of closest approach. Therefore,

$$\xi_{12} = \sqrt{\xi_{11} \xi_{22}}$$

(2.29)

$$\sigma_{12} = \frac{1}{2} (\sigma_{11} + \sigma_{22})$$

(2.30)

The parameter $\xi$ cannot be directly obtained from the atomic radial distribution function. The parameter $\sigma^-$ can be obtained from the atomic radial distribution function by assuming $\sigma^-$ corresponds to the point where the atomic radial distribution function begins to rise rapidly from a negligible value to give the first nearest neighbor shell. However, the leading edge of the first nearest neighbor shell is smeared by the finite limits of the Fourier integral. Clayton and Heaton (18) in their study on liquid krypton give a graphic example of how $\sigma^-$, the leading edge of the first neighbor shell and $r^*$, the
maximum of the first neighbor shell, depend on the finite upper limit of integration, $s_m$.

The Lennard-Jones potential is a two body potential. A potential of mean force which takes into account the presence of all the other molecules in the liquid has been described by Kirkwood (66). For dilute samples such as gases the relation between the radial distribution function and the potential of mean force $\phi(r)$ is,

$$\hat{c}(r) = \hat{c}_0 \exp\left(-\frac{\phi(r)}{kT}\right)$$

(2.31)

Stirpe and Thompson (20) have calculated the potential of mean force using equation (2.31). If equation (2.31) is differentiated with respect to $r$, the maximum of the first shell of $\hat{c}(r)$ should coincide with the minimum of the potential $\phi(r)$. For liquids the maximum of $\hat{c}(r)$ is temperature dependent, while $\phi(r)$ is not a function of temperature. Therefore, it is doubtful whether equation (2.31) is meaningful for liquids.
III. EXPERIMENTAL EQUIPMENT AND PROCESSES

3.1 The Cryostat and Spectrometer

The cryostat, the spectrometer, and the associated gas and liquid handling apparatus were designed, built, and used earlier by the x-ray laboratory of this department for diffraction studies on liquid helium. The cryostat and spectrometer are well described in W. Gordon's (67) dissertation. Figure 2 shows a cross sectional view of the cryostat. The liquid air chamber was in thermal contact with the copper skirt extending below it; the skirt acted as a radiation shield for the coolant chamber. The space between the outer walls and the radiation shield as well as the space between the radiation shield and the coolant chamber were kept at a pressure of 6 to 8 x 10^{-7} mm of Hg. The coolant chamber was filled with liquid nitrogen. The vapor pressure of the liquid nitrogen in the coolant chamber was kept at 73 ± 1 cm of Hg for the series of experiments at 77 degrees K and approximately 10 cm for those at 64 degrees K. The temperature was kept within ±0.15 degrees K by controlling the vapor pressure of the coolant. A radiation shield at the coolant chamber temperature surrounded the beryllium sample tube which
Fig. 2 Cryostat Cross Section
was 25.4 mm long and 2.92 mm in radius. The radiation entered and exited through windows 1 through 7, Figure 2. The windows were made of beryllium foil.

The spectrometer was mounted directly below the cryostat with the axis of the cylindrical sample tube coinciding with the spectrometer axis, Figure 3. Slits 1 and 2 defined the entrance beam, while slits 3 and 4 defined the scattered beam. Slit widths were 0.50 mm. The divergences of the entrance and of the exit beams are shown in Figure 4. Gordon (67) computes a lateral resolving power of one half degree (one third degree maximum crossfire for each pair of slits). The spectrometer has not been readjusted since the liquid helium experiments, therefore, this value of one half degree can be accepted as the lateral resolving power for the present series of experiments.

The detector drive train for the spectrometer was modified so that the detector could be driven automatically by a programmed device. Figure 5, lower center, shows the detector servomotor, while Figure 6 shows clearly the electrical counter that translated the position of the detector into electrical signals which the programmer used. Figure 5 shows an open box with the Ross filter device which, however, was not used for the present series of experiments. Instead of the filter a LiF crystal was used as a monochromator; the crystal can be seen on the axis of the spindle, left
Fig. 3
LIQUID DIFFRACTION SPECTROMETER
Central Ray Tracing
Fig. 4 X-Ray Beam Width Relative to Sample Tube Size
Fig. 5 Spectrometer Photograph, a.
Fig. 6 Spectrometer Photograph, b.
Figure 6. Figure 7 shows the cryostat and the spectrometer.

The x-ray tube used was a commercial Machlett A2 line focus tube with a molybdenum target. X-ray intensities from this tube monitored under constant x-ray tube voltage and current showed a slow downward drift in intensity. This drift in one direction can be explained by gradual tube contamination.

The LiF crystal monochromator was set approximately 2 3/4" from the window of the x-ray tube. The spectrometer scale reading of the Bragg angle was 10.1 degrees.

The scintillation detector used a NaI(Tl) crystal of dimensions 1.5 x 0.5 x 12 mm. When the pulse height analyzer was set to accept 98% of the Mo Kα radiation, the background was 0.9 counts/min.

3.2 Electronics

The X-Ray Power Supply. The voltage regulator adequately met the preset specification of 0.1% drift per twelve hours. In the construction (68) of the regulator the design of Jermotz and Pepinsky (69) was used. The drift in voltage as monitored through a 10^5 to 1 voltage divider was never greater than 5 parts in 10,000 during a twelve hour period. Any drift greater than this figure indicated worn reference batteries. Standard performance could again be maintained when the worn batteries were replaced.
Fig. 7 Spectrometer and Cryostat Photograph.
Current regulation proved to be troublesome and barely met the 0.1% criterion. The current regulating element for this feedback system was the emission limited x-ray tube filament. The current through the x-ray tube was controlled by regulating the temperature of the filament. The thermal inertia of the 15 watt filament together with the stray and built in capacitances gave the system a resonance frequency in the region of 2 to 5 cycles. Since m-derived filters at these frequencies require bulky inductors, a three stage RC pi network was designed to cut gain for the frequencies higher than 2 cycles to prevent the system from oscillating. The pi filter was also used to minimize the 60 cycle pickup produced by the grounding system of the unregulated power supply. The x-ray power supply chassis is isolated from the ac power ground but unshielded from 60 cycle pickup. The 10 volt dc error signal for the current regulator has a 5 volt peak to peak 60 cycle component in it. The filter placed at the input of the servoamplifier provides about 80 db of 60 cycle rejection.

Figure 8 is a schematic for the current regulator. The circuit is a standard balanced dc amplifier using an 0G3/85A2 tube as a reference. The output tubes were 6L6GC tubes acting in the triode mode. These tubes acted as 60 cycle push-pull impedance tubes. The impedances of these tubes are controlled by the amplified error signal. The
impedance tubes are in series (through an isolation transformer) with the filament of the x-ray tube and an unregulated current source. This current source heats the x-ray tube filament to produce x-ray tube current. The x-ray tube current is detected and compared to a set reference by the servoamplifier. If there is a difference, an error signal is produced, amplified, and sent to the grids of the output tubes resulting in a change of impedance of these tubes in a direction which minimizes the error signal.

The voltage and current monitored continuously showed no proportional relation between electrical power input and x-ray intensity for small changes. This can be explained by the large amount of 60 cycle and other noise in the sampled voltages. After filtering, the error signal showed little resemblance to the sampled signal. Waveform affects the average value of the signal. Gross changes in the order of 1% in electrical power input to the tube could be detected in the x-ray intensity, but 0.1% changes were not reflected accurately. Accordingly, little emphasis was placed on the electrical power input as a measure of good intensity regulation, and more care was taken to monitor the x-ray beam by direct recording of its intensity.

The Detection Assembly. The detection system was composed of a photomultiplier which detected the light pulses from a crystal scintillator, a White cathode
follower preamp, a linear amplifier, a pulse height analyzer, and a scaler.

The photomultiplier, EMI 9542S, was a conventional fourteen stage in line tube with a one inch circular photosensitive surface. Linearity of response versus counting rate showed a deviation of 1% at 4000 counts per second. This mediocre linearity response can be attributed to the low dynode string current which was about 40 microamperes. The photomultiplier was run with a negative ground, and since the amplifier accepted only positive pulses, the signal was picked from the second to the last dynode and ground.

The preamp was a standard White cathode follower which used a 5965 tube; the main purpose of the preamp was impedance matching. The amplifier which had a double delay line pulse shaping circuit was designed by G. G. Kelley of Oak Ridge National Laboratory and was manufactured by Hamner Electronics Company. The pulse height analyzer included in the main chassis of the amplifier used the regular Fairstein and Porter circuit. In the present experiments the pulse height analyzer was set to accept 98 percent of the crystal monochromatized radiation.

A one megacycle counter-timer, Computer Measurement Corp. Model 226B, recorded the detected pulses that came through the pulse height analyzer. A preset time of 100
seconds was employed for most of the work, and in a few cases where the intensities were low, 1000 second intervals were used. Stop pulses from this unit triggered the control circuits in the automatic programmer.

The high voltage for the photomultiplier was provided by a John Fluke Co. Model 405 power supply of conventional design. The selected output voltage was 1320 volts; the plate voltage of the photomultiplier was 1030 volts.

With the exception of temperature effects the components of the detecting chain operated satisfactorily. There was no compensation for the effects of rapid temperature changes. A recalibration made approximately every three weeks corrected for seasonal temperature changes and for other causes of drift as, for example, the aging of the components. The best estimate of the drift, as reflected in a change of amplification, is a 0.1% change in amplification between calibration checks. Shifts in amplification were compensated by changing the amplifier gain rather than the voltage to the photomultiplier.

3.3 The Programmer

In a simple diffraction experiment using monochromatic radiation there are two independent variables: the scattering angle and the recording time. The programming system must store the predetermined assembly of variables in a memory and reproduce the assembly when it is called for.
An asynchronous system capable of storing 100 pieces of angular information and 20 pieces of recording time information is required. For this limited capacity a patch panel memory is sufficient.

Stepper switches were chosen for the transfer functions, because the compactness, the serial/parallel feature, and the simplicity of stepper switches far outweighed their unattractiveness as electromechanical devices.

The function of the programmer can be divided into two subfunctions corresponding to the control of the program's two independent variables. The first subfunction is to move the detector to a preset angle which is stored in the patch panel memory, and the second subfunction is to record the intensity at this angle in periods of 100 seconds until a preset number of counting cycles is completed. The programmer should then seek the next preset angle and repeat the process and so on until all of the stored variables are sampled. After each count cycle is completed, the totalized counts must be recorded on a recording device.

The angle seeking subassembly was an analog servo system; a schematic of the circuit is shown in Figure 9. The detector was coupled to an angle recording device which was a Veeder-Root counter with electrical contacts similar to a ten position rotary switch. Each position corresponded to a decimal digit. There were three switches in one
Fig. 9 Servo Amplifier Schematic
counter hooked in series mechanically by ten-to-one gear trains. Each switch corresponded to a decade. The smallest increment of the counter was one tenth of a revolution which corresponded to approximately a tenth of a degree in the scattering angle.

A voltage divider string was hooked to the ten position switches to give a staircase reference, each position on the switch corresponding to a step on the staircase. Since the decades were sampled serially, all three switches could be tied to the same divider string.

There were three stepper switches controlling the transfer functions. The main program stepper sampled the columns on the patch panel, the decade stepper serially sampled analog voltages on the angle indicator, and the count cycle stepper totalized the number of count cycles completed in one column on the patch panel. The program patch panel contained $3^4$ columns of stored information. The program stepper switch sampled one column at a time, the command to go to the next column coming when all the functions in a column were completed.

The following is a description of a typical sequence of events. The program stepper samples a command line on the patch panel. The patch panel is wired to give three reference voltages corresponding to the digits desired in the three decade positions: tens, units, and tenths of
degrees. The decade stepper samples one of the voltages beginning with the most significant decade. This stepper also samples the voltage coming from the angle recorder. The voltages from the two sources are compared by a servo-amplifier which drives a motor if there is a difference in signal levels. The motor drives the detector and the angle recorder in the proper direction to minimize the error. When the error signal reaches zero, the decade stepper steps to the next most significant decade and repeats the process. The stepping process is accomplished by the activation of a thyatron which energizes the decade stepper when a null signal is received from the servo-amplifier. When all three decades are satisfactorily sampled, the servoamplifier input is shorted and command control is turned over to the counting system.

The counter-timer was a scaler inhibited from starting during the servo cycle by application of a large negative bias to the gate control grid of a gating tube in the start circuit of the scaler. The conventional way of inhibiting start is to inhibit reset, but the above method was chosen because it was necessary to place a blank space between information from different angle blocks when the parallel printer was used. There was no way of placing angular identification on the record when using this printer. The blank was put in during the servo cycle by
a print command. In order to get a blank using the printer, all the decimal counting units must be reading zero, that is it must be reset. Therefore, the inhibit reset could not be used to inhibit start.

The scaler had its own time base from 1 microsecond to 1000 seconds in steps of factors of ten. Once the appropriate time period was chosen, the scaler totaled the counts coming through the window of the analyzer during this time period. The stop pulse at the end of the counting period initiated the following sequence of events. The stop pulse commands the printer to print the number of counts registered by the scaler, signals the filter reversing mechanism to change the filter (if a Ross filter system is used), and fires a thyratron that activates a relay which in turn advances the count cycle stepper by one position on every alternate pulse of the thyratron.

One count cycle was defined as a pair of recordings, a record through each filter of the Ross filter system. When the crystal monochrometer was used, the filter reversal system was disabled, however, one count cycle was still defined as a pair of recordings.

The count cycle stepper acted as a tally box and recorded the number of count cycles completed. After the predetermined number of count cycles was completed, the following steps were initiated. The program stepper steps
to the next line, the decade stepper is reset to be in position to start a new servo cycle, and the count cycle stepper is reset to zero again. All thirty-four control lines on the patch panel functioned in the manner described above. Instructions for wiring the patch panel are given in Appendix C. Figures 10 and 11 are schematics of the programming system.

The programmer worked satisfactorily after details such as the appropriate level of the error signal to give reliable nulling were straightened out. Another critical area that required attention was the proper amount of electrical damping needed in the most sensitive decade controlled by the servoamplifier. The programmer is completely interlocked so the misuse of the push buttons or switches on the control panel cannot cause trouble by jamming or "burning out" the components. The only place where such trouble can occur is in the wiring of the patch panel since there are two types of voltages present; a low level dc voltage and a 110 ac voltage. The board is divided into two sections, a distinct line running between them, one section using the low level dc voltage the other using the 110 ac voltage. As long as there are no wires crossing the boundary line, there will be no damage. Any two points within one section may be connected with a wire without damage, but the desired results can be produced only by proper wiring.
Fig. 10 Programmer Control Panel Schematic
Fig. 11 Programmer Patch Panel Schematic
One problem was never satisfactorily solved: the variation in contact resistance in the stepper switches. At the 110 ac voltage level encountered in the control circuits, the contact resistance variation caused no problems, but it was a continual source of trouble in the low dc voltage circuits. This trouble originated from dust and dirt particles getting between the stator points and the wiper arm. It was found to be more beneficial to clean these points with CCl$_4$ and to lubricate them with Dow Corning 3 Compound than to follow the manufacturer's instructions on cleaning and lubrication. Whereas a cleaning and lubrication were required every three weeks when the manufacturer's instructions were followed, the same service was only necessary every two months when CCl$_4$ and Dow Corning 3 Compound were used.

3.4 The Data Recording System

The outputs of the scaler and the angle encoder were recorded on 1" perforated tape. The punching of the tape was done either by a Friden Motorized Tape Punch or by a Friden SFD Flexewriter. The Flexewriter punched as well as typed the recorded data. It was necessary to convert the parallel output of the scaler and the angle encoder into serial form in order to use the tape system. A Dymec Model 2540 Coupler performed the converting function. A subunit containing a diode matrix was necessary to convert
the decimal code of the angle encoder into binary code acceptable to the coupler. A similar unit performed the same function for the Ross filter identification. Each tape record contained the following information: four digits of angular identification, a tab, a digit for filter identification, a tab, six digits of intensity information, and finally, a carriage return or end of record mark.

3.5 The Reduction of Bulk Data

Two symbolic programs were developed by Philip Myers of our X-Ray Laboratory to totalize and average the recorded data with an IBM 1620 computer.

Description of the Tape Run Program. The data tape is read by the IBM 1620 computer. Only "good" tape records are accepted. "Good" tape records are those which fit a specific format determined by an input data card. The format agrees with the tape format of the coupler-punch units of the recording system. For the tape record to be acceptable each tab, information, and end of record mark must be numeric, in the proper position, and of the right length.

Since there are two types of records, filter and crystal monochromatized data, there is a provision for either type of information. An input information card selects the proper method of handling the data. In the crystal monochromator mode all intensity records at a particular angle are summed and averaged. In the filter
monochromator mode the records through filter A are summed separately from those through filter B, and the difference between the totals through A and B is averaged. In both cases the program does the averaging after completing the reading of an angle block of information. The end of a block after which a card is punched is denoted by a change in angle in the next tape record. The punched card contains the following information: the scattering angle, the total counts through filter A, the total counts through filter B (this column is zero in the crystal monochromator mode), the difference of the totals through A and B, the number of count cycles, the average number of counts per cycle, a card identification number, and finally, a run identification.

Description of the Intensity Normalization Program.

The output of the tape run program is sorted according to angle. There may be many cards with the same angular identification. This sorting does not destroy the chronological order in a particular block of records recorded at the same angle. During the experiment the x-ray intensity is monitored at a specific check angle every two hours or so. Therefore, there will be a large number of cards with the check angle identification. The check angle intensity is usually high (around 20,000 per count cycle); therefore, by scanning this group of data one can detect any change in intensity. The chronological positions of the intensity
changes are noted, and the check angle intensities between positions of change are averaged to compute the magnitudes of the changes. The cards can now be resorted back to their original chronological order by means of the card identification numbers. Since the chronological positions of intensity changes are known, the cards, which are now in chronological order, can be divided into groups of constant intensity. These groups are identified with a normalization identification number. The first run through the computer called Normalization Pass One (NP1) punches a new card for every input card; the output card contains the same information as the input card with the addition of a normalization identification number.

The output of NP1 is now sorted according to angle order. A table of normalization values corresponding to the proper normalization ID number is stored in the computer. Normalization Pass Two (NP2) takes a card record in a given angle block, multiplies it by its proper normalization number, and totalizes the intensities in the angle block. When the last record of the angle block is reached, the total is divided by the sum of count cycles to give an average intensity per angular setting. The output of NP2 will contain one card of information per observed angle. A typical experiment will have 125 cards corresponding to records at 125 different angles. This output card has the
following data: the angle, the unnormalized sum of A counts, the unnormalized sum of B counts (zero for the crystal system), the difference of the sums of A and B counts, the total number of count cycles, the normalized average intensity, normalization pass ID number, card ID number, and finally, run ID number.

**Exception.** The spectrometer slit system had to be changed for small scattering angles, i.e., scattering angles less than five degrees, to assure measurement of the proper portion of the diffracted intensity cone (70). The use of shorter slits for these small angles was required; the intensities were later normalized to the regular slit intensities. However, since the normalization factors also multiplied the background, the background had to be subtracted before the multiplication. Since the diffraction analysis program subtracts the normal background from the data at each angle, it was necessary to add back the normal background to the small angle corrected data. The final correction to the data at these small angles as the cards came from NP2 was,

\[ C = I_{ss} - B(R/r - 1) \]

where,

- \( C \) = correction
- \( I_{ss} \) = short slit intensity
- \( B \) = background
R = tall slit over short slit ratio
r = tall slit time period over short slit time period ratio.
IV. PREPARATION OF THE DATA FOR FOURIER INVERSION

The corrections necessary in order that the intensity curve can be analyzed by Fourier inversion to yield the radial distribution function are,

1) Subtraction of the normal background.
2) Subtraction of the contribution of the scattering from the sample container.
3) Correction for transmission effects.
4) Scattering volume correction.
5) Spectrometer scale correction.
6) Polarization correction.
7) Normalization to absolute units.

All of the above corrections are made in the liquid diffraction analysis program discussed in Appendix D: An exact step by step examination of the correction procedure can be made since the program is written in Fortran.

4.1 Background Correction

The background correction is straightforward. The normally occurring background was monitored at regular intervals. The small volume of the scintillating crystal (0.5 mm thick, 1.5 mm wide, 12 mm long) was responsible for
the low background of 0.90 counts per minute when the pulse height analyzer was set to accept 98% of the Mo Kα radiation. The background was scaled to the proper time interval and subtracted from the total intensity at each angle.

5.2 Corrections for Container Scattering

The correction for the scattering from the beryllium walls of the container is more difficult to make. Calculations show that the walls should enter into the scattering volume for scattering angles less than 17 degrees. This is more or less justified by experiment. The scattering from the empty container was measured after each run, while the transmission of the sample was measured during a sample fill or sample removal. The contribution of the scattering from the walls to the total intensity during a run can be said to be equal to the scattering from the empty container times the transmission through the sample. Assuming that the scattering volume is centered at the center of the container (see section 3.1) and considering only first order effects, one can say that any ray scattered by the walls, whether it is the wall toward the source of x rays or toward the detector, has to traverse one full length through the sample. Therefore, the probability of a ray which is scattered by the walls getting through to the detector is just the transmission through the sample.
The scattering from the empty container changed with time. This has also been noticed in the earlier experiments on helium, Figure 12. The scattering from the container is small compared to the sample intensity for both oxygen and nitrogen. The change in wall scattering causes small variations in the final results, but these errors are within the one per cent standard.

4.3 Transmission Correction

On simple ray tracing diagrams the transmission through the sample can be considered constant in all directions except in the backward direction. In the backward direction the optical path through the sample is not necessarily one diameter. Closer examination by Sawada and Shaw (71), who took into consideration beam widths and divergences, resulted in little change to this approximation except in the widening of the so-called backward direction. This effect is a strong function of $b/r$, beam width to radius ratio. In the present case $b/r$ is in the order of 0.10, small enough to make transmission constant up to 160 degrees scattering angle.

Correction for absolute transmission is not necessary since all such factors are absorbed in the normalization to absolute electron units, a process described in section 7 of this chapter.

4.4 Scattering Volume Correction

The correction most difficult to justify is the
Beryllium Scattering

--- Gordon Curve A

\[ \triangle \triangle \triangle \text{Gordon Curve B (1954)} \]

\[ \times \times \times \text{Spring 1962} \]

\[ \circ \circ \circ \text{Present} \]

(No absolute intensity relationship between curves.)
correction for the size of the scattering volume. If the container were perfectly cylindrical and could be centered exactly over the axis of the spectrometer, and if the divergences of the incident and scattered x-ray beams could be exactly measured, then a theoretical scattering volume correction could be calculated. Gordon (72) has shown that if the divergences of the beams are neglected, the scattering volume is proportional to $lw_1w_2/sin\phi$, where $\phi$ is the scattering angle for angles greater than 17 degrees, $l$ is slit height, and $w_1$ and $w_2$ the incident and scattered beam widths respectively. Figure 13 shows that the two beams pivot about 0, and when the beams intersect at right angles, the cross sectional area common to both beams is $w_1w_2$. This area increases by a factor $1/sin\phi$ as $\phi$ decreases from 90 degrees to 0 degrees. However, the volume reaches a finite limit as a result of the cut off by the container wall.

The area outside the container when the container begins to cut off the rapidly increasing area $lw_1w_2/sin\phi$ can be calculated to be (72),

$$2(x^2tan\phi + x(w_2 - w_1)/2 + (w_2 - w_1)^2/tan\phi)$$

The symbols are defined in Figure 13. The first term is the area of an isosceles triangle outside the container formed by the intersecting beams of equal widths, and the two other terms are the contributions outside the container.
Cross-section of Excess Scattering Volume. (Not to scale.)

Fig. 13
resulting from the difference in beam widths.

Scattering from the empty container shows an anomalous bump around 6 degrees, see Figure 12. This bump moves after each alignment of the container and, therefore, is an indication of a shift in container position.

The volume correction factor, in consequence, must be experimentally determined. To do this a sample with a known scattering curve is placed in the container, and the scattering pattern of the sample is recorded. Any deviation from the known scattering pattern can be attributed to volume effects.

The inert gases are ideal substances for this experiment, because they show no interatomic structural effects and their scattering factors are available. Argon gas was chosen for this experiment.

It became apparent after investigation that the latest methods for calculation of the scattering factors must be used. The argon scattering factors of James and Brindley (38) differ as much as 10% from those of Berghuis et al. (25) at small values of $\sin \theta / \lambda$. Berghuis et al. included exchange effects in their calculations; these calculations were the only coherent scattering factors available for argon at this time.

Since incoherent scattering factors for argon including exchange effects were not available, the average of the
incoherent scattering factors of K\(^+\) and Cl\(^-\) as calculated by Freeman (34) were used. This averaging is not unreasonable, and for comparison a similar calculation was tried for neon since its incoherent scattering factors were known. Using the average of the incoherent factors of Na\(^+\) and F\(^-\), one finds the discrepancy to be in the order of one per cent for the published points.

Theoretical scattering factors are published at intervals of 0.1 in \(\sin \theta/\lambda\). These intervals are too coarse for direct comparison of the experimental curve to the theoretical curve except at the given points. Therefore, a fifth power polynomial was fitted to the theoretical points to fill in the intervals so that a comparison could be made.

The experimentally determined correction gave an almost exact fit to the theoretical correction for angles larger than the beryllium cut off angles, that is, the correction curve did not deviate by more than a few per cent from \(1/\sin \theta\). Inside of 20 degrees scattering angle the observed intensity is lower than it should be if the theoretical volume correction were to hold exactly. A comparison of volume corrections at three different times is given in Figure 14, a disassembly and a reassembly of the cryostat were made between these measurements. It is interesting to note the change in volume correction and
Volume Correction

- sin ϕ
- Geometrical correction
- Gordon's data (1954)
- X-X-Spring (1962) Cu K
- ○○ Present MoK

Fig. 14
the corresponding change in beryllium scattering, Figure 12. The volume correction factors were computed and normalized to the unit volume at $\phi = 90$ degrees.

4.5 Scale Correction

The electrical counter, which is connected to the spectrometer is coupled to the spectrometer by a gear train which does not rotate the counter exactly one revolution for 0.1 degree change in the detector position. The error is small but corresponds to an error of 0.4 degrees at the scattering angle of 90 degrees if the zeros coincide. In practice, the counter zero and the spectrometer scale zero are off by 0.016 degrees. The total correction is,

$$\phi_s = 0.99595\phi_c - 0.016$$

$\phi_s$ = spectrometer scale scattering angle  
$\phi_c$ = angle as read by the electrical counter

4.6 Polarization Correction

The polarization corrections is $(1 + \cos^2\phi_x\cos^2\phi)$ where $\phi_x$ is the scattering angle for the crystal monochromator and is a constant, while $\phi$ is the scattering angle of the sample. For filter monochromatization $\cos^2\phi_x$ is unity.

4.7 Normalization to Absolute Units

Finally, it is necessary to have an absolute scale of units. The most convenient unit in liquid diffraction work is the electron unit which is defined as the scattered
intensity from a free electron, the Thomson electron. The process of normalizing to electron units is an involved one and is discussed in the following paragraphs.

There are several ways to normalize the data to absolute units.

1) Direct graphical fitting of the observed curve to a theoretical curve (73).

2) Finding the intensity ratio between a gaseous sample and a liquid sample at a given angle and solving two simultaneous intensity equations for two unknowns (74).

3) Fourier inverting the intensity curve with an approximate normalization constant and by a process of iteration, minimizing the difference between successive normalization trials until there is a negligible difference between the trial constants (75).

4) Fourier inverting the unnormalized intensity data at a unique radial distance on the radial distribution curve and comparing the result to a known theoretical value. This unique distance is \( r = 0 \).

The fourth method which was used in the present work will be discussed. This method was originally set forth independently by Norman (76) and Krogh-Moe (77). Mendel
(42) used this method on the determination of order phenomena in liquids and amorphous solids. The procedure as outlined by Mendel is followed here. The observed intensity can be subdivided into,

$$I_t(s) = I_{coh}(s) + I_{inc}(s) + I_m(s) + I_{fl}(s)$$ \hspace{1cm} (4.1)

$I_t$ is the total scattered intensity.

$I_{coh}$ is the coherent scattering.

$I_{inc}$ is the incoherent scattering.

$I_m$ is the interatomic scattering.

$I_{fl}$ is the fluorescence radiation.

$I_{coh} + I_{inc} = I_{ind}$ is the total independent scattering.

The fluorescence contribution can be neglected because of the low $Z$ of the samples and the relatively high energy for which the pulse height analyzer of the detector is set. Fluorescence radiation from the slit material can enter the window of the analyzer, but the intensity after diffraction by the sample is so low that induced fluorescence from the slits is negligible.

Let $I_e$ be the corrected but unnormalized experimental intensity. Then

$$I_t(s) = \alpha N I_e(s)$$ \hspace{1cm} (4.2)

where $\alpha$ is the normalization constant per atom, and $N$ is the number of atoms in the sample volume. The structure sensitive part, $I_m$, of the intensity curve is
\[ I_m(s) = I_t(s) - NI_{\text{ind}}(s). \]  \hspace{1cm} (4.3)

The small angle contribution to the scattered intensity is very large, but this contribution dies out in the order of minutes away from the main beam (58), and hence, is never seen without interference from the main beam itself. This forward direction scattering is the contribution from the whole irradiated sample acting as one particle of uniform charge density, \(NZ/V\). The forward scattering \(I_o\) can be calculated

\[ I_o(s) = \int \frac{4\pi r^2(NZ/V)^2V\sin sr}{sr} dr \]  \hspace{1cm} (4.4)

and this value must be subtracted from \(I_t(s)\). Therefore, equation (4.2) must be slightly modified,

\[ I_t(s) = \alpha N I_e(s) + I_o(s) \]  \hspace{1cm} (4.5)

If there are \(N\) scattering centers, the structure sensitive intensity \(I_m\), equation (4.3), will be,

\[ I_m(s) = I_t(s) - NI_{\text{ind}}(s) \]
\[ = \alpha NI_e(s) + I_o(s) - NI_{\text{ind}}(s) \]  \hspace{1cm} (4.6)

The Fourier transform of \(I_m\) is \(\sigma_m(r)\), and the Fourier transform of equation (4.4) is \(4\pi r^2(NZ/V)^2V\). Then,

\[ \sigma_m(r) = \frac{2r}{\pi} N \int (\alpha I_e - I_{\text{ind}}) \sin sr \, ds \]
\[ + 4\pi r^2(NZ/V)^2V \]  \hspace{1cm} (4.7)

\(\sigma_m(r)\) is the interatomic charge distribution so for \(r\) much less than an atomic diameter, \(\sigma_m(0)\) is zero. Small overlap effects will be considered later. When \(r\to0\) equation (4.7) reduces to,
Since $\sigma_m(r)$ is zero long before $r$ is zero, the right side of equation (4.7) converges to zero. It can also be shown that the derivative with respect to $r$ of $\sigma_m/r$ is zero as $r$ approaches zero, so equation (4.8) is justified.

Finally,

$$\int s^2 (\alpha I_e - I_{\text{ind}}) ds = -2\pi^2 (N/V)Z^2$$ (4.8)

$$\int I_{\text{ind}}(s)s^2 ds - 2\pi^2 (N/V)Z^2$$

If the atoms are bonded, the effects of overlapping electron densities can be included with the inclusion of the overlap integral $I_{\text{ov}}$,

$$I_{\text{ov}}(s) = \sum \sum f_n(s)f_m(s)(\sin sr_{nm})/sr_{nm}$$ (4.10)

where $r_{nm}$ is the bond distance. A temperature factor exp($-Ds^2$) (78) multiplying the right side of equation (4.10) may be used in the evaluation of the overlap integral. For low temperatures $D$ is in the order of 0.002 Å. $D$ is calculated using the zero point oscillation frequency obtainable from Raman spectra. The normalization constant is now,

$$\alpha = \frac{\int (I_{\text{ind}}(s) + I_{\text{ov}}(s))s^2 ds - 2\pi^2 (N/V)Z^2}{\int I_e(s)s^2 ds}$$ (4.11)
V. SAMPLES, PROCESSES, AND THE RESULTS OF THE EXPERIMENTS

The liquid structures of seven different samples were analyzed. A single sample run consisted of taking data at every degree from 25 to 90 degrees scattering angle. Observations were made at every half degree from 5 to 25 degrees, while data were taken at every tenth of a degree over the main diffraction peak which usually occurred around 13 degrees when Mo Kα radiation was used. There were usually 125 observations per curve; the total time taken to run an experiment was approximately 150 hours.

Short slits were used for angles of 5 degrees or less (70). The short slit toward the sample was 2.5 mm tall, and the short slit toward the detector was 2.75 mm tall. These slits were placed adjacent to the permanent tall slits.

All data points have a minimum of 10,000 counts to give a fractional standard deviation of less than one percent per point. Since the regular background was approximately 1.6 counts per time interval of 100 seconds, the effect of the regular background in the counting time for a given accuracy was negligible compared to the minimum counting rate of 200 counts per 100 seconds. For angles
less than 20 degrees the scattering from the container walls, see Figure 12, had to be subtracted, and the counting time for small angles went up according to the graph in Appendix A.

After every run an empty container run was made to check to see whether the container had shifted or been contaminated. Contamination did occur in the fall of 1961, and a cleaning of the cryostat was required.

The first half of the liquid diffraction analysis program worked very well. There was never any difficulty in correcting the scattered intensity for the various factors mentioned in Chapter IV. The normalization method of Norman (76) and Krogh-Moe (77) worked satisfactorily. Because the overlap contribution amounted to one per cent of the theoretical intensity, see equation (4.13), the overlap term was corrected for molecular vibrations. The vibrations arise from the zero point energy of the molecules. The correction factor is exp\(-D_s^2\) (78) and in the temperature range of these experiments,

\[ D_s^2 = (2h/m\sqrt{\lambda})(\sin\theta/\lambda)^2 \]

where \( h \) is Planck's constant, \( m \) the reduced mass of the molecule, and \( \sqrt{\lambda} \) the zero point oscillation frequency of the molecule. The zero point oscillation frequencies of nitrogen and oxygen were taken from the work of Crawford,
Welsh, and Locke (79). For nitrogen $\nu = 2331 \text{ cm}^{-1}$, while for oxygen $\nu = 1556 \text{ cm}^{-1}$.

### 5.1 The Samples

In all, there were seven different samples. Two experiments were conducted just above the triple point of nitrogen at approximately 64 degrees K. The samples were pure oxygen and nitrogen. The other five experiments were conducted just below the standard boiling point of nitrogen. At this temperature, 77 degrees K, there were samples of nitrogen, oxygen, and mixtures of nitrogen and oxygen of nominal compositions 20/80, 50/50, and 80/20. By recording the vapor pressures of these mixtures and by using the tables published by Goldstein, Armstrong, and Roberts (80), one can calculate the exact composition of the mixtures. The nitrogen-oxygen ratios were 0.725/0.275, 0.48/0.52, and 0.19/0.81.

The atomic number densities for nitrogen and oxygen were taken from published data which agree with each other to one per cent. Rowlinson's data (81) were used in the final calculations. For mixtures the atomic number densities were corrected for non-linear mixing by the use of Knaap, Knoester, and Beenakker's study (47) on the volume change of mixing in binary mixtures.

The corrected and normalized scattered intensities for the seven samples are plotted in Figure 15. A
Fig. 15 Corrected Intensity Curves.
semi-logarithmic scale is used to show the details at large scattering angles. The undulations at the large angles are probably the result of the bonding of the atoms. There are significant shifts in the positions of the maxima which can be attributed to both the mixing effect and the temperature effect. The widths of the peaks, on the other hand, are mainly temperature sensitive.

The various samples will be identified in the following manner,

a. Pure nitrogen at 64 degrees K.

b. Pure nitrogen at 77 degrees K.

c. 72.5% nitrogen at 77 degrees K.

d. 48% nitrogen at 77 degrees K.

e. 19% nitrogen at 77 degrees K.

f. Pure oxygen at 77 degrees K.

g. Pure oxygen at 64 degrees K.

The broken lines of Figure 15 indicate the independent scattering curves of the respective samples.

5.2 The Calculation of Coordination Numbers

The calculation of coordination numbers is highly subjective, e.g., the discussion between Prins and Zarzycki (82) shows complete disagreement on how to interpret the radial distribution curves to get the coordination numbers.

The coordination number is the average number of particles which are in a spherical shell of thickness $\Delta r$.
at a distance \( r \) away from the(95,106),(975,129) central particle of the radial distribution function. Using a packing model of hard spheres, one can calculate the number of nearest neighbors at \( r^* \) the position of the minimum of an assumed potential. The problem is not a straightforward integration of \[ 4\pi r^2 \rho(r)dr \] from \( r_1 \) to \( r_2 \) because of the overlapping of shells. Arguments (83) can be made to show that the radial distribution function should have a symmetrical distribution about the maxima of the curve \( \rho(r) \). The small \( r \) side of the first shell of molecules is well defined on the curve \( \rho(r) \) even in the case of samples with diatomic molecules, and a mirror reflection about the maximum will then define the first shell. The second shell can be defined by subtracting the first shell from the curve; the small \( r \) side of the second shell is then delineated. Another reflection can be performed to define the second shell, but little is gained from studying the more distant neighbors because of the accumulating errors. The outline of the shells can then be replotted as \( r^2 \rho(r) \) and integrated to get the coordination numbers.

Henshaw and Hurst (84) describe an analytic method to obtain the coordination numbers. However, their assumption of a Gaussian distribution of the molecules in the shells and their use of the Debye-Waller temperature factor (85) which implies a solid-like configuration make their approach questionable.
5.3 The Electronic Radial Distribution Function

The electronic radial distribution functions for the seven samples were calculated using the experimental data, which were normalized to Freeman's theoretical scattering factors for oxygen and nitrogen \(31, 33\). The electronic radial distribution functions were very smooth with no spurious bumps or ripples, see Figure 16, interfering with the interpretation of the results. Coordination numbers for the bonded atom and the molecules in the first shell could be calculated easily using the symmetric distribution function \(\sigma(r)/r\). No test was made to determine the shape of the distribution in the first shell of \(\sigma(r)/r\) to see whether it was Gaussian, but the flatness of the peaks indicated a non-Gaussian distribution.

The bond distance of the diatomic molecule as well as the mean distance to the first shell of molecules were easily distinguishable. The next nearest shell, however, did not show a maximum on the curve \(\sigma(r)/r\), so the mean distance to the second neighbor shell could not be computed directly. The distance from the origin to the maximum of the peaks on the curve \(\sigma(r)/r\) should give the average internuclear distance of each of the peaks according to Viervoll \(86\). The diatomic bond distances measured in this manner give values that are consistently larger than
Fig. 16 Electronic Radial Distribution Functions.
those taken by other means (87). Viervoll claims a larger than expected internuclear distance is the result of the finite limit of the Fourier integral. The difference is approximately plus 3% for both the nitrogen and oxygen bonds.

The nearest neighbor shell distances for the pure liquids give values larger than those expected from Lennard-Jones theory (88). Part of this can be attributed to the fact that internuclear distances are not necessarily intermolecular distances. If half the diatomic bond distances are subtracted from the first shell distances, then the numbers are too small, see Table 1. The discrepancy is probably the result of the assumption of spherical symmetry of the molecules in the Lennard-Jones theory.

The first neighbor shell distances of the pure liquids shift with temperature in the expected direction, i.e., a dilation of the shells with temperature increase. The assumption that the maximum of the first neighbor shell on the radial distribution curve corresponds to the position of the minimum of the Lennard-Jones potential is then hard to justify. To first order the potential is temperature independent. Green (89) can be consulted for a more precise treatment of the relation between the radial distribution function and models of potentials.
TABLE 1
Electronic Radial Distribution Function Parameters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature Degrees K.</th>
<th>Composition Per cent $N_2$</th>
<th>Distance to peaks on $\alpha(r)/r$ curve</th>
<th>Coordination number Atoms per peak</th>
<th>$r_1$ distance minus 1/2 $r_0$ distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>64</td>
<td>100% $N_2$</td>
<td>1.12 ± 0.02 4.25 ± 0.02</td>
<td>0.86 ± 0.02 23.7 ± 0.5</td>
<td>3.69</td>
</tr>
<tr>
<td>b</td>
<td>77</td>
<td>&quot;</td>
<td>1.12 ± 0.02 4.29 ± 0.02</td>
<td>0.85 ± 0.02 23.5 ± 0.5</td>
<td>3.73</td>
</tr>
<tr>
<td>c</td>
<td>77</td>
<td>72.5%</td>
<td>1.16 ± 0.02 4.27 ± 0.02</td>
<td>0.83 ± 0.02 25.6 ± 0.5</td>
<td>3.69</td>
</tr>
<tr>
<td>d</td>
<td>77</td>
<td>48%</td>
<td>1.18 ± 0.02 4.17 ± 0.02</td>
<td>0.86 ± 0.02 25.7 ± 0.5</td>
<td>3.58</td>
</tr>
<tr>
<td>e</td>
<td>77</td>
<td>19%</td>
<td>1.22 ± 0.02 4.08 ± 0.02</td>
<td>0.89 ± 0.02 25.3 ± 0.5</td>
<td>3.47</td>
</tr>
<tr>
<td>f</td>
<td>77</td>
<td>100% $O_2$</td>
<td>1.24 ± 0.02 4.03 ± 0.02</td>
<td>0.90 ± 0.02 25.1 ± 0.5</td>
<td>3.41</td>
</tr>
<tr>
<td>g</td>
<td>64</td>
<td>&quot;</td>
<td>1.24 ± 0.02 3.90 ± 0.02</td>
<td>0.90 ± 0.02 24.2 ± 0.5</td>
<td>3.28</td>
</tr>
</tbody>
</table>

$r_0$ identifies the bonded atom peak.

$r_1$ identifies the nearest neighbor shell.
In the mixtures c, d, and e the average diatomic bond distances of Table 1 scale linearly with concentration when a simple calculation is made. Therefore, the first nearest neighbor shell distances should likewise scale linearly with concentration if linear mixing is assumed. However, the first nearest neighbor distances do not scale linearly with concentration but show dilations on mixing. Direct measurements (47) on binary mixtures of nitrogen and oxygen show volume contractions on mixing. Therefore, the dilations of the shell distances must be accompanied by an increase in the number of molecules in the shells. Although the coordination numbers from electronic distributions are faulty, below, the relative values between these numbers are probably valid. Relative coordination numbers do show an increase in the average number of molecules in the nearest neighbor shell over what would be expected from linear mixing.

Figure 17 shows the electron density distribution with the mean electron density subtracted. This figure shows the effect of mixing more clearly than Figure 16. In general, Figure 17 does not show gross or apparent features that can be attributed to a volume contraction on mixing.

The coordination numbers for the bonded atoms from the electron density distributions were not unity but about ten
Fig. 17 Deviation of the Electronic Density from the Mean Electronic Density.
per cent too low, see Table 1. The discrepancies cannot be attributed to poor normalizations or incorrect mean density values for the next neighbor peaks show an overabundance of atoms, i.e., coordination numbers of 24 or more. The error probably lies in the way the coordination numbers have been calculated. The \( r \) dependence of the charge distribution was assumed to be transferrable to the pair correlation function. This then makes it an electronic pair correlation function. Division by \( Z^2 \) will not necessarily make it an atomic pair correlation function.

5.4 The Atomic Radial Distribution Function

The atomic distribution functions for the pure liquids at the two temperatures are shown in Figure 18. Radial distances of the diatomic bonds and of the nearest neighbor shell as well as the coordination numbers of the various peaks in the curves are listed in Table 2.

The positions of the maxima of the peaks except those of the bonded atoms are difficult to determine because of the flatness and in some cases concaveness of the tops of the peaks in the radial distribution curves of nitrogen and oxygen. These peaks do not show symmetry when plotted as \( r \ell (r) \). Consequently, the average radial distances to the shells are not precise and do not agree with the distances calculated from the electronic radial distribution curves. The atomic bond distances, on the other hand, agree well
Fig. 13 Atomic Radial Distribution Curves.
TABLE 2

Atomic Radial Distribution Function Parameters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature Degrees K.</th>
<th>Composition</th>
<th>Distance to peaks on $4\pi r^2(r)$ curve</th>
<th>Coordination number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Distance in A.</td>
<td>Atoms per peak</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$r_0$          $r_1$</td>
<td>$r_0$          $r_1$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>±.02          ±0.1</td>
<td>±.02          ±0.5</td>
</tr>
<tr>
<td>f</td>
<td>77</td>
<td>100% O$_2$</td>
<td>1.24          3.87</td>
<td>1.16          21.2</td>
</tr>
<tr>
<td>g</td>
<td>64</td>
<td>100% O$_2$</td>
<td>1.24          3.84</td>
<td>1.16          21.5</td>
</tr>
<tr>
<td>b</td>
<td>77</td>
<td>100% N$_2$</td>
<td>1.12          4.22</td>
<td>1.10          20.3</td>
</tr>
<tr>
<td>a</td>
<td>64</td>
<td>100% N$_2$</td>
<td>1.12          4.16</td>
<td>1.09          20.9</td>
</tr>
</tbody>
</table>

$r_0$ identifies the bonded atom peak.
$r_1$ identifies the nearest neighbor peak.
with those calculated from the electronic density distributions, see Table 1 and 2. In the case of non-monatomic samples the distances calculated from the electronic distribution functions are probably more reliable than those calculated from atomic distribution functions because of the symmetry of the peak consideration.

The asymmetrical character of the first nearest neighbor shell for oxygen and nitrogen indicates that the assumption of spherical symmetry of the nitrogen and oxygen molecules is not good. Spherical symmetry of the molecules should give sharp symmetric peaks similar to those found for monatomic liquids (17-20). The apparent resolution of the nearest neighbor peak into two peaks could indicate a preferred orientation of an elongated molecule with a component of the major axis in the radial direction.

The positions of the peaks of the bonded atoms do not shift with temperature for both samples. The distances to the nearest neighbor shells do not have the simple correlation with temperature as do the distances from the electronic distribution curves. This difference can be attributed to the lack of preciseness in estimating the center of the nearest neighbor peaks; this lack of preciseness in estimating the center of the peaks is very apparent when one tries to calculate coordination numbers.
The coordination numbers show only a slight, if any, temperature effect between 64 and 77 degrees K. The values of the coordination number for oxygen compare reasonably well with those taken from neutron diffraction data (44), but the coordination number for nitrogen is much lower than the value 23.6 atoms taken from neutron data (43). Since the coordination number for oxygen was 26.0 atoms in the same series of experiments when the nitrogen data was taken, there is reason to believe that 20.3 atoms is a better figure. Recent studies (90) of liquid nitrogen at seven atmospheres, and 80 degrees K. using x-ray diffraction techniques give a coordination number of 30 atoms for the first neighbor shell. A tighter configuration than closest packing is possible because of the non-spherical molecules and the high pressure. However, the accuracy of this data is questionable since the bond distance for the bonded atoms in this study is 1.22 A, which is too large, much larger than a reasonable estimate of the statistical error would allow.

Except for the ripples between the peak corresponding to the bonded atom and the first shell of molecules, the atomic distribution curves are relatively devoid of obviously spurious structure. The small peak on curve g at 5.2 A is probably spurious. Peaks at the same relative position on atomic distribution curves are considered spurious (18).
5.5 Error Estimates

The normalization to absolute units has been satisfactory. The method of Norman (76) and Krogh-Moe (77) using both atomic and electronic density distribution processes gave factors which agreed to better than 0.1%. The intensity curves normalized by these factors fit well graphically with the independent scattering curves at large scattering angles, see Figure 15.

The error estimates of Tables 1 and 2 are not based on the overall accuracy. Rather, they describe the limit of accuracy in estimating the various values from the inverted curve. The peaks of the electronic distribution function can be easily spotted; while those of the atomic distribution curve are less recognizable due to the flatness of the peaks and the asymmetry of the peaks of this curve. Likewise, the area under the peaks of the electronic distribution function can be easily obtained because of the symmetry, however, the diffuseness of the shells makes the boundaries of the shells hard to fix. The peaks of the atomic distribution function, on the other hand, are sharper, but the asymmetry of the peaks in the case of diatomic fluids affects the choice of a center of symmetry, and therefore, affects the boundaries of the shell.

Coordination numbers in general are not very precise. For example, studies of liquid helium give a value of
9.7 for the nearest neighbors when neutron diffraction methods are used, but 10.6 is the number obtained from x-ray data (74). In both experiments temperature and pressure were nearly identical. Questions as to whether the symmetry criterion should be applied to the \( r \rho(r) \) or the \( r^2 \rho(r) \) curves should also be resolved before the coordination numbers can be reliable. Symmetry in \( r \rho(r) \) was used as the standard in these experiments. As things now stand, coordination numbers cannot be trusted to better than \( \pm 10\% \), and even this is an optimistic figure.
VI. DISCUSSION

Spurious Peaks. Figure 18 shows two small but distinct ripples between the first peak identified as the bonded atom peak and the next large peak identified as the nearest neighbor peak. These ripples can be attributed to the finite upper limit of the Fourier integral (54). The peaks are ghosts of the peaks of the bonded atoms, and the number of ghost peaks in a given interval is a function of the upper limit of integration $s_m$. A direct way to show this is to find the theoretical radial distribution function for the diatomic molecule.

The intensity $I$ scattered by two identical bonded atoms is (92),

$$I = 2r^2(1 + (\sin sr*/sr*))$$

(6.1)

where $f$ is the coherent scattering factor for the atom, $r*$ is the bond distance and $s = 4 \sin \theta/\lambda$. The intensity $I$ can be inserted into equation (2.31), $N$ is now equal to 2 (for the two bonded atoms), and $\rho_b$ is 0. The result is the atomic radial distribution equation,

$$4\pi r^2 \rho(r) = (2r/\pi) \int_0^{s_m} s(\sin sr*/sr*)ds$$

(6.2)

This equation can be integrated directly to give,
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$4\pi r^2\rho(r) = \frac{(r/r^*)(\sin(r-r^*)s_m}{(r-r^*)} - \frac{\sin(r+r^*)s_m}{(r+r^*)}$  

(6.3)

The right side of equation (6.3) has the form of a generalized function (93) for as $s_m$ approaches infinity the second term on the right averages to zero, while the first term on the right takes on the shape of an infinite narrow spike centered at $r=r^*$. Equation (6.3) is plotted in Figure 19 for two values of $s_m$ together with experimental curves taken from the present oxygen data. It is apparent that as $s_m$ gets larger the main peak at $r=r^*$ gets taller and narrower, while the periods of the flanking oscillations get smaller; and in the limit $s_m=\infty$, the oscillations average to zero, while the main peak is a delta function. There are two ghost peaks in the present experimental data because $s_m$ was 12.6 A$^{-1}$. Henshaw's data (44) show a single ghost peak because his limit of integration was 7.6 A$^{-1}$.

$O_3$ and $O_4$ Molecules. When the coordinator number for the bonded atom of the oxygen molecule is calculated from the theoretical radial distribution function, equation (6.3), with $s_m = 4\pi$, the value is 1.17. This value compares favorably with the coordination number 1.16 calculated from the experimental curves at 64 and 77 degrees K. The area
Fig. 19 Radial Distribution Curves of the $O_2$ Molecule.
under the peak at \( r=r^* \) is larger than unity because of the finite limits of integration and not because of the presence of \( O_4 \) molecules. This lack of \( O_4 \) molecules in liquid oxygen has also been indicated by infrared measurements (94).

Kanda and Sugawara have shown that \( O_3 \) is not produced in a measurable quantity by x-ray irradiation of liquid oxygen (95). The present data support this conclusion. According to infrared data (96), the oxygen atoms in an ozone molecule are located at the corners of an isosceles triangle, and the possibility of an equilateral triangle configuration is definitely ruled out. If the concentration of \( O_3 \) molecules is temperature sensitive, then the average bond distance of the bonded atom in liquid oxygen should also be a function of temperature. The present data give, within the limits of accuracy of the experiments, a constant bond distance for oxygen at 64 and 77 degrees K.

A search of the literature produced no reference to measurements on the structure of the \( O_4 \) molecule. Henshaw (44) assumes a tetrahedral configuration with equal spacing between atoms. If this configuration for \( O_4 \) is accepted, the radial distribution function, obviously, will not show a changing bond distance with changing concentration of \( O_4 \). But if the \( O_4 \) molecules lack this symmetry, the method described above for detecting \( O_3 \) can be used to detect \( O_4 \) molecules.
**Liquid Structure.** Since the calculations of the Lennard-Jones parameters as tabulated by Hirshfelder, Curtiss, and Bird (88) assume spherical symmetry of the molecules, the distances calculated from atomic and electronic distribution functions need not agree with their data. The Lennard-Jones parameters are calculated from second virial coefficient and viscosity data. Second virial coefficients are not sensitive to the shape of the molecules. The parameter $r^*$, the position of the minimum of the potential, calculated from viscosity data is smaller when asymmetry of the molecules is considered than when it is not considered (97).

The inverse of the standard liquid diffraction analysis procedure has been tried with moderate success (98). The liquid structure theory of Born and Green (99) is used to calculate the intensity scattered by liquids. The scattering curves derived by this method agree reasonably in shape with the intensity curves obtained from x-ray diffraction of liquids. But again, it is the small differences that count. When the intensity curves are Fourier inverted, the radial distributions derived from the theoretical curves do not agree well with the curves derived from the experimental intensity curves.

**Errors.** Extremely accurate radial distribution functions are needed to predict the thermodynamic
properties of fluids. Green in his article on the structure of liquids (100) says,

Theoretical methods offer indirect methods of computing the equation of state and the internal energy of a simple liquid, and hence the thermodynamic functions. Indeed, thermodynamic variables depend so sensitively on the radial distribution function, especially in the repulsive part of the intermolecular field, that an error of 0.1% in the latter can easily lead to an error of 20% in the former. Such computations, therefore, provide a much more exacting test of accuracy than even direct comparison with the distribution functions derived from diffraction experiments.

At present, the radial distribution curves are certainly not good to 0.1%. If the accuracy of the shape of the radial distribution curve where the curve rises from a negligible value to give the nearest neighbor shell is so critical, then the thermodynamic functions calculated from distribution functions derived from diffraction data are valueless. The shape of the shells depends strongly on the finite limits of the Fourier integral (18). Increased resolution of the shells is obtained by increasing the limit of integration. Pings and Paalman (90) argue against increasing the upper limit of integration on the grounds that an increase introduces spurious peaks. Such peaks, however, are explainable as shown in the case of the small peaks flanking the bonded atom peaks of the present study. Instead of limiting the resolution to get rid of these "truncation" peaks, it would be better if a correction could be found for
them. Along this line, modification functions that decrease resolution such as the artificial temperature function should be avoided if information in addition to radial distances and coordination numbers is desired.

Finite termination or truncation errors are discussed by several authors. Klug and Alexander (53) have compiled the effects of various errors typical of Fourier transforms such as truncation errors, spurious peaks, and bad normalization. Viervoll (87) gives a detailed analysis of errors in the electronic distribution function.

Quantitative analysis of the accuracy of curves of Fourier inverted data is highly speculative. A measure of the accuracy of experimental data is readily available, but there is no one to one correspondence between the errors of the diffraction curve and the errors of the distribution function obtained through the Fourier inversion process. There is only a rough relation between the large \( s \) values of the intensity curve and the small \( r \) values of the distribution function.

In the case of the atomic distribution function, the integrand of the Fourier integral shows an increase in the estimated error as \( s \) increases. The error in the integrand is in the experimentally determined \( i(s) \), where
\[
i(s) = \frac{I}{f^2} - 1 \quad (I \text{ is the experimentally observed coherent}
\]
scattering with a standard deviation per point of 0.01); the systematic error in $f^2$ is assumed to be negligible compared to the error in $I$. For $s > 6 \, \text{A}^{-1}$, $I$ approaches $f^2$ and the value of $i(s)$ approaches zero. The constant term 1 in $i(s)$ is analogous to a dc common mode signal in electronics. Any noise (statistical fluctuation) will be a larger fraction of the signal (structure factor of the liquid) being measured when the common mode is subtracted from the total signal. The signal to noise ratio is large at the main diffraction peak and small for large $s$ values. When the integrand $s i(s)$ of the Fourier integral is plotted, the statistical fluctuation at the peak is approximately 2% of the peak value while for $s > 7 \, \text{A}^{-1}$ the estimated fluctuation is approximately 30% of the slowly undulating peaks. The values of the estimated fluctuations follow the electronic analogy and are rms figures. Therefore, if there is variable accuracy in the integrand curve, there is no way of estimating the accuracy of each point on the inverted curve.

The data-taking procedure in x-ray diffraction experiments should allow for the increasing weight given to the large $s$ values of the integrand of the Fourier integral. The present criterion of equal statistical weight for all observed points should be modified to conform to the statistical requirements of the Fourier inversion process. This
change in standard of accuracy will be feasible only if there is a more intense source of monochromatic x rays.
APPENDIX A

\[ F.S.D. = \sqrt{\frac{A+B}{A-B}} \]

\[ A = \text{Signal and Background} \]

\[ B = \text{Background} \]

\[ r = \frac{A}{B} \]

\[ A-B = \frac{1+1/r}{1-1/r} \left(\frac{1}{F.S.D.}\right)^2 \]

Fig. 20 Fractional Standard Deviation of a Composite of Two Poisson Distributions.
APPENDIX B

X-Ray Counting Efficiency

The Scintillation Detector Versus the Proportional Counter. For the initial phases of these experiments proportional counters were used to detect the diffracted x-ray beam. A change to a scintillation detection system was made in the summer of 1961. The scintillating crystal was NaI(Tl) of dimensions 0.5 x 1.5 x 12.0 mm, and the photomultiplier used was an EMI 9542S. Table 3 gives a comparison of the two types of detectors taken under identical conditions.

The comparison was made using Cu Kα radiation. The scintillation detector efficiency will show an even greater advantage over the proportional counter efficiency, if the comparison were made using molybdenum radiation. The counting efficiency at 0.711 A will remain the same as the efficiency at 1.54 A for the scintillation detector, but the efficiency of the proportional counter will drop considerably at the shorter wavelength. The background of the scintillation detector will also drop to approximately 0.9 counts/min mainly through the increased resolution, approximately 45%, which allows for a smaller window setting. There is no corresponding resolution gain in the proportional counter system.
TABLE 3

Comparison of the Proportional Counter and the Scintillation Detector

<table>
<thead>
<tr>
<th>Test</th>
<th>Krypton Proportional Counter</th>
<th>NaI(Tl) Scintillation Detector</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu Kα efficiency.</td>
<td>4200</td>
<td>7500</td>
</tr>
<tr>
<td>Counts/100 secs. at the liquid N₂ peak.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Background.</td>
<td>5.5/min.</td>
<td>1.9/min.</td>
</tr>
<tr>
<td>Total amplification through the electronic system necessary to give 35 volt pulses.</td>
<td>39,000</td>
<td>1000</td>
</tr>
<tr>
<td>Drift sensitivity; shift in pulse height distribution/% drift in detector voltage.</td>
<td>2.65 v/%</td>
<td>2.30 v/%</td>
</tr>
<tr>
<td>Resolution</td>
<td>16%</td>
<td>67%</td>
</tr>
</tbody>
</table>

Increasing the Reflective Power of a Crystal. The reflective power of a crystal can be increased by reworking the surface of the crystal. Birks and Seal (101) increased the reflective power of LiF by plastic deformation, while Priestly (102) used abrasion and ultrasonic treatment...
to get a gain of 10 from LiF at the Mo Kα wavelength. The present experiment showed an over-all gain of five by the method of ultrasonic treatment and by abrasion. An Alcar ultrasonic soldering gun was used in the ultrasonic treatment. Table 4 gives before and after comparisons of the reflective power of a LiF crystal.

TABLE 4

Effects of Surface Treatment on the Reflective Power of the LiF Crystal Monochromator

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Before Treatment Cts/100 secs</th>
<th>After Treatment Cts/100 secs</th>
<th>Gain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultrasonic treatment</td>
<td>2900</td>
<td>9250</td>
<td>3.12</td>
</tr>
<tr>
<td>Abrasion (Carborundum 3/F) and ultrasonic treatment</td>
<td>9250</td>
<td>15,250</td>
<td>1.65</td>
</tr>
</tbody>
</table>

Total Gain 5.26
APPENDIX C

Programming the Patch Panel

Figure 21 gives the wiring point layout. Lines 1 to 14 carry low voltage dc. Lines 15 to 20 carry 110 volts ac. Line 15 is not used and marks the boundary between the two sections. The points on line 15, however, are wired for 110 volts ac, therefore, no external wires should be plugged into them. There are 34 columns on the patch panel corresponding to 34 separate program instructions.

The Angle Positioning Section. Lines 1 to 11 carry the reference voltages that correspond to the digits of the three decades. The reference voltage lines are numbered 0 to 9 corresponding to the digits in a decade. The thirty-four points on a line are tied in common to a single voltage corresponding to a single digit. Therefore, the function of each of the first 11 lines is independent of program position. There are two lines of 0's since this is the digit most frequently used.

Line 12 is connected to the most significant decade (tens), 13 to the next most significant decade (units), and 14 to the least significant decade (tenths). A column of decades represents one angular setting allowing a maximum
of 34 settings. The three lines in any one column are sampled in sequence by the decade stepper and are compared to the corresponding decade on the angle indicator on the spectrometer. To program the angle positioning section a wire from each decade position is wired to the digit desired.

**The Count Cycle Section.** Line 15 is not used. Lines 16, 17, and part of lines 19 and 20 are connected to the count cycle stepper. These lines are broken into twenty groups from one to twenty corresponding to the number of count cycles. The groups are wired to the corresponding position on the count cycle stepper which steps one position after each count cycle. The wiper arm of the count cycle stepper is connected to the program advance and reset circuits. Line 18 called count cycle hot is wired to the program stepper. This stepper energizes the point on line 18 corresponding to the program stepper position. Therefore, to operate, a wire is connected from the count cycle hot to the desired count cycle point. Then, when the count cycle stepper reaches this point, a signal is sent to step the programmer to the next column.

**Other Control Functions.** The lower right corner has twelve points that are used for control functions.

R. Column 34, lines 19 and 20. If these points are wired together, the programmer automatically steps
from home to program position 1. This enables the pro-
gressor to recycle from position 34 to 1. This wire is
usually left connected.

XI. Columns 30 and 31, lines 19 and 20. When wires
are connected between lines 19 and 20 on both columns, the
count cycles are multiplied by one.

X2. Columns 32 and 33, lines 19 and 20. When wires
are connected between lines 19 and 20 on both columns, the
count cycles are multiplied by two; n.b., either XI or
X2 must be used, but not both at once.

Column 29, line 19. To get the programmer to return
to position 1 after completing in sequence any set of N
columns for N < 34, connect column 29, line 19 to the count
cycle hot on column N+1. In combination with R any sequence
of m columns, 1 ≤ m ≤ 34, can be made to repeat itself.

Column 31 or 33, line 19. If a constant number of
count cycles is desired for all program positions, connect
a wire from the number of count cycles desired to either
column 31 or 33, line 19. The choice depends on whether
XI or X2 is being used; n.b., if at the same time the count
cycle hot points are wired to count cycle points, the num-
ber of count cycles completed at any program position will
be the lesser of the two choices of count cycles. For ex-
ample, if column 33, line 19 is wired for 10 count cycles,
and program position 1 is wired for 8 count cycles, then
8 count cycles will be completed before the programmer steps to program position 2. However, if position 2 is now wired for 15 count cycles, only 10 count cycles will be completed before the programmer steps to the next column.
Fig. 21 Patch Panel Board
APPENDIX D

The Liquid Diffraction Analysis Program

The features of this program will not be discussed in detail because the program is written in IBM Fortran. A flow diagram is given in the following pages, and a list of variable names and their definitions are given so that the program can be analyzed easily. All input format and the order of stacking data cards are given in Table 6, so that anyone can use the program.

The program is written for the IBM 7090 computer and the attending peripheral equipment maintained by the Numerical Computation Laboratory of The Ohio State University. The computer has a 32 K word storage capacity and four tape units for the programmer's use.

Input cards are transferred to tape in preparation for use by the 7090, therefore, input data format is limited for the most part by card format. Output printed format is limited to the line size of the printer, which allows 120 characters per line.

Preliminaries. The COMMON statement includes all variables used in common by the main program and all the
functions and subroutines. To avoid confusion all COMMON statements for the main program, subroutines, and functions are identical.

The DIMENSION statement gives the array sizes. The array size of most of the input arrays is 200, while the interpolated data and the output data have an array size of 500.

The IF Box. The IF box contains all the IF statements that control the flow of the program. At each fork the program transfers to the IF box to ask for directions. Questions that are asked include the point of entry, whether to continue or to stop, and whether to print or to punch computed data. The yes or no replies are put into the program by an input data card called the IF card.

Point of Entry. The program has two points of entry. The first accepts uncorrected intensity data from the output of the IBM 1620 normalization program. The other point of entry is for corrected intensity data where acceptable data is in the form $\sin \theta/\lambda$ versus intensity. The point of entry is determined by the IF box. Both points of entry in the same problem are not acceptable, and the problem is scrapped if the IF card permits both points of entry.

Exit Points. In addition to the normal exit there are several other exit points controlled by the IF box or by errors in the program. Exit is accomplished by reading all
input data cards until NEOR is reached. NEOR, the last data card contains a 9 in column 72.

Interpolation. The integration for the Fourier inversion operation is done using Simpson's one third rule. The range of integration has to be divided into an even number of equal intervals, whose size must be small enough to accommodate all the fluctuations in the curve to be integrated. The experimental intensity curves have points at intervals that do not satisfy any of the above requirements for a valid integration using Simpson's rule. Therefore, the experimental intensity curves must be recalculated at points that will be determined by the requirements of Simpson's rule.

To do this a Lagrangian interpolation (103) is used. Points on the experimental curve have been measured in such a manner as to follow closely the fluctuations in the intensity curve, i.e., portions of the curve with rapid fluctuations have observed points at close intervals, while smoother portions have observed points at larger intervals.

The interpolation routine fits a fifth power polynomial to six points on the curve. Any point falling within the range of these six points can then be evaluated. The six points are chosen so that they bracket the point chosen to be interpolated, with three points of the independent variable having values less than the point to be
interpolated and three points having values greater than the interpolation point. As the point of interpolation moves successively along the intensity curve, so do the six points that bracket it. At the extremes of the range the first six points or the last six points are used.

There is no explicit smoothing done on the experimental data for two reasons. First, the observed points already have a fractional standard deviation of less than 0.01, and second, any smoothing routine will be complicated because the type of smoothing depends on the portion of the curve to be smoothed. The least squares method is not readily applicable to the entire curve since there is no analytic expression to which it could be fitted. Any regression method of curve fitting will be inordinately laborious due to the complicated structure of the intensity curves.

The interpolation routine takes the observed curve with approximately 125 points and computes from them 500 new points at equally spaced intervals spanning the range.

Integration. The Simpson's one third rule is used for all integrations in this program. The independent variable in the integration process is \( s = 4 \sin \theta/\lambda \). For Mo K\( \alpha \), the radiation used for the present experiments, the maximum \( \sin \theta/\lambda \) is close to 1.0A\(^{-1}\). This gives an interval
\( \Delta s = 0.025 \, \text{A}^{-1} \). There has been no measure of the accuracy of Simpson's method of integration using this size interval, but Gordon claims an accuracy of better than one per cent using an interval of 0.035 \( \text{A}^{-1} \), and integrating over only half the range given above. Mendel (42) used intervals of 0.062 and 0.120 \( \text{A}^{-1} \) for his work, but he does not quote the accuracy of his integration. The greatest error in too large an interval size will be in the analysis of the higher Fourier components at the larger \( r \) values. Since the largest \( r \), \( r_{\text{max}} \), is 10 \( \text{A} \), the highest Fourier component when \( s = s_{\text{max}} = 4 \pi \) is \( r_{\text{max}} s_{\text{max}} = 40 \pi \). This value divided into 500 intervals will give a sampled point every 0.25 radians or approximately every 15 degrees. The numerically integrated area under a sine curve samples at this rate will have an error of less than 1%.

Execution of the Program. The first data card which contains the title PROBNO is read and printed. The identifications of the IF station numbers are than printed. The next card, the IF card which contains the IF switch information is then read and printed. The intensity correction parameters and the intensity cards are read next. The intensity arrays as well as all other input arrays are read by first reading a card that tells the program the size of the arrays. Cards are read until the array size is equalled.
For the intensities at angles less than the beryllium cutoff angle a beryllium scattering correction is made. The proper beryllium correction is sought in the array previously read in. If the correction is not in the tables, then the interpolation function finds as appropriate correction. The beryllium correction is multiplied by the transmission factor before it is used to correct the intensity. If necessary the beryllium data can be further modified by a scale factor. The small natural background is subtracted at this point.

For angles larger than the beryllium cutoff angle there is no beryllium scattering correction, but there is natural background subtraction.

Once the subtractive corrections are made, then multiplicative corrections can be made. The volume correction for angles larger than the beryllium cutoff angle is simply \( \sin\theta \), while for angles smaller than the cutoff angle the correction is found in the volume correction table; interpolation is used if necessary. The polarization correction which is analytic is also made at this point. The scattering angle is corrected to the true spectrometer scattering angle and converted into radians by the arithmetic statement function PHIRF. The scattering angle is then converted to the reduced units \( \sin\theta \).

The program reads the parameters for the interpolation subroutine and for the theoretical scattering factors.
Interpolation is done in intervals designated by DELSTO, and begins at the value given by STOLO, which is usually 0.0. MAXSTO gives the total number of intervals, therefore, MAXSTO x DELSTO gives the maximum \( \sin \theta / \lambda \) and defines the upper limit of the integration function. MINSTO is not used in the interpolation process and is used only to indicate the lower limit of the integration function. MINSTI and MAXSTI are the indices of the limits of integration of the integration subroutine.

Some of the parameters read in next are redundant if the point of entry is 1 but are necessary if the entry is made at 2. The variable names starting with Q's and \( \rho \)'s are identified in the variable name list. They are associated with the theoretical scattering factors. If the sample is monatomic \( r_{\text{FRAC}} \), \( r_{\text{BFRAC}} \), and \( Q_{\text{BFRC}} \) must be zero. The other \( r \) parameters can have any values.

The different intensity and scattering are interpolated over the whole curve by \( r_{\text{OLAT1}} \). If the sample is monatomic, zero's are stored in \( r_{\text{COHI}} \) and \( r_{\text{INCI}} \). Recoil factors are calculated, and then the scattering factors are added to give the independent scattering, \( \text{FINDEP} \).

Now the overlap integral is calculated if the atoms are bonded. Before the use of the integration function the number of intervals is checked to see whether it is odd or even. There must be an even number of intervals, or the problem is
dumped. The program checks to see what kind of normalization factors are to be used. If external normalization factors are desired, NORMEX should be equal to 1; and the factors ALPHAl and GAMMA1 are used. IGAMAL will be 1 if the same normalization factor is desired for both the atomic and electronic distribution functions. Then the various integrals of the type, \( \int s^2 I(s) \, ds \) are calculated and combined to determine ALPHA the scale factor to convert experimental intensity to absolute units for the atomic radial distribution. GAMMA is calculated for the electronic radial distribution. ZBAR is calculated. ALPHA and GAMMA are now used to convert the observed intensity to electron units, and the various types of intensities, \( i(s) = \text{XINTM, SINTL, or XINTA} \), are calculated in preparation for the Fourier inversion.

Through the use of the Fourier inversion subroutine the three different types of intensity functions XINTM, XINTL, and XINTA are inverted to give the following corresponding radial distribution functions: the interatomic electron distribution function, the interatomic electron distribution function between atoms belonging to different molecules, in short, the intermolecular distribution function, and finally, the atomic distribution function.

The temperature factor \( \exp(-\lambda s^2) \) is left out in the calculation of the electronic distribution functions by the
arithmetic statement \( C = 0.0 \). For the atomic distribution function the temperature factor may be included by the appropriate input value for \( A \).

The outputs of the Fourier inversion subroutine are operated on by factors \( R_I \) and \( R_I^* \) to give the various convenient types of distribution functions that can be plotted easily. Finally, the problem exits by searching for the last card as stated earlier. When it successfully finds \( \text{NEOR} \), it prints the statement END OF PROBLEM and goes to statement 100, which begins the next problem. At the end of the last problem an ungracious but effective exit is made when the program tries to read more data. An "end of file" mark is put in by the Numerical Computation Lab at the end of every job.

**Functions and Subroutines**

**PHIRF(Z).** Arithmetic statement function that corrects the nominal recorded angle to true spectrometer angle and converts it to radians.

**POLATE(PHI, XRINT, MXINT, X)** takes the curve with variables \( PHI \) and \( XRINT \) and interpolates for the independent variable point \( X \), a value \( f(X) \) which is stored in the address given to this function. Since this function fits a fifth power polynomial to six points as stated above, the range of the six points must be predetermined. The range is fixed by \( L \) and \( MXINT \).

**SUM1(STOLI, XRINTI, MINSTO, MAXSTO, DELSTO).** This function
gives the value of \( \int s^2 I(s) ds \) using Simpson's formula. The arrays \( STOLI \) and \( XRINTI \) define \( I(s) \), \( s = 4\pi STOLI \), and \( ds = 4\pi \text{DELSTO} \). The limits of integration are implied in \( \text{MINSTO} \) and \( \text{MAXSTO} \).

\text{POLATI(STOL, XRINT, STOLO, STOLI, XRINTI, MAXSTO, DELSTO)}.

This subroutine finds values at equal intervals for the interpolated curve \( STOLI \) vs. \( XRINTI \) from the input curve \( STOL \) vs. \( XRINT \). The process can be initiated anywhere along the curve; the initial point is designated by \( STOLO \) and index 1 and terminated by the maximum index \( \text{MAXSTO} \).

\( \text{DELSTO} \) is the increment along the curve. This subroutine calls on the function \( \text{POLATE} \) to do the actual interpolation.

\text{FOUINV(STOLI, XINTA, MINSTI, MAXSTI, DELSTO, RO, MINR, MAXR, DELR, A, RI, DIFDIS)}.

This subroutine Fourier inverts the curve \( STOLI \) vs. \( XINTA \) to give the point \( \text{DIFDIS} \) at \( RI \). This process is repeated until the whole range of \( RI \) defined by \( RO \), \( \text{MINR} \), \( \text{MAXR} \), and \( \text{DELR} \) is covered. Again, \( RO \) and \( \text{MINR} \) define the initial point and \( \text{MAXR} \) the terminal point with \( \text{DELR} \) defining the interval. The range of integration is defined by a running index bounded by \( \text{MINSTO} \) and \( \text{MAXSTO} \) and by interval \( \text{DELSTO} \). \( A \) is the coefficient in the temperature factor \( \exp(-As^2) \).
Flow Diagram for the Liquid Diffraction Analysis Program

100 Read and write PROBNO, the title.
Read IF switch control card, write IF switch identification, and IF switch settings.
Check for an ambiguity in the point of entry.

No Yes

1000 Check if entry is through 1.

Yes No

1001 Check if entry is through 2.

Yes No

1011 Read intensity correction parameters, PHIBC, WVLT, POLX, TRNSM, BKGN, SCFAC, BESCA.
Read intensity arrays, MXINT, PHI, XRINT: MXBE, PHIBE, BEINT: MXVOLC, PHIV, VOLC.
Calculate the proper intensity corrections, calling the interpolate function if necessary. Calculate STOL for each PHI.

1003 Is the intensity printout desired?(1)

Yes No

119 Write PHI, CORR, STOL, XRINT.

1004 Punch intensity cards? (1)

Yes No

121 Punch PHI, CORR, STOL, XRINT.

1005 Go on? (1)

Yes No

131 Read arrays MXINT, FAKE, FAKE, STOL XRINT.
Read interpolation and integration parameters, MINSTO, MAXSTO, DELSTO, STOLO: MINSTI, MAXSTI, MINR, MAXR, DELR, RO: ADNSTY, A, WVLT: NORMEX, IGAMAL, ALPHAL, GAMMAL.
Reach charge and mole fraction QZ, QFRAC, PZ, PFRAC.
Read molecular bond information
QBFRAC, QBOND, PBFRAC, PBOND, QPFRC, QPFBD, D.
Read Q scattering factors MAXQ, QSTOL, QCOH, QINC.
Is there a second element?
Yes No

Read MAXP, PSTOL, PCOH, PINC.

Interpolate at equal intervals the curves STOL, XRINT to give STOLI, XRINTI.

1006 Go on? (2)
Yes No

1007 Print the interpolated intensity? (2)
Yes No

1042 Print STOLI, XRINTI.
Go to exit.

143 Interpolate at equal intervals the curves QCOH, QINC to QCOHI, QUNCI.
Is there a second element?
Yes No

Interpolate at equal intervals the curves PCOH, PINC to give PCOH, PINCI.
Go to 146

145 Fill arrays PCOH, PINC with zeros.

146 Calculate recoil factors RECFAC and the independent scattering factors
QINDEP, PINDEP, FINDEP, QPCOH2, AINDEP, AXRINT.
Calculate the overlap integrals
OVRLPI, OVRLPT.

1008 Print theoretical scattering factor? (3)
Yes No

Print theoretical scattering factors
STOLI, QINDEP, PINDEP, FINDEP, OVRLPI.
Check integration interval for evenness.
Yes No

Print problem error.
Got to exit.
Print normalization parameters from input data. Check NORMEX for external normalization parameters and use the parameters if they are present.

If one of two parameters are external, check ALPHAI and GAMMAI to see which one it is. If ALPHA is necessary, generate EXPSUM, FINDSM, and OVLPSM. Check IGAMMAL if GAMMA is necessary. If necessary, generate AXPSM, AINDSM. Print EXPSUM, FINDSM, OVLPSM, ALPHA, AXPSM, AINDSM, and GAMMA.

Calculate and print XINTA, XINTI, XINTM, XINTL.

Go on? (3)  
Yes  No

Calculate the electron density distribution? (4)  
Yes  No

Calculate the atomic distribution? (6)  
Yes  No

Fourier invert XINTM to get interatomic electron density distributions SIGMAM, SGMAM1, SGMAM2, SIGMA, SIGMA1, SIGMAO.

Print the interatomic electron distribution? (4)  
Yes  No

Print RI, SIGMA, SIGMA1, SIGMAO; RI, SIGMAM, SGMAM1, SGMAM2.

Punch interatomic electron density? (4)  
Yes  No

Punch RI, SIGMA, SIGMA1, SIGMAO; RI, SIGMAM, SGMAM1, SGMAM2.

Go on? (4)  
Yes  No

Calculate intermolecular electron distribution SIGMAL, SGMAL1, SGMAL2.
1017 Print intermolecular electron distributions? (5)
   Yes No
208 Print RI, SIGMAL, SGMAL1, SGMAL2.
1018 Punch intermolecular electron distributions? (5)
   Yes No
209 Punch RI, SIGMAL, SGMAL1, SGMAL2.
1019 Go on? (5)
   Yes No
211 Calculate atomic distributions RADDIS, AVEDIS, SYMDIS, DIFDIS.
1020 Print atomic distributions? (6)
   Yes No
212 Print RI, AVEDIS, SYMDIS, RADDIS, DIFDIS.
1021 Punch atomic distributions? (6)
   Yes No
213 Punch RI, AVEDIS, SYMDIS, RADDIS, DIFDIS
999 Exit routine, read all data cards until card containing 9 in column 72 is reached. Then go to 100.
### TABLE 5

Liquid Diffraction Program Variable Names.

**Main Program**

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Temperature factor used in Fourier inversion subroutines.</td>
</tr>
<tr>
<td>ADNSTY</td>
<td>Average atomic density.</td>
</tr>
<tr>
<td>AINDEP</td>
<td>Independent scattering factors divided by coherent scattering factors.</td>
</tr>
<tr>
<td>AINDSM</td>
<td>Value of integrate function with integrand AINDEP.</td>
</tr>
<tr>
<td>ALPHAI</td>
<td>External normalization factor for electron distribution.</td>
</tr>
<tr>
<td>AVEDIS</td>
<td>Average distribution of atoms.</td>
</tr>
<tr>
<td>AXRINT</td>
<td>Experimental intensity divided by coherent scattering.</td>
</tr>
<tr>
<td>B</td>
<td>B is the number equal to the number of integration intervals and must be an even number.</td>
</tr>
<tr>
<td>BEINT</td>
<td>Array of scattered beryllium intensities.</td>
</tr>
<tr>
<td>BESCA</td>
<td>Scale factor to correct BEINT, Usually 1.0.</td>
</tr>
<tr>
<td>BETA</td>
<td>Used in recoil factor calculation, ( =2h\gamma/mc ).</td>
</tr>
<tr>
<td>C</td>
<td>Temperature factor for electron distribution, it is always equal to 0.0.</td>
</tr>
<tr>
<td>COMPOS</td>
<td>Composition identification, 72 Hollerith.</td>
</tr>
<tr>
<td>CORR</td>
<td>Correction to be applied to the intensity data.</td>
</tr>
<tr>
<td>D</td>
<td>Temperature factor for the molecular bonds.</td>
</tr>
<tr>
<td>DELR</td>
<td>Interval on radial distribution curve.</td>
</tr>
<tr>
<td>DELSTO</td>
<td>Interpolation interval for intensity and scattering factor curves, also the interval for the integration routines.</td>
</tr>
<tr>
<td>DIFDIS</td>
<td>Difference distribution, ( =4\pi r^2(\tau(r)-r_0) ).</td>
</tr>
<tr>
<td>EXPSUM</td>
<td>Value of integrate function for the experimental intensity curve.</td>
</tr>
<tr>
<td>FAKE</td>
<td>Dummy so the 1620 cards can be read.</td>
</tr>
<tr>
<td>FINDEP</td>
<td>Independent scattering curve.</td>
</tr>
<tr>
<td>GAMMA</td>
<td>Normalization factor for atomic distribution.</td>
</tr>
<tr>
<td>GAMMA1</td>
<td>External normalization factor for atomic distribution.</td>
</tr>
<tr>
<td>I</td>
<td>Running index for various arrays.</td>
</tr>
<tr>
<td>IGAMMAL</td>
<td>The check whether GAMMA should equal ALPHA.</td>
</tr>
<tr>
<td>IGO1ON</td>
<td>If switch names to control exit points.</td>
</tr>
<tr>
<td>IGO2ON</td>
<td>&quot; &quot; &quot; &quot; &quot; &quot;</td>
</tr>
<tr>
<td>IGO3ON</td>
<td>&quot; &quot; &quot; &quot; &quot; &quot;</td>
</tr>
<tr>
<td>IGO4ON</td>
<td>&quot; &quot; &quot; &quot; &quot; &quot;</td>
</tr>
<tr>
<td>IGO5ON</td>
<td>&quot; &quot; &quot; &quot; &quot; &quot;</td>
</tr>
<tr>
<td>Code</td>
<td>Description</td>
</tr>
<tr>
<td>------</td>
<td>-------------</td>
</tr>
<tr>
<td>INT01</td>
<td>If switch name to control entry point.</td>
</tr>
<tr>
<td>INT02</td>
<td>Fourier inversion entry point.</td>
</tr>
<tr>
<td>INT04</td>
<td>Fourier inversion subroutine.</td>
</tr>
<tr>
<td>INT05</td>
<td>Fourier inversion subroutine.</td>
</tr>
<tr>
<td>INT06</td>
<td>Fourier inversion subroutine.</td>
</tr>
<tr>
<td>IPNCH1</td>
<td>If switch name to control punching.</td>
</tr>
<tr>
<td>IPNCH4</td>
<td>Interpolated curves.</td>
</tr>
<tr>
<td>IPNCH5</td>
<td>Interpolated curves.</td>
</tr>
<tr>
<td>IPNCH6</td>
<td>Interpolated curves.</td>
</tr>
<tr>
<td>IPRNT1</td>
<td>If switch name to control printing.</td>
</tr>
<tr>
<td>IPRNT2</td>
<td>Integrate function with integrand OVRLPI.</td>
</tr>
<tr>
<td>IPRNT3</td>
<td>Times temperature factor.</td>
</tr>
<tr>
<td>IPRNT4</td>
<td>Times temperature factor.</td>
</tr>
<tr>
<td>IPRNT5</td>
<td>Times temperature factor.</td>
</tr>
<tr>
<td>IPRNT6</td>
<td>Times temperature factor.</td>
</tr>
<tr>
<td>MAXP</td>
<td>Maximum number of cards, P scattering factors.</td>
</tr>
<tr>
<td>MAXQ</td>
<td>Maximum index of radial distribution curve.</td>
</tr>
<tr>
<td>MAXR</td>
<td>Maximum index of radial distribution curve.</td>
</tr>
<tr>
<td>MAXSTI</td>
<td>Fourier inversion subroutine.</td>
</tr>
<tr>
<td>MAXSTO</td>
<td>Fourier inversion subroutine.</td>
</tr>
<tr>
<td>MINR</td>
<td>Lower index of radial distribution curve, usually 1.</td>
</tr>
<tr>
<td>MINSTI</td>
<td>Fourier inversion subroutine.</td>
</tr>
<tr>
<td>MINSTO</td>
<td>Fourier inversion subroutine.</td>
</tr>
<tr>
<td>MXBE</td>
<td>Maximum number of beryllium intensity cards.</td>
</tr>
<tr>
<td>MXINT</td>
<td>Interpolated cards.</td>
</tr>
<tr>
<td>MXVOLC</td>
<td>Interpolated cards.</td>
</tr>
<tr>
<td>NCHECK</td>
<td>Check for even number of integration intervals.</td>
</tr>
<tr>
<td>NEOR</td>
<td>End of run designation, contains 9 in column 72.</td>
</tr>
<tr>
<td>NORMEX</td>
<td>Check for external normalization factors.</td>
</tr>
<tr>
<td>OVLPMS</td>
<td>Value of integrate function with integrand OVRLPI.</td>
</tr>
<tr>
<td>OVRLPI</td>
<td>Overlap integrals for bonded atoms.</td>
</tr>
<tr>
<td>OVRLPT</td>
<td>Overlap integrals for bonded atoms.</td>
</tr>
<tr>
<td>PBFRAC</td>
<td>Fraction of P type bonds.</td>
</tr>
<tr>
<td>PBOND</td>
<td>Bond distance between P type atoms.</td>
</tr>
<tr>
<td>PCOH</td>
<td>P type coherent scattering factors.</td>
</tr>
<tr>
<td>PCOHI</td>
<td>Interpolated factors.</td>
</tr>
<tr>
<td>PFRAC</td>
<td>Mole fraction of P type atoms.</td>
</tr>
<tr>
<td>PHI</td>
<td>Scattering angle.</td>
</tr>
<tr>
<td>PHIBC</td>
<td>Beryllium cutoff angle.</td>
</tr>
<tr>
<td>PHIBE</td>
<td>Scattering angle for beryllium scattering.</td>
</tr>
<tr>
<td>PHIV</td>
<td>Volume correction.</td>
</tr>
<tr>
<td>PI</td>
<td>3.1415927</td>
</tr>
<tr>
<td>PINC</td>
<td>P type incoherent scattering factors.</td>
</tr>
<tr>
<td>PINCI</td>
<td>Independent factors.</td>
</tr>
<tr>
<td>PINDEP</td>
<td>Independent factors.</td>
</tr>
<tr>
<td>POLX</td>
<td>Polarization factor for crystal monochromator.</td>
</tr>
</tbody>
</table>
**TABLE 5—Continued**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PROBNO</td>
<td>Name of problem, 72 Hollerith.</td>
</tr>
<tr>
<td>PSTOL</td>
<td>sinθ/λ, P type scattering factors.</td>
</tr>
<tr>
<td>PZ</td>
<td>Charge of P type atoms.</td>
</tr>
<tr>
<td>QBFRAC</td>
<td>Fraction of Q type bonds.</td>
</tr>
<tr>
<td>QCOH</td>
<td>Q type coherent scattering factors.</td>
</tr>
<tr>
<td>QCRI</td>
<td>&quot; &quot; &quot; &quot; , interpolated.</td>
</tr>
<tr>
<td>QCONST</td>
<td>Bond distance between Q type atoms.</td>
</tr>
<tr>
<td>QFRAC</td>
<td>Mole fraction of Q type atoms.</td>
</tr>
<tr>
<td>QINC</td>
<td>Q type incoherent scattering factors.</td>
</tr>
<tr>
<td>QINC1</td>
<td>&quot; &quot; &quot; &quot; , interpolated.</td>
</tr>
<tr>
<td>QINDEP</td>
<td>&quot; independent &quot;</td>
</tr>
<tr>
<td>QPBFRAC</td>
<td>Fraction of QP type bonds.</td>
</tr>
<tr>
<td>QPBOND</td>
<td>Bond distance between Q and P type atoms.</td>
</tr>
<tr>
<td>QSTOL</td>
<td>sinθ/λ, Q type scattering factors.</td>
</tr>
<tr>
<td>QZ</td>
<td>Charge of Q type atoms.</td>
</tr>
<tr>
<td>RADDIS</td>
<td>Atomic radial distribution.</td>
</tr>
<tr>
<td>RECFAC</td>
<td>Recoil factor.</td>
</tr>
<tr>
<td>RI</td>
<td>Independent variable, radial distribution function.</td>
</tr>
<tr>
<td>RO</td>
<td>Lower limit of the radial distribution curves, usually 0.0.</td>
</tr>
<tr>
<td>S</td>
<td>4π sinθ/λ</td>
</tr>
<tr>
<td>SCFAC</td>
<td>Scale factor for uncorrected intensity, usually 1.0.</td>
</tr>
<tr>
<td>SIGMA</td>
<td>Electronic radial distribution function.</td>
</tr>
<tr>
<td>SIGMA0</td>
<td>4πr^2ADNSTY times Z^2</td>
</tr>
<tr>
<td>SIGMA1</td>
<td>SIGMA/RI</td>
</tr>
<tr>
<td>SIGMA2</td>
<td>SIGMA1/RI^2</td>
</tr>
<tr>
<td>SIGMA3</td>
<td>SIGMA1/RI</td>
</tr>
<tr>
<td>SIGMA4</td>
<td>SIGMA1/RI^2</td>
</tr>
<tr>
<td>STOL</td>
<td>sinθ/λ</td>
</tr>
<tr>
<td>STOL1</td>
<td>STOL, interpolated.</td>
</tr>
<tr>
<td>STOLO</td>
<td>Initial value for interpolation subroutine, usually 0.0.</td>
</tr>
<tr>
<td>SYMDIS</td>
<td>Symmetric radial distribution function.</td>
</tr>
<tr>
<td>TRNSM</td>
<td>Transmission of sample.</td>
</tr>
<tr>
<td>VOLC</td>
<td>Volume correction for scattering angles less than the beryllium cutoff angle.</td>
</tr>
<tr>
<td>WVLTT</td>
<td>Wavelength in angstroms.</td>
</tr>
<tr>
<td>X</td>
<td>Independent variable for the point of interpolation.</td>
</tr>
<tr>
<td>XINTA</td>
<td>Intensity to be Fourier inverted for the atomic distribution.</td>
</tr>
<tr>
<td>XINTL</td>
<td>Intensity to be Fourier inverted for the inter-atomic distribution.</td>
</tr>
<tr>
<td>SINTM</td>
<td>Intensity to be Fourier inverted for the inter-atomic distribution.</td>
</tr>
</tbody>
</table>
TABLE 5--Continued

XPRINT  X-ray intensity, input intensity data.
XPRINTI Corrected intensity, interpolated.
ZBAR    Average charge per atom.

Interpolate Function

J   Running index to identify the point of interpolation.
K   Running index along the six points used for interpolation.
KF  Last of the six points of the interpolation.
KI  First " " " " " "
KIA Re-identification of the running index for a given K and L.
L   After K is fixed, L is a running index from 1 to 6 to determine the contribution from the fixed K.
MXL2 Upper limit of J.
YDMR Contribution to the denominator of YK.
YNMR " " " numerator of YK.
YK  " " " dependent variable at K.
Y   Interpolated value.

Integrate Function

MAXS Upper limit during the integration.
MINS Lower limit during the integration.
OFAC Initial factor, first term in Simpson's integration.
SEFAC Sum of even factors.
SOFAC Sum of odd factors.
S   Independent variable.
TFAC Terminal factor.

Interpolate Subroutine

None.

Integrate Subroutine

Essentially, this subroutine has the same names as the Integrate Function.
## TABLE 6
Stacking arrangement of the Input Data Cards

<table>
<thead>
<tr>
<th>Order</th>
<th>Format</th>
<th>Variable Names</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12A6</td>
<td>PROBNO</td>
</tr>
<tr>
<td>2</td>
<td>19I2</td>
<td>INTO1, INTO2, IPRNT1, IPNCH1, IGO1ON, IPRNT2, IGO2ON, IPRNT3, IGO3ON, INTO4, INTO6, IPRNT4, IPNCH4, IGO4ON, IPRNT5, IPNCH5, IGO5ON, IPRNT6, IPNCH6</td>
</tr>
<tr>
<td>3*</td>
<td>7F10.6</td>
<td>PHIBC, WVLIT, POLX, TRNSM, BKGND, SCFAC, BESCA</td>
</tr>
<tr>
<td>4*</td>
<td>I10</td>
<td>MXINT</td>
</tr>
<tr>
<td>5*</td>
<td>1XF3.1, 36XF9.4</td>
<td>PHI, XRINT</td>
</tr>
<tr>
<td>6*</td>
<td>I10</td>
<td>MXBE</td>
</tr>
<tr>
<td>7*</td>
<td>1XF3.1, 36XF9.4</td>
<td>PHIBE, BEINT</td>
</tr>
<tr>
<td>8*</td>
<td>I10</td>
<td>MXVOLC</td>
</tr>
<tr>
<td>9*</td>
<td>F10.6, F10.8</td>
<td>PHIV, VOLC</td>
</tr>
<tr>
<td>10</td>
<td>12A6</td>
<td>COMPOS</td>
</tr>
<tr>
<td>111</td>
<td>2I10, 2F10.6</td>
<td>MINSTO, MAXSTO, DELSTO, STOLO</td>
</tr>
<tr>
<td>12</td>
<td>4I10, 2F10.6</td>
<td>MINSTI, MAXSTI, MINR, MAXR, DELR, RO</td>
</tr>
<tr>
<td>13</td>
<td>3F10.6</td>
<td>ADNSTY, A, WVLT</td>
</tr>
<tr>
<td>14</td>
<td>2I10, 2F10.6</td>
<td>NORMEX, IGAMAL, ALPHA1, GAMMA1</td>
</tr>
<tr>
<td>15</td>
<td>4F10.6</td>
<td>QZ, QFRAC, PZ, PFRAC</td>
</tr>
<tr>
<td>16</td>
<td>7F10.6</td>
<td>QBFRAC, QBOND, PBFRAC, PBOND, QPBFRAC, QPBOND, D</td>
</tr>
</tbody>
</table>
TABLE 6--Continued

<table>
<thead>
<tr>
<th>Order</th>
<th>Format</th>
<th>Variable Names</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>I10</td>
<td>MAXQ</td>
</tr>
<tr>
<td>18</td>
<td>3F10.6</td>
<td>QSTOL, QCOH, QINC</td>
</tr>
<tr>
<td>19**</td>
<td>I10</td>
<td>MAXP</td>
</tr>
<tr>
<td>20**</td>
<td>3F10.6</td>
<td>PSTOL, PCOH, PINC</td>
</tr>
<tr>
<td>21</td>
<td>71X11</td>
<td>NEOR</td>
</tr>
</tbody>
</table>

*Omit these cards if entry is through point 2. In their place put,

| 110   |         | MXINT         |
| 4E14.6|         | FAKE, FAKE, STOL, XRINT |

**Omit these cards if PFRAC = 0.0.
SOURCE PROGRAM FOR XRAY DIFFRACTION ANALYSIS OF LIQUIDS CONTAINING ONE OR TWO ELEMENTS  
MODEL T DESIGNED SEPTEMBER 10, 1962 XRAY LAB PHYSICS OSU 

COMM   PHI, XRINT, PHIBE, BEINT, PHIV, VOLC, CORR, STOL, QSTOL,  
1   QCOH, QINC, PSTOL, PCOH, PINC, STOLI, XRINTI, QINDEP,  
2   PINDEP, FINDEP, OVRILPI, XINTM, RI, SIGMAM, SGMAM1, SGMAM2  
3   , XINTL, SGML, SGMAL1, SGML2, XINTA, DIFDIS, RADDIS,  
4   SYMDIS, AVEDIS, PROBNO, QCOHI, QINCI, PCOHI, PINCI,  
5   WVLT, MXINT, MXBE, MXVOLC, ADNSTY, A, X, MINSTO, MAXSTO,  
6   DELSTO, STOLO, R0, MINR, MAXR, DELR, MAXQ, MAXP, C,  
7   AINDEP, AXRINT, AINDSM, AXPSUM, OVRLPT, MINSTI, MAXSTI  
DIMENSION PROBNO(12), PHI(200), XRINT(200), PHIBE(200), BEINT(200)  
1   * PHIV(200), VOLC(200), CORR(200), STOL(200), QSTOL(200),  
2   QCOH(100), QINC(100), PSTOL(100), PCOH(100), PINC(100),  
3   STOLI(500), XRINTI(500), QINDEP(500), PINDEP(500),  
4   FINDEP(500), OVRILPI(500), XINTM(500), RI(500),  
5   SIGMAM(500), SGMAM1(500), SGMAM2(500), XINTL(500),  
6   SIGMAL(500), SGML(500), SGML2(500), XINTA(500),  
7   DIFDIS(500), RADDIS(500), SYMDIS(500), AVEDIS(500),  
8   COMPOS(12), QCOHI(500), QINCI(500), PCOHI(500),  
9   PINCI(500), SIGMA(500), SIGMA1(500), SIGMA2(500)  
DIMENSION QPCOH2(500), AINDEP(500), AXRINT(500), OVRLPT(500),  
1   TINDOV(500), SIGMA0(500)  

1 FORMAT (12A6)  
2 FORMAT (1H1/ /20X12A6)  
3 FORMAT (1912)  
4 FORMAT (1H09X8THDIAGNOSTIC, 1=INTENSITY CORRECTION, 2=INTERPOLATE  
1 INTENSITY, 3=INDEPENDENT SCATTERING/*10X99H4=INTERATOMIC ELECTRON  
2 DISTRIBUTION, 5=INTERMOLECULAR ELECTRON DISTRIBUTION, 6=ATOMIC DI  
3 STRIBUTION, 10X11H1=YES, 0=NO)  
5 FORMAT (24XH1,13XH2,13XH3,13XH4,13XH5,13XH6)  
6 FORMAT (20X5HENTER13,6X5HENTER13,6X5HPRINT13,6X2HD03XI3,6X5HPRINT1
13:6X2HD03X13)
7 FORMAT (20X5HPRINT13,6X5HPRINT13,6X5HGO ONI3,6X5HPRINT13,6X5HPUNCH
1I3,6X5HPRINT13)
8 FORMAT (20X5HPUNCH13,6X5HGO ONI3,20X5HPUNCH13,6X5HGO ONI3,6X5HPUNC
1HI3)
9 FORMAT (20X5HGO ONI3, 34X5HGO ONI3)
10 FORMAT (10X51HERROR IN POINT OF ENTRY. STOP PROBLEM. GO TO EXIT. )

C

PHIRF(Z)=(Z*0.995960+0.016)*0.0174533

100 READ INPUT TAPE 5, 1, PROBNO
WRITE OUTPUT TAPE 6, 2, PROBNO
READ INPUT TAPE 5, 3, INTO1, INTO2, IPRNT1, IPNCH1, IGO1ON,
1 IPRNT2, IGO2ON, IPRNT3, IGO3ON, INTO4, INTO6, IPRNT4, IPNCH4,
2 IGO4ON, IPRNT5, IPNCH5, IGO5ON, IPRNT6, IPNCH6
WRITE OUTPUT TAPE 6, 4
WRITE OUTPUT TAPE 6, 5
WRITE OUTPUT TAPE 6, 6, INTO1, INTO2, IPRNT3, INTO4, IPRNT5, INTO6
WRITE OUTPUT TAPE 6, 7, IPRNT1, IPRNT2, IGO3ON, IPRNT4, IPNCH5,
1IPRNT6
WRITE OUTPUT TAPE 6, 8, IPNCH1, IGO2ON, IPNCH4, IGO5ON, IPNCH6
WRITE OUTPUT TAPE 6, 9, IGO1ON, IGO4ON

C

IF BOX, THE IF BOX CONTROLS THE PROGRAM FLOW ACCORDING TO THE IF
CARD DIRECTIONS.

C

IF ENTRANCE.
IF (INT01-INT02) 1001, 1000, 1001
1000 WRITE OUTPUT TAPE 6, 10
 GO TO 999
1001 IF (INT01-1) 1002, 111, 1002
1002 IF (INT02-1) 999, 131, 999
C IF COMMANDS AFTER INTENSITY CORRECTIONS
1003 IF (IPRNT1-1) 1004, 119, 1004
1004 IF (IPNCH1-1) 1005, 121, 1005
1005 IF (IGO1ON-1) 999, 132, 999
C IF COMMANDS AFTER INTENSITY INTERPOLATED
1006 IF (IGO2ON-1) 1007, 143, 1007
1007 IF (IPRNT2-1) 999, 142, 999
   IF COMMANDS AFTER INDEPENDENT SCATTERING
1008 IF (IPRNT3-1) 149, 153, 149
1009 IF (IGO3ON-1) 999, 1012, 999
   IF COMMANDS FOR RADIAL DISTRIBUTION CALCULATION. 4=INTERATOMIC,
   5=INTERMOLECULAR, 6=ATOMIC
1012 IF (INTO4-1) 1013, 201, 1013
1013 IF (INTO6-1) 999, 211, 999
1014 IF (IPRNT4-1) 1015, 203, 1015
1015 IF (IPNCH4-1) 1016, 204, 1016
1016 IF (IGO4ON-1) 1013, 206, 1013
1017 IF (IPRNT5-1) 1018, 208, 1018
1018 IF (IPNCH5-1) 1019, 209, 1019
1019 IF (IGO5ON-1) 999, 211, 999
1020 IF (IPRNT6-1) 1021, 212, 1021
1021 IF (IPNCH6-1) 999, 213, 999
   START INTENSITY CORRECTION CALCULATIONS
   11 FORMAT (7F10.6)
12 FORMAT (I10)
13 FORMAT (1XF3.1, 36XF9.4)
14 FORMAT (F10.6, F10.8)
111 READ INPUT TAPE 5, 11, PHIBC, VWLT, POLX, TRNSM, BKGND, SCFAC,
1     BESCA
READ INPUT TAPE 5, 12, MXINT
READ INPUT TAPE 5, 13, (PHI(I), XRINT(I), I=1, MXINT)
READ INPUT TAPE 5, 12, MXBE
READ INPUT TAPE 5, 13, (PHIBE(I), BEINT(I), I=1, MXBE)
READ INPUT TAPE 5, 12, MXVOLC
READ INPUT TAPE 5, 14, (PHIV(I), VOLC(I), I=1, MXVOLC)

DO 115 I=1, MXINT
X=PHI(I)
IF (PHI(I)-PHIBC) < 112, 113, 113
112 XRINT(I)=XRINT(I)-BKGD-TRNSM*BESCA*(POLATE(PHIBE, BEINT, MXBE,X)
1 -BKGD)
   CORR(I)=POLATE(PHIV, VOLC, MXVOLC, X)/(1.0+POLX*(COSF(PHIRF(X))
1**2))
   GO TO 114
113 XRINT(I)=XRINT(I)-BKGD
   CORR(I)=SINF(PHIRF(X))/(1.0+POLX*(COSF(PHIRF(X))**2))
114 XRINT(I)=XRINT(I)*CORR(I)*SCFAC
115 STOL(I)=SINF(PHIRF(X)/2.0)/WVLT

THE FOLLOWING PUNCH FORMAT FOLLOWS 1620 PUNCH FORMAT
15 FORMAT (4E14.7,16X4HI,C..I4)
16 FORMAT (1H1//40X33HOUTPUT OF INTENSITY CORRECTION//25X3HPHI13X9
   1INTENSITY9X10HSINE THE1A8X9HCORRECTED/41X10HCORRECTION8X10HOVER L
   2AMDA8X9HINTENSITY//25X3HPHI16X4HCORR14X4HSTOL13X5HXINT)
17 FORMAT (50(20XE14.8, 3E18.8/). 1H1///25X3HPHI16X4HCORR14X4HSTOL13
   1X5HXINT)
   GO TO 1003
119 WRITE OUTPUT TAPE 6, 16
   WRITE OUTPUT TAPE 6, 17, (PHI(I), CORR(I), STOL(I), XRINT(I), I=1
   1MXINT)
120 GO TO 1004
121 WRITE OUTPUT TAPE 7, 15, (PHI(I), CORR(I), STOL(I), XRINT(I), I,
   1 I=1, MXINT)
122 GO TO 1005

INTERPOLATION OF INTENSITY DATA
18 FORMAT (I10)
19 FORMAT (4E14.6)
20 FORMAT (12A6)
21 FORMAT (1H1//20X12A6//)
22 FORMAT (2I10, 2F10.5)
61 FORMAT (4I10,2F10.5)
23 FORMAT (20X2HQZ5X1H=E14.6,8X2HPZ5X1H=E14.6/20X5HQFRAC2X1H=E14.6,
1 8X5HPFRAC2X1H=E14.6/20X5HQBOND2X1H=E14.6,8X5HPBOND2X1H=E14.6,8X6
2HQPBOND1X1H=E14.6/20X6HQFRAC1X1H=E14.6,8X6HPFRAC1X1H=E14.6,8X6HQBOND2X1H=E14.6
3PBFRAC1X1H=E14.6//20X43HTEMPERATURE FACTOR FOR MOLECULAR BONDS. D =
4E14.7// 20X43H AVERAGE ATOMIC NUMBER DENSITY. ADNSTY = E14.7/
5 20X43HTEMPERATURE FACTOR. FOURIER INVERSION A = E14.7/
6 20X43HWAVELENGTH OF RADIATION WVLT = E14.7)

24 FORMAT (4F10.6)
25 FORMAT (3F10.6)
26 FORMAT (7F10.6)
27 FORMAT (I10)
131 READ INPUT TAPE 5. 18. MX I  NT
READ INPUT TAPE 5. 19. (FAKE, FAKE, STOL(I), XRINT(I), I=1, MXINT)
132 READ INPUT TAPE 5, 20, COMPOS
WRITE OUTPUT TAPE 6, 21, COMPOS
READ INPUT TAPE 5, 22, MINSTO, MAXSTO, DELSTO, STOLO
READ INPUT TAPE 5, 23, MINSTI, MAXSTI, MINR, MAXR, DELR, ROC
READ INPUT TAPE 5, 24, ADNSTY, A, WVLT
READ INPUT TAPE 5, 25, NORMEX, IGAMAL, ALPHA1, GAMMA1
READ INPUT TAPE 5, 26, QZ, QFRAC, PZ, PFRAC
READ INPUT TAPE 5, 27, OBFRAC, QBOND, PBFRAC, PBOND, OPBFRC,
1 OPBOND, D
WRITE OUTPUT TAPE 6, 23, QZ, PZ, QFRAC, PFRAC, QBOND, PBOND,
1 QPBOND, QFRAC, PFRAC, OPBFRC, PBOND, D, ADNSTY, A, WVLT
READ INPUT TAPE 5, 28, MAXQ
READ INPUT TAPE 5, 29, (QSTOL(I), QC0H(I), QINC(I), I=1, MAXQ)
IF (QFRAC-0.0) 133, 141, 133
133 READ INPUT TAPE 5, 27, MAXP
READ INPUT TAPE 5, 25, (PSTOL(I), PCOH(I), PINC(I), I=1, MAXP)
29 FORMAT (1HO/5OX22HINTERPOLATED INTENSITY)
30 FORMAT (1HO/3X5HSTOLI,6X6HXINTI,4(7X5HSTOLI,6X6HXINTI))
31 FORMAT (5O15(2X7.5,E15.8)),1H1///4X5HSTOLI,6X6HXINTI,4(7X5HSTOL
1I,6X6HXINTI))
141 CALL POLAT(KSTOL, XRINT, MXINT, STOLO, STOLI, XRINTI, MAXSTO,
1 DELSTO)
GO TO 1006
142 WRITE OUTPUT TAPE 6, 29
WRITE OUTPUT TAPE 6*30
WRITE OUTPUT TAPE 6*31 (STOL(I), XRINT(I), I=1, MAXSTO)
GO TO 999
143 CALL POLAT1(QSTOL, QCOH, MAXQ, STOL, STOL, QCOHI, MAXSTO, DELSTO
1)
CALL POLAT1(QSTOL, QINC, MAXQ, STOL, STOL, QINCI, MAXSTO, DELSTO
1)
IF (PFRAC=0.0) 144, 145, 144
144 CALL POLAT1(PSTOL, PCOH, MAXP, STOL, STOL, PCOH, MAXSTO, DELSTO
1)
CALL POLAT1(PSTOL, PINC, MAXP, STOL, STOL, PINC, MAXSTO, DELSTO
1)
GO TO 147
145 DO 146 I=1, MAXSTO
PCOH(I)=0.0
146 PINC(I)=0.0
147 PI=3.1415927
BETA=2.0*0.662377*WVLT/(9.10721*2.99790)
DO 148 I=1, MAXSTO
RECFAC=1.0/((1.0+BETA*(STOL(I)**2))**3)
QPCOH2(I)=QFRAC*(QCOHI(I)**2)+PFRAC*(PCOH(I)**2)
QINDEP(I)=QCOHI(I)**2+RECFAC*QINCI(I)
PINDEP(I)=PCOH(I)**2+RECFAC*PINCI(I)
FINDEP(I)=QFRAC*QINDEP(I)+PFRAC*PINDEP(I)
AINDFP(I)=FINDEP(I)/QPCOH2(I)
S=4.0*PI*STOL(I)
OVRLP(I)=(QBFRC*((QCOHI(I)**2)*SINF(QBOND*S)/(QBOND*S))
1 +PBFRC*((PCOH(I)**2)*SINF(PBOND*S)/(PBOND*S))
2 +QBFRC*((QCOHI(I)*PCOH(I)**2)*SINF(QPBOND*S)/(QPBOND*S))
3 *EXP(-D*(S**2))
TND0V(I)=OVRLP(I)+FINDEP(I)
AXRINT(I)=XRINT(I)/QPCOH2(I)
148 CONTINUE
GO TO 1008
36 FORMAT (1H1//45X30HTHEORETICAL SCATTERING FACTORS/1H012X10HSINE T
1HETA8X11HINDEPENDENT9X11HINDEPENDENT9X12HTOTAL INDEP.8X10HINDEP. A
WRITE OUTPUT TAPE 6, 36
WRITE OUTPUT TAPE 6, 37, (STOL(I), QINDEP(I), PINDEP(I),
1 FINDEP(I), TINDOV(I), I = 5, MAXSTO, 5)

CHECK ON INTEGRATION INTERVAL. THERE MUST BE AN EVEN NUMBER OF
INTERVALS.

WRITE OUTPUT TAPE 6, 28
GO TO 999

WRITE OUTPUT TAPE 6, 32
WRITE OUTPUT TAPE 6, 33, (STOL(I), QINDEP(I), PINDEP(I),
1 FINDEP(I), TINDOV(I), I = 5, MAXSTO, 5)

CHECK ON INTEGRATION INTERVAL. THERE MUST BE AN EVEN NUMBER OF
INTERVALS.

WRITE OUTPUT TAPE 6, 28
GO TO 999

WRITE OUTPUT TAPE 6, 32
WRITE OUTPUT TAPE 6, 33, (STOL(I), QINDEP(I), PINDEP(I),
1 FINDEP(I), TINDOV(I), I = 5, MAXSTO, 5)

CHECK ON INTEGRATION INTERVAL. THERE MUST BE AN EVEN NUMBER OF
INTERVALS.

WRITE OUTPUT TAPE 6, 28
GO TO 999

WRITE OUTPUT TAPE 6, 32
WRITE OUTPUT TAPE 6, 33, (STOL(I), QINDEP(I), PINDEP(I),
1 FINDEP(I), TINDOV(I), I = 5, MAXSTO, 5)

CHECK ON INTEGRATION INTERVAL. THERE MUST BE AN EVEN NUMBER OF
INTERVALS.

WRITE OUTPUT TAPE 6, 28
GO TO 999

WRITE OUTPUT TAPE 6, 32
WRITE OUTPUT TAPE 6, 33, (STOL(I), QINDEP(I), PINDEP(I),
1 FINDEP(I), TINDOV(I), I = 5, MAXSTO, 5)

CHECK ON INTEGRATION INTERVAL. THERE MUST BE AN EVEN NUMBER OF
INTERVALS.

WRITE OUTPUT TAPE 6, 28
GO TO 999

WRITE OUTPUT TAPE 6, 32
WRITE OUTPUT TAPE 6, 33, (STOL(I), QINDEP(I), PINDEP(I),
1 FINDEP(I), TINDOV(I), I = 5, MAXSTO, 5)

CHECK ON INTEGRATION INTERVAL. THERE MUST BE AN EVEN NUMBER OF
INTERVALS.

WRITE OUTPUT TAPE 6, 28
GO TO 999

WRITE OUTPUT TAPE 6, 32
WRITE OUTPUT TAPE 6, 33, (STOL(I), QINDEP(I), PINDEP(I),
1 FINDEP(I), TINDOV(I), I = 5, MAXSTO, 5)

CHECK ON INTEGRATION INTERVAL. THERE MUST BE AN EVEN NUMBER OF
INTERVALS.

WRITE OUTPUT TAPE 6, 28
GO TO 999

WRITE OUTPUT TAPE 6, 32
WRITE OUTPUT TAPE 6, 33, (STOL(I), QINDEP(I), PINDEP(I),
1 FINDEP(I), TINDOV(I), I = 5, MAXSTO, 5)

CHECK ON INTEGRATION INTERVAL. THERE MUST BE AN EVEN NUMBER OF
INTERVALS.

WRITE OUTPUT TAPE 6, 28
GO TO 999

WRITE OUTPUT TAPE 6, 32
WRITE OUTPUT TAPE 6, 33, (STOL(I), QINDEP(I), PINDEP(I),
1 FINDEP(I), TINDOV(I), I = 5, MAXSTO, 5)

CHECK ON INTEGRATION INTERVAL. THERE MUST BE AN EVEN NUMBER OF
INTERVALS.

WRITE OUTPUT TAPE 6, 28
GO TO 999

WRITE OUTPUT TAPE 6, 32
WRITE OUTPUT TAPE 6, 33, (STOL(I), QINDEP(I), PINDEP(I),
1 FINDEP(I), TINDOV(I), I = 5, MAXSTO, 5)

CHECK ON INTEGRATION INTERVAL. THERE MUST BE AN EVEN NUMBER OF
INTERVALS.

WRITE OUTPUT TAPE 6, 28
GO TO 999

WRITE OUTPUT TAPE 6, 32
WRITE OUTPUT TAPE 6, 33, (STOL(I), QINDEP(I), PINDEP(I),
1 FINDEP(I), TINDOV(I), I = 5, MAXSTO, 5)

CHECK ON INTEGRATION INTERVAL. THERE MUST BE AN EVEN NUMBER OF
INTERVALS.

WRITE OUTPUT TAPE 6, 28
GO TO 999

WRITE OUTPUT TAPE 6, 32
WRITE OUTPUT TAPE 6, 33, (STOL(I), QINDEP(I), PINDEP(I),
1 FINDEP(I), TINDOV(I), I = 5, MAXSTO, 5)

CHECK ON INTEGRATION INTERVAL. THERE MUST BE AN EVEN NUMBER OF
INTERVALS.

WRITE OUTPUT TAPE 6, 28
GO TO 999

WRITE OUTPUT TAPE 6, 32
WRITE OUTPUT TAPE 6, 33, (STOL(I), QINDEP(I), PINDEP(I),
1 FINDEP(I), TINDOV(I), I = 5, MAXSTO, 5)

CHECK ON INTEGRATION INTERVAL. THERE MUST BE AN EVEN NUMBER OF
INTERVALS.

WRITE OUTPUT TAPE 6, 28
GO TO 999

WRITE OUTPUT TAPE 6, 32
WRITE OUTPUT TAPE 6, 33, (STOL(I), QINDEP(I), PINDEP(I),
1 FINDEP(I), TINDOV(I), I = 5, MAXSTO, 5)

CHECK ON INTEGRATION INTERVAL. THERE MUST BE AN EVEN NUMBER OF
INTERVALS.

WRITE OUTPUT TAPE 6, 28
GO TO 999

WRITE OUTPUT TAPE 6, 32
WRITE OUTPUT TAPE 6, 33, (STOL(I), QINDEP(I), PINDEP(I),
1 FINDEP(I), TINDOV(I), I = 5, MAXSTO, 5)

CHECK ON INTEGRATION INTERVAL. THERE MUST BE AN EVEN NUMBER OF
INTERVALS.

WRITE OUTPUT TAPE 6, 28
GO TO 999

WRITE OUTPUT TAPE 6, 32
WRITE OUTPUT TAPE 6, 33, (STOL(I), QINDEP(I), PINDEP(I),
1 FINDEP(I), TINDOV(I), I = 5, MAXSTO, 5)

CHECK ON INTEGRATION INTERVAL. THERE MUST BE AN EVEN NUMBER OF
INTERVALS.
EXPSUM = SUM1(STOLI, XRINTI, MINSTO, MAXSTO, DELSTO)
FINDSM = SUM1(STOLI, FINDEP, MINSTO, MAXSTO, DELSTO)
OVLPSM = SUM1(STOLI, OVRPLI, MINSTO, MAXSTO, DELSTO)
ALPHA = (FINDSM + OVLPSM - 2.0*(PI**2)*ADNSTY*(ZBAR**2))/EXPSUM

FORMAT (1H019X8HEXPSUM =E15.7/20X8HFINDSM =E15.7/20X8HOVLPSM =E15.7/20X4HZBAR =E15.7/20X5HALPHA =E15.7)
WRITE OUTPUT TAPE 6, 33, EXPSUM, FINDSM, OVLPSM, ZBAR, ALPHA

IF (IGAMAL =-1) 162, 161, 162
GAMMA = ALPHA
GO TO 165

IF (GAMMA = 0.0) 163, 164, 163
GAMMA = GAMMA
GO TO 165

AXPSUM = SUM1(STOLI, AXRINT, MINSTO, MAXSTO, DELSTO)
AINDSM = SUM1(STOLI, AINDEP, MINSTO, MAXSTO, DELSTO)
GAMMA = (AINDSM - 2.0*(PI**2)*ADNSTY)/AXPSUM

FORMAT (1H019X8HAXPSUM =E15.7/20X8HAINDSM =E15.7/20X5HGAMMA =E15.7)
WRITE OUTPUT TAPE 6, 64, AXPSUM, AINDSM, GAMMA

DO 166 I=1, MAXSTO
XINTA(I) = (GAMMA*XINTI(I) - FINDEP(I))/QPCOH2(I)
XRINTI(I) = ALPHA*XRINTI(I)
XINTM(I) = XRINTI(I) - FINDEP(I)
XINTL(I) = XRINTI(I) - TINDOV(I)

FORMAT (1H1///50X18HINTENSITY PRINTOUT/1H012X10HSINE THETA9X12HEXP EXPERIMENTAL7X12HINTENSITY IN8X14HINTENSITY LESS6X13HINTENSITY FOR13 2X10OVER LAMDA1X9HINTENSITY8X14HELECTRON UNITS6X13HMOLEC. CONTR.5 3X18HATOMIC RAD. DISTR.1X14HSTOLI15X6HRINTI14X5HXINTM15X5HXINT 4L15X5HXINTA)
34 FORMAT (50(5X5E20.7,/) ,1H1///15X5HSTOLI15X6HRINTI14X5HXINTM15X5H 1XINTL15X5HXINTA)
WRITE OUTPUT TAPE 6, 34
WRITE OUTPUT TAPE 6, 35, (STOLI(I), XRINTI(I), XINTM(I), XINTL(I),
XINTA(I), I=5, MAXSTO, 5)
GO TO 1009
INTERATOMIC FOURIER INVERSION

201 C=0.0
CALL FOUINV(STOLI, XINTM, MINSTI, MAXSTI, DELSTO, RO, MINR, MAXR, 1  DELR, C, RI, SIGMAM)
DO 202 I=MINR, MAXR
SIGMAO(I)=4.0*PI*(RI(I)**2)*ADNSTY*(ZBAR**2)
SIGMA(I)=SIGMAM(I)+SIGMAO(I)
SIGMA1(I)=SIGMA(I)/RI(I)
SIGMA2(I)=SIGMA1(I)/RI(I)
SGMAM1(I)=SIGMAM(I)/RI(I)
SGMAM2(I)=SGMAM1(I)/RI(I)
GO TO 1014
202 SIGMAM2(I)=SGMAM1(I)/RI(I)
GO TO 1014
38 FORMAT (1H1///40X42HELECTRON DENSITY DISTRIBUTION, INTERATOMIC//26 1X2HRI17X5HSIGMA15X6HSIGMA114X6HSGMAM1)
39 FORMAT (50(15X4E20.7,/),1H1///26X2HRI17X5HSIGMA15X6HSIGMA114X6HSGMAM1)
40 FORMAT (4E14.6,16X4H1.A,14)
50 FORMAT (1H1///30X63HSIGMAM IS THE DEPARTURE FROM THE AVERAGE ELECT 1RON DISTRIBUTION.//26X2HRI17X6HSIGMA14X6HSIGMA14X6HSGMAM2)
60 FORMAT (50(15X4E20.7,/),1H1///26X2HRI17X6HSIGMA14X6HSGMAM114X6HSGMAM2)
51 FORMAT (4E14.6, 16X4HIA-D,14)
203 WRITE OUTPUT TAPE 6, 38
WRITE OUTPUT TAPE 6, 39, (RI(I), SIGMA(I), SIGMA1(I), SIGMAO(I)), 1  I=MINR, MAXR
WRITE OUTPUT TAPE 6, 50
WRITE OUTPUT TAPE 6, 51, (RI(I), SIGMAM1(I), SGMAM1(I), SGMAM2(I)), 1  I=MINR, MAXR)
GO TO 1015
204 WRITE OUTPUT TAPE 7, 40, (RI(I), SIGMA(I), SIGMA1(I), SIGMAO(I)), I 1  I=MINR, MAXR
WRITE OUTPUT TAPE 7, 50, (RI(I), SIGMAM1(I), SGMAM1(I), SGMAM2(I)), 1  I, I=MINR, MAXR)
GO TO 1016
INTERMOLECULAR FOURIER INVERSION

206 C=0.0
CALL FOINV(STOLI, XINTL, MINSTI, MAXSTI, DELSTO, RO, MINR, MAXR,
1 DELR, C, RI, SIGMAL)
DO 207 I=MINR, MAXR
  SGMAL1(I)=SIGMAL(I)/RI(I)
207 SGMAL2(I)=SGMAL1(I)/RI(I)
GO TO 1017
41 FORMAT (1H1///40X45HELECTRON DENSITY DISTRIBUTION, INTERMOLECULAR/
  1/26X2HR117X6HSIGMAL14X6HSGMAL114X6HSIGMAL2)
42 FORMAT (50(15X4E20.7///),1H1///26X2HR117X6HSIGMAL14X6HSGMAL114X6HS
  1GMAL2)
208 WRITE OUTPUT TAPE 6* 41
43 FORMAT (4E14.6,16X4H.I.,14)
WRITE OUTPUT TAPE 6* 42, (RI(I), SIGMAL(I), SGMAL1(I), SGMAL2(I),
1 I=MINR, MAXR)
GO TO 1018
209 WRITE OUTPUT TAPE 7* 43, (RI(I), SIGMAL(I), SGMAL1(I), SGMAL2(I),
1 I, I=MINR, MAXR)
GO TO 1019

ATOMIC RADIAL DISTRIBUTION

211 CALL FOINV(STOLI, XINTA, MINSTI, MAXSTI, DELSTO, RO, MINR, MAXR,
1 DELR, A, RI, DIFDIS)
DO 214 I=MINR, MAXR
  AVEDIS(I)=4.0*PI*(RI(I)**2)*ADNSTY
  RADDIS(I)=DIFDIS(I)+AVEDIS(I)
214 SYMDIS(I)=RADDIS(I)/RI(I)
GO TO 1020
44 FORMAT (1H1///45X26HATOMIC RADIAL DISTRIBUTION//16X2HR117X6HAVEDIS
  114X6HDIFDIS14X6HSYMDIS14X6HRADDIS)
45 FORMAT (50(15X5E20.7///),1H1///16X2HR117X6HAVEDIS14X6HDIFDIS14X6HSY
  1MDIS14X6HRADDIS)
46 FORMAT (4E14.6,16X4HRADD,14)
212 WRITE OUTPUT TAPE 6, 44
WRITE OUTPUT TAPE 6, 45, (RI(I), AVEDIS(I), DIFDIS(I), SYMDIS(I),
1 RADDIS(I), I=MINR, MAXR)
GO TO 1021
213 WRITE OUTPUT TAPE 7, 46, (RKI), AVEDIS(I), SYMDIS(I), RADDIS(I),
1 I, I=MINR, MAXR)
47 FORMAT (71X11)
48 FORMAT (1H019X12A6)
49 FORMAT (20X20HEND OF THIS PROBLEM.)
999 DO 998 I=1, 2000
READ INPUT TAPE 5, 47, NEOR
IF (NEOR-9) 998, 997, 998
998 CONTINUE
997 WRITE OUTPUT TAPE 6, 48, PROBNO
WRITE OUTPUT TAPE 6, 49
GO TO 100
END

INTERPOLATION FUNCTION

FUNCTION POLATE(PHI, XRINT, MXINT, X)
COMMON PHI, XRINT, PHIBE, BEINT, PHIV, VOLC, CORR, STOL, QSTOL,
1 QC0H, QINC, PST0L, POC0H, PINC, STOLI, XRINTI, QINDEP,
2 PINDEP, FINDEP, OVR1PI, XINTM, RI, SIGMAM, SGMAM1, SGMAM2
3 XINTL, SIGMAI, SGMAL1, SGMAL2, XINTA, DIFDIS, RADDIS,
4 SYMDIS, AVEDIS, PROBNO, QC0HI, QINCI, PC0HI, PINCI,
5 WLT, MXINT, MXBE, MXV0LC, ADNSTY, A, X, MINSTO, MAXSTO,
6 DELSTO, ST0LO, RO, MINR, MAXR, DELR, MAXQ, MAXP, C,
7 AINDEP, AXINT, AXINDSM, AXPSUM, OVRLPT
DIMENSION PROBNO(12), PHI(200), XRINT(200), PHIBE(200), BEINT(200)
1 PHIV(200), VOLC(200), CORR(200), STOL(200), QSTOL(200),
2 QC0H(100), QINC(100), PST0L(100), POC0H(100), PINC(100),
3 ST0LI(500), XRINTI(500), QINDEP(500), PINDEP(500),
4 FINDEP(500), OVR1PI(500), XINTM(500), RI(500),
5 SIGMAI(500), SGMAL1(500), SGMAL2(500), XINTL(500),
SIGMA(500), SGMA1(500), SGMA2(500), XINTA(500),
DIFDIS(500), RADDIS(500), SYMDIS(500), AVEDIS(500),
COMPOS(12), QCOHI(500), QINCI(500), PCOH(500),
PQCI(500), SIGMA(500), SIGMA1(500), SIGMA2(500)
DIMENSION QPCOH2(500), AINDEP(500), AXINT(500), OVRLPT(500)

IF (PHI(3) - X) 111, 110, 116
Y = XRINT(3)
GO TO 130
MXL2 = MXINT - 2
IF (PHI(MXL2) - X) 117, 112, 113
Y = XRINT(MXL2)
GO TO 130
DO 115 J = 3, MXINT
IF (PHI(J) - X) 115, 114, 118
Y = XRINT(J)
GO TO 130
CONTINUE
KI = 1
KF = 6
GO TO 120
KI = MXINT - 5
KF = MXINT
GO TO 120
KI = J - 3
KF = J + 2
DO 123 K = KI, KF
YDMR = 1.0
YNMR = 1.0
DO 122 L = 1, 6
KIA = KI - 1 + L
IF (X - PHI(KIA)) 21, 20, 21
Y = XRINT(KIA)
GO TO 130
IF (KIA - K) 121, 122, 121
YNMR = YNMR*(X - PHI(KIA))
YDMR=YDMR*(PHI(K)-PHI(KIA))
122 CONTINUE
YK=YK+XINT(K)*YNMR/YDMR
123 CONTINUE
Y=YK
130 POLATE=Y
RETURN
END

C INTEGRATE FUNCTION

FUNCTION SUM1(STOLI, XRINTI, MINSTO, MAXSTO, DELSTO)
COMMON PHI, XRINT, PHIBE, BEINT, PHIV, VOLC, CORR, STOL, QSTOL,
1 QCoh, QINC, PSTOL, PCOH, PINC, STOLI, XRINTI, QINDEP,
2 PINDEP, FINDEP, OVRLPI, XINTM, RI, SIGMA1, SIGMA2, SIGMA3
3 XRINT, SIGMAL1, SIGMAL2, XINTA, DIFDIS, RADDIS,
4 SYMDIS, AVEDIS, PROBNO, QCohi, QINCI, PCOH, PINC,
5 WVLT, MXINT, MXBE, MXVOLC, ADNSTY, A, X, MINSTO, MAXSTO,
6 DELSTO, STOLO, RO, MINR, MAXR, DELR, MAXQ, MAXP, C,
7 AINDEP, AXRINT, AINDSM, AXPSUM, OVRLPT
DIMENSION PROBNO(12), PHI(200), XRINT(200), PHIBE(200), BEINT(200)
1 , PHIV(200), VOLC(200), CORR(200), STOL(200), QSTOL(200),
2 QCoh(100), QINC(100), PSTOL(100), PCOH(100), PINC(100),
3 STOLI(500), XRINTI(500), QINDEP(500), PINDEP(500),
4 FINDEP(500), OVRLPI(500), XINTM(500), RI(500),
5 SIGMA1(500), SIGMA2(500), SIGMA3(500), XINTA(500),
6 XRINT, SIGMAL1, SIGMAL2, XINTA(500),
7 DIFDIS(500), RADDIS(500), SYMDIS(500), AVEDIS(500),
8 COMPOS(12), QCohi(500), QINCI(500), PCOH(500),
9 PINC(500), SIGMA1(500), SIGMA2(500)
DIMENSION QPCOH2(500), AINDEP(500), AXRINT(500), OVRLPT(500)
PI=3.1415927
MINS=MINSTO+1
MAXS=MAXSTO-1
SOFAC =0.0
DO 1 J=MINS, MAXS, 2
S = STOLI(J) * 4.0 * PI
1
SOFAC = SOFAC + XRINTI(J) * (S ** 2)
MINS = MINSTO + 2
MAXS = MAXSTO - 2
SEFAC = 0.0
DO 2 J = MINS, MAXS, 2
S = STOLI(J) * 4.0 * PI
2
SEFAC = SEFAC + XRINTI(J) * (S ** 2)
OFAC = XRINTI(MINSTO) * ((STOLI(MINSTO) * 4.0 * PI) ** 2)
TFAC = XRINTI(MAXSTO) * ((STOLI(MAXSTO) * 4.0 * PI) ** 2)
SUM1 = (OFAC + 4.0 * SOFAC + 2.0 * SEFAC + TFAC) * 4.0 * PI * DELSTO / 3.0
RETURN
END

INTERPOLATION SUBROUTINE

SUBROUTINE POLAT1(STOL, XRINT, MXINT, STOLO, STOLI, XRINTI, MAXSTO,
1 DELSTO)
COMMON PHI, XRINT, PHIBE, BEINT, PHIV, VOLC, CORR, STOL, QSTOL,
1 QCOH, QINC, PSTOL, PCOH, PINC, STOLI, XRINTI, QINDEP,
2 PINDEP, FINDEP, OVRLPI, XINTM, RI, SIGMAM, SGMAM1, SGMAM2
3 XINTL, SIGMAL, SGMAL1, SGMAL2, XINTA, DIFDIS, RADDIS,
4 SYMDIS, AVEDIS, PROBNO, QCOH, QINCI, PCOH, PINCI,
5 WVLT, MXINT, MXBE, MXVOLC, ADNSTY, A, X, MINSTO, MAXSTO,
6 DELSTO, STOLO, RO, MINR, MAXR, DELR, MAXQ, MAXP, C,
7 AINDEP, AXRINT, AINDSM, AXPSUM, OVRLPT
DIMENSION PROBNO(12), PHI(200), XRINT(200), PHIBE(200), BEINT(200)
1 PHIV(200), VOLC(200), CORR(200), STOL(200), QSTOL(200),
2 QCOH(100), QINC(100), PSTOL(100), PCOH(100), PINC(100),
3 STOLI(500), XRINTI(500), QINDEP(500), PINDEP(500),
4 FINDEP(500), OVRLPI(500), XINTM(500), RI(500),
5 SIGMAM(500), SGMAM1(500), SGMAM2(500), XINTL(500),
6 SIGMAL(500), SGMAL1(500), SGMAL2(500), XINTA(500),
7 DIFDIS(500), RADDIS(500), SYMDIS(500), AVEDIS(500),
8 COMPOS(12), QCOHI(500), QINCI(500), PCOHI(500),
9 PINCI(500), SIGMA(500), SIGMAL(500), SIGMA2(500)
DIMENSION QPCOH2(500), AINDEP(500), AXRINT(500), OVRLPT(500)
X=STOLO
DO 1 I=1, MAXSTO
X=X+DELSTO
XRINTI(I)=POLATE(STOL, XRINT, MXINT, X)
1 STOL(I)=X
RETURN
END

FOURIER INVERSION SUBROUTINE

SUBROUTINE FOUINV(ST0LI, XINTA, MINSTO, MAXSTO, DELSTO, RO, MINR, MAXR, DELR, A, RI, DIFDIS)
COMMON PHI, XRINT, PHIBE, BEINT, PHIV, VOLC, CORR, STOL, QSTOL, QCOH, QINC, PSTOL, PCOH, PINC, STOLI, XRINTI, QINDEP,
PINDEP, FINDEP, OVRLPI, XINTM, RI, SIGMAM, SGMAM1, SGMAM2, XINTL, SIGMAL, SGMAL1, SGMAL2, XINTA, DIFDIS, RADDIS,
SYMDIS, AVEDIS, PROBNO, QCOHI, QINCI, PCOHI, PINCI,
WVLT, MXINT, MXBE, MXVOLC, ADNSTY, A, X, MINSTO, MAXSTO,
DELSTO, STOLO, RO, MINR, MAXR, DELR, MAXQ, MAXP, C,
AINDEP, AXRINT, AINDSM, AXPSUM, OVRLPT, MINSTI, MAXSTI
DIMENSION PROBNO(12), PHI(200), XRINT(200), PHIBE(200), BEINT(200),
PHIV(200), VOLC(200), CORR(200), STOL(200), QSTOL(200),
QCOHI(100), QINCI(100), PSTOL(100), PCOH(100), PINC(100),
STOLI(500), XRINTI(500), QINDEP(500), PINDEP(500),
FINDEP(500), OVRLPI(500), XINTM(500), RI(500),
SIGMAM(500), SGMAM1(500), SGMAM2(500), XINTL(500),
SIGMAL(500), SGMAL1(500), SGMAL2(500), XINTA(500),
DIFDIS(500), RADDIS(500), SYMDIS(500), AVEDIS(500),
COMPOS(12), QCOHI(500), QINCI(500), PCOHI(500),
PINC(500), SIGMA1(500), SIGMA2(500)
DIMENSION QPCOH2(500), AINDEP(500), AXRINT(500), OVRLPT(500)
PI=3.1415927
R=RO
DO 3 I=MINR, MAXR
R=R+DELR

DIMENSION QPCOH2(500), AINDEP(500), AXRINT(500), OVRLPT(500)
X=STOLO
DO 1 I=1, MAXSTO
X=X+DELSTO
XRINTI(I)=POLATE(STOL, XRINT, MXINT, X)
1 STOL(I)=X
RETURN
END

FOURIER INVERSION SUBROUTINE

SUBROUTINE FOUINV(ST0LI, XINTA, MINSTO, MAXSTO, DELSTO, RO, MINR, MAXR, DELR, A, RI, DIFDIS)
COMMON PHI, XRINT, PHIBE, BEINT, PHIV, VOLC, CORR, STOL, QSTOL, QCOH, QINC, PSTOL, PCOH, PINC, STOLI, XRINTI, QINDEP,
PINDEP, FINDEP, OVRLPI, XINTM, RI, SIGMAM, SGMAM1, SGMAM2, XINTL, SIGMAL, SGMAL1, SGMAL2, XINTA, DIFDIS, RADDIS,
SYMDIS, AVEDIS, PROBNO, QCOHI, QINCI, PCOHI, PINCI,
WVLT, MXINT, MXBE, MXVOLC, ADNSTY, A, X, MINSTO, MAXSTO,
DELSTO, STOLO, RO, MINR, MAXR, DELR, MAXQ, MAXP, C,
AINDEP, AXRINT, AINDSM, AXPSUM, OVRLPT, MINSTI, MAXSTI
DIMENSION PROBNO(12), PHI(200), XRINT(200), PHIBE(200), BEINT(200),
PHIV(200), VOLC(200), CORR(200), STOL(200), QSTOL(200),
QCOHI(100), QINCI(100), PSTOL(100), PCOH(100), PINC(100),
STOLI(500), XRINTI(500), QINDEP(500), PINDEP(500),
FINDEP(500), OVRLPI(500), XINTM(500), RI(500),
SIGMAM(500), SGMAM1(500), SGMAM2(500), XINTL(500),
SIGMAL(500), SGMAL1(500), SGMAL2(500), XINTA(500),
DIFDIS(500), RADDIS(500), SYMDIS(500), AVEDIS(500),
COMPOS(12), QCOHI(500), QINCI(500), PCOHI(500),
PINC(500), SIGMA1(500), SIGMA2(500)
DIMENSION QPCOH2(500), AINDEP(500), AXRINT(500), OVRLPT(500)
PI=3.1415927
R=RO
DO 3 I=MINR, MAXR
R=R+DELR
SOFAC=0.0
MINS=MINSTO+1
MAXS=MAXSTO-1
DO 1 J=MINS, MAXS, 2
S=4.0*PI*STOLI(J)
1 SOFAC=SOFAC+XINTA(J)*SINF(R*S)*FXPF(-A*(S**2))*S
MINS=MINSTO+2
MAXS=MAXSTO-2
SEFAC=0.0
DO 2 J=MINS, MAXS, 2
S=4.0*PI*STOLI(J)
2 SEFAC=SEFAC+XINTA(J)*SINF(R*S)*FXPF(-A*(S**2))*S
S=4.0*PI*STOLI(MINSTO)
OFAC=XINTA(MINSTO)*SINF(R*S)*FXPF(-A*(S**2))*S
S=4.0*PI*STOLI(MAXSTO)
TFAC=XINTA(MAXSTO)*SINF(R*S)*FXPF(-A*(S**2))*S
DIFDIS(I)=((2.0*R/PI)*(OFAC+4.0*SOFAC+2.0*SEFAC+TFAC)*4.0*PI*
1 DELSTO/3.0
3 RI(I)=R
RETURN
END
LIST OF REFERENCES

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AUTOBIOGRAPHY

The author, Horace Wataru Furumoto, of this dissertation was born on the thirteenth of December, 1931 in Honolulu, Hawaii. He received his primary education in the public school system of Honolulu and completed his secondary education at St. Louis High School in Honolulu. California Institute of Technology furnished him his undergraduate training, and he received his B.S. degree in physics in 1955. After two years of military service with the USAF he enrolled in the Graduate School of The Ohio State University to continue his education in physics. He graduated with a doctoral degree in the spring of 1963.