Fourier Analysis of X-Ray Scattering from Polyatomic Liquids

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It is shown that the Fourier integral analysis of x-ray scattering for liquids with polyatomic molecules containing like atoms may be simplified if the x-ray diffraction curve is corrected by subtraction of the gas scattering of the single molecules before the analysis is made. The method is tested by an analysis of Katzoff's data for benzene. The distribution function obtained indicates that a given molecule is surrounded by six neighbors in the plane of the benzene ring, with a mean separation of centers of about 6.7A. The neighbors of a given molecule are oriented with respect to the molecule. The parallel planes of flat molecules are separated by a distance of 3.7A. The structure is very similar to the crystal structure of hexamethyl benzene.

THE atomic distribution in a liquid may be determined from x-ray diffraction data[1] by application of the Zernike-Prins equation, which may be written in the form

$$q(r) = \frac{2r}{\pi} \int_0^\infty \frac{k(I - NTf^2)}{NTf^2} \sin kr \, dk, \qquad (1)$$

where $q(r)$ is a radial distribution function giving the excess number of atoms over the average at distance r. (The average number of atoms at distance r is given by the value of $4\pi r^2 \rho$, where ρ is the number of atoms in unit volume.) k is the function, $4\pi/\lambda \sin \theta$, where λ is the wave-length and θ is one-half the angle between direct beam and scattered beam. I is the observed intensity, corrected for polarization and for modified radiation. N is the number of irradiated atoms, and T the Thompson scattering per free electron. f is the atomic structure factor.

Two difficulties are encountered in the application[2] of Eq. (1) to the scattering obtained from a liquid containing polyatomic molecules:

1. In order to correct for modified radiation and to express the intensity in the same units as f^2, it is necessary to assume that the atoms scatter independently at large angles. Because of the gas scattering of single molecules this assumption is not valid, for at the largest angles attainable the scattering curve shows maxima and minima[3] due to interference in radiation from atoms within the same molecule. When Eq. (1) is used it is necessary to select arbitrarily a point at which independent scattering is assumed.

2. Because of the gas scattering, the curve $k(I - NTf^2)/NTf^2$ does not damp to zero amplitude in the experimentally attainable region, and it is impossible to perform the integration over the limits of zero to infinity.

These difficulties may both be eliminated if the observed intensity curve is corrected by subtracting from it the gas scattering of the single molecules. This operation gives a hypothetical scattering curve which would be obtained if there were no interference due to atoms within the same molecule. Use of a modified scattering curve necessitates the following revision of the method for calculating the distribution function:

If the Debye equation for the scattering of atoms at fixed distances is applied to a polymolecular system the summation may be made in two operations, one over the atoms in the single molecule, the other over atoms in neighboring molecules. In a system of N molecules, each containing m like atoms, the intensity is given by the relation

$$I = T \sum_1^{mN} \sum_1^{mN} f_i f_j \frac{\sin kr_{ij}}{kr_{ij}} = NT \sum_1^m \sum_1^m f_i f_j \frac{\sin kr_{ij}}{kr_{ij}}$$
$$\text{gas scattering} \cdot$$
$$+ m(N-1)T \sum_{m+1}^{mN} f_i f_j \frac{\sin kr_N}{kr_N}$$
$$\text{liquid scattering}$$

where r_N is the distance from a given atom to an

[1] F. Zernike and J. A. Prins, Zeits. f. Physik **41**, 184 (1927); P. Debye and H. Menke, Physik. Zeits. **31**, 797 (1930); B. E. Warren, Phys. Rev. **44**, 969 (1933).

[2] See W. C. Pierce, J. Chem. Phys. **3**, 252 (1935).

[3] In electron diffraction from gases, where the effective wave-length is very short, as many as 10–12 maxima and minima can be observed in the scattering curve. Only the first few of these can be observed in x-ray scattering, because of the longer wave-lengths employed.
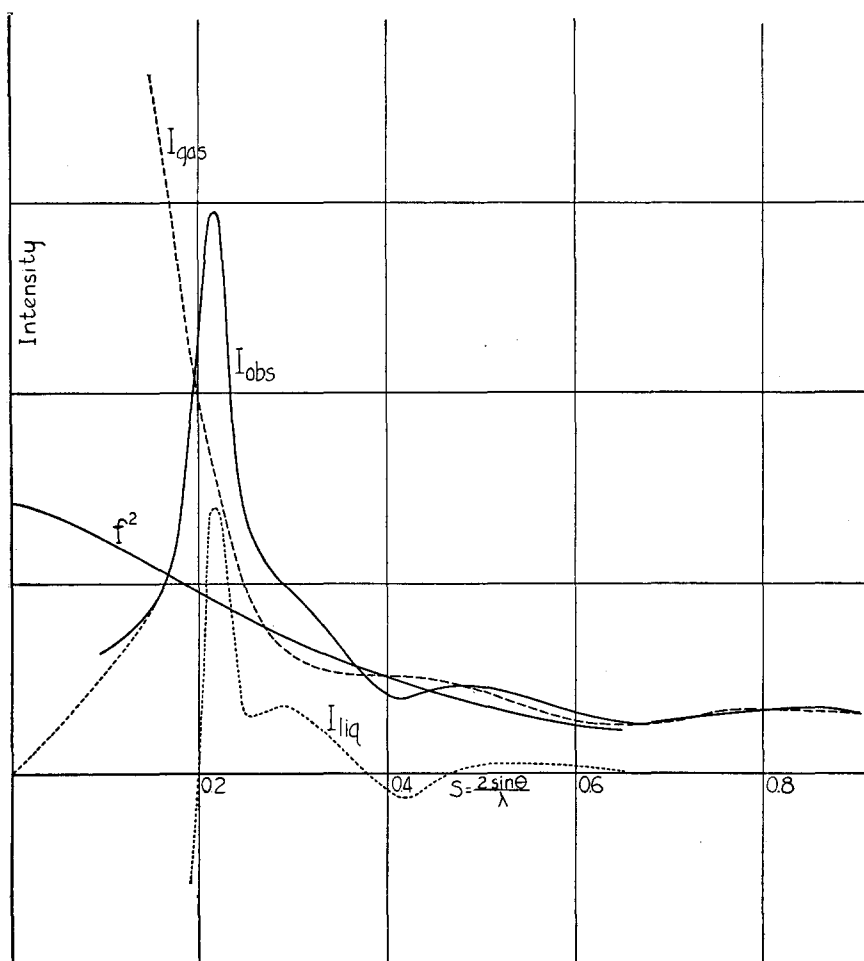
FIG. 1. Method for correcting the experimental scattering curve for the gas scattering of single molecules.

atom in a neighboring molecule. If the atoms are all alike and if every atom has on the average the same surroundings with respect to the atoms of neighboring molecules, the expression reduces to the form

$$I = I_{gas} + m(N-1)Tf^2 \sum_{m+1}^{mN} \frac{\sin kr_N}{kr_N}.$$

As an approximation we may replace $N-1$ by N and replace the single summation over fixed distances by an integral containing the probability function $p'(r)$, which gives the number of atoms in other molecules at radial distance r from a given atom. Then

$$I = I_{gas} + mNTf^2 \int_0^{\infty} p'(r)dr \frac{\sin kr}{kr}$$

$p'(r)$ may be split into two portions

$$p'(r) = \underset{\text{average}}{4\pi r^2 \rho} + \underset{\text{excess}}{q'(r)}.$$

Therefore,

$$\frac{I - I_{gas}}{mNTf^2} = E' = \int_0^{\infty} 4\pi r^2 \rho dr \frac{\sin kr}{kr} + \int_0^{\infty} q'(r)dr \frac{\sin kr}{kr}.$$

The first integral is zero except when k is zero, and may be neglected for the finite scattering observed. Therefore

$$E' = \frac{1}{k} \int_0^{\infty} \frac{q'(r)}{r} \sin kr \, dr.$$

This equation may be solved by the Fourier integral theorem,

$$q'(r) = \frac{2r}{\pi} \int_0^\infty kE' \sin kr\, dr. \qquad (2)$$

Eq. (2) must be considered as an approximation since the assumption is made that each atom has the same number of neighboring atoms, at the same distances. For liquids containing only one kind of atom, in molecules which are relatively far apart, the approximation seems to be justified. The equation may even be applied to scattering by liquids containing two kinds of atoms if they are sufficiently comparable in scattering power, as are carbon and oxygen atoms. It is not, however, applicable to the scattering of such a liquid as carbon tetrachloride, where the atoms are greatly different in scattering power.

In order to test the validity of the suggested modification, the x-ray scattering data of Katzoff for benzene[4] were analyzed. The method for making the corrections is shown in Fig. 1. A gas scattering curve was constructed for coherent radiation, using the structure factor for $C^-(Z=7)$ and neglecting the contribution of the hydrogen atoms. To this was added the incoherent scattering calculated for 6 CH, and the combined curve was equated to the experimental curve at a large value of s, by multiplication of the amplitude with a constant factor. It was found that the calculated gas scattering curve approximately fitted the experimental curve at all s values beyond 0.7. By subtraction of the I_{gas} curve from I_{obs}, a curve was obtained for I_{liq}, and this was used for calculation of the distribution function, $q'(r)$. The integration of Eq. (2) was performed graphically for the r values shown in Fig. 2, which gives the distribution function obtained. Since the kE' curve damps to zero at a k value of approximately 4, the integration of Eq. (2) is much more readily performed than that of Eq. (1).

A radial distribution curve was constructed by adding $q'(r)$ values to the average number of atoms at radial distance r. This curve has values of zero up to r distances of about 3.1A, then rises abruptly to the first maximum at about 4.3A. Lack of either positive or negative values at r distances less than 3A supports the belief that the distribution function obtained in the analysis

[4] S. Katzoff, J. Chem. Phys. 2, 841 (1934).

is valid, since if the agreement is fortuitous the combination of density data with x-ray data would probably give an oscillatory curve at values near zero.

The $q'(r)$ curve was used as the basis for construction of a model of the liquid arrangement. A close packing of spherical molecules was rejected, since this leads to a radial distribution widely at variance with the one found. Excellent agreement between model and x-ray distribution functions was found for an arrangement of flat molecules in planes, with the separation of planes about 3.7A. In a plane each molecule is surrounded by six neighbors with an average distance of closest approach about 4.3A. The distance apart of centers is about 6.7A. Molecules in adjacent planes do not lie directly above one another, but in a pyramidal arrangement so that the upper molecule is symmetrically placed with respect to three molecules in the lower plane. This model, which was worked out on the assumption that the average distance of closest approach corresponds to the first peak in the $q'(r)$ curve, is very similar to the crystal structure found for hexamethyl benzene and has the same distance between planes. The postulated planes are not of large extent, but merely refer to the average condition of the molecules surrounding a designated center, and throughout the liquid there will be found a random arrangement of
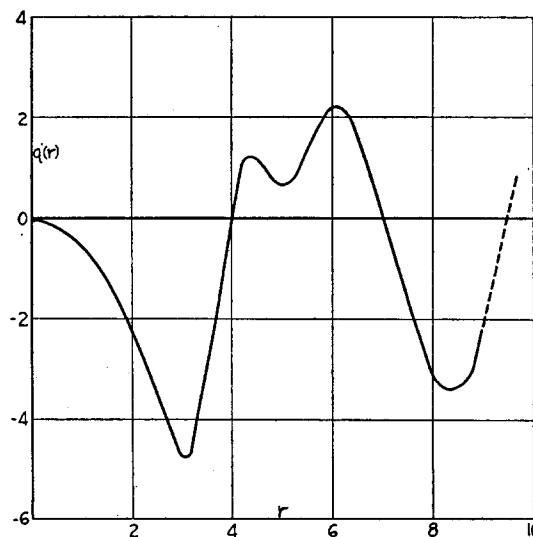

FIG. 2. Distribution function for liquid benzene. $q'(r)$ gives the excess number of atoms, not in the same molecule, at distance r.

planes. Since the atoms do not occupy fixed lattice positions within a plane the Bragg equation cannot be used for calculation of the linear separation of the planes.

The proposed model for the structure in liquid benzene differs from the model employed by Katzoff[4] chiefly in the assumption that the molecules lie flat in planes. Katzoff employed a model based upon crystal structure, in which the molecules lie in planes 3.4A apart and are tilted with respect to the plane. This difference is reflected in the atomic distribution curves obtained in the two cases. Although the $q'(r)$ curve of Fig. 2 qualitatively resembles the distribution curve deduced by Katzoff, the two are not in the same units. Conversion to the same units gives curves which are not in quantitative agreement, although both curves show the double peak observed at 4–7A in Fig. 2. This similarity is due to the assumption employed in both structures that neighboring molecules are oriented within a plane and that upper and lower planes contain molecules likewise oriented. Although the method

used here is a little more direct than the one employed by Katzoff the writer does not feel that the resolution obtained in x-ray scattering from a liquid is sufficient to enable one to make definite conclusions as to the uniqueness of either structure.

Katzoff and others have commented upon the bulge at the bottom of the first strong peak in the diffraction pattern (at $s=0.3$). This bulge is also found in the diffraction pattern of benzene derivatives. In the corrected liquid scattering curve of Fig. 1 the bulge becomes relatively more prominent than in the total scattering. It is undoubtedly due, as suggested by Katzoff, to a predominance of interatomic distances of about 4A—a condition which is caused by the orientation of neighboring flat molecules. The absence of this bulge in the diffraction pattern of cyclohexane and of long chain compounds supports this view.

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Calculation of the Rate of Elementary Association Reactions

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An upper limit for the rate of association reactions is found by determining the probability of a decrease of the relative energy of two atoms below zero energy, under the influence of a third body. The relation of this approximate calculation to the rigorous solution of the problem is discussed in Section 2. The results are applied to the recombination of J atoms, measured by Rabinowitch and Wood. Numerically, the agreement is quite good; however, the calculated values are somewhat too low, which cannot be explained by an inaccuracy of the method. Reasons for the discrepancy other than the possible nonadiabatic character of the reaction are discussed.

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THE transition state method[1] allows the calculation of the rate of reactions which involve an activation energy. The assumptions which one has to make in order to apply this method are (1) that the reaction shall not involve a jump in the quantum state of the electrons,[2]

(2) that classical mechanics be applicable to the motion of the nuclei (or that the ordinary way of taking into account quantum effects be justifiable) and, (3) that the number of systems crossing the activated state be the number of systems reacting. This last condition is always satisfied at sufficiently low temperatures and if the energy surfaces are not too complicated, the temperature at which their validity ceases will be rather high.[3] The common feature of the reactions to

[1] Cf. for previous literature e.g. M. G. Evans and M. Polanyi, Trans. Faraday Soc. **31**, 876 (1935).
[2] The possibility of chemical reactions without quantum jumps in the state of the electronic system has been first realized by F. London, *Sommerfeld Festschrift* (S. Hirzel, 1928), p. 104.
[3] Cf. for a closer discussion of these conditions, E. Wigner, Trans. Faraday Soc. (1937).