The Interpretation of X-Ray Diffraction Patterns of a Fluid at Various Densities*

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It is shown that existing calculations for the intensity of x-rays diffracted by a fluid at various densities can be applied only over a small range of densities, and it is pointed out that this is due to the distribution of atoms about any one atom chosen for the calculation. The distribution is discussed qualitatively for gases and liquids, and a reasonable approximation to the true distribution is assumed. From this a set of intensity *vs.* angle curves are drawn for several densities. These curves are compared with Stewart's experimental curves for ether at various densities.

1. INTRODUCTION

X-RAY diffraction patterns of gases and of liquids have been studied by many investigators, but relatively little work has been done on the diffraction patterns of a fluid at various densities. For a review of gas diffraction, one should refer to the paper of Wollan,[1] and for a review of liquid diffraction, reference should be made to the article by Debye and Menke.[2] A calculation of the diffraction effects of a gas at various densities was made by Debye[3] in 1925, but the results of this calculation are applicable only to a relatively rare gas. Excellent experimental studies of the x-ray diffraction by ether at various densities have been made by Stewart[4] and Spangler,[5] and the results of these studies are interpreted qualitatively in terms of the cybotactic theory. Recently, Harvey[6] has made a brief preliminary report of work on the diffraction of x-rays by nitrogen at high pressure.

Debye's calculation showed that diffraction effects in a gas should occur simply because two atoms cannot approach each other closer than a certain minimum interatomic distance, a. Upon the assumption of no atoms at a distance less than a from any one atom, and a continuous distribution of atoms thereafter, this calculation led to the result that the intensity of x-rays diffracted by a gas should depend upon the density of the gas. The equation for the intensity of coherent x-rays scattered from a monatomic gas is

$$I = Kf^2\{1-(\Omega/V)\Phi(sa)\}, \tag{1}$$

where f is the atomic scattering factor, $s = (4\pi \sin \theta)/\lambda$, Ω/V is proportional to the ratio of the actual density to the maximum density of the gas, and

$$\Phi(sa) = \frac{3}{(sa)^2}\left\{\frac{\sin sa}{sa} - \cos sa\right\}. \tag{2}$$

A plot of the intensity of x-rays *vs.* sa at several values of Ω/V and using an arbitrary f^2, is shown in Fig. 1. Although the general manner of variation with density is in accord with experiment, the shapes of the curves for high values of Ω/V do not agree with those of available experimental curves. Moreover, the definition of Ω is such that $\Omega/V=1$ corresponds to the case of a gas under pressure, but considerably removed from the liquid case. Thus, for very dense gases, or for liquids, this equation would lead to negative values for the intensity. The cause for these discrepancies at high densities is obviously that the assumption of having continuous distribution of matter beyond the smallest distance of approach of two atoms is not valid for a fluid at high densities.

2. DERIVATION OF MORE SUITABLE EQUATION

In the present paper, an attempt is made to find an expression which will more nearly approximate the experimental curves for x-ray diffraction by a fluid at various densities. Use

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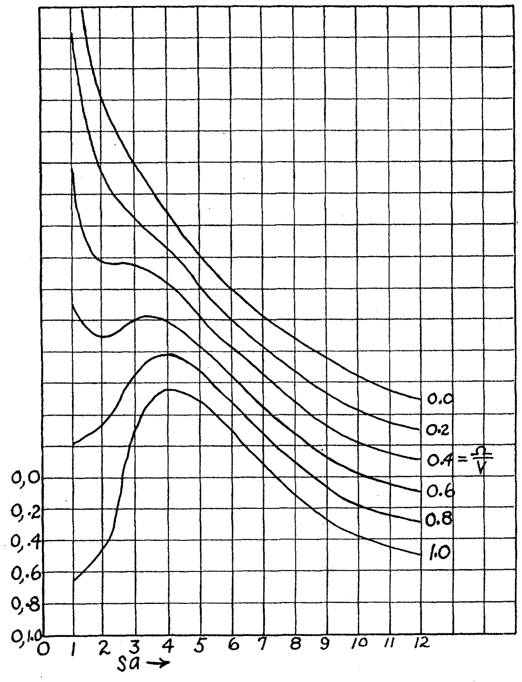

FIG. 1. Plots of Debye's equation for several values of Ω/V.

is made of the method of Zernike and Prins,[7] which has been applied successfully to certain gases, liquids and solids. Consider a monatomic substance, having spherical atoms, in which each atom is surrounded in the same way as every other atom. If x-rays are incident upon this substance, the intensity of coherent scattered x-rays as a function of angle is given by

$$I=Nf^2\left\{1+\int_0^\infty 4\pi r^2 g(r)[(\sin sr)/sr]dr\right\}, \quad (3)$$

where f is the atomic scattering factor, r is the distance measured from any one atom, and $g(r)$ is the density distribution function of atoms about any one atom. Thus, in order to calculate the intensity, I, it is necessary to know the atomic scattering factor f, and the density distribution function, $g(r)$. It can be seen that this equation will result in essentially Debye's equation, if the integration of the second term is taken with the lower limit a, and with $g(r)$ a constant. A more reliable calculation of the intensity could be made, however, if the density distribution function were known, or if a more reasonable approximation to it were made.

The general features of the distribution of atoms about any one atom in a gas or liquid can be seen from several considerations. For a gas, the density distribution can be calculated from Morse's[8] potential function, and this shows that there will be no atoms closer than a certain minimum distance and that there will be a slight concentration of atoms at about this distance, beyond which the density of atoms will rapidly become constant. For a liquid, in which the atoms are approximately close packed, the same minimum distance of approach should exist, and there should be a marked concentration of atoms at this distance, with a deficiency of atoms just beyond, after which the density distribution curve should oscillate about the average density a few times before becoming constant. Experimental support for this type of distribution may be found in the work of Debye and Menke[2] on mercury.

The calculation of the intensity of coherent scattered x-rays by a fluid can be made if the true density distribution function is known, or if a reasonable approximation to it is assumed. Fig. 2(a) shows a typical distribution curve for a gas, and Fig. 2(b) represents an assumed distribution, which leads to the equation

$$I=Nf^2\left\{1+M\frac{\sin sa}{sa}+\int_a^\infty 4\pi r^2\rho\frac{\sin sr}{sr}dr\right\}. \quad (4)$$

Integration of the last term of this equation results in $(4\pi/3)a^3\rho\Phi(sa)$ where $\Phi(sa)$ is defined by Eq. (2), and ρ is the constant average density in atoms per unit volume. The upper limit of this integral gives rise to no observable diffraction effects, as long as it is large compared to the interatomic distance, a. This can be seen from plots of $\Phi(sr)$, for this function is appreciable only for small values of sr, and if r is very large, s must be very small; that is, diffraction effects due to matter at very large r are confined to very small angles. The coefficient of this term represents the amount of matter removed from

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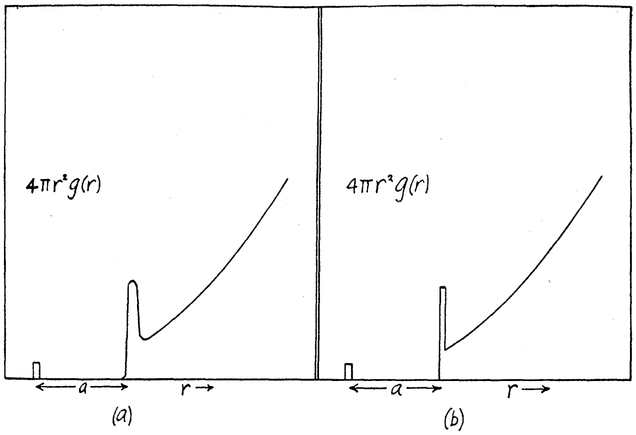

FIG. 2. Density distribution of atoms about any one in a gas, (a) as calculated, (b) as assumed.

the sphere of radius a in the continuous distribution. The coefficient of the second term, M, must equal the amount of matter removed from the sphere of radius a, less the one atom at the origin. The closest packing of spheres is the face centered cubic arrangement, and in this case, the volume per atom is $a^3/2^{\frac{1}{2}}$ so that $(4\pi a^3/3 - a^3/2^{\frac{1}{2}})\rho$ represents the amount of matter to be concentrated at a distance a. Thus, one obtains

$$I=Nf^2\left\{1+\left(\frac{4\pi}{3}a^3-\frac{a^3}{2^{\frac{1}{2}}}\right)\rho\frac{\sin sa}{sa}-\frac{4\pi}{3}2^{\frac{1}{2}}\frac{a^3}{2^{\frac{1}{2}}}\rho\Phi(sa)\right\}. \quad (5)$$

If $a^3/2^{\frac{1}{2}}$ is the volume per atom, in closest packing, then the density of close packed atoms would be $\rho_0=2^{\frac{1}{2}}/a^3$, the maximum density of the substance. Introducing this, and simplifying,

$$I=Nf^2\{1+(\rho/\rho_0)[4.92(\sin sa)/sa-5.92\Phi(sa)]\}. \quad (6)$$

Curves plotted from this equation show that for values of ρ/ρ_0 less than 0.5, better qualitative agreement with experimental curves is obtained than with Debye's equation, but for higher values of ρ/ρ_0, negative intensities at small angles appear. These negative intensities are obviously due to the crude approximation of density distribution for the liquid. The density distribution for a liquid should be roughly of the type shown in Fig. 3(a), and for purposes of calculation, that shown in Fig. 3(b) has been

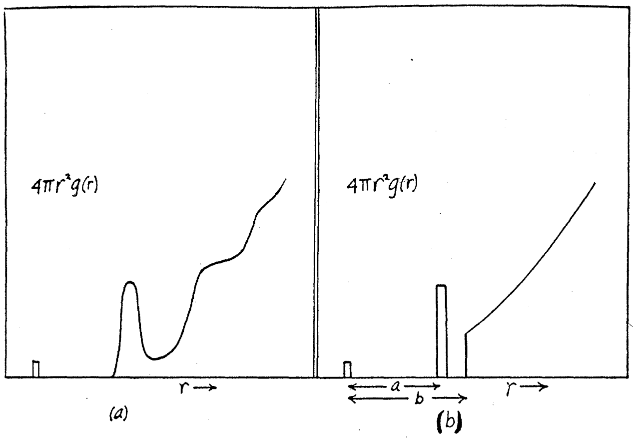

FIG. 3. Density distribution of atoms about any one atom in a liquid, (a) as it probably is and (b) as assumed.

assumed. This distribution leads to the equation

$$I = Nf^2\left\{1 + M\frac{\sin sa}{sa} + \int_b^\infty 4\pi r^2 \rho \frac{\sin sr}{sr} dr\right\}, \quad (7)$$

which becomes

$$I = Nf^2\{1 + (\rho/\rho_0)[K_1(\sin sa)/sa - K_2\Phi(sb)]\}, \quad (8)$$

where the coefficients K_1 and K_2 depend upon the ratio b/a. The ratio $b/a = 1.18$ has been found to be both reasonable and suitable, and this results in a value of $K_2 = 9.7$. However, this value of K_2 is too large, partly because of the assumption of close packing and partly because of neglect of density variations beyond the first concentration and first dip. To allow for these two effects we arbitrarily take a somewhat smaller value for K_2. K_1 is then immediately fixed by the condition that all the matter removed from the continuous distribution must equal the excess in the concentrations. The equation obtained in this way is

$$I = Nf^2\{1 + (\rho/\rho_0)[5(\sin sa)/sa - 6\Phi(1.18sa)]\}. \quad (9)$$

The maximum intensity will occur at a definite value of sa, so that the scattering angle for maximum intensity will depend upon a, the smallest distance of approach of atoms, and will depend on the density only inasmuch as the factor f^2 tends to shift the peaks for small density towards small angles.

3. Application of Equation to Experimental Results

From Eq. (9), plots of intensity *vs.* sa may be made for several values of ρ/ρ_0, and compared with experimental results. Such plots are shown in Fig. 4(b), for which plots, a value of f was used to approximate the effective f for ether. For comparison with experimental curves, one should have data on a monatomic gas for which the scattering factor is known, but no such data exist. However, experimental curves for ether at various densities have been obtained by G. W. Stewart and R. D. Spangler, and a set of their curves, which they very kindly sent us, is reproduced in Fig. 4(a). Similarities between the calculated and experimental curves can be seen. By means of certain arbitrary refinements, one can produce nearly exact fits between the curves, but it is felt that such manipulation in the case of ether is meaningless.

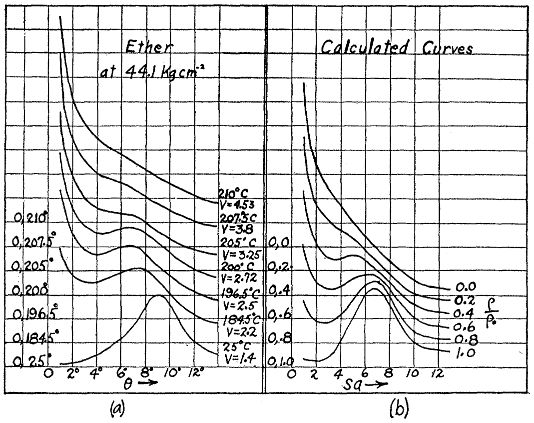

FIG. 4. Plots of intensity *vs.* θ, in the case of ether curves and *vs.* sa in the case of curves calculated from Eq. (9).

4. Summary

The interpretation, here presented, of the diffraction of x-rays by fluids at various densities is based on the ordinary theory of x-ray diffraction, but it cannot be made rigorous without a more complete knowledge of the density distribution of atoms about any one atom in gases and liquids, and the manner in which it changes in going from the gas to the liquid state. However, by introducing reasonable approximations to these distributions, it is shown that the general characteristics of diffraction curves of a fluid at various densities can be predicted.