Interatomic and Intermolecular Scattering in Gas Electron Diffraction†

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(Received March 29, 1965)

The effect of interatomic and intermolecular scattering on the total intensity of electrons scattered from a narrow beam of atoms or molecules in the gaseous state can be written as:

$$I_T(s) = I(s)\left\{1 + 4\pi\left(\frac{N}{V}\right) \times \int_0^\infty dr r^2 [e^{-V(r)/kT} - 1]\frac{\sin sr}{sr} + 4\pi\left(\frac{N}{V}\right)\int_0^\infty dr r^2 \frac{\sin sr}{sr}\right\} \quad (1)$$

in the first Born approximation, where $I(s)$ is the usual Debye intensity expression for scattering from atoms or molecules.[1] In Eq. 1, N refers to the number of atoms or molecules in the volume, V, undergoing scattering. It should be noted that Eq. 1 is the equation previously derived by Debye and Menke[2] for the X-ray scattering from liquids. The second term on the right of the equal sign in Eq. 1 represents electron scattering from a pair of atoms separated by distances close to the position of the minimum of the interatomic or intermolecular potential, $V(r)$. The third term represents the scattering of electrons from atom pairs separated by large distances and makes no contribution to the intensity.[1] Since the second term on the right of the equal sign in Eq. 1 makes a periodic contribution to the differential scattering cross section, it is of interest to investigate this term in order to ascertain if corrections for its effect on the electron diffraction analysis are needed.

It is convenient to define a reduced molecular intensity function for interatomic or intermolecular scattering as:

$$N(s) = 9.221 \times 10^{-2}(P_0/T) \times \int_0^\infty dr r^2 [e^{-V(r)/kT} - 1]\frac{\sin sr}{sr} \quad (2)$$

where P_0 is the average pressure in the gas beam in fractions of an atmosphere, and T is the temperature in degrees of atoms or molecules in the gas beam. In Fig. 1 $N(s)$ is calculated for an argon gas beam with $P_0 = 10^{-2}$ atm. and $T = 300°K$. The $V(r)$ potential is approximated by a Lennard-Jones 6-12 expression using parameters obtained from Ref. 3. It is obvious from Fig. 1 that interatomic or intermolecular effects at sample pressures of the order of 10 mmHg will usually not create any difficulty in the analysis of electron diffraction data. On the other hand, an interesting question arises as to whether or not the potential function, $V(r)$, can be obtained experimentally by carrying out electron diffraction experiments with high beam pressures. This appears to be a feasible experiment provided gas pressures greater than

† Contribution Number 1286 from the Chemical Laboratories of Indiana University.

* This author wishes to thank the U. S. Educational Commission in Japan, the John Simon Guggenheim Foundation, and the Alfred P. Sloan Foundation for their support.

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2) P. Debye and H. Menke, *Physik. Z.*, **31**, 797 (1930).

3) R. H. Fowler and E. A. Guggenheim, "Statistical Themodynamics," Cambridge at the University Press, London, Cambridge, England (1939), Chapter VII, Table 3, p. 285.

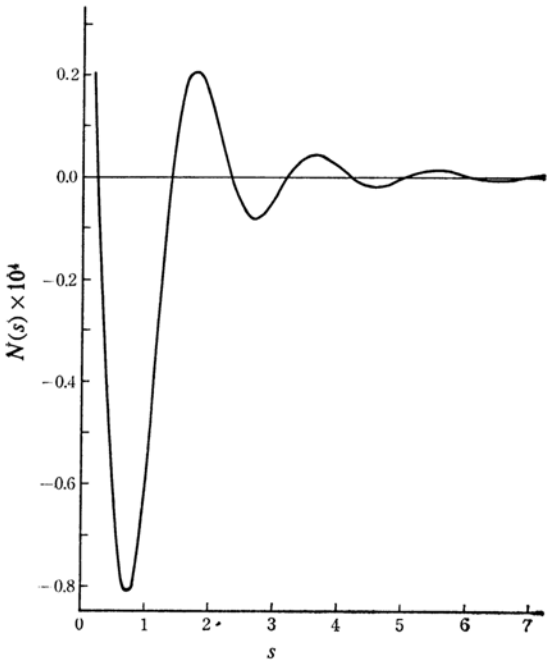

Fig. 1

1 atm. can be obtained while conditions for an optimum diffraction experiment are maintained. That is, the volume of gas undergoing scattering must be small (i. e., 10^{-3} cubic mm.), and the vacuum in the diffraction chamber should be at least 10^{-4} mm. of Hg away from the beam. At high pressures of the gas beam it is possible, in the case of many atoms and molecules, to obtain diffraction pictures in a few hundredths of a second with 40 kV. electrons. By taking a diffraction photograph during the instant following the formation of a gas beam by expansion through a small orifice (~0.1 mm.), it should be possible to maintain a reasonably good chamber pressure during the course of the exposure.

It is also important to consider the effect of multiple scattering on Eq. 1. The Karles[4] have discussed such effects previously; it appears, on the basis of their analysis, that such effects mainly contribute to the background term, $I(s)$, in a smooth fashion. It is, of course, possible for coherent contributions of these effects to the frequency such as those in Eq. 2 to arise from multiple scattering from closely-grouped clusters of three or more atoms. However, Bunyan[5] has shown that the intensity from triple scattering, for extremely heavy atoms, amounts to probably no more than 10% of the coherent scattering intensity from a cluster of three atoms in close proximity. Since in gases, even at fairly high pressures, there must be many more clusters with two atoms than with three atoms, the appearance of coherent features from multiple scattering seems rather improbable.

It is also important to note that the amplitude of $N(s)$ depends, in a sensitive manner, on the depth of the energy minimum of $V(r)$. This means that an increase in the density of the potential minimum of $V(r)$ will greatly enhance the amplitude of $N(s)$. Thus, the possibility of observing the function $N(s)$ experimentally for krypton or xenon should be even better than for argon.

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