the lower energy electrons and the rate at which the spectrum changes becomes less and less. In fact, at distances of a meter or more, the changes in the shape of the spectrum are too small to be measured with this low resolution spectrometer.

White[2] has already made some measurements in a similar experiment, using shielded ionization chambers, and found that the spectrum is still changing as far out from the source as 135 cm. These data do not, however, contradict the results of the present experiment since the ionization chambers are sensitive mostly to very soft radiation, so soft in fact as to have had no effect in this experiment. Furthermore, the spectra of photons calculated by Spencer and Fano[1] show the features of both experiments. The calculated spectra show a peak below 100 kev the height of which, relative to the high energy portion of the spectrum, is still changing at large distances; this component is primarily the one measured by White.[2] On the other hand, the shape of the calculated spectra at high energies change very slowly with distance, too slowly for any variation to be observed with the spectrometer used in the present experiment.

The author wishes to thank Mr. Eaton and the staff of the Hydraulics Laboratory for their hospitality and for their many courtesies. It is a pleasure to thank both Dr. U. Fano and Dr. L. V. Spencer for their many illuminating discussions.

---

PHYSICAL REVIEW VOLUME 86, NUMBER 4 MAY 15, 1952

# The Radial Distribution Function in Liquid Helium*

P. J. PRICE
*Department of Chemistry, Duke University, Durham, North Carolina*

(Received January 10, 1952)

It is pointed out that the Ornstein-Zernike-Gibbs formula, which is commonly used to connect the intensity of coherent scattering of radiation in a liquid with the thermodynamic functions, is not valid for liquid helium. Alternative formulas involving the radial distribution function are discussed.

IN the coherent scattering of radiation by a monatomic liquid, the scattered intensity is proportional to[1]

$$1+n\int[g(r)-1]e^{i(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{r}}d^3\mathbf{r}, \tag{1}$$

where $n$ is the number density, $g(r)$ the radial distribution function, and $\mathbf{k}_1$ and $\mathbf{k}_2$ the incident and scattered wave vectors. Consequently, for large wavelengths the scattering cross section is multiplied by the factor

$$S(T)\equiv 1+n\int_a^\infty(g-1)4\pi r^2dr, \tag{2}$$

and the scattered intensity can be related to the thermodynamic magnitudes of the liquid by the formula

$$S=nkT\chi_T, \tag{3}$$

where $\chi_T$ is the isothermal compressibility. This formula (3) is valid for "classical" conditions, but has recently been applied to the analysis of scattering in liquid helium.[2]

It is the present purpose to point out that this application to a *quantum* liquid is incorrect. To see this, we break down (3) into the two equations from which it derives. Consider a small fixed cell of volume $v$ in the liquid, which is supposed homogeneous, and define the function $f(\mathbf{r})$ such that $f$ is unity when $\mathbf{r}$ ends in the cell and zero otherwise; and hence the function $F=\sum_t f(\mathbf{r}_t)$, summed over the position-vectors $\mathbf{r}_t$ of the atoms, whose expectation is the average of the number of atoms in the cell, $\langle F\rangle=\overline{F}_{ii}=nv$. Then the fluctuation of the expectation of $F$, over the probability distribution of the $\mathbf{r}_t$, can be shown to be given by (2):

$$[\langle F^2\rangle-\langle F\rangle^2]/\langle F\rangle=S. \tag{4}$$

This result (4) is true equally for "classical" and "quantum" conditions [as is (1)], and depends on the assumptions that (i) there is a radius $a$ beyond which $g(r)$ tends to its (normalized) limit of unity, and such that $\int_a^\infty(g-1)4\pi r^2dr$ is negligible; and (ii) $v$ is large compared with $4\pi a^3/3$ and small compared with the volume of the whole liquid. For a quantum liquid the left-hand side of (4) must remain finite even at absolute zero, owing to the zero-point motion of the atoms, since the probability distribution of the atoms is essentially positive. This shows that (3) cannot then be true, since for a quantum liquid $n\chi_T$ remains finite, and hence $nkT\chi_T$ becomes zero, when $T\to 0$. Another case to which the same argument applies is that of the ideal Fermi gas. To arrive at (3) we would have to combine (4) with

---

* This work was begun at the Royal Society Mond Laboratory, Cambridge, England, where it was supported by the Department of Scientific and Industrial Research, and it was completed under contract between the ONR and Duke University. I would like to express my thanks to Professor F. London for the hospitality of his department.

[1] A general reference on the results (1)–(5) is: J. de Boer, Reports on Progress in Physics 12, 305 (1949), §10.

[2] Goldstein, Sommers, King, and Hoffman, Proceedings of the International Conference on Low Temperature Physics, Oxford, 1951, p. 88; see L. Goldstein, Phys. Rev. 84, 466 (1951), Fig. 1.

the Gibbs formula for the fluctuation of the number of atoms $N_v$ in the cell,

$$[\overline{N_v{}^2}-(\overline{N_v})^2]/\overline{N_v}=nkT\chi_T, \tag{5}$$

by equating their left-hand sides. It is this step which is clearly not permissible in general, because (5) refers to a thermal fluctuation *between* different quantum states (what is meant by "fluctuation" in statistical thermodynamics); while the average $\langle\ \rangle$ in (4) is given by a trace of the von Neumann density matrix, and at absolute zero becomes an expectation of the ground state. There is no difference when the variable in question is the energy, or another constant of the motion, but for the local density these two fluctuations are the same only in the classical (high temperature) limit.

In the absence of an adequate understanding of the excitations of a quantum liquid, an at least plausible formula to replace (3) in the low temperature range may be constructed as follows. We suppose that only "phonon" excitations are involved in the density fluctuation, and attribute $S(T)-S(0)$ to their effect. A phonon causes a fluctuation of the mass density $\rho$, for which we suppose the macroscopic formula

$$\text{energy density}=c^2\overline{(\delta\rho)^2}/\rho, \tag{6}$$

where $c$ is the velocity of sound, to hold.[3] Accordingly, putting $U\equiv E(T)-E(0)$, where $E$ is the total energy density, we would expect

$$S(T)-S(0)=U_{\text{phon}}/\rho c^2 \tag{7}$$

to give the variation of (2) at low temperatures. Using the specific heat data of Kramers[4] for liquid helium, (7) gives

$$S(T)-S(0)=1.05\times 10^{-4}\ \text{deg}^{-4}T^4. \tag{7$'$}$$

The tentative formula (7) may be compared with an exact one, valid for both classical and quantum conditions. If $K$ is the kinetic-energy density and $\phi(r)$ the potential of the interaction between two atoms, then the energy equation gives

$$E=K+\tfrac{1}{2}n^2\int g(r)\phi(r)d^3\mathbf{r},$$

and the virial theorem[5] gives

$$3p=2K-\tfrac{1}{2}n^2\int g(r)r\phi'(r)d^3\mathbf{r}.$$

Eliminating $K$ between these two equations,

$$2E-3p=\tfrac{1}{2}n^2\int g(r)[2\phi+r\phi']d^3\mathbf{r}. \tag{8}$$

From Kramers' results, the change in $g(r)$ below 0.6° implied by (8) is consistent with that given by (7′), in dependence on $T^4$, and also in order of magnitude. The implications of (8) at higher temperatures are also of interest. For liquid helium at saturated vapor pressure the left-hand side of (8) is $-43.7$ atmos at absolute zero, and increases by 0.3 atmos up to 1.4° and by a further 7.8 atmos between 1.4° and the lambda-point. This large increase of (8), and hence appreciable change in $g(r)$, in the high temperature range of helium II suggests (if (7) is correct at lower temperatures) that either the other kinds of excitation of the liquid also induce density fluctuations or they are strongly coupled to the "phonons" so that the energy contribution of the latter increases faster than the Debye expression. The increase of (8) seems to demand a large change in $g(r)$ between 3 and 6A. On the other hand the absence of a latent heat at the lambda-transition implies, by (8), that $g(r)$ is continuous through it, as expected.

Applied to a gas, (3) leads to an expression for the second virial coefficient,

$$B(T)=\lim_{n\to 0}\left\{\tfrac{1}{2}N\int[1-g(r)]d^3\mathbf{r}\right\}, \tag{9}$$

which has been used[6] to obtain a formula for $B(T)$ under quantum conditions. It appears from the discussion above that this application of (9) is not permissible.

*Note added in proof:*—It is conceivable that $a$ (the range beyond which $g=1$) is, for liquid helium, some orders of magnitude greater than the range of $\phi$, corresponding to a long-range order of quantal origin. This would lead to unusual effects in the scattering of radiation, in the soft x-ray to visible range; and would make possible anomalies in the scattering of light, as a function of temperature, not reflected in the left-hand side of Eq. (8).

---

[3] This step was made, long ago, for solids: A. Einstein, Ann. Physik **33**, 1275 (1910). It is curious how close this paper came to anticipating the Debye theory.

[4] H. C. Kramers, Proceedings of the International Conference on Low Temperature Physics, Oxford, 1951, page 93; and private communication.

[5] There has been some controversy over the applicability of the virial theorem in quantum conditions. See H. S. Green, Proc. Roy. Soc. (London) **A194**, 244 (1948); P. J. Price, Phil. Mag. **41**, 948 (1950).

[6] B. Beth and G. E. Uhlenbeck, Physica **4**, 915 (1937).