DEGENERACY IN NON-RELATIVISTIC BOSE-EINSTEIN STATISTICS

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ABSTRACT. Simple and direct proofs (substantially following Kennard and Condon) are given of the three distribution laws, *viz.*, Maxwell-Boltzmann, Fermi-Dirac and Bose-Einstein distribution. The properties of Bose-Einstein degenerate gas are discussed and compared with those of Fermi-Dirac degeneracy.

The thermal anomaly exhibited by helium at 2·19° Abs.—generally known as the λ-point*—has been the subject of many investigations during recent years. At this temperature helium shows a discontinuity in its specific heat, indicating a characteristic type of phase transition.† It has been found that its viscosity decreases suddenly at the λ-point, and the entropy difference between the liquid and the solid phase tends towards zero with decreasing temperature, showing that the liquid phase goes into a peculiar state below the λ-point. Recently Allen and Jones [1] have discovered that a transfer of momentum accompanies heat flow (the so-called fountain effect) in He II while Daunt and Mendelssohn's investigations [2] show that a large part of the heat must be carried by some form of material transport.

These unusual characteristics of liquid helium II have led F. London [3] to propose a new theory based on a peculiar condensation phenomenon of an ideal Bose-Einstein gas mentioned by Einstein [4] some years ago in his well-known papers on the degeneracy of an ideal gas. This interesting discovery of Einstein, however, was seriously questioned and adversely criticised by Uhlenbeck [5] and remained buried in Einstein's papers for many years. The credit of resuscitating it goes to F. London [6] who not only proved the correctness of Einstein's view but has also applied it in formulating a theory of condensation mechanism which has established, for the first time, the connection of Bose-Einstein degene-

* The λ-point temperature decreases with increase of pressure (about 1/50°C per atmosphere). When the pressure is increased to about 25 atmospheres, liquid He II passes into the solid state.

† See Ehrenfest, *Text-book of Thermodynamics*, 1937, pp. 128-133.

racy with the problem of liquid helium. Uhlenbeck [7] also has now withdrawn his former objection to Einstein's suggestion.

According to F. London He II may be regarded as a degenerate Bose-Einstein gas, *i.e.*, as a system in which one fraction of the substance is distributed over the excited states in a way determined by the temperature while the rest is condensed in the lowest energy level. If N_0 denotes the number of atoms condensed in the lowest energy state and $(N-N_0)$ the number of energetic particles, *i.e.*, the particles distributed over the excited states, then

$$\frac{N_0}{N}=\left[1-(T/T_0)^{\frac{3}{2}}\right]$$

where T_0 indicates the "temperature of degeneracy." The phenomenon of Bose-Einstein degeneracy has received only a desultory attention so far, partly because it appeared to be devoid of any practical significance, all real gases being condensed before the temperature T_0 and also because the magnitude of the various physical effects, *e.g.*, Joule-Thomson effect, Effusion, Thermal transpiration, etc., exhibited by an ideal Bose-Einstein gas is extremely small. However, the very smallness of an effect adds to it, at times, a special importance and interest. It will therefore be not altogether useless—and particularly because of the recent attempts at the application of degenerate Bose-Einstein statistics to the problem of He II—to discuss the phenomenon of Bose-Einstein degeneracy in detail, contrasting it with Fermi-Dirac degeneracy and (classical) non-degeneracy. The present paper is mainly intended to serve as a necessary background for subsequent papers dealing with physical properties of degenerate Bose-Einstein gas. We accordingly begin with a simple proof (substantially following Kennard [9] and Condon[8])* of the three distribution laws, *viz.*, Maxwell-Boltzmann, Bose-Einstein and Fermi-Dirac distribution. The second section is devoted to the derivation of expressions for the number and energy of particles of an ideal Bose-Einstein gas in the state of degeneracy as well as non-degeneracy. The continuity of the energy curve from the non-degenerate to the degenerate region, the discontinuity of the specific heat at $T=T_0$ and the dependence of pressure on concentration are discussed in the third section and expressions for entropy (non-degenerate and degenerate) are also derived in the end.

1. THE DISTRIBUTION LAWS*

We know that the wave function of any free particle enclosed in a cube of volume $V=L^3$ is

$$\psi=C\sin\frac{l\pi x}{L}\sin\frac{m\pi y}{L}\sin\frac{n\pi z}{} \qquad \ldots (1)$$

* The proof is here extended to include Bose-Einstein statistics. Kennard has dealt with the classical statistics, and Condon has included the Fermi-Dirac statistics also.

characterised by the energy value

$$E_{l,m,n} = \frac{h^2}{8mL^2}(l^2+m^2+n^2). \quad \cdots (2)$$

The normalisation constant C is easily found to be

$$C = 2\left(\frac{2}{V}\right)^{\frac{1}{2}}. \quad \cdots (3)$$

Let us now consider an assembly of ν similar non-interacting particles in the cube. The state of the assembly will be characterised by 3ν quantum numbers (l_1, m_1, n_1), (l_2, m_2, n_2), (l_3, m_3, n_3) ......, etc., one bracket for each of the ν particles. The energy of the assembly will be

$$W_k = \frac{h^2}{8m\,L^2}\sum_{r=1}^{r=\nu}(l_r^2+m_r^2+n_r^2). \quad \cdots (4)$$

The number of independent wave functions of energy less than or equal to W, *i.e.*, $W_k \leqq W$, will be $\frac{1}{2^{3\nu}}$ times the volume of a 3ν-dimensional sphere of radius $\left(\frac{8m\,L^2W}{h^2}\right)^{\frac{1}{2}}$. This is easily seen if we note that to each state there corresponds a unit volume in a space of 3ν dimensions (with co-ordinates l_1, m_1, n_1; l_2, m_2, n_2; etc.). The factor $\frac{1}{2^{3\nu}}$ arises, for we are concerned with only the positive values of l_r, m_r, n_r. Thus the number of states (independent wave functions) * of energy $\leqq$ W is

$$C_\nu(W) = \frac{1}{\Gamma\left(\frac{3\nu}{2}+1\right)}\left(\frac{2\pi mL^2W}{h^2}\right)^{\frac{3\nu}{2}}. \quad \cdots (5)$$

The number of wave functions lying between W and W + dW will therefore be

$$C_\nu'(W)dW = \frac{\left(\frac{2\pi mL^2W}{h^2}\right)^{\frac{3\nu}{2}}}{\Gamma\left(\frac{3\nu}{2}+1\right)}\cdot\frac{3\nu}{2}\,\frac{dW}{W}. \quad \cdots (6)$$

* This is the total number of wave functions neglecting symmetry restrictions that characterise Fermi and Bose Statistics.

We have now to introduce the concept of temperature and this can be done in two ways : (*i*) by an appeal to the second law of thermodynamics in one form or the other, (*ii*) by using the property of a classical perfect gas, that the average energy per particle, for it, is $\frac{3}{2}kT$. We shall follow here the second alternative and consider the system (or the assembly) whose law of energy distribution has to be investigated in thermal contact with a perfect gas thermometer.

In the case of a perfect gas we can rewrite (6) in a form suited to subsequent applications. In this case $W=\frac{3}{2}\nu kT$, and for w very small compared to W, we have from (6)

$$\frac{C_\nu'(W-w)}{C_\nu'(W)}=\left(1-\frac{w}{W}\right)^{\frac{3\nu}{2}-1}=e^{-\frac{w}{kT}} \qquad \ldots \quad (6a)$$

Suppose a system A has energy levels w_0, w_1, w_2, ...and the corresponding weight factors* g_0, g_1, g_2, ... Let us find the probability $P(a)$ that this system A has energy w_a. Let the total energy of the composite assembly, the system A in thermal contact with the perfect gas thermometer, be W to $W+dW$. The energy associated with the system A is w_a and with the perfect gas thermometer (containing ν particles), $W-w_a$ to $(W-w_a)+dW$. The number of wave functions such that A is in the state of energy w_a and the ν particles are in the state of energy $(W-w_a)$ to $(W-w_a)+dW$ will be

$$=g_a.C_\nu'(W-w_a)dW \qquad \ldots \quad (7)$$

and therefore the probability P(*a*) will be

$$P(a)=\frac{g_a.C_\nu'(W-w_a)dW}{\sum_s g_s.C_\nu'(W-w_s)dW} \qquad \ldots \quad (8)$$

where $\sum_s$ denotes the sum over all the states of A. Let the probability of A being in the state of lowest energy w_0 be P(o);

then,
$$P(o)=\frac{g_0.C_\nu'(W-w_0)dW}{\sum_s g_s.C_\nu'(W-w_s)dW} \qquad \ldots \quad (9)$$

* The weight factor of a state denotes the number of distinct wave functions corresponding to that state.

and using (6*a*) we have
$$\frac{P(a)}{P(o)}=\frac{g_a}{g_o}\cdot\frac{e^{-\frac{w_a}{kT}}}{e^{-\frac{w_o}{kT}}} \qquad \ldots \quad (10)^*$$

or
$$P(a)=c.g_a e^{-\frac{w_a}{kT}} \qquad \ldots \quad (11)$$
where c is a constant.

If the system A is a free particle, then from (6) applied to one particle, we have the number of states lying in the kinetic energy range ϵ, $\epsilon+d\epsilon$,
$$a(\epsilon)d\epsilon = g_a = \left(\frac{2\pi m L^2}{h^2}\right)^{\frac{3}{2}}\cdot\frac{1}{\Gamma(\frac{3}{2})}.w_a^{\frac{1}{2}}dw_a \qquad \ldots \quad (12)$$
and therefore (omitting the subscripts),
$$P(w)=bw^{\frac{1}{2}}dw.e^{-\frac{w}{kT}} \qquad \ldots \quad (13)$$
where b is a constant.

This is Maxwell's distribution law. The constant b can be easily determined by the normalisation condition that
$$\int_o^\infty P(w)dw=b\int_o^\infty w^{\frac{1}{2}}\;dw.e^{-\frac{w}{kT}} \qquad \ldots \quad (14)$$
or
$$b=\frac{2}{\sqrt{\pi}}(kT)^{-\frac{3}{2}} \qquad \ldots \quad (15)$$

We shall now derive the distribution law for Fermi-Dirac and Bose-Einstein Statistics. We suppose the system A, referred to in the above discussion, to consist of an assembly of N similar (indistinguishable) particles—this assembly being in thermal contact with the perfect gas thermometer. Let ϵ_r ($r=1, 2, \ldots$) denote the eigen-values of the energy of a particle in the assembly A, and N_r the number of particles in the energy state ϵ_r. Then
$$N=\Sigma N_r\;;\;w_a=\Sigma\epsilon_r N_r \qquad \ldots \quad (16)$$
where w_a is the total energy of the assembly A.

Let us think of a particular particle-energy-state ϵ_s and let $\underset{(N_s)}{\Sigma}F$ represent the sum (for any function F) taken over all those states of the assembly for which, in the energy-level ϵ_s, there are N_s particles (no more and no less), *i.e.*, the sum extends over all possible values of w_a consistent with this one restriction that there be N_s particles in the level ϵ_s.

* It will be noticed that the exponential factors arise because the system is in contact with classical perfect gas thermometer and shares energy with it.

Writing * $$F = e^{-w_a/kT}$$
and $$w_a = w_a' + N_s\epsilon_s \quad \Bigg\} \quad \dots (17)$$

we have $$\sum_{(N_s)} e^{-\frac{w_a}{kT}} = e^{-\frac{N_s\epsilon_s}{kT}} \sum_{(N_s)} e^{-\frac{w_a'}{kT}}. \quad \dots (18)$$

$\sum_{(N_s)} e^{-\frac{w_a'}{kT}}$ is the sum for an $(N - N_s)$-particle assembly from which the state ϵ_s is excluded (*i.e.*, this sum is independent of ϵ_s).

Let $$\sum_{(N_s)} e^{-\frac{w_a'}{kT}} \Big/ \sum_{(N_s-1)} e^{-\frac{w_a'}{kT}} = A, \quad \dots (19)$$

then A being the ratio of the sums for $(N - N_s)$-particle and $[(N-N_s)+1]$-particle assemblies (the state ϵ_s being excluded for both) will be independent of N_s as N is very large compared to N_s.†

Let us first find the distribution law for the case of Fermi-Dirac statistics. In this case no two particles can be in the same quantum state, and therefore the allowed values of N_s are only 0 and 1. For some of the states of the assembly, there will be a particle in the level ϵ_s, $(N_s = 1)$ and for the rest, the level ϵ_s will be unoccupied, $(N_s = 0)$. We have to find the average value of N_s for all possible states of the assembly.

Noting, from (11), that the probability factor associated with each state of the assembly is proportional to $e^{-\frac{w_a}{kT}}$, the expression for the average value of N_s will be, using (17) and (19),

$$\bar{N}_s = \frac{\sum_{(0)} 0 \times e^{-\frac{w_a}{kT}} + \sum_{(1)} 1 \times e^{-\frac{w_a}{kT}}}{\sum_{(0)} e^{-\frac{w_a}{kT}} + \sum_{(1)} e^{-\frac{w_a}{kT}}} = \frac{1}{\frac{1}{A} \cdot e^{\frac{\epsilon_s}{kT}} + 1} \quad \dots (20)$$

* $\sum e^{-\frac{w_a}{kT}}$ is known as the partition function.

† Strictly, there are states for which N_s will be comparable to N, but these states, because of the exponential factor $e^{-\frac{N_s\epsilon_s}{kT}}$, will be ineffective in our calculations. [See equation (22).]

or the number $N(\epsilon)d\epsilon$ of the particles lying in the energy range ϵ to $\epsilon+d\epsilon$ is

$$N(\epsilon)d\epsilon = \bar{N}_\epsilon\, a(\epsilon)d\epsilon = \frac{a(\epsilon)d\epsilon}{\frac{1}{A}e^{\frac{\epsilon}{kT}}+1} \qquad \ldots \quad (21)$$

where $a(\epsilon)$ is given by (12).

We now consider the case of Bose-Einstein Statistics. In this case there is no restriction on the number of particles in the same quantum state, *i.e.* no restriction on the value of N_s. The average value will therefore be given by

$$N_s = \frac{\sum\limits_{(0)} 0 \times e^{-\frac{w_a}{kT}} + \sum\limits_{(1)} 1 \times e^{-\frac{w_a}{kT}} + \sum\limits_{(2)} 2 \times e^{-\frac{w_a}{kT}} + \ldots\ldots}{\sum\limits_{(0)} e^{-\frac{w_a}{kT}} + \sum\limits_{(1)} e^{-\frac{w_a}{kT}} + \sum\limits_{(2)} e^{-\frac{w_a}{kT}} + \ldots\ldots} \qquad \ldots \quad (22)$$

which on using (17) and (19) reduces to

$$N_s = \frac{Ae^{-\frac{\epsilon_s}{kT}}\left[1+2Ae^{-\frac{\epsilon_s}{kT}}+3A^2e^{-\frac{2\epsilon_s}{kT}}+\ldots\right]}{\left[1+Ae^{-\frac{\epsilon_s}{kT}}+A^2e^{-\frac{2\epsilon_s}{kT}}+\ldots\ldots\right]}$$

$$= \frac{Ae^{-\frac{\epsilon_s}{kT}}\left(1-Ae^{-\frac{\epsilon_s}{kT}}\right)^{-2}}{\left(1-Ae^{-\frac{\epsilon_s}{kT}}\right)^{-1}}$$

$$= \frac{1}{\frac{1}{A}e^{\frac{\epsilon_s}{kT}}-1}. \qquad \ldots \quad (23)$$

The number $N(\epsilon)d\epsilon$ of particles lying in the energy range ϵ, $\epsilon+d\epsilon$, is

$$N(\epsilon)d\epsilon = \bar{N}_\epsilon\, a(\epsilon)d\epsilon = \frac{a(\epsilon)d\epsilon}{\frac{1}{A}e^{\frac{\epsilon_s}{kT}}-1} \qquad \ldots \quad (24)$$

where $a(\epsilon)$ is given by (12).

To obtain the distribution law for a classical assembly in this way, we have to note that for a classical assembly all states are accessible, whereas for a Bose-assembly the "symmetry requirement" imposes a severe restriction on the number of the accessible states.—*This restriction from the view-point of the phase-cells means that in classical statistics the particles are distinguishable from each other while in quantum statistics they are indistinguishable.* Therefore, the number of states for a $(N-N_s)$-particle assembly (classical) will be proportional to $N!/N_s!N-N_s!$, the number of ways of selecting $(N-N_s)$ particles out of the total number N, and thus instead of (19) we have

$$\sum_{(N_s)} e^{-\frac{w_a}{kT}} \Big/ \sum_{(N_s-1)} e^{-\frac{w_a}{kT}} = e^{-\frac{\epsilon_s}{kT}} \frac{A}{N_s}$$

or

$$\sum_{(N_s)} e^{-\frac{w_r}{kT}} \Big/ \sum_{(0)} e^{-\frac{w_r}{kT}} = e^{-\frac{N_s\epsilon_s}{kT}} \frac{A^{N_s}}{N_s!}.$$

and

$$\frac{\sum_{(N_s)}}{\sum_{(1)}} = e^{-\frac{(N_s-1)}{kT}} \frac{A^{(N_s-1)}}{N_s!}.$$

Thus, for a classical assembly (22) simply reduces to

$$\bar{N}_s = \frac{\sum_{(1)}}{\sum_{(0)}} = Ae^{-\frac{\epsilon_s}{kT}},$$

which is the classical distribution law.

2. We shall now proceed to derive the thermodynamical properties of a Bose-Einstein assembly consisting of N similar non-interacting particles occupying a volume V. The distribution law, on substituting in (24) for $a(\epsilon)d\epsilon$ from (12) becomes

$$N(\epsilon)d\epsilon = \frac{2\pi(2m)^{\frac{3}{2}}V}{h^3} \frac{\epsilon^{\frac{1}{2}}d\epsilon}{1/Ae^{\epsilon/kT}-1} \quad \dots \quad (25)$$

and

$$N = \int_0^\infty N(\epsilon)d\epsilon. \quad \dots \quad (26)$$

Defining a dimensionless number A_0 (usually called the degeneracy-discriminant) by the relation

$$A_0 = \frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{\frac{3}{2}} \quad \dots \quad (27)$$

we have from (25) and (26), $A_0 = F(A)$, where

$$F(A)=\frac{2}{\sqrt{\pi}}\int_0^\infty \frac{u^{\frac{1}{2}}du}{1/Ae^u-1}=\sum_{n=1}^{\infty}\frac{A^n}{n^{\frac{3}{2}}} \quad \text{for } A<1 \text{ and } u=\epsilon/kT \quad \ldots \quad (28)$$

Now A cannot be greater than unity, otherwise the expression (25) for $N(\epsilon)$ would be negative, for some values of ϵ, which is inadmissible. The maximum (admissible) value of F(A) is F(1) which is given by

$$F(1)=\zeta\left(\frac{3}{2}\right)=1+\frac{1}{2^{\frac{3}{2}}}+\frac{1}{3^{\frac{3}{2}}}+\frac{1}{4^{\frac{3}{2}}}+\ldots=2{\cdot}612 \quad \ldots \quad (29)$$

where $$\zeta(t)=\frac{1}{(t-1)!}\int_0^\infty \frac{x^{t-1}dx}{e^x-1}$$

denotes the Riemann zeta-function.*

Therefore, no solution A(T) of equation (28) can be found for which $A_0>$ 2·612 *i.e.*, for which

$$N>\frac{V}{h^3}(2\pi mkT)^{\frac{3}{2}}2{\cdot}612$$

or

$$T<T_0$$

where $$T_0=\left(\frac{n}{2{\cdot}612}\right)^{\frac{2}{3}}\frac{h^2}{2\pi mk}=\left(\frac{A_0}{2{\cdot}612}\right)^{\frac{2}{3}}T, \quad \ldots \quad (30)$$

n being the number of particles per unit volume. If m denotes the mass of the He-atom, N the Avogadro-number and V a molecular volume of 27·6 cm^3 for liquid He II, then

$$T_0=3{\cdot}13°K.$$

The total energy E is given by

$$E=N\epsilon=\frac{2\pi(2m)^{\frac{3}{2}}V}{h^3}\int_0^\infty \frac{\epsilon^{\frac{3}{2}}d\epsilon}{1/A\cdot e^{\epsilon/kT}-1}$$

$$=\frac{kTV}{h^3}\cdot\frac{2}{\sqrt{\pi}}(2\pi mkT)^{\frac{3}{2}}\int_0^\infty \frac{u^{\frac{3}{2}}du}{1/A\cdot e^u-1} \quad \ldots \quad (31a)$$

$$=\frac{kTV}{h^3}\frac{2}{\sqrt{\pi}}(2\pi mkT)^{\frac{3}{2}}\int_0^\infty u^{\frac{3}{2}}duAe^{-u}(1-Ae^{-u})^{-1}$$

or $$E=\frac{3}{2}\cdot\frac{kTV}{h^3}(2\pi mkT)^{\frac{3}{2}}A\left[1+\frac{A}{2^{\frac{5}{2}}}+\frac{A^2}{3^{\frac{5}{2}}}+\ldots\right]^{\dagger} \quad \ldots \quad (31b)$$

* For a table of values of the Riemann zeta-function, see the Appendix.

† This result is obtained by making use of the relation

$$\int_0^\infty u^n e^{-ru}du=\frac{1}{r^{n+1}}\Gamma(n+1)$$

Now from (28) we have

$$A_0 = A\left[1 + \frac{A}{2^{\frac{3}{2}}} + \frac{A^2}{3^{\frac{3}{2}}} + \frac{A^3}{4^{\frac{3}{2}}} + \ldots\right] \quad \ldots \quad (32)$$

Let us write

$$A = A_0 + aA_0^2 + bA_0^3 + cA_0^4 + dA_0^5 + \ldots \quad \ldots \quad (33a)$$

and

$$A_0 = A + qA^2 + rA^3 + sA^4 + tA^5 + \ldots$$

Then substituting the first series in the second, we get

$$A_0 = A_0 + A_0^2(a+q) + A_0^3(b+2aq+r)$$
$$+ A_0^4(c + a^2q + 2bq + 3ar + s)$$
$$+ A_0^5(d + 2abq + 2cq + 3a^2r + 3br + 4as + t) + \ldots$$

Equating coefficients of equal powers of A_0 on both sides of the above equation, we have

$$\left.\begin{array}{l} a = -q,\ b = 2q^2 - r,\ c = -s + 5qr - 5q^3, \\ d = 14q^4 - 21q^2r + 6qs + 3r^2 - t \end{array}\right\} \quad \ldots \quad (33b)$$

or for the particular case we are considering,

$$\left.\begin{array}{l} a = \left(-\frac{1}{2^{\frac{3}{2}}}\right) = -0{\cdot}353553 \\ b = \left(\frac{1}{4} - \frac{1}{3^{\frac{3}{2}}}\right) = 0{\cdot}057550 \\ c = \left(-\frac{1}{8} + \frac{5}{2^{\frac{3}{2}}\,3^{\frac{3}{2}}} - \frac{5}{2^{\frac{9}{2}}}\right) = -0{\cdot}005764 \end{array}\right\} \quad \ldots \quad (34)$$

Substituting for A in terms of A_0 in the energy equation (31*b*) we have

$$E = \frac{3}{2}RT\left[1 + A_0\left(a + \frac{1}{2^{\frac{5}{2}}}\right) + A_0^2\left(b + \frac{2a}{2^{\frac{5}{2}}} + \frac{1}{3^{\frac{5}{2}}}\right)\right.$$
$$\left. + A_0^3\left(c + \frac{a^2+2b}{2^{\frac{5}{2}}} + \frac{3a}{3^{\frac{5}{2}}} + \frac{1}{4^{\frac{5}{2}}}\right) + \ldots\ldots\right]$$

which after substituting the values of *a*, *b*, *c* from (34) reduces to

$$E = \frac{3}{2}RT\,[1 - 0{\cdot}1768A_0 - 0{\cdot}0033A_0^2 - 0{\cdot}00011A_0^3 - \ldots] \quad \ldots \quad (35)$$

or replacing A_0 by (T_0/T) with the help of (30), we obtain the non-degenerate Bose-Einstein expression for energy

$$E_+ = \frac{3}{2}RT\,[1 - 0{\cdot}462(T_0/T)^{\frac{3}{2}} - 0{\cdot}0225(T_0/T)^3 - 0{\cdot}00197(T_0/T)^{\frac{9}{2}} - \ldots] \quad \ldots \quad (36)$$

and

$$C_{v+}=\left(\frac{dE}{dT}\right)_v=\frac{3}{2}R\left[1+0{\cdot}231\left(\frac{T_0}{T}\right)^{\frac{3}{2}}\right.$$

$$\left.+0{\cdot}045\left(\frac{T_0}{T}\right)^{3}+0{\cdot}0069\left(\frac{T_0}{T}\right)^{\frac{9}{2}}+\ldots\ldots\right] \quad \ldots \quad (37)$$

Equations (36) and (37) are the same as equations (7b) and (8b) appearing in F. London's paper (*Phy. Rev.* 1938, *54*, p. 950) except for a numerical error in the coefficients of $\left(\frac{T_0}{T}\right)^{\frac{9}{2}}$.

Let us now derive the degenerate expression for energy. In the degenerate case when $T \leqq T_0$, A becomes equal to unity * and (31a) reduces to

$$E_-=\frac{kTV}{h^3}\frac{2}{\sqrt{\pi}}(2\pi mkT)^{\frac{3}{2}}\int_0^{\infty}\frac{u^{\frac{3}{2}}du}{e^u-1} \quad \ldots \quad (38)$$

But from (30) $\qquad (2\pi mkT)^{\frac{3}{2}}=\frac{nh^3}{2{\cdot}612}\left(\frac{T}{T_0}\right)^{\frac{3}{2}}$

Hence we have

$$E_-=\frac{2}{2{\cdot}612}\frac{RT}{\sqrt{\pi}}\left(\frac{T}{T_0}\right)^{\frac{3}{2}}\int_0^{\infty}\frac{u^{\frac{3}{2}}du}{e^u-1} \quad \ldots \quad (39)$$

$$=\frac{3}{2}RT(T/T_0)^{\frac{3}{2}}\frac{\zeta(2{\cdot}5)}{\zeta(1{\cdot}5)}$$

$$=0{\cdot}514\cdot\frac{3}{2}RT\cdot(T/T_0)^{\frac{3}{2}} \quad \ldots \quad (40)$$

and

$$C_{v-}=\left(\frac{dE}{dT}\right)_-=\frac{15}{4}\cdot 0{\cdot}514\,R(T/T_0)^{\frac{3}{2}} \quad \ldots \quad (41)$$

It will be of interest to note the ratio of the energy and the specific heats for the degenerate Bose and Fermi Statistics. In the case of the Bose Statistics, exact expressions are obtained for the degenerate case, but for Fermi Statistics, exact expressions cannot be obtained and the various physical quantities are expressed as a power series in (1/log A). In comparing degenerate Bose and Fermi Statistics, we take, in the latter case, only the first term of the series. We then have

$$E_-(\text{Fermi})=\frac{3}{10}\frac{h^2}{m}N\left(\frac{3n}{4\pi}\right)^{\frac{2}{3}}$$

$$=\frac{3}{5}\left(\frac{3}{4\pi}\right)^{\frac{2}{3}}\pi\left[\zeta\left(\frac{3}{2}\right)\right]^{\frac{2}{3}}RT\left(\frac{T_0}{T}\right) \quad \ldots \quad (42)$$

* Unity is the maximum value A can take. It cannot exceed unity, otherwise N(ε) will become negative for some values of ε which is inadmissible.

and $$C_{v-}(\text{Fermi}) = \frac{\pi^2 mk}{h^2}\,RT\left(\frac{4\pi}{3n}\right)^{\frac{2}{3}}$$

$$= \frac{\pi}{2}\left(\frac{4\pi}{3}\right)^{\frac{2}{3}}\;\frac{R}{[\zeta(\frac{3}{2})]^{\frac{2}{3}}}\;\left(\frac{T}{T_0}\right) \qquad \ldots (43)$$

and therefore, $$\frac{E_-(\text{Bose})}{E_-(\text{Fermi})} = \left[\frac{5}{2}\left(\frac{4}{3\sqrt{\pi}}\right)^{\frac{2}{3}}\zeta\left(\frac{5}{2}\right)\right] \times \frac{1}{A_0^{\frac{5}{3}}}$$

$$= 2{\cdot}77\left(\frac{1}{A_0^{\frac{5}{3}}}\right) \qquad \ldots (44)$$

and $$\frac{C_{v-}(\text{Bose})}{C_{v-}(\text{Fermi})} = \zeta\left(\frac{5}{2}\right)\frac{15}{2\pi}\left(\frac{3}{4\pi}\right)^{\frac{2}{3}}\;\frac{1}{A_0^{\frac{1}{3}}} = \frac{1{\cdot}23}{A_0^{\frac{1}{3}}} \qquad \ldots (45)$$

3. If we plot E/RT against T/T_0 using the non-degenerate expression

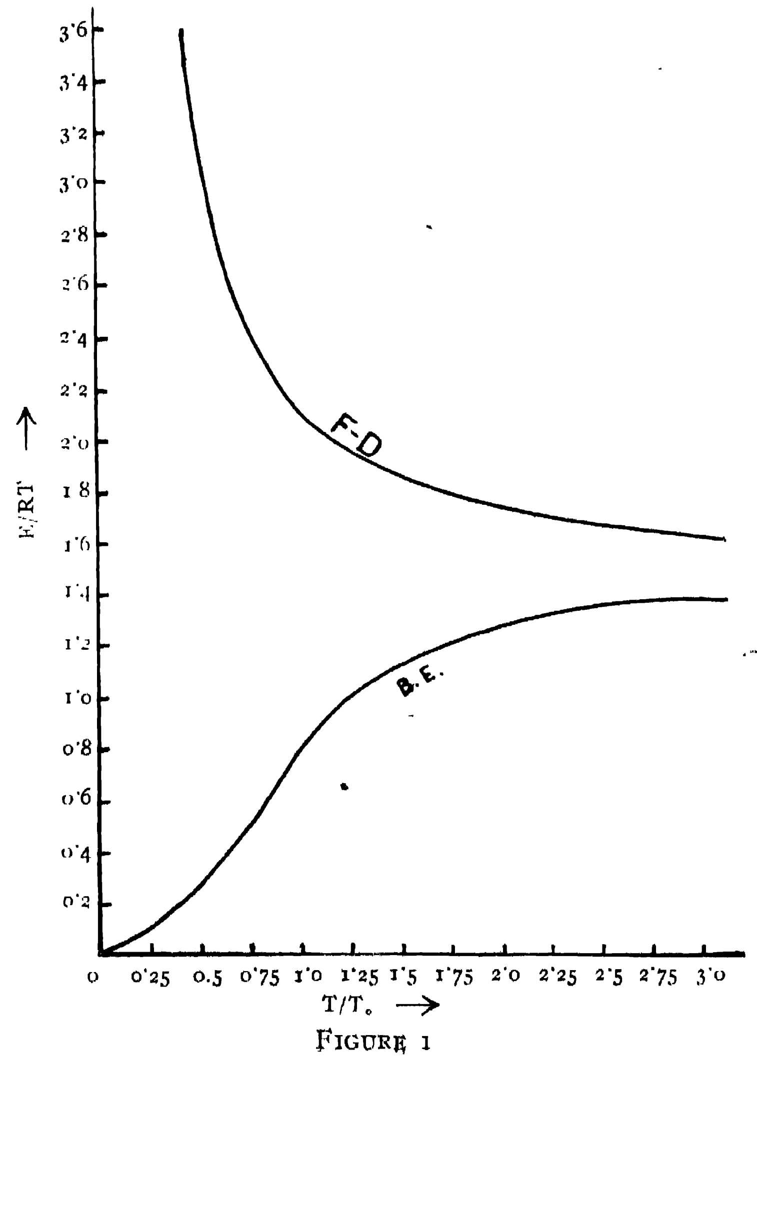

FIGURE 1

(36) for E_+ in the region in which $T > T_0$ and the degenerate expression (40) for E_- in the region of $T < T_0$, we obtain the lower curve in figure 1. The upper curve (given for the sake of comparison) is a plot of E/RT against T/T_0 for the Fermi-Dirac Statistics. This is obtained with the help of the data from Stoner's paper (*Phil. Mag.*, 1938, Vol. 25, p. 907). It can be easily seen that the two branches corresponding to E_+ and E_- in the lower curve are continuous at $T = T_0$ with a continuous tangent. This result can be theoretically verified by differentiating with respect to T, the expressions (36) and (40) and noting that $(dE/dT)_+$ becomes equal to $(dE/dT)_-$ when $T = T_0$.

The second derivative of E, however, is discontinuous and the run of the specific heat (C_v) curve has therefore a break at $T = T_0$. This is clearly shown in figure 2, where (C_v/R) is plotted against (T/T_0) following F. London. Differentiating the expressions for $(C_v)_+$ and $(C_v)_-$ and putting $T = T_0$ we get

$$\frac{d}{dT}(C_v)_+ = -0{\cdot}77\,\frac{R}{T_0} \tag{46}$$

and

$$\frac{d}{dT}(C_v)_- = 2{\cdot}89\,\frac{R}{T_0} \tag{47}$$

From the values of the two tangents given by (46) and (47), the angle of discontinuity between the two branches $(C_v)_+$ and $(C_v)_-$ at $T = T_0$ is easily found to be (about) 71°. For comparison, the specific heat curve for the

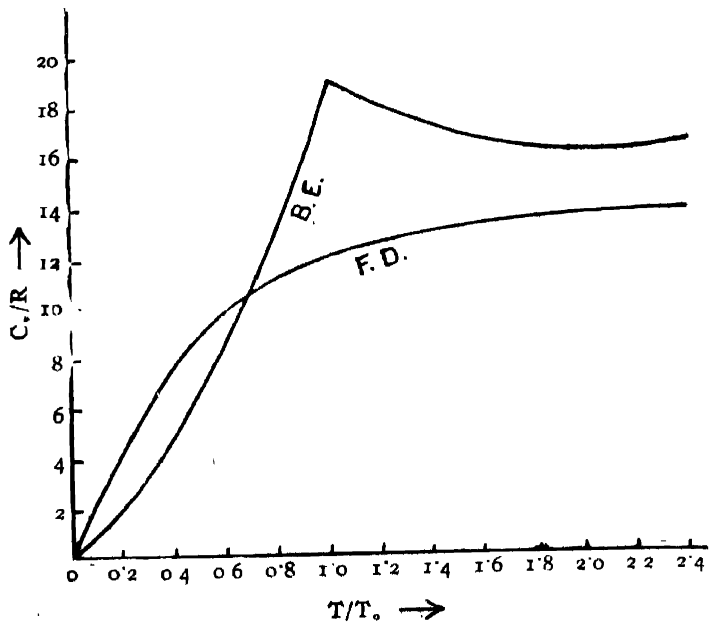

FIGURE 2

Fermi-Dirac Statistics is also plotted in figure 2 from the data in Stoner's paper referred to above.

From the relation $p=\frac{2}{3}\frac{E}{V}$ we get

$$p_+=\frac{RT}{V}\left[1-\frac{0\cdot462}{cVT^{\frac{3}{2}}}-\frac{0\cdot0225}{(cVT^{\frac{3}{2}})^2}-\frac{0\cdot00197}{(cVT^{\frac{3}{2}})^3}\cdots\right] \quad \ldots \quad (48)$$

and

$$p_-=0\cdot514cRT^{\frac{5}{2}} \quad \ldots \quad (49)$$

where

$$c=\frac{2\cdot612}{N}\left(\frac{2\pi mk}{h^2}\right)^{\frac{3}{2}}. \quad \ldots \quad (50)$$

To get the expressions for the free energy F, we make use of the Gibbs-Helmholtz relation

$$F=E+T\left(\frac{dF}{dT}\right)_V \quad \ldots \quad (51)$$

then

$$\frac{d}{dT}\left(\frac{F}{T}\right)=-\frac{E}{T^2}$$

and

$$F=-T\int_0^T\frac{E}{T^2}\,dT \quad \ldots \quad (52)$$

Substituting the values of E_+ and E_- from (36) and (40) in the above equation, we get

$$F_+=-\frac{3}{2}RT\left[ln\left(\frac{T}{T_0}\right)+0\cdot308\left(\frac{T_0}{T}\right)^{\frac{3}{2}}+0\cdot0075\left(\frac{T_0}{T}\right)^3+0\cdot00044\left(\frac{T_0}{T}\right)^{\frac{9}{2}}+\ldots\right] \quad \ldots \quad (53)$$

and

$$F_-=-\frac{\zeta(\frac{5}{2})}{\zeta(\frac{3}{2})}RT\left(\frac{T}{T_0}\right)^{\frac{3}{2}} \quad \ldots \quad (54)$$

as obtained by F. London.

The entropy S is given by the well-known relation

$$F=E-TS \quad \ldots \quad (55)$$

Hence

$$S_+=\left(\frac{E-F}{T}\right)_+=\frac{3}{2}R\left[1+ln\left(\frac{T}{T_0}\right)-0\cdot154\left(\frac{T_0}{T}\right)^{\frac{3}{2}}-0\cdot015\left(\frac{T_0}{T}\right)^3-0\cdot0016\left(\frac{T_0}{T}\right)^{\frac{9}{2}}-\ldots\right] \quad \ldots \quad (56)$$

and

$$S_-=\frac{5}{2}R\left(\frac{T}{T_0}\right)^{\frac{3}{2}}\frac{\zeta(2\cdot5)}{\zeta(1\cdot5)}=\frac{5}{2}0\cdot514RcT^{\frac{3}{2}}V \quad \ldots \quad (57)$$

The entropy for a degenerate Fermi gas is (to a first approximation) given by the expression

$$S_{-}\,(\text{Fermi}) = \frac{Rk\pi^2 Tm}{h^2}\left(\frac{4\pi}{3n}\right)^{\frac{2}{3}}$$

$$= \frac{\pi}{2}\left(\frac{4\pi}{3}\right)^{\frac{2}{3}} \frac{R}{[\zeta(\frac{3}{2})]^{\frac{2}{3}}} \left(\frac{T}{T_0}\right) \qquad \ldots \quad (58)$$

and hence

$$\frac{S_{-}\,(\text{Bose})}{S_{-}\,(\text{Fermi})} = 5\left(\frac{3}{4\pi^{\frac{5}{2}}}\right)^{\frac{2}{3}} \frac{\zeta(\frac{5}{2})}{A_0^{\frac{1}{3}}} \qquad (59)$$

$$= 0{\cdot}821\,\frac{1}{A_0^{\frac{1}{3}}}. \qquad \ldots \quad (60)$$

APPENDIX

Values of ζ-function for different values of x.

x $\quad \zeta(x) = \Sigma \frac{1}{n^x}$;

$\frac{3}{2}$ $\quad$ 2·612 ;

2 $\quad$ 1·645 $= \frac{\pi^2}{6}$;

$\frac{5}{2}$ $\quad$ 1·341 ;

3 $\quad$ 1·202 ;

$\frac{7}{2}$ $\quad$ 1·127 ;

4 $\quad$ 1·0823 $= \frac{\pi^2}{90}$;

$\frac{9}{2}$ $\quad$ 1·0573 ;

5 $\quad$ 1·0369.

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