The Bose-Einstein Condensation for Charged Particles in a Magnetic Field

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The condensation and accumulation phenomena of charged Bose-Einstein particles in a magnetic field are examined, neglecting electrostatic interactions. For weak fields a single condensation occurs at the same temperature as that for uncharged particles; for strong fields there is a separate lower accumulation temperature, indicating the accumulation of particles in the lowest translational state. The total energy, free energy, and polarization are calculated, and applied to the properties of a gas of electron pairs, and a solution of deuterons in a metal, these being systems whose low temperature behavior might show a Bose-Einstein condensation. It is shown that the Bose-Einstein condensation of free electron pairs cannot provide a theory of superconductivity.

INTRODUCTION

IN the preceding paper[1] the distinction was made between a condensation in the thermodynamic sense, and an accumulation in the statistical mechanical sense. In this paper we use the conceptions and approximations there discussed to examine the properties of charged Bose-Einstein particles in a magnetic field, neglecting the effect of electrostatic interactions but including, where required, spin and intrinsic magnetic moment. We shall calculate the distribution of the population over the different classes of states, the total energy, the free energy, and the polarization.

We repeat here two expressions from I for convenience. To replace a sum by an integral we have

$$\sum_{m=a}^{b} f(m) = \int_{a-\frac{1}{2}}^{b+\frac{1}{2}} f(m)dm - f'(m)/24 \Big|_{a}^{b}. \quad (1)$$

It is valid to use this approximation provided that for every point n within the interval, $a \leq n \leq b$

$$f(n+\tfrac{1}{2}) - f(n-\tfrac{1}{2}) - f'(n) \ll f(n). \quad (2)$$

For f of the form $1/(\exp(E(n)/kT+\alpha)-1)$, i.e. the B. E. integrand, it was found that if this criterion failed for one value of n in the interval (usually the lowest one) we could expect an abrupt accumulation of particles in the corresponding quantum state, and possibly a condensation. If it failed for every value we could expect a gradual accumulation in the lowest state.

THE GAS OF IONS IN A MAGNETIC FIELD, WITHOUT SPIN

Consider an assembly of N particles of mass m, charge e in a cylindrical container of volume V, radius R, height L with a magnetic field H along the axis. It is assumed that the energy levels which the particles occupy are given by the strength of the magnetic field and dimension L alone. Thus, we neglect electrostatic interactions, and ask: What is the behavior of this system as a function of the thermodynamic variables H and T? The

energy levels are given by[2]

$$E(l, n_1, n_3) = \mu H(2(l+\tfrac{1}{2}) + n_1 + |n_1|) + \epsilon n_3^2$$
$$\epsilon = h^2/8mL^2, \quad \mu = eh/4\pi mc. \quad (3)$$

Let

$$g = \pi e H R^2/hc.$$

α is determined by

$$N = \sum_{n_1=-g}^{-1} \sum_{l=0}^{\infty} \sum_{n_3=1}^{\infty} 1/(\exp(E(l, n_1, n_3)/kT+\alpha)-1), \quad (4)$$

where the limits of summation on n_1, the azimuthal quantum number are determined by correspondence principle arguments.[2,3] l is the orbital quantum number and n_3 the translational quantum number for motion along the field.

Definitions and Approximations

In evaluating (4) we will utilize the following definitions (see Fig. 1):

(1) $\quad U(p,\alpha) = (1/\Gamma(p+1))$

$$\times \int_0^{\infty} dz z^p/(\exp(z+\alpha)-1) \quad (5)$$

$$= \sum_{j=1}^{\infty} \exp(-\alpha j)/j^{p+1}. \quad (6)$$

(2) The temperature T_{01}, below which we must write separately the lowest term $(l=0)$ in the integration over l (failure of Eq. (2))

$$T_{01} = (N/VU(\tfrac{1}{2}, 0))^{\frac{2}{3}}(h^2/2\pi mk). \quad (7)$$

T_{01} is also the condensation temperature in the absence of a field.[4]

(3) T_{02} is defined as the temperature below which, for $l=0$, we must write separately the lowest term $(n_3=1)$ in the integration over n_3. It is defined so that

$$2gkT_{02}/3 = N,$$

[1] M. F. M. Osborne, Phys. Rev. **76**, 396 (1949), hereafter referred to as I.

[2] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Clarendon Press, Oxford, 1932), pp. 354, 358.
[3] L. Landau, Zeits. f. Physik **64**, 262 (1930).
[4] F. London, Phys. Rev. **54**, 947 (1938).

or

$$T_{02} = 3\epsilon Nhc/2\pi keHR^2 \qquad (8)$$

$$= 3h^3 Nc/16LVmeHk. \qquad (9)$$

Note that T_{02} depends on N/V, and also varies inversely as H and the dimensions of the system L in the direction of H. Roughly speaking T_{02} is the accumulation temperature of a one dimensional problem (see Fig. 1 of I), where the phenomenon is complicated by the presence of a magnetic field.

(4) T_H is defined as the temperature at which the spacing of the magnetic levels is of the order of magnitude of the thermal energy, $\mu H/kT_H = 1$. When this is true it is certainly no longer valid to integrate over *any* of the magnetic levels. Note that this circumstance is not realized abruptly but gradually, so that T_H marks off an accumulation band rather than an accumulation temperature.

(5) For purposes of mathematical completeness rather than physical significance, we define a temperature T_t at which the average kinetic energy is equal to the average spacing of the translational levels ($\epsilon/kT_t = 1$), and it is then no longer valid to integrate over any of the translational levels.

(6) H_c is defined as a critical field for which $T_{01} = T_{02}$

$$H_c = (N/V)^{\frac{1}{3}}(U(\tfrac{1}{2}, 0))^{\frac{1}{3}}hc\pi/8Le. \qquad (10)$$

For $H > H_c$ the accumulations at T_{01} and T_{02} occur separately. For $H < H_c$, the two accumulations occur at the same temperature T_{01} (case C). For $H < H_c$, $T_{02} > T_{01}$, and T_{02} is then simply a parameter by means of which the population of the lowest magnetic and higher translational states may simply be expressed as NT/T_{02}, an expression valid only for $T < T_{01}$.

Three other points should be noted in interpreting the formula which follows:

(1) The approximate behavior of the U functions for small parameter values, summarized in I, especially the fact that for

$$p = 0, \quad \alpha \rightarrow 0, \quad U(p, \alpha) \rightarrow -\ln\alpha, \qquad (11)$$

$$p < 0, \quad \alpha \rightarrow 0, \quad U(p, \alpha) \rightarrow \alpha^p. \qquad (12)$$

(2) The behavior of α in the neighborhood of the accumulation temperatures. Generally speaking, when a lowest energy term E_{low} has to be split off from an integration, in the separated term $\alpha \rightarrow -E_{low}/kT$ in just such a way that $(\alpha + E_{low}/kT)$ has the value to make the total population N. This is the explanation for the appearance of $\alpha + \mu H/kT$ and $\alpha + \mu H/kT + \epsilon/kT$ as effective normalization constants. A slightly different way of putting point (2) is as follows: if we have a series of complicated terms for N such as (14) or (17) which have a simple dependence on T, and only *one* of which is *sensitive* to α, then those terms effectively independent of α have the given dependence of population on T, and α is just such a complicated function of T to make the population of the term in which it does appear signifi-

cantly vary as N minus the rest of the terms. Thus, if α only appears effectively in one term, we do not have to solve for α to get the relative populations of the different classes of states. This point will become apparent from the summary below, and be very useful in evaluating expressions for the total and free energy.

(3) In deriving the equations below, the lower limit of integration on n_3 must be chosen with care. In (13) for example, the lower limit zero for n_3 is a valid approximation, in some of the others, a half integral value as dictated by (1) must be used.

The Distribution of the Population

We can now write the expressions for α in the different regions of Fig. 1 as follows: N has been divided out so that the terms give the relative fractions of the populations in the different classes of states.

In region A

$$1 = (T/T_{01})^{\frac{3}{2}}U(\tfrac{1}{2}, \alpha)/U(\tfrac{1}{2}, 0), \qquad (13)$$

valid for

$$\alpha > \mu H/kT \ll 1, \quad T > T_{01}.$$

There is no accumulation in any particular class of states.

In region B

$$1 = (2T_H/T_{01})(T/T_{01})^{\frac{1}{2}}U(-\tfrac{1}{2}, \alpha + \mu H/kT)/U(\tfrac{1}{2}, 0)$$
$$+ (T/T_{01})^{\frac{3}{2}}U(\tfrac{1}{2}, \alpha + 2\mu H/kT)/U(\tfrac{1}{2}, 0), \qquad (14)$$

valid for

$$\epsilon/kT < \alpha + \mu H/kT, \quad \alpha < \mu H/kT \ll 1, \quad T_{02} < T < T_{01}.$$

Since

$$U(\tfrac{1}{2}, \alpha + 2\mu H/kT) \simeq U(\tfrac{1}{2}, 0), \qquad (15)$$

the two terms of (14) vary like $1 - (T/T_{01})^{\frac{1}{2}}$, $(T/T_{01})^{\frac{3}{2}}$,
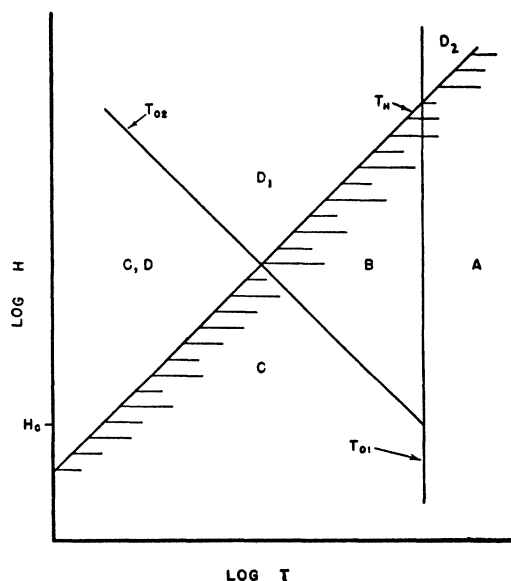

FIG. 1. (Schematic for Fig. 2.) Phase diagram for a gas of ions in a magnetic field.

these being the fractions of total population in ground magnetic and all higher magnetic states. From (14) we find

$$\alpha + \mu H/kT \simeq (\mu H/kT)^2 (T/T_{01})^3 \ll \mu H/kT. \quad (16)$$

In region C

$$1 = (3T_t/2T_{02})/(\alpha + \mu H/kT + \epsilon/kT) + T/T_{02}$$
$$+ (T/T_{01})^{\frac{3}{2}} U(\tfrac{1}{2}, \alpha + 2\mu H/kT)/U(\tfrac{1}{2}, 0) \quad (17)$$

valid for

$$-\epsilon/kT < \alpha + \mu H/kT < \epsilon/kT,$$
$$T_H < T < \text{(the smaller of } T_{01}, T_{02})$$

here also

$$U(\tfrac{1}{2}, \alpha + 2\mu H/kT) \simeq U(\tfrac{1}{2}, 0), \quad (18)$$

and the relative population of the states are

$$1 - (T/T_{01})^{\frac{3}{2}} - T/T_{02}, \quad T/T_{02}, \quad (T/T_{01})^{\frac{3}{2}}, \quad (19)$$

in ground magnetic and ground translational, ground magnetic and higher translational, and higher magnetic and all translational states, respectively. Equation (19) is valid only if the first term is positive. Equation (17) is valid to the extent that $(2/3)\epsilon/kT$ represents the integral over n_3 for $l = 0$ in (4), which is only approximately true (best when $|\alpha + \mu H/kT| \ll \epsilon/kT$). A detailed examination of this approximation will show that T/T_{02} in (19) indicates an abrupt accumulation in about the sense that T_{02}' in Fig. 1 of I represented an abrupt accumulation for the two-dimensional gas—perhaps not quite as abrupt. T_{02}, therefore, represents in Fig. 1 the center of a narrow accumulation band.

In region C, D

$$1 = (3/2)(T_t/T_{02})/(\alpha + \mu H/kT + \epsilon/kT) + T/T_{02}$$
$$+ 2(T_H/T_{01})(T/T_{01})^{\frac{3}{2}}$$
$$\times U(-\tfrac{1}{2}, \alpha + 3\mu H/kT)/U(\tfrac{1}{2}, 0), \quad (20)$$

valid if

$$\mu H/kT \gg 1, \quad -\epsilon/kT < \alpha + \mu H/kT < \epsilon/kT, \quad T < T_H.$$

This expression assumes that almost all the particles are in the first two magnetic states. This implies that

$$U(-\tfrac{1}{2}, \alpha + 3\mu H/kT) \simeq \exp(-2\mu H/kT)$$
$$= \exp(-2T_H/T). \quad (21)$$

The relative population of ground translational and lowest magnetic, higher translational and ground magnetic, and next lowest magnetic and all translational states are

$$1 - T/T_{02} - (2T_H/T_{02})(T/T_{01})^{\frac{3}{2}} \exp(-2T_H/T),$$
$$T/T_{02}, \quad (2T_H/T_{02})(T/T_{01})^{\frac{3}{2}} \exp(-2T_H/T), \quad (22)$$

respectively. The first member of (22) must be positive.

In regions D_1 and D_2 we have α determined by

$$1 = (2T_H/T_{01})(T/T_{01})^{\frac{3}{2}} [U(-\tfrac{1}{2}, \alpha + \mu H/kT)$$
$$+ U(-\tfrac{1}{2}, \alpha + 3\mu H/kT)]/U(\tfrac{1}{2}, 0). \quad (23)$$

This assumes the population is almost entirely confined to the two lowest magnetic states, which these two terms represent. There is no accumulation in the lowest

translational state as was the case in region CD. In region D_1 we may use the approximation

$$U(-\tfrac{1}{2}, \alpha + \mu H/kT) \simeq (\pi/(\alpha + \mu H/kT))^{\frac{1}{2}},$$
$$U(-\tfrac{1}{2}, \alpha + 3\mu H/kT) \simeq \exp(-2\mu H/kT), \quad (24)$$

i.e.

$$(\alpha + \mu H/kT) \ll 1, \quad \mu H/kT \gg 1.$$

The relative populations are

$$1 - (2T_H/T_{01})(T/T_{01})^{\frac{3}{2}} \exp(-2T_H/T), \quad (25)$$
$$(2T_H/T_{01})(T/T_{01})^{\frac{3}{2}} \exp(-2T_H/T).$$

In region D_2, the approximations (24) are not valid, and we must use exact expressions for the U functions.

In calculating Eqs. (13)–(25), the second term of (1) is neglected.

The Total Energy

We can also calculate expressions for the total energy

$$U = \sum_{l, n_1, n_3} E(l, n_1, n_3) n(l, n_1, n_3)$$

N_0 is Avogadro's number, R the gas constant.

In region A

$$U = (N/N_0)(3RT/2)(T/T_{01})^{\frac{3}{2}} U(\tfrac{3}{2}, \alpha)/U(\tfrac{1}{2}, 0). \quad (26)$$

In region B

$$U = (N/N_0)[RT_H(1 - (T/T_{01})^{\frac{3}{2}})$$
$$+ (RTT_H/T_{02})(T/T_{01})^{\frac{3}{2}} U(\tfrac{1}{2}, \alpha + \mu H/kT)/U(\tfrac{1}{2}, 0)$$
$$+ (3RT/2)(T/T_{01})^{\frac{3}{2}} U(\tfrac{3}{2}, \alpha + 2\mu H/kT)/U(\tfrac{1}{2}, 0)$$
$$+ 2RT_H(T/T_{01})^{\frac{3}{2}} U(\tfrac{1}{2}, \alpha + 2\mu H/kT)/U(\tfrac{1}{2}, 0)]. \quad (27)$$

In region C

$$U = (N/N_0)[R(T_H + T_t)(1 - (T/T_{01})^{\frac{3}{2}} - (T/T_{02}))$$
$$+ RTT_H/T_{02}$$
$$+ (3\pi^{\frac{1}{2}}RT/8)(T_t/T)^{\frac{1}{2}}(T/T_{02}) U(\tfrac{1}{2}, \alpha + \mu H/kT)$$
$$+ (3RT/2)(T/T_{01})^{\frac{3}{2}} U(\tfrac{3}{2}, \alpha + 2\mu H/kT)/U(\tfrac{1}{2}, 0)$$
$$+ 2RT_H(T/T_{01})^{\frac{3}{2}} U(\tfrac{1}{2}, \alpha + 2\mu H/kT)/U(\tfrac{1}{2}, 0)]. \quad (28)$$

In region CD

$$U = (N/N_0)[R(T_H + T_t)(1 - T/T_{02} - (2T_H/T_{01})$$
$$\times (T/T_{01})^{\frac{3}{2}} U(-\tfrac{1}{2}, \alpha + 3\mu H/kT)/U(\tfrac{1}{2}, 0))$$
$$+ RTT_H/T_{02}$$
$$+ (3\pi^{\frac{1}{2}}/8)(RT^2/T_{02})(T_t/T)^{\frac{1}{2}} U(\tfrac{1}{2}, \alpha + \mu H/kT)$$
$$+ (3RT_H^2/T_{01})(T/T_{01})^{\frac{1}{2}}$$
$$\times U(-\tfrac{1}{2}, \alpha + 3\mu H/kT)/U(\tfrac{1}{2}, 0)$$
$$+ (3\pi^{\frac{1}{2}}/8)(RT^2/T_{02})(T_t/T)^{\frac{1}{2}}$$
$$\times U(\tfrac{1}{2}, \alpha + 3\mu H/kT)]. \quad (29)$$

In regions D_1, D_2

$$U = (N/N_0)[RT_H(1 - 2(T_H/T_{01})(T/T_{01})^{\frac{3}{2}}$$
$$\times U(-\tfrac{1}{2}, \alpha + 3\mu H/kT)/U(\tfrac{1}{2}, 0))$$
$$+ RT(T_H/T_{01})(T/T_{01})^{\frac{1}{2}} U(\tfrac{1}{2}, \alpha + \mu H/kT)/U(\tfrac{1}{2}, 0)$$
$$+ 6RT_H(T/T_{01})^{\frac{1}{2}} U(-\tfrac{1}{2}, \alpha + 3\mu H/kT)/U(\tfrac{1}{2}, 0)$$
$$+ RT(T/T_{01})^{\frac{1}{2}}(T_H/T_{01})$$
$$\times U(\tfrac{1}{2}, \alpha + 3\mu H/kT)/U(\tfrac{1}{2}, 0)]. \quad (30)$$

The same approximations as in the corresponding equa-

tions for α also hold. The form of the above equations, when all the terms are written in the form const.$\times RT$ $\times$function of temperature ratios, is convenient when they are used with a diagram such as Fig. 1. Given an H, T point of interest, one can quickly estimate the values of different terms by reading the temperatures T_{01}, T_H, T_{02} at which a horizontal line through the H, T point of interest crosses the T_{01}, T_H or T_{02} line.

Equations (26)–(30) may be substantially simplified and condensed by using the valid approximations for each set, especially the facts that for all regions but B and D_2, $\alpha + \mu H/kT$ is very small and $U(p, \alpha) \simeq U(p, 0)$ for $\alpha \ll 1$ and $p > 0$. However, they have been left in the form given so that the energy contribution of each type of level may be more explicitly identified, and the validity of the approximations more critically examined.

THE GAS OF IONS IN A MAGNETIC FIELD, WITH SPIN

The Relative Populations of the States

Let us reconsider the above problem when it is assumed that the particles have an intrinsic magnetic moment μ', and a spin I. In that case, we have to sum over $2I+1$ additional levels $\mu'H$ apart, in addition to the levels given in (3) above. The expression determining α becomes

$$N = \sum_{l=0}^{\infty} \sum_{n_3=1}^{\infty} \sum_{\sigma=-I}^{I} g/(\exp(E(\sigma, n_3, l)/kT + \alpha) - 1) \quad (31)$$

with

$$E(\sigma, n_3, l) = \mu'H\sigma/I + \epsilon n_3{}^2 + 2(l+\tfrac{1}{2})\mu H,$$
$$\epsilon = h^2/8mL_z{}^2, \quad \mu = eh/4\pi mc.$$

Note that m refers to the (arbitrary) mass of the particle, so that in discussing particular particles such as deuterons μ'/μ is *not* the conventionally tabulated value for the intrinsic magnetic moment, but the mass number times it.

If all summations can be replaced by integrals, as will be the case so long as $\alpha > \mu H/kT$, (31) becomes

$$N = (2I+1)V(2\pi mkT)^{\frac{3}{2}}U(\tfrac{3}{2}, \alpha)/h^3. \quad (32)$$

When $\alpha < \mu H/kT$, it is no longer valid to replace the sum over the first terms of l by an integration. The behavior of α in this circumstance is a little subtle, but strict attention to the criterion (2) for integration, together with the expectation that α will approach close to the negative of the lowest energy state divided by kT, will show that when it no longer becomes valid to integrate over the first term of the l-summation, it will no longer be valid to integrate over the first term of the σ-summation either. Under these circumstances, splitting off the first term of the l- and σ-summation, (31) gives

$$1 = (2\mu H/kT(2I+1))(T/T_{0\sigma})^{\frac{3}{2}}U(-\tfrac{1}{2}, \alpha_0)/U(\tfrac{1}{2}, 0)$$
$$+ (\sum_{\sigma'=1}^{2I} (2\mu H/kT(2I+1)))(T/T_{0\sigma})^{\frac{3}{2}}$$
$$\times U(-\tfrac{1}{2}, \alpha_0 + \mu'H\sigma/I)/U(\tfrac{1}{2}, 0)) + (T/T_{0\sigma})^{\frac{3}{2}}. \quad (33)$$

In (33) we have the following definition. $T_{0\sigma}$ is the condensation temperature in the absence of a field H. It is the solution of (32) for $\alpha = 0$. $\alpha_0 = \alpha + \mu H/kT - \mu'H/kT$ is the effective normalization constant, and the first term of (33) is the only term sensitive to its value. It can be shown, as in the case of (16), that $\alpha_0 \ll \mu H/kT$. This together with the fact that $U(-\tfrac{1}{2}, \alpha_0) \simeq \alpha_0{}^{-\frac{1}{2}}$ will show that the terms of the summation in (33) are all small compared to the first term of (33).

The three terms of (33) represent the following classes of states:

(a) $l=0$, $\sigma = -I$, lowest magnetic and lowest spin, all translational.

(b) $l=0$, $\sigma = -I+1$ to $+I$, lowest magnetic and all higher spins, all translational.

(c) $l=1$ to ∞, $\sigma = -I$ to $+I$, excited magnetic, all spins, all translational.

The approximate relative orders of magnitude of the populations of these states are (a) $1-(T/T_{0\sigma})^{\frac{3}{2}}$, (b) Order $(\mu'H/kTI)^{\frac{1}{2}}$ (small), (c) $(T/T_{0\sigma})^{\frac{3}{2}}$.

The Free Energy and Polarization

We can now calculate the free energy $F = U - TS$ and magnetic polarization P. For $T > T_{0\sigma}$ and defining $\beta = \mu H/kT$, $\beta' = \mu'H/kTI$, $\gamma = \epsilon/kT$

$$F = -NkT\alpha + (gkT/4\beta)(\pi/\gamma)^{\frac{1}{2}}[-(2I+1)U(\tfrac{3}{2}, \alpha)$$
$$- \beta'^2(2I+1)^3U(-\tfrac{1}{2}, \alpha)/24$$
$$+ \beta'^2 U(-\tfrac{1}{2}, \alpha)/24$$
$$+ \beta^2(2I+1)U(-\tfrac{1}{2}, \alpha)/6]. \quad (34)$$

In obtaining (34) we have expressed $\sum_{\sigma=-I}^{I} U(\tfrac{3}{2}, \alpha + \beta'\sigma)$

as an integral, using (1), including the correction term and also expanded this U function as a Taylor series about α.

For $T < T_{0\sigma}$

$$F = -NkT\alpha - gkT(\pi/\gamma)^{\frac{1}{2}}[\sum_{\sigma=-I}^{I} U(\tfrac{1}{2}, \alpha + \beta + \sigma\beta')$$
$$- \sum_{\sigma=-I}^{I} U(\tfrac{3}{2}, \alpha + 2\beta + \sigma\beta')/4\beta$$
$$+ \beta \sum_{\sigma=-I}^{I} U(-\tfrac{1}{2}, \alpha + 2\beta + \sigma\beta')/24]. \quad (35)$$

The polarization, for $T > T_{0\sigma}$, is given by[5]

$$P = -(\partial F/\partial H)_\alpha/V,$$

$$P = (g(\pi/\gamma)^{\frac{1}{2}}\mu(2I+1)/V)$$
$$\times [(2I+1)^2(\mu'/\mu I)^2U(-\tfrac{1}{2}, \alpha)/48$$
$$- (\mu'/\mu I)^2U(-\tfrac{1}{2}, \alpha)/48 - U(-\tfrac{1}{2}, \alpha)/12] \quad (36)$$

[5] See N. F. Mott and H. Jones, *Properties of Metals and Alloys* (Clarendon Press, Oxford, 1936), p. 204.
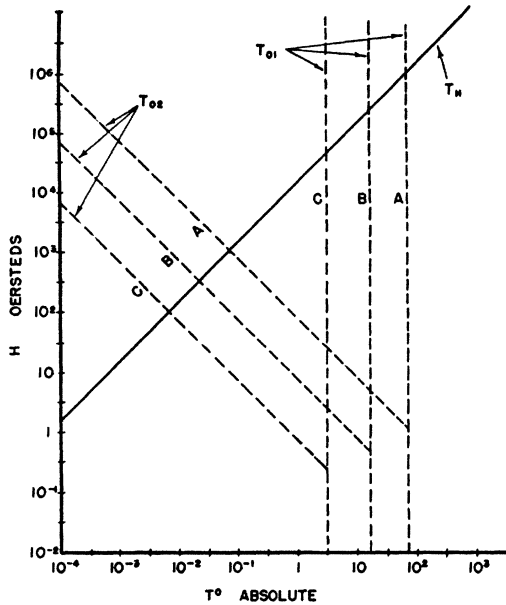
FIG. 2. Phase diagram for electron pairs. (A) 10^{19} pairs/cm^3, (B) 10^{18} pairs/cm^3, (C) 10^{17} pairs/cm^3. The Z dimension, along H, has been taken as 1 cm.

and for $T < T_{0\sigma}$

$$P = (g(\pi/\gamma)^{\frac{1}{2}}/V) \sum_{\sigma=I}^{I} [\mu U(\tfrac{1}{2}, \alpha+\beta+\sigma\beta')/2\beta$$

$$- (\mu+\mu'\sigma/I)U(-\tfrac{1}{2}, \alpha+\beta+\sigma\beta')/2$$

$$- (2\mu+\mu'\sigma/I)U(\tfrac{1}{2}, \alpha+2\beta+\sigma\beta')/4\beta$$

$$- \mu U(-\tfrac{1}{2}, \alpha+2\beta+\sigma\beta')/12$$

$$+ (2\mu+\mu'\sigma/I)\beta U(-\tfrac{3}{2}, \alpha+2\beta+\sigma\beta')/24]. \quad (37)$$

Limiting Form for High Temperature

For high temperatures $\alpha \gg 1$, $U(\tfrac{1}{2}, \alpha) \simeq U(\tfrac{3}{2}, \alpha)$ $\simeq U(-\tfrac{1}{2}, \alpha) \simeq \exp(-\alpha)$ and the polarization is, using (32) and (36)

$$P = \mu'^2 HN(I+1)/3IkTV - N\mu^2 H/3VkT. \quad (38)$$

For $I = \frac{1}{2}$

$$P = N\mu'^2 H/kTV - N\mu^2 H/3kTV \quad (39)$$

and these two terms can just be interpreted as the spin paramagnetism and the Langevin diamagnetism as given by Maxwell-Boltzmann statistics, which provides a convenient check on our work.

For $T < T_{0\sigma}$, the polarization is, using Eqs. (37) and (33) and neglecting quantities of order $(\mu H/kT)^{\frac{1}{2}}$

$$P = N(\mu'-\mu)(1-(T/T_{0\sigma})^{\frac{1}{2}})/V. \quad (40)$$

This expression has the quite plausible physical interpretation that there are $N(1-(T/T_{0\sigma})^{\frac{1}{2}})$ particles in the ground state of spin and circulation about the magnetic field, each of which contributes a positive magnetic moment μ' and a negative (diamagnetic) moment μ. In

obtaining Eqs. (34)–(40) one has to include the correction term of Eq. (1) in replacing sums by integrals and also must utilize the approximate expressions for the U functions with small parameter.

Interpretation and Limitations of Formulas

It is appropriate to ask at this point if the temperature T_{01} (or $T_{0\sigma}$, for particles with spin) is a condensation temperature or merely an accumulation temperature, such as T_{02}. In the limiting case of no magnetic field we know that T_{01} is a condensation temperature. We also know that as the magnetic field increases and we go up along the T_{01} line (Fig. 1) eventually we reach the T_H band, in which we know there is a gradual accumulation in the ground magnetic state. Therefore, somewhere between 0 magnetic field and a magnetic field so strong that $kT_{01} \sim \mu H$, T_{01} ceases to be a condensation temperature and becomes an accumulation temperature. However, examination of the mathematics shows that it is fairly abrupt except in the immediate neighborhood of T_H. The exact problem of the field strength for which T_{01} ceases to be a condensation temperature has not been examined, though one might conjecture that it lies near H_c.

In the case of the accumulation temperature T_{02}, it should be observed that it is a function of N/V as $N \to \infty$ but it also depends on how $V \to \infty$ because of the factor L. If the thickness of the specimen $L \to \infty$, $T_{02} \to 0$, otherwise it remains finite. This again is an example of how statistical mechanics shows the dependence of thermodynamic properties on geometry.

One can also point out here a limitation on the validity of the expressions derived above. It has been stated at the beginning that the magnetic field which determines the energy levels in which the particles move is H. Strictly speaking this is not true since the effective field acting on the particles is $H_{eff.} = H - \lambda P$ where λ is the depolarizing factor depending on the shape of the specimen, but in any event is not greater than 4π. However, it is valid to use H for $H_{eff.}$ if P is small compared to H. Now P, the polarization, was calculated to be $\sim (N\mu/V)(\mu H/kT)$ above the condensation temperature T_{01} and $\sim N\mu/V$ below it. If this latter expression is small compared to the applied H then the condition of applicability is met. As will be seen in the discussion of the numerical examples, this is the case for most problems of interest. $\mu \sim 10^{-20}$ for electron pairs, and $\mu \sim 10^{-23}$ for deuterons. For these examples the number of particles per unit volume has to be greater than 10^{20}, 10^{23}, respectively, for the theory to fail for fields less than one oersted.

Experimental Methods

We might now make a few remarks on the most suitable way in which these effects could be detected by measurement. Evidently, the orders of magnitude of the polarizations below and above the condensation tem-

perature are as $N\mu/V$ and as $(N\mu/V)\mu H/kT$, with $\mu H/kT \ll 1$. Now above the condensation temperature the phenomena are essentially the same as though determined by Maxwell-Boltzmann statistics, where Curie's law applies. Hence, for $T \gg T_{01}$, or $T \gg T_{0\sigma}$ as may be relevant, Bose-Einstein effects could not be distinguished from any others in which the susceptibility is independent of H and varies as $1/T$.

Experimentally, this means that the susceptibilities are of the order 10^{-6} and can best be detected by a weighing method in a strong inhomogeneous field. However, below the condensation temperature the polarization is essentially constant, or the susceptibility P/H varies as $1/H$. It is also larger by a quantity of order $kT/\mu H$ from what it is above. This means that it is not profitable in a weighing method to use a strong magnetic field since the force on the specimen would depend only on the gradient of the magnetic field and be independent of H. Also the fact that the polarization is so very much larger means that it would be simpler to detect it. Thus, a simple measurement of the self-induction of a coil around a specimen supposed to contain this peculiar gas would begin to change abruptly by a small amount as soon as the temperature T_{01} was reached. For the case of a needle-shaped specimen (depolarizing factor $\lambda=0$) filling a coil of inductance L_0, below the condensation temperature T_{01} the inductance would become $L=L_0(1+4\pi P/H)$ where H is the applied field, V the volume and P the total polarization as given by (40). This shows that the percentage change in the inductance would be larger the smaller H, with the restriction for applicability that $P/H \ll 1$.

Applications

Let us now consider some possible applications of these calculations. It was suggested by London,[4] among others, that superconductivity might be explained as a condensation phenomenon of Bose-Einstein particles and Ogg has added definiteness to this suggestion by supposing that these particles are electron pairs. Let us see whether or not this hypothesis is in accordance with the above calculations. Using twice the mass and charge of the electron, we see that for the condensation temperature to fall in the range of superconducting temperature, say less than $10°$ absolute, the concentration of particles must be $N/V < 10^{18}$. How large is the polarization under these conditions? It is of order $N\mu/V \simeq 10^{-2}$. However, it is one of the essential features of superconductivity that the material be perfectly diamagnetic, or that the $4\pi P$ be equal and opposite to the applied magnetic field H. This calculation shows that the polarization can never be larger than 10^{-2} oersteds, and since in practice superconductors are diamagnetic up to several hundred oersteds, we must reject this hypothesis, or modify in such a way that the accumulation takes place in states of much higher l than the lowest. This calculation does not exclude the possibility that there

can be electron pairs either in a metal or in a metal-ammonia solution. If there are, and if they are mobile and can be treated as Bose-Einstein particles, then one can look for their condensation temperature in the manner described above, by a small fairly abrupt (like $1-(T/T_{01})^{\frac{1}{3}}$) change in the self-induction of a coil with diminishing temperature. It would be interesting to see if this effect can actually be observed, as it is intimately tied up with the vexatious question as to how far and in what particulars one can go in treating particles which are not free and do interact as though they were free and did not interact. This is done in the treatment of valence electrons inside a metal by Fermi-Dirac statistics. Figure 2 gives the phase diagram corresponding to Fig. 1, for particles of zero spin and twice the electronic mass and charge.

A second possibility for testing the above formulas is suggested by London's refinement of his theory of liquid helium. In order to fit the observations of the specific heat of He with a theoretical specific heat calculated by Bose-Einstein statistics, London[6] proposed that the helium atoms be divided into two classes. One of these was to be treated as a crystalline lattice obeying a Debye T^3 law, the other fraction was to be treated as a Bose-Einstein gas which occupied the allowed levels formed by this lattice. It was the condensation phenomenon of the second class of particles which accounted for the λ-phenomenon of liquid helium. Now the number of possible particles available to observation of condensation phenomenon are relatively limited, because the condensation temperature diminishes with increasing mass and for helium, already one of the lightest particles, it is $\sim 3°K$. One other possibility is deuterons, and fortunately, we have a mechanism whereby these might be treated as a gas just as the valence electrons of a metal are treated. It is known that certain metals[7,8] (Ce, Th, Zr, Ti, Ta, V, Pd, Cb, La) absorb large amounts of hydrogen and presumably also deuterium. These solutions cannot be strictly considered as chemical compounds, since the proportion increases with decreasing temperature. Therefore, it is suggested that for deuterium a fraction of the particles (as deuterons) may be treated as a Bose-Einstein gas in the sense that they can be imagined to be distributed throughout the metallic lattice rather than at fixed points, and for these we could seek a condensation temperature. If as many as 10^{+21} deuterons/cc could be considered free, the condensation temperature would be $\sim 1°K$.

A possible encouragement for this point of view can be taken for the case of hydrogen and palladium. Here it is known that the absorption of hydrogen by palladium

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[6] F. London, J. Phys. Chem. 43, 49 (1939).

[7] F. Ephraim, *Inorganic Chemistry*, 4th Rev. Ed. by P. C. L. Thorne and E. R. Roberts (Nordeman Publishing Company, New York, 1943), p. 875. There is a most striking correlation between the hydride forming and superconducting elements, the explanation of which is unknown.

[8] A. Sieverts, Zeits. f. angew Chem. 21, 37 (1929).

decreases the susceptibility in a linear fashion to zero and that beyond that point the susceptibility remains zero.[9,10] This has been interpreted that the protons fill up the d levels (0.55 holes per atom). Presumably the excess ones wander about the lattice, and part of them could be treated as a gas of free particles in the desired way.[11] There is also evidence that hydrogen dissolved in the

[9] See reference 5, p. 200.

[10] B. Svenson, Ann. d. Physik 18, 294 (1933).

[11] It was pointed out to the author by S. Liebson that if one had a case where the "free proton theory of the hydrides" was approximately valid, one might expect that at very low temperatures there would be proton superconductivity, not to mention the formation of proton pairs!

metal is dissolved as protons and if this were also true for deuterium the deuterons stripped of their external electrons could be considered as Bose-Einstein particles.

These considerations are at best speculative, and ignore completely interactions and the periodic nature of the potential in which the particles move. They do suggest that an experimental study of the relative low temperature behavior of solutions of hydrogen in a metal and of deuterium in a metal would be most illuminating in revealing the effect of the two different statistics on the behavior of the system, and in indicating the nature of possible modifications in the theoretical approach to such problems which might be made.

On the Electromagnetic Surface Wave of Sommerfeld*

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It is proved that Sommerfeld's well-known electromagnetic surface wave does not exist in the radiation of a Hertzian dipole over a plane earth because it does not fulfill the so-called "radiation condition." The path of integration chosen by Sommerfeld is correct, but there is another saddle-point overlooked by this author which just annuls the surface wave due to the residue. These results are in agreement with Burrow's measurements.

IN a well-known paper published in 1909, Sommerfeld[1] treated the problem of the propagation of radio-waves along the surface of the (plane) earth. If we make the (ψ, ϕ) plane coincide with the plane of the earth surface (the z axis pointing upwards) and if we consider a vertically oscillating dipole in the air at the point $z=r=0$, the Hertzian vector Π describing the electromagnetic field may be expressed as follows:

$$\Pi = \frac{e^{ik_1R}}{R} = \int_0^\infty \frac{J_0(\lambda r)\lambda d\lambda \exp[-z(\lambda^2-k_1^2)^{\frac{1}{2}}]}{(\lambda^2-k_1^2)^{\frac{1}{2}}};$$
$$z>0. \quad (1)$$

For $z<0$ we have a similar formula with k_2 replacing k_1. Here k_1 and k_2 denote the wave numbers of the upper and lower medium (air and earth). Taking into account the radiation reflected by the earth, we get in the upper medium (air), for the resulting Hertzian function

$$\Pi_1 = \text{const.} \int_0^\infty \frac{J_0(\lambda r) \exp[-z(\lambda^2-k_1^2)^{\frac{1}{2}}]\lambda d\lambda}{k_1^2(\lambda^2-k_2^2)^{\frac{1}{2}}+k_2^2(\lambda^2-k_1^2)^{\frac{1}{2}}}. \quad (2)$$

Setting

$$J_0(\lambda r) = \frac{1}{2}[H_0^{(1)}(\lambda r) + H_0^{(2)}(\lambda r)], \quad (3)$$

where H and J are the usual cylindric functions. We can displace the path of integration of the integrand of (2) containing $H_0^{(1)}$ into the upper part of the complex

plane λ, and the path of integration containing $H_0^{(2)}$ we can shift into the lower half-plane λ. The integrals effected along the circle of infinite diameter are zero, the two integrals conducted along the imaginary axis compensate each other. As the integrand of (2) has no singularities in the lower quadrant, we have left only the following integral in the upper half-plane λ:

$$\text{const.} \int \frac{H_0^{(1)}(\lambda r) \exp[-z(\lambda^2-k_1^2)^{\frac{1}{2}}]\lambda d\lambda}{k_1^2(\lambda^2-k_2^2)^{\frac{1}{2}}+k_2^2(\lambda^2-k_1^2)^{\frac{1}{2}}} \quad (4)$$

conducted along the following three paths (Fig. 1): (a) Along the loop 1 around the branch-cut going from the branch point k_1 of (4) to infinity in the upper half-plane; (b) along the loop 2 around the branch-cut going from the branch point k_2 of (4) to infinity; (c) and along the circle 3 around the pole P of (4). Path 1 provides the so-called space-wave; path 2 gives no appreciable contribution; path 3 gives rise to the famous surface wave expressed by:

$$w_0 = \text{const.}e^{isr} \exp[-z(s^2-k_1^2)^{\frac{1}{2}}]/r^{\frac{1}{2}}, \quad (5)$$

s being the pole of the integrand of (4) defined by:

$$s = k_1 \sin\phi_B; \quad \phi_B = \tan^{-1}(k_2/k_1), \quad (6)$$

ϕ_B being the Brewester angle.

In 1919 Weyl[2] tackled the same problem but with a different mathematical approach. His solution contains

* For a preliminary report see T. Kahan and G. Eckart, Comptes rendus 226, 1513 (1948).

[1] A. Sommerfeld, Ann. d. Physik 28, 665 (1909).

[2] H. Weyl, Ann. d. Physik 60, 481 (1919).