

and, therefore, since $(\psi_0)_{S_0} = \psi_0(r_0)$.

$$\epsilon = [V(r_0) - E_0] \psi_0^2(r_0) v. \quad (12)$$

From Eqs. (11) and (12) we see that the first-order perturbation energy is zero if the sphere S_0 is only deformed without a change of volume.

§5

Higher approximations

The higher approximations cannot usually be calculated without solving a partial differential equation.

We do not intend to go into any detail of this question. We just want to mention that it is possible to eliminate the potential from the Schrödinger equation. In order to demonstrate that, we proceed thus: We insert

$$\psi = \psi_0 f$$

into Eq. (2) and observe that ψ_0 obeys Eq. (1). We then obtain for f the differential equation:

$$\text{div}(\psi_0^2 \text{grad } f) + \epsilon \psi_0^2 f = 0.$$

In cases where the function ψ_0 has a simple form, this transformation may be of advantage.³

On the Bose-Einstein Condensation

F. LONDON

*Institut Henri Poincaré, University of Paris, France**

(Received October 12, 1938)

A proof is given of the condensation phenomenon of a Bose-Einstein gas. A preliminary discussion of its transport properties is outlined with a view to its possible bearing on the problem of liquid helium.

INTRODUCTION

IN his well-known papers¹ on the degeneracy of an ideal gas, Einstein mentioned a peculiar condensation phenomenon of the ideal "Bose-Einstein" gas. This very interesting discovery, however, has not appeared in the textbooks, probably because Uhlenbeck in his thesis² questioned the correctness of Einstein's argument. Since, from the very first, the mechanism appeared to be devoid of any practical significance, all real gases being condensed at the temperature in question, the matter has never been examined in detail; and it has been generally supposed that there is no such condensation phenomenon.

In discussing some properties of liquid helium, I recently realized that Einstein's statement has been erroneously discredited; moreover, some

support could be given to the idea that the peculiar phase transition ("λ-point"), that liquid helium undergoes at 2.19°K, very probably has to be regarded as the condensation phenomenon of the Bose-Einstein statistics, distorted, of course, by the presence of molecular forces and by the fact that it manifests itself in the liquid and not in the gaseous state. In a preliminary note,³ the course of the specific heat of an ideal Bose-Einstein gas was reproduced, but no proof was communicated. As, since then, I have been asked several times for a proof and as even the correctness of the result has been questioned anew, it might perhaps be justified, on this occasion to publish a quite elementary demonstration of the condensation mechanism, discussing only briefly here the possible connection of the Bose-Einstein degeneracy with the problem of liquid helium.⁴

* At present at Duke University, Durham, North Carolina.

¹ A. Einstein, *Ber. Berl. Akad.* 261 (1924); 3 (1925).

² G. E. Uhlenbeck, *Dissertation* (Leiden, 1927).

³ F. London, *Nature* **141**, 643 (1938).

⁴ In a recent paper Uhlenbeck has withdrawn his former objection. G. E. Uhlenbeck and B. Kahn, *Physica* **5**, 399 (1938).

§1. THE DEGENERACY OF THE BOSE-EINSTEIN GAS

We start from the well-known fundamental formula for the most probable distribution in a Bose-Einstein gas:

$$N_i = \frac{g_i}{e^{\beta \epsilon_i + \alpha} - 1}$$

Here $\beta = 1/kT$, g_i = statistical weight of the state of energy ϵ_i ; the parameter α has to be determined as a function of T by the condition

$$N = \sum_i N_i = \sum_i \frac{g_i}{e^{\beta \epsilon_i + \alpha} - 1} \quad (1)$$

N = total number of particles. It may be mentioned that α is proportional to Gibb's potential ζ ; it is $\zeta = -\alpha kT$. For free particles of the mass M , without spin, in a given volume V , one usually assumes

$$\epsilon_p = (p^2/2M), \quad g(p)dp = (4\pi V/h^3)p^2dp$$

and obtains

$$N = \frac{4\pi V}{h^3} \int_0^\infty \frac{p^2 dp}{e^{\alpha + p^2/2MkT} - 1} = \frac{V}{h^3} (2\pi MkT)^{3/2} F(\alpha), \quad (2)$$

where

$$F(\alpha) = \frac{2}{\pi^{3/2}} \int_0^\infty \frac{z^3 dz}{e^{\alpha+z} - 1} = e^{-\alpha} + \frac{e^{-2\alpha}}{2^{3/2}} + \frac{e^{-3\alpha}}{3^{3/2}} + \frac{e^{-4\alpha}}{4^{3/2}} + \dots$$

Here α must be positive; otherwise some of the N_i would be negative, which, of course, is not admissible. Now $F(\alpha)$ is a monotonously decreasing function, its maximum value being $F(0) = 2.612$. Therefore, no solution $\alpha(T)$ of Eq. (2) can be found for

$$N > \frac{V(2\pi MkT)^{3/2}}{h^3} 2.612,$$

i.e., for

$$T < T_0,$$

where

$$T_0 = \left(\frac{N}{2.612V} \right)^{2/3} \frac{h^2}{2\pi Mk} \quad (3)$$

For M = mass of the He-atom and for a molar volume of 27.6 cm³ one obtains $T_0 = 3.13^\circ\text{K}$.

Equation (1), however, obviously always has a solution $\alpha(T)$, for each temperature T , with positive N_i . The difference of the behavior of Eqs. (1) and (2) comes from the neglect caused by the substitution of the sum by an integral. This can easily be seen if one takes, e.g., the discontinuous energy values of a cubic volume of linear dimension L (periodic boundary conditions):

$$\epsilon_{k,l,m} = (k^2 + l^2 + m^2)(h^2/2ML^2)$$

$$k, l, m = 0, \pm 1, \pm 2, \dots$$

and substitutes them into (1):

$$N = \sum_{k,l,m} \frac{1}{e^{\sigma(k^2+l^2+m^2)+\alpha} - 1}, \quad (1a)$$

where
$$\sigma = \frac{h^2}{2L^2MkT} = \frac{1.90\pi}{N^{2/3}} \frac{T_0}{T}$$

Here the right-hand side is again a monotonously decreasing function of α , which, however, is not bounded by a finite limit when $\alpha \rightarrow 0$. Consequently Eq. (1') has, for each temperature T , a solution $\alpha(T)$.⁵ The difference between (1a) and (2) is due to the fact that in (2) the lowest state $k=l=m=0$ (or $p=0$), incorrectly acquires the statistical weight zero, and therefore it becomes entirely suppressed. It is just this *one* term in the sum (1a) which is decisive for the behavior in the limit $\alpha \rightarrow 0$, viz., at lowest temperatures. It will therefore be sufficient to treat this lowest term of the sum separately; the other terms may, without detriment, be replaced by an integral.

We collect the states with $k^2 + l^2 + m^2 \leq \rho^2$ where the value of ρ may be chosen in such a way, that the difference between the integral from ρ to ∞ and the sum from ρ to ∞ is negligible (say $\rho \sim 10$). The mean energy of these states is

$$\bar{\epsilon}_0 = \frac{3}{10} \frac{\rho^2 h^2}{ML^2} = \frac{3}{5} \epsilon \quad \text{where} \quad \epsilon = \frac{h^2 \rho^2}{2ML^2}$$

and their number is given by

$$g_0 = (4\pi/3)\rho^3.$$

⁵ From this fact Uhlenbeck² was led to the conclusion that no condensation phenomenon should exist.

Then we may write, in a better approximation than (2),

$$N = \frac{g_0}{e^{\beta\epsilon_0 + \alpha} - 1} + \frac{4\pi V}{h^3} \int_{\rho h/L}^{\infty} \frac{p^2 dp}{e^{\alpha + p^2/2MkT} - 1}$$

or with $\alpha' = \beta\epsilon_0 + \alpha = \frac{3}{5}\beta\epsilon + \alpha$:

$$1 = \frac{g_0/N}{e^{\alpha'} - 1} + \left(\frac{T}{T_0}\right)^{\frac{3}{2}} \frac{2}{\pi^{\frac{1}{2}} F(0)} \times \int_{\beta\epsilon}^{\infty} \frac{z^{\frac{3}{2}} dz}{e^{z + \alpha' - 3/5 \cdot \beta\epsilon} - 1}. \quad (4)$$

The first term of the right-hand side must not be negative, since it gives the number of atoms in the cell of the g_0 lowest states. Therefore in any case $\alpha' > 0$. It may be remarked that the quantity $\beta\epsilon = (h^2 p^2 / 2ML^2 kT)$ is always a very small number [= (5.97/N^{2/3}) $\rho^2(T_0/T)$].

Now we have to distinguish two entirely different cases:

(1) $T > T_0$. In this case α' comes out to be a number of the order of magnitude 1. Consequently, the first term of the right-hand side of (4) is of the order $1/N$ and may be neglected compared with the second term. In the latter we may neglect $\beta\epsilon \ll \alpha'$ and obtain

$$(T_0/T)^{\frac{3}{2}} = [F(\alpha')/F(0)] \quad \text{for } T > T_0, \quad (4a)$$

which is equivalent to (2).

(2) $T < T_0$. The second term of the right-hand side of (4) is in any case smaller than $(T/T_0)^{\frac{3}{2}}$. In particular for $T < T_0$, it is smaller than 1. Thus the first term is required to make up for the rest; consequently, since the numerator of this term is very small, its denominator must be equally small, *viz.*, of the order $1/N$, this means $\alpha' \sim 1/N$; in the second term α' may now be neglected compared with $\beta\epsilon \sim 1/N^{\frac{2}{3}}$ and we can write for (4):

$$1 = \frac{g_0}{N\alpha'} + \left(\frac{T}{T_0}\right)^{\frac{3}{2}} \frac{2}{\pi^{\frac{1}{2}} F(0)} \int_{\beta\epsilon}^{\infty} \frac{z^{\frac{3}{2}} dz}{e^{z - 3/5 \cdot \beta\epsilon} - 1} \quad (4b)$$

$$= \frac{g_0}{N\alpha'} + \left(\frac{T}{T_0}\right)^{\frac{3}{2}} [1 - 0.173(\beta\epsilon)^{\frac{1}{2}} + \dots]$$

or

$$\alpha' = \frac{g_0}{N} [1 - (T/T_0)^{\frac{3}{2}} (1 - 0.173(\beta\epsilon)^{\frac{1}{2}} + \dots)]^{-1}, \quad (5)$$

valid as long as

$$N[1 - (T/T_0)^{\frac{3}{2}}] \gg 1 \quad \text{or for } T_0 - T \gg \frac{2}{3N} T_0,$$

i.e., practically for all temperatures $T < T_0$.

The number of particles in the lowest cell becomes

$$N_0 = N[1 - (T/T_0)^{\frac{3}{2}} (1 - 0.173(\beta\epsilon)^{\frac{1}{2}} + \dots)]$$

$$= N[1 - (T/T_0)^{\frac{3}{2}}] + 0.422 \rho N^{\frac{2}{3}} T/T_0 + \dots$$

We see that in first approximation this expression is independent of ρ , i.e., independent of $g_0 = (4\pi/3)\rho^3$, the number of states we have collected in the lowest cell. Therefore, $N(1 - (T/T_0)^{\frac{3}{2}})$ atoms, i.e., a *finite fraction of all atoms* will be assembled in the *one* lowest state. In the spherical shell of radius ρ and thickness $d\rho$ around the lowest state, there will be only $0.422 N^{\frac{2}{3}} T/T_0 d\rho$ molecules.

Accordingly, the distribution among the lowest quantum states, characterized by the quantum numbers k, l, m (see (1a)), may be written:

$$N_{k, l, m} = \frac{N[1 - (T/T_0)^{\frac{3}{2}}]}{1 + (k^2 + l^2 + m^2) N^{\frac{2}{3}} 29.8 T_0/T [1 - (T/T_0)^{\frac{3}{2}}]}$$

If N is finite, the function $\alpha(T)$ is, of course, an analytic function. However, for increasing values of N , the third derivative of α , near $T = T_0$, becomes greater and greater. In the limit $N \rightarrow \infty$, $N/V = \text{constant}$, the function $\alpha(T)$ has a discontinuous second derivative. It consists of two branches which do not cohere analytically. One gets $\alpha = 0$ for $T \leq T_0$, while for $T \geq T_0$ the function $\alpha(T)$ is given by the inversion of (4a). Taking $N = \text{Avogadro's number}$, and $V = \text{molecular volume}$, we may, for $T < T_0$, write simply:

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

(number of atoms in the lowest state) (6a)

$$N(E)dE = (2\pi V/h^3)(2M)^{\frac{3}{2}}(E^{\frac{1}{2}}dE/(e^{\beta E} - 1)).$$

(number of atoms of the interval
($E, E + dE$) where $E > 0$) (6b)

Therefrom we obtain the energy U per molecular

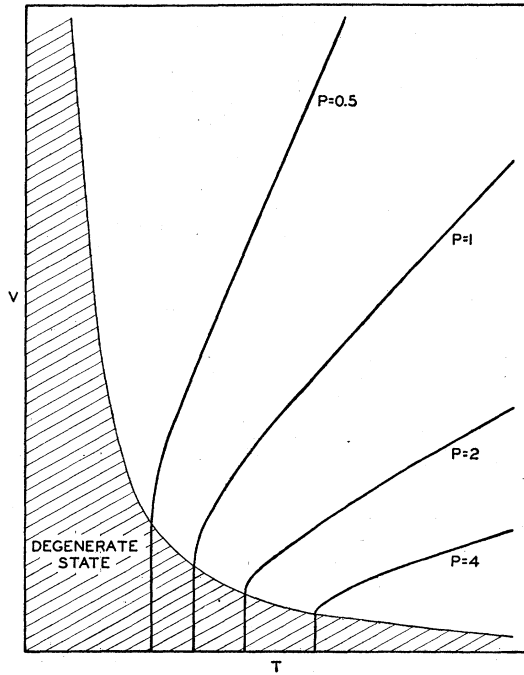


FIG. 1. Isobars of a Bose-Einstein gas.

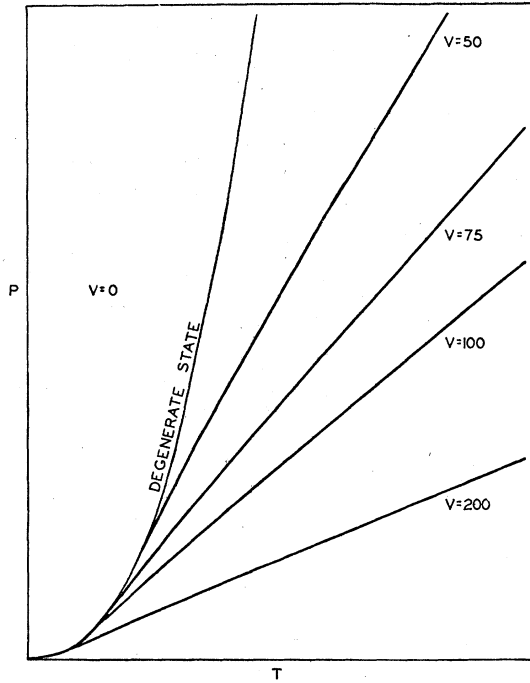


FIG. 2. Isochores of a Bose-Einstein gas.

volume and for $T < T_0$:

$$U_- = \int_0^\infty EN(E)dE = \frac{3}{2}RT \left(\frac{T}{T_0}\right)^{\frac{3}{2}} \frac{\zeta(2.5)}{\zeta(1.5)}$$

$$= -\frac{3}{2}0.514RT \left(\frac{T}{T_0}\right)^{\frac{3}{2}} = -\frac{3}{2}0.514RCT^{5/2}V, \quad (7a)$$

where $C = \frac{2.612}{N} \left(\frac{2\pi Mk}{h^2}\right)^{\frac{3}{2}} \approx \frac{1}{153}$ for He

and
$$\zeta(k) = \frac{1}{(k-1)!} \int_0^\infty \frac{x^{k-1}dx}{e^x - 1}.$$

denotes the Riemann zeta-function ($\zeta(\frac{3}{2}) = 2.612$; $\zeta(\frac{5}{2}) = 1.341$).

For $T \geq T_0$, Einstein has previously given the semi-convergent expansion:

$$U_+ = \frac{3RT}{2} \{1 - 0.462(T_0/T)^{\frac{3}{2}} - 0.0225(T_0/T)^3 - 0.0114(T_0/T)^{9/2} - \dots\}. \quad (7b)$$

The two branches U_+ and U_- are continuous at $T = T_0$ with a continuous tangent, but the second derivative is discontinuous. Thus the specific

heat c_v has a *break* at $T = T_0$ (see Fig. 4):

$$c_{v-} = -\frac{15}{4}0.514R(T/T_0)^{\frac{3}{2}} \quad (8a)$$

$$c_{v+} = \frac{3}{2}R \{1 + 0.231(T_0/T)^{\frac{3}{2}} + 0.045(T_0/T)^3 + 0.040(T_0/T)^{9/2} + \dots\}. \quad (8b)$$

The free energy

$$F = -T \int_0^T \frac{U}{T^2} dT$$

is found to be:

$$F_- = -0.514RT(T/T_0)^{3/2} = -0.514CRT^{5/2}V \quad (9a)$$

$$F_+ = -\frac{3}{2}RT \{ \ln(T/T_0) + 0.308(T_0/T)^{3/2} + 0.0075(T_0/T)^3 + 0.0025(T_0/T)^{9/2} + \dots \}, \quad (9b)$$

from which one gets the pressure $p = -\partial F/\partial V$

$$p_- = 0.514CRT^{5/2} \quad (10a)$$

$$p_+ = \frac{RT}{V} \left[1 - \frac{0.462}{CVT^{\frac{3}{2}}} - \frac{0.0225}{(CVT^{\frac{3}{2}})^2} - \frac{0.0114}{(CVT^{\frac{3}{2}})^3} - \dots \right]. \quad (10b)$$

This is in agreement with the Virial theorem: $pV = \frac{2}{3}U$.

§2. CONDENSATION IN MOMENTUM SPACE

Attention has already been directed to the remarkable result (10a), that for $T < T_0$ the pressure is independent of density, just as in the case of a van der Waals gas in the transition region below the critical point. However, this independence of density is quite accidental for the Bose-Einstein gas,⁶ and it is somewhat misleading to interpret this behavior in analogy with a van der Waals gas by saying that for $T < T_0$ a fraction of the molecules condenses into a state of zero volume and does not contribute to the density.⁴ Indeed, in the transition region of the van der Waals gas, a fraction of the molecules is condensed into a state of considerably

smaller volume and, since it is separated by gravitation from the other molecules, it does not contribute to the density of the gaseous phase. At this point the analogy fails completely, or is rather to be found in a more remote sense. The supernumerary molecules of a degenerate Bose-Einstein gas which we have denoted by N_0 and which indeed may be considered as belonging to a particular phase, do not, of course, disappear mysteriously from space; they do contribute to the density as any other molecules. They do *not contribute, however, to the pressure*, since their kinetic energy (and momentum), is zero. If one likes analogies, one may say that there is actually a *condensation, but only in momentum space*, and not in ordinary space, i.e., an equilibrium of two phases, *one* containing the molecules N_0 of momentum zero and occupying in the space of momenta, a zero volume; and *another one* showing a distribution over all momenta similar to that which is realized for $T > T_0$. In ordinary space, however, no separation of phases is to be noticed.

In a certain respect the molecules of the condensed phase having the momentum zero, show also a characteristic peculiarity as to their behavior in ordinary space. Since their wave functions are constant over the whole volume, they are particularly inappropriate for forming wave packets of the size of molecular dimensions by superposition of neighboring wave functions (i.e., wave functions of comparable small energy, so

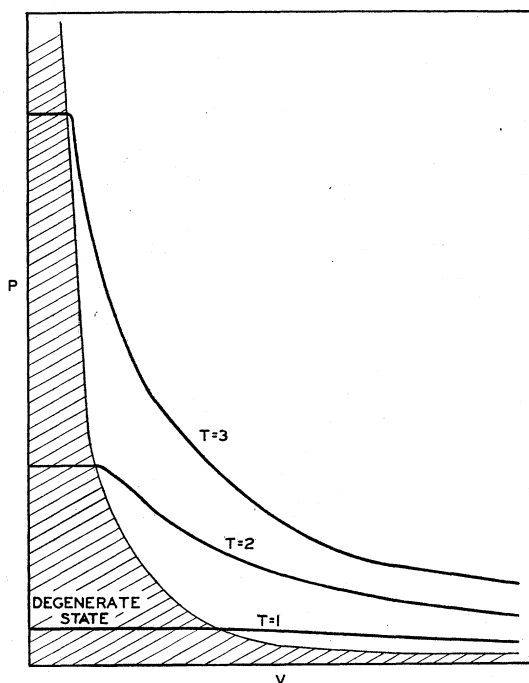


FIG. 3. Isotherms of an ideal Bose-Einstein gas.

⁶ This independence of density holds only for an "ideal" Bose-Einstein gas, but is no longer realized as soon as a molecular interaction is taken into account, for instance by adding a term $U_0(V)$ to the energy, representing a mean van der Waals field smeared over the total volume accessible to the molecules. In this case the condensation for constant volume proceeds as before and the specific heat c_v is exactly the same as given by (8). The pressure, however, will no longer be independent of V . It will be given by

$$p = 0.514 CRT^{5/2} - \partial U_0 / \partial V$$

and for constant pressure the gas will in this case no longer condense to the volume zero.

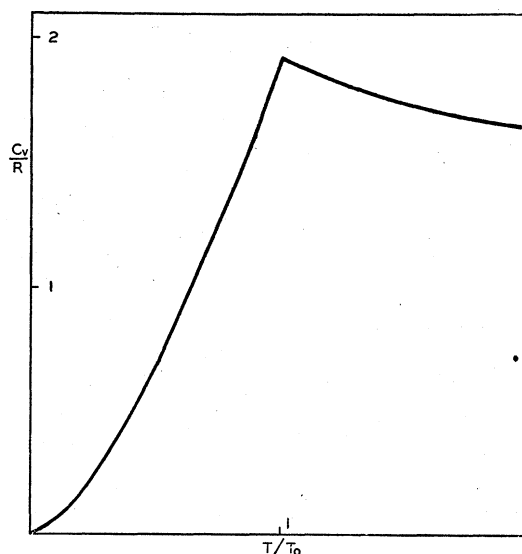


FIG. 4. Specific heat of an ideal Bose-Einstein gas.

that the energy distribution of the whole remains unchanged). These molecules therefore will represent a peculiar omnipresence in the total volume at their disposal. Accordingly it will not be allowable to treat their motion in external fields (pressure gradient, etc.), on the lines of Ehrenfest's theorem (approximate validity of classical mechanics for small wave packets), which theorem has been the general basis of the usual corpuscular treatment of the transport phenomena. Here we have before us just the opposite limiting case, namely, wave packets of a very *small extension* in the space of momenta, but which in ordinary space are spread over a region comparable with the extension of the inhomogeneities of macroscopic fields.

The quantum dynamics of this limiting case has been investigated very little. Only one interesting special case has so far been discussed in connection with superconductivity. It has been shown⁷ that the macroscopic description given for this phenomenon leads to a relation between electric current and magnetic field, which is identical with that which would be valid in an enormous diamagnetic atom of the dimensions of the metal. Now it is well known that diamagnetism cannot be explained on the basis of classical dynamics of electrons. The currents in a diamagnetic atom are not given by progressive de Broglie waves (or progressive wave packets), as in the usual treatment of the ordinary conductivity phenomena. These currents are represented rather by standing waves; they come from that term in the expression for the electric current which contains the vector potential of the magnetic field, and their structure is intimately connected with the spatial extension of the *quantum states* (the diamagnetic susceptibility is known to be proportional to $\langle r^2 \rangle_M$). For the superconductivity in particular it can be shown that the macroscopic phenomena may be interpreted very simply by the assumption of a peculiar coupling in the space of momenta, producing, below a certain critical temperature, a fixation of momentum, as if there were something like a condensed phase in the space of momenta. Thus far, however, it has not yet been possible to base that assumption on a molecular model by the general theory of electrons in metals.

⁷ F. London and H. London, *Physica* **2**, 341 (1935); F. London, *Proc. Roy. Soc.* **A152**, 24 (1935).

Now the degenerate Bose-Einstein gas provides a good example of a molecular model for such a condensed state in space of momenta, such as seems needed for the superconductive state. Though this fact cannot, of course, be applied to explain superconductivity, as electrons do not obey Bose statistics, it is remarkable on the other hand that the transport properties (viscosity,⁸ thermal conductivity⁹), of liquid helium, when passing the λ -point actually change in a very conspicuous manner; thus one speaks of a "superfluidity" and of a super-heat-conductivity."

§3. SUPERFLUIDITY

We have already emphasized that one might certainly not be justified in formally applying the ordinary corpuscular theory¹⁰ of transport phenomena of a Bose-Einstein gas to this case of degeneracy where the *mean de Broglie wave-length of the particles is comparable with the macroscopic dimensions of the whole system*. On the present occasion, however, it may perhaps be permissible to discuss, with all due reserve, the question of what would be the effect if, in Sommerfeld's theory of conductivity,¹¹ the Fermi statistics are formally replaced by the Bose-Einstein statistics, and in particular, what would happen at the transition to the degenerate state. One may presume that our attempt will prove as much justified as the classical treatment of diamagnetism on the basis of the Larmor theorem.

In order to fix our ideas and to have a definite, though highly idealized, model, we may depict liquid helium as a metal in which ions and electrons are replaced by particles of the *same* kind, namely both by He atoms. Each He atom may move in a self-consistent (van der Waals) field formed by the other atoms. The states of this system might perhaps, to a certain approxima-

⁸ E. F. Burton, *Nature* **135**, 265 (1935); Wilhelm, Misener and Clark, *Proc. Roy. Soc. (London)* **A151**, 342 (1935); E. F. Burton, *Nature* **142**, 72 (1938); P. Kapitza, *Nature* **141**, 74 (1938); J. F. Allen and A. D. Misener, *Nature* **141**, 75 (1938); B. V. Rollin, VII. Congrès Internat. du Froid **1**, 187 (1936); Kikoin and Lasarew, *Nature* **142**, 912 (1938); J. G. Daunt, and K. Mendelssohn, *Nature* **141**, 911 (1938); **142**, 475 (1938).

⁹ W. H. Keesom and A. P. Keesom, *Physica* **2**, 557 (1935); B. V. Rollin, *Physica* **3**, 296 (1936); W. H. Keesom and A. P. Keesom, *Physica* **3**, 359 (1936); J. F. Allen, R. Peierls and M. Z. Uddin, *Nature* **140**, 62 (1937).

¹⁰ G. E. Uhlenbeck and E. A. Uehling, *Phys. Rev.* **43**, 552 (1933).

¹¹ A. Sommerfeld, *Zeits. f. Physik* **47**, 1 (1928).

tion, be divided into two classes: one, being more of the *Bloch-type* (progressive modulated Schrödinger waves), corresponding to the *electronic states* of the metal and representing a transport of matter; the other one, more of the *Debye-type* (quantized acoustical or elastic waves), corresponding to the *vibrations of the ionic lattice*. In this picture the *fluidity* of the liquid would correspond to the electric *conductivity* of the electrons in a metal; the friction would be due to the dissipation of progressive Bloch waves by inelastic reflection on the Debye waves. Let us finally make the assumption that for these inelastic collisions there exists a mean free path l which is independent of the velocity v for small values of v .

We do not want to insist here on the details of this conception, which is certainly open to much criticism, though perhaps it may prove useful for describing some properties of liquids in general. At any rate it is desirable to know what would be the result if in the theory of metals the Fermi statistics are formally replaced by Bose statistics, even if one does not think of a possible connection with liquid helium, and even if it is more than doubtful whether one is allowed to apply the ordinary collision theory to this limiting case in which the mean value of the de Broglie wavelength is comparable with the macroscopic dimensions of the whole system.

The well-known formula for the electric conductivity $\sigma \sim \langle l/v \rangle_{av}$ would yield the value $\sigma = \infty$ in the case where a finite fraction of all particles has zero velocity. But actually one has to apply a special consideration for the slowest particles. A particle of mass M and of initial velocity v_0 , chosen in the direction of the field F , needs the time τ to traverse the mean free path l :

$$l = v_0\tau + (1/2M)F\tau^2,$$

$$\text{or } \tau = (M/F)[(v_0^2 + 2lF/M)^{1/2} - v_0].$$

The mean change of velocity due to the action of F during this time τ will therefore be given by

$$\langle \delta v_0 \rangle_{av} = \frac{1}{2M} F\tau = \frac{1}{2} [(v_0^2 + 2lF/M)^{1/2} - v_0]. \quad (11)$$

In general (particularly in the case of Fermi statistics, and also in the case $T > T_0$ for the Bose statistics), one is accustomed and entitled to disregard the few particles with $Mv_0^2/2 \lesssim lF$

and one may write instead of (11):

$$\langle \delta v_0 \rangle_{av} = \frac{l}{2Mv_0} \cdot F \quad \text{for } Mv_0^2/2 \gg lF, \quad (11a)$$

which gives the above-mentioned formula for σ .

In the case of the Bose degeneracy ($T < T_0$), however, we are not allowed to neglect the *finite fraction* of particles with $v_0 = 0$. For these we obtain

$$\langle \delta v_0 \rangle_{av} = (lF/2M)^{1/2} \quad \text{for } Mv_0^2/2 \ll l \cdot F. \quad (11b)$$

This contribution is, for ordinary values of F , enormously greater than (11a). One may say the "conductivity," *viz.*, the *fluidity* (defined as derivative of the current with respect to F), becomes *infinite* for $F \rightarrow 0$, and this abruptly, as soon as $T < T_0$. For a fixed value of F , the current will be proportional to N_0/N , i.e., proportional to the fraction of atoms of velocity zero.

The particles N_0 , having the energy zero, will not appreciably contribute to the transport of energy, and therefore, we should not expect a particularly great increase of the *heat conductivity* when passing to the degenerate state.

§4. THERMOMECHANICAL EFFECT

But there is another mechanism which may produce a transfer of heat.¹² The van der Waals forces between the walls and the He atoms are much stronger than those between the He atoms themselves. In a layer, L , of perhaps 10A, or 100A, or even greater thickness along the walls, the van der Waals field will be appreciably stronger than in the interior, I , of the liquid. In this layer the concentration of the degenerate atoms will therefore be much greater than in the interior, the entropy in the layer, S_L , will be much smaller than in the interior, S_I . Thus we have a situation quite analogous to a thermocouple: namely, two different conductors, L and I , in conducting contact.

If q mols of helium pass at a temperature T from I to L they will go into a state of greater order, and the heat

$$Q = T(S_I - S_L)q \quad (12)$$

will be set free. This will occur in a *reversible manner*, quite as in the case of the Peltier effect. Relating all transfer of energy or matter to unit

¹² H. London, Nature **142**, 612 (1938).

of time and to unit of cross section, we may write

$$Q = T(S_I - S_L)J, \quad (12a)$$

where J is the current density. The "Peltier coefficient" is accordingly given by

$$\Pi_{I, L} = T(S_I - S_L). \quad (13)$$

Assuming for S the expression for an ideal degenerate Bose gas, which is given by (7) (9)

$$S_- = \frac{U_- - F_-}{T} = (5/2)0.514CRT^{5/2}V, \quad (14)$$

we obtain for the Peltier coefficient

$$\Pi_{I, L} = (5/2)0.514CRT^{5/2}(V_I - V_L). \quad (15)$$

Now the arrangement for measuring heat conductivity can simply be considered as a thermocouple consisting of the two "metals" L and I . If we heat at one point of the wall and cool at another one, in such a way that the temperature at the two points may be kept constant at T_1 and T_2 respectively, we may produce a "thermoforce" Φ given, according to W. Thomson's well-known thermodynamic relation, by the formula

$$\Phi = \int_{T_1}^{T_2} \frac{\Pi_{I, L}}{T} dT = \int_{T_1}^{T_2} (S_I - S_L) dT$$

or with (14):

$$\Phi = (T_2 - T_1)(5/2)0.514CRT_1^{3/2}(V_I - V_L). \quad (16)$$

This "thermoforce" will produce very great circulation of matter, since the "internal resistance" of the thermoelement is extraordinarily small, and, therefore, the consumption of heat for maintaining even the smallest temperature differences will also be very great. This process, therefore, will appear like an enormous conduction of heat; the "conductivity," however, will depend very strongly on the gradient of temperature. For the lowest temperatures, the helium atoms will everywhere be almost completely degenerate, in the layer as well as in the interior of the liquid. There will be no difference of entropy between the different parts of the liquid, the "thermoforce" will disappear—as it must according to Nernst's Law—and there will no longer be a production of circulation in the liquid. Only ordinary heat conductivity (chiefly by the Debye vibrations), will remain. Nevertheless the great fluidity, since it is proportional to the number N_0 of degenerate atoms, will persist

down to the lowest temperatures; only the driving thermoforce and the Peltier heat will disappear.

All this is in qualitative agreement with the experiments, particularly with those of Keesom and Saris,¹³ and of Kürti and Simon,¹³ on the heat conductivity of He at the lowest temperatures, which below 0.6°K, has been found to become "normal" again, i.e., small and independent of the gradient of temperature. In fact, this transition to normal heat conductivity occurs in just that region where the thermal anomaly of the specific heat, connected with the λ -point, ceases and passes over into an ordinary Debye T^3 -law for the specific heat.

This mechanism of reversible transformation of heat into mechanical energy gives a very simple explanation also for the so-called "fountain phenomenon" observed by Allen and Jones,¹⁴ and interprets it as a pump driven by a thermoelement. It may be remarked that according to (12) the flow of matter in the capillary layer has to have the opposite direction to the transfer of heat, if the entropy in the capillary layer is smaller than in the normal liquid. In fact this connection between the directions of the flow of heat and of the flow of matter has actually been observed in the experiment of Allen and Jones. The same has been found in the Knudsen manometer experiment of H. London.¹²

The idea that the transport phenomena of He II might be reversible processes has first been discussed by L. Tisza.¹⁵ The thermodynamic relation (12) has recently been given by H. London.¹² Though it might appear that the logical connection between the facts will not be qualitatively very different from the one we have sketched here, it is obvious that the theoretical basis given thus far is not to be considered more than a quite rough and preliminary approach to the problem of liquid helium, limited chiefly by the lack of a satisfactory molecular theory of liquids.

The author wishes to express his thanks to Professor P. Gross for his hospitality in the Chemistry Department of Duke University, and for his kind interest in this work.

¹³ W. H. Keesom, A. D. Keesom, and B. F. Saris, *Physica* 5, 281 (1938); N. Kürti and F. Simon, *Nature* 142, 207 (1938).

¹⁴ J. F. Allen and H. Jones, *Nature* 141, 243 (1938).

¹⁵ L. Tisza, *Nature* 141, 913 (1938).