Now Ω_0 can be put into the following form

$$\Omega_0=\Omega_0'\Omega_0''$$

where Ω_0' depends only on the variables of the transverse photons and Ω_0'' depends only on those of the longitudinal photons belonging to the vacuum. Equation (41) becomes

$$A^{(l)}(k)\Omega_0''=0, \quad A^{*(l)}(k)\Omega_0''=0. \tag{42}$$

Since, as pointed out in the footnote before, the solution Eq. (40) does not depend on the exact form of Ω_0'', the factor Ω_0'' can simply be omitted from Eq. (40). This means that instead of choosing Ω_0 to satisfy Eq. (41), one can simply consider it as independent of the variables of the longitudinal photons. In other words, vacuum is considered as containing no longitudinal photons at all. This is just the convention adopted in the usual treatment in which the longitudinal field has been replaced by the Coulomb interaction.

In conclusion, the author wishes to express his thanks to Professor Bethe for helpful suggestions and discussions and also to Professor Feynman for detailed exposition of his theory before publication.

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The Bose-Einstein Condensation for Thin Films

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The distinction is made between a condensation temperature in the thermodynamic sense, where the thermodynamic functions have a discontinuity, and an abrupt accumulation (in the statistical mechanical sense) of particles in the ground state of a system. The criterion for the latter is that an integral will not approximate one term of a sum. The problem of a thin film of gas is solved to illustrate this distinction. For films thicker than a critical thickness a condensation occurs at the same temperature as that for bulk material. The thinner films are effectively two dimensional and have an abrupt accumulation temperature lower than the bulk condensation temperature. Films of liquid helium are briefly considered.

INTRODUCTION

CONSIDERABLE interest has been provoked by London's proposal[1] that the λ-phenomenon of helium is a Bose-Einstein condensation, or accumulation of a finite fraction of all the particles in the ground state of a potential hole of macroscopic dimensions. Tisza[2] has extended this suggestion to discuss helium in terms of the hydrodynamics of a two-fluid system, and more recently Ogg[3] has proposed that phenomena which he has observed in metal-ammonia solutions and possibly also the phenomenon of superconductivity might be explained by the condensation of a gas of electron pairs formed from the free electrons of the material. It is the purpose of this paper to examine in some detail the conditions under which these condensations occur and to discuss some examples of physical interest. The particular examples we shall discuss are: (1) Three-dimensional gas of uncharged particles in a thin film, (2) Two-dimensional gas, and in a subsequent paper (3) Gas of charged particles in a magnetic field, neglecting electrostatic interactions.

Condensation and Accumulation Temperatures

In classical thermodynamics a condensation temperature implies a discontinuity in one of the thermodynamic functions which describe the system. Such discontinuities are also described by phase changes of first, second, third order, depending on whether the function or one of its higher derivatives becomes discontinuous.

From the standpoint of statistical mechanics we shall define an accumulation temperature T_0 as a temperature at which a finite fraction of all particles begin to accumulate in just one state or set of states with the same energy. By "finite" fraction we mean less than, but not a great deal less than unity, or very much greater than $1/N$, N being the total number of particles. We can speak of an "abrupt" accumulation if the fraction in a given state changes from "small" to "finite" in a small temperature range $\Delta T \ll T_0$. Such finite fractions can usually be expressed as $1-(T/T_0)^n$, $T<T_0$. We speak of a gradual accumulation if it occurs over a range $\Delta T \simeq T_0$. Only in the first case would it be appropriate to speak of a well-defined accumulation temperature, in the second case one might speak of an accumulation temperature band. Consider the expression for N, the total number of particles in a Bose-Einstein assembly.

$$\begin{aligned} N &= \sum_{k,l,m} 1/(\exp(E(k,l,m)/kT+\alpha)-1) \\ &= \sum_{k,l,m} f(E(k,l,m),\alpha,T), \end{aligned} \tag{1}$$

where k, l, m are quantum numbers specifying the level of energy $E(k, l, m)$ and α is defined implicitly as a function of T by this relation.

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[1] F. London, Phys. Rev. 54, 947 (1938).

[2] L. Tisza, Phys. Rev. 72, 838 (1947).

[3] R. A. Ogg, Preliminary Report to ONR, "Electronic Processes in Liquid Dielectric Media. The Constitution of Metal Ammonia Solutions." April 11, 1948, p. 20.

If the value of $\sum_{k,l,m} f(E(k,l,m),\alpha,T)$ can be replaced by $\int\int\int dkdldmf(E(k,l,m),\alpha,T)$ there is no accumulation of particles in any particular energy state. In general, on replacing a sum by an integral we have

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

valid provided

$$f(n+\tfrac{1}{2})-f(n-\tfrac{1}{2})-f'(n)\ll f(n), \qquad (3)$$

where $a<n<b$, and n refers to any of the three indices k, l, m of summation.

The condition in Eq. (3) may fail in either of two ways: (a) If it fails for every value of n in the interval a, b, (as will be the case if in (1) kT is of the order of the spacing of the levels), then there is a gradual accumulation of the particles with diminishing temperature in the lowest energy state; (b) (3) may fail only for the lowest value of n in the interval a, b. If the value of the temperature at which this occurs is well defined, we have an abrupt accumulation of particles in the lowest state. If this accumulation temperature depends only on N/V as $N\rightarrow\infty$, i.e. is independent of the size of the system, we may expect discontinuities in the thermodynamic properties at this temperature. It is then a condensation temperature. This was first shown by Einstein,[4] and subsequently examined in detail by others.[5] Even when weak interactions between the particles are included the condensation occurs.[6]

THE IDEAL GAS IN A THIN FILM

In order to illustrate these points, let us consider the case of an ideal three-dimensional Bose-Einstein gas confined to a thin film. We shall show, using the above consideration, how thin the film must be for the well-known three-dimensional condensation to be prevented, and that for still thinner films (effectively two-dimensional gas[7]) an *abrupt accumulation* can still occur.

For the thin film, the expression for the total number of particles of mass M' in a box ($\psi=0$ on walls) of dimensions

$$L_x=L_y=L, \quad L_z=L/M, \quad M\gg 1$$

is

$$N=\sum_{k,l,m=1}^{\infty} 1/(\exp((k^2+l^2+m^2M^2)\epsilon/kT+\alpha)-1), \qquad (4)$$
$$\epsilon=h^2/8M'L^2.$$

Assuming for the moment that all these summations can be replaced by integrals (despite the large energy interval in m), we shall first examine the conditions under which the lower limits of integration on k, l, m can be replaced by 0, instead of $\frac{1}{2}$ as required by (2). This will give us an expression for N equivalent to that for a cubical box, plus correction terms which when large indicate that the film is too thin to be considered a three-dimensional system. The condition for largeness of the correction term will turn out to be the same as the condition forbidding replacement of a sum (over m) by an integral. From (4)

$$N=\int_{\frac{1}{2}}^{\infty}\int_{\frac{1}{2}}^{\infty}\int_{\frac{1}{2}}^{\infty} dkdldm\Big/ (\exp((k^2+l^2+m^2M^2)\epsilon/kT+\alpha)-1). \qquad (5)$$

Letting

$$k^2+l^2+M^2m^2=\rho^2, \quad \eta=(\tfrac{1}{2}+M^2/4)^{\frac{1}{2}}\simeq M/2$$

$$N=(1/M)\int_{\eta}^{\infty}(\pi/2)\rho^2d\rho/(\exp(\rho^2\epsilon/kT+\alpha)-1), \qquad (6)$$

where the factor $\pi/2$ is a consequence of the fact we use box rather than periodic boundary conditions, and so integrate only over one octant in k, l, m space. Letting $\rho=\rho'+\eta$, and expanding that part of the exponential which is linear in ρ', and using the definition

$$U(p,\alpha)=(1/\Gamma(p+1))\int_0^{\infty} dzz^p/(\exp(z+\alpha)-1)$$
$$=\sum_{j=1}^{\infty}\exp(-\alpha j)/j^{p+1}, \qquad (7)$$

we find, after some manipulation

$$\begin{aligned}N=(\pi/2M)(kT/\epsilon)^{\frac{3}{2}}[&\Gamma(3/2)U(\tfrac{1}{2},\eta^2\epsilon/kT+\alpha)/2\\ &+\eta(\epsilon/kT)^{\frac{1}{2}}U(0,\eta^2\epsilon/kT+\alpha)\\ &+\eta^2\Gamma(1/2)(\epsilon/2kT)U(-\tfrac{1}{2},\eta^2\epsilon/kT+\alpha)]\\ &+\text{Order }(\eta(\epsilon/kT)^{\frac{1}{2}}). \qquad (8)\end{aligned}$$

The four terms of (8) come in order from the three terms of $\rho^2=\rho'^2+2\eta\rho'+\eta^2$ in the numerator of (6) and the linear term in ρ' in the expansion of the denominator, the last being valid so long as $\eta\epsilon\rho'/kT$ is small in the region of the principal contribution to the integrand. This is so if $\eta\epsilon/kT$ is small. If one takes into account the following properties of the U functions,

$$U(\tfrac{1}{2},\alpha)\simeq U(\tfrac{1}{2},0),$$
$$U(0,\alpha)\simeq -\ln\alpha,$$
$$U(-\tfrac{1}{2},\alpha)\simeq\alpha^{-\frac{1}{2}},$$

for

$$0<\alpha\ll 1, \qquad (9)$$

and compares the above formulas with those of reference 1, one can easily verify the following statements. T_{01} is the condensation temperature for the three-dimensional case given in reference 1.

(1) For $\alpha>0$ and $\eta\epsilon/kT\ll 1$, $T>T_{01}$, the 2nd, 3rd,

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[4] A. Einstein, Ber. Berl. Akad. (1924), 261; (1925), 3.

[5] R. H. Fowler and H. Jones, Camb. Phil. Soc. Proc. 34, 573 (1938).

[6] L. I. Shiff, Phys. Rev. 59, 758 (1941).

[7] Correspondence and conversation with F. London on this problem led to the distinction between "condensation" and "accumulation."

and 4th terms of Eq. (8) are negligible, and the first term gives just the conditions for determining α for the gas in a cubical box, given in reference 1.

(2) For $\alpha \leq 0$ and $\eta\epsilon/kT \ll 1$, the 2nd, 3rd and 4th terms of (8) are still negligible, and the first term determines the condensation temperature T_{01} as given in reference 1. Below this temperature, the condition (3) for integrating k, l or m fails for $k=l=m=1$. The first term of the summation must be separated from the integral, and α is determined by

$$\alpha+(2+M^2)\epsilon/kT=1/N(1-(T/T_{01})^{\frac{3}{2}}.$$

(3) For $\eta\epsilon/kT \simeq 1$, there is no condensation phenomenon. The 2nd, 3rd and 4th terms are not negligible, but (8) cannot be used to determine α, as $\eta\epsilon/kT \simeq 1$ is just the condition for a gradual accumulation in the lowest z direction level ($m=1$) and the failure of the integration condition (3) for all values of m.

(4) For $\eta\epsilon/kT \gg 1$ practically all of the particles are in the $m=1$ state, the gas can properly be considered as two dimensional, and must be reexamined for integrability on k and l.

Application to Liquid Helium

Before proceeding to a discussion of the two-dimensional case we can estimate for helium how thin a film has to be before condensation will be prevented. If $\eta\epsilon/kT \simeq 1$ we find for $T=T_{01}=3.4°$ (theoretical), $L_z \simeq 10^{-7}$ cm. This is small compared to the observed thickness of 5.10^{-6} cm for superfluid helium films.[8] Therefore, the observed thickness of superfluid helium films is not in contradiction with the idea that superfluidity is a consequence of a Bose-Einstein condensation. This calculation ignores the effect of the surface forces of the material on which the film lies in modifying the energy levels.

THE TWO DIMENSIONAL IDEAL GAS

Though primarily of academic interest, this problem has been the subject of some controversy, and is illuminating in showing the distinction between an abrupt accumulation and a condensation. It is also suggestive of the nature of the effects of geometry and impurities. The expression determining α for a square film is

$$N=\sum_{k,\,l=1}^{\infty} 1/(\exp((k^2+l^2)\epsilon/kT+\alpha)-1),$$
$$L_x=L_y=L, \quad \epsilon=h^2/8mL^2. \tag{10}$$

If the conditions (3) for replacing the sums over k, l by integrals are met we have

$$N=\int_{\frac{1}{2}}^{\infty}\int_{\frac{1}{2}}^{\infty} dkdl\Big/ (\exp((k^2+l^2)\epsilon/kT+\alpha)-1) \tag{11}$$
$$=-(\pi kT/4\epsilon)\ln(1-\exp(-\alpha')), \tag{12}$$

where by definition

$$\alpha' \equiv \epsilon/kT+\alpha.$$

The expression (12), determining α, unlike its three dimensional analogue, does have a solution for α for all values of T. In fact for α small (low temperatures) we find

$$\alpha=\exp(-4\epsilon N/\pi kT)-\epsilon/kT, \tag{13}$$

or in terms of α'

$$\alpha'=\exp(-T_{01}'/T), \tag{14}$$

where by definition

$$T_{01}'=h^2N/2\pi mkS,$$
$$S=L_xL_y.$$

T_{01}' is very nearly the condensation temperature for a three-dimensional gas whose surface density is the same as that for the two dimensional case. But T_{01}' is not a condensation temperature in this problem.

However, it is not legitimate, in view of the integration criterion (3) to use the above expression (13) for $\alpha < \epsilon/kT$. When $\alpha < \epsilon/kT$, we must use

$$N=1/(\exp(2\epsilon/kT+\alpha)-1)$$
$$+\int_{3/2}^{\infty}\int_{3/2}^{\infty} dkdl\Big/ (\exp((k^2+l^2)\epsilon/kT+\alpha)-1), \tag{15}$$

$$N=1/(\alpha'+3\epsilon/2kT)$$
$$-(\pi kT/4\epsilon)\ln(1-\exp(-5\epsilon/2kT-\alpha')). \tag{16}$$

In Eq. (16) the first term represents the population of the ground state and the second term represents the population of all the higher states. We shall continue the discussion in terms of α' since it is the behavior of this quantity as a function of T, rather than α, which will simplify the argument. Let us ask at what temperature T_{02}', where we expect $T_{02}' \ll T_{01}'$, Eqs. (16) and (12) give different results for α', so that for $T < T_{02}'$ we must use the more exact expression Eq. (16).

T_{02}' is a temperature such that $\alpha'(T_{02}')=(5\epsilon/2)/kT_{02}'$. To see this we first observe that by (14) α' is a very violent function of the temperature for $T \ll T_{01}'$. Thus, since $T_{02}' \ll T_{01}'$, at temperatures slightly above T_{02}', α' dominates the logarithm in (16), and (16) and (12) are equivalent. However, at temperatures slightly less than T_{02}' in (16), the logarithm in Eq. (16) is practically independent of α'. Then (16) and (12) give different results for α', so one must use the more exact expression, Eq. (16), in which α' will primarily be determined by the first term.

Finally, we remark that the condition to determine T_{02}', $\alpha'(T_{02}')=5\epsilon/2kT_{02}'$ giving the temperature at which (16) and (12) begin to disagree, and the condition to use Eq. (16) given by $\alpha \simeq \epsilon/2kT_{02}'$ for the failure of the integration condition in Eq. (3), will in practice give almost exactly the same numerical value for T_{02}'. The reason for this is that α' is such a violent function of the

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[8] J. G. Daunt and K. Mendelssohn, Proc. Roy. Soc. **170**, 423, 429 (1939).

temperature in the vicinity of T_{02}' that both of the equalities $\alpha'(T)=5\epsilon/2kT$ and $\alpha(T)=\epsilon/2kT$ are met in a very small temperature range.

Let us now determine what the relative populations of the ground, and all higher states are, above and below T_{02}'. Above T_{02}', since the right-hand side of Eq. (12) (the total population) and the second term of Eq. (16) agree, we see that the population of the ground state (1st term of Eq. (16)) is negligibly small. Below T_{02}' we have that the population of the higher states (2nd term of Eq. (16)), since $\alpha' \ll \epsilon/kT$, is $\simeq MT \ln MT$, where $M \sim k/\epsilon$ is *large*. Now $MT \ln MT$ varies approximately linearly in T, since its principal variation with T is in the factor of the logarithm. Moreover, it must provide, at the temperature T_{02}', practically all of the particles N, since above T_{02}' few of the particles are in the ground state. Therefore, we are compelled to conclude that, for $T<T_{02}'$ the population of the higher states must vary approximately like NT/T_{02}', and since the total number of particles must add up to N the ground state population varies like $N(1-T/T_{02}')$. In other words, since in Eq. (16), the second term is independent of α' (for $T<T_{02}'$, $\alpha' \ll 5\epsilon/2kT$) and is linear in T (like NT/T_{02}'), α' in the first term must vary in just such a way that the first term makes the total number of particles add up to N.

We, therefore, conclude that T_{02}' must be an accumulation temperature. We do not yet know how abrupt it is, and if it is also a condensation temperature.

To answer these questions we first determine T_{02}' by substituting $\alpha'=5\epsilon/2kT$, $T=T_{02}'$ in (16) and solving for T_{02}'. Doing this one finds

$$T_{02}'=T_{01}'(1+\delta)/\ln N, \tag{17}$$

where δ is small, of order $1/\ln N$. This shows that T_{02}' is not a condensation temperature since $T_{02}' \to 0$ as $N \to \infty$.

As an accumulation temperature T_{02}' is moderately "abrupt." To show this one calculates from Eq. (16) the relative population of ground and excited state *at* the temperature T_{02}', and also the maximum departure from linearity in T of the second term of (16), as α' varies in the range $\alpha'=5\epsilon/2kT$ to $\alpha'=-3\epsilon/2kT$ (the lowest allowed value according to first term of (16)). Doing this one finds that the band of transition ΔT from condition "above" T_{02}' (negligible number of particles in ground state) to condition "below" T_{02}' (the ground state population $\simeq N(1-T/T_{02}')$) is given by

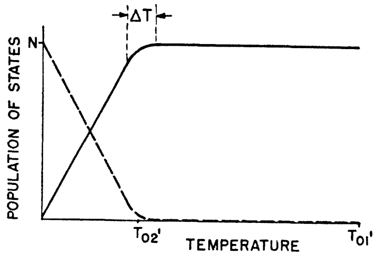

FIG. 1. Populations of the ground state (broken line) and all higher states (full line) of a two-dimensional B. E. gas. T_{01}' is the approximate condensation temperature of a three-dimensional B. E. gas of the same surface density.

$$\Delta T \simeq T_{02}'/\ln N.$$

This means T_{02}' is a moderately abrupt accumulation temperature. Thus, if one had a "surface gram molecule" of material, $N=(N_{\text{Avogadro}})^{\frac{2}{3}}$ the accumulation at T_{02}' would occur at a temperature of 1/35 the corresponding three-dimensional condensation temperature, and in a temperature range about 3 percent of T_{02}' wide. All these conclusions are summarized in Fig. 1.

To interpret these results, one can say that in any physical situation where these calculations would be applicable, the results would be sensitive to any boundaries or impurities on the surface which would tend to modify the lowest energy state and break up the total number of particles N into subsystems. Effects of this type really represent the essence of surface and geometry effects in calculating from a statistical mechanical standpoint the properties of matter in the bulk. For example, one ordinarily considers the condensation temperature of water to be independent of the amount of material, but a moment's reflection shows that this is only approximately true. For small drops the condensation temperature (water-steam) is higher because of the increased pressure of surface tension. In this case, the condensation temperature also goes down (but not to zero) with an increased amount of material.