

Statistical Mechanics and the Partition of Numbers. I. The Transition of Liquid Helium

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the same as the spectrum derived from thin-target radiation. Even quantitatively we should expect the resemblance to be close, considering the equivalence of electrons and photons revealed in the Weizsäcker-Williams method.

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Statistical mechanics and the partition of numbers

I. The transition of liquid helium

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The existing theory of 'Bose-Einstein condensation' is compared with some results obtained from the theory of partition of numbers. Two models are examined, one in which the energy levels are all equally spaced, the other being the perfect gas model. It is concluded that orthodox theory can be relied upon at very high and at very low temperatures, also that the condensation phenomenon is a real one, but that it is not correctly described by orthodox theory, the position of the transition temperature and the form of the specific heat anomaly both being given wrongly.

1. INTRODUCTION

It has long been recognized that the central problem of statistical mechanics, the determination of the number of ways in which a given amount of energy can be shared out among the different possible states of an assembly, is essentially a problem of the same type as that of the determination of the number of partitions of a number into integral parts under certain restrictions. The application by Fowler and Darwin, in the former writer's great book *Statistical mechanics*, of the powerful methods of complex variable theory that had already proved so successful in analytic number theory, served to underline this affinity, which has been explicitly mentioned by a number of writers, for example, Auluck & Kothari (1946). In the present paper, some of the methods of partition theory will be applied to a study of the 'Bose-Einstein condensation' of a perfect gas. This problem has been chosen for study because a recent paper by Schubert (1946) has thrown doubt on the validity of orthodox theory. The difficulty arises when one attempts to use the Fowler-Darwin

method of steepest descents to determine the coefficient of x^N in the generating function $\prod_r (1 - xz^{E_r})^{-1}$, where E_r is the energy of the r th state. In the Fowler-Darwin method, this is done by means of a contour integration with respect to the variable x , the contour being a circle of radius λ encircling the origin, λ being chosen so that the circle passes through the saddle-point of the integrand on the real axis. The results of orthodox theory now follow if it can be shown that the main contribution to the contour integral comes from a small region of the circle in the neighbourhood of the real axis. If so, it then follows that the occupation number of the r th state, of weight ϖ_r , is given by the well-known expression $\bar{N}_r = \frac{\varpi_r \lambda e^{-E_r/kT}}{1 - \lambda e^{-E_r/kT}}$, and, if this may be assumed, the detailed theory of the Bose-Einstein condensation can be rigorously proved as was done by London (1938), and Fowler & Jones (1938).

The contour used by Fowler and Darwin is the circle $x = \lambda e^{i\alpha}$, and their procedure is to expand the integrand in the form $\exp(\sum_r A_r \alpha^r)$, where A_1 vanishes because $x = \lambda$ is a saddle-point of the integrand. In general A_2 is large and negative, and it is possible to find a small value α_0 of α such that $A_2 \alpha_0^2$ has become numerically very large, while the terms involving A_3, A_4, \dots are still negligibly small, on account of the fact that they involve higher powers of α . The results of orthodox theory now follow if it can be shown that:

(a) The remainder of the circle $\pi > |\alpha| \geq \alpha_0$ contributes to the integral an amount that is negligibly small compared with the contribution of the region of the circle $|\alpha| \leq \alpha_0$.

(b) The expansion of the integrand as the exponential of a power series in α is convergent in the region $|\alpha| \leq \alpha_0$.

Assumption (a) does not seem to have been critically examined, but Schrödinger (*Statistical thermodynamics*) has examined at length the analogous case of integration over the z -variable in classical statistics, and has proved that here the analogous assumption introduces no physically significant error. Assumption (b) has been examined by Schubert (1946) and by Fraser (unpublished) for the perfect gas model, who find that, for temperatures in the region of the alleged transition temperature, the expansion of the integrand used by Fowler and Darwin fails to converge in part of the range of $|\alpha| \leq \alpha_0$. The reason for this is that the integrand has a singularity at $\lambda = 1$, so that when the saddle-point approaches the unit circle, as it does in this temperature region, the circle of convergence of the expansion of the integrand becomes insufficient to include the whole of the range of $|\alpha| \leq \alpha_0$, and the Fowler-Darwin method breaks down. It is, however, still possible that the orthodox formula $\bar{N}_r = \frac{\varpi_r \lambda e^{-E_r/kT}}{1 - \lambda e^{-E_r/kT}}$ is universally true, and it is the purpose of this paper to examine this question by methods which do not involve contour integration over the variable x .

A recent attempt by Leibfried (1947) to show that the orthodox formula for \bar{N}_r is always valid for the perfect gas model must be rejected as completely fallacious, the fallacy being that one cannot differentiate an asymptotic expansion without a careful examination of the remainder term, still less may one differentiate the

leading term after rejecting all the others, as Leibfried attempts to do. Because each term is negligible compared with the one before it, it does not follow that the same is true of their derivatives.

The investigation now to be described seems to show conclusively that the orthodox expression for the occupation number \bar{N}_r is not universally valid and that the true distribution law is more complicated. The orthodox law appears to be valid at very high and at very low temperatures, but for the two distributions of energy level examined there is a region of intermediate temperatures where it fails. It is not yet possible to say whether this failure always occurs in Bose-Einstein statistics, or whether it is confined to models which would, on orthodox theory, show a condensation phenomenon.

The two models studied are, first, one in which the energy-levels are equally spaced. The consequences of this model are examined, first, if the orthodox expression for the occupation number is assumed, secondly, making no such assumption but using the analytic theory of the partition of numbers. It is concluded that the orthodox expression gives incorrect results in the transition region (in particular that there is no 'sharp' specific heat anomaly). The second model studied is the more complicated one of the perfect gas, which cannot yet be solved so completely by partition methods, but again the orthodox expression is shown to be invalid for a certain range of temperatures.

2. A MODEL WITH EQUALLY SPACED LEVELS

This model has already been considered by Auluck & Kothari (1946) in connexion with their work on the partition of numbers, the problem they consider being the 'radiation problem', that is, the sharing of a fixed amount of energy between N harmonic oscillators of equal frequency. We shall consider the rather different problem of N particles obeying Bose-Einstein statistics distributed among infinitely many energy-levels $0, \epsilon, 2\epsilon, 3\epsilon, \dots$ of uniform spacing ϵ , in such a way that the total energy is ϵE . Auluck & Kothari find expressions for $p_N(E)$, the number of ways of dividing an integer E into N or less integral parts, from the statistical mechanics of harmonic oscillators, and obtain results agreeing with those obtained for $p_N(E)$ by purely mathematical methods, so that for the radiation problem the use of the method of steepest descents for the evaluation of their integrals seems justified. In our problem, we shall obtain results differing widely from those given by orthodox theory.

The generating function for $p_N(E)$ is

$$\sum_N \sum_E p_N(E) x^N z^E = 1/(1-x)(1-xz)(1-xz^2)(1-xz^3)\dots \quad (1)$$

In our problem, if \bar{N}_r is the mean occupation number of the state with energy $r\epsilon$ referred to the lowest state as zero, the generating function for $\bar{N}_r p_N(E)$ is easily seen to be

$$\frac{xz^r}{1-xz^r} \frac{1}{(1-x)(1-xz)(1-xz^2)\dots} \quad (2)$$

According to orthodox theory we now apply the method of contour integration with steepest descents to pick out the appropriate powers of x and z in these two expressions, and obtain for the ratio the expression

$$\bar{N}_r = \frac{\lambda \theta^{\epsilon}}{1 - \lambda \theta^{\epsilon}}, \quad (3)$$

where λ and θ^{ϵ} are the values of x and z respectively at the saddle-point.

In this particular model, the coefficient of x^N can be picked out exactly, so that the contour integration with respect to x is not really necessary. We shall first assume the accuracy of equation (3), and that the spacing of the levels ϵ is independent of N . In these circumstances we obtain a discontinuity in the specific heat at the transition temperature. (If we wanted to discuss the 'two-dimensional Bose-Einstein gas', which can be approximated to by a spacing of energy-levels at equal intervals, we should have to allow ϵ to tend to zero like $1/A$, where A is the area within which the molecules are confined. For a constant surface density of particles N/A , this would make ϵ tend to zero like $1/N$ as the assembly became very large, and, in these circumstances it is well known that no discontinuity appears.)

We shall then compare these results with those obtained by a method that does not assume the validity of equation (3), and does not necessitate the use of a contour integral to determine the coefficient of x^N . In Schubert's (1946) discussion of a perfect gas, it was the corresponding contour integration that was found to be impossible by the method of steepest descents, and we shall find evidence of a similar failure here, which may be traced to the fact that, if N is large compared with $E^{\frac{1}{2}}$, the function $p_N(E)$ varies so slowly with N that it is not surprising that the method of steepest descents fails. On the other hand, $p_N(E)$ always increases very rapidly with E , and the contour integration with respect to z , to determine the coefficient of z^E , seems to be always possible by the method of steepest descents. A corresponding result is implicitly assumed by Schubert (1946) for the perfect gas.

The result of the amended treatment of the equally spaced model is that there is certainly a range of temperatures just above absolute zero for which the occupation numbers of all states but the lowest are independent of N , and that there is a transition temperature above which the fact that N is finite begins to affect the occupation numbers, but that this effect certainly cannot be described by a *single* parameter λ in the manner of equation (3). Furthermore, this transition temperature is much lower than that predicted by orthodox theory based on equation (3). It seems probable that the transition is of an unfamiliar type, in that it is not associated with a discontinuity of any finite derivative of the partition function, but our present knowledge of the behaviour of the function $p_N(E)$ is not sufficient to enable us to be quite certain of this.

Finally, some results are obtained for the perfect gas model. It is first shown that, in the 'classical' limiting case of high temperatures, the consequences of equation (3) are practically equivalent to some well-known results on the representation of large numbers as sums of integral squares. Secondly, it is shown that equation (3) is correct at sufficiently low temperatures, but that the transition temperature again lies much lower than it would according to orthodox theory, so that the transition temperature

for a perfect gas of particles of mass equal to that of a helium atom would lie well below 1°K . If, however, the assumption of a perfect gas were replaced by the more realistic assumption that a typical helium atom is confined within a 'cage' of dimensions of the order of magnitude of the atomic distances in liquid helium, then *this* model would be expected to have a transition temperature of the order of 1 to 2°K .

3. A MODEL WITH EQUALLY SPACED ENERGY-LEVELS. ORTHODOX TREATMENT

We consider an assembly containing infinitely many energy-levels spaced at equal intervals ϵ above the lowest one, each being capable of being occupied any number of times. We let the total number of particles be N and the total energy ϵE . It is not claimed that this model represents any actual physical situation, but it does exhibit in what way the orthodox and exact treatments fail to agree. According to the orthodox theory we have

$$N = \sum_{r=0}^{\infty} \frac{\lambda \theta^{r\epsilon}}{1 - \lambda \theta^{r\epsilon}}, \quad E = \sum_{r=0}^{\infty} \frac{r \lambda \theta^{r\epsilon}}{1 - \lambda \theta^{r\epsilon}}. \quad (4)$$

If we keep ϵ finite, it is never possible to represent these sums as tending to integrals, but they can be summed without much difficulty by Poisson's formula, which enables one to sum a series if one can sum the series formed by applying the Fourier transform to each term. We apply this process to the series for N after removing the first term, and to the series for E . We obtain, putting $\lambda = 1/A$, $\theta = e^{-1/kT}$,

$$\begin{aligned} N - \frac{1}{A-1} - \frac{1}{2A} \frac{1}{e^{\epsilon/kT} - 1} &= \sum_{l=-\infty}^{+\infty} \int_0^{\infty} \frac{e^{2\pi i l t}}{A e^{\epsilon(1+l)/kT} - 1} dt \\ &= \sum_{s=1}^{\infty} \sum_{l=-\infty}^{+\infty} \int_0^{\infty} e^{2\pi i l t} A^{-s} e^{-s(t+1)\epsilon/kT} dt \\ &= \sum_{s=1}^{\infty} \sum_{l=-\infty}^{+\infty} \frac{A^{-s} e^{-s\epsilon/kT}}{(s\epsilon/kT) + 2\pi i l} \\ &= \frac{kT}{\epsilon} \sum_{s=1}^{\infty} \frac{A^{-s} e^{-s\epsilon/kT}}{s} + \frac{2\epsilon}{kT} \sum_{s=1}^{\infty} \sum_{l=1}^{\infty} \frac{s A^{-s} e^{-s\epsilon/kT}}{(s\epsilon/kT)^2 + 4\pi^2 l^2} \\ &= -\frac{kT}{\epsilon} \log \left(1 - \frac{e^{-\epsilon/kT}}{A} \right) + \frac{\epsilon}{kT} \frac{1/A e^{\epsilon/kT}}{(1 - 1/A e^{\epsilon/kT})^2} O(1). \end{aligned} \quad (5)$$

The corresponding equation for E is

$$\begin{aligned} E - \frac{1}{2A} \frac{1}{e^{\epsilon/kT} - 1} &= \sum_{l=-\infty}^{+\infty} \int_0^{\infty} \frac{(t+1) e^{2\pi i l t}}{A e^{\epsilon(t+1)/kT} - 1} dt \\ &= \sum_{s=1}^{\infty} \sum_{l=-\infty}^{+\infty} \int_0^{\infty} (t+1) e^{2\pi i l t} A^{-s} e^{-s(t+1)\epsilon/kT} dt \\ &= \sum_{s=1}^{\infty} \sum_{l=-\infty}^{+\infty} \frac{A^{-s} e^{-s\epsilon/kT}}{(s\epsilon/kT) + 2\pi i l} + \sum_{s=1}^{\infty} \sum_{l=-\infty}^{+\infty} \frac{A^{-s} e^{-s\epsilon/kT}}{[(s\epsilon/kT) + 2\pi i l]^2} \\ &= \frac{kT}{\epsilon} \sum_{s=1}^{\infty} \frac{A^{-s} e^{-s\epsilon/kT}}{s} + \left(\frac{kT}{\epsilon} \right)^2 \sum_{s=1}^{\infty} \frac{A^{-s} e^{-s\epsilon/kT}}{s^2} \\ &\quad + \frac{2\epsilon}{kT} \sum_{s=1}^{\infty} \sum_{l=1}^{\infty} \frac{s A^{-s} e^{-s\epsilon/kT}}{(s\epsilon/kT)^2 + 4\pi^2 l^2} + 2 \sum_{s=1}^{\infty} \sum_{l=1}^{\infty} \frac{A^{-s} e^{-s\epsilon/kT} [(s\epsilon/kT)^2 - 4\pi^2 l^2]}{[(s\epsilon/kT)^2 + 4\pi^2 l^2]^2}. \end{aligned} \quad (6)$$

We know that A may never be less than unity because this would make the occupation number of the lowest state infinite. Equation (6) shows that, to make E a large number, we must have $\epsilon/kT = O(1)$. The third and fourth terms in equation (6) (right-hand side) are then at most $O(kT/\epsilon)$, as is the term $\frac{1}{2}(A e^{\epsilon/kT} - 1)^{-1}$, while the first term on the right-hand side is $O\left(\frac{kT}{\epsilon} \log\left(\frac{kT}{\epsilon}\right)\right)$ and the second term is $O\left(\frac{kT}{\epsilon}\right)^2$. On the right-hand side of equation (5), the second term can only become large if A is nearly unity, in which case it is of order kT/ϵ , but the first term is then of order $\frac{kT}{\epsilon} \log\left(\frac{kT}{\epsilon}\right)$. If, for example, we have A equal to $1 + \frac{O(1)}{N^{\frac{1}{2}}}$, then, in the limiting case of a very large assembly, the second and third terms on the left-hand side are negligible compared with N , and we shall have

$$N \sim \frac{kT}{\epsilon} \log\left(\frac{kT}{\epsilon}\right), \quad E \sim \left(\frac{kT}{\epsilon}\right)^2 \sum_{s=1}^{\infty} \frac{1}{s^2} = \frac{\pi^2}{6} \left(\frac{kT}{\epsilon}\right)^2. \quad (7)$$

If now A takes the slightly smaller value $1 + \frac{O(1)}{N}$, the expression for E is practically unaffected, but the term $1/(A-1)$ in equation (5) now contributes effectively to N . Thus, we have a situation very similar to that in the orthodox theory of the perfect gas, the energy at a given temperature being no longer affected by N when this number rises above the value $\frac{\sqrt{6}}{\pi} E^{\frac{1}{2}} \log E$, any further increase merely affecting A , but, as the change in A is only of the order of $1/N$, the only term in equations (6) and (7) to be significantly affected is the term $1/(A-1)$, which determines the occupation number of the very lowest level.

The nature of the anomaly that occurs can be found by differentiating the expression (4) for E with respect to temperature, and summing the resulting series for $\partial E/\partial T$, by means of Poisson's formula. This gives an expression for the specific heat in terms of $\partial A/\partial T$, and the latter quantity can be evaluated by differentiating the series (4) for N with respect to temperature, using the fact that N is constant, so that the series for $\partial N/\partial T$ must vanish. Both these series can be summed by the same process as that used for equations (5) and (6), that of picking out the dominant terms in the transformed series. Below the transition temperature the quantity $\partial A/\partial T$ is negligibly small, while just above the transition temperature it is, in the limiting case of very large N and E , given by the simple expression $1/T_0$, where T_0 is the transition temperature as determined by equation (7). The discontinuity in $\partial A/\partial T$ leads to a negative discontinuity in the specific heat, which drops discontinuously from the value $\frac{\pi^2}{3} \frac{k^2}{\epsilon}$ just below the transition temperature to the value $\left(\frac{\pi^2}{3} - 1\right) \frac{k^2}{\epsilon}$ just above this temperature. The analysis is rather lengthy on account of the fact that both the transformed series contain a great many terms whose orders of magnitude all have to be examined, so it is omitted, as it contains no features of any special interest.

This model thus gives a discontinuity in the specific heat itself, in contrast with the discontinuity in the derivative of the specific heat found for the perfect gas. The

slightly more drastic nature of the discontinuity is due to the fact that we are supposing the separation of the energy-levels to remain finite, while in the perfect gas, the spacing of the levels becomes zero for a very large assembly.

4. A MORE EXACT TREATMENT OF THE MODEL WITH EQUALLY SPACED ENERGY-LEVELS

In this treatment we abandon equation (3) and return to the exact equations (1) and (2). For this simple model, one of the integrations by the method of steepest descents can be avoided by algebraic means. In equation (1), putting xz for x we obtain

$$\sum_N \sum_E p_N(E) x^N z^{E+N} = 1/(1-xz)(1-xz^2)(1-xz^3)\dots = (1-x) \sum_N \sum_E p_N(E) x^N z^E. \quad (8)$$

Equating coefficients of x^N , we find

$$\sum_E p_{N-1}(E) z^E = (1-z^N) \sum_E p_N(E) z^E,$$

so that

$$\sum_E p_N(E) z^E = 1/(1-z)(1-z^2)\dots(1-z^N). \quad (9)$$

Expanding the first factor in expression (2) in powers of x , and remembering that expression (2) may also be written as $\sum_N \sum_E \bar{N}_r p_N(E) x^N z^E$, we obtain

$$\sum_E \bar{N}_r p_N(E) z^E = \frac{z^r(1-z^N) + z^{2r}(1-z^N)(1-z^{N-1}) + \dots}{(1-z)(1-z^2)\dots(1-z^N)}. \quad (10)$$

One can prove formally the applicability of the saddle-point method to determine the ratio of the coefficients of z^E in (9) and (10). An outline of this proof is as follows:

The contour integral $\oint \frac{dz}{z^E(1-z)(1-z^2)\dots}$ has been intensively studied, e.g. by Hardy's *Ramanujan* (1940, chap. VIII), using the following method of evaluating such integrals. A given radius R (< 1) of the contour is chosen, and the contour is divided into arcs each of which arcs is associated with one of the rational fractions in the Farey series of order n , this Farey series consisting of those rational fractions whose denominators are not greater than n . Each rational fraction p is associated with a point on the unit circle whose polar angle is $2\pi p$, which point is a singularity of $f(z)$. The function $f(z) = \frac{1}{(1-z)(1-z^2)\dots}$ is transformed by the formulae of elliptic function theory, and it is shown that, in each arc of the contour, it is sufficiently accurate to replace $f(z)$ by its asymptotic form in the neighbourhood of the point on the unit circle associated with this arc, a different transformation formula holding for each arc, according to the particular polar angle $2\pi p$. The investigation shows that the main contribution to the contour integral is always given by the arc in the neighbourhood of the real axis associated with the singularity $z = 1$ of $f(z)$, in other words that, to use Hardy's language, this singularity of $f(z)$ is by far the 'heaviest' one. The contributions to the contour integral associated with the other rational singularities of $f(z)$ are together negligible compared with this one (however large

n may be). For any given value of n , it can further be shown that the error in the evaluation of the contour integral can even be made less than unity if n is made sufficiently large and all the corresponding singularities are considered.

Thus, for the contour integral containing $f(z)$, we can show quite rigorously, first that the only contribution of physical importance for a very large assembly comes from the immediate neighbourhood of the real axis, secondly that $f(z)$ can always be expressed in a form that converges on the whole of the arc corresponding to $z = 1$, so that both our conditions (a) and (b) above (p. 362) would be satisfied if the integrand contained $f(z)$. This situation is not changed by replacing $f(z)$ by the function

$\frac{1}{(1-z)(1-z^2)\dots(1-z^N)}$ which only means that the essential singularities of $f(z)$ on the unit circle are replaced by poles of order N , $\frac{1}{2}N$, $\frac{1}{3}N$, etc., nor does multiplication of the integrand by the function $z^r(1-z^N) + z^r(1-z^N)(1-z^{N-1}) + \dots$ (which has at most a simple pole at $z = 1$) affect the position of the saddle-point, because the integrand itself has a pole of order N at $z = 1$ and is therefore varying with extreme rapidity in this neighbourhood.

We thus obtain the following expression for \bar{N}_r .

$$\bar{N}_r = \theta^{er}(1 - \theta^{Ne}) + \theta^{2er}(1 - \theta^{Ne})(1 - \theta^{(N-1)e}) + \dots \quad (r \geq 1), \quad (11)$$

where θ^e is the value of z at the saddle-point. This argument fails for the very lowest state, $r = 0$, but, as a matter of fact, expression (11) is valid in this case also. To prove this, we have

$$\bar{N}_0 = N - \sum_{r=1}^{\infty} \bar{N}_r = N - \frac{\theta^e(1 - \theta^{Ne})}{1 - \theta^e} - \frac{\theta^{2e}(1 - \theta^{Ne})(1 - \theta^{(N-1)e})}{1 - \theta^{2e}} - \dots$$

(using equation (11) for \bar{N}_r and summing from $r = 1$ to infinity), which gives

$$\bar{N}_0 = (1 - \theta^{Ne}) + (1 - \theta^{NE})(1 - \theta^{(N-1)E}) + \dots$$

by setting $p = \theta^e$ in the identity

$$N \equiv \frac{1-p^N}{1-p} + \frac{(1-p^N)(1-p^{N-1})}{1-p^2} + \dots$$

This identity may be proved as follows: Let k_N stand for the expression

$$k_N = \frac{1-p^N}{1-p} + \frac{(1-p^N)(1-p^{N-1})}{1-p^2} + \dots$$

Then

$$\begin{aligned} k_N - k_{N-1} &= p^{N-1} + p^{N-2}(1-p^{N-1}) + p^{N-3}(1-p^{N-1})(1-p^{N-2}) + \dots \\ &\quad + (1-p^{N-1})(1-p^{N-2}) \dots (1-p) \\ &= p^{N-1} + (1-p^{N-1})(k_{N-1} - k_{N-2}). \end{aligned}$$

Now $k_2 - k_1$ is identically unity, therefore so are $k_3 - k_2$, $k_4 - k_3$, etc., and since k_1 is unity it follows that k_N is identically equal to N and therefore that equation (11) is also true for $r = 0$.

For $N > E$, the terms in expression (10) that involve z^N and higher powers of z can contribute nothing to the coefficient of z^E , while, until N drops to a value com-

parable with $E^{\frac{1}{2}}$, they give a contribution to expression (11) that vanishes in comparison with the main terms. For N less than E , the expression for \bar{N}_r therefore takes the form

$$\bar{N}_r \approx \theta^{er} + \theta^{2er} + \theta^{3er} + \dots = \frac{\theta^{er}}{1 - \theta^{er}}, \quad (12)$$

which agrees with the very low temperature expression for \bar{N}_r according to orthodox theory provided that we make the customary identification $\theta = e^{-1/kT}$. For T very large, expression (11) agrees with the 'classical' expression $\theta^{er}/(1 + \theta^e + \theta^{2e} + \dots)$ for \bar{N}_r , provided that we can neglect θ^e in comparison with unity. The customary relation between θ and T therefore gives us results that agree with orthodox theory both for very high temperatures and for a finite range of energies above absolute zero, thus justifying this identification of θ .

We now examine whether expression (11) can be made to agree with orthodox theory in the region of the transition temperature predicted by the orthodox theory. We notice first of all the following relation between the values of \bar{N}_r for two consecutive values of N , which follows easily from expression (11),

$$\bar{N}_r(N) = \theta^{er}(1 - \theta^{Ne})(1 + \bar{N}_r(N-1)). \quad (13)$$

If orthodox theory were correct in the transition region, then it would be possible to express the occupation numbers in the form

$$\bar{N}_r(N) = \frac{\lambda_{N,r} \theta^{re}}{1 - \lambda_{N,r} \theta^{re}}, \quad (14)$$

where $\lambda_{N,r}$ may be written $1 - \delta_{N,r}$, where $\delta_{N,r}$ is a small quantity which may depend on N , but whose leading term must be independent of r . Substituting expression (14) into equation (13), expressing the λ 's in terms of the δ 's, and neglecting products of the δ 's,

$$\delta_{N,r} = \theta^{Ne}(1 - \theta^{re}) + \theta^{re} \delta_{N-1,r} + O(\theta^{2Ne}), \quad (15)$$

which implies that the leading terms in $\delta_{N,r}$ must take the following form:

$$\begin{aligned} \delta_{N,r} &\approx \frac{(1 - \theta^{re})(\theta^{Ne} - \theta^{Nr\epsilon})}{1 - \theta^{(r-1)\epsilon}} \quad (r \geq 2) \\ &\approx N\theta^{Ne}(1 - \theta^e) \quad (r = 1). \end{aligned} \quad (16)$$

Equation (16) shows clearly that $\delta_{N,r}$ is *not* independent of r , a different degeneracy parameter $\lambda_{N,r}$ appearing for each energy level, and it must be concluded that orthodox theory is not correct, at least not in the supposed transition region where $\lambda_{N,r}$ should be nearly unity.

Orthodox theory therefore cannot be used in the transition region, where we can point to two other discrepancies with the treatment we have just given. In the first place, the onset of the transition is not located correctly. Orthodox theory (equation (7)) predicts that the transition should take place when N is proportional to $E^{\frac{1}{2}} \log E$, while the exact theory shows that the transition must set in, in the sense of the occupation numbers of the state other than the lowest becoming functions of N as well as of E , when N becomes less than E . In the second place, orthodox theory pre-

dicts a jump in the specific heat, while the exact theory certainly predicts an anomaly, but not one corresponding to a phase-transition of any finite order. The following is the asymptotic expression for $p_N(E)$, which can be obtained from equation (9) by using an asymptotic expression for the function $1/(1-z)(1-z^2)\dots(1-z^N)$ in the neighbourhood of the singularity $z = 1$, as in the classical work on the partition of numbers of Hardy & Ramanujan (1918). It can also be obtained, as was done by Auluck & Kothari (1946), from the accepted statistical mechanical formulae for the distribution of energy among simple harmonic oscillators. Auluck, Chowla & Gupta (1942) have obtained a similar result by methods which do not use a contour integral at all.

$$p_N(E) \sim \frac{1}{4\sqrt{3}E} \exp \left[\pi \sqrt{\frac{2E}{3}} - \frac{\sqrt{(6E)}}{\pi} \exp \left(-\frac{\pi N}{\sqrt{(6E)}} \right) \right] \quad (N \gg E^{\frac{1}{2}}). \quad (17)$$

By the Boltzmann formula the entropy S is given by the expression $S = k \log p_N(E)$, which reduces to $k \log p(E)$ when $N \geq E$. The quantity $k \log \left(\frac{p_N(E)}{p(E)} \right)$ is therefore the defect in entropy caused by the fact that N is finite, which will lead to a specific heat anomaly as E passes through the value N . (The temperature is determined by the usual relation $T = \partial S / \partial E$.) The form of equation (17) suggests that none of the derivatives of S with respect to E or T are discontinuous as E passes through the value N , so that no discontinuity of co-operative type is to be expected. This result is not yet formally proved, on account of the difficulties of differentiating asymptotic expressions, but an elementary argument can be used to establish it. The numbers $p_E(E)$ and $p_{E-1}(E)$ only differ by unity, namely by the one partition in which E is divided into E parts, all of them unity. There is therefore, for E large, no significant discontinuity in the first derivative of $\log p_N(E)$. A similar argument can be applied to the second, third and higher derivatives by counting up the number of partitions that we lose in going from $p_{E-1}(E)$ to $p_{E-2}(E)$, $p_{E-3}(E)$, etc. It is therefore extremely likely that there is no actual discontinuity in any finite derivative of S . This situation seems to be rather like what one would observe supposing that one had a transition temperature T_c , with no anomaly in the entropy below T_c , but an extra term proportional to $\exp \left(\frac{B}{T_c - T} \right)$, where B is a constant, above T_c . Such an extra term would not give any discontinuity in the specific heat or in any of its derivatives, and, from an experimental point of view, would be indistinguishable from a 'smooth' specific heat anomaly.

Equation (17) is of interest from another point of view, in indicating a possible reason for the failure of the saddle-point method when applied to the variable x in equations (1) and (2), namely, that in the transition region the value of $p_N(E)$ is changing extremely slowly with N . This, combined with the fact that the saddle-point value of x is nearly unity means that, for a fixed E , expression (1) contains a very large number of terms $\sum_N p_N(E) x^N$ all of which are of the same order of magnitude, so that one cannot necessarily replace the logarithm of this series by the logarithm of a single term with sufficient approximation. Since $p_N(E)$ always varies extremely rapidly with the variable E , no such effect occurs to spoil the validity of the z -integration.

We have still to examine the behaviour of \bar{N}_0 according to the exact theory, as equation (11) gives no direct information on this point. Equation (10), however, is valid, giving us

$$\sum_E N_0 p_N(E) z^E = \frac{(1-z^N) + (1-z^N)(1-z^{N-1}) + \dots}{(1-z)(1-z^2)(1-z^3) \dots (1-z^N)}. \quad (18)$$

Let f_N stand for the series

$$(1-z^N) + (1-z^N)(1-z^{N-1}) + \dots$$

Then we have the following relation

$$f_N = (1-z^N)(1+f_{N-1}). \quad (19)$$

Now set $f_N = N - g_N$ and equation (19) becomes

$$g_N = Nz^N + (1-z^N)g_{N-1}. \quad (20)$$

If we now set

$$g_N = h_N(1-z)(1-z^2) \dots (1-z^N)$$

we obtain from equation (20)

$$h_N - h_{N-1} = \frac{Nz^N}{(1-z)(1-z^2) \dots (1-z^N)}, \quad (21)$$

which gives us the following expression for h_N :

$$h_N = \frac{Nz^N}{(1-z)(1-z^2) \dots (1-z^N)} + \frac{(N-1)z^{N-1}}{(1-z) \dots (1-z^{N-1})} + \dots + \frac{z}{1-z}. \quad (22)$$

Equation (18) may now be written

$$\sum_E \bar{N}_0 p_N(E) z^E = \frac{N}{(1-z)(1-z^2) \dots (1-z^N)} - h_N \quad \text{or} \quad \sum_E (N - \bar{N}_0) p_N(E) z^E = h_N, \quad (23)$$

since, from equation (9), $p_N(E)$ is the coefficient of z^E in $1/(1-z)(1-z^2) \dots (1-z^N)$. We already know that $p_N(E)$ becomes independent of N if $N \geq E$, and equation (22) shows that the coefficient of z^E in h_N becomes independent of N when $N \geq E$. Thus, we have shown that the quantity $N - \bar{N}_0$, that is to say, the total number of systems in states other than the lowest one is independent of N for N greater than E , but begins to depend on N as soon as N passes through this value. Thus, we have succeeded in confirming, by a purely algebraic method, the result proved above by contour integration, namely, that the anomaly sets in at N equals E .

It thus seems to be definitely established that orthodox theory cannot be relied on for any correct results in the transition region, the occupation numbers, the nature of the specific heat anomaly, and the energy content at which the transition sets in all being incorrect. One further remark about this model may be of interest. Let us make the usually correct, but not self-evident, assumption that the statistical mean state (obtained by averaging over all accessible states) is identical with the most probable state. Let us fix N_0 the occupation number of the lowest state. Then the remaining states can be occupied in $P_{N-\bar{N}_0}(E)$ ways, where $P_k(E)$ is the number of ways of partitioning E into exactly k non-zero parts. The behaviour of this function

has been studied by Auluck *et al.* (1942). It is clearly an increasing function of k when k is small, and a decreasing function of k when k is becoming comparable with E . Thus, if N is below the value that makes $P_N(E)$ a maximum, we shall get the greatest number of arrangements if we make \bar{N}_0 zero, whereas if N is greater than this value, we shall get the largest number of arrangements if we choose \bar{N}_0 so that $P_{N-\bar{N}_0}(E)$ takes the maximum value. The precise behaviour of the function $P_k(E)$ is not known, but Auluck *et al.* present theoretical and numerical evidence in support of the view that there is a single maximum in the region $k \sim \frac{1}{\pi} \sqrt{\left(\frac{3E}{2}\right) \log E}$. If their conjecture proves correct, it will mean that the condensation sets in (according to the assumption that the mean state is identical with the most probable state) for a value of N differing by a factor of 2 from that predicted by the saddle-point method, and widely different from that predicted by the exact theory. It therefore seems that it is possible to construct models for which the most probable state is not identical with the mean state.

5. SOME PRELIMINARY RESULTS FOR THE 'PERFECT BOSE-EINSTEIN GAS' MODEL

There seems to be a very general relation between N the number of particles and the total energy for which a condensation sets in. In any model, let ϵ_0 be the energy-separation between the state of lowest energy and the first excited state, either or both of which may be multiple. Let $E\epsilon_0$ be the total energy. If E is less than N , there is clearly no possible arrangement of the particles for which the ground state does not contain at least one particle. If we add more particles, keeping the energy constant, we do not introduce any new possible ways in which the excited states can be occupied, the new arrangements are simply reproductions of the old ones, differing only from them by having more particles in the ground state. If the ground state is single, an exact one-to-one correspondence can be set up between the new and the old arrangements, but the correspondence is no longer exact if the ground state is multiple, as the occupation of different sub-states of the ground state does produce a few more arrangements. If the ground state is single, then the average number of particles in the excited states is quite unaffected by adding more particles, provided $N > E$, while the average increase in the number in the ground state is just the number of particles added. It is interesting to work out the energy at which degeneracy sets in in the perfect Bose-Einstein gas according to this argument. (In this model, the ground state is single.) The separation between the ground state and the first excited state, if the gas is in a cubical box of side d , is given by the expression $3h^2/8md^2$, so that we have the following relation between N and E for degeneracy to set in. It is not possible to calculate the transition temperature, because we have no knowledge of the behaviour in this region of the function corresponding to $p_N(E)$ in the simple model.

$$N = E, \quad \text{with} \quad \epsilon_0 = \frac{3h^2}{8md^2}. \quad (24)$$

We can, however, make a comparison with the position of the transition region as given by the orthodox theory by writing down the expressions for critical number of

atoms per unit volume as a function of temperature, and for energy content as a function of temperature and eliminating T between these two equations. These two equations are well known, see, for example Mayer & Mayer (1940, chap. 16):

$$N = \frac{(2\pi m)^{\frac{3}{2}}}{h^3} (kT)^{\frac{3}{2}} d^3 \sum_j \frac{1}{j^{\frac{3}{2}}}, \quad (25)$$

$$E\epsilon_0 = \frac{(2\pi m)^{\frac{3}{2}}}{h^3} (kT)^{\frac{3}{2}} d^3 \sum_j \frac{1}{j^{\frac{3}{2}}}. \quad (26)$$

Eliminating T between them, we find the following relation between N and E :

$$N^{\frac{2}{3}} = 0.17 E. \quad (27)$$

This differs from relation (24) by a factor of the order of $N^{\frac{2}{3}}$, so that an exact theory would give a transition beginning at a temperature far below 1°K . This investigation suggests, however, that the 'cell' model of a liquid, or some similar conception, rather than the perfect gas assumption, would, if investigated properly, be found to lead to a relationship between N and E very similar to equation (27), and may therefore be expected to lead also to a transition temperature in the right region. For suppose that each atom is supposed to be confined by the interactions with its neighbours in a volume of order of magnitude l^3 or d^3/N which is one atom's share of the total volume, then the spacing of the first excited state above the ground state is now of the order of magnitude $3h^2/8ml^2$ which differs from the perfect gas model by a factor d^2/l^2 or $N^{\frac{2}{3}}$, which is just the order of magnitude of the discrepancy between equations (24) and (27), so that the cell model, worked out properly, should give a transition temperature in the proper region.

The perfect gas model is mathematically equivalent to a certain problem in the partition of numbers into sums of squares, a subject that has been much studied by mathematicians. Unfortunately, the results hitherto available only seem to be applicable to the high temperature region, and we shall state the mathematical problem involved, in the hope that it may stimulate further work by mathematicians. Finally, we shall show the equivalence of existing theory of a perfect gas at high temperatures with certain well-known results on the representation of numbers as sums of squares. A 'representation' differs from a partition in two important respects, namely that the order of arrangement of the squares is considered, each possible order being regarded as a different representation, also the squares of negative numbers are reckoned to be different from those of positive numbers.

The mathematical problem is as follows: The energy-levels available to particles inside a cubical box of side d are given by the expression $(r^2 + s^2 + t^2) \frac{h^2}{8md^2}$, which we write $\frac{h^2}{8md^2} K(r, s, t)$ for brevity. Each of these levels may be occupied an integral number of times, or not at all. We require to know the asymptotic form for the number of distinct partitions of an integer E , representing the ratio of the total energy to the lowest possible energy-separation $h^2/8md^2$, into a sum of the numbers $K(r, s, t)$, where the order in which the K 's are arranged is ignored, but, on the other hand, K 's like $K(1, 2, 3)$, $K(2, 1, 3)$ are distinct from one another, and such K 's have

to be reckoned as 'different', in spite of the fact that they are numerically equal. In all cases, the r, s, t are positive integers (not zero).

The following result is well known, being taken from Hardy (1940),

$$S_{3N}(E) \sim \frac{\pi^{\frac{3}{2}N}}{\Gamma(\frac{3}{2}N)} E^{\frac{3}{2}N-1} \quad (28)$$

giving the number of representations of the number E as the sum of $3N$ squares. Since some of these squares may be zero, we must replace this expression, which is really the sum of the number of representations of E as $3N, 3N-1, 3N-2, \dots$, etc., non-zero squares by the expression

$$T_{3N}(E) \sim \sum_{r=0}^{\infty} \frac{\pi^{\frac{3N-r}{2}}}{\Gamma(\frac{3N-r}{2})} (-1)^r E^{\frac{3N-r}{2}-1} \quad (29)$$

which may also be written

$$T_{3N}(E) \sim S_{3N}(E) \left[1 - O\left(\frac{N^{\frac{1}{2}}}{E^{\frac{1}{2}}}\right) \right] \quad (30)$$

and the correction is thus negligible as long as $E \gg N$.

Having removed the representations involving zero squares, the next task is to remove those involving the squares of negative integers, which since the zero squares have been allowed for, simply involves dividing expression (28) by 2^{3N} . Finally, we have to allow for the fact, that, in expression (28), the same partition into squares written in a different order is counted as different. In our problem, the $3N$ squares have to be divided into N groups of three each. A permutation *within* a group of three, or an exchange of one or two squares *between* two groups of three leads, in general, to a new physical state, but a reshuffling of the *order* in which the groups of three are taken does not lead to a new physical state. Thus, the number of physically different partitions is obtained by dividing expression (28) by a further factor $N!$ giving us finally

$$Q_N(E) \sim \frac{\Pi^{\frac{3}{2}N}}{\Gamma(\frac{3}{2}N)} \frac{E^{\frac{3}{2}N-1}}{N! 2^{3N}}. \quad (31)$$

The last step would be invalidated if too many of the groups of three in a typical partition were identical. I have not succeeded in making even an 'order of magnitude' estimate of the error due to this, but it seems certain on physical grounds that it becomes rapidly less important as E increases.

From expression (31), we can calculate the number of partitions which contain a state of energy $\epsilon_1 K(r, s, t)$, where ϵ_1 is the 'energy step' $\hbar^2/8md^2$. Clearly it is the number of partitions of $E - K(r, s, t)$ into $N-1$ groups of three squares, so that the probability of finding the state (r, s, t) in a typical partition is obtained by replacing N by $N-1$ and E by $E - K(r, s, t)$ in expression (31), and then dividing this by the expression (31) as it stands, which is the total number of partitions without restriction, we obtain

$$\bar{N}_{r,s,t} \sim \frac{N(\frac{3}{2}N)^{\frac{3}{2}}}{E^{\frac{3}{2}}} \frac{8}{\pi^{\frac{3}{2}}} \left(1 - \frac{K(r, s, t)}{E} \right)^{\frac{3}{2}N - \frac{3}{2}} \quad (32)$$

This is to be compared with the 'classical' expression

$$\bar{N}_{r,s,t} \sim N \exp \left[-\frac{\epsilon_1 K(r,s,t)}{kT} \right] / \int \int \int_0^\infty \exp \left[-\frac{(r^2+s^2+t^2)\epsilon_1}{kT} \right] dr ds dt, \quad (33)$$

and it can be seen that these two expressions agree in the limiting case of large T , provided that $E\epsilon_1 \sim \frac{3}{2}NkT$, which is the classical relation between temperature and energy content in a perfect gas.

We may thus conclude that the behaviour of the perfect gas model is qualitatively similar to that of the model with equally spaced levels, in that orthodox theory describes the situation correctly at very high temperatures but breaks down in the supposed transition region. A. R. Fraser (unpublished) has proved a rather stronger result than the one we have just obtained, namely that orthodox theory gives correct results at least down to a temperature not greater than 1.5 times the supposed transition temperature. R. B. Dingle (unpublished) has further shown that, for any model, there is a finite region of temperature starting from absolute zero, within which orthodox theory is correct.

6. CONCLUSION

The two models studied show the same general type of behaviour, namely the existence of an intermediate temperature region within which the results of orthodox theory are unreliable, the orthodox expression for the occupation numbers of the energy levels being only an approximation in this range. The investigation has confirmed the existence of the phenomenon of 'condensation into the lowest energy-level', though the perfect gas model worked out properly, would give a transition temperature far below 1° K for a perfect gas of helium atoms. On the other hand, we have seen that the 'cell' model of a liquid may well have such a transition at a temperature agreeing with the transition temperature for liquid helium, so the investigation gives us no reason to doubt either the reality of the condensation phenomenon or its relevance to the liquid helium problem.

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