ON BOSE-EINSTEIN CONDENSATION

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ABSTRACT. This paper contains a proof that the description of the phenomenon of Bose-Einstein condensation is the same whether (1) an open system is contemplated and treated on the basis of the grand canonical ensemble, or (2) a closed system is contemplated and treated on the basis of the canonical ensemble without recourse to the method of steepest descents, or (3) a closed system is contemplated and treated on the basis of the canonical ensemble using the method of steepest descents. Contrary to what is usually believed, it is shown that the crucial factor governing the incidence of the condensation phenomenon of a system (open or closed) having an infinity of energy levels is the density of states $N(E) \propto E^n$ for high quantum numbers, a condition for condensation being $n > 0$. These results are obtained on the basis of the following assumptions: (i) For large volumes V (*a*) all energy levels behave like $V^{-\theta}$, and (*b*) there exists a finite integer M such that it is justifiable to put for the jth energy level $E_j = cV^{-\theta}j^{\tau}$, and to use the continuous spectrum approximation, whenever $j \geqslant M$; c, θ, τ are positive constants. (ii) All results are evaluated in the limit in which the volume of the gas is allowed to tend to infinity, keeping the volume density of particles a finite and non-zero constant. The present paper also serves to coordinate much of previously published work, and corrects a current misconception regarding the method of steepest descents.

1. *Introduction.* Recent rigorous discussions of the phenomenon of Bose-Einstein condensation (2, 3, 5, 10, 12) lead one to ask the following questions.

(*a*) De Groot and collaborators (2) have assumed what is usually referred to as the Bose-Einstein distribution function, i.e. $1/\{\exp[E_j/kT - \alpha] - 1\}$, stating that they 'are not concerned with its foundation or accuracy'. Hence they have shown by rigorous methods that *no* condensation phenomenon occurs for one- or two-dimensional rectangular boxes, but that it does occur for three-dimensional rectangular boxes. In view of the apparently deficient foundation of their work, one wants to know precisely what the significance of their results is, and what factor governs the incidence of condensation. Their answer to this latter question is that 'the differences between the various cases are caused by the different behaviour of a certain series...', and cannot therefore be given any immediate physical interpretation. We show here that their conclusions are exactly those one would expect for an open system treated by the grand canonical ensemble, and that a condition for the incidence of condensation is that $n > 0$ in the law $N(E) \propto E^n$ for the density of energy states at high quantum numbers. For non-interacting particles in a w-dimensional box $n = \frac{1}{2}w - 1$, so that condensation can occur only for $w > 2$.

(*b*) Fraser (5) has recently shown that for a closed system, treated on the basis of the canonical ensemble, one may expect condensation, provided the energy difference between the lowest two energy levels satisfies

$$(E_2 - E_1)/kT \sim N^{-\gamma} \quad (\gamma < 1).$$

One wants to know if closed and open systems always yield identical results for Bose-Einstein systems (this cannot be expected generally, since the appropriate distribution

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functions are not identical), and, if so, why Fraser's condition for condensation is violated by one- and two-dimensional rectangular boxes. These considerations are supplied in this paper, where it is shown that the grand-canonical ensemble and the canonical ensemble lead to the same result, provided an infinite gas having a fixed volume density of particles is contemplated.*

(*c*) Schubert (10) has thrown doubt on the validity of the method of steepest descents as applied to the problem of Bose-Einstein condensation in closed systems. This conclusion was based on the belief that the first-order correction term to the mean occupation number usually given, and this occupation number, become both of the same order of magnitude at the lowest temperatures. We show here that this belief, which has so far gone unchallenged (3, 5), is in error. The first-order correction term to each of the mean occupation numbers, as obtained by the method of steepest descents, does in fact not diverge in the limit considered by these authors. Our conclusion is that the *total* correction term to the mean occupation number usually given may indeed have an appreciable effect in the case of *finite* systems (as, for instance, investigated by Temperley (12)), but that this effect should vanish when transition is made to the limit of an infinite system having a fixed volume density of particles.

(*d*) One finally wants to know the reason why the rigorous procedures, which involve limiting processes, do not yield results which are fundamentally different from those obtained by London (7), who used the continuous-spectrum approximation, but did not require a limiting process.

In § 2 a mathematical approach is outlined which is sufficiently powerful to handle the questions outlined in (*a*) (cf. §§ 3 and 4), (*b*) (cf. §§ 5 and 6) and (*d*) (cf. § 9). The problem discussed under (*c*) is dealt with in §§ 7 and 8. A brief statement of results is given in the abstract, their fuller discussion being postponed to § 9.

Consider now the usual limiting process (to be referred to as 'L') in which the number of particles N of a perfect Bose-Einstein gas and its volume V both tend to infinity so as to keep the density $\rho = N/V$ a finite and non-zero constant. N may be the number of particles in a *closed* system. Alternatively, it may be the average number of particles in an *open* system (treated on the basis of the grand canonical ensemble). In either case one may define a *condensation temperature* T_0 in the limit L by the condition

$$\lim_{N,V\to\infty} \frac{n_1}{N} \begin{cases} > 0 & \text{for} \quad 0 \leqslant T < T_0, \\ = 0 & \text{for} \quad T_0 < T, \end{cases}$$

n_j being the mean occupation number of the jth quantum state. The value of the limit at $T = T_0$ is left unspecified. It is shown in this paper that, subject to assumptions (10) and (11) (below), the value of the above limit, and hence the value of T_0 (if it exists), is the same whether one is dealing with a closed or with an open system.

We note that, since an infinitely large number of particles cannot be shared out among a finite number of states without allotting to at least one state a non-zero fraction of particles, and since further $n_1 \geqslant n_2 \geqslant \ldots$ for any set of fixed conditions, it follows that a Bose-Einstein system having a *finite* number of quantum states is, in

* A more general theorem linking these two methods will appear shortly in the *Physical Review*.

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the limit L, condensed at all temperatures. In the sequel only systems having an *infinity* of quantum states will therefore be considered.

2. *General considerations.* Consider a physical system whose energy states

$$E_j \quad (j = 1, 2, \ldots)$$

form a denumerable set such that $E_1 < E_2 \leqslant E_3 \leqslant \ldots$. By allowing the equality sign we remove the need for a degeneracy factor in the expressions for the mean occupation numbers. We shall assume that E_1 is a non-degenerate state for finite systems,* that the other degeneracies are finite if the volume is finite, that E_j is finite if j is finite, and that in the limit L finite energies tend to the zero of the energy scale. Let the mean occupation number of the jth state be

$$n_j = [f_j(E_j) - 1]^{-1}, \tag{1}$$

where

$$1 \leqslant f_1(E_1) \leqslant f_2(E_2) \leqslant \ldots \tag{2}$$

to ensure that $n_1 \geqslant n_2 \geqslant \ldots \geqslant 0$. The density $\rho = N/V$ of the gas, assumed finite and non-zero, is given by

$$\rho - V^{-1} \sum_{j=M}^{\infty} [f_j(E_j) - 1]^{-1} = V^{-1} \sum_{j=1}^{M-1} [f_j(E_j) - 1]^{-1}, \tag{3}$$

where $M \geqslant 2$ is here, and throughout the rest of this paper, an arbitrary finite integer. Multiplying both sides of (3) by $f_1(E_1) - 1$ and proceeding to the limit, the right-hand side of (3) vanishes in virtue of (2) *for all finite* M. Writing $f_1(0)$ for the value of $f_1(E_1)$ in the limit L, one finds

$$\left\{\rho - \lim_{N, V \to \infty} \left(V^{-1} \sum_{j=M}^{\infty} [f_j(E_j) - 1]^{-1}\right)\right\} \{f_1(0) - 1\} = 0, \tag{4}$$

provided that the limit which occurs in (4) exists when $f_1(0) \neq 1$.

It is convenient to define a critical temperature T_c by the requirement that in the limit L

$$f_1(0) \begin{cases} > 1 & \text{for} \quad T > T_c, \\ = 1 & \text{for} \quad T \leqslant T_c. \end{cases} \tag{5}$$

By (1) and (5) n_1/N vanishes in the limit L if $f_1(0) > 1$, so that $T > T_c$ implies $T > T_0$, i.e.

$$T_c \geqslant T_0. \tag{6}$$

We shall find (equations (21) and (36)) that in fact the equality sign holds for both open and closed systems.

3. *Open systems.* Interpreting N as the average total number of particles of an open system contained in a volume V, and ρ as the corresponding density, it is known (15) from arguments based on the grand canonical ensemble that

$$f_j(E_j) = \exp\left[\frac{E_j}{kT} - \alpha\right], \quad \alpha \leqslant \frac{E_1}{kT}, \tag{7}$$

where α is the chemical potential divided by kT. (4) becomes

$$\left\{\rho - \lim_{N, V \to \infty} \left(V^{-1} \sum_{j=M}^{\infty} \left[\exp\left(\frac{E_j}{kT} - \alpha\right) - 1\right]^{-1}\right)\right\} \{e^{-\alpha} - 1\} = 0, \tag{8}$$

* This assumption is not essential. If g be the (finite) degeneracy of the lowest energy level of the finite system, it must be understood that if $g > 1$, then throughout the rest of this paper the finite integer M which occurs must satisfy $M > g$, and that n_1 is the mean occupation number of the lowest *energy level*, while the remaining n_j's refer to *quantum states*.

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and T_c is given by

$$\rho = \lim_{N, V \to \infty} \left\{ V^{-1} \sum_{j=M}^{\infty} \left[\exp \frac{E_j}{kT_c'} - 1 \right]^{-1} \right\}. \tag{9}$$

We shall write T_c', T_0' for the value of T_c, T_0 on the basis of the grand canonical ensemble, and assume that the limits which occur exist.

We shall now make the following assumptions:

(i) all energy levels behave as $V^{-\theta}$ for large volumes, (10)

(ii) for sufficiently large j and V one can put $E_j = cV^{-\theta} j^{\tau}$, (11)

where c, θ, τ are finite positive constants. (10) and (11) hold for most problems which are likely to arise. The energy spectrum can be approximated by a continuum to any desired accuracy by choosing V large enough; by choosing M large enough one can use (11) and the corresponding density-of-states function. Hence, replacing the sum in (8) by an integration, and passing to the limit,

$$\left\{ \rho - \Gamma\left(1 + \frac{1}{\tau}\right) \left(\frac{kT}{c}\right)^{1/\tau} G_{1/\tau - 1}(\alpha) \right\} \{ e^{-\alpha} - 1 \} = 0 \quad \text{if} \quad \theta = \tau, \tag{12}$$

where, for $k > -1$ and $\alpha \leqslant 0$,

$$G_k(\alpha) \equiv \frac{1}{\Gamma(k+1)} \int_0^{\infty} \frac{x^k \, dx}{e^{x-\alpha} - 1} = \sum_{s=1}^{\infty} \frac{e^{s\alpha}}{s^{k+1}}, \tag{13}$$

and $\Gamma(x)$ denotes the usual gamma function. Also, by direct integration and the definition $\sum_{j=1}^{\infty} j^{-k} \equiv \zeta(k)$ of the Riemann zeta function,

$$G_{-1}(\alpha) = \frac{1}{e^{\alpha} - 1}, \quad G_0(\alpha) = \log \frac{e^{-\alpha}}{e^{-\alpha} - 1}, \quad G_k(0) = \zeta(k+1) \quad \text{for } k > 0. \tag{14}$$

The case $\theta \neq \tau$, for which it is easily verified that α must be permanently zero, is of no practical interest, and will not be considered further until §6. T_c' is given by

$$\frac{\rho}{\Gamma(1 + 1/\tau)} \left(\frac{c}{kT_c'}\right)^{1/\tau} = G_{1/\tau - 1}(0), \tag{15}$$

and α by

$$\frac{\rho}{\Gamma(1 + 1/\tau)} \left(\frac{c}{kT}\right)^{1/\tau} = G_{1/\tau - 1}(\alpha) \quad \text{for} \quad T \geqslant T_c' \quad \text{and by} \quad \alpha = 0 \quad \text{for} \quad T \leqslant T_c'. \tag{16}$$

The temperature derivatives of α are, by (13) and (16),

$$\left.\begin{aligned} \frac{d\alpha}{dT} &= \frac{1}{\tau T} \frac{G_{1/\tau - 1}(\alpha)}{G_{1/\tau - 2}(\alpha)}, \\ \frac{d^2\alpha}{dT^2} &= \frac{G_{1/\tau - 1}(\alpha)}{\tau^2 T^2 G_{1/\tau - 2}^3(\alpha)} \left[(1 + \tau) \, G_{1/\tau - 2}(\alpha) - G_{1/\tau - 1}(\alpha) \, G_{1/\tau - 3}(\alpha) \right] \end{aligned}\right\} \tag{17}$$

for $T \geqslant T_c'$, and are both zero for $T \leqslant T_c'$. If $T_c' > 0$ exists, the two portions of the (α, T) curve join continuously at $T = T_c'$, but the derivatives (17) need not do so, as may be verified by allowing T to tend to $T_c'+$ and comparing the result with the values (zero) which one obtains by letting T tend to $T_c'-$. The calculation is simplified by the result, due to de Groot *et al.* (2),* that

$$\text{for} \quad k < 0 \quad G_k(\alpha) \to \Gamma(-k) \, (1 - e^{\alpha})^k \quad \text{as } \alpha \to 0. \tag{18}$$

* De Groot *et al.* would write $R_{k+1}(e^{\alpha})$ for $G_k(\alpha)$.

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From (14), (17) and (18), Table 1, which gives the results of these calculations, has been constructed. It is seen that the discontinuities become less marked, and eventually disappear, as τ increases.

Table 1

$\theta = \tau$ given by	T_c' given by	$\frac{d\alpha}{dT}$ at T_c'	$\frac{d^2\alpha}{dT^2}$ at T_c'	Dimension $2/\tau = w$ of corresponding rectangular box
$0<\tau<\frac{1}{2}$	$\frac{\rho}{\Gamma(1+1/\tau)}\left(\frac{c}{kT_c'}\right)^{1/\tau} = \zeta(1/\tau)$	Finite discontinuity	Finite discontinuity	$w>4$
$\tau=\frac{1}{2}$		continuous		4
$\frac{1}{2}<\tau<\frac{2}{3}$				
$\tau=\frac{2}{3}$			Finite discontinuity	3
$\frac{2}{3}<\tau<1$			Continuous	—
$\tau=1$	0	No condensation		2
$1<\tau$				1

Suppose now that $\theta = \tau < 1$. Then by (7)

$$\frac{n_1}{N} = 1 - N^{-1}\sum_{j=2}^{\infty}\left[\exp\left(\frac{E_j}{kT}-\alpha\right)-1\right]^{-1}. \tag{19}$$

But
$$0 \leqslant \frac{1}{N}\left[\exp\left(\frac{E_j}{kT}-\alpha\right)-1\right]^{-1} \leqslant \frac{1}{N}\left[\exp\left(\frac{E_j-E_1}{kT}\right)-1\right]^{-1},$$

so that for large enough V and finite j the right-hand side is by (10)

$$\frac{1}{\rho V}\frac{kT}{E_j-E_1} = \text{constant} \times \frac{kT}{\rho}V^{\tau-1},$$

and tends to zero as $V\to\infty$. One may therefore in the limit L replace $j=2$ by $j=M$ in (19). Proceeding to the limit, choosing M large enough for (11) to hold, and using (15), one finds

$$\lim_{N,V\to\infty}\frac{n_j}{N} = \begin{cases} 1-(T/T_c')^{1/\tau} & \text{for } j=1, \text{ if } T\leqslant T_c', \\ 0 & \text{for } j=1, \text{ if } T\geqslant T_c', \\ 0 & \text{for finite } j>1 \text{ and all temperatures.} \end{cases} \tag{20}$$

This shows that the condensation temperature is

$$T_c' = T_0'. \tag{21}$$

The average energy E per particle of the gas is given by a sum of terms of the form

$$\frac{E_j}{N}\left[\exp\left(\frac{E_j}{kT}-\alpha\right)-1\right]^{-1} \leqslant \frac{E_j}{N}\left[\exp\left(\frac{E_j-E_1}{kT}\right)-1\right]^{-1}. \tag{22}$$

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As before one can show that in the limit L the right-hand side of (22) tends to zero for finite j and all θ. Choosing M large enough to justify the use of (11) one finds if $\theta = \tau$

$$E = \lim_{N,V\to\infty} \left\{ N^{-1} \sum_{j=M}^{\infty} E_j \left[\exp\left(\frac{E_j}{kT} - \alpha\right) - 1 \right]^{-1} \right\}$$
$$= \Gamma\left(\frac{1}{\tau}\right) \frac{kT}{\rho} \left(\frac{kT}{c}\right)^{1/\tau} G_{1/\tau}(\alpha). \tag{23}$$

Using the results

$$\frac{dE}{dT} = \left(\frac{\partial E}{\partial T}\right)_{\alpha} + \left(\frac{\partial E}{\partial \alpha}\right)_{T} \frac{d\alpha}{dT}, \text{ etc.}$$

for the temperature derivatives of E, we see that the discontinuities in E and its temperature derivatives are of the same kind as the corresponding discontinuities in α and its temperature derivatives.

4. *Open systems: comparison with previous work.* De Groot *et al.* (2) considered energy levels in a w-dimensional box of sides $a_1, \ldots, a_w$ given by

$$E_{j_1 \ldots j_w} = \frac{h^2}{8m} \sum_{i=1}^{w} \frac{j_i^2 - 1}{a_i^2}. \tag{24}$$

It can readily be shown that in this case one must put in (10) and (11)

$$\theta = \tau = 2/w, \quad c = \left[\Gamma\left(1 + \frac{w}{2}\right)\right]^{2/w} \frac{h^2}{2\pi m}. \tag{25}$$

Their results follow now in all details from those of §3 (cf. Table 1). This calls for comment, as they avoided explicitly any discussion of the foundation of their work, which merely assumed a distribution function (7). Their *mathematical procedure* was therefore equivalent to what it would have been if they had argued on the basis of the grand canonical ensemble, thus generalizing in all respects the first convincing demonstration of Bose-Einstein condensation by Fowler and Jones (4). One may therefore interpret the total number of particles in their closed system as the fixed average number of particles in an open system. De Groot's paper is then rigorously founded on the grand canonical ensemble, without requiring additional alterations.

It must be emphasized, however, that the gain in mathematical simplicity obtained by the use of the grand canonical ensemble is, according to some workers, offset in the theory of Bose condensation by the fact that these ensembles apply to *open* systems, while they regard any container of liquid helium as representing an (almost) closed system. The relation, indicated in this section, between previous work and the grand canonical ensemble may, however, be of interest.

Another recent paper (13) deals with somewhat different aspects of open Bose-Einstein systems from those discussed here.

5. *Closed systems.* In this case (1, 8)

$$f_j(E_j) = \frac{Z_{N+1} n_{N+1,j}}{Z_N n_{N,j}} \exp\frac{E_j}{kT}, \quad \frac{Z_{N+1} n_{N+1,j}}{Z_N n_{N,j}} \geqslant \exp\frac{E_1}{kT} \tag{26}$$

for all j and N, N being now the total number of particles in a closed system of volume V. Z is the partition function and the suffixes N, $N+1$ refer to the number of particles

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confined in the volume V. By (4) we have that at any temperature, writing T_c'', T_0'' for the value of T_c and T_0 in closed systems,

either $$\rho = \lim_{N,V\to\infty}\left\{V^{-1}\sum_{j=M}^{\infty}\left[\frac{Z_{N+1}n_{N+1,j}}{Z_N n_{N,j}}\exp\frac{E_j}{kT}-1\right]^{-1}\right\} \quad (T>T_c''), \tag{27}$$

or $$\lim_{N,V\to\infty}\left[\frac{Z_{N+1}n_{N+1,1}}{Z_N n_{N,1}}\exp\frac{E_1}{kT}\right]=1 \quad (T\leqslant T_c''), \tag{28}$$

or both (27) and (28) are fulfilled. As each of the three factors in the expression (28) approaches a finite and non-zero limiting value independently of the other two, one can write (28)

$$\lim_{N,V\to\infty}\left(\frac{Z_{N+1}}{Z_N}\right)=\lim_{N,V\to\infty}\left(\frac{n_{N,1}}{n_{N+1,1}}\right) \quad (T\leqslant T_c''). \tag{29}$$

By (5), (27) and (29), T_c'' is given by

$$\rho = \lim_{N,V\to\infty}\left\{V^{-1}\sum_{j=M}^{\infty}\left[\frac{n_{N,1}n_{N+1,j}}{n_{N+1,1}n_{N,j}}\exp\frac{E_j}{kT_c''}-1\right]^{-1}\right\}. \tag{30}$$

The condition for open and closed systems to have the same value of T_c is, by (9) and (30),

$$\lim_{N,V\to\infty}\left\{\frac{n_{N,1}n_{N+1,j}}{n_{N+1,1}n_{N,j}}\right\}=1 \quad \text{for all } j\geqslant M \text{ at } T=T_c''. \tag{31}$$

It was shown by Fraser (5) that

$$\frac{n_{N+1,j}}{n_{N,j}}\geqslant 1, \quad \frac{Z_{N+1}}{Z_N}\geqslant\exp\left(-\frac{E_1}{kT}\right) \quad (\text{all } N,V,j,T). \tag{32}$$

It follows that $$1<\frac{n_{N+1,j}}{n_{N,j}}<\frac{\Sigma_k n_{N+1,k}}{\Sigma_k n_{N,k}}=\frac{N+1}{N},$$

so that $$\lim_{N,V\to\infty}\left(\frac{n_{N+1,j}}{n_{N,j}}\right)=1 \quad (\text{all } j, \text{ all } T), \tag{33}$$

and, therefore, by (31), $$T_c'=T_c''. \tag{34}$$

Comparing (7) and (26), using (32), we see that the theory of §3 applies to closed systems from equation (8) onwards, provided one puts

$$e^{-\alpha}=Z_{N+1}/Z_N. \tag{35}$$

If the argument of §3 is repeated with this substitution, one finds the analogue of (21), $T_c''=T_0''$, so that by (21) and (34) $$T_0'=T_0''. \tag{36}$$

This shows that the condensation temperature is, when it exists, the same for closed and for open systems. The value of n_j/N is at any temperature in the limit L also the same in both cases.

6. *Closed systems: comparison with previous work.* A rigorous treatment of Bose condensation in closed systems has been given by Fraser (5). His basic assumption was that $(E_2-E_1)/kT$ is or order $N^{-\gamma}$, where $\gamma<1$. As, in the present notation, $N=\rho V$, where ρ is a constant, this is equivalent to supposing that a condition of the form (10) with $$0<\theta<1 \tag{37}$$ holds. Fraser showed this assumption to be *sufficient* for the existence of a critical temperature, which we shall denote by T_F'', given by

$$\rho\sim V^{-1}\sum_{j=2}^{\infty}\left[\exp\frac{E_j-E_1}{kT_F''}-1\right]^{-1}, \tag{38}$$

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such that a finite fraction of particles is in the first energy level in the limit L, provided $T < T''_F$. (For simplicity we shall in this and the following section occasionally use the sign $\sim$ to denote 'equality in the limit L', and suppose that the limits involved exist.) He also showed that

$$1 + \frac{1}{n_{N,j}} \sim \begin{cases} \frac{Z_N}{Z_{N-1}} \exp \frac{E_j}{kT} & (\theta < 1;\ \text{all } j;\ T > T''_F), \quad (39) \\ \exp \frac{E_j - E_1}{kT} & (\theta < 1;\ j \geqslant 2;\ T < T''_F). \quad (40) \end{cases}$$

$n_{N,1}$ is determined for $T < T''_F$ by the condition $\Sigma_j n_{N,j} = N$.

We must inquire how these results are related to those of §5. In virtue of (30), (33) and (38) $T''_F = T''_c$, so that T''_F gives in fact the condensation temperature as defined in §1. It would appear, however, from (37) that Fraser's argument would lead one to expect a condensation temperature also if $\theta \neq \tau$, in contradiction with the results of §§3 and 5, provided only $\theta < 1$. That this is not so on the basis of (10) and (11) may be seen by noting that for $\theta < 1$ we have from (38), and by a repetition of the argument applied to equation (19),

$$\rho \sim V^{-1} \sum_{j=M}^{\infty} \left[\exp \frac{E_j - E_1}{kT''_F} - 1 \right]^{-1} \sim \Gamma(1 + 1/\tau) \left(\frac{kT''_F}{c} \right)^{1/\tau} V^{\theta/\tau - 1} G_{1/\tau - 1}(0).$$

It follows that, as $V \to \infty$, $T''_F \to 0$ if $\theta > \tau$, $T''_F \to \infty$ if $\theta < \tau \leqslant 1$, and T''_F is undefined if $\theta < \tau$, $1 < \tau$.

This shows that the assumption that a temperature range exists for which (27) holds, and that another one exists for which (28) holds (i.e. the assumption of a finite and non-zero T''_c) can be self-contradictory if $\theta \neq \tau$, and one must go back to an equation of the form (4) to see under what conditions it can be satisfied at all (cf. §3).

One may also use Fraser's equations to verify that the condition $\theta < 1$ for condensation is also *necessary*. His condition for condensation is $N > N_c$ (in his notation), i.e.

$$\rho V > \sum_{j \geqslant 2} \left[\exp \frac{E_j - E_1}{kT} - 1 \right]^{-1}. \quad (41)$$

Any term in the sum having finite j goes to infinity as V^θ when $V \to \infty$, i.e. less rapidly than the left-hand side of (41) only if $\theta < 1$, as was to be proved.

In conclusion, it seems worth verifying, owing to the importance of (33), that equations of this kind are also involved in Fraser's paper. By (26)

$$\exp\left(-\frac{E_j}{kT}\right) = \frac{Z_{N+1}}{Z_N} \frac{n_{N+1,j}}{1 + n_{N,j}} = \frac{Z_N}{Z_{N-1}} \frac{n_{N,j}}{1 + n_{N-1,j}} = \ldots,$$

so that

$$1 + \frac{1}{n_{N,j}} = \frac{Z_N}{Z_{N-1}} \frac{1 + n_{N,j}}{1 + n_{N-1,j}} \exp \frac{E_j}{kT} \quad (\text{all } N, V, j, T). \quad (42)$$

By (39), (40) and (42) we have for $\theta < 1$

$$n_{N,j} \sim n_{N-1,j}\ (\text{all } j,\ T > T''_F);\ \frac{Z_N}{Z_{N-1}} \frac{1 + n_{N,j}}{1 + n_{N-1,j}} \sim \exp\left(-\frac{E_j}{kT}\right) \quad (j \geqslant 2;\ T < T''_F).$$

In virtue of (32) these relations imply for $\theta < 1$

$$n_{N,j} \sim n_{N-1,j} \quad (\text{all } j \text{ if } T > T''_F;\ j \geqslant 2 \text{ if } T < T''_F), \qquad \frac{Z_N}{Z_{N-1}} \sim \exp\left(-\frac{E_1}{kT}\right) \quad (T < T''_F), \quad (43)$$

and this proves our assertion.

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7. *The saddle-point method.* Another mathematical technique for treating finite closed systems is provided by the saddle-point method (9), when expressions $n_{N,j} = D^{(0)}_{N,j} + D^{(1)}_{N,j}$ are obtained for the mean occupation numbers. They are valid in the limit in which the number of particles in the system is allowed to tend to infinity. $D^{(0)}_{N,j}$ is the usual Bose function $(t_{N,j} - 1)^{-1}$, where $t_{N,j} = y_N^{-1} \exp(E_j/kT)$. y_N gives the position of the saddle-point, and we shall call $D^{(1)}_{N,j}$ the first-order correction term. For finite systems these relations hold only approximately, so that one may define a further term $D^{(2)}_{N,j}$ by the equation $n_{N,j} = D^{(0)}_{N,j} + D^{(1)}_{N,j} + D^{(2)}_{N,j}$. We shall denote the total correction term $D^{(1)}_{N,j} + D^{(2)}_{N,j}$ by $-\Delta_{N,j}$.

The technique can be applied to results obtained on the basis of the canonical ensemble (9). The constant which occurs in the exponent as a multiplier of the energy levels is therefore $1/kT$. It follows that E_j/kT ($= \eta_j$, say) occurs in the same sense here and in §5, and both treatments must lead to similar results. Hence

$$n_{N,j} = [y_N^{-1} \exp \eta_j - 1]^{-1} - \Delta_{N,j} = \left[\frac{Z_{N+1} n_{N+1,j}}{Z_N n_{N,j}} \exp \eta_j - 1\right]^{-1}, \tag{44}$$

$$N + 1 = \sum_k [y_N^{-1} \exp \eta_k - 1]^{-1} = \sum_k \left[\frac{Z_{N+2} n_{N+2,k}}{Z_{N+1} n_{N+1,k}} \exp \eta_k - 1\right]^{-1}. \tag{45}$$

(45) defines the position of the saddle point. In the limit L the limiting values of y_N^{-1} and of Z_{N+2}/Z_{N+1} must satisfy by (33) and (45) the same equation for a given physical system and a given temperature, so that

$$y_N^{-1} \sim Z_{N+2}/Z_{N+1} \sim Z_{N+1}/Z_N. \tag{46}$$

The last relation follows from the result (5)

$$\frac{Z_{N+2}}{Z_{N+1}} < \frac{Z_{N+1}}{Z_N} < \frac{N+2}{N+1} \frac{Z_{N+2}}{Z_{N+1}}. \tag{47}$$

Using (46) in (44), one finds

$$\lim_{N, V \to \infty} \Delta_{N,j} = 0 \quad (\text{all } j, \text{ all } T), \tag{48}$$

and the argument of §3 can in the limit L again be carried through, this time on the basis of equations (44) and (48). The result

$$\Sigma_k \Delta_{N,k} = 1 \tag{49}$$

is, by (44) and (45), valid for *finite* systems.

8. *The saddle-point method: comparison with previous work.* Schubert (10, 3) stated that the first-order terms $D^{(1)}_{N,j}$ can diverge as $T \to 0$. Since $D^{(1)}_{N,j}$ is a component in $\Delta_{N,j}$, this statement makes (48) and (49) very surprising (though it does not necessarily contradict these equations). We shall show, however, that his statement is incorrect. The complete expression for $D^{(1)}_{N,j}$ (10, 3) may most conveniently be written

where

$$\left.\begin{aligned} D^{(1)}_{N,j} &= P_{N,j} + Q_{N,j} - P_{N,j} \Sigma_k Q_{N,k}, \\ P_{N,j} &= F_{N,j}/\Sigma_k F_{N,k}, \quad F_{N,j} = \frac{t_{N,j}}{(t_{N,j} - 1)^2}, \\ Q_{N,j} &= \frac{t_{N,j}(t_{N,j} + 1)}{2(t_{N,j} - 1)^3 \Sigma_k F_{N,k}}. \end{aligned}\right\} \tag{50}$$

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For finite systems $0 \leqslant E_1 < E_2 \leqslant E_3 \ldots$, and, since the saddle-point is on the positive axis, $1 \leqslant t_{N,1} < t_{N,2} \leqslant t_{N,3} \leqslant \ldots$. Suppose $t_{N,1} \to 1$ as $T \to 0$. Then

$$t_{N,j} = t_{N,1} \exp\left(\frac{E_j - E_1}{kT}\right) \to \infty \text{ for } j \geqslant 2, \quad F_{N,j} \to \begin{cases} \dfrac{t_{N,1}}{(t_{N,1}-1)^2} \to \infty & \text{for } j = 1, \\ 0 & \text{for } j \geqslant 2, \end{cases}$$

$$P_{N,j} \to \begin{cases} 1 \text{ for } j = 1, \\ 0 \text{ for } j \geqslant 2, \end{cases} \quad Q_{N,j} \to \begin{cases} \dfrac{1}{t_{N,1}-1} \to \infty & \text{if } j = 1, \\ 0 & \text{if } j \geqslant 2. \end{cases}$$

Hence, for finite systems,

$$D^{(1)}_{N,j} \to 1 + Q_{N,1} - Q_{N,1} = 1, \quad D^{(1)}_{N,j} \to 0 \quad \text{for } j \geqslant 2. \tag{51}$$

Thus $\sum_k D^{(1)}_{N,k} \to 1$, so that, by (49), $\sum_k D^{(2)}_{N,k} \to 0$. This *suggests* that the first-order correction terms are in fact small at low temperatures, and that the second-order correction terms are even smaller.

Dingle (3) pointed out that non-divergence of the mean occupation number does not ensure that an argument is satisfactory, since a finite mean occupation number may be the result of differentiating a divergent series for the corresponding partition function. The appropriate equation is in the present case (3)

$$\log Z_N = -N \log y_0 - \tfrac{1}{2} \log 2\pi - \sum_i \log \frac{t_{N,i} - 1}{t_{N,i}} - \tfrac{1}{2} \log \left(\sum_j F_{N,j}\right) + \ldots$$

and must be examined next. It is found, as in the argument leading to (51), that, as $T \to 0$ and for finite systems,

$$\log Z_N \to -N \log y_0 - \tfrac{1}{2} \log 2\pi - \tfrac{1}{2} \log \left[\frac{(t_{N,1}-1)^2}{t^2_{N,1}} \frac{t_{N,1}}{(t_{N,1}-1)^2}\right] - \tfrac{1}{2} \sum_{j=2} \log \frac{t_{N,j}-1}{t_{N,j}} + \ldots$$
$$= -N \log y_0 - \tfrac{1}{2} \log 2\pi + \ldots.$$

None of the first-order correction terms diverges.

We add a brief remark about the reformulation of Bose statistics as an intermediate statistics (6, 11) which Schubert was investigating. The mean occupation number as evaluated by the method of steepest descent is in this case

$$n_{N,j} = \frac{1}{t_{N,j}-1} - \frac{a_j + 1}{t^{a_j+1}_{N,j} - 1} - \Delta_{N,j}(a_j), \tag{52}$$

a_j being the maximum number of particles allowed into the state E_j. For $a_1 = a_2 = \ldots = 1$ one obtains Fermi, for $a_1 = a_2 = \ldots = \infty$ Bose statistics. These statistics yield with $a_j = N, N+1, \ldots$ for all j an infinity of alternative ways of formulating Bose statistics, as the value of a_j is clearly indifferent when it exceeds the total number of particles in the gas. The expressions (52) are then *equivalent* with those which one obtains by the traditional method, the *formal difference* being fully compensated by the influence which the a_j's have on the $\Delta_{N,j}(a_j)$'s and on the position of the saddle-point. It may be shown in detail that for fixed and finite N each of the infinity of new treatments contains a very narrow region of temperature in which the first-order correction terms to the mean occupation numbers diverge, while they are finite outside this range. The critical region is shifted to lower temperatures as the a_j's are increased. If $a_j > 2N$ for all j the critical region corresponds to $n_1 > N$, a condition which cannot be realized.

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Thus, if $a_j > 2N$, and this includes the traditional way of formulating Bose statistics (when $a_j = \infty$), none of the first order correction terms can diverge in the physically relevant range. As has been pointed out before (10, 14), the introduction of the parameters a_j, is of no physical significance. The above remarks suggest that the only conditions under which they may possibly become useful is when it is desired to have a simple mathematical device for shifting the position of the saddle-point.

The present results, which assume $\theta > 0$, cannot be compared with those of Temperley (12), who investigated a finite system of equally spaced volume-independent levels (i.e. $\theta = 0$). Under these conditions (49) rather than (48) holds, so that the neglect of the correction terms in the method of steepest descent introduces errors, and (51) suggests that these errors may be most marked for the lowest energy level. These are just Temperley's findings.

9. *Conclusion.* It is convenient to classify the quantum states of a finite Bose-Einstein system as follows: (*a*) the lowest (non-degenerate) level, (*b*) the states $E_2 \leqslant E_3 \leqslant \ldots \leqslant E_{M-1}$, (*c*) the remaining states. The states of group (*b*) have *in the limit* L a negligible influence on many of the macroscopic properties of the system. By (8) and (9) they do not influence the value of the chemical potential, its variation with temperature, the question whether a condensation temperature exists, or its value when it does exist. By the arguments following (19) and (22) they do not influence the fraction of particles in the lowest level, or the average energy per particle. In fact, the fraction of particles in the levels of group (*b*) is in the limit L *always* vanishingly small. This circumstance is responsible for the fact that the continuous spectrum approximation, used by London (7) for the levels of group (*b*) and (*c*) *without making a transition to the limit* L, has been so successful in giving results, which were subsequently confirmed by more accurate methods *involving a limiting procedure* (2, 5); for his treatment is readily seen to be mathematically equivalent to applying the continuous spectrum approximation (when the volume is large) to the states of group (*c*) with M large, while ignoring the states of group (*b*), and then proceeding to the limit L.

The relationship with the continuous-spectrum approximation can be clarified by a simple example which shows, in addition, that the density of states for very high quantum numbers determines the incidence of condensation. Suppose the energy levels of a physical system can be described by the density-of-states curve

$$N(E) = \begin{cases} aE^p & (0 \leqslant E < E_M), \\ bE^q & (E_M \leqslant E). \end{cases}$$

Using the grand canonical ensemble, the density of the gas is

$$\rho = V^{-1}\left\{a(kT)^{p+1}\int_0^{E_M/kT} \frac{x^p dx}{e^{x-\alpha}-1} + b(kT)^{q+1}\int_{E_M/kT}^{\infty} \frac{x^q dx}{e^{x-\alpha}-1}\right\}.$$

In the limit L, $E_M \to 0$ and the first term disappears, so that the condensation temperature, if it exists, is determined by an equation of the form (15), $1/\tau - 1$ being replaced by q. Thus q, not p, determines the incidence of condensation, the value of E_M, however large, being irrelevant, as long as it is finite. This agrees with a basic result of the preceding sections.

A conclusion of this type is in contradiction with physical intuition, which suggests that states of infinitely high quantum numbers are unlikely to play a dominant part

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in physical phenomena (such as the λ-point of liquid helium). As the above example shows, the origin of this paradox resides in the limiting process L (in conjunction with assumption (11)). While it is precisely due to this mathematical device that the differences between treatments based on the canonical and those based on the grand canonical ensemble disappear, and a consistent picture emerges, it does at the same time endow the levels of group (c) with a mathematical importance which is unlikely to represent any physical phenomena exhibited by actual (finite) systems, where the particle interactions make the present considerations inapplicable.

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