On The Einstein Condensation

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ABSTRACT

Exact series expressions for the thermodynamic quantities of an ideal Bose gas are found in terms of the theta function of Jacobi. The Einstein condensation thus can be treated by rigorous mathematical argument. The nature of the "integral approximation" and its modification, employed in the usual treatment of the problem, is clearly revealed. For finite volume, the exact expansions of pressure and density in powers of the activity converge in an entirely different way than do the integral approximation expansions. The modified integral approximation, however, becomes exact in the limit $V \to \infty$, $N \to \infty$, $V/N \to$ const.

On The Einstein Condensation*

The phenomenon of the Einstein condensation of an ideal boson system is well known. In the usual procedure of evaluating the thermodynamic quantities, one uses the "integral approximation", in which the summations over energy eigenvalues of an individual boson, appearing in the series expressing the thermodynamic quantities, are replaced by integrals. This approximation, which gives the correct results in the region of the homogeneous phase in the case of an infinite system, requires an artificial modification to account for the condensation region. The modification is made by treating the terms corresponding to the ground state of the individual boson separately from the others.(1)

In the present report we show that an exact mathematical treatment of the Einstein condensation is feasible, and therefore the nature of the usual "integral approximation" and its modification is revealed.

The fundamental expressions in the Bose-Einstein statistics for N, p and E, denoting respectively the total number of bosons, the pressure and the total energy of the system, are:

$$N = \sum_i \frac{g_i}{z^{-1} e^{\beta E_i} - 1} , \tag{1}$$

$$p = \sum_i \frac{1}{z^{-1} e^{\beta E_i} - 1} \left(-\frac{\partial E_i}{\partial V} \right) , \tag{2}$$

$$E = \sum_i \frac{E_i g_i}{z^{-1} e^{\beta E_i} - 1} , \tag{3}$$

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where

$\beta = 1/kT$

k = Boltzmann constant

T = absolute temperature

z = activity = $\exp(\beta\mu)$

μ = chemical potential

E_i = the energy of the i-th individual boson state, which is a function of the volume V

g_i = the degeneracy of the i-th individual boson state.

The summation is taken over all boson states.

The expressions (1), (2) and (3), as is well known, can be derived either from the canonical or grand canonical ensemble method. In the grand canonical ensemble the independent variables are V, β and z, but in the canonical ensemble the independent variables are V, β and N, therefore z changes with V. This familiar fact is important in the later discussion of the limiting process $V \to \infty$.

Let us now choose the volume of the system to be a cubic box with side length $L = V^{1/3}$, and impose periodic boundary conditions upon the wave functions of the individual boson. The energy E_i then takes the following form:

$$E_i = E_0 (n_x^2 + n_y^2 + n_z^2) , \qquad (4)$$

where

$$E_0 = h^2 / (2mV^{2/3}) , \qquad (5)$$

(m = mass of each boson, h = Planck's constant), and n_x, n_y and n_z are

integers, including zero. To each E_i there is generally more than one set of integers, (n_x , n_y , n_z), satisfying (4), the number of which is evidently g_i (We assume here that the spin of each boson is zero. If each boson has a spin S, then the degeneracy of each state will be $2S + 1$ times more).

From (4) and (5) we get immediately

$$-\frac{\partial E_i}{\partial V} = \frac{2}{3} E_i V^{-1} .$$

Hence (2) and (3) have the following relation

$$E = \frac{3}{2} PV , \tag{6}$$

which holds also for the ideal Boltzmann or Fermi gas.

Since the lowest energy, E_1, in (4) is zero, an inspection of (1), (2) and (3) shows that z must be always smaller than unity, i.e. the range of z is $0 \quad z \quad 1$. Hence we can expand each term of the series in (1) and (2) (consequently (3) by (6)) in power series in z and interchange the order of the summation in the resulted repeated series, which can be shown to be allowable.(2) Thus we have

$$N = \sum_{l=1}^{\infty} z^l \left(\sum_i g_i e^{-l\beta E_i} \right) \tag{7}$$

$$P = \frac{2}{3} V^{-1} \sum_{l=1}^{\infty} z^l \left(\sum_i g_i E_i e^{-l\beta E_i} \right) \tag{8}$$

In the "integral approximation" the two series in the parentheses of (7) and (8) are approximated by the following replacement:

$$\sum c_l (\quad) \to \int_0^\infty g(E)\,dE\,(\quad),$$

where

$$g(E) = 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} E^{1/2}$$

This approximation, in a crude sense, amounts to taking the limit of infinite volume in each term of the series in z in (7) and (8), while the correct limiting procedure should sum the series before letting $V \to \infty$. This raises a mathematical question about the interchange of the order of these operations and a physical question about the correct volume dependence of thermodynamic properties of the ideal boson system.

We now show that the two series

$$I = \sum_i g_i e^{-l\beta E_i}, \tag{9}$$

$$J = -\frac{\partial I}{\partial l\beta} = \sum_i g_i E_i e^{-l\beta E_i}, \tag{10}$$

can be exactly expressed in terms of the theta function, $\theta(x)$, which is defined by

$$\theta(x) = \sum_{n=-\infty}^{\infty} e^{-\pi n^2 x}, \tag{11}$$

and its derivative. In fact, by (4) and (5), we have

$$I = \sum_{n_x=-\infty}^{\infty} \sum_{n_y=-\infty} \sum_{n_z=-\infty} e^{-\beta E_0 (n_x^2 + n_y + n_z^2)}$$

$$= \left(\sum_{n=-\infty}^{\infty} e^{-\beta E_0 n^2} \right)^3 = \theta^3\left(\frac{\beta E_0}{\pi}\right) = \theta^3\left(\frac{\beta \lambda^2}{V^{2/3}}\right), \tag{12}$$

where

$$\lambda = h\sqrt{\beta/2\pi m}. \tag{13}$$

The theta function has the following properties: $\theta(\chi)$ is a monotonically decreasing function in $0 < \chi < \infty$; $\theta(\chi) \to 0$, as $\chi \to 0$; $\theta(\chi) \to 1$, as $\chi \to \infty$. See Fig. 1. Besides it satisfies the following important functional relation:(3)

$$\theta(x) = \frac{1}{\sqrt{x}}\,\theta\left(\frac{1}{x}\right). \tag{14}$$

Hence (12) becomes

$$I = V \lambda^{-3} \beta^{-3/2}\, \theta^3\left(\frac{V^{2/3}}{\beta\lambda^2}\right). \tag{15}$$

By (15), (10) then becomes

$$J = \frac{3}{2} V \lambda^{-3} \beta^{-1} \beta^{-5/2}\, \Psi\left(\frac{V^{2/3}}{\beta\lambda^2}\right), \tag{16}$$

where

$$\Psi(x) \equiv \theta^3(x) + 2x\,\theta'(x)\,\theta^2(x). \tag{17}$$

The function $\psi(x)$ has the following properties: $0 < \psi(x) < 1$ for $0 < x < 1$; $\psi(x) \to 1$, as $x \to \infty$; $\psi(x) \approx 4\pi x^{-5/2} e^{-\pi/x} \to 0$, as $x \to 0$. See Fig. 1.

Substituting (15) and (16) into (7) and (8) respectively, we obtain the exact expressions for N and p for any finite V:

$$\frac{1}{v} = \frac{N}{V} = \lambda^{-3} \sum_{l=1}^{\infty} l^{-3/2} \theta^3\left(\frac{V^{2/3}}{l\lambda^2}\right) z^l, \tag{18}$$

$$p = \lambda^{-3}\beta^{-1} \sum_{l=1}^{\infty} l^{-5/2} \psi\left(\frac{V^{2/3}}{l\lambda^2}\right) z^l, \tag{19}$$

where v is the specific volume (number of particles per unit volume)$^{-1}$

The series (18) and (19) are convergent for $z < 1$ for any finite V, and as $z \to 1$, $1/v \to 0$ but p remains finite. The p-v curve has no singular point as long as V is finite. See Fig. 2, curve (a).

From (18) and (19) we notice that in the usual integral approximation one replaces the functions $\theta^3\left(\frac{V^{2/3}}{l\lambda^2}\right)$ and $\psi\left(\frac{V^{2/3}}{l\lambda^2}\right)$ by unity for all $l = 1, 2, 3 \ldots\ldots$ The replacement of $\theta^3\left(\frac{V^{2/3}}{l\lambda^2}\right)$ by 1 is a good approximation only for those $l \ll V^{2/3}/\lambda^2$ since $\theta(x) \approx 1$ for $x \gg 1$. For $l \gg V^{2/3}/\lambda^2$ we have from (14) that $\theta^3\left(\frac{V^{2/3}}{l\lambda^2}\right) \approx l^{3/2}\lambda^3 V^{-1} \gg 1$, hence it is not justified. In fact for $l \gg V^{2/3}/\lambda^2$, the series (18) behaves like the series

$$\frac{1}{V} \sum_{l \gg V^{2/3}\lambda^{-2}} z^l$$

which diverges as $z \to 1$, in contrast to the finiteness of the corresponding series in the "integral approximation". Thus in considering the system in a finite volume, the integral approximation is good only for sufficiently small values of z. Likewise the replacement of $\psi\left(\frac{V^{1/3}}{\ell\lambda^2}\right)$ by 1 is good also for $\ell \ll V^{2/3}\lambda^{-2}$, but not for $\ell \gg V^{2/3}\lambda^{-2}$, since there $\psi\left(\frac{V^{2/3}}{\ell\lambda^2}\right) \approx 0$. However, in this case the exact series (19) converges more rapidly than the corresponding approximate one, and the numerical error is always small. We notice that as V becomes larger, the larger is the range of z in which the integral approximation is applicable.

To show the condensation phenomenon of the ideal boson system, we have to consider the properties of the system in the limit $V \to \infty$. The expressions for 1/v and p to be investigated, from (18) and (19), now are:

$$\frac{1}{v} = \lambda^{-3} \lim_{V\to\infty} \sum_{\ell=1}^{\infty} \ell^{-3/2} \theta^3\left(\frac{V^{2/3}}{\ell\lambda^2}\right) z^\ell , \tag{20}$$

$$p = \lambda^{-3}\beta^{-1} \lim_{V\to\infty} \sum_{\ell=1}^{\infty} \ell^{-5/2} \psi\left(\frac{V^{2/3}}{\ell\lambda^2}\right) z^\ell . \tag{21}$$

A sufficient condition that the "lim" in (20)and (21) can be placed inside the summation sign is that the series in (20 and (21) be uniformly convergent with respect to V near $V = \infty$. To test this condition two cases have to be considered, according to whether (20) and (21) are originally regarded as derived from the canonical or grand canonical ensemble method. In the latter case z is an independent variable,

therefore the only V dependent factors in each term of the series in (20) and (21) are $\theta^3\left(\frac{V^{2/3}}{2\lambda^2}\right)$ and $\psi\left(\frac{V^{2/3}}{2\lambda^2}\right)$ respectively. In the former case z is a dependent variable, therefore varies with V also.

Let us first consider the case where z is an independent variable, along with β and V. Then it can be easily shown by the Weierstrass' M-test[4] that both the series in (20) and (21) are uniformly convergent with respect to V near $V = \infty$ for all z in $0 \leq z < 1$. Since $\lim \theta(x) = \lim \psi(x) = 1$ as $x \to \infty$, we thus from (20) and (21) obtain the limiting expressions for 1/v and p:

$$\frac{1}{v} = \lambda^{-3} \sum_{l=1}^{\infty} l^{-3/2} z^l , \tag{22}$$

$$p = \lambda^{-3} \beta^{-1} \sum_{l=1}^{\infty} l^{-5/2} z^l . \tag{23}$$

These expressions are exactly the same as those obtained by "integral approximation". This means that the "integral approximation" is justified for calculating the thermodynamic quantities of the ideal boson system in the limiting case of infinite volume. The p-v curve by (22) and (23) is shown in Fig. 2, curve (b). Notice that the curve is regular, extending from $v = \infty$ to the point

$$v = v_c \equiv \lambda^{-3} \sum_{l=1}^{\infty} l^{-3/2} = 2.612\, \lambda^{-3} ,$$

$$p = p_c \equiv \lambda^{-3} \beta^{-1} \sum_{l=1}^{\infty} l^{-5/2} = 1.341\, \lambda^{-3} \beta^{-1} .$$

There is no extension of the curve to the condensation region $v < v_c$, which can be expressed analytically in (22) and (23). This is a general characteristic of the grand canonical ensemble method, which exhibits only thermodynamic relations of the homogeneous phases in the limit $V \to \infty$. That the missing part $v < v_c$ is the condensation region can be seen only through the graphical observation that as V becomes larger the curve (a) in Fig. 2 is nearer to the horizontal dotted line, i.e. p tends to p_c throughout the region $v < v_c$. But just as the limit is reached, the horizontal part of the isotherm disappears, for (22) converges to a finite value for $0 \leq z \leq 1$.

Next we consider z as depending on V besides v and β. We then regard (20) and (21) as being derived from the canonical ensemble method. To emphasize this we write z as z(V). Because of its absolute convergence, we can rewrite the series in (20) in the following form:

$$\frac{\lambda^3}{V} \cdot \frac{z(V)}{1 - z(V)} + \sum_{l=1}^{\infty} l^{-3/2} \phi\left(\frac{V^{2/3}}{l\lambda^2}\right) z^l, \tag{24}$$

where

$$\phi(x) \equiv \theta^3(x) - x^{-3/2}.$$

The function $\phi(x)$ has similar properties to $\psi(x)$; i.e. $0 < \phi(x) < 1$ for $0 < x < 1$; $\phi(x) \to 1$, as $x \to \infty$; $\phi(x) \approx 6 x^{-5/2} e^{-\pi/x} \to 0$, as $x \to 0$.

By these properties of $\phi(x)$ and those of $\psi(x)$, it is easy to show, again by the Weierstrass M-test, that the series in (24) and (21) are

uniformly convergent with respect to V near $V = \infty$. Thus we have

$$\frac{1}{v} = \lim_{V\to\infty} \frac{1}{V} \cdot \frac{z(V)}{1 - z(V)} + \lambda^{-3} \sum_{l=1}^{\infty} l^{-3/2} \lim_{V\to\infty} \phi\left(\frac{V^{2/3}}{l\lambda^2}\right) z^l(V), \tag{25}$$

$$p = \lambda^{-3}\beta^{-1} \sum_{l=1}^{\infty} l^{-5/2} \lim_{V\to\infty} \psi\left(\frac{V^{2/3}}{l\lambda^2}\right) z^l(V). \tag{26}$$

Two regions of v have to be considered separately:

a) For $v > v_c$. In this case we must have

$$z_\infty \equiv \lim_{V\to\infty} z(V) < 1.$$

For otherwise the series in (25) would become $1/v_c$ as $V \to \infty$. Consequently from (25) we get $1/v > 1/v_c$, which is contradictory to our choice of the region of v. Thus from (25) and (26) we obtain

$$\frac{1}{v} = \lambda^{-3} \sum_{l=1}^{\infty} l^{-3/2} z_\infty^l, \tag{27}$$

$$p = \lambda^{-3}\beta^{-1} \sum_{l=1}^{\infty} l^{-5/2} z_\infty^l, \tag{28}$$

which are identical to (22) and (23). Thus we have reproduced the p-v curve shown in Fig. 2, curve (b).

b) For $v < v_c$. $z(V)$ then must tend to 1 as $V \to \infty$ in such a way, from (25), that

$$\lim_{V\to\infty} \frac{1}{V} \cdot \frac{z(V)}{1 - z(V)} = \frac{1}{v} - \frac{1}{v_c}.$$

Hence (26) becomes

$$p = \lambda^{-3}\beta^{-1}\sum_{l=1}^{\infty} l^{-5/2} = p_c ,$$

which is independent of v. Thus the region $v < v_c$ has a constant pressure, characterizing the condensation phenomenon.

The p-v curve of the cases (a) and (b) discussed above is shown in Fig. 3. The curve consists of two regular curves which meet at the singular point $v = v_c$, $p = p_c$. The canonical ensemble method is thus contrasted with the grand canonical ensemble one by being capable of describing the condensation analytically.

We note that in the usual method in order to account for the condensation region one modifies the "integral approximation" by rewriting the expression for λ^3/v in the form of (24) and approximating $\phi\left(\frac{V^{2/3}}{\chi\lambda^2}\right)$ by 1. This "modified integral approximation" which gives the results we obtained in the canonical ensemble method by some mathematically less rigorous arguments may, according to our above discussions, be regarded not as a modification to the "integral approximation", but as an entirely different approach to the problem by using a different (i.e. canonical) ensemble method.

References

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FIGURE CAPTIONS

Fig. 1: The functional behaviors of $\theta(x)$, $\psi(x)$ and $\phi(x)$.

Fig. 2: Curve (a) is the isotherm at finite volume. Curve (b) is the isotherm at infinite volume obtained from the grand canonical ensemble method. The dotted line is missing in the process $V \to \infty$.

Fig. 3: The isotherm at infinite volume obtained from the canonical ensemble method. The horizontal line shows the region of condensation.

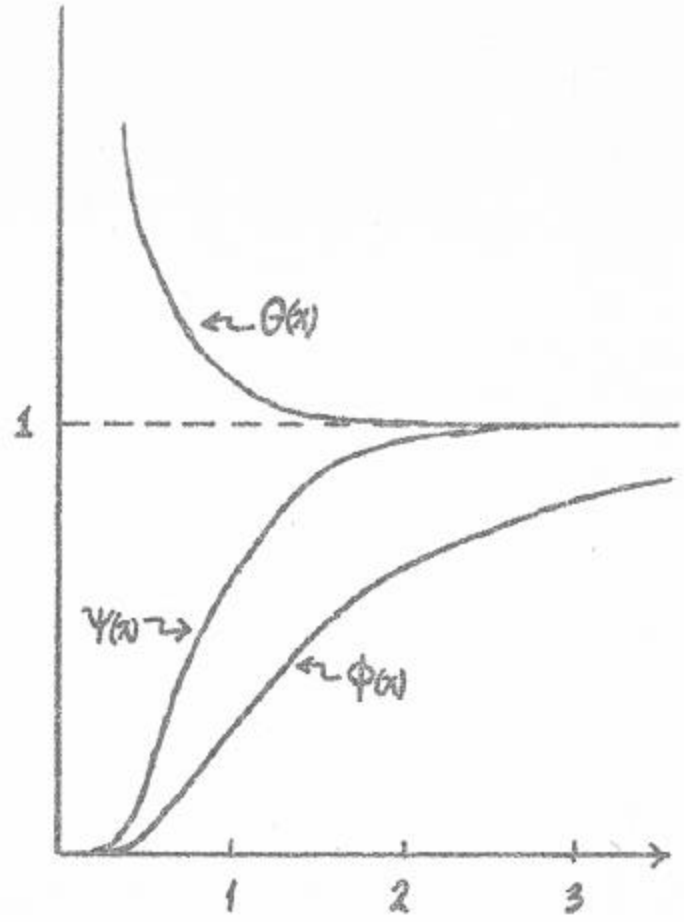

Fig. 1

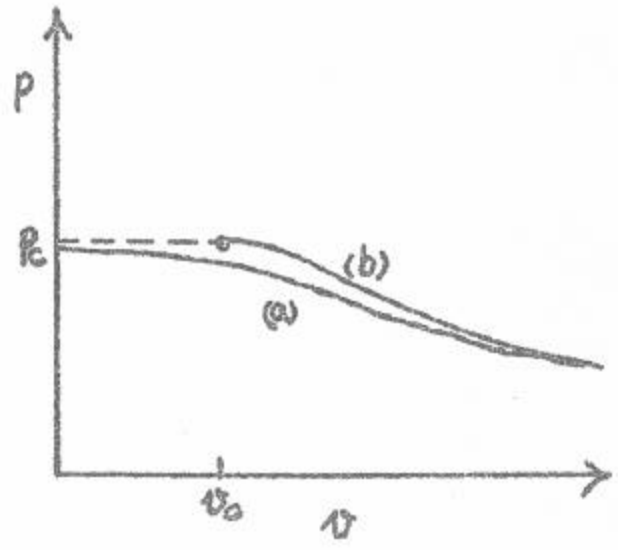

Fig 2

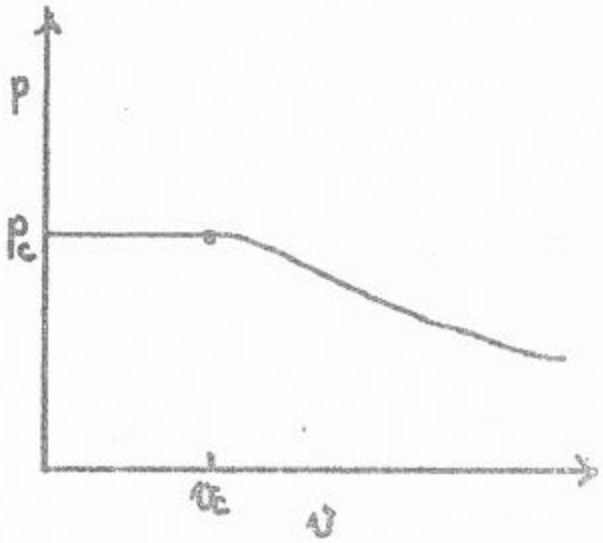

Fig. 3