

Bose-Einstein condensation

e-content for B.Sc Physics (Honours)

B.Sc Part-III

Paper-VI

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Bose-Einstein condensation

For an ideal Bose gas of N molecules in a volume V the most probable no. of particle with energy ϵ_i is given by

$$\bar{n}_i(\epsilon_i) = \frac{g_i}{e^{\alpha + \beta \epsilon_i} - 1}$$

where $\beta = \frac{1}{kT}$ & $\alpha = -\frac{\mu}{kT}$, μ = chemical pot. of the system, g_i is the degeneracy in the i^{th} state level. The value of μ can be determined as the fn. of N & T by the relation

$$N = \sum_{i=1}^{\infty} \bar{n}_i = \sum_{i=1}^{\infty} \frac{g_i}{e^{(\epsilon_i - \mu)/kT} - 1} \quad \text{--- (1)}$$

We must have $\bar{n}_i \geq 0$ because the no. of particle can not be negative. Therefore for boson gas at all temp. μ greater than zero. For all ϵ_i $e^{(\epsilon_i - \mu)/kT} \geq 1$. At the ground state if we choose $\epsilon_i = 0$. Then $e^{-\mu/kT} \geq 1$. This suggests that μ is negative or equal to zero ($\mu \leq 0$). For photon $\mu = 0$.

If we replace the summation by integration we have to replace g_i by the density of states. Therefore,

$$g(\epsilon) d\epsilon = \frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2} d\epsilon \quad \text{--- (2)}$$

Therefore eqn. (1) becomes

$$N = \int_0^{\infty} \frac{2\pi V}{h^3} (2m)^{3/2} \frac{\epsilon^{1/2}}{\frac{1}{\eta_a} e^{\beta \epsilon} - 1} d\epsilon$$

where $\eta_a = e^{\beta \mu} \leq 1$ known as absolute activity.

We put $\epsilon/kT = x$

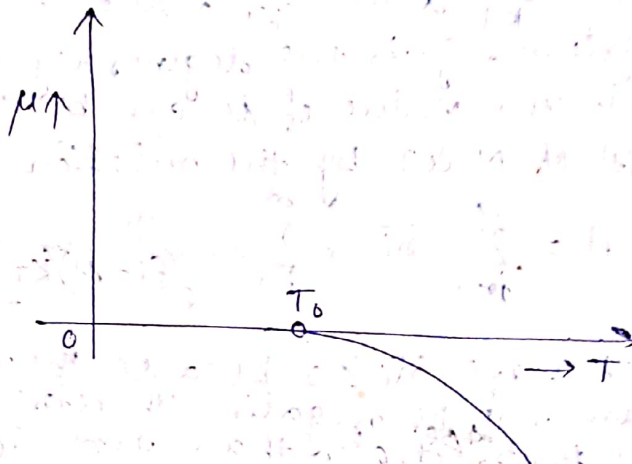
$$\therefore d\epsilon = kT dx$$

$$\begin{aligned} N &= \frac{2\pi V}{h^3} (2m)^{3/2} (kT)^{3/2} \int_0^{\infty} \frac{x^{1/2} dx}{\frac{1}{\eta_a} e^x - 1} \\ &= \frac{V}{\lambda^3} F_{3/2}(\eta_a) \quad \text{--- (3)} \end{aligned}$$

where $\lambda = \frac{h}{(2\pi mKT)^{1/2}}$

$$F_{3/2}(\eta_a) = \frac{2}{\sqrt{\pi}} \int_0^{\infty} \frac{x^{1/2} dx}{\frac{1}{\eta_a} e^x - 1}$$

Eqⁿ ③ has no solution for $T < T_0$. μ can not be positive nor it become 've' again. The only possibility is for μ to make equal to zero.



The variation of μ vs T is shown in the fig. The difficulty occurs here due to the improper change of the sum into integral. At very low temp. this causes a serious error as large contribution is coming from the 1st few terms in eqⁿ ①. For a boson gas there is no restriction on the no. of particle that can belong to a single state. Hence the large contribution comes from the 1st few terms in eqⁿ ①. In fact for $T \rightarrow 0$ the 1st term \bar{n}_0 approaches to the total no. of particle N . Because

$$\lim_{T \rightarrow 0} \bar{n}_0 = N = \frac{1}{e^{(\epsilon_0 - \mu)/KT} - 1}$$

$$\approx \frac{KT}{\epsilon_0 - \mu} \quad [\bar{n}_0 = \text{large}]$$

Thus for very low temp. μ is very close to ϵ_0 . So the population in the ground state is very large. This phenomenon is known as Bose-Einstein condensation. The reason behind the BE condensation is the behavior of chemical

potential μ of the boson gas at low temp. It must be noted that the condensation refers to the condensation in momentum space and not in actual condensation in the gas.

For $T \rightarrow 0$ the sum $(N - \bar{n}_0)$ can be approximated by the integral without any serious error.

$$\begin{aligned} \therefore N - \bar{n}_0 &= \sum_i \bar{n}_i \\ &\approx \frac{2\pi V}{h^3} (2m)^{3/2} \int_0^\infty \frac{e^{-\beta \epsilon} \epsilon^{1/2} d\epsilon}{\frac{1}{n_a} e^{\beta \epsilon} - 1} \\ &= \frac{V}{\lambda^3} F_{3/2}(n_a) \quad \text{--- (5)} \end{aligned}$$

Replacing V , we get,

$$\begin{aligned} N - \bar{n}_0 &= N \left(\frac{T}{T_0} \right)^{3/2} \frac{F_{3/2}(n_a)}{2.612} \\ \therefore \bar{n}_0 &= N \left[1 - \left(\frac{T}{T_0} \right)^{3/2} \frac{F_{3/2}(n_a)}{2.612} \right] \end{aligned}$$

For low temp. μ is very close to zero and we can put $n_a = 1$.

$$\therefore \bar{n}_0 = N \left[1 - \left(\frac{T}{T_0} \right)^{3/2} \right] \quad \boxed{\bar{n}_0 = N_0}$$

So the no. of particle in the excited state

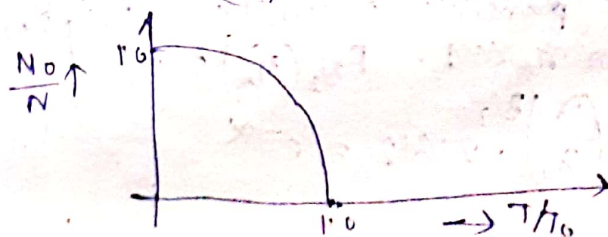
$$N' = N - \bar{n}_0 = N \left(\frac{T}{T_0} \right)^{3/2}$$

At $T = T_0$, $\bar{n}_0 = 0$ at $T = 0$, $\bar{n}_0 = N$.

So as the temp. decreases below T_0 , more and more particle begin to occupy ground state. The BE gas then degenerates and we are in the quantum region characterised by $\mu \rightarrow 0$.

At temp $T = T_0$ is called degeneracy temp.

The plot (N_0/N) vs (T/T_0) is shown in the fig.



An alternative definition T_0 we can define at critical volume V_0 such that at temp T

$$N = \frac{V_0}{\lambda^3} F_{3/2}(\eta_a = 1)$$

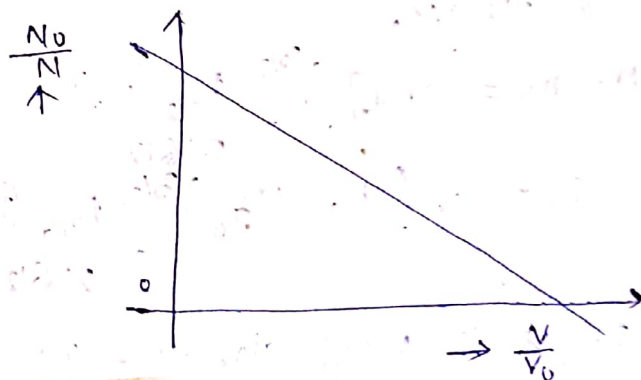
$$= V_0 \left(\frac{2\pi mKT}{h^2} \right)^{3/2} \times 2.612$$

$$\therefore N = N_0 + N \frac{V}{V_0} \cdot \frac{F_{3/2}(\eta_a)}{2.612}$$

$$\approx N_0 + N \frac{V}{V_0}$$

$$\therefore N_0 = N \left(1 - \frac{V}{V_0} \right) \quad (V < V_0)$$

A plot of $\frac{N_0}{N}$ vs $\frac{V}{V_0}$ is shown in fig.



For $T > T_0$ we have $\eta_a < 1$ and the contribution of 1st term in eqn (1) [N_0 becomes negligible] and the 2nd term increases as $T^{3/2}$ when the box gas is heated above T_0 . Therefore

$$N = \frac{V}{\lambda^3} F_{3/2}(\eta_a)$$

$$\text{Now } F_{3/2}(\eta_a) = \left(\frac{T_0}{T} \right)^{3/2} F_{3/2}(\eta_a = 1)$$

$$\therefore N = \frac{V}{\lambda^3} \left(\frac{T_0}{T} \right)^{3/2} \times 2.612$$

For $T \gg T_0$ the ground state is practically empty and most of the particles occupy the higher excited state. For $\eta_a \ll 1$, $F_{3/2}(\eta_a) \approx \eta_a$

$$\therefore \eta_a = \left(\frac{\lambda}{\lambda_0} \right)^{3/2} \cdot 2.612 = e^{-\alpha}$$

$$\therefore f \lambda^3 = e^{-\alpha} \text{ (classical limit).}$$

$$\text{where } f = \frac{N}{V}$$

Therefore the BE gas behaves as MB gas.

Indistinguishable

Energy of the boson gas:

The internal energy of the boson gas is given by

$$U = \sum_i \epsilon_i \tilde{n}_i = \int_0^\infty \epsilon d n$$

$$= \int_0^\infty \frac{\epsilon g(\epsilon) d\epsilon}{e^{(\epsilon-\mu)/kT} - 1}$$

$$= \frac{2\pi V}{h^3} (2m)^{3/2} \int_0^\infty \frac{\epsilon^{3/2} d\epsilon}{e^{(\epsilon-\mu)/kT} - 1}$$

$$= \frac{V kT}{\lambda^3} \cdot \frac{2}{\sqrt{\pi}} \int_0^\infty x^{3/2} \left(\frac{1}{\eta_a} e^x - 1 \right)^{-1} dx$$

$$\text{where } \epsilon/kT = x.$$

$$\text{and, } \eta_a = e^{\beta\mu} \leq 1.$$

$$= \frac{3}{2} kT \cdot \frac{V}{\lambda^3} f_{5/2}(\eta_a)$$

$$\text{where, } f_{5/2}(\eta_a) = \frac{1}{\frac{3}{4} \sqrt{\pi}} \int_0^\infty x^{3/2} \left(\frac{1}{\eta_a} e^x - 1 \right)^{-1} dx$$

$$= \frac{1}{\frac{3}{4} \sqrt{\pi}} \int_0^\infty \eta_a e^{-x} x^{3/2} (1 - \eta_a e^{-x})^{-1} dx$$

$$= \frac{1}{\frac{3}{4} \sqrt{\pi}} \int_0^\infty \eta_a e^{-x} x^{3/2} (1 + \eta_a e^{-x} + \eta_a^2 e^{-2x} + \dots) dx$$

$$= \eta_a + \frac{\eta_a^2}{2^{5/2}} + \frac{\eta_a^3}{3^{5/2}} + \dots$$

$$= \sum_{n=1}^{\infty} \frac{\eta_n^n}{n^{5/2}}$$

We shall consider two cases,
 i) for $T < T_0$ (degenerate gas)
 ii) for $T > T_0$ (nondegenerate gas).

for $T < T_0$, $\eta_n = 1$. and,
 $f_{5/2}(\eta_n = 1) = \zeta(5/2)$

Therefore,

$$U_- = \frac{3}{2} K T \frac{V}{\lambda^3} \zeta(5/2)$$

We have, $N = \frac{V}{\lambda^3} \zeta(3/2)$

$$\begin{aligned} \therefore U_- &= \frac{3}{2} N K T \frac{(T/T_0)^{3/2} \zeta(5/2)}{\zeta(3/2)} \\ &= \frac{3}{2} N K T (T/T_0)^{3/2} \frac{1.341}{2.612} \\ &= \frac{3}{2} N K T (T/T_0)^{3/2} \times 0.51. \end{aligned}$$

From the above expression it is clear that the energy of the Bose gas is less than that of the ideal MB gas.

For $T > T_0$,

$$U_+ = \frac{3}{2} K T \frac{V}{\lambda^3} f_{5/2}(\eta_n)$$

We have $N = \frac{V}{\lambda^3} f_{3/2}(\eta_n)$

$$\begin{aligned} \therefore U_+ &= \frac{3}{2} N K T \frac{f_{5/2}(\eta_n)}{f_{3/2}(\eta_n)} \\ &= \frac{3}{2} N K T \left[1 - 2^{-5/2} \frac{f_{5/2}(\eta_n)}{f_{3/2}(\eta_n)} - 2 \left(3^{-5/2} - 2^{-5/2} \right) \frac{f_{5/2}(\eta_n)}{\{f_{3/2}(\eta_n)\}^2} - \dots \right] \end{aligned}$$

$$\therefore U_+ = \frac{3}{2} NKT \left[1 - 0.462 \left(\frac{T_0}{T} \right)^{3/2} - 0.023 \left(\frac{T_0}{T} \right)^5 \right].$$

This shows that the energy of Bose gas is less than the Fermi gas.

Specific heat of Bose-gas \Rightarrow

we have,

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

we have two cases -

i) $T < T_0$

ii) $T > T_0$.

For $T < T_0$

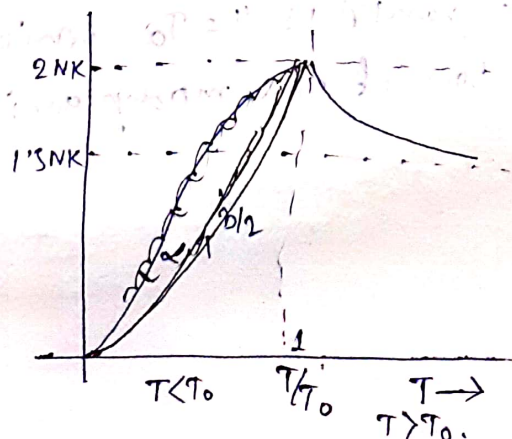
$$C_V = \frac{15}{4} NK \left(T/T_0 \right)^{3/2} \times 0.51.$$

$$= 1.926 NK \left(T/T_0 \right)^{3/2}$$

For $T > T_0$

$$C_{V+} = \frac{3}{2} NK \left[1 + 0.2281 \left(\frac{T_0}{T} \right)^{3/2} + \dots \right].$$

If we plot C_V Vs T



The sp. heat curve shows a kink which indicates that the Bose condensation is the 1st order phase transition.

Entropy of Bose gas \Rightarrow

We have entropy

$$S = \int \frac{C_v dT}{T}$$

We have two cases-

i) $T < T_0$

ii) $T > T_0$

For $T < T_0$,

$$S_-(T) = \int_0^T \frac{C_v dT}{T}$$

$$= \frac{2}{3} \times 1.926 NK \left(\frac{T}{T_0} \right)^{3/2}$$

For $T > T_0$

$$S_+(T) = S(T_0) + \int_{T_0}^T \frac{C_{v+} dT}{T}$$

$$= S(T_0) + \frac{2}{3} NK \left[\ln \left(\frac{T}{T_0} \right) + \frac{2}{3} \times 0.231 \right]$$

$$\left(1 - \frac{T_0}{T} \right)^{3/2} + \dots$$

The entropy shows a certain drop for $T < T_0$ and it vanishes at $T = T_0$ which is consistent with 3rd law of thermodynamics.

Pressure of ideal Bose gas.

We have,

$$P = \frac{2}{3} \frac{U}{V}$$

We have two cases: i) $T < T_0$
ii) $T > T_0$.

for $T < T_0$

$$P_- = \frac{2}{3} \frac{U_-}{V} = NK \left(\frac{T}{T_0} \right)$$

We have used $V/V_0 = (T/T_0)^{3/2}$

for $T > T_0$

$$P_+ = \frac{2}{3} \frac{U_+}{V} = \frac{NKT}{V} \left[1 - 0.462 \frac{V_0}{V} - \dots \right]$$

For condensation in a gas as we decrease the temp. the pressure also decreases.

Example Consider a gas composed of fixed no. of boson (N) in a container of volume V . Show that the α of such a system always $\rightarrow -ve$ & it is strictly increasing fn of T .

We have; $N = \int_0^\infty dn$

$$= \int_0^\infty \frac{g(E) dE}{e^{\alpha} + e^{E/KT}}$$

$$= \frac{2\pi V (2m)^{3/2}}{h^3} \int_0^\infty \frac{E^{1/2} dE}{e^{\alpha} e^{E/KT}}$$

If α is $\rightarrow -ve$ then at the ground the the occupation no. is $\rightarrow -ve$ which can not happen α must non negative.

put, $\alpha = E/KT$

$$E = KTR$$

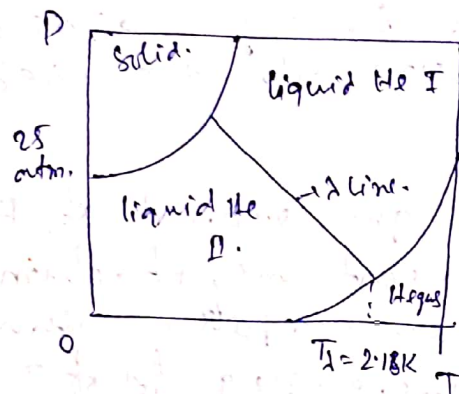
$$dE = KT dR$$

$$= \frac{2\pi V}{h^3} (2\pi m kT)^{3/2} \left[\int_0^\infty \frac{x^{1/2} dx}{e^{x-\alpha} - 1} \right]$$

As T increase the 1st term increases. So the value of the integral has to decrease, because the no. of particles is fixed. Therefore, α must increase as we increase the temp.

Liquid helium (λ transition) \Rightarrow

An ${}^4\text{He}$ atom contains two protons and two neutrons so it obeys BE condensation. Thus liquid ${}^4\text{He}$ undergoes BE condensation. The phase diagram of ${}^4\text{He}$ is shown in fig.



As liq. ${}^4\text{He}$ is cooled in vapour, it begins to show dramatic change in its property at $T = 2.18\text{ K}$. For $T > T_\lambda$ it is a normal liq. called Helium-I. For $T < T_\lambda$, the liq. ${}^4\text{He}$ begins to show some remarkable property such as zero viscosity and zero entropy. It is called superfluid. The transition between ${}^4\text{He I} - {}^4\text{He II}$ is called λ transition. The λ -transition is the form of Bose condensation.