PHYS 3014: Statistical Mechanics

Lecture Notes
Part 15

Bose Gas : Bose - Einstein Condensation

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Bose Gas

We know that in the classical limit, an ideal Bose gas becomes an ideal Boltzmann gas i.e classical ideal gas. The condition is

$$n\lambda^3 << 1$$

or, $$\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2} << 1$$, λ is mean thermal wavelength of the particles.

It is fulfilled as high temperature and low densities. But when temperature decreases or for high densities, behaviour of system shows departure from classical behaviour and when $n\lambda^3$ becomes of the order of unity, the behaviour of system changes significantly different from classical one and quantum effects dominate leading to interesting phenomenon which is not observed in classical system.

For a ideal Bose gas, N is no. of particles in Volume V, at temperature T and pressure P, the no. of particles with energy ϵ is

$$\bar{n}_\epsilon = \frac{1}{e^{\frac{\epsilon-\mu}{kT}} - 1}$$

Total no. of particles

$$N = \sum_\epsilon \bar{n}_\epsilon = \sum_\epsilon \frac{1}{e^{\frac{\epsilon+\mu}{kT}} - 1} = N_0 + N_1 + N_2 + \cdots$$

Summation is over all energy levels.

We define $z = e^{\beta\mu}$ as fugacity or absolute activity of the system. It defines the behaviour or activity of the system. In terms of fugacity,

$$N = \sum_\epsilon \bar{n}_\epsilon = \sum_\epsilon \frac{1}{z^{-1} e^{\beta\epsilon} - 1} \quad \cdots\cdots (1)$$

For Bose gas, $n_\epsilon \geq 0$ i.e the no. of particles in an energy level can not be negative. Therefore for all temperatures, $\epsilon - \mu$ must be greater than zero for all energy values i.e

$$e^{\frac{\epsilon-\mu}{kT}} \geq 1$$

$$\Rightarrow e^{-\frac{\mu}{kT}} \geq 1 \qquad , \epsilon \text{ can not be negative}$$

It means that $\mu \leq 0$

Therefore the limiting value of fugacity of the system is

$$0 \leq z \leq 1$$

$\mu = -\infty \Rightarrow e^{\frac{\mu}{kT}} = 0$

$\mu = 0 \Rightarrow e^{\frac{\mu}{kT}} = 1$

It is equivalent to the fact that bosons seem to experience attractive potential and no energy is needed to add another bosons to the system.

If $\mathcal{Z}$ is the grand partition function of the system then we have for bose gas:

$$\frac{PV}{KT} \equiv \ln \mathcal{Z} = -\sum_{\epsilon} \ln\left(1 - e^{\beta(\mu-\epsilon)}\right)$$

$$\text{or,} \quad \frac{PV}{KT} = -\sum_{\epsilon} \ln\left(1 - z e^{-\beta\epsilon}\right) \quad --- \quad (2)$$

The two equations (1) and (2) defines the behaviour of the system having absolute activity z. With the given value of z. system displays its characteristic behaviour. With the given value of z, the two equations also gives other thermodynamic quantities associated with the system.

For large V, the spectrum of the single particle states is almost continuous. So the summation in equation ① and ② may be replaced by integrations.

$$\sum_{\epsilon} \rightarrow \int g(\epsilon)\, d\epsilon$$

The total no. of states $\Gamma(E) = \frac{2\pi V}{h^3}(2m)^{3/2}\int \epsilon^{1/2}\, d\epsilon$

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

is the single particle density of state.

when we replace summation by integration then automatically a zero weightage is assigned to the energy level $\epsilon = 0$ as $g(0) = 0$. This is incorrect quantum mechanically as a statistical weight unity must be assigned to each non-degenerate single particle state in the system. The state $\epsilon = 0$ plays a special role in Bose gas. So we take term containing $\epsilon = 0$ out of the sum before carrying integration. we have

$$\frac{P}{KT} = -\frac{2\pi}{h^3}(2m)^{3/2}\int_0^\infty \epsilon^{1/2} \ln\left(1 - z e^{-\beta\epsilon}\right) d\epsilon - \frac{1}{V}\ln(1-z) \quad \text{--- (3)}$$

and $$\frac{N}{V} = \frac{2\pi}{h^3}(2m)^{3/2}\int_0^\infty \frac{\epsilon^{1/2}\, d\epsilon}{z^{-1}e^{\beta\epsilon} - 1} + \frac{1}{V}\cdot\frac{z}{1-z} \quad \text{--- (4)}$$

For evaluating integration lower limit is still be taken as 0 as state $\epsilon = 0$ is not giving any contribution to the integral.

In equation (4) $N_0 = \frac{z}{1-z}$ represents the contribution of the level $\epsilon \neq 0$ to the total no. of particles of the system.

The value of z lies between 0 and 1. When $z \ll 1$, the last terms in the integrals (3) and (4) are negligible.

When value of μ increases from $-\infty$ or temperature decreases, value of z increases from 0. Now when value of z assumes close to unity, the value of $\frac{N_0}{V}$ i.e $\frac{1}{V}\frac{z}{1-z}$ becomes a significant fraction of $\frac{N}{V}$. N_0 is the no. of particles in state $\epsilon = 0$. When $z = 0$, $N_0 = 0$, further increase of value of z results to increasing non-zero value of N_0 in the state $\epsilon = 0$. The accumulation of macroscopic fraction of the given particles into a single state $\epsilon = 0$ leads to the phenomenon called as Bose-Einstein condensation.

Equation ④ can be written as

$$\frac{N}{V} = \frac{2\pi}{h^3}(2mKT)^{3/2}\int_0^\infty \frac{x^{1/2}\,dx}{z^{-1}e^x - 1} + \frac{N_0}{V} \quad ---⑤ \qquad , \quad N_0 = \frac{z}{1-z}, \quad \beta\epsilon = x$$

or $\quad N = N_{ex} + N_0$

Define Bose-Einstein function

$$g_\nu(z) = \frac{1}{\Gamma\nu}\int_0^\infty \frac{x^{\nu-1}\,dx}{z^{-1}e^x - 1} \quad , 0 < z \leq 1$$

$$= z + \frac{z^2}{2^\nu} + \frac{z^3}{3^\nu} + \cdots$$

$$= \sum_K \frac{z^K}{K^\nu}, \quad 0 \leq z \leq 1$$

value of $g_\nu(z) \to \infty$ for $\nu \leq 1$ and $z \to 1$. It remains finite for $\nu > 1$ for all value $0 \leq z \leq 1$.

Using this function, eqn (5) becomes

$$\frac{N - N_0}{V} = \frac{(2\pi m K T)^{3/2}}{h^3} \cdot \frac{1}{\sqrt{\pi} \cdot \frac{1}{2}} \int_0^\infty \frac{x^{1/2} \, dx}{z^{-1} e^x - 1}$$

$$= \frac{1}{\lambda^3} g_{3/2}(z) \quad , \quad \lambda = \frac{h}{\sqrt{2\pi m K T}} \quad \text{--- (6)}$$

Now,

$N - N_0 = N_{ex}$, where $N_{ex} = V \dfrac{(2\pi m K T)^{3/2}}{h^3} g_{3/2}(z)$

The number of particles in the excited states will depend on the value of z.

$g_{3/2}(0) = 0$ and $g_{3/2}(1) \simeq 2.612 = \zeta\left(\frac{3}{2}\right)$ Zeta function

for $\mu = -\infty, z = 0$ for $\mu = 0, z = 1$

It means that excited states $\epsilon \neq 0$ for a given value of V and T can accomodate max. number of particles equal to

$$N_{ex}^{max} = \frac{V}{\lambda^3} \zeta\left(\frac{3}{2}\right) \quad --- \quad 6(a)$$

For all values $g_{3/2}(z) \leq \zeta\left(\frac{3}{2}\right)$
$0 \leq z \leq 1$

So at equilibrium, for a given V and T, the number of particles in all the excited states taken together are bounded as

$$N_{ex} \leq V \frac{(2\pi mKT)^{3/2}}{h^3} \zeta\left(\frac{3}{2}\right) \quad --- \quad (7)$$

As long as the actual number of particles in the system for a given V and T is less than this limiting value, all the particles in the system are distributed among the excited states and if actual number of particles exceeds this limiting value, the excited states can accomodate only $N_{ex}^{max} = \frac{V}{\lambda^3}$ and the rest will be pushed into the ground state $\epsilon = 0$ whose capacity in all circumstances is practically unlimited.

$$N_0 = N - \frac{V}{\lambda^3} \zeta\left(\frac{3}{2}\right) \quad \text{---} \; (8)$$

For $N >> 1$

$N_0 \simeq N$ and $N_0 = \frac{z}{1-z}$ gives $z = \frac{N_0}{N_0+1} \simeq 1 - \frac{1}{N_0}$

So value of z is almost unity. When its value is not very close to unity, $N_0 = \frac{z}{1-z}$ can be neglected.

The phenomenon in which a macroscopically large number of particles are accumulating in a single quantum state $\epsilon = 0$ is referred to the phenomenon of Bose-Einstein Condensation. It is purely of a quantum origin and takes place in momentum space.

The condition for onset of Bose-Einstein condensation is

$$N > V \frac{(2\pi m K T)^{3/2}}{h^3} \zeta\left(\tfrac{3}{2}\right) \quad --- (9)$$

If we keep N and V constant and vary temperature T, the condition will be

$$T < T_c = \frac{h^2}{2\pi m k}\left[\frac{N}{V \zeta\left(\frac{3}{2}\right)}\right]^{2/3} \quad --- (10)$$

T_c is a characteristic temperature that depends upon the particle mass m and the particle density $\frac{N}{V}$ in the system. It is known as Bose temperature or critical temperature. It is the temperature which corresponds to the value of $z = 1$ for a given value of V and N.

Now

$$N = N_0 + N\left(\frac{T}{T_c}\right)^{3/2} \qquad \text{by (8) and (10)}$$

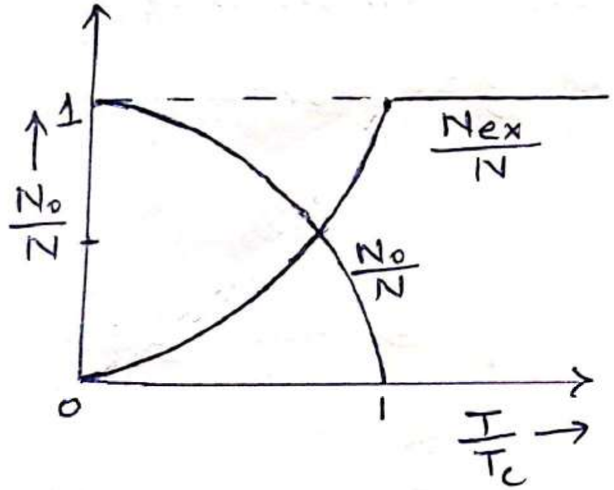
or

$$N_0 = N\left[1 - \left(\frac{T}{T_c}\right)^{3/2}\right] \quad \text{---- (11)}$$

For $T < T_c$, the system can be considered as a mixture of two phases

(i) a normal phase consisting of $N_{ex} = N\left(\frac{T}{T_c}\right)^{3/2}$ particles distributed among excited states $\epsilon \neq 0$ and (ii) a condensed phase consisting of

$N_0 = N - N_{ex}$ particles accumutated in the ground state $\epsilon = 0$.



For $T > T_c$, we have normal phase alone, the number of particles in the ground state $\frac{z}{1-z}$ is negligible in Comparison to total number N.

In the case when T starts from zero and approaching T_c i.e $T \rightarrow T_c$ from below the condensed fraction vanishes as

$$\frac{N_0}{N} = 1 - \left(\frac{T}{T_c}\right)^{3/2}$$

$$\doteq 1 - \left(\frac{T_c - \Delta T}{T_c}\right)^{3/2}, \quad \Delta T = T_c - T$$

$$\simeq 1 - \left[1 - \frac{3}{2}\frac{\Delta T}{T_c}\right] = \frac{3}{2}\left(\frac{T_c - T}{T_c}\right)$$

References:

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Thank You

For any questions/doubts/suggestions and submission of assignments

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