Lecture IV - Bose-Einstein condensation

As we have discussed previously, the quantum limit in which the Bose-Einstein and Fermi-Dirac are relevant occurs for low temperatures or high densities, in such a way that

$$\frac{N}{V}\cdot\frac{h^3}{(2\pi m k_B T)^{3/2}} \gtrsim 1,$$

in contrast with the regime $\frac{N}{V}\frac{h^3}{(2\pi m k_B T)^{3/2}} \ll 1$ in which the quantum effects are irrelevant,

For a system of free bosons, the thermodynamic properties are given by

$$\frac{P}{k_B T} = \frac{1}{V}\ln \Xi(z,T,V) = -\frac{1}{V}\sum_{\epsilon}\ln\left(1-z e^{-\beta\epsilon}\right)$$

and

$$N = \sum_{\epsilon}\langle n_\epsilon\rangle = \sum_{\epsilon}\frac{1}{z^{-1}e^{\beta\epsilon}-1}, \quad (*)$$

with z being the fugacity $z = e^{\beta\mu}$.

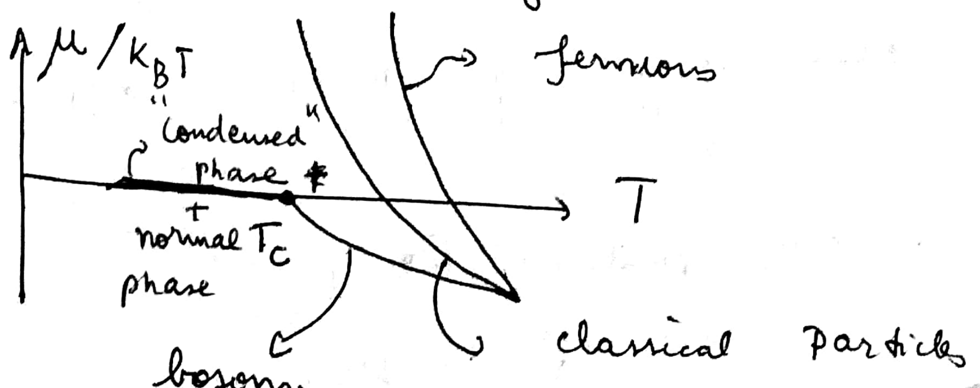
Above relations have remarkable differences when compared with fermions.
As we have discussed previously, since $\langle n_\epsilon\rangle$ is strictly positive, $e^{\beta(\epsilon-\mu)} > 1$ for all values of energy.

Thus, it implies that $e^{+\beta\mu} \lesssim 1$ and hence the chemical potential of bosons is always negative and at most zero.

As we shall see, (see e.g. *) by decreasing T for a fixed N, the chemical potential increases until reaching its maximum value $\mu = 0$ at a "critical / transition" temperature T_c, giving rise to the Bose-Einstein condensation phenomenon.

As $T \leq T_c$ and $\mu = 0$, there is the emergence of a "regime" characterized by a macroscopic density of particles at the ground state coexisting with a macroscopic density of particles at the excited levels. It is worth mentioning that this is remarkably different from the "normal regime" in which every (individual) energy levels have a occupation fraction approaching to zero.

Schematically, the chemical potential of bosons, fermions and ideal gas are sketched in the below figure



For high temperatures $\mu < 0$ and particles are distributed over the levels characterized by no macroscopic occupations in a given energy level. (normal phase). By decreasing T (the temperature) the chemical potential increasing (for a given N) and $T = T_0$ marks its vanishment (for bosons) and the Bose-Einstein phenomenon gives rise in which the ground state has a macroscopic density of particles.

A complementar information is achieved by examining the pressure and N/V (density) in normal and condensed phase.

In the normal phase, expressions for $\frac{P}{K_B T}$ and $\frac{N}{V}$ are given by

$$\frac{N}{V} = \sum_{\epsilon} \frac{1}{e^{\beta(\epsilon-\mu)} - 1}, \quad \frac{P}{K_B T} = -\frac{1}{V} \sum_{\epsilon} \ln\left(1 - e^{-\beta(\epsilon-\mu)}\right) \quad (1),$$

whereas in the condensed phase

$$\frac{N}{V} = \frac{1}{V} \frac{1}{e^{-\beta\mu} - 1} + \frac{1}{V} \sum_{\epsilon \neq 0} \frac{1}{e^{\beta(\epsilon-\mu)} - 1} \quad (2)$$

and.

$$\frac{P}{K_B T} = -\frac{\ln(1-e^{+\beta\mu})}{V} - \frac{1}{V}\sum_{\epsilon\neq 0} \ln\left(1-e^{-\beta(\epsilon-\mu)}\right) \quad (3).$$

respectively

Note that the first term in the right side of Eq. (2) diverges as $\mu \to 0$, consistent with a macroscopic fraction $\frac{N_0}{V}$ of particles $\left(N_0 = \frac{1}{e^{-\beta\mu}-1}\right)$ in the ground state.

Now we are in position to discuss the main thermodynamic properties of a gas of free bosons described by the spectrum of energy $\epsilon_{\vec{k}} = \frac{\hbar^2 k^2}{2M}$.

By assuming that $\sum_{\vec{k}} \longrightarrow \frac{V}{(2\pi)^3}\int d^3\vec{k}$

we then have that (for $V \to \infty$)

$$\sum_{\vec{k}} \ln\left(1-z\, e^{-\frac{\beta\hbar^2k^2}{2M}}\right) \longrightarrow \frac{V}{(2\pi)^3}\, 4\pi \int_0^\infty k^2 \ln\left(1-z\, e^{-\frac{\beta\hbar^2k^2}{2M}}\right) dk$$

and

$$\frac{N}{V} = \frac{1}{V}\sum_{\vec{k}} \frac{1}{z^{-1} e^{\frac{\beta\hbar^2k^2}{2M}}-1} \longrightarrow \frac{1}{(2\pi)^3}\, 4\pi \int_0^\infty \frac{k^2}{z^{-1} e^{\frac{\beta\hbar^2k^2}{2M}}-1}\, dk$$

where $z = e^{\beta\mu}$.

By taking $\epsilon = \frac{\hbar^2 k^2}{2M}$ above expressions can be rewritten in the "energy space"

$$\frac{P}{K_B T} \rightarrow \frac{1}{(2\pi)^2}\left(\frac{2M}{\hbar^2}\right)\int_0^\infty \epsilon^{1/2} \ln\left(1 - z e^{-\beta\epsilon}\right) d\epsilon$$

$$\frac{N}{V} \rightarrow \frac{1}{(2\pi)^2}\left(\frac{2M}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\epsilon^{1/2}}{z^{-1}(e^{\beta\epsilon} - 1)} d\epsilon$$

Another way of interpreting is that The Bose-Einstein emerges at $T \leq T_C$ and $\mu \to 0$ in which the term $\frac{1}{V}\frac{1}{e^{-\beta\mu} - 1} \equiv \frac{N_0}{V}$ becomes important and the fraction density of excited levels $\frac{1}{(2\pi)^2}\left(\frac{2M}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\epsilon^{1/2}}{e^{\beta(\epsilon-\mu)} - 1} d\epsilon$ "reaches" its maximum value in such a way that all "excess" of particles has to occupy the ground state. That is, the Bose-Einstein condensation yields at $\mu = 0$ for $T \leq T_c$ in which

$$N > \frac{1}{(2\pi)^2}\left(\frac{2M}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\epsilon^{1/2}}{e^{\beta\epsilon} - 1} d\epsilon$$

The integral can be evaluated by recalling that

$$\frac{1}{e^{\beta\epsilon}-1} = e^{-\beta\epsilon}\sum_{n=0}^{\infty}\left(e^{-\beta\epsilon}\right)^{n}$$ and

hence $$\int_0^{\infty}\frac{\epsilon^{1/2}}{e^{\beta\epsilon}-1}\,d\epsilon = \int_0^{\infty}\sum_{n=0}^{\infty}\epsilon^{1/2}e^{-\beta(n+1)\epsilon}\,d\epsilon$$

Each integral are a gaussian integral

and therefore $$\sum_{n=0}^{\infty}\int_0^{\infty}\epsilon^{1/2}e^{-\beta\epsilon(n+1)}\,d\epsilon = \frac{\sqrt{\pi}}{2\beta^{3/2}}\underbrace{\sum_{n=0}^{\infty}\frac{1}{(1+n)^{3/2}}}_{\zeta(\frac{3}{2})}$$

and then

$$N > V\left(\frac{2\pi m K_B T}{h^3}\right)^{3/2}\zeta\left(\frac{3}{2}\right) \qquad (5)$$

From above expression, the condensation temperature T_0 is given by the limit of above expression:

$$T_0 = \left(\frac{N}{V}\frac{1}{\zeta(3/2)}\right)^{2/3}\frac{h^2}{(2\pi m K_B T)}$$

Once again, all fraction density $\frac{N_0}{V}$ exceding the maximum value $\left(\frac{2\pi m K_B T}{h^3}\right)^{3/2}\zeta(\frac{3}{2})$ has to occupy the ground state when $\mu \to 0$.

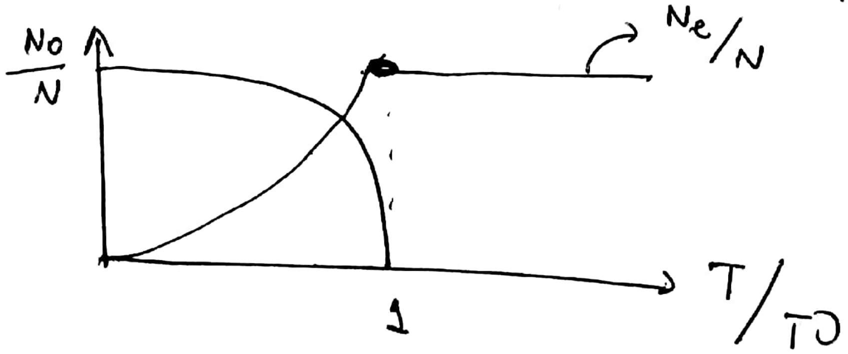
Below T_0, the system is characterized by the coexistence between the "normal phase" and the "condensed phase". For $T < T_0$, Eq (5) can be rewritten as

$$\frac{N}{V} = \frac{N_0}{V} + T^{3/2}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \zeta\left(\tfrac{3}{2}\right),$$

Which can be rewritten as

$$\frac{N_0}{N} = 1 - \left(\frac{T}{T_0}\right)^{3/2}.$$

Graphically, the fraction of particles in the ground ~~state~~ and the excited $(N-N_0)$ states have the following shapes



There are some similarities between the Bose-Einstein phenomenon and the behavior of Helium-4. It can have two phases, a normal and a superfluid phase.

The phase transition, giving rise to the superfluid phase, is second-order and yields at $T_\lambda = 2{,}17\ \mathrm{K}$ and $P_\lambda = 1\ \mathrm{atm}$, whose specific volume

$v_\lambda = 46,2\ \mathring{A}^3$. By assuming (approximately) that the Helium-4 can be treated as an ideal gas and by using its parameters, we find $T_0 \cong 3,14\,K$, a value which is close to $2,17\,K$. This means that the superfluid phase shares some similarities with the Bose-Einstein phenomenon at the condensed phase. However, the present description (a system of non-interacting particles) is few realist.

Thermodynamic Properties

(1) Normal phase ($\mu < 0$ and $T < T_0$).

In such a case the fraction of molecules/particles at the ground state is neglible and expressions for $\frac{N}{V}$ and $\frac{P}{K_B T}$ reads.

$$\frac{N}{V} \to \frac{1}{(2\pi)^2}\left(\frac{2M}{\hbar^2}\right)^{3/2}\int_0^\infty \sum_{n=0}^{\infty} \epsilon^{1/2}\left(e^{-\beta(\epsilon-\mu)}\right)^{n+1} d\epsilon$$

$$= \frac{1}{(2\pi)^2}\left(\frac{2M}{\hbar^2}\right)^{3/2}\frac{1}{2\beta^{3/2}}\sum_{n=0}^{\infty}\frac{z^{n+1}}{(n+1)^{3/2}}$$

$$= \frac{1}{\lambda^3}\, g_{3/2}(z), \quad \text{where}$$

$$\frac{1}{\lambda^3} = \left(\frac{2M\pi K_B T}{h^2}\right)^{3/2} \quad \text{and} \quad g_{3/2}(z) = \sum_{n=0}^{\infty}\frac{z^{n+1}}{(n+1)^{3/2}}$$

denotes the Bose-Einstein function.

The expression for the pressure is more cumbersome. In particular,

$$\frac{P}{k_B T} \rightarrow \frac{1}{(2\pi)^3} \left(\frac{2M}{\hbar^2} \right)^{3/2} \int_0^\infty \epsilon^{1/2} \ln(1 - z e^{-\beta\epsilon}) \, d\epsilon$$

Since $\ln(1 - z e^{-\beta\epsilon}) = \left(z e^{-\beta\epsilon} + \frac{z^2}{2} e^{-2\beta\epsilon} + \dots \right)$, we have that

$$\frac{P}{k_B T} \Rightarrow \frac{1}{(2\pi)^2} \left(\frac{2M}{\hbar^2 \beta} \right)^{3/2} \sum_{n=0}^{\infty} \int_0^\infty \epsilon^{1/2} \frac{z^n}{n} e^{-n\beta\epsilon} \, d\epsilon$$

and finally

$$\frac{P}{k_B T} = \frac{1}{\lambda^3} \sum_{n=0}^{\infty} \frac{z^{n+1}}{(n+1)^{5/2}}$$

$g_{5/2}(z)$

The mean energy in the grand canonical can be evaluated from formulae

$$u = -\frac{\partial}{\partial \beta} \ln \Xi(z, V, \beta) = -\frac{\partial}{\partial \beta} \left[\frac{V}{\lambda^3} g_{5/2}(z) \right]$$

$$= \frac{3}{2} \frac{V}{\beta \lambda^3} g_{5/2}(z).$$

The specific heat at constant volume $C_V(T, N)$.

is given by $C_V = \frac{1}{N}\left(\frac{\partial u}{\partial T}\right)_{V,N}$ or

even $$C_V = -\frac{K_B \beta^2}{N}\left(\frac{\partial u}{\partial \beta}\right)_{V,N}.$$

Since in the present case $u = u(\beta, z)$ and not $u = u(\beta, N)$ we can appeal to the "reduction of derivatives recipe" in such a way that

$$\left(\frac{\partial u}{\partial \beta}\right)_N = \underbrace{\left(\frac{\partial u}{\partial \beta}\right)_z}_{1} + \underbrace{\left(\frac{\partial u}{\partial z}\right)_\beta}_{2} \widetilde{\left(\frac{\partial z}{\partial \beta}\right)_N}$$

where $$\left(\frac{\partial z}{\partial \beta}\right)_N = -\frac{\overbrace{(\partial N/\partial \beta)_z}^{3}}{\underbrace{(\partial N/\partial z)_\beta}_{4}}$$

The following derivatives are given as follows:

$$(1) = -\frac{3}{2}\cdot\frac{5}{2}\frac{V}{\beta^2\lambda^3} g_{5/2}(z)$$

$$(2) = \frac{3}{2}\frac{V}{\beta\lambda^3}\sum_{n=0}^{\infty}\frac{(n+1)}{(n+1)^{5/2}} z^n = \frac{3}{2z}\frac{V}{\beta\lambda^3} g_{3/2}(z)$$

$$(3) = -\frac{3}{2}\frac{1}{\lambda^3\beta} g_{3/2}(z)$$

$$(4) = \frac{1}{\lambda^3}\sum_{n=0}^{\infty}\frac{(n+1)\, z^n}{(n+1)^{3/2}} = \frac{1}{z\lambda^3} g_{1/2}(z)$$

Thereby

$$C_V = \frac{3}{2}\frac{k_B}{N}\left[\frac{5}{2}\frac{V}{\lambda^3} g_{5/2}(z) - \frac{3}{2}\frac{V}{\lambda^3}\frac{g^2_{3/2}(z)}{g_{1/2}(z)}\right]$$

or

$$C_V = \frac{3}{2} k_B \left[\frac{5}{2}\frac{g_{5/2}(z)}{g_{3/2}(z)} - \frac{3}{2}\frac{g_{3/2}(z)}{g_{1/2}(z)}\right]$$

For $T \to \infty$

$$g_{5/2}(z) \approx z$$

$$g_{3/2}(z) \approx z$$

$$g_{1/2}(z) \approx z$$ and then

$$C_V \to \frac{3}{2} k_B$$ (consistent with the equipartition principle)

at the transition Temperature, $z = 1$ and

$$g_{5/2}(1) \Rightarrow \zeta(5/2) = 1.342$$

$$g_{3/2}(1) \Rightarrow \zeta(3/2) = 2.612$$

$$g_{1/2}(1) \longrightarrow \infty$$

and $C_V \longrightarrow \frac{3}{2} k_B \left[\frac{5}{2}\frac{1.342}{2.612}\right]$ which

is finite!, but $C_V(T_0) > \underbrace{C_V(T \to \infty)}_{\text{classical}}$

Pressure

For $T \to \infty$ $\left.\begin{array}{l} P \to \frac{k_B T}{\lambda^3} z \text{ and} \\ N \to z/\lambda^3 \end{array}\right\} \Rightarrow PV = N k_B T$ (ideal gas)

(2) Coexistence region ($\mu = 0$ and $T \leq T_0$)

The above expressions become:

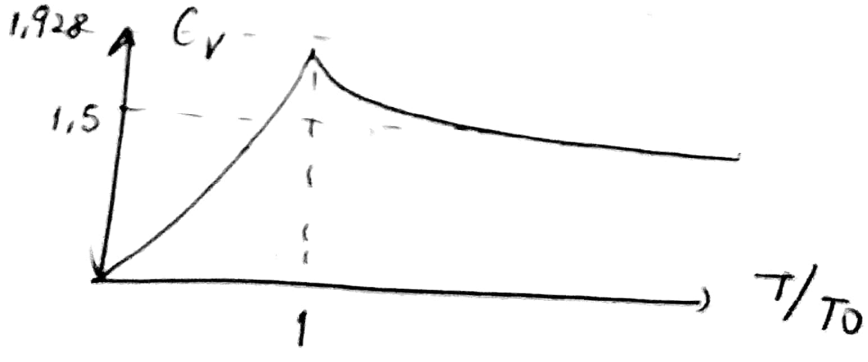
$$u = \frac{3}{2} \frac{V}{\beta \lambda^3} g_{5/2}(1) = \frac{3}{2} V C T^{5/2} g_{5/2}(1)$$

↳ where $C^{-1} = \left(\frac{h^2}{2 m \pi k_B} \right)^{3/2}$

$$\underbrace{N_e}_{\substack{\text{fraction of} \\ \text{particles occupying} \\ \text{the excited states}}} = \frac{V}{\lambda^3} g_{3/2}(1).$$

$$C_V = \frac{1}{N} \left(\frac{\partial u}{\partial T} \right)_{V,N} = \frac{1}{N} \frac{15}{4} V C g_{5/2}(1) T^{3/2}$$

Hence $C_V \to 0$ when $T \to 0$ and C_V has the following shape



Finally, the pressure along the coexistence line is given by

$$\frac{p}{k_B T} \longrightarrow -\frac{\ln(1-z)}{V} + \frac{1}{\lambda^3} g_{5/2}(z).$$

Since $\frac{z}{1-z}$ can be identified as the total number of particles in the ground state

$$\frac{\ln(1-z)}{V} \Rightarrow \frac{\ln(1+N_0)}{V} \longrightarrow 0 \quad \text{when } V \to \infty$$

Hence, in the condensed phase + normal phase the particles occupying the ground state does not contribute for the system pressure. The pressure comes from only particles occupying the excited states (normal phase).

$$\text{Hence } P \Rightarrow \frac{1}{\beta\lambda^3} g_{5/2}(1) \quad \text{and}$$

$P \to 0$ when $T \to 0$, which is in contrast with the ideal Fermi gas.