Physics 415 - Lecture 34: Bose Gas and Bose-Einstein Condensation

April 16, 2025

Summary

- Bose Gas (BG): Gas of weakly interacting particles obeying Bose-Einstein (BE) statistics.
- GCE description (fixed T, μ, V):
  - Grand Partition Function: $\mathcal{Z} = \prod_r \left(\sum_{n_r=0}^{\infty} e^{-\beta(\epsilon_r-\mu)n_r}\right) = \prod_r \frac{1}{1-e^{-\beta(\epsilon_r-\mu)}}$. Converges only if $\epsilon_r - \mu > 0$ for all r, i.e., $\mu < \epsilon_{min}$. Usually $\epsilon_{min} = 0$, so $\mu < 0$.
  - Grand Potential: $\Phi = -T \ln \mathcal{Z} = T \sum_r \ln(1 - e^{-\beta(\epsilon_r-\mu)})$.
  - Mean occupation number: $\overline{n}_r = \frac{1}{e^{\beta(\epsilon_r-\mu)}-1}$.
- Sum over states $r \to g \int d\epsilon \rho(\epsilon)$, where $\rho(\epsilon) = \frac{V}{4\pi^2}(\frac{2m}{\hbar^2})^{3/2}\sqrt{\epsilon}$ (spatial DOS) and $g = 2J+1$ is spin degeneracy.
  - $\Phi = gT \int_0^\infty d\epsilon \rho(\epsilon) \ln(1 - e^{-\beta(\epsilon-\mu)})$.
  - $N = \sum_r \overline{n}_r = g \int_0^\infty d\epsilon \rho(\epsilon) \frac{1}{e^{\beta(\epsilon-\mu)}-1}$. This determines $\mu(T, N, V)$.

Bose-Einstein Condensation (BEC)

Properties of the Bose gas at low temperatures are dramatically different from those of the Fermi gas. We will see the phenomenon of Bose-Einstein condensation = macroscopic occupation of the ground state, even for $T > 0$.

For this discussion, set the zero of energy such that the lowest single-particle state has $\epsilon_0 = 0$. The condition for convergence of $\mathcal{Z}$ then requires $\mu < 0$.

Consider the evolution of μ as T changes, determined by the constraint on the total number of particles N.

$$N = g \int_0^\infty d\epsilon \frac{\rho(\epsilon)}{e^{\beta(\epsilon-\mu)} - 1}$$

Substitute $\rho(\epsilon) = AV\sqrt{\epsilon}$ and change variables $x = \beta\epsilon$:

$$N = gAV \int_0^\infty \frac{\sqrt{\epsilon} d\epsilon}{e^{\beta\epsilon}e^{-\beta\mu} - 1} = gAVT^{3/2} \int_0^\infty \frac{\sqrt{x} dx}{z^{-1}e^x - 1}$$

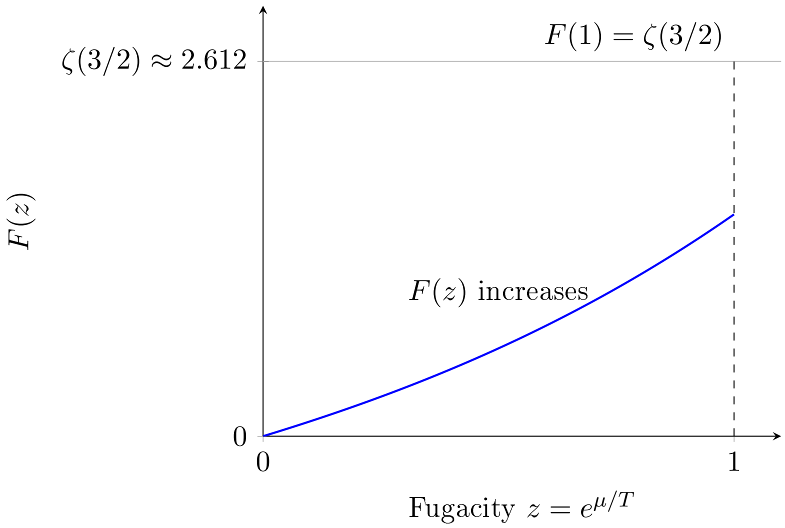
where $z = e^{\beta\mu} = e^{\mu/T}$ is the fugacity. Using $AV = \frac{V}{2\pi^2}(\frac{2m}{\hbar^2})^{3/2}\sqrt{2} = \frac{V}{2\pi^2}(\frac{mT\lambda_{th}^2}{\pi\hbar^2 T})^{3/2}$? No. Use $AVT^{3/2} = \frac{V}{2\pi^2}(\frac{m}{\hbar^2})^{3/2}\sqrt{2}T^{3/2} = \frac{V}{2\pi^2}(\frac{mT}{2\pi\hbar^2})^{3/2}\frac{(2\pi)^{3/2}}{\sqrt{2}}2\pi^2$? No. Use $\lambda_{th} = h/\sqrt{2\pi mT}$.

$$N = g\frac{V}{\lambda_{th}^3}\left[\frac{2}{\sqrt{\pi}}\int_0^\infty \frac{\sqrt{x}dx}{z^{-1}e^x - 1}\right]$$

Let $F(z) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\sqrt{x}dx}{z^{-1}e^x - 1}$.

$$n = \frac{N}{V} = \frac{g}{\lambda_{th}^3} F(z)$$

Since $\mu < 0$, the fugacity $z = e^{\mu/T}$ lies in the range $0 < z < 1$. The function $F(z)$ behaves as follows:



$F(z)$ increases monotonically with z, from $F(0) = 0$ to a maximum finite value $F(1)$. $F(1) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\sqrt{x}dx}{e^x - 1}$. This integral evaluates to $\Gamma(3/2)\zeta(3/2) = (\sqrt{\pi}/2)\zeta(3/2)$. So, $F(1) = \frac{2}{\sqrt{\pi}}(\frac{\sqrt{\pi}}{2})\zeta(3/2) = \zeta(3/2) \approx 2.612$, where ζ is the Riemann zeta function.

Now consider fixed density n. The relation is $n\lambda_{th}^3/g = F(z)$. As T decreases, $\lambda_{th} \propto 1/\sqrt{T}$ increases, so $n\lambda_{th}^3/g$ increases. To maintain the equality, $F(z)$ must increase, which means $z = e^{\mu/T}$ must increase (i.e., μ must become less negative, approaching 0).

However, there is a limiting value, since $z \leq 1$ (or $\mu \leq 0$). This limit is reached when $n\lambda_{th}^3/g$ reaches its maximum possible value $F(1)$. This occurs at a critical temperature T_c:

$$n\frac{\lambda T_c^3}{g} = \zeta(3/2)$$

$$\frac{N}{V}\frac{1}{g}\left(\frac{2\pi\hbar^2}{mT_c}\right)^{3/2} = \zeta(3/2)$$

Solving for T_c:

$$T_c(n) = \frac{2\pi\hbar^2}{m}\left(\frac{n}{g\zeta(3/2)}\right)^{2/3} \approx \frac{3.313}{g^{2/3}}\frac{\hbar^2}{m}n^{2/3}$$

(T_c in energy units).

What happens for $T < T_c$? The equation $n\lambda_{th}^3/g = F(z)$ seems impossible to satisfy, since $n\lambda_{th}^3/g > \zeta(3/2)$ but $F(z) \leq \zeta(3/2)$. Demanding $\mu = 0$ ($z = 1$) would imply $N = g\int d\epsilon\rho(\epsilon)/(e^{\beta\epsilon} - 1)$ which gives a number of particles $N_{ex} = N(T/T_c)^{3/2} < N$. Where are the other particles?

Resolution: The replacement of the sum $\sum_r$ by the integral $\int d\epsilon\rho(\epsilon)$ is invalid for the ground state $\epsilon_0 = 0$, because $\rho(\epsilon) \propto \sqrt{\epsilon} \to 0$ as $\epsilon \to 0$, effectively ignoring the ground state. We must treat the ground state ($r = 0, \epsilon_0 = 0$) separately in the sum:

$$N = \sum_r \overline{n}_r = \overline{n}_0 + \sum_{r>0} \overline{n}_r$$

$$N = \frac{1}{e^{\beta(0-\mu)} - 1} + \sum_{r>0} \frac{1}{e^{\beta(\epsilon_r-\mu)} - 1}$$

Let $N_0 = \overline{n}_0$ be the number of particles in the ground state. The sum over excited states $r > 0$ can be accurately replaced by the integral for large V:

$$N_{\epsilon>0} = \sum_{r>0} \overline{n}_r \approx g \int_0^\infty d\epsilon \frac{\rho(\epsilon)}{e^{\beta(\epsilon-\mu)} - 1} = N \left(\frac{T}{T_c}\right)^{3/2} \frac{F(z)}{F(1)}$$

So, $N = N_0 + N_{\epsilon>0}$.

For $T > T_c$, we must have $\mu < 0$ ($z < 1$). In this regime, $N_0 = 1/(z^{-1} - 1)$. Since $z < 1$, $z^{-1} > 1$, N_0 is finite and non-macroscopic. So effectively $N \approx N_{\epsilon>0}$, and the equation $n\lambda_{th}^3/g = F(z)$ determines z (and μ). For $T < T_c$, the excited states cannot accommodate all N particles if $\mu < 0$. The equation $N = N_0 + N_{\epsilon>0}$ can only be satisfied if the chemical potential becomes essentially fixed at $\mu = 0$ ($z = 1$), allowing the ground state occupation N_0 to become macroscopic. For $T < T_c$, we set $\mu = 0$. Then:

$$N_{\epsilon>0} = g \int_0^\infty d\epsilon \frac{\rho(\epsilon)}{e^{\beta\epsilon} - 1} = g \frac{V}{\lambda_{th}^3} F(1) = g \frac{V}{\lambda_{th}^3} \zeta(3/2)$$

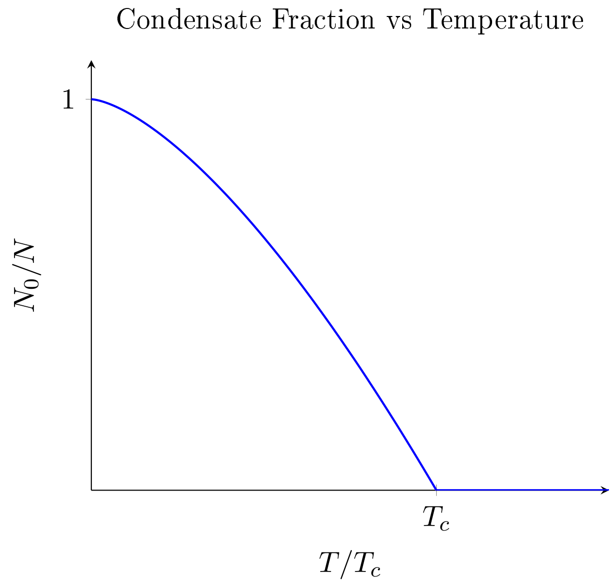
Using $N = g \frac{V}{\lambda T_c^3} \zeta(3/2)$, we get:

$$N_{\epsilon>0} = N \frac{\lambda T_c^3}{\lambda_{th}^3} = N \left(\frac{T}{T_c}\right)^{3/2}$$

The number of particles in the ground state (the condensate) is:

$$N_0(T) = N - N_{\epsilon>0} = N \left[1 - \left(\frac{T}{T_c}\right)^{3/2}\right] \quad (\text{for } T \leq T_c)$$

$N_0(T) = 0$ for $T > T_c$. This macroscopic occupation of the $\epsilon_0 = 0$ state below T_c is **Bose-Einstein Condensation**.



Thermodynamics below T_c

For $T < T_c$, we have $\mu = 0$. **Energy:** The condensate particles (N_0) are in state $\epsilon_0 = 0$ and do not contribute to energy.

$$E = \sum_{r>0} \overline{n}_r \epsilon_r = g \int_0^\infty d\epsilon \frac{\rho(\epsilon)\epsilon}{e^{\beta\epsilon} - 1}$$

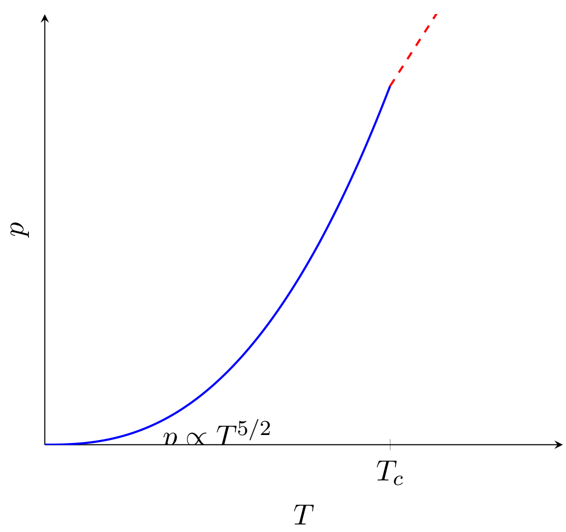
The integral can be evaluated: $E = gV(\frac{m}{2\pi\hbar^2})^{3/2}T^{5/2}[\Gamma(5/2)\zeta(5/2)]$. $E = N\frac{(3/2)\zeta(5/2)}{\zeta(3/2)}T_c(T/T_c)^{5/2} \approx 0.770NT_c(T/T_c)^{5/2}$. Let $E(T_c)$ be the energy at $T = T_c$. Then $E(T) = E(T_c)(T/T_c)^{5/2}$ for $T < T_c$.

Pressure: Using $pV = \frac{2}{3}E$:

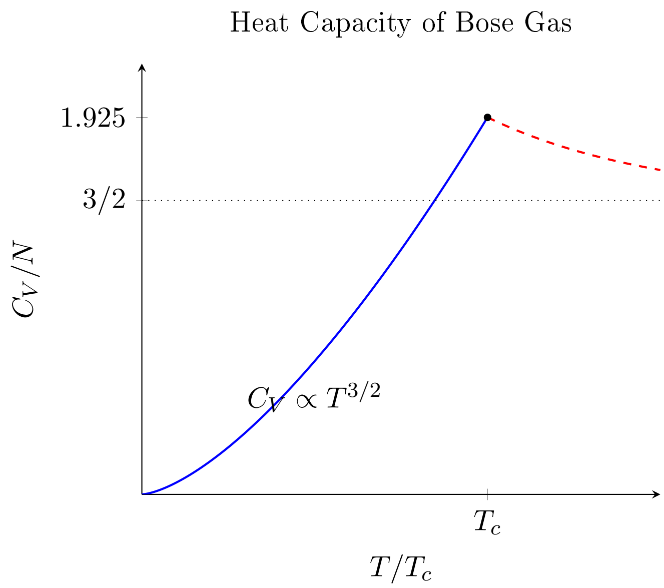
$$p(T) = \frac{2}{3}\frac{E(T)}{V} = p(T_c)\left(\frac{T}{T_c}\right)^{5/2}$$

where $p(T_c) = \frac{2}{3}E(T_c)/V \approx 0.513nT_c$. Note that for $T < T_c$, the pressure $p(T)$ depends only on T, not on V or n. This is because adding more particles (increasing n) at fixed $T < T_c$ only increases the condensate fraction N_0; the number of excited particles $N_{\epsilon>0}$ and thus the pressure remains unchanged.

Pressure vs Temperature for Bose Gas



Heat Capacity: $C_V = (\partial E/\partial T)_V$. For $T < T_c$: $C_V = \frac{\mathrm{d}}{\mathrm{d}T}[E(T_c)(T/T_c)^{5/2}] = E(T_c)\frac{5}{2}T^{3/2}/T_c^{5/2} = \frac{5}{2}\frac{E(T)}{T}$. $C_V(T) = C_V(T_c)(T/T_c)^{3/2}$, where $C_V(T_c) = \frac{5}{2}E(T_c)/T_c \approx 1.925N$. Compare to classical value $C_V = \frac{3}{2}N = 1.5N$. Note $C_V(T_c) > 1.5N$. The specific heat shows a cusp at $T = T_c$, where the slope $\partial C_V/\partial T$ is discontinuous.



(Note: The cusp is specific to non-interacting particles. Interactions tend to modify the singularity, e.g., making it stronger like in superfluid ^{4}He).

Qualitative argument for $C_V \sim T^{3/2}$: At low T, only low energy states $\epsilon \lesssim T$ are significantly excited. Number of excited states $N_{excited} \approx g \int_0^T \rho(\epsilon) d\epsilon \propto V \int_0^T \sqrt{\epsilon} d\epsilon \propto VT^{3/2}$. Each carries energy $\sim T$. Total excitation energy $\Delta E \sim N_{excited} T \propto T^{5/2}$. $C_V = dE/dT \propto T^{3/2}$. ✓

BEC in the Real World

- BEC of dilute alkali gases (^{87}Rb, ^{23}Na, ^{7}Li...) first observed in 1995 (Cornell/Wieman, Ketterle). These are closest to the ideal BEC theory developed here.
- Superfluidity of liquid ^{4}He (below $T \approx 2.17$ K). ^{4}He atoms are bosons. While liquid interactions are strong, the phenomenon is understood as a BEC.
- Superfluidity of liquid ^{3}He (below $T \approx 2$ mK). ^{3}He atoms are fermions. Fermions first "pair" up (like electrons in superconductivity) to form effective bosons, which then undergo BEC.
- Superconductivity: Electrons (fermions) in a metal form "Cooper pairs" (effective bosons) which undergo BEC, leading to superconductivity.