Lecture 10

Ideal quantum gases

$$H = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} \qquad \vec{p}_i = \text{(quantum) momentum of the } i^{\text{th}} \text{ particle}$$

Consider spinless particles for simplicity.

Single-particle energy: $\epsilon_{\vec{p}} = \dfrac{p^2}{2m}$,

$p = |\vec{p}\,|$.

as before, $\vec{p} = \dfrac{2\pi\hbar}{L}\vec{n}$, where $L = V^{1/3}$

$$\vec{n} = (n_1, n_2, n_3) \quad , \quad \underset{i=1,2,3}{n_i} = 0, \pm 1, \pm 2, \dots$$

$V \to \infty \Rightarrow$ possible values of $\vec{p}$ form a continuum, yielding:

$$\sum_{\vec{p}} \Rightarrow \frac{V}{h^3}\int d^3p$$

<u>Note</u>:

$$\begin{cases} \underbrace{u_{\vec{p}}(\vec{r})}_{\text{single-particle wavefunction}} = \dfrac{1}{\sqrt{V}}\underbrace{e^{i\vec{p}\cdot\vec{r}/\hbar}}_{\text{plane wave}} \\ u_{\vec{p}}(\vec{r}+\vec{n}L) = u_{\vec{p}}(\vec{r}) \end{cases}$$

$$\int d^3r\, u^*_{\vec{p}}(\vec{r})\, u_{\vec{p}'}(\vec{r}) = \delta_{\vec{p}\vec{p}'}$$

Finally,
$$
\begin{cases}
E = \sum_{\vec{p}} n_{\vec{p}} \epsilon_{\vec{p}}, \\
N = \sum_{\vec{p}} n_{\vec{p}}
\end{cases}
$$

$$
n_{\vec{p}} = \begin{cases} 0, 1, 2, \ldots & \text{bosons} \\ 0, 1 & \text{fermions} \end{cases}
$$

The $\sum_{\vec{p}} n_{\vec{p}} = N$ makes canonical ensemble difficult $\Rightarrow$ use grand canonical ensemble:

$z^{\sum_{\vec{p}} n_{\vec{p}}}$

$$
\Sigma(z, V, T) = \sum_{N=0}^{\infty} z^N \sum_{\substack{\{n_{\vec{p}}\} \\ \sum_{\vec{p}} n_{\vec{p}} = N}} e^{-\beta \sum_{\vec{p}} n_{\vec{p}} \epsilon_{\vec{p}}} =
$$

$z = e^{\beta\mu} \leftarrow$ fugacity

$$
= \sum_{N=0}^{\infty} \sum_{\substack{\{n_{\vec{p}}\} \\ \sum_{\vec{p}} n_{\vec{p}} = N}} \prod_{\vec{p}} \left(z e^{-\beta \epsilon_{\vec{p}}} \right)^{n_{\vec{p}}} =
$$

$$
= \sum_{n_0} \sum_{n_1} \ldots \left[\left(z e^{-\beta\epsilon_0} \right)^{n_0} \left(z e^{-\beta\epsilon_1} \right)^{n_1} \ldots \right] =
$$

$n_0 \uparrow$ labels $\vec{p}$-states

$$
= \prod_{\vec{p}} \left(\sum_{n} \left(z e^{-\beta\epsilon_{\vec{p}}} \right)^n \right).
$$

$\uparrow$ sum over $\begin{cases} n = 0, 1, 2, \ldots & \text{bosons} \\ n = 0, 1 & \text{fermions} \end{cases}$

Thus,

$$\Sigma(z,V,T) = \begin{cases} \prod_{\vec{p}} \dfrac{1}{1-z e^{-\beta\epsilon_{\vec{p}}}} & \text{Bose} \\ \prod_{\vec{p}} (1+z e^{-\beta\epsilon_{\vec{p}}}) & \text{Fermi} \end{cases}$$

Equations of state (EoS):

$$\beta p V = \log \Sigma = \begin{cases} -\sum_{\vec{p}} \log(1-z e^{-\beta\epsilon_{\vec{p}}}) & \text{Bose} \\ \sum_{\vec{p}} \log(1+z e^{-\beta\epsilon_{\vec{p}}}) & \text{Fermi} \end{cases}$$

Moreover,

$$\underset{\text{known}}{N} = z\frac{\partial}{\partial z}\log\Sigma = \begin{cases} \sum_{\vec{p}} \dfrac{z e^{-\beta\epsilon_{\vec{p}}}}{1-z e^{-\beta\epsilon_{\vec{p}}}} & \text{Bose} \\ \sum_{\vec{p}} \dfrac{z e^{-\beta\epsilon_{\vec{p}}}}{1+z e^{-\beta\epsilon_{\vec{p}}}} & \text{Fermi} \end{cases}$$

can be used to find z and plug it back into the EoS

Finally,

$$\langle n_{\vec{p}}\rangle = \frac{1}{\Sigma}\sum_{N=0}^{\infty} z^N \sum_{\substack{\{n_{\vec{p}}\} \\ \sum_{\vec{p}} n_{\vec{p}} = N}} n_p e^{-\beta\sum_{\vec{p}}\epsilon_{\vec{p}} n_{\vec{p}}} =$$

$$= \frac{\partial}{\partial(-\beta\epsilon_{\vec{p}})}\log\Sigma = \begin{cases} \dfrac{z e^{-\beta\epsilon_{\vec{p}}}}{1-z e^{-\beta\epsilon_{\vec{p}}}} & \text{Bose} \\ \dfrac{z e^{-\beta\epsilon_{\vec{p}}}}{1+z e^{-\beta\epsilon_{\vec{p}}}} & \text{Fermi} \end{cases}$$

Note that

$$N = \sum_{\vec{p}} \langle n_{\vec{p}} \rangle \quad , \text{ as expected:}$$

$$\sum_{\vec{p}} \langle n_{\vec{p}} \rangle = \langle \underbrace{\sum_{\vec{p}} n_{\vec{p}}}_{N} \rangle = \langle N \rangle = N$$

Now, consider the $V \to \infty$ limit.

<u>Ideal</u> <u>Fermi</u> <u>gas</u>:

$$\frac{pV}{k_B T} = \frac{V}{h^3} \int \underbrace{d^3p}_{4\pi p^2 dp} \log\left(1 + z e^{-\beta \epsilon_p}\right), \text{ or}$$

$$\underbrace{}_{} = x^2 \Rightarrow p = \sqrt{\frac{2m}{\beta}}\, x$$

$$\frac{p}{k_B T} = \frac{4\pi}{h^3} \int_0^\infty dp\, p^2 \log\left(1 + z e^{-\frac{\beta p^2}{2m}}\right).$$

Next,

$$N = \frac{V}{h^3} \int d^3p \frac{z e^{-\beta \epsilon_p}}{1 + z e^{-\beta \epsilon_p}}, \text{ or}$$

$$\frac{1}{v} = \frac{4\pi}{h^3} \int_0^\infty dp\, p^2 \frac{1}{1 + z^{-1} e^{\beta p^2 / 2m}}.$$

Introduce $\lambda = \sqrt{\frac{2\pi\hbar^2}{m k_B T}}$, then

$$\frac{p}{k_B T} = \frac{\pi^{3/2}}{h^3} \frac{4}{\sqrt{\pi}} \left(\frac{2m}{\beta}\right)^{3/2} \int_0^\infty dx\, x^2 \log\left(1 + z e^{-x^2}\right) =$$

$$= \underbrace{\frac{(2\pi)^{3/2}}{(2\pi\hbar)^3}}_{\frac{1}{(2\pi\hbar^2)^{3/2}}} (m k_B T)^{3/2} \underbrace{\frac{4}{\sqrt{\pi}} \int_0^\infty dx \ldots}_{f_{5/2}(z)} \equiv$$

$\boxed{=} \frac{1}{\lambda^3} f_{5/2}(z)$, where

$$f_{5/2}(z) = \sum_{\ell=1}^{\infty} \frac{(-1)^{\ell+1} z^\ell}{\ell^{5/2}} .$$

Likewise, it can be shown that

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

$$f_{3/2}(z) = \underbrace{z \frac{\partial}{\partial z}}_{\text{see eq's for } N \text{ above}} f_{5/2}(z) = \sum_{\ell=1}^{\infty} \frac{(-1)^{\ell+1} z^\ell}{\ell^{3/2}} .$$

$\underline{\text{Ideal Bose gas}}$:

in this case, $\log(1 - z e^{-\beta\epsilon_{\vec{p}}})$ (in $\log \Sigma$) diverges for $\vec{p} = 0$ ($\epsilon_{\vec{p}} = 0$) as $z \to 1$.

This term, which is responsible for Bose-Einstein condensation, needs to be treated separately (i.e., split off from the integral). Then

$$\begin{cases} \dfrac{P}{k_B T} = -\dfrac{4\pi}{h^3} \displaystyle\int_0^\infty dp\, p^2 \log(1 - z e^{-\beta p^2/2m}) - \dfrac{1}{V} \log(1-z), \\[2ex] \dfrac{1}{v} = \dfrac{4\pi}{h^3} \displaystyle\int_0^\infty dp\, p^2 \dfrac{1}{z^{-1} e^{\beta p^2/2m} - 1} + \dfrac{1}{V} \dfrac{z}{1-z} \end{cases}$$

It can be shown that

$$\begin{cases} \dfrac{P}{k_B T} = \dfrac{1}{\lambda^3} g_{5/2}(z) - \dfrac{1}{V} \log(1-z), \\ \dfrac{1}{v} = \dfrac{1}{\lambda^3} g_{3/2}(z) + \dfrac{1}{V} \dfrac{z}{1-z}, \quad \text{where} \end{cases}$$

$$g_{5/2}(z) = -\frac{4}{\sqrt{\pi}} \int_0^\infty dx\, x^2 \log(1 - z e^{-x^2}) = \sum_{\ell=1}^{\infty} \frac{z^\ell}{\ell^{5/2}},$$

$$g_{3/2}(z) = z \frac{\partial}{\partial z} g_{5/2}(z) = \sum_{\ell=1}^{\infty} \frac{z^\ell}{\ell^{3/2}}.$$

Since $\langle n_{\vec{p}} \rangle = \dfrac{z e^{-\beta \epsilon_{\vec{p}}}}{1 - z e^{-\beta \epsilon_{\vec{p}}}}$,

$$\frac{z}{1-z} = \underbrace{\langle n_0 \rangle}_{\text{average occupancy of the } \vec{p}=0 \text{ level}}$$

If $\dfrac{\langle n_0 \rangle}{V}$ is finite (i.e., a finite fraction of all particles occupy the $\vec{p}=0$ level), this term cannot be neglected.

Now, consider

$$\mathcal{U}(z,V,T) = \frac{1}{\Sigma} \sum_{N=0}^{\infty} z^N \sum_{\substack{\{n_{\vec p}\} \\ \sum_{\vec p} n_{\vec p} = N}} \left[\left(\sum_{\vec p} n_{\vec p} \epsilon_{\vec p} \right) e^{-\beta \sum_{\vec p} n_{\vec p} \epsilon_{\vec p}} \right] =$$

$$= -\frac{\partial}{\partial \beta} \underbrace{\log \Sigma}_{\frac{pV}{k_B T}} .$$

Then $$\frac{\mathcal{U}}{V} = -\frac{\partial}{\partial \beta}(\beta p) = -p - \beta \frac{\partial p}{\partial \beta} \overset{\text{Fermi}}{=}$$

$$= -\frac{1}{\beta\lambda^3} f_{5/2}(z) - \beta \frac{\partial}{\partial \beta}\left(\frac{1}{\beta \lambda^3}\right) \times f_{5/2}(z) =$$

$$= -\frac{1}{\beta\lambda^3} f_{5/2}(z) - \beta \left[-\frac{1}{\beta^2 \lambda^3} + \frac{1}{\beta} \frac{(-3)}{\lambda^4} \frac{\partial \lambda}{\partial \beta} \right] f_{5/2}(z) =$$

$$= \frac{3}{\lambda^4} \frac{\lambda}{2\beta} f_{5/2}(z) = \frac{3}{2} \frac{k_B T}{\lambda^3} f_{5/2}(z)$$

$$\lambda = \underset{\text{const}}{A} \sqrt{\beta} \rightarrow \frac{\partial \lambda}{\partial \beta} = A \frac{1}{2\sqrt{\beta}} = \frac{\lambda}{2\beta}$$

Likewise, $$\frac{\mathcal{U}}{V} \underset{\text{Bose}}{=} \frac{3}{2} \frac{k_B T}{\lambda^3} g_{5/2}(z) .$$

Note that the $\frac{\log(1-z)}{V}$ term did not contribute.

Finally,

$\frac{U}{V} = \frac{3}{2} p$ for both Fermi and Bose (if the $\frac{\log(1-z)}{V}$ term can be neglected)

Then $\underbrace{U = \frac{3}{2} p V}_{\text{in both cases}}$, same as classical ideal gas