Lecture #14

We now wish to find the partition function for non-interacting Fermions and bosons. (9)

$$Z = Q_N(T,V) = \sum_{\{n_i\}} e^{-\beta E(\{n_i\})} \quad , E = \sum_i \epsilon_i n_i$$

ϵ_i are single-particle energies

sum over all $\{n_i\}$ such that $\sum_i n_i = N$

Kronecker δ

$$= \sum_{\{n_i\}} \delta\left(\sum_i n_i - N\right) e^{-\beta E(\{n_i\})} \quad \text{[difficult to do]}$$

Go to the Grand canonical ensemble.

$$\Xi = \sum_{N=0}^{\infty} z^N Q_N; \quad z = e^{\beta\mu} \quad ; \text{ write } z^N = \prod_i z^{n_i}$$

$$= \sum_{\{n_i\}} \sum_{N=0}^{\infty} \prod_i z^{n_i} \delta\left(\sum_i n_i - N\right) e^{-\beta E(\{n_i\})}$$

$$\sum_{\{n_i\}} \left[\prod_i z^{n_i}\right] e^{-\beta \sum_i n_i \epsilon_i} = \quad \left(e^{\Sigma} = \prod e\right)$$

$$\sum_{\{n_i\}} \prod_i \left(z e^{-\beta \epsilon_i}\right)^{n_i}, \text{ the sum is now unconstrained}$$

$$= \sum_{n_0=0}^{\infty} \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \left[\left(z e^{-\beta\epsilon_0}\right)^{n_0} \left(z e^{-\beta\epsilon_1}\right)^{n_1} \cdots\right]$$

n_i = # of particles w/ energy ϵ_i

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

In the Bose-Einstein case $n_\epsilon = 0, 1, 2, \ldots$ while in the Fermi-Dirac case, $n_\epsilon = 0$ or 1 only [Pauli-exclusion]

FD ($n_i = 0, 1$)

$$\Xi = \prod_i \left(1 + z e^{-\beta\epsilon_i}\right)$$

$$= \prod_i \left(1 + e^{-\beta(\epsilon_i - \mu)}\right)$$

BE $n_i \in \mathbb{Z}^+$

$$\sum_{n_i=0}^{\infty} \left(z e^{-\beta\epsilon_i}\right)^{n_i} = \frac{1}{1 - z e^{-\beta\epsilon_i}}$$

$$\therefore \Xi = \prod_i \left(\frac{1}{1 - z e^{-\beta\epsilon_i}}\right) = \prod_i \left[\frac{1}{1 - e^{-\beta(\epsilon_i - \mu)}}\right]$$

Therefore $-\frac{\Psi}{kT} = \frac{PV}{kT} = \ln \Xi$

sign in different convention

$$= \begin{cases} \sum_i \ln\left(1 + e^{-\beta(\epsilon_i - \mu)}\right) & \text{FD} \\ -\sum_i \ln\left(1 - e^{-\beta(\epsilon_i - \mu)}\right) & \text{BE} \end{cases}$$

Combine the expressions as:

$$\ln \Xi = \pm \sum_i \ln\left[1 \pm e^{-\beta(\varepsilon_i - \mu)}\right]$$

+ is for FD
− is for BE

Compare this w/ classical result:

Consider single particle states labeled by energy ϵ_i, with n_i = # particles in state i

$$E = \sum_i n_i \varepsilon_i, \quad N = \sum_i n_i$$

⇒ if the particles are distinguishable, then the number of ways to distribute the particles

$$\Omega = \frac{N!}{n_1! n_2! \cdots n_N!}, \text{ so}$$

$$Z = Q_N = \sum_{\{n_i\}} \delta\left(N - \sum_i n_i\right) \frac{N!}{n_1! n_2! \cdots n_N!} e^{-\beta \sum_i \varepsilon_i n_i}$$

Recall "correct Boltzmann counting"
⇒ remove factor of $N!$

$$\Rightarrow Q_N = \sum_{\{n_i\}} \delta\left(N - \sum_i n_i\right) \prod_i \frac{1}{n_i!} \left(e^{-\beta \epsilon_i}\right)^{n_i}$$

→ Classically we weight state $\{n_i\}$ with $\frac{1}{n_1! n_2! \cdots n_N!}$, but QM weight is 1!

Go to Grand Canonical picture.

$$\Xi = \sum_{N=0}^{\infty} z^N Q_N = \sum_{\{n_i\}} \prod_i \frac{1}{n_i!} \left(z e^{-\beta\epsilon_i}\right)^{n_i}$$

$$= \prod_i \sum_{n_i=0}^{\infty} \frac{1}{n_i!} \left(z e^{-\beta\epsilon_i}\right)^{n_i}$$

$$= \prod_i \operatorname{Exp}\left[z e^{-\beta\epsilon_i}\right] = e^{z \sum_i e^{-\beta\epsilon_i}}$$

$$= e^{z Q_1} \quad ; \; Q_1 = \sum_i e^{-\beta\epsilon_i}$$ is single-particle partition function.

$$\therefore \; \frac{-\Psi}{kT} = \frac{PV}{kT} = \ln \Xi = z Q_1$$

Average Occupation numbers of Bose/Fermi Gas.

$$\langle N \rangle = \frac{1}{\beta}\frac{\partial}{\partial \mu} \ln \Xi = z \frac{\partial \ln \Xi}{\partial z}\Big|_{T,V}$$

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln \Xi \Big|_{z,V} \quad ; \text{Recall } \ln \Xi = \pm \sum_i \ln\left(1 \pm z e^{-\beta \epsilon_i}\right)$$

$$\therefore \langle N \rangle = \pm z \sum_i \frac{\pm e^{-\beta\epsilon_i}}{1 \pm z e^{-\beta\epsilon_i}} = \sum_i \frac{z e^{-\beta\epsilon_i}}{1 \pm z e^{-\beta\epsilon_i}}$$

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

$$\therefore \langle N \rangle = \sum_i \left(\frac{1}{e^{\beta(\epsilon_i - \mu)} \pm 1}\right)$$

$$\langle E \rangle = -\left(\frac{-}{+}\right) \sum_i \frac{(-)(\pm)\, e^{-\beta\epsilon_i} z \epsilon_i}{1 \pm z e^{-\beta\epsilon_i}} = \sum_i \frac{z e^{-\beta\epsilon_i} \epsilon_i}{1 \pm z e^{-\beta\epsilon_i}}$$

$$\therefore \langle E \rangle = \sum_i \frac{\epsilon_i}{e^{\beta(\epsilon_i - \mu)} \pm 1}$$

Recall $N = \sum_i n_i$, $E = \sum_i \epsilon_i n_i$

$$\Rightarrow \langle n_i \rangle = \frac{1}{e^{\beta(\epsilon_i - \mu)} \pm 1} \qquad \begin{array}{l} + \text{ FD} \\ - \text{ BE} \end{array}$$

is the average <u>occupation</u> of each state.

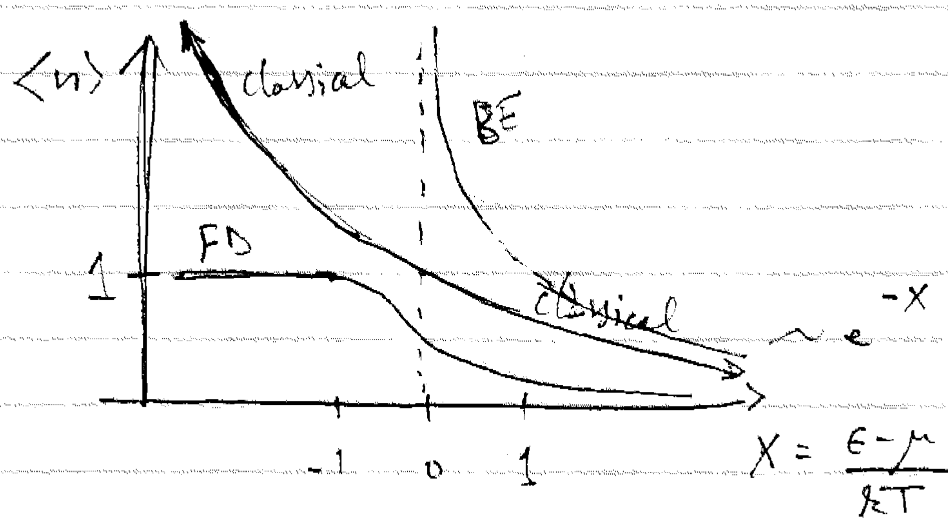
Classically, $\ln \Xi = \sum_i z\, e^{-\beta\epsilon_i}$

$$\therefore \langle N \rangle = z \frac{\partial}{\partial z}\left(\sum_i z e^{-\beta\epsilon_i}\right) = \sum_i z e^{-\beta\epsilon_i}$$

$$\therefore \langle N \rangle = \ln \Xi = \frac{PV}{kT} = N \quad \text{(ideal gas law)}$$

$$\langle E \rangle = -\frac{\partial}{\partial\beta} \sum_i z e^{-\beta\epsilon_i} = z \sum_i \epsilon_i e^{-\beta\epsilon_i}$$

$$\therefore \langle n_i \rangle = e^{-\beta(\epsilon_i - \mu)}$$



$$\langle n \rangle = \frac{1}{e^{\beta(\epsilon-\mu)} \pm 1} \qquad \begin{matrix} + \text{ FD} \\ - \text{ BE} \end{matrix}$$

$$= \frac{1}{e^{x} \pm 1} \rightarrow \begin{cases} \infty & x \to 0 \quad \text{for BE} \\ 1 & x \ll 0 \quad \text{FD} \\ 0 & x \gg 0 \quad \text{FD} \\ \frac{1}{2} & x = 0 \quad \text{FD} \end{cases}$$

Transition in FD is over $|\epsilon - \mu| \sim kT$

Review: Partition Functions

$$\ln \Xi = \pm \sum_i \ln\left(1 \pm e^{-\beta(\epsilon_i - \mu)}\right) \qquad \begin{matrix} +FD \\ -BE \end{matrix}$$

$$= \pm \sum_i \ln\left[1 \pm z\, e^{-\beta\epsilon_i}\right]$$

Classical $\ln \Xi = \sum_i z e^{-\beta\epsilon_i}$

$\ln \Xi_{\text{quant}} \to \ln \Xi_{\text{classical}}$ if $z = e^{\beta\mu} \ll 1$

or $\beta\mu \ll 0$ or T large on energy scales.

$\Rightarrow$ chemical potential is negative in classical limit

Occupation #:

Quant $\langle n_i \rangle = \dfrac{1}{e^{\beta(\epsilon_i - \mu)} \pm 1}$

classical $\langle n_i \rangle = e^{-\beta(\epsilon_i - \mu)}$

$\Rightarrow$ need $\beta(\epsilon_i - \mu) \gg 0$ to get classical limit

N.B. for Bosons $\epsilon_i - \mu \geq 0$ because $\langle n_i \rangle \geq 0$

$\Rightarrow$ $\boxed{\mu \leq \epsilon_{min}}$ for Bosons