We are now ready to compute the Partition function for non-interacting fermions + bosons

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

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

$$= \sum_{\{n_i\}} \delta\left(\sum_i n_i - N\right) e^{-\beta \sum_i \epsilon_i n_i}$$

↑ sum over all $\{n_i\}$, constraint now handled by the δ-function

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

Because of the constraint $\sum_i n_i = N$ it is difficult to carry out the summation. ⇒ go to <u>grand canonical</u> ensemble

$$\mathcal{L}(T,V,z) = \sum_{N=0}^{\infty} z^N Q_N \qquad z^N = z^{\sum n_i} = \prod_i z^{n_i}$$

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

do $\sum_N$ first to eliminate δ-function

$$\mathcal{L} = \sum_{\{n_i\}} \prod_i \left(z e^{-\beta\epsilon_i}\right)^{n_i}$$

↑ unconstrained sum over all sets of occupation numbers

$$\mathcal{L} = \prod_i \left(\sum_n (z e^{-\beta \epsilon_i})^n \right)$$

sum over all possible occupations of state i

product over all single particle eigenstates

For FD, $n = 0, 1$

$$\Rightarrow \sum_{n=0}^{1} (z e^{-\beta \epsilon_i})^n = 1 + z e^{-\beta \epsilon_i}$$

FD $$\boxed{\mathcal{L} = \prod_i (1 + z e^{-\beta \epsilon_i}) = \prod_i (1 + e^{-\beta(\epsilon_i - \mu)})}$$ $z = e^{\beta \mu}$

For BE, $n = 0, 1, 2, \ldots$

$$\Rightarrow \sum_{n=0}^{\infty} (z e^{-\beta \epsilon_i})^n = \frac{1}{1 - z e^{-\beta \epsilon_i}}$$

BE $$\boxed{\mathcal{L} = \prod_i \left(\frac{1}{1 - z e^{-\beta \epsilon_i}} \right) = \prod_i \left(\frac{1}{1 - e^{-\beta(\epsilon_i - \mu)}} \right)}$$

$$-\frac{\Sigma}{k_B T} = \frac{PV}{k_B T} = \ln \mathcal{L} = \sum_i \ln(1 + e^{-\beta(\epsilon_i - \mu)}) \quad \text{FD}$$

$$= -\sum_i \ln(1 - e^{-\beta(\epsilon_i - \mu)}) \quad \text{BE}$$

can combine above expressions as

$$\ln \mathcal{L} = \pm \sum_i \ln(1 \pm e^{-\beta(\epsilon_i - \mu)})$$

where (+) is for FD, (−) is for BE

Compare these to what one has <u>Classically</u>

If single particle states are labeled by energy ϵ_i with

$$E = \sum_i n_i \epsilon_i \qquad n_i = \#\text{ particles in state } i$$

$$N = \sum_i n_i$$

Then if the particles are <u>distinguishable</u>, then for N particles with n_1 in state 1, n_2 in state 2, etc, the number of microstates corresponding to a given set of occupation numbers $\{n_i\}$ would be

$$\frac{N!}{n_1!\, n_2! \cdots} = \#\text{ ways to distribute } N \text{ particles so that } n_i \text{ are in state } i$$

So we would have

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

But we now recall Gibb's correction factor $1/N!$ for <u>indistinguishable</u> particles, to get in this case

$$Q_N = \sum_{\{n_i\}} \delta\left(\sum_i n_i - N\right) \frac{1}{n_1!\, n_2! \cdots} e^{-\beta \sum_i \epsilon_i n_i}$$

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

Grand canonical

no constraint on $\{n_i\}$

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

$\left(z^N = \prod_i z^{n_i}\right)$

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

Classical Gibbs $\boxed{\mathcal{Z} = \prod_i \exp\left[z e^{-\beta\epsilon_i}\right] = \prod_i \exp\left[e^{-\beta(\epsilon_i-\mu)}\right]}$

$$\frac{PV}{k_B T} = \ln \mathcal{Z} = \sum_i e^{-\beta(\epsilon_i - \mu)}$$

$$= z \sum_i e^{-\beta\epsilon_i} = z Q_1$$

1 body canonical partition func $Q_1 = \sum_i e^{-\beta\epsilon_i}$

Note: $\frac{PV}{k_B T} = z Q_1$

also $N = z \frac{\partial}{\partial z} \ln Q = z Q_1$

$\Rightarrow \frac{PV}{k_B T} = N$

$PV = N k_B T$

ideal gas law!

Average Occupation Numbers

$$\langle N \rangle = \frac{1}{\beta}\frac{\partial}{\partial\mu}(\ln \mathcal{Z})_{T,V} = z\left(\frac{\partial \ln \mathcal{Z}}{\partial z}\right)_{T,V}$$

$$\langle E \rangle = -\left(\frac{\partial}{\partial\beta}\ln \mathcal{Z}\right)_{z,V}$$

const z, not const μ

$$\ln \mathcal{Z} = \pm \sum_i \ln(1 \pm z e^{-\beta\epsilon_i}) \qquad \begin{matrix} +\ FD \\ -\ BE \end{matrix}$$

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

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

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

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

Now $N = \sum_i n_i$ so $\langle N \rangle = \sum_i \langle n_i \rangle$

and $E = \sum_i n_i \epsilon_i$ so $\langle E \rangle = \sum_i \epsilon_i \langle n_i \rangle$

comparing with the above we get

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

Classically

$$\ln \mathcal{Z} = \sum_i z e^{-\beta \epsilon_i}$$

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

$$= \ln \mathcal{Z} = \frac{PV}{k_B T}$$

again we get the ideal gas law! $PV = N k_B T$

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

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

__Quantum__: $\ln \mathcal{L} = \pm \sum_i \ln\left(1 \pm e^{-\beta(\epsilon_i - \mu)}\right)$

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

__Classical__ $\ln \mathcal{L} = \sum_i z e^{-\beta \epsilon_i}$

we see that quantum → classical in the limit $\boxed{z \ll 1}$
(then $\ln(1 \pm z e^{-\beta\epsilon_i}) \approx z e^{-\beta \epsilon_i}$)

$$z = e^{\beta\mu} \ll 1 \implies \beta\mu \ll 0$$

__Occupation numbers__

__quantum__ $\langle n_i \rangle = \dfrac{1}{e^{\beta(\epsilon_i - \mu)} \pm 1} \qquad \begin{matrix} + \text{FD} \\ - \text{BE} \end{matrix}$

__classical__

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

we see that quantum → classical for states i such that $e^{\beta(\epsilon_i - \mu)} \gg 1$

$$\Rightarrow \beta(\epsilon_i - \mu) \gg 0 \quad \text{or} \quad \epsilon_i \gg \mu$$

Note: for bosons we need $(\epsilon_i - \mu) > 0$
so that $\langle n \rangle$ always is positive. For free particles where $\epsilon_k = \dfrac{\hbar^2 k^2}{2m}$ and $\epsilon = 0$ is the smallest energy this $\Rightarrow \mu < 0$

<u>Classical</u> non interacting particles

<u>phase space approach</u>

$$\mathcal{L} = \sum_{N=0}^{\infty} z^N Q_N = \sum_{N=0}^{\infty} \frac{(z Q_1)^N}{N!} \qquad Q_N = \frac{Q_1^N}{N!}$$

$$= e^{zQ_1} \quad \Rightarrow \quad \boxed{\ln \mathcal{L} = z Q_1}$$

Q_1 is single particle partition function

where $Q_1 = \int \frac{d^3q \int d^3p}{h^3} e^{-\beta p^2/2m} = \frac{V}{h^3} (2\pi m k_B T)^{3/2}$

define $\lambda = \left(\frac{h^2}{2\pi m k_B T} \right)^{1/2}$ thermal wavelength

$$\Rightarrow \boxed{Q_1 = \frac{V}{\lambda^3}}$$

<u>occupation number approach</u>

$$\mathcal{L} = \sum_{\{n_i\}} z^N \prod_i \left[\frac{1}{n_i!} (e^{-\beta \epsilon_i})^{n_i} \right] = \prod_i \left(\sum_{n_i} \frac{(z e^{-\beta \epsilon_i})^{n_i}}{n_i!} \right)$$

$$= \prod_i e^{(z e^{-\beta \epsilon_i})}$$

$$\ln \mathcal{L} = \sum_i z e^{-\beta \epsilon_i} = z \sum_i e^{-\beta \epsilon_i} = \boxed{z Q_1 = \ln \mathcal{L}}$$

same as in phase space approach

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

For quantized particles in a box, $\vec{p} = \hbar \vec{k}$, where $k_\alpha = \frac{2\pi}{L} n_\alpha \quad \alpha = x, y, z, \; n_\alpha$ integer.

$\Rightarrow \Delta k = \dfrac{2\pi}{L}$ spacing between k vectors

$$\Delta p = \frac{2\pi\hbar}{L} = \frac{h}{L} \quad \text{where } h = 2\pi\hbar \text{ is Planck's constant}$$

$$Q_1 = \sum_i e^{-\beta\epsilon_i} = \sum_{\vec{p}} e^{-\beta p^2/2m} = \frac{1}{(\Delta p)^3}\int d^3p\, e^{-\beta p^2/2m}$$

$$= \left(\frac{L}{h}\right)^3 (2\pi m k_B T)^{3/2} \qquad L^3 = V$$

$$= \frac{V}{h^3}(2\pi m k_B T)^{3/2}$$

$$\boxed{Q_1 = \frac{V}{\lambda^3}} \quad \text{where } \lambda = \left(\frac{h^2}{2\pi m k_B T}\right)^{1/2}$$

exact same result as in phase space method, but here we see that the phase space division h, which classically is arbitrary in the phase space method, should be taken as Planck's constant once we quantize the single particle states.

Validity of classical limit

We saw that the quantum partition functions $\mathcal{L}$ agreed with classical result in the limit $z \ll 1$.

Classically $N = z\left(\dfrac{\partial \ln \mathcal{L}}{\partial z}\right) = z\dfrac{\partial}{\partial z}(zQ_1) = zQ$

so $z = \dfrac{N}{Q_1} = \dfrac{N}{V}\lambda^3 = n\lambda^3$

where $n = \frac{N}{V}$ is the particle density.

We can define $n = 1/\ell^3$ where ℓ is the average spacing between particles. Then

$$z = \left(\frac{\lambda}{\ell}\right)^3$$

and the condition $z \ll 1$ becomes

$$\left(\frac{\lambda}{\ell}\right)^3 \ll 1 \quad \text{or} \quad \ell \gg \lambda$$

Classical limit applies when interparticle spacing is very much larger than thermal wavelength.

Agrees with our earlier calculation of $\langle \vec{r}_1 \vec{r}_2 | \hat{\rho} | \vec{r}_1 \vec{r}_2 \rangle$ where we saw that the effect of quantum statistics on spatial correlations was only significant for distances $r_{12} < \lambda$.

Since $\lambda \sim 1/\sqrt{T}$, as T decreases, λ increases, and quantum effects become more important.

Equivalently, classical results should be OK provided

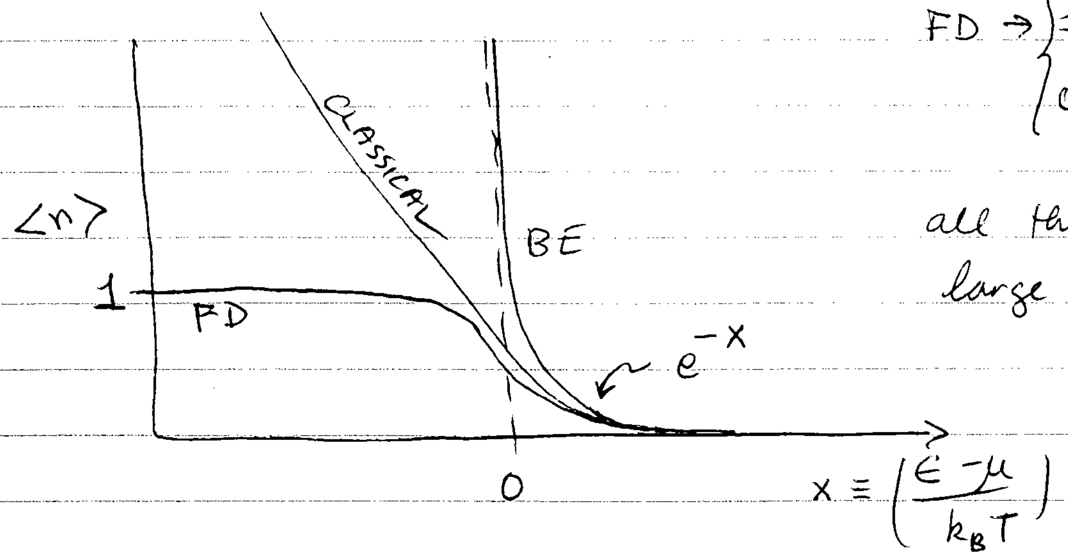
$$\ell \gg \lambda \Rightarrow k_B T \gg \frac{h^2}{2\pi m \ell^2}$$

Classical limit is a low T, or equivalently low density (large ℓ) limit.

BE diverges as $\left(\frac{\epsilon-\mu}{k_B T}\right) \to 0$

FD $\to \begin{cases} 1 & \text{for } \left(\frac{\epsilon-\mu}{k_B T}\right) \ll 0 \\ 0 & \text{for } \left(\frac{\epsilon-\mu}{k_B T}\right) \gg 0 \end{cases}$

all three equal at large $(\epsilon-\mu)/k_B T$



For FD, $\langle n \rangle$ goes from 1 to 0 in an energy width of $O(k_B T)$

Harmonic Oscillator vs boson

Recall for harmonic oscillator $\epsilon_n = \hbar\omega(n+1/2)$

We found

average level excitation

$$\langle n \rangle = \frac{\sum_n e^{-\beta\hbar\omega(n+1/2)}\, n}{\sum_n e^{-\beta\hbar\omega(n+1/2)}} = \frac{\sum_n e^{-\beta\hbar\omega n}\, n}{\sum_n e^{-\beta\hbar\omega n}}$$

$$= \frac{-1}{\hbar\omega}\frac{\frac{\partial}{\partial\beta}\left(\sum_n e^{-\beta\hbar\omega n}\right)}{\sum_n e^{-\beta\hbar\omega n}} = \frac{-1}{\hbar\omega}\frac{\partial}{\partial\beta}\ln\left[\frac{1}{1-e^{-\beta\hbar\omega}}\right]$$

$$= \frac{1}{\hbar\omega}\frac{\partial}{\partial\beta}\ln\left(1-e^{-\beta\hbar\omega}\right)$$

$$= \frac{1}{\hbar\omega}\,\frac{\hbar\omega\, e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} = \frac{1}{e^{\beta\hbar\omega}-1}$$

Looks just like boson occupation number with $\epsilon = \hbar\omega$ and chemical potential $\mu = 0$.

$\Rightarrow$ quantized harmonic oscillators obey same statistics as bosons, with $\mu = 0$

we say that excitation level n of the oscillator is the same as n quanta or n "particles" of excitation.

Applies to: elastic oscillations of a solid $\leftrightarrow$ "phonons"
oscillation of electromagnetic waves $\leftrightarrow$ "photons"

Sound modes in solid

$$\omega = c_s |\vec{k}| \qquad c_s = \text{speed of sound}, \ \vec{k} = \text{wave vector}$$

$$\Rightarrow \text{phonon modes} \quad \langle n_k \rangle = \frac{1}{e^{\beta \hbar c_s k} - 1}$$

electromagnetic waves

$$\omega = c|\vec{k}|, \qquad c = \text{speed of light}, \ \vec{k} = \text{wave vector}$$

$$\text{photon modes} \quad \langle n_k \rangle = \frac{1}{e^{\beta \hbar c k} - 1}$$

Another way to see $\mu = 0$. Phonons and photons are not conserved particles - they can be created and destroyed

Chemical equilibrium

Suppose $n_1 A_1 + n_2 A_2 \leftrightarrow n_3 A_3$
chemical reaction among species A_1, A_2, A_3

What determines equilib concentrations of A_1, A_2, A_3?
Consider total entropy as function of N_1, N_2, N_3
numbers of A_1, A_2, A_3

$S(N_1, N_2, N_3)$ N_i adjust to maximize S

$$dS = 0 = \sum_i \frac{\partial S}{\partial N_i} dN_i = \sum_i -\frac{\mu_i}{T} dN_i$$ (all species in equilib at common T)

Now if ~~2~~ N_3 ~~changes by~~ decreases by $-dN$
Then N_1 and N_2 increase by $\frac{n_1}{n_3} dN$ and $\frac{n_2}{n_3} dN$
respectively.

or if
$$dN_3 = -n_3 dN$$
$$dN_1 = n_1 dN$$
$$dN_2 = n_2 dN$$

So
$$-\frac{\mu_1}{T} dN_1 - \frac{\mu_2}{T} dN_2 - \frac{\mu_3}{T} dN_3 = 0$$

$$\Rightarrow \mu_1 n_1 + \mu_2 n_2 - \mu_3 n_3 = 0$$

$$\boxed{\mu_1 n_1 + \mu_2 n_2 = \mu_3 n_3}$$

atom + photon $\leftrightarrow$ atom

$$\Rightarrow \mu_{atom} + \mu_{photon} = \mu_{atom} \Rightarrow \mu_{photon} = 0$$