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

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

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

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

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

Classically, the state $|n_1, n_2, \ldots\rangle$ which counts with weight 1 in QM, counts with weight $\dfrac{1}{n_1!\,n_2!\cdots}$.

This is because classically, when we divide by $N!$ to avoid over counting, that is really only correct for states in which each particle is at a different point in phase space. If two or more particles were at exact same point in phase space, then we should not correct our counting. This is not important classically since the probability for any two particles to be at the exact same point in the continuous phase space is vanishingly small. But in QM where energy eigenstates can be discrete, this can make a difference. (see Bose condensation)

Grand canonical

$$\mathcal{L} = \sum_{N=0}^{\infty} z^N Q_N = \underbrace{\sum_{\{n_i\}}}_{\text{no constraint on } \{n_i\}} \prod_i \frac{1}{n_i!}\left(z e^{-\beta\epsilon_i}\right)^{n_i}$$

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

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

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

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

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

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

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

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

$PV = N k_B T$

ideal gas law!

Same result as from old approach

$$\mathcal{L} = \sum_N z^N Q_N = \sum_N z^N \frac{Q_1^N}{N!} = e^{z Q_1}$$

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

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

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

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

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

$\Rightarrow$ need negative μ

Occupation numbers

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

classical

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

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

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

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

Classical non interacting particles

phase space approach

$$\mathcal{L} = \sum_{N=0}^{\infty} z^N Q_N = \sum_{N=0}^{\infty} \frac{(zQ_1)^N}{N!} \qquad Q_N = \frac{Q_1^N}{N!}$$

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

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

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

occupation number approach

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

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

$$\ln \mathcal{L} = \sum_i z e^{-\beta\epsilon_i} = z \sum_i e^{-\beta\epsilon_i} = \boxed{zQ_1 = \ln \mathcal{L}}$$

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
$k_\alpha = \frac{2\pi}{L} n_\alpha$ $\alpha = x, y, z$, n_α integer.

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

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

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

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

$L^3 = V$

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

$\boxed{Q_1 = \frac{V}{\lambda^3}}$ 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 <u>phase space division h</u>, which classically is arbitrary in the phase space method, <u>should be taken as Planck's constant</u> once we quantize the single particle states.

<u>Validity of classical limit</u>

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

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

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

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 - for a system with <u>fixed density n</u>.

Equivalently, classical results should be OK provided

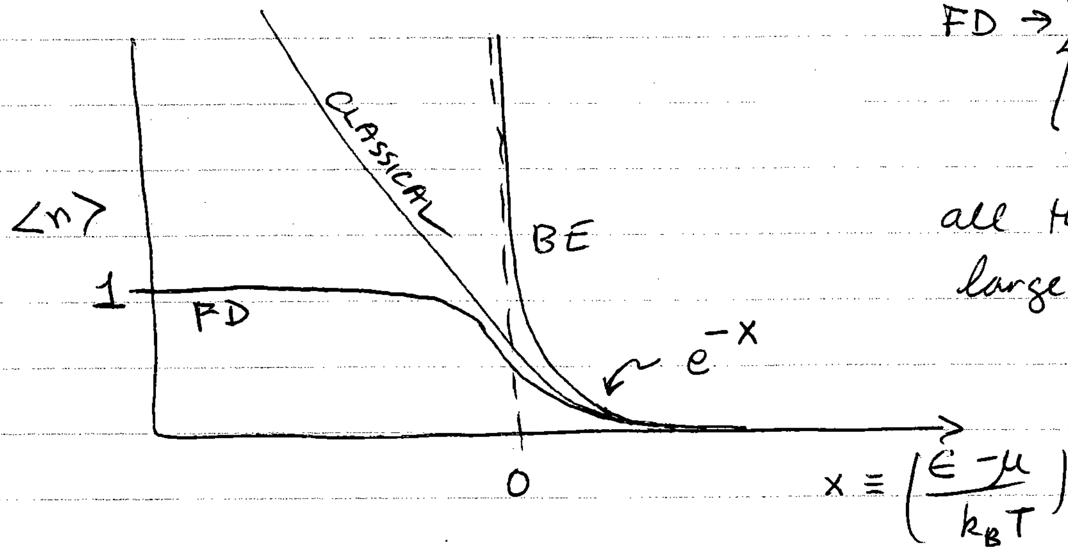
$$\ell \gg \lambda \implies k_B T \gg \frac{h^2}{2\pi m \ell^2}$$

Classical limit is a ~~large~~ 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 $O(k_B T)$

<u>Harmonic Oscillator vs boson</u>

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

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"

<u>Sound modes in solid</u>

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

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

<u>electromagnetic waves</u>

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

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

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

$$e + \gamma \rightarrow e \qquad \text{electron scattered by absorbing a photon}$$

chemical equilib $\Rightarrow \mu_e + \mu_\gamma = \mu_e \rightarrow \mu_\gamma = 0$ chemical pot of photon