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

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

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

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

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

can combine above expressions as

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

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

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

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 for non-interacting classical particles using occupation number represatation

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

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

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

$$= \exp\left[z Q_1\right]$$

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

"i" labels the single particle states

$$\left.\begin{aligned} \frac{pV}{k_BT} &= \ln \mathcal{Z} = z Q_1 \\ N &= z \frac{\partial \ln \mathcal{Z}}{\partial z} = z Q_1 \end{aligned}\right\} \Rightarrow \frac{pV}{k_BT} = N$$

got ideal gas law independent of what the single particle energy values ϵ_i are.

Recall, above is the same result we got from our earlier classical phase space calculation of $\mathcal{Z}$

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

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

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

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

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

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

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

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

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

Classically

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

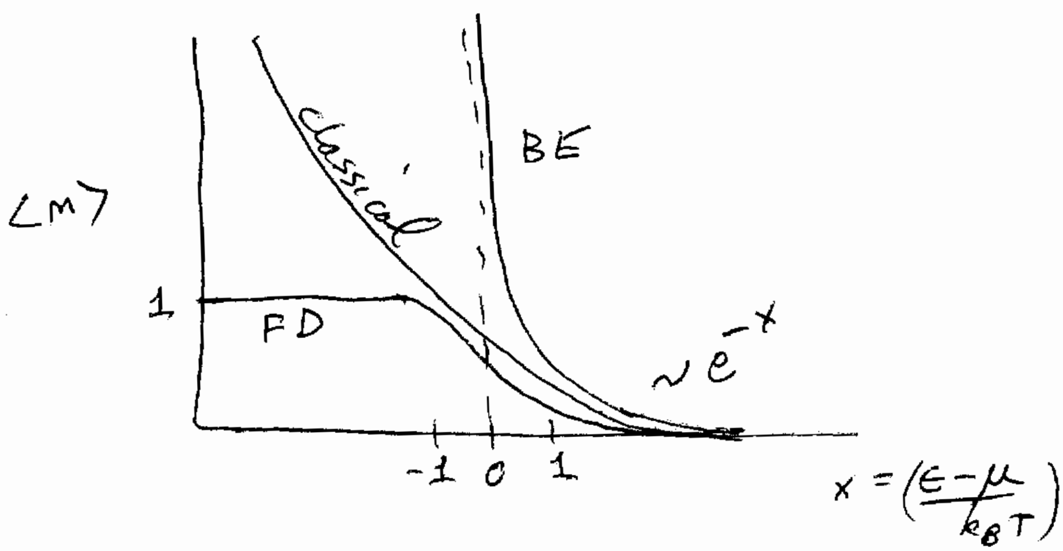
$$\langle N \rangle = z \frac{\partial}{\partial z}\left(\sum_i z e^{-\beta\epsilon_i}\right) = z \sum_i e^{-\beta \epsilon_i} = \sum_i z e^{-\beta\epsilon_i}$$

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

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

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

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



$\langle n \rangle$ for BE diverges as $x \to 0$

$\langle n \rangle$ for FD $\to \begin{cases} 1 & \text{for } x \ll 0 \\ 0 & \text{for } x \gg 0 \end{cases}$

all three expressions for $\langle n \rangle \sim e^{-x}$ at large x

for FD $\langle n(x) \rangle$ goes from 1 to 0 ~~over~~ an interval of order $\sim O(1)$, ie $|\epsilon - \mu| \sim k_B T$

Review – Partition Functions

Quantum $\ln \mathcal{Z} = \pm \sum_i \ln(1 \pm e^{-\beta(\epsilon_i - \mu)})$ $\quad$ + FD, − BE

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

Classical

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

sum "i" is over all single particle energy levels

from above we see that quantum result → classical result in the limit $z \ll 1$, since $\ln(1+\delta) \approx \delta$, when $\delta \ll 1$. $z = e^{\beta\mu} \ll 1 \Rightarrow \beta\mu \ll 0$.
⇒ chemical potential is negative in the classical limit

Occupation numbers

quantum $\langle n_i \rangle = \dfrac{1}{e^{\beta(\epsilon_i - \mu)} \pm 1}$ $\quad$ + FD, − BE

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

we see that quantum → classical for states i such that $e^{\beta(\epsilon_i - \mu)} \gg 1 \Rightarrow \beta(\epsilon_i - \mu) \gg 0$
$\Rightarrow (\epsilon_i - \mu) \gg k_B T$

Note: Since $\langle n_i \rangle$ must always be positive, and for bosons $\langle n_i \rangle = 1/[e^{\beta(\epsilon_i - \mu)} - 1]$ it therefore follows that we must always have $(\epsilon_i - \mu) > 0$ for any state i, for bosons. For free particles the smallest ϵ_i is usually $\epsilon_i = 0$, so we conclude that $\mu < 0$ always must hold for bosons (or $\mu < \epsilon_{min}$)

Comparison of Classical and Quantum Ideal Gas

meaning of the "arbitrary" phase space factor h^3

Classical phase space approach

We had $$\mathcal{L} = \sum_{N=0}^{\infty} z^N Q_N = \sum_{N=0}^{\infty} \frac{(zQ_1)^N}{N!} = e^{zQ_1}$$

$$\ln \mathcal{L} = zQ_1$$

where Q_1 is the single particle partition function for a free particle

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

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

is the thermal wavelength

In above classical calculation, h^3 was an arbitrary phase space factor.

Quantum sum over energy levels in "classical" limit

We now compare the above to the result we get using the occupation number formulation, in which one sums over the single particle energy levels ϵ_i. Since we want to compare to classical limit, we will use the expression we got in the $z \ll 1$ limit ie:

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

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

only now, instead of integrating over continuous phase space, we will sum over the quantized energy levels of a quantum mechanical particle in a box of volume $V = L^3$

Eigenstates of the particle in a box are specified by a quantized wave vector $\vec{k}$

$$\left.\begin{array}{ll}\text{momentum} & \vec{p} = \hbar\vec{k} \\ \text{energy} & \epsilon = \dfrac{\hbar^2 k^2}{2m}\end{array}\right\} \text{ with } k_\alpha = \frac{2\pi}{L} n_\alpha, \quad \alpha = x, y, z$$

n_α integer

integer number of wavelengths must fit in the box

$$Q_1 = \sum_{\vec{k}} e^{-\beta\epsilon(\vec{k})} = \sum_{\vec{k}} e^{-\beta\hbar^2k^2/2m}$$

the spacing between the allowed values of k_α is $\Delta k = \frac{2\pi}{L}$. So we can write

$$Q_1 = \sum_{\vec{k}} e^{-\beta\hbar^2k^2/2m} \simeq \frac{1}{(\Delta k)^3}\int_{-\infty}^{\infty} d^3k\, e^{-\beta\hbar^2k^2/2m}$$

approximating sum by an integral

$$Q_1 = \left(\frac{L}{2\pi}\right)^3 \left(\frac{2\pi m k_B T}{\hbar^2}\right)^{3/2} = V\left(\frac{2\pi m k_B T}{(2\pi\hbar)^2}\right)^{3/2}$$

use $2\pi\hbar = h$ Planck's constant

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

We get exactly the same result as the classical phase space method, provided we identify the classically arbitrary phase space factor h as Planck's constant.

Quantum mechanics $\Rightarrow$ h in classical statistical mechanics should be taken as Planck's constant

Validity of the classical limit

We found that the quantum partition functions $\mathcal{L}$ (for FD or BE) agreed with the classical result in the limit $z \ll 1$. Now we will see the physical meaning of this condition.

Classically: $N = z\left(\frac{\partial \ln \mathcal{L}}{\partial z}\right)_{T,V} = z \frac{\partial}{\partial z}(zQ_1) = zQ_1$

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

where $n = \frac{N}{V}$ is the density of particles

Define $n \equiv 1/l^3$ where l is roughly the average spacing between particles. Then

$z = \left(\frac{\lambda}{l}\right)^3$ and $z \ll 1 \Rightarrow \lambda \ll l$.

Classical results are good approx when thermal wavelength λ is smaller than the typical spacing between particles l.

physical meaning of thermal wave length λ.

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

$$\Rightarrow \hbar^2 k^2 = \frac{h^2}{(2\pi)^2} \cdot (2\pi)^2 \frac{2\pi m k_B T}{h^2} = 2\pi m k_B T$$

$$\frac{\hbar^2 k^2}{2m} = \pi k_B T$$ ~ typical thermal energy of a classical particle at temperature T.

So λ is the de Broglie wavelength of a typical particle taken from a classical Maxwell distribution at temperature T.

$\Rightarrow$ Quantum effects can be ignored, and classical results give a good approximation, when $\lambda \ll \ell$, ie when the quantum de Broglie wavelength of the typical particle is much less than the average spacing between particles.

Since $\lambda \sim 1/\sqrt{T}$, as T decreases λ increases.

$\Rightarrow$ For a gas of fixed density $n = 1/\ell^3$, quantum effects become more important as <u>T decreases</u>.
At fixed T, quantum effects become more important as density n increases (so ℓ decreases).

$\Rightarrow$ Classical limit is a high-T, low density, limit