Grand Canonical for non-interacting classical particles using occupation number representation

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

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

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

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

where $Q_1 = \sum_i e^{-\beta\epsilon_i}$ is single particle partition function
"i" labels the single particle states

$$\frac{pV}{k_BT} = \ln \mathcal{Z} = z Q_1$$

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

$\Rightarrow \frac{pV}{k_BT} = N$

get 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 $\mathcal{Z}$

$$\mathcal{Z} = \sum_N z^N Q_N = \sum_N z^N \frac{Q_1^N}{N!} = e^{zQ_1}$$

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

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

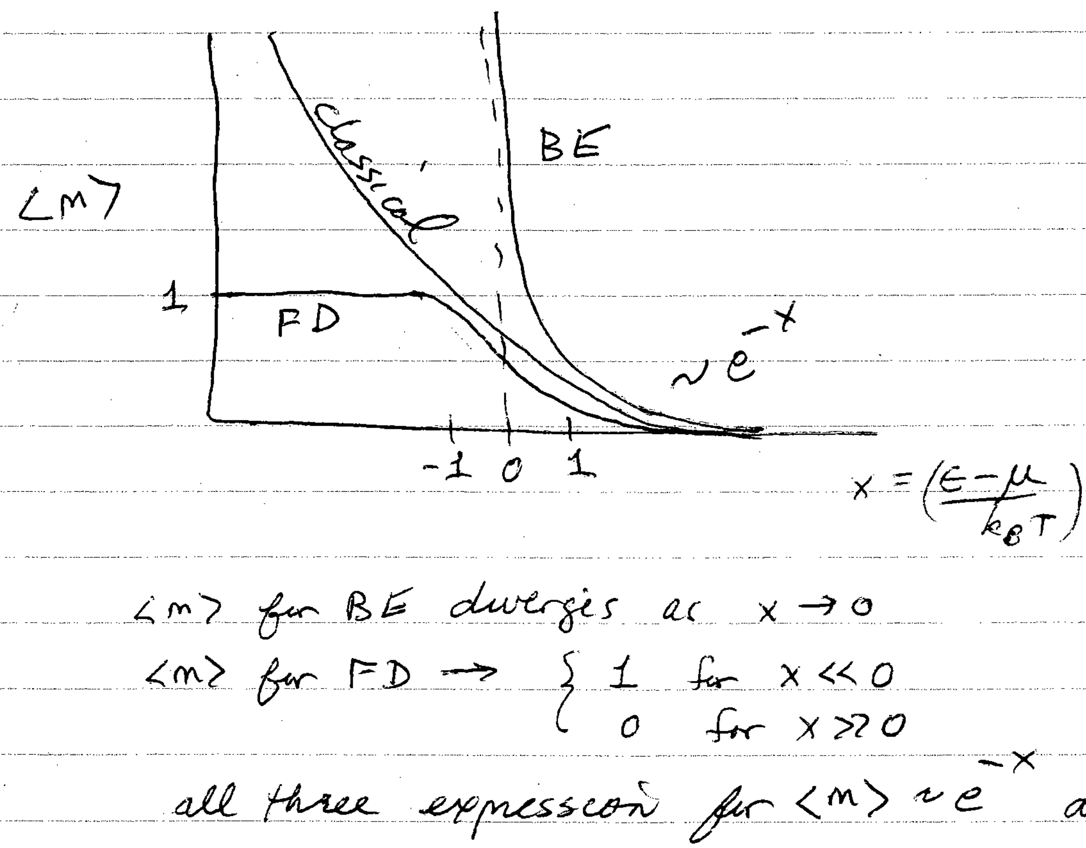
$$\langle N \rangle = z \frac{\partial}{\partial z}\left(\sum_i z e^{-\beta \epsilon_i}\right) = z \sum_i e^{-\beta \epsilon_i} = \sum_i z e^{-\beta \epsilon_i}$$

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

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

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

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



$\langle n \rangle$ 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:

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

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

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 $\vec{k}$

momentum $\vec{p} = \hbar \vec{k}$ } with $k_\alpha = \frac{2\pi}{L} n_\alpha$, $\alpha = x, y, z$
energy $\epsilon = \frac{\hbar^2 k^2}{2m}$ } n_α integer

integer number of wavelengths must fit in the box

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

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

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

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 $\mathcal{Z}$ (for FD or BE) agreeded with the classical result in the limit $z \ll 1$. Now we will see the physical meaning of this condition.

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

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

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

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 $\lambda \ll l$, 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 $n = 1/l^3$, 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

Harmonic Oscillator vs boson

Recall our earlier result for the quantized harmonic oscillator

$$\epsilon_n = \hbar\omega(n+\tfrac{1}{2})$$

We found:

average level of excitation $\rightarrow$

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

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

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

$$\langle n\rangle = \frac{1}{e^{\beta\hbar\omega}-1}$$

Compare to occupation number of a boson of energy ϵ

$$\langle n\rangle = \frac{1}{e^{\beta(\epsilon-\mu)}-1}$$

We see that average level excitation of the harmonic oscillator has exactly the same form as the average ~~number~~ number of bosons with energy $\epsilon = \hbar\omega$, if the boson chemical potential is taken to be $\mu = 0$.

⇒ 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 ⟷ "phonons"
oscillation of electromagnetic waves ⟷ "photons"

<u>Sound modes in solid</u>

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

⇒ phonon modes $\langle n_k \rangle = \dfrac{1}{e^{\beta\hbar c_s k} - 1}$

<u>electromagnetic waves</u>

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

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

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

$e + \gamma \to e$ $\quad$ electron scattered by absorbing a photon

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