\[ L = \prod_i \left( \sum_n (z e^{-\beta E_i})^n \right) \]

sum over all possible occupations of state \( i \)

product over all single particle eigenstates

For FD, \( n = 0, 1 \)

\[ \Rightarrow \sum_{n=0}^\infty (z e^{-\beta E_i})^n = 1 + z e^{-\beta E_i} \]

FD \[ L = \prod_i \left( 1 + z e^{-\beta E_i} \right) = \prod_i \left( 1 + e^{-\beta (E_i - \mu)} \right) \]

\( z = e^{\beta \mu} \)

For BE, \( n = 0, 1, 2, \ldots \)

\[ \Rightarrow \sum_{n=0}^\infty (z e^{-\beta E_i})^n = \frac{1}{1 - z e^{-\beta E_i}} \]

BE \[ L = \prod_i \left( \frac{1}{1 - z e^{-\beta E_i}} \right) = \prod_i \left( \frac{1}{1 - e^{-\beta (E_i - \mu)}} \right) \]

\[ -\frac{\sum}{k_B T} = \frac{PV}{k_B T} = \ln L = \sum_i \ln \left( 1 + e^{-\beta (E_i - \mu)} \right) \quad \text{FD} \]

\[ = -\sum_i \ln \left( 1 - e^{-\beta (E_i - \mu)} \right) \quad \text{BE} \]

can combine above expressions as

\[ \ln L = \pm \sum_i \ln \left( 1 \pm e^{-\beta (E_i - \mu)} \right) \]

where (+) is for FD, (-) is for BE
Compare these to what one has \textit{Classically}.

If single particle states are labeled by energy $E_i$ with

$$E = \sum E_i n_i \quad n_i = \# \text{ particles in state } i$$

$$N = \sum n_i$$

Then if the particles are distinguishable, 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

$$Q_N = \sum_{E_n_i \geq 0} \delta (\sum E_i n_i - N) \frac{N!}{n_1! n_2! \cdots} e^{-\frac{\beta \sum E_i n_i}{\epsilon}}$$

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

$$Q_N = \sum_{E_n_i \geq 0} \delta (\sum E_i n_i - N) \frac{1}{n_1! n_2! \cdots} e^{-\frac{\beta \sum E_i n_i}{\epsilon}}$$

$$= \sum_{E_n_i \geq 0} \delta (\sum E_i n_i - N) \prod_i \left( \frac{1}{n_i!} (e^{-\beta E_i})^{n_i} \right)$$
Classically, the state $|n_1, n_2, \cdots \rangle$
which counts with weight $1$ in QM, counts with weight $\frac{1}{n_1! n_2! \cdots}$.

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 representation:

\[ z = \sum_{N=0}^{\infty} \frac{z^N}{N!} \rho_N = \prod_i \left( z e^{-\beta\varepsilon_i} \right)^{n_i} = \prod_i \left[ \sum_{n=0}^{\infty} \frac{1}{n!} \left( z e^{-\beta\varepsilon_i} \right)^n \right] = \prod_i \exp \left[ z e^{-\beta\varepsilon_i} \right] = \exp \left[ z \sum_i e^{-\beta\varepsilon_i} \right] = \exp \left[ z \Omega_1 \right] \]

where \( \Omega_1 = \sum_i e^{-\beta \varepsilon_i} \) is single particle partition function, "i" labels the single particle states.

\[ \frac{pV}{k_B T} = \ln z = z \Omega_1 \]

\[ N = z - \frac{z \ln z}{z} - z \Omega_1 \]

\[ \Rightarrow \frac{pV}{k_B T} = N \]

Get ideal gas law independent of what the single particle energy values \( \varepsilon_i \) are.

Recall, above is the same result we got from our earlier classical phase space calculation of \( z \):

\[ z = \sum \frac{z^N}{N!} \rho_N = \sum \frac{z^N \Omega_1^N}{N!} = e^{z \Omega_1} \]
Average Occupation Numbers

\[ \langle N \rangle = \frac{1}{Z} \frac{1}{\partial \beta} (\ln Z)_{T,V} = \frac{z}{Z} \left(\frac{2 \ln Z}{z} \right)_{T,V} \]

\[ \langle E \rangle = -\frac{\partial}{\partial \beta} (\ln Z)_{Z,V} \]

\[ \text{const} \ z \text{, not const} \ \mu \]

\[ \ln Z = \pm \sum \ln (1 \pm Z e^{-\beta E_i}) + FD \]

\[ \langle N \rangle = \pm Z \sum \frac{e^{-\beta E_i}}{1 \pm Z e^{-\beta E_i}} = \sum \frac{Ze^{-\beta E_i}}{1 \pm Ze^{-\beta E_i}} \]

\[ \langle N \rangle = \sum \left(\frac{1}{1 \pm Ze^{-\beta E_i}}\right) = \sum \left(\frac{1}{e^{\beta (E_i - \mu)} + 1}\right) \]

\[ \langle E \rangle = \pm \sum \frac{Ze_i e^{-\beta E_i}}{1 \pm Z e^{-\beta E_i}} = \sum \frac{Ze_i e^{-\beta E_i}}{1 \pm Ze^{-\beta E_i}} \]

\[ \langle E \rangle = \sum \left(\frac{E_i}{1 \pm e^{-\beta E_i}}\right) = \sum \frac{E_i}{e^{\beta (E_i - \mu)} + 1} \]

Now \( N = \sum n_i \) so \( \langle N \rangle = \sum \langle n_i \rangle \)

and \( E = \sum n_i E_i \) so \( \langle E \rangle = \frac{\sum E_i \langle n_i \rangle}{z} \)

company with the above we get

\[ \langle n_i \rangle = \frac{1}{e^{\beta (E_i - \mu)} + 1} + FD \]

\[ \text{FD} - BE \]
Classically

\[ \ln Z = \sum_i z e^{-\beta e_i} \]

\[ \langle N \rangle = \frac{\partial}{\partial z} \left( \sum_i z e^{-\beta e_i} \right) = z \sum_i e^{-\beta e_i} = Z z e^{-\beta e} \]

\[ = \ln Z = \frac{PV}{k_B T} \] again we set the ideal gas law! \( PV = Nk_B T \)

\[ \langle E \rangle = -\frac{2}{\beta} \sum_i z e^{-\beta e_i} = \sum_i \epsilon_i z e^{-\beta e_i} \]

\[ \Rightarrow \langle n_i \rangle = z e^{-\beta e_i} = e^{-\beta (\epsilon_i - \mu)} \]

\[ \langle m \rangle \] for BE diverges as \( x \to 0 \)

\[ \langle m \rangle \] for FD \( \to \begin{cases} 1 & \text{for } x << 0 \\ 0 & \text{for } x > 0 \end{cases} \)

all three expression for \( \langle m \rangle = e^{-x} \) at large \( x \)

for FD \( \langle n(x) \rangle \) goes from 1 to 0 over an interval of order \( \sim O(1) \), i.e. \( |\epsilon - \mu| \sim k_B T \)
**Review - Partition Functions**

**Quantum**
\[
\ln Z = \pm \sum_i \ln \left(1 \pm e^{-\beta (E_i - \mu)} \right) + \text{FD} - \beta E
\]

\[
= \pm \sum_i \ln \left(1 \pm z e^{-\beta E_i} \right)
\]

**Classical**
\[
\ln Z = \sum_i z E_i
\]

sum "i" is over all single particle energy levels.

From above, we see that quantum result \(\rightarrow\) classical result

in the limit \(z \ll 1\), since \(\ln(1+z) \approx z\),

when \(z < 1\), \(z e^{-\beta \mu} \ll 1 \Rightarrow \beta \mu \ll 0\).

\(\Rightarrow\) chemical potential is negative in the classical limit.

**Occupation numbers**

**Quantum**
\[
\langle n_i \rangle = \frac{1}{e^{\beta (E_i - \mu)} + 1} + \text{FD} - \beta E
\]

**Classical**
\[
\langle n_i \rangle = e^{-\beta (E_i - \mu)}
\]

We see that quantum \(\rightarrow\) classical for states \(E_i\)

such that \(e^{\beta (E_i - \mu)} \gg 1 \Rightarrow \beta (E_i - \mu) \gg 0\)

\(\Rightarrow (E_i - \mu) \gg k_B T\)

**Note:** Since \(\langle n_i \rangle\) must always be positive, and

for bosons \(\langle n_i \rangle = \sqrt{e^{\beta (E_i - \mu)} - 1}\), it therefore follows that we must always have \((E_i - \mu) > 0\)

for any state \(i\), for bosons. For free particles, the smallest \(E_i\)

is usually \(E_i \approx 0\), so we conclude that \(\mu < 0\)

always must hold for bosons (or \(\mu < \varepsilon_{\text{min}}\)).
Comparison of Classical and Quantum Ideal Gas

meaning of the "arbitrary" phase space factor $\hbar^3$

Classical phase space approach

We had

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

$$ \ln L = zQ_1 $$

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

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

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

where $\lambda = \left(\frac{\hbar^2}{2\pi m k_B T}\right)^{1/2}$

in the thermal wavelength

In above classical calculation, $\hbar^3$ 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 $E_i$.

Since we want to compare to classical limit, we will use the expression we got in the $E \ll 1$

limit $E_i$:

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

$$ \ln L = zQ_1 = z \sum_i e^{-\beta E_i} $$
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 $\mathbf{k}$

momentum $\mathbf{p} = \hbar \mathbf{k}$

energy $\epsilon = \hbar^2 k^2 / 2m$

with $k_\alpha = \frac{2\pi \nu_\alpha}{L}$, $\nu = x, y, z$

integer number of wavelengths must fit in the box

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

the spacing between the allowed values of $\mathbf{k}$ is

$$\Delta k = \frac{2\pi \nu}{L}$$

so we can write

$$Q_1 = \sum_\mathbf{k} e^{-\beta \hbar^2 k^2 / 2m} \approx \frac{1}{(\Delta k)^3} \int_0^{\infty} d^3 k e^{-\beta \hbar^2 k^2 / 2m}$$

approximately sum by an integral

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

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

$$Q_1 = V \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} = \frac{V}{\lambda^3}, \quad \lambda = \left( \frac{h^2}{2\pi m k_B T} \right)^{3/2}$$
We get exactly the same result as the classical phase space method, provided we identify the classically arbitrary phase space factor \(\hbar\) as Planck's constant.

Quantum mechanics \(\Rightarrow \hbar\) in classical statistical mechanics should be taken as Planck's constant.

Validity of the classical limit

We found that the quantum partition functions \(Z\) (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: \(N = Z \frac{Z}{e^{\frac{Z}{2}}/N} = Z \frac{\frac{Z}{2}}{e^{\frac{Z}{2}}} = Z Q_1\)

So \(Z = \frac{N}{Q_1} = \frac{N}{V} \lambda^3 = m \lambda^3\)

where \(M = \frac{N}{V}\) is the density of particles.

Define \(m = \frac{1}{N} \lambda^3\) where \(\lambda\) is roughly the average spacing between particles. Then

\[\lambda = \left(\frac{m}{\lambda}\right)^{\frac{1}{2}}\]

and \(Z \ll 1 \Rightarrow \lambda \ll \lambda\).

Classical results are good approx when thermal wavelength \(\lambda\) is smaller than the typical spacing between particles \(\lambda\).
The physical meaning of thermal wave length $\lambda$:

\[ \lambda = \left( \frac{\hbar^2}{2\pi m k_B T} \right)^{\frac{1}{2}} \Rightarrow \frac{k}{\lambda} = \frac{2\pi}{\hbar} = \frac{2\pi m k_B T}{\hbar^2} \]

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

\[ \frac{\hbar^2}{2m} = \pi k_B T \sim \text{typical thermal energy of a classical particle at temperature } T. \]

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

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

\[ \Rightarrow \text{As } T \text{ decreases, } \lambda \text{ increases. For a gas of fixed density } m = \frac{1}{V}, \text{ quantum effects become more important as } T \text{ decreases. At fixed } T, \text{ quantum effects become more important as density } m \text{ increases (so } \ell \text{ decreases).} \]

\[ \Rightarrow \text{Classical limit is a high-} T, \text{ low-density, limit.} \]