Micro canonical \[ E \text{ fixed} \quad N \text{ fixed} \quad T = \frac{2}{3} E \ln N(e) \]

Canonical \[ E \text{ fluctuates} \quad N \text{ fixed} \]

Grand Canonical \[ E \text{ fluctuates} \quad N \text{ fluctuates} \]

In canonical \[ T \text{ controls } \langle E \rangle \quad \langle E \rangle = -\frac{2}{3} E \ln Z \]

In grand canonical \[ \mu \text{ controls } \langle N \rangle \]

Different Ensembles are equivalent for large \( N \).
Calculations become easier \( \downarrow \)

\( N \) two level systems in canonical ensemble.
All independent \[ Z_N = (Z_i)^N \quad Z_i = e^{+\beta e} + e^{-\beta e} \]

\[ \langle E \rangle = -\frac{2}{3} \ln Z_N = -N \frac{2}{3} \ln 2 = -N E \tanh \beta e \]

Easy.

Micro Canonical Ensemble calculation is much harder!

Basically lose independence of the different two level systems because of constraint \( E_1 + E_2 + \ldots + E_N = \text{Total} \).
Microcanonical vs Canonical for TLS

\[ E = -N \varepsilon \quad N(E) = 1 \]
\[ -N \varepsilon + 2N \varepsilon \quad N(E) = N \]
\[ -N \varepsilon + 4N \varepsilon \quad N(E) = \frac{1}{2} N(N-1) \]

\[ E = -N \varepsilon + 2n \varepsilon \quad N(E) = \binom{N}{n} = \frac{N!}{n!(N-n)!} \]

Canonical \quad \langle E \rangle = -N \varepsilon \tanh \beta \varepsilon \quad \text{(trivial!)}

\[ \frac{1}{T} = \frac{N}{2} \varepsilon \ln n(E) \]
\[ E = -N \varepsilon + 2n \varepsilon = (-N + 2n) \varepsilon \]
\[ n = \left( \frac{E}{\varepsilon} + N \right)^{\frac{1}{2}} \]

\[ \ln N(E) = N \ln n - n \ln n - (N-n) \ln (N-n) \]

\[ \frac{d}{d \varepsilon} \left( \frac{3}{2} \varepsilon \ln n(E) \right) = \frac{d}{d \varepsilon} \left( \frac{n^{\frac{3}{2}}}{e} \right) \]
\[ = \frac{1}{2} \varepsilon \left\{ -\ln n - 1 + \ln (N-n) + 1 \right\} \]
\[ = \frac{1}{2} \varepsilon \ln \left[ \frac{N-n}{n} \right] \]

\[ \frac{3 \varepsilon}{T} = \ln \left( \frac{N-n}{n} \right) \]

\[ \frac{2 \varepsilon}{T} = \frac{N-n}{n} = \frac{2n}{N-n-1} = e^{\beta \varepsilon} \]
\[ \frac{N}{\beta} = 1 + e^{2 \beta \varepsilon} \]
\[ \frac{n}{N} = (1 + e^{2 \beta \varepsilon})^{-1} \]
\[ \frac{1}{2} \left( \frac{E}{\varepsilon} + N \right)^{\frac{1}{2}} = (1 + e^{2 \beta \varepsilon})^{-1} \]
\[ \frac{E}{\varepsilon} + N = 2N(1 + e^{2 \beta \varepsilon})^{-1} \]
Calculations in Microcanonical ensemble were much harder than canonical ensemble because particles shared a constant energy. Thus what particle 1 does affects all the others. There is an "interaction" because of the constraint \( E_1 + E_2 + E_3 + \ldots = E = \text{fixed} \).

Thus we had no simple noninteracting limit where

\[
Z_N = \left( \frac{Z}{10} \right)^{N/\text{Nth power}}
\]

\( Z \) in particles \( \rightarrow \) single particle

We face a similar dilemma with quantum particles because of indistinguishability / Pauli principle.

Working in "grand canonical ensemble" will make things easy again.
Let's understand what the problem is with a simple example. Consider one classical particles in 3 energy levels: $E_1, E_2, E_3$.

Clearly, $Z = e^{-\beta E_1} + e^{-\beta E_2} + e^{-\beta E_3}$

For two classical, distinguishable particles, $A, B$.

We have 9 possible configurations:

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>AB</th>
<th>B</th>
<th>A</th>
<th>B</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_2$</td>
<td></td>
<td>AB</td>
<td>B</td>
<td>A</td>
<td>B</td>
<td>A</td>
</tr>
<tr>
<td>$E_1$</td>
<td>AB</td>
<td>A</td>
<td>B</td>
<td>A</td>
<td>B</td>
<td>B</td>
</tr>
</tbody>
</table>

$Z = e^{-2\beta E_1} + e^{-2\beta E_2} + e^{-2\beta E_3} + 2e^{-\beta (E_1 + E_2)} + \ldots$

$Z = (e^{-\beta E_1} + e^{-\beta E_2} + e^{-\beta E_3})^2$

So we explicitly see we did not ever need to consider a two-particle system but just each single particle individually and multiply $Z_1 \cdot Z_1 = Z_1^2$.
But quantum mechanics (Pauli + indistinguishability)

\[ Z = e^{-\beta E_1} + e^{-\beta E_2} + e^{-\beta E_3} \text{ still } Z \]

**Bosons**

\[ Z = e^{-2\beta E_1} + e^{-2\beta E_2} + e^{-2\beta E_3} + 1 + e^{-\beta(E_1+E_2)} \]

No factor of 2

\[ Z \neq Z^2 - 1 \]

Similar failure for fermions:

\[ Z = e^{-\beta(E_1+E_2)} + e^{-\beta E_3} + e^{-\beta(E_2+E_3)} \]
This problem is solved by removing restriction of fixed particle number. In a way it is similar to

\[ \text{Microcanonical} \rightarrow \text{Canonical} \]

Fixed, shared \( E \) \quad Unshared \( E \)

Temperature instead

\[ \text{Canonical} \rightarrow \text{grad-canonical} \]

Fixed, shared \( N \) \quad Unshared \( N \)

Chemical potential instead

\[ \text{Less familiar!} \]

"Grad potential"

\[ Q = \sum_{N=0}^{\infty} \frac{1}{N!} e^{\beta \mu N} z_N \]

\[ \Rightarrow \quad \text{allow any # of partition functions for } N \text{ particles} \]

For non-interacting particles \( z_N = z_1^N \), so

\[ Q = \sum_{N=0}^{\infty} \frac{1}{N!} e^{\beta \mu N} z_1 = e^{\beta \mu} z_1 \]

Looks awkward \( S = e^{\beta \mu} \) " fugacity"
To understand what \( \mu \) is, let's compute \( <N> \):

\[
<N> = \frac{1}{\Omega} \sum_{N=0}^{\infty} \frac{1}{N!} e^{\beta N} \chi_N^2 N
\]

This is the analog of \( <E> = \sum E_i p_i \):

\[
= \frac{1}{\Omega} \sum_{N=0}^{\infty} \frac{1}{N!} e^{\beta N} \chi_N^2 N = \beta <N>
\]

Consider \( \frac{\partial}{\partial \mu} \ln \Omega = \frac{1}{\Omega} \sum_{N=0}^{\infty} \frac{1}{N!} e^{\beta N} \chi_N^2 N = \beta <N> \)

Thus \( <N> = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln \Omega \) so one practical understanding of \( \mu \) is that it gives the average particle density according to this approximation.

But perhaps more physically, we can see that large \( \mu \) gives large \( \chi_N^2 \) and hence favors having more particles, so \( \mu \) is what allows you to deal the density, in very much the rare way that temperature favors occupying higher energy levels and allows you to deal \( <E> \).
Canonical Ensemble

\[ F = -\frac{1}{\beta} \ln Z \quad \text{Free energy} \]

Grand canonical Ensemble

\[ Z = \beta \mu N \]

\[ N = \frac{\partial Z}{\partial \mu} \]

\[ P = \frac{\partial Z}{\partial V} \quad \text{like} \quad P = -\frac{\partial F}{\partial V} \]

Recall \[ Z = \left( \int d^3p \int d^3r e^{-\beta p^2/2m} \right)^N \]

\[ Z = \sqrt{N} \left( 2\pi m k_B T \right)^{3N/2} \]

\[ F = -\frac{1}{\beta} \ln Z = -N\frac{1}{\beta} \ln V - \frac{3N}{2} \ln \left( 2\pi m k_B T \right) \]

\[ \phi = -\frac{\partial F}{\partial V} = \frac{N}{\beta V} \]

\[ \Rightarrow \quad \phi V = N k_B T \]
Really desire \( z \) to be dimensionless

\[
\sum_{\text{configurations}} e^{-\beta E}
\]

\( \int d^3r \int d^3p \quad \text{exp} \)

Unit of angular momentum

So divide by \( h^3 \)

\[
\lambda = \frac{\lambda^{3N}}{N}
\]

\[
\lambda = \frac{\hbar}{(2\pi m k_B T)^{1/2}} \quad \text{``de Broglie-Bohm'' wavelength}
\]
Ideal gas in GCE

\[ z = e^{\beta V} \]

\[ Q = \sum_{n=0}^{\infty} e^{\beta \mu N} \frac{N!}{N!} = e^{\frac{3}{4} \frac{V}{\lambda_T^3}} \]

\[ \lambda_T = \frac{3}{2 \pi m k_B T} \]

\[ \beta = -\frac{1}{\beta} \ln Q \]

\[ = -k_B T \frac{3}{\lambda_T^3} \frac{V}{(\lambda_T^3)} \]

\[ P = -\frac{\partial E}{\partial V} = +k_B T \frac{3}{\lambda_T^3} \frac{V}{(\lambda_T^3)} \]

\[ \langle N \rangle = -\frac{\partial E}{\partial \mu} = +k_B T \frac{3}{\lambda_T^3} \beta \frac{V}{(\lambda_T^3)} \]

\[ = \beta V P \]

\[ PV = N k_B T \quad \text{Recover ideal gas law!} \]

Also notice

\[ \frac{\langle N \rangle}{V} = \frac{3}{(\lambda_T^3)} \]

\[ \frac{1}{\lambda^3} \quad \lambda = \text{interparticle spacing} \]

\[ 3 = e^{\beta \mu} = \left( \frac{\lambda}{\lambda_T} \right)^3 \quad \text{is large} \]
We had \( \langle N \rangle = 3 \frac{V}{(\lambda_T)^3} \)

\[ 3 = \frac{1}{\lambda_T^3} \langle N \rangle \frac{1}{V} \]

\[ \frac{1}{\lambda_T^3} \quad \lambda_T = \text{interparticle spacing} \]

\[ \lambda_T = \frac{\hbar}{(2\pi m k_B T)^{1/2}} \]

\[ = 6 \times 10^{-34} / \left( \frac{2\pi}{32} \cdot 1.67 \times 10^{-27} \cdot 1.3 \times 10^{-23} \cdot 300 \right)^{1/2} \]

\[ = 1.6 \times 10^{-11} \text{ m} \]

\( \text{In solid} \quad 1 \AA = 10^{-10} \text{ m} \)

\( \text{In an at T=0} \quad 10 \AA \sim 10^{-9} \text{ m} \)

\[ \lambda_T l^3 \sim 10^{-2} \quad \Rightarrow \mu \text{ is large and negative} \]

\[ \epsilon^{\beta \mu} \sim 10^{-2} \]

\( E_i = \frac{P^2}{2m} > 0 \)

\( \mu \sim -4.6 \text{ KBT} \quad \text{Recall} \quad \langle E \rangle = \frac{3}{2} k_B T \)

So \( e^{\beta (\mu - E_i)} < 10^{-2} \)
$g_{\text{solid}} \quad \rho \sim 1 \text{ g/m}^3$

$\sim 1 \text{ g/cm}^3 = \frac{6 \times 10^{23} \text{ atoms}}{18 \text{ g m}} = \frac{10^{23} \text{ atoms}}{3 \text{ cm}^3}$

$\frac{1}{\rho^3} \sim 10^{24/30} \quad \frac{1}{l} \sim 10^{8/3} \quad \frac{1}{cm}$

$\frac{1}{l} \sim 10^{10/3} \quad \frac{1}{m}$

$l \sim 3 \times 10^{-10} \text{ m} \text{ for } \text{H}_2\text{O liquid}$

**Gas**

$PV = N k_B T$

$10^5 \frac{1}{(1.38 \times 10^{-23})(300)} = \frac{N}{V}$

$1 \text{ atm} = \frac{10^5 N}{m^2}$

$\frac{10^{26}}{4} \sim \frac{N}{V} \sim \frac{10^{27}}{40} \frac{1}{m} \sim \frac{10^9}{3}$

$\ell \sim 3 \times 10^{-7} \text{ m}$
Discrete Energy levels $E_1, E_2, \ldots$

Classically

\[
\sum_{N=0}^{\infty} \frac{Z_N e^{\beta \mu N}}{N!} = 1
\]

\[
\begin{array}{ccc}
0 & 1 & 1 \\
1 & (e^{-\beta E_1} + e^{-\beta E_2} + \ldots) & e^{\beta \mu} \frac{1}{2!} \\
2 & \left( e^{-\beta E_1} \right)^2 & e^{2 \beta \mu} \frac{1}{2!}
\end{array}
\]

\[
Q = \sum_{N=0}^{\infty} \frac{Z_N (Z_i)^N}{N!} = e^{\beta Z_i}
\]

With fugacity $Z_i = e^{\beta \mu}$

\[
Z_1 = \sum_{i} e^{-\beta E_i}
\]

\[
\mathcal{Z} = -\frac{1}{\beta} \ln Q = -\frac{1}{\beta} \ln Z_1 = -\frac{1}{\beta} \sum_i e^{\beta (\mu - E_i)}
\]

\[
\langle N \rangle = \sum_i e^{\beta (\mu - E_i)} = \sum_i \eta_i
\]

Small for classical system
GCE fermions

\[ N = Z_N e^{\beta \mu N / N!} \]

0 \quad 1 \quad 1

1 \quad e^{-\beta E_1} + e^{-\beta E_2} + \ldots \quad e^{\beta \mu}

2 \quad e^{-\beta(E_1+E_2)} + e^{-\beta(E_1+E_3)} + e^{-\beta(E_2+E_3)} + \ldots \quad e^{2 \beta \mu}

\[ Q = 1 + e^{\beta (\mu - E_1)} + e^{\beta (\mu - E_2)} + e^{\beta [(\mu - E_1) + (\mu - E_2)]} + \ldots \]

\[ = (1 + e^{\beta (\mu - E_1)}) (1 + e^{\beta (\mu - E_2)}) \ldots = \prod_{i} (1 + e^{\beta (\mu - E_i)}) \]

Clearly, each \( E_i \) can appear only 1 time in product.

\[ \Omega = -\frac{1}{\beta} \ln Q = -k_B T \sum_i \ln (1 + e^{\beta (\mu - E_i)}) \]

\[ \langle N \rangle = -\frac{\partial \Omega}{\partial \mu} = \sum_i \left(1 + e^{\beta (\mu - E_i)}\right)^{-1} e^{\beta (\mu - E_i)} \]

\[ \text{Importance Indep. sum} = \sum_i \frac{1}{e^{\beta (E_i - \mu)} + 1} \]

\[ a \text{ Ni Fermi-Dirac Distribution} \]
GCE Bosons

\[ N \equiv Z_N e^{\beta M N} \]

\[ Z = e^{-\beta E_1} + e^{-\beta (E_1 + E_2)} e^{2 \beta M} + e^{-2 \beta E_2} + \ldots \]

\[ Q = \left( \frac{1 + e^\beta (\mu - E_1)}{1 + e^\beta (\mu - E_2)} \right)^{-1} \]

\[ S = -\frac{1}{\beta} \ln Q = k_B T \sum_i \ln \left( 1 - e^\beta (\mu - E_i) \right) \]

\[ \langle N \rangle = -\frac{\partial S}{\partial \mu} = \sum_i \frac{e^\beta (\mu - E_i)}{1 - e^\beta (\mu - E_i)} = \sum_i \frac{1}{e^\beta (\mu - E_i) - 1} \]

Base Emission distribution