GRAND CANONICAL ENSEMBLE

Calculations in Microcanonical ensemble were much harder than canonical ensemble because particles shared a constant energy. Thus what particle I does affects all the others. There is an "interaction"

because of the constraint $E_1 + E_2 + E_3 + ... = E = \text{fixed}$

Thus we had no simple noninteracting limit where

$$Z_N = Z^{N \rightarrow \infty} \text{N}^{\text{th}} \text{ power}$$

$$\frac{Z}{N \text{ particles}} \text{ single particle}$$

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 particle 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:

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<th>AB</th>
<th>BA</th>
<th>A</th>
<th>B</th>
<th>A</th>
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<tbody>
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<td>$E_3$</td>
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<td>$E_2$</td>
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<td>$E_1$</td>
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$Z = e^{-2\beta E_1} + e^{-2\beta E_2} + e^{-2\beta E_3} + 2e^{-\beta(E_1+E_2)} + \cdots$

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

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)

merges us up!

\[ z_1 = e^{-\beta E_1} + e^{-\beta E_2} + e^{-\beta E_3} \]

still but

**Bosons**

\[ E_3 \]

\[ E_2 \]

\[ E_1 \]

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

\[ \Delta \]

No factor of 2

\[ \neq \ z^2 \neq 1 \]

Similar failure for fermions:

**Fermions**

\[ E_3 \]

\[ E_2 \]

\[ E_1 \]

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

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

**Microcanonical** \( \rightarrow \) **Canonical**

- Fixed, shared \( E \) \( \rightarrow \) Unshared \( E \)
- Temperature instead

**Canonical** \( \rightarrow \) **Graduated canonical**

- Fixed, shared \( N \) \( \rightarrow \) Unshared \( N \)
- Chemical potential instead

Less familiar!

"Graduated potential" \( \rightarrow \) chemical potential

\[
Q = \sum_{N=0}^{\infty} \frac{1}{N!} e^{\beta N} z_N^2
\]

\( z_N \) is the partition function for \( N \) particles

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

\[
Q = \sum_{N=0}^{\infty} \frac{1}{N!} e^{\beta N} z_1^N = e^{\beta z_1^2}
\]

Looks awkward \( \mathcal{Z} = e^{\beta z_1} \) "fugacity"
To understand what $\mu$ is let's compute $\langle N \rangle$

$$\langle N \rangle = Q^{-1} \sum_{N=0}^{\infty} \frac{1}{N!} e^{\beta N} \beta N N$$

This is the analog of $\langle E \rangle = \sum E_i p_i$$ = 2^{-1} \sum E_i e^{-\beta E_i}$

Consider $\frac{2}{3} \mu$ and $\alpha = Q^{-1} \sum_{N=0}^{\infty} \frac{1}{N!} e^{\beta N} \beta N N \alpha = \beta \langle N \rangle$

Thus $\langle N \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln \alpha < \infty$ one practical understanding of $\mu$

Analogy of $\langle E \rangle = -\frac{2}{3} \ln \beta$

But perhaps more physically we can see that

large $\mu$ gives large $e^{\beta N}$ and hence favors

having more particles, so $\mu$ is what allows you to
dial the density, in very much the same way that

temperature favors occupying higher energy levels and allows

you to dial $\langle E \rangle$. 
Canonical Ensemble

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

Grand canonical Ensemble

\[ \mathcal{Z} = -\frac{1}{\beta} \ln \Omega \]

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

\[ P = -\frac{\partial \mathcal{Z}}{\partial V} \]

like \( P = -\frac{\partial F}{\partial V} \)

Recall

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

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

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

\[ \beta = -\frac{\partial F}{\partial V} = \frac{N \frac{1}{\beta}}{V} \]

\[ \Rightarrow PV = Nk_B T \]
Really desire $z$ to be dimensionless

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

\[ \int d^3r \int d^3p \leq \text{unit of angular momentum} \times p \]

So divide by $\hbar^3$

\[ z = \frac{V^N}{\lambda_r^{3N}} \]

\[ \lambda_r = \frac{\hbar}{\sqrt{2\pi mk_B T}} \]

"de Broglie length"
Ideal gas vs. GCE

\[ S = e^\beta \mu \]

\[ Q = \sum_{N=0}^{\infty} e^{\beta \mu N} \frac{Z_N}{N!} = e^{3V/(\Delta T)^3} \]

\[ \Delta = -\frac{1}{\beta} \ln Q = -k_B T \frac{3V}{(\Delta T)^3} \]

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

\[ N = -\frac{\partial S}{\partial \mu} = +k_B T \frac{3\beta V}{(\Delta T)^3} = \beta V P \]

\[ PV = Nk_BT \quad \text{Recover ideal gas law!} \]