GRAND CANONICAL ENSEMBLE

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

$$\underbrace{Z_N}_{N \text{ particles}} = \underbrace{Z_1}_{\text{single particle}}^{N \leftarrow N\text{th power}}$$

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

Working in "grand canonical ensemble" will make things easy again

GCE-2

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

E_3			AB			B	A	B	B
E_2		AB		B	A			A	A
E_1	AB			A	B	A	B		

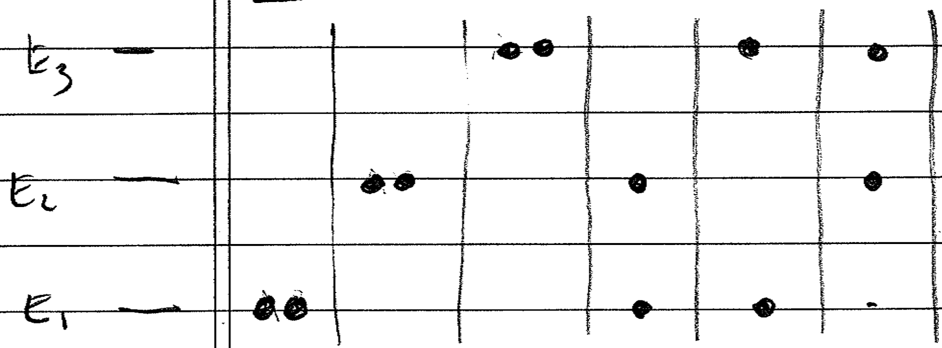
$$Z = e^{-2\beta E_1} + e^{-2\beta E_2} + e^{-2\beta E_3} + 2e^{-\beta(E_1 + E_2)} + \dots$$

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

So we explicitly see we did <u>not</u> 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) messes us up! $Z_1 = e^{-\beta E_1} + e^{-\beta E_2} + e^{-\beta E_3}$ still but

BOSONS

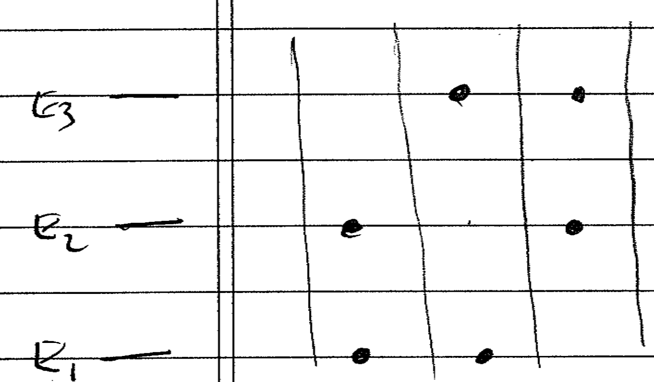


$$Z = e^{-2\beta E_1} + e^{-2\beta E_2} + e^{-2\beta E_3} + 1\, e^{-\beta(E_1+E_2)} + \ldots$$

NO FACTOR OF 2

$$\neq Z_1^2 \; !$$

similar failure for fermions:



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

GCE-4

This problem is solved by removing restriction of fixed particle number. In a way it is similar to

Microcanonical → Canonical

Fixed, shared E → Unshared E, T

Temperature instead

Canonical → grand canonical

Fixed shared N → Unshared N

chemical potential instead

less familiar!

"Grand potential"

chemical potential

$$Q \equiv \sum_{N=0}^{\infty} \frac{1}{N!} e^{\beta \mu N} Z_N$$

allow any # of particles

partition function for N particles

For noninteracting particles $Z_N = Z_1^N$ so

$$Q = \sum_{N=0}^{\infty} \frac{1}{N!} e^{\beta \mu N} Z_1^N = e^{e^{\beta \mu} Z_1} \quad !$$

Looks awkward $\xi \equiv e^{\beta \mu}$ "fugacity"

To understand what μ is let's compute $\langle N \rangle$

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

This is the analog of $\langle E \rangle = \sum E_i p_i$

$$= Z^{-1} \sum E_i e^{-\beta E_i}$$

Consider $\frac{\partial}{\partial \mu} \ln Q = Q^{-1} \sum_{N=0}^{\infty} \frac{1}{N!} e^{\beta \mu N} \beta N Z_N = \beta \langle N \rangle$

Thus $\langle N \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln Q$ ← so one practical understanding of μ is that it gives average particle # according to this eqn

(analog of $\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z$)

But perhaps more physically we can see that large μ gives large $e^{\beta \mu N}$ and hence favors having more particles, so μ 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 $\langle E \rangle$.

GCE-5A

Canonical Ensemble

$$F \equiv -\frac{1}{\beta} \ln Z \qquad \text{Free energy}$$

Grand canonical Ensemble

$$\Omega = -\frac{1}{\beta} \ln Q$$

$$N = -\partial\Omega/\partial\mu$$

$$P = -\partial\Omega/\partial V$$

like $P = -\partial F/\partial V$

Recall

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

$$= V^N (2\pi m k_B T)^{3N/2}$$

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

$$P = -\frac{\partial F}{\partial V} = \frac{N}{\beta}\frac{1}{V}$$

$$\Rightarrow \quad PV = N k_B T$$

GCE-5B

Really desire Z to be dimensionless

$$\sum_{\{\text{configurations}\}} e^{-\beta E}$$

$$\int d^3r \int d^3p \leftarrow \text{units of } \overset{r \times p}{\text{angular momentum}}$$

so divide by h^3

$$Z = V^N / \lambda_T^{3N}$$

$$\lambda_T \equiv h / (2\pi m k_B T)^{1/2}$$ "de Broglie thermal wavelength"

Ideal gas in GCE

$$\xi \equiv e^{\beta\mu}$$

$$Q = \sum_{N=0}^{\infty} e^{\beta\mu N} Z_N \,{}^1/_{N!} = e^{\xi V/(\lambda_T)^3}$$

$$Z_N = (V/\lambda_T^3)^N \qquad \lambda_T = h/(2\pi m k_B T)^{1/2}$$

$$\Omega = -{}^1/_\beta \ln Q$$

$$= -k_B T \,\xi V/(\lambda_T)^3$$

$$P = -\partial\Omega/\partial V = +k_B T \,\xi/(\lambda_T)^3$$

$$N = -\partial\Omega/\partial\mu = +k_B T \,\xi \beta \, V/(\lambda_T)^3$$

$$= \beta V P$$

$PV = Nk_BT$ Recover ideal gas law!