E1

Microcanonical	E fixed	N fixed	$T = \frac{\partial}{\partial E} \ln N(E)$
canonical	E fluctuates	N fixed	
Grand Canonical	E fluctuates	N fluctuates	

In canonical T controls $\langle E \rangle$ $\quad \langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z$

In grand canonical μ controls $\langle N \rangle$

Different Ensembles are equivalent for large N.

Calculations become easier ↓

N two level systems in canonical ensemble.

All independent $\quad Z_N = (Z_1)^N \quad\quad Z_1 = e^{+\beta\epsilon} + e^{-\beta\epsilon}$

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z_N = -N \frac{\partial}{\partial \beta} \ln Z_1 = -N\epsilon \tanh \beta\epsilon.$$

Easy!

Micro Canonical Ensemble calculation is much harder!

Basically lose independence of the different two level systems because of constraint $E_1 + E_2 + \dots E_N = E_{TOTAL}$.

E2 //

Microcanonical vs Canonical for TLS

ϵ —
$-\epsilon$ —

$E = -N\epsilon \qquad N(E) = 1$

$-N\epsilon + 2\epsilon \qquad N(E) = N$

$-N\epsilon + 4\epsilon \qquad N(E) = \tfrac{1}{2} N(N-1)$

$$E = -N\epsilon + 2n\epsilon \qquad N(E) = \binom{N}{n} = N!/n!\,(N-n)!$$

Canonical $\qquad \langle E\rangle = -N\epsilon \tanh\beta\epsilon$ (trivial!)

$1/T \equiv \partial/\partial E \ \ln N(E) \qquad E = -N\epsilon + 2n\epsilon = (-N+2n)\epsilon$

$$n = \left(\frac{E}{\epsilon} + N\right)\frac{1}{2}$$

$$\ln N(E) = N\ln N - n\ln n - (N-n)\ln(N-n)$$

$$\frac{\partial}{\partial E}\ln N(E) = \frac{\partial n}{\partial E}\frac{\partial}{\partial n}\ln N$$

$$= \frac{1}{2\epsilon}\left\{-\ln n - 1 + \ln(N-n) + 1\right\}$$

$$= \frac{1}{2\epsilon}\ln\left[\frac{N-n}{n}\right]$$

$$\frac{2\epsilon}{T} = \ln\left(\frac{N-n}{n}\right)$$

$$e^{2\epsilon/T} = \frac{N-n}{n} = \frac{N}{n} - 1 = e^{2\beta\epsilon}$$

$$\frac{N}{n} = 1 + e^{2\beta\epsilon}$$

$$\frac{n}{N} = (1+e^{2\beta\epsilon})^{-1}$$

$$\frac{1}{2}\left(\frac{E}{\epsilon} + N\right)\frac{1}{N} = (1+e^{2\beta\epsilon})^{-1}$$

$$\frac{E}{\epsilon} + N = 2N(1+e^{2\beta\epsilon})^{-1}$$

$$\frac{E}{\epsilon} = N\left(\frac{2}{1+e^{2\beta\epsilon}} - 1\right)$$

$$= N\,\frac{2-1-e^{2\beta\epsilon}}{1+e^{2\beta\epsilon}}$$

$$= N\,\frac{1-e^{2\beta\epsilon}}{1+e^{2\beta\epsilon}}$$

$$\frac{E}{\epsilon} = -N\tanh\beta\epsilon \quad \checkmark\checkmark$$

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		

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

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

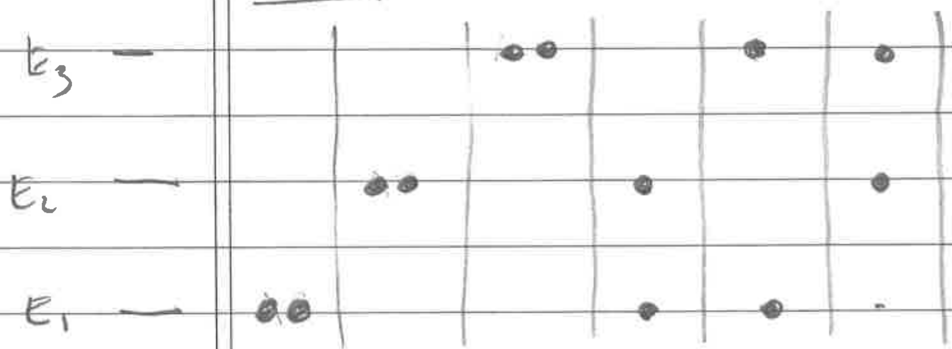
So we explicitly see we did <u>not</u> ever need to consider a two particle system but just each single particle individually and multiply $Z_1 \cdot Z_1 = Z_1^2$

GCE-3

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

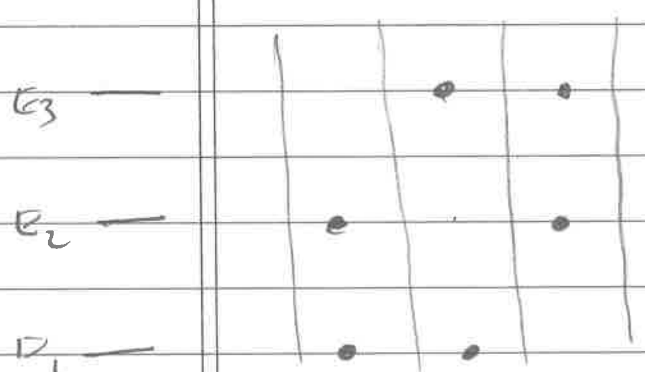


$$Z = e^{-2\beta E_1} + e^{-2\beta E_2} + e^{-2\beta E_3} + 1\, e^{-\beta(E_1+E_2)} + \ldots$$

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 $\longrightarrow$ Canonical
Fixed, shared E $\quad$ Unshared E, Temperature instead

Canonical $\longrightarrow$ grandcanonical
Fixed shared N $\quad$ Unshared N
chemical potential instead

less familiar !

"Grand potential"

chemical potential

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

allow any # of particles

partition function for N particles

For noninteracting particles $Z_N = Z_1^N$ so

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

Looks awkward $\quad \mathfrak{z} \equiv e^{\beta\mu}$ "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

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

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

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

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

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

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

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

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

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

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"

GCE - 6

Ideal gas in GCE

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

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

$$\lambda_T = h/(2\pi m k_B T)^{1/2}$$

$$\Omega = -1/\beta \ln Q$$

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

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

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

$$= \beta V P$$

$$PV = N k_B T$$ Recover ideal gas law!

Also notice $\underbrace{\langle N \rangle / V}_{1/\ell^3} = \xi/(\lambda_T)^3$

ℓ = interparticle spacing

$$\xi = e^{\beta\mu} = \left(\ell/\lambda_T\right)^3$$ is <u>large</u>

9CE 6A

We had $\langle N \rangle = \mathfrak{z}\, V/(\lambda_T)^3$

$$\mathfrak{z} = \lambda_T^3 \langle N \rangle / V$$

$1/\ell^3$ $\quad \ell$ = interparticle spacing

$$\lambda_T = h/(2\pi m k_B T)^{1/2}$$

$$= 6\cdot 10^{-34} / (2\pi\ 32\ 1.67\cdot 10^{-27}\ 1.38\cdot 10^{-23}\ 300)^{1/2}$$

O_2 molecules

$$= 1.6\cdot 10^{-11}\ m$$

ℓ in solid $\sim 1 \text{Å} = 10^{-10}\ m$

ℓ in air at STP $\sim 10 \text{Å} \sim 10^{-9}\ m$

$\lambda_T / \ell \sim 10^{-2}$ $\Rightarrow \mu$ is large and negative

$e^{\beta\mu} \sim 10^{-2}$

$E_i = p^2/2m \geq 0$

$\mu \sim -4.6\ k_B T$ $\qquad$ Recall $\langle E \rangle = 3/2\ k_B T$

so $e^{\beta(\mu - E_i)} < 10^{-2}$

9CE6B

H_2O liquid

Solid $\quad \rho \sim 1\ gm/cm^3$

$$\sim 1\ gm/cm^3 \ \frac{6 \cdot 10^{23}\ \text{atoms}}{18\ gm} = \frac{10^{23}}{3}\ \frac{\text{atoms}}{cm^3}$$

$$1/\ell^3 \sim 10^{24}/30 \qquad 1/\ell \sim 10^8/3\ \ 1/cm$$

$$1/\ell \sim 10^{10}/3\ \ 1/m$$

$\ell \sim 3 \cdot 10^{-10}\ m$ for H_2O liquid

gas $\quad PV = N k_B T$

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

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

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

$\ell \sim 3 \cdot 10^{-9}\ m$

GCE-7

Discrete Energy levels $E_1, E_2, \ldots$

Classically

N	Z_N	$e^{+\beta\mu N}$	$1/N!$
0	1	1	1
1	$(e^{-\beta E_1} + e^{-\beta E_2} + \ldots)$	$e^{+\beta\mu}$	1
2	$(\quad\downarrow\quad)^2$	$e^{2\beta\mu}$	$1/2!$

$$Q = \sum_{N=0}^{\infty} \xi^N (z_1)^N \, 1/N! = e^{\xi z_1}$$

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

$$z_1 \equiv \sum_i e^{-\beta E_i}$$

$$\Omega = -1/\beta \ln Q = -1/\beta \, \xi z_1 = -1/\beta \sum_i e^{\beta(\mu - E_i)}$$

$$\langle N \rangle = 1/\beta \, \partial/\partial\mu \ln Q = -\partial\Omega/\partial\mu$$

$$= \sum_i e^{\beta(\mu - E_i)} = \sum n_i$$

small for classical system

GCE 8

GCE fermions

N	Z_N	$e^{\beta\mu N}$ $\cancel{1/N!}$ No!
0	1	1
1	$e^{-\beta E_1} + e^{-\beta E_2} + \ldots$	$e^{\beta\mu}$
2	$e^{-\beta(E_1+E_2)} + e^{-\beta(E_1+E_3)} + \ldots$	$e^{2\beta\mu}$

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

$$= \left(1 + e^{\beta(\mu-E_1)}\right)\left(1 + e^{\beta(\mu-E_2)}\right)\ldots = \prod_i \left(1 + e^{\beta(\mu-E_i)}\right)$$

clearly each E_i can appear only 1 time in product.

$$\Omega = -1/\beta \ln Q = -k_B T \sum_i \ln\left(1 + e^{\beta(\mu-E_i)}\right)$$

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

IMPT: Indep sum!

$$= \sum_i \frac{1}{e^{\beta(E_i-\mu)}+1}$$

n_i Fermi-Dirac Distribution!

GCE 9

QCE BOSONS

N	Z_N	$e^{\beta\mu N}$	$\cancel{1/N!}$ NO!
0	1	1	
1	$e^{-\beta E_1} + e^{-\beta E_2} + \ldots$	$e^{\beta\mu}$	
2	$e^{-2\beta E_1} + e^{-\beta(E_1+E_2)} + e^{-2\beta E_2} + \ldots$	$e^{2\beta\mu}$	

$$Q = \left(1 + e^{\beta(\mu - E_1)} + e^{2\beta(\mu - E_1)} + \ldots\right)$$

$$\left(1 + e^{\beta(\mu - E_2)} + e^{2\beta(\mu - E_2)} + \ldots\right) \ldots$$

$$= \prod_i \left(1 - e^{\beta(\mu - E_i)}\right)^{-1}$$

Signs differ from FERMIONS

$$\Omega = -\tfrac{1}{\beta} \ln Q = +k_B T \sum_i \ln\left(1 - e^{\beta(\mu - E_i)}\right)$$

Signs differ from FERMIONS

$$\langle N \rangle = -\frac{\partial \Omega}{\partial \mu} = \sum_i \frac{e^{\beta(\mu - E_i)}}{1 - e^{\beta(\mu - E_i)}} = \sum_i \frac{1}{e^{\beta(E_i - \mu)} - 1}$$

Bose Einstein distribution