STATISTICAL MECHANICS

Mean value $\bar{u} = \dfrac{u_1 + u_2 + \cdots + u_5}{5}$

$$\bar{u} = \sum_{i=1}^{N} P_i(u_i)\, u_i$$

$\sum_{i=1}^{N} P_i = 1 \longrightarrow$ Normalisation

$\rightarrow \overline{(u_i - \bar{u})} = \bar{u} - \bar{U} = 0$

$\rightarrow \overline{(u_i - \bar{u})^2} = u_i^2 + \bar{u}^2 - 2u_i\bar{u}$

$$= \bar{u}^2 + \bar{u}^2 - 2\bar{u}^2$$

$$= \overline{u^2} - \bar{u}^2 > 0$$ (Dispersion of u)

→ Ensemble

→ A collection of equivalent states.

$$P(u_i) \rightarrow P(x)$$

$$P_x(x)dx \rightarrow x \;\; dx + dx$$

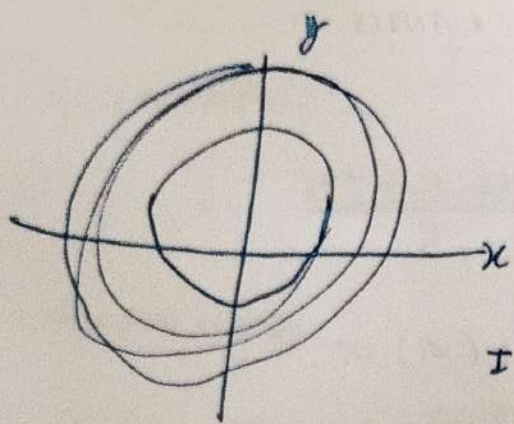
Gaussian Integral

$$I = \int_{-\infty}^{\infty} e^{-ax^2} dx$$

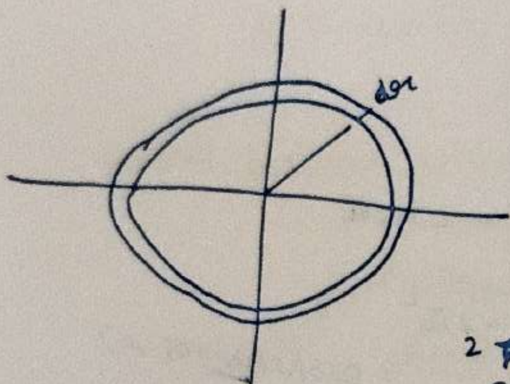
$$I^2 = \int_{-\infty}^{\infty} e^{-ax^2} dx \int_{-\infty}^{\infty} e^{-ay^2} dy$$

$$I^2 = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-a(x^2+y^2)} dx\, dy$$

$x \quad y$



$$I^2 = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-a(x^2+y^2)}\,dx\,dy$$



Polar coordinates

$x = r\cos\theta$

$y = r\sin\theta$, $x^2+y^2=r^2$

$$= \int_{\theta=0}^{2\pi}\int_{r=0}^{\infty} e^{-ar^2}\, r\,dr\,d\theta$$

$$\cancel{= 2\pi \int_0^{\infty} e^{-at}\,dt}$$

$$\Rightarrow 2\pi \int_0^{\infty} e^{-ar^2}\, r\,dr$$

$$I^2 = \frac{\pi}{a}$$

$$I = \sqrt{\frac{\pi}{a}}$$

L-7

D. TONG : cambridge univ

F. Ref

$$P(x)dx = \frac{1}{\sqrt{2\pi}\,\sigma} e^{-\frac{(x-\mu)^2}{2\sigma^2}} dx$$

$\sigma, \mu \to$ constant parameters

$$\int_{-\infty}^{\infty} P(x)dx = 1.$$

$$\overline{(x-\mu)} = \frac{1}{2\pi\sigma}\int_{-\infty}^{+\infty}(x-\mu)\, e^{-\frac{(x-\mu)^2}{2\sigma^2}} dx$$

odd f^n

$$\overline{(x-\mu)} = 0$$

$$\bar{x} - \mu = 0$$

$$\boxed{\Rightarrow \bar{x} = \mu}$$

$$\overline{(x-\mu)^2} = \frac{1}{2\pi\sigma}\int_{-\infty}^{\infty}(x-\mu)^2 e^{-\frac{(x-\mu)^2}{2\sigma^2}} dx$$

$a = \frac{1}{2\sigma^2}$

$$= \frac{1}{2\pi\sigma}\int_{-\infty}^{\infty}(x-\mu)^2 e^{-a(x-\mu)^2} dx$$

$$= \frac{\cancel{1}}{\cancel{2}} \frac{\partial}{\partial a} \underbrace{\int_{-\infty}^{\infty} e^{-a(x-\mu)^2} dx}$$

$\left\{ \frac{\partial}{\partial a}(e^{ax}) = x e^{ax} \right\}$

a & x are ind^{nt}.

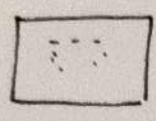
$$= \frac{\cancel{1}}{\cancel{a}} \frac{\partial}{\partial a}\left(\sqrt{\frac{\pi}{a}}\right)$$

$$\boxed{\overline{(x-\mu)^2} = \sigma^2}$$

Postulates of stats
Phase space
Accessible space
Ω
Thermal eq^m

STATISTICAL Postulates:
Prob of a particular micro state is same for all such ~~state~~ states.

Accessible states:

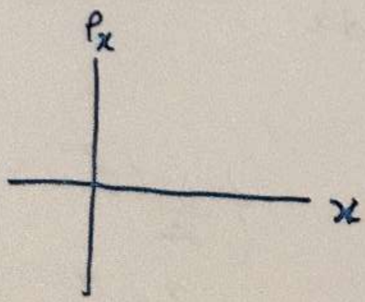


Spin $\frac{1}{2}$ particle

+ ↑ ↕ H
− ↓

				energy = −H of a spin
+	+	+	3	−3H
+	−	+	2	−H
+	+	−	1	+H
−	+	+		
				3H
−	−	+		
−	+	−		
+	−	−		
−	−	−		

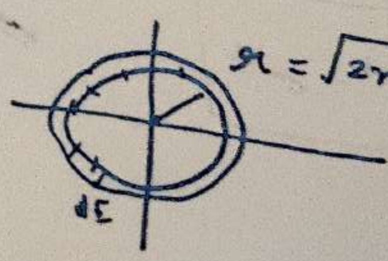
Phase space



1 particle in 1-dim^n

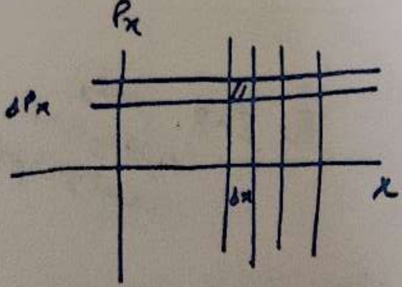
$$p_x = m\frac{dq}{dt} = m\dot{x}$$

$$E = \frac{m}{2}(\dot{x}^2 + \dot{y}^2)$$
$$= \frac{p_x^2}{2m} + \frac{p_y^2}{2m}$$



$r = \sqrt{2mE}$

E, E+dE



$\delta x \, \delta p_x = h_0$

in quantum mechanics

$dx \, \delta p_x$ = Planck's constant

N - no of particles in 3 dim state

6N - phase space. $\left[\begin{array}{l} 3(x, y, z) \\ 3(p_x, p_y, p_z) \end{array} \right.$

$m\ddot{x} = -Kx$

$x = A \cos(\omega t + \phi)$

$\omega^2 m = K$

$\boxed{\omega = \sqrt{\frac{K}{m}}}$

$p_x = m\dot{x}$

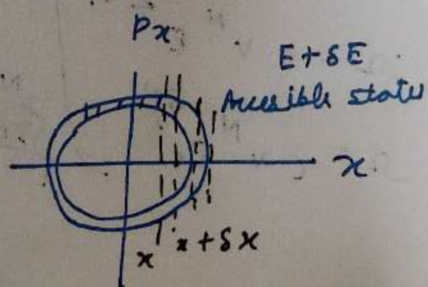
$= -mA\omega \sin(\omega t + \phi)$

$E = \frac{1}{2} m\dot{x}^2 + \frac{1}{2} K x^2$

$= \frac{p_x^2}{2m} + \frac{1}{2} K x^2$

$1 = \frac{p_x^2}{2mE} + \frac{1}{2}\frac{Kx^2}{E}$

$1 = \frac{p_x^2}{2mE} + \frac{x^2}{\frac{2E}{K}}$



Accessible state $\Omega(E)$

ideal gas

N molecules

$$E = \sum_{i=1}^{N} \frac{1}{2} m \dot{x}_i^2 = \sum_{i=1}^{N} \frac{p_i^2}{2m}$$

$E = \sum_i KE_i$ only as they are ideal gas particles

$\Omega(E)$ having Energy b/w E & $E + \delta E$.

$$\Omega \sim \iiint_{E}^{(E+\delta E)} (dx_1\, dy_1\, dz_1)(dx_2\, dy_2\, dz_2) \ldots \ldots (dx_n, dy_n, dz_n) \to x$$

$(dx_i\, dy_i\, dz_i = V)$

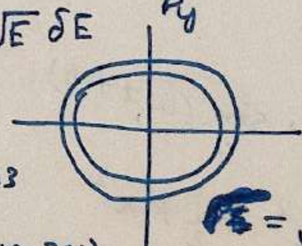
$$(dp_{x_1}, dp_y, dp_{z_1}) \ldots \ldots (\quad)_N \to p_x$$

$$\left[\begin{array}{l} \Omega \sim V^N \cdot E^{\frac{3N}{2}-1} \\ \Omega = C\, V^N E^{\frac{3N}{2}-1} \\ \Omega = C\, V^N E^{\frac{3N}{2}} \end{array}\right]$$

$N \sim 10^{23}$

$\left\{\frac{3N}{2} - 1 \sim \frac{3N}{2}\right\}$

$2\pi\sqrt{E}\,\delta E$



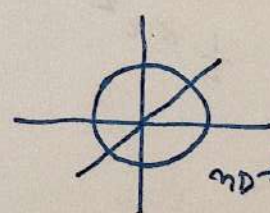
E, $E + \delta E$

$= \sqrt{p_x^2 + p_y^2} = \sqrt{E}$

2D $\sim r$

3D $\sim r^2$

$\vdots$

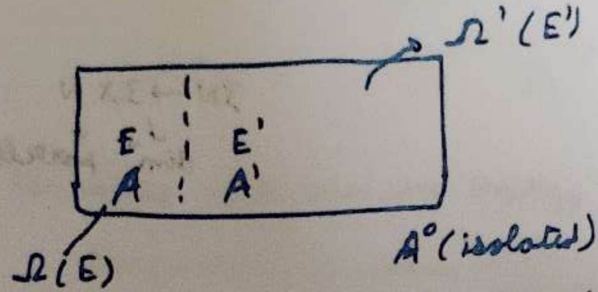


nD $\to r^{n-1}$ of momentum shell

$\to$ Ω for ideal gas (N-particles) with energy b/w E & $E + \delta E$.

$\sqrt{E} = \sqrt{p_x^2 + p_y^2 + p_z^2}$

Ω is very rapidly varying function of V & E.



No of states of total system s.t. A has energy E

$A^\circ = A + A'$

$E^\circ = \text{constant} = E + E'$

$$\Omega^\circ(E) = \Omega(E)\,\Omega'(E')$$

$$= \Omega(E)\,\Omega'(E_\circ - E)$$

$$\ln \Omega^\circ(E) = \ln \Omega(E) + \ln \Omega'(E')$$

$$\frac{d}{dE}\ln \Omega^\circ(E) = \frac{d}{dE}\ln(\Omega E) + \frac{d}{dE}\ln \Omega'(E')$$

$$0 = \frac{d\Omega(E)}{dE} + \frac{d\Omega'(E')}{dE'}\left(\frac{dE'}{dE}\right)$$

$$\left\{ E^\circ(\text{const}) = E + E' \Rightarrow \frac{dE'}{dE} = -1 \right\}$$

$$0 = \frac{d\Omega(E)}{dE} - \frac{d\Omega'(E')}{dE'}$$

$$\beta = \frac{d(\Omega(E))}{dE}\Big|_{\bar{E}}$$

$$\beta(E) = \frac{d\Omega(E)}{dE}\Big|_{\bar{E}} = \frac{d\Omega'(E')}{dE'}\Big|_{\bar{E}'}$$

$$\beta(E) = \frac{1}{kT}\Big|$$

$$\beta(E) = \beta'(E')$$

$$T = T'$$

k → boltzmann const.

$\boxed{S = k\ln\Omega}$ → definition of entropy

$$k\beta = k\frac{d\ln\Omega}{dE} = \frac{d\,k\ln\Omega}{dE} = \frac{dS}{dE}$$

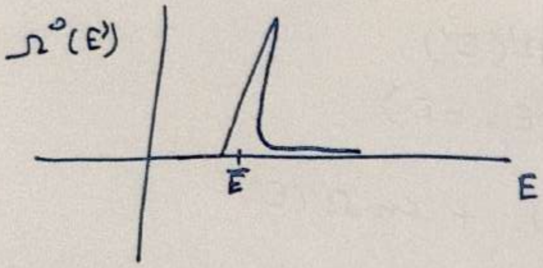
$$\frac{k}{kT} = \frac{\partial S}{\partial E}$$

$$\frac{\partial S}{\partial E} = \frac{1}{T}$$

$$\frac{\partial S}{\partial E} = \frac{1}{T}$$

$$3N \to \underbrace{3}_{\text{dim}^n} \times \underbrace{N}_{\text{particles}}$$

$$\Omega^{0}(E) = \Omega(E)\,\Omega'(E^{0} - E)$$



$$\ln \Omega \sim N \ln V + \frac{3N}{2} \ln E$$

L-8

$\frac{E}{N} = \frac{3}{2} kT$

$\ln\Omega \sim N\ln V + \frac{3}{2} N \ln E$

$\frac{\partial \ln\Omega}{\partial E} = \frac{1}{kT} = \beta \Rightarrow \frac{3}{2} N \frac{1}{E} = \frac{1}{kT}$

$\frac{E}{N} = \frac{3}{2} kT$

Per degree of freedom avg energy $\sim \frac{1}{2} kT$

Equipartition Theorem

$E' = E^{\circ} - E$

$$\ln(\Omega^{\circ}(E)) = \ln\Omega(E) \cdot \ln\Omega(E')$$

Expand $\ln\Omega(E)$ about $\bar{E}$.

$$\ln\Omega(E) = \ln\Omega(\bar{E}) + \left.\frac{\partial \ln\Omega}{\partial E}\right|_{E}(E-\bar{E})$$

(Taylor's)

$$+ \frac{1}{2}\left.\frac{\partial^2 \ln\Omega}{\partial E^2}\right|_{E}(E-\bar{E})^2 + \dots$$

$$\left\{\frac{\partial^2 \ln\Omega}{\partial E^2} = -\frac{3N}{2E^2}\right\}\left[-\frac{\partial^2 \ln\Omega}{\partial E^2} = \lambda\right]$$

$$\ln\Omega(E) = \ln\Omega(\bar{E}) + \beta(E)\eta - \lambda(\bar{E})\eta^2$$

$$\ln\Omega'(E') = \ln(\bar{E}') + \beta'(\bar{E}')\eta' - \lambda'(\bar{E}')\eta'^2$$

$[E' - \bar{E}' = \eta']$ $\quad E \to E'$

$$\left\{\begin{array}{l} E^{\circ} - E - (E^{\circ} - \bar{E}) = \eta' \\ -(E^{\circ} - \bar{E}) = \eta' \end{array}\right\} \quad \eta = -\eta'$$

$$\ln\Omega'(E') = \ln(\bar{E}') - \beta'(E')\eta' - \frac{1}{2}\lambda'(\bar{E}')\eta^2$$

$$\ln(\Omega\Omega') = \ln(\Omega E)\Omega'(\bar{E}') + (\beta_E - \beta'_E)\eta - \frac{1}{2}(\lambda + \lambda')\eta^2$$

$$\ln \frac{\Omega \Omega'}{\Omega(E)\Omega'(E')} = -\frac{1}{2} \lambda^2 \eta^2$$

$$\lambda = \frac{-\partial^2}{\partial E^2} \ln \Omega$$

$$P(E) = \left(P(E)\, P'(E')\right) e^{-\frac{1}{2}\lambda^2 \eta^2}$$

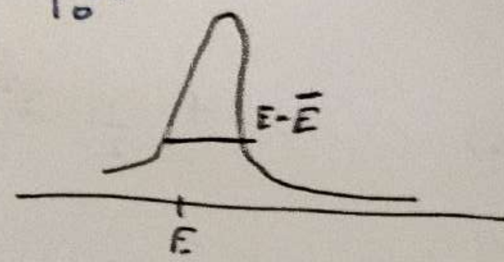
$$\lambda = -\frac{3N}{2} \bar{E}^2$$

$$P(E) = c\, e^{-\frac{\lambda}{2}(E-\bar{E})^2}$$

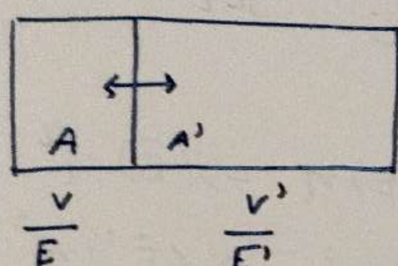
Exponentially damped

$$\lambda \sim \frac{f}{E^2}$$

$$\frac{(E-\bar{E})^2}{(E)^3} > \frac{1}{f} = \frac{1}{10^{23}}$$



$$\left(\frac{E-\bar{E}}{\bar{E}}\right)$$



$V + V' = V^{\circ}$ (fixed)

$E + E' = E^{\circ}$ (fixed)

Thermal eqm
Mechanical eqm

$$\Omega^{\circ}(E, V; E', V') = \Omega(E, V)\, \Omega'(E', V')$$

$$\ln \Omega^{\circ}(E, V; E', V') = \ln \Omega(E, V) + \ln \Omega'(E', V')$$

$\left(d \ln \Omega^{\circ} = 0 \right.$ max^{m} cond^{n} $\left. \right)$

$$0 = \left.\frac{\partial \ln \Omega}{\partial E}\right|_{\bar{E}} dE + \left.\frac{\partial \ln \Omega'}{\partial V}\right|_{\bar{V}} dV$$

$$+ \left.\frac{\partial \ln \Omega}{\partial E'}\right|_{\bar{E}'} dE' + \left.\frac{\partial \ln \Omega}{\partial V'}\right|_{\bar{V}'} dV'$$

$dE = -dE'$, $dV = -dV'$

$$0 = \frac{\partial \ln \Omega}{\partial E}\Big|_E dE + \frac{\partial \ln \Omega'}{\partial E}\Big|_V dV - \frac{\partial \ln \Omega}{\partial E'}\Big|_E dE' - \frac{\partial \ln \Omega}{\partial E'}\Big|_V dV'$$

$\beta(\bar{E}) = \beta'(\bar{E}')$ $\qquad \frac{\partial \ln \Omega}{\partial E} = \beta$

$\beta = \beta'$, $p = p'$ $\qquad \frac{\partial \ln \Omega}{\partial V} = \beta p \to$ pressure

$\Rightarrow \beta p = \beta' p'$

$$d \ln \Omega = \beta dE + \beta p dV$$
$$= \beta (dE + p dV) = \beta dq$$
$$= \beta T dS$$
$$= \frac{T dS}{kT} = \frac{dS}{k}$$

$dS = d(k \ln \Omega)$

LHS = RHS hence TRUE

$(S = k \ln \Omega)$

$k \, d \ln \Omega = dS \Rightarrow d \, k \ln \Omega = dS$

$$\Omega = C V^N E^{\frac{3N}{2}}$$
$$\Omega \sim V^N E^{\frac{3N}{2}}$$

$$\ln \Omega = \ln C + N \ln V + f(E)$$

$$\frac{\partial \ln \Omega}{\partial V} = \frac{N}{V}$$

$\left\{ \beta p = \frac{\partial \ln \Omega}{\partial V} = \frac{N}{V} \right.$

$\left. pV = \frac{N}{\beta} = NkT \right\}$

(*) Microcanonical distⁿ Ensemble

Canonical distⁿ

Grand canonical distⁿ

(*) Isolated system (noninteracting)

$E_r \to E \to$ energy

$r \to$ microstate

$\boxed{E_r}$ $E = E_r$

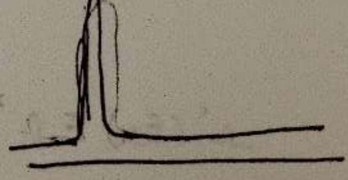
$E_r \to C$

$E = E_r$

$\to P(E_r) = C$

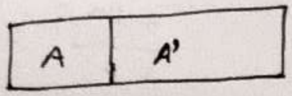
$\to E \neq E_r \to f(E) = 0$

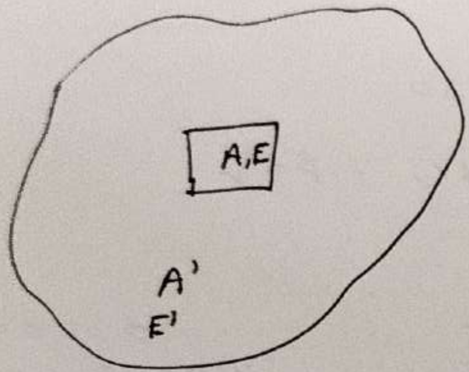
$E = E \pm E_r$



$\sum_r P_r = 1$ (Micro canonical Ensemble)

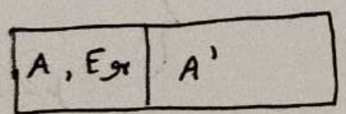
⊛ Canonical Ensemble (distrⁿ)





$E << E'$

A → small compared to A'.
(Reservoir, Heat Bath)



Ⓐ $E_r \to E_r$ if it is in a specific microstate.

Probability that A is in specific microstate A_r.

$$A^0 = A + A'$$

$$\Omega^0(E_r) = \underbrace{\Omega(E_r)}_{=1}\Omega'(E') \qquad E^0 = E_r + E'$$

$$\Omega^0(E_r) = \Omega'(E') = \Omega'(E^0 - E_r)$$

$$\ln(\Omega^0) = \ln\{\Omega'(E^0 - E_r)\}$$

$$= \ln \Omega'(E^0) - \frac{\partial \ln \Omega'}{\partial E_r}\Big|_{E^0} E^r$$

$$+ \quad (\quad) E^r$$ → neglected b/c $E_r << E$.

$$\boxed{\ln \frac{\Omega}{\Omega'}\Big|_{E_0} = -\beta E_r}$$

$$\boxed{\frac{\partial \ln \Omega'}{\partial E_r} = \beta}$$

$$P_r(E_r) = c\, e^{-\beta E_r} = c\, e^{-\frac{E_r}{KT}}$$

If system (A) is connected to a heat bath / Reservoir of Tempr T.

Then the system energy $\frac{E^r}{KT}$ will not be large.

we can get c

$$\sum_r P_r = 1 = c \sum_r e^{-\beta E_r}$$

$$P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

canonical Distn

$e^{-\beta E_r}$ → Boltzmann Factor

$$Z = \sum_r e^{-\beta E_r}$$

→ Partition fn

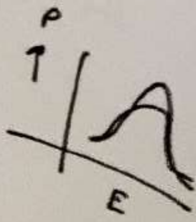
L-9

Boltzmann Distribution

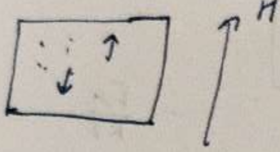
$$P(E_r) = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

$$\beta = \frac{1}{KT}$$

$$\frac{E_r}{KT}$$



A system of spin $\frac{1}{2}$ particle in an external magnetic field.



Energy of a magnetic moment in $\bar{H}$.

$$E = -\bar{\mu}\cdot\bar{H} = -\mu H\cos\theta.$$

$\uparrow$ $E_+ = -\mu H$, $\downarrow\theta$ $E_- = +\mu H$

$$p^+ = \frac{e^{-\beta E_+}}{\Sigma} = \frac{e^{+\beta\mu\cdot H}}{\Sigma}$$

$$p^- = \frac{e^{-\beta E_-}}{\Sigma} = \frac{e^{-\beta\mu\cdot H}}{\Sigma}$$

$$\bar{\mu} = \frac{\sum_r \mu_r e^{-\beta E_r}}{\sum e^{-\beta E_r}} = \frac{\mu\left(e^{\beta\mu H} - e^{-\beta\mu H}\right)}{\left(e^{\beta\mu H} + e^{-\beta\mu H}\right)}$$

$$\left\{\bar{\mu} = (\mu_+)P_+ + (\mu_-)P_-\right\}$$

$$\bar{\mu} = \mu \tanh(\beta \mu H) = \mu \tanh\left(\frac{\mu H}{kT}\right)$$

$n = \dfrac{\text{No of spin } \frac{1}{2}}{V}$, $\bar{\mu}_{total} = n \tanh\left(\dfrac{\mu H}{kT}\right)$

avg magnetic moment

$$\bar{\mu} = \frac{\mu\left(e^{\frac{\mu H}{kT}} - e^{-\frac{\mu H}{kT}}\right)}{\left(e^{\frac{\mu H}{kT}} + e^{-\frac{\mu H}{kT}}\right)}$$

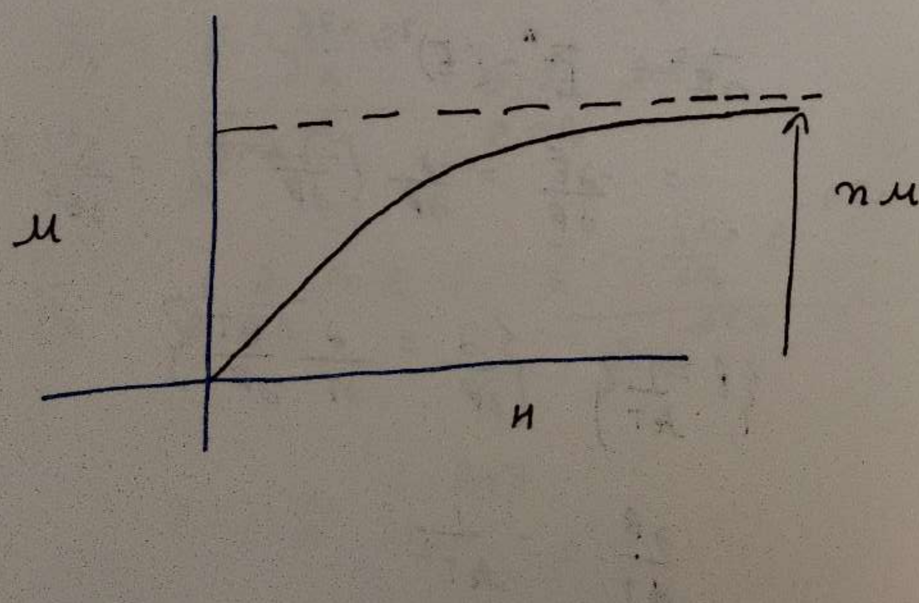
→ $\dfrac{\mu H}{kT} \gg 1$ very large H

$\boxed{\bar{\mu} = n\mu}$ → large H

→ $\dfrac{\mu H}{kT} \ll 1$ T very large

$$\bar{\mu} \approx n\mu \frac{\left(1 + \frac{\mu H}{kT}\right) - \left(1 - \frac{\mu H}{kT}\right)}{1 + \frac{\mu H}{kT} + 1 - \frac{\mu H}{kT}}$$

$$\bar{\mu} = \frac{n\mu^2 H}{kT}$$ curie's Law



Partition function // Boltzmann dist

$$\boxed{Z = \sum_r e^{-\beta E_r}} \qquad Z = e^{-\beta E_+} + e^{-\beta E_-}$$

$$\bar{E} = \frac{\sum_r E_r e^{-\beta E_r}}{\sum e^{-\beta E_r}} = -\frac{\partial}{\partial \beta} \ln Z$$

$$\overline{E^2} = \frac{\sum_r E_r^2 e^{-\beta E_r}}{Z} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}$$

$$= \frac{\partial}{\partial \beta} \underbrace{\left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right)}_{\frac{\partial}{\partial \beta} \ln Z = -\bar{E}} + \underbrace{\left(\frac{1}{Z^2} \left(\frac{\partial Z}{\partial \beta} \right)^2 \right)}_{(-\bar{E})^2}$$

$$\overline{E^2} = -\frac{\partial}{\partial \beta} (\bar{E}) + \bar{E}^2$$

$$\overline{\Delta E^2} = \overline{E^2} - (\bar{E})^2$$

$$= \frac{-\partial \bar{E}}{\partial \beta} = \frac{-\partial}{\partial \beta} \left(\frac{-\partial}{\partial \beta} \ln Z \right) = \frac{\partial^2}{\partial \beta^2} \ln Z$$

$$\left\{ \beta = \frac{1}{kT} \right\} \quad \left\{ \frac{\partial}{\partial \beta} = \frac{\partial}{\partial T} \frac{\partial T}{\partial \beta} \right\}$$

$$\frac{\partial \beta}{\partial T} = -\frac{1}{kT^2}$$

$$\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial E}{\partial T} \frac{\partial T}{\partial \beta} = -kT^2 \frac{\partial \bar{E}}{\partial T}$$

$$\overline{E^2} - \bar{E}^2 = kT^2 \frac{\partial \bar{E}}{\partial T}$$

$$(E-\bar{E})^2$$

$$dW = p\,dV = \text{force} \times \text{displmt}$$

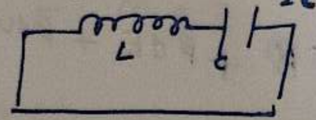
$$= \sum_{\alpha=1}^{n} X_\alpha \, dq_\alpha$$

X_α → generalised force

dq_α → generalised displmt.

$$\frac{1}{2} L I^2 \qquad \frac{q^2}{2C}$$

$L \quad \frac{ml}{t^2}$



$$I = \frac{dq}{dt}$$

$$H = \frac{1}{2} L \left(\frac{dq}{dt}\right)^2 + \frac{1}{2}\frac{Q^2}{C}$$

$$[Q] \neq [L]$$

$$\frac{1}{2} m \left(\frac{dx}{dt}\right)^2 + \frac{1}{2} k x^2$$

$$\text{force} = -\frac{dU}{dx}$$

we get

$$\left[\begin{array}{l} q \to \text{volume} \\ p = \frac{1}{\beta}\frac{\partial}{\partial V} \ln Z \end{array} \right]$$

$$dW = \underbrace{-\frac{\partial E}{\partial q}}_{\text{force}} \cdot dq$$

$$\bar{X}_q = \frac{\sum_r -\frac{\partial E_r}{\partial q} e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} = \frac{1}{\beta}\frac{\partial}{\partial q} \ln Z$$

$$\bar{X}_q = \frac{1}{\beta}\frac{\partial}{\partial q} \ln Z = \frac{\sum_r -\frac{\partial E_r}{\partial q} e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

$$p = \frac{1}{\beta}\frac{\partial}{\partial V} \ln Z$$

$$Z \sim \int e^{(-\dots)} \, dp \, dx$$

$$\ln Z = \ln(T_1) + N \ln V$$

$$d \ln Z = \frac{\partial \ln Z}{\partial \beta} d\beta + \frac{\partial \ln Z}{\partial q} dq$$

$$= -\bar{E}\, d\beta + \underbrace{\beta X\, dq}_{dW}$$

$$\left[\bar{X} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial q} \quad q \to \text{volume} \right]$$

$$= -\bar{E}\, d\beta + \beta\, dW$$

$$= -d(E\beta) + \beta\, dE + \beta\, dW$$

$$= -d(E\beta) + \beta(dq)$$

$$d\ln Z = -d(\beta E) + \beta T dS$$

$$\cancel{= d(\ln Z + \beta E)}$$

$$d(\ln Z + \beta E) = \beta T dS = \frac{1}{k} dS$$

$$k \ln Z + k\beta E = S$$

$$k \ln Z + \frac{E}{T} = S$$

$$TS = kT\ln Z + E \qquad \{F = E - TS\}$$

$$F = -kT\ln Z$$

$$F = -kT\ln Z$$

$$\boxed{\dot{x} = \frac{dx}{dt}}$$

$$= p_i^2/2m + U(r_1, r_2 \cdots r_n)$$

$$E = \frac{1}{2} m \dot{r}_i^2 + U(r_1, r_2, \cdots r_n)$$

$$Z = \int e^{-\beta E_r} d^3p_1\, d^3p_2 \cdots d^3p_n\, d^3r_1 \cdots d^3r_n$$

$$Z = \int e^{-\beta \Sigma(\frac{1}{2} m p_i^2 + U)} d^3p_1\, d^3p_2 \cdots d^3p_n * d^3r_1 \cdots d^3r_n$$

$$P(p_1, \ldots, r_1, \ldots) \propto e^{-\beta \Sigma \left(\frac{1}{2} m p_i^2 + U\right)}$$

$$P(r_1, r_2, \ldots r_N) \int dp$$

$$E = \frac{p_i^2}{2m} + m g z$$

$$P \sim e^{-\beta \frac{p^2}{2m}} \cdot e^{-\beta m g z} \, dp_x \, dp_y \, dp_z \, dx \, dy \, dz$$

$$\frac{P(z)}{dz} \sim e^{-\beta m g z} \, dz$$

~~Partition f^n~~

Partition f^n for Z harmonic oscillator (classical) one dim^n x, p

$$E = \frac{p^2}{2m} + \frac{1}{2}\lambda x^2$$

$$Z = \int e^{-\beta\left(\frac{p^2}{2m} + \frac{\lambda}{2}x^2\right)} dp \, dx$$

$$= \int_{-\infty}^{\infty} e^{-\beta\left(\frac{p^2}{2m}\right)} dp \; e^{-\frac{\lambda}{2}x^2} dx$$

$$= \int_{-\infty}^{\infty} e^{-\left(\frac{p^2}{2kTm}\right)} dp \cdot e^{-\frac{\lambda}{2}x^2} dx$$

on calcula^n

$$Z = \sqrt{\frac{(2p)^2 m}{\lambda}} \; \frac{1}{\beta}$$

$$\bar{E} = -\frac{\partial}{\partial \beta} \ln Z = \frac{\partial}{\partial \beta} \ln \beta$$

$$= \frac{1}{\beta} = kT$$

$$\boxed{\bar{E} = kT}$$

Quantum Harmonic Oscillator

$$Z = \sum_n e^{-\beta E_n}$$

$$E_n = \left(n + \frac{1}{2}\right)\hbar \omega \qquad n = 0, 1, \ldots$$

$$\omega = \sqrt{\frac{\lambda}{m}}$$

$$n = 0$$

$$E_0 = \frac{1}{2}\hbar \omega$$

L-10

Quantum HO $\rightarrow \bar{E} = kT$ (Classical)

$$E_n = \left(n+\tfrac{1}{2}\right)\hbar\omega \qquad \omega = \sqrt{\frac{k}{m}}$$

(quantum) $\qquad n = 0, 1, 2, \ldots$

$$Z = \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-\beta\left(n+\frac{1}{2}\right)\hbar\omega}$$

$$= e^{-\frac{1}{2}\beta\omega\hbar}\sum_{n=0}^{\infty} e^{-\beta n\hbar\omega} = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}$$

$$= \frac{1}{2}\hbar\omega + \frac{-e^{-\beta\hbar\omega}(-\hbar\omega)}{1-e^{-\beta\hbar\omega}}$$

$$\left\{ \begin{aligned} \bar{E} &= \frac{-\partial}{\partial\beta}\ln Z \\ &= \frac{-\partial}{\partial\beta}\left[\left(-\frac{1}{2}\beta\hbar\omega - \ln\left(1-e^{-\beta\hbar\omega}\right)\right)\right] \end{aligned} \right\}$$

$$= \hbar\omega\left(\frac{1}{2} + \frac{e^{-\frac{\hbar\omega}{kT}}}{1-e^{-\beta\hbar\omega}}\right)$$

$T \rightarrow$ large $\qquad e^{-\frac{\hbar\omega}{kT}} \longrightarrow 1$

$$\left\{ \begin{aligned} \frac{e^{-\hbar\omega/kT}}{1-e^{-\hbar\omega/kT}} &= \frac{1-\frac{\hbar\omega}{kT}}{1-1+\frac{\hbar\omega}{kT}} \\ &= \frac{kT}{\hbar\omega} - 1 \end{aligned} \right\}$$

$T \to$ large if $T \to$ large value

$kT >> \hbar\omega$ $\to$ classical limit

$\cancel{\bar{E}} = \cancel{\frac{\hbar\omega}{2}} + \cancel{kT\hbar\omega} = \hbar(\omega)\left(\frac{1}{2} + \frac{kT}{\hbar\omega}\right)$

$\bar{E} = \cancel{kT\hbar\omega}$

$$= \frac{\hbar\omega}{2} + kT$$

$$\simeq kT$$

Q.H.O

$T \to$ large $\bar{E} = kT$

High temp^{r}

$T \to$ small $\Rightarrow E = \hbar\omega\left(\frac{1}{2} + e^{-\frac{\hbar\omega}{kT}}\right)$

Solid system

Classical $\cdot$ $\bar{E} = kT3N$

$$C_V = \frac{\partial\bar{E}}{\partial T} = 3NR$$

$C_V = 3R$ Dulong Petite Law

Quantum:

$$E = 3N\omega\hbar\left(\frac{1}{2} + \frac{e^{-\frac{\hbar\omega}{kT}}}{1 - e^{-\frac{\hbar\omega}{kT}}}\right)$$

on calc^{n}

we get

$$C_V = 3R\left(\frac{\theta_E}{T}\right)^2 \frac{e}{\left(e^{\frac{\theta_E}{T}} - 1\right)^2}$$

$\theta_E = \frac{\hbar\omega}{k}$ Einstein Temp^{r}

$T \to$ Small

$$E = \hbar\omega\left(\frac{1}{2} + e^{-\frac{kT}{\hbar\omega}}\right)$$

PTO

classical

$$\bar{E} = kT\, 3N$$

$$C_v = \frac{\partial \bar{E}}{\partial T} = 3NR$$

$$C_v = 3R \qquad \text{Dulong Petit law}$$

~~Stat~~

$$E = 3N\hbar\omega\left(\frac{1}{2} + e^{-\frac{kT}{\hbar\omega}}\right)$$

$$C_v = \frac{\partial \bar{E}}{\partial T} = 3N\hbar\omega\left[\, e^{-\frac{\hbar\omega}{kT}} \,\right]$$

$$\frac{\theta_E}{T} << 1 \quad \Big| \quad T >> \theta_E$$

$$C_v = 3R \left(1 + \frac{\theta_E}{T}\right)^{\to 0} = 3R$$

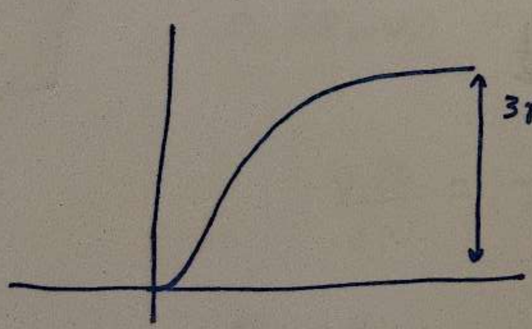
= Classical Result at $T >> \theta_E$ (high) Einstein Temp^n.

T → small

$$\frac{\theta_E}{T} >> 1, \quad \theta_E >> T$$

$$C_v = 3R\left(\frac{\theta_E}{T}\right) e^{-\frac{\theta_E}{T}}$$

$$T \to 0, \quad C_v \to 0$$



[illegible]

↓

Indistinguishable

Classical

↓

Distinguishable

2 particles $_{A,B}$, 3 boxes

AB	0	0
0	AB	0
0	0	AB
A	B	0
B	A	0
A	0	B
0	A	B
0	B	A
B	A	0
B	0	A

$$P_r\big|_{AB} = \frac{3}{9} = \frac{1}{3}$$

$$P_r\big|_{A \neq B} = \frac{6}{9} = \frac{2}{3}$$

$$\frac{P_r\big|_{AB}}{P_r\big|_{A\neq B}} = \frac{1/3}{2/3} = \frac{1}{2}$$

Quantum Behaviour

Bosons → integral spin
0, 1, 2, ...

Fermions → $\frac{1}{2}$ integral spin

Bosons

A A	o	o
o	A A	o
o	o	A A
A	A	o
A	o	A
o	A	A

$P_{AA} = \frac{3}{6} = \frac{1}{2}$

$P_{A-A} = \frac{1}{2}$

$\frac{P_{AA}}{P_{A-A}} = 1$

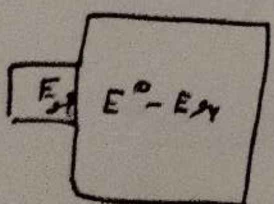
Bosons try to stay with each other

Fermions (Don't like each other)

A	A	o
o	A	A
A	o	A

$P_{AA} = 0$

Canonical Distr^n

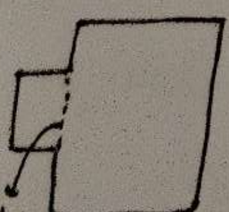


$$\Omega = \Omega(E^\circ - E_r)$$

$$= \Omega(E_0) - \frac{\partial \Omega}{\partial E}\Big|_{E_0} E_r$$

$$e^{-\beta E_r}$$

Grand Canonical Dist^n



Particle exchange allow

$$\Omega(E^\circ - E_r, N^\circ - N_r)$$

$$\Omega(E_0, N_0) - \frac{\partial \Omega}{\partial E}\Big|_{E_0} E_r - \frac{\partial \Omega}{\partial N}\Big|_{N_0} N_r$$

$-\beta\mu$

$$\frac{\partial \Omega}{\partial N} = -\beta\mu$$

$$P_r = e^{-\beta E_r + \beta\mu N_r}$$

$$Z_{\text{grand partition}} = \sum e^{-\beta(\mu r - E_r)}$$

f^n

Boson

$$Z \rightarrow \bar{n}_r = \frac{1}{e^{\beta(E_r-\mu)}-1}$$

Fermions

$$Z \rightarrow \bar{n}_r = \frac{1}{e^{\beta(E_r-\mu)}+1}$$

avg no. of particles $\sum N_r e^{-\beta E_r + \mu N_r}$

L-10 end

L-11

How To Deal with Interacting Systems

$$pV = nRT \xrightarrow{\text{Real gas}} \left(p - \frac{a}{V^2}\right)(V-b) = \cancel{nR}T$$

Vander Walls.

$$E = \sum \frac{p_i^2}{2m} + U(r_1, r_2, \dots r_n)$$

$$Z \sim \frac{\int d^3p \cdots d^3r \cdots e^{-\beta\left(\sum \frac{p_i^2}{2m} + U(r_1 \dots r_n)\right)}}{(N!)}$$

$$\left[\cancel{U(r_1 \dots r_n) = {}^N C_2\, U(r_1 - r_2)}\right] = (p\text{ integral}) \int d^3r_1 \dots d^3r_N\, e^{-U(r_1, \dots r_N)}$$

some

we can't isolate like $\int dr_i\, e^{-U(r_i)}$

$$\left[\text{Harmonic oscillator classical} \quad \int e^{-kx^2} dx\right]$$

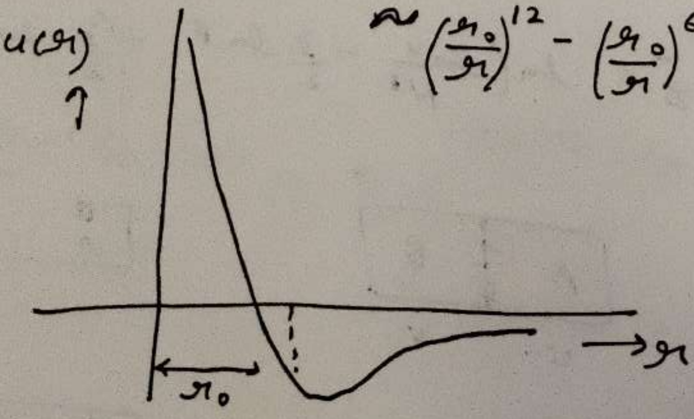
Real gas (weakly interacting)

1. Pairwise
2. Depends only on $|r_i - r_j|$
3.

$${}^N C_2\, U(r_1 - r_2) = U(r)$$

Lennard-Jones

$$\sim \left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^6$$



How then did N! come?

Gibbs Paradox / ideal gas $\quad Z = \int \cdots$

$$\ln Z = N\left(\ln V - \frac{3}{2}\ln\beta + \frac{3}{2}\ln\left(\frac{2\pi m}{h_0^2}\right)\right)$$

$$\bar{p} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V} = \frac{1}{\beta}\frac{N}{V}$$

$$\bar{E} = \frac{-\partial}{\partial\beta}\ln Z = \frac{3N}{2\beta} = \frac{3}{2}NkT$$

$$S = k(\ln Z + \beta\bar{E})$$

$$S = Nk\left(\ln V + \frac{3}{2}\ln T + \sigma\right)$$

Extensive Parameters // N, V, E, S

Non extensive : T, P, μ

$$\bar{Z} = \frac{Z}{N!}$$

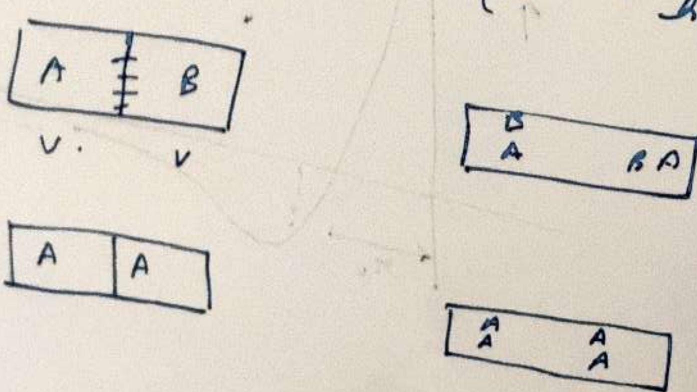
$$\ln\bar{Z} = N\left(\ln V + \frac{3}{2}\ln\beta + \frac{3}{2}\ln\left(\frac{2\pi m}{h_0}\right)\right) - \ln(N!)$$

$\left\{\right.$ very large N

$\log N! = N\log N - N$

Stirling's formula $\left.\right\}$

$$\ln\bar{Z} = N\left(\ln\frac{V}{N} - \frac{3}{2}\ln\beta + \left(\frac{3}{2}\ln\left(\frac{2\pi m}{h_0}\right) + 1\right)\right)$$



MATTHEW SCHWARZ // Statistical Mechanics Spring 2021.

free

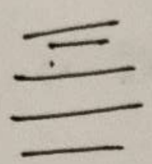
occupation no. of system of bosons or fermions

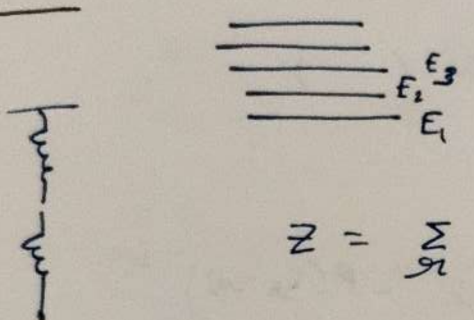
$m_r = \dots$

System of non interacting quantum particles.

QHO, $E_n = \left(n+\frac{1}{2}\right)\hbar\omega$

Discrete





$$Z = \sum_r e^{-\beta E_r}$$

$$E_r = \sum_r n_r \varepsilon_r$$

$$E_r' = \sum n_r' \varepsilon_r$$

$\sum n_r = N$

$$Z = \sum_{(r_1, \dots)} e^{-\beta \sum n_r E_r}$$

Grand Partition f^n , chemical potential

$$\Omega = \sum_{(\dots)} e^{-\beta(E_r - \mu N_r)}$$

$$= \sum_{\{\dots\}} e^{-\beta \sum_{n_r} n_r(\varepsilon_r - \mu)} = \sum e^{-\beta \sum_{n_r} n_r(\varepsilon_r - \mu)}$$

$$= \prod_r \sum_{n_r=0}^{\infty} e^{-\beta n_r(\varepsilon_r - \mu)} \qquad \varepsilon_r \text{ fixed}$$

$$\boxed{N = \frac{1}{\beta}\frac{\partial \ln \Omega}{\partial \mu}}$$

<u>Bosons</u>

$$\Omega = \sum_{n_r=0}^{\infty} \left(\frac{1}{1-e^{-\beta(\varepsilon_r-\mu)}}\right)\left(\frac{1}{1-e^{-\beta(\varepsilon_r^2-\mu)}}\right)$$

$$\ln \Omega = \ln(\quad) + \ln(\quad)$$

$$n_r = \frac{-1}{\beta}\frac{\partial \ln \Omega}{\partial \epsilon_r}$$

$$= \frac{-1}{\beta}\frac{\partial}{\partial \varepsilon_r} \ln\left(1-e^{-\beta(\varepsilon_r-\mu)}\right)^{-1}$$

$$n_{r_b} = \frac{1}{\beta}\frac{\cancel{+}-e^{-\beta(\varepsilon_r-\mu)}(-\beta)}{1-e^{-\beta(\varepsilon_r-\mu)}} \qquad n_r = e^{\beta(\varepsilon_r-\mu)} - 1$$

<u>Fermions</u>

$$n=0, n=1$$

$$1 + e^{-\beta(\varepsilon_r-\mu)}$$

Fermi-Dirac

$$n_r^F = \frac{1}{e^{\beta(\varepsilon_r \mp \mu)}+1}$$

<u>Fermions</u>

Bosons

$$n_r^{\text{Bose-Einstien}} = \frac{1}{e^{\beta(\varepsilon_r-\mu)}}$$

Photons are also Bosons, ($\mu = 0$)

$$n_r^{\text{photons}} = \frac{1}{e^{\beta \varepsilon_r} - 1}$$ Planks Radiation Law

$n_r \to$ small

Large Temp^r

Maxwell Boltzmann

$$n_r^{MB} = e^{-\beta(\varepsilon_r - \mu)}$$

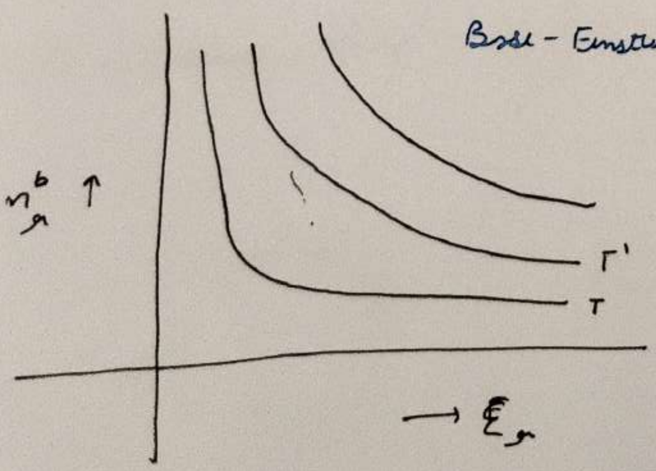
$$n_r^{B\text{-}E} = e^{\frac{(\varepsilon_r - \mu)}{kT}} - 1$$

$$n_r^{F\cdot D} = \frac{1}{e^{\frac{\varepsilon_r - \mu}{kT}} + 1}$$

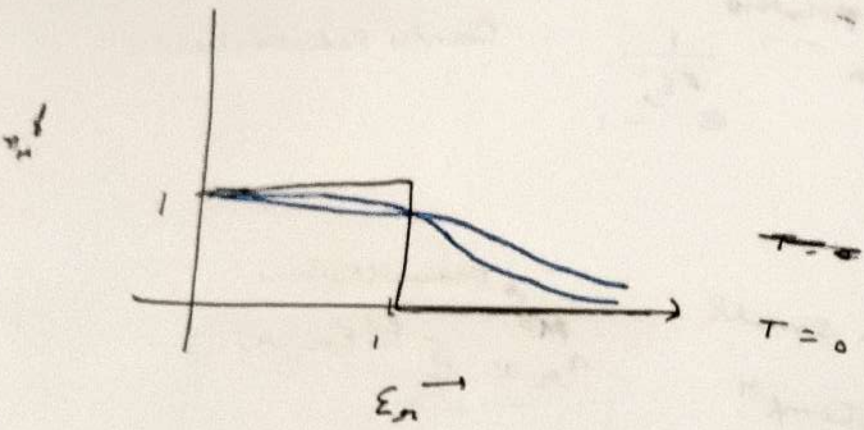
$$n_r^{B\text{-}E} = \bar{e}^{\beta(\varepsilon_r - \mu)}$$

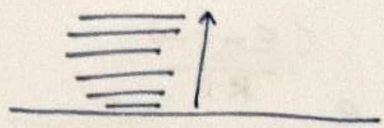
μ must be < 0
else if $\mu > 0$
it must be $\mu < \varepsilon_r$.

Bose - Einstein condensation



Bosons





Ising Model → ferromagnetism.

Phase Trans^n

L—11 ends

Paramagnet

L-12

ISING MODEL

Proposed originally by Lenz to show ferromagnetism.

Paramagnetism → If no external field ⇒ no net mag moment in the sample   spin → non interacting

spin → interacting

N no. of interacting things in external field B $= -J \sum_{\substack{i=1 \\ i>j}}^{M} s_i s_j - \mu_B \sum_{i=1}^{N} s_i$

J → constant

J > 0 → ferromagnetic

J < 0 → Anti-ferro

$s_i = +1, -1$

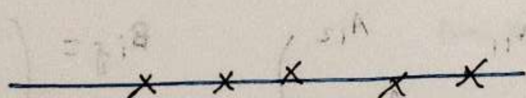
Ising model approxⁿ

① 1D-Model system.

② Nearest neighbour approxⁿ.

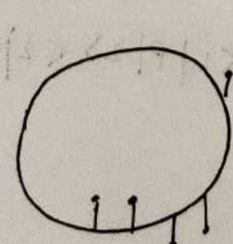
③ Periodic Boundary condⁿ $s_1 = s_{N+1}$

1- Dimensional chain

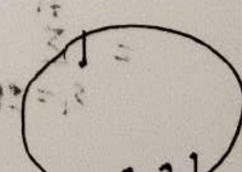


N no of interacting things $= -J \sum_{i=1}^{M} s_i s_{i+1}$

E_1



E_2



$$Z = \sum_r e^{-\beta E_r} = \sum_{s_1=+1}^{-1} \sum_{s_2=+1}^{-1} \cdots \sum_{s_N=+1}^{-1} \exp(B(\alpha))$$

$$\alpha = \left[J \sum_{i=1}^{N} s_i s_{i+1} - \mu \sum s_i \right]$$

$$Z = \sum_{\mathfrak{n}} e^{-\beta E_{\mathfrak{n}}}$$

$$= \sum_{s_1=+1}^{-1} \sum_{s_2=+1}^{-1} \cdots \sum_{s_N=+1}^{-1} \exp \beta \left[J \sum_{i=1}^{N} s_i s_{i+1} + \mu \sum s_i \right]$$

$$= \sum_{s_1=1}^{-1} \sum_{s_2=+1}^{-1} \cdots \sum_{s_N=+1}^{-1} \exp \beta \left[J \sum_{i=1}^{N} s_i s_{i+1} + \frac{\mu}{2} \sum_i (s_i + s_{i+1}) \right]$$

$$\rightarrow \langle 1 | P | 2 \rangle = e^{\beta (J s_1 s_2 + \frac{\mu}{2} (s_1 + s_2))}$$

$$\langle 1 | P | 1 \rangle = e^{\beta (J + \mu)}$$

$$\langle 1 | P | -1 \rangle = e^{-\beta J}$$

$$\langle -1 | P | +1 \rangle = e^{-\beta J}$$

$$\langle -1 | P | -1 \rangle = e^{\beta (J - \mu)}$$

2X2 Matrix

$$A_{ij} = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \qquad B_{ij} = \begin{pmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{pmatrix}$$

$$C_{ij} = A_{ik} B_{kj}$$

$$= \sum_{s_1=\pm 1}^{+1} \sum_{s_1=-1}^{+1} \sum_{s_2} \langle 1 | P | 2 \rangle \langle 2 | P | 3 \rangle \langle 2 | P | 4 \rangle \cdots$$

$$\cdots \langle \ | N | \rangle$$

$$\begin{pmatrix} \langle 1|P|1\rangle & \langle 1|P|2\rangle \\ \langle 2|P|1\rangle & \langle 2|P|2\rangle \end{pmatrix}$$

Trace of a matrix : sum of diagonal elements.

$$Tr(A) = \sum_{i=1} A_{ii}$$

$$AB = C$$

$$C_{ij} = \sum_k A_{ik} B_{kj}$$

$$Z = Tr(\overbrace{P \cdot P \cdot \ldots \ldots P}^{N \text{ times}})$$

$$\left[\begin{array}{l} Tr(AB) = Tr(BA) \\ Tr(ABC) = Tr(BCA) = Tr(CAB) \end{array}\right\} \text{ Cyclic Property of Trace.}\Big]$$

$$Z = Tr(D^{-1} \overbrace{PP \ldots P}^{N} D)$$

D → another 2x2.

$$= Tr[\underbrace{D^{-1} P D}_{\text{Diagonal Matrix}} D^{-1} P D D^{-1} \ldots]$$

Similarity Transform^n

$$D^{-1}PD = \begin{pmatrix} \checkmark & 0 \\ 0 & \checkmark \end{pmatrix}$$

$$Z = \text{Trace}\,\overbrace{(D^{-1}PD)}^{\text{diagonal}}(D^{-1}PD) \ldots$$

$$= \text{Trace} \begin{pmatrix} \lambda^+ & 0 \\ 0 & \lambda^- \end{pmatrix}\begin{pmatrix} \lambda^+ & 0 \\ 0 & \lambda^- \end{pmatrix} \ldots\ldots$$

N times

$$= \text{Trace}\begin{pmatrix} (\lambda^+)^N & 0 \\ 0 & (\lambda^-)^N \end{pmatrix} = (\lambda^+)^N + (\lambda^-)^N$$

$$\begin{pmatrix} e^{\beta(J+\mu B)} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J-\mu B)} \end{pmatrix} = P_{2\times 2}$$

for $\boxed{\mu = 1}$

$$|P_{2\times 2} - \lambda I_{2\times 2}| = 0$$

K Huang — stat mech

Martin Schwartz — L-18 Lect series

$$\lambda^2 - 2\lambda \underset{\text{multiply}}{e^{\beta J} \times} \cosh(\beta B) + 2\sinh(2\beta J) = 0$$

$$\lambda_\pm\ e^{\beta J}\left[\cosh(\beta B) \pm \sqrt{\cosh^2(\beta B) - 2e^{-\beta J}\sinh(2\beta J)}\right.$$

$$\lambda_+ > \lambda_-$$

$$Z = (\lambda^+)^N + (\lambda^-)^N$$

$$= (\lambda^+)^N \left(1 + \left(\frac{\lambda^-}{\lambda^+}\right)^N\right)$$

$$\ln Z = N \ln \lambda^+ + \ln\left(1 + \left(\frac{\lambda^-}{\lambda^+}\right)^N\right)$$

$$\simeq N \ln \lambda^+$$

$$Z \sim \frac{e^{+\beta (J(\ ) - \beta\mu \sum_i s_i)}}{\sum s_i \ e^{-\beta(\ )}}$$

$$\frac{1}{N\beta} \frac{\partial \ln Z}{\partial B} = (\bar{\mu})$$

$$\bar{\mu} = \frac{1}{\beta N} \frac{\partial \ln Z}{\partial B} = \frac{\sinh(\beta\mu B)}{\sqrt{\cosh^2(\beta\mu B - 2e^{-2\beta J} \sinh(2\beta J)}}$$

1-D ising model in nearest neighbour approx^n & periodic boundary result.

No interaction b/w the spins $\Rightarrow J = 0$

earlier model of paramagnetism.

If $B = 0$ we get $\bar{\mu} = 0 \Rightarrow$ No residual magnetism.

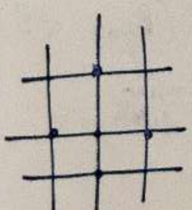
$F = U - TS^{\uparrow \text{ maximise}}$ | Free energy minimize

$\downarrow$ minimise F

$\downarrow$ minimum

In 2-D or 3-D

Till midsem Here only



Mean field ~~approach~~ Model

L-12 ends