Maa Omwati Degree Collage

Hassanpur

NOTES

Subject:- Statistical Machanics

B.SC Sem:-IV

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UV notes

Statistical mechanics

[redacted]

20/4/15

STATISTICAL MECHANICS

↳ A branch of physics explains the macroscopic behaviour in terms of microscopic variable.

$$\text{Macro} \xrightarrow{SM} \text{Micro}$$

[Macroscopic Variable] state variable.

↳ variables require to describe the system.

Extensive variable

Depends on mass.

eg: E, N, V, S ....

Additive property

$E = E_1 + E_2$ ---

$S = S_1 + S_2$ ----

Intensive variable

Independent of mass.

T, P, density, Refractive index ...

vary spatially

$P = P_0 + \rho g h$.

Microscopic variable

↳ Position & momentum of constituent particle of the system

$(\vec{x_i} \cdot \vec{p_i})$

phase space

=> Macro & micro state

① coins {H, T} $p = 1/2$, $q = 1/2$

1) 1 coin => $2^1 = 2$ # no: of microstate.

2) 2 coins => $2^2 = 4$ # no: of micro

3) 3 coin => $2^3 = 8$ # no: of micro.

No: of microstate 2^N

Macro

Binomial $(p+q)^N$

$(p+q)^1 = p+q$ # Macro 2.

$(p+q)^2 = p^2+2pq+q^2$ # macro 3

$(p+q)^3 = p^3+3p^2q+3pq^2+q^3$

macro 3.

No: of macrostate N+1

micro

② Dice {1, 2, 3, 4, 5, 6}

1) 1 Dice # micro $= 6^1 = 6$

2) 2 Dice # micro $= 6^2 = 36$

3) 3 Dice # micro $6^3 = 64$

No: of micro state 6^N.

Macro.

1 Dice (min to max) = 1 to 6 = 6

2 Dice (min to max)

(1+1) to (6+6) 2 to 12 = 11

3 Dice (3 to 18) = 16.

No: of macrostate 5N+1

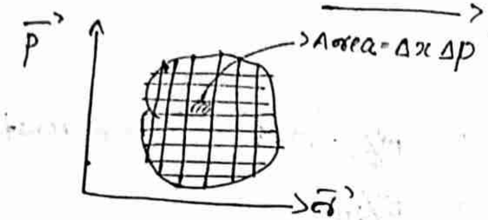
Macrostate

└> Specification of the system.

Microstate

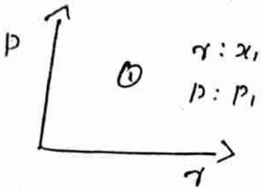
└> No: of arrangement.

⟹ PHASE SPACE



⟶ position & momentum space.

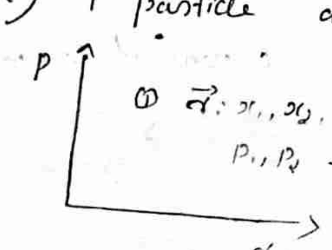
1) 1 particle dof = 3



① $r : x_1\ x_2\ x_3 = 3$
$p : p_1\ p_2\ p_3 = 3$
Dimension of phase space: 6

Volume
$(\Delta x_1 \Delta p_1)(\Delta x_2 \Delta p_2)(\Delta x_3 \Delta p_3)$
$\downarrow h \quad \downarrow h \quad \downarrow h$
Volume $= h^3$

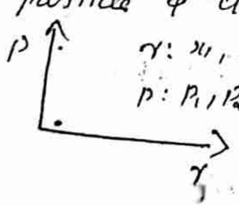
2) 1 particle dof = f.



① $\vec{r} : x_1, x_2, x_3 \ldots x_f = f.$
$p_1, p_2 \ldots p_f = f$
Dimension of the phase space $= 2f$

$(\Delta x_1 \Delta p_1)(\Delta x_2 \Delta p_2) \ldots$
$h \quad h \ldots$
volume $= h^f$

3) N particle & dof 3



$r : x_1, x_2, x_3 \ldots x_{3N} = 3N$
$p : p_1, p_2, \ldots p_{3N} = 3N$
Dimension of phase space $= 6N$.

) N particles & dof = f
$\vec{r} : x_1, x_2 \ldots x_{fN} = fN$
$\vec{p} : p_1\ p_2 \ldots p_{Nf} = fN$

$\boxed{\text{Dimension of phase space} = 2fN}$

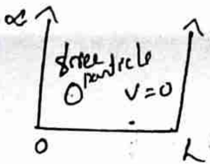
Volume ⟶ JS
energy × time

ume $(\Delta x_1 \Delta p_1)(\Delta x_2 \Delta p_2) \ldots fN$

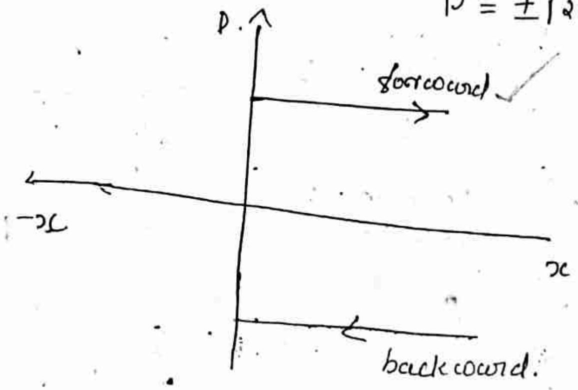
$\boxed{\text{Volume} = h^{fN}}$

⟹ Phase space diagrams

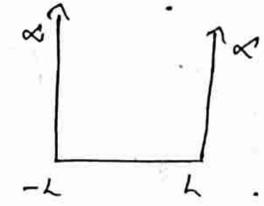
1. 1D box.

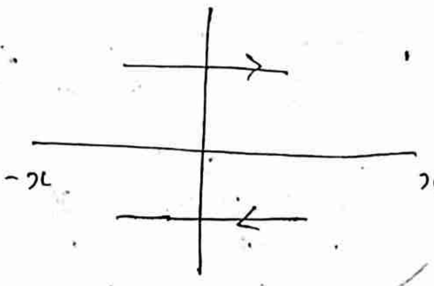


$E = p^2/2m + V$ x is const.
$= p^2/2m$
$p = \pm\sqrt{2mE}$



ansymmetric 1D box





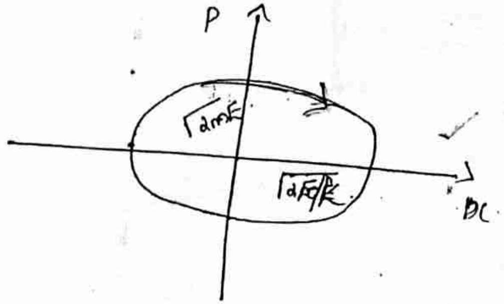
symmetric

LHO

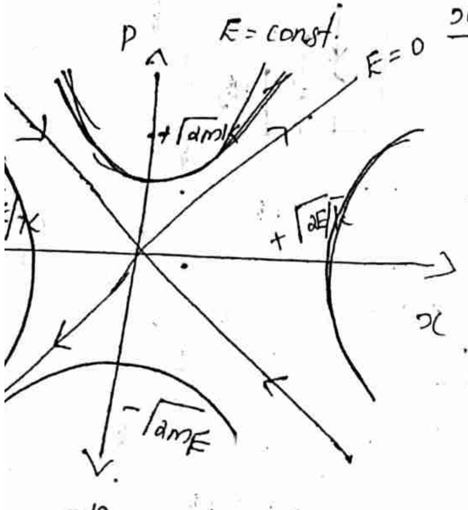
$$E = \frac{p^2}{2m} + \frac{1}{2} k x^2$$

$$\frac{p^2}{2mE} + \frac{x^2}{2E/k} = 1$$

$$\frac{x^2}{\left(\sqrt{2E/k}\right)^2} + \frac{p^2}{\left(\sqrt{2mE}\right)^2} = 1 \quad \text{eq}^n \text{ of ellipse.}$$



) $E = p^2/2m - \frac{1}{2} k x^2$. $\quad V = -\frac{1}{2} k x^2$.



$x = 0$

$p = \pm\sqrt{2mE}$

$p = 0$

$x = \pm\sqrt{2E/k}$.

$E = 0$

$p^2 = kmx^2$

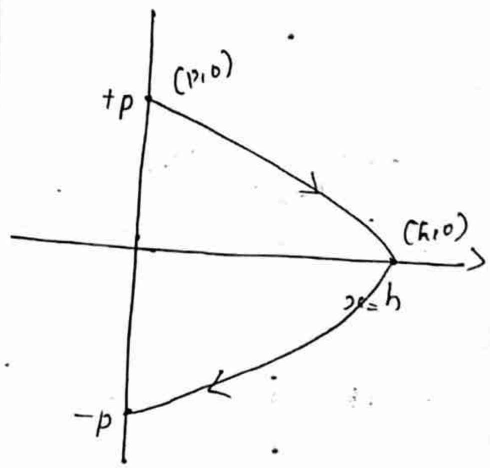
$p = \pm\sqrt{mk}\, x$.

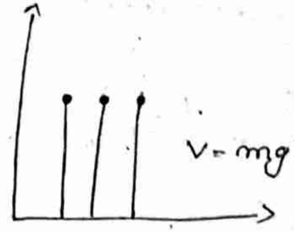
$Y = mx$

st line passing through origin

⇒ Bouncing ball

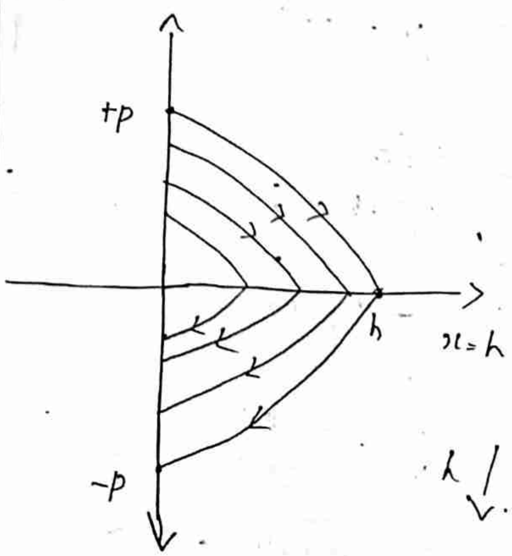
1) Elastic collision

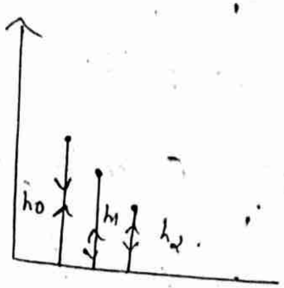




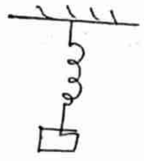
$E = \frac{p^2}{2m} + mgh$.

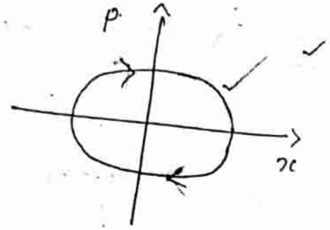
2) Inelastic collision





⟹ SHO

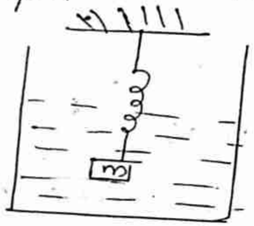


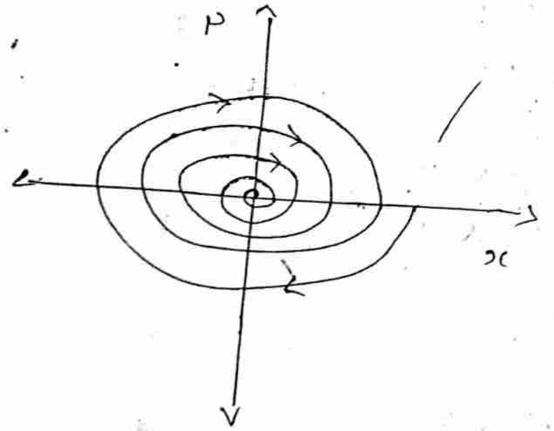


x −ve ⟹ p +ve

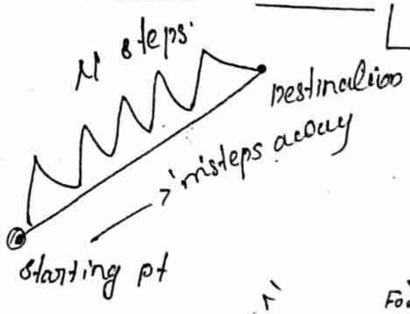
x +ve ⟹ p −ve.

⟹ Damped oscillator





⟹ Random walk problem ↳ [To study molecular Dispersions]



N steps → Forward N_1, backward N_2.

$N_1 + N_2 = N$ —— (1)

distance covered $N_1 - N_2$

$N_1 - N_2 = m$ —(2)→ reach home.

(1) + (2) ⟹ $2N_1 = N + m$

$N_1 = \frac{N+m}{2}$

(1) − (2) ⟹ $2N_2 = N - m$

$N_2 = \frac{N-m}{2}$.

$P_n^N = {}^NC_n \, p^n q^{N-n}$.

$P_{N_1}^N = {}^NC_{N_1} \, p^{N_1} q^{N-N_1}$

$p = q = 1/2$

$P_{N_1}^N = \frac{N!}{N_1!(N-N_1)!} (1/2)^{N_1} (1/2)^{N-N_1}$

$P(N) = \frac{N!}{N_1! N_2!} (1/2)^N$

$$\boxed{P_m^N = \frac{N!}{\left(\frac{N+m}{2}\right)!\left(\frac{N-m}{2}\right)!} (1/2)^N}$$

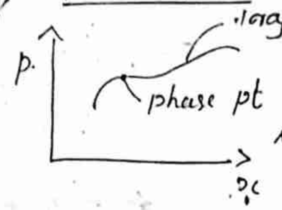
LIOUVILLE'S THEOREM

Real space

flow of incompressible.

$\vec{\nabla}\cdot\vec{J} = 0.$

phase space



$\vec{\nabla}\cdot\vec{J} = 0$

no source & no sink.

Statement: - density of phase space is const $\frac{d\rho}{dt} = 0$.

space (Real space).

$$\vec{\nabla}\cdot\vec{J} = \sum_i \frac{\partial}{\partial x_i}\rho v_i \qquad \left[\because \vec{J} = ne\,v_d. = \rho v\right]$$

$$\vec{\nabla}\cdot\vec{J} = \sum_i \frac{\partial J_i}{\partial x_i} = \frac{\partial}{\partial x}J_x + \frac{\partial}{\partial y}J_y + \frac{\partial}{\partial z}J_z.$$

$$\vec{\nabla}\cdot\vec{J} = \sum_i \frac{\partial}{\partial x_i}\rho v_i$$

$$\vec{\nabla}\cdot\vec{J}\Big|_{Real} = \sum_i \frac{\partial}{\partial q_i}(\rho\dot{q}_i).$$

$$\boxed{\vec{\nabla}\cdot\vec{J}\Big|_{Real} = \sum_{i=1}^{3}\frac{\partial}{\partial q_i}\rho\dot{q}_i}$$

↓ Analogy.

$$\vec{\nabla}\cdot\vec{J}\Big|_{phase\ space} = \sum_i \frac{\partial}{\partial q_i}\rho\dot{q}_i + \sum_i \frac{\partial}{\partial p_i}\rho\dot{p}_i.$$

$$= \sum_i\left[\rho\frac{\partial \dot{q}_i}{\partial q_i} + \dot{q}_i\frac{\partial\rho}{\partial q_i} + \rho\frac{\partial \dot{p}_i}{\partial p_i} + \dot{p}_i\frac{\partial\rho}{\partial p_i}\right]$$

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \quad , \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}$$

$$\therefore \vec{\nabla}\cdot\vec{J} = \sum\left[\rho\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial H}{\partial p_i}\frac{\partial\rho}{\partial q_i} + \rho\frac{\partial \dot{p}_i}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial\rho}{\partial p_i}\right]$$

$$= \sum\left[\rho\frac{\partial}{\partial q_i}\frac{\partial H}{\partial p_i} + \frac{\partial H}{\partial p_i}\frac{\partial\rho}{\partial q_i} - \rho\frac{\partial\partial H}{\partial q_i\partial p_i} - \frac{\partial H}{\partial q_i}\frac{\partial\rho}{\partial p_i}\right]$$

$$= \sum\left[\frac{\partial H}{\partial p_i}\frac{\partial\rho}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial\rho}{\partial p_i}\right]$$

$$\vec{\nabla}\cdot\vec{J} = \{\rho, H\}.$$

eqn of continuity = $\vec{\nabla}\cdot\vec{J} = -\partial\rho/\partial t.$

$$\vec{\nabla}\cdot\vec{J} + \partial\rho/\partial t = 0.$$

$$\{\rho, H\} + \partial\rho/\partial t = 0.$$

eqn of motion $\frac{d\rho}{dt} = \{\rho, H\} + \partial\rho/\partial t = 0.$

$$\frac{d\rho}{dt} = 0$$

$$\rho = \text{const}$$

$\therefore$ density of phase space is const.

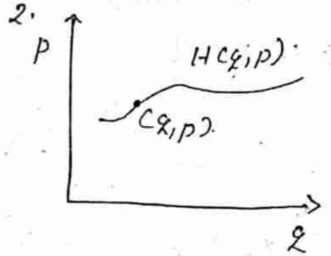
ie, local density of representative pts as observed by an observer moving with of representative pts remains const.

The representative pts moves in phase space as an incompressible fluid moves in real space.

-> properties of phase space:

1. $\frac{d\rho}{dt} = 0 \implies \rho = \text{const.}$

2.



$H(q,p)$

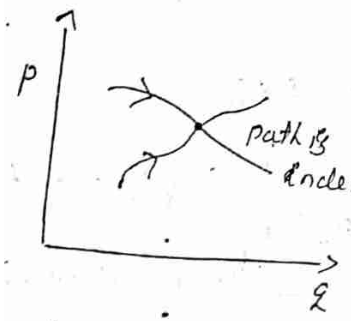
$\dot{q} = \frac{\partial H}{\partial p}$ $\dot{p} = -\frac{\partial H}{\partial q}$

$\int \dot{q}\,dt = \int \frac{\partial H}{\partial p} dt$ $\int \dot{p}\,dt = -\int \frac{\partial H}{\partial q} dt$

↳ solving (q, p).

exactly soluable.

- path of the particle is deterministic.



No two trajectories intersect each other.

There are no sources and no sink is phase space. (attractors)

=> Relation b/w thermodynamics & statistics

System equilibrium (stable / unstable)

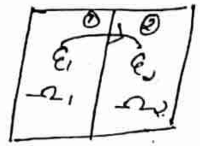
Thermodynamic pt of view

Entropy [S].

S_{max} = more disorder.

S_{min} = more order

closed system



statistics

Probability [P]

[most probable state]

↳ Ω_{max}. (microstate)

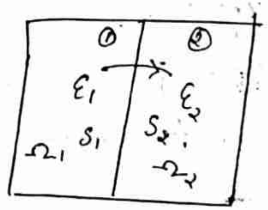
5 students

2	2	1

$\Omega/\omega = \frac{N!}{n_1! n_2! n_3!} = \frac{5!}{2!2!1!} = 30.$

3	2	0

$\Omega/\omega = \frac{N!}{n_1! n_3!} = 10$



1) S is extensive $\implies S_{total} = S_1 + S_2$.

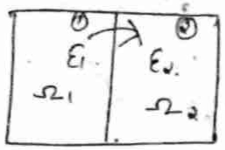
$\left.\begin{array}{l}\Omega_1 = \Omega_1(\varepsilon_1) \\ \Omega_2 = \Omega_2(\varepsilon_2)\end{array}\right\} \varepsilon_1 + \varepsilon_2 = \text{const}.$

2) P is multiplicative $\implies \Omega$ is multiplicative

$\implies \Omega = \Omega_1 \Omega_2$.

$\Omega_{max} = d\Omega = 0$

Statistics



Energy is exchanging.

$\Omega = \Omega_1 \Omega_2$

equilibrium = $d\Omega_{max} = 0$.

$\varepsilon_1 + \varepsilon_2 = const$

$\varepsilon_1 = -\varepsilon_2$

$\frac{\partial \varepsilon_2}{\partial \varepsilon_1} = -1$

$$\frac{d\Omega_{max}}{d\varepsilon} = \frac{\partial \Omega_1}{\partial \varepsilon_1}\Omega_2 + \Omega_1 \frac{\partial \Omega_2}{\partial \varepsilon_1} = 0$$

$$= \Omega_2 \frac{\partial \Omega_1}{\partial \varepsilon_1} + \Omega_1 \frac{\partial \Omega_2}{\partial \varepsilon_2}\frac{\partial \varepsilon_2}{\partial \varepsilon_1} = 0$$

$$= \Omega_2 \frac{\partial \Omega_1}{\partial \varepsilon_1} - \Omega_1 \frac{\partial \Omega_2}{\partial \varepsilon_2} = 0.$$

$\div\, \Omega_1\Omega_2$.

$$\frac{d\Omega}{d\varepsilon} = \frac{1}{\Omega_1}\frac{\partial \Omega_1}{\partial \varepsilon_1} - \frac{1}{\Omega_2}\frac{\partial \Omega_2}{\partial \varepsilon_2} = 0.$$

$\frac{\partial \ln f(x)}{\partial x} = \frac{1}{f(x)}\frac{\partial f}{\partial x}$

$\frac{1}{K_B T} = \beta = \frac{\partial \ln \Omega}{\partial \varepsilon}$

statistics

$\frac{1}{K_B T} = \beta = \frac{\partial \ln \Omega}{\partial \varepsilon}$

$$\frac{1}{\Omega_1}\frac{\partial \Omega_1}{\partial \varepsilon_1} = \frac{1}{\Omega_2}\frac{\partial \Omega_2}{\partial \varepsilon_2}.$$

$$\underbrace{\frac{\partial}{\partial \varepsilon_1}\ln \Omega_1}_{\beta_1} = \underbrace{\frac{\partial}{\partial \varepsilon_2}\ln \Omega_2}_{\beta_2} \Rightarrow \frac{1}{KT_1} = 1/KT_2$$

$\underline{T_1 = T_2}$

Thermodynamic pt of view

$\boxed{TDS}$ $\quad dS = \frac{dQ}{T}$

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

statistic

$\frac{1}{K_B T} = \beta = \frac{\partial \ln \Omega}{\partial E}$

$$\frac{\partial \ln \Omega}{\partial \varepsilon} = \frac{1}{K_B T} \quad —①$$

$$\partial S = \frac{\partial E}{T} \quad —②$$

$$① \times ② \Rightarrow \frac{\partial \ln \Omega}{\partial \varepsilon} \times \frac{\partial \varepsilon}{T} = \frac{1}{K_B T}\partial S.$$

$$\partial \ln \Omega = \frac{\partial S}{K_B}.$$

$$K_B \partial \ln \Omega = \partial S.$$

$$\partial (K_B \ln \Omega) = \partial S$$

Boltzmann's hypothesis → $\boxed{S = K_B \ln \Omega}$ → Bridge eqn b/w thermodynamics & statistics

⟹ Application

2

a) N spin - ½ particle.

Ω (no: of microstate) = $(\text{Basis})^N$

$\therefore$ Basis $2S+1 = 2$.

$\Omega = 2^N$

$S = K_B \ln \Omega = K_B \ln 2^N$

$\underline{\underline{S = N K_B \ln 2}}$ ✓

b) N spin - 1 particle.

$\Omega = (2S+1)^N = 3^N$

$S = K_B \ln \Omega$

$S = K_B \ln 3^N$

$\underline{\underline{S = N K_B \ln 3}}$ ✓

⟹ Relation b/w S & P

m_1 ε_1	m_2 ε_2
m_3 ε_3	m_4 ε_4

n

No: of microstate Ω (No: of arrangement) → No: of permutation $= \dfrac{n!}{m_1!\, m_2! \cdots}$

$$\Omega = \frac{n!}{m_1!\, m_2! \cdots} = \frac{n!}{\prod_s m_s}$$

$S = k_B \ln \Omega.$

$$S = K_B \ln \frac{n!}{\prod_s m_s!}$$

$\ln a + \ln b + \ln c = \ln abc$

$\ln \prod_s m_s = \sum_s \ln m_s$ ✓

$\left[\because \sum_s m_s = n\right]$

Stirling approximation

$\boxed{\ln n! = n \ln n - n.}$

$\ln \prod_s m_s = \sum_s \ln m_s$

$$S = K_B \ln n! / \prod_s m_s!$$

$$= K_B \left[\ln n! - \ln \prod_s m_s!\right],$$

$$= K_B \left[n \ln n - n - \ln \prod_s m_s!\right]$$

$$= K_B \left[n \ln n - n - \sum_s \ln m_s!\right]$$

$$= K_B \left[n \ln n - n - \sum_s (m_s \ln m_s - m_s)\right]$$

$$S = k_B \left[n\ln n - n - \sum_s (m_s \ln m_s + n) \right] \quad 9.$$

$$= k_B \left[n \ln n - \sum_s (m_s \ln m_s) \right]$$

$$\text{probability} = \frac{\text{favourable}}{\text{total}} = \frac{m_s}{n}$$

$$P_s = m_s / n$$

$$m_s = n P_s$$

$$S = k_B \left[n \ln n - \sum P_s n \ln P_s n \right]$$

$$= k_B \left[n \ln n - \sum P_s n (\ln P_s + \ln n) \right]$$

$$= k_B \left[n \ln n - \sum \left[P_s n \ln P_s + P_s n \ln n \right] \right]$$

$$= k_B \left[n \ln n - \sum_s P_s n \ln P_s - \overset{\to 1}{\left(\sum P_s\right)} n \ln n \right]$$

$$= -k_B \sum_s P_s n \ln P_s$$

Specific system $= -k_B \sum_s P_s \ln P_s$

$$S = -n k_B \sum_s P_s \ln P_s$$

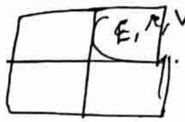
$$S = -n k_B \sum_s P_s \ln P_s$$

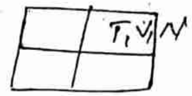
$$\boxed{S_{\text{each system}} = -k_B \sum_s P_s \ln P_s}$$

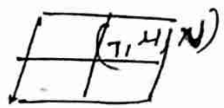
⟹ Ensemble theory

~~Ensm~~ Ensembles

Micro canonical	canonical	Grand canonical
(Insulated walls)	(rigid walls)	(permiable walls)
Isolated	closed	open
No exchang of E & N	exchange of E only	exchange of E & N







EVN — (E, N, V)   TVN — (N, V, T) TVN   (T, μ, V) TVμ

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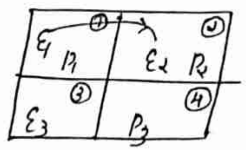
CANONICAL ENSEMBLE [Energy only exchanged]
⟶ (N, V, T)



① $\sum_s P_s = 1 \implies \sum_s P_s - 1 = 0.$

$\sum_s P_s - 1 = 0$ —— (1).

2) $\sum_s E_s P_s = E$

$\sum_s E_s P_s - E = 0$ —— (2)

eq (1) λ_1 + eq (2) λ_2.

$$\lambda_1 \left(\sum_s P_s - 1 \right) + \lambda_2 \left(\sum_s E_s P_s - E \right) = 0.$$

$$f(P_s) = S + \lambda_1 \left(\sum_s P_s - 1 \right) + \lambda_2 \left(\sum_s E_s P_s - E \right)$$

⟶ $-k_B \sum_s P_s \ln P_s$

Equilibrium state (most probable state) 19

P_s max.

$f(P_s)$ is also max.

$$\frac{\partial f(P_s)}{\partial P_s} = 0$$

$$f(P_s) = -K_B \sum_s P_s \ln P_s + \lambda_1 \left(\sum_s P_s - 1 \right) + \lambda_2 \left(\sum_s \varepsilon_s P_s - E \right) =$$

$$\frac{\partial f(P_s)}{\partial P_s} = -K_B \left(\ln P_s + \frac{P_s}{P_s} \right) + \lambda_1 + \lambda_2 (\varepsilon_s) = 0$$

$$-K_B (\ln P_s + 1) + \lambda_1 + \lambda_2 (\varepsilon_s) = 0$$

$$\ln P_s + 1 = \frac{\lambda_1 + \lambda_2 (\varepsilon_s)}{K_B}$$

$$\ln P_s = \frac{\lambda_1 + \lambda_2 \varepsilon_s}{K_B} - 1 \qquad P_s = A e^{\beta \varepsilon_s}$$

$$\cancel{P_s = e^{\left(\frac{\lambda_1 + \lambda_2 \varepsilon_s}{K_B} - 1 \right)}}$$

$$\ln P_s = \left(\frac{\lambda_1}{K_B} - 1 \right) + \left(\frac{\lambda_2 \varepsilon_s}{K_B} \right)$$

$$P_s = e^{\left(\frac{\lambda_1}{K_B} - 1 \right)} \times \frac{\lambda_2 \varepsilon_s}{K_B}$$

$$= e^{(\lambda_1/K_B - 1)} \times e^{\lambda_2 \varepsilon_s / K_B}$$

$$P_s = A e^{\left(\frac{\lambda_2}{K_B} \right) \varepsilon_s} \quad -\beta$$

$$= A e^{-\beta \varepsilon_s}$$

$$\sum_s P_s = 1$$

$$\sum_s A e^{-\beta \varepsilon_s} = 1$$

$$A = \frac{1}{\sum_s e^{-\beta \varepsilon_s}}$$

$$\boxed{P_s = \frac{e^{-\beta \varepsilon_s}}{\sum_s e^{-\beta \varepsilon_s}}} \quad //$$

$\rightarrow Z$ ~~notation~~

Probability of finding the system with energy ε_s.

2 ——— N_2 ——— ε_2.

1 ——— N_1 ——— ε_1

$$P_1 = \frac{e^{-\beta \varepsilon_1}}{\underbrace{\sum_s e^{-\beta \varepsilon_s}}_{\rightarrow Z}}$$

Z ["zustand summe" sum over states partition f^n]

$$P_1 = \frac{e^{-\beta \varepsilon_1}}{Z}$$

$$P_2 = \frac{e^{-\beta \varepsilon_2}}{Z}$$

$$\frac{P_2}{P_1} = e^{-\beta (\varepsilon_2 - \varepsilon_1)}$$

$\beta = 40\ eV^{-1}$

At room temp ($T = 300K$)

$$\beta = \frac{1}{K_B T} = 40\ eV^{-1}$$

Prob.

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1. H_2 atom. (at room temp)

-3.4 eV ——— P_2 ——— ε_2

-13.6 eV ——— P_1 ——— ε_1

$$\frac{N_2}{N_1} = \frac{P_2}{P_1} = e^{-\beta(\varepsilon_2 - \varepsilon_1)}$$

$$\frac{P_2}{P_1} = e^{-\beta(10.2)}$$

$$= e^{-40(10.2)}$$

$$\frac{102}{4} \quad 408$$

$$\frac{P_2}{P_1} = e^{-408}$$

$$\frac{P_2}{P_1} = \frac{1}{e^{408}}$$

1st state ~~B~~ is most populated.

$$\boxed{N = N_0 e^{-\beta\varepsilon}} \rightarrow \text{Boltzmann law.}$$

2. At room temp find the ratio of

Q

1. A system has N distinguishable particle each particle can occupy one of the two non degenerate state, with energy diff. is 0.1eV. If system is in thermal equilibrium at room temp. Find the fraction of particle in the higher to lower state.

N_2 ——— ε_2

$\} \; 0.1$ eV $\quad \Delta E = \varepsilon_2 - \varepsilon_1 = 0.1$ eV.

N_1 ——— ε_1

$$\frac{N_2}{N_1} = e^{-\beta\Delta E}$$

$$= e^{-40(0.1)}$$

$$= e^{-4}$$

$$\frac{N_2}{N_1} = \frac{1}{e^4}$$

HW. At what temp would we find about half as many Hydrogen atom in the 1st excited state as in the ground state.

-3.4 ———

$\} \; 10.2$ eV

-13.6 eV ———

$$\frac{N_2}{N_1} = \frac{1}{2} = e^{-\beta\Delta E}$$

$$\Rightarrow \frac{1}{2} = e^{-\frac{1}{K_B T} 10.2\text{eV}}$$

$$2 = e^{\frac{10.2\text{eV}}{K_B T}}$$

$$\ln(2) = 10.2\text{eV}$$

$$T = \frac{10.2\text{eV}}{\cancel{0.6931} \times 0.693 \times 1.38 \times 10^{-23}}$$

$$T = \frac{10.2 \times 1.6 \times 10^{-19} \times 10^{23}}{0.693 \times 1.38}$$

$$=$$

CANONICAL

Partition f^n Z "sum over all possible state"

$$Z = \sum_s e^{-\beta \epsilon_s}$$

System = "Discrete system"
→ Discrete energy states

Non degenerate

$$\epsilon_3,\ \epsilon_2,\ \epsilon_1 \qquad g = 1$$

$$Z = \sum_s e^{-\beta \epsilon_s}$$

$$Z = e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2} + e^{-\beta\epsilon_3}$$

$$\boxed{P = \frac{e^{-\beta\epsilon_s}}{\sum_s e^{-\beta\epsilon_s}}} = \frac{e^{-\beta\epsilon_s}}{Z}$$

Degenerate

$$\epsilon_2 \quad g_2 = 3$$

$$\epsilon_1 \quad g_1 = 2$$

$$Z = \sum_s g_s e^{-\beta\epsilon_s}$$

$$Z = 2e^{-\beta\epsilon_1} + 3e^{-\beta\epsilon_2}$$

$$\boxed{P = \frac{g_s e^{-\beta\epsilon_s}}{\sum_s g_s e^{-\beta\epsilon_s}}} \qquad P_s = \frac{g_s e^{-\beta\epsilon_s}}{Z}$$

1. A system has two energy levels with energies E & $2E$. The lower level is fourfold while the upper level is double degenerate. If there are N non-interacting particles of the system. The fraction of particle in the upper level is

$$g_1 = 4 \qquad g_2 = 2.$$

$$g_2 = 2 \quad E_2 = 2E$$

$$g_1 = 4 \quad E_1 = E$$

$$Z = \sum_s g_s e^{-\beta\epsilon_s}$$

$$= 4e^{-\beta E} + 2e^{-2\beta E}$$

$$P_1 = \frac{g_1 e^{-\beta\epsilon_1}}{Z}$$

$$P_1 = \frac{4e^{-\beta E}}{4e^{-\beta E} + 2e^{-2\beta E}} \Rightarrow P_1 = \frac{4}{4 + 2e^{-\beta E}}$$

$$P_2 = g_2 e^{-\beta\epsilon_2}/Z$$

$$P_2 = \frac{2e^{-2\beta E}}{4e^{-\beta E} + 2e^{-2\beta E}} = \frac{2}{2 + e^{-\beta E}}$$

$$\Rightarrow P_2 = \frac{2}{4e^{\beta E} + 2}$$

$$P_2 = \frac{1}{1 + 2e^{\beta E}}$$

G.2012.

2. Consider a system whose 3 energy levels are given by 0, ε, & 2ε. The energy level ε is 2 fold degenerate & other two are nondegenerate. Find Z.

$g_3 = 1$ 2ε
$g_2 = 2$ ε
$g_1 = 1$ 0

$$Z = \sum_s g_s e^{-\beta \varepsilon_s}$$

$$Z = 1 + 2e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}$$

Z =

$$Z = (1 + e^{-\beta\varepsilon})^2$$

3. Consider a system of 2 non-interacting classical particles which can occupy any of the three levels with energy 0, ε, 2ε with degeneracies 1, 2, 4 respectively find Z & also find the corresponding probabilities.

$$\cancel{Z = d\,d} \quad Z = \sum_s g_s e^{-\beta\varepsilon_s}$$

$$Z = (1 + 2e^{-\beta\varepsilon} + 4e^{-2\beta\varepsilon})^2$$

$$P_s = \frac{g_s e^{-\beta\varepsilon_s}}{\sum g_s e^{-\beta\varepsilon_s}}$$

$$P_1 = \frac{1}{(1 + 2e^{-\beta\varepsilon} + 4e^{-2\beta\varepsilon})^2}$$

$$P_2 = \frac{2e^{-\beta\varepsilon}}{(1 + 2e^{-\beta\varepsilon} + 4e^{-2\beta\varepsilon})^2}$$

$$P_3 = \frac{4e^{-2\beta\varepsilon}}{(1 + 2e^{-\beta\varepsilon} + 4e^{-2\beta\varepsilon})^2}$$

$1 + 4e^{-2\beta\varepsilon} + 16e^{-4\beta\varepsilon} + 4e^{-\beta\varepsilon} + 8e^{-2\beta\varepsilon} + 16e^{-3\beta\varepsilon}$

$(a+b+c)^2$
$= a^2 + b^2 + c^2 + 2ab + 2ac + 2bc$

$\Rightarrow$ Discrete system

For N particle.

$$\boxed{Z_N = [Z_1]^N}$$

Non-Degenerate

1. $Z = \sum_s e^{-\beta\varepsilon_s}$

2. $P_s = \frac{e^{-\beta\varepsilon_s}}{Z} = \frac{e^{-\beta\varepsilon_s}}{\sum_s e^{-\beta\varepsilon_s}}$

3. $$\boxed{\langle f \rangle = \sum_s f P_s = \frac{\sum_s f e^{-\beta\varepsilon_s}}{\sum_s e^{-\beta\varepsilon_s}}}$$

$$\langle E \rangle = \sum_s \varepsilon_s P_s = \frac{\sum_s \varepsilon_s e^{-\beta\varepsilon_s}}{\sum_s e^{-\beta\varepsilon_s}}$$

Degenerate

1. $Z = \sum_s g_s e^{-\beta\varepsilon_s}$

2. $P_s = \frac{g_s e^{-\beta\varepsilon_s}}{Z}$

3. $\langle f \rangle = \sum_s f_s P_s$

$$\boxed{\langle f \rangle = \frac{\sum_s f g_s e^{-\beta\varepsilon_s}}{\sum_s g_s e^{-\beta\varepsilon_s}}}$$

$$\langle E \rangle = \frac{\sum_s \varepsilon_s g_s e^{-\beta\varepsilon_s}}{\sum_s g_s e^{-\beta\varepsilon_s}}$$

Continuous system [classical]

$$Z = \sum_s e^{-\beta \varepsilon_s} \Rightarrow \text{"Dimensionless quantity"}$$

$$\sum \longrightarrow \int dq_i \, dp_i$$

$dq_i \rightarrow [dx\,dy\,dz]$, $dp_i \rightarrow [dp_x\,dp_y\,dp_z]$

$$Z_{cont} = \frac{1}{h^3} \int e^{-\beta E} \, dq_i \, dp_i$$

$\frac{1}{h^3} \rightarrow$ Dimensionless term.

$$\boxed{Z_{class} = \frac{1}{h^3} \int e^{-\beta \hat{H}} \, dq_i \, dp_i}$$

$Z_{class} \rightarrow$ 1 particle.

$$Z_N = [Z_1]^N$$

Note

① $Z = \sum_s e^{-\beta \varepsilon_s}$

Consider $\ln Z = \ln \sum_s e^{-\beta \varepsilon_s}$

$$\frac{\partial \ln Z}{\partial \varepsilon_s} = \frac{\partial}{\partial \varepsilon_s} \ln \sum_s e^{-\beta \varepsilon_s}$$

$$= \frac{1}{\sum_s e^{-\beta \varepsilon_s}} \times e^{-\beta \varepsilon_s}(-\beta)$$

$$\frac{\partial \ln Z}{\partial \varepsilon_s} = \frac{e^{-\beta \varepsilon_s}}{Z}(-\beta)$$

$$\boxed{-\frac{1}{\beta}\frac{\partial \ln Z}{\partial \varepsilon_s} = P_s} \longrightarrow \boxed{P_s = -k_B T \frac{\partial \ln Z}{\partial \varepsilon_s}}$$

2) $Z = \sum_s e^{-\beta \varepsilon_s}$

Consider $\ln Z = \ln \sum_s e^{-\beta \varepsilon_s}$

$$\frac{\partial \ln Z}{\partial \beta} = \frac{\partial}{\partial \beta} \ln \left(\sum_s e^{-\beta \varepsilon_s}\right)$$

$$= \frac{1}{\sum_s e^{-\beta \varepsilon_s}} \sum_s e^{-\beta \varepsilon_s}(-\varepsilon_s)$$

$$= -\frac{\sum_s \varepsilon_s e^{-\beta \varepsilon_s}}{\sum_s e^{-\beta \varepsilon_s}}$$

$$\boxed{U = -\frac{\partial}{\partial \beta} \ln Z}$$

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Relation b/w Z & F (Helmholtz free energy).

Thermodynamic potential = U, F, G, H

(G → const pressure; F → const. volume; Calculable energy)

1st law of TD - $dQ = dU + dW - \mu dN$.

($dW \to pdV$)

$dQ = dU + pdV - \mu dN$.

$TdS = dU + pdV - \mu dN$.

Rel^n b/w U & F.

$F = U - TS$.

$dF = dU - TdS - SdT$

$dF = TdS - pdV + \underline{\mu dN} - TdS - SdT$

$dF = -pdV \cancel{+} SdT + \mu dN$.

$dF = -pdV - SdT + \mu dN$

$\boxed{\left.\frac{\partial F}{\partial V}\right|_{T,N} = -p} \implies p = -\left.\frac{\partial F}{\partial V}\right|_{T,N}$.

$\boxed{\left.\frac{\partial F}{\partial T}\right|_{V,N} = -S} \implies S = -\left.\frac{\partial F}{\partial T}\right|_{V,N}$

$\boxed{\left.\frac{\partial F}{\partial N}\right|_{T,V} = \mu}$

$F = U - TS$.

$S = -\partial F/\partial T$

$F = U + T\frac{\partial F}{\partial T}$

$T^2\frac{d}{dT}\left(\frac{F}{T}\right) = T^2 F\left(\frac{-1}{T^2}\right) - T^2 \times \frac{1}{T}\frac{\partial F}{\partial T}$

$-T\frac{\partial F}{\partial T} = -F - T^2\frac{d}{dT}\left(\frac{F}{T}\right) \implies T\frac{\partial F}{\partial T} = F + T^2 \ldots$

$F = U + F + T^2\frac{d}{dT}\left(\frac{F}{T}\right)$

$U = -T^2\frac{d}{dT}\left(\frac{F}{T}\right)$ —— (1)

we know

$U = -\frac{\partial}{\partial \beta}\ln Z$.

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

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

$U = \frac{\cancel{\ldots}}{k_B T^2}\frac{\partial}{\partial T}\ln Z$.

$U = \frac{\cancel{\ldots}}{k_B T^2}\frac{\partial}{\partial T}\ln Z$ —— (2)

$\boxed{U = k_B T^2\frac{\partial}{\partial T}\ln Z}$

$$k_B T^2 \frac{\partial}{\partial T} \ln Z = -T^2 \frac{d}{dT}\left(\frac{F}{T}\right)$$

$$\boxed{F = -k_B T \ln Z}$$

$$\ln Z = -F/k_B T$$

$$\boxed{Z = e^{-\beta F}}$$

Canonical ensemble (summary)

1. $Z = \sum_s e^{-\beta \varepsilon_s}$.

2. $P_s = \frac{e^{-\beta \varepsilon_s}}{Z} = -k_B T \frac{\partial}{\partial \varepsilon_s} \ln Z$ $\qquad C_V = \frac{\partial U}{\partial T}$

3. $U = \sum_s \varepsilon_s P_s = \frac{\sum_s \varepsilon_s e^{-\beta \varepsilon_s}}{\sum_s e^{-\beta \varepsilon_s}}$

$U = -\frac{\partial}{\partial \beta} \ln Z$.

4. $F = -k_B T \ln Z$ $\Longrightarrow U = k_B T^2 \frac{\partial}{\partial T} \ln Z$.

5. $p = -\frac{\partial F}{\partial V}\Big|_{T,N}$ $\quad S = -\frac{\partial F}{\partial T}\Big|_{V,N}$ $\quad \mu = +\frac{\partial F}{\partial N}\Big|_{V,T}$

6. $F = U - TS$.

1. A system in thermal equilibrium has energies 0, & ε. Find Z & also find the physical quantities of the system.

② ———— ε.

① ———— 0

1) $Z = \sum_s e^{-\beta \varepsilon_s}$.

$= 1 + e^{-\beta \varepsilon}$.

$U = -\frac{\partial}{\partial \beta} \ln Z = -\frac{\partial}{\partial \beta} \ln(1 + e^{-\beta \varepsilon})$

$= -\frac{1}{1 + e^{-\beta \varepsilon}} \times e^{-\beta \varepsilon}(-\varepsilon)$

$U = \frac{\varepsilon e^{-\beta \varepsilon}}{1 + e^{-\beta \varepsilon}}$

$F = -k_B T \ln Z. = -k_B T \ln(1 + e^{-\beta \varepsilon})$

$S = -\partial F/\partial T$.

$F = U - TS$.

$$S = \frac{U - F}{T} = \frac{\frac{\varepsilon e^{-\beta \varepsilon}}{1 + e^{-\beta \varepsilon}} + k_B T \ln(1 + e^{-\beta \varepsilon})}{T}$$

$$S = \frac{\varepsilon\, e^{-\beta\varepsilon}}{T\left(1+e^{-\beta\varepsilon}\right)} + k_B \ln\left(1+e^{-\beta\varepsilon}\right)$$

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$$C_v = \frac{\partial u}{\partial T}$$

$$C_v = \frac{\partial}{\partial T}\left(\frac{\varepsilon\, e^{-\varepsilon/k_BT}}{1+e^{-\varepsilon/k_BT}}\right)$$

$$= \frac{\left(1+e^{-\varepsilon/k_BT}\right)\varepsilon\, e^{-\varepsilon/k_BT} \times \left(\frac{+\varepsilon}{k_BT^2}\right) - \varepsilon\, e^{-\varepsilon/k_BT}\left(e^{-\varepsilon/k_BT} \times \frac{\varepsilon}{k_BT^2}\right)}{\left(1+e^{-\varepsilon/k_BT}\right)^2}$$

$$= \frac{\frac{\varepsilon^2 e^{-\varepsilon/k_BT}}{k_BT^2} + \frac{\varepsilon^2 e^{-2\varepsilon/k_BT}}{k_BT^2} - \frac{\varepsilon^2 e^{-2\varepsilon/k_BT}}{k_BT^2}}{\left(1+e^{-\varepsilon/k_BT}\right)^2}$$

$$= \frac{\varepsilon^2 e^{-\varepsilon/k_BT}}{k_BT^2\left(1+e^{-\varepsilon/k_BT}\right)^2}$$

2.

ε

0

$-\varepsilon$

$$Z = \sum_s e^{-\beta\varepsilon_s}$$

$$\frac{e^{\beta\epsilon}+e^{-\beta\epsilon}}{2} = \cosh\beta\epsilon$$

$$Z = e^{\beta\epsilon} + 1 + e^{-\beta\epsilon}$$

$$= 1 + 2\cosh\beta\epsilon.$$

$$Z = 1 + 2\cosh\beta\epsilon.$$

$$U = -\frac{\partial}{\partial\beta}\ln z.$$

$$= -\frac{\partial}{\partial\beta}\ln\left(1+2\cosh\beta\epsilon\right)$$

$$= -\frac{1}{1+2\cosh\beta\epsilon} \times 2\sinh\beta\varepsilon \times \varepsilon$$

$$= \frac{-2\varepsilon\sinh\beta\epsilon}{1+2\cosh\beta\epsilon}$$

$$F = -k_BT\ln z.$$

$$= -k_BT\ln\left(1+2\cosh\beta\epsilon\right)$$

$$F = U - TS.$$

$$S = \frac{U-F}{T} = \frac{-2\varepsilon\sinh\beta\epsilon}{T\left(1+2\cosh\beta\epsilon\right)} + k_B\ln\left(1+2\cosh\beta\epsilon\right)$$

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$$C_v = \frac{\partial U}{\partial T}$$

$$= \frac{(1+2\cosh\beta\epsilon)\left(-2\epsilon^2\cosh\beta\epsilon \times \frac{-1}{k_B T^2}\right) + 2\epsilon\sinh\beta\epsilon\left(2\sinh\beta\epsilon \times \frac{-\epsilon}{k_B T^2}\right)}{(1+2\cosh\beta\epsilon)^2}$$

$$= \frac{\frac{+2\epsilon^2}{k_B T^2}\cosh\beta\epsilon + \frac{4\epsilon^2}{k_B T^2}\cosh^2\beta\epsilon - \frac{4\epsilon^2}{k_B T^2}\sinh^2\beta\epsilon}{(1+2\cosh\beta\epsilon)^2}$$

$$= \frac{\frac{4\epsilon^2}{k_B T^2} + \frac{2\epsilon^2}{k_B T^2}\cosh\beta\epsilon}{(1+2\cosh\beta\epsilon)^2}$$

$$= \frac{\frac{2\epsilon^2}{k_B T^2}(2+\cosh\beta\epsilon)}{(1+2\cosh\beta\epsilon)^2} = \frac{\frac{\epsilon^2}{k_B T^2}\left(4+e^{\beta\epsilon}+e^{-\beta\epsilon}\right)}{\left(1+e^{-\beta\epsilon}+e^{-\beta\epsilon}\right)^2}$$

$\Longrightarrow$ <u>Quantum oscillators</u>

$$V(x) = \frac{1}{2}kx^2$$

$$H = \frac{p^2}{2m} + \frac{1}{2}kx^2$$

$$\langle \hat{H} \rangle = E = \left(n+\tfrac{1}{2}\right)\hbar\omega$$

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

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

$$= \sum_n e^{-\beta n\hbar\omega} \times e^{-\frac{\beta\hbar\omega}{2}}$$

$$= e^{-\frac{\beta\hbar\omega}{2}} \sum_n e^{-\beta n\hbar\omega}$$

$$= e^{-\frac{\beta\hbar\omega}{2}}\left[1 + e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} + \cdots\right]$$

$\Downarrow$

GP

$$S_\infty = \frac{a}{1-r} = \frac{1}{1-e^{-\beta\hbar\omega}}$$

$$\frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}$$

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

$$Z = \frac{1}{e^{\frac{\beta\hbar\omega}{2}} - e^{-\frac{\beta\hbar\omega}{2}}}$$

$$\boxed{Z = \frac{1}{2\sinh\left(\frac{\beta\hbar\omega}{2}\right)}}$$

$$\frac{a}{1-r} \qquad S_\infty = \frac{a}{1-}$$

$$\frac{a}{1-r}$$

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

2 cosh

2

$$U = -\frac{\partial}{\partial\beta}\ln Z.$$

$$= -\frac{\partial}{\partial\beta}\ln\left(\frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}\right)$$

$$\cancel{= -\frac{\partial}{\partial\beta}\left[\ln\left(1 - e^{-\beta\hbar\omega}\right)\right)}$$

$$= -\frac{\partial}{\partial\beta}\left(\ln e^{-\beta\hbar\omega/2} - \ln\left(1 - e^{-\beta\hbar\omega}\right)\right]$$

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

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

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

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

$$F = -k_BT\ln Z.$$

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

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

$$S = \frac{U - F}{T}$$

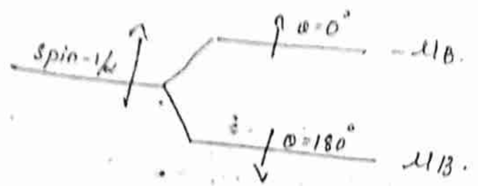
$$= \frac{\cancel{\frac{\hbar\omega}{2}} + \frac{\hbar\omega e^{-\beta\hbar\omega}}{\left(1 - e^{-\beta\hbar\omega}\right)} + \cancel{\frac{\hbar\omega}{2}} + k_BT\ln\left(1 - e^{-\beta\hbar\omega}\right)}{T}$$

$$= \cancel{\frac{\hbar\omega}{T}} + \frac{\hbar\omega}{T}\frac{e^{-\beta\hbar\omega}}{\left(1 - e^{-\beta\hbar\omega}\right)} + k_B\ln\left(1 - e^{-\beta\hbar\omega}\right)$$

$$S = \frac{\hbar\omega}{T}\frac{e^{-\beta\hbar\omega}}{\left(1 - e^{-\beta\hbar\omega}\right)} - k_B\ln\left(1 - e^{-\beta\hbar\omega}\right)$$

→ Paramagnetic system

Spin-½ particle kept in a magnetic field.



$PE = -\mu \cdot B$

$E = -\mu B \cos\theta.$

$Z = \sum_s e^{-\beta E_s} = e^{-\beta(-\mu B)} + e^{-\beta(\mu B)}$

$Z = e^{-\beta\mu B} + e^{\beta\mu B}.$

$\left[\frac{e^{\beta\mu B} + e^{-\beta\mu B}}{2} = \cosh\beta\mu B \right]$

$Z = 2\cosh\beta\mu B.$

$U = -\frac{\partial}{\partial\beta} \ln Z.$

$= -\frac{\partial}{\partial\beta} \ln(2\cosh\beta\mu B)$

$= \frac{-1}{2\cosh\beta\mu B} 2\sinh\beta\mu B \times \mu B.$

$= -\mu B \tanh\beta\mu B.$

$U = -\mu B \tanh\beta\mu B$

$F = -K_B T \ln Z.$

$F = -K_B T \ln 2\cosh(\beta\mu B)$

$S = \frac{U - F}{T}$

$= \frac{-\mu B \tanh\beta\mu B + K_B T \ln 2\cosh(\beta\mu B)}{T}$

$= \frac{-\mu B}{T} \tanh\beta\mu B + K_B \ln(2\cosh(\beta\mu B))$

Magnetization $[M]$

$M = -\frac{\partial F}{\partial B}.$

$M = K_B T \frac{\partial}{\partial B} \ln 2\cos(\beta\mu B)$

$= K_B T \frac{2\sinh\beta\mu B \times \mu\beta}{2\cos\beta\mu B}$

$= \mu \tanh\beta\mu B$

$M = -\frac{\partial F}{\partial B}$

U/B

$M = -U/B$

$U = -MB$

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classical system.

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↳ continuous energy

$$Z = \sum_s e^{-\beta E_s}$$

$$E = \sum_{i=1}^{3} \frac{p_i^2}{2m} + U$$

$$Z_1 = \sum_s e^{-\beta E_s} = \frac{1}{h^3} \int e^{-\beta E}\, dq_i\, dp_i$$

$$= \frac{1}{h^3} \int e^{-\beta\left[\sum_{i=1}^{3} \frac{p_i^2}{2m} + U\right]} dq_i\, dp_i$$

$$= \frac{1}{h^3} \int_{-\infty}^{\infty} e^{-\beta\left[\frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}\right]} dp_x\, dp_y\, dp_z \times \int_{-\infty}^{\infty} e^{-\beta U}\, dq_i$$

$$= \frac{1}{h^3} \int_{-\infty}^{\infty} e^{-\frac{\beta p_x^2}{2m}} dp_x \int_{-\infty}^{\infty} e^{-\frac{\beta p_y^2}{2m}} dp_y \int_{-\infty}^{\infty} e^{-\frac{\beta p_z^2}{2m}} dp_z \times \int_{-\infty}^{\infty} e^{-\beta U}\, dq_i$$

$$\left[\because \int_{-\infty}^{\infty} e^{-ax^2} = \sqrt{\pi/a}\right]$$

$$\therefore Z = \frac{1}{h^3} \sqrt{\frac{2\pi m}{\beta}} \times \sqrt{\frac{2\pi m}{\beta}} \times \sqrt{\frac{2\pi m}{\beta}} \cdot \int_{-\infty}^{\infty} e^{-\beta U}\, dq_i$$

$$= \frac{1}{h^3} \left(\frac{2\pi m}{\beta}\right)^{3/2} \int_{-\infty}^{\infty} e^{-\beta U}\, dq_i$$

$$= \frac{1}{h^3} (2\pi m k_B T)^{3/2} \int_{-\infty}^{\infty} e^{-\beta U}\, dq_i$$

$$\boxed{Z_{cl}^{3D} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \int_{-\infty}^{\infty} e^{-\beta U}\, dq_i}$$

$$Z_{cl}^{1D} = \left(\frac{2\pi m k_B T}{h^2}\right)^{1/2} \int_{-\infty}^{\infty} e^{-\beta U}\, dx$$

eg: 1.) Gravitation potential.

$U = mgz$ (z axis)

$$Z_{cl}^{3D} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \int_{0}^{\infty} e^{-\beta m g z}\, dz$$

$$\boxed{Z_{cl}^{3D} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \frac{1}{\beta m g}}$$

2) Ideal gas $U = 0$.

$$Z_{id}^{3D} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \int_{-\infty}^{\infty} \underbrace{dx\, dy\, dz}_{dz \,\to\, \text{Real space}}$$

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

For N ~~particle~~ molecule

$$Z = (Z_1)^N = V^N \left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2}$$

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

Ideal gas

$$Z = V^N \left(\frac{2\pi m K_B T}{h^2}\right)^{3N/2}$$

1) $F = -K_B T \ln Z$

$$= -K_B T \left[N \ln V + \frac{3N}{2} \ln\left(\frac{2\pi m K_B T}{h^2}\right)\right]$$

2) $U = -\frac{\partial}{\partial \beta} \ln Z$

$$= -\frac{\partial}{\partial \beta}\left[N \ln V + \frac{3N}{2} \ln\left(\frac{2\pi m K_B T}{h^2}\right)\right]$$

$$= -\frac{\partial}{\partial \beta}\left[N \ln V + \frac{3N}{2} \ln\left(\frac{2\pi m}{\beta h^2}\right)\right]$$

we know:

$$\frac{\partial}{\partial x} \ln x = \frac{1}{x}$$

$$\frac{\partial}{\partial x} \ln ax = \frac{1}{x}$$

$$U = -\frac{\partial}{\partial \beta}\left[N \ln V - \frac{3N}{2} \ln\left(\frac{\beta h^2}{2\pi m}\right)\right]$$

$$= \frac{3N}{2} \frac{1}{\beta}$$

$$U = \frac{3N K_B T}{2}$$

$$C_v = \frac{\partial U}{\partial T} = \frac{3}{2} N K_B$$

Avarage value of a quantity

Discrete:

$$\langle A \rangle = \sum_s A P_s$$

$$\langle A \rangle = \frac{\sum_s A e^{-\beta \varepsilon_s}}{\sum e^{-\beta \varepsilon_s}}$$

continuous $\longrightarrow \sum - \int$.

$$\therefore \langle A \rangle = \frac{\int A e^{-\beta E} dq_i \, dp_i}{\int e^{-\beta E} dq_i \, dp_i}$$

eg:

$$\langle x \rangle = \frac{\int x \, e^{-\beta E} dx \, dp_x}{\int e^{-\beta E} dx \, dp_x} \qquad E \to \frac{p_x^2}{2m} + V(x)$$

$$\langle x \rangle = \frac{\int x \, e^{-\beta\left(\frac{p_x^2}{2m} + V(x)\right)} dx \, dp_x}{\int e^{-\beta\left(\frac{p_x^2}{2m} + V(x)\right)} dx \, dp_x}$$

CSIR

1. A particle is confined to the region $x \geq 0$ by a pot. which increases linearly $U(x) = U_0 x$. The mean position of the particle.

$$\langle x \rangle = \frac{\int x e^{-\beta E} dx\, dp_x}{\int e^{-\beta E} dx\, dp_x}$$

$$E = \frac{p_x^2}{2m} + U_0 x.$$

$$\langle x \rangle = \frac{\int x e^{-\beta\left(\frac{p_x^2}{2m} + U_0 x\right)} dx\, dp_x}{\int e^{-\beta\left(\frac{p_x^2}{2m} + U_0 x\right)} dx\, dp_x}$$

$$\left| \int_{-\infty}^{\infty} e^{-ax} = 1/a \qquad \int_{-\infty}^{\infty} x e^{-ax} = 1/a^2 \right.$$

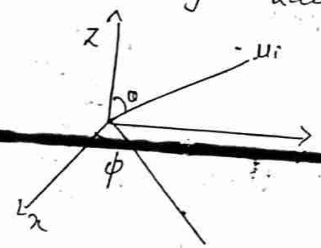
$$= \frac{\int_0^\infty x e^{-\beta U_0 x} dx \times \int_0^\infty e^{-\beta \frac{p_x^2}{2m}} dp_x}{\int_0^\infty e^{-\beta \frac{p_x^2}{2m}} dp_x \times \int_0^\infty e^{-\beta U_0 x} dx}$$

$$= \frac{\int_0^\infty x e^{-\beta U_0 x} dx}{\int_0^\infty e^{-\beta U_0 x} dx} = \frac{\frac{1}{(\beta U_0)^2}}{1/\beta U_0}$$

$$\langle x \rangle = \frac{1}{\beta U_0} \checkmark$$

⟹ Paramagnetic system (classical theory) [Langevin]

1. Consider a system of non interacting spins each has classical magnetic moment magnitude μ. The Hamiltonian of the system in an external magnetic field is $H_{m} = \sum_{i=1}^{N} \vec{\mu}_i \cdot \vec{H}$. Find Z and also find magnetization.



$$E = \sum_i^N \vec{\mu}_i \cdot \vec{H}$$

$$E = \mu H \cos\theta.$$

$$Z = \sum e^{-\beta E}$$

$$= \sum e^{-\beta \mu H \cos\theta}$$

(θ, ϕ are changing, No phase space concept)

$$\sum \longrightarrow \int \sin\theta\, d\theta\, d\phi$$

$$Z = \int_0^\pi \int_0^{2\pi} e^{-\beta \mu H \cos\theta} \sin\theta\, d\theta\, d\phi.$$

$$= 2\pi \int_0^\pi e^{-\beta \mu H \cos\theta} \sin\theta\, d\theta.$$

Let $\cos\theta = x$. $-\sin\theta\, d\theta = dx$. $x = 1$, -1

$$= 2\pi \int_{-1}^{+1} e^{-\beta \mu H x} dx$$

$$= 2\pi \left. \frac{e^{-\beta \mu H x}}{-\beta \mu H} \right|_{-1}^{1} = \frac{2\pi}{\beta \mu H}\left[-e^{-\beta \mu H} + e^{\beta \mu H} \right]$$

$$Z = \frac{2\pi}{\beta\mu H}\left[e^{\beta\mu H} - e^{-\beta\mu H}\right]$$

$$= \frac{4\pi}{\beta\mu H}\cdot\sinh(\beta\mu H)$$

$$\boxed{Z = \frac{4\pi}{\beta\mu H}\sinh(\beta\mu H)}$$

$$F = -K_BT\ln Z = -K_BT\left(\ln\frac{4\pi}{\beta\mu H}\sinh\beta\mu H\right).$$

$$\boxed{M = -\frac{\partial F}{\partial H}}$$

$$F = -K_BT\left[\ln\frac{4\pi}{\beta\mu H} + \ln\sinh\beta\mu H\right]$$

$$M = K_BT\frac{\partial}{\partial H}\left[-\left(\ln\frac{\beta\mu H}{4\pi}\right) + \ln\sinh\beta\mu H\right]$$

$$= K_BT\left[\frac{\cosh\beta\mu H}{\sinh\beta\mu H}\times\beta\mu - \frac{1}{H}\right]$$

$$= K_BT\left[\cot\beta\mu H\times\beta\mu - 1/H\right].$$

$$M = \mu\cot\beta\mu H - \frac{K_BT}{H}$$

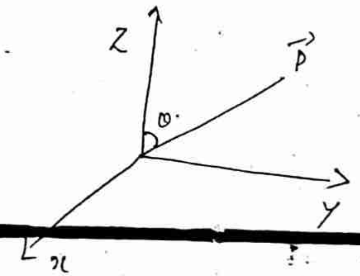
$$M = K_BT\beta\mu\left[\cot\beta\mu H - \frac{1}{\beta\mu H}\right].$$

$$\boxed{M = \mu.\left[\coth\beta\mu H - \frac{1}{\beta\mu H}\right]}$$

$$L(x) = \coth x - \frac{1}{x}$$

$$\therefore \boxed{M = \mu L(\beta\mu H)}$$

2. Write down a general expression for the average macroscopic polarization $\vec{P}$. (dipol momentum /unit volume) for a dilute system for n molecule /unit volume at temp T in uniform Electric field E.



$$PE = -\vec{P}\cdot\vec{E}$$

$$E = -PE\cos\theta.$$

$$E = -PE\cos\theta.$$

$$Z = \Sigma e^{-\beta E}$$

$$= \Sigma e^{+\beta PE\cos\theta}.$$

$$Z = \int_0^{2\pi}\int_0^{\pi} e^{\beta PE\cos\theta}\sin\theta\, d\theta\, d\phi$$

$$= 2\pi\int^{\pi} e^{\beta PE\cos\theta}\sin\theta\, d\theta$$

$$= 2\pi\int_{-1} e^{\beta PEx}\,dx \qquad \text{Let } \cos\theta = x,\ -\sin\theta\, d\theta = dx$$

$$= 2\pi\left.\frac{e^{\beta PEx}}{\beta PE}\right|_{-1}^{1}$$

$$Z = \frac{2\pi}{\beta p E}\left(e^{\beta p E} - e^{-\beta p E}\right) \quad 2c''$$

$$= \frac{4\pi}{\beta p E} \sinh \beta p E$$

$$\ln z = \ln \frac{4\pi}{\beta p E} + \ln \sinh \beta p E$$

$$F = -k_B T \ln z$$

$$= -k_B T \left(\ln \frac{4\pi}{\beta p E} + \ln \sinh \beta p E\right)$$

$$\boxed{\vec{p} = -\frac{\partial F}{\partial E}}$$

$$\vec{p} = -k_B T \left[-\ln \frac{\beta p E}{4\pi} + \ln \sinh \beta p E\right]$$

$$= k_B T \left[\frac{\cosh \beta p E}{\sinh \beta p E} \times \beta p - \frac{1}{E}\right]$$

$$= k_B T \left[\beta p \coth \beta E - \frac{1}{E}\right]$$

$$\vec{p} = p \coth \beta p E - \frac{k_B T}{E}$$

For n particle.

$$\boxed{\vec{p} = p n \coth \beta p E - \frac{n k_B T}{E}}$$

3) A zipper has N links. Each link has 2 states; state 1 means it is closed and has zero energy & state 2 means it is open with energy E. The zipper can only un zip from the left & the s^{th} link cannot open unless all the links to its left (1, 2, ... s-1) are already open. Find the partition fn of the system.

N links

1) closed $E = 0$

2) open $E = E$.

$$Z = \sum e^{-\beta \epsilon}$$

1) all closed $E = 0$

2) 1^{st} link is open $E = \epsilon$.

2^{nd} link is open $E = 2\epsilon$.

3^{rd} link is open $E = 3\epsilon$.

n^{th} link is open $E = n\epsilon$.

$$Z = 1 + e^{-\beta \epsilon} + e^{-2\beta \epsilon} + \cdots$$

$$= \sum_{n=0}^{N} e^{-n\beta E}$$

$\rightarrow$ GP $\quad S_n = \dfrac{a(1-r^n)}{1-r}$

$$Z = \frac{1 - e^{-(N+1)\beta E}}{1 - e^{-\beta E}} \qquad r = e^{-\beta E}, \quad n = N+1$$

4) consider 10 atom filled at lattice sites, each atom can have magnetic moment μ_0 or $-\mu_0$ in x direction. $f(\mu)$ denote the probability the the magnetic moment of the system is μ. Assuming statistical mechanics to hold, then the value of $f(\ldots)/f(0)$ is

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10 → 6 (μB), 4 ($-\mu B$)

$$\Omega = \frac{10!}{6!\,4!}$$

10 → 5 (μB), 5 ($-\mu B$)

$$\Omega = \frac{10!}{5!\,5!}$$

$$\frac{f(2\mu_B)}{f(0)} = \frac{5!\,5!}{6!\,4!} = \frac{5}{6}$$

21) 1000 particles at a temp T are distributed among three energy levels $E_0 = 0$, $E_1 = kT$ & $E_2 = 2kT$. What is the total energy of the system?

$$Z_N = \left(1 + e^{-\beta k_B T} + e^{-2\beta k_B T}\right)^{1000}$$

$$U = -\frac{\partial}{\partial \beta}\ln Z = 1000\left(\frac{e^{-\beta k_B T} \times k_B T + e^{-2\beta k_B T} \times 2k_B T}{1 + e^{-\beta k_B T} + e^{-2\beta k_B T}}\right)$$

$$= 1000\, k_B T\, \frac{\left(e^{-1} + 2e^{-2}\right)}{\left(1 + e^{-1} + e^{-2}\right)} = \frac{k_B T\left(1 + 2e^{-1}\right)}{\left(1 + e + e^{-1}\right)}$$

$$E = 1000 k_B T\, \frac{e^{-1}\left(1 + 2e^{-1}\right)}{\left(1 + e^{-1} + e^{-2}\right)}$$

22) A large isolated system of N weakly interacting particle is in thermal equilibrium. Each particle has only 3 possible non-degenerate states of energies 0, E & $3E$ ~~possible~~ when the system is at an absolute temp $T \gg E/k$, where k is Boltzmann's const, the average energy of each particle is

$$Z = 1 + e^{-\beta E} + e^{-3\beta E}.$$

$$Z^N = \left(1 + e^{-\beta E} + e^{-3\beta E}\right)^N.$$

$$U = -\frac{\partial}{\partial \beta}\ln Z.$$

$$= -\frac{\partial}{\partial \beta}\left(\ln\left(1 + e^{-\beta E} + e^{-3\beta E}\right)\right)$$

$$= \left(\frac{e^{-\beta E}\, E + e^{-3\beta E} \times 3E}{1 + e^{-\beta E} + e^{-3\beta E}}\right)$$

$T \gg E/k$

$kT \gg E$

$1 \gg E/k_B T$

$$= \frac{E + 3E}{3} = 4E/3$$

28) A gas of N identical classical non-interacting atoms is held in a potential $V(r) = \alpha r$ where $r = (x^2 + y^2 + z^2)^{1/2}$. The gas is in thermal equilibrium at temp. T. Find the single particle partition f^n Z_1 of an atom in the gas. Express your answer in the form $Z_1 = A T^{\alpha} a^{-2}$

$$Z = V^N\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2} \int e^{-\beta a r} \, r^2 \, dr$$

$$= V^N\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2} \int_0^\infty e^{-\beta a r} r^2 \, dr$$

$$= V^N\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2} \frac{2!}{(\beta a)^3}$$

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

$N = 1$

$$Z = A\, T^{9/2} a^{-3}$$

31. A dilute system at T.P. consist 50 independent distinguished particles; has three energy level of energy $0, \varepsilon \,\&\, 2\varepsilon$, with degeneracies of 300, 600, & 1200 respectively. The system is at a const temp. $T = \varepsilon/k_B$, where k_B is Boltzmann's const. The molecular partition f^n for this system is.

$$Z = \sum_s g_s e^{-\beta \varepsilon_s} = 300 + 600 e^{-\frac{\varepsilon}{k_B \varepsilon/k_B}} + 1200 e^{-\frac{2\varepsilon}{k_B \varepsilon/k_B}}$$

$$= 300 + 600 e^{-1} + 1200 e^{-2}$$

$$\simeq 683$$

33) N particle distributed among two states $E = 0$ & $E = k_B T$. The probability of occupation of $E = 0$ level at temp T is

$$Z = 1 + e^{-1}$$

$$P_0 = \frac{1}{1+e^{-1}} = \frac{e^1}{e^1+1} = \frac{e}{1+e}$$

35) A system has a fixed number of particles. N. Suppose the energy scale is shifted by an arbitrary const η. The new and the old partition f^n, z' & z will be related as.

$$Z = \sum e^{-\beta \varepsilon_s N}$$

$$Z' = \sum_s e^{-\beta \eta \varepsilon_s N} e^{-\beta \varepsilon_s N}$$

$$Z' = e^{-\beta \varepsilon_s \eta N} Z.$$

$$Z' = e^{-\beta \varepsilon_s \eta N} Z$$

36. A system in thermal equilibrium at temp T consist of a large no: N_0 of subsystems each of which can exist only in 2 states of energy E_1 & E_2, where $E_2 - E_1 = \varepsilon$ where k is the Boltzmann const. The internal energy of this system at any temp T is given by $E_1 N_0 + \frac{N_0 \varepsilon}{1+e^{\varepsilon/k_BT}}$. The heat capacity of the system is given by which of the following expressions?

$$U = E_1 N_0 + \frac{N_0 \varepsilon}{1+e^{\varepsilon/k_BT}}$$

$$C_V = \frac{\partial U}{\partial T}$$

$$= \frac{N_0 \varepsilon}{\left(1+e^{\varepsilon/k_BT}\right)^2} \times e^{\varepsilon/k_BT} \times \frac{\varepsilon}{k_BT^2}$$

$$= \frac{N\varepsilon^2}{k_BT^2} \frac{e^{\varepsilon/k_BT}}{\left(1+e^{\varepsilon/k_BT}\right)^2}$$

$$= Nk\left(\frac{\varepsilon}{kT}\right)^2 \frac{e^{+\varepsilon/k_BT}}{\left(1+e^{+\varepsilon/k_BT}\right)^2}$$

$$= Nk_B\left(\frac{\varepsilon}{k_BT}\right)^2 \frac{e^{\varepsilon/k_BT}}{\left(1+e^{\varepsilon/k_BT}\right)^2}$$

37) A system of N localized, non-interacting spin ½ ions [redacted] external magnetic field H. If the system is in equilibrium at temp T, then Helmholtz energy of the system is

$$Z = e^{\beta\mu H} + e^{-\beta\mu H}$$

$$= 2\cosh\beta\mu H$$

$$Z^N = (2\cosh\beta\mu H)^N$$

$$F = -k_BT\ln Z = -Nk_BT\ln\left(2\cosh\frac{\mu H}{k_BT}\right)$$

41) Assuming that only ground state & the 1st excited state of a SH 1D oscillator are appreciable populated, the mean energy of the oscillator is.

$$Z = e^{-\frac{\hbar\omega}{2k_BT}} + e^{-\frac{3\beta\hbar\omega}{2k_BT}}$$

$$\ln Z = \ln\left(e^{\frac{-\hbar\omega}{2k_BT}} + e^{\frac{-3\beta\hbar\omega}{2}}\right)$$

$$U = -\frac{\partial}{\partial \beta} \ln Z.$$

$$= \frac{\left(e^{-\frac{\beta \hbar\omega}{2}} \times \frac{\hbar\omega}{2} + e^{-\frac{3\beta\hbar\omega}{2}} \times \frac{3}{2}\hbar\omega\right)}{e^{-\frac{\beta\hbar\omega}{2}} + e^{-\frac{3\beta\hbar\omega}{2}}}$$

$$= \frac{\hbar\omega}{2} \frac{\left(e^{-\frac{\beta\hbar\omega}{2}} + 3e^{-\frac{3\beta\hbar\omega}{2}}\right)}{e^{-\frac{\beta\hbar\omega}{2}} + e^{-\frac{3\beta\hbar\omega}{2}}}$$

$\frac{-3}{2} + \frac{1}{2}$

$$= \frac{\hbar\omega}{2}\left[\frac{1+3e^{-\beta\hbar\omega}}{1+e^{-\beta\hbar\omega}}\right]$$ //.

46 An ensemble of quantum harmonic oscillator is kept at a finite temp $T = 1/k_B\beta$. The Z of a single oscillator with energy level $(n+\frac{1}{2})\hbar\omega$ is given by.

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

$$= e^{-\frac{\beta\hbar\omega}{2}} \sum_n e^{-\beta n\hbar\omega}.$$

$$= e^{-\frac{\beta\hbar\omega}{2}}\left[1 + e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} + \cdots\right]$$

$$Z = \frac{e^{-\frac{\beta\hbar\omega}{2}}}{1-e^{-\beta\hbar\omega}}$$ ✓ ✓

GP

$S_\infty = \frac{a}{1-r}$

$= \frac{1}{1-e^{-\beta\hbar\omega}}$

50. The average energy of a equilibrium quantum mechanical SHO of frequency ω at temp T is given by.

$$Z = \frac{e^{-\frac{\hbar\omega}{2k_BT}}}{1-e^{-\frac{\hbar\omega}{k_BT}}}$$

$$\ln Z = -\frac{\beta\hbar\omega}{2} - \ln\left(1 - e^{-\hbar\omega/k_BT}\right)$$

$$U = -\frac{\partial}{\partial\beta}\ln Z.$$

$$= \frac{\hbar\omega}{2} + \frac{e^{-\frac{\hbar\omega}{k_BT}} \times \hbar\omega}{1-e^{-\hbar\omega/k_BT}}$$

$$U = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/k_BT}-1}$$

51. A simple harmonic oscillator has energy level $E_n = (n+\frac{1}{2})\hbar\omega$, for a 2D oscillators $n = n_x + n_y$. where $E_{n_x} = (n_x+\frac{1}{2})\hbar\omega_x$, $E_{n_y} = (n_y+\frac{1}{2})\hbar\omega_y$.

~~where~~ [illegible]

The partition fn of the system is given by $(\alpha = \hbar\omega\beta)$

27/4/15

1. The systems has 2 normal modes of vibration with frequencies ω_1 & $\omega_2 = 2\omega_1$. What is the probability that at temp T the system has an energy less than $4\hbar\omega_1$ ($E < 4\hbar\omega_1$) [consider $x = e^{-\beta\hbar\omega}$ & Z is the partition fn).

ω_1 & $\omega_2 = 2\omega$.

2D Harmonic oscillator

$$E = (n_1 + 1/2)\hbar\omega_1 + (n_2 + 1/2)\hbar\omega_2.$$
$$= (n_1 + 1/2)\hbar\omega_1 + (n_2 + 1/2)2\hbar\omega_1$$
$$= (n_1 + 1/2)\hbar\omega_1 + (2n_2 + 1)\hbar\omega_1$$
$$= (n_1 + 2n_2 + 3/2)\hbar\omega_1.$$

n_1, n_2	$(n_1 + 2n_2 + 3/2)$		deg.
0, 0	$3/2\ \hbar\omega$	$3/2\ \hbar\omega$	1
0, 1	$\cancel{7/2}\ \hbar\omega$	$5/2\ \hbar\omega$	1
1, 0	$5/2\ \hbar\omega$	$7/2\ \hbar\omega$	2
2, 0	$7/\hbar\omega$		

$g=2$ — $7/2\hbar\omega$

$g=1$ — $5/2\ \hbar\omega$

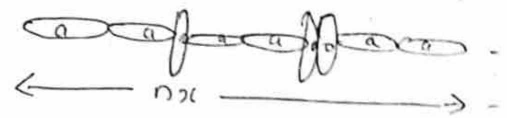
$g=1$ — $3/2\ \hbar\omega$

$$p = e^{-\beta E_S}/Z.$$
$$= \frac{e^{-3/2\beta\hbar\omega} + e^{-\beta 5/2\hbar\omega} + 2e^{-7/2\beta\hbar\omega}}{Z}$$
$$= e^{-3/2\beta\hbar\omega}\frac{(1 + x + 2x^2)}{Z}$$
$$= x^{3/2}(1 + x + 2x^2)/Z$$

1. Consider a 1D chain consisting $n \gg 1$ segments as shown in the figure. Let the length of ~~each segment be 'a' when the dimension~~ of the segment is ∥el to the chain & zero when segment is vertical. Each segment has just two states a horizontal orientation of vertical orientation & each of the state is non degenerate. The distance b/w two ends of the chain is nx.

~~(a) Find the entropy~~ of the system.

b) Find the average length of the system.



Let us suppose there are 'm' horizontal links.

length $= ma = nx$.

$\therefore m = \frac{nx}{a}$.

$S = k\ln\Omega$ | Ω = no. of arrangement.

$$\Omega = \frac{n!}{m!(n-m)!}$$

$$S = k\ln\frac{n!}{\frac{nx}{a}!\left(n - \frac{nx}{a}\right)!}$$

$$\ln\Omega = \ln n! - \ln(m!) - \ln(n-m)!$$
$$= n\ln n - n - [m\ln m - m + (n-m)\ln(n-m) - (n-m)]$$

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$$\ln \Omega = n\ln n - n - m\ln m + m - (n-m)\ln(n-m) + n - m$$

$$= n\ln n - m\ln m - (n-m)\ln(n-m).$$

$$= n\ln n - \frac{nx}{a}\ln\frac{nx}{a} - \left(n-\frac{nx}{a}\right)\ln\left(n-\frac{nx}{a}\right)$$

$$S = k\ln\Omega$$

$$= k\ln\frac{n!}{\frac{nx}{a}!\left(n-\frac{nx}{a}\right)!}$$

b)

$\longrightarrow F.$

0 — V $E = Fd = F\times 0 = 0$

length a — H $E = Fd = F\times a = Fa.$

$\therefore$

$$Z = 1 + e^{-\beta Fa}.$$

$$\langle L\rangle = \sum_s l_s P_s = l_V P_V + l_H P_H.$$

$$= \frac{0 + a e^{-\beta Fa}}{1 + e^{-\beta Fa}} = \frac{a e^{-\beta Fa}}{1+e^{-\beta Fa}}$$

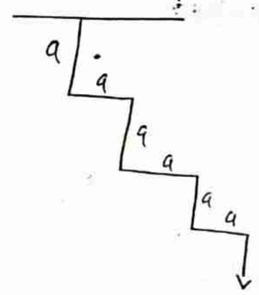
$\langle L\rangle = a P_{av}.$

Trick

$$\boxed{\langle L\rangle = L \times P_{bav}.}$$

$$\boxed{\langle N\rangle = N \times P_{bav}}$$

3.) A 1D chain consist of a set of N rods, each of length a. When stretched by a load each rod can align either $\parallel$el or ~~[illegible]~~ $\perp$r to the length of the chain. The energy of a rod is $-\varepsilon$ when it is $\parallel$el & $+\varepsilon$ when it is $\perp$r to the length. Find the average length.?



$-\varepsilon \longrightarrow \parallel$el

$\varepsilon \longrightarrow \perp$r.

$$Z = e^{\beta\varepsilon} + e^{-\beta\varepsilon}.$$

$$\langle L\rangle = L P_{bav}$$

$$= \frac{L e^{\beta\varepsilon}}{Z}.$$

$$= \frac{L e^{\beta\varepsilon}}{e^{\beta\varepsilon} + e^{-\beta\varepsilon}}.$$

$L \approx Na.$

$$\langle L\rangle = \frac{Na\, e^{\beta\varepsilon}}{e^{\beta\varepsilon}+e^{-\beta\varepsilon}}$$

$$\langle L\rangle = \frac{Na}{1+e^{-2\beta\varepsilon}}$$

⇒ <u>classical system</u>

$$Z = \sum e^{-\beta \epsilon_s}$$

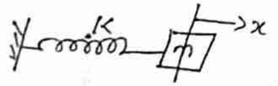
$$Z_{cl} = \frac{1}{h^3}\int e^{-\beta E}\, dq_i\, dp_i$$

$$E = KE + PE$$

$$E = \sum_i \frac{p^2}{2m} + U$$

$$Z_{cl}^{3D} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \int_{-\infty}^{\infty} e^{-\beta U}\, dq_i$$

classical. LHO



$$U = \tfrac{1}{2}Kx^2 = \tfrac{1}{2}m\omega^2 x^2$$

$$Z_{cl}^{1D} = \left(\frac{2\pi m k_B T}{h^2}\right)^{1/2} \int_{-\infty}^{\infty} e^{-\frac{\beta m\omega^2 x^2}{2}}\, dx$$

$$= \left(\frac{2\pi m}{h^2\beta}\right)^{1/2}\sqrt{\frac{2\pi}{\beta m\omega^2}}$$

$$= \frac{2\pi}{h\omega\beta}$$

$$Z_{cl}^{1D} = \frac{1}{\beta\omega\hbar} = \frac{1}{\beta\hbar\omega}$$

For N oscillator

$$Z = \left(\frac{1}{\beta\hbar\omega}\right)^N$$

$$Z_{Qua} = \left(\frac{1}{2\sinh\frac{\beta\hbar\omega}{2}}\right)^N$$

⇒ Ideal gas.

$$Z_{cl}^{3D} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\int_{-\infty}^{\infty} e^{-\beta U}\, dq_i$$

$$U = 0$$

$$Z_{cl}^{3D} = V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$$

$$Z_{1mol}^{3D} = [Z_1^N] = V^N\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}}$$

$$F = -k_B T \ln Z$$

$$= -Nk_B T\left[\ln V + \frac{3}{2}\ln\left(\frac{2\pi m k_B T}{h^2}\right)\right]$$

$$S = -\frac{\partial F}{\partial T}$$

$$= Nk_B\left[\ln V + \tfrac{3}{2}\ln\left(\frac{2\pi m k_B T}{h^2}\right)\right] + Nk_B T\cdot\frac{3}{2}\frac{1}{T}$$

$$= Nk_B\left[\ln V + \tfrac{3}{2}\ln\left(\frac{2\pi m k_B T}{h^2}\right) + \tfrac{3}{2}\right]$$

$\Rightarrow$ Gibb's Paradox

$\boxed{\begin{matrix} F & V \\ S & N \end{matrix}}$ $\rightarrow$ identical particle.

$N' \Rightarrow 2N$
$V' \Rightarrow 2V$

$\left.\begin{matrix} F' = 2F \\ S' \Rightarrow 2S \end{matrix}\right\}$ since F & S are extensive

$$F = -Nk_BT\left[\ln V + \tfrac{3}{2}\ln\left(\frac{2\pi m k_BT}{h^2}\right)\right].$$

$$F' = -2Nk_BT\left[\ln 2V + \tfrac{3}{2}\ln\left(\frac{2\pi m k_BT}{h^2}\right)\right]$$

$$= -2Nk_BT\left[\ln V + \tfrac{3}{2}\ln\left(\frac{2\pi m k_BT}{h^2}\right) + \ln 2\right]$$

$$= 2F - 2Nk_BT\ln 2.$$

$$\underline{\underline{F' \neq 2F}}.$$

$$S = Nk_B\left[\ln V + \tfrac{3}{2}\ln\left(\frac{2\pi m k_BT}{h^2}\right) + \tfrac{3}{2}\right]$$

$$S' = 2Nk_B\left[\ln V + \tfrac{3}{2}\ln\left(\frac{2\pi m k_BT}{h^2}\right) + \tfrac{3}{2} + \ln 2\right]$$

$$S' = 2S + 2Nk_B\ln 2.$$

$$\underline{\underline{S' \neq 2S}}$$

This paradox is due the identical behaviour of gas molecules.

Gibbs introduced a factor $(N!)$ to indicates identical behaviour of the classical particles.

MPC = No. of way $= \dfrac{3!}{1!1!1!}$

PPM = ,, $= \dfrac{3!}{2!1!}$

PPP = ,, $= \dfrac{3!}{3!}$

3D Identical Ideal gas.

$$Z_N = [Z_1]^N \xrightarrow[\text{factor}]{\text{Gibbs}} Z_N = \frac{[Z_1]^N}{N!}$$

[classical identical particle]

$$F = -k_BT\ln Z.$$

$$F = -Nk_BT\left[\ln(V/N) + \tfrac{3}{2}\ln\left(\frac{2\pi m k_BT}{h^2}\right) + 1\right]$$

$$S = -\frac{\partial F}{\partial T}$$

$$S = Nk_B\left[\ln(V/N) + \tfrac{3}{2}\ln\left(\frac{2\pi m k_BT}{h^2}\right) + 1\right] + Nk_BT \times \frac{3/2}{T}$$

$$= Nk_B\left[\ln(V/N) + \tfrac{3}{2}\ln\left(\frac{2\pi m k_BT}{h^2}\right) + \tfrac{5}{2}\right]$$

$N \rightarrow 2N$
$V \rightarrow 2V$

$$S' = 2Nk_B\left[\ln(V/N) + \tfrac{3}{2}\ln\left(\frac{2\pi m k_BT}{h^2}\right) + \tfrac{5}{2}\right]$$

$$\underline{\underline{S' = 2S}}$$

$$Z_N = \frac{V^N}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2}.$$

$$F = -k_B T \ln Z.$$

$$= -N k_B T\left[\ln V + 3/2 \ln\left(\frac{2\pi m k_B T}{h^2}\right)\right] + k_B T \ln N!$$

$$F = -N k_B T\left[\ln V + 3/2 \ln\left[\frac{2\pi m k_B T}{h^2}\right]\right] + N k_B T \ln N - N k_B T$$

$$F = -N k_B T\left[\ln(V/N) + 3/2 \ln\left(\frac{2\pi m k_B T}{h^2}\right) + 1\right]$$

$F = 2N$
$V = 2V$

$$F' = -2N k_B T\left[\ln(V/N) + 3/2 \ln\left(\frac{2\pi m k_B T}{h^2}\right) + 1\right]$$

$F' = 2F$

Gibbs factor is introduced ~~because~~ because of indistinguishable nature of classical particle.

28/4/15 **Energy fluctuations of canonical ensemble.**

Canonical.

$$U = \frac{\sum_s \varepsilon_s e^{-\beta \varepsilon_s}}{\sum_s e^{-\beta \varepsilon_s}} \qquad \left[\because U = \sum_s \varepsilon_s P_s\right]$$

$$\frac{\partial u}{\partial \beta} = \frac{\sum_s e^{-\beta \varepsilon_s} \times \sum_s \varepsilon_s e^{-\beta \varepsilon_s} \times (-\varepsilon_s) - \sum_s \varepsilon_s e^{-\beta \varepsilon_s} \times \sum_s e^{-\beta \varepsilon_s} \times (-\varepsilon_s)}{\left(\sum_s e^{-\beta \varepsilon_s}\right)^2}$$

$$= -\frac{\sum_s \varepsilon_s^2 e^{-\beta \varepsilon_s}}{\sum_s e^{-\beta \varepsilon_s}} + \frac{\left(\sum_s \varepsilon_s e^{-\beta \varepsilon_s}\right)^2}{\left(\sum_s e^{-\beta \varepsilon_s}\right)^2}$$

$$= -\frac{\sum_s \varepsilon_s^2 e^{-\beta \varepsilon_s}}{\sum_s e^{-\beta \varepsilon_s}} + \left(\frac{\sum_s \varepsilon_s e^{-\beta \varepsilon_s}}{\sum_s e^{-\beta \varepsilon_s}}\right)^2.$$

$$= -\langle \varepsilon_s^2 \rangle + \langle \varepsilon_s \rangle^2.$$

$$-\frac{\partial u}{\partial \beta} = \langle \varepsilon_s^2 \rangle - \langle \varepsilon_s \rangle^2.$$

$$-\frac{\partial u}{\partial \beta} = (\Delta \varepsilon_s)^2$$

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

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

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

$\therefore KT^2\frac{\partial U}{\partial T} = (\Delta E)^2$

$\Delta E = \sqrt{K_B T^2 C_V}$
$\downarrow$
rms fluctuations.

<u>Relative fluctuations</u>

$$\boxed{\frac{\Delta E}{E} = \frac{\sqrt{K_B T^2 C_V}}{U}}$$

eg: Ideal gas. $U = 3/2\, N K_B T$

$\therefore C_V = 3/2\, N K_B$.

$$\frac{\Delta E}{E} = \frac{\sqrt{K_B T^2 \times 3/2\, N K_B}}{3/2\, N K_B T}$$

$$= \sqrt{\frac{2}{3N}}$$

Generally $U \propto N$
$C_V \propto N$

$$\frac{\Delta E}{E} \propto \frac{1}{\sqrt{N}}$$

$N \to \infty$. $\frac{\Delta E}{E} \to 0$. [There is no fluctuation]

Conc:

$\therefore$ <u>If $N \to \infty$, any canonical ensemble behaves like a microcanonical ensemble.</u> [there is no change of interaction]

$\Rightarrow$ <u>Partition function of an ideal gas.</u>

$$Z_1^{cl}{}_{(3D)} = \left(\frac{2\pi m K_B T}{h^2}\right)^{3/2} \int_{-\infty}^{\infty} e^{-\beta u}\, dq_i$$

Ideal gas (mono atomic)
$\hookrightarrow$ dof $= 3$ i.e. translational).

$$Z_1 = \left(\frac{2\pi m K_B T}{h^2}\right)^{3/2}$$

$$Z_N = \frac{[Z_1]^N}{N!} = \frac{V^N}{N!}\left(\frac{2\pi m K_B T}{h^2}\right)^{3N/2}.$$

<u>Diatomic</u>

DOF $= 3N - C = 5$ (3 trans + 2 rotat)

$Z_{total} = Z_{trans} \times Z_{rotat}$.

<u>Translational</u>

$$Z_{trans}^{mono} = \frac{V^N}{N!}\left(\frac{2\pi m K_B T}{h^2}\right)^{\frac{3N}{2}}$$

$$Z_{trans}^{dia} = \frac{V^N}{N!}\left(\frac{2\pi (m_1+m_2) K_B T}{h^2}\right)^{\frac{3N}{2}}$$

Rotational

$$E = \frac{\langle J^2 \rangle}{2I} = \frac{\hbar^2 J(J+1)}{2I}$$

$$Z_{rot} = \sum_s g_s e^{-\beta \epsilon_s} \qquad \text{degeneracy } (2J+1)$$

$$Z_{rot} = \sum_J (2J+1) e^{-\frac{\beta \hbar^2}{2I} J(J+1)}$$

$$e^{-\frac{\beta \hbar^2}{2I}} = e^{-\frac{\hbar^2}{2k_B T I}}$$

$\theta = \frac{\hbar^2}{2k_B I}$ (characteristic temperature), $\frac{\hbar^2}{2k_B I} = \theta$.

$$\boxed{Z_{rot} = \sum_J (2J+1)\, e^{-\frac{\theta}{T} J(J+1)}}$$

$$Z_{rot} = \sum_J (2J+1)\, e^{-\frac{\theta_r}{T} J(J+1)}$$

$J = 0, 1, 2, 3 \ldots$

case I At low temp $\Rightarrow$ Energy level are discrete.

$$Z_{rotal} = 1 + 3e^{-\frac{2\theta_r}{T}} + 5e^{-\frac{6\theta_r}{T}} + \ldots$$

case 2 At high temp $\Rightarrow$ energy levels are continue.

$\therefore \sum \longrightarrow \int dJ$

$$Z_{rot} = \int_0^\infty (2J+1)\, e^{-\frac{\theta_r}{T} J(J+1)}\, dJ$$

$$Z_{rot} = \int_0^\infty e^{-\frac{\theta_r}{T} x}\, dx$$

$$= \frac{T}{\theta_r} \qquad \theta_r = \frac{\hbar^2}{2k_B I}$$

$$= \frac{T\, 2k_B I}{\hbar^2}$$

$$\boxed{Z_{rot}^{\text{high temp}} = \frac{2k_B T I}{\hbar^2}} \qquad Z_{rot} = \frac{2 I k_B T}{\hbar^2}$$

$$Z_{rot}\ (\text{at high temp}) = \frac{2kIT}{\hbar^2} \qquad Z_{rot} = \frac{2 I k_B T}{\hbar^2}$$

Generally

$$\boxed{Z_{rot}^{hp} = \frac{1}{\underbrace{\sigma}_{\text{symmetry}}} \frac{2k_B T I}{\hbar^2}}$$

Hetero molecule $\sigma = 1$ fold symmetry

Homo $\sigma = 2$ fold symmet.

$$Z_{rot}^{Homo} = \frac{k_B T I}{\hbar^2}$$

$$Z_{ro}^{het} = \frac{2k_B T I}{\hbar^2}$$

Ortho & Para molecules

H_2 molecule. $\quad (H)^{e^-} + (H)^{e^-} \quad s_1 = 1/2 \quad s_2 = 1/2$

$S = 0, 1$

$\uparrow\uparrow \; [S=1]$ — symmetric — ortho molecule

$\uparrow\downarrow \; [S=0]$ — antisymmetric — para molecule.

$\psi_{total} = \psi^{J}_{space} \times \psi_{spin}$

$\psi_{Antisy.} = $ A.sy $\times$ Symmetric

Symmetric $\times$ Antisymmetric

$\pi = (-)^J$

$$\psi^{(J)}_{space} = \begin{cases} \text{symmetric} & J = 0, 2, 4 \ldots \\ \text{Antisymmetric} & J = 1, 3, 5, 7 \ldots \end{cases}$$

$\psi_{ortho} = \psi_{space} \times \psi_{spin}$

Antisymmetric $\quad$ symmetric

$J = 1, 3, 5 \ldots \quad$ Sym $(S=1)$

$$\boxed{Z_{ortho} = \sum_{J=1,3,5..} (2J+1)\, e^{\frac{-\beta\hbar^2}{2I} J(J+1)}}$$

$\psi_{para} = \psi_{space} \times \psi_{spin}$

Symmetric $\quad$ A. symmetric

$J = 0, 2, 4 \ldots \quad (S=0)$

$$\boxed{Z_{para} = \sum_{J=0,2,4..} (2J+1)\, e^{\frac{-\beta\hbar^2}{2I} J(J+1)}}$$

$\Rightarrow$

DISTRIBUTIONS

Distributions of identical particles.

classical ✓ — Distinguishable. ✓ — $\langle r \rangle \gg \lambda$.

obey maxwell Boltzmann's statistics ✓

Quantum ✓ — ✓ Indistinguishable. — $\langle r \rangle \ll \lambda$.

Fermions ✓ — obey Fermi Dirac statistics ✓ — * Either one particle ✓ or No particle.

Boson ✓ — obey Bose Einstien stati ✓ — No restrictio

* How to write Z.

TIP write the z for ~~…~~ one particle:

* $Z_N = [Z_1]^N$

Note: If there are N Indistinguishable particle

$$Z_N = \frac{[Z_1]^N}{N!}$$ ✓

* How to write Z. ✓

Distribute the particle ✓

find the energy of states.

$$Z = \Sigma e^{-\beta \epsilon_s}$$

1. 3 states 2 particle

1) MB statistics. (a,b)

		b	a	b	a			ab
b	b			a	b		ab	
a	a	a	b			ab		

No: of way 9

2) FD statistics (a,b)

	a	a
a	a	
a		a

No: of ways = 3

BE statistic

	a	a			aa
a	a			aa	
a		a	aa		

No: of ways = 6

3 states 3 particle

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1) MB

c	b	c	a	a	b			abc
b	b	a	b	c	a		abc	
a	a	b	c	b	c	abc		

				c	ab
c	ab	b	~~ac~~	ab	c
ab	c	ac	b		

b	ac			a	bc
ac	b	a	bc	bc	a
		bc	a		

2) FD

a

a

a

BE

a			a	aa			aaa	a
a	a	aa	aa	a		aaa		
a	aa	a			aaa			aa

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1. Consider a system of 2 atoms each having three quantum states of energies 0, ε, 2ε. The system is in contact with a heat reservoir at temp T. Write the partition f^n if particles obey

a) MB statistics & distinguishable.
b) MB statistics & Indistinguishable.
c) FD statistics
d) BE statistics.

a) $Z_1 = 1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon}$

$Z_N = [Z_1]^N \Rightarrow Z_2 = \left(1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon}\right)^2$.

b) $Z_N = \dfrac{[Z]^N}{N!} = \dfrac{1}{2!}\left(1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon}\right)^2$.

c) $Z = e^{-\beta\epsilon} + e^{-2\beta\epsilon} + e^{-3\beta\epsilon}$

2ε		a	a
ε	a		a
0	a	a	
	ε	2ε	3ε

d)
$Z = 1 + e^{-\beta\epsilon} + 2e^{-2\beta\epsilon} + e^{-3\beta\epsilon} + e^{-4\beta\epsilon}$

$= 1 + e^{-\beta\epsilon}\left(1 + 2e^{-\beta\epsilon} + e^{-2\beta\epsilon} + e^{-3\beta\epsilon}\right)$

2ε		a	a			aa
ε	a	a			aa	
0	a		a	aa		
	ε	3ε	2ε	0	2ε	4ε

Gate

2. There are four energy levels E, 2E, 3E & 4E where E > 0. Find the canonical partition f^n of 2 particles if the particles are.

a) classical particle.
b) Fermions
c) Bosons

a) $Z_1 = e^{-\beta E} + e^{-2\beta E} + e^{-3\beta E} + e^{-4\beta E}$.

$Z_2 = [Z_1]^N = \left(e^{-\beta E} + e^{-2\beta E} + e^{-3\beta E} + e^{-4\beta E}\right)^2$.

b)

4E			a		a	a
3E		a		a		a
2E	a			a	a	
E	a	a	a			
	3E	4E	5E	5E	6E	7E

$Z = e^{-3\beta E} + e^{-4\beta E} + 2e^{-5\beta E} + e^{-6\beta E} + e^{-7\beta E}$.

c)

4E			a		a	a				aa
3E		a		a		a			aa	
2E	a			a	a			aa		
E	a	a	a				aa			
	3E	4E	5E	5E	6E	7E	2E	4E	6E	8E

$Z = e^{-2\beta E} + e^{-3\beta E} + 2e^{-4\beta E} + 2e^{-5\beta E} + 2e^{-6\beta E} + e^{-7\beta E} + e^{-8\beta E}$.

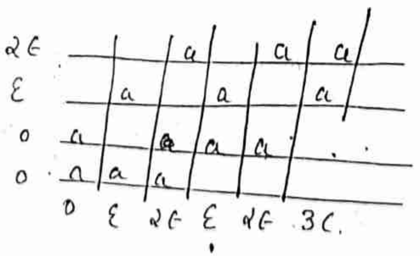
3. You are given system of two[41] identical particles which may occupy any of the three energy levels $E_n = n\epsilon$, $n = 0, 1, 2$. The lowest energy ~~energy~~ state is doubly degenerate. Find the Z if they obey

a) FD

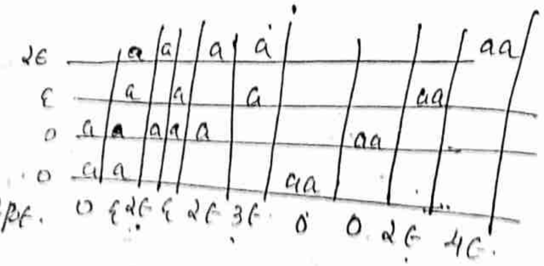
b) BE

c) MB.

a) $Z = 1 + 2e^{-\beta\epsilon} + 2e^{-2\beta\epsilon} + e^{-3\beta\epsilon}$.



b)



$Z = 3 + 2e^{-\beta\epsilon} + 3e^{-2\beta\epsilon} + e^{-3\beta\epsilon} + e^{-4\beta\epsilon}$.

c) $Z_1 = 2 + e^{-\beta\epsilon} + e^{-2\beta\epsilon}$

$Z_2 = [Z_1]^2 = \left(2 + e^{-\beta\epsilon} + e^{-2\beta\epsilon}\right)^2$

$\Rightarrow$ MB - ~~sta~~ Distribution [classical]

$$N \begin{cases} n_l \text{ ---------- } n_l \text{ ---------- } n_l \epsilon_l \\ \vdots \\ 3 \text{ ---------- } n_3 \text{ ---------- } \epsilon_3 \text{ ---------- } n_3 \epsilon_3 \\ 2 \text{ ---------- } n_2 \text{ ---------- } \epsilon_2 \text{ ---------- } n_2 \epsilon_2 \\ 1 \text{ ---------- } n_1 \text{ ---------- } \epsilon_1 \text{ ---------- } n_1 \epsilon_1 \end{cases}$$

1) $n_1 + n_2 + n_3 + \cdots n_l = N$

$$\sum_i n_i = N \text{ [const]} \text{ ——— (1)}$$

2) $n_1\epsilon_1 + n_2\epsilon_2 + n_3\epsilon_3 + \cdots n_l\epsilon_l = E$.

$$\sum_i n_i E_i = E \text{ [const]} \text{ ——— (2)}$$

TD Probability.
No: of arrangements
No: of microstates } W.

$N \Rightarrow$ No: of ways of arranging n_1 particle $W_1 = \frac{N!}{n_1!(N - n_1)!}$

$(N - n_1) \Rightarrow$ no: of way of arranging n_2 particle.

$$W_2 = \frac{(N - n_1)!}{n_2!\,(N - n_1 - n_2)!}$$

$(N - n_1 - n_2)! \Rightarrow$ no: of way of arranging n_3 particle

$$W_3 = \frac{(N-n_1-n_2)!}{n! \, (N-n_1-n_2-n_3)!} \quad 4^2$$

$$W_{MB} = W_1 \times W_2 \times W_3 \times \cdots$$

$$W_{MB} = \frac{N!}{n_1! \, \cancel{(N-n_1)!}} \times \frac{\cancel{(N-n_1)!}}{n_2! \, (N-n_1-n_2)!} \times \cdots$$

$$W_{MB} = \frac{N!}{n_1! \, n_2! \, n_3! \cdots}$$ [without degeneracy]

With degeneracy

eg: 3 states & 2 particle (a, b)

Level									
3			b	a	a	b			ab
2	b	a	a	b				ab	
1	a	b			b	a	ab		

No: of way = 9 = 3^2.

Generally $= (g_i)^{n_i}$

3 ———

2 $n_2 \quad g_2$ ——— $\quad g_2^{n_2} \times \frac{(N-n_1)!}{n_2! \, (N-n_1-n_2)!}$

1 $n_1 \quad g_1$ ——— $\quad (g_1)^{n_1} \times \frac{N!}{n_1! \, (N-n_1)!}$

$$W_{MB} = \frac{N!}{n_1! \, n_2! \cdots} \times (g_1)^{n_1} \times (g_2)^{n_2} \times \cdots$$

$$\boxed{W_{MB} = N! \prod_i \frac{(g_i)^{n_i}}{n_i!}}$$

1. Five distinguishable particle are distributed in three non-degenerate state with energy $0, \varepsilon, 2\varepsilon$ the most probable state that has total energy 4ε is

$\boxed{5}$ particle.

0	ε	2ε
n_1	n_2	n_3

$$n_1 \times 0 + n_2 \varepsilon + n_3 \times 2\varepsilon = 4\varepsilon.$$

$$\therefore n_2 + 2n_3 = 4.$$

$W = N!/n_1! n_2! \cdots$

n_1	n_2	n_3	
2	2	1	$W_1 = \frac{5!}{2!2!1!} = 30$
1	4	0	$W_2 = \frac{5!}{4!1!0!} = 20$
3	0	2	$W_3 = \frac{5!}{3!2!0!} = 5$

Most probable state 2, 2, 1

2) 8 particle, 4 states & $E_{total} = 5E$. 4)

0	ϵ	2ϵ	3ϵ
n_1	n_2	n_3	n_4

$$n_1 \times 0 + n_2 \times \epsilon + n_3 \times 2\epsilon + n_4 \times 3\epsilon = 5\epsilon.$$

$$n_2 + 2n_3 + 3n_4 = 5E.$$

n_1	n_2	n_3	n_4
8	8	∅	∅
5	1	2	0
6	0	1	1
4	3	1	0
3	5	0	0

$W_5 = \frac{8!}{\cancel{3!3!1!1!}} = 1120$

160
×7
1120
8×7×5×4

$W_3 =$

3. Five distinguishable particle distributed with intrinsic probability. 1/3 each. The energy of the particle in cell one is 0, cell two is ε & cell three is 2ε & cell four 3ε. The most probable state.

a) (3, 2, 0) b) (3, 1, 1) c) (2, 2, 1) d) (4, 1, 0)

0	ϵ	2ϵ
n_1	n_2	n_3

$$n_1 \times 0 + n_2 \times \epsilon + n_3 \times 2\epsilon = 3\epsilon.$$

$$\boxed{n_2 + 2n_3 = 3\epsilon}$$

check the option which satisfy the above cond^n.

(3, 2, 0) $n_2 + 2n_3 = 2\epsilon$ ✗

(3, 1, 1) $n_2 + 2n_3 = 3\epsilon$ ✓

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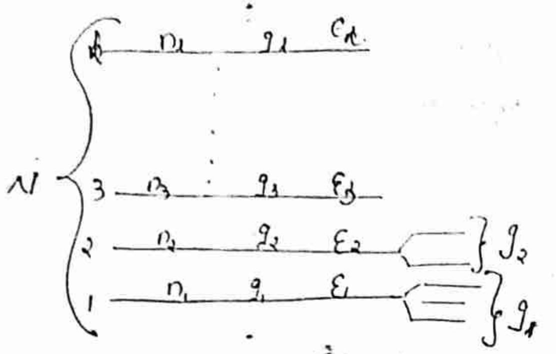
⟹ FD Distribution



$\sum_i n_i = N$ [const]

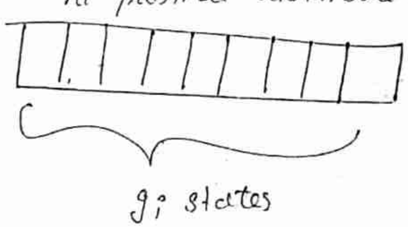
$\sum n_i \epsilon_i = E$ [const]

i^{th} state.

i^{th} n_i particle g_i ϵ_i

i^{th} n_i g_i ϵ_i

n_i particle distribute in g_i states



No: of way $= {}^{g_i}C_{n_i}$

$W_{total} = \prod_i {}^{g_i}C_{n_i}$

$$\boxed{W_{FD} = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!}}$$

For FD

$(g_i - n_i)!$ → > 0

$g_i - n_i \geq 0$

$g_i \geq n_i$

$$\boxed{W_{BE} = \prod_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}}$$

$$\boxed{W_{BE} = \prod_i \frac{(n_i + g_i)!}{n_i!\, g_i!}}$$

1. Consider a gas of weakly interacting particle in a states with degeneracy four & 3 particle. no: of ways of selecting the particle in MB, FD & BE distributions respectively.

a) $W_{MB} = \prod (g_i)^{n_i}$

$= (4)^3$

$= 64$

$\frac{16}{8}$

b) $FD = \prod \frac{g_i!}{n_i!(g_i - n_i)!}$

$= \frac{4!}{3!(4-3)!} = 4$

c) $W_{BE} = \prod \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} = \frac{6!}{3!\,3!} = 20$

CSIR

2. The no: of way in which N identical bosons can be distributed in to two levels.

$W_{BE} = \prod_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} = \frac{(N+1)!}{N!}$

$= (N+1)$

5

TD probability

$N!$

$$W_{MB} = N! \prod_i \frac{(g_i)^{n_i}}{n_i!}$$

$$W_{FD} = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!} = \prod_i {}^{g_i}C_{n_i} \quad FD = \prod_i {}^{g_i}C_{n_i}$$

$$W_{BE} = \prod_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \simeq \prod_i \frac{(n_i + g_i)!}{n_i! g_i!}$$

Entropy

$S = k_B \ln W$.

MB :

$$S = k_B \ln \left[N! \prod_i \frac{(g_i)^{n_i}}{n_i!} \right] \qquad \ln \prod_i = \sum \ln$$

$$S = k_B \left[\ln N! + \sum \ln \frac{(g_i)^{n_i}}{n_i!} \right]$$

$$= k_B \left[N \ln N - N + \sum n_i \ln g_i - n_i \ln n_i + n_i \right]$$

$$\boxed{S = k_B \left[N \ln N + \sum n_i \ln (g_i / n_i) \right]}$$

FD

$$W = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!}$$

$$S = k_B \ln W$$

$$= k_B \ln \left[\prod_i \frac{g_i!}{n_i!(g_i - n_i)!} \right]$$

$$= k_B \sum \ln \left[\frac{g_i!}{n_i!(g_i - n_i)!} \right]$$

$$= k_B \sum g_i \ln g_i - g_i - \left[\ln n_i! + \ln (g_i - n_i)! \right]$$

$$= k_B \sum g_i \ln g_i - g_i - \left[n_i \ln n_i - n_i + (g_i - n_i) \ln (g_i - n_i) - (g_i - n_i) \right]$$

$$= k_B \sum g_i \ln g_i - g_i - n_i \ln n_i + n_i + (g_i + n_i) \ln (g_i - n_i) + (g_i - n_i)$$

$$= k_B \sum g_i \ln g_i - n_i \ln n_i + (g_i - n_i) \ln (g_i - n_i)$$

$$= k_B \sum g_i \ln \frac{g_i}{g_i - n_i} + n_i \ln \frac{g_i - n_i}{n_i}$$

$$\boxed{S = k_B \sum n_i \ln \left(\frac{g_i}{n_i} - 1 \right) - g_i \ln \left(\frac{g_i}{g_i} - \frac{n_i}{g_i} \right)}$$

$$S = k_B \sum n_i \ln \left(\frac{g_i}{n_i} - 1 \right) - g_i \ln \left(1 - \frac{n_i}{g_i} \right)$$

BE

$$W = \prod_i \frac{(n_i + g_i)!}{n_i!\, g_i!}$$

$S = K_B \ln W$

$$= K_B \sum \ln \frac{(n_i + g_i)!}{n_i!\, g_i!}$$

$$= K_B \sum_i \ln (n_i + g_i)! - [\ln n_i! + \ln g_i!]$$

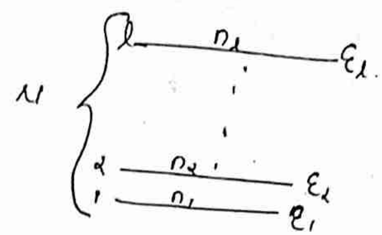
$$= K_B \sum_i (n_i + g_i) \ln (n_i + g_i) - (n_i + g_i) - [n_i \ln n_i - n_i + g_i \ln g_i - g_i]$$

$$= K_B \sum_i (n_i + g_i) \ln (n_i + g_i) - n_i \ln n_i - g_i \ln g_i$$

$$= K_B \sum_i n_i \ln \left(\frac{g_i + n_i}{n_i}\right) + g_i \ln \frac{(n_i + g_i)}{g_i}$$

$$\boxed{= K_B \sum_i n_i \ln \left(\frac{g_i}{n_i} + 1\right) + g_i \ln \left(1 + \frac{n_i}{g_i}\right)}$$

$\Longrightarrow$ Distribution f^n $f(\varepsilon) = \frac{n_i}{g_i}$



$N = \sum_i n_i = \text{const.}$

$\therefore dN = \boxed{\sum_i dn_i = 0} \quad \text{—— (1)}$

$E = \sum_i \epsilon_i n_i \Rightarrow \text{const.}$

$dE = \boxed{\sum_i dn_i \epsilon_i = 0} \quad \text{—— (2)}$

$W = W(n_1, n_2, n_3 \dots n_l)$

For most probable state $\Longrightarrow W_{max}$.

$(\ln W)_{max} \Rightarrow d \ln W = 0. \quad \text{—— (3)}$

$$\frac{\partial}{\partial n_1} \ln W\, dn_1 + \frac{\partial}{\partial n_2} \ln W\, dn_2 + \dots \frac{\partial}{\partial n_i} \ln W\, dn_i =$$

$$\sum_i \frac{\partial}{\partial n_i} \ln W\, dn_i = 0$$

(1) $\times \alpha \Longrightarrow \alpha \sum_i dn_i = 0. \quad \text{—— (4)}$

(2) $\times \beta \Longrightarrow \beta \sum_i dn_i \epsilon_i = 0 \quad \text{—— (4)}$

(3)+(4) $\Longrightarrow \alpha\, dn_i + \beta \sum_i dn_i \epsilon_i = 0.$

$$\sum_i (\alpha + \beta \epsilon_i)\, dn_i = 0. \quad \text{—— (5)}$$

$$\sum_i \frac{\partial}{\partial n_i} \ln w \, dn_i = \sum_i (\alpha + \beta \epsilon_i) \, dn_i$$

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$$\boxed{\frac{\partial}{\partial n_i} \ln w = (\alpha + \beta \epsilon_i)}$$

MB distribution

$$w_{MB} = N! \prod_i \frac{(g_i)^{n_i}}{n_i!}$$

$$\ln w = \ln N! + \sum \ln \frac{(g_i)^{n_i}}{n_i!}$$

$$\ln w = \ln N! + \sum n_i \ln g_i - n_i \ln n_i + n_i$$

$$\frac{\partial}{\partial n_i} \ln w = 0 + \ln g_i - \frac{n_i}{n_i} - \ln n_i + 1$$

$$= \ln g_i - \ln n_i$$

$$\frac{\partial}{\partial n_i} \ln w = \ln(g_i/n_i) = \alpha + \beta \epsilon_i$$

$$\frac{g_i}{n_i} = e^{\alpha + \beta \epsilon_i}$$

$$\boxed{f(\epsilon) = \frac{n_i}{g_i} = \frac{1}{e^{\alpha + \beta \epsilon_i}}}$$

FD

$$\frac{\partial}{\partial n_i} \ln w = \alpha + \beta \epsilon_i$$

$$w_{FD} = \prod_i \frac{g_i!}{n_i! (g_i - n_i)!}$$

$$\ln w = \sum \ln \left(\frac{g_i!}{n_i! (g_i - n_i)!} \right)$$

$$= \sum \ln g_i! - [\ln n_i! + \ln (g_i - n_i)!]$$

$$= \sum \ln g_i! - [n_i \ln n_i - n_i + (g_i - n_i) \ln (g_i - n_i) - (g_i - n_i)]$$

$$= \sum \ln g_i! - n_i \ln n_i + (g_i - n_i) \ln (g_i - n_i) + g_i$$

$$\frac{\partial}{\partial n_i} \ln w = -\frac{n_i}{n_i} - \ln n_i + \frac{g_i}{(g_i - n_i)} + \ln(g_i - n_i) + \frac{n_i}{(g_i - n_i)}$$

$$= -1 + \ln \left(\frac{g_i - n_i}{n_i} \right) + \frac{1}{(g_i - n_i)} (g_i - n_i)$$

$$= \ln \left(\frac{g_i}{n_i} - 1 \right)$$

$$= \ln \left(\frac{g_i}{n_i} - 1 \right)$$

$$\frac{g_i}{n_i} - 1 = e^{\alpha + \beta \epsilon_i} \implies \frac{g_i}{n_i} = e^{\alpha + \beta \epsilon_i} + 1$$

$$\boxed{f(\epsilon) = \frac{n_i}{g_i} = \frac{1}{1 + e^{\alpha + \beta \epsilon_i}} = \frac{1}{e^{\alpha + \beta \epsilon_i} + 1}}$$

BE

$$W = \prod \frac{(n_i+g_i)!}{n_i!\, g_i!}$$

BE

$$\ln W = \sum \ln(n_i+g_i)! - [\ln n_i! + \ln g_i!]$$

$$= \sum (n_i+g_i)\ln(n_i+g_i) - (n_i+g_i) - n_i\ln n_i + n_i - g_i\ln g_i + g_i$$

$$= \sum (n_i+g_i)\ln(n_i+g_i) - n_i\ln n_i - g_i\ln g_i$$

$$\frac{\partial}{\partial n_i}\ln W = \ln(n_i+g_i) + \frac{n_i}{(n_i+g_i)} + \frac{g_i}{(n_i+g_i)} - \frac{n_i}{n_i} - \ln n_i$$

$$= \ln(n_i+g_i) - \ln n_i + 1 - 1$$

$$\frac{\partial}{\partial n_i}\ln W = \ln\left(1+\frac{g_i}{n_i}\right) = \alpha + \beta\epsilon_i$$

$$1 + \frac{g_i}{n_i} = e^{\alpha+\beta\epsilon_i}$$

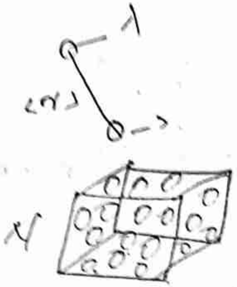
$$\frac{g_i}{n_i} = e^{\alpha+\beta\epsilon_i} - 1$$

$$\boxed{f(\epsilon) = \frac{n_i}{g_i} = \frac{1}{e^{\alpha+\beta\epsilon_i} - 1}}$$

***

VALIDITY OF FD & BE & MB

Condition for applying MB-statistics



$\langle r \rangle \gg \lambda.$

mean separation $\gg \lambda.$

Avg. vol. $= \frac{V}{N}.$

Avg. length $= (\text{Avg. vol})^{1/3}$

$$= \left(\frac{V}{N}\right)^{1/3}$$

$$\langle r \rangle = \left(\frac{V}{N}\right)^{1/3}.$$

$$\left(\frac{V}{N}\right)^{1/3} \ggg \lambda.$$

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{3mk_BT}}$$

$$\left(\frac{V}{N}\right)^{1/3} \gg \frac{h}{\sqrt{3mk_BT}}$$

$$\left(\frac{V}{N}\right)^{1/3} \gg \left(\frac{h^2}{3mk_BT}\right)^{1/2}.$$

$$\frac{V}{N} \gg \left(\frac{h^2}{3mk_BT}\right)^{3/2}.$$

$$1 \gg \frac{N}{V}\left(\frac{h^2}{3mk_BT}\right)^{3/2}.$$

$$\left(\frac{3}{2\pi}\right)^{3/2} \gg \frac{N}{V}\left(\frac{h^2}{3mk_BT}\right)^{3/2} \times \left(\frac{3}{2\pi}\right)^{3/2}$$

$$1 \gg \left(\frac{h^2}{2\pi m k_0 T}\right)^{3/2} \frac{N}{V}$$

$$\frac{1}{\lambda_0} = \left(\frac{2\pi\hbar^2}{m k_0 T}\right)$$

$$e^{-\alpha} \ll 1$$

$$\left(\frac{h^2}{2\pi m k_0 T}\right)^{3/2} \frac{N}{V} \ll 1$$

$$\left(\frac{h^2}{2\pi m k_0 T}\right)^{3/2} \frac{N}{V} \ll 1$$

$$e^{-\alpha} \ll 1$$

1/5/15

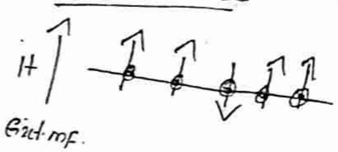
ISING MODEL. [A collection of spins]

→ Apply to a canonical ensemble & slight more to micro canonical ensemble.

Model consist of spin variable $\{S_i\}$, which takes values $+1\ (\uparrow)$ or $-1\ (\downarrow)$

⟹ spins have two types of interactions.

1D Lattice



Mutual interaction

$-J \sum_{ij} S_i S_j$

with ext. mag. field ($\to \mu B$)

$-h \sum_i S_i$

$$\boxed{H = -J \sum_{ij} S_i S_j - h \sum_i S_i}$$

$\boxed{J}$

$J > 0$

$S_i = \uparrow$ & $S_{i+1} = \uparrow$

$S_i = \downarrow$ & $S_{i+1} = \downarrow$

Ferro magnetic material

$J < 0$

$S_i = \uparrow \Rightarrow S_{i+1} = \downarrow$

$S_i = \downarrow \Rightarrow S_{i+1} = \uparrow$

anti ferro.

$\boxed{h}$

$h > 0$

$S_i \Rightarrow \uparrow$

parallel

$h < 0$

$S_i \Rightarrow \downarrow$

anti parallel

mutual   magnetic field

~~2 states~~

2 lattice sites : [2 spins]

s_1 s_2.

Case 1   No mutual interaction [$J=0$]

$H = -h \sum_i s_i = -h(s_1+s_2)$.

Basis 2 $\uparrow\downarrow$

$\therefore$ No. of array $(2)^N = \underline{\underline{2^2}}$
4

$\uparrow\uparrow \Longrightarrow \hat{H} = -2h$

$\uparrow\downarrow \Longrightarrow \hat{H} = 0$

$\downarrow\uparrow \Longrightarrow \hat{H} = 0$

$\downarrow\downarrow \Longrightarrow \hat{H} = 2h$.

$\hat{H} = \sum e^{-\beta E_s} = \sum e^{-\beta H}$

$= 2 + e^{-\beta(2h)} + e^{-\beta(2h)} = 2 + e^{2\beta h} + e^{-2\beta h}$.

$= 2 + e^{2\beta\mu B} + e^{-2\beta\mu B}$

$\hat{H} = \underline{\underline{2 + e^{2\beta\mu B} + e^{-2\beta\mu B}}}$

(3 spins)

microstates $-2^3 = 8$.

$H = -h\sum_i s_i = -h(s_1+s_2+s_3)$

$\uparrow\uparrow\uparrow$ $H = -h(3) = -3h$.

$\uparrow\uparrow\downarrow$ $H = -h$

$\uparrow\downarrow\uparrow$ $H = -h$

$\uparrow\downarrow\downarrow$ $H = h$

$\downarrow\uparrow\downarrow$ $H = h$

$\downarrow\downarrow\uparrow$ $H = -h$

$\downarrow\uparrow\uparrow$ $H = +h$

$\downarrow\downarrow\downarrow$ $H = 3h$

$\hat{H} = e^{-3\beta h} + 3e^{-\beta h} + 3e^{\beta h} + e^{3\beta h}$

$\hat{H} = e^{3\beta\mu B} + 3e^{\beta\mu B} + 3e^{-\beta\mu B} + e^{-3\beta\mu b}$

$\Longrightarrow$ Pauli paramagnetic (spin ½) ($J=0$)

$\hat{H} = -h\sum_i s_i = -hs$.

$\uparrow$ $\hat{H} = -h$

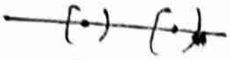
$\downarrow$ $\hat{H} = h$

$Z = e^{-\beta h} + e^{\beta h}$. $= e^{\beta\mu B} + e^{-\beta\mu B}$.

$Z = \underline{\underline{2\cosh(\beta\mu B)}}$ For N particle $Z_N = (2\cosh\beta\ldots$

case 2 $\quad J \neq 0.$

eg: 2 lattice sites (2 spins) $\quad$ 51



$S_1 \quad S_2$

$$\hat{H} = -J \sum S_i S_{i+1} - h \sum_i S_i$$

$$= -J (S_1 S_2) - h(S_1 + S_2)$$

micro states $\quad 2^2 = 4$

$\uparrow \uparrow \quad H = -J - 2h$

$\uparrow \downarrow \quad H = J$

$\downarrow \uparrow \quad H = J$

$\downarrow \downarrow \quad H = J + 2h.$

$$Z = \sum e^{-\beta \epsilon_j} = e^{\beta(J+2h)} + 2 e^{-\beta J} + e^{-\beta(J+2h)}$$

$$Z = e^{-\beta(J+2\mu B)} + 2 e^{-\beta J} + e^{-\beta(J+2\mu B)}$$

2) 3 lattice site.

$$H = -J \sum_i S_i S_{i+1} - h \sum_i S_i$$

micro states

$$= -J (S_1 S_2 + S_1 S_3 + S_{23}) - h (S_1 + S_2 + S_3)$$

$$\underline{\underline{2^3 = 8}}$$