

Can deal with the microscopic & macroscopic world.

Macro

$$(P, T, V)$$

Pressure, temp, Vol

Thermodynamics.

Micro

$$\{\vec{r}\} = (\vec{r}_1, \vec{r}_2, \dots)$$

$$\{\vec{p}\} = (\vec{p}_1, \dots, \vec{p}_n)$$

$\uparrow \leftrightarrow \Delta v$ . kinetic energy

Extending concepts to

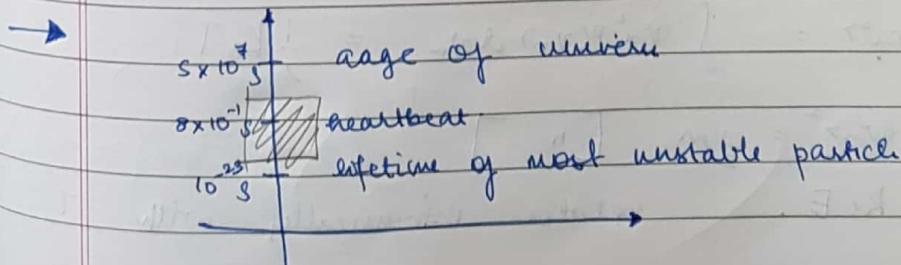
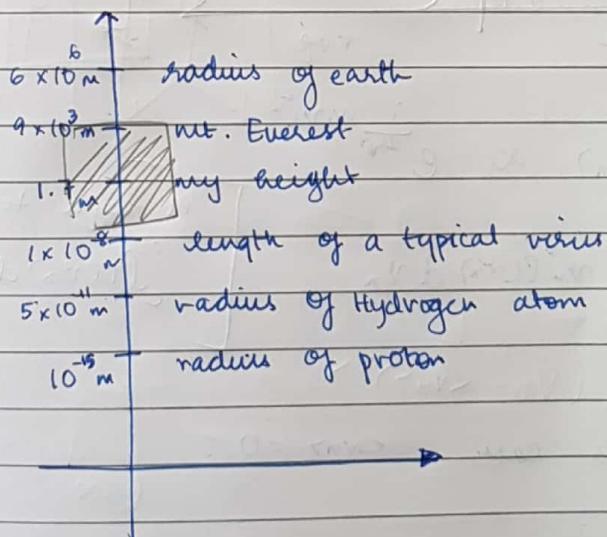
~ length scales  $10^{-18}$  m to  $10^{18}$  m.

~ Time scales  $10^{-15}$  s to years

- Classical mechanics (large length scales)
- Quantum mechanics (smaller length scales)

■ Science is based on measurements & observations

→ A length scale:



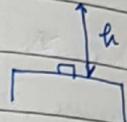
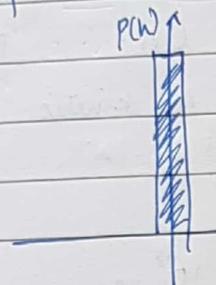
$$\langle \text{var} \rangle = \text{avg. of (var)}$$

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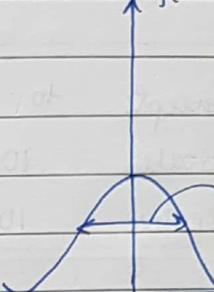
Measurements do not give you unique value

For eg: consider a corn bread on a hot plate

Expected curve:-

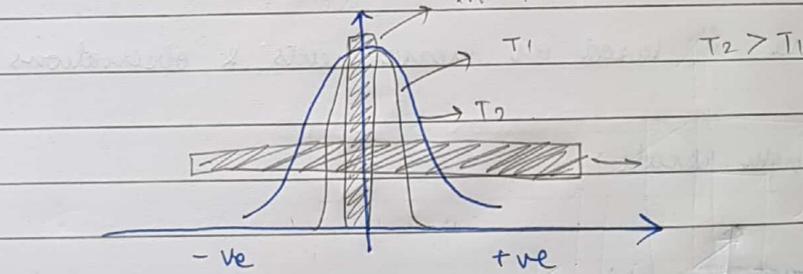


$$P(h)$$



→ Maxwell Boltzmann dist curve

At  $T \rightarrow 0$ ,



$$\text{Now, } P(v_n) \propto e^{-\frac{mv_n^2}{2k_B T}}$$

Gives us we  $\langle v_n^2 \rangle = \int_{-\infty}^{\infty} v_n^2 P(v_n) dv_n$   
standard deviation

at high temperature  
 $\int_{-\infty}^{\infty} P(v_n) dv_n \neq 0$

$$= \langle (v_n - \langle v_n \rangle)^2 \rangle$$

$$\text{In this case } \langle v_n \rangle = 0.$$

NOW,

$$\langle v_n^2 \rangle = \int_{-\infty}^{\infty} v_n^2 P(v_n) dv_n = \frac{1}{2} k_B T$$

$$\frac{1}{2} m \langle v_n^2 \rangle = \frac{1}{2} m ["]$$

K.E. relates intrinsically with T

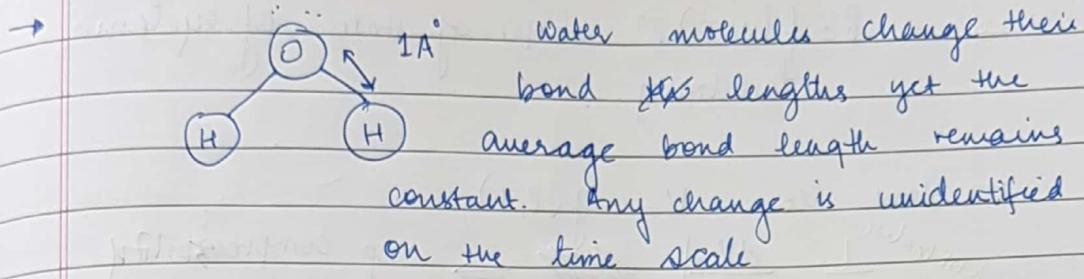
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ink! Mathematical model

classmate

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Proof that the H<sub>2</sub>O molecules are vibrating: drop ink, it diffuses.

- Stability of Graphite & Diamond

- Graphite is more stable than diamond
- Diamond always tries to go back to the graphite form.
- Gibbs Free energy function is used to determine stability.

~ Cooling water rapidly will form water glass.  
This is where kinetics comes into play!

To understand any system we could use 4 parameters

Energy	Matter	Waves	Mathematics
Bond Energy Thermodynamic Heat Work free energy	Statistical mechanics Solid state physics Matter	Bohr System is made of particles define the micro state of the system	Electromagnetic waves Particle waves Quantum Mech.

Law:

PV = nRT

Equation of State of a gas:

P = f(V, T)

In the thermodynamic world we have 4 parameters

P, V, T,  $\lambda$  considered constant.

Each can be expressed as a function of the other law

$P = f(V, T) \rightarrow$  Eqn of state of system  
+ arbitrary.

Now let  $V = g(P, T)$ .

Normalized  
to get ratio  $V \frac{dV}{dP} \cancel{\Big|_T} \rightarrow$  rep compressibility

when  $P \rightarrow P + dP$   
 $V \rightarrow V + dV$

### • Matter:

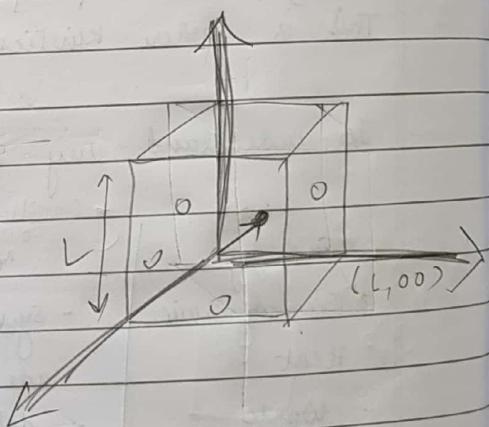
- System consists of  $N$  particles
- Positions & momenta of particles known
- Microscopic variables

Expt:  $N$  particles in the system

Let co-ordinates of particle

$$\vec{r} \rightarrow (x_i, y_i, z_i)$$

$$\text{also } \left. \begin{array}{l} 0 \leq x_i \leq L \\ 0 \leq y_i \leq L \\ 0 \leq z_i \leq L \end{array} \right\} + i$$



$$\text{Volume } V = L^3$$

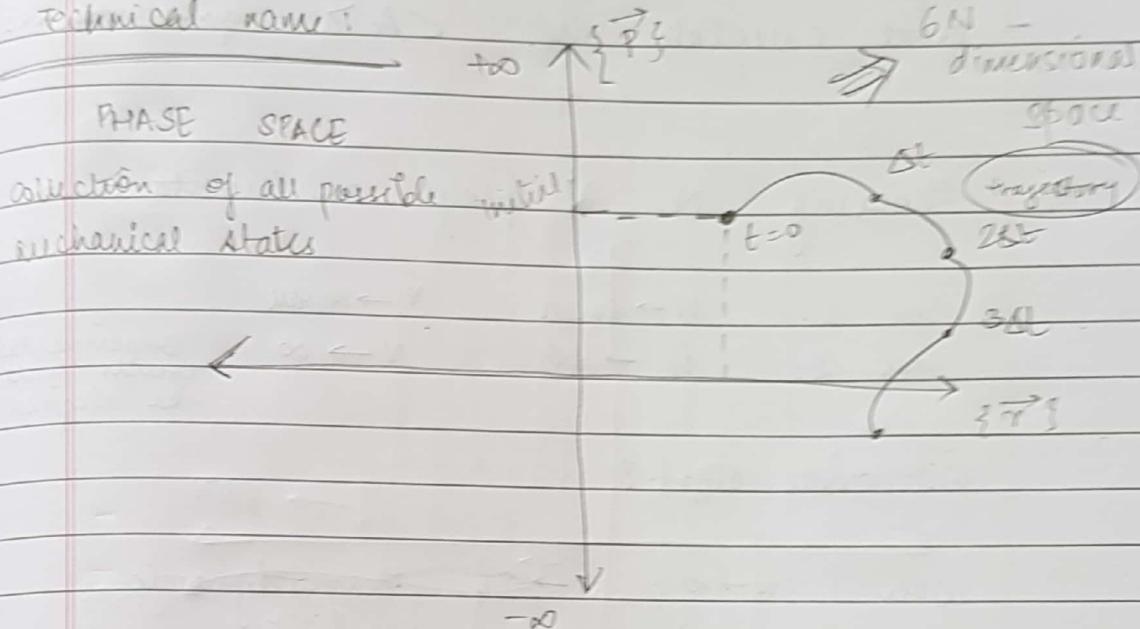
Notation:  $\{\vec{r}\} = (\bar{x}_1, \bar{y}_1, \bar{z}_1, x_2, y_2, z_2, \dots, \bar{x}_N, \bar{y}_N, \bar{z}_N)$   
( $3N$  components)

$$\vec{r}_i = (x_i, y_i, z_i)$$

Similarly:  $\{\vec{p}\} = (\bar{p}_{x1}, \bar{p}_{y1}, \bar{p}_{z1}, \dots, \bar{p}_{xN}, \bar{p}_{yN}, \bar{p}_{zN})$   
( $3N$  components)

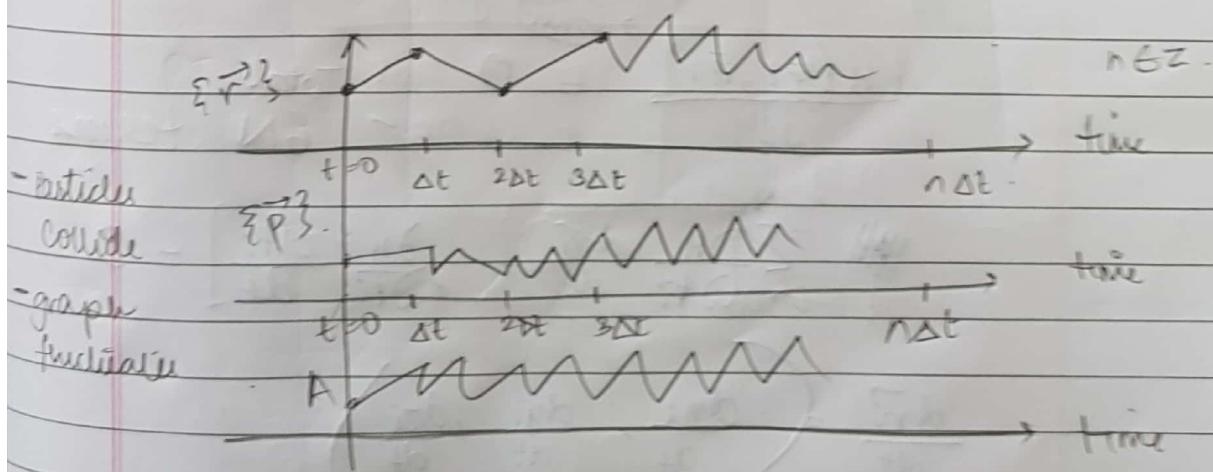
Now constructing a plane with  $\{\vec{r}\}$  on  $x$ -axis &  $\{\vec{p}\}$  on  $y$ -axis.

Technical name:



- A given pt. on this space rep. a mechanical state of the system.
- The system is going to evolve.
- When a particle moves, the system changes its state.
- All thermodynamic properties can be expressed in terms of the co-ordinates & momenta of particles.

arbitrary prop  $\leftarrow A = A(\{\vec{r}\}, \{\vec{p}\})$



- A is a simple scalar function giving a single number
- Next calculate the  $\langle A \rangle$  → comparable to experimental results
- choosing  $N, V$  plays an important role

Case 1:  $N \rightarrow \text{small}$        $V \rightarrow \text{small}$

Case 2:  $N \rightarrow \infty$        $V \rightarrow \infty$

Experimental results will be aligned.

Will results differ?

with  $N \rightarrow \infty; V \rightarrow \infty \}$  thermodynamic limit  
 $\frac{N}{V} = \text{finite}$

$$\rightarrow H(\{\vec{r}\}, \{\vec{p}\}) = U(\{\vec{r}\}) + k(\{\vec{p}\})$$

↑ scalar function      ↑ potential energy func.  
★ Hamiltonian function      (Interaction b/w particles)  
 (Total energy of system)

Consider an isolated system → Doesn't exchange energy with the surroundings

$$\frac{dH(\{\vec{r}\}, \{\vec{p}\})}{dt} = 0 \quad \text{Total } 6N \text{ terms}$$

$$\cancel{\frac{dH}{dt}} = \sum_{i=1}^N \left[ \frac{\partial H}{\partial r_i} \cdot \frac{dr_i}{dt} + \frac{\partial H}{\partial p_i} \cdot \frac{dp_i}{dt} \right] = 0$$

$$\frac{d\vec{r}_i}{dt} = \left( \frac{dx_i}{dt}, \frac{dy_i}{dt}, \frac{dz_i}{dt} \right)$$

$\vec{F}_i$  $\frac{\partial H}{\partial r_i}$  $\frac{\partial r_i}{\partial t}$ 

$$= - \cancel{\frac{\partial H}{\partial r_i}} \frac{d p_i}{d t}$$

force

Hamiltonian

eqn.

$$\frac{\partial H}{\partial p_i} = \frac{d r_i}{d t}$$

$$\frac{d r_i}{d t}$$

velocity

Recap:

→ microstate of a system consisting of N particles ( $\vec{r}, \vec{p}$ )

$$\vec{r} = (x_1, y_1, z_1, x_2, y_2, z_2, \dots) \rightarrow S_N$$

$$\vec{p} = (p_{x1}, p_{y1}, p_{z1}, \dots, p_{xN}, p_{yN}, p_{zN})$$

in the hamiltonian scale:

$$\vec{F}_i = \frac{d \vec{p}_i}{d t} = - \cancel{\frac{\partial H}{\partial r_i}} = \boxed{- \frac{\partial U(\vec{r})}{\partial r_i}}$$

negative gradient of pot. energy

The direction of decrease in pot. energy is the direction of force

$$\text{Here } \vec{F}_i = F_{xi} \hat{i} + F_{yi} \hat{j} + F_{zi} \hat{k}$$

$$F_{xi} = \cancel{8} - \frac{\partial U}{\partial x_i}$$

$$F_{yi} = - \frac{\partial U}{\partial y_i}$$

$$F_{zi} = - \frac{\partial U}{\partial z_i}$$

for individual components.

Displace the  $i^{\text{th}}$  atom by an incremental amt ie:

$$x_i \rightarrow x_i + \delta x_i$$

$$y_i \rightarrow y_i + \delta y_i$$

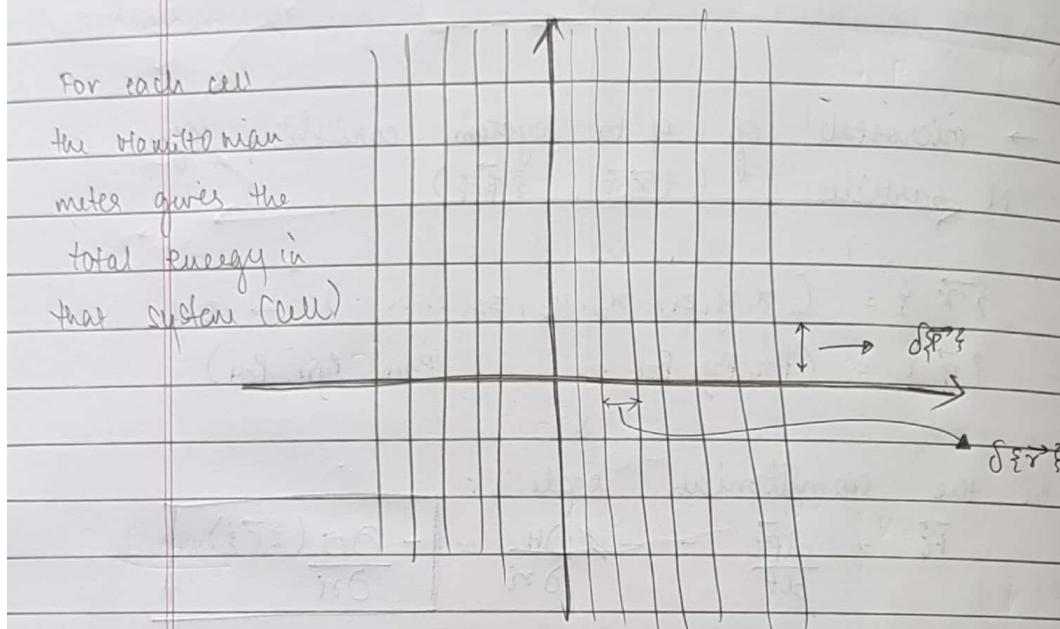
$$z_i \rightarrow z_i + \delta z_i$$

∴ change in pot energy is :-

$$U(x_i + \delta x_i, y_i + \delta y_i, z_i + \delta z_i) - U(x_i, y_i, z_i)$$

Aim : to convert the  $bN$  dimension space to  $1D$

For each cell  
the Hamiltonian  
matrix gives the  
total energy in  
that system (cell)



$$\delta z_i \rightarrow 0 \quad \delta z_i \rightarrow 0 \text{ arbitrarily small}$$

ENERGY

dig.

$E_{max}$  (highest energy)

$E_i \rightarrow \Omega(E_i)$  with  
no. of cells  
 $E_i$

$$E_{min} + 2\delta E$$

$$E_{min} + \delta E$$

$E_{min}$  (lowest energy)

$$\delta E \rightarrow 0$$

Two overlapping particles could have ~~as~~ energy <sup>classmate</sup>

(E<sub>i</sub>) No. of microstates accessible to the system with energy E<sub>i</sub>

Boltzmann's claim :-

Entropy S of a system

$$S \propto \ln(\Omega(E_i))$$

microscopic

$$\xleftarrow{\text{thermodynamic quantity}} S = k_B \ln(\Omega(E_i))$$

Boltzmann const.

↓ statistical measure

→ This can be used to reason why ice has lower entropy than water. All atoms are frozen with 0 velocity & no change in momentum, all particles in ice are in one mechanical state. Then  $S = k_B \ln(1) = 0$  (or tending to 0)

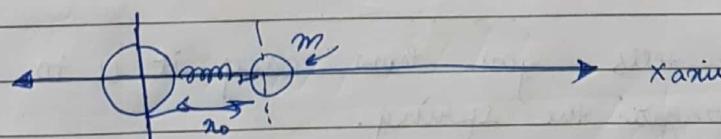
On heating,  $\ln(E_i)$  increases. For an isolated system acceptable energy levels are where energy of the microstate is E<sub>i</sub>

▲ Determine  $\Omega(E_i)$  for:

① Model 1: One-dimensional harmonic oscillator

② Ideal Gas.  $U(\vec{r}) = 0$

Model 1: Consider a heavy atom attached to a light O atom let a spring bond exist.



lighter atom will execute harmonic motion on being displaced.

Constructing phase space for model 1:

Area  
 $= Sx \times Sp.$

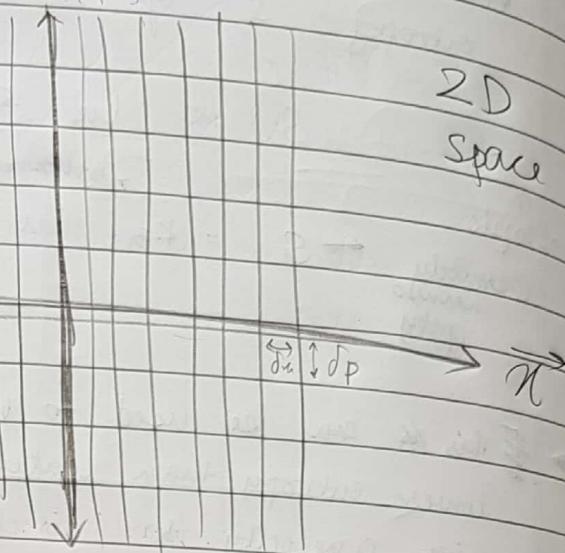
dim ↑

angular  
 momentum ←

$d\theta dp = h$

2D

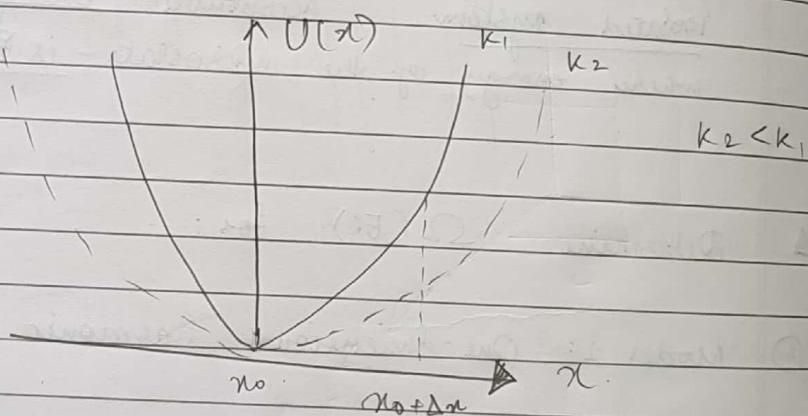
Space



$$H(x, p) = \frac{p^2}{2m} + \frac{1}{2} K(x - x_0)^2 = E$$

Initial energy

Pot energy:



$$U(x) = \frac{1}{2} K (x - x_0)^2$$

$\downarrow$   
spring const.

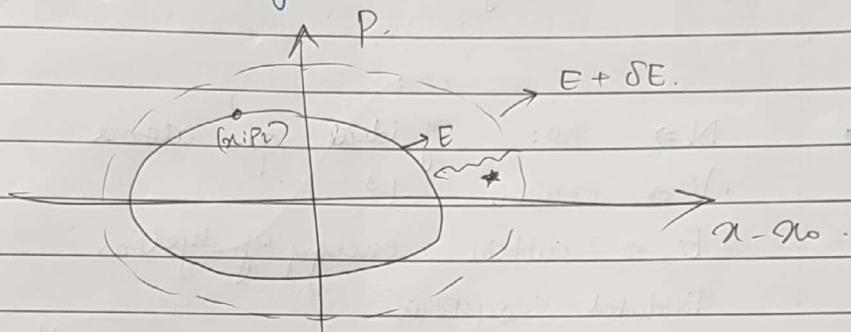
$$\left. \frac{d^2 U}{dx^2} \right|_x = k.$$

K tells you how easy it is to compress/elongate the spring.

Rearranging:-

$$\frac{(x - x_0)^2}{\left(\frac{\sqrt{2E}}{k}\right)^2} + \frac{P^2}{\left(\frac{\sqrt{2ME}}{k}\right)^2} = 1 \rightarrow \text{Ellipse}$$

The pts. on the circumference of this ellipse are all the accessible states. These are the states visited by the system.



$$\Omega(E) \propto \text{Circumference of Ellipse}$$

$$\Omega(E) \propto \pi \left( \frac{\sqrt{2E}}{k} + \frac{\sqrt{2ME}}{k} \right)$$

$$\text{i.e.: } \Omega(E) \propto E^{1/2}$$

No. of microstates can increase with the energy of the system & consequently increase the entropy of the system.

\* : relaxation time : how fast the system can come back to the ground state

→ For crystals at low temp:-

$$\begin{aligned} \Omega(E) &\rightarrow 1 \\ \Rightarrow S &\rightarrow 0 \end{aligned}$$

→ Ideal Gas (Model 1) :-

$$H(\vec{r}_1, \vec{p}_1) = U(\vec{r}_1) + K(\vec{p}_1)$$

if  $U(\vec{r}_1) = 0$  atoms do not interact with each other  $\Rightarrow$  ideal gas  
 Only energy that excites particles is thermal energy

- $N \Rightarrow$  no: of ideal gas atoms
- $V \Rightarrow$  volume  $L^3$
- $E \Rightarrow$  initial energy of system  
 Isolated system

It is a  $6N$  dimension space.

Vol. of a  $6N$  dimensional space

$$\delta\vec{r}_1 \delta\vec{p}_1$$

$=$

$$\delta x_1, \delta p_{x_1}, \delta y_1, \delta p_{y_1}, \delta z_1, \delta p_{z_1} \dots$$

$$\delta x_N, \delta p_{x_N}, \delta y_N, \delta p_{y_N}, \delta z_N, \delta p_{z_N}$$

$$= h^{3N} \quad h \rightarrow 0$$

$h$  is arbitrary in classical mechanics

$h$  is called Planck's const in quantum mechanics

Aim : calculate  $S(E)$

But here more parameters exist

SO calc:  $S(N, V, E)$

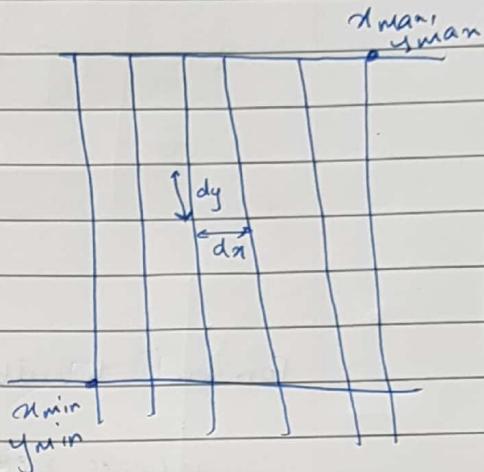
$\Omega$ : No: of accessible microstates.

System visits those states in which energy = E.  
Check each cell.

Calc integral :-

$$\int_{x_{\min}}^{x_{\max}} \int_{y_{\min}}^{y_{\max}} dx dy .$$

visit all ~~for~~ cells in  $6N$  dimensional phase



[Idea: Calc total area,  $\div$  by area of 1 cell  $\Rightarrow$  total no: of particles]

$$\iint \delta(H-E) \delta \vec{r} \delta \vec{p}$$

$\downarrow$   $\downarrow$  Hamiltonian  $\int (H-E) = 1$  when  $H=E$   
 $3N$   $3N$  integrals integrals.  $\downarrow$   $= 0$  otherwise  
 $\downarrow$  direct delta function

$$\Omega(N, V, E) = \frac{1}{h^{3N}} \iint \delta(H-E) \delta \vec{r} \delta \vec{p} .$$

$\downarrow$   
counting cells that satisfy this condition

The Hamiltonian function:

$$H(\vec{r}, \vec{p}) = \frac{1}{m} \sum_{i=1}^N \vec{p}_i \cdot \vec{p}_i$$

$\downarrow$   
mass of an atom

$$0 \leq x_i, y_i, z_i \leq L .$$

$$\Omega(N, V, E) = \frac{1}{h^{3N}} \int_{\{\vec{r} = 0\}} d\vec{r} \int_{\{\vec{p} = 0\}} \delta(H-E) d\vec{p}$$

$$= \frac{1}{h^{3N}} \cancel{V^N} \int_{\{\vec{p} = 0\}} \delta(H-E) d\vec{p}$$

visiting only  
the momentum  
space of dim =  $3N$

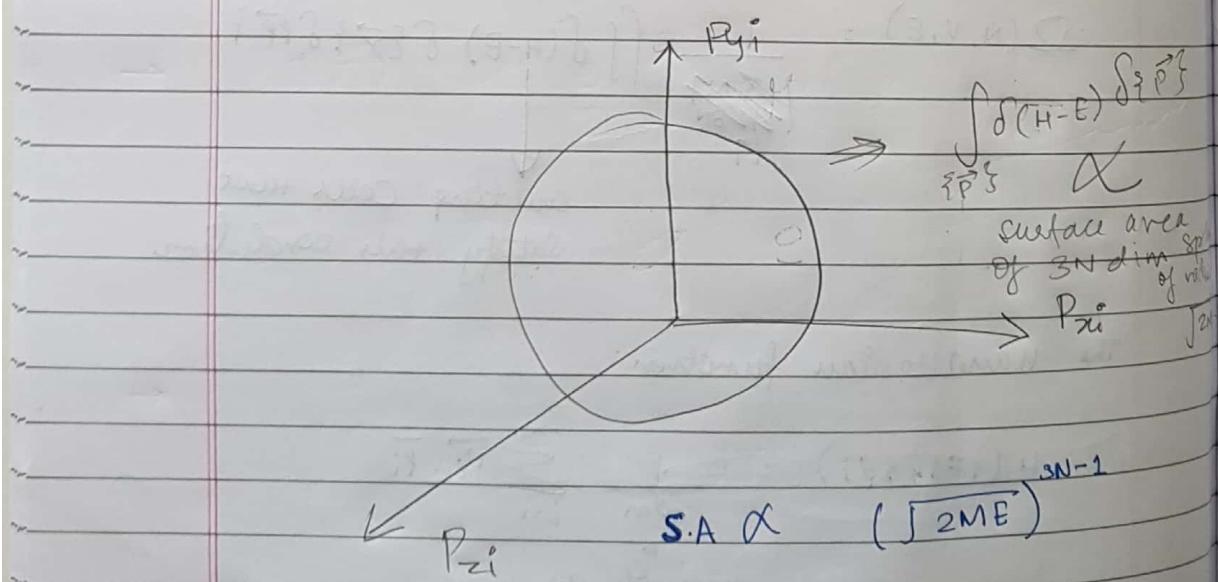
For the hamiltonian :-

$$H(\{\vec{r}\}, \{\vec{p}\}) = \frac{p_{x_1}^2}{2m} + \frac{p_{y_1}^2}{2m} + \frac{p_{z_1}^2}{2m} + \dots + \frac{p_{x_N}^2}{2m} + \frac{p_{y_N}^2}{2m} + \frac{p_{z_N}^2}{2m} = E$$

Also:-

$$p_{x_1}^2 + p_{y_1}^2 + p_{z_1}^2 + \dots + p_{x_N}^2 + p_{y_N}^2 + p_{z_N}^2 = (\sqrt{2mE})^2$$

This is the eqn of a  $3N$  dimensional sphere of radius  $\sqrt{2mE}$ .



$$\Omega(N, V, E) \propto V^N E^{-2} h^{3N}$$

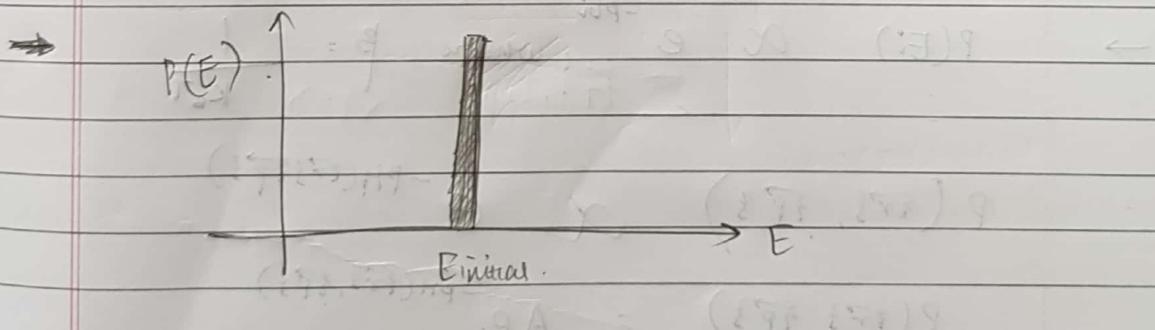
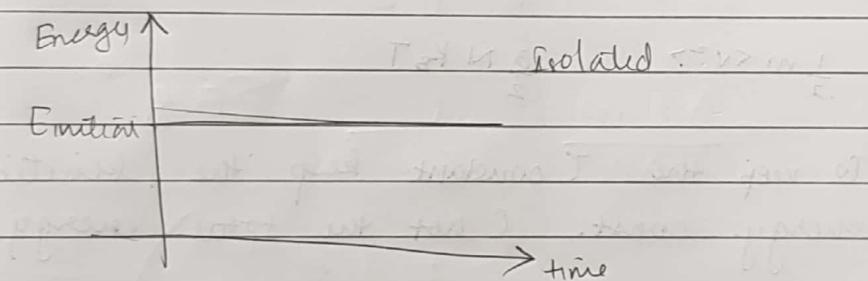
No: of accessible microstates increases with volume with Energy

Increasing no: of atoms increase no: of accessible microstates

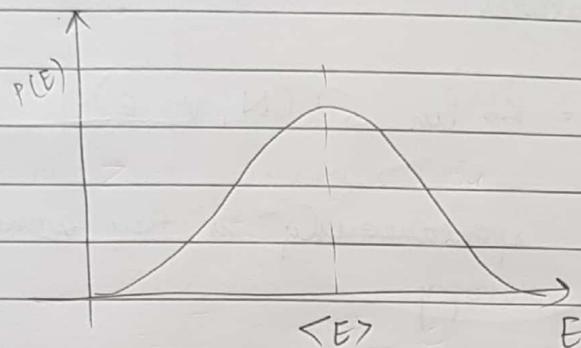
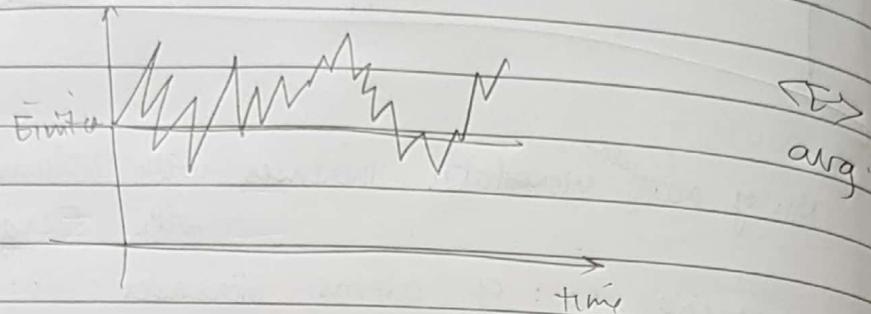
$$S = k_B \ln \Omega(N, V, E).$$

→ Gasses expand spontaneously as they want to increase their entropy

→ For an isolated system:-



For a closed system:-



$$\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} N k_B T$$

To keep the  $T$  constant keep the kinetic energy const. (not the total energy)

$$\rightarrow P(E_i) \propto e^{-\beta E_i}, \text{ where } \beta = \frac{1}{k_B T}$$

$$P(\vec{r}_1, \vec{p}_1) \propto e^{-\beta H(\vec{r}_1, \vec{p}_1)}$$

$$P(\vec{r}_1, \vec{p}_1) = A e^{-\beta H(\vec{r}_1, \vec{p}_1)}$$

$$\iint_{\vec{r}_1, \vec{p}_1} P(\vec{r}_1, \vec{p}_1) d\vec{r}_1 d\vec{p}_1 = 1$$

$$P(\{\vec{r}\}, \{\vec{p}\}) = e^{-\beta H(\{\vec{r}\}, \{\vec{p}\})}$$

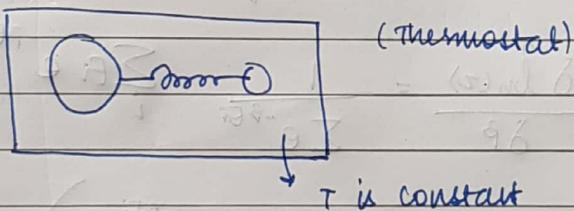
$\int \int \dots \int$

$$Z = \frac{1}{h^{3N}} \int \int \dots \int \left( e^{-\beta H(\{\vec{r}\}, \{\vec{p}\})} d\vec{r} d\vec{p} \right)$$

$Z$  is called the partition function of the system.

Given  $Z$  we can calculate all thermodynamic properties of the system.

→ Model-1: One dimensional Harmonic Oscillator (closed)

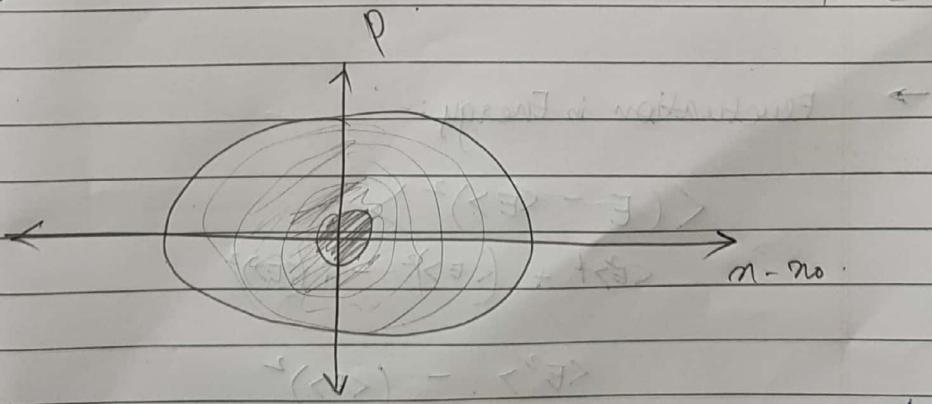


$$H(x, p) = \frac{1}{2} K(x - x_0)^2 + \frac{p^2}{2m}$$

$$P(x, p) \propto e^{-\frac{p^2}{2m} - \frac{K(x - x_0)^2}{2}}$$

Max prob when  $x = x_0$  or  $p = 0$

comb of 2 Gaussian func.



$$Z = \frac{1}{\beta h^{3N}} \iiint e^{-\beta E} d^3 p_1 d^3 p_2 d^3 p_3$$

Continuous :

$$Z = \sum_{i=1}^{\text{no. of microstates}} e^{-\beta E_i}$$

Discrete.

→ From  $Z$  we can calculate thermodynamic properties of the system :-

$$Z = \sum_i e^{-\beta E_i}$$

$$\ln Z = \ln \left( \sum_i e^{-\beta E_i} \right)$$

$$-\frac{\delta \ln(Z)}{\delta \beta} = \frac{1}{\sum_i e^{-\beta E_i}} \sum_i E_i e^{-\beta E_i}$$

$$= \sum_i E_i \left( \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}} \right) \quad \dots (1)$$

$$= \sum_i E_i P(E_i) = \langle E \rangle$$

↳ internal energy of the system

→ Fluctuation in Energy :-

$$\langle (E - \langle E \rangle)^2 \rangle$$

$$\langle E^2 \rangle + \langle E \rangle^2 - 2 \langle E \rangle^2$$

$$\langle E^2 \rangle - \langle E \rangle^2$$

Consider

$$\sum E_i e^{-\beta E_i} = -z \frac{\partial \ln z}{\partial \beta}$$

$$\frac{\partial}{\partial \beta} \left[ \sum_i E_i e^{-\beta E_i} \right] = -\frac{\partial}{\partial \beta} \left( z \frac{\partial \ln z}{\partial \beta} \right)$$

$$-\sum_i E_i^2 e^{-\beta E_i} = -\left(\frac{\partial z}{\partial \beta}\right) \frac{\partial \ln z}{\partial \beta}$$

$$= -z \frac{\partial^2 \ln z}{\partial \beta^2}$$

$$\sum_i E_i^2 \left( \frac{e^{-\beta E_i}}{z} \right) = \left( \frac{1}{z} \frac{\partial z}{\partial \beta} \right) \left( \frac{\partial \ln z}{\partial \beta} \right) + \frac{\partial^2 \ln z}{\partial \beta^2}$$

$$\langle E^2 \rangle = \left( \frac{\partial \ln z}{\partial \beta} \right)^2 + \frac{\partial^2 \ln z}{\partial \beta^2}$$

$$\langle E^2 \rangle = (\langle E \rangle)^2 + \frac{\partial^2 \ln z}{\partial \beta^2}$$

$$\langle E^2 \rangle - (\langle E \rangle)^2 = \frac{\partial^2 \ln z}{\partial \beta^2}$$

$$= -\frac{\partial}{\partial \beta} \left( \frac{\partial \ln z}{\partial \beta} \right) = -\frac{\partial}{\partial \beta} \langle E \rangle$$

Now  $\beta = \frac{1}{k_B T}$

$$\langle E^2 \rangle - (\langle E \rangle)^2 = \frac{\left( -\frac{\partial}{\partial T} \langle E \rangle \right)}{\left( \frac{\partial \beta}{\partial T} \right)}$$

$$\left\{ C_V = -\frac{\partial \langle E \rangle}{\partial T} \rightarrow \text{heat capacity} \right\}$$

$$\langle E^2 \rangle - (\langle E \rangle)^2 = \frac{C_V}{(\frac{\partial P}{\partial T})}$$

Energy fluctuation is related to the heat capacity of the system.

$$\left(\frac{\partial P}{\partial T}\right)$$

$$\frac{\partial \ln P}{\partial T} = \frac{C_V}{k_B T}$$

- Energy fluctuation is related to the heat capacity of the system.
- $C_V$  is always positive as  $C_V = \frac{\partial \langle E \rangle}{\partial T}$  and  $\langle (E - \langle E \rangle)^2 \rangle$  is positive
- Fluctuation in energy can be calculated at constant temperature.

### ▲ For an isolated system:-

*isolated*

- entropy  $S = k_B \ln \Omega$
- $S = -k_B \sum_i p_i \ln p_i \rightarrow$  Expectation  
*Prob of finding the system in  $i^{th}$  microstate*
- $\underline{-k_B \langle \ln p_i \rangle}$

If the system was isolated

$$p_i = \frac{1}{\Omega} \quad (\text{The prob of equal a priori probabilities})$$

*all states equally probable*

Closed systems  $\rightarrow$  energy exchange only  
 Open systems  $\rightarrow$  both energy & matter

classmate

Date \_\_\_\_\_  
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For a closed system :-  $P_i = e^{-\frac{E_i}{k_B T}} / Z$

$$S = -k_B \sum_i \left( \frac{e^{-\frac{E_i}{k_B T}}}{Z} \right) (-\beta E_i - \ln Z)$$

*Sum over microstates* =  $\beta k_B \sum_i E_i P_i + k_B \ln Z \sum_i P_i$

$$= \frac{1}{k_B T} \sum_i E_i P_i + k_B \ln Z \underbrace{\sum_i P_i}_{=1}$$

$$S = \frac{1}{T} \langle E \rangle + k_B \ln Z$$

$$-k_B T \ln Z = \langle E \rangle - TS$$

RHS  $\rightarrow$  Helmholtz free energy  $A = U - TS$ .

$\therefore A = -k_B T \ln Z$   $\rightarrow$  In terms of the partition func.

Keeping all parameters - no: of moles, V, T const  
 & ~~then~~ <sup>only</sup> Helmholtz free energy will be minimized

$$S = -k_B \sum_i P_i \ln P_i \quad \text{If } P_i = 1 \text{ then } S = 0$$

Whenever the P.D is delocalized ~~the~~ ie: prob is distributed to various states entropy increases  
 You don't know where the system exactly is at a given pt. of time.

## MICROSCOPIC DEFINITION OF PRESSURE:

$$P_i = - \frac{\partial E_i}{\partial V} = - \left[ \frac{(E_i(v + \Delta v)) - E(v)}{\Delta v} \right]_{\Delta v \rightarrow 0}$$

↑  
Pressure of  
the microstate i

expand the vol. of the system & measure the energy of the same microstate. This change is the microscopic defn of pressure.

$$\langle P_i \rangle = \sum_i P_i P_i = \frac{1}{Z} \frac{\partial \ln Z}{\partial V}$$

### For an ideal gas (closed)

$N \Rightarrow$  no: of ideal gas atoms.

$V \Rightarrow$  volume.

$T \Rightarrow$  temperature

$$H(\{\vec{r}\}, \{\vec{p}\}) = \frac{1}{2m} \sum_{j=1}^N \vec{p}_j \cdot \vec{p}_j$$

↑ Pot energy  
↓ Total KE

To calc Z:-

$$Z = \frac{1}{h^{3N}} \int \int e^{-\frac{p_i \vec{r}_i \cdot \vec{p}_i}{2m}} d\vec{r}_i d\vec{p}_i$$

$$= \frac{1}{h^{3N}} \int_{\vec{r}_1} \int_{\vec{p}_1} d\vec{r}_1 d\vec{p}_1 \int_{\vec{r}_2} \int_{\vec{p}_2} \cdots \int_{\vec{r}_N} \int_{\vec{p}_N} d\vec{r}_N d\vec{p}_N$$

$\uparrow \frac{N}{2m} \sum_{i=1}^N \vec{p}_i \cdot \vec{p}_i$

$\uparrow 3N \text{ terms}$

$$Z = \frac{1}{h^{3N}} V^N \left( \int_{n=-\infty}^{\infty} e^{-\frac{\beta n^2}{2}} \right)^{3N}$$

$$Z = \frac{1}{h^{3N}} V^N \left( \sqrt{\frac{2m\pi}{\beta}} \right)^{3N}$$

$$= \frac{1}{h^{3N}} V^N \left( 2m\pi k_B T \right)^{3N/2}$$

$$\langle P \rangle = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V}$$

$$\langle P \rangle = \frac{1}{\beta} \frac{N}{V}$$

$$\boxed{\langle P \rangle V = N k_B T} \rightarrow \text{Ideal Gas eqn of state}$$

→ Feynman's trick to solve ① :-

$$I = \int_{n=-\infty}^{\infty} e^{-\alpha n^2} dn.$$

$$I = \int_{y=-\infty}^{\infty} e^{-\alpha y^2} dy$$

$$I^2 = \iint_{n=-\infty}^{\infty} e^{-\alpha(n^2+y^2)} dndy$$

$$n^2 + y^2 = r^2 \\ dndy = r dr d\theta$$

$$n = r \cos \theta \\ dn = r \cos \theta dr \\ d\theta = -r \sin \theta dr$$

Transforming  
to polar coords

~~Method~~

$$\begin{aligned} I &= \int_0^\infty \int_0^{2\pi} e^{-\alpha r^2} r dr d\theta \\ &= 2\pi \int_0^\infty e^{-\alpha r^2} d\left(\frac{r}{\alpha}\right)^2 \\ &= \pi \int_0^\infty e^{-\alpha u} du. \end{aligned}$$

→ Recap:

∫ Integrand has nothing but 1.

- Non-interacting particles (ideal gas)

$$Z \propto \int_{\vec{r}_1}^{\vec{r}_N} d\vec{r}_1 \int_{\vec{p}_1}^{\vec{p}_N} e^{-\frac{P}{k_B T} \sum_i \vec{p}_i \cdot \vec{r}_i}$$

→ Ideal gas eqn.

$$\left\langle P \right\rangle = \frac{N}{V} k_B T = \rho : \text{no: density of the system no: of atoms per unit volume.}$$

- For Interacting systems:-

$$Z \propto \int_{\vec{r}_1}^{\vec{r}_N} e^{-\frac{1}{2} \sum_{i=1}^N \sum_{j \neq i} \frac{1}{r_{ij}} \vec{p}_i \cdot \vec{p}_j}$$

The pot energy can be written as a sum of pairwise  $\frac{1}{r_{ij}}$  energy of the particles

∴ The equation of state becomes:-

*looking derivation if read.*

$$\begin{aligned} \left\langle P \right\rangle &= \rho + B_2(T) \rho^2 + B_3 \rho^3 \dots \\ &= \boxed{\sum_{i=1}^{\infty} B_i(T) \rho^i} \rightarrow \text{Virial Eqn of State.} \end{aligned}$$

- All coefficients  $B_i(T)$  depend on the temperature of the system.
- The co-efficients are called virial co-efficients.
- By inc. the vol the system is diluted when  $\rho \downarrow$  the system behaves like an ideal gas.

★ This is valid only for dilute systems.

Vol in Volume increases  $\rho$  decrease

binary  
solution

$$U_{\text{eff}} = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N u_{ij} \xi_i \xi_j \rightarrow \text{for dilute systems}$$

$\downarrow$        $i \neq j$

overcounting

- Sum over all pairs of interactions for dilute systems

Subbing ① in the  $\Sigma$  or  $\int$  formula you can derive the virial eqn of state

### • THERMODYNAMICS:

In the thermodynamic world, atoms & molecules do not exist.

→ Laws of Thermodynamics:

I: The internal energy of a system can be changed by 2 means

- supply or extract heat to/from the system
- work done on the system or by the system

$$dU = dW + dQ \rightarrow \text{Conservation of energy.}$$

Convention :-

→ Work done by sys =  $-dW$

→ Work done on sys =  $+dW$

Exm,

→ Heat supplied to sys =  $+dQ$

→ Heat extracted from sys =  $-dQ$

II:

→ Spontaneous processes

→ Change in entropy of a spn process

→ doesn't give absolute value. Given only the change

Statement 1:

$$(\Delta S)_{\text{total}} \geq 0$$

$$(\Delta S)_{\text{total}} = (\Delta S)_{\text{sys}} + (\Delta S)_{\text{surroundings}}$$

→ Entropy of any spontaneous process must increase.

When any spontaneous process is carried out, slowly it is extremely reversible process (Quasistatic process). Then  $(\Delta S)_{\text{total}} = 0$  ∵ no change.

Statement 2:

Clausius Inequality (System specific)

$$\text{Change in entropy of the system} \leftarrow (\Delta S)_{\text{system}} \geq \frac{dQ}{T} \rightarrow \text{heat supplied at a given temp } T$$

Equality valid for rev processes & not for Irreversible processes.

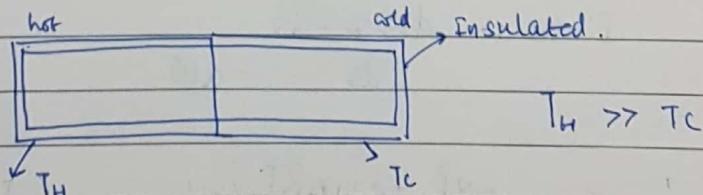
**III:** Second law didn't mention anything about the absolute value of entropy. [only  $(\Delta S)_{\text{total}} = 0$  /  $(\Delta S)_{\text{sys}} = 0$ ]

Third law states that :-  $T \rightarrow 0 : S \rightarrow 0$  universal law.

→ Consider the following 2 spontaneous Processes.

- ① Heat flow.
- ② Gas Expansion

Proc 1: 2 identical metal blocks. (Reversible)



→ Let case 1: heat flow from colder object to hotter one.

$$\text{Change in entropy of} \quad = -\frac{dQ}{T_c}$$

the colder object

$$\text{Change in entropy of} \quad - \frac{dQ}{T_h}$$

hotter object

$$\text{Total change} : \Delta S = dQ \left[ \frac{1}{T_h} - \frac{1}{T_c} \right]$$

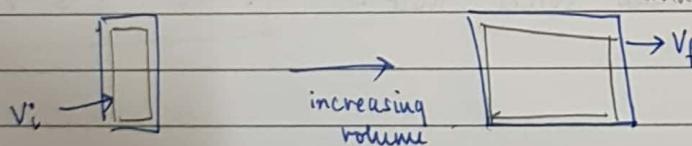
$$T_h \gg T_c \quad \frac{1}{T_h} \ll \frac{1}{T_c}$$

$$\therefore \Delta S < 0 \quad \dots \# \text{contradiction}$$

Heat flow from colder to hotter object is not a spontaneous process.

→ Let Case 2: heat flow from hotter to colder object  
 $\Delta S > 0$

Proc 2: free expansion of ideal gas.



isolated, isothermally

$$\text{Case 1: } V_f \not\propto V_i$$

$$\text{Case 2: } V_f \propto V_i$$

∴ Isothermal:- change in internal energy =  $\Delta U = 0$

I<sup>st</sup> law :-  $dQ = dU + dW$

$$dQ = -dW$$

$$P = \frac{nRT}{V}$$

$$W = PdV$$

classmate

Date \_\_\_\_\_

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$$\Delta S = nR \ln\left(\frac{V_f}{V_i}\right)$$

If  $V_f < V_i$

$\Rightarrow \Delta S$  is negative (not spontaneous).  
Violates second law.

If  $V_f > V_i$

$\Delta S$  is positive

→ Consider freezing of water

i.e.: liquid water  $\rightarrow$  solid ice

$S_{\text{liquid}} > S_{\text{ice}}$

Is II<sup>nd</sup> law violated?

### • THERMODYNAMIC POTENTIALS :-

- i) Internal energy  $U$
- ii) Enthalpy  $H$
- iii) Helmholtz free energy  $A$
- iv) Gibbs free energy  $G$ .

~ Rewrite the II<sup>nd</sup> law in terms of the thermodynamic potentials.

$$\boxed{dS \geq \frac{dq}{T}}$$

(i) At constant volume  $\Rightarrow dq = dV$

$$dS \geq \frac{dU}{T}$$

$$TdS - dU > 0$$

(ii) For constant entropy

$$ds = 0$$

$$\Rightarrow \cancel{(dU)}_{P,V} (dU)_{V,S} < 0$$

∴ This indicates it always minimizes the internal energy.

→ Here constant entropy is hard to achieve so we'll change our approach.

~ Define enthalpy as

$$\boxed{H = U + PV}$$

$$dH = dU + PdV + VdP$$

~~i~~ const vol:

$$dH = dq + Vdp$$

- ~~i~~ Constant Pressure
- ~~ii~~ Constant entropy

~~ii~~ Const pressure:

$$(dH)_{P,V} = \cancel{dq} - \cancel{dp}$$

$$dH = \underbrace{dq - pdV}_{\text{from 1st law}} + pdV + Vdp = 0$$

$$(dH)_P = dq$$

$$ds \geq \frac{dH}{T}$$

$$TdS - dH \geq 0$$

$$(dH)_{P,S} \leq 0$$

Processes carried out at constant pressure & constant entropy would minimize the enthalpy of the system.

### ~ Helmholtz Free Energy :-

$$A = U - TS$$

- i) Const vol
- ii) Const temp.

Const vol is difficult to achieve at high temp. because thermal expansion is expected.

$$\frac{dA}{dT} \quad (dA)_{V,T} \leq 0$$

Process carried out at constant volume and Temp would minimize the Helmholtz free energy.

### ~ Gibbs Free Energy

$$G = U + PV - TS$$

$$U = \underbrace{\frac{dq}{T}}_{\text{temp}} + \underbrace{\frac{dW}{P}}_{=0 \text{ press}} = 0$$

- i) Constant Temp
- ii) Const Pressure.

$$(dG)_{P,T} \leq 0$$

∴

$$\boxed{\begin{aligned} U &= U(S, V) \\ H &= H(S, P) \\ A &= A(T, V) \\ G &= G(T, P) \end{aligned}}$$

$$G(T, p) > G(T, p)$$

phase 1

phase 2.

⇒ Phase with the least  $G$  at a given  $T$  &  $p$  is the most stable phase.

To compare stabilities, you must have the same no: of molecules.

$G$  would vary with no: of moles of the substance  
∴  $G$  is sensitive to no: of moles of substance

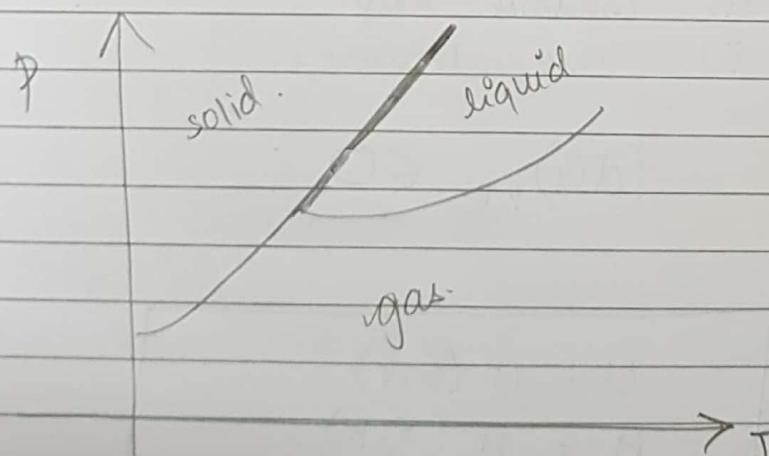
∴ Introduce a new func. called Chemical Potential

$$\mu(T, p) = \frac{G(T, n)}{n} \quad \text{where } n : \text{no: of moles}$$

Hence better to use  $\mu$  than  $G$

modification: The phase with the least  $\mu$  at given  $P$  &  $T$  would be the most stable phase.

→ Phase Diagram:



- At the phase boundaries, the both the phases are stable.
- crossing the boundary phase transition.
- Gibbs Free Energy is most convenient to measure

$$\mu_{\text{gas}}(T, P) = \mu_{\text{liquid}}(T, P).$$

$$\mu_{\text{solid}}(T, P) = \mu_{\text{liquid}}(T, P).$$

→ Triple Point:  $\mu_{\text{gas}}(T, P) = \mu_{\text{liquid}}(T, P) = \mu_{\text{solid}}(T, P)$