

### Grading Scheme

Mid - I - 20%

Mid - II - 20%

End sem - 40%

Assignments / quizzes - 20%

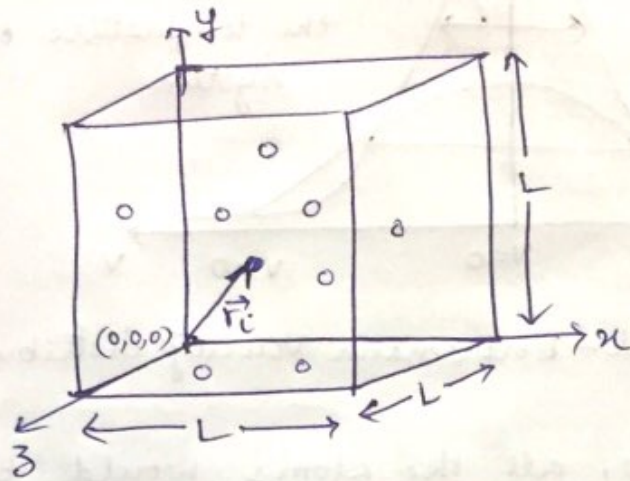
Part - I -

→ Statistical Mechanics and Thermodynamics.

## SCIENCE-II

### Statistical Mechanics and thermodynamics -

positions of atoms in an ordered system can be known



$$\vec{r}_i = (x_i, y_i, z_i) \quad , \quad i = 1, 2, 3, \dots, N \quad (N \rightarrow \text{number of atoms in the system})$$

Volume,  $V = L^3$

(where,  $L$  = length of the box),

$$0 \leq x_i \leq L$$

$$0 \leq y_i \leq L$$

$$0 \leq z_i \leq L$$

$$\text{Number density, } \rho = \frac{N}{V}$$

→ Error depends on the number of samples.

$$\text{error} \propto \frac{1}{\sqrt{N}} \quad \left[ \begin{array}{l} \text{larger the system,} \\ \text{better will be the} \\ \text{statistics} \end{array} \right]$$

Ideal Case -

$$\text{So, } N \rightarrow \infty, \quad V \rightarrow \infty \quad (\text{infinitely extended large system})$$

$$\left( \rho = \frac{N}{V} \sim \text{finite} \right)$$

→ Thermodynamic limit\*

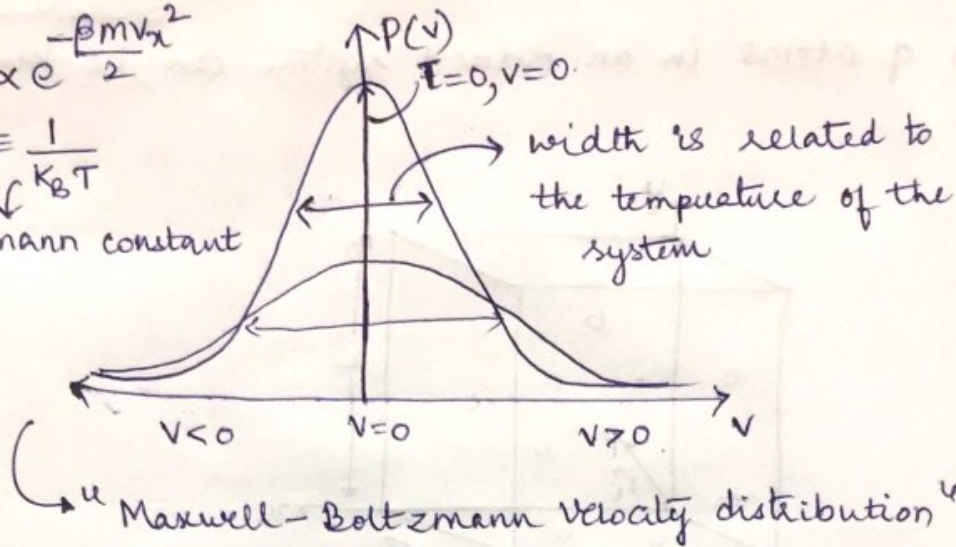
Atoms have to be assigned velocities; where

$T \rightarrow$  temperature of the system.

$$P(v_x) \propto e^{-\frac{\beta m v_x^2}{2}}$$

$$\beta \equiv \frac{1}{k_B T}$$

Boltzmann constant



If temperature = 0, all the atoms would be frozen  
 $v = 0$ .

$\rightarrow$  Width of the distribution  $\equiv$  second moment

$$\langle v_x^2 \rangle = A \int_{-\infty}^{\infty} v_x^2 \cdot e^{-\frac{\beta m v_x^2}{2}} \cdot dv_x, \quad A \equiv \text{Normalisation Constant}$$

Kinetic Energy.

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

width  $\propto T$

$$P(v_x) = A e^{-\frac{\beta m v_x^2}{2}}$$

$\Rightarrow$  Velocities of atoms,

$$\vec{v}_i = (v_{x,i}, v_{y,i}, v_{z,i}) \quad \forall i$$

Systems can be -

1. Isolated, NVE or microcanonical system
2. Closed, NVT or canonical system.
3. Open,



### Isolated

1. Total energy will be conserved ( $E$ )
2.  $N$  should be fixed
3.  $V$  should be fixed



Constant energy system

### closed

1. Total energy can change but temp. ( $T$ ) should be constant
2.  $N$  should be fixed
3.  $V$  should be fixed



constant temperature system

### Open

1. Energy exchange is possible with surroundings
2.  $N$  can vary
3.  $V$  can be fixed

→ Total energy is given by the Hamiltonian function

$$H(\{\vec{r}_i\}, \{\vec{v}_i\})$$

where,  $\{\vec{r}_i\} = (\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_N)$   $\nearrow$   $3N$  variables.

$\downarrow$   $\{\vec{v}_i\} = (\vec{v}_1, \vec{v}_2, \vec{v}_3, \dots, \vec{v}_N)$

set of positions and velocities

System of  $N$  atoms  $\rightarrow 3N + 3N = 6N$  variables.

$$H(\{\vec{r}_i\}, \{\vec{v}_i\}) = U(\{\vec{r}_i\}) + K(\{\vec{v}_i\})$$

potential energy function

Kinetic energy function

→ Atoms are not static, they move, so  $r_i$  &  $v_i$  are going to vary as a function of time,  $\{r_i(t), v_i(t)\}$

Consider an isolated system -

$$\frac{dH(\{\vec{r}_i(t)\}, \{\vec{v}_i(t)\})}{dt} = 0$$

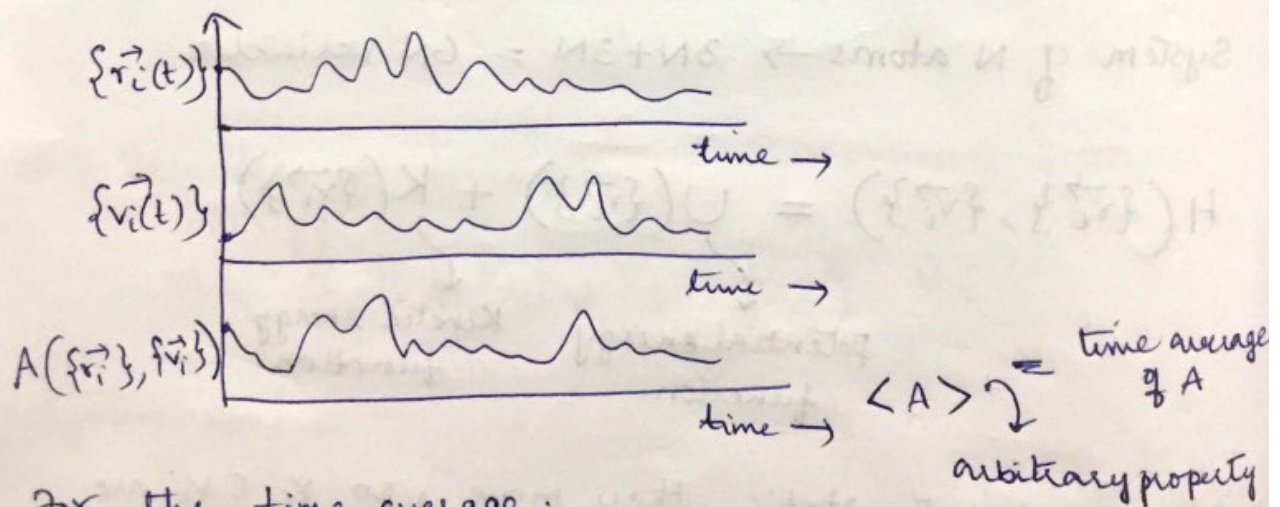
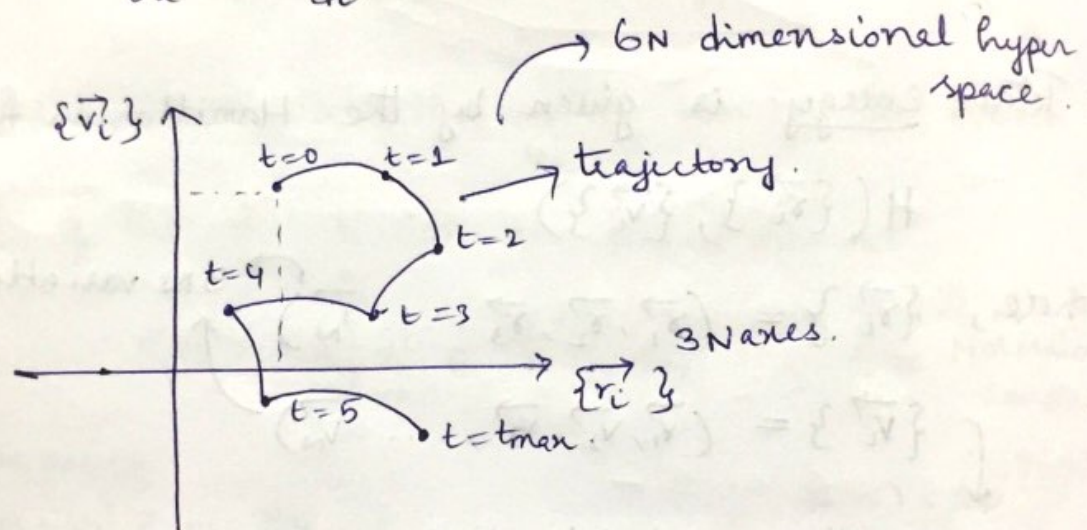
[Total energy is  
Conserved]

$$\rightarrow \frac{dH(x, v)}{dt} = 0$$

$$\frac{\partial H}{\partial x} \cdot \frac{\partial x}{\partial t} + \frac{\partial H}{\partial v} \cdot \frac{\partial v}{\partial t} = 0$$

$$\Rightarrow \frac{\partial H}{\partial v} = \frac{dx}{dt}$$

$$\frac{\partial H}{\partial x} = -\frac{dv}{dt}$$



for the time average;

$$t_{\max} \rightarrow \infty$$



## Thermodynamics — macroscopic

$P \rightarrow$  Pressure

$V \rightarrow$  Volume

$T \rightarrow$  Temperature

$n \rightarrow$  number of moles

function. [different for different systems]  
 $P = f(V, T, n)$

Equation of state of the system.

$\rightarrow$  macroscopic thermodynamic properties.

For ideal gas;

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

For Ex: isothermal compressibility.  
[change of volume with pressure.]

## Statistical Mechanics — microscopic

$\{\vec{r}_i\} \rightarrow$  position of atom " $i$ " [cannot be precisely measured]  
 $\sim$  microscopic variable.

$\{\vec{p}_i\} \Rightarrow \vec{p}_i = m_i \vec{v}_i \rightarrow$  velocity of atom  $i$

mass of atom  $i$

linear momentum of atom " $i$ "

### Classical Mechanics

$$\rightarrow L(q, \dot{q}) = K(\dot{q}) - U(q)$$

Kinetic energy function

Potential energy

Lagrangian

### \* Hamiltonian Mechanics =

$$H(q, p) = K(p) + U(q)$$

$\downarrow$   
Total energy of the system  $\sim$  has a physical meaning.

Hamilton's equations of motion —

$$\frac{dp}{dt} = -\frac{\partial H}{\partial q}$$

$$\frac{dq}{dt} = \frac{\partial H}{\partial p}$$

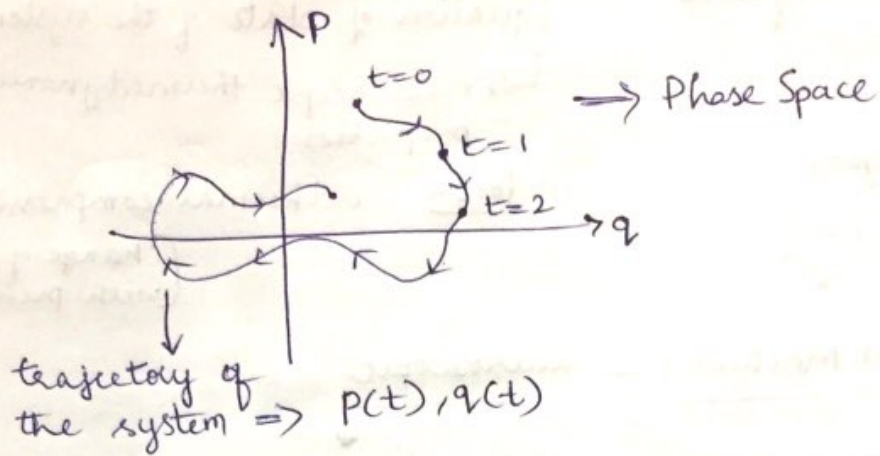
$\rightarrow \dot{q} = \frac{dq}{dt}$   
Lagrange's equation of motion —

$$\Rightarrow \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}} \right) = \frac{\partial L}{\partial q}$$

$$K(\dot{q}) = \frac{1}{2} m \dot{q}^2$$

# Classical Statistical Mechanics

- classical laws of motion
- Precisely locate the positions and momenta of particles.



## Phase Space of an N-particle system -

$N$  - No. of atoms in the system.

$$\{\vec{r}_i(t)\} = (x_1(t), y_1(t), z_1(t), x_2(t), y_2(t), z_2(t), \dots, x_N(t), y_N(t), z_N(t))$$

↓  
3N variables

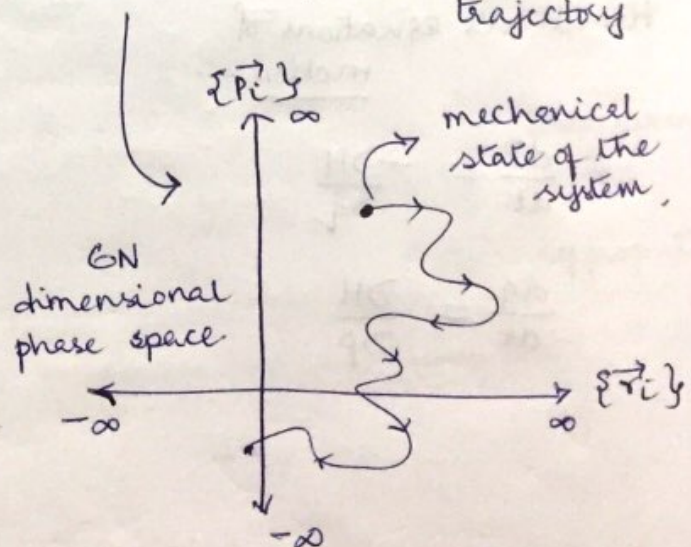
$$\{\vec{p}_i(t)\} = (p_{1x}, p_{1y}, p_{1z}, p_{2x}, p_{2y}, p_{2z}, \dots, p_{Nx}, p_{Ny}, p_{Nz})$$

↓  
3N variables.

Phase Space  $\Rightarrow$   $6N$  dimensional space  $\leftarrow (N \sim 10^{23})$   
trajectory



$\Rightarrow$  A given point in phase space denotes a mechanical state of the system.





# Hamilton's equations of motion for an N-particle system

For N-particle system  $\rightarrow$

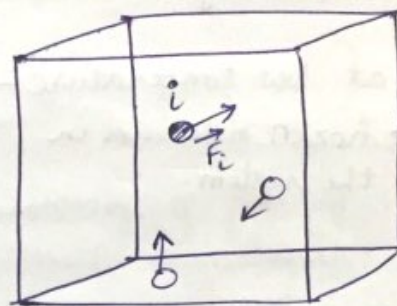
$$\begin{pmatrix} \frac{dP_{1,x}}{dt} \\ \frac{dP_{1,y}}{dt} \\ \frac{dP_{1,z}}{dt} \\ \vdots \end{pmatrix} = \begin{pmatrix} -\frac{\partial H}{\partial x_1} \\ -\frac{\partial H}{\partial y_1} \\ -\frac{\partial H}{\partial z_1} \\ \vdots \end{pmatrix}$$

$\leftarrow 3N$  equations.

$$\frac{dP}{dt} = -\frac{\partial H}{\partial q}$$

$$\frac{dq}{dt} = \frac{\partial H}{\partial p}$$

$$\begin{pmatrix} \frac{dx_1}{dt} \\ \frac{dy_1}{dt} \\ \vdots \end{pmatrix} = \begin{pmatrix} \frac{\partial H}{\partial P_{1,x}} \\ \frac{\partial H}{\partial P_{1,y}} \\ \vdots \end{pmatrix}$$

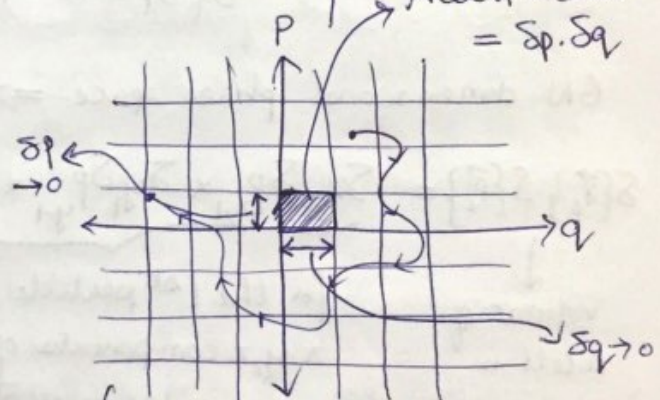


$$\vec{F}_i = F_{i,x} \hat{i} + F_{i,y} \hat{j} + F_{i,z} \hat{k}$$

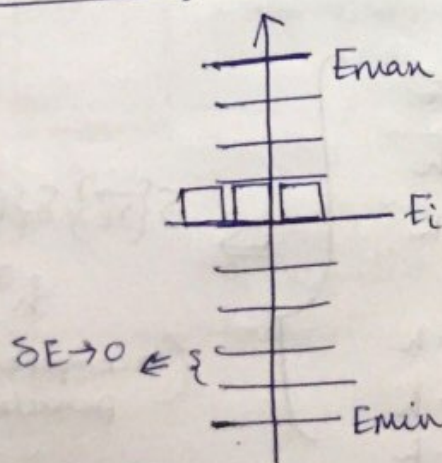
Force on atom  $i$

each cell represents a mechanical state of the system  
Area of a cell =  $\Delta p \cdot \Delta q$

where,  $F_{i,x} = -\frac{\partial H}{\partial x_i}$   
 $F_{i,y} = -\frac{\partial H}{\partial y_i}$   
 $F_{i,z} = -\frac{\partial H}{\partial z_i}$



Energy level diagram -



Energy is measured in each and every cell.  
and the cells are stacked acc to their energy values on the ladder.  
 $E_i \Rightarrow \Omega(E_i)$   
 $\downarrow$   
number of cells with energy,  $E_i$ .



\* From the energy level diagram, we can calculate the average energy of the system.

For an isolated system prepared initially with an energy  $E_i \Rightarrow S \propto \ln \Omega(E_i)$

Boltzmann's Entropy formula  $\equiv$

$$S = k_B \ln \Omega(E_i)$$

$\downarrow$  entropy  $\downarrow$  Boltzmann's constant  $\uparrow$  Statistical quantity.

thermodynamic quantity.

Solids, at low temperature  $\rightarrow$  have zero entropy as  $\Omega(E_i) = 1$   
 $\rightarrow$  frozen molecules in the system.  
 $S = k_B \ln \Omega(E_i) = 0$

Area of a cell =  $\Delta q \cdot \Delta p \Rightarrow$  dimension of angular momentum  
 $\Delta q \cdot \Delta p = h, h \rightarrow 0$ .

$6N$  dimensional phase space  $\Rightarrow$

$$\Delta\{\vec{r}_i\} \Delta\{\vec{p}_i\} = \underbrace{\Delta x_1 \Delta p_{x,1} \times \Delta y_1 \Delta p_{y,1} \times \Delta z_1 \Delta p_{z,1}}_{\text{for the 1st particle, } x, y, z \text{ components of angular momentum.}} \times \dots \times \Delta x_N \Delta p_{x,N} \times \Delta y_N \Delta p_{y,N} \times \Delta z_N \Delta p_{z,N}$$

$\downarrow$   
Volume of a cell in  $6N$  dimensional phase space.

$$\Delta x_1 \Delta p_{x,1} = h$$

$$\Delta y_1 \Delta p_{y,1} = h$$

$$\Delta z_1 \Delta p_{z,1} = h$$

$$\vdots$$

$$\Delta x_N \Delta p_{x,N} = h$$

$$\Delta y_N \Delta p_{y,N} = h$$

$$\Delta z_N \Delta p_{z,N} = h$$

$$\Rightarrow \Delta\{\vec{r}_i\} \Delta\{\vec{p}_i\} = h^{3N}$$

(3 components per particle)

$6N$  dimensional space  $\equiv$  hypercube

$\downarrow$   
Volume,  $\delta\{\vec{r}_i\} \delta\{\vec{p}_i\} = h^{3N}$

optimum size of the cell  $\rightarrow$

For quantum systems,  $h \Rightarrow$  Planck's constant.

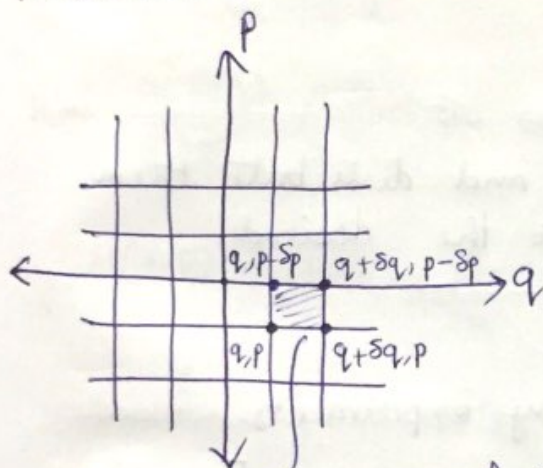
uncertainty principle - in position and momentum

$$\delta x \delta p_x \geq h$$

In principle, the least uncertainty  $= h = \delta x \delta p_x$

but for classical systems,  $h$  - arbitrary.

1 dimension  $\rightarrow$



mechanical state  
of the system  
[microstate of the  
system]

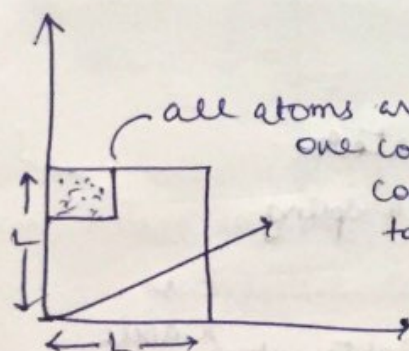
probability  
 $\uparrow$

$$P(q \rightarrow q + \delta q, p \rightarrow p + \delta p)$$

$\downarrow$

Probability of finding the  
system in a mechanical  
state between  $p$  and  $p + \delta p$   
and  $q$  and  $q + \delta q$ .

$\rightarrow$  If this probability does not change  
with time (for all mechanical states)  
then the system is said to be in  
equilibrium with the surroundings.



all atoms are compressed to  
one corner of the box and when the  
constraint is released, the atoms move  
to the unoccupied part.

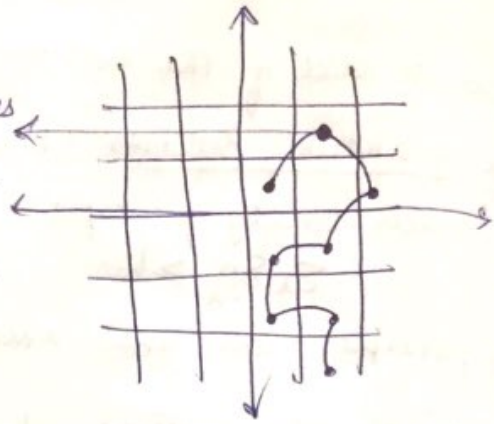
Relaxation time - Time taken by the system to reach  
the equilibrium state from an initial  
state.



## Mechanics — Time evolution of a single system (proposed by Boltzmann).

→ System can visit the same state many times.

$n_i$  = number of times the system visited the  $i$ th mechanical state in time steps =



$$* P_i = \frac{n_i}{M}$$

↓  
probability of finding the system in  $i$ th mechanical state

## Ensemble Approach (by Gibbs)

→ prepare  $M$  identical systems and distribute them in phase space according to the desired probability distribution.

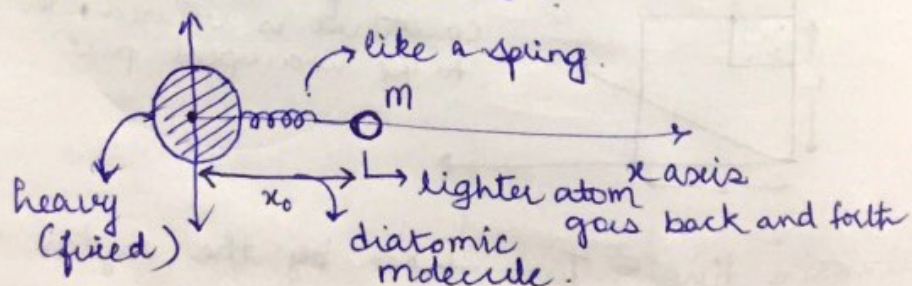
↓ should have infinitely many experiments.

~ Ergodic hypothesis  $\Rightarrow$  time average = Ensemble average

( $t_{\max} \rightarrow \infty$   
Number of  $\rightarrow \infty$   
ensembles)

## Model Systems —

1. One dimensional harmonic oscillation.



Undisturbed bond length — equilibrium bond length ( $x_0$ )

$$H(x, p) = U(x) + K(p)$$

mass of lighter atom =  $m$

$$= U(x) + \frac{p^2}{2m}$$

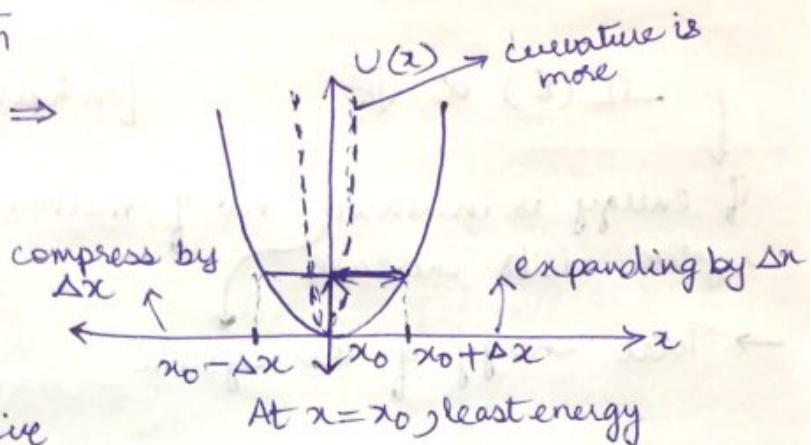
$U(x)$  for the system  $\Rightarrow$

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

where  $K$  - spring constant

$K \equiv$  second derivative of  $U(x)$  w.r.t  $x$

$$K = \frac{d^2 U(x)}{dx^2} \quad (\text{gives the curvature at that point})$$



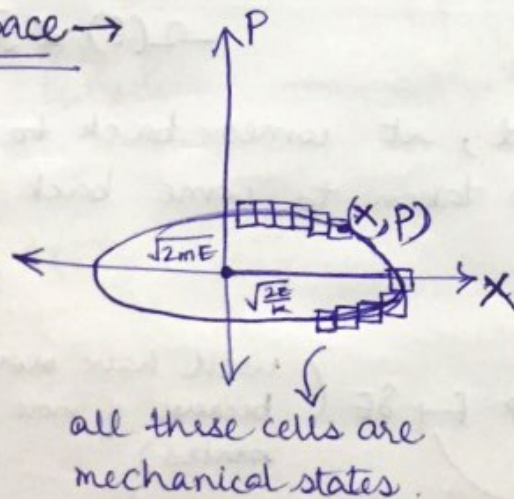
$$H(x, p) = U(x) + \frac{p^2}{2m}$$

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

(System is prepared with initial energy,  $E$ )

$\rightarrow$  Isolated system, let initial energy be  $E$

Phase space  $\rightarrow$



$$\frac{(x-x_0)^2}{\left(\frac{\sqrt{2E}}{\sqrt{K}}\right)^2} + \frac{p^2}{(\sqrt{2mE})^2} = 1$$

Equation of an ellipse

$$\rightarrow X = x - x_0$$

trajectory  $\equiv$  elliptical orbit

\* All the possible mechanical states fall on the circumference of the ellipse.

$E, K$  can control the width and height of the ellipse



$$\Omega(E) \propto \text{circumference of the ellipse } (\pi(a+b))$$

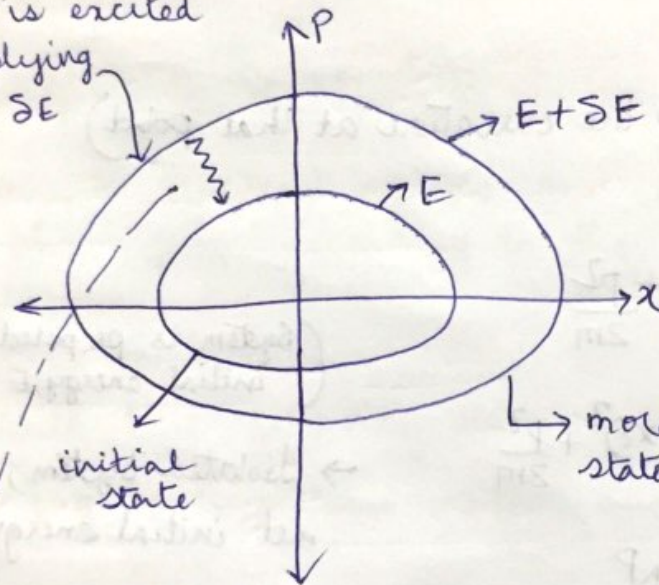
$$\propto \pi\left(\sqrt{2mE} + \sqrt{\frac{2E}{k}}\right)$$

$$\Omega(E) \propto \sqrt{E} \quad [\text{on fixing } m \& k]$$

if energy is increased, no. of mechanical states the system visits increase

→ Total energy of the system.

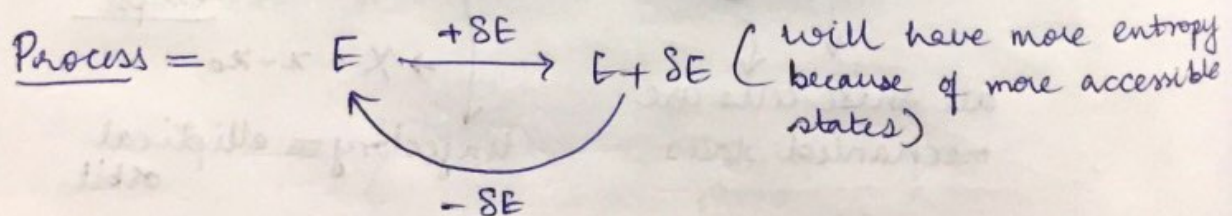
system is excited by supplying energy,  $\Delta E$



more no. of accessible states

$$\Omega(E) \propto \sqrt{E}$$

When energy is removed, it comes back to the ground state. The time taken to come back is called Relaxation time.



Time taken to go from  $(E + \Delta E)$  ellipse to  $E$  ellipse is called the relaxation time

## Time average and ensemble average -

→ Any arbitrary property can be expressed as a function of  $\{\vec{r}_i\}$  and  $\{\vec{p}_i\}$

$$A(\{\vec{r}_i\}, \{\vec{p}_i\})$$

Compute average of  $A$ ,  $\langle A \rangle$  (denotes average of  $A$ )

$$\Rightarrow \langle A \rangle = \frac{1}{h^{3N}} \int \int_{\{\vec{r}_i\}, \{\vec{p}_i\}} A(\{\vec{r}_i\}, \{\vec{p}_i\}) \cdot P(\{\vec{r}_i\}, \{\vec{p}_i\}) \cdot d\{\vec{r}_i\} \cdot d\{\vec{p}_i\}$$

angular  
momentum  
of dimension  
 $3N$

$$\left[ \text{Average of } x, \langle x \rangle = \int x P(x) dx \right]$$

(variables determining the quantity.)

$$\int_{\{\vec{r}_i\}} \equiv \int \int \int \int \int \int \dots \int \int \int \int_{x_1 y_1 z_1 x_2 y_2 z_2 \dots x_N y_N z_N}$$

3N-dimensional.

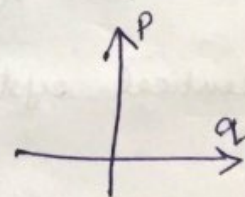
$$\int_{\{\vec{p}_i\}} \equiv \int \int \int \int \int \int \dots \int \int \int \int_{p_{x1} p_{y1} p_{z1} \dots p_{xN} p_{yN} p_{zN}}$$

$$\Rightarrow \int \int_{\{\vec{r}_i\}, \{\vec{p}_i\}} \Rightarrow \text{Set of } 6N \text{ integrals.}$$

$$\frac{1}{h^{3N}} \cdot \int \int_{\{\vec{r}_i\}, \{\vec{p}_i\}} d\{\vec{r}_i\} \cdot d\{\vec{p}_i\}$$

gives the number of microstates in the phase space.

[visiting all the microstates in the phase space]



$$\text{Area of phase space} = \int \int_{q, p} dq \cdot dp$$

No. of microstates in phase space  $\equiv$

$$\frac{\text{Area of phase space}}{\text{Area of microstates}}$$



How to determine  $P(\{\vec{r}_i\}, \{\vec{p}_i\})$



- Probability of finding the system in a given microstate [given, set of  $r$ s and set of  $p$ s]  
 $\{\vec{r}_i\}, \{\vec{p}_i\}$

Approaches -

1) Time evolution of a single system. — "Boltzmann"

$$P_{\text{time}}(\{\vec{r}_i\}, \{\vec{p}_i\}) = \frac{n(\{\vec{r}_i\}, \{\vec{p}_i\})}{M_t} \rightarrow \text{no. of times it has visited the particular microstate } (\{\vec{r}_i\}, \{\vec{p}_i\}) \text{ out of } \underline{M_t} \text{ steps}$$

$\langle A \rangle$  calculated using  $P(\{\vec{r}_i\}, \{\vec{p}_i\}) = \frac{n(\{\vec{r}_i\}, \{\vec{p}_i\})}{M_t}$   
is called the time-average of  $A$ .

2) Ensemble Approach — "Gibbs"

$$P_{\text{ensemble}}(\{\vec{r}_i\}, \{\vec{p}_i\}) = \frac{n_{\text{systems}}(\{\vec{r}_i\}, \{\vec{p}_i\})}{M_{\text{systems}}}$$

$n_{\text{systems}} \equiv$  no. of systems that fall on the given state,  $(\{\vec{r}_i\}, \{\vec{p}_i\})$

$M$  identical systems [with same particles]

Ergodic hypothesis  $\leftarrow P_{\text{time}}(\{\vec{r}_i\}, \{\vec{p}_i\}) = P_{\text{ensemble}}(\{\vec{r}_i\}, \{\vec{p}_i\})$

$M_t \rightarrow \infty$  (time evolution)

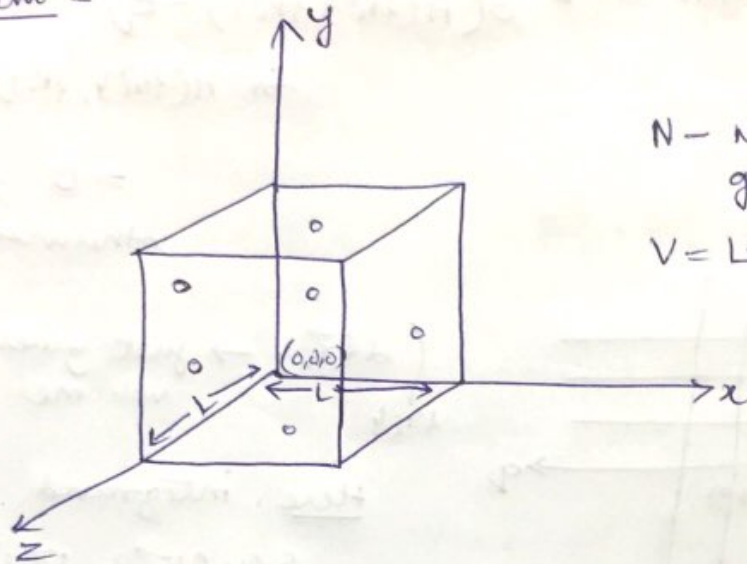
$M_{\text{systems}} \rightarrow \infty$  (ensemble approach)

Since the probabilities are equal, averages will also be equal.

$$\Rightarrow \langle A \rangle_{\text{time}} = \langle A \rangle_{\text{ensemble}}$$

Case 2: Ideal gas of  $N$  Particles.

System -



$N$  - number of ideal gas atoms

$V = L^3 \equiv$  Volume of the box

$$\begin{cases} 0 \leq x \leq L \\ 0 \leq y \leq L \\ 0 \leq z \leq L \end{cases}$$

Box constraints

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

$$U(\{\vec{r}_i\}) = 0 \quad (\text{ideal gas}) \quad \leftarrow \text{Particles do not interact with each other.}$$

$$K(\{\vec{p}_i\}) = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m}$$

$\Rightarrow E$  is the energy of the system in the initial state and it is kept isolated, particles are going to rearrange but total energy will be constant.

$$H(\{\vec{r}_i\}, \{\vec{p}_i\}) = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} = E \quad (\text{constant})$$

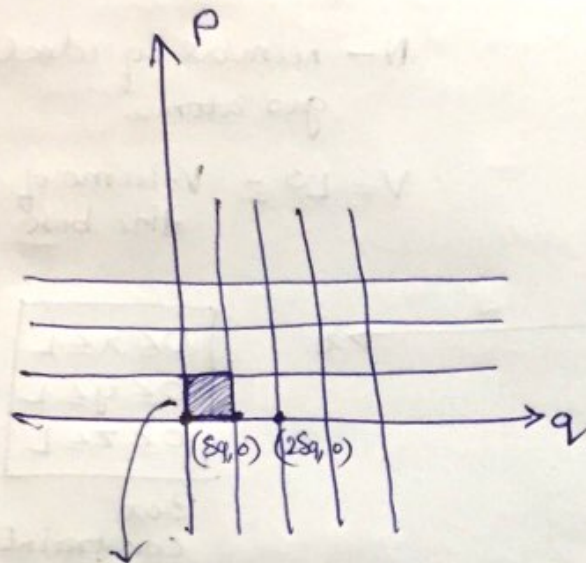
Let the system evolve, phase space under constant energy conditions.



→ Calculate the number of accessible microstates  $\Omega(E)$  of the system,

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

$\delta \equiv$  delta function.  $\rightarrow \delta(H(\{\vec{r}_i\}, \{\vec{p}_i\}) - E) = 1$  ;  
for  $H(\{\vec{r}_i\}, \{\vec{p}_i\}) = E$



if it's  $E$ , then this mechanical state will be counted, else will be zero and that state will be rejected.

$= 0$  ;  
otherwise .  
 $\int d\{\vec{r}_i\} \rightarrow$  just gives the volume.

Here, integrand  $\delta(H(\{\vec{r}_i\}, \{\vec{p}_i\}))$  depends only on  $\{\vec{p}_i\}$

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

Volume of the box

$$\int_{\{\vec{r}_i\}} d\{\vec{r}_i\} = \int \int \int \dots \int_{x_1, y_1, z_1} \dots \int_{x_N, y_N, z_N}$$

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

- If volume is increased or number of particles are increased, system will have more entropy.

For the momentum integral,

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

$$\boxed{\delta(H-E) = 1, \text{ if } H=E.}$$

$$\Rightarrow p_{x,1}^2 + p_{y,1}^2 + p_{z,1}^2 + p_{x,2}^2 + \dots + p_{x,N}^2 + p_{y,N}^2 + p_{z,N}^2 = (\sqrt{2mE})^2$$

↓

Equation of 3N dimensional sphere of radius  $\sqrt{2mE}$

Surface Area of the sphere  $\propto R^{3N-1}$

[R - Radius of the 3N dimensional sphere]

$$\begin{aligned} \text{3D-} \\ \text{area} &\propto r^{3-1} \\ \text{3ND-} \\ \text{area} &\propto r^{3N-1} \end{aligned}$$

$$\text{Surface Area of the sphere} \propto (\sqrt{2mE})^{3N-1}$$

$$\propto (\sqrt{E})^{3N-1}$$

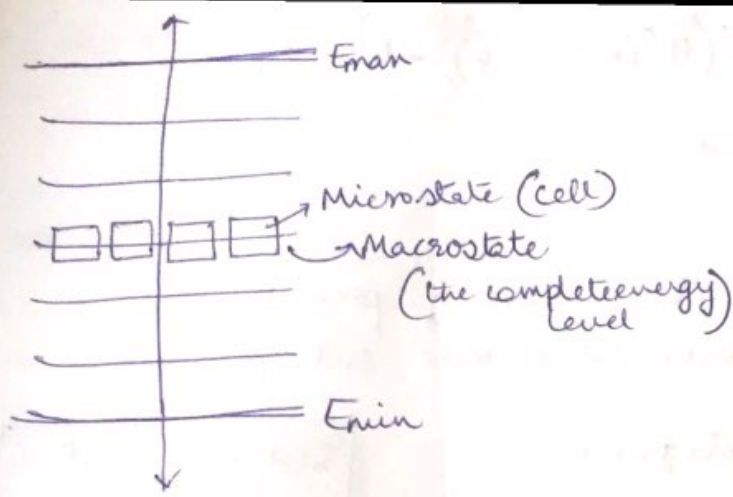
$$\Omega(E) \propto \frac{V^N}{h^{3N}} \cdot E^{\frac{3N-1}{2}}$$

No. of accessible microstates can be varied by varying  $V, N, E$  for an ideal gas.

$$\Omega(N, V, E) = \frac{V^N}{h^{3N}} E^{\frac{3N-1}{2}}$$

$$S(\text{entropy}) = K_B \ln(\Omega(N, V, E))$$





### Closed Systems →

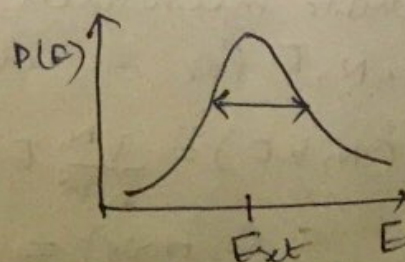
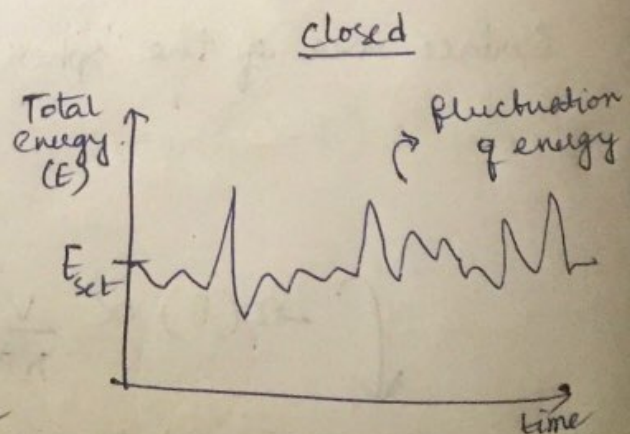
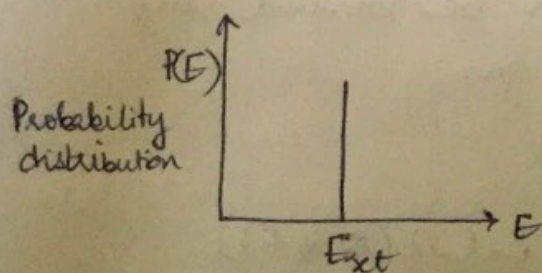
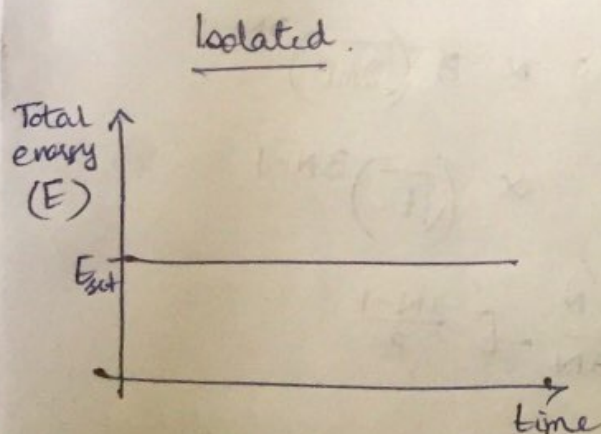
- Can exchange energy with the surroundings to maintain constant temperature.

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

average kinetic energy of the system ↳ Boltzmann constant

⇒ constant average kinetic energy ⇒ constant  $T$

→ System would visit different energy levels ( $\alpha$ ) different macrostates.



→ Probability curve depends on the extent of exchange.

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

$$\downarrow \quad \text{where } \beta = \frac{1}{k_B T}$$

Probability of finding the system in the microstate  $(\{\vec{r}_i\}, \{\vec{p}_i\})$ .

⇒ Normalise  $P(\{\vec{r}_i\}, \{\vec{p}_i\}) \equiv$

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

$$\rightarrow \text{where } Z = \frac{1}{h^{3N}} \int \int_{\{\vec{r}_i\} \{\vec{p}_i\}} e^{-\beta H(\{\vec{r}_i\}, \{\vec{p}_i\})} d\{\vec{r}_i\} d\{\vec{p}_i\}.$$

Normalisation constant, Partition function

Microstates with lower energy – higher probability  
and vice versa – higher energy – lower probability

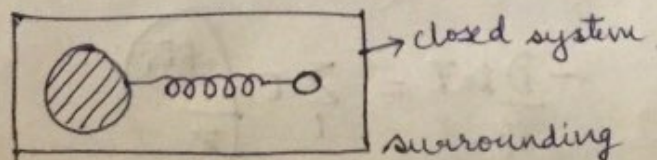
For discrete cases –

$$Z = \sum_{i=1}^{N_{\text{microstates}}} e^{-\beta E_i} \quad \text{(discrete microstates as in quantum systems)}$$

$$P(E_i) = \frac{e^{-\beta E_i}}{Z}$$

Model Systems :-

(1.) 1-dimensional harmonic oscillator.

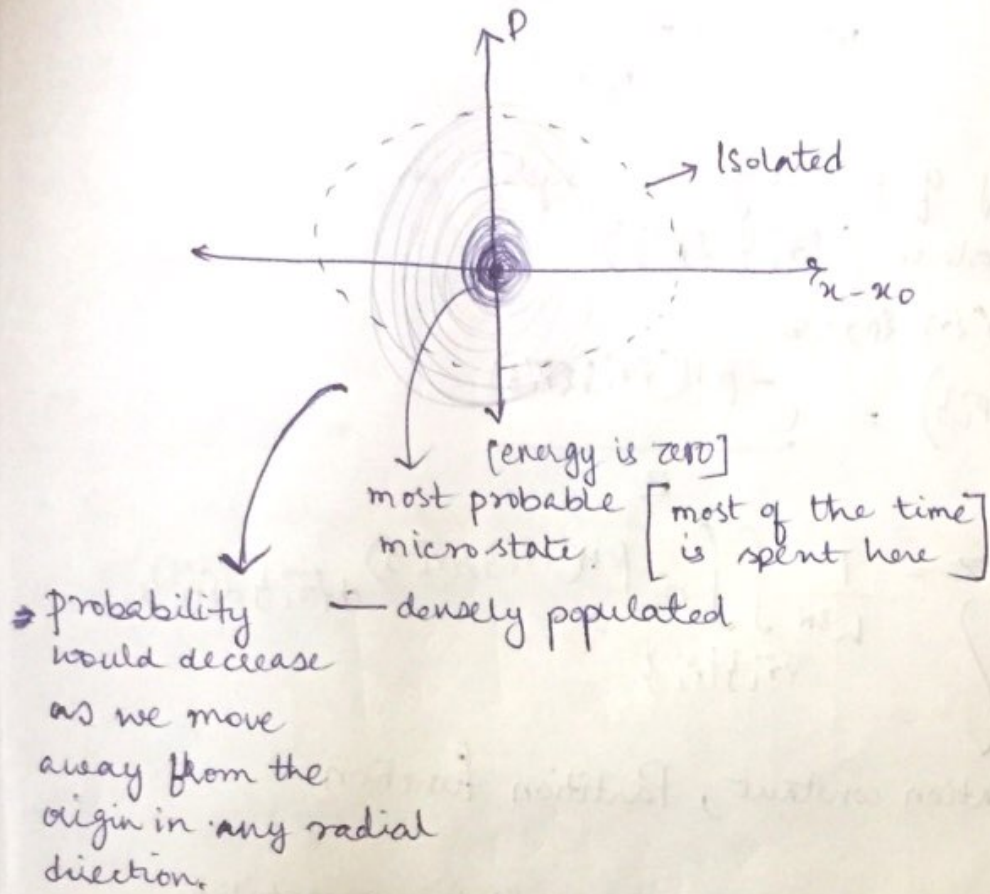


$$H(x, p) = \frac{1}{2} K (x - x_0)^2 + \frac{p^2}{2m}$$

$$P(x, p) \propto e^{-\beta \left[ \frac{1}{2} K (x - x_0)^2 + \frac{p^2}{2m} \right]}$$



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



Given  $Z$ , how do we determine thermodynamic properties of the system?

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

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

$$-\frac{\partial}{\partial \beta} \ln Z = \frac{1}{\sum_i e^{-\beta E_i}} \sum_i E_i e^{-\beta E_i}$$

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

probability of finding in the energy  $E_i$

$$= \sum_i E_i P(E_i) \rightarrow \text{average energy of the system}$$

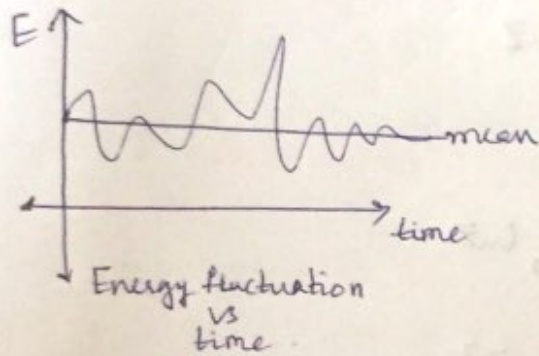
$$= \langle E \rangle$$

Mean Energy  
Mean of the fluctuating energy

$$\boxed{-\frac{\partial \ln Z}{\partial \beta} = \langle E \rangle}$$

⇒ Internal Energy of the system.

⇒ Internal Energy = Heat supplied to the system at constant volume.



Variance or fluctuation -

$$\text{deviation} \equiv E_i - \langle E \rangle$$

$$\text{Fluctuation} = \langle (E_i - \langle E \rangle)^2 \rangle$$

↓  
for each microstates.

⇒ Variance in energy -

$$\langle (E_i - \langle E \rangle)^2 \rangle = \langle E_i^2 + \langle E \rangle^2 - 2E_i \langle E \rangle \rangle$$

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

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

easy to compute

Consider,  $\sum_i E_i e^{-\beta E_i}$

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

$$-\frac{1}{Z} \frac{\partial}{\partial \beta} \left( \sum_i E_i e^{-\beta E_i} \right) = \sum_i \frac{E_i^2 e^{-\beta E_i}}{Z} = \sum_i E_i^2 P(E_i) = \langle E_i^2 \rangle$$



$$\langle E_i^2 \rangle = -\frac{1}{Z} \frac{\partial}{\partial \beta} \left( \sum_i E_i e^{\beta E_i} \right)$$

$$= -\frac{1}{Z} \frac{\partial}{\partial \beta} \left( -Z \frac{\partial \ln Z}{\partial \beta} \right)$$

$$= \frac{\partial}{\partial \beta} \left( \frac{\partial \ln Z}{\partial \beta} \right)$$

$$= \frac{1}{Z} \left[ \frac{\partial Z}{\partial \beta} \cdot \frac{\partial \ln Z}{\partial \beta} + Z \frac{\partial^2 \ln Z}{\partial \beta^2} \right]$$

$$= \frac{1}{Z} \frac{\partial Z}{\partial \beta} \cdot \frac{\partial \ln Z}{\partial \beta} + \frac{\partial^2 \ln Z}{\partial \beta^2}$$

$$= \left[ \frac{\partial \ln Z}{\partial \beta} \right]^2 + \frac{\partial^2 \ln Z}{\partial \beta^2}$$

$$\langle E_i^2 \rangle = \langle E \rangle^2 + \frac{\partial^2 \ln Z}{\partial \beta^2}$$

variance  $\equiv \langle E_i^2 \rangle - \langle E \rangle^2 = \frac{\partial^2 \ln Z}{\partial \beta^2}$   
or  
fluctuation.

$$= \frac{\partial}{\partial \beta} \left[ \frac{\partial \ln Z}{\partial \beta} \right]$$

$$= -\frac{\partial \langle E \rangle}{\partial \beta}$$

$$\therefore \boxed{\langle E_i^2 \rangle - \langle E \rangle^2 = -\frac{\partial}{\partial \beta} \langle E \rangle}$$

since,  $\beta = \frac{1}{k_B T}$

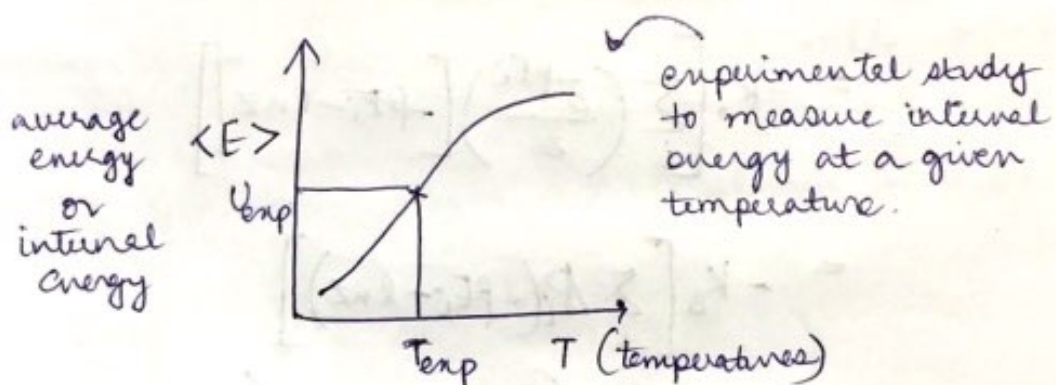
$$\langle E^2 \rangle - \langle E \rangle^2 = -\frac{\partial}{\partial T} \langle E \rangle \cdot \left( \frac{\partial \beta}{\partial T} \right)$$

$$\Rightarrow \boxed{\langle E^2 \rangle - \langle E \rangle^2 = k_B T^2 \frac{\partial \langle E \rangle}{\partial T}}$$

width of energy distribution  $\propto$  derivative of energy w.r.t temperature  
 $\sim$  Heat Capacity

$$C_V = \frac{\partial \langle E \rangle}{\partial T}, \text{ Heat Capacity}$$

$$\boxed{\langle E^2 \rangle - \langle E \rangle^2 = k_B T^2 C_V}$$



But,  $C_V = \frac{\partial \langle E \rangle}{\partial T}$ , from this equation, you get the heat capacity directly.

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

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

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

Entropy -

$$S \equiv -k_B \sum_i P_i \ln P_i \quad \left[ \text{Shannon's entropy} \right]$$

over all microstates.

loss of information

For an isolated system,  $P_i = \frac{1}{\Omega} \rightarrow$  Number of accessible microstates



$P_i = \frac{1}{\Omega} \rightarrow$  Postulate of equal a priori probabilities.

Boltzmann entropy formula  $\equiv$

$$S = k_B \ln \Omega$$

$\uparrow$

entropy  $\equiv$  average of logarithm of probability.

For closed systems -  $P(\{\vec{r}_i\}, \{\vec{p}_i\}) = \frac{e^{-\beta H(\{\vec{r}_i\}, \{\vec{p}_i\})}}{Z}$

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

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

$$= -k_B \left[ \sum_i P_i (-\beta E_i - \ln Z) \right]$$

$$= k_B \beta \sum_i P_i E_i + k_B \ln Z \sum_i P_i$$

$\downarrow$  average energy       $\downarrow$  1

$$S = k_B \beta \langle E \rangle + k_B \ln Z$$

$$= k_B \left( \frac{1}{k_B T} \right) \langle E \rangle + k_B \ln Z$$

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

$$ST = \langle E \rangle + k_B T \ln Z$$

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

In thermodynamics;

$$\text{Helmholtz's free energy, } F = U - TS$$

$\downarrow$   
internal energy

Microscopic definition of Helmholtz free energy  $\rightarrow$

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

$E$  - can change  
 $T$  - constant  
 $V$  - cannot change

Thermodynamic potential  
that is optimised at fixed  
 $N, V, T$ .

- (increase entropy / <sup>decrease</sup> minimise energy)
- Any spontaneous process at fixed  $N, V, T$  will minimise  $F$  (Helmholtz's free energy) out of 4 diff energy functions.

$\Rightarrow$  Entropy of spontaneous process should always increase

Internal Energy,  $\bar{U} = \langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$

Heat Capacity,  $C_V = \frac{1}{k_B T^2} \frac{\partial^2 \ln Z}{\partial \beta^2}$

Helmholtz free energy,  $F = -k_B T \ln Z$

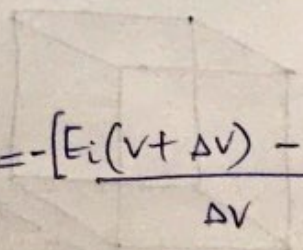
Entropy,  $S = \frac{\langle E \rangle}{T} + k_B \ln Z$

all these  
thermodynamic  
quantities  
are related  
to  $Z$ .

Pressure: For a given microstate, we can calculate the change in energy w.r.t change in volume of the system,  $V$ .

Pressure of  $i$ th microstate;

$$P_i = -\frac{\partial E_i}{\partial V} = -\frac{[E_i(V + \Delta V) - E_i(V)]}{\Delta V}, \Delta V \rightarrow 0$$





→ Different microstates have different pressure, so we calculate the average pressure.

$$\begin{aligned} \langle P \rangle &= \sum_i P_i p_i \\ \text{average (or) macroscopic pressure} &= - \sum_i \left( \frac{\partial E_i}{\partial V} \right) \frac{e^{-\beta E_i}}{Z} \end{aligned}$$

We know that;

$$\frac{\partial \ln Z}{\partial V} = \frac{\partial \ln Z}{\partial Z} \cdot \frac{\partial Z}{\partial V} \quad , Z = \sum_i e^{-\beta E_i}$$

$$= \frac{1}{Z} \cdot \sum_i e^{-\beta E_i} \left( -\beta \frac{\partial E_i}{\partial V} \right)$$

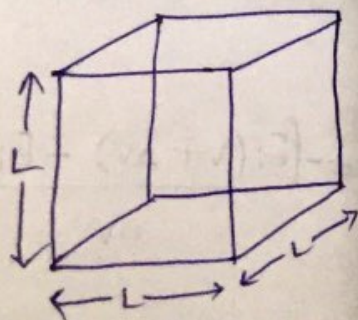
$$= -\beta \sum_i \frac{\partial E_i}{\partial V} \left( \frac{e^{-\beta E_i}}{Z} \right)$$

$$\frac{\partial \ln Z}{\partial V} = \beta \left[ + \sum_i \underbrace{\left( \frac{\partial E_i}{\partial V} \right)}_{P_i} \underbrace{\left( \frac{e^{-\beta E_i}}{Z} \right)}_{p_i} \right]$$

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

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

Ideal gas [closed system] -



$N$  - Number of ideal gas atoms.

$V$  - Volume  $= L^3$

$T$  - fixed temperature

## Calculation of Partition function -

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

for an ideal gas  $\Rightarrow H(\{\vec{r}\}, \{\vec{p}\}) = \frac{1}{2m} \sum_{i=1}^N \vec{p}_i \cdot \vec{p}_i$   
 $\downarrow$   
 independent of the positions.

$$Z = \frac{1}{h^{3N}} \int_{\{\vec{r}\}} d\{\vec{r}\} \int_{\{\vec{p}\}} e^{-\beta \sum_{i=1}^N \vec{p}_i \cdot \vec{p}_i} d\{\vec{p}\}$$

$$= \frac{1}{h^{3N}} \cdot V^N \int_{\{\vec{p}\}} e^{-\beta \sum_{i=1}^N \frac{\vec{p}_i \cdot \vec{p}_i}{2m}} d\{\vec{p}\}$$

$V$  - Volume of 1 particle

$V^N$  - for all  $N$  particles

$$= \frac{1}{h^{3N}} \cdot V^N \left[ \int_{-\infty}^{\infty} e^{-\beta \frac{x^2}{2m}} dx \right]^{3N}$$

3 components of  $P$

$3N \rightarrow$  for all  $N$

$x$  - dummy variable

$\hookrightarrow$  one component of momentum.

$$\int e^{-\beta \sum_{i=1}^N \vec{p}_i \cdot \vec{p}_i} = \int e^{-\beta \sum_{i=1}^N [p_{i,x}^2 + p_{i,y}^2 + p_{i,z}^2 + \dots + p_{i,x}^2 + p_{i,y}^2 + p_{i,z}^2]}$$

$$= \left( \int e^{-\beta \frac{x^2}{2m}} \right)^{3N}$$

independent

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty}$$

$3N$  such, product of integrals



$$= \frac{1}{h^{3N}} \cdot V^N \left[ \int_{-\infty}^{\infty} e^{-\frac{\beta x^2}{2m}} dx \right]^{3N}$$

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

Partition function for an ideal gas.

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

→ Dilute gases can be treated as ideal gases.

> Calculate the pressure,  $\langle P \rangle$

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

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

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

$$= \frac{N}{\beta V}$$

$$\langle P \rangle V = N \cdot k_B T$$

Ideal gas equation of state  
(for any system)  
we could derive.