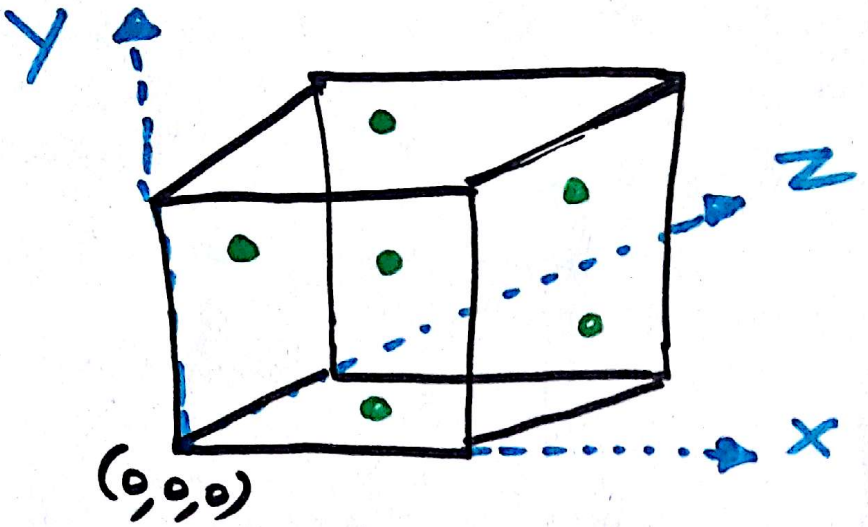
MICROSCOPIC VIEW :-



$V \rightarrow$ FINITE

$N \rightarrow$ FINITE

$\mathcal{C} \rightarrow$ FINITE

→ POSITIONS OF ATOMS $(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$

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

HERE, $\vec{r}_i = (x_i, y_i, z_i)$ GIVES THE COORDINATES OF ATOM i

→ VELOCITIES OF ATOMS $(\vec{v}_1, \vec{v}_2, \ldots, \vec{v}_N)$

$$\{\vec{v}\} = (\vec{v}_1, \vec{v}_2, \ldots, \vec{v}_N)$$

HERE, $\vec{v}_i = (v_{x,i}, v_{y,i}, v_{z,i})$ IS THE VELOCITY OF ATOM i

→ MASSES $(m_1, m_2, \ldots, m_N)$

ASSUME $m_1 = m_2 = \ldots = m_N = m$

→ MOMENTA $(\vec{p}_1, \vec{p}_2, \ldots, \vec{p}_N)$

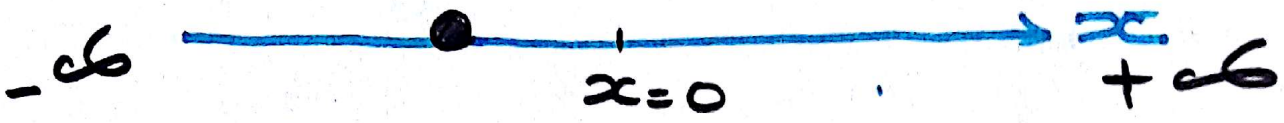
$$\{\vec{p}\} = (\vec{p}_1, \vec{p}_2, \ldots, \vec{p}_N)$$

$$\vec{p}_i = m_i \vec{v}_i$$

→ MICROSCOPIC STATE OF THE SYSTEM

$(\{\vec{r}\}, \{\vec{p}\}) \Rightarrow 6N$ VARIABLES

EXAMPLE : ONE DIMENSIONAL SYSTEM

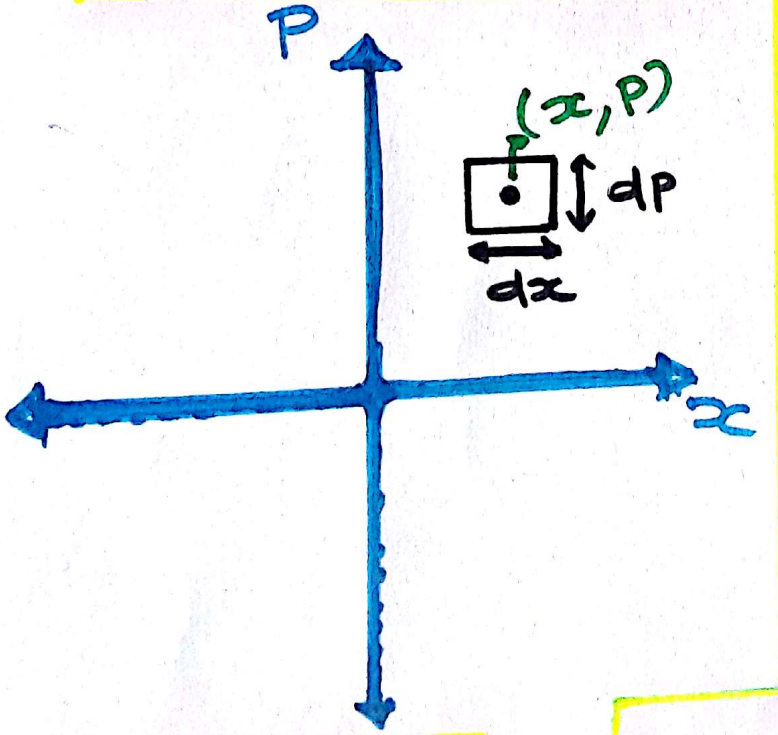


$(x, p) \Rightarrow$ MICROSTATE

HERE p IS THE MOMENTUM OF THE ATOM

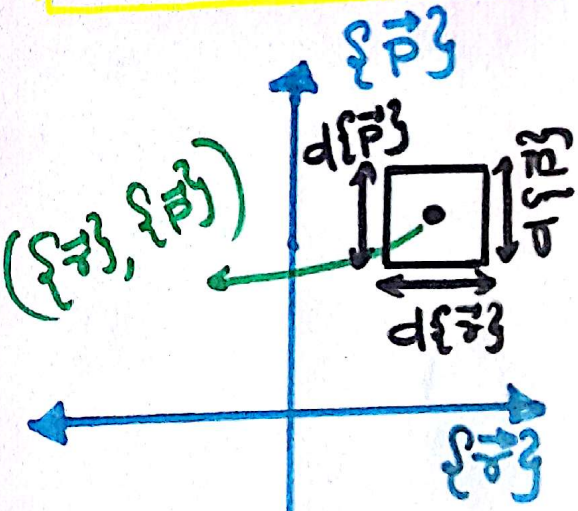
→ PHASE SPACE : COLLECTION OF MICROSTATES

ONE DIMENSIONAL



$dx\,dp = h$

MANY-BODY SYSTEM



HERE

$d\{\vec{r}\} \equiv dx_1\, dy_1\, dz_1 \ldots dx_N\, dy_N\, dz_N$

$d\{\vec{p}\} \equiv dp_{x_1}\, dp_{y_1}\, dp_{z_1} \ldots dp_{x_N}\, dp_{y_N}\, dp_{z_N}$

$d\{\vec{r}\}\, d\{\vec{p}\} = h^{3N}$

→ HAMILTONIAN :

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

U: POTENTIAL ENERGY, K: KINETIC ENERGY

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

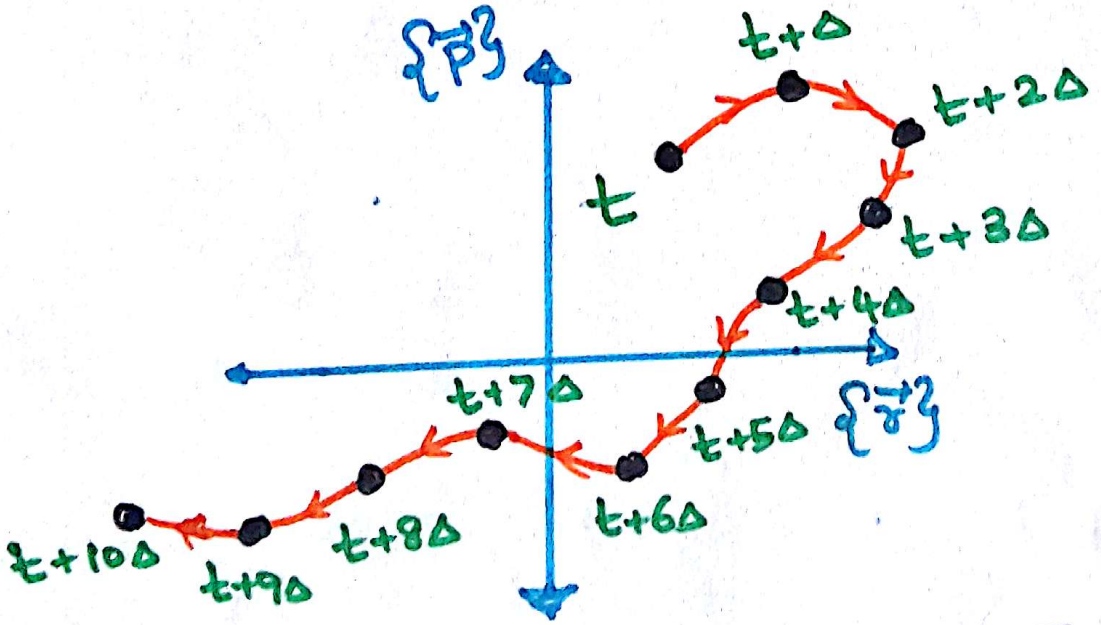
$U(\{\vec{r}\})$ ⇒ INTERACTIONS BETWEEN ATOMS

→ $\{\vec{r}\}$ AND $\{\vec{p}\}$ CHANGE WITH TIME.

$$\{\vec{r}(t)\} = (\vec{r}_1(t), \vec{r}_2(t), \ldots, \vec{r}_N(t))$$

$$\{\vec{p}(t)\} = (\vec{p}_1(t), \vec{p}_2(t), \ldots, \vec{p}_N(t))$$

SYSTEM CHANGES ITS MICROSTATE WITH TIME (DYNAMICS)



WHAT GOVERNS THIS TIME EVOLUTION?

COMPARE TRAJECTORIES OF SOLIDS, LIQUID, GAS

→ HAMILTON'S EQUATIONS :

$$\frac{\partial H}{\partial \vec{r}_i} = -\frac{d\vec{P}_i}{dt} = -\vec{F}_i \quad \text{(FORCE)}$$

$$\frac{\partial H}{\partial \vec{P}_i} = \frac{d\vec{r}_i}{dt} = \vec{V}_i \quad \text{(VELOCITY)}$$

$$\frac{d\vec{P}_i}{dt} = -\frac{\partial H}{\partial \vec{r}_i} \Rightarrow \begin{aligned} \frac{dP_{xi}}{dt} &= -\frac{\partial H}{\partial x_i} = F_{xi} \\ \frac{dP_{yi}}{dt} &= -\frac{\partial H}{\partial y_i} = F_{yi} \\ \frac{dP_{zi}}{dt} &= -\frac{\partial H}{\partial z_i} = F_{zi} \end{aligned}$$

$$\frac{d\vec{r}_i}{dt} = \frac{\partial H}{\partial \vec{P}_i} \Rightarrow \begin{aligned} \frac{dx_i}{dt} &= \frac{\partial H}{\partial P_{xi}} = V_{xi} \\ \frac{dy_i}{dt} &= \frac{\partial H}{\partial P_{yi}} = V_{yi} \\ \frac{dz_i}{dt} &= \frac{\partial H}{\partial P_{zi}} = V_{zi} \end{aligned}$$

FOR ONE-DIMENSIONAL SYSTEM :

$$\frac{dP}{dt} = -\frac{\partial H}{\partial x}, \quad \frac{dx}{dt} = \frac{\partial H}{\partial P}$$

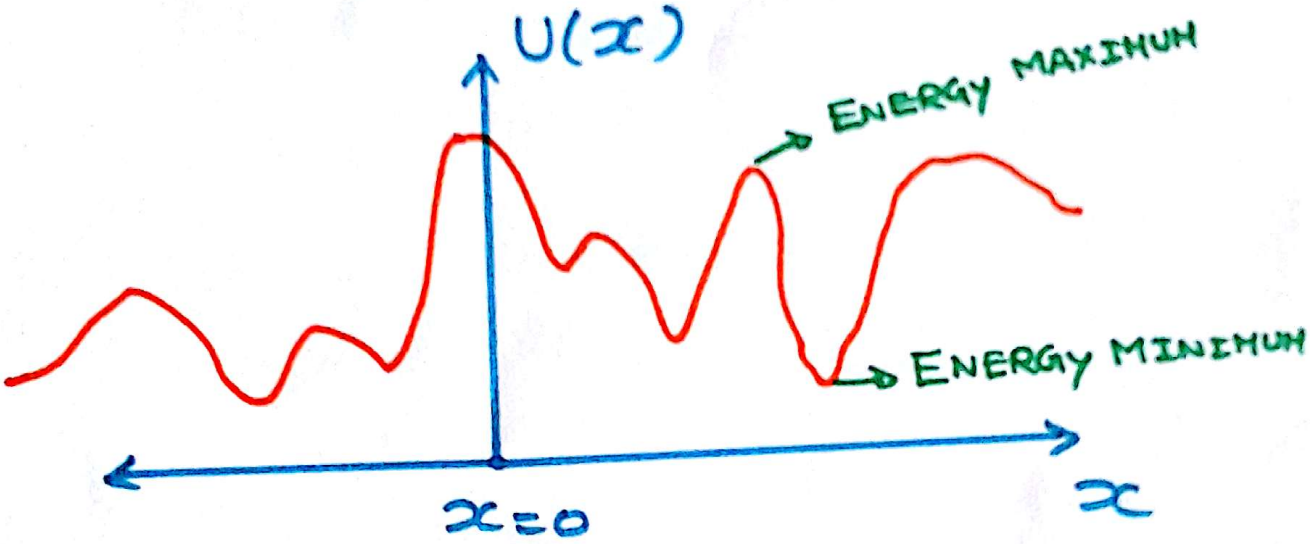
$$\frac{dH}{dt} = \frac{\partial H}{\partial x}\frac{dx}{dt} + \frac{\partial H}{\partial P}\frac{dP}{dt} = 0$$

- $H(x, P)$ = CONSTANT OF MOTION

$H(\{\vec{r}\}, \{\vec{P}\})$ = CONSTANT OF MOTION
ISOLATED SYSTEM

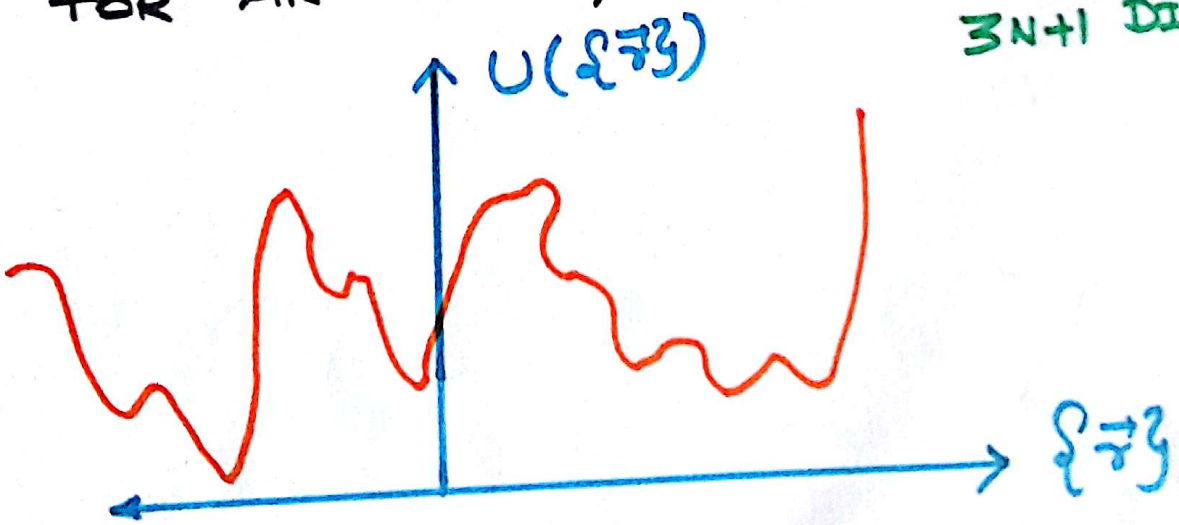
POTENTIAL ENERGY $U(\{\vec{r}\})$

- CONSIDER ONE-DIMENSIONAL SYSTEM
  - ⇒ POTENTIAL ENERGY $U(x)$
  - ⇒ POTENTIAL ENERGY SURFACE



$$\frac{dp}{dt} = -\frac{\partial H}{\partial x} = -\frac{\partial U}{\partial x} = F$$

- FOR AN N-BODY SYSTEM



$$\frac{d\vec{p}_i}{dt} = -\frac{\partial H}{\partial \vec{r}_i} = -\frac{\partial U}{\partial \vec{r}_i} = \vec{F}_i$$

PAIR-WISE INTERACTION

- CONSIDER A PAIR OF ATOMS i AND j
- r_{ij} ⇒ DISTANCE BETWEEN i AND j
- THEIR INTERACTION ENERGY AT r_{ij}

$$U(r_{ij}) \Rightarrow \text{PAIR-WISE INTERACTION}$$

- FOR A SYSTEM OF N ATOMS, THERE ARE $\frac{N(N-1)}{2}$ PAIRS OF ATOMS
- $$U(\{\vec{r}\}) = \sum_{i=1}^{N} \sum_{j>i}^{N} U(r_{ij})$$

SUM OF INTERACTIONS OF ALL PAIRS

- $\Omega(r)$ ⇒ NUMBER OF PAIRS OF ATOMS WITH AN INTERATOMIC SEPARATION OF r (INTERACTING SYSTEM)
- $\Omega_{IDEAL}(r)$ ⇒ NUMBER OF PAIRS OF ATOM WITH A SEPARATION OF r IN AN IDEAL GAS (NON-INTERACTING SYSTEM)
- $$g(r) = \frac{\Omega(r)}{\Omega_{IDEAL}(r)}$$; $g(r) = 1$? $g(r) > 1$? $g(r) < 1$?