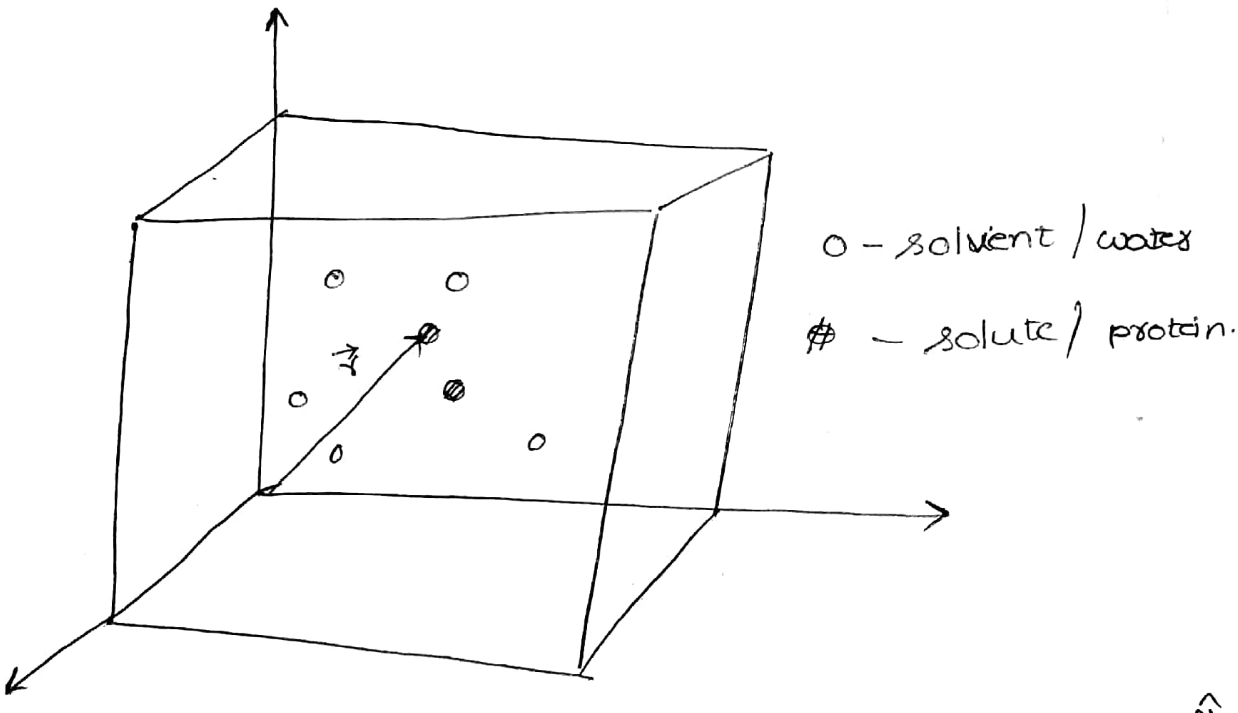
for 3D

$$\rho(\vec{r},t) = \frac{e^{-(x^2+y^2+z^2)/4Dt}}{(4\pi Dt)^{3/2}}$$

$$\boxed{\rho(\vec{r},t) = \frac{e^{-r^2/4Dt}}{(4\pi Dt)^{3/2}}}$$

* General approach to study dynamics at microscopic level



$$\vec{r}_i(t) = x_i(t)\hat{i} + y_i(t)\hat{j} + z_i(t)\hat{k}$$

$$\forall i$$

$\{\vec{r}_i\}$ = set of positions of all atoms.

$\|^{ly}$ define set of particle.

$\{\vec{p}(t)\} \rightarrow$ set of momentums of particles.

H $\hookrightarrow$ hamiltonian (or) Total-energy.

$$H(\{\vec{r}(t)\},\{\vec{p}(t)\}) = \underbrace{U(\{\vec{r}(t)\})}_{\text{potential energy function}} + \underbrace{K(\{\vec{p}(t)\})}_{\text{kinetic energy function}}$$

1 Dimension:

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

$$dH/dt = \frac{dU(x)}{dt} + \frac{dK(p)}{dt}$$

$$= -\vec{F}.\vec{V} + \frac{dK(p)}{dp}.\frac{dp}{dt}.$$

$$= \sum\vec{F}.\vec{V} + \sum\frac{\vec{P}}{m}.\vec{F}$$

for an isolated system:

Total energy is conserved $H(x,p) = \text{const}$

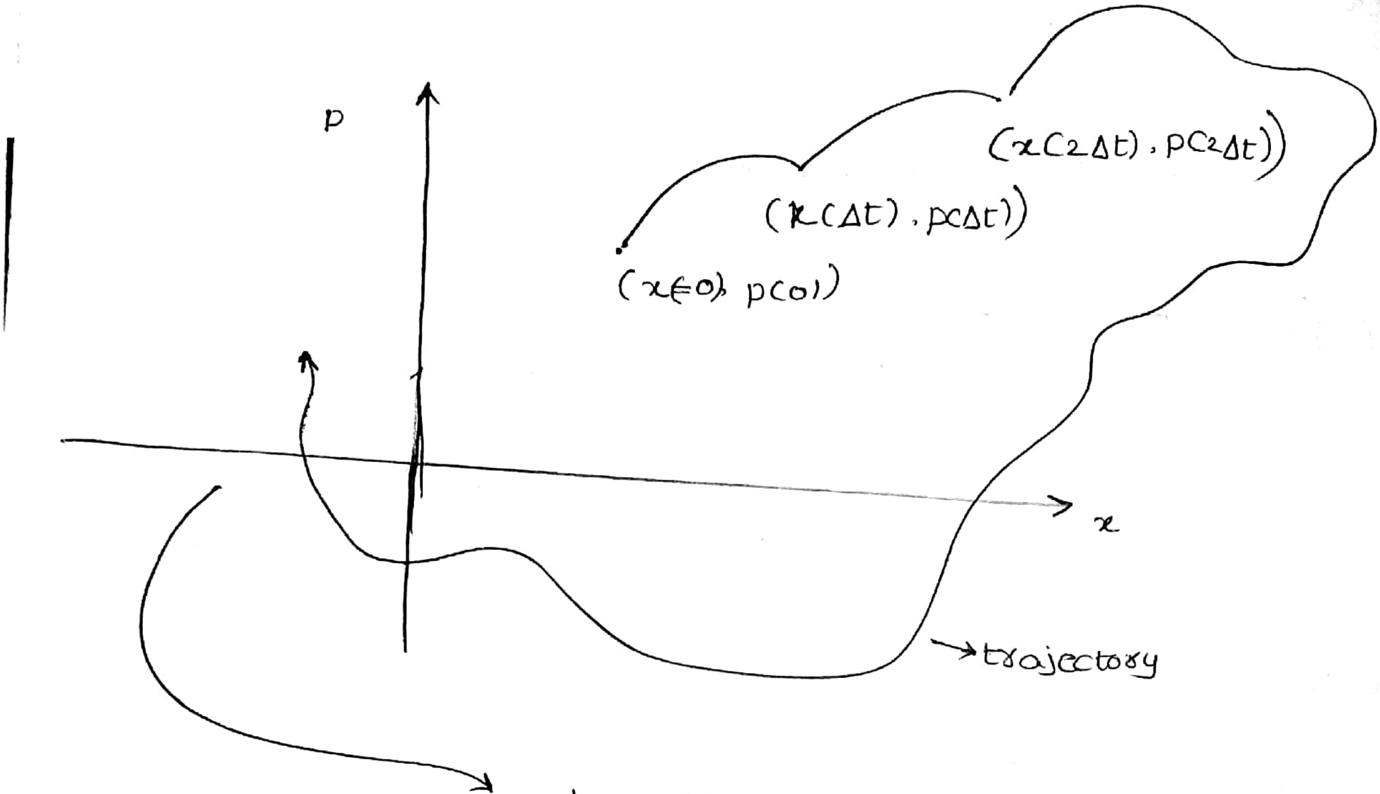
$$\frac{dH}{dt} = 0$$

$$\cancel{-\vec{\nabla}U.\vec{V}} \quad -\frac{dU}{dx}.\frac{dx}{dt} = \frac{dK(p)}{dp}\frac{dp}{dt}.$$

Hamilton's equation:

$$\frac{dp}{dt} = -\frac{dU}{dx}.$$

$$\frac{dx}{dt} = \frac{dk}{dp}.$$



phase Space (2D)

for 1D:

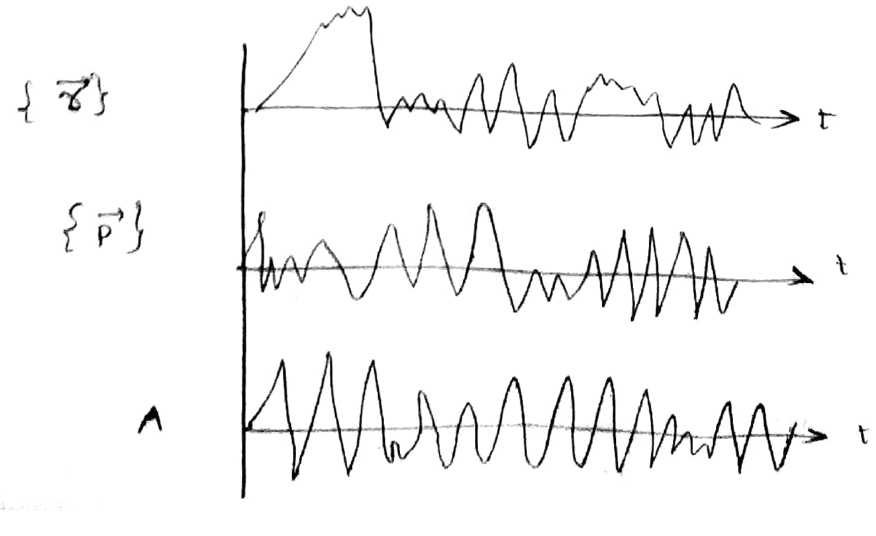
phase space (x, p)

for a system of N particles:

phasespace $(x_1, y_1, z_1, \ldots, x_N, y_N, z_N, p_{x_1}, p_{y_1}, p_{z_1}, \ldots, p_{x_N}, p_{y_N}, p_{z_N})$

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

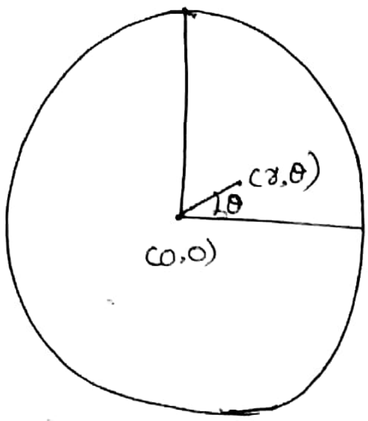
arbitary property.



$$\langle A \rangle = \frac{\sum_{i=0}^{t_{max}} A_i}{t_{max}}$$

comparable to experimental results.

2D:



$\vec{r} = x\hat{i} + y\hat{j}$

$|\vec{r}| = r$

N-random walkers.

(number of molecules)

intial cond^n - start at centre

2 random numbers

$rand_1$ (r)

$rand_2$ (θ)

* Statistical thermal physics:

Hamilton's equations:

$dx/dt = \partial H/\partial p$. $dp/dt = -\partial H/\partial x$

$\langle A(x,p)\rangle_{time}$ can be found if x, p as function of time is known.

$$x(t+\Delta t) = \frac{x(t)}{0!} + \frac{\dot{x}(t)\,\Delta t}{1!} + \frac{\ddot{x}(t)\,\Delta t^2}{2!} + \dots$$

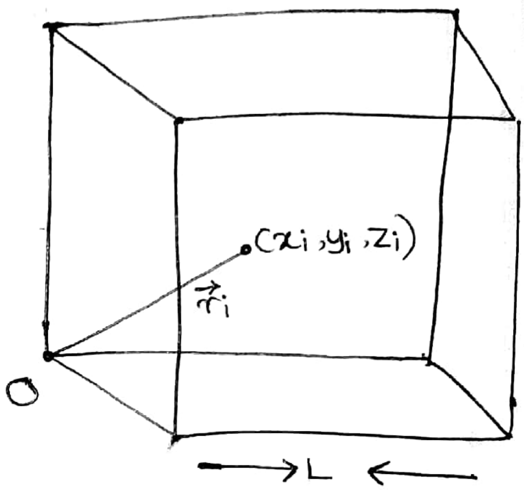
$$x(t+\Delta t) = \sum_{n=0}^{\infty} \frac{d^n x(t)}{dt^n} \frac{(\Delta t)^n}{n!}$$

$$p(t+\Delta t) = \sum_{i=0}^{\infty} \frac{d^i p(t)}{dt^i} \frac{(\Delta t)^i}{i!}$$

equations of kinetics and dynamics.

N particles:

$H(\{\vec{r}, \vec{p}\})$



Potential energy: $U(\{\vec{r}_i\})$

Kinetic energy: $K(\{\vec{p}_i\})$

$\{\vec{r}_i\} = (\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n)$ $\quad \vec{r}_i = x_i\hat{i} + y_i\hat{j} + z_i\hat{k}$.

$\{\vec{p}_i\} = (\vec{p}_1, \vec{p}_2, \dots, \vec{p}_n)$ $\quad \vec{p}_i = p_{x,i}\hat{i} + p_{y_i}\hat{j} + p_{z_i}\hat{k}$

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

$$dx_i/dt = \partial H / \partial p_{x,i}$$

$$\Rightarrow \quad d\vec{r}_i/dt = \partial H / \partial \vec{p}_i$$

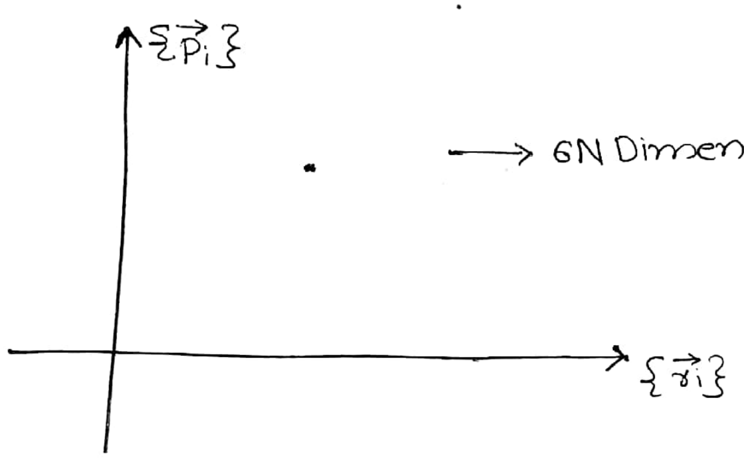
$$\begin{bmatrix} dx_i/dt \\ dy_i/dt \\ dz_i/dt \end{bmatrix} = \begin{bmatrix} \partial H/\partial p_{x,i} \\ \partial H/\partial p_{y,i} \\ \partial H/\partial p_{z,i} \end{bmatrix}$$

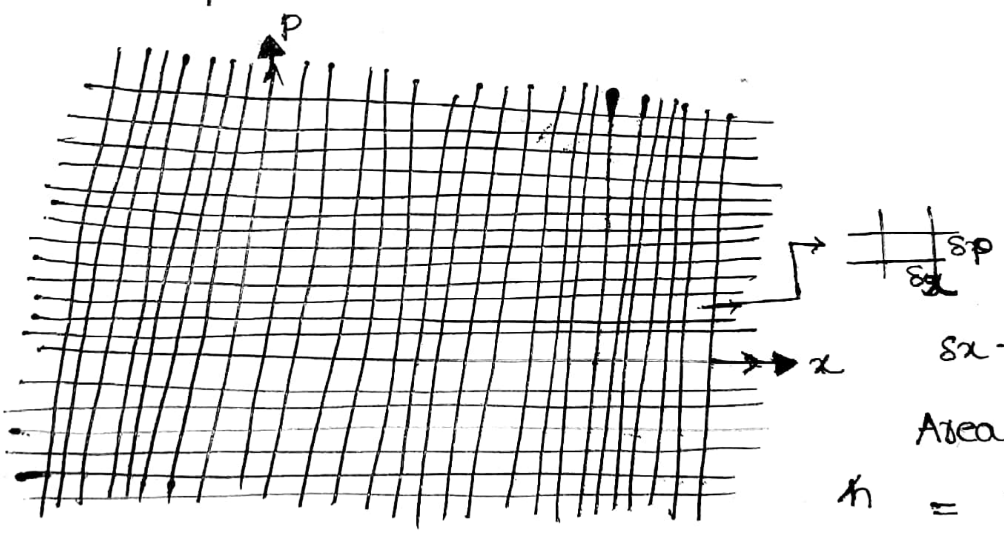
$$d\vec{p}_i/dt = -\partial H/\partial \vec{x}_i$$

$$\begin{bmatrix} dp_{i,x}/dt \\ dp_{i,y}/dt \\ dp_{i,z}/dt \end{bmatrix} = \begin{bmatrix} -\partial H/\partial x_i \\ -\partial H/\partial y_i \\ -\partial H/\partial z_i \end{bmatrix}$$

we will have 6N equations. describing equations of motion.

phase space – 6 N dimensions.





$\delta x \to 0$ $\delta p \to 0$

Area of cell

$\hbar = \delta x . \delta p.$

↓

angular moment unit

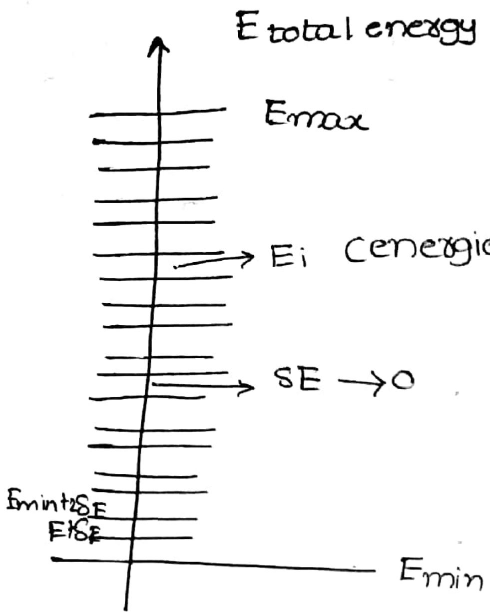
$\Rightarrow \hbar = h/2\pi$

$= \delta x \delta p.$ $h \to$ plank's constant

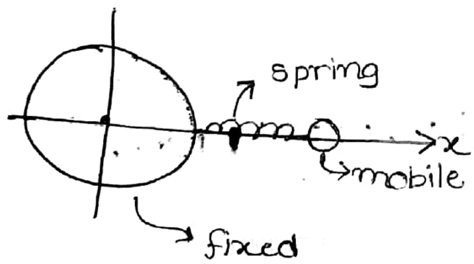
Each cell is called micro state of sys[illegible]

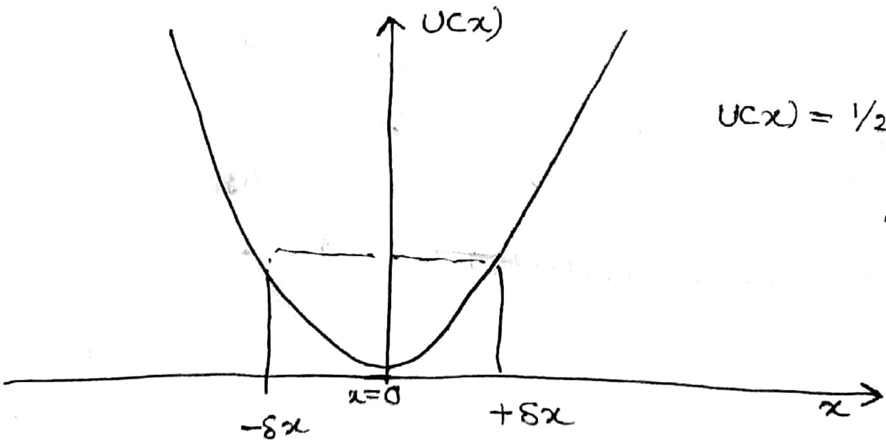
cell can be assumed as a point[illegible]

Set of all micro states forms a macro st[illegible]



* 1D Harmonic oscillator:





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

↓ (k)

spring constant.

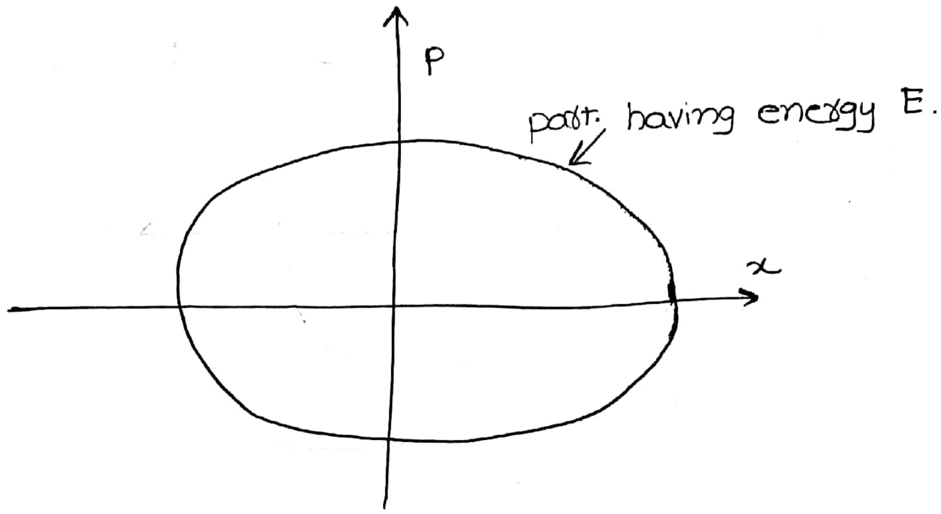
$\boxed{dH/dt = 0}$

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

$$E = \tfrac{1}{2} kx^2 + \tfrac{1}{2} p^2/m$$

$$x^2 \Big/ \left(\sqrt{\tfrac{2E}{k}}\right)^2 + p^2 \Big/ \left(\sqrt{2mE}\right)^2 = 1$$

↳ ellipse if energy E is constant.



* Boltzman's equation:

entropy $\boxed{S \propto \ln(\Omega(E))}$ statiscal number.

$\Omega(E) \rightarrow$ number of states at energy E.

thermodynamic number

$\Rightarrow \boxed{S = k_B \ln \Omega(E)}$ $k_B \rightarrow$ Boltzman's constant.

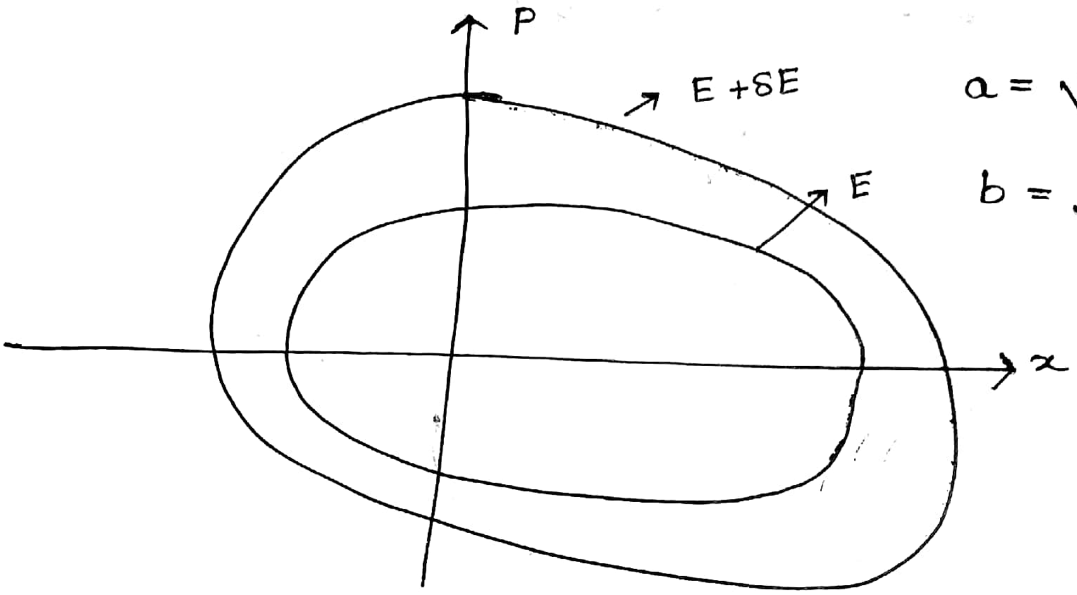
Case - 1 : 1D Harmonic oscillator:

$$\Rightarrow \left(x \Big/ \sqrt{2E/k}\right)^2 + \left(p \Big/ \sqrt{2mE}\right)^2 = 1$$

$$\boxed{d^2U/dx^2 = k}$$

$\hookrightarrow$ curvature of U.

Prob of being at E = $1/\Omega(E)$.



$a = \sqrt{2E/k}$

$b = \sqrt{2mE}$

$A = \pi a b \quad \Rightarrow dA = \pi(b\,da + \pi a\,db)$

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

$$= \pi\left(2\sqrt{\frac{m}{k}}\right)\delta E$$

$$\boxed{dA = \frac{2\pi\sqrt{m}}{\sqrt{k}}\,\delta E}$$

$\Rightarrow$ no. of ~~states~~ poss states in $E, E+\delta E$ = $\frac{2\pi\sqrt{m}}{\sqrt{k}}\delta E \propto (E)$

$dS = \frac{2\pi\sqrt{m}}{\sqrt{k}}\delta E \;\; \delta(E)$

$\Rightarrow S \propto \log \Omega(E)$

$\Omega(E) \propto$ circumference of ellipse

$\propto \sqrt{E}$

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

Number of accessible micro states increases with E.

$\Rightarrow$ Entropy increases with E.

entropy is zero when system has only one state.

$$\boxed{S = -\sum_i p_i \ln p_i}$$ (Information entropy).

$$\boxed{S = -k_B \sum_i p_i \ln p_i}$$ (thermodynamic entropy).

probability of system in ith state.

for an isolated system $\Omega(E)$ states.

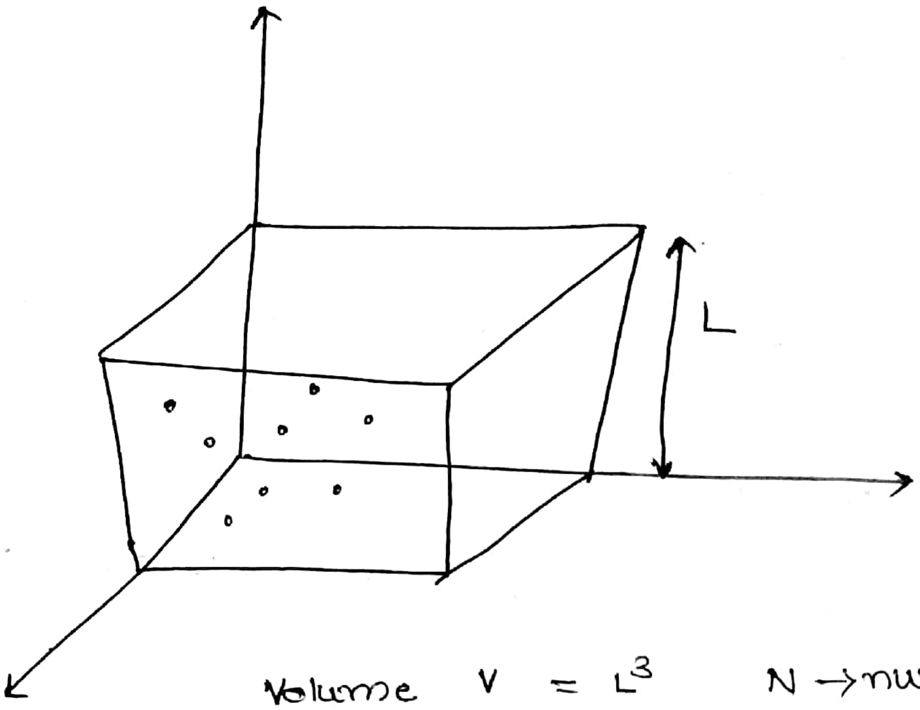
$$\boxed{p_i = 1/\Omega(E)}$$

$$S = -k_B \sum \frac{1}{\Omega} \ln \frac{1}{\Omega}$$

$$\Rightarrow \boxed{S = k_B \ln \Omega(E)}$$

Scanned by CamScanner

cubic cylinder: gas cylinder



Volume $V = L^3$ $N \rightarrow$ number of particles

$0 \le x_i \le L$

$0 \le y_i \le L$

$0 \le z_i \le L$

$$H(\{\vec{r}_i\}, \{\vec{p}_i\}) = \sum_{i=1}^{N} \left(\frac{\vec{p}_i \cdot \vec{p}_i}{2m} + \frac{k\, \vec{r}_i \cdot \vec{r}_i}{2} \right)$$

$$\boxed{H(\{\vec{r}\}, \{\vec{p}\}) = \frac{1}{2m} \sum_{i=1}^{N} \vec{p}_i \cdot \vec{p}_i + U(\{\vec{r}\})}$$

$\boxed{U(\{\vec{r}\}) = 0}$ $\Rightarrow$ an ideal gas.

$$H(\{\vec{r}\}, \{\vec{p}\}) = 1/2m \sum_{i=1}^{N} p_{x,i}^2 + p_{y,i}^2 + p_{z,i}^2 =$$

$$\sum_{i=1}^{N} p_{x,i}^2 + p_{y,i}^2 + p_{z,i}^2 = \left(\sqrt{2mE}\right)^2$$

→ 3N - dimensional sphere of

radius = $\sqrt{2mE}$.

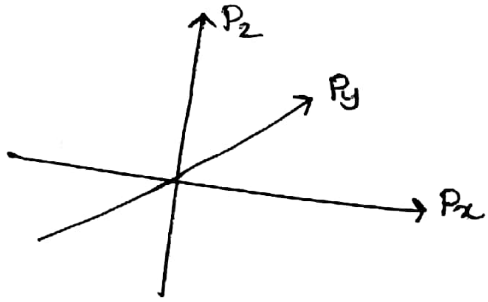
* calculate $\Omega(E)$:

$$\cancel{\Omega(E)} \int_{\{\vec{r}\}=0}^{L} \int_{\{\vec{p}\}=-\infty}^{\infty} d\{\vec{r}\}\{\vec{p}\} \rightarrow \text{all states}$$

$$\Omega(E) \propto \int_{\{\vec{r}\}=0}^{L} \int_{\{\vec{p}\}=-\infty}^{\infty} \delta\left(H(\{\vec{r}\},\{\vec{p}\}) - E \right) d\{\vec{r}\}\, d\{\vec{p}\}$$

$$\cancel{\Omega(E) = L^3 \, 4\pi (2mE)}$$

$$\cancel{\boxed{\Omega(E) = 8\pi m E L^3}}$$



$$\Omega(E) \propto \int_{\{\vec{r}\}=0}^{L} d\{\vec{r}\} \int_{\{\vec{p}\}=-\infty}^{\infty} \delta\left(\frac{\sum \vec{p}^2}{2m} - E \right) d\{\vec{p}\}$$

$$\propto V^N \times (2mE)^{\frac{3N-1}{2}}$$

$$\Omega(E) = V^N \times (2mE)^{\frac{3N-1}{2}} \times C(N)$$

1 particle

$$\boxed{\Omega(E) = 8\pi m L^3}$$

$\Omega(N, V, E)$ = number of accessible microstates.

case-1: 1D Harmonic oscillator.

$$\Omega(N,V,E) \propto \sqrt{E}.$$

case-2: N particles 3D with no internal energy

$$\boxed{\Omega(N,V,E) \propto V^N \left(\sqrt{E}\right)^{3N-1}}$$

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

NVE ensemble

(or)

Micro canonical ensemble.
(Isolated system)

$S(N,V,E)$

$$dS = \left.\frac{\partial S}{\partial E}\right|_{N,V} dE + \left.\frac{\partial S}{\partial N}\right|_{V,E} dN + \left.\frac{\partial S}{\partial V}\right|_{N,E} dV$$

$dS \longrightarrow$ change in entropy.
due to small changes

E,N

$$\frac{\partial S}{\partial E}\Big|_{N,V} = k_B \boxed{\cancel{3N/2E}} \left(\frac{3N-1}{2E}\right) = k_B \frac{\partial \ln\Omega}{\partial E}\Big|_{N,V}$$

$$\boxed{\cancel{\frac{\partial y}{\partial E}}} \quad \frac{\partial S}{\partial V}\Big|_{E,N} = k_B\, N/V = k_B \frac{\partial \ln\Omega}{\partial V}\Big|_{E,N}$$

$$\frac{\partial S}{\partial N}\Big|_{E,V} = k_B \left(\ln E + 3/2 \ln N\right) = k_B \frac{\partial \ln\Omega}{\partial N}\Big|_{E,V}$$

from conventional thermodynamics:

$$T\,dS = dE + P\,dV - \underbrace{\mu\, dN}_{\text{chemical potential.}}$$

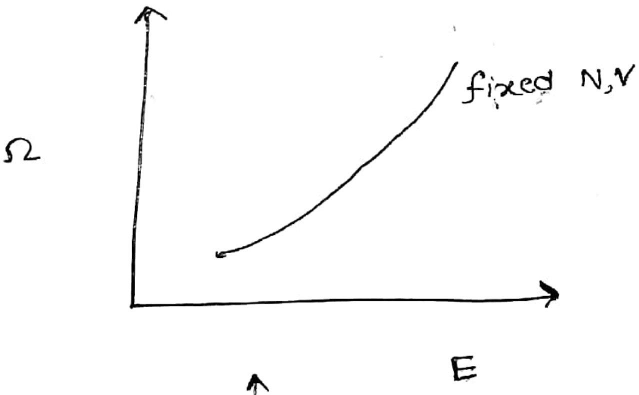
$$dS = \frac{dE}{T} + \frac{P\,dV}{T} - \frac{\mu\, dN}{T}$$

from ① & ②

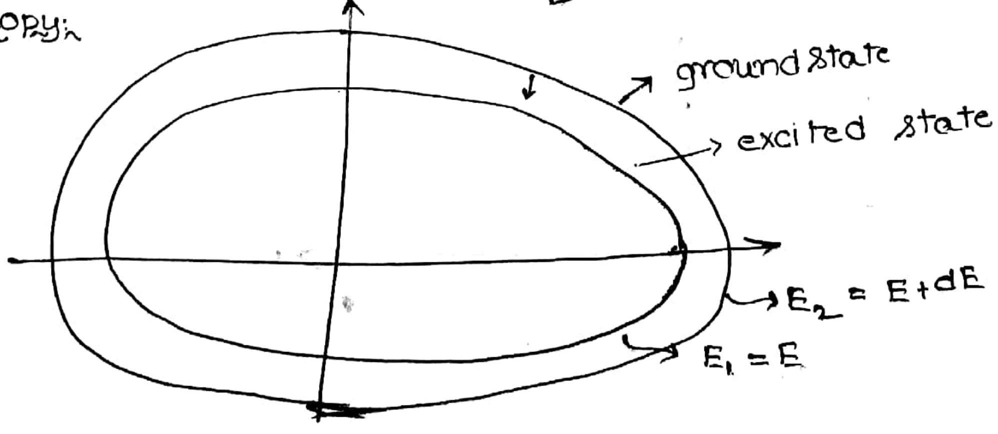
$$P/k_BT = \frac{\partial \ln\Omega}{\partial V}\Big|_{E,N}$$

$$1/k_BT = \frac{\partial \ln\Omega}{\partial E}\Big|_{N,V}$$

$$-\mu/k_BT = \frac{\partial \ln\Omega}{\partial N}\Big|_{E,V}$$



Spectroscopy:



dE *

Relaxation: from excited state to ground st

$$\boxed{\langle k \rangle \propto T}$$

* Closed system,

N = const.

V = const

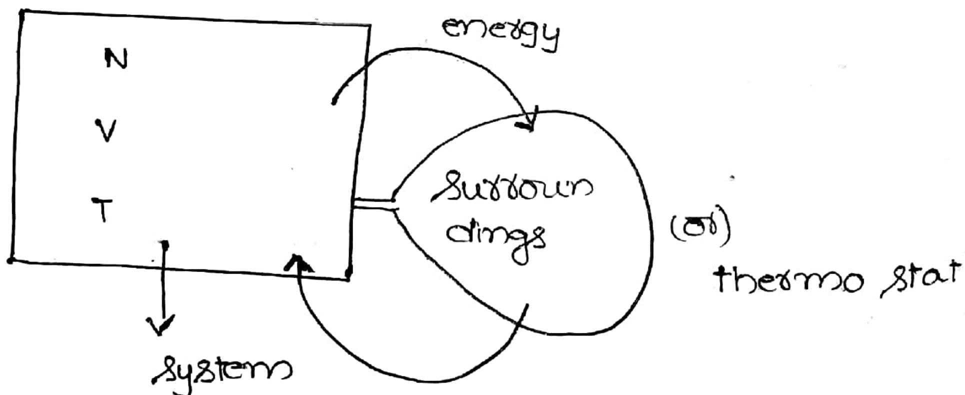
$E \rightarrow$ varies.

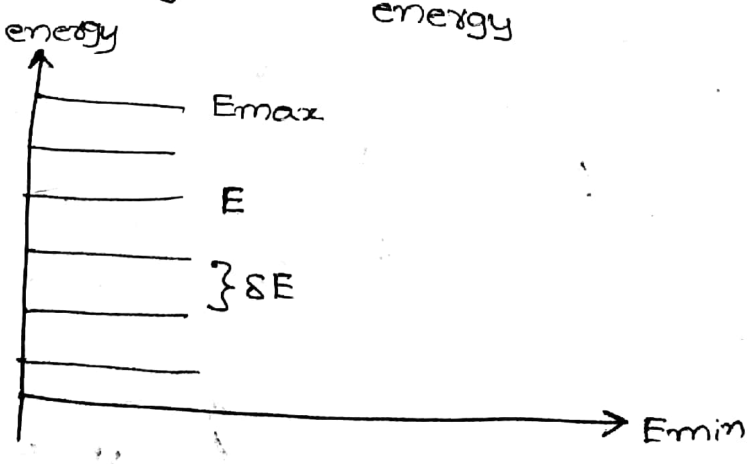
T = const

NVT ensemble

(or)

canonical ensemble





$P_i \propto e^{-\beta E_i}$ (Boltzmann) $\beta \equiv 1/k_B T$

consider both system and surrounding as one system (isolated system).

Normalization constant $= \sum_i e^{-\beta E_i}$

$$\Rightarrow \boxed{P_i = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}}$$

continous $P(\{\vec{r}\},\{\vec{p}\}) = \dfrac{e^{-\beta H(\{\vec{r}\},\{\vec{p}\})}}{\frac{1}{h^{3N}} \iint_{\{\vec{r}\}\{\vec{p}\}} e^{-\beta H(\{\vec{r}\},\{\vec{p}\})}}$

$$\boxed{Z \equiv \sum_i e^{-\beta E_i}}$$ → discrete

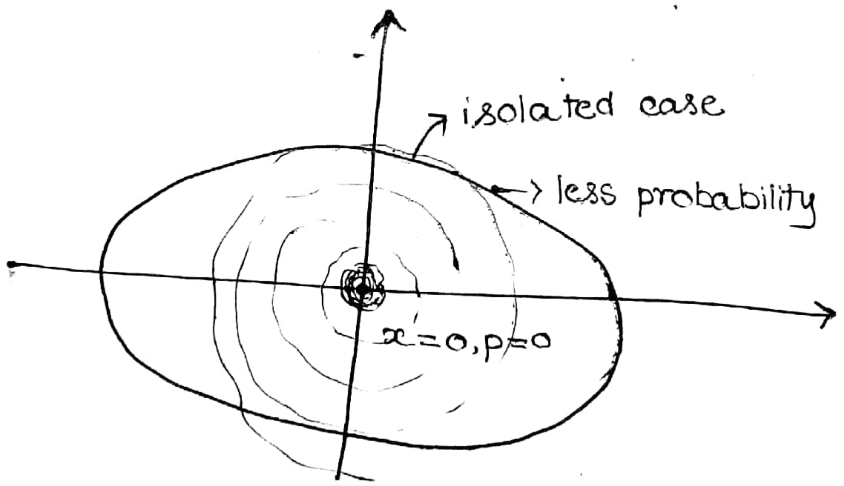
Z → partition function.

case-1 : 1D Harmonic oscillator.
(closed system)

$$H(x,p) = \tfrac{1}{2} k x^2 + p^2/2m.$$

$\cancel{P(x,p)}$ $P(x,p)$

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



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

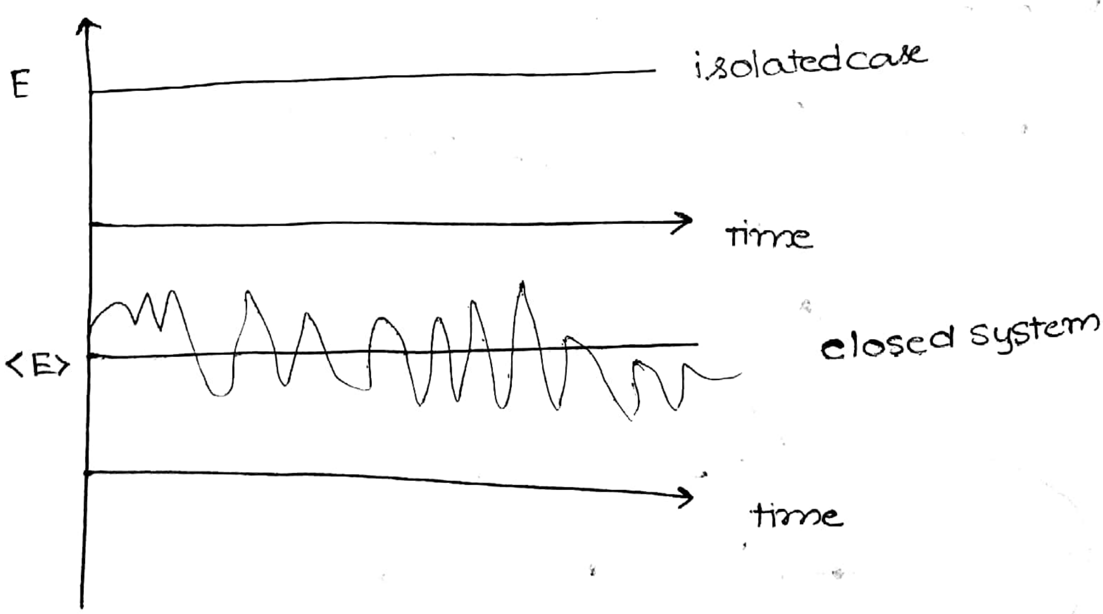
$$\ln Z = \ln \left(\sum e^{-\beta E_i} \right)$$

$$-\frac{\partial \ln Z}{\partial \beta} = \frac{1}{\sum e^{-\beta E_i}} \left(\sum_i E_i \, e^{-\beta E_i} \right)$$

$$= \frac{\sum E_i \, e^{-\beta E_i}}{\sum e^{-\beta E_i}}$$

$$= \sum E_i P_i$$

$$-\frac{\partial \ln Z}{\partial \beta} = \langle E \rangle \quad \text{(Internal energy)}$$

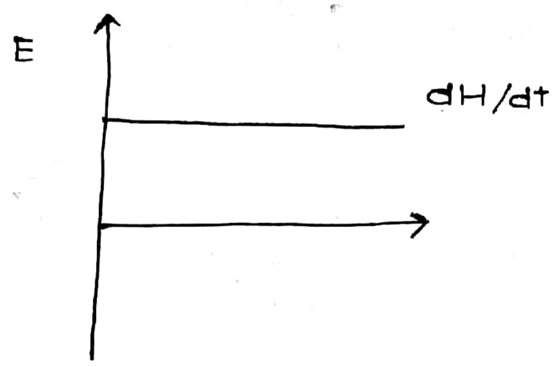


Isolated

1) const energy

$dH/dt = 0$

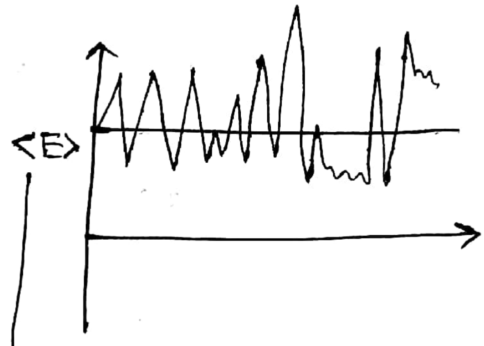
2)



Closed

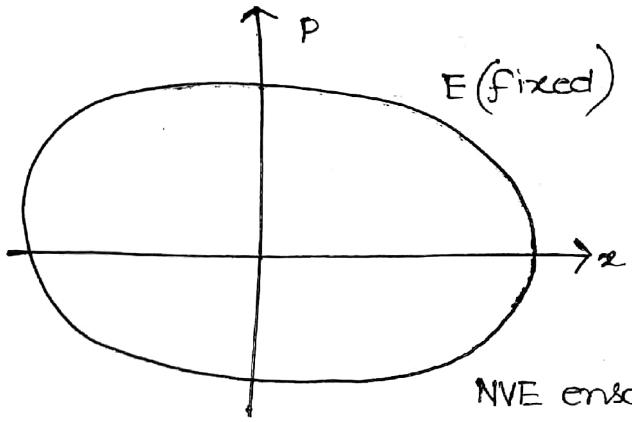
energy exchange

$dH/dt \neq 0$

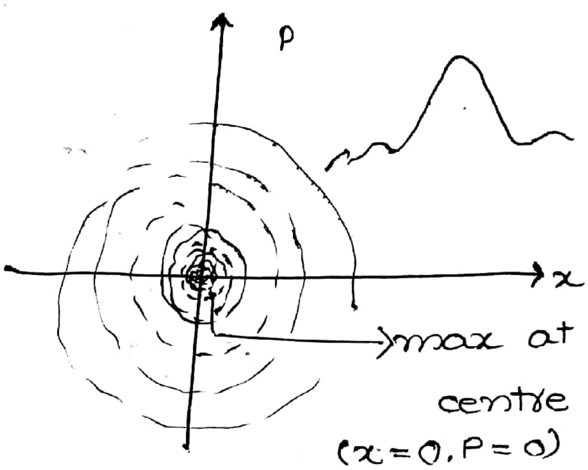


Internal Energy.

case:- 1) 1D Harmonic oscillator



NVE ensemble



NVT ensemble

$P_j \propto e^{-\beta H_j}$

↳ jth state

Normalization const.

$$Z = \sum_j e^{-\beta E_j}$$

2)

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

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

↳ continous.

Internal energy-

$$Z = \sum_j e^{-\beta E_j}$$

$$\ln Z = \ln\left(\sum_j e^{-\beta E_j}\right)$$

$$\Rightarrow \quad -\frac{\partial \ln Z}{\partial \beta} = \frac{1}{\sum_j e^{-\beta E_j}}\left(\sum E_j e^{-\beta E_j}\right)$$

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

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

$\langle \Delta E^2 \rangle$

if $\sigma_E^2 = 0$ - Isolated System

consider

$$\sum_j E_j e^{-\beta E_j} = -Z \frac{\partial \ln Z}{\partial \beta}$$

$$\Rightarrow \quad +\sum_j E_j^2 e^{-\beta E_j} = +\frac{\partial \ln Z}{\partial \beta}\frac{\partial Z}{\partial \beta} + Z\frac{\partial^2 \ln Z}{\partial \beta^2}$$

$$\langle E^2 \rangle \cancel{E_j} = \left[\left(\frac{\partial \ln Z}{\partial \beta}\right)^2 + \frac{\partial^2 \ln Z}{\partial \beta^2}\right]$$

$$\Rightarrow \quad \langle E^2 \rangle - \langle E \rangle^2 = \frac{\partial^2 \ln Z}{\partial \beta^2}$$

$$\Rightarrow \quad \boxed{\partial^2 \ln z / \partial \beta^2 = \langle \Delta E^2 \rangle}$$

$$\therefore \quad \boxed{\langle E \rangle = -\partial \ln z / \partial \beta} \qquad \boxed{\langle \Delta E^2 \rangle = \frac{\partial^2 \ln z}{\partial \beta^2}}$$

$$\Rightarrow \quad \boxed{\langle \Delta E^2 \rangle = -\frac{\partial \langle E \rangle}{\partial \beta}}$$

$$\boxed{\beta \equiv 1/k_B T}$$

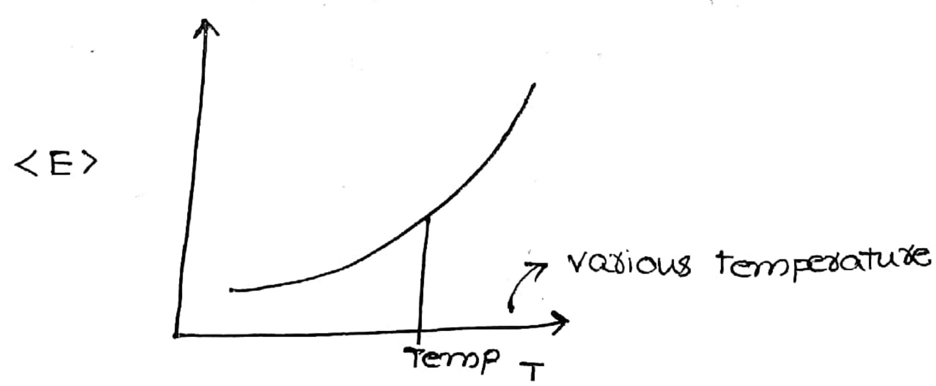
k_B → Boltzmann constant

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

$\frac{\partial \langle E \rangle}{\partial T}$ → heat capacity at const. volume.

$$\Rightarrow \quad \boxed{\langle \Delta E^2 \rangle = k_B C_V T^2}$$

experimental measurement of C_V



Theoritically: C_V is calculated from $\langle \Delta E^2 \rangle$ at a given temperature.

$C_V \geq 0$ as $\langle \Delta E^2 \rangle \geq 0$

$\Rightarrow \partial E / \partial T \geq 0$

$\Rightarrow \langle E \rangle \uparrow$ with T.

$C_V \propto \partial^2 \ln Z / \partial \beta^2$

$$S = -k_B \sum_j P_j \ln P_j$$

$$P_j = \frac{e^{-\beta E_j}}{Z}$$

$$\Rightarrow S = \frac{-1}{T} \sum \langle E \rangle + \frac{\ln Z}{\beta} = \frac{\langle E \rangle}{T}$$

$$\Rightarrow \cancel{S = \langle E \rangle / T} \qquad \boxed{S = \frac{\langle E \rangle}{T} + \ln Z \, k_B}$$

$$\boxed{TS = \langle E \rangle + \ln Z / \beta}$$

$$U - TS = -\ln Z / \beta = -k_B T \ln Z$$

from thermodynamics
Helmotz free energy (F)

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

$$\boxed{F = -\ln Z / \beta}$$

Pressure:-

$$P_j = -\frac{\partial H(\{\vec{r}\}, \{\vec{p}\})}{\partial V}$$

$\langle P \rangle$ — is measured experimentally.

$$\langle P \rangle = \sum_j P_j \, \mathcal{P}_j$$

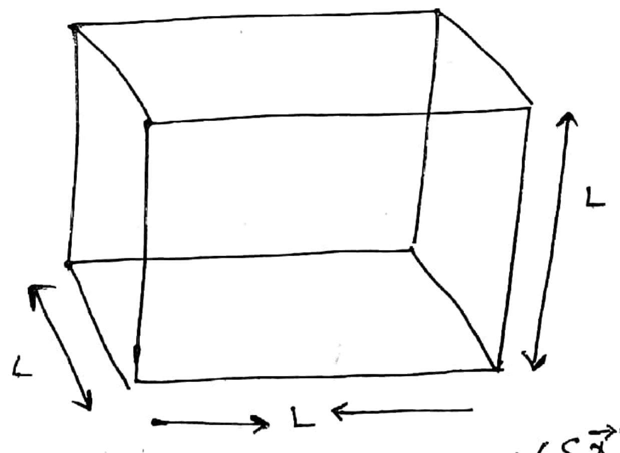
$$= - \sum_j \left(\frac{\partial E_j}{\partial V} \right) \frac{e^{-\beta E_j}}{Z}$$

$$\partial \ln Z / \partial V = \cancel{\left(\frac{\partial \beta}{\partial V}\right) \left(\frac{\sum E_j e^{-\beta E_j}}{Z} \right)}$$

$$= \cancel{- \langle E \rangle \, \partial \beta / \partial V} - \beta \sum_j \frac{\partial E_j}{\partial V} \frac{e^{-\beta E_j}}{Z}.$$

$$\Rightarrow \boxed{\langle P \rangle = \frac{\partial \ln Z}{\beta \, \partial V}}$$

case - 2 : ideal gas system N atoms in volume V



$U(\{\vec{r}\}) = 0$

$$H(\{\vec{r}\}, \{\vec{p}\}) = \frac{1}{2m} \sum_i \vec{p}_i \cdot \vec{p}_i$$

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

$$\boxed{Z = Z_r Z_p}$$

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$$z_r = \int_{\{\vec{r}\}} d\{\vec{r}\} = L^{3N} = V^N$$

$$z_p = \int_{\{\vec{p}\}} e^{-\beta(\sum_i \vec{p_i}\cdot\vec{p_i})} d\{\vec{p}\}$$

$$= e\left(\sqrt{\pi/\beta}\right)^{3N}$$

$$= \left(2\pi m/\beta\right)^{3N/2}$$

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

$$Z = \left[\frac{\sqrt{2\pi m}\ L}{\hbar\sqrt{\beta}}\right]^{3N}$$

$$Z = \left[\frac{\sqrt{2\pi m}\ L}{\hbar\ \sqrt{\beta}}\ \cancel{k_B}T\right]^{3N} = \left(\frac{\sqrt{2\pi k_B T m}\,L}{\hbar}\right)^{3}$$

$$\langle E\rangle = -\frac{\partial \ln Z}{\partial\beta} = +\frac{3N}{\hbar\sqrt{\beta}}\ \frac{1}{2\sqrt{\beta}}$$

$$\boxed{\langle E\rangle = \frac{3N}{2\hbar\beta}} \Rightarrow \langle E\rangle = \frac{3T}{2}$$

$$\boxed{\langle \Delta E^2\rangle = \frac{3N}{2\hbar\beta^2}}$$

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$$\boxed{C_V = \frac{3N k_B}{2\hbar}}$$

$$\cancel{\langle P \rangle = \left(\frac{\sqrt{2\pi m}}{\beta \hbar}\right)^{3N} N V_1^{N-1}}$$

$$\boxed{\cancel{\langle P \rangle = N \left(\frac{\sqrt{2\pi m}}{\beta \hbar}\right)^{3N} V^{N-1}}}$$

$$\Rightarrow \quad \cancel{\langle P \rangle V = N \left[\frac{\sqrt{2\pi m}}{\beta \hbar}\right]^{3N}} V^N \frac{1}{\beta} \frac{N}{V}$$

$$\cancel{= NRT}$$

$$\langle P \rangle = \partial \ln z / \beta \partial V$$

$$= \frac{\partial \left(3N \left(\ln \left(\sqrt{\frac{2\pi m}{\beta \hbar^2}}\right)\right) + N \ln V\right)}{\beta \, \partial V}$$

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

$$\Rightarrow \quad \langle P \rangle V = kNT = nRT$$

$$\therefore \quad \boxed{\langle P \rangle V = nRT}$$

$$\langle E \rangle = -\partial \ln z / \partial \beta = \frac{3N}{2\beta} = \frac{3}{2} nRT$$

$$\boxed{\langle E \rangle = 3nRT/2}$$

$$\langle \Delta E^2 \rangle = \frac{3N}{2} \beta^{-2}$$

$$\boxed{\langle \Delta E^2 \rangle = \frac{3N}{2\beta^2}}$$

$$\boxed{C_V = \frac{3nR}{2}}$$

C_V is independent of temparature.

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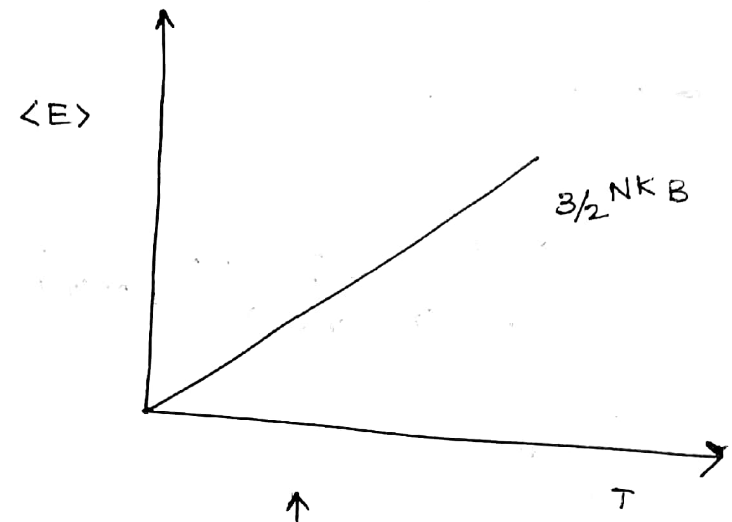
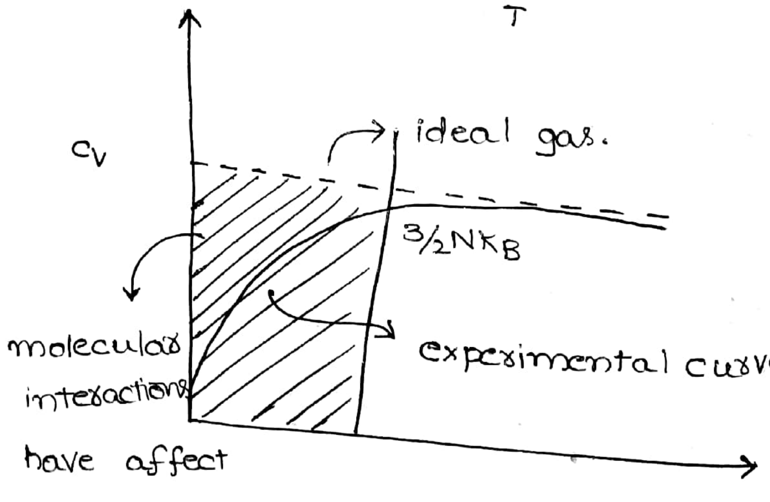
All macroscopic quantities can be calculated using microscopic values.

* Real gas:

$U(\{\vec{r}\}) \neq 0.$

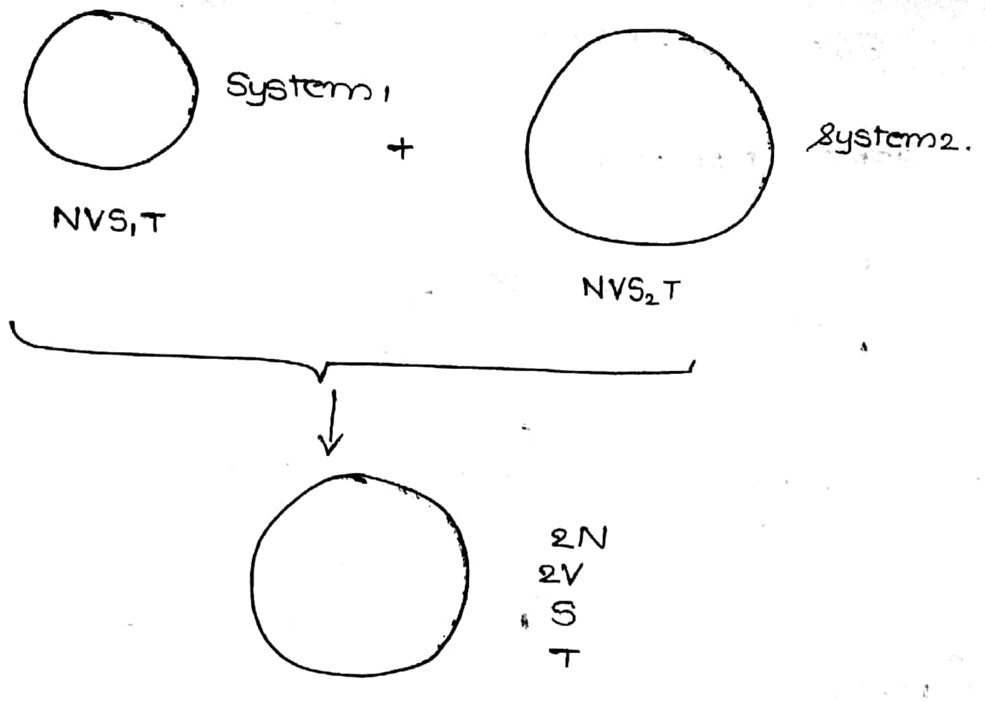
$\Rightarrow \boxed{PV/T = nR}$





$U\{\vec{r}\}$ not relevant at high temp.

entropy is an extensive property.



$$S = -k_B \sum_j P_j \ln P_j$$

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

$$\cancel{S_1 + S_2 = 2 k_B}$$

$$S_1 = k_B (\ln z + \beta \langle E \rangle) \qquad S_2 = k_B (\ln z + \beta \langle E \rangle)$$

$$S = k_B (\ln z + \beta \langle E \rangle)$$

$$= k_B \left(\ln z + \frac{1}{k_B T} \frac{3}{2} \frac{N}{\beta}\right)$$

$$S = k_B (\ln z + 3N/2)$$

$$\cancel{\ln z = \ln \left[\frac{\sqrt{2\pi m}}{\hbar \sqrt{\beta}} L \right]^{3N} = 3N \ln}$$

$$S = \frac{k_B 3N}{2} \cancel{\times 2} + k_B \ln\left[z\left(1 + e^{-\beta E}\right)\right]$$

$$S_1 = k_B \ln z + 3 k_B N/2 \qquad S_2 = k_B \ln z + 3 k_B N/2.$$

$$S_1 + S_2 = 2 k_B \ln z$$

for ideal gas

$S - (S_1 + S_2) = 2Nk_B \ln 2$

GIBBS PARADOX

$$\boxed{Z_{correct} = Z / N!}$$

$$\boxed{S - (S_1 + S_2) = 0}$$

$$\boxed{\begin{array}{c} \ln N! \simeq N \ln N - N \\ N \to \infty \end{array}}$$

$N \to \infty$ $\quad V \to \infty$

$\boxed{N/V = \text{finite}}$

thermodynamic limit

* Non-ideal gas: