## General Approach to study Thermodynamics at microscopic limit

$\vec{r_i}$ $= x_i \hat{i} + y_i \hat{j} + z_i \hat{k}$
(position of $i^{th}$ atom)

$\vec{r}(t) = x(t)\hat{i} + y(t)\hat{j} + z(t)\hat{k}$
Position of particle changes with time

$\{\vec{r}\}$: set of positions of atoms

$\{\vec{r}\} = \{\vec{r_1}, \vec{r_2}, \ldots \vec{r_n}\}$

$\{\vec{r}(t)\} = \{\vec{r_1}(t), \vec{r_2}(t), \ldots \vec{r_n}(t)\}$

Set of momentum:

$\{\vec{p}(t)\} = \{\vec{p_1}(t), \vec{p_2}(t), \ldots \vec{p_n}(t)\}$

- Maxwell - Boltzmann distribution gives velocity

$H \rightarrow$ Hamiltonian of system (total energy)

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

$$\Rightarrow \frac{dH}{dt} = \frac{dU(u)}{dt} + \frac{dK(p)}{dt}$$

$$= \frac{dU}{du}\underbrace{\left(\frac{du}{dt}\right)}_{\text{velocity}} + \frac{dK(p)}{dp}\cdot\underbrace{\left(\frac{dp}{dt}\right)}_{\text{force}}$$

If system is isolated, total energy : constant

$dH = 0$

$\Rightarrow$

$$\frac{dU}{dx} \cdot \frac{dx}{dt} + \frac{dK}{dp} \cdot \frac{dp}{dt}$$

## Hamilton's Equations

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

$$\frac{dx}{dt} = \frac{dK}{dp}$$

Hamilton's equation of motion

- space formed by $x$ & $p$ is called phase space

for $N$ exp' particle system, $6N$ - dimension phase space.

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- for one particle in one dimension:

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

$$\frac{dx}{dt} = \frac{\partial H}{\partial p} = \frac{\partial K}{\partial p}$$

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

- for $N$ particles in 3 dimensions:

$U(\{\vec{r_i}\})$ : potential energy function

$K(\{\vec{p_i}\})$ : kinetic energy function

Hamilton's equations:

$$\frac{d\vec{p_i}}{dt} = \frac{\partial H}{\partial \vec{p_i}}$$

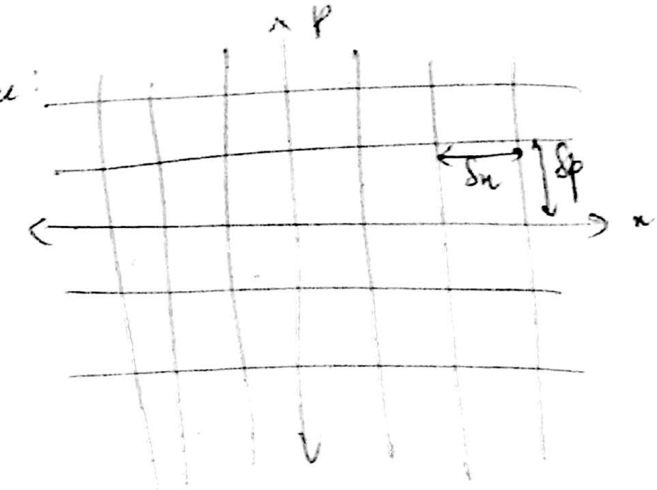
$$\begin{bmatrix} \frac{d\vec{x_i}}{dt} \\ \frac{d\vec{y_i}}{dt} \\ \frac{d\vec{z_i}}{dt} \end{bmatrix} = \begin{bmatrix} \frac{\partial H}{\partial p_{xi}} \\ \frac{\partial H}{\partial p_{yi}} \\ \frac{\partial H}{\partial p_{zi}} \end{bmatrix}$$

And, $\frac{\partial \vec{p_i}}{\partial t} = \frac{\partial U}{\partial \vec{x_i}}$

$$\Rightarrow \begin{bmatrix} \frac{d\vec{p_{ix}}}{dt} \\ \frac{d\vec{p_{iy}}}{dt} \\ \frac{dp_{iz}}{dt} \end{bmatrix} = \begin{bmatrix} \frac{\partial U}{\partial x_i} \\ \frac{\partial U}{\partial y_i} \\ \frac{\partial U}{\partial z_i} \end{bmatrix}$$

<u>for 1 dimension case of a particle.</u>

Phase space:




Area of phase space

$= \delta p \, \delta x$ (angular momentum)

$= \hbar$

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

- <u>Microstate:</u>

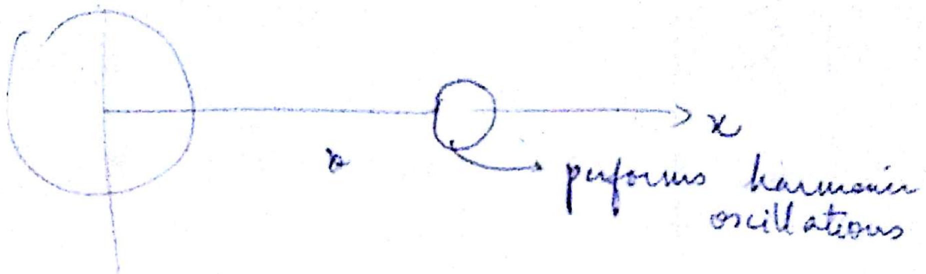
  Each 'cell' in phase space.

## Energy Level Diagram

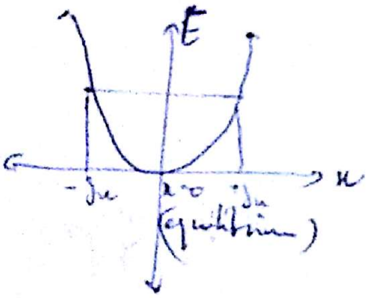
- Given energy level : MACRO STATE
- A macro state has many micro states attached to it

### Model System :

- 1-D harmonic oscillator (isolated)




$U(x) = \frac{1}{2}kx^2$ ; $k$ = spring constant




for this system,

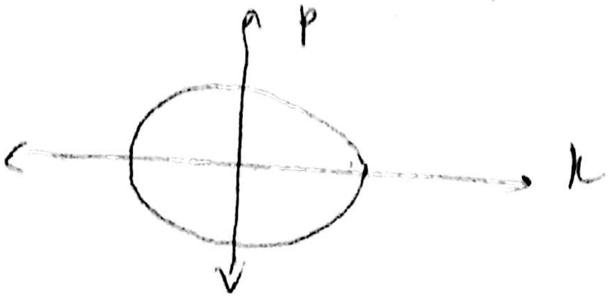
$H(x,p) = U(x) + K(p)$

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

(constant, as isolated system)

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

Phase space trajectory is ellipse (of ~~mm~~ energy E)




## Boltzmann's Law:

~~$S \propto \ln(E)$~~

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

$S$: entropy

$\Omega$: Statistical measure, number of microstates with energy $E$

$$\Rightarrow \quad S = k_B \ln(\Omega(E))$$

↓

Boltzman's constant

## Model:

1-D Harmonic Oscillator

$$U(x) = \frac{kx^2}{2}, \quad K(p) = \frac{p^2}{2m}$$

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

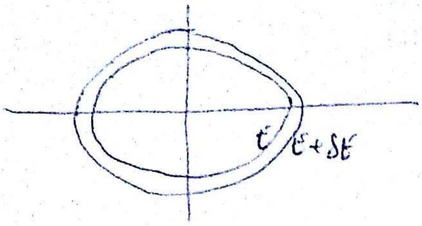
$$\frac{x^2}{\left(\sqrt{\frac{2E}{k}}\right)^2} + \frac{p^2}{\left(\sqrt{2mE}\right)^2} = 1$$

↓

ellipse

We wish to find $\Omega(E)$

probability of a state $= \dfrac{1}{\Omega(E)}$ (Hypothesis: each microstate is equiprobable)




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

$b = \sqrt{2mE}$

Now, circumference of ellipse : $2\pi \sqrt{\dfrac{a^2+b^2}{2}}$

$$= 2\pi \sqrt{\dfrac{\frac{2E}{k} + 2mE}{2}}$$

$$\propto \sqrt{E}$$

Also, $\Omega(E) \propto$ circumference

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

$\Rightarrow$ number of microstates increases with $E$

$\Rightarrow$ $S$ increases with $E$.

- Information entropy : $-\sum_i p_i \ln(p_i)$

  $\downarrow$

  probability of system to be in $i^{th}$ state

- Thermodynamic entropy $(S)$ : $k_B \times$ (info entropy)

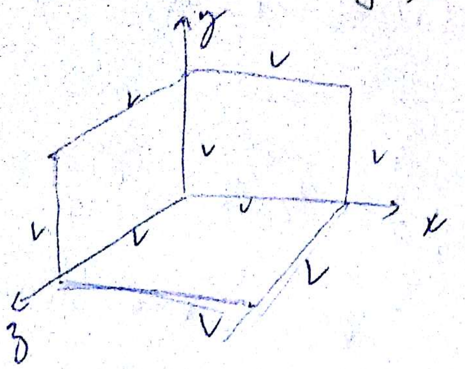
$$= k_B \sum_i \frac{1}{\Omega} \ln(\Omega) \qquad (p_i = \Omega)$$

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

...del:

gas cylinder (ideal gas)






N particles
identical mass m.

$L \leq x_i \leq L$
$L \leq y_i \leq L$
$L \leq z_i \leq L$

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

$$= \sum_{i=1}^{N} \frac{|\vec{p_i}|^2}{2m} + u(\{\vec{r}\})$$

- for our system, assume particles don't interact (ideal gas model)

$$\therefore \quad u(\{\vec{r}\}) = 0$$

$$\Rightarrow \quad H(\{\vec{r}\}, \{\vec{p}\}) = \frac{1}{2m} \sum_{i=1}^{N} \left( p_{x_i}^2 + p_{y_i}^2 + p_{z_i}^2 \right) = E$$

(isolated, hence constant)

$$\Rightarrow \sum_{i=1}^{N} \left( p_{x_i}^2 + p_{y_i}^2 + p_{z_i}^2 \right) = \left( \sqrt{2mE} \right)^2$$

$\therefore$ Hypersphere in phase space, radius $= \sqrt{2mE}$.

- To calculate $\Omega(E)$, visit all microstates over phase space, and only sum over those with energy $E$.

$$\Rightarrow \quad \Omega(E) \propto \int_0^L \int_{-\infty}^{\infty} \underbrace{\delta\left( H(\{\vec{r}\}\{\vec{p}\}) = E \right)}_{\text{delta function}} d\{\vec{p}\}\, d\{\vec{r}\}$$

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

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

Now, for 1 particle, $\int_{\{\vec{r}\}=0}^{L} d\vec{r} = \int_0^L \int_0^L \int_0^L dx \cdot dy \cdot dz = L^3$

$\therefore$ for N particles $= L^{3N} = V^N$ $\quad (V = L^3 \text{ (volume)})$

$$\Rightarrow \Omega(E) \propto V^N \int_{\{p\}=-\infty}^{\{p\}=+\infty} \delta\left(\sum_1^N (p_{ix}^2 + p_{iy}^2 + p_{iz}^2) - E\right) d\{p\}$$

Now, surface area of N-dimensional sphere with radius $r$ is $\propto r^{N-1}$

Also, $\int_{\{p\}=-\infty}^{\{p\}=\infty} \delta\left(\sum (p_{ix}^2 + p_{iy}^2 + p_{iz}^2) - E\right) d\{p\} \propto$ (circumference of hypersphere)

$$\Rightarrow \Omega(E) \propto V^N \left(\sqrt{2mE}\right)^{3N}.$$

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

## Ensembles :

### N,V,E Ensemble

- Systems with constant N, V, E
- Also called ~~ideal~~ isolated systems.

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

$\Rightarrow$ $\cancel{\text{Now, } \left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{k_B}{\Omega(N,V,E)}}$

Now,

$$\left(\frac{\partial S}{\partial E}\right)_{N,V} = \left(\frac{\partial k_B \ln(\Omega)}{\partial E}\right)_{N,V}$$

$$\left(\frac{\partial S}{\partial V}\right)_{N,E} = k_B\left(\frac{\partial \ln(E)}{\partial V}\right)_{N,E}$$

$$\left(\frac{\partial S}{\partial N}\right)_{V,E} = k_B\left(\frac{\partial \ln(E)}{\partial N}\right)_{V,E}$$

### From conventional Thermodynamics:

$$TdS = dE + PdV - \mu dN$$

Comparing,

$$\Rightarrow \frac{1}{T} = k_B\left(\frac{\partial \ln \Omega}{\partial E}\right)_{N,V} \Rightarrow \left(\frac{\partial \ln(\Omega)}{\partial E}\right)_{N,V} = \frac{1}{k_B T}$$

$$\Rightarrow \frac{P}{T} = k_B\left(\frac{\partial \ln \Omega}{\partial V}\right)_{N,E} \Rightarrow \left(\frac{\partial \ln \Omega}{\partial V}\right)_{N,E} = \frac{P}{k_B T}$$

$$\Rightarrow \frac{-\mu}{T} = k_B\left(\frac{\partial \ln \Omega}{\partial N}\right)_{V,E} \Rightarrow \left(\frac{\partial \ln \Omega}{\partial N}\right)_{V,E} = \frac{-\mu}{k_B T}$$

## Closed System

System can exchange energy, not particles from the ~~energy~~ Surroundings

## NVT Ensemble:

N, V, T fixed

E → vary

- System exists in different energy levels

$$p_i \propto e^{-\beta E_i} \quad , \quad \beta = \frac{1}{k_B T}$$

(probability of system in state i)

$$\Rightarrow \quad p_i = \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}}$$

⇒ $\vec{p}_i$ ~~≈~~ $\mathcal{R}$ for discrete System.

- For continuous system,

$$P_i = P\left(\{\vec{r}_i\}, \{\vec{p}_i\}\right) = \frac{e^{-\beta H(\{\vec{r}_i\}, \{\vec{p}_i\})}}{\frac{1}{h^{3N}} \iint_{\{\vec{r}\}\{\vec{p}\}} e^{-\beta H(\{\vec{r}\}, \{\vec{p}\})} \, d\{\vec{r}\} \, d\{\vec{p}\}}$$

## Partition function (Z)

for discrete:

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

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

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Differentiating (w.r.t $\beta$).

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

$$\Rightarrow \quad \frac{-\partial \ln Z}{\partial \beta} = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} \quad \begin{array}{l} \longrightarrow \sum_k x f(x) \\ \longrightarrow \text{sum of probabilities} \end{array}$$

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

$\langle E \rangle$ : internal energy : avg. energy of closed system.

## for continuous:

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

## Properties using Partition function 'Z':

for DISCRETE ENERGY STATES:

1) Internal Energy ($\langle E \rangle$)

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

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

differentiating w.r.t. $\beta$,

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

$$\Rightarrow \frac{-\partial \ln Z}{\partial \beta} = \sum_j E_j \left( \frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} \right) = \langle E \rangle$$

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

2.) Heat capacity $\left( \frac{\partial \langle E\rangle}{\partial T} \right.$ : rate of change of internal energy with ~~time~~ Temp $\left. \right)$.

We know that:

$$\frac{-\partial \ln Z}{\partial \beta} = \sum_j E_j \frac{e^{-\beta E_j}}{\underbrace{\sum e^{-\beta E_i}}_{Z}}$$

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

differentiating w.r.t. $\beta$,

$$\Rightarrow +\left[\frac{\partial Z}{\partial \beta}\cdot \frac{\partial \ln Z}{\partial \beta} + Z\frac{\partial^2}{\partial \beta^2}\ln Z\right] = +\sum_j E_j^2 e^{-\beta E_j}$$

$$\Rightarrow \frac{1}{Z}\cdot\frac{\partial Z}{\partial \beta}\cdot\frac{\partial \ln Z}{\partial \beta} + \frac{\partial^2 \ln Z}{\partial \beta^2} = \sum_j E_j^2 \underbrace{\left(\frac{e^{-\beta E_j}}{Z}\right)}_{P_i}$$

$$\Rightarrow \text{Now, } \frac{\partial \ln Z}{\partial \beta} = \left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right)$$

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

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

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

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

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

$$\Rightarrow \quad \langle (\Delta E)^2 \rangle = \frac{-\partial \langle E \rangle}{\partial T} \cdot \frac{\partial T}{\partial \beta}$$

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

$$\Rightarrow \quad \langle (\Delta E)^2 \rangle = \frac{+\partial \langle E \rangle}{\partial T} \cdot \left( \frac{+1}{\beta^2 k_B} \right)$$

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

$$\Rightarrow \quad \boxed{\frac{\partial \langle E \rangle}{\partial T} = \frac{1}{k_B T^2} \langle (\Delta E)^2 \rangle}$$

$\downarrow$

Heat Capacity.

3) Entropy & Free Energy

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

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

$$\Rightarrow \quad S = -k_B \sum_j \left[ \frac{e^{-\beta E_j}}{Z} \ln\left( \frac{e^{-\beta E_j}}{Z} \right) \right]$$

$$\Rightarrow \quad S = +k_B \sum_j \left( \frac{e^{-\beta E_j}}{Z} \left( +\beta E_j + \ln Z \right) \right)$$

$$\Rightarrow S = k_B \left( \beta \sum_j P_j E_j + \ln Z \sum_j P_j \right)$$

$$\Rightarrow S = k_B \left( \beta \langle E \rangle + \ln Z \right)$$

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

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

$$\Rightarrow TS = \langle E \rangle + k_B T \ln Z$$

$$\Rightarrow \boxed{\langle E \rangle - TS = -k_B T \ln Z}$$

Now, Gibb's free energy = $F$

$\therefore$ we know that

$$F = \langle E \rangle - TS$$

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

4) Pressure

$$\text{Pressure} = P = \frac{-\partial H}{\partial V} \left( \{\vec{x}\}, \{\vec{p}\} \right)$$

$$\langle P \rangle = -\sum_j P_j \, \underbrace{P(E_j)}_{\text{Pressure at energy } E_j}$$

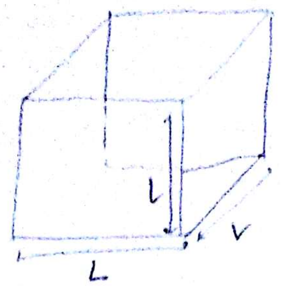
$$\langle P \rangle = \sum_j \frac{\partial E_j}{\partial V} \frac{e^{-\beta E_j}}{Z}$$

Now, $\dfrac{\partial \ln Z}{\partial V} = \dfrac{1}{Z} \dfrac{\partial Z}{\partial V} = \dfrac{1}{Z} \dfrac{\partial \left( \sum e^{-\beta E_i} \right)}{\partial V} = \sum_j \left( -\beta \left( \dfrac{\partial E_i}{\partial V} \right) \right) \dfrac{e^{-\beta E_j}}{Z}$

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

$$\Rightarrow \boxed{\langle P \rangle = k_B T \left( \frac{\partial (\ln Z)}{\partial \beta} \right)}$$

<u>Ideal-Gas System</u>:




N atoms,
Confined in volume $V = L^3$
Closed system.

Since ideal gas, $U(\{\vec{r}\}) = 0$

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

$$\Rightarrow Z = \frac{1}{h^{3N}} \iint_{\{\vec{r}\}\{\vec{p}\}} e^{-\frac{\beta}{2m} \sum_{i=1}^{N} \vec{p_i} \cdot \vec{p_i}} \, d\{\vec{p}\} \, d\{\vec{r}\}$$

$$Z_r = \int_{\{\vec{r}\}} d\{\vec{r}\} = \left( \int_x \int_y \int_z dz \, dy \, dx \right)^N = V^N$$

$$Z_p = \int_{\{\vec{p}\}} e^{-\frac{\beta}{2m} \left( \sum_{i=1}^{N} \vec{p_i} \cdot \vec{p_i} \right)} \, d\{\vec{p}\}$$

$$\Rightarrow Z_p = \int_{\{\vec{p}\}} e^{-\frac{\beta}{2m} \left( \sum_{i=1}^{N} p_{x_i}^2 + p_{y_i}^2 + p_{z_i}^2 \right)} \, d\{\vec{p}\}$$

These are 3N integrals of equal value

$$\Rightarrow Z_p = \left( \int_{-\infty}^{\infty} e^{-\frac{\beta}{2m} x^2} \, dx \right)^{3N}$$

$$\Rightarrow \quad Z_p = \left(\sqrt{\frac{2m\pi}{\beta}}\right)^{3N}$$

$$\Rightarrow \quad Z_p = \left(2\pi m k_B T\right)^{\frac{3N}{2}}$$

And, $Z = \frac{1}{h^{3N}} Z_x \cdot Z_p$

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

## Ideal Gas Equation:

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

$$\Rightarrow \quad \langle P \rangle = \frac{1}{\beta} \frac{\partial}{\partial V} \left( -\ln(h^{3N}) + N \ln V + \frac{3N}{2} \ln(2\pi m k_B T) \right)$$

$$\Rightarrow \quad \langle P \rangle = \frac{1}{\beta} \frac{\partial (N \ln V)}{\partial V}$$

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

$$\Rightarrow \quad \langle P \rangle V = \frac{N}{\beta} \qquad \left(\beta = \frac{1}{k_B T}\right)$$

$$\Rightarrow \quad \boxed{\langle P \rangle V = k_B N T}$$

↳ Ideal Gas equation

Similarly $Z$ (for continuous energy states) for

for $N=1$, 2D box

$$= \frac{1}{h^2} \iint_{\{p\}\{r\}} e^{-\frac{\beta}{2m}\sum p_i^2} \cdot d\{r\}\, d\{p\}$$

$$= \frac{1}{h^2} \cdot Z_r \cdot Z_p$$

$$Z_r = \left( \int_0^L \int_0^L dx\, dy \right)^1 = L^2$$

$$Z_p = \left( \int_{-\infty}^{\infty} e^{-\frac{\beta}{2m} p_x^2}\, dx \right)^2 = \left( \sqrt{\frac{2m\pi}{\beta}} \right)^2 = 2m k_B T \pi$$

$$\Rightarrow \boxed{Z = 2\pi \frac{L^2}{h^2} m k_B T.}$$

- In general, for $N$ particles in 3-D system

SAME AS IDEAL GAS.

$$Z = \sigma V^N \quad (\sigma \text{ does not depend on } V)$$

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

$$\Rightarrow \boxed{\langle P \rangle \cdot V = k_B T N}$$

<u>for ideal gas:</u>

$$\langle E \rangle = \frac{-\partial}{\partial \beta} \ln Z = \frac{-\partial}{\partial \beta} \left[ \ln \sigma + N \ln V \right]$$

$$\sigma = \left( 2\pi m k_B T \right)^{\frac{3N}{2}} = \left( \frac{2\pi m}{\beta} \right)^{\frac{3N}{2}}$$

$$\Rightarrow \langle E \rangle = \frac{-\partial}{\partial \beta} \left[ \frac{3N}{2} \ln (2\pi m) - \frac{3N}{2} \ln \beta + N \ln V \right]$$

$$\Rightarrow \langle E \rangle = \frac{+\partial}{\partial \beta}\left(\frac{3}{2}\ln\beta\right) + \left(-\frac{\partial}{\partial\beta}(N\ln V)\right)$$

$$\frac{\partial(\ln V)}{\partial\beta} = \frac{1}{V}\frac{\partial V}{\partial \beta} = \frac{1}{V}\underbrace{\frac{\partial V}{\partial T}}_{= 0 \text{ (assuming)}}\frac{\partial T}{\partial \beta}$$

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

$$C_v = \frac{\partial \langle E \rangle}{\partial T} = \frac{3Nk_B}{2}$$ Dulong Petit's law.

## Gibb's Paradox


$$S_1 + S_2 = S_3$$

$$S = k_B \sum_j P_j \ln(P_j)$$

$$\Rightarrow S = k_B\left[\ln(Z) + \beta\langle E \rangle\right]$$ (previously calculated)

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

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

$$S_1 = S_2 = S$$

$$S_3 = k_B\left[2N\ln 2V + 3N\ln(2\pi m k_B T) - 6N\ln h\right]$$

$$S_1 - S_2 = K_B[2N\ln 2V - 2N\ln V]$$
$$= K_B[2N\ln 2]$$

This does not follow the extensive property of entropy.

Reason: Over counting of same ~~pattern~~ particles (assuming them to be different)

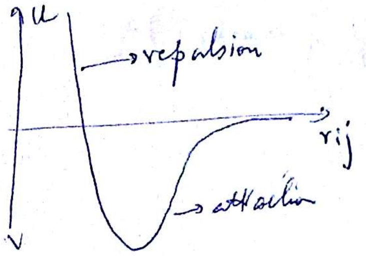
$$\therefore \boxed{Z_{correct} = \frac{Z}{N!}}$$

## Analysis of Real Gases:

$u(\{\vec{r}\}) \neq 0$

Energy b/w 2 particles $= u = 4\epsilon\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$

($\epsilon$: width of attraction region
$\sigma_{ij} = \sigma = \frac{\sigma_i + \sigma_j}{2}$
(diameter avg))




for minimum u,

$$\frac{du}{dr_{ij}} = 0 \Rightarrow 4\epsilon\left[\frac{12}{(r_{ij})^2}\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{11} + \frac{6}{(r_{ij})^2}\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{5}\right] = 0$$

$$\Rightarrow \boxed{r_{ij} = 2^{1/6}\sigma}$$

for $u = 0$, $\boxed{r_{ij} = \sigma}$

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

$$= \frac{1}{2m}\sum_{i=1}^{N}|p_i|^2 + U(\{\vec{r}\})$$

$U(\{\vec{r}\}) = U_{12} + U_{13} + \ldots U_{nn}$ (Pairwise P.E)

$$\rightarrow U(\{\vec{r}\}) = \frac{1}{2}\sum_{j=1}^{N}\sum_{\substack{k=1 \\ j\neq k}}^{n} U_{jk}$$

↳ to avoid repetition

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

$$Z = \frac{1}{h^{3N}} Z_K Z_U$$

$$Z_K = \frac{1}{N!}\int_{\{\vec{p}\}} e^{-\beta\frac{1}{2m}\sum_{i=1}^{N}\vec{p}_i^{\,2}}\, d\{\vec{p}\} = \frac{1}{N!}(2\pi m k_B T)^{\frac{3N}{2}}$$

$$Z_U = \int_{\{\vec{r}\}} e^{-\beta U(\{\vec{r}\})}\, d\{\vec{r}\}$$

For an ideal gas, $U(\{\vec{r}\}) = 0$

But now, $U(\{\vec{r}\}) \neq 0$

$$\langle U\rangle = \frac{\int_{\{\vec{r}\}} e^{-\beta U\{\vec{r}\}}\, U\{\vec{r}\}\, d\{\vec{r}\}}{\int_{\{\vec{r}\}} e^{-\beta U(\{\vec{r}\})}\, d\{\vec{r}\}} = -\frac{\partial}{\partial\beta}\ln(Z_U)$$

Lecture - 9

$\frac{\partial}{\partial \beta} \ln Z_U = -\langle U \rangle$ —— (1)

We know when $T \to \infty \Rightarrow \frac{1}{k_B T} \to 0$, real gas behaves as ideal gas

$$\therefore \lim_{T \to \infty} Z_U \longrightarrow V^N$$

(for real gas)

Integrating (1),

$$\Rightarrow \int_{\beta=0}^{\beta} \frac{\partial}{\partial \beta}(\ln Z_U)\, d\beta = -\int_0^{\beta} \langle U \rangle\, d\beta$$

$$\Rightarrow \ln(Z_U(\beta)) - \ln(Z_U(0)) = -\int_0^{\beta} \langle U \rangle\, d\beta$$

$$\Rightarrow \ln Z_U(\beta) - N \ln V = -\int_0^{\beta} \langle U \rangle\, d\beta$$

$\langle U \rangle = \frac{N(N-1)}{2} \langle u \rangle$ ; $\langle u \rangle$ = avg. energy per pair

$N \to \infty$, $V \to \infty$, $\langle U \rangle \approx \frac{N^2}{2} \langle u \rangle$

Now, $$\langle u \rangle = \frac{\int_{\vec{R}} e^{-\beta u(\vec{R})}\, u(\vec{R})\, d\vec{R}}{\int_{\vec{R}} e^{-\beta u(\vec{R})}\, d\vec{R}}$$ (3D integral)

$$\Rightarrow \langle u \rangle = \frac{-\partial}{\partial \beta} \left[ \ln \left( \int_{\vec{R}} e^{-\beta u(\vec{R})}\, d\vec{R} \right) \right]$$

Now, $\int_{\vec{R}} e^{-\beta u(\vec{R})} d\vec{R} = \int_{\vec{R}} \left(1 + e^{-\beta u(\vec{R})} - 1\right) d\vec{R}$

$$= \underbrace{\int_{\vec{R}} d\vec{R}}_{\text{integral over 3D space}} + \underbrace{\int_{\vec{R}} \left(e^{-\beta u(\vec{R})} - 1\right) d\vec{R}}_{I(\beta)}$$

$$= V + I(\beta)$$

$$\langle u \rangle = -\frac{\partial}{\partial \beta}\left(\ln\left(\int_{\vec{R}} e^{-\beta u(\vec{R})} d\vec{R}\right)\right)$$

$$\Rightarrow \langle u \rangle = -\frac{\partial}{\partial \beta} \ln\left(V + I(\beta)\right)$$

$$\Rightarrow \langle u \rangle = -\frac{\partial}{\partial \beta} \ln\left(V\left(1 + \frac{I(\beta)}{V}\right)\right)$$

$$\Rightarrow \langle u \rangle = \frac{-\partial \ln V}{\partial \beta} - \frac{\partial}{\partial \beta} \ln\left(1 + \frac{I}{V}\right)$$

as $V$ is fixed, $\frac{\partial \ln V}{\partial \beta} = 0$

$$\Rightarrow \langle u \rangle = \frac{-\partial}{\partial \beta} \ln\left(1 + \frac{I}{\beta}\right)$$

$$\ln\left(\frac{I}{V} + 1\right) \approx \frac{I}{V} + \dots$$

$$\Rightarrow \langle u \rangle = \frac{-\partial}{\partial \beta}\left(\frac{I}{V}\right) = -\frac{1}{V}\frac{\partial I}{\partial \beta}$$

$$\Rightarrow \langle U \rangle = \frac{N^2 \langle u \rangle}{2} = \frac{-N^2}{2V}\frac{\partial I}{\partial \beta}$$

$$\ln(Z_u) = N \ln V - \int_0^{\beta} \langle U \rangle \, d\beta$$

$$\Rightarrow \ln(Z_u) = N \ln V + \frac{1}{2}\frac{N^2}{V} I(\beta)$$

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

$$\Rightarrow \langle P \rangle = \frac{1}{\beta}\frac{\partial}{\partial V} \ln(Z_u)$$

$$\Rightarrow \langle P \rangle = \frac{1}{\beta}\left[ \frac{N}{V} + \frac{1}{2}\frac{N^2(-1)}{V^2} I(\beta) \right]$$

$$\Rightarrow \underbrace{\frac{\langle P \rangle}{k_B T} = \frac{N}{V}}_{\text{Ideal Gas}} - \underbrace{\frac{1}{2}\frac{N^2}{V^2} I(\beta)}_{\text{contraction}}$$

$$\Rightarrow \frac{\langle P \rangle}{k_B T} = \rho - \frac{1}{2}\rho^2 I \qquad \left(\rho = \frac{N}{V} = \text{density}\right)$$

In general,

$$\frac{\langle P \rangle}{k_B T} = \rho + B_1(T)\rho^2 + B_3(T)\rho^3 + \cdots$$

$\downarrow$

Virial Eq$^n$.