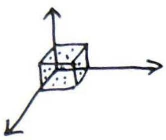
Stability – $G(T,P) = 0$: Gibb's Free energy

P, V, T : $\left.\dfrac{dV}{dP}\right|_T$: Compressibility

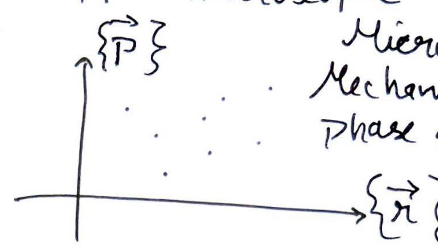
Normalize : $\dfrac{1}{V} \left.\dfrac{dV}{dP}\right|_T$

Matter $\longrightarrow$ Approach N particles. r, P – microscopic



$x_i, y_i, z_i \in [0, L]$

$r_i = (x_i, y_i, z_i)$



Microstates
Mechanical states
phase space

$N, V \to$ Finite or ∞.

- Total energy : Hamiltonian : $H(\{\vec{r}\}, \{\vec{P}\})$

ISOLATED : No exchange. H constant over time.

$$\frac{d}{dt} H(\{\vec{r}\}, \{\vec{P}\}) = 0$$

$$\sum_{i=1}^{N} \left\{ \frac{\partial H}{\partial \vec{r}_i} \cdot \frac{\partial \vec{r}_i}{\partial t} + \frac{\partial H}{\partial \vec{P}_i} \cdot \frac{\partial \vec{P}_i}{\partial t} \right\} = 0$$

$$\frac{\partial \vec{r}_i}{\partial t} = \left(\frac{\partial x_i}{\partial t}, \frac{\partial y_i}{\partial t}, \frac{\partial z_i}{\partial t} \right)$$

$$\left.\begin{aligned} \frac{\partial H}{\partial \vec{r}_i} &= -\frac{d\vec{P}_i}{dt} \\ \frac{\partial H}{\partial \vec{P}_i} &= \frac{d\vec{r}_i}{dt} \end{aligned}\right\} \text{Hamilton's Eqns.}$$

$\frac{d\vec{P}_i}{dt} \to$ Force

$\frac{d\vec{r}_i}{dt} \to$ Acceleration

$$H(\{\vec{r}\}, \{\vec{P}\}) = \underbrace{U(\{\vec{r}\})}_{\text{potential}} + \underbrace{K(\{\vec{P}\})}_{\text{kinetic.}}$$

thermal

$$\frac{d\vec{P}_i}{dt} = \frac{-\partial H}{\partial \vec{r}_i} = \vec{F}_i = \underset{-\partial U/\partial x_i}{\underset{\parallel}{F_{x,i}}}\,\hat{i} + \underset{-\partial U/\partial y_i}{\underset{\parallel}{F_{y,i}}}\,\hat{j} + \underset{-\partial U/\partial z_i}{\underset{\parallel}{F_{z,i}}}\,\hat{k}$$

$$= \frac{-\partial U}{\partial \vec{r}_i} \quad \text{as} \quad \frac{\partial K(\{\vec{P}\})}{\partial \vec{r}_i} = 0$$

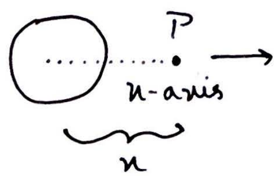
$\Omega(E_i)$: Number of cells with energy E_i.
System travel between such cells — microstate change

$$\boxed{\begin{aligned} &\text{Boltzmann Entropy: } S \propto \ln(\Omega(E_i)) \\ &S = K_B \ln(\Omega(E_i)) \end{aligned}}$$

$\Omega(E_i) \to 1$ for ice.

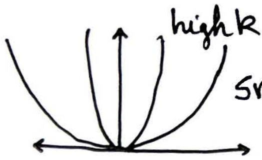
*

{1D : Harmonic Oscillator}



m : Mass of • atom.

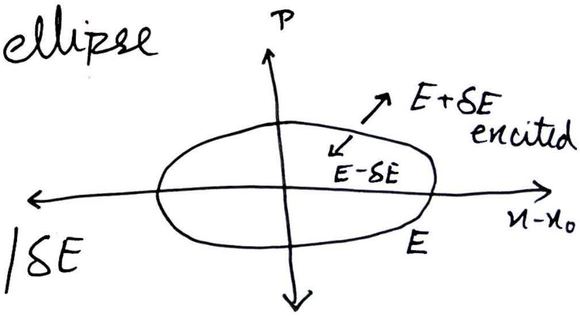
$$H(\{\vec{r}\}, \{\vec{P}\}) \longrightarrow H(x, P) = \underbrace{\frac{P^2}{2m}}_{\text{Kinetic}} + \underbrace{\frac{1}{2}k(x - x_0)^2}_{\text{Potential } U(x)} = E_{init} = E \text{ (const)}$$



high k → spring in train coaches

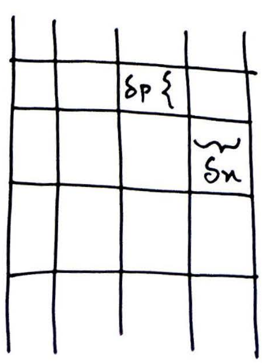
small k : ease of compression

$$\to \frac{P^2}{(\sqrt{2mE})^2} + \frac{(x - x_0)^2}{\left(\sqrt{\frac{2E}{k}}\right)^2} = 1 \quad \text{ellipse}$$



$\Omega(E)$ = circumference of ellipse / δE

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



Area

$= \delta x \cdot \delta p$

$= h$

→ Angular Momentum

{Ideal Gas} [Isolated] $H(\{\vec{r}\},\{\vec{p}\}) = \underbrace{U(\{\vec{r}\})}_{=\,0} + K(\{\vec{p}\})$

* Volume of 6N-dimensional cell $= \delta\{\vec{r}\}.\delta\{\vec{p}\}$

$$= \underline{\delta x_1\, \delta P_{x_1}}\ \underline{\delta y_1\, \delta P_{y_1}}\ \underline{\delta z_1\, \delta P_{z_1}} \ldots\ldots \underline{\delta x_N\, \delta P_{xN}}\ \underline{\delta y_N\, \delta P_{yN}}\ \underline{\delta z_N\, \delta P_{zN}}$$

$= h^{3N}$. $h \to 0$. Planck's Constant in Quantum

$\boxed{\Omega(E)}$ → All accessible microstates with energy E.

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

Dirac Delta Func – Indicator. 1 if $H = E$, 0 else

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

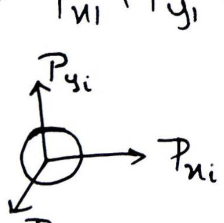
$$= \frac{1}{h^{3N}} . V^N \left[\int_{\{\vec{p}\}} \delta(H-E)\, \delta\{\vec{p}\} \right]$$

∴ Find $\vec{p}$'s such that:

$$\frac{P_{x1}^2}{2m} + \frac{P_{y_1}^2}{2m} + \cdots + \frac{P_{zN}^2}{2m} = E$$

$$\Rightarrow P_{x1}^2 + P_{y_1}^2 + \ldots + P_{zN}^2 = \left(\sqrt{2mE}\right)^2$$

As $H(\{\vec{r}\},\{\vec{p}\}) = \dfrac{\sum_{i=1}^{N} \vec{p}.\vec{p}}{2m}$



$\int_{\{\vec{p}\}} \delta(H-E)\,\delta\{\vec{p}\} \propto$ Surface Area of 3N-dime sphere of radius $\sqrt{2mE}$

$$\propto \left(\sqrt{2mE}\right)^{3N-1}$$

$$\propto E^{(3N-1)/2}$$

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

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

Relation: * $\frac{1}{2} m \langle v^2 \rangle = \frac{3N}{2} k_B \cdot T$.

keep T constant $\equiv$ keep average kinetic energy of system constant

$P[E_i] = P$[Finding system in a given energy level with energy E_i]

* $P[E_i] \propto e^{-\beta E_i}$, $\beta = 1/k_B \cdot T$

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

$$\left[\int_{\{\vec{r}\}} \int_{\{\vec{p}\}} P(\{\vec{r}\}, \{\vec{p}\})\, d\{\vec{r}\}\, d\{\vec{p}\} = 1\right]$$

integrating both sides.

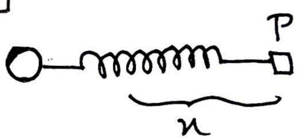
$$\underbrace{\int_{\{\vec{r}\}\{\vec{p}\}} P(\{\vec{r}\}, \{\vec{p}\})\, d\{\vec{r}\}\, d\{\vec{p}\}}_{=1} = \frac{1}{C} \int_{\{\vec{r}\}} \int_{\{\vec{p}\}} e^{-\beta H(\{\vec{r}\}, \{\vec{p}\})}\, d\{\vec{r}\}\, d\{\vec{p}\}$$

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

$\rightarrow$ Partition Function.

$\boxed{\text{Closed}}$

[Model – Harmonic Oscillator.]

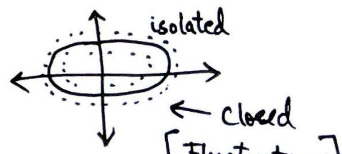


, Mass($\square$) = m

Constant T

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

$$P[x, p] \propto e^{-\beta E} = e^{-\frac{\beta}{2} k (x - x_0)^2} \cdot e^{-\beta p^2/2m}$$



$$\bar{Z} = \sum_{i=1}^{\text{number of microstates}} e^{-\beta E_i} \qquad \ln(Z) = \ln\left(\sum_i e^{(-\beta E_i)}\right)$$

Differentiate w.r.t β

$$\frac{\partial}{\partial \beta}(\ln Z) = \frac{1}{\sum_i e^{-\beta E_i}} \sum_i - E_i e^{-\beta E_i} = \frac{-1}{Z} \sum_i \left(E_i \cdot e^{-\beta E_i}\right) \quad \text{— (i)}$$

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

$$= \langle E \rangle$$ Internal energy

Mean total energy of the system

Variance : $\langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2$

$$\sum E_i \cdot e^{-\beta E_i} = - Z \frac{\partial}{\partial \beta}(\ln Z) \quad \text{— from (i)}$$

$$\hookrightarrow \frac{\partial}{\partial \beta}\left[\sum E_i \cdot e^{-\beta E_i}\right] = \frac{\partial}{\partial \beta}\left\{ - Z \frac{\partial}{\partial \beta}(\ln Z) \right\}$$

$$\Rightarrow \sum_i E_i \cdot (-E_i) e^{-\beta E_i} = -\left[\frac{\partial}{\partial \beta}(Z) \cdot \frac{\partial}{\partial \beta}(\ln Z) + Z \frac{\partial^2 (\ln Z)}{\partial \beta^2} \right]$$

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

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

$$\Rightarrow \sum_i E_i^2 \, P[E_i] = \left\{ \frac{\partial}{\partial \beta}(\ln Z) \right\}^2 + \frac{\partial^2}{\partial \beta^2}(\ln Z)$$

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

$$\Rightarrow \text{variance}(E) = \frac{\partial^2}{\partial \beta^2}(\ln Z).$$

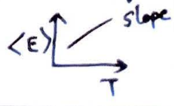
$$= -\frac{\partial}{\partial \beta}\left(-\frac{\partial}{\partial \beta} \ln Z\right) = -\frac{\partial}{\partial \beta} \langle E \rangle$$

$$= \frac{-\frac{\partial}{\partial T}\langle E \rangle}{\frac{\partial \beta}{\partial T}} = \frac{+\frac{\partial}{\partial T}\langle E \rangle}{+\frac{1}{K_B T^2}} = C_V . K_B . T^2$$

$$\beta = \frac{1}{K_B . T}$$

$$\frac{\partial \beta}{\partial T} = \frac{1}{K_B} \cdot \frac{-1}{T^2}$$

$$C_V = \frac{\partial}{\partial T} \langle E \rangle \ *$$



Closed : $S = -K_B \sum_i P_i \ln P_i$

$\hookrightarrow P$[finding system in ith microstate]

{Isolated : $S = K_B \ln(\Omega)$}

Closed : $P_i = \dfrac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} = \dfrac{e^{-\beta E_i}}{Z}$

{Isolated : $P_i = \dfrac{1}{\Omega}$}

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

$$= -K_B \sum_i P_i (-\beta E_i - \ln Z)$$

$$= K_B . \beta \sum_i P_i E_i + K_B \sum_i \ln Z \, P_i$$

$$= K_B . \beta . \langle E \rangle + K_B . \ln Z$$

$$= \cancel{K_B} . \frac{1}{\cancel{K_B} . T} \langle E \rangle + K_B \ln Z$$

$$\Rightarrow S = \frac{\langle E \rangle}{T} + K_B \ln(Z)$$

$$\Rightarrow \langle E \rangle - TS = -K_B T . \ln(Z)$$

$$\downarrow$$

$$U - TS = -K_B . T . \ln(Z)$$

Helmholtz Free Energy $A = U - TS = -K_B . T . \ln(Z)$.

Defn: Pressure of system at microstate i. $\mathbb{P}_i = -\frac{\partial}{\partial V} E_i$

$$\langle \mathbb{P} \rangle = \underbrace{\sum_i \mathbb{P}_i P_i = \frac{1}{\beta} \frac{\partial}{\partial V} (\ln Z)}$$

$$\left[\begin{aligned} &= \sum_i -\frac{\partial}{\partial V} E_i \cdot P_i = -\frac{\partial}{\partial V} \sum E_i \cdot P_i = -\frac{\partial}{\partial V} \langle E \rangle \\ &= -\frac{\partial}{\partial V}\left(-\frac{\partial}{\partial \beta} \ln Z\right) = \frac{\partial^2}{\partial V \, \partial \beta} (\ln Z) \end{aligned} \right]$$

Closed: Ideal Gas:

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

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

$$= \frac{1}{h^{3N}} \underbrace{\int_{\{\vec{r}\}} d\{\vec{r}\}}_{V^N} \cdot \int_{\{\vec{p}\}} e^{-\beta \left[\frac{1}{2m} \sum_i \vec{P}_i \cdot \vec{P}_i\right]} d\{\vec{p}\}$$

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

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

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

$\therefore$ $\langle \mathbb{P} \rangle V = N K_B T$
ideal gas eqn of state.

$$\left[I = \int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}} \right]$$