Partition Function

"Counts # states in a system"

Microcanonical

System w/ constant N, V, E

E.g. follows Hamilton's equations

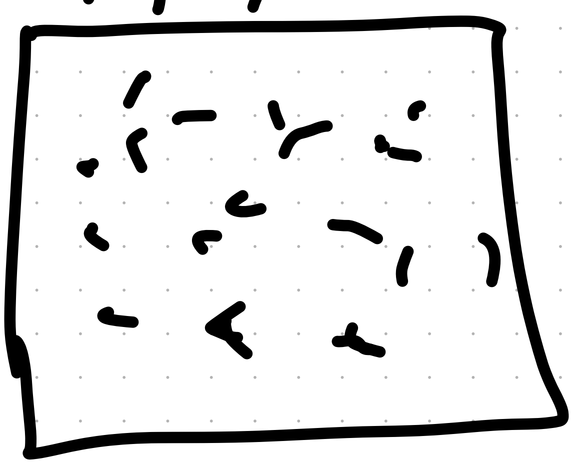
Every state w/ E equally likely

$$\Omega(N, V, E) \propto \int d\vec{X}\ \underbrace{\delta(\mathcal{H}(\vec{X}) - E)}_{\text{units } \frac{1}{E}}$$

$$d\vec{X} = \underbrace{dq_1 dq_2 \dots dq_{3N}\ dp_1 dp_2 \dots dp_{3N}}$$

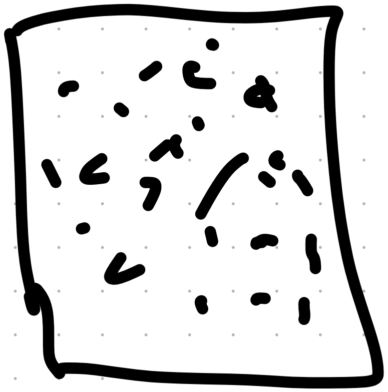
prefactor $\dfrac{E_0}{N!\,h^{3N}}$

N, V, E



Isolated N particles

Connected to thermodynamics:



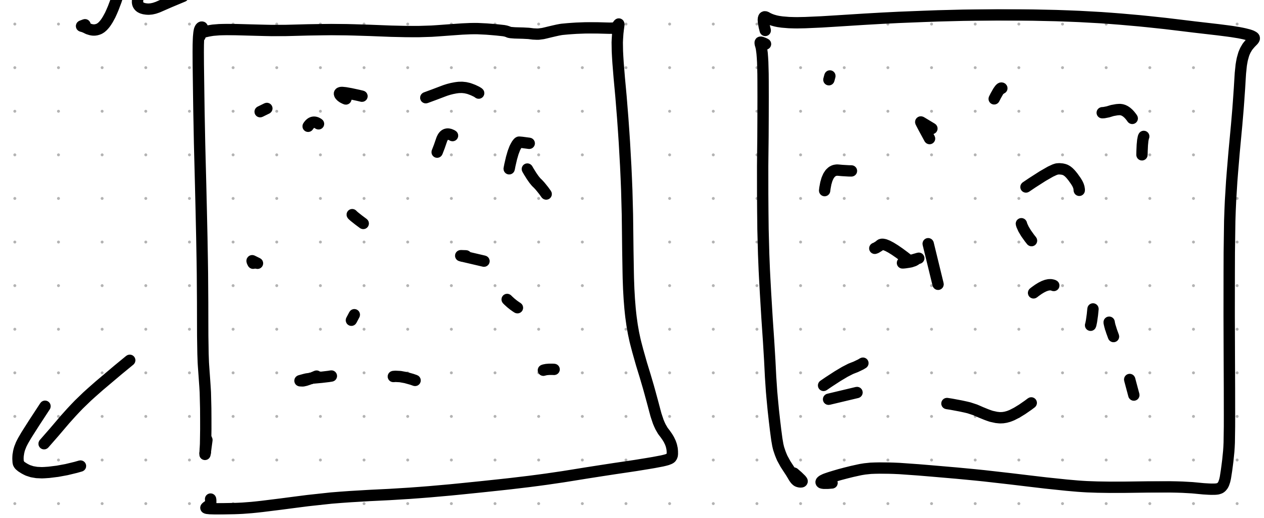
has $\Omega(N, V, E)$ states

N, V, E

<u>Isolated</u>

2 copies

Ω Ω



N, V, E N, V, E

$$\Omega(\overset{N_1+N_2}{2N}, \overset{V_1+V_2}{2V}, \overset{E_1+E_2}{2E}) = \Omega(\overset{N_1,\ V_1,\ E_1}{N, V, E}) \cdot \Omega(\overset{N_2\ V_2\ E_2}{N, V, E})$$

Extensive function:

Eg Energy, Entropy

multiply by X if X copies

$$\Omega(2N, 2V, 2E) = f\big(\underbrace{\Omega(N, V, E)}\,\Omega(N, V, E)\big)$$

$$f(\quad) = 2\, f(\quad)$$

$$f(x^2) = 2 f(x)$$

* logarithm

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

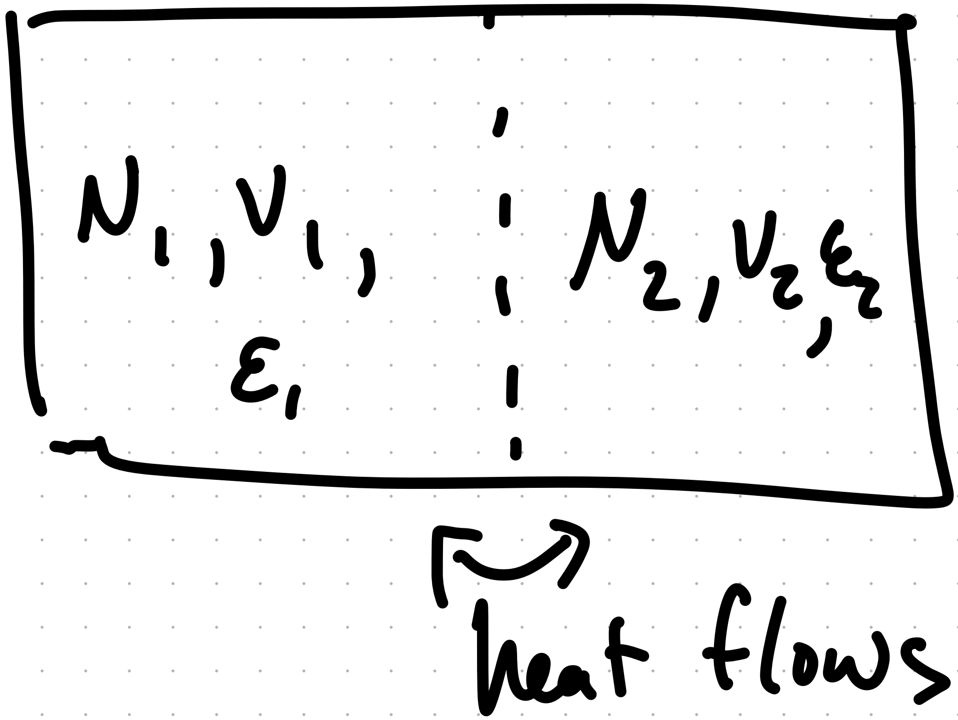
entropy

$$\Omega(N_1 + N_2, V_1 + V_2, E_1 + E_2)$$

$$= \Omega(N_1, V_1, E_1)\,\Omega(N_2, V_2, E_2)$$

$$\log(\;) = \log \Omega(N_1, V_1, E_1)$$

$$+ \log \Omega(N_2, V_2, E_2)$$



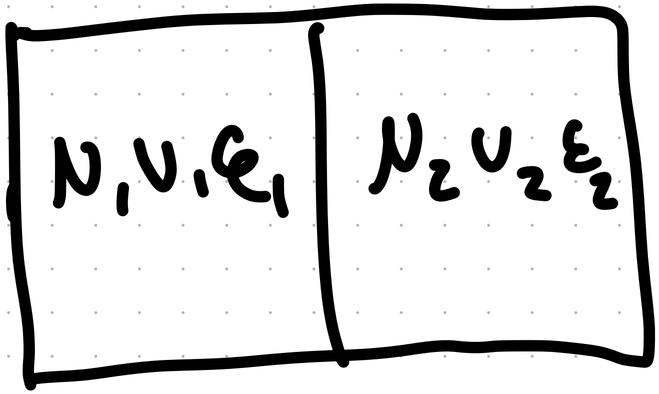
$\mathcal{E}_{total} = \mathcal{E}_1 + \mathcal{E}_2$

constant

$\mathcal{E}_1$ can be $0 \rightarrow \mathcal{E}_1 + \mathcal{E}_2$

Which $\mathcal{E}_1, \mathcal{E}_2$ most likely

$\Rightarrow$ most states $\Rightarrow$ biggest Ω



Max Ω

$$\frac{d\Omega}{dE_1} = 0$$

also do $\dfrac{d\log(\Omega)}{dE_1} = 0$

b/c log is monotonically increasing function

$= \Omega_{left}\,\Omega_{right}$

$$0 = \left(\frac{d\log\Omega(N_1+N_2,\, V_1+V_2,\, E_1+E_2)}{dE_1}\right)_{N_1, V_1, N_2 V_2}$$

$$0 = \left(\frac{d \log \Omega(N_1, V_1, E_1)}{dE_1}\right)_{N_1, V_1} + \left(\frac{d \log \Omega(N_2, V_2, E_2)}{dE_1}\right)$$

const $N_2\ V_2$

$$-\left(\frac{d \log \Omega(N_2, V_2, E_{tot} - E_1)}{dE_1}\right)_{N_2, V_2} = \left(\frac{d \log \Omega(N_1, V_1, E_1)}{dE_1}\right)_{N_1, V_1}$$

$$E_2 = E_{tot} - E_1$$

$$dE_2 = -dE_1$$

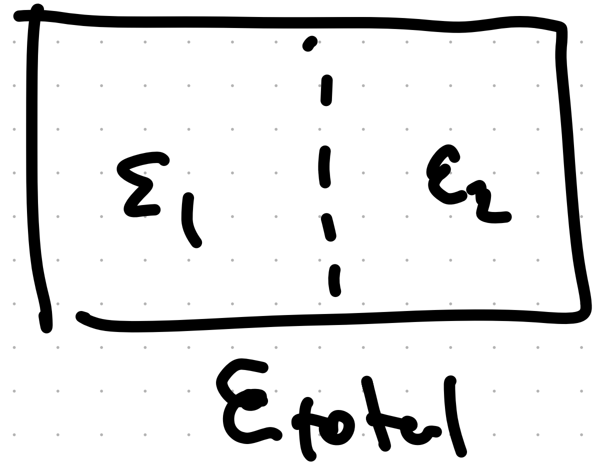
$$\left(\frac{d \log \Omega(N_2, V_2, E_2)}{dE_2}\right)_{N_2, V_2} = \left(\frac{d \log \Omega(N_1, V_1, E_1)}{dE_1}\right)$$

when # states is maximized
then this is true

heat flows until $\left(\frac{d \log \Omega}{dE}\right)_{N,V}$ is equal

heat flows until temperature
is equal

Classical thermo



$$\frac{1}{T} = \left(\frac{\partial S}{\partial \varepsilon}\right)_{N,V}$$

$$S(N, V, \varepsilon) = k_B \log \Omega(N, V, \varepsilon)$$

① 2 bodies in contact equalize $1/T$ at eq.

② Entropy is maximized for a closed system at eq.

Basic thermo reminder

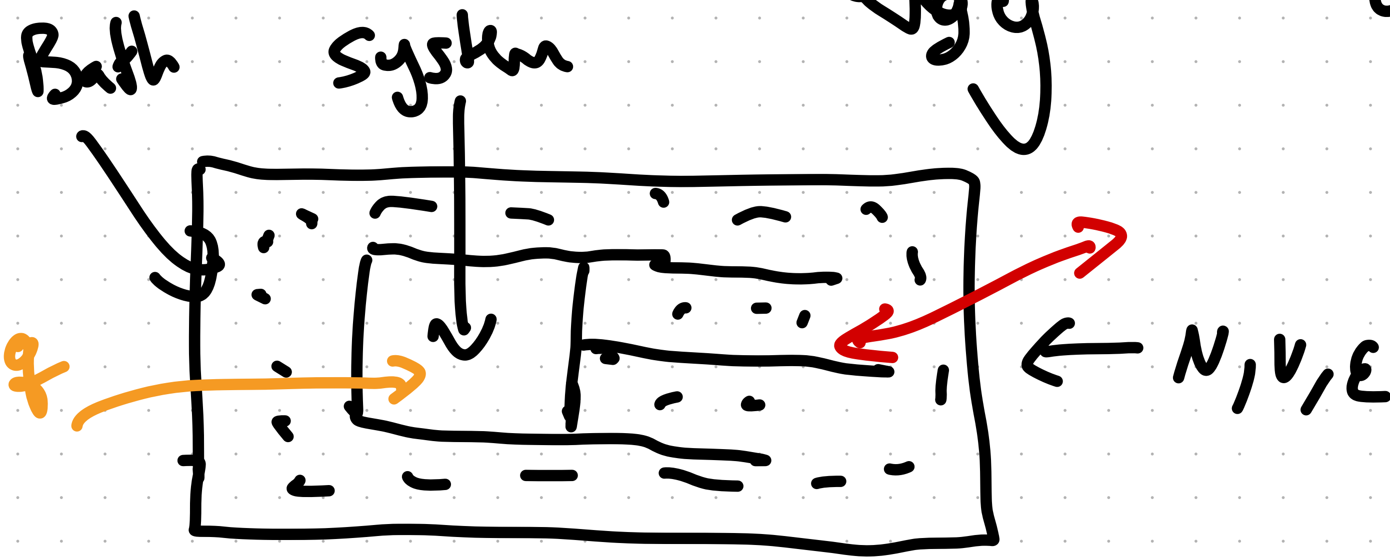
1st law — conservation of energy

$$dE = \delta q - \delta w$$

dE ← change in energy

δq ← heat into system

δw ← done by the system



$$d\mathcal{E} = \delta q - \delta w \Big\} \; q, w \text{ are not}$$

Energy is a "state function"

Path from state a to b

$$\int_a^b d\mathcal{E} = \mathcal{E}_b - \mathcal{E}_a = \int_a^b (\delta q - \delta w)$$

$$\delta w = -P d\underline{V} + \mu d\underline{N}$$

2nd law of thermo

① heat is not a state function

Exists "S" $= \delta q / T$

this is a state function

$$S(b) - S(a) = \int_a^b \delta q / T$$

for any path

(2) quasistatic process

Isolated system

(no heat flow)

$$\Delta S = 0$$

(3) non quasistatic process

$$\Delta S \geq 0$$

$$dS = \frac{\delta q}{T} = \frac{dE}{T} + \frac{\delta w}{T}$$

$$dE = \delta q - \delta w$$

Chain rule

$S(N, V, E)$

$$\frac{\partial S}{\partial x} = \frac{\partial S}{\partial N}\frac{\partial N}{\partial x} + \frac{\partial S}{\partial V}\frac{\partial V}{\partial x} \cdots$$

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

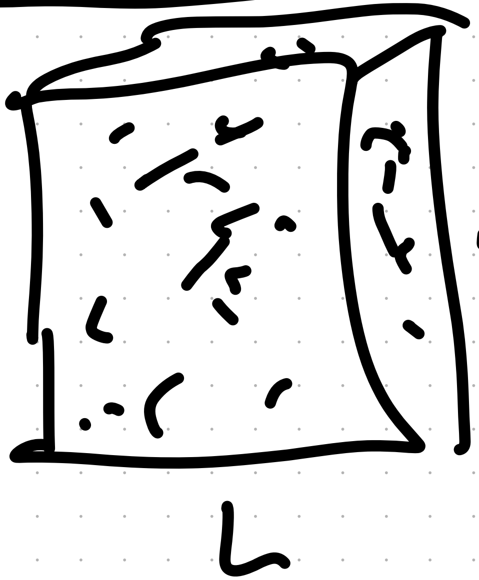
$$dS = \left(\frac{\partial S}{\partial N}\right)_{V,E} dN + \left(\frac{\partial S}{\partial V}\right)_{N,E} dV + \left(\frac{\partial S}{\partial E}\right)_{N,V} dE$$

$$dS = \left(\frac{1}{T}\right) dE + \underbrace{\frac{1}{T}\delta w}_{+\frac{P}{T}dV - \frac{\mu}{T}dN}$$

$$\left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T} \qquad \left(\frac{\partial S}{\partial V}\right)_{N,E} = P/T$$

$$\left(\partial S/\partial N\right)_{V,E} = -\mu/T$$

Microcanonical Ensemble



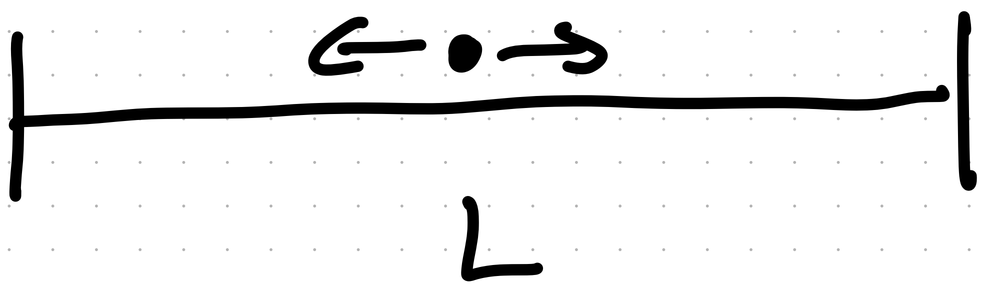
N, V, E

$V = L^3$

$S = ?$

ideal gas

$\mathcal{H} = KE = \sum p_i^2/2m$



q, p

$\mathcal{H} = p^2/2m$

$$\Omega = C \underbrace{\int_0^L dq}\int_{-\infty}^{\infty} dp \; \delta\big(\underbrace{\mathcal{H}((q,p)}_{p^2/2m} - \varepsilon\big)$$

$$= CL \int_{-\infty}^{\infty} dp \; \delta\left(\frac{p^2}{2m} - \varepsilon\right)$$

$$p = \sqrt{2m}\, y \qquad dp = \sqrt{2m}\, dy$$

$$= \sqrt{2m}\, CL \int_{-\infty}^{\infty} dy \; \delta(y^2 - \varepsilon)$$

$$= \sqrt{2m}\, CL \int_{-\infty}^{\infty} dy\, \delta(y^2 - \varepsilon)$$

[Appendix A.15 $\quad \delta(x^2 - a^2) = \frac{1}{2|a|}\left[\delta(x-a) + \delta(x+a)\right]$

$$\delta(f(x)) = \sum_{\substack{k \\ \text{roots}}} \frac{\delta(x - x_k)}{|f'(x_k)|}$$]

$$= \sqrt{2m}\, CL \cdot \frac{1}{2\sqrt{\varepsilon}} \int_{-\infty}^{\infty} dy \left[\delta(y - \sqrt{\varepsilon}) + \delta(y + \sqrt{\varepsilon})\right]$$

$$= \sqrt{\frac{2m}{\varepsilon}} \cdot L \cdot \underbrace{C}_{\frac{\varepsilon_0}{(1)! \cdot h'}} = \frac{\varepsilon_0 L}{h} \sqrt{2m/\varepsilon}$$

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

$$[\quad \int_{-\infty}^{\infty} \delta(y \pm \sqrt{\varepsilon})\, dy = 1$$

$$\mathcal{H} = \sum_{i=1}^{N} \vec{p}_i^{\,2}/2m \quad \text{in 3d}$$

$$\Omega(N, V, E) = \frac{E_0}{h^{3N} N!} \int_{-\infty}^{\infty} dp_1\, dp_2 \cdots dp_{3N} \int_0^{L} dq^{3N}$$

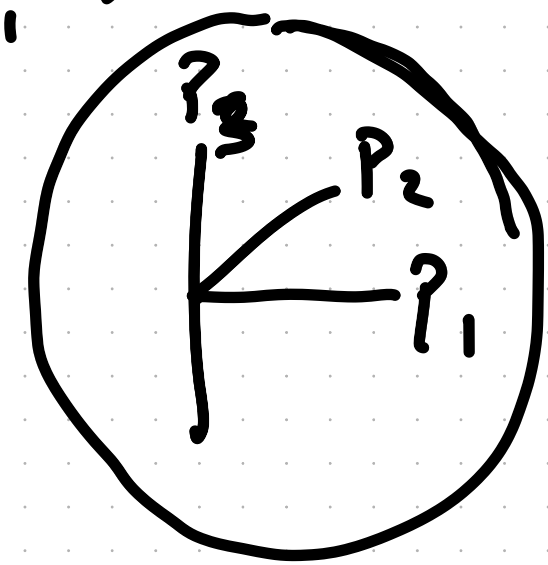
$$\delta\left(\sum_{i=1}^{N} p_i^2/2m - E\right)$$

$$\int_0^L dq^{3N} = \int_0^L dq_1 \int_0^L dq_2 \cdots \int_0^L dq_{3N} = L^{3N} = \left(L^3\right)^N$$

$$= V^N$$

$$\Omega = \frac{\varepsilon_0 V^N}{h^{3N} N!} \int_{-\infty}^{\infty} dp^{3N}\, \delta\left(\sum \frac{p_i^2}{2m} - E\right)$$

$$p_i = \sqrt{2m}\, y_i$$



large N

$$\Omega \approx \frac{\varepsilon_0}{N!}\left[V\left(\frac{4\pi m E e}{3N}\right)^{3/2}\right]^N$$

$$\Omega \approx \frac{\varepsilon_0}{N!}\left[V\left(\frac{4\pi m \varepsilon e}{3N}\right)^{3/2}\right]^N$$

$$S = k_B \ln \Omega$$

$$\frac{1}{k_B T} = \frac{\partial \ln \Omega}{\partial \varepsilon} = \frac{\partial \ln\left(\varepsilon^{3N/2}\right)}{\partial \varepsilon} + \cancelto{0}{\frac{\partial \ln(\;)}{\partial \varepsilon}}$$

$$= \frac{3}{2} N \frac{\partial \ln \varepsilon}{\partial \varepsilon} = \frac{3N}{2\varepsilon}$$

$$\Rightarrow \quad \varepsilon = \frac{3}{2} N k_B T = \frac{3}{2} nRT$$

$$\Omega \approx \frac{\varepsilon_0}{N!}\left[V\left(\frac{4\pi m \varepsilon e}{3N}\right)^{5/2}\right]^N$$

$$P/T = \left(\frac{\partial S}{\partial V}\right) = k_B \frac{\partial \log \Omega}{\partial V}$$

$$= k_B \frac{\partial \log (V^N)}{\partial V}$$

$$= k_B N \cdot \frac{\partial \log V}{\partial V} = \frac{k_B N}{V}$$

$$\Rightarrow \boxed{PV = N k_B T}$$