Lecture 8 - Second law & Boltzmann Entropy

Carnot cycle: $\sum q_i^{rev}/T_i = 0$

Suggests $dS = dq^{reversible}/T$

Heat produced by a process, can't be less than the reversible path

(Isolated system) $dS \geq dq/T \iff \Delta S_{A\to B} \geq \int_{A\to B} dq/T$

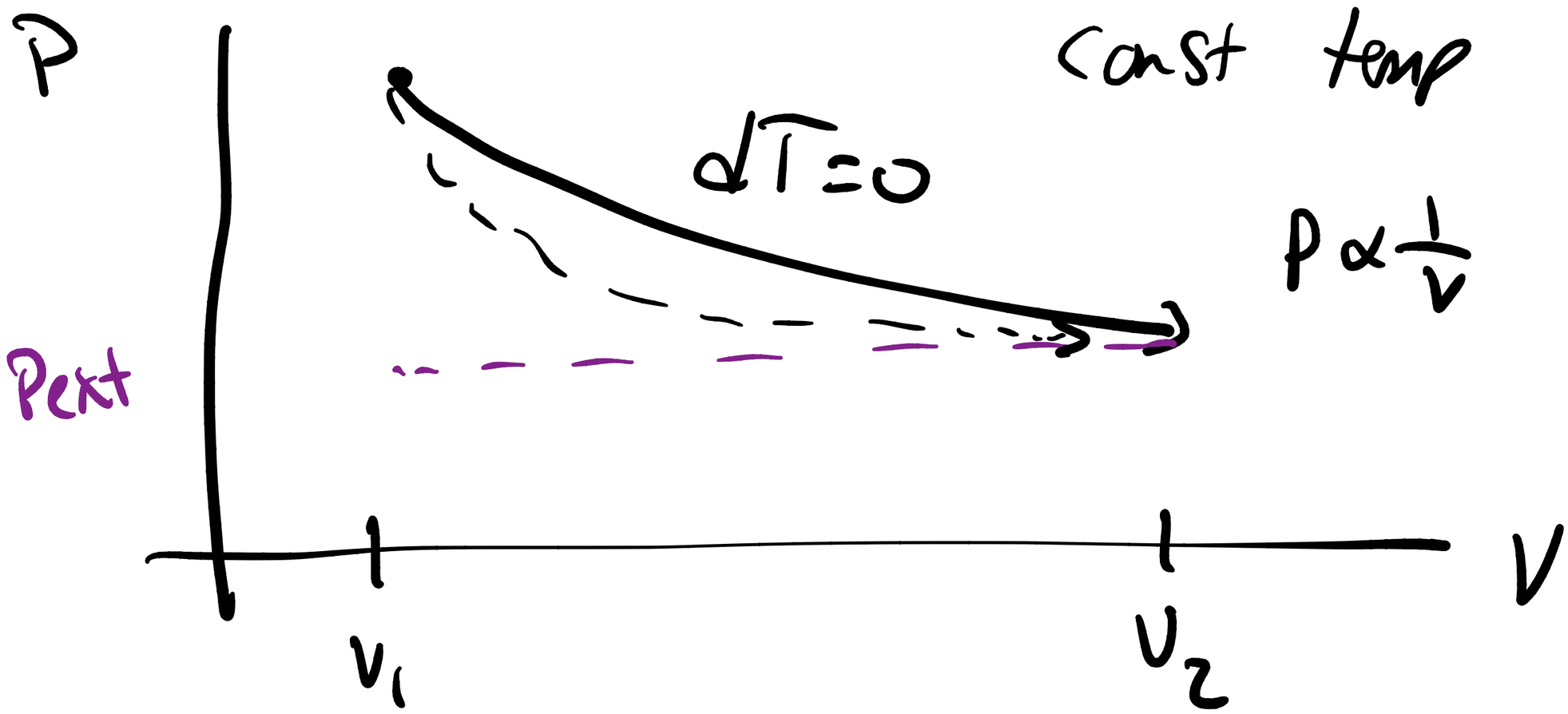
[Second law of thermodynamics]

What is an irreversible process?

Reversible $A \to B$, infinitely small steps

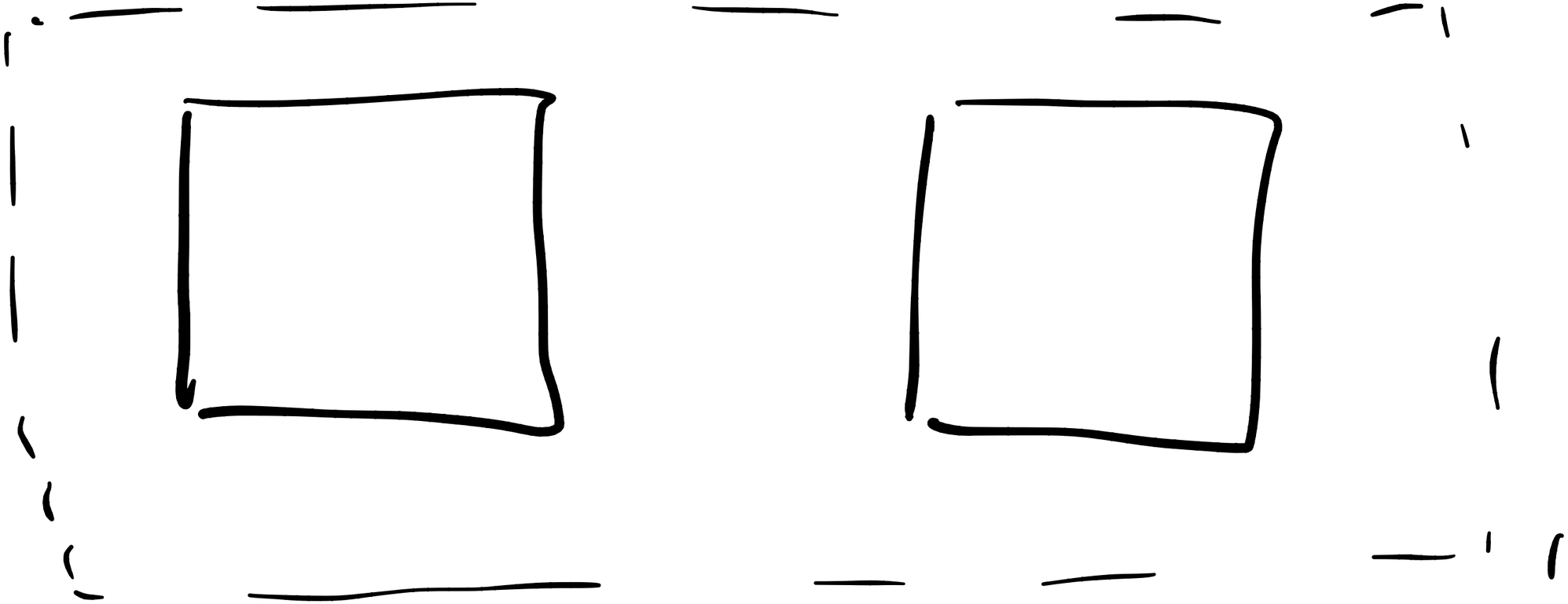
Suddenly change the conditions

Usually lose energy to heat/friction



Work has to be less ←

Spontaneous process → moving to equilibrium



$$dE = dq + dw$$

$$dq_1 = -dq_2$$

$$dS = \frac{dq_1^{rev}}{T_1} + \frac{dq_2^{rev}}{T_2} = dq_1^{rev}\underbrace{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}_{\text{sign?}}$$

sign?

Postulate: heat goes from hot to cold

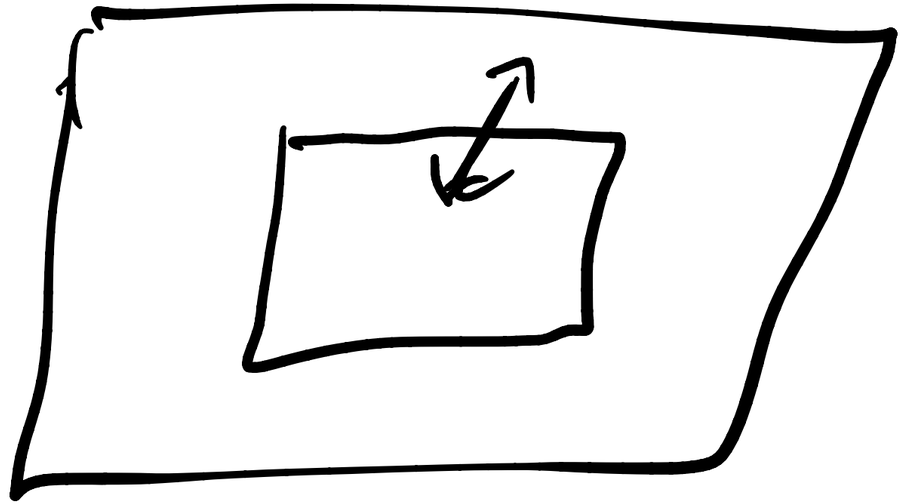
if $T_1 > T_2$, $dq_1 < 0$ & $\frac{1}{T_1} - \frac{1}{T_2} < 0$ $\Big\}$ $dS > 0$

if $T_1 < T_2$, $dq_1 > 0$ & $\frac{1}{T_1} - \frac{1}{T_2} > 0$

At equilibrium $dS = 0$

Spontaneous in isolation: $dS > 0$ ← entropy is produced

Consider non-isolated:



$$dS_{sys} = dS_{produced} + dS_{exchange}$$

$$= dS_{prod} + dq/T$$

for reversible change

$$dS = dq^{rev}/T$$

everything else $dS_{prod} > 0$

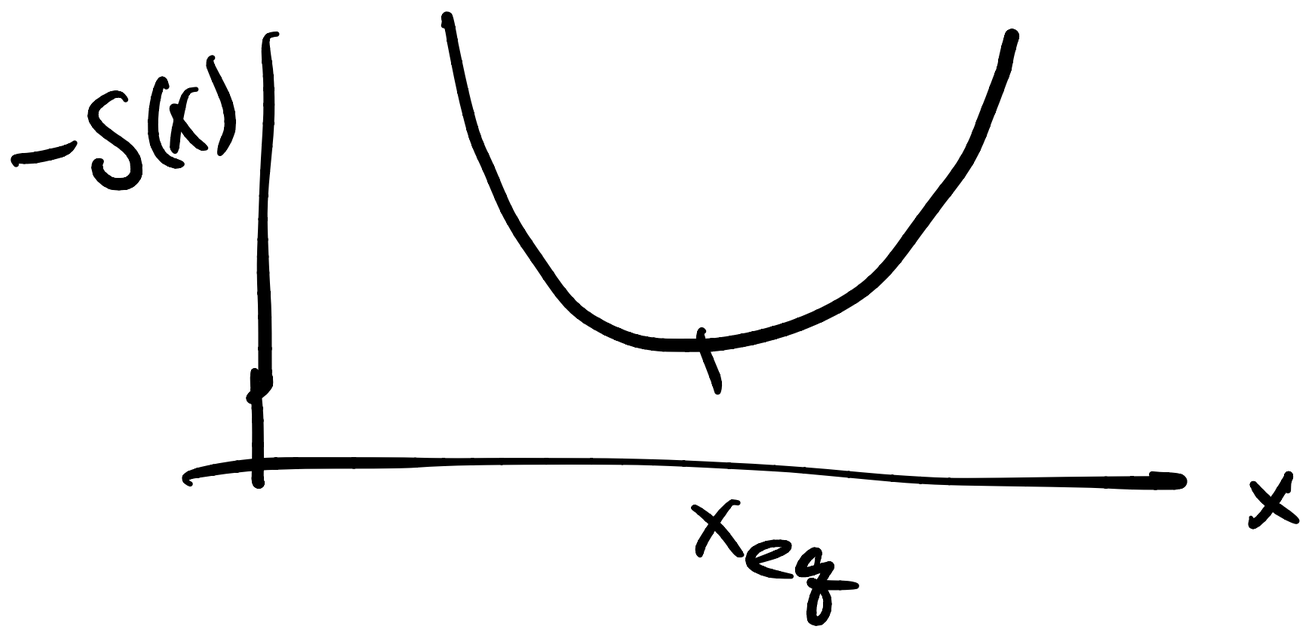
so $dS \geq dq^{rev}/T$

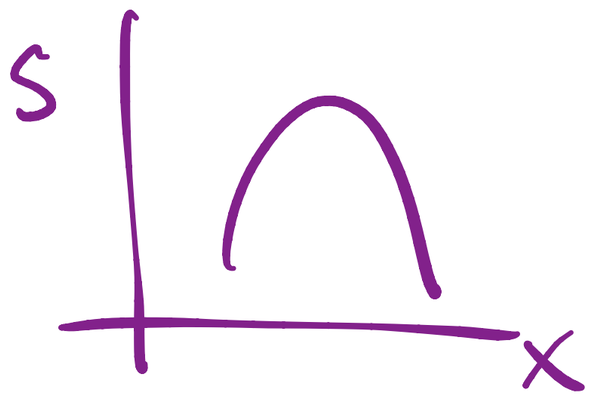
Universe is an isolated system

$$dS_{universe} \geq 0$$ for any process

preview because entropy is always increasing for isolated system

$-S$ kind of like a "potential" for a process or reaction





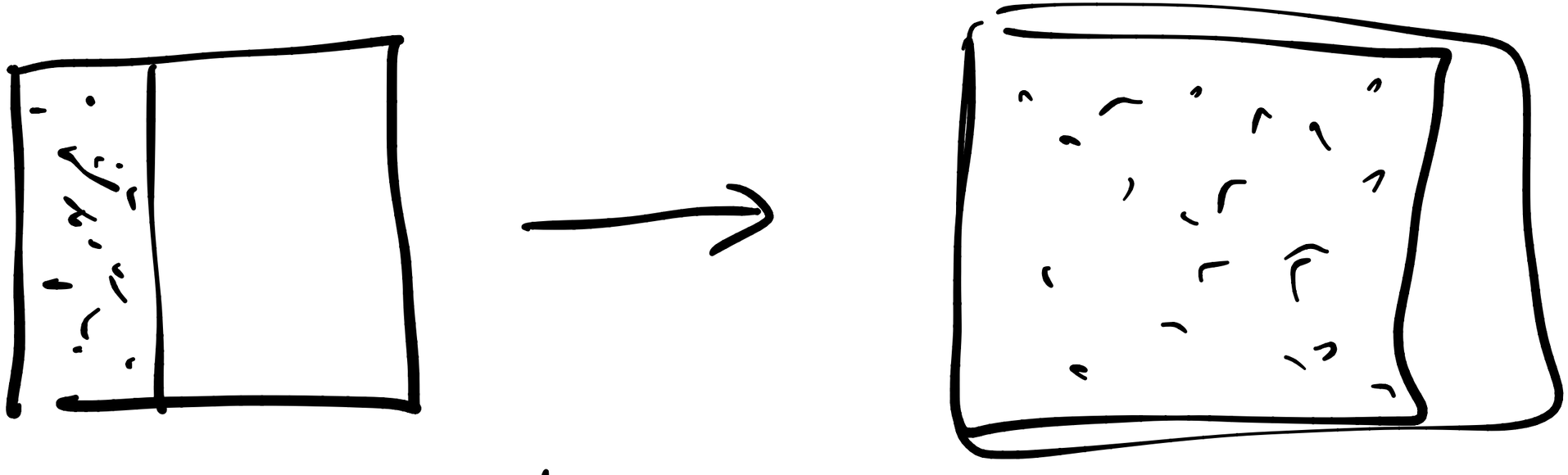
← progress

Molecular interpretation:

Entropy = disorder ?

Boltzmann wanted to connect

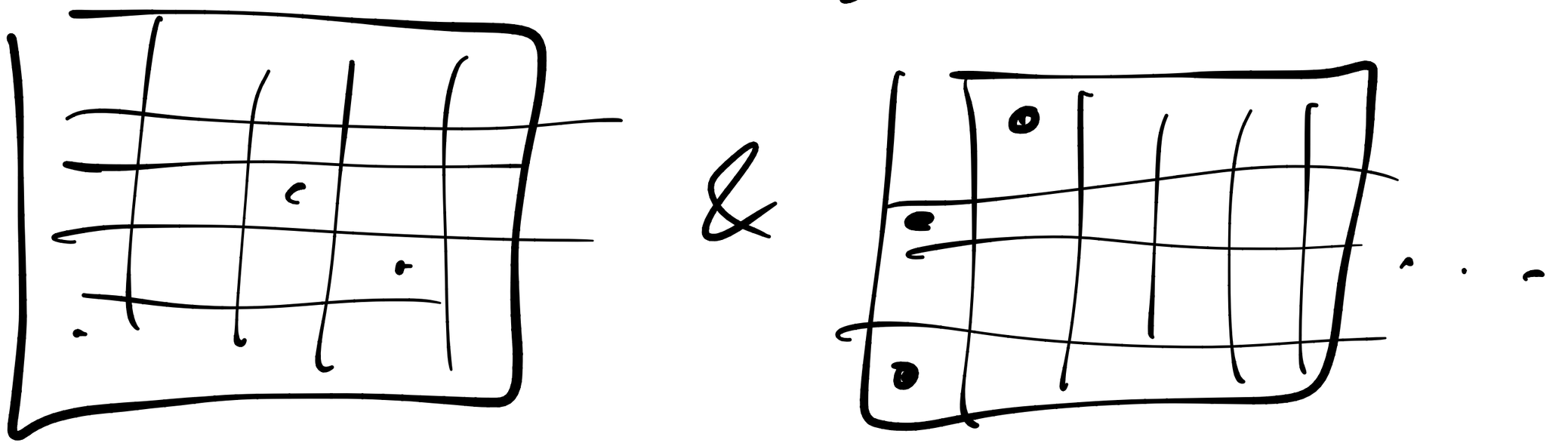
Molecular motion → thermodyamics



Seems to violate mechanics

Solution to paradox:

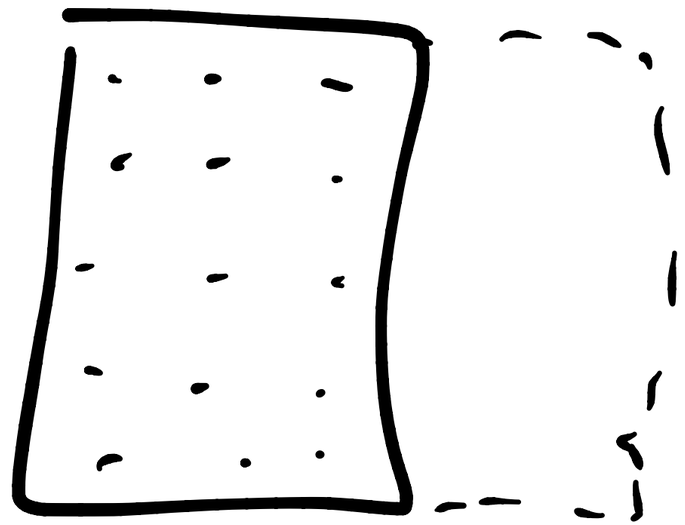
postulate: every state w/ same energy is equally likely for an isolated system



etc

N molecules in a box of volume V $\leftrightarrow$ N_V

why is it that



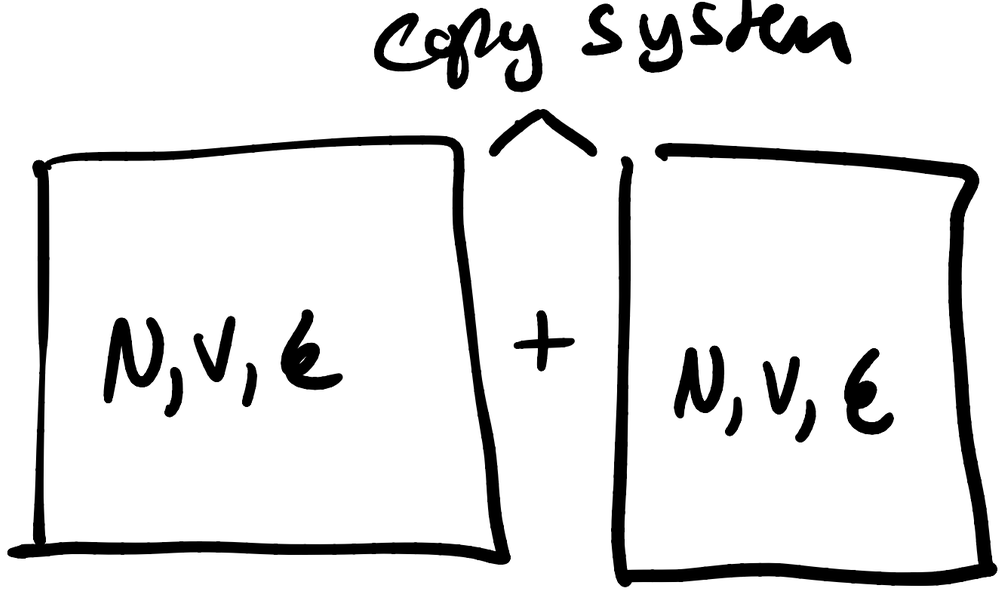
why do molecules expand?

"microstates" → observable like density

↳ system tries to increase # of states

↳ entropy increases

Is # states like entropy, Ω



Ω is not extensive. N, V, ϵ, S double

$$\Omega(\text{State 1} + \text{State 2}) = \Omega(\text{State 1}) \cdot \Omega(\text{State 2})$$

What if $S \propto \log \Omega$

$S = k \ln \Omega$ $\pm$ ~~$\frac{1}{2}$~~ ← not here

if only 1 state, $S = 0$

k turns out to be $R/N_A = k_B$

see this by driving ideal gas law

On HW: M molecule in N sites
can't overlap, $\Omega = \binom{N}{M}$

Simpler case, m molecules in N sites

can go anywhere:

$$\Omega = N \times N \times N \cdots = N^m$$

(if distinguishable

$\left(\frac{N^m}{m!}\right)$ ndish

$$S = k \ln \Omega = m k \ln N$$

$$= nR \ln N \Leftarrow nR \ln V$$

$$S(V_2) - S(V_1) = nR \ln (N_2/N_1) \quad \ldots$$

1st law $$dE = dQ + dW$$

$$= TdS - PdV$$

$$dS = \frac{1}{T}dE + \frac{P}{T}dV$$

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

$S = nR\ln V$

$$\frac{nR}{V} = \frac{P}{T} \Rightarrow PV = nRT$$

$k = R/N_A$