

Lecture 8 - Second law & Boltzmann Entropy

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

Suggests $dS = \frac{dq_{\text{reversible}}}{T}$

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

$$\text{(Isolated system)} \quad dS \geq dq/T \quad \Leftrightarrow \quad \Delta S \geq \int_{A \rightarrow B} dq/T$$

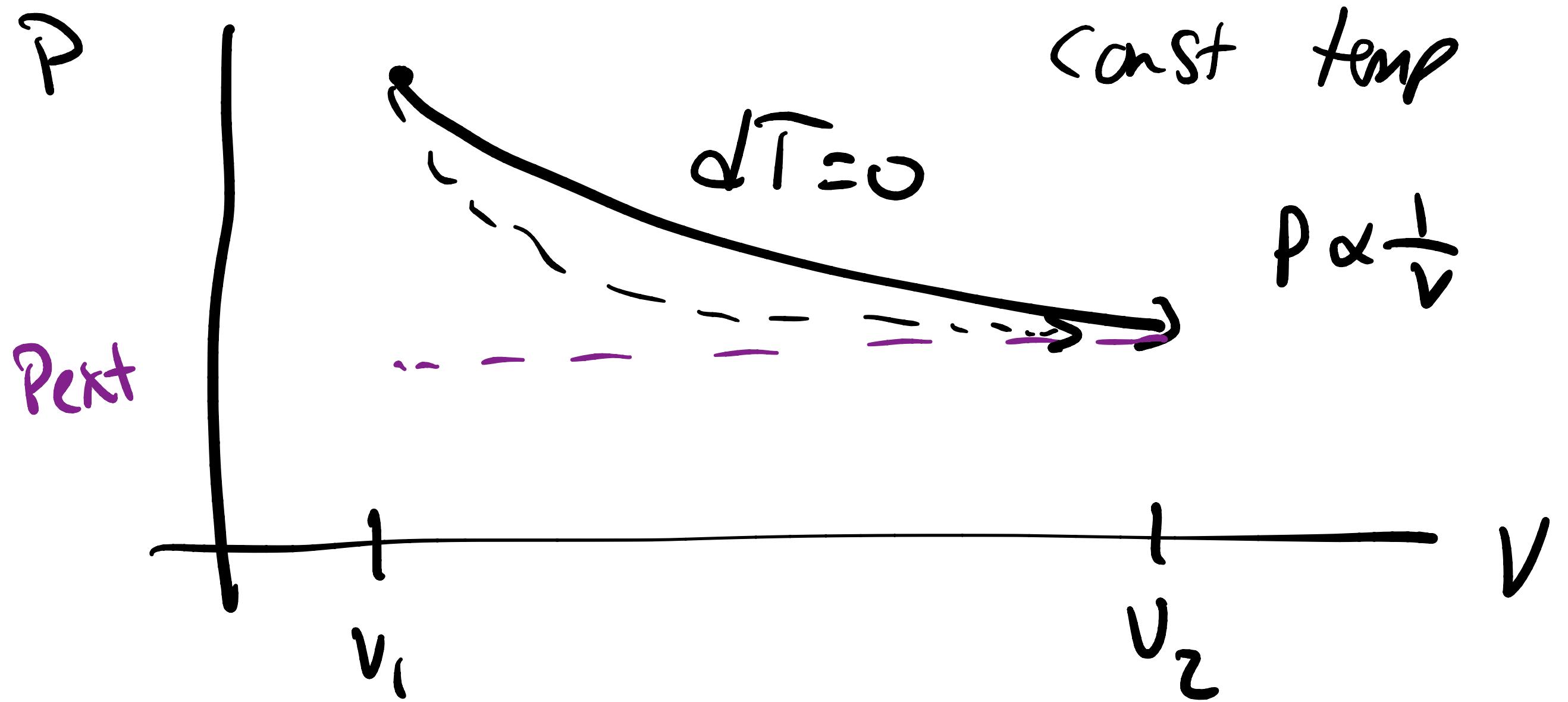
[Second law of thermodynamics]

What is an irreversible process?

Reversible $A \rightarrow B$, infinitely small steps

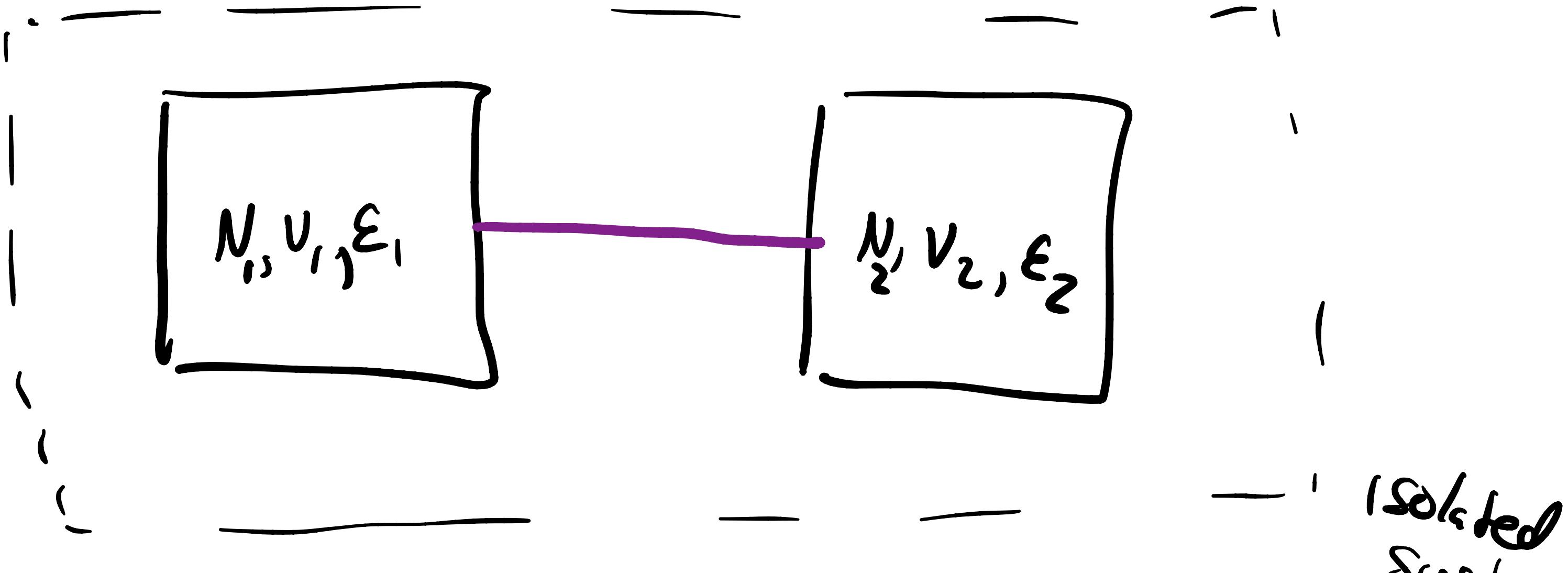
Suddenly change the conditions

Usually lose energy to heat/friction



Work has to be less \leftarrow

Spontaneous process \rightarrow moving to equilibrium



$$\epsilon_{\text{total}} = \epsilon_1 + \epsilon_2$$

also, $d\omega = 0$
isolated system

$$d\epsilon_{\text{total}} = 0 = d\epsilon_1 + d\epsilon_2 \Rightarrow d\epsilon_1 = -d\epsilon_2$$

$$dE = dg + d\omega$$

$$dg_1 = -dg_2$$



$$dS = \frac{dg_1^{\text{rev}}}{T_1} + \frac{dg_2^{\text{rev}}}{T_2} = dg_1^{\text{rev}} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

\underbrace{\hspace{10em}}_{\text{Sign?}} \quad \underbrace{\hspace{10em}}_{\text{Sign?}}

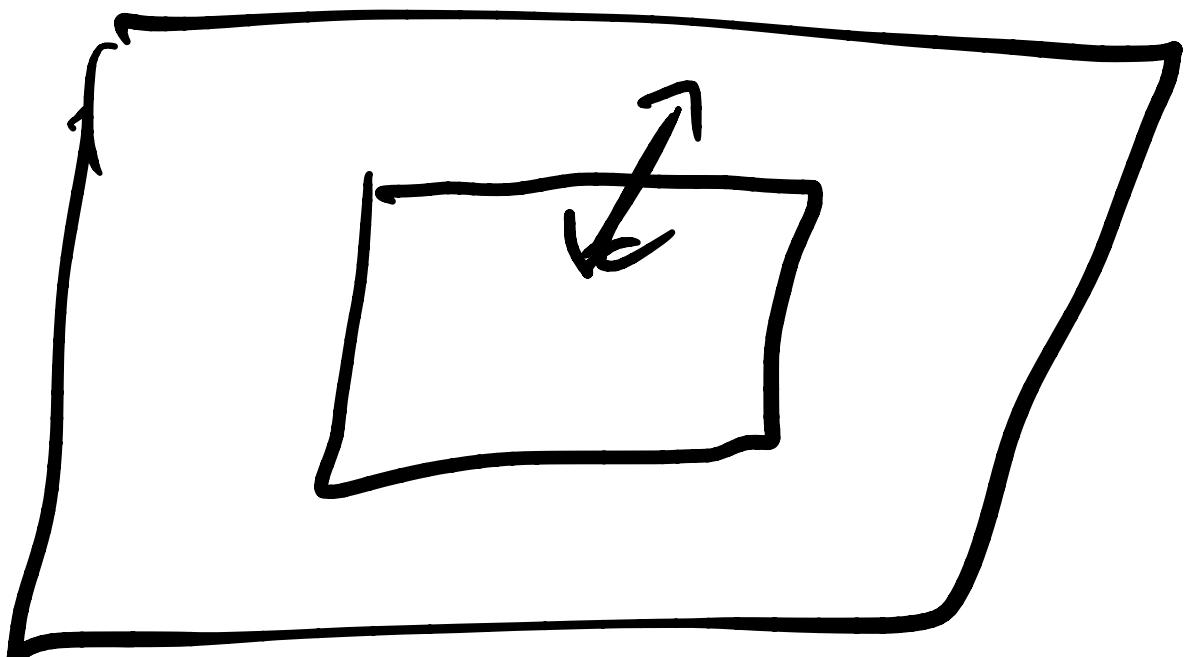
Postulate: heat goes from hot to cold

$$\begin{aligned} \text{If } T_1 > T_2, \quad dg_1 < 0 \quad \& \quad \frac{1}{T_1} - \frac{1}{T_2} < 0 \quad \left. \right\} dS > 0 \\ \text{If } T_1 < T_2, \quad dg_1 > 0 \quad \& \quad \frac{1}{T_1} - \frac{1}{T_2} > 0 \quad \left. \right\} dS > 0 \end{aligned}$$

At equilibrium $dS = 0$ entropy
is
produced

Spontaneous \rightarrow Isolation: $dS > 0$

Consider non-isolated:



$$\begin{aligned} dS_{\text{sys}} &= dS_{\text{produced}} \\ &\quad + dS_{\text{exchange}} \\ &= dS_{\text{prod}} + d\dot{Q}_T \end{aligned}$$

for reversible change

$$dS = \frac{df^{rev}}{T}$$

everything else $dS_{prod} > 0$

$$\text{so } dS \geq \frac{df^{rev}}{T}$$

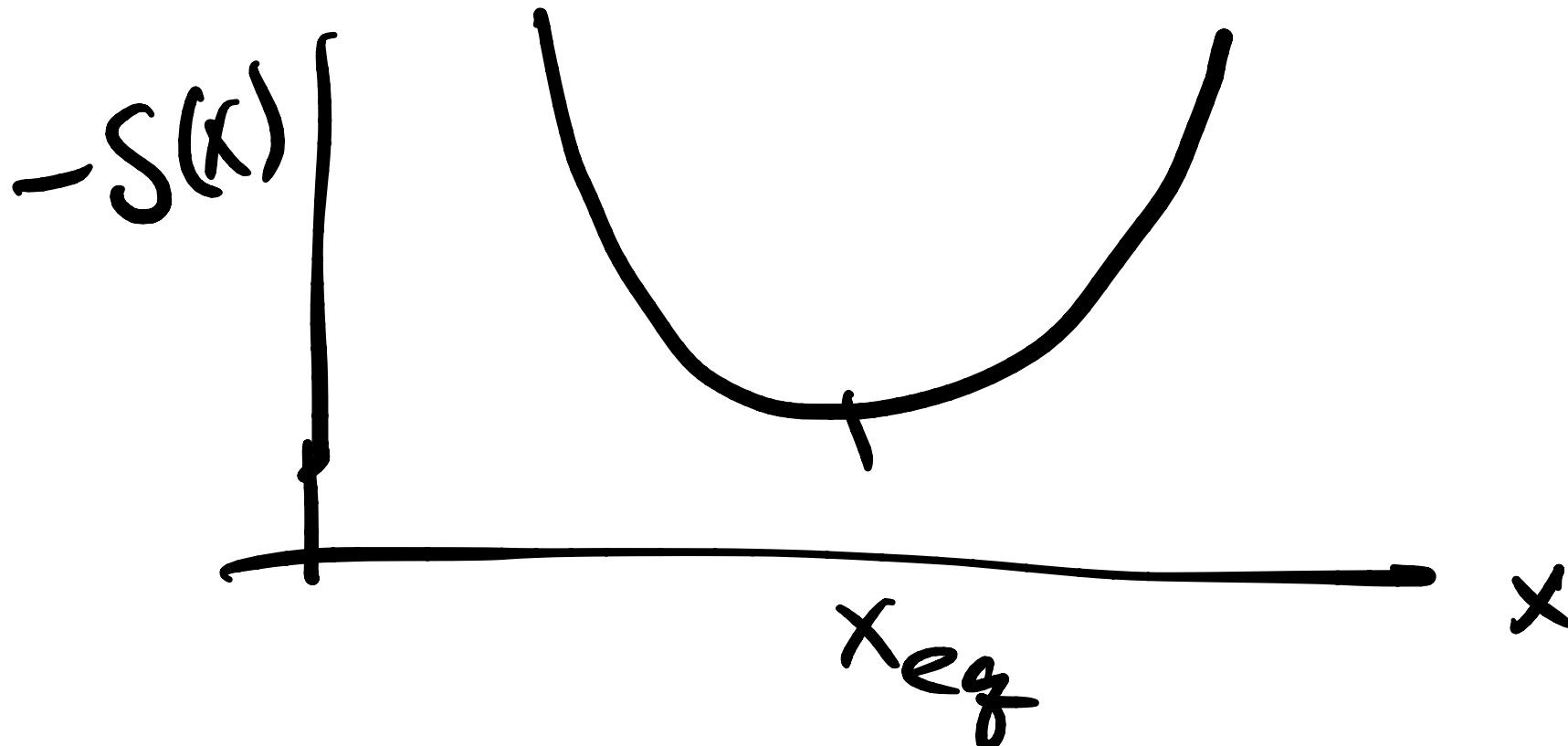
Universe is an isolated system

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

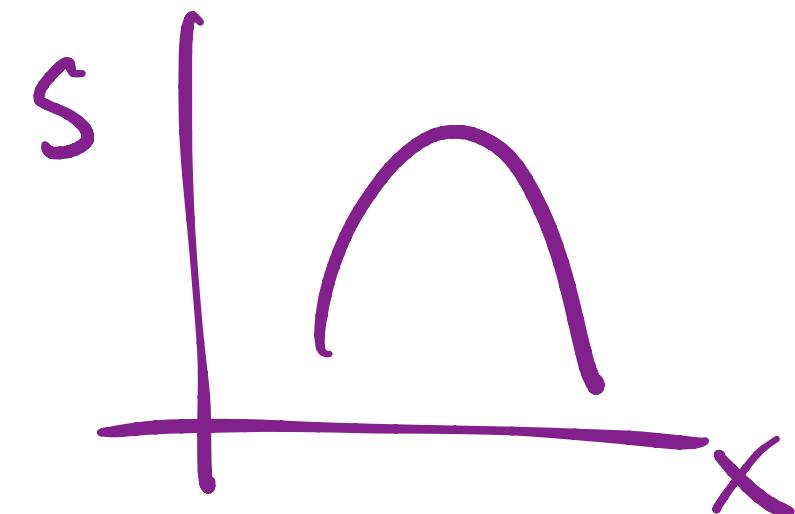
preview

because entropy is always increasing for isolated systems

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



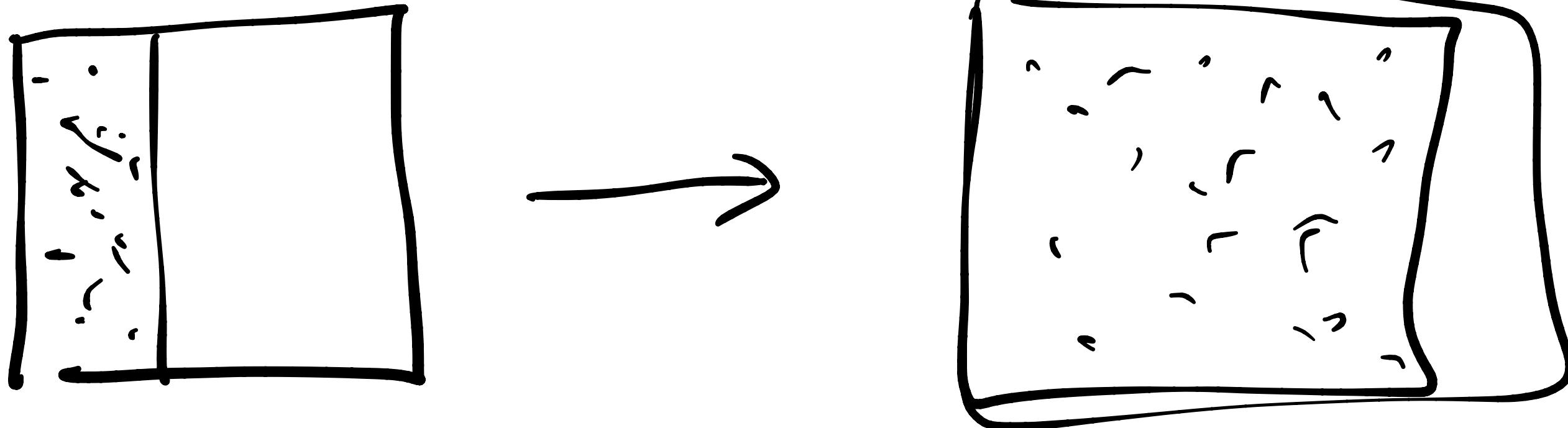
← progress



Molecular interpretation:

Entropy \approx disorder?

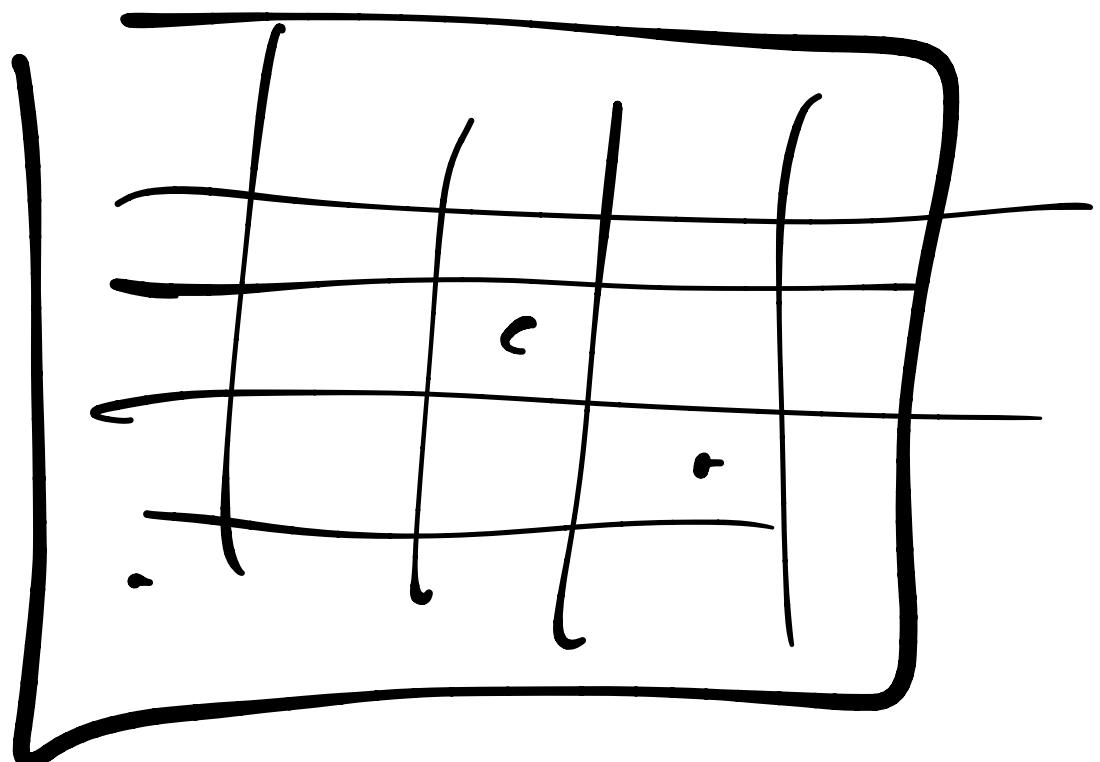
Boltzmann wanted to connect
molecular motion \rightarrow thermodynamics



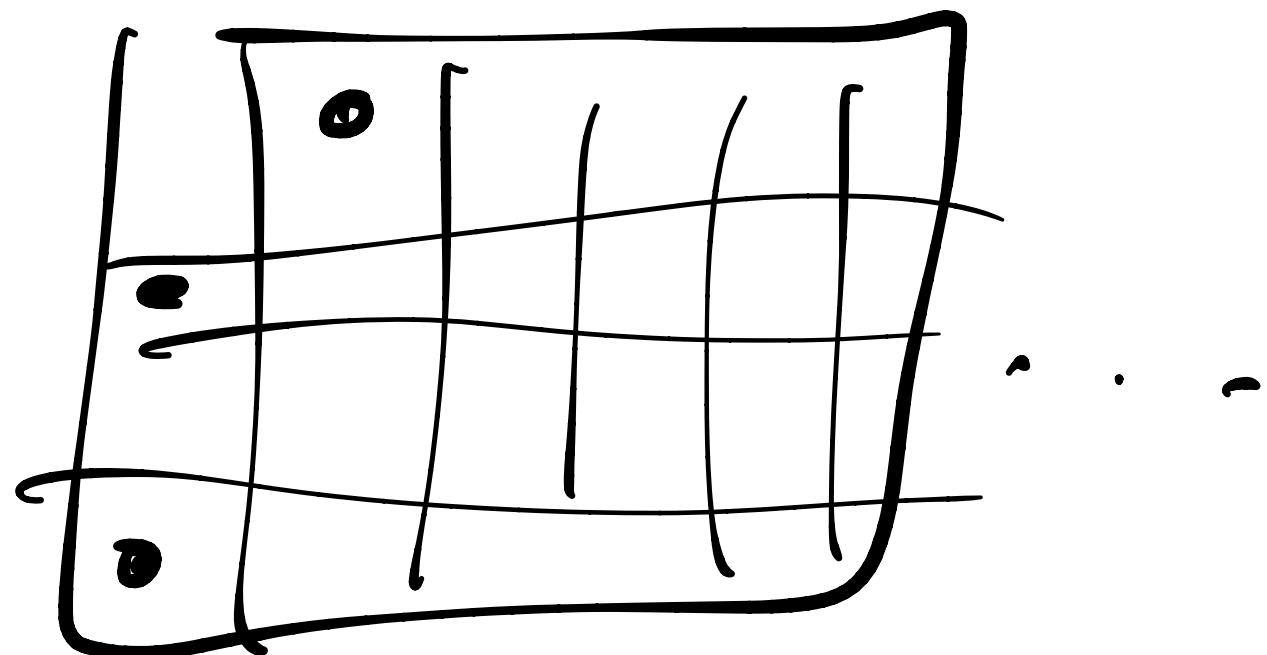
Seems to violate mechanics

Solution to paradox:

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



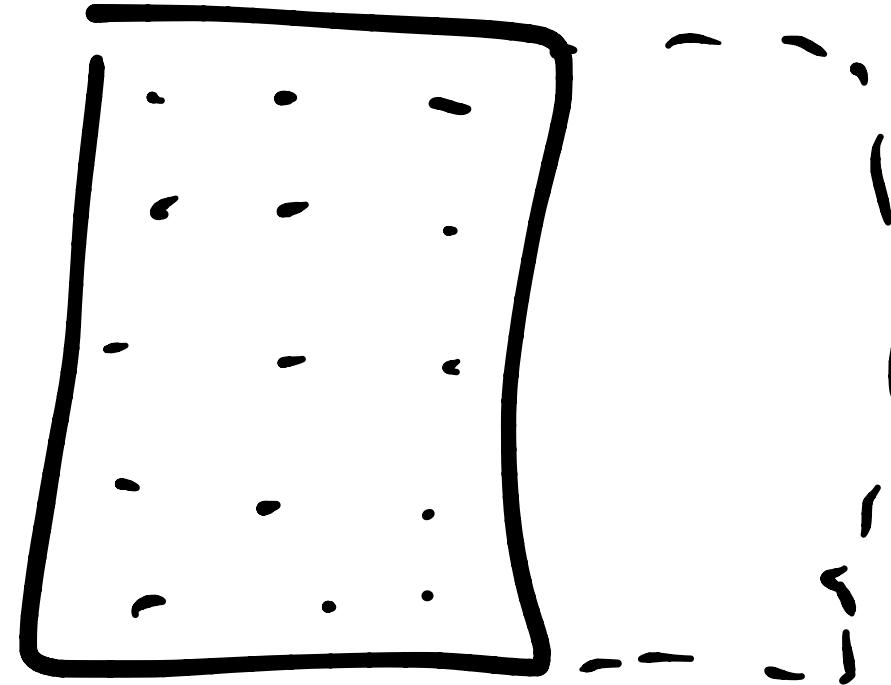
&



etc

M molecules in a box of volume $V \leftrightarrow N_v$

Why is it that

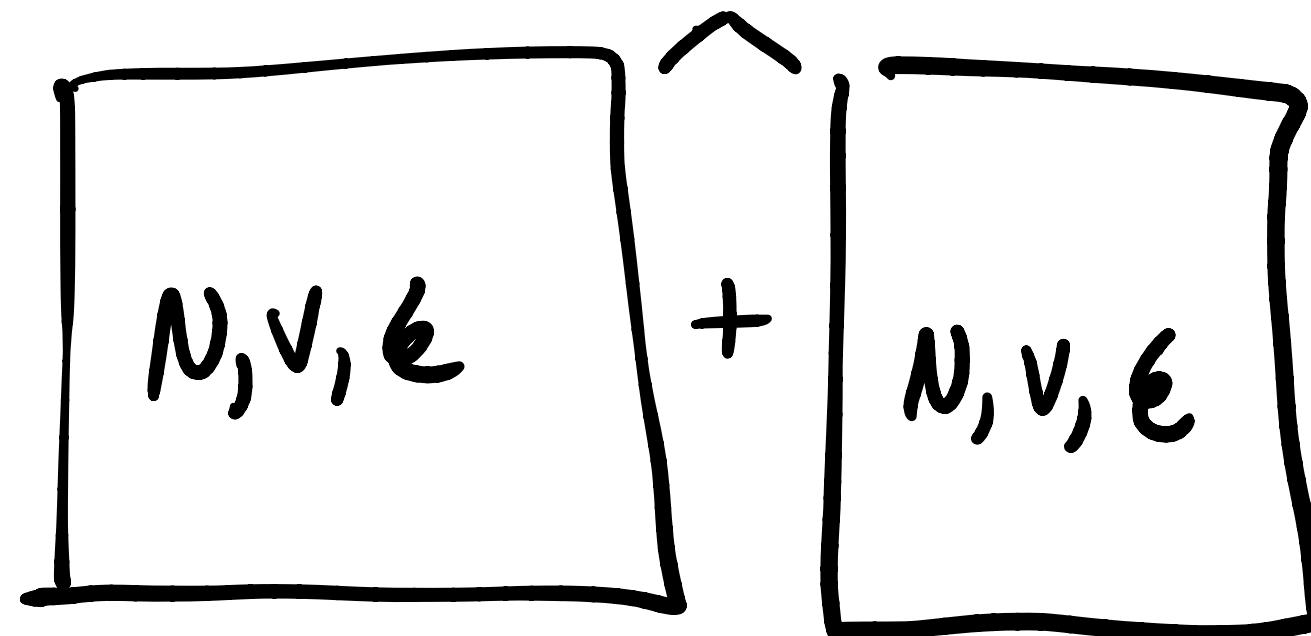


why do molecules expand?

"microStates" \rightarrow observable like density

\hookrightarrow system tries to increase # of states
 \hookrightarrow entropy increases

Is $\#$ states like entropy, \mathcal{R}
copy system



\mathcal{R} is not extensive. N, V, E, S double

$$\mathcal{R}(\text{state 1} + \text{state 2}) = \mathcal{R}(\text{state 1}) \cdot \mathcal{R}(\text{state 2})$$

What if $S \propto \log \mathcal{R}$

$$S = k \ln \mathcal{R} \quad \cancel{+ \infty} \leftarrow \text{not here}$$

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 on N sites
can't overlap, $\mathcal{R} = \binom{N}{M}$

Simpler case, m molecules in N sites

can go anywhere:

$$\mathcal{R} = N \times N \times N \cdots = N^m \quad \text{if distinguishable}$$

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

$$S = k \ln \mathcal{R} = m k \ln N \\ = n R \ln N < n R \ln V$$

$$S(v_2) - S(v_1) = n R \ln \left(\frac{N_2}{N_1} \right) \dots$$

1st law

$$dE = dg + dw \\ = TdS - PdV$$

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

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

$$S = nR \ln V$$

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

$$\underbrace{k}_{\sim} = R/N_A$$