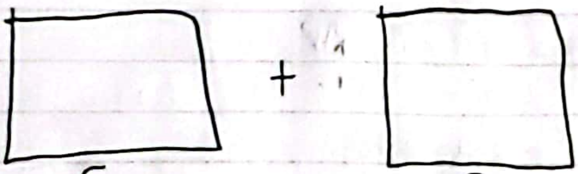
Lecture 20

Last time: Exam! Class: 67 ± 18
review: 72 ± 17

Review: S and w

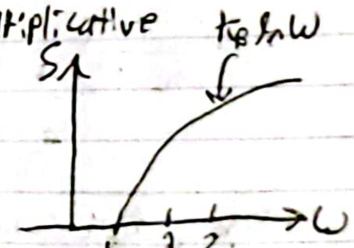
System 1



E_1 V_1 w_1 + E_2 V_2 w_2

extensive vs. multiplicative

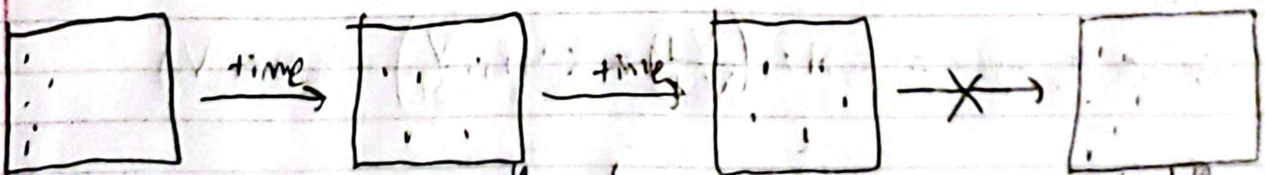
$E = E_1 + E_2$, $V = V_1 + V_2$ } extensive
$w = w_1 \cdot w_2$ } multiplicative



Def: $S \equiv k_b \ln w$ where k_B is a positive #
$\Rightarrow S = S_1 + S_2$ (extensive
$\Rightarrow$ w can be uniquely retreived from S

$\ln(ab) = \ln a + \ln b$
$\ln(\,)$ is a monotonic function

Today: derive 2nd and 3rd laws



$\underbrace{w = (10^4)^{10^{19}} \text{ of these}}$ ... $\left(\frac{1}{2}\right)^{10^{19}}$ fewer of these

$\Rightarrow W(t>0) \geq w(t=0)$ ($\lim N \to \infty$)
$\Rightarrow S(t>0) \geq S(t=0)$ $\therefore \Delta S \geq 0$ 2nd law of thermodynamics

Why the k_B?

In the 19th century it was not realized that temperature is the "energy per degree of freedom"; so really temperature should have units Joules; E/T should be unitless, but actually has units of J/K.

$0k \to 0J$

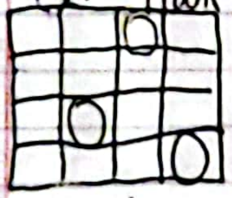
$1k \to 1.38 \times 10^{-38} J = k_B$

$S = (1.38 \times 10^{-23}) \ln w \ (J/k)$ instead of $S = \ln W$.

Entropy not for 1 particle, but for a mole

$$S\left(\frac{J}{mol \cdot K}\right) = \left(6.022 \times 10^{23} \frac{molecules}{mol}\right)\left(1.38 \times 10^{23} J/k\right) \ln w$$
$$= 8.31 \ J/(mol \cdot k) \cdot \ln w = R \cdot \ln w$$

ex: HW 52.3 Entropy of a gas in a box?



$$W \approx \left(\frac{M}{N}\right)^N \text{ if } M >> N >> 1$$

Using Sterling's Approx. here

$M = \frac{V}{V_0}$

$$\approx \left(\frac{V}{V_0 N}\right)^N$$

N

$$\Rightarrow S = k_B \ln W = = k_B N \ln\left(\frac{V}{V_0 N}\right) = k_B N \ln\left(\frac{V}{N}\right) - k_B N \ln(V_0)$$

S increases slowly ($\ln$) with volume, and it is extensive

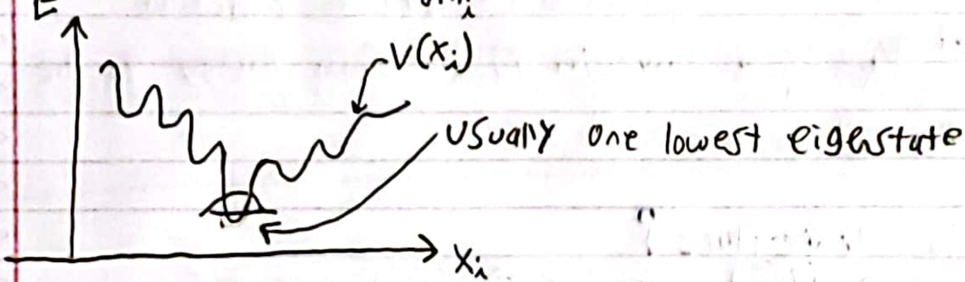
We started out with $\rho_j = \frac{1}{W}$

$S = k_B \ln W = -k_B W \cdot \frac{1}{W} \ln\left(\frac{1}{W}\right) = -k_B W \cdot \rho_j \ln(\rho_j)$

$= -k_B \sum_{j=1}^{W} \rho_j \ln \rho_j$

More microstates → more disorder → higher entropy

3rd law $\mathcal{H} = \sum \frac{p_i^2}{2m_i} + V(x_i)$



$\lim_{E \to min} W = 1 \Rightarrow \lim_{E \to min} S = 0 \to$ 3rd law of thermodynamics