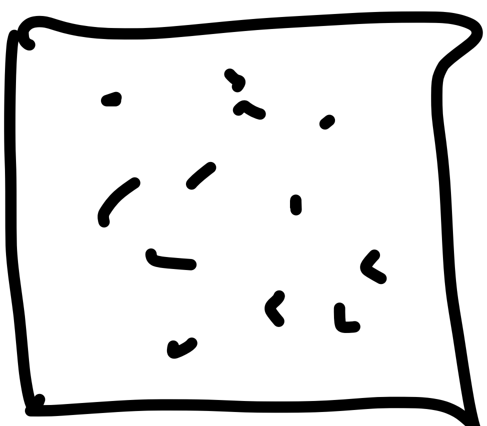
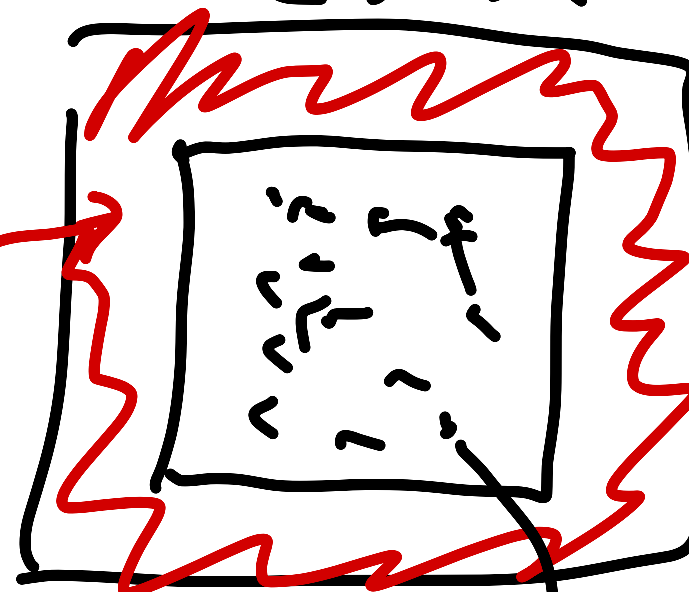
Lecture 4 - Thermo Review

Last time:

- Microcanonical partition function





• Asserted that (microcanonical)

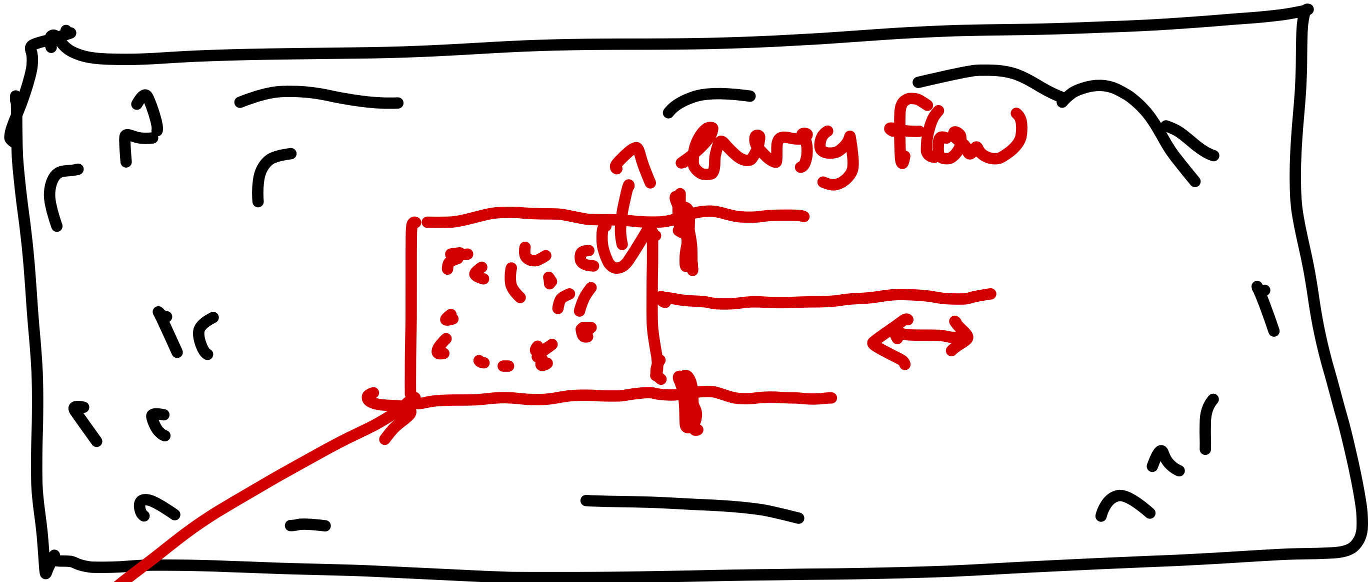
$$S = k_B \ln \Omega(N, V, E)$$

Thermo review

① First law: conservation of energy. Energy isn't created or destroyed

What is the system we're studying

Classic scenario:



closed, isolated N, U, E constant

System we care about

const N, V, T

System - does not have const E

another statement:

for a system

change E_{system} = heat flows in − work done by system

change E_{surr} = − change E_{system}

$$\boxed{dE_{system} = \delta q - \delta w}$$

δq ↑ heat in

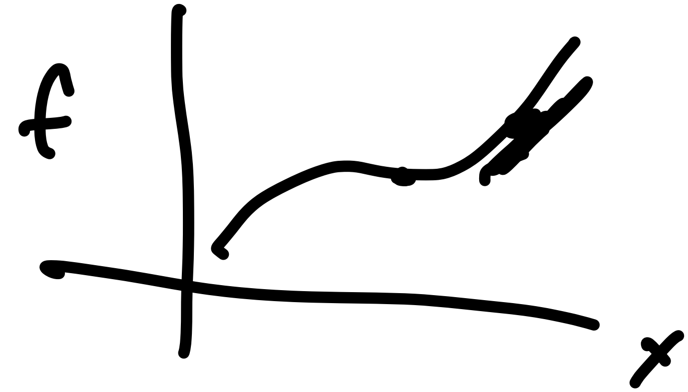
δw ↑ work done

Reminder: "infintessible" (eg dE)

response of a function to a tiny change in argument

$f(x)$ is a function

df



$$f(x+\Delta x) \approx f(x) + \Delta x \frac{df}{dx} + \cancel{\frac{1}{2}\Delta x^2 \frac{d^2 f}{dx^2}} \dots$$

$$df = \lim_{\Delta x \to dx} f(x+\Delta x) - f(x) = \left(\frac{df}{dx}\right) dx$$

$f(x,y)$ what is df

$$f(x+\Delta x, y+\Delta y) = f(x) + \Delta x \left(\frac{\partial f}{\partial x}\right)_y + \Delta y \left(\frac{\partial f}{\partial y}\right)_x + \cdots$$

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy \quad (+ \cdots)$$

connected to chain rule, eg

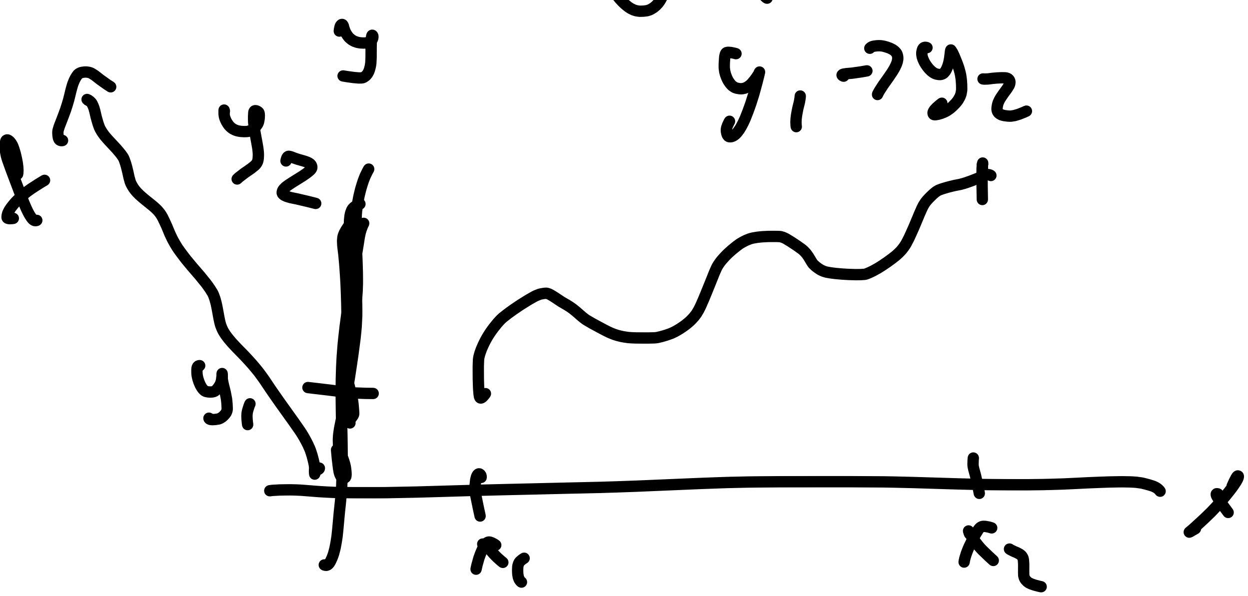
$$\frac{df(x,y)}{dt} = \left(\frac{\partial f}{\partial x}\right)\left(\frac{\partial x}{\partial t}\right) + \left(\frac{\partial f}{\partial y}\right)\left(\frac{\partial y}{\partial t}\right)$$

Thermodynamics ~ want to know change in f along a thermodynamic path

$$\Delta f = f(x_2, y_2) - f(x_1, y_1)$$

$$= \int_{\substack{x_1 \to x_2 \\ y_1 \to y_2}} df$$

(eg $E(V,T)$)



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

Energy is a "state variable"
heat, work are not

$$\Delta E = \int_{path} \delta q - \delta w$$

different kinds of work $\quad -\left(\frac{\partial u}{\partial r}\right)$

mechanical, chemical

classical mech.

$$w = \int_{path} F \cdot dr \qquad dw = F \cdot dr$$

$$dw = -\left(\frac{\partial u}{\partial r}\right) dr$$ energy

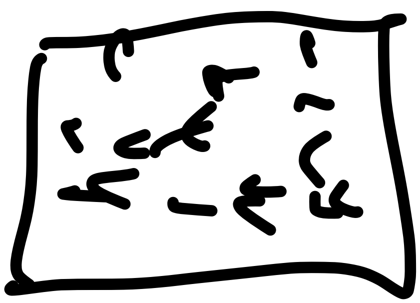
$$\mathcal{E}(A, B, C)$$ (think $A, B, C = N, V, T$)

$$d\mathcal{E} = \left(\frac{\partial \mathcal{E}}{\partial A}\right)_{B,C} dA + \left(\frac{\partial \mathcal{E}}{\partial B}\right)_{A,C} dB + \left(\frac{\partial \mathcal{E}}{\partial C}\right)_{A,B} dC$$

1st law $\quad d\mathcal{E} = \delta q - \delta w$

always

$$\Rightarrow -\delta w = \sum_i \left(\frac{\partial \mathcal{E}}{\partial \lambda_i}\right) d\lambda_i$$



imagine

closed isolated system — $\delta q = 0$

Real example

$$-w = -PdV + \mu dN$$

chemical work

② 2nd law:

heat is a not a state function

exist a quantity $dS = \underbrace{\frac{\delta Q}{T}}$

• state function, "entropy"

$$S(b) - S(a) = \int_{a \to b} \frac{\delta Q}{T}$$

units of $[E]/[T]$

$$d\mathcal{E} = \delta q - \delta w$$

$$= \delta q + \sum_i \left(\frac{\partial \mathcal{E}}{\partial \lambda_i}\right) d\lambda_i$$

divide by T

$$\frac{1}{T} d\mathcal{E} = \underbrace{\frac{\delta q}{T}}_{dS} + \frac{1}{T} \sum_i \left(\frac{\partial \mathcal{E}}{\partial \lambda_i}\right) d\lambda_i$$

$$dS = \frac{1}{T} d\mathcal{E} - \frac{1}{T} \sum_i \left(\frac{\partial \mathcal{E}}{\partial \lambda_i}\right) d\lambda_i$$

$$dS = \frac{1}{T}\,dE - \frac{1}{T}\sum_i \left(\frac{\partial E}{\partial \lambda_i}\right) d\lambda_i$$

in microcanonical ensemble

S depends only on N, V, E

infintesibles - chain rule ..

$S(N,V,E) \rightarrow$

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

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

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

$$dS = \frac{1}{T}\,dE - \frac{1}{T}\underbrace{\left(\frac{\partial E}{\partial N}\right)}_{\mu} dN - \frac{1}{T}\underbrace{\left(\frac{\partial E}{\partial V}\right)}_{-P} dV$$

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

$$\left(\frac{\partial S}{\partial V}\right) = +\frac{P}{T}$$

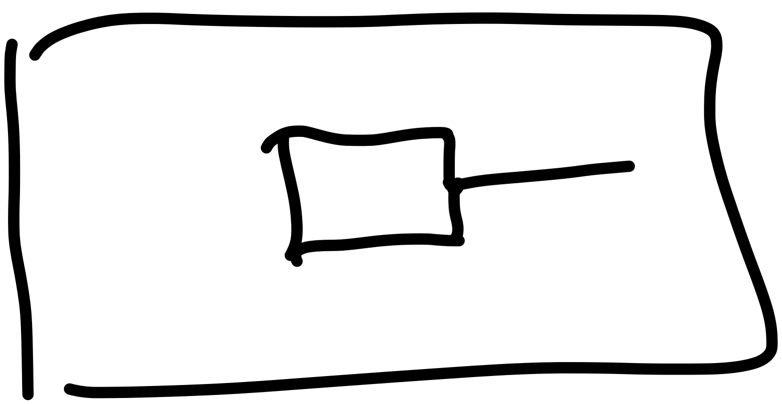
- $\Delta S \geq 0$ for any process

  $\Delta S = 0$ for a reversible path

includes isolated systems

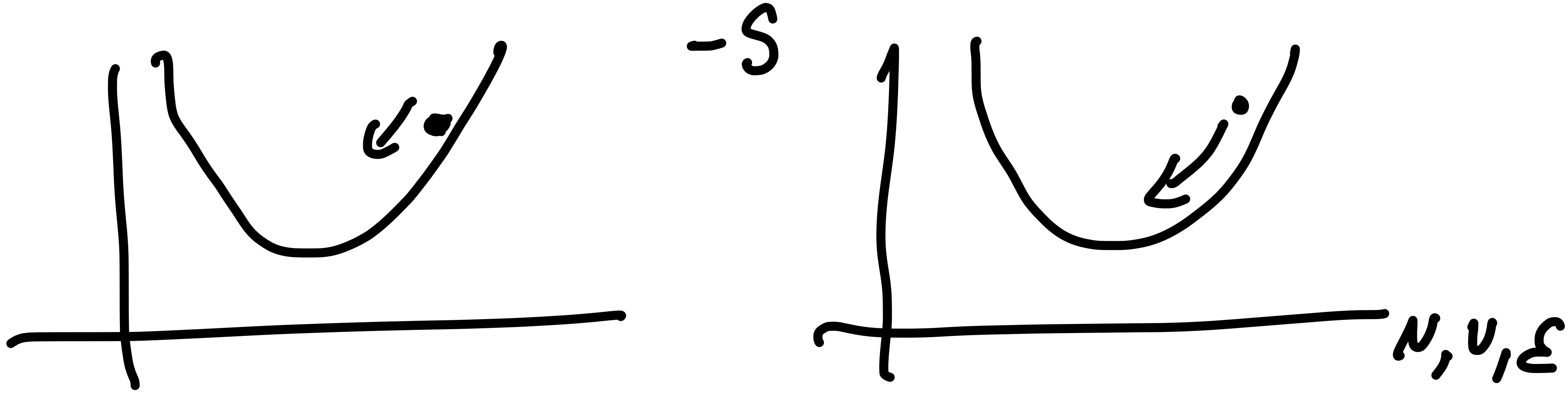
universe = isolated system

constant energy



Isolated system

Can think of S is $[-S]$
a "thermodynamic potential"
for microcanonical ensemble



entropy will maximize as
we approach equilibrium

Next time: S for ideal gas
ideal gas law from S ...