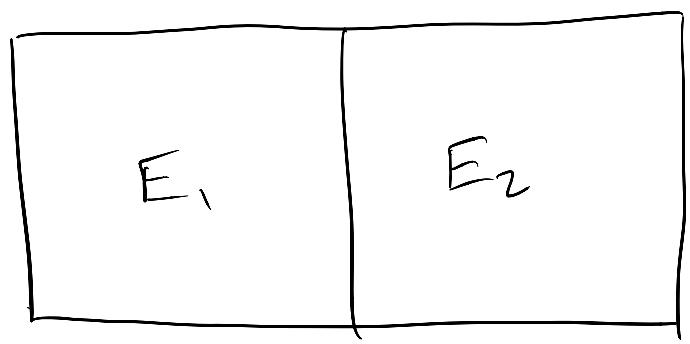
Moving on to energy, entropy

Chapter 2

First law of thermodynamics

Conservation of Energy



E : internal energy

$E = E_1 + E_2$ $\rightarrow$ extensive

linearly additive

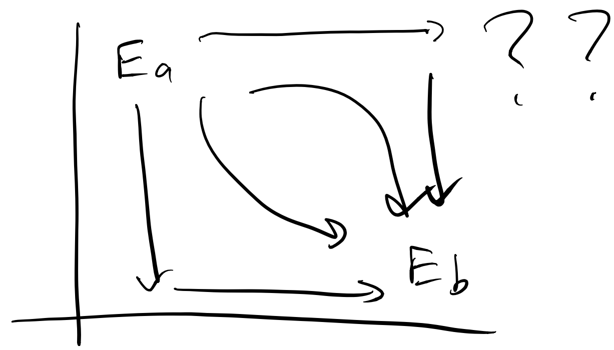
follows $f(\lambda x) = \lambda f(x)$

If energy in the system has changed it can be the result of energy flow to the system. (transfer)

- heat flow across boundaries
- work energy flow.

funny delta is a differential for a path-dependent variable

$$\boxed{dE = \delta Q + \delta W}$$



If you know states, you don't necessarily know how you got there.

$$\delta W = \underline{f} \cdot d\underline{X}$$

$\underline{f}$: force applied to the system

$\underline{X}$: mechanical extensive variable

$$\underline{f} \cdot d\underline{X} = f_1\, dX_1 + f_2\, dX_2 + f_3\, dX_3 + \ldots$$

classically

$$\delta W = -P_{ext}\, dV$$ pressure volume work.

Both work and heat are types of energy transfer. Once mechanical work or heat causes a change in E, and E is the only measurable quantity, there is no way to distinguish the contributions from the two transfer processes that change internal energy.

2nd law of thermodynamics

"Tendency to increase disorder"

There is an extensive function of state, $S(E, \underline{X})$, which is a monotonically increasing function of E. If state B is adiabatically accessible from state A, then $S_B \geq S_A$.

Adiabatically accessible?

no heat flow across system boundaries.

adiabatically accessible (no heat)

irreversible processes

$S_B > S_A$

$(S_B - S_A) > 0$

$\Delta S^{irreversible}_{adiabatic} > 0$

reversible processes

$B \rightarrow A$ could be carried out.

$\left.\begin{array}{l} S_A \geq S_B \\ S_B \geq S_A \end{array}\right\} S_A = S_B$

$(S_B - S_A) = 0$

$\Delta S^{reversible}_{adiabatic} = 0$

$$\Delta S_{adiabatic} \geq 0$$

$S(E, \underline{X})$ is entropy $\rightarrow$ function of state we are interested in things that change $\rightarrow$ In - Out

total derivative of S?

$$d\left(S(E, \underline{X})\right) =$$

$$\left(\frac{\partial S}{\partial E}\right)_{\underline{X}} dE + \left(\frac{\partial S}{\partial \underline{X}}\right)_E \cdot d\underline{X}$$

stick w/ Reversible

Recall $dE = \left(\delta Q_{rev}\right) + \underline{f} \cdot d\underline{X}$

$$dS = \left(\frac{\partial S}{\partial E}\right)_{\underline{X}} \delta(Q_{rev}) + \left[\frac{\partial S}{\partial \underline{X}}\Big|_E + \left(\frac{\partial S}{\partial E}\right)\Big|_{\underline{X}} \underline{f}\right] \cdot dX$$

but 1st, what is δQ_{rev} for adiabatic reversible?

$$\delta(Q_{rev}) = 0$$

$$0 = \left(\frac{\partial S}{\partial \underline{x}}\right)_E + \underbrace{\left(\frac{\partial S}{\partial E}\right)_{\underline{X}}} \underline{f}$$

$S(E, \underline{X})$ is a monotone increasing function of E.

means $\left(\frac{\partial S}{\partial E}\right)_{\underline{X}} \geq 0$

$$\left(\frac{\partial S}{\partial E}\right)_{\underline{X}} \in (0, \infty)$$

$\swarrow$

$$\left(\frac{\partial E}{\partial S}\right)_{\underline{X}} \in [0, \infty)$$

$$\left(\frac{\partial E}{\partial S}\right)_{\underline{X}} \geq 0$$

$$\boxed{\left(\frac{\partial E}{\partial S}\right)_{\underline{X}} \equiv T}$$