next step: introduce a thermodynamic formalism to keep track of system properties (i.e. energy) + relate them to currents

state n $\Rightarrow$ energy E_n ← subscript: state prop.

mean energy at time t $\quad \langle E \rangle_t = \sum_n p_n(t) E_n$

simpler notation $\quad E(t) \equiv \langle E \rangle_t$

↑ avg: no subscript

$$\frac{d}{dt} E(t) = \sum_n \underbrace{\frac{dp_n}{dt}}_{\sum_m J_{nm}(t)} E_n = \sum_{n,m} J_{nm}(t) E_n$$

$J_{mn}(t) = -J_{nm}(t)$

$$= \frac{1}{2} \sum_{n,m} J_{nm}(t) E_n + \frac{1}{2} \sum_{\substack{n,m \\ n \to m \\ m \to n}} J_{mn}(t) E_m$$

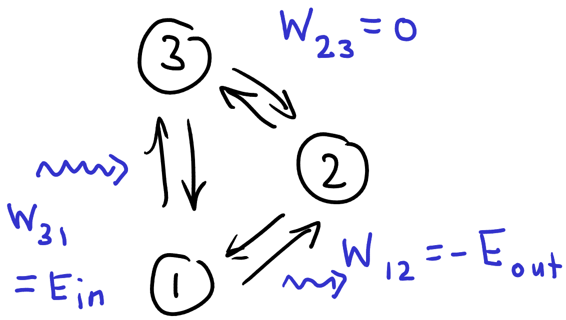
$$\underbrace{\frac{d}{dt} E(t)}_{\text{"power"}} = \frac{1}{2} \sum_{n,m} \underbrace{J_{nm}(t)}_{\text{"current"}} \underbrace{(E_n - E_m)}_{\text{"potential difference" b/t } n \text{ + } m}$$

in general: state property A_n

avg. $\quad A(t) = \sum_n p_n(t) A_n$

rate of change $\quad \frac{dA(t)}{dt} = \frac{1}{2} \sum_{nm} J_{nm}(t)(A_n - A_m)$

$$= \dot{A}(t)$$



assume A_n exists:

$$W_{31} = A_3 - A_1$$

$$W_{12} = A_1 - A_2 = A_1 - A_3$$

$$W_{23} = A_2 - A_3 = 0$$

$$\Rightarrow W_{31} = -W_{12}$$

$$E_{in} = E_{out}$$

in general, not true

edge property B_{nm} (i.e. work W_{nm})

define a "production rate" associated w/ edges:

$$\mathring{B}(t) \equiv \frac{1}{2} \sum_{nm} J_{nm}(t) B_{nm}$$

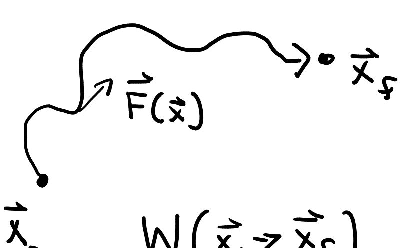
i.e. $$\mathring{W}(t) = \frac{1}{2} J_{31}(t) W_{31} + \frac{1}{2} J_{12}(t) W_{12}$$

abuse of notation: $\mathring{B}(t)$ exists (by definition), but there is no $B(t)$ in general, so $\dot{B}(t) \neq \frac{dB}{dt}$

exception: if the edge property is "conservative" then there exists some associated state property A_n such that

$$B_{nm} = A_n - A_m$$

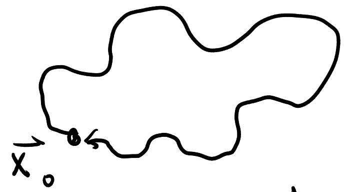
$$\Rightarrow \dot{B}(t) = \frac{dA}{dt} \quad \text{where} \quad A(t) = \sum_n p_n(t) A_n$$



$$W(\vec{x}_0 \to \vec{x}_f) = \int_{\vec{x}_0}^{\vec{x}_f} \vec{F}(\vec{x}) \cdot d\vec{x}$$

conservative: $\vec{F}(\vec{x}) = -\vec{\nabla} U(\vec{x}) \Rightarrow W(\vec{x}_0 \to \vec{x}_f) = U(\vec{x}_f) - U(\vec{x}_0)$

for conserv. case:



$$W(\vec{x}_0 \to \vec{x}_0) = 0$$

Special edge property: $I_{nm}(t) \equiv k_B \ln \dfrac{\Omega_{nm}\, p_m(t)}{\Omega_{mn}\, p_n(t)}$

"irreversibility"

$$= k_B \ln \frac{\text{avg. \# } m \to n \text{ jumps / time}}{\text{avg. \# } n \to m \text{ jumps / time}}$$

closely related to $J_{nm}(t) = \Omega_{nm} P_m(t) - \Omega_{mn} p_n(t)$

when "forward" jumps $(m \to n)$ are much more likely than "reverse" ones $(n \to m)$

$\Rightarrow$ $I_{nm}(t)$ is large + positive

$J_{nm}(t)$ is large + positive

when "reverse" much more likely than "forward"

$I_{nm}(t)$ is large + negative

$J_{nm}(t)$ is " "

$$\dot{I}(t) = \frac{1}{2} \sum_{nm} J_{nm}(t)\, I_{nm}(t) = \text{sum of positive (or zero) terms}$$

production rate

$$\Rightarrow \boxed{\dot{I}(t) \geq 0}$$

valid for any system at any time

physical intuition: $\dot{I}(t) = 0$ if and only if

$$I_{nm}(t) + J_{nm}(t) = 0$$

for every n,m trans.

$$\Leftrightarrow \Omega_{mn} p_n(t) = \Omega_{nm} p_m(t)$$

for every connected edge

$$\Rightarrow \frac{dp_n}{dt} = \sum_m J_{nm}(t) = 0$$

$$\boxed{\dot{I}(t) = 0 \Rightarrow \text{ESS}}$$

we can think of $\dot{I}(t)$ as a "distance" from an ESS

$\dot{I}(t) > 0$

- $\to$ NESS: $\frac{dp_n}{dt} = 0$ but $J_{nm}(t) \neq 0$ for some (n,m)
- $\to$ not in a stat. state: $\frac{dp_n}{dt} \neq 0$

connect to other physical quantities:

$$I_{nm}(t) = k_B \ln \frac{\Omega_{nm} p_m(t)}{\Omega_{mn} p_n(t)}$$

heat from env. $m \to n$

$$\frac{\Omega_{nm}}{\Omega_{mn}} = e^{-\beta Q_{nm}}$$

$$= e^{-\beta(E_n - E_m - W_{nm})}$$

$$= -\frac{1}{T} Q_{nm} + k_B \ln \frac{p_m(t)}{p_n(t)}$$

$$= -\frac{1}{T} Q_{nm} + \left(S_n(t) - S_m(t)\right)$$

$S_n(t) = -k_B \ln p_n(t)$

new state func.

"surprisal"

how "surprised" you are to see state n

$0 \le p_n(t) \le 1$

$S_n(t)$ is large + positive when $p_n(t) \approx 0$

≈ 0 when $p_n(t) \approx 1$

multiply by $\frac{1}{2} J_{nm}(t)$ + $\sum_{nm}$ $\Rightarrow$

$$\dot{\mathcal{I}}(t) = -\frac{\dot{Q}(t)}{T} + \dot{S}(t)$$

prod. rate of "irreversibility"

mean rate of heat into sys.

rate of change of entropy

where $\dot{S}(t) = \frac{d}{dt} S(t)$

$S(t) = \sum_n p_n(t) S_n(t)$

$= -k_B \sum_n p_n(t) \ln p_n(t)$

mean surprisal

"entropy"

Gibbs entropy formula