state property A_n

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

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

$\equiv \mathring{A}(t)$ dot notation: current × edge prop.

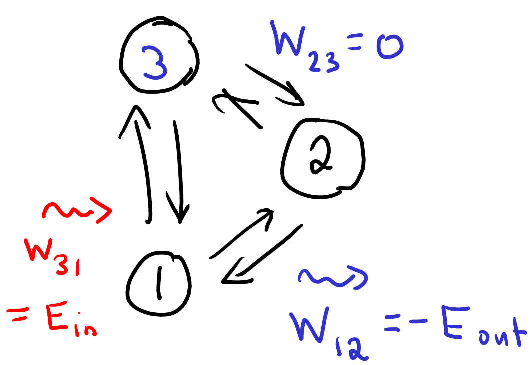
edge property B_{nm} (i.e. work W_{nm})

end ↑ ↑ start

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

"production rate" associated w/ edge property

i.e. work W_{nm}



$$\mathring{W}(t) = \frac{1}{2} [J_{31} W_{31} + J_{13} W_{13} + J_{12} W_{12} + J_{21} W_{21}]$$

↑ net power input into sys.

$J_{31} = -J_{13}$ etc.

$W_{31} = -W_{13}$

$= J_{31} E_{in} + J_{12} (-E_{out})$

proof by contradiction:

assume A_n exists

$W_{31} = A_3 - A_1$

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

$W_{23} = A_2 - A_3$

$= 0$

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

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

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

$E_{out} = E_{in}$

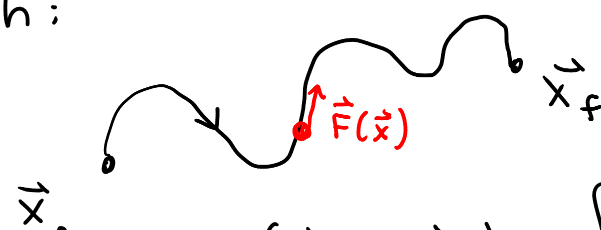
not true in general

exception: if the edge property is "conservative" — there exists some state property A_n such that $B_{nm} = A_n - A_m$ for all (n,m)

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

$$A(t) = \sum_n p_n(t) A_n$$

classical mech:

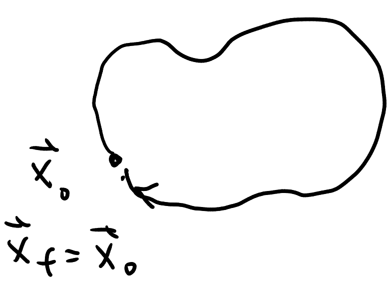


$$W(\vec{x}_0 \rightarrow \vec{x}_f) = \int_{\vec{x}_0}^{\vec{x}_f} \vec{F}(\vec{x}) \cdot d\vec{x}$$

conservative: $\vec{F}(\vec{x}) = -\vec{\nabla} U(\vec{x})$

$$\Rightarrow W(\vec{x}_0 \rightarrow \vec{x}_f) = U(\vec{x}_f) - U(\vec{x}_0)$$

indep. of path



cons. case: $W(\vec{x}_0 \rightarrow \vec{x}_0) = 0$

equiv: any cons. edge property

$$\sum_{\text{loop}} B_{nm} = 0$$

Boltzmann const: units J/k

Special edge property:

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

"irreversibility" $= k_B \ln \dfrac{\text{avg. \# of } m \to n \text{ jumps / time}}{\text{avg. \# of } n \to m \text{ jumps / time}}$

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

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

$$I_{nm}(t) > 0$$
$$J_{nm}(t) > 0$$

when "reverse" more likely than "forward":

$$I_{nm}(t) < 0$$
$$J_{nm}(t) < 0$$

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

prod. rate of irrev.

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

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

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

for every (n,m) trans.

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

for every connected edge

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

$\dot{I}(t) = 0 \Rightarrow$ stationary state w/ all currents $= 0$ $\Rightarrow$ ESS

$\dot{I}(t) > 0 \Rightarrow \begin{cases} \text{NESS} & \frac{dp_n}{dt} = 0 \text{ but } J_{nm} \neq 0 \text{ for at least some edges} \\ \text{not in a stat. state} & \frac{dp_n}{dt} \neq 0 \end{cases}$

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