

Thermodynamic formalism:

state $n \Rightarrow$ energy E_n subscript: property of state

- mean energy
at time t

$$\langle E \rangle_t = \sum_n p_n(t) E_n$$

Simpler notation: $E(t) \equiv \langle E \rangle_t$
no subscript: avg over all states

$$\frac{d}{dt} E(t) = \frac{d}{dt} \sum_n p_n(t) E_n = \sum_n \underbrace{\frac{dp_n}{dt}}_{J_{nm}(t)} E_n$$

$$\begin{aligned} J_{nm}(t) &= -J_{mn}(t) \\ &= \sum_{n,m} J_{nm}(t) E_n \\ &= \frac{1}{2} \sum_{n,m} J_{nm}(t) E_n + \frac{1}{2} \sum_{n,m} J_{nm}(t) E_n \end{aligned}$$

$$\frac{d}{dt} E(t) = \frac{1}{2} \sum_{n,m} \left[J_{nm}(t) E_n + \overset{n \rightarrow m}{\underset{m \rightarrow n}{J_{mn}(t) E_m}} \right]$$

$$\text{"power"} = \frac{1}{2} \sum_{n,m} \underbrace{J_{nm}(t)}_{\text{"current"}} \underbrace{[E_n - E_m]}_{\text{"potential diff" b/t } n \text{ \& } m}$$

$$\sum_{a=1}^N \sum_{b=1}^N B_{ab}$$

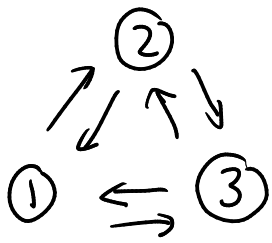
"

$$\sum_{n=1}^N \sum_{m=1}^N B_{nm} = B_{11} + B_{12} + B_{21} + B_{13} + B_{31} + \dots + B_{NN}$$

prevents
double counting

double sum over
all edges of net

"potential
diff" b/t n & m



$$J_{21} = -J_{12}$$

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

c.t.c.

$$J_{12}(E_1 - E_2)$$

$$= J_{21}(E_2 - E_1)$$

$$\frac{d}{dt} E = \sum_{n,m} J_{nm} E_n$$

$$= J_{12} E_1 + J_{21} E_2$$

$$+ J_{13} E_1 + J_{31} E_3$$

$$+ J_{23} E_2 + J_{32} E_3$$

$$= J_{12} (E_1 - E_2)$$

$$+ J_{13} (E_1 - E_3)$$

$$+ J_{23} (E_2 - E_3)$$

$$= \frac{1}{2} J_{12} (E_1 - E_2) + \frac{1}{2} J_{21} (E_2 - E_1)$$

$$+ \frac{1}{2} J_{13} (E_1 - E_3) + \frac{1}{2} J_{31} (E_3 - E_1)$$

$$+ \frac{1}{2} J_{23} (E_2 - E_3) + \frac{1}{2} J_{32} (E_3 - E_2)$$

in general:

state property A_n

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

rate of
change

$$\frac{dA(t)}{dt} = \frac{1}{2} \sum_{n,m} J_{nm}(t) (A_n - A_m)$$

RHS: $\equiv \dot{A}(t)$

edge property

B_{nm} (i.e. current J_{nm})
work W_{nm}

define a "production rate" assoc.
w/ edges

$$\dot{B}(t) \equiv \frac{1}{2} \sum_{n,m} J_{nm}(t) B_{nm}$$

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

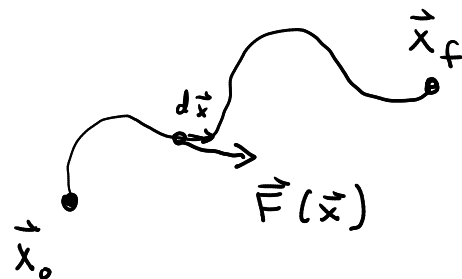
exception: certain edge properties B_{nm}
are "conservative" meaning there
exists an associated state prop.
such that $B_{nm} = A_n - A_m$

in this case: $\dot{B}(t) = \frac{dA}{dt}$

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

inspiration: notation of conservative force
in classical mechanics

force field $\vec{F}(\vec{x})$



Work
over a
path

$$W(\vec{x}_0 \rightarrow \vec{x}_f)$$

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

← general def'n

conservative:

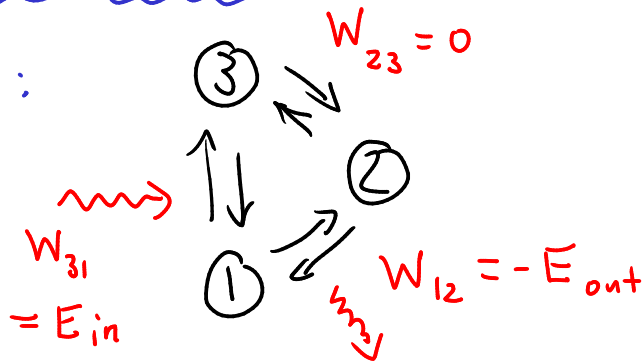
$$\vec{F}(\vec{x}) = -\vec{\nabla} U(\vec{x})$$

↑ potential

$$= U(\vec{x}_0) - U(\vec{x}_f) \Rightarrow \text{if } \vec{x}_f = \vec{x}_0 \text{ (closed loop)}$$

analogous: $B_{nm} = A_n - A_m$ $W(\vec{x}_0 \rightarrow \vec{x}_0) = 0$

example:



for this set of W_{nm} does a state func.

A_n exist

s.t. $W_{nm} = A_n - A_m$?

proof by contradiction: assume A_n exists

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

$$W_{12} = A_1 - A_2 = A_1 - A_3 = -W_{31}$$

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

$$\Rightarrow W_{12} = -W_{31} \Rightarrow E_{in} = E_{out}$$
$$-E_{out} = -E_{in}$$

in general not

true $\Rightarrow$ work here is not conservative

alternatively:

total work around loop:

$$W_{31} + W_{23} + W_{12} = E_{in} - E_{out} \neq 0$$

in general

special edge property "irreversibility"

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

by convention

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

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

Cases: When "forward" jumps ($m \rightarrow n$) are much more likely than "reverse" ($n \rightarrow m$):

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

irreversibility
production
rate

$$\dot{I}(t) = \frac{1}{2} \sum_{nm} J_{nm}(t) I_{nm}(t)$$

= sum over ≥ 0 terms

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

valid for any system
at any time