PHYS 320/420 : Lecture 20

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

$$\frac{dE}{dt} = \sum_{nm} J_{nm} E_n \qquad (*)$$

$$= \frac{1}{2} \sum_{nm} J_{nm} (E_n - E_m)$$

example:

$$J_{nm} = \Omega_{nm} p_m - \Omega_{mn} p_n$$

$$J_{nn} = 0 \;, \quad J_{nm} = -J_{mn}$$

$$(1) \rightleftarrows (2) \rightleftarrows (3)$$

$$(*) = J_{12} E_1 + J_{21} E_2 + J_{23} E_2 + J_{32} E_3$$

$$(**) = J_{12}(E_1 - E_2) + J_{23}(E_2 - E_3)$$

using $J_{21} = -J_{12}$, $J_{32} = -J_{23}$

$$(***) = J_{21}(E_2 - E_1) + J_{32}(E_3 - E_2)$$

$$(*) = \frac{1}{2}\left[(**) + (***)\right] = \frac{1}{2} \sum_{nm} J_{nm}(E_n - E_m)$$

General definitions:

state (n) has property A_n

(energy, etc.)

avg. of that property in sys at time t $= A(t) \equiv \sum_n P_n(t) A_n$

$$\dot{A}(t) = \frac{dA}{dt} = \frac{1}{2} \sum_{nm} J_{nm}(t) (A_n - A_m)$$

transition $m \rightarrow n$ has property B_{nm}

"production rate" $\dot{B}(t) \equiv \frac{1}{2} \sum_{nm} J_{nm}(t) B_{nm}$

abuse of notation: sometimes $\dot{B}(t)$ exists, & no $B(t)$

exception: special case where $\underbrace{B_{nm}}_{\text{trans. property}} = \underbrace{A_n - A_m}_{\text{diff. in state properties}}$

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

where

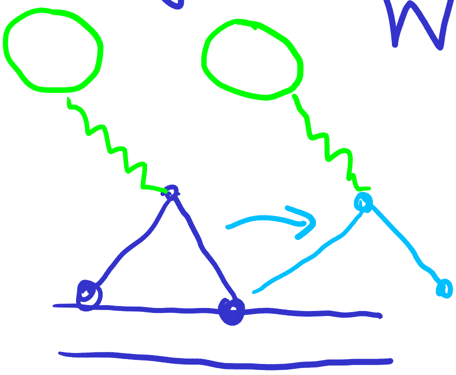
$$A(t) = \sum_n p_n(t) A_n$$

is well defined

example: work done by sys during $m \to n$ transition

$$W_{nm}$$

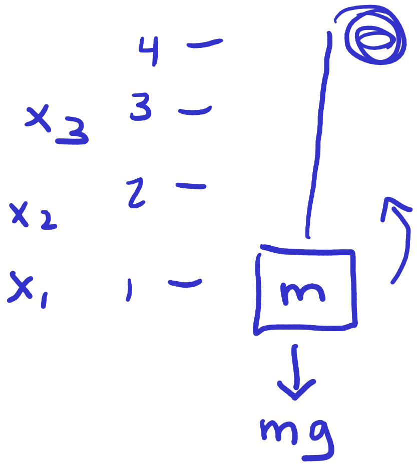
motor protein doing work on cargo



$$\dot{W}(t) = \frac{1}{2} \sum_{nm} J_{nm} W_{nm}$$

= rate of mean work done by sys

= power output of sys



$$W_{21} = mg(x_2 - x_1)$$

$$= mg x_2 - mg x_1$$

$$= U_2 - U_1$$

Let's define another transition property associated w/ any allowable trans. ($\Omega_{nm} \neq 0 \Leftrightarrow \Omega_{mn} \neq 0$):

define "irreversibility" $I_{nm}(t)$

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

by convention

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

If "reverse" jumps $n \to m$ are much less likely than "forward" $m \to n$ jumps $\Rightarrow I_{nm}(t)$ is large

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

$$= \frac{k_B}{2} \sum_{nm} (\Omega_{nm} p_m - \Omega_{mn} p_n) \ln \frac{\Omega_{nm} p_m}{\Omega_{mn} p_n}$$

every term has form: $(x-y)\ln\frac{x}{y}$

$$= \begin{cases} >0 & \text{if } x \neq y \\ =0 & \text{if } x = y \end{cases}$$

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

for us this is equiv. to 2nd law of thermodynamics (we will explain soon!)

valid at all times for all systems
(note: indep. of det. balance relation)
does not require stationary state

Note: $\mathring{I}(t) = 0$ can only happen if $\Omega_{nm} p_m(t) = \Omega_{mn} p_n(t)$ for every connected (n,m)

$\Rightarrow J_{nm}(t) = 0$ for every (n,m)

This can only happen if the system is in equilibrium (ESS)

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

What happens if detailed balance condition is also true?

$$\frac{\Omega_{nm}}{\Omega_{mn}} = e^{-\beta(E_n - E_m)} \qquad \beta = \frac{1}{k_B T}$$

$$\mathring{I} = \frac{k_B}{2} \sum_{nm} J_{nm} \ln \frac{\Omega_{nm}}{\Omega_{mn}} \frac{p_m}{p_n}$$

$$= \frac{-1}{2T} \sum_{nm} J_{nm} (E_n - E_m)$$

$$+ \frac{k_B}{2} \sum_{nm} J_{nm} \ln \frac{p_m}{p_n}$$

$$= -\frac{\mathring{E}}{T} + \frac{1}{2} \sum_{nm} J_{nm} \Big[\underbrace{-k_B \ln p_n}_{S_n(t)} - \underbrace{(-k_B \ln p_m)}_{S_m(t)} \Big]$$

$S_n(t)$ = "entropy" of state n

$$\mathring{I} = -\frac{\mathring{E}}{T} + \mathring{S} \quad \text{where} \quad \mathring{S}(t) = \frac{d}{dt} S(t)$$

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

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

"mean" entropy of system

$\Rightarrow$ typically called entropy of system

define $F(t) = E(t) - T S(t)$

$=$ Helmholtz free energy

$$-T\mathring{I} = \mathring{E} - T\mathring{S} = \mathring{F}$$

$F(t)$ must have slope ≤ 0

b/c $\mathring{F} = -T\dot{I}$ and $T > 0$

$\dot{I} \geq 0$

this free energy must dec. or stay constant over time