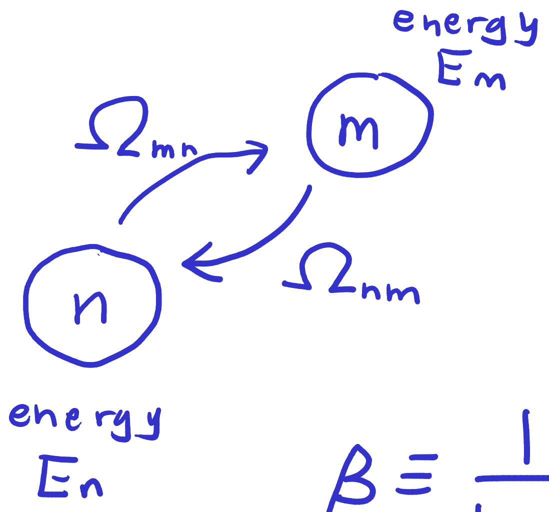
PHYS 320/420 Lecture 17



$$\frac{\Omega_{mn}}{\Omega_{nm}} = e^{-\beta \overbrace{(E_m - E_n)}}$$

energy change in sys $n \to m$

= energy taken from env. to make this possible (if $E_m > E_n$)

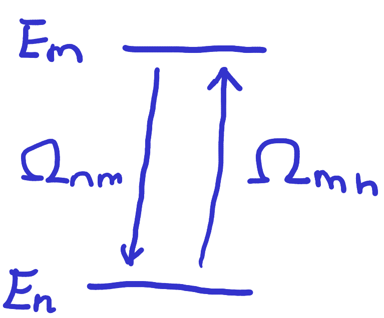
or released to env. (if $E_m < E_n$)

$$\beta \equiv \frac{1}{k_B T}$$

used to define "temperature": measure of how willing the env. is to donate energy

$$\beta = -\frac{V_E}{D_E} > 0$$ for env. that prefer to take energy ($w^- > w^+$)

$\Rightarrow T > 0$ for such environments



case: $E_m > E_n$

$\beta > 0 \quad (T > 0)$

$$\frac{\Omega_{mn}}{\Omega_{nm}} = e^{\underbrace{-\beta}_{>0}\underbrace{(E_m - E_n)}_{>0}} < 1$$

$$\Omega_{mn} < \Omega_{nm}$$

for pos. temp env. ("greedy", unwilling to loan energy)

$\Rightarrow$ sys. going uphill in energy is less likely than going downhill

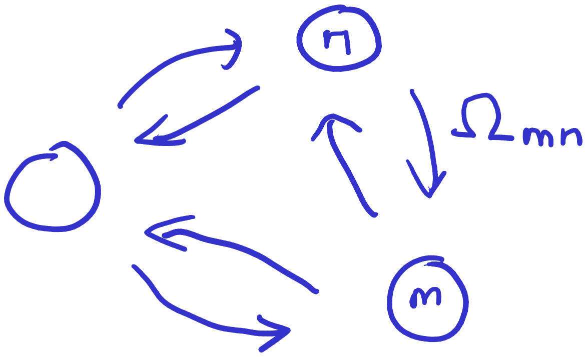
as T increases $\Rightarrow$ $\beta = \frac{1}{k_B T}$ decrease

$T \to \infty \Rightarrow \beta \to 0$

inf. temp $+\infty \Rightarrow \Omega_{mn} = \Omega_{nm}$

Two pillars of the course:

i) state dynamics via the master equ:



$$\frac{dp_n}{dt} = \sum_m \Omega_{nm} p_m$$

ii) transition rates Ω_{mn} are connected to energy exchange w/ environment:

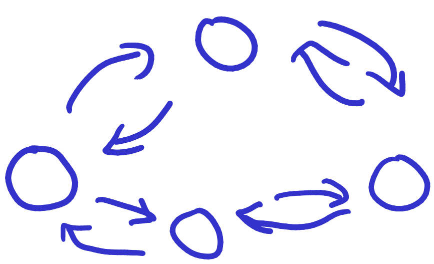
$$\frac{\Omega_{mn}}{\Omega_{nm}} = e^{-\beta \underbrace{(E_m - E_n)}}$$

to do: look at all possible ways an environment can donate energy:

- absorption of a photon
- absorption of heat from surroundings
- "chemical energy": binding / modification / unbinding of molecules from environment

What are implications?

focus on biochemical cycles like



and ask how we can move around these cycles (mostly) in one direction

$\Rightarrow$ this will require a flow of energy from the environment

$\Rightarrow$ tell us something about nature of life vs. non-life, + possible origins of life

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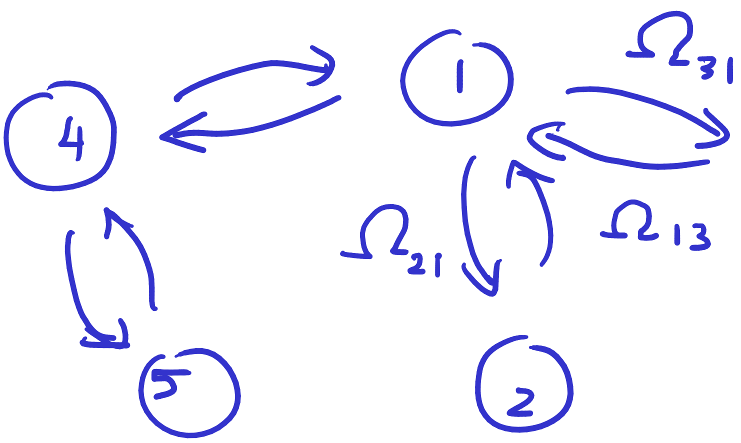


$\Omega_{23} = \Omega_{32} = 0$ (not connected)

note: not all states can transition to each other (system-specific property)

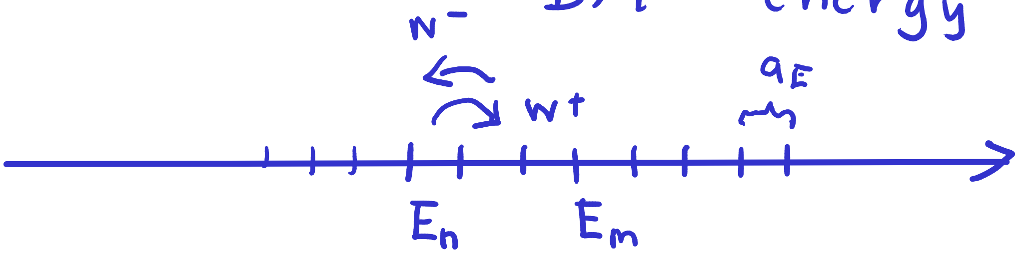
but det. balance implies

if Ω_{mn} exists then Ω_{nm} (reverse trans.) must be possible + satisfy that ratio

$\Rightarrow$ all arrows must go both ways

Ω's are properties of system trans.

w^+, w^- : properties of the environment transitioning b/t energy states



tran in sys. energy must occur b/c of env. energy donation or taking

w^+: rate at which you are likely to gain a_E from env. in time step δt

w^-: " " " lose "

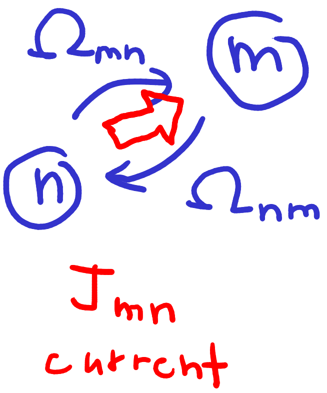
connection:
$$\frac{\Omega_{mn}}{\Omega_{nm}} = e^{-\beta(E_m - E_n)}$$

$$\beta = -\frac{V_E}{D_E} = \frac{-(w^+ - w^-)a_E}{\frac{1}{2}(w^+ + w^-)a_E^2}$$

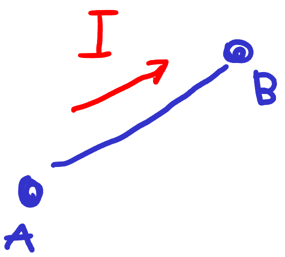
Let's start by describing how cycles work:

$\Rightarrow$ introduce the notion of "probability currents" similar to electric currents

take any two connected states in our network



$$J_{mn}(t) = \underbrace{\Omega_{mn} p_n(t)}_{\substack{\text{avg. \# of} \\ n \to m \text{ trans.} \\ \text{per unit time}}} - \underbrace{\Omega_{nm} p_m(t)}_{\substack{\text{avg. \# of} \\ m \to n \text{ trans.} \\ \text{per unit time}}}$$



= net "probability flow" from $n \to m$

$\equiv$ "current" b/t $n \to m$

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

(like in E+M we can choose arbitrarily which dir. is + current)