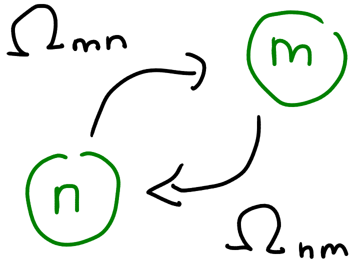
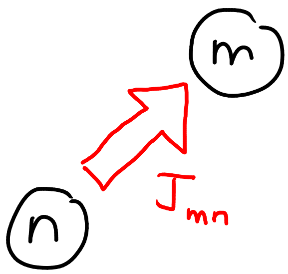


$$\frac{\Omega_{nm}}{\Omega_{mn}} = e^{-\beta(E_n - E_m)}$$

local detailed balance (LDB)

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

(net) probability current b/t states:



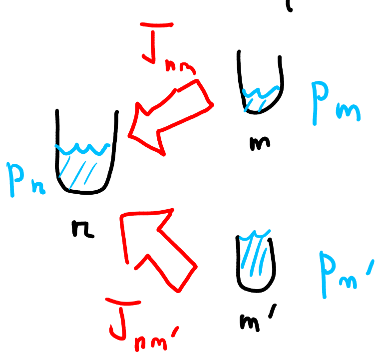
current from $n \to m$:

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

by construction: $J_{nm}(t) = -J_{mn}(t)$

$J_{nn}(t) = 0$

master equation:



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

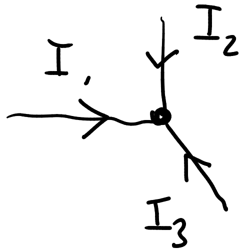
$$= \sum_{m\neq n} \Omega_{nm} p_m + \underbrace{\Omega_{nn}}_{-\sum_{m\neq n}\Omega_{mn}} p_n$$

$$= \sum_{m\neq n} \underbrace{[\Omega_{nm} p_m - \Omega_{mn} p_n]}_{J_{nm}}$$

$$\Rightarrow \boxed{\frac{dp_n}{dt} = \sum_m J_{nm}}$$

conserv. of prob.

= sum of currents into state n from all other states m



$$I_1 + I_2 + I_3 = 0$$

to get analog of Kirchoff's first law ("sum of currents into any state is zero")

$\Rightarrow$ special case: $\dfrac{dp_n}{dt} = 0$ for all n

stationary state

$\Rightarrow$ $p_n(t)$ constants indep. of time

$= p_n^s$

$$0 = \sum_m J_{nm}^s$$

stationary current

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

two types of stationary states:

1) equilibrium stat. state (ESS)

all $J_{nm}^s = 0$

(all forward trans. are balanced by their reverse)

2) non-equilibrium stat. state (NESS)

at least some $J_{nm}^s \neq 0$

Will show:

- living things require NESS
- NESS necessarily require energy input from env.

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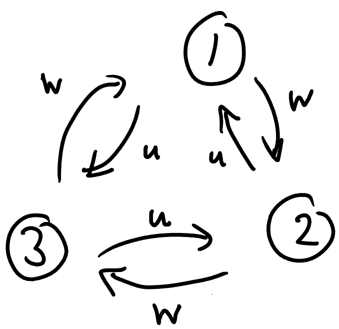
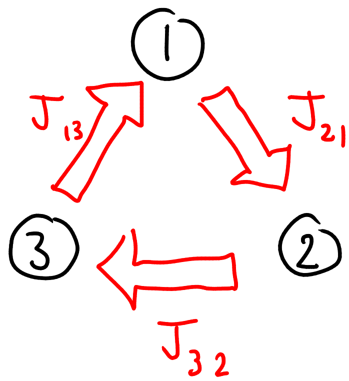
example:





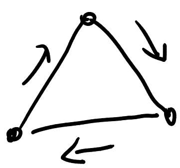
solve for stat. state:

$$0 = \sum_m J^s_{nm}$$

$$0 = J^s_{13} + J^s_{12} = J^s_{13} - J^s_{21}$$

$$0 = J^s_{21} + J^s_{23} = J^s_{21} - J^s_{32}$$

$$0 = J^s_{32} + J^s_{31} = J^s_{32} - J^s_{13}$$



$$J^s_{13} = J^s_{21}$$

$$J^s_{21} = J^s_{32}$$

$$J^s_{32} = J^s_{13}$$

$$J^s_{13} = J^s_{21} = J^s_{32} = \text{const.} = J$$

to find prob. p^s_n for all & value of J

$$\left.\begin{aligned} J &= J^s_{21} = w p^s_1 - u p^s_2 \\ J &= J^s_{32} = w p^s_2 - u p^s_3 \\ J &= J^s_{13} = w p^s_3 - u p^s_1 \\ & p^s_1 + p^s_2 + p^s_3 = 1 \end{aligned}\right\} \begin{array}{l} \text{4 eqn} \\ \text{4 unk} \end{array}$$

$\Rightarrow \quad p_1^s = p_2^s = p_3^s = \frac{1}{3} \qquad J = \frac{1}{3}(w-u)$

if $u = w$: $\quad J = 0 \quad$ (ESS)

$u \neq w$: $\quad J \neq 0 \quad$ (NESS)

consider LDB:

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

$$\frac{w}{u} = e^{-\beta(E_2 - E_1)}$$

$$\frac{w}{u} = e^{-\beta(E_3 - E_2)}$$

$$\frac{w}{u} = e^{-\beta(E_1 - E_3)}$$

multiply together: $\quad \frac{w^3}{u^3} = 1 \Rightarrow \frac{w}{u} = 1$

LDB $\Rightarrow$ ESS

claim: for <u>any</u> network where LDB looks like $\frac{\Omega_{nm}}{\Omega_{mn}} = e^{-\beta(E_n - E_m)}$

only thermal energy exchange w/ env, at temp. T

$\Rightarrow$ stat. state <u>must</u> be ESS

$$J_{nm}^s = \Omega_{nm} p_m^s - \Omega_{mn} p_n^s = 0 \qquad \text{ESS}$$

for all connected (n,m)

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

def'n of ESS

LDB

there always exist a sol'n that satisfies ESS:

$$\boxed{p_n^s = \frac{e^{-\beta E_n}}{Z}} \qquad p_m^s = \frac{e^{-\beta E_m}}{Z}$$

norm. const.

Boltzmann equil. prob. dist.

$$\sum_n p_n^s = 1 \Rightarrow Z = \sum_n e^{-\beta E_n}$$

LDB $\Longleftrightarrow$ ESS