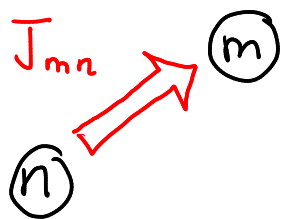


$$\frac{\Omega_{mn}}{\Omega_{nm}} = e^{-\beta(E_m - E_n)}$$

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



current from  $n \rightarrow m$ :

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

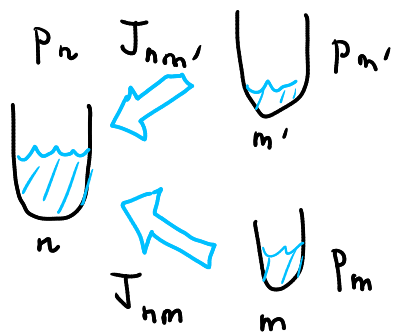
by construction:

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

$$J_{nn}(t) = 0$$

master eqn:

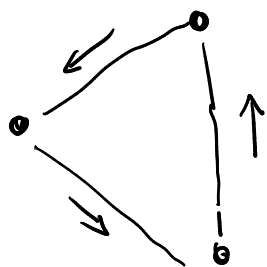
$$\begin{aligned} \frac{dp_n}{dt} &= \sum_m \Omega_{nm} p_m(t) \\ &= \sum_{m \neq n} \Omega_{nm} p_m + \underbrace{\Omega_{nn} p_n}_{-\sum_{m \neq n} \Omega_{mn} p_n} \end{aligned}$$



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

$$\frac{dp_n}{dt} = \sum_m J_{nm}(t) = \text{Sum of all currents into } n \text{ from other } m$$

Conservation of probability equation



special case: stationary state  
(typically occurs when  $t \rightarrow \infty$ )

$$\frac{dp_n}{dt} = 0 \quad \text{for all } n \Rightarrow p_n(t) \text{ indep. of time}$$

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

$$p_n(t) = p_n^s$$

in stationary state:

master equ:  $0 = \sum_n J_{nm}^s$  Kirchoff's first law

two ways to have a stationary state:

- 1) all currents are zero:  $J_{nm}^s = 0$   
for all connected  $(n,m)$  in net

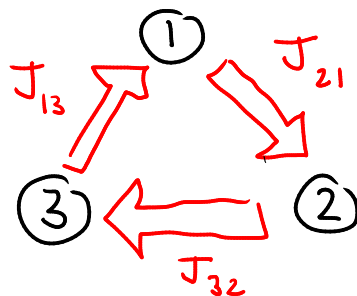
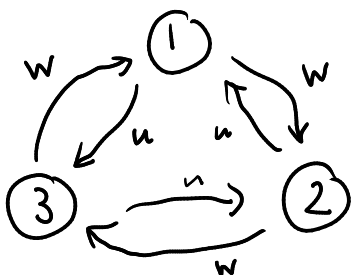
equilibrium stationary state (ESS)

- 2) non-equilibrium stat. state (NESS) at least some  $J_{nm}^s \neq 0$

will show:

- living organisms need NESS
- NESS necessarily require energy input from environment

example:



characterize stat. state

sum of currents into any node = 0

$$0 = J_{13}^S + J_{12}^S = J_{13}^S - J_{21}^S \Rightarrow J_{13}^S = J_{21}^S$$

$$0 = J_{21}^S + J_{23}^S = J_{21}^S - J_{32}^S \Rightarrow J_{21}^S = J_{32}^S$$

$$0 = J_{32}^S + J_{31}^S = J_{32}^S - J_{13}^S = J_{21}^S = J_{13}^S$$

all currents  $J_{13}^S = J_{21}^S = J_{32}^S = \text{const} \equiv \underline{J}$

to find  $p_n^S$  & value of  $J$ , write down def'n's of currents:

$$J = J_{21}^S = w p_1^S - u p_2^S \quad p_1^S + p_2^S + p_3^S = 1$$

$$J = J_{32}^S = w p_2^S - u p_3^S \quad 4 \text{ eqn's, } 4 \text{ unkn.}$$

$$J = J_{13}^S = w p_3^S - u p_1^S$$

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

if  $u = w$  :  $J = 0 \Rightarrow \text{ESS}$

$u \neq w$  :  $J \neq 0 \Rightarrow \text{NESS}$

if only energy is exchanged w/ env:

LDB  $\frac{w}{u} = \frac{\Omega_{21}}{\Omega_{12}} = e^{-\beta(E_2 - E_1)}$

$$\frac{w}{u} = \frac{\Omega_{32}}{\Omega_{23}} = e^{-\beta(E_3 - E_2)}$$

$$\frac{w}{u} = \frac{\Omega_{13}}{\Omega_{31}} = e^{-\beta(E_1 - E_3)}$$

$$\frac{W^3}{u^3} = 1 \Rightarrow \frac{W}{u} = 1$$

LDB  $\Rightarrow$  only an ESS is possible here



claim: for any network where only energy exchange occurs at temp.  $T$

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

$\Rightarrow$  stat. state has to be ESS

proof: show stationary currents are all zero

$$J_{nm}^s = \Omega_{nm} p_m^s - \Omega_{mn} p_n^s \stackrel{?}{=} 0$$

if  $= 0 \Rightarrow \frac{\Omega_{nm}}{\Omega_{mn}} = \frac{p_n^s}{p_m^s} = e^{-\beta(E_n - E_m)}$   
↖ LDB ↗  
 for all connected  $(n, m)$

there always a solution for

$p_n^s$  where this is true:

$$p_n^s = \frac{e^{-\beta E_n}}{Z}$$

$$p_m^s = \frac{e^{-\beta E_m}}{Z}$$

normaliz.  
const.

Boltzmann  
equil. solution

$$\sum_n p_n^s = 1$$

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