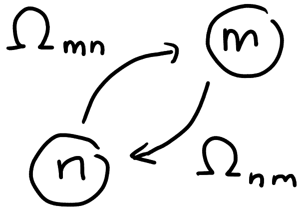
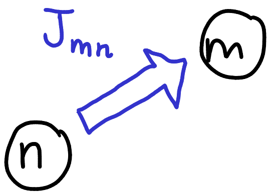


$$\frac{\Omega_{nm}}{\Omega_{mn}} = e^{-\beta(E_n - E_m)}$$

local detailed balance (LDB)

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



current from $n \to m$:

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

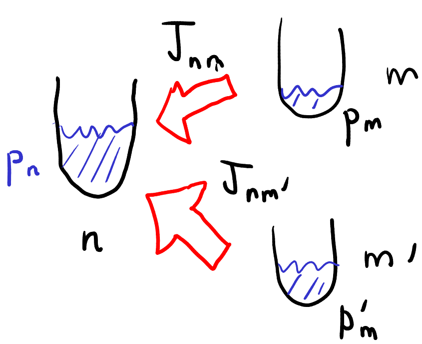
by construction: $J_{nm}(t) = -J_{mn}(t)$

$J_{nn}(t) = 0$

master eqn:

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

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



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

$$\Rightarrow \boxed{\frac{dp_n}{dt} = \sum_m J_{nm}(t)} = \text{sum of currents into state } n \text{ from all other states } m$$

conservation of prob.

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

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

are indep. of time

two types: 1) equilibrium stationary state (ESS):

all $J^s_{nm} = 0$

currents in stat. state

2) non-equilibrium stat. state (NESS):

at least some $J^s_{nm} \neq 0$

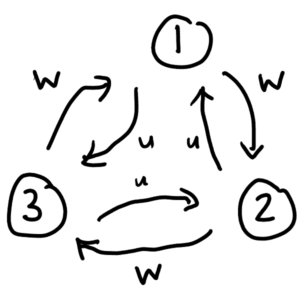
will show:
- living things require NESS
- NESS necessarily require energy input from environment

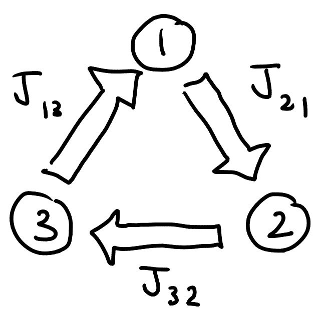
in stat. state, master eqn becomes:

$$0 = \sum_m J^s_{nm} \quad \text{for all state } n$$

"Kirchoff's first law": sum of currents into any state $= 0$

example:





solve for stat. state:

$$0 = J^s_{13} + J^s_{12} = J^s_{13} - J^s_{21}$$
$$0 = J^s_{21} + J^s_{23} = J^s_{21} - J^s_{32}$$
$$0 = J^s_{32} + J^s_{31} = J^s_{32} - J^s_{13}$$

$\Rightarrow \quad J_{13}^{s} = J_{21}^{s} \qquad J_{21}^{s} = J_{32}^{s} \qquad J_{32}^{s} = J_{13}^{s}$

$\Rightarrow \quad J_{13}^{s} = J_{21}^{s} = J_{32}^{s} = \text{constant} \equiv J$

to find prob's + the value of J,
use definitions of currents:

$$\left.\begin{aligned} J_{21}^{s} &= w p_1^s - u p_2^s = J \\ J_{32}^{s} &= w p_2^s - u p_3^s = J \\ J_{13}^{s} &= w p_3^s - u p_1^s = J \\ p_1^s &+ p_2^s + p_3^s = 1 \end{aligned}\right\} \begin{array}{c} \text{4 eqn's} \\ \text{for} \\ \text{4 unknowns:} \\ J, p_1^s, p_2^s, p_3^s \end{array}$$

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

if $u = w$: $\quad J = 0 \quad \Rightarrow$ ESS

$u \neq w$: $\quad J \neq 0 \quad \Rightarrow$ NESS

Consider LDB: $\quad \dfrac{w}{u} = e^{-\beta(E_2 - E_1)}$

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

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

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

LDB $\Rightarrow$ only an ESS is possible!

claim: for <u>any</u> network where LDB looks like:

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

only energy exchange w/ envir. at temp. T

$\Rightarrow$ stat. state must be ESS

show: ESS currents are all zero

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

LDB

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

for all connected (m, n)

def'n of ESS

there always exists a solution that satisfies ESS

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

norm. constant

Boltzmann equ.

universal ESS sol'n

$$\sum_n p_n^s = 1$$

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

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

To get an NESS we need to modify LDB:

will argue:

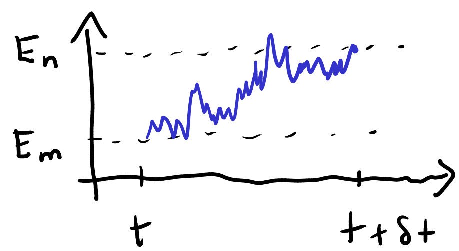
$$\frac{\Omega_{nm}}{\Omega_{mn}} = e^{-\beta(E_n - E_m - W_{nm})}$$

$\uparrow$ "work" done during $m \to n$ trans.

where $W_{nm} \neq \Phi_n - \Phi_m$ for any state func. Φ_n

How to get this extra term?

recall:



$\Omega_{nm}\delta t \propto$ prob. that env. takes us from E_m to E_n in δt (donates $E_n - E_m$ energy)

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

Q_{nm} = how much energy we need from env. in $m \to n$ trans.

= "heat"

Imagine we have "help" from another energy source:

$$Q_{nm} = E_n - E_m - \underbrace{W_{nm}}_{\text{energy from other source} \equiv \text{"work"}}$$

$W_{nm} > 0$: help
work into sys.

$W_{nm} < 0$: hurt
work output from sys.

main takeaway:
new LDB condition

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