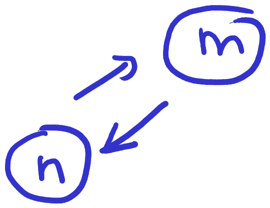
PHYS 320/420: Lecture 18

Current:



$$J_{mn}(t)$$

$$= \Omega_{mn} p_n(t) - \Omega_{nm} p_m(t)$$

$\sim$ net probability flow
(# trans. per unit time)
from $n \to m$

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

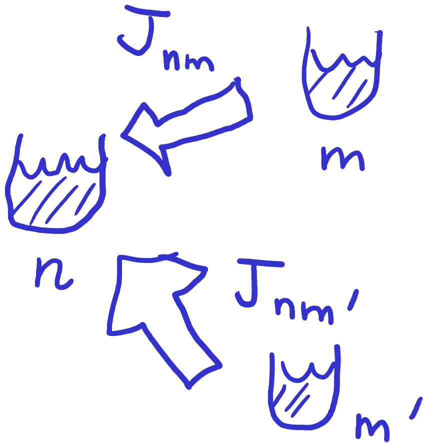
$$= \sum_{m \neq n} \Omega_{nm} p_m + \underbrace{\Omega_{nn}}_{-\sum_{m \neq n} \Omega_{mn}} p_n$$

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

$$\boxed{\frac{dp_n}{dt} = \sum_{m \neq n} J_{nm}}$$

"conservation of probability"

rate at which prob. in state n change = sum of currents from all other states into n



Special class of solutions to master equation:

<u>stationary states</u>:

the case where all state prob. no longer change in time $\Rightarrow$ $P_n(t) \to p_n^s$

time ind. const. (could be diff. for each n)

$$\frac{dp_n^s}{dt} = 0 = \sum_{m \neq n} J_{nm}^s$$

currents flowing into each state must cancel

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

stationary states

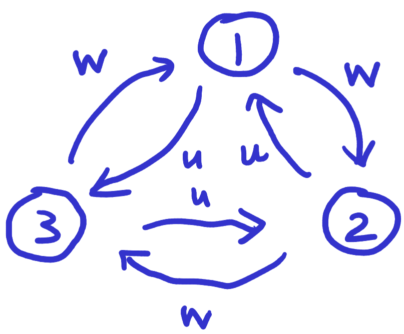
1) equilibrium stat. state (ESS): all $J^s_{nm} = 0$

2) non-equil. state state (NESS): at least one $J^s_{nm} \neq 0$

Things that we will show:

- Living things necessarily require NESS.
- NESS necessarily require an energy flow from environment.

Example: 3 state cycle



$$0 = \frac{dp_1^s}{dt} = J^s_{12} + J^s_{13}$$

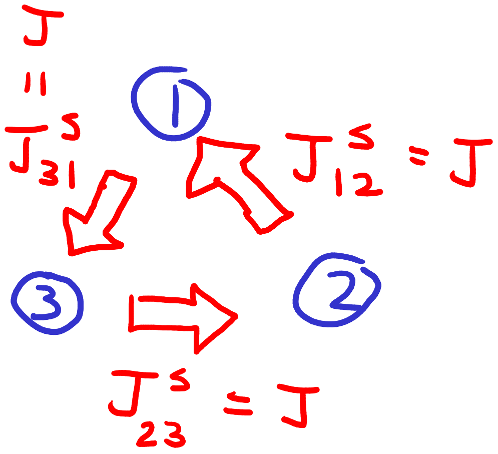
$$0 = \frac{dp_2^s}{dt} = J^s_{21} + J^s_{23}$$

$$0 = \frac{dp_3^s}{dt} = J^s_{31} + J^s_{32}$$

solving for stat. state

$$\Rightarrow \quad J^s_{12} = -J^s_{13} \qquad J^s_{21} = -J^s_{23} \qquad J^s_{31} = -J^s_{32}$$

$$J^s_{12} = J^s_{31} = J^s_{23} = J \quad \text{constant}$$



$$J^s_{12} = \overbrace{u p^s_2}^{\#\, 2\to 1 \text{ trans.}/\text{time}} - \overbrace{w p^s_1}^{\#\, 1\to 2 \text{ trans.}/\text{time}} = J$$

$$J^s_{31} = u p^s_1 - w p^s_3 = J$$

$$J^s_{23} = u p^s_3 - w p^s_2 = J$$

$$p^s_1 + p^s_2 + p^s_3 = 1$$

4 eqns for 4 unknowns (J, p^s_1, p^s_2, p^s_3)

$$\Rightarrow \quad p^s_1 = p^s_2 = p^s_3 = \frac{1}{3} \qquad J = \frac{1}{3}(u-w)$$

if $u = w$: $J = 0 \Rightarrow$ all currents are zero

$\Rightarrow$ ESS

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

Factor in detailed balance:

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

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

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

$\Rightarrow$ multiply all 3 equations:

$$\frac{w^3}{u^3} = 1 \Rightarrow w = u \Rightarrow$$ only ESS is possible!

For a general network that satisfies det. balance condition, the stat. solution is always ESS:

$$J_{nm}(t) = J_{nm}^s \overset{}{\underset{ESS}{=}} 0 = \Omega_{nm} p_m^s - \Omega_{mn} p_n^s$$

$$\Rightarrow \frac{\Omega_{nm}}{\Omega_{mn}} = \frac{p_n^s}{p_m^s}$$

det. balance $\Rightarrow$ $$e^{-\beta(E_n - E_m)} = \frac{p_n^s}{p_m^s}$$

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

partition func. $\parallel$ Z = const. indep. of n

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

Boltzmann equil. distribution describing ESS for a sys. w/ envir. at temp T

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

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

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

Z is a normalization const.