Current:

\[ J_{mn}(t) = \Omega_{mn} p_n(t) - \Omega_{nm} p_m(t) \]

\( \sim \) net probability flow

(\# trans. per unit time)

from \( n \to m \)

\[
\frac{dp_n}{dt} = \sum_m \Omega_{nm} p_m \\
= \sum_{m \neq n} \Omega_{nm} p_m + \Omega_{nn} p_n - \sum_{m \neq n} \Omega_{mn} p_n \\
= \sum_{m \neq n} \left[ \Omega_{nm} p_m - \Omega_{mn} p_n \right]
\]

\[
\frac{dp_n}{dt} = \sum_{m \neq n} J_{nm}
\]
"conservation of probability"

\[ J_{nm} \]

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

\[ J_{nm}, \quad J_{nm'} \]

Special class of solutions to master equation:

**stationary states**:

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

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

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

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

\[ \begin{align*}
1) \text{ equilibrium stat. state (ESS)}: \quad & \text{all } J_{nm}^S = 0 \\
2) \text{ non-equil. state state (NESS): } \quad & \text{at least one } J_{nm}^S \neq 0
\end{align*} \]

Things that we will show:

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

Example: 3 state cycle

\[ \begin{align*}
o = \frac{dp_1^S}{dt} &= J_{12}^S + J_{13}^S \\
o = \frac{dp_2^S}{dt} &= J_{21}^S + J_{23}^S \\
o = \frac{dp_3^S}{dt} &= J_{31}^S + J_{32}^S
\end{align*} \]

solving for stat. state

\[ J_{12}^S = -J_{13}^S, \quad J_{21}^S = -J_{23}^S, \quad J_{31}^S = -J_{32}^S \]
\[ J_{12}^s = J_{23}^s = J_{31}^s = J \quad \text{constant} \]

\[ J_{12}^s = u p_2^s - w p_1^s = J \]

\[ J_{31}^s = u p_1^s - w p_3^s = J \]

\[ J_{23}^s = u p_3^s - w p_2^s = J \]

\[ p_1^s + p_2^s + p_3^s = 1 \]

4 eqns for 4 unknowns \((J, p_1^s, p_2^s, p_3^s)\)

\[ p_1^s = p_2^s = p_3^s = \frac{1}{3} \quad J = \frac{1}{3} (u-w) \]

if \(u = w\): \(J = 0 \Rightarrow \text{all currents are zero} \Rightarrow \text{ESS} \)

if \(u \neq w\): \(J \neq 0 \Rightarrow \text{NESS} \)

Factor in detailed balance:

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

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

\[ \frac{w}{u} = e^{-\beta (E_1 - E_3)} \]
multiply all 3 equations:
\[ \frac{w^3}{u^3} = 1 \Rightarrow u = w \Rightarrow \text{only ESS is possible!} \]

For a general network that satisfies det. balance condition, the stat. solution is always ESS:
\[ J_{nm}(t) = J_{nm}^s = 0 = \Omega_{nm} p_{m}^s - \Omega_{mn} p_{n}^s \]

\[ \Rightarrow \frac{\Omega_{nm}}{\Omega_{mn}} = \frac{p_{n}^s}{p_{m}^s} \]

det. balance \[ \Rightarrow e^{-\beta(E_n - E_m)} = \frac{p_{n}^s}{p_{m}^s} \quad \text{partition func.} \]

\[ p_{n}^s = \frac{e^{-\beta E_n}}{Z} \]
\[ p_{m}^s = \frac{e^{-\beta E_m}}{Z} \]

\[ \beta = \frac{1}{k_B T} \]

Z = const. independent of n

Boltzmann equil. distribution describing ESS for a sys. w/ envir. at temp T
\[ \sum' \rho_n = 1 = \sum' \frac{e^{-\beta E_n}}{Z} = \frac{1}{Z} \sum' e^{-\beta E_n} \]

\[ Z = \sum e^{-\beta E_n} \]

\( Z \) is a normalization constant.