Return to our system trajectory:

\[ P(y_0, y_1, \ldots, y_i, y_{i+1}) = \text{joint prob. of (i+1) long trajectory} \]

Markovian approximation:

\[ P(y_{i+1} | y_0, y_1, \ldots, y_i) = P(y_{i+1} | y_i) \]

independent of \( y_0, \ldots, y_{i-1} \)

only dependent on \( y_i \)
generally can choose $S\tau$ sufficiently large that this is approximately true.

Rewriting the condition:

$$\frac{P(y_0, \ldots, y_i, y_{i+1})}{P(y_0, \ldots, y_i)} = P(y_{i+1} | y_i)$$

$$\Rightarrow P(y_0, \ldots, y_i, y_{i+1}) = P(y_{i+1} | y_i) P(y_0, \ldots, y_i)$$

$$= P(y_{i+1} | y_i) P(y_i | y_{i-1}) P(y_0, \ldots, y_{i-1})$$

$$\Rightarrow \prod_{j=0}^{i} P(y_{j+1} | y_j) P(y_0)$$

prescription to construct joint probabilities

Every dynamical theory so far has been Markovian:

$$P(y, t+\delta t) = \text{right-hand side that depends on } P(y', t) \text{ only for some } y'$$

$\Rightarrow$ this includes classical mechanics + Hamilton's equations

Explicitly:

$$P(y_{i+1} | y_0) = \frac{P(y_0, y_{i+1})}{P(y_0)} = \frac{\int dy_1 \cdots dy_i P(y_0, \ldots, y_{i+1})}{P(y_0)}$$

$$= \int dy_1 \cdots dy_i \prod_{j=0}^{i} P(y_{j+1} | y_j)$$

$$= \int dy_i \frac{P(y_{i+1} | y_i) \left[ \int dy_i \cdots y_{i-1} \prod_{j=0}^{i-1} P(y_j | y_{j-1}) \right]}{P(y_0)}$$

$\Rightarrow P(y_{i+1} | y_0) = \int dy_i P(y_{i+1} | y_i) P(y_i | y_0)$

Chapman
Kolmogorov
for discrete states: \( y_i = \text{integer } n \), \( 1 \leq n \leq N \)

\[ P(y_{i+1} | y_i) \Rightarrow W_{mn} \quad \text{N\times N matrix} \]

= probability to transition to state \( m \) in time interval \( \delta t \)
given initially in state \( n \)

\[ P(y) \Rightarrow P_n \quad \text{N-comp. vector} \]

What can we say about \( P(y_i | y_0) \)?

\[ y_i = m \quad 1 \leq m \leq N \]
\[ y_0 = n \quad 1 \leq n \leq N \]

1) \( P(y_i | y_0) = N \times N \) matrix

2) \( P(y_i | y_0) \) depends only on time difference \( t_i - t_0 = i \delta t \)

assuming external environment parameters do not change in time

\[ m \]
\[ \Rightarrow \]
\[ P(m | n) \]
\[ \Rightarrow \]
\[ m_n \]

if environment is the same, initial time makes no difference:

homogeneous Markov process

\[ P(y_i | y_0) \Rightarrow P_{mn}(t) \quad \text{prob. to observe } m \text{ after time } t \]
\[ \text{if started in } n \text{ at time } 0 \]

\[ P(y_i | y_{i-1}) \Rightarrow P_{mm'}(\delta t) = W_{mm'}, \delta t \quad W_{mm'} > 0 \]

\[ \sum_{y_i} P(y_i | y_{i-1}) = 1 \]
\[ \sum_{m} S_{t} W_{mm'} = 1 \]

prob. per unit time to transition from \( m' \rightarrow m \) over time interval \( \delta t \)
Chapman-Kolmogorov:
\[ P_{mn}(t+s\tau) = \sum_{m'=1}^N W_{mm'} s\tau P_{m'n}(t) \]
\[ \approx P_{mn}(t) + \frac{dP_{mn}(t)}{dt} s\tau = s\tau \sum_{m'=1}^N W_{mm'} P_{m'n}(t) \]
\[ P_{mn}(t) \sum_{m'} W_{m'm} \]
\[ = 1 \text{ for any } m \]
\[ \Rightarrow \]
\[ \frac{dP_{mn}(t)}{dt} = \sum_{m'} \left[ W_{mm'} P_{m'n}(t) - W_{m'm} P_{mn}(t) \right] \]

**Gain-loss equation:**
\[ p(y_i) = \sum_{y_0} p(y_i | y_0) p(y_0) \Rightarrow p_{n}(t) = \sum_{n} p_{mn}(t) p_{n}(0) \]
\[ \Omega_{mn} = W_{mn} - \delta_{mm'} \left( \sum_{m''} W_{m''m} \right) \]
\[ \Omega = W - \frac{\hat{H}}{s\tau} \]
\[ \Rightarrow \]
\[ \frac{dP_{mn}(t)}{dt} = \sum_{m'} \Omega_{mm'} P_{m'n}(t) \]
\[ \Omega_{mn} > 0 \text{ (prob!)} \]
\[ \sum_{m} \Omega_{mm'} = \sum_{m} W_{mm'} - \sum_{m''} W_{m''m'} = 0 \]
\[ W = \begin{pmatrix} W_{11} & W_{12} & W_{13} \\ W_{21} & W_{22} & W_{23} \\ W_{31} & W_{32} & W_{33} \end{pmatrix} \quad \sum_i W_{i1} = \frac{1}{\delta t}, \text{ etc.} \]

\[ W_{11} = 1 - W_{21} - W_{31} \]

\[ \Omega = \begin{pmatrix} -W_{24} - W_{31} & W_{12} & W_{13} \\ W_{21} & -W_{12} - W_{32} & W_{23} \\ W_{31} & W_{32} & -W_{13} - W_{23} \end{pmatrix} \]

**Neat aspect:**

\[
\frac{d\hat{p}(t)}{dt} = \Omega \hat{p}(t) \quad \hat{p} = N \text{ comp. vector}
\]

**Solution:**

\[
\hat{p}(t) = e^{\Omega t} \hat{p}(0)
\]

Matrix exponential

\[
P_m(t) = \sum_{m'} \left[ e^{\Omega t} \right]_{mm'} P_{m'}(0)
\]

Initial distribution

\[ P_m(t) = \sum_n \left[ e^{\Omega t} \right]_{mn} P_n(0) \]

**Note:**

If \( P_{m'}(0) = \delta_{m'n} \) initial state definitely \( n \) then this becomes an equation for:

\[
P_{mn}(t) = \sum_{m'} \left[ e^{\Omega t} \right]_{m'n} P_{m'}(0)
\]

\[ \Rightarrow \text{components of } e^{\Omega t} \text{ are conditional prob's } P_{mn}(t) \]

Simple example:

1. \[ k \rightarrow 2 \]

Poisson process

\[ \Omega = \begin{pmatrix} -k & 0 \\ k & 0 \end{pmatrix} \Rightarrow P(t) = \left[ e^{\Omega t} \right]
\]

\[ P_{21}(t) = 1 - e^{-kt} \]

Regardless of initial cond.
Master equation + kinetic networks

$s_t = 1s: \text{ time step}$

\[
W = \begin{pmatrix}
1 & 2 & 3 \\
0.9 & 0.2 & 0.7 \\
0.1 & 0.3 & 0 \\
0 & 0.5 & 0.3 \\
\end{pmatrix}
\]

\[
\text{master: } \frac{dp_{mn}}{dt} = \sum_{m'} [W_{mm'}p_{m'n} - W_{m'm}p_{mn}]
\]

\[\text{define } \Omega_{mm'} = \begin{cases} W_{mm'} & m \neq m' \\ -\sum_{m' \neq m} W_{m'm} & m = m' \end{cases}\]

\[\frac{dp_{mn}}{dt} = \sum_{m'} \Omega_{mm'} p_{m'n} \]

\[\Omega = \begin{pmatrix}
-0.1 & 0.2 & 0.7 \\
0.1 & -0.7 & 0 \\
0 & 0.5 & -0.7 \\
\end{pmatrix}\]

\[\sum_{m} \Omega_{mm'} = 0\]

Solution:

\[p_{mn}(t) = [e^{\Omega t}]_{mn}\]

where

\[e^{\Omega t} = I + \Omega t + \frac{t^2}{2!} \Omega^2 + \ldots\]

if you have initial distrib. \(p_n(0)\)

\[p_m(t) = \sum_{n} [e^{\Omega t}]_{mn} p_n(0)\]

\[\frac{dP}{dt} = \Omega P\]

If you have observable \(A\) which has values \(a_m\) in state \(m\)
\[ \langle A(t) \rangle = \sum_{m} \text{amp}_{m}(t) \]
\[ = \sum_{m,m'} a_{m} [\text{e}^{\Omega t}]_{mm'} p_{m'}(0) \]

All of physics is solved!

\[ \dot{P} = \Omega P \]
\[ \dot{P}^T = \dot{P}^T \Omega^T \]

\[ \Rightarrow \text{transpose of master equation gives:} \]

adjoint master equation:

\[ \frac{dP_{nm}(t)}{dt} = \sum_{m'} P_{nm'} \Omega_{m'm} \quad \text{← note: we can sum both sides over final states} \]

\( P \) matrix satisfies both master equations.

adjoint:

\[ \frac{dP_{nm}(t)}{dt} = \sum_{m'} (P_{nm'} - P_{nm}) W_{m'm} \]

\( W \) is irreducible if its kinetic network is connected. [a path b/t any two states, ignoring arrow direction]

\( W = \begin{pmatrix} M & 0 \\ 0 & \text{I} \end{pmatrix} \) Here \( W \) is decomposable.

\( = \text{two non-interacting systems} \)

\( \Rightarrow \text{block diagonal} \)
First major conclusion: the dynamical result:

Theorem I. If $W$ is not decomposable, $P_{mm}(t) \to P_{n}^{s}$ as $t \to \infty$.

Proof: look at adjoint equation:

- $W_{mm} \geq 0$
- if $P_{nm} < P_{nm'}$ for all $m' \neq m$, then $\frac{dP_{nm}}{dt} > 0$ where $W_{mm} \neq 0$
- if $P_{nm} > P_{nm'}$ for all $m' \neq m$, then $\frac{dP_{nm}}{dt} < 0$ where $W_{mm} \neq 0$

Adjoint equation drives convergence of all $P_{nm}(t)$ as $t \to \infty$ toward some constant $P_{n}^{s}$.

When $P_{nm}(\infty) = P_{n}^{s}$ for all $m$, then $\frac{dP_{nm}}{dt} = 0$.

Example:

$P = e^{\Omega t} = \begin{pmatrix}
  k_{1} \& k_{2} \\
  k_{2} \& k_{1}
\end{pmatrix}
\begin{pmatrix}
  k_{2} + k_{1} e^{-\left(k_{1} + k_{2}\right) t} \\
  k_{2} + k_{1} e^{-\left(k_{1} + k_{2}\right) t}
\end{pmatrix}$
as \( t \to \infty \):

\[
P_{1n}(t) \to p_1^s = \frac{k_2}{k_1 + k_2}
\]

\[
P_{2n}(t) \to p_2^s = \frac{k_1}{k_1 + k_2}
\]

Note that \( p_m^s \) is solution to master equation.

with \( \frac{dp_m^s}{dt} = 0 \Rightarrow \)

\[
0 = \sum_m \left[ W_{mm}' p_m^s - W_{mm} p_m^s \right]
\]

\[\text{gain} \]

\[\text{loss} \]

\[
\begin{align*}
[m = 1] & \Rightarrow W_{12} p_2^s - W_{21} p_1^s = 0 \\
& = k_2 & = k_1
\end{align*}
\]

\[
\sum_m \Omega_{mm}' p_m^s = 0 \Rightarrow p_m^s \text{ is right e-vec of } \Omega \text{ w/e-val zero}
\]

\[
\sum_m \Omega_{mm}' p_m^s = 0 \Rightarrow p_m^s \text{ is right e-vec of } \Omega \text{ w/e-val zero}
\]

\[
\frac{W_{mm}}{W_{mm}'} \sum_m \Omega_{mm}' p_m^s + \sum_{m \neq m} W_{mm}' p_m^s = 0
\]

\[
\frac{W_{mm}}{W_{mm}'} \sum_m \Omega_{mm}' p_m^s + \sum_{m \neq m} W_{mm}' p_m^s = 0
\]

\[
\text{frac of time spent in state } 2 = \frac{k_1}{k_1 + k_2}
\]

as \( t \to \infty \), system constantly changing its state,

but prob. to be in a given state at any time \( t \Rightarrow \) constant.

probabilities are stationary, system is not in general.

Note that in our example,

\( P_{mn}(t) > 0 \) for all times \( t > 0 \).
Profound corollary #1: if $W$ corresponds to

- **Strongly connected network** (irreducible)
  - there is a path between any two states following the arrows
  - $p_{mn}(t) > 0$ for all $t > 0, m, n$
  - $p_{mn}(\infty) = p_{ms}^S > 0$ for all $m$

- No zero probs in stationary distribution and the distribution is unique
- Every state in the system is recurrent (it will be visited $\infty$ times as $t \to \infty$).
- The system is **ergodic**.

Counterexamples:

- $k_2 = 0$: $p_1^S = 0$, $p_2^S = 1$
- $k_2 = 0$: $p_1^S = 0$, $p_2^S = 1$, $p_3^S = 0$
  - More than one possible stationary distribution:
  - $p_1^S = 0$, $p_2^S = 1$, $p_3^S = 0$
  - $p_1^S = 0$, $p_2^S = 0$, $p_3^S = 1$

States that have zero prob. as $t \to \infty$ are called **transient states**. $p_n^S = 0$

The remainder are called **absorbing**.

In general, can group a network into strongly connected subsets:

- Those subsets with at least one external outgoing arrow will be transitory.
the others will be absorbing:
in at least one stationary distribution
their prob's will be nonzero

⇒ thus generally we can focus on strongly connected subsets
Broad view:

Ensemble = many copies of the whole system that are prepared at time $t=0$ and allowed to evolve in time.

Each ensemble is defined by its preparation: the initial states $n$ are drawn from some distribution $P_n(0)$, where $\sum P_n(0) = 1$.

$P_n(0) = \delta_{ni}$ pure ensemble: every copy starts in the same state $i$.

$P_n(0) = \sum_i \alpha_i$ otherwise, it is called a mixed ensemble: can have different starting states.

For system with matrix $\Omega$:

$P_m(t) = \sum_{m'} [e^{\Omega t}]_{mm'} P_{m'}(0)$ in general.

$P_m(t) = [e^{\Omega t}]_{mi}$ if pure ensemble $P_m(0) = \delta_{mi}$.

$\equiv P_{mi}(t)$
All p's in this course are fractions of ensembles!
We cannot solve analytically what a single copy of the system does: requires numerical kinetic Monte Carlo.

Types of systems:
- Connected
- Non-ergodic
- Ergodic (strongly connected):
  \( p_m(t=\infty) = p_m^s > 0 \) for all ensembles (\( p_m^s \) unique)
- Splitting:
  \( p_m(t=\infty) = \text{diff. values for diff. ensembles} \)
- Non-splitting:
  \( p_m(t=\infty) = p_m^s \geq 0 \) for all ensembles (\( p_m^s \) unique)

Classify by different \( p_m^s \)
Poisson life-and-death example

\[ \Omega = \begin{pmatrix} -k & 0 \\ k & 0 \end{pmatrix} \]

\[ P = e^{\Omega t} = \begin{pmatrix} e^{-kt} & 0 \\ 1 - e^{-kt} & 1 \end{pmatrix} \]

\[ P_{11} = e^{-kt} \]

\[ \text{prob. of staying at 1 in time interval } \Delta t \text{ is: } W_{11} \Delta t = 1 - e^{-kt} \]

prob. of 1 \rightarrow 2 transition in time interval \( \Delta t \) is \( k \Delta t \):

\[ W_{12} \Delta t = k \Delta t \]

\[ t \rightarrow \infty, \quad \begin{pmatrix} 0 & 0 \\ 1 & 1 \end{pmatrix} \]

alternative deriv:

\[ P_{11} = \left(\frac{1 - k \Delta t}{\Delta t}\right)^n \]

\( n \) large \( \Rightarrow e^{-kt} \) as \( \Delta t \rightarrow 0 \)

\[ P_{11}(t) \Rightarrow \text{in ensemble of systems starting at 1 at time 0,} \]

the fraction that are at 1 in time \( t \)

\[ \text{you cannot solve for individual trajectories analytically,} \]

only numerically by kinetic Monte Carlo.
Aside: splitting system

\[ \Omega = \begin{pmatrix} -k_a - k_b & 0 & 0 \\ k_a & 0 & 0 \\ k_b & 0 & 0 \end{pmatrix} \]

\[ k_T = k_a + k_b \]

\[ P = e^{\Omega t} = e^{t \Omega} \]

\[ = \begin{pmatrix} e^{-k_T t} & 0 & 0 \\ \frac{k_a}{k_T} (1 - e^{-k_T t}) & 1 & 0 \\ \frac{k_b}{k_T} (1 - e^{-k_T t}) & 0 & 1 \end{pmatrix} \]

as \( t \to \infty \):

\[ \begin{pmatrix} 0 & 0 & 0 \\ \frac{k_a}{k_T} & 1 & 0 \\ \frac{k_b}{k_T} & 0 & 1 \end{pmatrix} \]

\( P_{21}(\infty) \neq P_{22}(\infty) \neq P_{23}(\infty) \) different stationary states

if you start with some arbitrary \( p_n(0) \)

\[ P_2(\infty) = \sum \frac{e^{t \Omega}}{k_T} P_{2n}(\infty) p_n(0) \]

\[ = \frac{k_a}{k_T} P_1(0) + P_2(0) \] for different starting dist.

as \( t \to \infty \): \( p_m(\infty) \) depends on initial preparation in a splitting system
Another viewpoint: \( \vec{p} = (p_1, p_2, \ldots) \)

\[
\frac{d\vec{p}}{dt} = \Omega \vec{p}
\]

Stationary \( \vec{p} \) satisfies:

\[
\frac{d\vec{p}_s}{dt} = 0 = \Omega \vec{p}_s
\]

right e-vec of \( \Omega \) w/ e-val 0

If \( \Omega \) has 1 such e-vec (non-splitting, connected)

\[\Rightarrow \vec{p}_s = C \hat{v} \]

\( \hat{v} \) set by normalization \( \sum p_n^2 = 1 \)

If there are more than one: \( \hat{v}_1, \hat{v}_2 \)

i.e. \[\hat{v}_i = \begin{pmatrix} 0 \\ 1 \\ \vdots \end{pmatrix} \quad \hat{v}_2 = \begin{pmatrix} 0 \\ 0 \\ \vdots \end{pmatrix} \]

any normalized \( \vec{p}_s = C_1 \hat{v}_1 + C_2 \hat{v}_2 \) is a stationary distribution!

Special property of ergodic \( \Omega \): \( \hat{v} \) is one

and \( v_n \neq 0 \) for all \( n \)