Markov Chains

Algorithms for Using Model Equilibration:

\[ 2^N \text{ States } \{ S_i \} \]

Transition Rules:

\[ P_{S_i \rightarrow S_j} = \text{Probability } S_j \text{ at } t+1 \]

given \( \{ S_i \} \) at time \( t \).

Will it reach thermal equilibrium?

Red & Green Bacteria (HW 3.1)

1001 states \# red = 0, \ldots, 1000 = \alpha

Transition rates \( P_{\alpha+1 \rightarrow \alpha}, P_{\alpha-1 \rightarrow \alpha}, P_{\alpha \rightarrow \alpha} \)

What is the long-time limit?
Generalize to Markov Chain.

- Finite set of states \( \mathcal{X} \times \mathcal{Y} \)
- Markovian Assumption: Future evolution depends only on current state, no memory
- Transition probabilities for next time step \( P_{x \rightarrow y} \): \( \bar{P}_{n+1} = P \cdot \bar{P}_n \)

\( 0 \leq P_{x \rightarrow y} \leq 1 \) (No negative rates)

- \( \sum_{x} P_{x \rightarrow y} = 1 \) (Probability conserved)
- \( P_{x \rightarrow y} \neq P_{y \rightarrow x} \) usually (Not symmetric! Can't diagonalize.)

Right eigenvectors: \( P \cdot \bar{p}_x = \lambda \cdot \bar{p}_x \)

Left eigenvectors: \( \sigma_x^T \cdot P = \lambda \sigma_x^T \)

- Math Truth: To each distinct eigenvalue, there is at least one left & right eigenvector.
Theorem 1: $P$ has a right eigenvector $p^*$ with eigenvalue one. (Stationary probability distribution $p^*_n = p^*$.)

Proof: $P$ has a left eigenvector $\omega^T = (1, 1, ..., 1)$

\[
\omega^T P = \sum_x \omega_x P_{x\to y} = \sum_x p_{x\to y} = 1
\]

$\omega$ goes somewhere

So it must have a right eigenvector.

Theorem 2: $P$ has no eigenvalues $|\lambda| > 1$.

Proof: Suppose $p_\lambda$, $|\lambda| > 1$, eigenvector.

First, $\sum_\lambda p_{\lambda} = \sum_\lambda (P p_\lambda)^\omega = \lambda \sum_\lambda p_{\lambda} \Rightarrow \sum_\lambda p_{\lambda} = 0.

Thus at least one element of $p_\lambda < 0$: let the most negative element be $-\frac{1}{A}$. Consider

\[
(p^* + \frac{\varepsilon}{A} p_\lambda)^n = P^n (p^* + \frac{\varepsilon}{A} p_\lambda) = p^* + \frac{\varepsilon}{A} \lambda^n p_\lambda
\]

Good probability distribution: positive for $0 < \varepsilon < 1$, $\sum p^* = 1$.

$\Rightarrow$ eventually goes negative, contradiction.

$\Rightarrow$ No $|\lambda| > 1$, 
Markov chains can have more than one stationary probability distribution.

**HW 3.1** has two eigenvectors with \( \lambda = 1 \). **Hint**

Energy conservation \( \rightarrow \) one \( p \) for each energy.

KAM theorem \( \rightarrow \) one \( p \) for each torus.

An ergodic Markov chain is one where every state \( \alpha \) can evolve into every other state \( \beta \) in a finite number of steps.

**Theorem** (too messy to prove here): An ergodic Markov chain has a unique stationary state \( p^* \), with right eigenvalue one.

All other eigenvalues < 1.

**Theorem**: If \( P \) is ergodic, then \( \lim_{n \to \infty} P^n p = p^* \) for any initial probability distribution \( p \).

**Proof**: \( p = p^* + \sum_{x} \alpha_x p_x \quad p^n p = p^* + \sum_{x} \alpha_x p^n_x \quad \to 0 \) as \( n \to \infty \)

True anyway.

Why bogus? Can't find complete set of right eigenvectors. (Can, if detailed balance assumed.)
One more specialization for stat mech:

**Detailed Balance**

A Markov chain satisfies detailed balance, if

$$p_{\alpha \rightarrow \beta} e^{-\frac{E_\beta}{kT}} = p_{\beta \rightarrow \alpha} e^{-\frac{E_\alpha}{kT}}$$

for some function $E_\beta$ and all $\alpha, \beta$.

Net flux $\alpha \rightarrow \beta$ equals flux $\beta \rightarrow \alpha$

$$p_\alpha = e^{-\frac{E_\alpha}{kT}} / Z$$

(Not true of magnetic systems, classical trajectories $x = p/m$)

To guarantee convergence to canonical ensemble, sufficient for computer algorithm to be

- Markovian (no memory)
- Ergodic (can reach everywhere)
- Satisfy detailed balance