Stat. Phys. IV: lecture 7

Spring 2025

Transition Rate and Probability

We consider a Markov process continuous in time with discrete states n.

$$W(n_1, n_2) = \lim_{\Delta t \to 0} \frac{P(n_1, 0 \mid n_2, \Delta t)}{t} = \frac{\partial}{\partial t} P(n_1, 0 \mid n_2, \Delta t)\Big|_{\Delta t = 0}$$

is the transition rate to jump from state.
Then we can assume transition probability with short-time expansion:

$$P(n_1, 0 \mid n_2, t) = W(n_1, n_2)t + \mathcal{O}(t^2)$$

Can also introduce the exit rate out of state u_1:

$$a(n_1) = \sum_{n_1 \neq n_2} W(n_1, n_2)$$

Mesoscopic Master Equation

Equation of motion of $P(n_1|n_2, \Delta t)$

$$P(n_1 \mid n_2, \Delta t) = (1 - a(n_1)\Delta t)\delta_{n_1 n_2} + (1 - \delta_{n_1 n_2})W(n_1, n_2)\Delta t$$

- Stay in state n_1: $n_1 = n_2 \Rightarrow 1 - a(n_2)\Delta t$
- Jump from n_1 to n_2: $n_1 \neq n_2 \Rightarrow W(n_1, n_2)\Delta t$

For a homogeneous Markov process, the transition probability is independent of time, and given with the Chapman-Kolmogorov equations:

$$P(n_1, n_3; t + \Delta t) = \sum_{n_2} P(n_1 \mid n_2, t) \cdot P(n_2 \mid n_3, \Delta t)$$

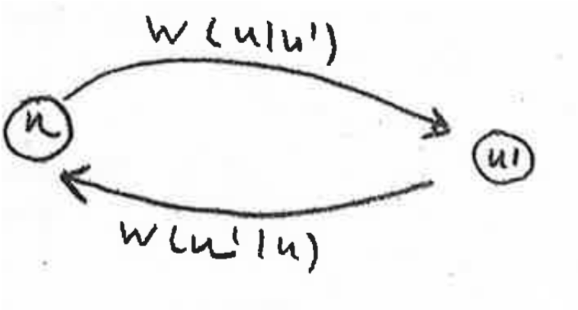
Mesoscopic Master Equation

$$\frac{\partial}{\partial t} P(n, t) = \sum_{n'} \left(P(n', t)W(n'|n) - P(n, t)W(n|n') \right)$$

Stationary process

For a stationary process

$$\sum_{n'} P^s(n')W(n'|n) - P^s(n)W(n|n') = 0$$



Example 1: birth and death process

Only transitions between adjacent states are allowed:

$$W(n|n+1) = g_n \quad \text{and} \quad W(n|n-1) = r_n.$$

Birth-death process

$$\frac{\partial}{\partial t} P(n,t) = g_{n-1} P(n-1,t) + r_{n+1} P(n+1,t) - (g_n + r_n) P(n,t)$$

- Population evolution: $\frac{d}{dt}\langle n \rangle = \langle g_n \rangle - \langle r_n \rangle$
- Steady state solution: $P^s(n) = P^s(0) \prod_{n'=1}^{n} \frac{g_{n'-1}}{r_{n'}}$

Example 2: radioactive decay

Birth-death process with $g_n = 0$, $r_n = n\gamma$.

Radioactive decay

$\frac{\partial}{\partial t} P(n,t) = (n+1)\gamma P(n+1,t) - n\gamma P(n,t)$

- Population evolution: $\langle n(t) \rangle = n_0 e^{-\gamma t}$
- Fluctuations of the population: $\langle (\Delta n)^2(t) \rangle = n_0(n_0 - 1)e^{-2\gamma t} + n_0 e^{-\gamma t}$

Example 3: Photons

Absorption and emission of photons from a two level system $g_n = \lambda(n+1), \quad \lambda = \gamma N_2$, $r_n = \mu n, \quad \mu = \gamma N_1$.

Burgess solution:

$$P_n^s = c(\frac{\lambda}{\mu})^n$$

- The distribution needs to satisfy Boltzmann statistics:

$$\frac{\lambda}{\mu} = \frac{N_2}{N_1} = e^{-\frac{E_1-E_2}{k_B T}} = e^{-\frac{\hbar\omega}{k_B T}}$$

Boltzmann distribution

$$P_n^s = (1 - e^{-\beta\hbar\omega})e^{-\beta\hbar\omega n}$$

Leads to:

Bose distribution

$$\langle n_s \rangle = \frac{1}{e^{\beta\hbar\omega} - 1}$$

Detailed Balance

Detailed balance condition:

$$P_n^{\mathsf{eq}} W(n' \mid n) = P_{n'}^{\mathsf{eq}} W(n \mid n') \quad \forall n, n'$$

For canonical thermal equilibrium:

$$P_n^{\mathsf{eq}} \propto d_n e^{-E_n/k_B T}$$

Hence for the simple case $dn' = dn$ detailed balance:

$$\frac{W(n \to n')}{W(n' \to n)} = e^{-(E_{n'} - E_n)/k_B T}$$

Monte-Carlo algorithm

Simulation of system fluctuations in thermal equilibrium:

- (i) Choose a state (random or by prescription)
- (ii) Calculate $\Delta E = E_{n'} - E_n$
- (iii) If $\Delta E < 0 \rightarrow W_{n,n'} = 1$
  If $\Delta E > 0 \rightarrow W_{n,n'} = e^{-\Delta E/KT}$

$$W_{n,n'} = min(1, X), \quad X = e^{-\Delta E/KT}$$

- (iv) reset

Next week's presentation

Verification of the Crooks fluctuation theorem and recovery of RNA folding free energies

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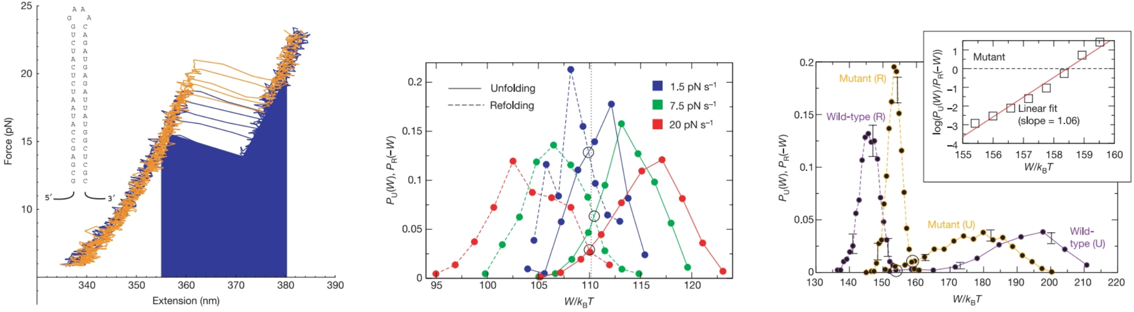

Questions for next week's paper presentation

- What is the Monte Carlo method and how is it implemented?
- What is the advantage of the Metropolis - Hastings (MH) algorithm compared to a classical Monte Carlo sampling?
- Prove that MH algorithms converges to the desired distribution you want to sampled from?
- How would you draw a sample from a Markov chain obtained by MH algorithms?
- Explain the application of the algorithm that is presented in the paper.