TUTORIAL 05

7CCMCS04
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Problem 5.1 *from Exam 2019* Consider an N-state stochastic system. Let $\mathsf{N}_t \in \Omega \coloneqq \{1, 2, \dots, N\}$ describe its state at time t. We define $P_i(t)$ as the probability that the system's state N_t at time t is i and denote with W_{ij} the rate at which the system moves from state j to state i. The state probabilities evolve according to the set of master equations

$$\frac{\mathrm{d}\, P_i}{\mathrm{d}\, t} = \sum_{j(\neq i)} (W_{ij} P_j - W_{ji} P_i) \qquad \forall\, i \in \Omega.$$

a. Show that, using the convention $\sum_j W_{ji} = 0$, the above set of equations can be cast in the vector equation

$$\frac{\mathrm{d}\, |\boldsymbol{P}(t)\rangle}{\mathrm{d}\, t} = \boldsymbol{W} |\boldsymbol{P}(t)\rangle,$$

where $\boldsymbol{W}$ is the matrix of transition rates and $|\boldsymbol{P}(t)\rangle \coloneqq (P_1(t), \dots, P_N(t))^\top$ is the column vector of state probabilities. Show that $\boldsymbol{W}$ has always a zero eigenvalue, hence determine the corresponding right and left eigenvectors.

b. Show that $|\boldsymbol{P}(t)\rangle = \boldsymbol{K}(t)|\boldsymbol{P}(0)\rangle$, where the propagator $\boldsymbol{K}(t)$ should be expressed in terms of $\boldsymbol{W}$, and explain in words the meaning of the elements $K_{ij}(t)$ of the propagator matrix. Show that if $\boldsymbol{W}$ satisfies detailed balance with the stationary state $|\boldsymbol{\Pi}\rangle \coloneqq \lim_{t\to\infty} |\boldsymbol{P}(t)\rangle$, it must allow a complete set of orthonormal eigenvectors, $\{\langle \boldsymbol{\phi}^a|, |\boldsymbol{\psi}^a\rangle\}$, such that

$$\boldsymbol{W}|\boldsymbol{\psi}^a\rangle = \mu_a |\boldsymbol{\psi}^a\rangle \quad \text{and} \quad \langle \boldsymbol{\phi}^a|\boldsymbol{W} = \mu_a \langle \boldsymbol{\phi}^a|,$$

where μ_a with $a = 1, \dots, N$ are the eigenvalues of $\boldsymbol{W}$. Finally, express $P_i(t)$ in terms of the eigenvalues and eigenvectors of $\boldsymbol{W}$.

Hint: Any $N\times N$ symmetric matrix $\boldsymbol{A}$ has a complete set of orthonormal eigenvectors $\{|\boldsymbol{\chi}^a\rangle\}_{a=1}^N$ such that $\boldsymbol{A}|\boldsymbol{\chi}^a\rangle = \mu_a |\boldsymbol{\chi}^a\rangle$, and, denoting $\langle \boldsymbol{\chi}^a|$ the row vector obtained trasposing $|\boldsymbol{\chi}^a\rangle$, $\langle \boldsymbol{\chi}^a|\boldsymbol{A} = \mu_a \langle \boldsymbol{\chi}^a|$ and $\langle \boldsymbol{\chi}^a|\boldsymbol{\chi}^b\rangle = \delta_{ab}$. The eigenvalues μ_a are invariant under similarity transformations of the form $\boldsymbol{B}^{-1}\boldsymbol{A}\boldsymbol{B}$.

c. We define $\theta_i(t)$ a state occupation variable, which takes value 1 when the state of the system at time t, N_t, is equal to i, and zero otherwise. Express the correlation function (with $t' < t$)

$$C_{ij}(t, t') = \langle\!\langle \theta_i(t)\theta_j(t') \rangle\!\rangle = \mathbb{E}[\theta_i(t)\theta_j(t')] - \mathbb{E}[\theta_i(t)]\mathbb{E}[\theta_j(t')]$$

in terms of the propagator, and show that at stationarity it is only a function of the time difference $\tau = t - t'$. Show that in this case the correlation function is given by a superposition of $N - 1$ exponential

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functions of τ, that should be specified. For which range of values of τ, will the system lose memory of its state at the earlier time t'?

Problem 5.2 *from Exam 2016* Consider a Markov process with two states, 1 and 2. Let $P_1(t)$ be the probability that the system is in the state 1 at time t and $P_2(t) = 1 - P_1(t)$. If the system is in state 1 at time t it will randomly move to state 2 with rate α; conversely, if it is in state 2 it will randomly move to state 1 with rate β.

a. Write down the combined Master equations for $P_1(t)$ and $P_2(t)$. Show that these can be cast in a vector equation

$$\frac{\mathrm{d}\,|\boldsymbol{P}(t)\rangle}{\mathrm{d}\,t} = \boldsymbol{W}|\boldsymbol{P}(t)\rangle$$

with $|\boldsymbol{P}(t)\rangle = \binom{P_1(t)}{P_2(t)}$ and the matrix $\boldsymbol{W}$ enclosing the transition rates. Summarize the salient features of matrix $\boldsymbol{W}$.

b. Find the steady state probability vector $|\boldsymbol{\Pi}\rangle$ and show that it is the right eigenstate associated to eigenvalue $\lambda = 0$ of $\boldsymbol{W}$. Find the left eigenstate associated with $\lambda = 0$.

c. Show that the steady state probability vector satisfies detailed balance with the transition rates of the process. Explain why this is always the case with a two-state process. Show that the Kullback-Leibler distance

$$\mathrm{KL}(\boldsymbol{P}(t)\|\boldsymbol{\Pi}) = \sum_{i=1}^{2} P_i(t) \ln \frac{P_i(t)}{\Pi_i}$$

between the time-dependent distribution $|\boldsymbol{P}(t)\rangle$ and the steady state distribution $|\boldsymbol{\Pi}\rangle$ is a non-increasing function of time, hence is a Lyapunov function for the dynamics considered (you may use that $\mathrm{KL}(\boldsymbol{P}(t)\|\boldsymbol{\Pi}) \geq 0$ without proof). Hence deduce that the dynamics converges to the steady state $|\boldsymbol{\Pi}\rangle$, i.e. $|\boldsymbol{\Pi}\rangle = \lim_{t\to\infty} |\boldsymbol{P}(t)\rangle$.

Hint: You may use, without proof, the inequality $(\mathrm{e}^x - \mathrm{e}^y)(x - y) \geq 0$, with equality holding only if $x = y$.

d. Show that the matrix $\boldsymbol{M}$ with elements

$$M_{ij} = \sqrt{\frac{\Pi_j}{\Pi_i}} W_{ij}$$

is symmetric and that the dynamics of the system can be rewritten as

$$\frac{\mathrm{d}\,|\boldsymbol{q}(t)\rangle}{\mathrm{d}\,t} = \boldsymbol{M}|\boldsymbol{q}(t)\rangle$$

for a suitable vector $|\boldsymbol{q}(t)\rangle$. Explain why it is always possible to diagonalize matrix $\boldsymbol{M}$ for a system that satisfies detailed balance.

e. Explain why, for a two-state ergodic Markov process, $\boldsymbol{W}$ itself must be diagonalizable. Hence, find the time-dependent distribution $|\boldsymbol{P}(t)\rangle$ for the initial conditions $P_1(0) = p_{01}$, $P_2(0) = p_{02}$, by diagonalizing $\boldsymbol{W}$. What is the relaxation time to the equilibrium steady state?

f. Define a three-state Markov process that does not satisfy detailed balance.

Problem 5.3 Equilibrium correlations normally decay with a characteristic decay time τ_C, as $C(\tau) = \mathrm{e}^{-\frac{|\tau|}{\tau_C}}$. Show that the power spectrum i.e. the Fourier transform of the correlation function) is

$$S(\omega) \sim \frac{1}{\omega^2\tau_C^2 + 1}.$$

Hint: You can either calculate the Fourier transform of $C(\tau)$ and show that it is equal to $S(\omega)$ or calculate the Inverse Fourier Transform of $S(\omega)$ and show that it equates $C(\tau)$. The inverse Fourier Transform can be calculated with the help of Cauchy's integral theorem.

Problem 5.4 *from Exam 2017* Consider a closed system of N molecules, each of which can be found in one of two isomerization states, A and B. We denote with k_1 and k_2 the rate at which a molecule transitions from state A to B and from B to A, respectively.

a. Write down the master equation for the probability mass $P_n(t)$ to have $\mathsf{N}_t = n$ particles in state A at time t and motivate your answer.

b Derive the equation of motion for the average number of particles $\mathbb{E}[\mathsf{N}_t]$ in state A at time t. Hence, show that the ratio between the equilibrium average numbers of molecules in state A and B, $n_A = \mathbb{E}[\mathsf{N}_\infty]$ and $n_B = N - \mathbb{E}[\mathsf{N}_\infty]$, respectively, is related to the reaction rates via

$$\frac{n_B}{n_A} = \frac{k_1}{k_2}.$$

c By solving the equation of motion for $\mathbb{E}[\mathsf{N}_t] = \sum_{n=1}^{\infty} nP_n(t)$, show that

$$\mathbb{E}[\mathsf{N}_t] = n_A + (\mathbb{E}[\mathsf{N}_0] - n_A)\,\mathrm{e}^{-\frac{t}{\tau}}$$

where the inverse relaxation time is

$$\tau^{-1} = k_1 + k_2.$$

d. We introduce a state variable $\sigma_i \in \{1, -1\}$ for each molecule $i = 1, \ldots, N$, denoting whether molecule i is in state A (1), or in state B (-1), so that the number of molecules in state A, in configuration $\boldsymbol{\sigma} = (\sigma_1, \ldots, \sigma_N)$, is $n(\boldsymbol{\sigma}) = \frac{1}{2}\sum_{i=1}^{N}(1 + \sigma_i)$. We assume that initially, the system is in equilibrium, described by

$$P_0(\boldsymbol{\sigma}) = \frac{1}{Z_0}\,\mathrm{e}^{-\beta H_0(\boldsymbol{\sigma})},$$

where β is an inverse noise level, H_0 is the equilibrium Hamiltonian and Z_0 is a normalization constant. At time $t = 0$, we apply a perturbation h that changes the number of molecules in state A from its equilibrium value n_A in the absence of perturbation, to their non-equilibrium value $\mathbb{E}[\mathsf{N}_t]$, for all $t > 0$. The Hamiltonian in the presence of the perturbation reads

$$H(\boldsymbol{\sigma}) = H_0(\boldsymbol{\sigma}) - hn(\boldsymbol{\sigma}).$$

Show that, for small h, the equilibrium distribution $P_h(\boldsymbol{\sigma})$ in the presence of the perturbation is given, to linear orders in h, by

$$P_h(\boldsymbol{\sigma}) = P_0(\boldsymbol{\sigma})\big(1 + \beta h(n(\boldsymbol{\sigma}) - n_A)\big).$$

Hence, show that the deviation of the average number of particles $\mathbb{E}[\mathsf{N}_t]$ in state A at time $t > 0$, from its equilibrium value n_{A} in the absence of perturbation, is given by

$$\mathbb{E}[\mathsf{N}_t] - n_{\mathrm{A}} = \beta h C_h(t)$$

where $C_h(t) = \mathbb{E}_h[(\mathsf{N}_t - n_{\mathrm{A}})(\mathsf{N}_0 - n_{\mathrm{A}})]$ is the correlation function obtained averaging via $\Pi^h_{\boldsymbol{\sigma}}$. Finally, show that,

$$\frac{\tilde{C}_h(s)}{C_h(0)} = \frac{1}{s + \tau^{-1}}$$

where $\tilde{C}_h(s)$ is the Laplace transform of the correlation function

$$\tilde{C}_h(s) = \int_0^\infty \mathrm{d}\,t\ \mathrm{e}^{-st}\, C_h(t),$$

and the relaxation time τ is given by

$$\tau = \int_0^\infty \frac{C_h(t)}{C_h(0)}\,\mathrm{d}\,t.$$