

TUTORIAL 05 — SOLUTIONS

7CCMCS04

A. ANNIBALE AND G. SICURO

PROBLEM 5.1

Let us proceed step by step.

- a. From $\sum_j W_{ji} = 0$, one has $W_{ii} = -\sum_{j(\neq i)} W_{ji}$. Substituting in the Master equation

$$\dot{P}_i = \sum_{j(\neq i)} W_{ij} P_j - \sum_{j(\neq i)} W_{ji} P_i = \sum_{j(\neq i)} W_{ij} P_j + W_{ii} P_i = \sum_j W_{ij} P_j.$$

This can indeed be written in vector notation

$$(1) \quad |\dot{\mathbf{P}}(t)\rangle = \mathbf{W}|\mathbf{P}(t)\rangle.$$

We can write $0 = \sum_j W_{ji} = \langle \mathbf{1} | \mathbf{W}$ hence $\langle \mathbf{1} |$ is the left eigenvector of \mathbf{W} associated to eigenvalue zero. Since probabilities are conserved at all times $\langle \mathbf{1} | \mathbf{P}(t) \rangle = \sum_n P_n(t) = 1 \forall t$, i.e., $\frac{d}{dt} \langle \mathbf{1} | \mathbf{P}(t) \rangle = 0$, \mathbf{W} has always a zero eigenvalue with left eigenvector $\langle \mathbf{1} |$. The corresponding right eigenvector is the stationary distribution $|\mathbf{\Pi}\rangle$, defined such that $\mathbf{W}|\mathbf{\Pi}\rangle = 0$.

- b. Equation (1) is a linear first order ODE. Its solution is $|\mathbf{P}(t)\rangle = e^{\mathbf{W}t} |\mathbf{P}(0)\rangle$. The propagator is then $\mathbf{K}(t) = e^{\mathbf{W}t}$. Since $P_i(t) = \sum_j K_{ij}(t) P_j(0)$ and, for any Markov process, $P_i(t) = \sum_j \mathbb{P}_{1|1}[\mathbf{N}_t = i | \mathbf{N}_0 = j] P_j(0)$, the entry $K_{ij}(t) = \mathbb{P}_{1|1}[\mathbf{N}_t = i | \mathbf{N}_0 = j]$ denotes the probability that the system is in state i at time t given that it was in state j at time 0. From the detailed balance relation $W_{ij}\Pi_j = W_{ji}\Pi_i$, we have

$$W_{ji} \sqrt{\frac{\Pi_i}{\Pi_j}} = W_{ij} \sqrt{\frac{\Pi_j}{\Pi_i}}.$$

Hence the matrix $M_{ij} = W_{ij} \sqrt{\frac{\Pi_j}{\Pi_i}}$ is symmetric, and related to \mathbf{W} by the orthogonal transformation $\mathbf{M} = \mathbf{D}^{-1/2} \mathbf{W} \mathbf{D}^{1/2}$, where $D_{ij} = \delta_{ij} \Pi_i$. This implies that \mathbf{M} has the same eigenvalues as \mathbf{W} and it has a complete set of orthonormal eigenvectors χ^a , such that

$$\mathbf{M}|\chi^a\rangle = \mu_a|\chi^a\rangle \quad \text{and} \quad \langle \chi^a | \mathbf{M} = \mu_a \langle \chi^a |.$$

This yields $\mathbf{D}^{-1/2} \mathbf{W} \mathbf{D}^{1/2} |\chi^a\rangle = \mu_a |\chi^a\rangle$ and $\langle \chi^a | \mathbf{D}^{-1/2} \mathbf{W} \mathbf{D}^{1/2} = \mu_a \langle \chi^a |$ or, rearranging, $\mathbf{W} \mathbf{D}^{1/2} |\chi^a\rangle = \mu_a \mathbf{D}^{1/2} |\chi^a\rangle$ and $\langle \chi^a | \mathbf{D}^{-1/2} \mathbf{W} = \mu_a \langle \chi^a | \mathbf{D}^{-1/2}$. This implies that the eigenvectors of \mathbf{W} , $|\psi^a\rangle = \mathbf{D}^{1/2} |\chi^a\rangle$ and $\langle \phi^a| = \langle \chi^a | \mathbf{D}^{-1/2}$ form a complete, orthonormal set:

$$\delta_{ab} = \langle \chi^a | \chi^b \rangle = \langle \phi^a | \mathbf{D}^{1/2} \mathbf{D}^{-1/2} |\psi^b\rangle = \langle \phi^a | \psi^b \rangle.$$

Therefore any function of \mathbf{W} allows a spectral decomposition. We have

$$\mathbf{K}(t) \equiv e^{\mathbf{W}t} = \sum_a e^{\mu_a t} |\psi^a\rangle \langle \phi^a|$$

and

$$|\mathbf{P}(t)\rangle = \sum_a e^{\mu_a t} |\psi^a\rangle \langle \phi^a| \mathbf{P}(0)\rangle$$

- c. Given a function $f(n)$ of the system's state n , we define the dynamical average

$$\begin{aligned} \mathbb{E}[f(\mathbf{N}_t)f(\mathbf{N}_{t'})] &= \sum_{ij} f(i)f(j) \mathbb{P}_2[\mathbf{N}_t = i, \mathbf{N}_{t'} = j] \\ &= \sum_{ij} f(i)f(j) \mathbb{P}_{1|1}[\mathbf{N}_t = i | \mathbf{N}_{t'} = j] P_j(t'), \end{aligned}$$

where the average is calculated over all the dynamical paths between the times t' and t . Since $\theta_i(t) = \delta_{\mathbf{N}_t, i}$ we have,

$$\begin{aligned} C_{ij}(t, t') &= \langle \theta_i(t) \theta_j(t') \rangle = \sum_{nm} \theta_i(n) \theta_j(m) \mathbb{P}_{1|1}[\mathbf{N}_t = n | \mathbf{N}_{t'} = m] P_m(t') \\ &\quad - \sum_n \theta_i(n) P_n(t) \sum_m \theta_j(m) P_m(t') \\ &= \mathbb{P}_{1|1}[\mathbf{N}_t = i | \mathbf{N}_{t'} = j] P_j(t') - P_i(t) P_j(t') \\ &= K_{ij}(t - t') P_j(t') - P_i(t) P_j(t'). \end{aligned}$$

At stationarity, one-time quantities are constant and $P_i(t) = \Pi_i \forall i$, so

$$C_{ij}(t, t') = \Pi_j [K_{ij}(t - t') - \Pi_i] = \Pi_j \left(\sum_{n=1}^N e^{\mu_n(t-t')} \psi_i^n \phi_j^n - \Pi_i \right),$$

showing that the two-time correlator becomes a function of the time difference $t - t'$ only. Ordering the eigenvalues $0 = \mu_1 > \mu_2 > \dots > \mu_N$ and using $|\psi^1\rangle = |\mathbf{\Pi}\rangle$ and $\langle \phi^1| = \langle \mathbf{1}|$, we obtain C_{ij} as a superposition of $N - 1$ exponential functions of the time difference $\tau = t - t'$

$$C_{ij}(\tau) = \Pi_j \sum_{a=2}^N e^{\mu_a \tau} \psi_i^a \phi_j^a.$$

Rearranging and taking the large τ limit

$$\begin{aligned} C_{ij}(\tau) &= \Pi_j e^{-|\mu_2|\tau} \left(\psi_i^2 \phi_j^2 + \mathcal{O}\left(e^{-(|\mu_3| - |\mu_2|)\tau}\right) \right) \\ &\sim \Pi_j e^{-|\mu_2|\tau} \psi_i^2 \phi_j^2. \end{aligned}$$

The correlation function will decay to a small value, meaning that the system has lost memory of its initial state, when the time separation $\tau \gg |\mu_2|^{-1}$.

PROBLEM 5.2

a. The master equations are

$$(2) \quad \frac{d P_1(t)}{d t} = -\alpha P_1(t) + \beta P_2(t)$$

$$(3) \quad \frac{d P_2(t)}{d t} = \alpha P_1(t) - \beta P_2(t).$$

which, in vector notation, can be written as

$$\frac{d |\mathbf{P}(t)\rangle}{d t} = \mathbf{W} |\mathbf{P}(t)\rangle \quad \text{with} \quad \mathbf{W} = \begin{pmatrix} -\alpha & \beta \\ \alpha & -\beta \end{pmatrix}.$$

We have $\sum_{i=1}^2 W_{ij} = 0$ for $j = 1, 2$.

b. The steady state distribution can be found setting $\dot{P}_1 = 0$ and $\dot{P}_2 = 0$ and using $P_1 + P_2 = 1$, so that

$$\Pi_1 = \frac{\beta}{\alpha + \beta}, \quad \Pi_2 = \frac{\alpha}{\alpha + \beta}$$

This is by definition the right eigenstate associated to eigenvalue zero of \mathbf{W} . The left one is $\langle \mathbf{1} |$ as the columns of \mathbf{W} sum to zero.

c. The steady state probabilities satisfy $\alpha \Pi_1 = \beta \Pi_2$. For two-state Markov process with non-zero rates, the steady state condition coincides with the detailed balance condition, as transitions can occur only between two states.

$$(4) \quad \begin{aligned} \frac{d \text{KL}(\mathbf{P}(t) \| \Pi)}{d t} &= \sum_n \dot{P}_n(t) \left(\ln \frac{P_n(t)}{\Pi_n} + 1 \right) = \sum_n \dot{P}_n(t) \ln \frac{P_n(t)}{\Pi_n} \\ &= \sum_{nm} W_{nm} P_m(t) \ln \frac{P_n(t)}{\Pi_n} \\ &= -(\alpha P_1(t) - \beta P_2(t)) \left(\ln \frac{P_1(t)}{\Pi_1} - \ln \frac{P_2(t)}{\Pi_2} \right) \\ &= \alpha P_1(t) \left(1 - \frac{\beta P_2(t)}{\alpha P_1(t)} \right) \ln \frac{\beta P_2(t)}{\alpha P_1(t)}. \end{aligned}$$

Using the identity provided in the Hint, this is strictly less than zero as long as $P_1(t) \neq \frac{\beta}{\alpha} P_2(t)$. However, $\text{KL}(\mathbf{P}(t) \| \Pi) \geq 0$, hence for $t \rightarrow \infty$, $|\mathbf{P}(t)\rangle$ must converge to $|\Pi\rangle$.

d. From $\dot{P}_n(t) = \sum_m W_{nm} P_m(t)$ we have $|\dot{\mathbf{q}}(t)\rangle = \mathbf{U} |\mathbf{q}(t)\rangle$ with $q_n(t) = \frac{P_n(t)}{\sqrt{\Pi_n}}$. By inspection: $U_{12} = U_{21} = \sqrt{\alpha\beta}$ hence \mathbf{U} is symmetric. For a system that satisfies detailed balance, $\Pi_n W_{mn} = \Pi_m W_{nm}$, hence

$$\sqrt{\frac{\Pi_n}{\Pi_m}} W_{mn} = \sqrt{\frac{\Pi_m}{\Pi_n}} W_{nm}$$

so matrix \mathbf{U} is always symmetric. Hence, it is always possible to diagonalise matrix \mathbf{U} , as via the spectral theorem, it has a complete set of orthonormal eigenvectors.

e. Since $\mu_1 = 0$, from the trace of \mathbf{W} , $\text{tr}[\mathbf{W}] = -(\alpha + \beta)$ we have

$$\mu_2 = -(\alpha + \beta)$$

Unless $\alpha + \beta = 0$, which cannot happen for ergodic systems, there are two real and distinct eigenvalues, hence the Jordan canonical form of \mathbf{W} is diagonal. The right eigenvector $|\psi^1\rangle$, associated to $\mu_1 = 0$ is found earlier as

$$\mathbf{W}|\psi^1\rangle = 0 \Rightarrow |\psi^1\rangle = \frac{1}{\beta + \alpha} \begin{pmatrix} \beta \\ \alpha \end{pmatrix} \equiv |\mathbf{\Pi}\rangle$$

(observe that we have normalised it). The right eigenvector associated to $\mu_2 = -(\alpha + \beta)$ found as

$$\mathbf{W}|\psi^2\rangle = -(\alpha + \beta)|\psi^2\rangle \Rightarrow |\psi^2\rangle = \begin{pmatrix} 1 \\ -1 \end{pmatrix}.$$

Writing $|\mathbf{P}(0)\rangle = c_1|\psi^1\rangle + c_2|\psi^2\rangle$,

$$|\mathbf{P}(t)\rangle = e^{\mathbf{W}t} |\mathbf{P}(0)\rangle = c_1|\psi^1\rangle + c_2 e^{-(\alpha+\beta)t} |\psi^2\rangle.$$

The constants are found imposing the initial conditions:

$$|\mathbf{P}(0)\rangle \equiv \begin{pmatrix} \frac{c_1\beta}{\alpha+\beta} + c_2 \\ \frac{c_1\alpha}{\alpha+\beta} - c_2 \end{pmatrix}$$

Also, using $P_1(0) + P_2(0) = 1$, we get $c_1 = 1$. Also,

$$c_2 = P_1(0) - \frac{\beta}{\beta + \alpha} = \frac{\alpha}{\alpha + \beta} - P_2(0).$$

This means that $c_2|\psi^2\rangle = \begin{pmatrix} P_1(0) - \Pi_1 \\ P_2(0) - \Pi_2 \end{pmatrix} = |\mathbf{P}(0)\rangle - |\mathbf{\Pi}\rangle$. Substituting, we can write

$$|\mathbf{P}(t)\rangle = |\mathbf{\Pi}\rangle + e^{-(\alpha+\beta)t} (|\mathbf{P}(0)\rangle - |\mathbf{\Pi}\rangle).$$

PROBLEM 5.3

From the Wiener–Khinchine theorem, we know that

$$C(\tau) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} S(\omega) e^{-i\omega\tau} = \lim_{R \rightarrow \infty} \int_{-R}^R \frac{d\omega}{2\pi} S(\omega) e^{-i\omega\tau}$$

Next we move to the z complex plane, with $z = \omega + i\omega'$ and consider the integral above over a close contour which consists of a segment $[-R, R]$ along the real axis, plus a semicircle C_R of radius R , centered in the origin:

$$\oint dz S(z) e^{-iz\tau} = \int_{-R}^R d\omega S(\omega) e^{-i\omega\tau} + \int_{C_R} dz S(z) e^{-iz\tau}.$$

The objective is to choose C_R in such a way that in the limit $R \rightarrow \infty$ the integral along the semicircle gives a vanishing contribution, which can be neglected (according to the Jordan's lemma), so that we can calculate the integral over the real axis simply by calculating the contour integral, which is easily done using Cauchy theorem. We note that $|S(z)| \rightarrow 0$ for $R \rightarrow \infty$ and the exponential provides an extra convergence factor to the integral if we choose the contour suitably. Given that $e^{-iz\tau} = e^{-i\omega\tau} e^{\omega'\tau}$, we need to choose $\omega' < 0$ for $\tau > 0$ (i.e., in this case we have close the path from below) and $\omega' > 0$ for $\tau < 0$ (we close the contour from above). For this choice, we have

$$\int_{-\infty}^{\infty} d\omega S(\omega) e^{-i\omega\tau} = \oint dz S(z) e^{-iz\tau} = 2\pi i \sum_k n_k \text{Res}[S(z_k) e^{-iz_k\tau}]$$

where z_k are the poles of $S(z)$ circled by the contour, n_k is the number of times that the contour circles the k th singularity, with plus sign if the singularity is circled counter-clockwise and minus otherwise. $S(z)$ has two poles, i.e., $z_{\pm} = \pm \frac{i}{\tau}$. For $\tau > 0$ our contour circles the poles in the negative imaginary axis (clockwise), while for $\tau < 0$ it circles the singularity in the positive semi-axis (counter-clockwise). Calculating the residues is left to the student. You will see that the contributions given by $\tau < 0$ and $\tau > 0$ are identical, as expected because in equilibrium $C(\tau) = C(-\tau)$.

PROBLEM 5.4

- a. Let us work out the loss term first. Starting from the state with n A molecules the system can do the following:
- switch to $n - 1$ A molecules via a transition of any of them from A to B at rate k_1 ;
 - switch to $n + 1$ A molecules via a transition of any of the $N - n$ B molecules from state B to A at rate k_2 .

In other words, from the state with $n + 1$ A molecules the system can go to n A molecules via a transition of any of the $n + 1$ molecules from A to B with rate k_1 . From $n - 1$ A molecules the system can go to n A molecules via a transition of any of the $N - (n - 1)$ B molecules from state B to A with rate k_2 . Hence the master equation is given by:

$$\frac{dP_n(t)}{dt} = -P_n(nk_1 + k_2(N - n)) + P_{n+1}k_1(n+1) + P_{n-1}k_2(N - (n-1)).$$

- b. Multiplying times n and summing over n

$$\frac{d\mathbb{E}[N_t]}{dt} = -\sum_n P_n(n^2k_1 + k_2(Nn - n^2)) + \sum_n P_{n+1}k_1n(n+1) + \sum_n P_{n-1}k_2(Nn - n(n-1)).$$

Shifting indices

$$\begin{aligned} \frac{d\mathbb{E}[N_t]}{dt} &= -(\mathbb{E}[N_t^2]k_1 + k_2(N\mathbb{E}[N_t] - \mathbb{E}[N_t^2])) \\ &\quad + k_1(\mathbb{E}[N_t^2] - \mathbb{E}[N_t]) + k_2(N(\mathbb{E}[N_t] + 1) - (\mathbb{E}[N_t^2] + \mathbb{E}[N_t])). \end{aligned}$$

Quadratic terms cancel, as expected from linear equations and we get

$$\frac{d\mathbb{E}[N_t]}{dt} = k_2N - (k_1 + k_2)\mathbb{E}[N_t].$$

At stationarity, $\mathbb{E}[N_t] = n_A$ and since the total number of molecules is constant $N = n_A + n_B$, by setting $\mathbb{E}[\dot{N}_t] = 0$ we obtain

$$k_2(n_A + n_B) = (k_1 + k_2)n_A \Rightarrow k_2 \left(1 + \frac{n_B}{n_A}\right) = k_1 + k_2 \Rightarrow \frac{n_B}{n_A} = \frac{k_1}{k_2}.$$

- c. Solve linear first-order ODE:

$$\begin{aligned} \frac{d\mathbb{E}[N_t]}{dt} + (k_1 + k_2)\mathbb{E}[N_t] &= k_2N \\ \frac{d}{dt}(\mathbb{E}[N_t]e^{(k_1+k_2)t}) &= k_2Ne^{(k_1+k_2)t} \\ \mathbb{E}[N_t]e^{(k_1+k_2)t} - \mathbb{E}[N_0] &= k_2N \frac{e^{(k_1+k_2)t} - 1}{k_1 + k_2}. \end{aligned}$$

Therefore

$$\begin{aligned} \mathbb{E}[N_t] &= e^{-(k_1+k_2)t} \mathbb{E}[N_0] + \frac{k_2N}{k_1 + k_2} (1 - e^{-(k_1+k_2)t}) \\ &= \frac{k_2N}{k_1 + k_2} + e^{-(k_1+k_2)t} \left(\mathbb{E}[N_0] - \frac{k_2N}{k_1 + k_2} \right). \end{aligned}$$

Finally

$$\frac{k_2N}{k_1 + k_2} = k_2 \frac{n_A + n_B}{k_1 + k_2} = n_A \left(1 + \frac{n_B}{n_A}\right) \frac{1}{k_1/k_2 + 1}$$

Using $n_B/n_A = k_1/k_2$, we find

$$\frac{k_2 N}{k_1 + k_2} = n_A$$

leading to the desired result.

- d. In the following, $\mathbb{E}_0[\bullet]$ is the expectation with respect to Π_{σ}^0 , asymptotic distribution at $t \rightarrow +\infty$, whilst $\mathbb{E}_h[\bullet]$ is the expectation with respect to Π_{σ}^h , stationary distribution at $t \rightarrow +\infty$. As usual, $\mathbb{E}[\bullet]$ will be the expectation with respect to $P_n(t)$. As in the question, $n_A^0 := \mathbb{E}_0[N]$ and we denote $n_A \equiv n_A^h := \mathbb{E}_h[N]$, asymptotic expected value. From

$$\begin{aligned} \Pi_{\sigma}^h &= \frac{e^{-\beta(H_0(\sigma) - hn(\sigma))}}{\sum_{\sigma} e^{-\beta(H_0(\sigma) - hn(\sigma))}} \approx \frac{e^{-\beta H_0(\sigma)}(1 + \beta hn(\sigma))}{\sum_{\sigma'} e^{-\beta H_0(\sigma')}(1 + \beta hn(\sigma'))} \\ &= \frac{e^{-\beta H_0(\sigma)}(1 + \beta hn(\sigma))}{Z_0(1 + \beta h\mathbb{E}_0[N])} = \Pi_{\sigma}^0(1 + \beta hn(\sigma))(1 - \beta h\mathbb{E}_0[N]) \\ &\simeq \Pi_{\sigma}^0(1 + \beta h(n(\sigma) - n_A)). \end{aligned}$$

This equation implies that, given an observable $A \equiv A(\sigma)$,

$$\mathbb{E}_h[A] = \mathbb{E}_0[A] + \beta h(\mathbb{E}_0[NA] - n_A \mathbb{E}_0[A])$$

But this also means that

$$\Pi_{\sigma}^0 \simeq \frac{\Pi_{\sigma}^h}{1 + \beta h(n(\sigma) - n_A)} \simeq \Pi_{\sigma}^h(1 - \beta h(n(\sigma) - n_A)).$$

Following the same steps as in the lecture slides, let $\mathbb{P}_{1|1}^h$ be the conditional probability in the presence of the field h . We find the non-equilibrium result

$$\begin{aligned} \mathbb{E}[N_t] &= \sum_{\sigma} n(\sigma) P_{\sigma}(t) \\ &= \sum_{\sigma} n(\sigma) \sum_{\sigma'} \mathbb{P}_{1|1}^h[\sigma_t = \sigma | \sigma_0 = \sigma'] \Pi_{\sigma'}^0 \\ &= \sum_{\sigma} n(\sigma) \sum_{\sigma'} \mathbb{P}_{1|1}^h[\sigma_t = \sigma | \sigma_0 = \sigma'] \Pi_{\sigma'}^h (1 - \beta h(n(\sigma') - n_A)) \\ &= n_A^h - \beta h(\mathbb{E}_h[N_t N_0] - n_A^h n_A). \end{aligned}$$

But from what we showed before $n_A^h = n_A^0 + O(h)$, so neglecting $O(h^2)$ terms and remembering that $n_A \equiv n_A^h$

$$\begin{aligned} \mathbb{E}[N_t] &= n_A + \beta h(\mathbb{E}_h[N_t N_0] - n_A^2) \\ &= n_A + \beta h \mathbb{E}_h[(N_t - n_A)(N_0 - n_A)] \equiv C_h(t) \end{aligned}$$

where $C_h(t)$ is the correlation function computed using Π_{σ}^h . From part a. we have

$$\mathbb{E}[N_t] = n_A + e^{-t/\tau}(\mathbb{E}[N_0] - n_A)$$

giving

$$e^{-t/\tau} = \frac{\mathbb{E}[N_t] - n_A}{\mathbb{E}[N_0] - n_A} = \frac{C_h(t)}{C_h(0)}.$$

Taking the Laplace transform, we have

$$\frac{\tilde{C}_h(s)}{C_h(0)} = \int_0^\infty dt \, e^{-(s+1/\tau)t} = \frac{1}{s + 1/\tau}.$$

In the $s \rightarrow 0$ limit we can recover therefore τ as

$$\tau = \lim_{s \rightarrow 0} \frac{\tilde{C}_h(s)}{C_h(0)} = \lim_{s \rightarrow 0} \int_0^\infty dt \, e^{-st} \frac{C_h(t)}{C_h(0)} = \int_0^\infty dt \, \frac{C_h(t)}{C_h(0)}.$$