This is a draft version of the lecture notes. We aim to keep improving it but at the current stage it is most likely far from perfect. Please contact us if you notice any typos, errors, subtle points, or if you have any questions or suggestions for improvements.

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7 Master equation

We will now, based on the Chapmann-Kolmogorov-Smoluchowski equation, write down an equation for the evolution of the transition probabilities $T_\tau(y_2|y_1)$. The transition probability for $\tau = 0$ and continuous variables is $T_0(y_2|y_1) = \delta(y_2 - y_1)$. Based on that, for small τ we write the following expansion

$$T_\tau(y_2|y_1) = (1 - \tau a_0(y_1))\,\delta(y_2 - y_1) + \tau W(y_2|y_1) + \mathcal{O}(\tau^2). \tag{7.1}$$

The coefficients $a_0(y_1)$ and $W(y_2|y_1)$ are not independent. From the normalization (or completeness) relation we find

$$a_0(y_1) = \int \mathrm{d}y_2\, W(y_2|y_1). \tag{7.2}$$

Comparing with (7.1) this has a simple interpretation. The probability of staying in state y_1, expressed through $1 - a_0(y_1)$ is decreased by the transition rates to all other states. The quantity $W(y_2|y_1)$ is interpreted as a transition amplitude from y_1 to y_2 in the unit time.

We can use now the Chapmann-Kolmogorov-Smoluchowski equation

$$T_{\tau+\tau'}(y_3|y_1) = \int \mathrm{d}y_2\, T_{\tau'}(y_3|y_2) T_\tau(y_2|y_1), \tag{7.3}$$

and substitute for $T_{\tau'}(y_3|y_2)$ the expansion from eq. (7.1). After reorganizing the terms we find

$$T_{\tau+\tau'}(y_3|y_1) - T_\tau(y_3|y_1) = \tau' \int \mathrm{d}y_2\, \left[W(y_3|y_2)T_\tau(y_2|y_1) - W(y_2|y_3)T_\tau(y_3|y_1)\right], \tag{7.4}$$

where we used (7.2) to eliminate $a_1(y_3)$. We divide now this expression by τ' and take the limit of $\tau' \to 0$ to find

$$\frac{\partial T_\tau(y_3|y_1)}{\partial \tau} = \int \mathrm{d}y_2\, \left[W(y_3|y_2)T_\tau(y_2|y_1) - W(y_2|y_3)T_\tau(y_3|y_1)\right] \tag{7.5}$$

It is customary to rewrite this equation using $P(y,t)$ for $T_\tau(y_2|y_1)$. However one has to keep in mind that $P(y,t)$ is a probability of transition to state y at time t, and not the

probability distribution at time t. The latter is $P(y,t) \times P_0(y)$ where $P_0(y)$ is the initial probability distribution at time $t = 0$. With the new notation,

$$\frac{\partial P(y,t)}{\partial t} = \int \mathrm{d}y' \, \left[W(y|y') T_\tau(y',t) - W(y'|y) P(y,t) \right]. \tag{7.6}$$

This is the master equation. Here it is written for continuous space of states. In the discrete case

$$\frac{p_n(t)}{\partial t} = \sum_{n'} \left[W_{nn'} p_{n'}(t) - W_{n'n} p_n(t) \right]. \tag{7.7}$$

Regardless of the form, the master equation can be interpreted as a gain-loss equation. Namely, the change to $p_n(t)$ is due to a balance of the processes which increase it and processes that decrease it.

7.1 Discrete master equation and matrix W

For the study of properties of the master equation it is convenient to introduce the following matrix

$$\mathbf{W}_{nn'} = W_{nn'}, \qquad \text{for } n \neq n', \tag{7.8}$$

$$\mathbf{W}_{nn} = -\sum_{n' \neq n} W_{n'n}. \tag{7.9}$$

Another way is

$$\mathbf{W}_{nn'} = W_{nn'} - \delta_{nn'} \sum_{n''} W_{n''n}. \tag{7.10}$$

The master equation then becomes

$$\dot{p}_n(t) = \sum_{n'} \mathbf{W}_{nn'} p_{n'}(t), \tag{7.11}$$

which in the matrix equation reads

$$\dot{p}(t) = \mathbf{W} p(t), \tag{7.12}$$

where $p(t) = (p_1(t), \ldots, p_d(t))$. We can formally solve this equation by writing

$$p(t) = e^{t\mathbf{W}} p(0). \tag{7.13}$$

Example We consider a two-state process. The matrix $\mathbf{W}$ has dimensions 2×2 and is characterized by two real numbers $a, b > 0$ such that

$$\mathbf{W} = \begin{pmatrix} -a & b \\ a & -b \end{pmatrix}. \tag{7.14}$$

To use the formal solution (7.13) we use the Taylor expansion of the exponential function. It will involve powers of $\mathbf{W}$ which we first analyze. Taking the square, we get

$$\mathbf{W}^2 = -(a+b)\mathbf{W}, \tag{7.15}$$

which results in a simple structure $\mathbf{W}^k = (-1)^{k-1}(a+b)^{k-1}\mathbf{W}$. We then have

$$e^{t\mathbf{W}} = \sum_{k=0}^{\infty} \frac{(t\mathbf{W})^k}{k!} = \mathbf{1} + \sum_{k=1}^{\infty} \frac{t^k(-(a+b))^{k-1}}{k!}\mathbf{W} = \mathbf{1} + \frac{1-e^{-t(a+b)}}{a+b}\mathbf{W}. \tag{7.16}$$

The solution to the master equation is then

$$p(t) = \left(\mathbf{1} + \frac{1-e^{-t(a+b)}}{a+b}\mathbf{W}\right) p(0), \tag{7.17}$$

and is explicit for a given choice of the initial state $p(0)$ and transition rates a, b. Let us analyze its large time limit. We find

$$\lim_{t\to\infty} p(t) = \left(\mathbf{1} + \frac{1}{a+b}\mathbf{W}\right) p(0) = \frac{1}{a+b}\begin{pmatrix} b & b \\ a & a \end{pmatrix} p(0) = \frac{c_1+c_2}{a+b}\begin{pmatrix} b \\ a \end{pmatrix}, \tag{7.18}$$

where $p(0) = (c_1, c_2)$. Because $p(0)$ is a vector of probabilities, $c_1 + c_2 = 1$. This shows that

$$\lim_{t\to\infty} p(t) = \frac{1}{a+b}\begin{pmatrix} b \\ a \end{pmatrix}, \tag{7.19}$$

independently of the initial conditions.

From the structure of the matrix $\mathbf{W}$ we can infer that there always exists a stationary state. The matrix $\mathbf{W}$ can be defined by two properties

$$\mathbf{W}_{nn'} \leq 0, \quad \text{for } n \neq n', \tag{7.20}$$

$$\sum_n \mathbf{W}_{nn'} = 0. \tag{7.21}$$

The second property implies that the vector $\psi = (1, 1, \dots)$ is a left-eigenvector with 0 eigenvalue. If a matrix has a left eigenvectors it implies that there exists a right eigenvector of the same eigenvalue.[1] This eigenvector, denoted ϕ represents a stationary state.

This observation can be further refined by considering matrices $\mathbf{W}$ of certain internal structure. We will analyze two cases.

- reducible: Matrix $\mathbf{W}$ is of the following form

$$\mathbf{W} = \begin{pmatrix} \mathbf{A} & \mathbf{0} \\ \mathbf{0} & \mathbf{B} \end{pmatrix}, \tag{7.22}$$

  with matrices $\mathbf{A}$ and $\mathbf{B}$ both square matrices and obeying properties (7.20). In this case $\mathbf{W}$ has two linearly independent eigenvectors with 0 eigenvalue

$$\mathbf{W}\begin{pmatrix} \phi_A \\ 0 \end{pmatrix} = 0, \qquad \mathbf{W}\begin{pmatrix} 0 \\ \phi_B \end{pmatrix} = 0. \tag{7.23}$$

[1] One way of seeing this is that the characteristic polynomials of $\mathbf{A}$ and $\mathbf{A}^T$ are the same.

- partially reducible: Matrix $\mathbf{W}$ is of the following form

$$\mathbf{W} = \begin{pmatrix} \mathbf{A} & \mathbf{D} \\ \mathbf{0} & \mathbf{B} \end{pmatrix}. \tag{7.24}$$

In this case the eigenvector with zero eigenvalue is $\phi = \begin{pmatrix} \phi_A \\ 0 \end{pmatrix}$. There is a flow of probability from b states to a states. The master equation for a b state reads

$$\dot{p}_b = \sum_{b'} B_{bb'} p_{b'}(t), \tag{7.25}$$

summing over b states gives

$$\sum_b \dot{p}_b = \sum_{b'} \left(\sum_b B_{bb'} \right) p_{b'}(t). \tag{7.26}$$

However $\sum_b B_{bb'} = -\left(\sum_a D_{ab'}\right) < 0$ because $D_{ab'} \geq 0$. Therefore the total probability of being in any state b decays in time.

7.2 Macroscopic equations

The Master equation is an equation for the probability. Instead we can write an equation for certain observable. For example, for the expectation value of the state y, namely

$$y(t) = \langle Y \rangle_t = \int y P(y,t) \mathrm{d}y. \tag{7.27}$$

From the master equation we find

$$\dot{y}(t) = \int y \frac{\partial P(y,t)}{\partial t} \mathrm{d}y = \int (y - y') W(y|y') P(y,t) \mathrm{d}y \, \mathrm{d}y'. \tag{7.28}$$

To understand the relating structure we define the jump moments

$$a_\nu(y) = \int (y' - y)^\nu W(y'|y) \mathrm{d}y', \tag{7.29}$$

then

$$\frac{\partial \langle Y \rangle_t}{\partial t} = \langle a_1(y) \rangle_t. \tag{7.30}$$

In a similar fashion we can derive an equation for the second moment

$$\frac{\partial \langle Y^2 \rangle_t}{\partial t} = \langle a_2(Y) \rangle_t + 2 \langle Y a_1(Y) \rangle_t, \tag{7.31}$$

or for the variance

$$\frac{\partial \sigma^2(t)}{\partial t} = \langle a_2(Y) \rangle_t + \langle (Y - \langle Y \rangle_t) a_1(Y) \rangle_t. \tag{7.32}$$

These equations depend not only on the first two moments of Y but also on higher moments. In fact, so far we have not done approximation and the equations depend on all the details

of the dynamic. We can now perform a sort of mean-field approximation, where we assume that fluctuations of Y around its mean value $\langle Y\rangle_t$ are small. We then have

$$\begin{aligned}\langle a_\nu(Y)\rangle_t &= a_\nu(\langle Y\rangle_t) + \underbrace{\langle a_\nu(Y)\rangle_t - a_\nu(\langle Y\rangle_t)}_{\text{assumed small}} \\ &= a_\nu(\langle Y\rangle_t) + (\langle Y - \langle Y\rangle_t)a'_\nu(\langle Y\rangle_t) + \mathcal{O}((Y - \langle Y\rangle_t)^2)\dots \end{aligned} \tag{7.33}$$

Upon this assumption we find the following closed set of equations for the first two moments

$$\frac{\partial y(t)}{\partial t} = a_1(y(t)) + \frac{1}{2}\sigma^2(t)a''_1(y), \tag{7.34}$$

$$\frac{\partial \sigma^2(t)}{\partial t} = a_2(y(t)) + 2\sigma^2(t)a'_1(y(t)). \tag{7.35}$$

Based on this equations we can inspect the validity of the approximation. To this end we estimate the value of $\sigma^2(t)$. We have, from the definition, that $a_2(y) > 0$ and we also expect that $a'_1(y) < 0$ cause otherwise the fluctuations would increase exponentially in time. Then for $\sigma^2 = a_2/2|a'_1|$ the fluctuations are stationary. We use this as an estimation for σ^2. In the equations for the average, the fluctuating term is small when

$$\left|\frac{\sigma^2}{2}a''_1\right| \ll |a_1|, \tag{7.36}$$

or using the estimation for σ^2,

$$\left|\frac{a_2 a''}{4a_1 a'_1}\right| \ll 1. \tag{7.37}$$

The jump moments can be computed according to eq. (7.29) from the knowledge of the transition rates $W(y'|y)$ and the condition can be checked without the need of solving the master equation.

7.3 One-step processes

We now consider an important class of master equations in which the transition rates connect only the neighbouring states. These are called one-step processes. In that case, the master equation can be written as

$$\dot{p}_n = r_{n+1}p_{n+1} + g_{n-1}p_{n-1} - (r_n + g_n)p_n. \tag{7.38}$$

We further divide the one-step processes into three classes:

- of infinite range, $-\infty < n < \infty$,
- of semi-infinite range, $n = 0, 1, 3, \dots,$
- of finite range, $n = 0, 1, \dots, N$.

In the case of semi-finite or finite ranges the equations at the border take a special form. For example

$$\dot{p}_0 = r_1 p_1 - g_0 p_0. \tag{7.39}$$

This can be incorporated into the general form (7.38) by setting $r_0 = 0$ and $g_{-1} = 0$. Similarly, for the upper boundary in the case of finite range we set $r_{N+1} = 0$ and $g_N = 0$.

For the one-step processes we can find a general form of the stationary step. To this end we introduce the following notation

$$\mathbf{E}f(n) = f(n+1). \tag{7.40}$$

With the help of the operator $\mathbf{E}$ the master equation becomes

$$\dot{p}_n = (\mathbf{E} - 1)r_n p_n + (\mathbf{E}^{-1} - 1)g_n p_n. \tag{7.41}$$

Example: We can observe the following identity

$$\sum_{n=0}^{N-1} g(n)\mathbf{E}f(n) = \sum_{n=1}^{N} f(n)\mathbf{E}^{-1}g(n), \tag{7.42}$$

which is similar to integration by parts. With this identity it is simple to derive an equation for the average $\langle n \rangle_t$,

$$\langle n \rangle_t = \sum_n p_n(t)n. \tag{7.43}$$

We have

$$\begin{aligned}\frac{\partial}{\partial t}\langle n \rangle_t &= \sum_n n(\mathbf{E} - 1)r_n p_n + \sum_n n(\mathbf{E}^{-1} - 1)g_n p_n \\ &= \sum_n r_n p_n(\mathbf{E}^{-1} - 1)n + \sum_n g_n p_n(\mathbf{E} - 1)n \\ &= -\langle r_n \rangle + \langle g_n \rangle,\end{aligned} \tag{7.44}$$

where the averages on the right hand have a meaning of an average transition amplitude to the left and to the right correspondingly.

The stationary state $\dot{p}^s_n = 0$ obeys then the following equation

$$0 = (\mathbf{E} - 1)r_n p^s_n + (\mathbf{E}^{-1} - 1)g_n p^s_n = (\mathbf{E} - 1)\left[r_n p^s_n - \mathbf{E}^{-1} g_n p^s_n\right]. \tag{7.45}$$

For this to be true for every n we need

$$r_n p^s_n - \mathbf{E}^{-1} g_n p^s_n = -J, \tag{7.46}$$

where J is a constant and has an interpretation of the probability current. For finite or semi-finite range the boundary equation reads

$$r_0 p^s_0 - g_{-1} p^s_{-1} = 0, \tag{7.47}$$

which means that in these cases the stationary state does not support any probability current. Therefore

$$r_n p^s_n = g_{n-1} p^s_{n-1}, \tag{7.48}$$

which is solved by

$$p^s_n = \frac{g_{n-1} g_{n-2} \cdots g_1 g_0}{r_n r_{n-1} \cdots r_2 r_1} p^s_0. \tag{7.49}$$

This formula works for finite and semi-finite ranges.

For infinite systems it is possible for $J \neq 0$ in the stationary state.

7.4 The detailed balance relation

For the proof of the detailed balance relation see van Kampen Chapter 5.6.

7.5 Applications of the master equation

We discuss now applications of master equations to model natural phenomena by considering few illustrative examples. Our aim here is to formulate the problem rather than solve it.

- *Radioactive decay:* The dynamic process here is a decay of a radioactive atom. We can write schematically
$$X \xrightarrow{\omega} Y, \tag{7.50}$$
where X is an radioactive atom, Y is a product of radioactive decay and ω is the transition rate. For an ensemble of atoms, we denote $p(n,t)$ the probability that n of them, at time t are still radioactive (have not yet decayed). Then the master equation is
$$\partial_t p(n,t) = (n+1)\omega p(n+1,t) - n\omega p(n,t). \tag{7.51}$$

- *Birth and death process:* This is a simple process in which particles are created from a reservoir and can also disappear. Schematically:
$$A \xrightarrow{\omega_A} X \xrightarrow{\omega} 0. \tag{7.52}$$
We can assume that the reservoir is infinite and the rate of birth is independent of the number of particles created. The master equation for probability $p(n,t)$ of the number n particles at time t is then
$$\partial_t p(n,t) = \omega_A(p(n-1,t) - p(n,t)) + \omega((n+1)p(n+1,t) - np(n,t)). \tag{7.53}$$
Note that the transition rate for the death process depends on the number of particles present, indeed the larger number of particles the larger chances that one of them disappear. Instead, the transition rate for the birth process, as assumed above, does not depend on the number of particles.

- *Chemical reactions:* We take a simple model of a chemical reaction in which particles X and Y can form a bound state XY. The molecule can then break up to and yield back particles X and Y. The scheme is
$$X + Y \rightleftarrows XY. \tag{7.54}$$
To simplify the description we assume that initially the numbers of particles X and Y are the same and equal N and there are no bound states. Because it takes both particles to create the bound state, their number always remain equal. The probability that there are n particles X or Y at time t we denote $p(n,t)$. Let us denote ω the rate at which particles X and Y form a molecule. For this process to happen they have to be next to each other. If we denote by V the volume of the container, the

probability that two particles are next to each other is n/V. Therefore, the transition rate for forming the bound state is $\omega n^2/V$. The reverse reaction is a single particle process and therefore the transition rate is simple $(N-n)\omega'$. The master equation is then

$$\begin{aligned}\partial_t p(n,t) =& \omega/V \left((n+1)^2 p(n+1,t) - n^2 p(n,t)\right) \\ &+ \omega' \left(N-n+1\right)p(n-1,t) - (N-n)p(n,t)\right). \end{aligned} \tag{7.55}$$