Markovian, Non-Markovian processes and the Master equation

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1 Markovian Master equation

In this section we are going to define Markovian processes or stochastic processes, fulfilling the Markovian assumption. Looking at the probability densities we will derive the Chapman-Kolmogorov equation. We can then expand the probability density in time and look at the short time behaviour, to derive the classical, Markovian Master equation. This part of the talk mainly follows the treatment in pp.156-196 of Honerkamp [3]

1.1 Markovian Processes and Chapman-Kolmogorov Equation

We will start by considering a stochastic process defined by states $z_i, t_i, i = 1, 2, ...$;
The probability of the system beeing in z_1 at time t_1 ist defined by: $\rho_1(z_1, t_1)$ and the conditional probabilities of beeing in z_2, t_2, after beeing in Z_1, t_1 or of beeing in z_n, t_n after $z_{n-1}, t_{n-1}; z_{n-2}, t_{n-2}, ..., z_1, t_1$ by:

$$\rho_2(z_2, t_2|z_1, t_1);$$

and

$$\rho_n(z_n, t_n|z_{n-1}, t_{n-1}; z_{n-2}, t_{n-2}; ...; z_1, t_1);$$

A Markovian process is one, without memory, or in other words a process in which the probability of jumping into a certain state only depends on the last state. Thus we can formulate the

Markovian assumption by:

$$\rho_n(z_n,t_n|z_{n-1},t_{n-1};z_{n-2},t_{n-2};...;z_1,t_1)=\rho_2(z_n,t_n|z_{n-1},t_{n-1});$$

The Chapman-Kolmogorov equation can now be derived by using the Markovian assumption:

$$\rho_3(z_3,t_3;z_1,t_1)=\int\rho_3(z_3,t_3;z_2,t_2;z_1,t_1)dz_2=\int\rho_2(z_3,t_3|z_2,t_2)\rho_2(z_2,t_2|z_1,t_1)\rho_1(z_1,t_1)dz_2$$

Thus we get the Chapman-Kolmogorov equation:

$$\rho_2(z_3,t_3|z_1,t_1)=\int\rho_2(z_3,t_3|z_2,t_2)\rho_2(z_2,t_2|z_1,t_1)dz_2;$$

Multiplying by ρ_1 and integrating over z_1 we get the C-K equation for ρ_1:

$$\rho_1(z_3,t_3)=\int\rho_2(z_3,t_3|z_2,t_2)\rho_1(z_2,t_2)dz_2;$$

1.2 Master Equation

Now we have the background to derive the Master equation which describes the time evolution of the probability density. To get its time derivative we look at the short time behaviour by making the expansion:

$$\rho_2(z,t+\tau|z'',t)=(1-a(z,t)\tau)\delta(z-z'')+w(z,z'',t)\tau+O(\tau^2);$$

Using the normalisation of the density we can relate the a to w by:

$$\int\rho_2(z,t+\tau|z'',t)dz=1\Rightarrow a(z',t)=\int w(z,z',t)dz;$$

Inserting the expansion into the Chapman-Kolmogorov equation we get:

$$\rho_2(z,t+\tau|z',t')=\int\rho_2(z,t+\tau|z'',t)\rho_2(z'',t|z',t')dz''=(1-a(z,t)\tau)\rho_2(z,t|z',t')+\tau\int w(z,z'',t)\rho_2(z'',t|z',t')dz''+O(\tau^2$$

Now we can use the $a-w-$ relation and take the limit $\tau\to 0$ to get the Master equation:

$$\frac{\partial\rho_2(z,t|z',t')}{\partial t}=\int w(z,z'',t)\rho_2(z'',t|z',t')dz'-\int w(z',z,t)\rho_2(z,t|z',t')dz';$$

We can finally multiply by $\rho_1(z',t')$ and integrate over z' to get the Master equation for ρ_1:

$$\frac{\partial\rho_1(z,t)}{\partial t}=\int w(z,z',t)\rho_1(z',t)dz'-\int w(z',z,t)\rho_1(z,t)dz';$$

Analogously we can look at a system with discrete states. We can easily redifine all the given quantities to describe discrete states, by:

$$z\to n;\rho_1(z,t)\to\rho_n(t);w(z,z',t)\to w_{n,n'}(t);$$

Then we get the discrete Master equation:

$$\partial_t\rho_n(t)=\sum_{n'}(w_{n,n'}(t)\rho_{n'}(t)-w_{n',n}(t)\rho_n(t));$$

The Master equation in this form is very easy to interpret. The change of the probability density in time is equal to the over all gain terms, or in other words, terms, adding to the state of interest, minus the loss terms. For convenience we can also write this as a Matrix equation, by ordering all transition rates $w_{n,n'}(t)$ into the matrix $V_{\alpha,\alpha'}$ and ordering the densities for different states in a vector. Then we get:

$$\partial_t\rho_\alpha(t)=\sum_{\alpha'}V_{\alpha,\alpha'}(t)\rho_{\alpha'}(t);$$

1.3 Examples

1.3.1 Liouville Equation and deterministic processes

As the first physical example and to show, how fundamental a method the Master equation is, were goint to formulate the Master equation for a deterministic system, or to be more specific, a Hamiltonian system. If a system is defined by a differential equation:

$$x' = f(x), x \in \mathbb{R}^n;$$

We can then define the density:

$$\rho_2(z,t|x_0,t_0) = \delta(z - x(t)), x(t_0) = x_o;$$

To check the short-time behaviour again we can expand the density to first order by:

$$\rho_2(z,t+\tau|z',t') = \delta(z-(z'-f(x))) = \delta(z-z') - f(z')\partial_z\delta(z-z')\tau + O(\tau^2);$$

$$\rightarrow w(z,z') = -f(z')\partial_z\delta(z-z')\tau;$$

$$\rightarrow a(z') = -\int f(z')\partial_t\delta(z-z')d^n z = 0;$$

With all this we can define the Master equation for deterministic systems:

$$\partial_t\rho_1(z,t) = \int(-f(z')\partial_z\delta(z-z'))\rho_1(z',t)d^n z' = -\partial_z(f(z)\rho_1(z,t));$$

We can now look specifically at a Hamiltonian system, defined by:

$$z = (p,q), z' = (-\partial_q H, \partial_p H);$$

$$\Rightarrow \partial_z\rho(p,q,t) = \frac{\partial H}{\partial q}\frac{\partial \rho}{\partial p} - \frac{\partial H}{\partial p}\frac{\partial \rho}{\partial q};$$

This is the Liouville equation, in the form known from Analytical Mechanics.

1.3.2 A simple Fokker-Planck equation

We can also use the Master equation to get the Focker-Planck equation. As the subject is very broad and a lengthy discussion of the Fokker-Planck equation would require much more space and time, we're going to restrict ourselves to a very simple, one-dimensional example.
Let's start with a Master equation for a one-dimensional system:

$$\partial_t\rho_n(t) = \alpha\rho_{n+1}(t) + \beta\rho_{n-1}(t) - (\alpha+\beta)\rho_n(t);$$

α is here defined as the rate for states to fall one one state to the next lower and thus the term $\alpha * \rho_{n+1}$ the number of states falling into n, from the upper ones. Analogously β is the rate of climbing into the next upper state. To get a more convenient form of the Fokker-Planck equation we rescale the system, by defining:

$$x = \frac{n}{L}, \Pi(x,t) = \rho_n(t), -L \leq n \leq L, 1 \ll L;$$

Thus we can rewrite the Master equation as:

$$\partial_t\Pi(x,t) = \alpha\Pi(x+\frac{1}{L},t) + \beta\Pi(x-\frac{1}{L},t) - (\alpha+\beta)\Pi(x,t);$$

And expanding in orders of $\frac{1}{L}$:

$$\partial_t \Pi(x,t) = (\alpha-\beta)\frac{1}{L}\frac{\partial}{\partial x}\Pi(x,t) - \frac{(\alpha-\beta)}{2}\frac{1}{L^2}\frac{\partial^2}{\partial^2 x}\Pi(x,t) + O(\frac{1}{L^3});$$

Looking at each order in the expansion we can give some interpretation: The first term is the first derivative of the density times the difference of "falling" and "climbing" rates. Depending on whether α or β is bigger, we will have some kind of drift into the direction of the upper or lower states. In the following were going to consider the static, or non-drifting case, by setting both rates equal. The second oder term describes a diffusion, which has to be proportional to both α and β. If we rescale again $\tau = \frac{t}{L^2}$ and set $\alpha = \beta$ er get the Fokker-Planck equation in its simplest form:

$$\frac{\partial}{\partial t}\Pi(x,t) = \frac{\partial}{\partial x^2}\Pi(x,t);$$

This equation, though being of very simple structure already describes some phenomena, like Random Walk and is one of the very few versions of the Fokker-Planck equation, that can be solved by a Gaussian.

2 Quantum Master equation

Now that we have looked at the classical Master equation, describing Markovian processes, we will consider quantum processes, or in particular a perturbed quantum system and and derive a more general form of the Master equation, that also describes Non-Markovian processes. So processes, where transition probabilities depend on not only the last, but possibly also previous states. In the end we will also see how bringing in the Markovian assumption into the Non-Markovian Master equation will again yield the previously derived form. We will also see that the Master equation for a perturbed quantum system yields the Fermi Golden Rule, when the system is restricted to be Markovian. Some mathmatical details are skipped in this part and can be read in [1].

2.1 Pauli Equation

Before getting to the Non-Markovian Master equation we start with the Pauli equation, which was the first quantum Master equation to be drived. First of all we start with the von Neumann equation with [.,.] defining the commutator and by defining the Liouville operator $\hat{L}$:

$$i\frac{\partial\hat{\rho}}{\partial t} = [\hat{H},\hat{\rho}] = \hat{L}\hat{\rho};$$

This can formally be solved by: $\hat{\rho}(t) = e^{-i\hat{H}(t-t')}\hat{\rho}(t_0)$; The time evolution in Heisenberg picture is given by: $\hat{\rho}(t+\tau) = e^{-i\tau\hat{H}}\hat{\rho}(t)e^{i\tau\hat{H}}$; Using the bracket notation we can now look at the diagonal elements:

$$\rho_{mm}(t+\tau) = \langle m|e^{-i\tau\hat{H}}\hat{\rho}(t)e^{i\tau\hat{H}}|m\rangle = \sum_{n,l}\langle m|e^{-i\tau\hat{H}}|n\rangle\langle n|\hat{\rho}(t)|l\rangle\langle l|e^{i\tau\hat{H}}|m\rangle;$$

If we now neglect off-diagonal elements and consider that the diagonal elements of the density matrix are probabilities $\rho_{mm} = P_m$, we get the Pauli equation:

$$P_m(t+\tau) = \sum_n \langle m|e^{-i\tau\hat{H}}|n\rangle\langle n|\hat{\rho}(t)|n\rangle\langle n|e^{i\tau\hat{H}}|m\rangle = \sum_n |\langle m|e^{-i\tau\hat{H}}|n\rangle|^2\rho_{nn}(t);$$

$$\Leftrightarrow P_m(t+\tau) = \sum_n Q_{mn}(\tau)P_n(t);$$

The problem with this equation is, that it is only valid for probabilities, constant in time, as can easily be seen, by plugging in $-\tau$ instead of τ, as both yield the same result.

2.2 The Van Hove method

To get the Van Hove equation, which is more general and seeks to get rid of the error of the Pauli equation. The derivation is completely analogous, but this time we start with a perturbed Hamiltonian: $\hat{H} = \hat{H}_0 + \lambda(t)\hat{W}$, with lamba being a small coupling, $\hat{W}$ the interaction term and $\hat{H}_0$ the unperturbed Hamiltonian, that we know the solution for. We can also assume that the density operator is initially diagonal, which can be done, as the basis can always be chosen such that it is diagonal at a certain time. But we can't guarantee its remaining diagonal. With all these considerations we get the Van Hove equation:

$$P_m(t) = \sum_{n,l} \langle m| e^{-i\hat{H}t} |n\rangle \langle n| \hat{\rho}(0) |l\rangle \langle l| e^{it\hat{H}} |m\rangle = \sum_n |\langle m| e^{-i(\hat{H}_0+\lambda(t)\hat{W})t} |n\rangle|^2 \rho_{nn}(0)$$

$$= \sum_n |\langle m| e^{-i(\hat{H}_0+\lambda(t)\hat{W})t} |n\rangle|^2 P_n(0);$$

2.3 Zwanzig and Nakajimas Solution

Now we are going to look at an Ansatz by Robert Zwanzig and Sadao Nakajima, for the Master equation, which will yield a formal solution and a very general form of the Master equation, for Non-Markovian processes. This will be achieved by starting from a perturbed Hamiltonian system, splitting ρ into diagonal and off-diagonal elements to get two coupled equations. Then a Greens function can be used to uncouple them and get one equation.

2.3.1

We can split the density matrix by defining the diagonalization operator $\hat{D}$:

$$\hat{\rho} = \hat{\rho}_d + \hat{\rho}_{od} = \hat{D}\hat{\rho} + (1 - \hat{D})\hat{\rho};$$

By applying $\hat{D}$ and $(1 - \hat{D})$ to the Von Neumann equation we get:

$$\partial_t \hat{\rho}_d = -i\hat{D}\hat{L}\hat{\rho}_d - i\hat{D}\hat{L}\hat{\rho}_{od};$$

$$\partial_t \hat{\rho}_{od} = -i(1 - \hat{D})\hat{L}\hat{\rho}_d - i(1 - \hat{D})\hat{L}\hat{\rho}_{od};$$

2.3.2 Green´s function and uncoupling the equations

To simplify the equations we got for the diagonal and off-diagonal parts we shall look at a Green´s function, solving equation of the type the off-diagonal equation has. A differential equation of the type:

$$\partial_t x + \alpha x = f(x);$$

Is solved by the function:

$$x(t) = x(0)e^{-\alpha t} + \int_0^t e^{-\alpha(t-t')} f(t')dt';$$

Applying this method to the off-diagonal equation we get:

$$\hat{\rho}_{od}(t) = e^{-i(1-\hat{D})\hat{L}t}\hat{\rho}_{od}(0) + \int_0^t e^{-i(1-\hat{D})\hat{L}(t-t')}(-i(1 - \hat{D})\hat{L}\rho_d\hat{(t')})dt';$$

We can plug this into the equation for the diagonal part to uncouple the equations:

$$\partial_t \hat{\rho}_d = -i\hat{D}\hat{L}\hat{\rho}_d - \hat{D}\hat{L}\int_0^t e^{-i(1-\hat{D})\hat{L}(t-t')}(1 - \hat{D})\hat{L}\hat{\rho}_d(t')dt';$$

2.3.3 Memory Kernel and the Non-Markovian Master Equation

As we have uncoupled the equations to the time development of the diagonal part of the density operator, we can now further investigate the structure of the equation. Looking at the integral we can see that it is an integral over ρ_d and a term containing some time development. It contains information from the initial time $t_0 = 0$ to the time t. It is the so called memory kernel $K(t-t')$:

$$K(t-t') = \hat{D}(\hat{L}_0 + \lambda\hat{L}_W)e^{-i(1-\hat{D})(\hat{L}_0+\lambda\hat{L}_W)(t-t')}(\hat{L}_0 + \lambda\hat{L}_W)$$

Considering that λ is very small we can simplify this term by dropping terms of higher than second order:

$$K(t-t') = \hat{D}(\hat{L}_0 + \lambda\hat{L}_W)e^{-i(1-\hat{D})\hat{L}_0(t-t')}(\hat{L}_0 + \lambda\hat{L}_W) = \lambda^2\hat{L}_W e^{-i\hat{L}_0(t-t')}\hat{L}_W;$$

We can further simplify the equation by taking a closer look at the first term:

$$\hat{D}\hat{L}\hat{\rho}_d = 0;$$

This can easily be checked by looking at the exact components of this term. As $\hat{L}$ is the commutator of a symmetric (Hamiltonian) and a diagonal operator, it vanishes. To get closer to the previous form of the Master equation we define: $\hat{M} = e^{-i(t-t')\hat{H}_0}[\hat{W}, \rho_d]e^{i(t-t')\hat{H}_0}$ and use the fact that the unperturbed Hamiltonian $\hat{H}_0$ is solved by: $\hat{H}_0|m\rangle = \epsilon_m|m\rangle$: Using that we can look at the matrix element of $\hat{M}$:

$$M_{mn} = e^{-i(t-t')\epsilon_m}(M_{mn}P_n - P_m M_{mn})e^{i(t-t'\epsilon_n)};$$

We can now calculate the diagonal elements of the Master equation:

$$\langle m|\,\partial_t\hat{\rho}_d\,|m\rangle = -\lambda^2\langle m|\int_0^t[\hat{W}, e^{-i(t-t')\hat{L}_0}[\hat{W}, \hat{\rho}_d]]dt'|m\rangle = -\lambda^2\int_0^t(\langle m|\,\hat{W}\hat{M}\,|m\rangle - \langle m|\hat{M}\hat{W}\,|m\rangle)dt'$$

$$= -\lambda^2\int_0^t\sum_n(W_{mn}M_{nm} - M_{mn}W_{nm})dt' = -2\lambda^2\int_0^t\sum_n|W_{mn}|^2[P_n - P_m]cos((t-t')(\epsilon-\epsilon'))dt';$$

We can finally define the new memory kernel $\Omega_{mn}(t-t') = |W_{mn}|^2 cos((t-t')(\epsilon-\epsilon'))$ to get the final form the Non-Markovian Master equation:

$$\partial_t P_m = \int_0^t\sum_n[\Omega_{mn}(t-t')P_n - \Omega_{nm}(t-t')P_m]dt';$$

We can see that the basic structure is the same as that of the discrete Non-Markovian Master equation we have described in the previous section. The striking difference is, that instead of "simple" transition amplitudes we have memory kernels, that do not only depend on the current time t but also on the "past" of the system, which we have to integrate over. In the next section we are going to see how this reduces to the Non-Markovian Master equation when we bring in the Markovian assumption.

2.4 Connection to the Markovian Master equation and the Fermi Golden Rule

Now that we have a very general form of the Master equation, we need to consider how the Markovian assumption. It can be formulated by $corr(t,t') = 0$, for $t \neq t'$ meaning that probabilities at different times are not correlated or by defining away the "memory" of the memory kernel, by: $\Omega_{mn}(t) = \delta(t)\int_0^t\Omega_{mn}(\tau)d\tau$; To apply this we will need to rewrite the Master equation in the interaction picture:

$$\partial_t P_m = -\lambda^2\int_0^t\sum_n[(W_{mn}e^{-i(t-t')(\epsilon_n-\epsilon_m)}W_{nm}(P_m - P_n)) - (e^{-i(t-t')\epsilon_m}(W_{mn}P_n - P_m W_{mn})e^{i(t-t')\epsilon_n})]dt' =$$

$$= -\lambda^2 \sum_n \int_0^t [W^I_{mn}(t-t')W^I_{nm}(0)(P_m - P_n) - W^I_{mn}(t-t')W^I_{nm}(0)(P_n - P_m)]dt';$$

We can now bring in the Markovian assumption by:

$$\int_0^t W^I_{mn}(t-t')W^I_{nm}(0)(P_m(t) - P_n(t))dt' = (P_m(t) - P_n(t)) \lim_{t\to\infty} \int_0^t W^I_{mn}(t-t')W^I_{nm}(0)dt';$$

Plugging this into the Master equation we can integrate over the exponential to get:

$$\partial_t P_m(t) = -\lambda^2 \sum_n (P_m(t) - P_n(t')) \lim_{t\to\infty} (\frac{|W_{mn}|^2}{i\omega_{nm}} (e^{-it\omega_{mn}} - e^{it\omega_{mn}})) =$$

$$= 2\pi\lambda^2 \sum_n (P_m - P_n)|W_{mn}|^2 \lim_{t\to\infty} (\frac{sin(\omega_{mn}t)}{\pi\omega_{mn}}) =$$

Taking the limit we get a delta function and the final result:

$$\partial_t P_m(t) = 2\pi\lambda^2 \sum_n (P_n - P_m)|W_{mn}|^2 \delta(\epsilon_m - \epsilon_n) = \sum_m [\Omega_{mn}P_n - \Omega_{nm}P_m];$$

We have finally arrived back at the discrete Non-Markovian Master equation. The omega matrix elements are the transition amplitudes. The element Ω_{mn} is the amplitude for transitions from the state n to m. We can further look at the exact expression it:

$$\Omega_{mn} = 2\pi|W_{mn}|^2 \delta(\epsilon_m - \epsilon_n);$$

We see that this is exactly the Fermi Golden Rule. The delta function can be interpreted as the energy conservation condition. Only same-energy transitions are allowed. This is quite beautiful a result, as we have only used the von Von Neumann equation for a very general, perturbed quantum system and the Markovian assumption.

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