Master equation, thermodynamics and fluctuation theorems

Seminar: Stochastic thermodynamics and biophysical applications

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Organiser: Berg, Bollenbach, Krug, Lässig, Maier, Sabass
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Speaker: Christopher Zachow

Motivation

Comparable to talk two we want to identify thermodynamic quantities at stochastic processes. Therefore we look at stochastic processes that are governed by the so called master equation and identify the stochastic entropy production. For specific types of states we formulate the famous fluctuation theorems and give some examples for observable non-equilibrium steady states.

At the beginning we want to look at a dummy system to motivate the master equation. Let us consider a particle on a finite lattice of size N with hardcore walls that can jump to the left or right with fixed rates W_+ and W_-. We can ask: Given an initial distribution for the particle, what is the probability to find the particle at site n at time t. The probability changes according to the following equation:

$$\partial_t P_n\left(t\right) = W_+ P_{n-1}\left(t\right) + W_- P_{n+1}\left(t\right) - \left(W_+ + W_-\right) P_n\left(t\right)$$

For a free particle both rates should equal which can be expressed as $\frac{W_+}{W_-} = 1$. In this setup we will get an equilibrium distribution for the particle $P_n^s = \frac{1}{N}$.

Now we apply a constant force F that pulls the particle to the right. Classically this constant force is the gradient of some potential and therefore we can associate an energy with each lattice site. We expect to observe the Boltzmann distribution as the equilibrium steady state distribution of this system. In equilibrium we expect no probability flow between sites which is called local detailed balance. This leads to transition rates of the form $\frac{P_n^s}{P_{n-1}^s} = \frac{W_+}{W_-} = \exp\left(\beta F a\right)$ with a the lattice constant. Since the force is constant the system will relax to a new equilibrium state, in the intermediate time it is in a NETS.

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$$\begin{aligned}
\partial_t P_n = 0 &= W_+ P_{n-1} + W_- P_{n+1} - \left(W_+ + W_-\right) P_n \\
&= W P_{n-1} + W \exp\left(-\beta F a\right) P_{n+1} - W\left(1 + \exp\left(-\beta F a\right)\right) P_n \\
\Rightarrow P_{n+1} &= \left(\exp\left(\beta F a\right) + 1\right) P_n - \exp\left(\beta F a\right) P_{n-1}
\end{aligned}$$

With the condition on the boundaries we get:

$$\partial_t P_0 = W_- P_1 - W_+ P_0 \qquad\qquad \partial_t P_{N-1} = W_+ P_{N-2} - W_- P_{N-1}$$
$$\Rightarrow P_1 = \exp\left(\beta F a\right) P_0 \qquad\qquad \Rightarrow P_{N-1} = \exp\left(\beta F a\right) P_{N-2}$$

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Using induction we finally get $P_n^s = P_0 \exp\left(\beta F a n\right)$ with P_0 a proper normalization constant. This

means that it is highly likely to find the particle on the right. We can now identify the associated energy ϵ_n with $\epsilon_n = -Fan$.

In a third setup we connect the ends of our lattice and make it a circle. Additionally we apply the same force as in the second setup. Because of the boundary conditions there is a stationary state with $P_n^s = \frac{1}{N}$ again which does not fulfil the detailed balance condition $\frac{W_+}{W_-} = \exp\left(\beta Fa\right) \neq 1$. Such a steady state is called a generic NESS (non-equilibrium steady state). In this setup we can identify the logarithm of the transition rates as the dissipated heat divided by temperature and therefore associate an entropy production with it.

$$\log\left(\frac{W_+}{W_-}\right) = \beta Fa = \frac{q}{T}$$

In the following we want to generalize these considerations and combine them with known results.
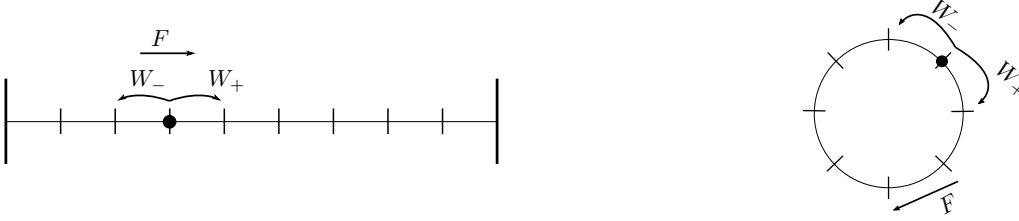
Single particle on lattice under different boundary conditions

Master equation

The prototype process above can be generalized to a discrete stochastic process in continuous time. Dynamics should be of Markovian type so that only the current state influences the next state of the system. The transition rates are given as W_{nm} resulting in the full master equation:

$$\partial_t P_n\left(t\right) = \sum_{n \neq m} W_{mn} P_m\left(t\right) - W_{nm} P_n\left(t\right)$$

One can also introduce the corresponding diagonal elements $W_{nn} = -\sum_{m,n \neq m} W_{nm}$ and interpret the master equation as a continuity equation with local probability flow $j_{nm}\left(t\right) = W_{mn} P_m\left(t\right) - W_{nm} P_n\left(t\right)$. Examples for systems that can be described with this equation are networks or a chemical reaction.

Reversibility

Now we want to put our system under external control. Normally the transition rates W_{nm} would not be explicitly time dependent. By changing the external parameter $\lambda\left(t\right)$ e.g. a magnetic field we change the transition rates $W_{nm}\left(t\right) = W_{nm}\left(\lambda\left(t\right)\right)$. To assure that the microscopic reversibility is given the probability rates for a given external parameter must fulfil the condition of detailed balance for the corresponding steady state:

$$\frac{W_{nm}\left(\lambda\left(t\right)\right)}{W_{mn}\left(\lambda\left(t\right)\right)} = \frac{P_n^s\left(\lambda\left(t\right)\right)}{P_m^s\left(\lambda\left(t\right)\right)}$$

This condition is equivalent to observing no local probability flow in the steady state. That implies that for every time t and corresponding parameter $\lambda\left(t\right)$ we have a steady state probability distribution which fulfils $\partial_t P_n^s\left(\lambda\left(t\right)\right)|_{\lambda(t)=const.} = 0$.

Trajectories

Before introducing the notion of energy and stochastic entropy we want to introduce the concept of a trajectory. Comparable to the continuous case we define a trajectory Γ as a sequence of states starting at n_i at time t_i and ending at n_f at time t_f. The jumps occur at intermediate times t_k für $k \in \{1, ..., M\}$.
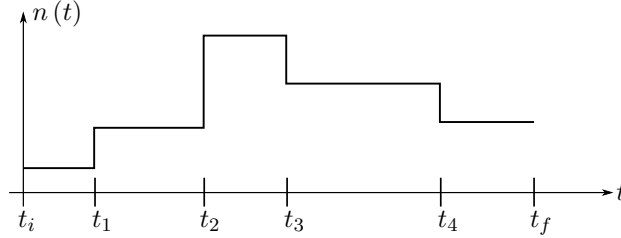
Example trajectory

Energy

For systems that obey the detailed balance condition at all times we can define an energy using the corresponding steady states:

$$\epsilon_n \left(\lambda \left(t \right) \right) = -T \log \left(P_n^s \left(\lambda \left(t \right) \right) \right)$$

The energy difference along a trajectory is given as $\triangle\epsilon = \epsilon_{n_f} \left(t_f \right) - \epsilon_{n_i} \left(t_i \right)$ and with the first law of thermodynamics can be split into two contributions work and heat. They are related to the shifting in energy levels (tuning of λ but no jump) and the jumps in energy levels (constant λ but jump).

$$w = \left[\epsilon_{n_i} \left(t_1 \right) - \epsilon_{n_i} \left(t_i \right) \right] + ... + \left[\epsilon_{n_f} \left(t_f \right) - \epsilon_{n_f} \left(t_M \right) \right]$$

$$q = \sum_{k=1}^{M} \epsilon_{n_k} \left(t_k \right) - \epsilon_{n_{k-1}} \left(t_k \right)$$

With this definition we can associate the logarithm of the transition rates with a heat flow by plugging in the definition for the energy and the detailed balance condition.

$$\frac{q}{T} = \sum_{k=1}^{M} \log \left(\frac{P_{n_{k-1}}^s \left(t_k \right)}{P_{n_k}^s \left(t_k \right)} \right)$$

$$= \sum_{k=1}^{M} \log \left(\frac{W_{n_{k-1} n_k} \left(t_k \right)}{W_{n_k n_{k-1}} \left(t_k \right)} \right)$$

From thermodynamics we know that a heat flow divided by temperature can be interpreted as an entropy.

Entropy

We now want to define stochastic entropy along a trajectory:

$$s \left(t \right) = -\log \left(P_{n(t)} \left(t \right) \right)$$

This quantity depends on the initial distribution and is time dependent due to two effects (relaxation and time-dependence of jumps). Therefore we can divide the total entropy along a trajectory $[t_i, t_f]$ into two parts (total and medium):

$$\triangle s = -\log\left(P_{n_f}(t_f)\right) + \log\left(P_{n_i}(t_i)\right)$$
$$= \triangle s_{tot} - \triangle s_{med}$$

The definition for the medium entropy change is motivated by the results for the definition of exchanged heat. It adds the contributions from the jumps and is as follows:

$$\triangle s_{med} = \sum_{k=1}^{M} \log\left(\frac{W_{n_{k-1}n_k}(t_k)}{W_{n_k n_{k-1}}(t_k)}\right)$$

This results in an total entropy production along a trajectory:

$$\triangle s_{tot} = \triangle s + \triangle s_{med} = -\log\left(P_{n_f}(t_f)\right) + \log\left(P_{n_i}(t_i)\right) + \sum_{k=1}^{M} \log\left(\frac{W_{n_{k-1}n_k}(t_k)}{W_{n_k n_{k-1}}(t_k)}\right)$$

Fluctuation Theorem

We now want to consider the inverse process and ask ourselves in which way the probabilities for forward and backward process equal each other. We start with the forward process in the time interval $[t_i, t_f]$ starting from a given initial distribution $P_n(t_i)$. We want to assume that jumps occur at times t_k and therefore the state does not change in the intermediate time. The probability for the trajectory $P(\Gamma)$ is then given as the product of probabilities for the jumps, the intermediate periods of staying in one state and beginning/end (identifying $t_0 = t_i$ and $t_{M+1} = t_f$).

$$P(\Gamma) = P_{n_i}(t_i) \exp\left(\int_{t_i}^{t_1} W_{n_i n_i}(t)\, dt\right)\left(\prod_{k=1}^{M} W_{n_{k-1}n_k}(t_k) \exp\left(\int_{t_k}^{t_{k+1}} W_{n_k n_k}(t)\, dt\right)\right)$$

In the backward process we start at the final distribution of the forward process and evolve to its initial distribution. The rates run backward in time and are therefore given as $W_{n_k n_{k-1}}(t_k)$. The probability for the reverse trajectory $\tilde{\Gamma}$ in the backward process is $\tilde{P}\left(\tilde{\Gamma}\right)$. The contributions to the reverse trajectory are more or less the same resulting in the ratio of both as:

$$\log\left(\frac{P(\Gamma)}{\tilde{P}\left(\tilde{\Gamma}\right)}\right) = \log\left(P_{n_i}(t_i)\right) - \log\left(P_{n_f}(t_f)\right) + \sum_{k=1}^{M} \log\left(\frac{W_{n_{k-1}n_k}(t_k)}{W_{n_k n_{k-1}}(t_k)}\right)$$

This can be identified as $\triangle s_{tot}$ and therefore we get:

$$\log\left(\frac{P(\Gamma)}{\tilde{P}\left(\tilde{\Gamma}\right)}\right) = \triangle s_{tot}$$

If we now average this probability over all possible trajectories we get the integral fluctuation theorem:

$$\langle \exp\left(-\triangle s_{tot}\right)\rangle_{\Gamma} = \left\langle \frac{\tilde{P}}{P}\right\rangle_{\Gamma} = \sum_{\Gamma} P(\Gamma)\frac{\tilde{P}(\Gamma)}{P(\Gamma)} = 1$$

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With Jensen's inequality we get the usual second law of thermodynamics $\triangle S_{tot} = \langle \triangle s_{tot} \rangle \geq 0$. We can also ask what is the probability to find a change in total stochastic entropy given a specific process.

$$P\left(\triangle s_{tot}\right) = \sum_{\Gamma} P\left(\Gamma\right) \delta\left(\triangle s_{tot} - \log\left(\frac{P\left(\Gamma\right)}{\tilde{P}\left(\tilde{\Gamma}\right)}\right)\right)$$

$$= \exp\left(\triangle s_{tot}\right) \sum_{\Gamma} \tilde{P}\left(\tilde{\Gamma}\right) \delta\left(\triangle s_{tot} - \log\left(\frac{P\left(\Gamma\right)}{\tilde{P}\left(\tilde{\Gamma}\right)}\right)\right)$$

$$= \exp\left(\triangle s_{tot}\right) \sum_{\tilde{\Gamma}} \tilde{P}\left(\tilde{\Gamma}\right) \delta\left(-\triangle s_{tot} - \log\left(\frac{\tilde{P}\left(\tilde{\Gamma}\right)}{P\left(\Gamma\right)}\right)\right)$$

$$= \exp\left(\triangle s_{tot}\right) \tilde{P}\left(-\triangle s_{tot}\right)$$

$$\Rightarrow \frac{P\left(\triangle s_{tot}\right)}{\tilde{P}\left(-\triangle s_{tot}\right)} = \exp\left(\triangle s_{tot}\right)$$

This means that it is exponentially more likely to see a stochastic entropy increase $\triangle s_{tot}$ in a process than to see the corresponding decrease in the reversed process. This equation is named detailed fluctuation theorem.

References

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