



BACHELOR THESIS

Notions of entropy and entropy production in non-equilibrium systems

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Konzepte von Entropie und Entropieproduktion in Nichtgleichgewichtssystemen

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1 Introduction

You should call it entropy [...] nobody knows what entropy really is, so in a debate you will always have the advantage.

John von Neumann
to Claude Shannon

Entropy has proved itself to be a key concept in the development of modern physics. Though having been under thorough investigation for 150 years, the use of entropy and its implications provide still a vivid field of research spreading over a wide area of approaches from philosophy over physics up to mathematics.

The origin of the term entropy can be traced back to the mid 19th century, where, as a *thermodynamic* quantity, entropy first appears in the works of Rudolf Clausius [1]. Inspired by engineering, he concerned himself with the question of how to optimally transform heat into useful work. Dealing with cyclic processes in thermodynamic state space, he showed that the exchanged amount of heat between a cool and a warm reservoir divided by their respective temperatures are equal to one another. He defined this variable as entropy, from the Greek word for change. In this text, entropy is a state variable only defined for thermodynamic equilibrium. With his definition, Clausius showed what is now known as the Second Law of Thermodynamics, namely that the change in entropy equals zero for a reversible process and that entropy can only increase in an irreversible process.

Thermodynamics is a theoretical framework initially derived for equilibrium systems. For non-equilibrium conditions, one can therefore not expect to arrive at valid predictions beyond *local equilibrium*, a condition that we take for granted in the following [2]. With the development of *statistical physics*, a first approach to entropy by taking into account the relation between the microscopic and macroscopic dynamics of a system was undertaken by Ludwig Boltzmann [3]. Known as *Boltzmann's principle*, entropy is a matter of counting microstates that lead to the same macrostate. This concept does not require an equilibrium system, since *counting* is an observational definition of entropy that can be applied to an arbitrary system state. The postulates of thermodynamics require that entropy is a non-decreasing function that is maximized in equilibrium and that is additive [4]. With Boltzmann's idea, the first postulate leads to functional

dependence on the number of microstates yielding one macrostate and the second postulate entails a logarithmic dependence [3].

Towards the end of the 19th century, equilibrium statistical physics prospered with the works of Josiah W. Gibbs. In the Gibbs picture of equilibrium statistical physics the concept of entropy is based on an ensemble average over the phase space in contrast to observations of a single system. Thereby, the term equilibrium becomes embedded in a stochastic framework: though the systems of the ensemble might still evolve in time, the *probability* to find a particular state within the ensemble is time invariant. Naturally, an entropy definition that is associated to the ensemble concept becomes a function of the ensemble probabilities [3].

During the 20th century, the idea of entropy was applied in mathematical statistics and information theory utilizing its inherent feature as measure of *uncertainty* or lack of *information*. Furthermore, within physics the concept of entropy transferred from statistical physics to other branches such as dynamical systems theory, where the amount of information produced by a system is measured by the Komogorov-Sinai entropy [5].

In the first decade of this century, the term *stochastic thermodynamics* has been coined [6, 7]. Here, one deals with open systems that are subject to strong fluctuations. This opposes the thermodynamic theory that is interested in performing the thermodynamic limit for large particle numbers. This novel approach discloses the statistical nature of thermodynamic principles such as the Second Law, since they are only valid on *average*. In the context of stochastic thermodynamics, thermodynamic quantities can be assigned to single trajectories and an ensemble is constructed out of all possible paths. All averages are then taken with respect to this trajectory ensemble. Being accompanied by experimental advances in the resolution and construction of ever finer structures, this development is catalized by a practical interest. Recent examples can especially be found in biophysics [6].

By the maximum entropy postulate, in equilibrium states the different ideas are expected to make the same predictions. However, the more general case of *non-equilibrium* plays the dominant role in most physical systems, a realm that cannot yet be explained in a self-consistent theory, though offers an interesting setup to investigate different notions of entropy. The idea behind entropy is based on a few principles, but on the contrary has a wide variety of applications. This gap leaves room for interpretation and misconception forcing a cautious approach to the use of the term entropy. By investigation of different entropy concepts the basic principles become evident leading

to a better understanding of where to apply which notion.

2 A Markov chain as a physical model

Many stochastic physical systems can be described in terms of Markov processes, i.e. are formulated in the language of probability theory [8]. In this thesis, we examine a discrete time Markov chain as a representant for a class of transport processes.

First, we introduce a transport model for which we divide the phase space Γ of some underlying dynamics into M different cells with mesoscopic length a . For simplicity just one spatial dimension is taken into account, which corresponds to translational invariance in all but one direction. From the mesoscopic point of view this *coarse-graining* is necessary because of our insufficient knowledge of the states $(x(t), p(t))$ in phase space.

We now impose a transport theory on that system in a sense that we only consider the particle exchange between these cells, where $N_{m,m+1}(t)/\tau$ is the number of particles per unit time that flow from cell m to cell $m + 1$, and we neglect any small-scale dynamics.

In this thermodynamic approach, in the spirit of [2], the particle current $j_m(t)$ over a time τ from cell m to cell $m + 1$ at a given time instant t can be defined as

$$j_m(t) = \frac{1}{\tau} [N_{m,m+1}(t) - N_{m+1,m}(t)]. \quad (2.1)$$

This system can also be considered from a stochastic point of view with simple stochastic dynamics between the coarse-grained states.

We begin by introducing a general Markov chain. We consider M states $[M] := \{1, \dots, M\}$ and construct a *jump process*. We imagine an ensemble of systems and assign an initial probability distribution $p_m(0)$, $m \in [M]$ over the discrete state space. The state of a randomly chosen system is then a random variable $X(t)$ and its time evolution becomes a stochastic process.

The evolution of the probability $p_i(t)$ of finding a system in state i at time t is governed by the *master equation* [8]

$$\partial_t p_i(t) = \sum_{j \in [M]} w_{ji} p_j(t) - w_{ij} p_i(t). \quad (2.2)$$

Here, w_{ij} is the transition rate from state i to state j with $\sum_{j \in [M]} w_{ij} = 1$. One defines

the probability current from state j to state i as

$$K_{ji}(t) = w_{ji} p_j(t) - w_{ij} p_i(t). \quad (2.3)$$

In equilibrium, the system fulfills the condition of *detailed balance*, i.e. $K_{ji}^{\text{eq}} = 0 \forall i, j \in [M]$. A more general *non-equilibrium steady state* (NESS) is reached, when its currents K_{ji}^* obey $\sum_{j \in [M]} K_{ji}^* = 0 \forall i \in [M]$ [9].

A Markov chain is said to be ergodic if every state can be reached from every other one (not necessarily with one step). An ergodic system has a unique stationary state [9].

In this thesis, we study the master equation Eq. (2.2) in discrete time. We use periodic boundary conditions for the states and to model the above transport process allow only nearest neighbor interaction by introducing a right transition rate r , a left transition rate l and a stay probability s with the probability constraint $l + r + s = 1$. For this model the master equation takes the form

$$p_m(\nu + 1) = r p_{m-1}(\nu) + l p_{m+1}(\nu) + s p_m(\nu). \quad (2.4)$$

In the language of linear algebra the evolution of the probability distribution of a Markov chain can be described by the equation

$$\mathbf{p}_m(\nu) = \mathbf{p}_m(0) \mathbf{W}^\nu, \quad (2.5)$$

where $\mathbf{p}_m(\nu) = (p_1(\nu), \dots, p_M(\nu))$ is the probability vector and $\mathbf{W} := (w_{ij})_{i,j \in [M]}$ is the $M \times M$ transition matrix with its elements denoting the one-step transition probabilities from state i to state j . For our transport model, \mathbf{W} becomes the circulant matrix

$$\mathbf{W} = \begin{pmatrix} s & r & 0 & \dots & 0 & 0 & l \\ l & s & r & 0 & \dots & 0 & 0 \\ 0 & l & s & r & 0 & \dots & 0 \\ & & & \vdots & & & \\ r & 0 & 0 & \dots & 0 & l & s \end{pmatrix} \quad (2.6)$$

We study this system as a minimal non-equilibrium model. We therefore define the transition probabilities as $r_m = l_m = g, s_m = s$ for all $m \in \{2, \dots, M\}$. For a given

2 A Markov chain as a physical model

ε with $\min\{r, l\} \geq \varepsilon \geq 0$ we let state 1 have the transition probabilities $s_1 = s, r_1 = g + \varepsilon, l_1 = g - \varepsilon$, such that the one step transition matrix $\mathbf{W} = (w_{ij})_{i,j \in [M]}$ of the Markov chain takes the form (perturbed Markov chain)

$$\mathbf{W} = \begin{pmatrix} s & (g + \varepsilon) & 0 & \dots & 0 & 0 & (g - \varepsilon) \\ g & s & g & 0 & \dots & 0 & 0 \\ 0 & g & s & g & 0 & \dots & 0 \\ & & & \vdots & & & \\ g & 0 & 0 & \dots & 0 & g & s \end{pmatrix} \quad (2.7)$$

In a physical context, our system is at one point coupled to an external field that induces a clockwise small drive of the probability current depending on the perturbation parameter ε . In the language of thermodynamics, we have thereby a clear understanding of the heat dissipation into the medium.

To enforce non-steady state conditions, we use the uniform distribution $p_m(0) = 1/M \forall m \in [M]$ as our initial distribution. In the corresponding physical setting, the system is in equilibrium for all times $\nu < 0$ and at $\nu = 0$ the external force is abruptly activated. For $\nu \geq 0$, the system then relaxes to its new steady state, the distribution of which depends on ε .

The same physical system can thus be investigated by a thermodynamic and by a stochastic approach. They correspond to two levels of coarse-graining. Whereas the former approach neglects small scale dynamics by assuming a homogeneous *particle* density, the latter is based on a completely stochastic theory using a *probability* density to approximate the dynamics.

3 Notions of entropy

The model system outlined in Sec. 2 enables us to study entropy concepts that are defined on different levels of coarse-graining. Following the historical development of ideas concerning the term *entropy*, we introduce notions of entropy that can be evaluated using the model.

3.1 Irreversible Thermodynamics (Transport Theory)

In order to construct a thermodynamic theory of our model system we require *local equilibrium*, i.e. a uniform particle density ρ_m in each cell. In the continuum limit of this transport process, particle conservation is expressed by the continuity equation for the particle density $\rho^{(N)}(x, t)$ and the particle current $j^{(N)}(x, t)$ at position $x = m a$ and time $t = \tau \nu$,

$$\partial_t \rho^{(N)}(x, t) = -\partial_x j^{(N)}(x, t). \quad (3.1)$$

For simplicity, we consider an isothermal system. The particle current is proportional to the concentration gradient, which itself is proportional to the change in the chemical potential difference μ of a binary mixture, such that the relation

$$j^{(N)} = -\kappa_\mu \partial_x \mu \quad (3.2)$$

holds true, combining the Gibbs-Duhem relation with the continuity equations for energy and particle number. The Second Law of Thermodynamics for the entropy density s with respect to volume can also be stated in form of a continuity equation [2]

$$\frac{\partial s}{\partial t} = -\partial_x j^{(S)} + \sigma^{\text{irr}}, \quad (3.3)$$

with $\sigma^{\text{irr}} \geq 0$ being the irreversible entropy production rate and $j^{(S)}$ being the entropy current. The change in entropy density s under the assumption of a constant internal

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energy is given by the Gibbs relation [2]

$$\begin{aligned}
 \frac{ds}{dt} &= -\mu \frac{d\rho^{(N)}}{dt} \\
 &= \mu \partial_x j^{(N)} \\
 &= -\partial_x \left[-\mu j^{(N)} \right] - j^{(N)} \partial_x \mu.
 \end{aligned} \tag{3.4}$$

This expression is valid in the moving reference frame with its origin at the center of mass, as can be seen by the use of the total derivative (cf. hydrodynamics). From comparison with Eq. (3.3) it follows that σ^{irr} is proportional to the *square* of the diffusive particle current.

$$\sigma^{\text{irr}} = \frac{1}{\kappa} (j^{(N)})^2, \quad j^{(S)} = -\mu j^{(N)} \tag{3.5}$$

Thermodynamics is a theory of *averages*, such as currents, and *second moments*, such as heat capacities, and is not formulated in a stochastic language. It uses vocabulary present in hydrodynamic transport theory such as flows of heat and entropy.

3.2 Boltzmann's line of thought

The Boltzmann entropy is an observable of a system with the entropy of a macrostate being proportional to the logarithm of the number microstates that compose this macrostate. A macroscopic state with Ω microscopic realizations has the entropy (k_B is Boltzmann's constant)

$$S_{\text{Boltzmann}} = k_B \log(\Omega) \tag{3.6}$$

In analogy, we now consider an *assembly* of particles. We fix the number N of particles with the state occupation numbers \mathcal{N}_m for $m \in [M] := \{1, \dots, M\}$. These are random variables with an average occupation number $N_m(t) = \langle \mathcal{N}_m(t) \rangle_{\Omega_N}$ at time t , where $\Omega_N = \{0, \dots, N\}$ is the sample space of all possible occupation numbers. An associated entropy per particle yields

$$\mathcal{S}_A(t) = - \sum_{m=1}^M \frac{\mathcal{N}_m(t)}{N} \ln \left(\frac{\mathcal{N}_m(t)}{N} \right). \tag{3.7}$$

As for the Boltzmann entropy, this entropy concept is traced back to observing and counting the occupation of states of a *single system*. Note that since $\mathcal{N}_m(t)$ are *random variables*, so is $\mathcal{S}_A(t)$. Considering the set $\{\mathcal{N}_m(t)\}_{m \in [M]}$ of occupation numbers as a system state, the time evolution can be described via a Markov process, since the particle occupation is only dependent on the previous time step. The average then has to be taken with respect to the joint probability density $\mathbb{P}(\mathcal{N}_1(t) = n_1, \dots, \mathcal{N}_M(t) = n_M)$, which, because of the independence of the particles can be traced back to the one particle evolution, i.e. the solution of Eq. (2.2).

$$\mathbb{P}(\mathcal{N}_1(t) = n_1, \dots, \mathcal{N}_M(t) = n_M; t) = \prod_{m=1}^M p_m^{n_m}(t) \quad (3.8)$$

Thus the average value of Eq. (3.7) is obtained as¹

$$S_A(t) = \langle \mathcal{S}_A(t) \rangle = \sum_{\substack{n_1, \dots, n_M \\ \sum_m n_m = N}} \frac{N!}{\prod_{m \in [M]} n_m!} \left(\prod_{m=1}^M p_m^{n_m}(t) \right) \sum_{m=1}^M \frac{n_m}{N} \ln \left(\frac{n_m}{N} \right), \quad (3.9)$$

where the combinatorial prefactor accounts for our dealing with identical particles, such that two particles in the same state are indistinguishable.

3.3 Gibbs' line of thought

In equilibrium statistical physics, the Gibbs entropy of some dynamics in phase space Γ with a density $\varrho(x, p)$ is expressed as [10]

$$S_G = - \int_{\Gamma} dx dp \varrho(x, p) \ln \left(\frac{\varrho(x, p)}{\varrho^*} \right). \quad (3.10)$$

In this equation, ϱ^* is a constant leading to a dimensionless argument of the logarithm. In our stochastic model system, we do not consider a phase space, but are only concerned with the state space of the stochastic process. By analogy, one can define the *Gibbs entropy* of the system as the state space average of the quantity $-\ln(p_m(t))$, where

¹Here and in the remainder of this thesis, we use a calligraphy font (\mathcal{S}) for random variables and the usual math font for the average of these variables ($S = \langle \mathcal{S} \rangle$).

3 Notions of entropy

$p_m(t)$ as the solution of Eq. (2.2) is the probability measure of the ensemble of systems:

$$S_G(t) = - \sum_{m=1}^M p_m(t) \ln(p_m(t)). \quad (3.11)$$

This equation is *not* an observable of one single system, but based on the ensemble notion and therefore by construction described by probability theory. Analogous to Eq. (3.10) this entropy expression is maximized for an equilibrium probability distribution [10]. In contrast to Eq. (3.10), Eq. (3.11) is a valid definition for an arbitrary probability distribution and is not restricted to (local) equilibrium.

The relation of the assembly entropy defined by Eq. (3.7) and the Gibbs entropy is explained in detail in Sec. ??.

3.4 Coarse-grained thermodynamic entropy

We consider the coarse-grained thermodynamic system introduced in Sec. 2. For each cell, the Gibbs entropy can be obtained by integrating over the phase space element Γ_m with density $\varrho(x, p)$ as introduced in Eq. (3.10):

$$S_m^{(G)} = - \int_{\Gamma_m} dx dp \varrho(x, p) \ln \left(\frac{\varrho(x, p)}{\varrho^*} \right). \quad (3.12)$$

Let ρ_m be the particle density of cell m , i.e. $\rho_m = (1/a) \int_{\Gamma_m} dx dp \varrho(x, p)$. An extensive coarse-grained thermodynamic entropy can be introduced as [11]

$$S_m^{(cg)} = a \rho_m \ln \left(\frac{\rho_m}{\rho^*} \right), \quad (3.13)$$

where a is the spatial extension of the cells and ρ^* is a constant such that the argument of the logarithm is dimensionless. This notion combines the thermodynamic approach of transport processes (cf. Sec. 3.1) and statistical physics (*phase space*). We will address the relation between Eqs. (3.12) and (3.13) in Sec. 9.1 when dealing with the entropy production.

3.5 Stochastic Thermodynamics

In the framework of stochastic thermodynamics, one can introduce a *trajectory ensemble* instead of a particle ensemble. In this context it makes sense to talk about an entropy of a single trajectory. The system entropy is afterwards attained by averaging over the trajectory sample space Ω_T . An entropy definition for a single trajectory $\omega(t = \nu\tau) = (\omega_0, \omega_1, \dots, \omega_\nu)$ up to ν discrete time steps of length τ has been postulated in [12] as

$$s_T(\nu) = -\ln(p_{\omega_\nu}(\nu)), \quad (3.14)$$

where ω_ν is the endpoint of a the trajectory ω evaluated at time $t = \nu\tau$ and $p(\omega_\nu)$ is the solution of the master equation evaluated along the trajectory and gives the probability to find the particle in state ω_ν at discrete time ν . This defines a random variable depending on the realization of a trajectory in the sample space Ω_T . For now, this definition appears arbitrary, but it is justified after taking the trajectory ensemble average (cf. Sec. 7), which is then computed as

$$S_T(\nu) = -\langle s_T(\nu) \rangle_{\Omega_T} = -\sum_{\omega \in \Omega_T} \tilde{p}(\omega) \ln(p_{\omega_\nu}(\nu)), \quad (3.15)$$

where $\tilde{p}(\omega)$ is the probability measure on Ω_T and $\langle \cdot \rangle_{\Omega_T}$ is the average taken with respect to that measure. Note that the trajectory entropy Eq. (3.14) is only described by the probability of a *state*. The assignment to a single trajectory becomes evident by looking at the entropy production, which we will explain in Sec. 7.2.

4 Aspects of non-equilibrium statistical physics

Characteristic for non-equilibrium is a non-vanishing probability current leading to a non-zero total entropy production. During the relaxation process, one wants to talk about thermodynamically relevant quantities, such as heat dissipation, and wants to recover important laws, such as the Second Law of Thermodynamics. This section introduces how thermodynamic ideas are implemented in stochastic systems.

4.1 Splitting of the Gibbs entropy production

When dealing with non-equilibrium systems, we want to investigate the non-zero total entropy production as implied by the Second Law of Thermodynamics. The time derivative $\dot{S}_{\text{sys}}(t)$ of the Gibbs entropy, Eq. (3.11), can be written as the difference of two physically meaningful terms, the total entropy production rate $\dot{S}_{\text{tot}}(t)$ and an external entropy flow into the medium $\dot{S}_{\text{med}}(t)$. With this splitting, each term can be investigated separately. In a NESS, the change of the system entropy, \dot{S}_{sys} , vanishes and the total entropy production is balanced by the medium flow [9].

The derivative of Eq. (3.11) gives the system entropy production in terms of the probability current $K_{ji}(t) = w_{ji} p_j(t) - w_{ij} p_i(t)$,

$$\begin{aligned}
 \dot{S}_{\text{sys}}(t) &= \dot{S}_G(t) \\
 &= - \sum_{i=1}^M \partial_t p_i(t) \ln(p_i(t)) - \underbrace{\sum_{i=1}^M p_i(t) \partial_t \ln(p_i(t))}_0 \\
 &= - \sum_{i,j \in [M]} w_{ji} p_j(t) \ln(p_j(t)) \\
 &= -\frac{1}{2} \sum_{i,j \in [M]} K_{ji}(t) \ln \left(\frac{p_j(t)}{p_i(t)} \right). \tag{4.1}
 \end{aligned}$$

The decomposition can be written as

$$\begin{aligned}
 \dot{S}_{\text{tot}}(t) &= \frac{1}{2} \sum_{i,j \in [M]} K_{ji}(t) \ln \left(\frac{w_{ji} p_j(t)}{w_{ij} p_i(t)} \right) \\
 &= \frac{1}{2} \sum_{i,j \in [M]} K_{ji}(t) \left[\ln \left(\frac{w_{ji}}{w_{ij}} \right) - \ln \left(\frac{p_j(t)}{p_i(t)} \right) \right] \\
 &= \dot{S}_{\text{med}}(t) + \dot{S}_{\text{sys}}(t). \tag{4.2}
 \end{aligned}$$

4.2 Statistical nature of the Second Law of Thermodynamics

We can also see that $\dot{S}_{\text{tot}}(t)$ fulfills the Second Law, since

$$\begin{aligned}
 \dot{S}_{\text{tot}}(t) &= \sum_{i,j \in [M]} w_{ji} p_j(t) \ln \left(\frac{w_{ji} p_j(t)}{w_{ij} p_i(t)} \right) \\
 &\geq \sum_{i,j \in [M]} w_{ji} p_j(t) \left(1 - \frac{w_{ij} p_i(t)}{w_{ji} p_j(t)} \right) \\
 &= \sum_{i,j \in [M]} K_{ji}(t) \\
 &= 0, \tag{4.3}
 \end{aligned}$$

where the sum over the currents vanishes due to probability conservation (closed system). Equality holds if and only if the system is in equilibrium and therefore fulfills detailed balance, $K_{ji} = 0 \forall i, j \in [M]$.

The Second Law arises here as a statistical principle for an ensemble. The next subsection treats the stochasticity for an observable quantity defined on single system instead of an ensemble.

4.2 Statistical nature of the Second Law of Thermodynamics

The statistical nature of the Second Law has been widely discussed for various special cases and as a general concept [13, 14]. To illustrate the idea, we cite the results for the special case of the entropy production along a trajectory as in Eq. (3.14).

Following [12], we define the quantity R as

$$R[\boldsymbol{\omega}; \mathbf{p}(0), \mathbf{p}(t)] := \ln \frac{\mathbb{P}(\omega_\nu | \omega_0) p(\omega_0)}{\mathbb{P}(\omega_\nu^r | \omega_0^r) p(\omega_0^r)} = \Delta s_{\text{med}} + \ln \frac{p(\omega_0)}{p(\omega_t)}, \tag{4.4}$$

where ω_ν is the position of a trajectory $\boldsymbol{\omega}$ after ν time steps, $\mathbf{p} = (p_m)_{m \in [M]}$ is the probability vector and the time reversed trajectory $\boldsymbol{\omega}^r$ is defined as $\omega_\nu^r := \omega_{t-\nu}$. The random variable R depends on the initial and final distributions $\mathbf{p}(0)$ and $\mathbf{p}(t)$ over the discrete state space and the chosen trajectory $\boldsymbol{\omega}$. Δs_{med} is the entropy flow over the time interval $[0, t]$. R can be identified with the total entropy production rate [14], $R = \Delta s_{\text{tot}}$, in accordance with the splitting introduced in the previous section. Therefore, entropy production can be viewed as the measure for microscopic breaking of the symmetry

5 Analytical solution of the model system

along a single trajectory². Let P be the probability distribution of Δs_{tot} . Then in a steady state the following fluctuation theorem holds true [14]:

$$\frac{P(-R)}{P(R)} = \frac{P(-\Delta s_{\text{tot}})}{P(\Delta s_{\text{tot}})} = e^{-\Delta s_{\text{tot}}}, \quad (4.5)$$

and in general, R fulfills the relation

$$\langle e^{-R} \rangle = 1. \quad (4.6)$$

This can be verified by directly calculating the average of definition (4.4) over the trajectory ensemble. For $R = \Delta s_{\text{tot}}$ this result is valid arbitrarily far from equilibrium. Hence, applying Jensen's inequality, $\langle \exp x \rangle \geq \exp \langle x \rangle$, we recover the Second Law,

$$-\langle \Delta s_{\text{tot}} \rangle = \langle -\Delta s_{\text{tot}} \rangle = \ln(\langle \exp(-\Delta s_{\text{tot}}) \rangle) \leq \ln(\langle \exp(-\Delta s_{\text{tot}}) \rangle) = \ln(1) = 0,$$

as a statement on the ensemble average of Δs_{tot} . This result emphasises the statistical nature of the Second Law: there might be entropy annihilating trajectories, but on average the Second Law is valid.

5 Analytical solution of the model system

In this section we find an analytical solution of the discrete time *master equation*, Eq. (2.4), that corresponds to the model introduced in Sec. 2. The solution allows for an insight into the effect the perturbation parameter ε has on the system dynamics.

5.1 Algebraic solution of the Master equation

We start our analysis by giving the solution to the general nearest neighbor jump process with all states having equivalent jump probabilities and periodic boundary conditions, which is governed by the equation

$$p_m(\nu + 1) = r p_{m-1}(\nu) + l p_{m+1}(\nu) + s p_m(\nu). \quad (5.1)$$

²A more detailed discussion of this idea is given in Sec. 7.2, when we come back to this point.

5.2 Solution of the perturbed non-steady state model

For the solution, the elements $w_{ij}^{(\nu)}$ of the ν -step transition matrix \mathbf{W} are needed, since then for a given initial distribution $\{p_m(0)\}_{m \in [M]}$ we get

$$p_m(\nu) = \sum_{i=1}^M w_{im}^{(\nu)} \cdot p_i(0). \quad (5.2)$$

For general transition matrices, Feller [15] outlines a solution relying on their eigen-system³. For circulant matrices, the eigenvalue problem has a particularly handy solution [16].

Let $\Theta := e^{2\pi i/M}$ be the M th root of unity. Then the eigenvalues of \mathbf{W} are given by

$$\lambda_k = s + r\Theta^k + l\Theta^{-k} \quad (5.3)$$

and the normalized eigenvectors are

$$\mathbf{v}_k = \frac{1}{\sqrt{M}}(1, \Theta^k, \Theta^{2k}, \dots, \Theta^{(M-1)k}). \quad (5.4)$$

The matrix elements of \mathbf{W} can then be expressed in the closed form

$$w_{ij}^{(\nu)} = \frac{1}{M} \sum_{k=1}^M \Theta^{(i-j)k} (r\Theta^k + l\Theta^{-k} + s)^\nu. \quad (5.5)$$

5.2 Solution of the perturbed non-steady state model

We now solve the perturbed model, as described in Sec. 2, with the transition matrix

$$\mathbf{W} = \begin{pmatrix} s & (g + \varepsilon) & 0 & \dots & 0 & 0 & (g - \varepsilon) \\ g & s & g & 0 & \dots & 0 & 0 \\ 0 & g & s & g & 0 & \dots & 0 \\ & & & \vdots & & & \\ g & 0 & 0 & \dots & 0 & g & s \end{pmatrix} \quad (5.6)$$

Feller's method is not applicable to this matrix to obtain a closed formula, since \mathbf{W} does not have a simple eigenvalue problem. We therefore developed a different strategy to get an expression for w_{ij} .

³Feller assumes pairwise distinct and non-zero eigenvalues, which is valid for our following considerations.

5 Analytical solution of the model system

The matrix \mathbf{W} can be decomposed as $\mathbf{W} = \mathbf{T} + \mathbf{N}$ into the matrices:

$$\mathbf{T} = \begin{pmatrix} s & g & 0 & \dots & 0 & 0 & g \\ g & s & g & 0 & \dots & 0 & 0 \\ 0 & g & s & g & 0 & \dots & 0 \\ & & & \vdots & & & \\ g & 0 & 0 & \dots & 0 & g & s \end{pmatrix} \quad \mathbf{N} = \begin{pmatrix} 0 & \varepsilon & 0 & \dots & 0 & 0 & -\varepsilon \\ 0 & 0 & 0 & 0 & \dots & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \dots & 0 \\ & & & \vdots & & & \\ 0 & 0 & 0 & \dots & 0 & 0 & 0 \end{pmatrix} \quad (5.7)$$

The circulant matrix $\mathbf{T} = (t_{ij})_{i,j \in [M]}$ resembles the unperturbed Markov process and \mathbf{N} is nilpotent of order 2, i.e. $\mathbf{N}^2 = 0$. Using induction, we start by proving that the ν -step transition matrix \mathbf{W}^ν can be written as

$$(\mathbf{T} + \mathbf{N})^\nu = \mathbf{T}^\nu \prod_{\mu=0}^{\nu-1} (\mathbf{1} + \mathbf{T}^{-\nu+\mu} \mathbf{N} \mathbf{T}^{\nu-1-\mu}). \quad (5.8)$$

Let $\nu = 1$. Then we have

$$\mathbf{T} (\mathbf{1} + \mathbf{T}^{-1} \mathbf{N}) = (\mathbf{T} + \mathbf{N}). \quad (5.9)$$

Assuming this holds true for all $1 \leq k \leq \nu$, we perform the induction step $\nu \rightarrow \nu + 1$:

$$\mathbf{T}^{\nu+1} \prod_{\mu=0}^{\nu} (\mathbf{1} + \mathbf{T}^{-\nu-1+\mu} \mathbf{N} \mathbf{T}^{\nu-\mu}) = \mathbf{T}^{\nu+1} \prod_{\mu=0}^{\nu} \mathbf{T}^{-1} (\mathbf{T} \mathbf{T}^{-1} + \mathbf{T}^{-\nu+\mu} \mathbf{N} \mathbf{T}^{\nu-\mu-1}) \mathbf{T} \quad (5.10)$$

$$(\mathbf{T} \mathbf{T}^{-1} \text{ between factors}) \quad = \mathbf{T}^{\nu+1} \mathbf{T}^{-1} \left[\prod_{\mu=0}^{\nu} (\mathbf{1} + \mathbf{T}^{-\nu+\mu} \mathbf{N} \mathbf{T}^{\nu-\mu-1}) \right] \mathbf{T} \quad (5.11)$$

$$= \left[\mathbf{T}^\nu \prod_{\mu=0}^{\nu-1} (\mathbf{1} + \mathbf{T}^{-\nu+\mu} \mathbf{N} \mathbf{T}^{\nu-\mu-1}) \right] (\mathbf{1} + \mathbf{N} \mathbf{T}^{-1}) \mathbf{T} \quad (5.12)$$

$$(\text{induction hypothesis}) \quad = (\mathbf{T} + \mathbf{N})^\nu (\mathbf{1} + \mathbf{N} \mathbf{T}^{-1}) \mathbf{T} \quad (5.13)$$

$$= (\mathbf{T} + \mathbf{N})^{\nu+1} \quad (5.14)$$

We recognize that by factoring out the product in Eq. (5.8), we are left with a non-negative power of the matrix \mathbf{T} between every two matrices of type \mathbf{N} , because for

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$\mu_2 > \mu_1$ we have products of the form

$$\mathbf{T}^{-\nu+\mu_2}\mathbf{T}^{\nu-\mu_1-1} = \mathbf{T}^{\mu_2-\mu_1-1}, \quad (5.15)$$

where $\mu_2 - \mu_1 - 1 \geq 0$.

We now want to prove the following identity, which will simplify Eq. (5.8):

$$\mathbf{N}\mathbf{T}^n\mathbf{N} = 0 \quad \forall n \in \mathbb{N}_0. \quad (5.16)$$

For $n = 0$, the expression gives $\mathbf{N}^2 = 0$. For $n > 0$, we define the matrix $\mathbf{A} := \mathbf{N}\mathbf{T}^n$ and write the matrix product explicitly.

$$A_{ij} = \sum_{k=1}^M n_{ik} t_{kj}^{(n)} \quad (5.17)$$

$$= \sum_{k=1}^M \delta_{i,1} \varepsilon (\delta_{k,2} - \delta_{k,M}) t_{kj}^{(n)} \quad (5.18)$$

$$= \varepsilon \delta_{i,1} (t_{2j}^{(n)} - t_{Mj}^{(n)}) \quad (5.19)$$

$$(\mathbf{A}\mathbf{N})_{ij} = \sum_{k=1}^M a_{ik} n_{kj} \quad (5.20)$$

$$= \sum_{k=1}^M \varepsilon \delta_{i,1} (t_{2k}^{(n)} - t_{Mk}^{(n)}) n_{kj} \quad (5.21)$$

$$= \sum_{k=1}^M \varepsilon \delta_{i,1} (t_{2k}^{(n)} - t_{Mk}^{(n)}) \delta_{k,1} \varepsilon (\delta_{j,2} - \delta_{j,M}) \quad (5.22)$$

$$= \varepsilon^2 \delta_{i,1} (t_{21}^{(n)} - t_{M1}^{(n)}) (\delta_{j,2} - \delta_{j,M}) \quad (5.23)$$

The elements $t_{21}^{(n)}$ and $t_{M1}^{(n)}$ are known from the unperturbed system as [15]

$$t_{ij}^{(n)} = \frac{1}{M} \sum_{k=1}^M \Theta^{k(i-j)} (g \Theta^k + g \Theta^{-k} + s)^n. \quad (5.24)$$

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Hence, the difference between the two expressions becomes

$$t_{21}^{(n)} - t_{M1}^{(n)} = \frac{1}{M} \sum_{k=1}^M \left[s (\Theta^k - \Theta^{-k}) + g (\Theta^{2k} - \Theta^{-2k}) \right] \left(g \Theta^k + g \Theta^{-k} + s \right)^{n-1} \quad (5.25)$$

$$= \frac{1}{M} 2i \sum_{k=1}^M \left[s \sin \left(2\pi \frac{k}{M} \right) + g \sin \left(4\pi \frac{k}{M} \right) \right] \left[s + 2g \cos \left(\frac{2\pi k}{M} \right) \right]^{n-1} \quad (5.26)$$

$$= 0, \quad (5.27)$$

The sum vanishes since it gives an imaginary value, though we know that the difference between the jump probabilities has to be real.

We define $\kappa := \nu - \mu$ and $\mathbf{N}_\kappa := \mathbf{T}^{-\kappa} \mathbf{N} \mathbf{T}^{\kappa-1}$, such that with the above result, Eq. (5.8) can be rewritten as

$$(\mathbf{T} + \mathbf{N})^\nu = \mathbf{T}^\nu [\mathbf{1} + \mathbf{N}_\nu + \mathbf{N}_{\nu-1} + \cdots + \mathbf{N}_1] \quad (5.28)$$

$$= \mathbf{T}^\nu + \sum_{\mu=0}^{\nu-1} \mathbf{T}^\mu \mathbf{N} \mathbf{T}^{\nu-\mu-1} \quad (5.29)$$

To obtain an analytical solution for the elements of this matrix, we are left with the derivation of the matrix elements of $\mathbf{T}^m \mathbf{N} \mathbf{T}^n \forall m, n \in \mathbb{N}$. Writing out the matrix product as before, we have

$$(\mathbf{T}^m \mathbf{N})_{ij} = t_{i1}^{(m)} \varepsilon (\delta_{j,2} - \delta_{j,M}) \quad (5.30)$$

and consequently

$$\begin{aligned} (\mathbf{T}^m \mathbf{N} \mathbf{T}^n)_{ij} &= t_{i1}^{(m)} \varepsilon (t_{2j}^{(n)} - t_{Mj}^{(n)}) \\ &= \frac{\varepsilon}{M^2} \sum_{k,l=1}^M \Theta^{(i-1)k-jl} (\Theta^{2l} - 1) \left(s + 2g \cos \left(2\pi \frac{k}{M} \right) \right)^m \left(s + 2g \cos \left(2\pi \frac{l}{M} \right) \right)^n \end{aligned} \quad (5.31)$$

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The elements of \mathbf{W}^ν can then be computed as

$$w_{ij}^{(\nu)} = t_{ij}^{(\nu)} + \sum_{\mu=0}^{\nu-1} (\mathbf{T}^\mu \mathbf{N} \mathbf{T}^{\nu-\mu-1})_{ij}. \quad (5.32)$$

As discussed in Sec. 2, we use a uniform initial distribution, $p_m(0) = 1/M \forall m \in [M]$. Since in Eq. (5.32) $t_{ij}^{(\nu)}$ is the matrix element of the unperturbed system whose steady state distribution is the uniform, the underlying distribution of the unperturbed system remains unchanged for all times, i.e. $t_m(\nu) = \sum_{i \in [M]} (1/M) t_{im}(\nu) = 1/M \forall \nu \geq 0$. The summation has therefore only to be carried out over the perturbation contribution such that the probability to find the system in state m after ν time steps is given by

$$p_m(\nu) = \frac{1}{M} + \frac{1}{M^3} \sum_{k,l,n=1}^M \varepsilon \Theta^{(n-1)k-ml} (\Theta^{2l} - 1) \cdot \sum_{\mu=0}^{\nu-1} \left(\frac{s + 2g \cos\left(2\pi \frac{k}{M}\right)}{s + 2g \cos\left(2\pi \frac{l}{M}\right)} \right)^\mu \left(s + 2g \cos\left(2\pi \frac{l}{M}\right) \right)^{\nu-1} \quad (5.33)$$

By evaluation of the finite geometric sum over μ , we arrive at

$$p_m(\nu) = \frac{1}{M} + \frac{1}{M^3} \sum_{k,l,n=1}^M \varepsilon \Theta^{(n-1)k-ml} (\Theta^{2l} - 1) \cdot \frac{\left(s + 2g \cos\left(2\pi \frac{l}{M}\right) \right)^\nu - \left(s + 2g \cos\left(2\pi \frac{k}{M}\right) \right)^\nu}{\left(s + 2g \cos\left(2\pi \frac{l}{M}\right) \right) - \left(s + 2g \cos\left(2\pi \frac{k}{M}\right) \right)}. \quad (5.34)$$

Notice that n is only present in one factor, so that we can perform this summation independently.

$$\sum_{n=1}^M \Theta^{(n-1)k} = \Theta^{-k} \frac{1 - \Theta^{kM}}{1 - \Theta^k} = \frac{1 - e^{2\pi i k}}{\Theta^k (1 - \Theta^k)} \quad (5.35)$$

This sum vanishes for all values of k other than M . For $k = M$ the sum equals M . Now we are only left with one sum over l ,

$$p_m(\nu) = \frac{1}{M} + \frac{\varepsilon M}{M^3} \sum_{l=1}^M \Theta^{-ml} (\Theta^{2l} - 1) \frac{\left(s + 2g \cos\left(2\pi \frac{l}{M}\right) \right)^\nu - (s + 2g)^\nu}{\left(s + 2g \cos\left(2\pi \frac{l}{M}\right) \right) - (s + 2g)}. \quad (5.36)$$

At first sight the last term in the sum, $l = M$, is indeterminate, since the second factor

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equals $0/0$. In the first term though there is a factor $(\Theta^{2l} - 1) = 0$ forcing the expression to vanish. Since we know that the probabilities are real numbers, we can take the real part of Eq. (5.36) to express the solution in terms of trigonometric functions as

$$p_m(\nu) = \frac{1}{M} + \frac{\varepsilon}{M^2} \sum_{l=1}^M \left[\cos \left(2\pi \frac{(2-m)l}{M} \right) - \cos \left(2\pi \frac{ml}{M} \right) \right] \frac{\left(s + 2g \cos \left(2\pi \frac{l}{M} \right) \right)^\nu - 1}{\left(s + 2g \cos \left(2\pi \frac{l}{M} \right) \right) - 1}. \quad (5.37)$$

5.3 Steady state distribution

The time evolution Eq. (5.37) of the probability distribution for a ring with $M = 20$ states with $g = 0.4$, $s = 0.2$, $\varepsilon = 0.1$ is visualized in Fig. 1.

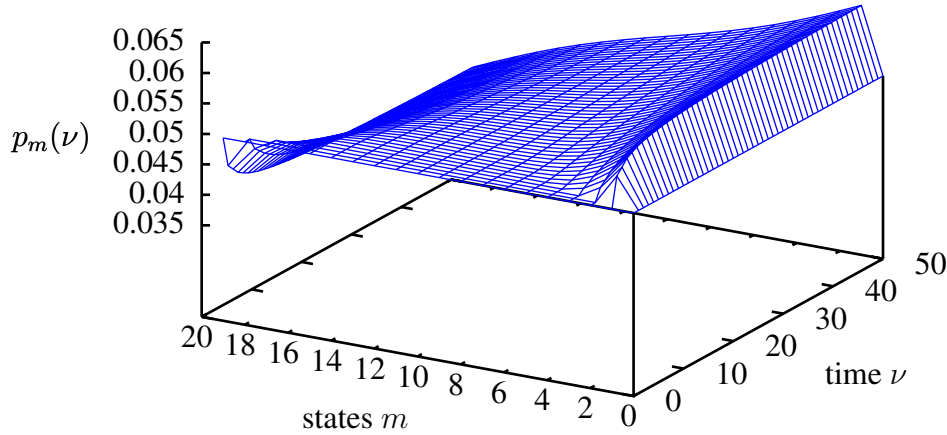


Figure 1: Time evolution of the probability distribution; $M = 20$ and $g = 0.4$, $s = 0.2$, $\varepsilon = 0.1$ for the uniform initial distribution.

The distribution converges to a linear saw tooth profile with a maximum at $m = 2$, a minimum at $m = M$ and an invariant probability $p_1 = 1/M$. For $r = l$, between all states other than $m = 1, 2, M$, there is the same steady state probability current. One therefore expects this linear slope, with a maximum and a minimum. In the

limit $\nu \rightarrow \infty$ the system relaxes to a steady state distribution. Let $\mathbf{p} = (p_m)_{m \in [M]}$ be the distribution vector. Then the steady state distribution can be determined as a left eigenvalue problem $\mathbf{p}^* = \mathbf{p}^* \mathbf{W}$, where $\mathbf{W} = (w_{ij})_{i,j \in [M]}$ is the transition matrix of the Markov chain. With our analytical solution Eq. (5.37), we can carry out the limit $\nu \rightarrow \infty$. Since the sum over l is finite, we can perform the limit $\nu \rightarrow \infty$ prior to summation. To evaluate this limit, we note that

$$\left| \left(s + 2g \cos \left(2\pi \frac{l}{M} \right) \right) \right| \leq 1. \quad (5.38)$$

For $s > 0$, equality holds if and only if $l = M$. Therefore

$$\lim_{\nu \rightarrow \infty} \left(s + 2g \cos \left(2\pi \frac{l}{M} \right) \right)^\nu = \begin{cases} 0, & l \in \{1, \dots, M-1\} \\ 1, & l = M \end{cases} \quad (5.39)$$

Since we have excluded the case $l = M$ in the summation in Eq. (5.37), the long-time limit $\forall m \in [M]$ in terms of trigonometric functions is given by

$$p_m^* = \frac{1}{M} + \frac{\varepsilon}{M^2} \sum_{l=1}^{M-1} \frac{\cos \left(2\pi \frac{(2-m)l}{M} \right) - \cos \left(2\pi \frac{ml}{M} \right)}{2g \left(1 - \cos \left(2\pi \frac{l}{M} \right) \right)} \quad (5.40)$$

This steady state distribution is plotted in Fig. 1.

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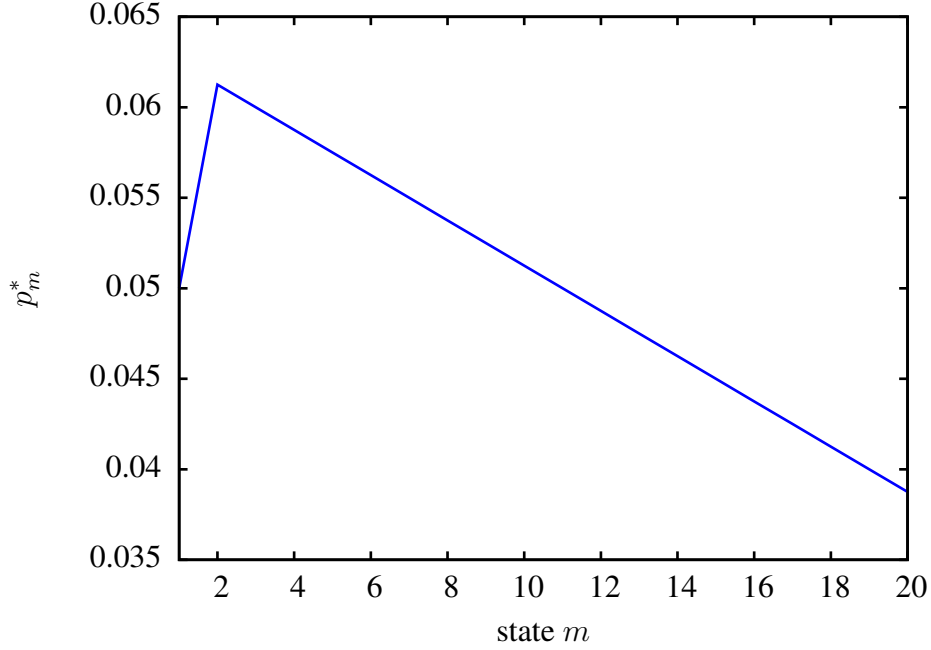


Figure 2: Steady state distribution for the system with $M = 20$ and $l = r = 0.4$, $s = 0.2$, $\varepsilon = 0.1$.

Instead of dealing with the trigonometric functions in Eq. (5.40), we choose a different approach to finding a descriptive functional dependence for the p_m^* . Solving a system of linear equations based on the steady state condition for the master equation describing a stochastic system with periodic boundary conditions, a general solution for the steady state distribution for arbitrary jump rates is outlined in [17].⁴ Defining

$$r_m = \frac{1}{w_{m,m+1}} \left[1 + \sum_{i=1}^{M-1} \prod_{j=1}^i \left(\frac{w_{m+j,m+j-1}}{w_{m+j,m+j+1}} \right) \right], \quad (5.41)$$

the steady state probabilities are given by

$$p_m^* = \frac{r_m}{\sum_{m=1}^M r_m}. \quad (5.42)$$

Most factors in Eq. (5.41) are equal to 1 because of the symmetry of our model system. The sum can therefore be expressed by considering the position of every summand

⁴Publication [17] deals with the case of zero stay probability. The proof though does not require this assumption and remains valid for our case. It is physically reasonable that the steady state distribution does only depend on the ratio of the jump probabilities.

relative to $m = 1$, which leads to

$$r_m = \frac{1}{g + \varepsilon \delta_{m1}} \left[1 + (M - m) + \frac{g - \varepsilon}{g + \varepsilon} (m - 1) \right], \quad (5.43)$$

$$\sum_{m=1}^M r_m = \frac{M^2}{g + \varepsilon}. \quad (5.44)$$

After some algebraic manipulations, we hence recover the curve depicted in Fig. 2.

$$p_m^* = \begin{cases} \frac{(g+\varepsilon)}{Mg} + (1-m)\frac{2\varepsilon}{M^2g} & , m \in \{2, \dots, M\} \\ \frac{1}{M} & , m = 1 \end{cases} \quad (5.45)$$

We can also classify the perturbation in terms of the steady state probability distribution and define $\Delta p^* := p_2 - p_M$ as the difference between the maximum and the minimum probability and $\bar{p}^* = 1/M$ as the average probability, such that the relative steady state dispersion,

$$\frac{\Delta p^*}{\bar{p}^*} = \frac{2(M-2)\varepsilon}{Mg}, \quad (5.46)$$

is a characteristic *system property* describing the perturbation.

5.4 Transport coefficients

With Eq. (5.37), we have found a mathematical solution to the master equation of our model system. In the Gibbs picture of the one-particle ensemble, let $X_{\mathbb{Z}}(\nu)$ be the stochastic process describing the position of the particle at discrete time ν with the integers \mathbb{Z} as the state space. We denote the probability to find a particle in state $k \in \mathbb{Z}$ at time ν by $p_k^{\mathbb{Z}}(\nu)$ and let $X(\nu)$ be the stochastic process of our model with the probabilities $p_m(\nu) = \sum_{j \in \mathbb{Z}} p_{(m+jM)}^{\mathbb{Z}}(\nu)$ as the solution of the master equation we have derived in Sec. 5.2. In order to assign a physical meaning to the stochastic transport process, we have to define the transport coefficients,

$$v = \lim_{\nu \rightarrow \infty} \langle \Delta X_{\mathbb{Z}}(\nu) \rangle \quad (5.47)$$

$$D = \lim_{\nu \rightarrow \infty} \frac{1}{2} \left(\langle (\Delta X_{\mathbb{Z}})^2(\nu) \rangle - \langle \Delta X_{\mathbb{Z}}(\nu) \rangle^2 \right). \quad (5.48)$$

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where the discrete time difference is $\Delta X_{\mathbb{Z}}(\nu) = X_{\mathbb{Z}}(\nu + 1) - X_{\mathbb{Z}}(\nu)$. The drift velocity v and the diffusion coefficient D characterize the asymptotic evolution of a sharp initial distribution. The drift velocity is the derivative of the average position and the diffusion coefficient is given by the change in time of the variance of the stochastic process $X_{\mathbb{Z}}(\nu)$, thereby describing the dispersion of the particle location.

We eventually want to characterize our model with periodic boundary conditions and uniform initial distribution. The above definition then describes how the center of mass of the initial distribution moves over \mathbb{Z} and how the distribution disperses. The coefficients cannot be directly defined on X itself, since the average values describing the motion of the probability distribution are not meaningful quantities due to periodic boundary conditions. Still, the coefficients derived via $X_{\mathbb{Z}}$ characterise X .

The drift velocity can be derived as

$$\begin{aligned}
 \langle \Delta X_{\mathbb{Z}}(\nu) \rangle &= \sum_{k \in \mathbb{Z}} k (p_k^{\mathbb{Z}}(\nu + 1) - p_k^{\mathbb{Z}}(\nu)) \\
 &= \sum_{k \in \mathbb{Z}} k [p_{k+1}^{\mathbb{Z}}(\nu) w_{k+1,k} + p_{k-1}^{\mathbb{Z}}(\nu) w_{k-1,k} - (w_{k,k+1} + w_{k,k-1}) p_k^{\mathbb{Z}}(\nu)] \\
 &= \sum_{k \in \mathbb{Z}} (k-1) w_{k,k-1} p_k^{\mathbb{Z}}(\nu) + (k+1) w_{k,k+1} p_k^{\mathbb{Z}}(\nu) - k (w_{k,k+1} + w_{k,k-1}) p_k^{\mathbb{Z}}(\nu) \\
 &= \sum_{m \in [M]} (w_{m,m+1} - w_{m,m-1}) \sum_{j \in \mathbb{Z}} p_{(m+j)M}^{\mathbb{Z}}(\nu) \tag{5.49}
 \end{aligned}$$

$$= \sum_{m \in [M]} (w_{m,m+1} - w_{m,m-1}) p_m(\nu) \tag{5.50}$$

Since $w_{m,m+1} - w_{m,m-1} = 0 \quad \forall m \neq 1$, and since $p_1 = 1/M \quad \forall \nu \geq 0$, this result is independent of time, and we get for the drift velocity:

$$v = \frac{2\varepsilon}{M} \tag{5.51}$$

Using $\langle (\Delta X_{\mathbb{Z}})^2(\nu) \rangle = \sum_{k \in \mathbb{Z}} k^2 (p_k^{\mathbb{Z}}(\nu + 1) - p_k^{\mathbb{Z}}(\nu))$, the same approach can be taken for the diffusion coefficient, though step (5.49) cannot be done. A derivation of a closed formula for the diffusion coefficient for general jump rates can be found in [17]. We cite an algebraically manipulated version of this expression, which will prove itself to

be more convenient in our calculation.

$$\begin{aligned}
 D = & \frac{1}{(\sum_{m \in [M]} r_m)^2} \left(v \sum_{m \in [M]} u_m \left(\sum_{k=m+1}^M (k-m)r_k + \sum_{j=1}^m (M-m+j)r_j \right) \right. \\
 & \left. + v M \sum_{m=1}^M w_{m,m+1} u_m r_m \right) \\
 & - \frac{v(M+2)}{2} - \frac{v^2}{2}
 \end{aligned} \tag{5.52}$$

In this expression, r_m are the coefficients (5.41) already discussed in the previous section, and the u_m are given by

$$u_m = \frac{1}{w_{m,m+1}} \left[1 + \sum_{i=1}^{M-1} \prod_{j=1}^i \left(\frac{w_{m-j+1,m-j}}{w_{m-j,m-j+1}} \right) \right]. \tag{5.53}$$

For our system they can be calculated yielding

$$u_m = \frac{1}{g} \left[\frac{g M - (1 - 2m + M)\varepsilon}{g + \varepsilon} \right]. \tag{5.54}$$

With these expression we derive the diffusion coefficient:

$$D = g - \frac{(M^2 + 6g - 1)}{3gM^2} \varepsilon^2. \tag{5.55}$$

6 Gibbs entropy

In this section we discuss in detail the Gibbs entropy, Eq. (3.11), in discrete time $t = \nu \tau$. It is not obvious how to discretize the continuous time derivative, which is why evaluate the different discretization concepts.

6.1 Discretization and entropy production splitting

We analyze the discretization of the continuous time Gibbs entropy,

$$S_G(t) = - \sum_{m=1}^M p_m(t) \ln(p_m(t)). \quad (6.1)$$

For our discussion, we want to postulate two axioms for the discretization of the derivative of this equation.

1. For a time $t = \nu \tau$, in the limit of a vanishing time step τ , the continuous time case has to be recovered.
2. The Second Law of Thermodynamics as a fundamental physical law has to be valid.

As outlined in Sec. 4.1, the change in entropy can be physically split into two parts. For the Second Law to hold, in any splitting the positive definite contribution

$$\Delta S_{\text{tot}}(t) = \sum_{i,j \in [M]} w_{ji} p_j(t) \ln \left(\frac{w_{ji} p_j(t)}{w_{ij} p_i(t)} \right) \quad (6.2)$$

has to denote the total irreversible entropy production.

6.1.1 Different discretizations of the time derivative

There are several possible discretizations of the derivative of Eq. (6.1), which we will evaluate with respect to these two axioms.

System entropy production in variation

The difference in Gibbs entropy over a time step of length τ can be written as a variation (var) of the system entropy:⁵

$$\begin{aligned}\Delta S_{\text{var}}(t) &= \frac{S_G(t + \tau) - S_G(t)}{\tau} \\ &= \frac{1}{\tau} \left[- \sum_{m \in [M]} p_m(t + \tau) \ln(p_m(t + \tau)) + \sum_{m \in [M]} p_m(t) \ln(p_m(t)) \right] \quad (6.3)\end{aligned}$$

System entropy production in measure difference

By considering $p_m(t)$ as a measure of the observable $-\ln(p_m(t))$ on the state space $[M]$, the entropy difference can be expressed in a measure difference (MD). Regarding the time domain, two definitions are possible,

$$\Delta S_{\text{MD}}(t) = - \sum_{m \in [M]} \frac{[p_m(t + \tau) - p_m(t)]}{\tau} \ln(p_m(t)) \quad (6.4)$$

$$\Delta S_{\text{MD}\tau}(t) = - \sum_{m \in [M]} \frac{[p_m(t + \tau) - p_m(t)]}{\tau} \ln(p_m(t + \tau)) \quad (6.5)$$

In the latter equation, the index τ indicates that the observable $-\ln(p_m(t + \tau))$ is evaluated at the later time $t + \tau$.

System entropy production in observable difference

The change in Gibbs entropy can be expressed as a difference in the observable (OD) over which the average is taken.

$$\Delta S_{\text{OD}}(t) = - \frac{1}{\tau} \sum_{m \in [M]} p_m(t) \ln \left(\frac{p_m(t + \tau)}{p_m(t)} \right) \quad (6.6)$$

$$\Delta S_{\text{OD}\tau}(t) = - \frac{1}{\tau} \sum_{m \in [M]} p_m(t + \tau) \ln \left(\frac{p_m(t + \tau)}{p_m(t)} \right) \quad (6.7)$$

Here again, the index τ signifies that the measure is taken at the later time.

⁵Note that $\Delta S_{\text{var}}(t)$ is an entropy difference per unit time τ . Here and in the remainder of this chapter Δ signifies an entropy change per time unit.

6.1.2 Evaluation of axiom 1: convergence to the continuous time derivative

Axiom 1 holds true for Eqs. (6.3), (6.4) and (6.5). Eq. (6.3) is the definition of the discrete time derivative and therefore naturally converges to the continuous time derivative of the Gibbs entropy.

We evaluate the time derivative of the continuous time Gibbs entropy using the chain rule,

$$\frac{dS_G}{dt} = - \sum_{m \in [M]} \frac{\partial p_m(t)}{\partial t} \ln(p_m(t)) - \sum_{m \in [M]} p_m(t) \frac{\partial \ln(p_m(t))}{\partial t}. \quad (6.8)$$

The latter sum in Eq. (6.8) vanishes because of probability conservation,

$$- \sum_{m \in [M]} p_m(t) \frac{\partial \ln(p_m(t))}{\partial t} = - \sum_{m \in [M]} \frac{\partial p_m(t)}{\partial t} = 0. \quad (6.9)$$

We now examine the continuous time limit of Eqs. (6.4) and (6.5). By definition of the discrete time derivative of $p_m(t)$ in the limit $\tau \rightarrow 0$, Eqs. (6.4) and (6.5) both converge to the derivative of the continuous time Gibbs entropy:

$$\lim_{\tau \rightarrow 0} \Delta S_{MD}(t) = \lim_{\tau \rightarrow 0} \Delta S_{MD_\tau}(t) = - \sum_{m \in [M]} \frac{\partial p_m(t)}{\partial t} \ln(p_m(t)) = \frac{dS_G}{dt}. \quad (6.10)$$

In order to compare the differences between the entropy change in variation, Eq. (6.3) and the entropy change in measure difference, Eqs. (6.4) and (6.5),

$$\Delta S_{\text{var}}(t) - \Delta S_{MD}(t) = -\frac{1}{\tau} \sum_{i \in [M]} p_i(t + \tau) \ln \left(\frac{p_i(t + \tau)}{p_i(t)} \right) \quad (6.11)$$

$$\Delta S_{\text{var}}(t) - \Delta S_{MD}(t) = -\frac{1}{\tau} \sum_{i \in [M]} p_i(t) \ln \left(\frac{p_i(t + \tau)}{p_i(t)} \right). \quad (6.12)$$

We expand the logarithms to first order which yields for Eq. (6.11)

$$\begin{aligned} \Delta S_{\text{var}}(t) - \Delta S_{MD}(t) &= \frac{1}{\tau} \sum_{i \in [M]} p_i(t + \tau) \left[\left(\frac{p_i(t)}{p_i(t + \tau)} - 1 \right) - \mathcal{O} \left(\frac{p_i(t)}{p_i(t + \tau)} - 1 \right)^2 \right] \\ &\approx \frac{1}{\tau} \sum_{i \in [M]} [p_i(t) - p_i(t + \tau)] = 0. \end{aligned} \quad (6.13)$$

The expansion of Eq. (6.12) to first order gives the same behavior with a different sign. Consequently, the differences vanish because of probability conservation in first order approximation.

Eqs. (6.6) and (6.7) do have the functional form of Eqs. (6.12) and (6.11), respectively. Therefore, in the continuum limit $\tau \rightarrow 0$, both notions tend to zero and do *not* converge to the continuous time derivative of the Gibbs entropy and thus violate axiom 1.

As a consequence, the discretization in observable difference, Eqs. (6.6) and (6.7) are not viable choices for the discretization.

6.1.3 Evaluation of axiom 2: Second Law of Thermodynamics

Eqs. (6.3), (6.4) and (6.5) are in accordance with axiom 1 and we now examine their behavior with respect to axiom 2 that concerns the splitting of these system entropy production terms.

Given these equations and $\Delta S_{\text{tot}}(t)$, the entropy exchange with the medium, ΔS_{med} , is already determined by the difference of $\Delta S_{\text{tot}}(t)$ and the respective equation among Eqs. (6.3), (6.4) and (6.5). Performing these subtractions, we arrive at the expressions for the entropy flow into the medium:

$$\Delta S_{\text{var,med}}(\nu) = \sum_{i,j \in [M]} p_j(\nu) w_{ji} \ln \left(\frac{p_i(\nu+1) w_{ji}}{p_i(\nu) w_{ij}} \right) \quad (6.14a)$$

$$\Delta S_{\text{MD,med}}(\nu) = \sum_{i,j \in [M]} p_j(\nu) w_{ji} \ln \left(\frac{w_{ji}}{w_{ij}} \right) \quad (6.14b)$$

$$\Delta S_{\text{MD}_\tau, \text{med}}(\nu) = \sum_{i,j \in [M]} p_j(\nu) w_{ji} \ln \left(\frac{p_i(\nu+1) p_j(\nu) w_{ji}}{p_i(\nu) p_j(\nu+1) w_{ij}} \right) \quad (6.14c)$$

In a steady state, Eqs. (6.14a)-(6.14c) coincide, but in a non-steady state, they take different values depending on the probability distribution.

As noted in Sec. 2, many physical systems can be described by discrete-time Markov chains. Within the theory of Markov chains, the interaction with the environment (*field*) is modelled by the structure of the transition matrix. Asymmetries in this matrix give rise to an external force and therefore *drive* the system (*battery*).

In the following, we want to determine which discretization of the Gibbs entropy is

most suitable to have a thermodynamic interpretation of Markov chains. We consider the specific case of an *isolated system*. In this systems there is neither particle nor heat exchange.

For discrete-time stochastic system to have a thermodynamic interpretation, there has to be a class of system parameters that corresponds to an isolated system. In this case, the entropy flow into the medium, $\Delta S_{\text{MD,med}}$, has to vanish for all times and irrespectively of the probability distribution.

Among Eqs. (6.14a)-(6.14c), the only expression which can possibly fullfill the independence of the probability distribution and of time is Eq. (6.14b). Eqs. (6.14a) and (6.14c) on the contrary *cannot* be made independent of the probability distribution for any choice of the matrix \mathbf{W} , except for the matrix with all elements equal to zero.

Therefore, to have a discretization that provides a physically meaningful interpretation of the Markov chain, Eqs. (6.14a) and (6.14c) have to be discarded as valid discretizations and the consistent discretization is acquired based on the *measure difference*,

$$\begin{aligned}\Delta S_{\text{MD}}(\nu) &= - \sum_{m \in [M]} [p_m(\nu + 1) - p_m(\nu)] \ln(p_m(\nu)) \\ &= - \sum_{m \in [M]} \sum_{n \in [M]} p_n(\nu) w_{nm} \ln(p_m(\nu)),\end{aligned}\quad (6.15)$$

with the entropy production splitting being

$$\Delta S_{\text{tot}}(\nu) = \sum_{i,j \in [M]} w_{ji} p_j(\nu) \ln \left(\frac{w_{ji} p_j(\nu)}{w_{ij} p_i(\nu)} \right) \quad (6.16)$$

$$\Delta S_{\text{MD,med}}(\nu) = \sum_{i,j \in [M]} p_j(\nu) w_{ji} \ln \left(\frac{w_{ji}}{w_{ij}} \right). \quad (6.17)$$

The equations in this splitting are equal to the continuous time expressions, such that results obtained for continuous time can be easily transferred to the discrete time setup. Furthermore, our analysis shows that if $w_{ij} = w_{ji} \quad \forall i, j \in [M]$, then $\Delta S_{\text{MD,med}} = \forall \nu$, and therefore Markov chains with a symmetric transition matrix correspond to isolated systems.

6.2 The perturbed Markov chain as an example for the entropy flow

Because of our argument for the discretization choice being based on the expression for the entropy flow into the medium, $\Delta S_{\text{MD,med}}$, we now want to further investigate this term using our model system in discrete time $\tau = 1$.

A comparison of the discretization in variation and in measure difference for the entropy exchange with the medium during the relaxation to the steady state is shown in Fig. 3.

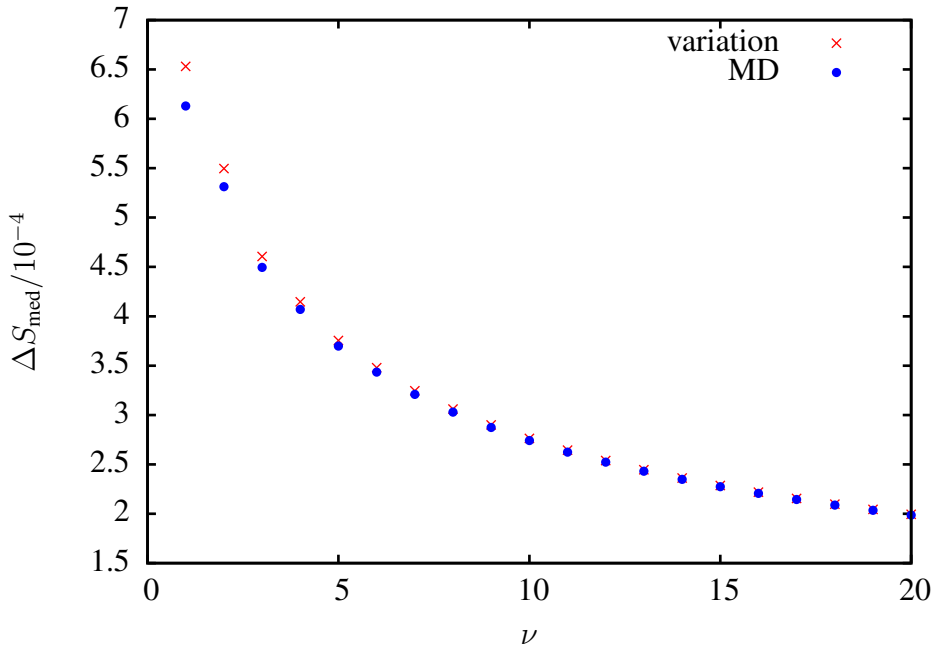


Figure 3: Comparison of the entropy flow discretization in variation, Eq. (6.14a), and in measure difference, Eq. (6.14b), during the relaxation from the uniform initial distribution to the steady state for $M = 50$, $s = 0.2$, $g = 0.4$, $\varepsilon = 0.1$.

For all times, the change in entropy Eq. (6.14a) is an upper bound to the change in entropy measured by the measure difference, Eq. (6.14b). As expected, the two discretizations converge to the same entropy change in the steady state, which can be seen by subtracting Eq. (6.14b) from Eq. (6.14a) to arrive at

$$\Delta S_{\text{var,med}} - \Delta S_{\text{MD,med}} = \sum_{i,j \in [M]} p_j(\nu) w_{ji} \ln \left(\frac{p_i(\nu+1)}{p_i(\nu)} \right). \quad (6.18)$$

The difference between the two expressions is further illustrated in Fig. 4, where the relative deviation is shown as a function of ν and ε . For all values of ε , this relative error is smaller than 0.1.

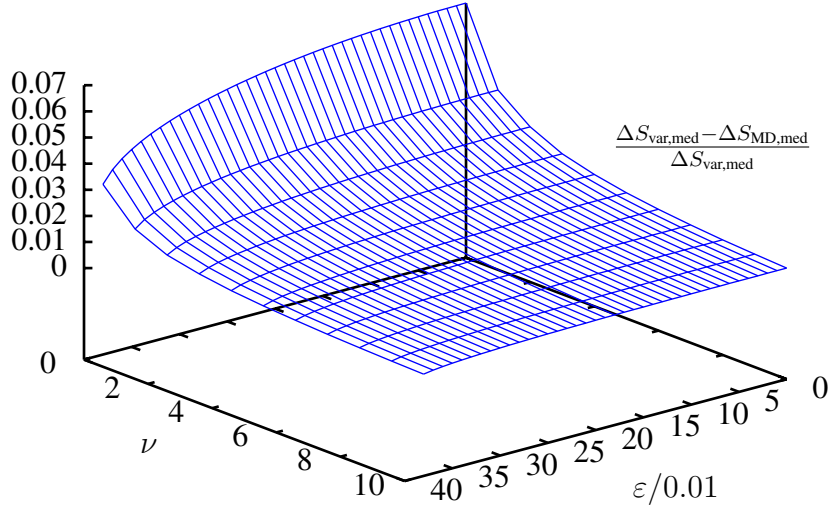


Figure 4: Relative difference between Gibbs entropy exchange with the medium in variation (var) and measure difference (MD) for the first 10 time steps over a perturbation range $\varepsilon \in [0.01, 0.39]$; $M = 50, \varepsilon = 0.1, g = 0.4, s = 0.2$.

The entropy flow into the medium, Eq. (6.17) can also be tracked analytically. Since most elements of the transition matrix (5.6) are symmetric, there are only three contributions left in the double sum. We are looking for a small drive $\varepsilon/g \ll 1$ and thus expand the expression to quadratic order in ε/g . For brevity of notation, we drop the time index ν in the following.

For $i = 1$, we have a contribution

$$\begin{aligned} c_1 &= p_M g \ln \left(\frac{g}{g - \varepsilon} \right) + p_2 g \ln \left(\frac{g}{g + \varepsilon} \right) \\ &= -p_M g \ln \left(1 - \frac{\varepsilon}{g} \right) - p_2 g \ln \left(1 + \frac{\varepsilon}{g} \right). \end{aligned} \quad (6.19)$$

6.2 The perturbed Markov chain as an example for the entropy flow

To second order in ε/g , we have⁶

$$c_1 \approx g p_M \left[\left(\frac{\varepsilon}{g} \right) + \frac{1}{2} \left(\frac{\varepsilon}{g} \right)^2 \right] - g p_2 \left[\left(\frac{\varepsilon}{g} \right) - \frac{1}{2} \left(\frac{\varepsilon}{g} \right)^2 \right] \quad (6.20)$$

For $i = 2$ the contribution to second order gives

$$\begin{aligned} c_2 &= p_1 (g + \varepsilon) \ln \left(1 + \frac{\varepsilon}{g} \right) \\ &\approx p_1 (g + \varepsilon) \left(\left(\frac{\varepsilon}{g} \right) - \frac{1}{2} \left(\frac{\varepsilon}{g} \right)^2 \right) \end{aligned} \quad (6.21)$$

and for the state $i = M$ we have

$$\begin{aligned} c_M &= p_1 (g - \varepsilon) \ln \left(1 - \frac{\varepsilon}{g} \right) \\ &\approx p_1 (g - \varepsilon) \left(- \left(\frac{\varepsilon}{g} \right) - \frac{1}{2} \left(\frac{\varepsilon}{g} \right)^2 \right). \end{aligned} \quad (6.22)$$

Adding up all contributions, we arrive at the total entropy flow for the system to quadratic (superscript (2)) approximation in ε :

$$\Delta S_{\text{MD,med}}^{(2)} = c_1 + c_2 + c_M = (p_M - p_2) \varepsilon + \frac{\varepsilon^2}{g} \left(\frac{1}{2} p_M + \frac{1}{2} p_2 + p_1 \right) \quad (6.23)$$

We now want to evaluate this expression taking into account the explicit structure for the probabilities, Eq. (5.36). Summing up the probabilities for $m = 2$ and $m = M$, we get

$$p_M + p_2 = \frac{2}{M} + \frac{\varepsilon}{M^2} \sum_{l=1}^{M-1} \frac{\left(s + 2g \cos \left(2\pi \frac{l}{M} \right) \right)^\nu - 1}{\left(s + 2g \cos \left(2\pi \frac{l}{M} \right) \right) - 1} (\Theta^{-2l} + \Theta^{-Ml})(\Theta^{2l} - 1). \quad (6.24)$$

The last factor can be rewritten to read $(\Theta^{-2l} + \Theta^{-Ml})(\Theta^{2l} - 1) = 2i \sin(2\pi (2l)/M)$. Knowing that this expression has to yield a real value we conclude that the sum over l has to vanish, such that $p_M + p_2 = 2/M$. To express the difference $p_M - p_2$, we note that $(\Theta^{-Ml} - \Theta^{-2l})(\Theta^{2l} - 1) = 2(\cos(2\pi (2l)/M) - 1)$. Using $s = 1 - 2g$ and

⁶The power series expansion of the natural logarithm is $\ln(1+x) = \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} x^n$.

6 Gibbs entropy

trigonometric identities, we get

$$\begin{aligned} p_M - p_2 &= \frac{\varepsilon}{M^2} \sum_{l=1}^{M-1} \left[\left(s + 2g \cos \left(2\pi \frac{l}{M} \right) \right)^\nu - 1 \right] \frac{(\cos(2\pi(2l)/M) - 1)}{g(\cos(2\pi l/M) - 1)} \\ &= \frac{2\varepsilon}{gM^2} \sum_{l=1}^{M-1} \left[\left(s + 2g \cos \left(2\pi \frac{l}{M} \right) \right)^\nu - 1 \right] \left(\cos \left(2\pi \frac{l}{M} \right) + 1 \right). \end{aligned} \quad (6.25)$$

With the value $p_1 = 1/M$, the approximation can hence be written as

$$\begin{aligned} \Delta S_{\text{MD,med}}^{(2)} &= \frac{2\varepsilon^2}{gM^3} \sum_{l=1}^{M-1} \left[\left(s + 2g \cos \left(2\pi \frac{l}{M} \right) \right)^\nu \left(\cos \left(2\pi \frac{l}{M} \right) + 1 \right) \right] \\ &\quad + \frac{4\varepsilon^2}{gM^2} \end{aligned} \quad (6.26)$$

In the long-time limit (cf. Sec. 5.3), this equation reduces to

$$\Delta S_{\text{MD,med}}^{(2),*} = \frac{4\varepsilon^2}{gM^2}. \quad (6.27)$$

Since we have derived a second order approximation for a steady state, one can expect to arrive at this result using transport theory with a time step length τ and a length scale $a = 1/M$. In terms of the relative steady state dispersion, Eq. (5.46), the entropy flow Eq. (6.27) can be rewritten as

$$\begin{aligned} \frac{\Delta S_{\text{MD,med}}^{(2),*}}{\tau} &= \frac{g}{\tau} \left(\frac{\Delta p^*/M}{\bar{p}^*} \right)^2 \\ &= \frac{a^2 g}{\tau} \left(\frac{\partial_x p^*}{\bar{p}^*} \right)^2. \end{aligned} \quad (6.28)$$

Comparison with Eq. (5.52) discloses, that $(a^2 g)/\tau$ is for small ε the diffusion coefficient. We thus have derived an entropy flow proportional to the *square* of the probability current, as predicted by transport theory.

In order to get an idea of the quality of the approximation Eq. (6.26), we look at the relative error

$$\frac{\Delta S_{\text{MD,med}}^{(2)} - \Delta S_{\text{MD,med}}}{\Delta S_{\text{MD,med}}}. \quad (6.29)$$

6.2 The perturbed Markov chain as an example for the entropy flow

We can see numerically that for a given perturbation ε , this error is *independent* of time. This allows us to calculate the error only as a function of the perturbation parameter. Even for a relatively strong perturbation of $\varepsilon = 0.1$, i.e. $\Delta p^* = \bar{p}^*/4$, Eq. (6.23) can be used as an adequate approximation with a relative deviation of less than 5%.

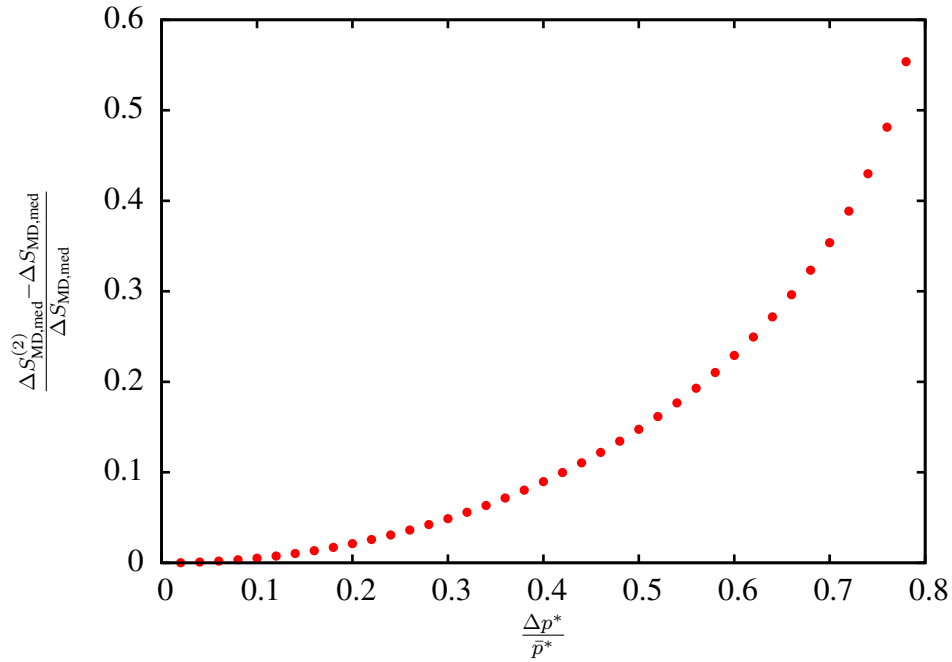


Figure 5: Relative error of the approximation to second order in ε in terms of relative steady state dispersion as calculated by Eq. (5.46)

7 Trajectory entropy

The trajectory entropy in the framework of stochastic thermodynamics is based on an ensemble of trajectories as opposed the one particle ensemble for the Gibbs entropy concept. In this section, we draw a connection between the ensemble averages taken over those distinct ensembles.

7.1 Relation between trajectory and Gibbs entropy

The following derivation shows for the discrete-time and discrete-state case of our model system that the average of the one-particle ensemble over the state space, (Eq. (3.11)) is equivalent to the average taken with respect to the trajectory ensemble (Eq. 3.15). In the derivation, ω_{ji} denotes a possible trajectory from j to i , $X(\nu)$ is the stochastic process describing the one-particle evolution and, $\mathbb{P}(\cdot)$ is the associated probability measure:

$$\begin{aligned}
S_T(\nu) &= - \sum_{\omega \in \Omega_T} \tilde{p}(\omega) \ln(p_{\omega_\nu}(\nu)) \\
&= - \sum_{i,j \in [M]} \sum_{\omega_{ji}} \tilde{p}(\omega_{ji}) \ln(p_i(\nu)) \\
&= - \sum_{i,j \in [M]} \mathbb{P}(X(\nu) = i | X(0) = j) \mathbb{P}(X(0) = j) \ln(p_i(\nu)) \\
&= - \sum_{i \in [M]} p_i(\nu) \ln(p_i(\nu)) \\
&= S_G(\nu)
\end{aligned} \tag{7.1}$$

The continuous-time is derived in [12].

7.2 Entropy splitting

In the following we accept the axiom introduced in Sec. 4.2 (cf. [14]): For single trajectories, the total entropy production is given by the symmetry breaking of the time reversal. This statement can be formalized as

$$\Delta s_{\text{tot}} = \ln \left(\frac{p_{\omega_0}(0) w_{\omega_0, \omega_1} w_{\omega_1, \omega_2} \cdots w_{\omega_{\nu-1}, \omega_\nu}}{p_{\omega_\nu}(\nu) w_{\omega_\nu, \omega_{\nu-1}} w_{\omega_{\nu-1}, \omega_{\nu-2}} \cdots w_{\omega_1, \omega_0}} \right). \tag{7.2}$$

The expression can be decomposed into the change of the system entropy, Δs_{sys} , and the entropy flow into the medium, Δs_{med} , via

$$\Delta s_{\text{tot}} = \underbrace{\ln \left(\frac{p_{\omega_0}(0)}{p_{\omega_\nu}(\nu)} \right)}_{\Delta s_{\text{sys}}} + \underbrace{\ln \left(\frac{w_{\omega_0, \omega_1} w_{\omega_1, \omega_2} \cdots w_{\omega_{\nu-1}, \omega_\nu}}{w_{\omega_\nu, \omega_{\nu-1}} w_{\omega_{\nu-1}, \omega_{\nu-2}} \cdots w_{\omega_1, \omega_0}} \right)}_{\Delta s_{\text{med}}}. \quad (7.3)$$

These changes, which are based on a trajectory of length $\nu \tau$, are derived over a time span $[0, \nu \tau]$. In order to compare the trajectory entropy change with the Gibbs entropy change, over a time instant τ , the latter has to be integrated over the times $\{0, \dots, \nu\}$. For the system entropy, we get

$$\begin{aligned} \langle \Delta s_{\text{sys}} \rangle &= \sum_{\omega} \tilde{p}(\omega) \ln \left(\frac{p_{\omega_0}(0)}{p_{\omega_\nu}(\nu)} \right) \\ &= \sum_{m_0 \in [M]} p_{m_0}(0) \sum_{m_1 \in [M]} w_{m_0, m_1} \cdots \sum_{m_\nu \in [M]} w_{m_{\nu-1}, m_\nu} \ln \left(\frac{p_{m_0}(0)}{p_{m_\nu}(\nu)} \right) \\ &= \sum_{m_0 \in [M]} p_{m_0}(0) \ln(p_{m_0}(0)) - \sum_{m_0 \in [M]} p_{m_0}(0) \sum_{m_1 \in [M]} w_{m_0, m_1} \cdots \sum_{m_\nu \in [M]} w_{m_{\nu-1}, m_\nu} \ln(p_{m_\nu}(\nu)) \\ &= \sum_{m \in [M]} p_m(0) \ln(p_m(0)) - \sum_{m \in [M]} p_m(\nu) \ln(p_m(\nu)) \\ &= S_{\text{var, sys}}^{\text{Gibbs}}(\nu) - S_{\text{var, sys}}^{\text{Gibbs}}(0), \end{aligned} \quad (7.4)$$

where we have used for arbitrary indices j, k that

$$\sum_{j, k \in [M]} p_j(\nu) w_{jk} = \sum_{k \in [M]} p_k(\nu + 1) \text{ and } \sum_{k \in [M]} w_{jk} = 1. \quad (7.5)$$

7 Trajectory entropy

By an analogous calculation, we find the averaged entropy flow to be equal to the *integrated* Gibbs entropy flow:

$$\begin{aligned}
\langle \Delta S_{\text{med}} \rangle &= \sum_{\omega} \tilde{p}(\omega) \sum_{\mu=0}^{\nu-1} \ln \left(\frac{w_{\omega_{\mu}, \omega_{\mu+1}}}{w_{\omega_{\mu+1}, \omega_{\mu}}} \right) \\
&= \sum_{m_0 \in [M]} p_{m_0}(0) \sum_{m_1 \in [M]} w_{m_0, m_1} \cdots \sum_{m_{\nu} \in [M]} w_{m_{\nu-1}, m_{\nu}} \sum_{\mu=0}^{\nu-1} \ln \left(\frac{w_{m_{\mu}, m_{\mu+1}}}{w_{m_{\mu+1}, m_{\mu}}} \right) \\
&= \sum_{m_0 \in [M]} p_{m_0}(0) \sum_{m_1 \in [M]} w_{m_0, m_1} \ln \left(\frac{w_{m_0, m_1}}{w_{m_1, m_0}} \right) \\
&+ \sum_{m_1 \in [M]} p_{m_1}(1) \sum_{m_2 \in [M]} w_{m_1, m_2} \ln \left(\frac{w_{m_1, m_2}}{w_{m_2, m_1}} \right) + \dots \\
&= \sum_{\mu=0}^{\nu-1} \sum_{m_{\mu}, m_{\mu+1} \in [M]} p_{m_{\mu}}(\mu) w_{m_{\mu}, m_{\mu+1}} \ln \left(\frac{w_{m_{\mu}, m_{\mu+1}}}{w_{m_{\mu+1}, m_{\mu}}} \right) \\
&= \sum_{\mu=0}^{\nu-1} \sum_{i, j \in [M]} p_i(\mu) w_{ij} \ln \left(\frac{w_{ij}}{w_{ji}} \right) \\
&= \sum_{\mu=0}^{\nu-1} S_{\text{MD, med}}^{\text{Gibbs}}(\mu) \tag{7.6}
\end{aligned}$$

We arrive at expressions for the change in Gibbs entropy that are equal to the continuous time case. Even though we have a *discrete time* trajectory, the system entropy production is the variational difference of the Gibbs entropy, as defined by Eq. (6.3), the medium entropy flow on the other hand is given by the expression for the measure difference discretization, Eq. (6.14b). Thus, the continuous time case expressions are recovered naturally by starting from Eq. (7.2)

Altogether, these findings justify our choice for the entropy production and the concept of an entropy assignment to a single trajectory, since the expressions for the Gibbs notion are reproduced after averaging over the trajectory ensemble. Furthermore, this argument underlines that the trajectory entropy notion does not yield any new information upon averaging. Its true value lies in the fact that enables to determine the entropy based on multiple observations of a single trajectories. On the one hand that this notion compatible with the Gibbs entropy, on the other hand it helps to prove strong results for systems that are arbitrarily far from equilibrium, such as an integral fluctuation theorem for the total entropy production, or a fluctuation theorem over a *finite* time (cf.

Sec. 4.2, [12]).

8 The assembly entropy

As an entropy concept based on a fluctuating random variable

8.1 Change in assembly entropy

For the discretization of the assembly entropy,

$$\mathcal{S}_A(\nu) = - \sum_{m=1}^M \frac{\mathcal{N}_m(\nu)}{N} \ln \left(\frac{\mathcal{N}_m(\nu)}{N} \right), \quad (8.1)$$

we take the average over the difference between the two random variables, $\Delta\mathcal{S}_A(\nu) := \mathcal{S}_A(\nu + 1) - \mathcal{S}_A(\nu)$ and we get

$$\begin{aligned} \langle \Delta\mathcal{S}_A(\nu) \rangle &= - \sum_{\sum_m \{n_m\} = N} \sum_{\sum_m \{n'_m\} = N} \mathbb{P} \left(\{\mathcal{N}_m(\nu + 1)\} = \{n'_m\}, \{\mathcal{N}_m(\nu)\} = \{n_m\} \right) \\ &\quad \cdot \sum_{m=1}^M \left[\frac{N!}{\prod_{m \in [M]} n'_m!} \frac{n'_m}{N} \ln \left(\frac{n'_m}{N} \right) - \frac{N!}{\prod_{m \in [M]} n_m!} \frac{n_m}{N} \ln \left(\frac{n_m}{N} \right) \right] \\ &= - \sum_{m=1}^M \left[\sum_{\substack{\{n'_m\} \\ \sum_m n'_m = N}} \frac{N!}{\prod_{m \in [M]} n'_m!} \mathbb{P} \left(\{\mathcal{N}_m(\nu + 1)\} = \{n'_m\} \right) \frac{n'_m}{N} \ln \left(\frac{n'_m}{N} \right) \right. \\ &\quad \left. - \sum_{\substack{\{n_m\} \\ \sum_m n_m = N}} \frac{N!}{\prod_{m \in [M]} n_m!} \mathbb{P} \left(\{\mathcal{N}_m(\nu)\} = \{n_m\} \right) \frac{n_m}{N} \ln \left(\frac{n_m}{N} \right) \right] \\ &= - \sum_{\substack{\{n_m\} \\ \sum_m n_m = N}} \frac{N!}{\prod_{m \in [M]} n_m!} \left[\mathbb{P} \left(\{\mathcal{N}_m(\nu + 1)\} = \{n_m\} \right) - \mathbb{P} \left(\{\mathcal{N}_m(\nu)\} = \{n_m\} \right) \right] \\ &\quad \cdot \left(\frac{n_m}{N} \ln \left(\frac{n_m}{N} \right) \right) \\ &= \langle \mathcal{S}_A(\nu + 1) \rangle_{\nu+1} - \langle \mathcal{S}_A(\nu) \rangle_{\nu}, \quad (8.2) \end{aligned}$$

8 The assembly entropy

where the index for the average emphasises that it depends only on the probability distribution for one single time step.

In Fig. 6, the average assembly entropy production is plotted.⁷

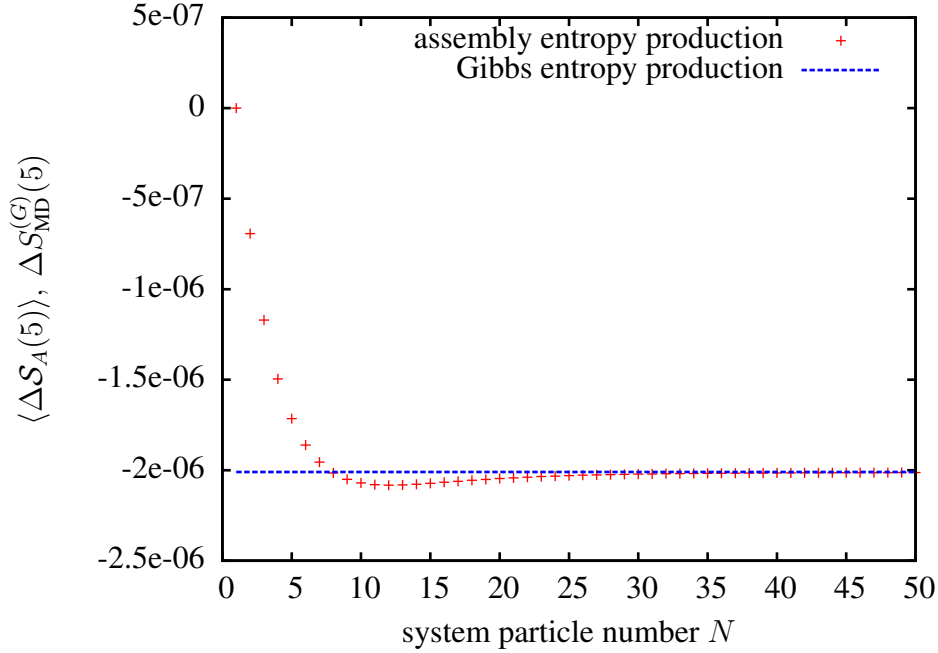


Figure 6: Assembly entropy production as a function of particle number for a system with $M = 4$ states averaged after $\nu = 5$ time steps; this corresponds to non-steady state conditions. The jump probabilities are $g = 0.4$, $s = 0.2$ with a perturbation $\varepsilon = 0.1$.

We can deduce a convergence to the Gibbs entropy in the long time limit, but this convergence is not monotone. As a function of the number of particles in the system, the average change in assembly entropy first drops below the change in the Gibbs ensemble entropy and then approaches it from below. The Gibbs entropy is based on the one-particle ensemble and is therefore independent of the number of particles in the system.

For one particle, the entropy is zero and there is no relaxation in time to expect, since it remains a sharp distribution. Furthermore, one can divide the particle axis in three parts. For $N < 8 = 2M$ particles, the assembly system entropy production is smaller than the Gibbs entropy and relaxes towards the Gibbs entropy production. In this regime, it is not possible to define a proper particle density, since up to this point, there is no

⁷To generate all possible occupation numbers for given total particle number N distributed over M states we have used the lexicographic Algorithm L described on page 358 in [18].

more than one particle per state. In the second phase, the assembly entropy production is smaller than the Gibbs entropy but converges towards it from below. In this regime, a meaningful particle density can be defined though the dynamics do on average not effect a single particle as the following argument shows:

For the relative maximum of the probability distribution, $p_2(5) - 1/M = 1/32$, gives the fraction of particles that are affected by the perturbation. We can see that 32 particles in the system are needed for the stochastic dynamics to have an average effect on the assembly. Observing Fig. 7 we can see that this is the particle number for which the assembly system entropy production has converged to the Gibbs system entropy production.

8.2 Convergence of the assembly entropy to the Gibbs entropy

In this section, we want to discuss the difference between the entropy notions based on a one-particle ensemble, S_G , and an assembly, S_A . Conceptually, they differ in the way how stochasticity is introduced. The Gibbs entropy is a *number* calculated by ensemble probabilities, whereas the assembly entropy is a *random variable* itself. The latter is only accessible via its probability density function. To investigate this concept, we need to specify the occupation numbers \mathcal{N}_m .

Because we are dealing with non-interacting particles, the occupation numbers can be written as a sum of independent, identically distributed (i.i.d.) random variables $Y_n^{(m)}(\nu)$, $n \in \{1, \dots, N\}$ that are 1 if particle n is in state m at time ν and 0 otherwise, i.e. $Y_n^{(m)}(\nu) \sim \text{Bernoulli}(p_m(\nu))$. Therefore the occupation numbers are binomially distributed, $\mathcal{N}_m(\nu) \sim \text{Binomial}(N, p_m(\nu))$. We show that the expectation value of the assembly entropy converges to the Gibbs entropy. This convergence is a direct implication of the first order *delta method* that is based on a Taylor expansion of a function of a random variable around its expectation value [19]. We use the notation $N(\mu, \sigma^2)$ for the normal distribution with mean μ and variance σ^2 in the following theorem:

Theorem. *Let Z_N be a sequence of random variables that satisfies $\sqrt{N}(Z_N - \theta) \rightarrow N(0, \sigma^2)$ in distribution⁸. For a given function g and a specific value of θ , suppose that $g'(\theta)$ exists and is not 0.*

⁸ $X_n \rightarrow X$ in distribution, if $\mathbb{P}(X_n \leq x) \rightarrow \mathbb{P}(X \leq x)$ as $n \rightarrow \infty$ [20].

Then,

$$\sqrt{N}(g(Z_N) - g(\theta)) \rightarrow N(0, \sigma^2[g'(\theta)]^2) \quad \text{in distribution.} \quad (8.3)$$

Since $\mathcal{N}_m(\nu)$ is binomially distributed with variance $\text{Var}(\mathcal{N}_m(\nu)) = N p_m(\nu)(1 - p_m(\nu))$ and expectation value $\mathbb{E}(\mathcal{N}_m(\nu)) = N p_m(\nu)$, we can apply this theorem by setting $Z_N := \mathcal{N}_m(\nu)/N$, $\theta = p_m(\nu)$ and $g(x) = x \ln(x)$. By the central limit theorem, we have the convergence $\sqrt{N}(\mathcal{N}_m/N - p) \rightarrow N(0, (1 - p)/p)$ in distribution. Together with the above theorem, this proves

$$\lim_{N \rightarrow \infty} \mathbb{E} \left(\frac{\mathcal{N}_m(\nu)}{N} \ln \left(\frac{\mathcal{N}_m(\nu)}{N} \right) \right) = p_m(\nu) \ln(p_m(\nu)) \quad (8.4)$$

Since $g(x) = x \ln(x)$ is a convex function, Jensen's inequality states for every random variable X that $\mathbb{E}(-g(X)) \leq -g(\mathbb{E}(X))$. Applying this inequality to $X = \mathcal{N}_m(\nu)/N$ proves that the Gibbs entropy is an upper bound on the assembly entropy.

The convergence is illustrated in Fig. 7.

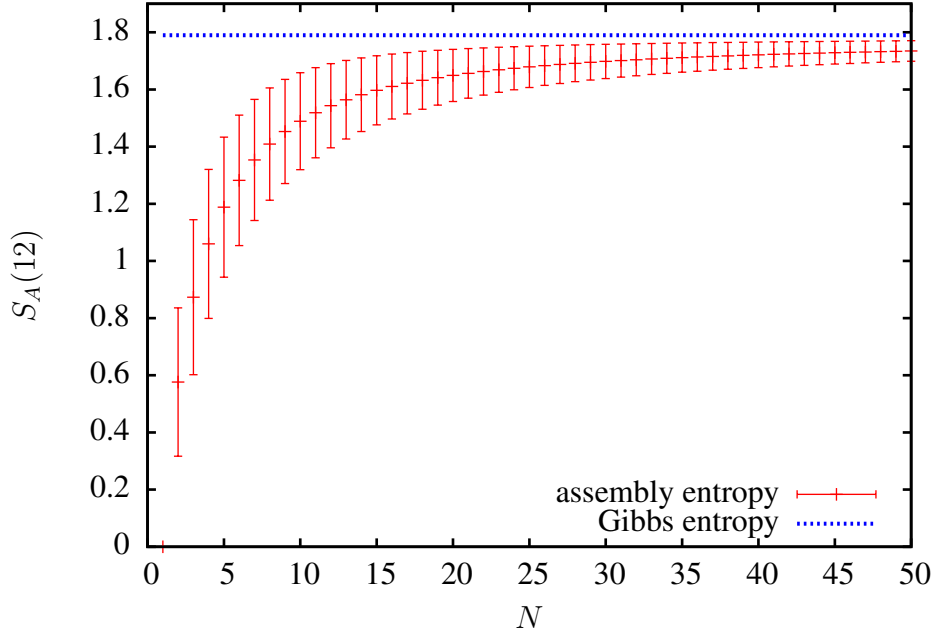


Figure 7: Convergence of the average assembly entropy to the Gibbs entropy of the system; $M = 6$ states after $\nu = 12$ time steps for jump rates $g = 0.4$, $s = 0.2$ and a perturbation $\varepsilon = 0.1$, i.e. $\Delta p^*/\bar{p}^* = 1/3$. The errorbars indicate the standard deviation of the random variable S_A . The Gibbs ensemble entropy of the system amounts to $S_G = 1.79$.

8.3 The Shannon entropy of the assembly entropy

We consider the assembly entropy Eq. (8.1). Since here entropy is a random variable, we can formally calculate the *Shannon information entropy* of this expression. For a given particle number N this reads

$$\begin{aligned}
 S_{\text{Sh}}(\mathcal{S}_A) &= - \sum_{\sum_m \{n_m\} = N} \mathbb{P}(\{\mathcal{N}_m(\nu)\} = \{n_m\}) \ln(\mathbb{P}(\{\mathcal{N}_m(\nu)\} = \{n_m\})) \\
 &= - \sum_{\sum_m \{n_m\} = N} p_1^{n_1} \dots p_M^{n_M} \ln(p_1^{n_1} \dots p_M^{n_M}) \\
 &= - \sum_{\sum_m \{n_m\} = N} p_1^{n_1} \dots p_M^{n_M} \sum_{k=1}^M \ln(p_k) \tag{8.5}
 \end{aligned}$$

8 The assembly entropy

We have demonstrated that in the limit $N \rightarrow \infty$ the assembly entropy becomes equal to the Gibbs entropy of the one particle ensemble. Using the Shannon entropy, a connection between the two notions can be drawn without discourse to this limit. Swapping the summation order, expression (8.5) can be rewritten to read

$$\begin{aligned} S_{\text{Sh}}(\mathcal{S}_A) &= - \sum_{k=1}^M N \left(\sum_{\substack{\{n_m\} \\ \sum_m n_m = N}} p_1^{n_1} \dots p_k^{n_k} \dots p_M^{n_M} \frac{n_k}{N} \right) \ln(p_k) \\ &= -N \sum_{k=1}^M \frac{\langle n_k \rangle}{N} \ln(p_k) \\ &= -N \sum_{k=1}^M p_k \ln(p_k) \\ &= N S_G \end{aligned} \tag{8.6}$$

Therefore, by adding one particle to the assembly, we loose an amount of information about the random variable \mathcal{S}_A equal to the Gibbs entropy of the one particle ensemble. This physically intuitive result supports the interplay between information theory and entropy.

9 Coarse-grained thermodynamic entropy

Hier wird es noch ein paar einleitende Worte geben.

9.1 Entropy production

We image our thermodynamic model system as introduced in Sec. 2. Let a be the length of the cells and τ the time between two consecutive observations of the system. Following [11], the system entropy production can be split into the total entropy production and an entropy flow into the medium,

$$\frac{\Delta S_m^{(cg)}(\nu)}{a\tau} = \frac{S_m^{(cg)}(\nu+1) - S_m^{(cg)}(\nu)}{a\tau} = \frac{\Delta S_{m,\text{tot}}^{(cg)}(\nu)}{a\tau} - \frac{\Delta S_{m,\text{med}}^{(cg)}(\nu)}{a\tau}, \quad (9.1)$$

where the entropy flow is the difference in Gibbs entropy of the cell and the total entropy production is the change in the difference between the Gibbs entropy and the coarse-grained thermodynamic entropy:

$$\begin{aligned} \Delta S_{m,\text{med}}^{(cg)}(\nu) &= S_m^{(G)}(\nu+1) - S_m^{(G)}(\nu) \\ \Delta S_{m,\text{tot}}^{(cg)}(\nu) &= (S_m^{(G)}(\nu) - S_m^{(cg)}(\nu)) - (S_m^{(G)}(\nu+1) - S_m^{(cg)}(\nu+1)) \end{aligned} \quad (9.2)$$

The idea is that $S_m^{(cg)}$ provides us with less information about the stochastic dynamics than the Gibbs entropy and tracks back to the difference in information content in phase space density $\varrho(x, p)$ and particle density ρ_m [11]. The total entropy production respects the Second Law of Thermodynamics (cf. [21]).

9.2 Coarse-grained entropy as a fluctuating variable

Instead of dealing with the average particle density ρ_m , we now want to investigate the coarse-grained entropy for fluctuating particle numbers (random variables). Let \mathcal{N}_m be the particle number of cell m that has a spatial extension a . Then the coarse-grained

entropy Eq. (3.13) reads⁹

$$\mathcal{S}_m^{(cg)} = \mathcal{N}_m \ln \left(\frac{\mathcal{N}_m}{a} \right). \quad (9.3)$$

The total entropy production of the system is calculated as [22]

$$\begin{aligned} \Delta \mathcal{S}_{m,\text{tot}}(\nu) &= -\mathcal{N}_m(\nu+1) \ln \left(\frac{\mathcal{N}_m(\nu+1)}{\mathcal{N}_m(\nu)} \right) \\ &\quad + \mathcal{N}_{m-1,m}(\nu) \ln \left(\frac{\mathcal{N}_{m-1,m}(\nu)}{\mathcal{N}_{m,m-1}(\nu)} \right) \\ &\quad + \mathcal{N}_{m+1,m}(\nu) \ln \left(\frac{\mathcal{N}_{m+1,m}(\nu)}{\mathcal{N}_{m,m+1}(\nu)} \right) \end{aligned} \quad (9.4)$$

Conceptually, Eq. (9.3) combines two distinct concepts, on the one hand, the formulation in terms of random variables that corresponds to *counting* particles, on the other hand a structure for the entropy expression that is based upon the definition of an ensemble via the Gibbs entropy. Eq. (9.4) does not fulfill the Second Law of Thermodynamics for an equilibrium state, $\langle \Delta \mathcal{S}_{m,\text{tot}} \rangle \neq 0$. Therefore, by combining both approaches, there is a correction term to the coarse-grained entropy that becomes dominant in equilibrium (cf. [22]).

We note that all appearing contributions are of the form $g(X, Y) = X \ln(X/Y)$ with X, Y being random variables. We want to take the average value $\mathbb{E}(g(X, Y))$ and analyze the fluctuations using the *delta method* introduced in Sec. 8.2. Here we extend this method by dealing with a bivariate function and an expansion up to second order around the expectation values $\mu_X := \mathbb{E}(X)$ and $\mu_Y := \mathbb{E}(Y)$.

$$\begin{aligned} g(X, Y) &\approx \mu_X \ln \left(\frac{\mu_X}{\mu_Y} \right) \\ &\quad + (X - \mu_X) \left(\ln \left(\frac{\mu_X}{\mu_Y} \right) + 1 \right) \\ &\quad + (Y - \mu_Y) \left(-\frac{\mu_X}{\mu_Y} \right) \\ &\quad + \frac{1}{2} \left[(X - \mu_X)^2 \frac{1}{\mu_X} + 2(X - \mu_X)(Y - \mu_Y) \left(-\frac{1}{\mu_Y} \right) + (Y - \mu_Y)^2 \frac{\mu_X}{\mu_Y^2} \right] \end{aligned} \quad (9.5)$$

⁹This equation is extensive in the particle number and may be normalized by the cell length a .

9.2 Coarse-grained entropy as a fluctuating variable

Because the expectation value of the terms linear in X and Y vanishes, we get the following approximation for the mean of the above expression.

$$\mathbb{E}(g(X, Y)) \approx \mu_X \ln \left(\frac{\mu_X}{\mu_Y} \right) + \frac{1}{2} \frac{\text{Var}(X)}{\mu_X} + \frac{1}{2} \frac{\text{Var}(Y)}{\mu_Y} \frac{\mu_X}{\mu_Y} - \frac{\text{Cov}(X, Y)}{\mu_Y} \quad (9.6)$$

The correction due to fluctuations depends on the relative dispersion of each variable, as expressed by quotient of the variance and the corresponding mean, on the quotient of the mean values of X and Y , as well as on the joint dispersion expressed by the covariance.

In Sec. 8.2 we have found that the occupation numbers are binomially distributed, $\mathcal{N}_m(\nu) \sim \text{Binomial}(N, p_m(\nu))$. An analogous argument can be put forward for the exchanged particles. We can express the random variable $\mathcal{N}_{m,m\pm 1}$ as a sum of i.i.d. Bernoulli variables, $\mathcal{N}_{m,m\pm 1}(\nu) = \sum_{n=1}^N Z_n^{(m,m\pm 1)}(\nu)$, where $Z_n^{(m,m\pm 1)}$ is 1 if particle n is in state m at time ν and in state $m \pm 1$ at time $\nu + 1$ and 0 otherwise. Hence, $Z_n^{(m,m\pm 1)}(\nu) \sim \text{Bernoulli}(q_m(\nu))$, with $q_m(\nu) = \mathbb{P}(X_n(\nu) = m, X_n(\nu + 1) = m \pm 1) = p_m(\nu)w_{m,m\pm 1}$. Consequently, we get $\mathcal{N}_{m,m\pm 1} \sim \text{Binomial}(N, p_m(\nu)w_{m,m\pm 1})$.

Now, we examine this expansion with respect to the particle number N and the number of states M . The expectation value and the variance of the binomial distribution both scale with N/M , since $p_m(\nu) \sim 1/M$, which is why the leading term of the approximation, Eq. (9.6), also has this scaling behavior. The fluctuating terms on the other hand are of order 1 since the factor N/M cancels. Thus the fluctuations do only give any notable contribution to a non-vanishing leading term if N/M is of order 1.

We first examine the random variables describing the exchanged particles and choose X and Y according to the summands in Eq. (9.4). Since these fluctuating quantities are just weakly correlated (see below) the last term in Eq. (9.6) is negligible. Furthermore, the statistical dispersion of the exchanged particles is approximately the same for all random variables. An example for the time $\nu = 3$ is illustrated in Fig. 8. The correlation matrix of the $3M$ random variables $\{\mathcal{N}_{m,m-1}(3), \mathcal{N}_{m,m}(3), \mathcal{N}_{m,m+1}(3)\}$, in this sequence for all m , is plotted. We can deduce that they are only weakly correlated with the correlation coefficient being between -0.2 and 0.2 . Also, there is a tendency towards negative correlation coefficients, which makes sense considering that we require particle conservation thus forcing the particles flows to be anti-proportionally correlated. The absolute value of the correlation coefficient is bounded from above by 0.2 . This holds true for all times ν .

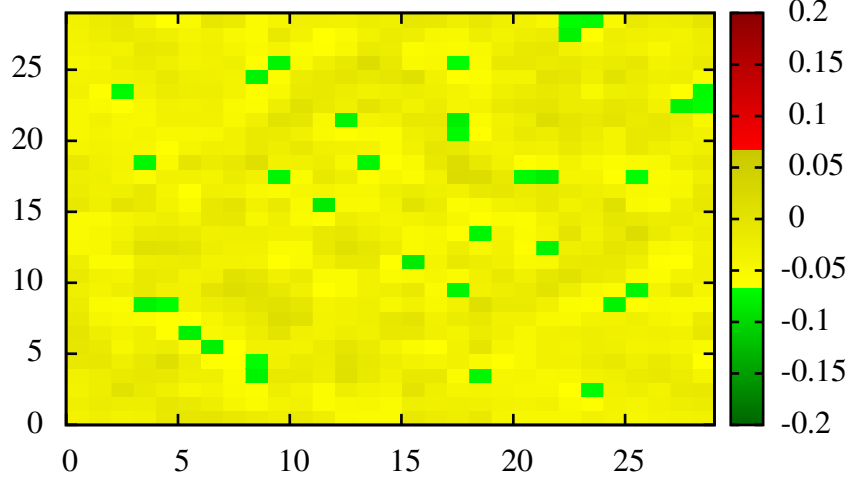


Figure 8: Correlationmatrix for the $3M$ variables $\{\mathcal{N}_{m,m-1}(3), \mathcal{N}_{m,m}(3), \mathcal{N}_{m,m+1}(3)\}$; $M = 10$ states, $N = 500$ particles, averaged over 700 simulations. Correlations of a random variable with itself are set to zero so that this value does not rescale the plot.

Hence, Eq. (9.6) can further be simplified as

$$\begin{aligned}
 \mathbb{E}(g(X, Y)) &= \mu_X \ln \left(\frac{\mu_X}{\mu_Y} \right) + \frac{1}{2} \text{Var}(Y) \left[\frac{\mu_Y^2 - \mu_X^2}{\mu_X \mu_Y^2} \right] \\
 &= \mu_X \ln \left(\frac{\mu_X}{\mu_Y} \right) + \frac{1}{2} \text{Var}(Y) \left[\underbrace{\frac{(\mu_Y - \mu_X)^2}{\mu_X \mu_Y^2}}_{\approx 0} + \frac{2\mu_X \mu_Y}{\mu_X \mu_Y^2} \right] \\
 &\approx \mu_X \ln \left(\frac{\mu_X}{\mu_Y} \right) + \frac{\text{Var}(Y)}{\mu_Y}, \tag{9.7}
 \end{aligned}$$

where we used that the squared difference of the mean is extremely small compared to the mean values.

For the particle occupation numbers $\{\mathcal{N}_m\}_{m \in [M]}$, the correlations and thus the covariance cannot be neglected. Already qualitatively this can be understood by bearing in mind that the occupation of one state m at a time $\nu + 1$ is comprised of the occupation numbers of the states $m, m \pm 1$ at time ν . Our previous observation concerning the approximate equality of their independent fluctuations though holds also true for these

random variables.

With our argumentation, an approximation of the expectation value of Eq. (9.4) in equilibrium can be written as

$$\begin{aligned}
 \langle \Delta \mathcal{S}_{m,tot}(\nu) \rangle \approx & -N_m(\nu+1) \ln \left(\frac{N_m(\nu+1)}{N_m(\nu)} \right) \\
 & + N_{m-1,m}(\nu) \ln \left(\frac{N_{m-1,m}(\nu)}{N_{m,m-1}(\nu)} \right) \\
 & + N_{m+1,m}(\nu) \ln \left(\frac{N_{m+1,m}(\nu)}{N_{m,m+1}(\nu)} \right) \\
 & - \frac{\text{Var}(\mathcal{N}_m(\nu))}{N_m(\nu)} + \frac{\text{Var}(\mathcal{N}_{m,m-1}(\nu))}{N_{m,m-1}(\nu)} + \frac{\text{Var}(\mathcal{N}_{m,m+1}(\nu))}{N_{m,m+1}(\nu)} \\
 & + \frac{\text{Cov}(\mathcal{N}_m(\nu+1), \mathcal{N}_m(\nu))}{N_m(\nu)}, \tag{9.8}
 \end{aligned}$$

where $N_m(\nu) = \langle (\mathcal{N}_m(\nu)) \rangle$.

10 Summary and Outlook

In this thesis, we have examined and compared different notions of entropy using a Markov chain as model system for coarse-grained transport processes. It enables us to clearly identify thermodynamic variables such as the heat exchanged with the surrounding medium, but on the other hand exhibits analytically manageable stochastic dynamics. We fully characterized the perturbed model system by finding an analytical solution to the evolution of the probability distribution and by calculating the transport coefficients, which give the stochastic dynamics a physical classification. The model permits the study of non-steady state many particle systems with interest in a perturbation parameter that allows to continually change the distance of the system from equilibrium and that can be interpreted as the coupling to an external medium.

We investigated the Gibbs entropy for this Markov chain in discrete time and showed that from a physical point of view the discretization of the continuous time derivative does not include isolated systems, because this would violate the Second Law of Thermodynamics. Therefore, we discarded the intuitive discretization of taking the variation in Gibbs entropy as viable description to establish a general correspondence between physical systems and Markov chains. Instead, we suggest to take the time derivative in *measure difference*, which would allow for a physical interpretation of isolated systems.

Additionally, the entropy splitting coincides with the time continuous case, which makes results obtained for these expressions available. We furthermore pointed out that with this discretization, symmetric transition matrices correspond to isolated systems, since they imply a vanishing entropy flow into the medium. It would be interesting to investigate whether one can further classify equivalence classes of transition matrices that can be identified with a certain type of physical system.

In analogy to Boltzmann's idea of counting particle occupation numbers, we introduced the assembly entropy as a fluctuating variable and showed mathematically that it converges to the Gibbs entropy for large particle numbers. This entropy concept might be interesting to study for systems with interacting particles and small particle numbers. In our dealing with the coarse-grained thermodynamic entropy, we quantified how the introduction of fluctuations to a thermodynamic entropy concept yields a correction to the Second Law of thermodynamics, because positive fluctuation contributions in the particle exchange add up to give a noticeable irreversible entropy production. Using the

delta method, we showed that fluctuations become important when the particle number per state becomes of order 1. A continuation of this work would include an adequate physical rescaling. In order to not change the physics of the system by adaptation of the cell size, characterizing quantities such as the transport coefficients have to stay the same, whereas the transition rates become a function of the time step size and the number of states.

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Hiermit erkläre ich, dass ich diese Abschlussarbeit selbständig verfasst habe, keine anderen als die angegebenen Quellen und Hilfsmittel benutzt habe und alle Stellen, die wörtlich oder sinngemäß aus veröffentlichten Schriften entnommen wurden, als solche kenntlich gemacht habe.

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Göttingen, den August 28, 2011

(Thomas Frerix)