An integral fluctuation theorem for systems with unidirectional transitions

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Received 24 June 2014
Accepted for publication 19 September 2014
Published 30 October 2014

Online at stacks.iop.org/JSTAT/2014/P10044
doi:10.1088/1742-5468/2014/10/P10044

Abstract. The fluctuations of a Markovian jump process with one or more unidirectional transitions, where $R_{ij} > 0$ but $R_{ji} = 0$, are studied. We find that such systems satisfy an integral fluctuation theorem. The fluctuating quantity satisfying the theorem is a sum of the entropy produced in the bidirectional transitions and a dynamical contribution, which depends on the residence times in the states connected by the unidirectional transitions. The convergence of the integral fluctuation theorem is studied numerically and found to show the same qualitative features as systems exhibiting microreversibility.

Keywords: stochastic particle dynamics (theory), current fluctuations

ArXiv ePrint: 1409.4037
1. Introduction

The last two decades have seen substantial advancement in our understanding of the thermodynamics of small out-of-equilibrium systems. Much of the progress was related to the study of fluctuations in such systems. In particular, it was found that many out-of-equilibrium processes satisfy fluctuation theorems [1–8]. These celebrated relations compare the probabilities of observing a realization of a process and its time-reversed or symmetry related counterpart. The ratio of these probabilities is expressed in terms of thermodynamic quantities such as entropy production or heat. A closely related set of results is termed work relations [9,10]. These focus on the fluctuations in the work done on the system when it is driven away from equilibrium.

Fluctuation theorems are valid for systems that are driven arbitrarily far from their thermal equilibrium. The discovery of fluctuation theorems has opened up new research directions and enhanced our qualitative and quantitative understanding of small systems in contact with thermal environments. The progress that has been made is summarized in several review articles [11–23].

One of the important concepts underlying fluctuation theorems is their ability to meaningfully and consistently assign thermodynamic interpretation to a single realization of a stochastic out-of-equilibrium process. This approach is sometimes referred to as stochastic thermodynamics. Sekimoto demonstrated that heat and work can be defined for a single realization of a process so that the first law is satisfied [24]. Seifert introduced the concept of a fluctuating system entropy and demonstrated that it allows us to obtain an exact fluctuation theorem [8]. Fluctuation theorems can be viewed as replacing the inequality of the second law of thermodynamics by an equality for the exponential average of a realization dependent fluctuating quantity [21]. The inequality is restored for the ensemble average of this quantity with the help of the Jensen inequality. More information about stochastic thermodynamics can be found in Seifert’s comprehensive review [23].

doi:10.1088/1742-5468/2014/10/P10044
Derivations of fluctuation theorems commonly use a direct comparison of the probabilities of a realization and that of its time reversed counterpart. For systems driven by a given force protocol, one similarly compares probabilities of realization of a forward process to that of its time reversed (backward) process driven by a time reversed force protocol. The same considerations can be applied for systems in the absence of time reversal symmetry, for instance due to the presence of a magnetic field. See [25] for a recent review. All of these approaches employ microreversibility, namely the fact that time inversion (combined with an inversion of momenta, driving protocol and possibly magnetic field) maps between allowed realizations of a forward and a backward process. In jump processes, microreversibility means that if the transition from state $i$ to state $j$ has a finite rate, $R_{ji} > 0$, then so does the reversed transition, $R_{ij} > 0$, where we assume absence of magnetic fields.

There are instances, however, where the simplest description of a natural process is one where microreversibility is violated. Consider an atom in an excited state that decays via spontaneous emission of a photon that escapes from the system. In many situations, it is useful to derive a reduced description for the atom in which the field serves as an external reservoir. For spontaneous emission, the empty field modes can be interpreted as a zero temperature reservoir. The reversed process, namely an excitation of the atom, requires the presence of photons but when there are no such photons, this reverse process will not occur. As a result, the reduced description has $R_{\text{emission}} > 0$ while $R_{\text{absorption}} = 0$. When the field modes are in a thermal state with finite temperature, the presence of stimulated processes restores microreversibility. Unidirectional transitions can be incorporated into models of heat engines and machines, which also include reversible transitions such as the model of a photosynthetic reaction center studied by Dorfman et al [26]. Irreversible jump processes are also used to model biological enzymes, which break down the substrate they move on such as cellulase (see e.g. [27]). In the following, we use this as motivation to study jump processes that violate microreversibility. We focus on the fluctuations in such systems and ask whether they satisfy a fluctuation theorem.

Fluctuations of systems with unidirectional transitions have generated limited interest so far. Ohkubo derived a fluctuation theorem, which also holds for irreversible systems [28]. It is based on posterior transition rates obtained with the help of Bayes’ theorem. A fluctuation theorem for a system of soft spheres with dissipative collisions was derived by Chong et al [29]. It applies to systems with continuous dynamics and, moreover, requires thermal initial conditions. Other approaches used to investigate fluctuation theorems in systems with an irreversible transition replace the vanishing rate by an effective finite rate using some coarse-graining of the dynamics. Ben-Avraham et al suggested measuring the state of the system in fixed time intervals [30]. This coarse graining in time allows for an effective backward rate, which is actually obtained from the combined contributions of allowed transitions that take the system to the other side of the irreversible transition. Zeraati et al chose to view the vanishing transition rate as being the limit of a very small but finite rate, which is small enough that it is unlikely to be observed in a finite time experiment [31]. This effective rate was then estimated using Bayes theorem, which, in turn, is then used to obtain a lower bound for the entropy production that depends on the observation time. Both of these approaches exhibit logarithmically diverging quantities that are ill defined in the limit where the coarse-graining is removed, namely for vanishing time intervals between measurements or infinite observation time.
Here, we employ an approach that does not suffer from such difficulties and show that an integral fluctuation theorem holds for systems with unidirectional jumps. This fluctuation theorem is based on a different treatment of reversible and irreversible transitions. It holds for a fluctuating quantity that is a sum of two contributions. The first is the usual fluctuating entropy production due to reversible transitions. The second is an unusual dynamical term, which depends on the fluctuating residence times in the states connected by the irreversible (unidirectional) transitions. This prescription avoids the difficulties of defining an entropy production for the irreversible terms that led to diverging expressions in coarse-grained approaches.

The structure of the paper is as follows. In section 2, we consider a simple example of a jump process with a single irreversible transition and derive the integral fluctuation theorem. The derivation is simple and can be easily applied to systems with more states, irreversible transitions, or time dependent transition rates. Such generalizations are straightforward and are stated without detailed proof in section 3. In section 4, we discuss the number of realizations needed for convergence of the exponential average appearing in the integral fluctuation theorem. We point out that estimates based on the identification of typical and dominant realizations developed for systems with reversible rates are also applicable here. We summarize our results in section 5.

2. A simple model

We introduce the integral fluctuation theorem with the help of a simple example of a Markovian jump process. The use of an example allows us to present the derivation without using unnecessarily complicated notations. The choice of the example is based on two requirements. We want the system to include one irreversible transition. In addition, we want at least one closed cycle of reversible transitions to allow for a steady state flux even in the absence of the irreversible transition. These considerations lead us to study a system with four states and one irreversible transition, which is the minimal model that has no more that one transition between states and satisfies the requirements. Generalizations to more general jump processes are possible and are described in section 3.

The possible transitions between the four states are characterized by the transition rates, with $R_{ij} \geq 0$ corresponding to the transition $j \rightarrow i$ (for $i \neq j$). When the transition between $i$ and $j$ is reversible, the combination $\ln \frac{R_{ij}}{R_{ji}}$ is interpreted as the entropy change in the reservoir during the transition [5]. (We use units where $k_B = 1$.) This identification is motivated by the fact that, for thermally activated rates, this term commonly has the form $\frac{E_i - E_j}{k_B T}$, with $E_i$ the energy of state $i$ and $T$ the temperature of the reservoir. This is an ill-defined quantity for unidirectional rates, where $R_{ij} > 0$ and $R_{ji} = 0$.

The simple model investigated in this section can be conveniently represented using a graph, which is depicted in figure 1. The black solid lines represent reversible (bidirectional) transitions. In contrast, the transition from state 2 to state 4 is irreversible, with rates $R_{42} > 0$ and $R_{24} = 0$.

The system’s probability distribution evolves according to a master equation, $\frac{dp}{dt} = Rp$, with $R_{ii} \equiv -\sum_{j \neq i} R_{ji} = -r_i$. Here, $p$ is the vector containing population of the four states and $R$ is the transition rate matrix. If left alone, the system relaxes to a
steady state, \(p^{ss}\). A history or, equivalently, a realization of the system is a list detailing the state of the system at any given time, including also the specific transitions it made during the entire realization. We denote a given realization by \(\gamma\). For example,

\[
\gamma = \left\{ 2 \xrightarrow{t_1} 3 \xrightarrow{t_2} \cdots 4 \xrightarrow{t_n} 1 \right\}
\]

(1)
corresponds to a realization where the system was initially at state 2 and stayed there until time \(t_1\). (This can be denoted equivalently by \(\gamma(t) = 2\) for \(0 \leq t < t_1\).) At time \(t_1\), the system makes a transition to state 3. Eventually, the system makes a transition from state 4 to state 1 at time \(t_n\). The system then stays in that state until the end of the observation at time \(t_f\). Since this is a Markovian jump process, the probability density of such a history is

\[
P(\gamma) = p_i(2)e^{-r_2t_1}R_{32}e^{-r_3(t_2-t_1)}\cdots R_{41}e^{-r_1(t_f-t_n)},
\]

(2)
where \(p_i\) denotes the initial probability distribution. We denote the final probability distribution by \(p_f\), namely the solution of the master equation at time \(t_f\) given the initial condition \(p_i\).

Let us denote the time reversed realization of \(\gamma\) by \(\overline{\gamma}\). For \(\gamma\) of equation (1), this is clearly

\[
\overline{\gamma} = \left\{ 1 \xrightarrow{t_f-t_n} 4 \xrightarrow{t_f-t_2} 3 \xrightarrow{t_f-t_1} 2 \right\}.
\]

(3)
We note that time reversal is a one-to-one mapping between realizations. However, many of the time reversed realizations are not allowed under the dynamics of the irreversible jump process depicted in figure 1 because they would make the forbidden 4 \(\rightarrow\) 2 transition. We note that there are approaches that derive integral fluctuation theorems by separating realizations into groups of regular and irregular realizations and calculating the weight of the latter [32], but a simpler approach is possible here. We view the reversed realizations \(\overline{\gamma}\) as obtained from an auxiliary dynamics in which one reverses the direction of the irreversible transition. For the simple example considered in this section, this auxiliary dynamics has \(\overline{R}_{24} = R_{42}\) and \(\overline{R}_{42} = 0\) and otherwise \(\overline{R}_{ij} = R_{ij}\) (for \(i \neq j\)). We intentionally avoid the more common terminology of ‘forward’ and ‘backward’ processes, which are best left for cases in which the backward process has a meaningful physical interpretation.

Importantly, the time reversal mapping between \(\gamma\) in the physical dynamics and \(\overline{\gamma}\) in the auxiliary dynamics is one-to-one. One can assign a probability density \(\overline{P}(\overline{\gamma})\) for realizations of the auxiliary dynamics. For the realization in equation (3), one finds

\[
\overline{P}(\overline{\gamma}) = p_i(1)e^{-\tau_1(t_f-t_n)}\overline{R}_{41} \cdots e^{-\tau_3(t_2-t_1)}\overline{R}_{23}e^{-\tau_2 t_1}.
\]

(4)

\[\text{doi:10.1088/1742-5468/2014/10/P10044}\]
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We note that \( r_i \neq r_i \) for the states linked by the unidirectional transition. It is crucial to point out that with the interpretation of irreversibility as coming from spontaneous emission, the auxiliary dynamics is not physical. It involves transitions taking the system from a low energy state to an excited state without energy input from the environment.

The auxiliary dynamics allows us to obtain a formal integral fluctuation theorem by defining

\[
\Sigma(\gamma) \equiv \ln \frac{P(\gamma)}{\overline{P}(\gamma)},
\]

and noting that

\[
\langle e^{-\Sigma} \rangle = \sum_{\gamma} e^{-\Sigma(\gamma)} P(\gamma) = \sum_{\gamma} \overline{P}(\gamma) = 1.
\]

Equation (6) is a mathematical identity. Fluctuation theorems of this type are of interest when they can be given an appealing physical interpretation. We show that it is possible to express \( \Sigma(\gamma) \) using only properties of the physical dynamics, suppressing any explicit dependence on the auxiliary dynamics.

To do so, we note that equation (6) is valid for any choice of the initial condition for the auxiliary dynamics. We therefore chose \( \overline{p}_i = p_f \), meaning that the initial distribution of the auxiliary dynamics is the same as the final distribution of the physical dynamics. A short calculation then finds

\[
\Sigma(\gamma) = \Delta S_{\text{rev}}(\gamma) + R_{42}(\tau_4(\gamma) - \tau_2(\gamma)).
\]

Here,

\[
\Delta S_{\text{rev}}(\gamma) = \sum_{i, \text{rev}} \ln \frac{R_{\gamma_i+1}^{\gamma_i+1}}{R_{\gamma_i}^{\gamma_i+1}} + \ln \frac{p_i(\gamma(0))}{p_f(\gamma(t_f))},
\]

where the first term on the right hand side is the sum of contributions to the medium entropy production from all the reversible transitions during the realization \( \gamma(t) \), while the second is the change of the fluctuating system entropy [8]. Note that the quantity \( \Sigma(\gamma) \) fluctuates from one realization to another. \( \tau_i(\gamma) \) in equation (7) denotes the (fluctuating) time that the system spends in state \( i \) during the realization. It can be written as \( \tau_i(\gamma) = \int dt \chi_i(\gamma(t)) \), where \( \chi_i = 1 \) for \( \gamma(t) = i \) and 0 otherwise.

The jump process depicted in figure 1 thus satisfies the integral fluctuation theorem

\[
\langle e^{-\Delta S_{\text{rev}} + R_{42}(\tau_4 - \tau_2)} \rangle = 1,
\]

which is accompanied by a second law like inequality

\[
\langle \Delta S_{\text{rev}} + R_{42}(\tau_4 - \tau_2) \rangle \geq 0.
\]

The quantity \( \Sigma \) satisfying the integral fluctuation theorem (9) has a simple physical interpretation, which is an interesting mixture of dynamical and thermodynamic quantities. The thermodynamic part, \( \Delta S_{\text{rev}} \), includes the change in medium entropy in the finite temperature reservoirs. The thermodynamic interpretation of this entropy production as resulting from, for example, energy exchanged with finite temperature reservoirs, is well understood, in contrast to the absence of a similar interpretation for irreversible transitions. The contribution of the irreversible transitions is dynamical and depends on residence times, namely the time that the system spends in the states connected by the transition. The structure of this dynamical term, a product of the
transition rate and residence times, is similar to the so-called traffic that contributes to the linear response of jump processes [33, 34]. Both the dynamical term in equation (9) and the traffic as considered in [33, 34] are given by time integrals of escape rates, but only the irreversible transition contributes to the dynamical part of $\Sigma$. Furthermore, the sign of the contribution depends on whether the irreversible transition points into or out of the state.

It is worthwhile to examine the inequality (10) more closely at steady state, where all the terms appearing in the inequality are linearly proportional to time, $\langle \Delta S_{\text{rev}} \rangle = q_{\text{rev}} t_f$ and $\langle \tau_i \rangle = p_{\text{ss}}(i) t_f$. The inequality (10) can be rewritten as

$$q_{\text{rev}} + R_{42} (p^{ss}(4) - p^{ss}(2)) \geq 0.$$  

(11)

Here, $q_{\text{rev}}$ is the reversible entropy production rate at steady state. Each reversible transition $i \rightarrow j$ contributes $\ln(R_{ji}/R_{ij})$ to the entropy production. At steady state, the mean rate of the $i \rightarrow j$ transition is $R_{ji} p_{\text{ss}}(i)$. Therefore,

$$q_{\text{rev}} = \sum_{(i,j) \text{rev}} [R_{ji} p_{\text{ss}}(i) - R_{ij} p_{\text{ss}}(j)] \ln(R_{ji}/R_{ij}),$$

(12)

where the sum is over all unordered pairs of states connected by a reversible transition. (For simplicity, we assume here that, at most, one transition connects any given pair of states.) Finally, with the help of the conservation laws for steady state fluxes, this inequality can be restated as

$$J_{14}^{ss} \ln \frac{R_{14} p^{ss}(4)}{R_{41} p^{ss}(1)} + J_{21}^{ss} \ln \frac{R_{21} p^{ss}(1)}{R_{12} p^{ss}(2)} + J_{34}^{ss} \ln \frac{R_{34} p^{ss}(4)}{R_{43} p^{ss}(3)} + J_{23}^{ss} \ln \frac{R_{23} p^{ss}(3)}{R_{32} p^{ss}(2)}$$

$$+ R_{42} p_{ss}(2) \left[ \ln \frac{p^{ss}(2)}{p^{ss}(4)} + \frac{p^{ss}(4)}{p^{ss}(2)} - 1 \right] \geq 0.$$  

(13)

The terms of the form $J_{ij}^{ss} \ln \frac{R_{ij} p^{ss}(j)}{R_{ji} p^{ss}(i)} = (R_{ij} p^{ss}(j) - R_{ji} p^{ss}(i)) \ln \frac{R_{ij} p^{ss}(j)}{R_{ji} p^{ss}(i)} \geq 0$ commonly appear in systems with reversible transitions and are interpreted as a product of flux and thermodynamic affinity. Interestingly, the presence of a unidirectional transition leads to the appearance of a different type of term in equation (13), namely the last term on the left hand side. This term is also non-negative since $\ln(x + \frac{1}{x} - 1 \geq 0$ for positive $x$. $R_{42} p^{ss}(2)$ is clearly the steady state flux of irreversible transitions. However, it is not clear whether $\ln \frac{p^{ss}(2)}{p^{ss}(4)} + \frac{p^{ss}(4)}{p^{ss}(2)} - 1 = \ln \left( \frac{\tau_4}{\tau_2} \right) + \frac{\tau_4}{\tau_2} - 1$, which depends on the ratio of likelihood to find the system at both sides of the unidirectional transition, can be meaningfully interpreted as some generalized affinity.

### 3. Possible generalizations

In this section, we briefly describe various generalizations of the integral fluctuation theorem, equation (9). The derivations are straightforward and most of the details are omitted.

We first note that there is some mathematical freedom in the choice of possible auxiliary dynamics. One can modify the magnitude of various transition rates in the auxiliary dynamics and equation (6) will still hold as long as the correct transitions are prohibited. However, this freedom to play with the magnitude of rates results in a $\Sigma$ whose
‘entropic’ and ‘dynamical’ parts have dubious physical interpretation. For instance, using an auxiliary dynamics with a modified value of $\bar{R}_{24}$ would result in contributions of $\ln \frac{\bar{R}_{42}}{\bar{R}_{24}}$ to the ‘entropy production’. However, such a physical interpretation is unjustified since the rate $\bar{R}_{24}$ has nothing to do with the dynamics of the physical system. Moreover, with this choice of auxiliary dynamics, $\Sigma$ depends on the rate $\bar{R}_{24}$ and the resulting integral fluctuation theorem no longer depends only on properties of the physical dynamics. The auxiliary dynamics used in section 2 was chosen to prevent the appearance of such difficulties and keep the physical interpretation of $\Sigma$ transparent. In that sense, the demand for consistent physical interpretation suggests that the auxiliary dynamics should have been the one used in section 2.

The derivation of equation (8) presented in section 2 never made use of the fact that there are only four states in the system. It applies to a jump process with any finite number of states as long as the initial and final probability distributions have finite values for all states. Even when some of the probabilities $p_{fi}, p_{fi}$ vanish, it is possible that the approach developed by Murashita et al. [32] may be of use, but this is beyond the scope of the current paper.

Another possible generalization is to a system with several unidirectional transitions. In this case, the auxiliary dynamics is one where all the irreversible rates have been reversed. Their contribution to the fluctuation theorem enters through the escape rates $r_i$ and $\bar{r}_i$. These escape rates are sums over all the rates of transitions leaving a state and the different irreversible transitions must thus contribute additively to the escape rates. The result is that several irreversible rates contribute additively to $\Sigma$ and the dynamic contribution has the form $\sum_\alpha R_{\alpha+\alpha-} \left[ r_{\alpha+}(\gamma) - r_{\alpha-}(\gamma) \right]$, where $\alpha$ runs over different irreversible transitions, which connect state $\alpha^-$ to state $\alpha^+$ and have the rate $R_{\alpha+\alpha-}$.

The last generalization we consider is to systems with time dependent rates. For such systems, the conditional probability factors expressing the probability to stay in a state have the form $\exp \left[ - \int_{t_i}^{t_{i+1}} dt R_{\alpha+\alpha-} \right]$, in contrast to factors of $\exp \left[ -r_{\alpha}(t_{i+1} - t_i) \right]$ appearing in autonomous systems. The resulting contribution to $\Sigma$ has dynamical terms of the form $\int dt R_{\alpha+\alpha-}(t) \left[ \chi_{\alpha+}(\gamma(t)) - \chi_{\alpha-}(\gamma(t)) \right]$ replacing the terms $R_{\alpha+\alpha-}.$

Based on these considerations, the integral fluctuation theorem (6) holds for time dependent jump processes with several irreversible transitions and, as long as the probability distribution is non-vanishing, $\Sigma$ takes the form

$$\Sigma(\gamma) = \Delta S_{rev}(\gamma) + \sum_\alpha \int dt R_{\alpha+\alpha-}(t) \left[ \chi_{\alpha+}(\gamma(t)) - \chi_{\alpha-}(\gamma(t)) \right].$$  \hspace{1cm} (14)

4. Convergence of the exponential average

Exponential averages such as the one in equations (6) and (9) often exhibit poor convergence. The underlying reason is the difference between typical and dominant realizations. Typical realizations are the ones that are likely during the process of interest and correspond to $\Sigma$ values in the vicinity of the maximum of $P(\Sigma)$. In contrast, dominant realizations are those for which $e^{-\Sigma}P(\Sigma)$ is maximal. Jarzynski discussed the convergence of exponential averages of this type using a gas in an expanding piston
An integral fluctuation theorem for systems with unidirectional transitions as an example [35]. He used the detailed version of the fluctuation theorem to argue that the dominant realizations are actually the (time-reversed) typical realizations of the corresponding reversed process. In addition, he derived a simple estimate for the number of realizations needed for convergence of the exponential average. The purpose of this section is to demonstrate that these considerations also apply to systems with unidirectional transitions and to numerically verify the validity of equation (9).

To do so, we simulate the jump process of section 2 using the Gillespie algorithm. This algorithm efficiently generates stochastic trajectories with the correct distribution by determining the time of the next transition, making use of the fact that the waiting times between jumps are distributed exponentially [36]. The transition rates were taken to be $R_{12} = 3$, $R_{21} = 0.24$, $R_{23} = 4$, $R_{32} = 1$, $R_{34} = 0.67$, $R_{43} = 2.1$, $R_{41} = 1$, $R_{42} = 0.78$ and $R_{42} = 2.3$. The jump process is assumed to be at steady state. For the parameters above, we find $p_{ss}(1) \simeq 0.5213$, $p_{ss}(2) \simeq 0.0515$, $p_{ss}(3) \simeq 0.0498$ and $p_{ss}(4) \simeq 0.3772$.

The numerically computed probability distribution of $\Sigma$ is depicted in the left panel of figure 2 for $t_f = 5$. This distribution was generated from $10^9$ different realizations of the process. This panel also depicts $e^{-\Sigma}P(\Sigma)$, which was calculated from $P(\Sigma)$. In addition, it shows the distribution $\overline{P}(-\Sigma)$, which was calculated by numerical simulation of the auxiliary dynamics with the suitable initial condition ($p^{ss}$). The latter two curves are expected to be identical. They are indeed very close to each other and the differences between them are possibly due to a combination of imperfect sampling of the tail of $P(\Sigma)$ and of errors introduced by binning the sparsely sampled region in the tail of $P(\Sigma)$. The spike at $\Sigma = 0$ is due to a discrete contribution to the probability density from the trajectories, which start at states 1 or 3 and never make a jump during the entire process. There are also discrete contributions at $R_{42}t_f$ and $-R_{42}t_f$ from trajectories spending the entire time at states 4 and 2, respectively. The weights of these contributions is smaller compared to the one at $\Sigma = 0$ because of the specific transition rates used in the numerics. In contrast to these discrete features, trajectories that make jumps lead to a continuous distribution due to the continuous nature of jump times. Therefore, the relative weight of discrete contributions to $P(\Sigma)$ is reduced when $t_f$ is increased. We note in passing that while the process we are interested in is stationary, the corresponding reference auxiliary is not stationary since $p^{ss} \neq \overline{p}^{ss}$.

The same curves are presented in the right panel of figure 2 for $t_f = 20$. A comparison of the two panels shows that when $t_f$ is increased, the dominant realizations are pushed further into the tails of $P(\Sigma)$. This is easily seen from the amount of overlap between $P(\Sigma)$ and $\overline{P}(\Sigma)$. Larger values of $t_f$ show even less overlap.

This reduced amount of overlap has a direct impact on the probability to reliably obtain dominant realizations with the correct weights and, hence, on the convergence of exponential average equation (9). For $t_f = 5$, the dominant region is well sampled by the simulation. In contrast, when $t_f = 20$, it is clear that the dominant region is only partially sampled and the sampling is rather noisy. In some spots, the simulation of the original process gives weights that are too low or too high. The leftmost part of the dominant region was never sampled. As a result we expect that a simulation based calculation of $\langle e^{-\Sigma} \rangle$ will give reasonable results for $t_f = 5$ and somewhat poor results for $t_f = 20$. Sampling of the latter can be improved by adding more realizations.

To check the validity and convergence of the exponential average (9), we used ensembles of $3 \times 10^6$, $3 \times 10^7$ and $3 \times 10^8$ realizations of the jump process of section 2.

doi:10.1088/1742-5468/2014/10/P10044
Here, $R_{42} = 0.3$, while the rest of the transition rates are identical to those used to generate figure 2. The results are presented in figure 3. The ensemble was divided into 30 sub-ensembles, which were summed separately and used to generate an effective standard deviation measuring the fluctuations between different sub-ensembles. It is clear that good convergence is obtained for small $t_f$, where the average is close to 1 and the standard deviation is small. When $t_f$ is increased, the fluctuations between sub-ensembles become noticeable. When $t_f$ is increased even further and the dominant region is pushed further into the tail of $P(\Sigma)$, the dominant region is typically under-sampled and the numerical simulation returns an average value that is substantially smaller than 1. Occasionally, this region is over sampled and then sometimes the simulation returns a value that can be larger than 1. This is the hallmark of poorly converged exponential averages of this type.

An estimate of the number of realizations needed for convergence was derived by Jarzynski [35]. For the jump process studied here, it is given by

$$N^* \approx e^{\Sigma_{\text{typ}}}, \quad (15)$$

where $\Sigma_{\text{typ}}$ is the typical value of $\Sigma$ in the auxiliary dynamics. This is an approximate criterion and we further simplify it by estimating $\Sigma_{\text{typ}}$ as if the auxiliary dynamics is at steady state. As mentioned earlier, this is not true since the auxiliary dynamics exhibits transient relaxation towards its steady state. We nevertheless make this approximation and obtain

$$\Sigma_{\text{typ}} \approx \left[ \bar{q}_{\text{rev}}^* + R_{42} (\bar{p}^*(2) - \bar{p}^*(4)) \right] t_f \simeq 0.6866 t_f. \quad (16)$$

By substituting equation (16) in equation (15), one can calculate the value $t_f^* = \ln N/0.6866$ so that the exponential average converges for a given number of realizations as long as $t_f < t_f^*$. The three vertical lines (dashed, solid and dash–dot) in figure 3 represent $t_f^*$ for $N = 3 \times 10^6$, $3 \times 10^7$ and $3 \times 10^8$, respectively. Since the estimate is approximate and we further ignored the possible contribution of transients, we expect this estimate to only work qualitatively. Indeed, all lines are roughly located in the transition region between times where the exponential average converges and the region where it does not. Overall, the numerical results presented in figure 3 qualitatively agree with our existing understanding of the difficulties in numerical estimation of exponential averages.
5. Summary

The stochastic coarse-grained dynamics of small systems in contact with external thermal reservoirs exhibit microreversibility, which ultimately stems from the time reversal symmetry of the underlying deterministic evolution. Nevertheless, there are situations in which it is useful to consider models that violate microreversibility. We have studied the fluctuations of jump processes in a system with one or more unidirectional rates. Such systems violate microreversibility and can be viewed as motivated by physical processes such as spontaneous relaxation in quantum systems. The usual formulation of fluctuation theorems cannot be used for irreversible systems since it involves contributions to the entropy production of the form \( \ln \frac{R_{ji}}{R_{ij}} \), which are not always defined.

For such systems, one can compare the dynamics to that of an auxiliary system in which the unidirectional transitions are flipped. However, this auxiliary dynamics has no simple physical interpretation; therefore, it is of interest to identify measures of fluctuations that can be expressed only in terms of the physical system. We have shown that it is possible to derive such an integral fluctuation, equation (9), which has a simple and appealing physical interpretation. The realization dependent quantity, \( \Sigma \), which appears in the exponent of equation (9) is a sum of a well-defined entropy production due to bidirectional transitions and a dynamical term that depends on the residence times in the states connected by the unidirectional transition. It can thus be viewed as including both thermodynamic and dynamical contributions.

The validity of equation (9) was checked numerically using simulations of the jump process. It is well-known that exponential averages show poor convergence when dominant
realizations are insufficiently sampled. This has been discussed in detail for systems exhibiting microreversibility [35] and our numerical results suggest that the same considerations can also be applied for systems with unidirectional transitions. When the numerical results converge they indeed support the validity of the integral fluctuation theorem.

Acknowledgments

We thank C Jarzynski and M Esposito for illuminating discussions. SR is grateful for support from the Israel Science Foundation (grant 924/11) and the US-Israel Binational Science Foundation (grant 2010363). This work was partially supported by the COST Action MP1209. UH acknowledges support from the Indian Institute of Science, Bangalore, India.

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doi:10.1088/1742-5468/2014/10/P10044 12