Entropy production in nonequilibrium steady states: A different approach and an exactly solvable canonical model

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(Received 4 May 2011; published 12 July 2011)

We discuss entropy production in nonequilibrium steady states by focusing on paths obtained by sampling at regular (small) intervals, instead of sampling on each change of the system's state. This allows us to directly study entropy production in systems with microscopic irreversibility. The two sampling methods are equivalent otherwise, and the fluctuation theorem also holds for the different paths. We focus on a fully irreversible three-state loop, as a canonical model of microscopic irreversibility, finding its entropy distribution, rate of entropy production, and large deviation function in closed analytical form, and showing that the observed kink in the large deviation function arises solely from microscopic irreversibility.

DOI: 10.1103/PhysRevE.84.011115 PACS number(s): 05.70.Ln, 05.20.−y, 05.40.−a

I. INTRODUCTION

Entropy production is a hallmark of nonequilibrium steady states. While entropy production is a system-dependent quantity, some remarkable universal properties emerge: For example, the probability distribution of the total entropy production satisfies a detailed fluctuation theorem in large classes of systems (see, e.g., Refs. [1–5]), and a kink appears in its large deviation function (and in that of related currents) at zero entropy production [6–12]. Initially, this kink has been attributed to specific properties of the systems under investigation, but a recent study indicates that it is a generic feature, related to the detailed fluctuation theorem [13]. We note that, in systems with microscopic reversibility, one finds numerical indications for the existence of a kink (defined as a jump of the first derivative of the rate function), but no analytical proof has yet been given. In contrast, a discontinuity in the derivative of the rate function is seen analytically for the asymmetric random walk when the backstep rate goes to zero [6], i.e., when the system becomes irreversible.

Most published works on fluctuation theorems and the related large deviation functions deal with systems that are *reversible* at the microscopic level: All transitions between states are bidirectional. However, sheared granular systems and chemical reactions, where the products are cleared rapidly, are two of many important cases where microscopic reversibility is broken. Few recent publications discuss fluctuation theorems for this type of system. Ohkubo has proposed a fluctuation theorem based on posterior probabilities [14], and Chong *et al.* showed that an integral fluctuation theorem can be derived without microscopic time reversibility [15].

Our aim in this paper is twofold. First, we propose the study of entropy production along trajectories sampled at regular (small) intervals instead of the usual sampling on each change in the system's state. This sampling is equivalent to the traditional technique, in the limit of vanishingly small intervals, and yields analogous results, including the fluctuation theorems. The advantage is that it enables direct analysis of systems with microscopic irreversibility and is more easily implemented in experiments and numerical studies. Second, we study the consequences of microscopic irreversibility by focusing on the smallest canonical example: a fully irreversible three-state loop. Thus, we find universal features of the entropy production and related quantities and demonstrate that the observed kink in the large deviation function at zero entropy is a feature of irreversibility.

II. ENTROPY PRODUCTION AND TWO KINDS OF SAMPLING

Consider a stochastic dynamical process in a system with a *discrete* set of states $A,B,C,\dots$, and with transition rates $k(X,Y)$ (from state X to Y). We denote the steady-state probability of being in state X by $\rho(X)$ and consider only systems with $\rho(X)>0$ for all states X.

A. Event sampling

Imagine the system starting from state X_0 (at the steady state) and progressing through the sequence $X_1,X_2,\dots,X_M$. No other states occur between X_i and X_{i+1}. The average time elapsed between two consecutive events is $\tau_i=1/k(X_i,X_{i+1})$. This is the kind of trajectory, or path, employed in previous work on the subject (see, e.g., Refs. [4,10,13,16]).

B. Interval sampling

We sample the system at M regular intervals $\tau,2\tau,\dots,M\tau$ and record its state at each sampling, thus, defining a trajectory $X_0,X_1,\dots,X_M$. The time gap between consecutive points on the trajectory is constant $\tau_i=\tau$. The system can be found in the *same* state on consecutive samplings, and it could also visit any number of states in between X_i and X_{i+1} [17]. One should note that this interval sampling is readily accessible in experiments, where one usually cannot record every transition between states, as would be needed for event sampling.

The total entropy production, in the steady state, is given by [18]

$$s_{tot}=\ln\frac{\rho(X_0)}{\rho(X_M)}+\ln\prod_i\frac{\omega(X_{i-1},X_i)}{\omega(X_i,X_{i-1})} \qquad (1)$$

for either kind of trajectory. For interval sampling, $\omega(X,Y)$ denotes the probability for finding the system in state Y, after time τ, having started at state X (at time zero). For event sampling, $\omega(X,Y)$ is replaced by $k(X,Y)$.

If the sampling rate is large enough, $1/\tau \gg \max_{X,Y} k(X,Y)$, the most likely outcome for consecutive samplings is $X_i = X_{i+1}$, and on the rare occasions that $X_i \neq X_{i+1}$, no other states are visited in between. Repeated visits to the same state do not contribute to the entropy (1), so $\tau \to 0$ interval sampling becomes equivalent to event sampling. Moreover, many of the properties found with the usual event sampling are reproduced by interval sampling, even for finite τ. For example, the detailed fluctuation theorem [4,5], $P(s_{tot})/P(-s_{tot}) = \exp(s_{tot})$, holds for both types of paths. A major advantage of interval sampling is that it lets us discuss situations of microscopic irreversibility: $X \to Y$, but $Y \not\to X$, and we focus on this idea.

III. THE THREE-STATE LOOP

For the sake of clarity and for a chance at a full analytical solution, we wish to study the simplest nonequilibrium system (with microscopic irreversibility). A two-state system with a nontrivial steady state [i.e., $\rho(A),\rho(B) > 0$] is, per force, an equilibrium system. Thus, we are led to consider the three-state system: $A \to B$, $B \to C$, $C \to A$, where we assume that all the rates are equal to 1, thus, defining our unit of time. We later argue that, despite its simplicity, this can be viewed as a canonical model for irreversibility.

Using the rate equations for the system, one finds

$$\omega_0 = \frac{1}{3} + \frac{2}{3}e^{-3\tau/2}\cos\left(\frac{\sqrt{3}}{2}\tau\right),$$
$$\omega_+ = \frac{1}{3} + \frac{1}{3}e^{-3\tau/2}\left[-\cos\left(\frac{\sqrt{3}}{2}\tau\right) + \sqrt{3}\sin\left(\frac{\sqrt{3}}{2}\tau\right)\right],$$
$$\omega_- = \frac{1}{3} + \frac{1}{3}e^{-3\tau/2}\left[-\cos\left(\frac{\sqrt{3}}{2}\tau\right) - \sqrt{3}\sin\left(\frac{\sqrt{3}}{2}\tau\right)\right], \tag{2}$$

where $\omega_0 \equiv \omega(A,A) = \omega(B,B) = \omega(C,C)$ denotes the *neutral* transitions, $\omega_+ \equiv \omega(A,B) = \omega(B,C) = \omega(C,A)$ are the *forward* transitions, and $\omega_- \equiv \omega(A,C) = \omega(B,A) = \omega(C,B)$ are the *reverse* transitions. Although these exact expressions can be employed in the subsequent calculations, we are interested in the limit $\tau \to 0$, and, in effect, we use their lower-order expansions: $\omega_0 = 1 - \tau + \tau^2/2 + \cdots$, $\omega_+ = \tau - \tau^2 + \cdots$, and $\omega_- = \tau^2/2 - \tau^3/2 + \cdots$. We have carefully verified that the final results are not affected. Note that the ratio $\omega_-/\omega_+ \approx \tau/2$, for the forbidden reverse direction, vanishes as $\tau \to 0$.

IV. PROBABILITY DISTRIBUTION OF ENTROPY PRODUCTION

Since $\rho(A) = \rho(B) = \rho(C) = 1/3$, the first term on the right-hand side of Eq. (1) does not contribute to s_{tot}. The remainder, which we denote simply by s, is the entropy produced in the thermal bath coupled to our system. Of the three types of terms that appear inside the product describing s, ω_0/ω_0, ω_+/ω_-, and ω_-/ω_+, only the last two contribute to s in equal and opposite amounts. Thus, s assumes a discrete spectrum of values: $s_m = m\,ds$ with $ds = \ln(\omega_+/\omega_-)$ and $m = 0, \pm 1, \pm 2, \ldots, \pm M$, where $m = N_+ - N_-$ is the excess number of forward (N_+) over reverse (N_-) transitions.

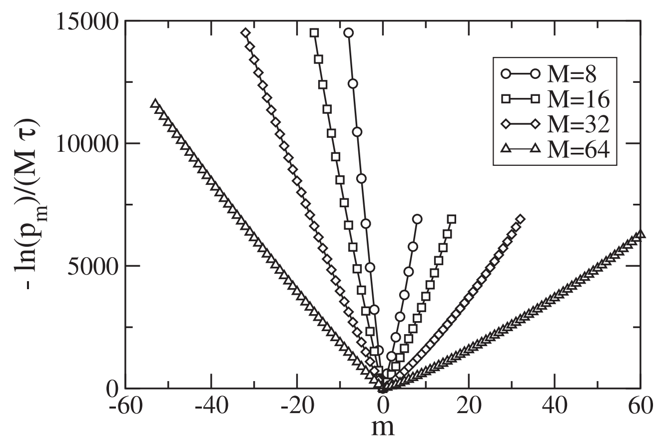

FIG. 1. The probability p_m as a function of m, the total number of forward and reverse transitions for the three-state loop where paths are sampled over M intervals of length $\tau = 0.001$. In order to make the different curves obtained for different values of M more easily distinguishable, we plot $-\ln(p_m)/(M\tau)$ where $M\tau$ is the total length of the path. One should note the emergence of a kink for increasing values of M.

The probability p_m of obtaining $s_m = m\,ds$ is the sum of the weights of all the trajectories consistent with that value. The weight of a trajectory with N_+-forward, N_--reverse, and N_0-neutral transitions is $\omega_0^{N_0}\omega_+^{N_+}\omega_-^{N_-}$. All values of N_+, N_-, N_0 must be counted, subject to the constraints $N_+ - N_- = m$ and $N_+ + N_- + N_0 = M$. For any finite M, one can work out explicit (cumbersome) expressions. Alternatively, the sums can easily be worked out numerically, see Fig. 1.

The problem can be approached more elegantly using the generating function $p(z) = \sum_m p_m z^m$. In our case, the generating function clearly is

$$p(z) = \left(\omega_0 + \omega_+ z + \frac{\omega_-}{z}\right)^M,$$

since its trinomial expansion yields all the possible combinations subject to the constraint $N_+ + N_- + N_0 = M$, and the z^m terms are precisely those where $N_+ - N_- = m$.

Upon making the substitution $z = e^{-\mu\,ds} = (\omega_-/\omega_+)^\mu$, the generating function assumes its usual interpretation,

$$p(e^{-\mu\,ds}) = \langle\exp(-\mu s)\rangle = \left(\omega_0 + \omega_+^{1-\mu}\omega_-^{\mu} + \omega_+^{\mu}\omega_-^{1-\mu}\right)^M. \tag{3}$$

The time evolution of this generating function is described by a linear operator whose lowest eigenvalue $\nu(\mu)$ allows one to compute quantities of interest [4,6,13]. For now, we ignore the linear operator itself, since we can obtain ν directly from

$$\nu(\mu) = \lim_{T\to\infty}\left[-\frac{1}{T}\ln\langle\exp(-\mu s)\rangle\right],$$

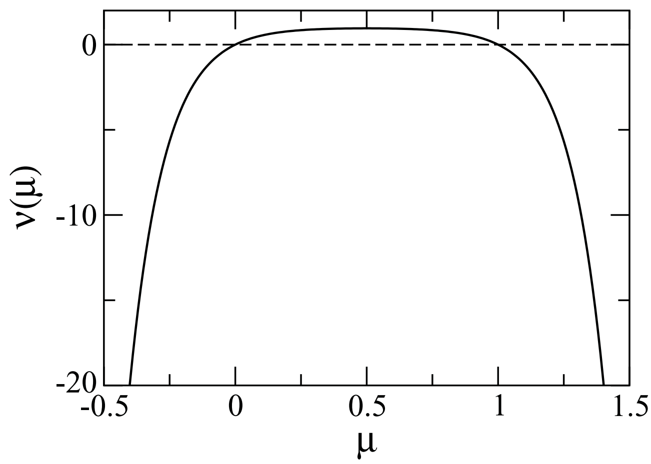

FIG. 2. The eigenvalue $\nu(\mu)$, plotted as a function of μ, for $\tau = 0.001$. The top of the curve becomes flatter as $\tau \to 0$.

where $T = M\tau$ is the total time length of each trajectory. Thus, we obtain

$$\nu(\mu) = -\tau^{-1} \ln\left(\omega_0 + \omega_+^{1-\mu}\omega_-^{\mu} + \omega_+^{\mu}\omega_-^{1-\mu}\right). \tag{4}$$

Interestingly, in our case, this limit is achieved for *any* value of M. This helps us discuss $T \to \infty$ ($M \to \infty$), even as $\tau \to 0$, for we can take the two limits independently. The fact that $\nu(\mu) = \nu(1-\mu)$ is a manifestation of the detailed fluctuation theorem [1–4]. The eigenvalue $\nu(\mu)$ is plotted in Fig. 2, for the case of $\tau = 0.001$. Using the low-order approximations for the ω's, we get

$$\nu(\mu) \approx 1 - (\tau/2)^{\mu} - (\tau/2)^{1-\mu}, \tag{5}$$

which compares very nicely with Eq. (4) when $\tau \to 0$.

The mean entropy production rate can now be derived from $\nu(\mu)$,

$$\langle \dot{s} \rangle = d\nu/d\mu|_{\mu=0} = \tau^{-1}(\omega_+ - \omega_-)\ln(\omega_+/\omega_-) \approx \ln(2/\tau), \tag{6}$$

where we have used $\omega_0 + \omega_+ + \omega_- = 1$, and the last expression is the dominant behavior as $\tau \to 0$. The fact that the approximate limit is the same as the entropy produced in a single forward transition is in agreement with the notion that backward steps are exceedingly rare as $\tau \to 0$ and do not contribute to the average.

The mean entropy production may also be computed from

$$\langle \dot{s} \rangle = \tau^{-1} \sum_{X,Y} \rho(X)\omega(X,Y) \ln \frac{\omega(X,Y)}{\omega(Y,X)}. \tag{7}$$

In general, the sum is dominated by the states P,Q yielding the fastest diverging $\omega(P,Q)/\omega(Q,P)$ ratio as $\tau \to 0$. The dominant contribution comes from an irreversible transition $P \to Q$ and $Q \not\to P$, since $\omega(Q,P) \to 0$ as $\tau \to 0$ in that case. It is in this sense that our model is canonical, for it suffices to focus on the effect of a single (dominant) irreversible transition, and ours is the smallest model that accomplishes that.

The fluctuation function $\chi(\sigma)$, of the *scaled* entropy $\sigma = s/\langle \dot{s} \rangle T$, is derived from an extremum of the Legendre transform of ν,

$$\chi(\sigma) = \max_{\mu}[\nu(\mu) - \langle \dot{s} \rangle \sigma\mu]. \tag{8}$$

It is possible to obtain a full analytic derivation of $\chi(\nu)$ for our simple model, but this results in cumbersome expressions. Instead, we illustrate the technique for the limit of small τ. The two derivations yield virtually indistinguishable curves for $\tau \lesssim 0.001$, while more insight is gained from the simpler approximation.

We begin by rewriting (the approximate) $\nu(\mu)$ as

$$\nu(\mu) = 1 - x - \frac{\tau}{2}x^{-1}, \qquad x \equiv (\tau/2)^{\mu},$$

and find μ_* that maximizes $\nu(\mu) - \langle \dot{s} \rangle \sigma\mu$ using the approximate limit $\langle \dot{s} \rangle = \ln(2/\tau)$,

$$x_* = \frac{\sigma + \sqrt{\sigma^2 + 2\tau}}{2}, \qquad \mu_* = \frac{\ln x_*}{\ln(\tau/2)}.$$

(The other root of the quadratic equation for x yields unphysical complex values.) Finally, setting $x = x_*$ and $\mu = \mu_*$ in $\nu(\mu) - \langle \dot{s} \rangle \sigma\mu$, we obtain

$$\chi(\sigma) = 1 - \sqrt{\sigma^2 + 2\tau} + \sigma \ln\left(\frac{\sigma + \sqrt{\sigma^2 + 2\tau}}{2}\right). \tag{9}$$

It is easy to check that this satisfies the symmetry relation $\chi(-\sigma) = \chi(\sigma) + \langle \dot{s} \rangle \sigma$, yet another manifestation of the detailed fluctuation theorem.

The limiting form of $\chi(\sigma)$ is universal,

$$\chi(\sigma) \longrightarrow 1 - \sigma + \sigma \ln \sigma, \quad \text{as } \tau \to 0, \qquad \sigma > 0, \tag{10}$$

and $\chi(\sigma) \to \infty$ for $\sigma < 0$, as $\tau \to 0$. The origin of the kink [6] in $\chi(\sigma)$ resides in $\sqrt{\sigma^2 + 2\tau}$, Eq. (9), which tends to $|\sigma|$ as $\tau \to 0$. Moreover, at the same limit, the logarithmic term diverges for $\sigma < 0$ but not for $\sigma > 0$. The kink can best be explored through the derivatives of $\chi(\sigma)$ [13],

$$\chi'(\sigma) = \ln\left(\frac{\sigma + \sqrt{\sigma^2 + 2\tau}}{2}\right), \qquad \chi''(\sigma) = \frac{1}{\sqrt{\sigma^2 + 2\tau}} \longrightarrow |\sigma|^{-1}, \tag{11}$$

as $\tau \to 0$. Note the existence of the limit $\tau \to 0$ for $\chi''(\sigma)$ for all $\sigma \neq 0$. For finite τ, the magnitude of the apparent jump in χ' is found to be on the order of $\chi'(1) - \chi'(-1) \to \ln(2/\tau)$. The large deviation function $\chi(\sigma)$ and its derivative are plotted in Fig. 3.

For our simple model, we were able to find the generating function (3) by inspection. For other systems, in general, it can be expressed as a matrix product,

$$\langle e^{-\mu s} \rangle = \mathbf{u}\mathbf{R}^M\mathbf{v}, \qquad \mathbf{R}_{X,Y} = \omega(X,Y)^{1-\mu}\omega(Y,X)^{\mu}, \tag{12}$$

where $\mathbf{u} = [\rho(A),\rho(B),\ldots]$ and $\mathbf{v}$ is a column vector of ones. Then, for $T \to \infty$,

$$\nu(\mu) = -\tau^{-1} \ln \lambda(\mu), \tag{13}$$

where $\lambda(\mu)$ is the largest eigenvalue of $\mathbf{R}$.

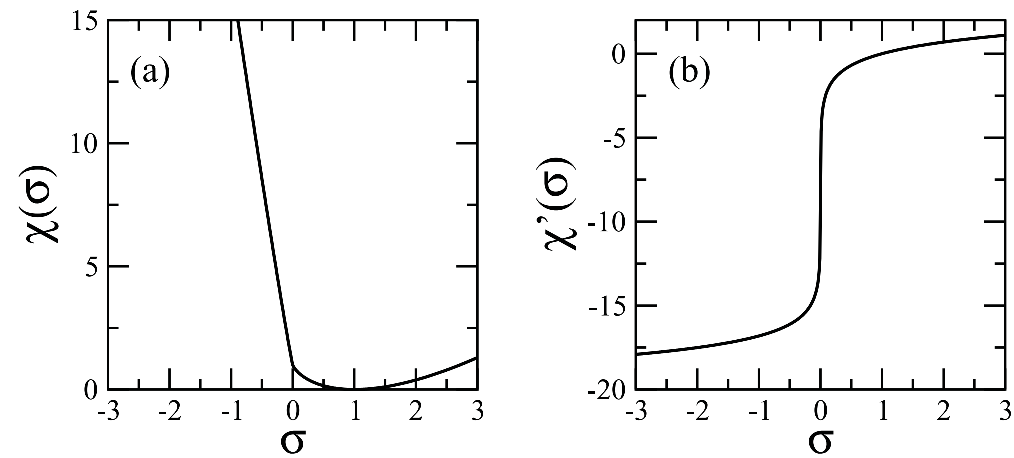

FIG. 3. The large deviation function (a), and its derivative (b), as a function of σ for $\tau = 10^{-7}$. The kink is more pronounced the smaller the value of τ.

A. N-state ring

It is easy to generalize the foregoing results to an N-state ring: $A_1 \to A_2, A_2 \to A_3, \ldots, A_N \to A_1$ ($N \geqslant 3$), where all rates are 1. The key ingredient arises from the fact that the forward transition probability (after time τ), from $A_k \to A_{k+1}$, is then $\approx\tau$, while the forbidden transition probability, for $A_k \to A_{k-1}$, is $\tau^{N-1}/(N-1)! \equiv \delta_N \tau$. All of the results valid for $N = 3$ can then be extended to general N, expressed as a function of δ_N. In particular,

$$\nu(\mu) = 1 - \delta_N^{\mu} - \delta_N^{1-\mu}, \tag{14}$$

from which follows:

$$\langle \dot{s} \rangle = \ln(1/\delta_N), \tag{15}$$

$$\chi(\sigma) = 1 - \sqrt{\sigma^2 + 4\delta_N} + \sigma \ln\left(\frac{\sigma + \sqrt{\sigma^2 + 4\delta_N}}{2}\right), \tag{16}$$

$$\chi'(\sigma)|_{\tau\to 0} = -\ln\left(\frac{\sigma + \sqrt{\sigma^2 + 4\delta_N}}{2}\right). \tag{17}$$

The results $\chi(\sigma > 0)|_{\tau\to 0} = 1 - \sigma + \sigma \ln \sigma$ and $\chi''(\sigma)|_{\tau\to 0} = 1/|\sigma|$ are universal.

B. Event sampling

The N-state ring can also be analyzed with event sampling, only that then one must postulate [13] a small backreaction rate ϵ for the forbidden transitions $A_k \to A_{k-1}$. It is easy to show that

$$\nu(\mu) = 1 + \epsilon - \epsilon^{\mu} - \epsilon^{1-\mu} \tag{18}$$

for all $N \geqslant 3$. Thus, the results from event sampling agree with those of interval sampling, in the limit of $\tau \to 0$, provided that one sets $\epsilon = \delta_N = \tau^{N-2}/(N-1)!$ (for the N ring). Thus, interval sampling endows ϵ with an actual physical meaning—indeed, for event sampling, there is no coherent prescription on how to choose independent ϵ's for the various irreversible transitions.

V. CONCLUSION

In this paper, we have proposed the use of interval sampling, a technique for studying entropy production in nonequilibrium steady states. Most importantly, interval sampling allows direct analysis of systems with microscopic irreversibility and is more easily implemented in experiments. We then focused on the smallest model possessing irreversibility—the three-state loop—and argued that it may serve as a canonical example for systems with microscopic irreversibility, such as driven granular systems, in general. In this way, we were able to identify universal features of entropy production, including its large deviation function and the kink at zero entropy production, which is seen to arise from irreversibility.

ACKNOWLEDGMENTS

This work was supported by the U.S. National Science Foundation through Grant No. DMR-0904999 as well as by the National Research Fund, Luxembourg, and was cofunded under the Marie Curie Actions of the European Commission (Grant No. FP7-COFUND).

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