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Time-Reversed Dynamical Entropy and Irreversibility in Markovian Random Processes

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A concept of time-reversed entropy per unit time is introduced in analogy with the entropy per unit time by Shannon, Kolmogorov, and Sinai. This time-reversed entropy per unit time characterizes the dynamical randomness of a stochastic process backward in time, while the standard entropy per unit time characterizes the dynamical randomness forward in time. The difference between the time-reversed and standard entropies per unit time is shown to give the entropy production of Markovian processes in nonequilibrium steady states.

KEY WORDS: Dynamical randomness; entropy per unit time; Kolmogorov Sinai entropy; entropy production; time reversal; nonequilibrium steady state; stochastic process; Markov chain; jump process; chemical reaction.

1. INTRODUCTION

Fluxes of matter or energy imposed at the boundaries of an open system explicitly break the time-reversal symmetry. Indeed, in nonequilibrium steady-states (NESS), the particles incoming at boundaries typically have a smooth probability distribution, although the outgoing particles have a probability distribution which depends on their interaction inside the system and are therefore, finely correlated. The time-reversed steady-state is in principle possible but highly improbable because it would require the incoming particles to have a probability distribution which is finely correlated according to the interaction they will have inside the system and, in general, the environment from where the particles come does not know about the interactions taking place inside the system.(1,2) Accordingly, in

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a NESS, the probability distribution of the microscopic trajectories inside the system differs from the probability distribution of the time-reversed trajectories so that the system is in an irreversible state. The irreversibility of a NESS thus finds its origin in the selection of the initial conditions for the trajectories incoming the open system. Most trajectories have an initial condition which is different from the initial condition of the time-reversed trajectory and, moreover, the stationary probability distribution of a NESS gives a different weight to the forward and backward trajectories. Therefore, the selection of initial conditions by the flux boundary conditions explicitly breaks the time-reversal symmetry at the statistical level of description as already noticed in refs. 1 and 2. The breaking of time-reversal symmetry may manifest itself for instance in some time correlation functions(3) and we may wonder if the time-reversal symmetry breaking would not also concern other properties closely related to both the dynamics and the thermodynamics.

In this regard, the irreversibility of a NESS is commonly characterized by the production of entropy inside the system. Previous work has given some hints that entropy production could be related to the dynamical randomness (alias chaos) taking place inside the system. Already, the escape-rate theory has shown that the transport properties can be related to the difference between the sum of positive Lyapunov exponents and the Kolmogorov–Sinai entropy per unit time, establishing a connection between irreversible properties and the characteristic quantities of dynamical systems theory.(2,4,5) However, the Lyapunov exponents cannot have their usual definition for random processes describing NESS because most trajectories spent a finite time inside the system between their incoming and outgoing times. Therefore, a general relationship between entropy production and some quantities of the type of those defined in dynamical systems theory has been missing.

The purpose of the present paper is to introduce a concept of *time-reversed entropy per unit time* similar to the standard entropy per unit time introduced by Shannon,(6) Kolmogorov,(7) and Sinai.(8) The aim is to characterize the dynamical randomness of the time-reversed trajectories of an open system and to show that, in a NESS, the entropy production is given by the difference between the time-reversed entropy per unit time and the standard entropy per unit time from dynamical systems theory. Our goal is thus to show that entropy production is due to the manifestation of the aforementioned breaking of the time-reversal symmetry at the level of the dynamical randomness of the microscopic trajectories.

The plan of the paper is the following. The concept of time-reversed entropy per unit time is introduced in Section 2. The relationship between the time-reversed and standard dynamical entropies and entropy production is proved for time-discrete Markov chains in Section 3 and for time-continuous jump processes in Section 4. The connection to recent work by Lebowitz and Spohn(9) and by Maes(10) is discussed in Section 5. The relationship is applied to reactive processes in Section 6. The connection to other relationships is discussed in Section 7. Conclusions are drawn in Section 8.

2. TIME-REVERSED ENTROPY PER UNIT TIME

The concept of entropy per unit time has been introduced in the context of random processes by Shannon(6) and, later, by Kolmogorov(7) and Sinai(8) in dynamical systems theory. The phase space of the system is partitioned into disjoint cells $\mathcal{C}_\omega$ forming the partition $\mathcal{P}=\{\mathcal{C}_1,\mathcal{C}_2,\dots,\mathcal{C}_N\}$. These cells can be considered as the sets of microstates of the total system corresponding to the states $\omega\in\{1,2,\dots,N\}$ of some measuring device observing the system. The system we consider is open so that the measuring device observes only the degrees of freedom which are internal to the system but not the degrees of freedom of the environment. The cells of the partition thus establish a coarse graining which is fine enough to observe the internal state of the system up to some resolution but not the state of the environment. The symbolic sequence $\boldsymbol{\omega}=\omega_0\omega_1\cdots\omega_{n-1}$ defines a *path* or *history* which is a set of trajectories visiting the cells $\mathcal{C}_{\omega_0}\mathcal{C}_{\omega_1}\cdots\mathcal{C}_{\omega_{n-1}}$ at the successive times $t_k=k\tau$ $(k=0,1,\dots,n-1)$.

The multiple-time probability to observe the system in the successive coarse-grained states $\omega_0\omega_1...\omega_{n-1}$ at regular time intervals τ is given by

$$p(\boldsymbol{\omega})=p(\omega_0\omega_1\dots\omega_{n-1})=\mu\left(\mathcal{C}_{\omega_0}\cap\Phi^{-\tau}\mathcal{C}_{\omega_1}\cap\cdots\cap\Phi^{-(n-1)\tau}\mathcal{C}_{\omega_{n-1}}\right), \tag{1}$$

where μ is an invariant measure of the time evolution Φ^t, which is supposed to be a time-reversal symmetric automorphism. The invariant measure μ used in Eq. (1) is assumed to be the stationary probability of the NESS. The standard entropy per unit time of the partition $\mathcal{P}$ is defined as the mean decay rate of the multiple-time probability (1) as(11)

$$\begin{aligned}h(\mathcal{P}) &\equiv \lim_{n\to\infty}-\frac{1}{n\tau}\sum_{\boldsymbol{\omega}}p(\boldsymbol{\omega})\ln p(\boldsymbol{\omega})\\ &=\lim_{n\to\infty}-\frac{1}{n\tau}\sum_{\omega_0\omega_1\dots\omega_{n-1}}p(\omega_0\omega_1\dots\omega_{n-1})\ln p(\omega_0\omega_1\dots\omega_{n-1}).\end{aligned} \tag{2}$$

According to the Shannon–McMillan–Breiman theorem$^{(11,12)}$, the multiple-time probability indeed decays according to

$$p(\omega_0\omega_1\dots\omega_{n-1}) \sim e^{-n\tau h(\mathcal{P})} \tag{3}$$

for almost all the trajectories if the process is ergodic. The entropy per unit time characterizes the dynamical randomness of the time evolution observed with the measuring device. The supremum of the dynamical entropy (2) over all the possible partitions $\mathcal{P}$ defines the Kolmogorov Sinai (KS) entropy per unit time of dynamical systems theory.$^{(7,8,11)}$ According to Pesin's theorem, the KS entropy is given by the sum of positive Lyapunov exponents.$^{(13)}$ Therefore, the dynamical entropy does not vanish at equilibrium in chaotic systems contrary to the entropy production and no proportionality may exist between these concepts.

In order to compare with the properties of the time-reversed trajectories, we consider the *time-reversed path* (or *time-reversed history)*: $\boldsymbol{\omega}^{\mathrm{R}} = \omega_{n-1}\dots\omega_1\omega_0$. We are interested by the probability

$$p(\boldsymbol{\omega}^{\mathrm{R}}) \equiv p(\omega_{n-1}\cdots\omega_1\omega_0) \tag{4}$$

of occurrence of the time-reversed path in the process taking place in the NESS. We define the *time-reversed entropy per unit time* as

$$\begin{aligned} h^{\mathrm{R}}(\mathcal{P}) &\equiv \lim_{n\to\infty} -\frac{1}{n\tau}\sum_{\boldsymbol{\omega}} p(\boldsymbol{\omega}) \ln p(\boldsymbol{\omega}^{\mathrm{R}}) \\ &= \lim_{n\to\infty} -\frac{1}{n\tau} \sum_{\omega_0\omega_1\dots\omega_{n-1}} p(\omega_0\omega_1\dots\omega_{n-1}) \ln p(\omega_{n-1}\dots\omega_1\omega_0). \end{aligned} \tag{5}$$

We emphasize that the average is taken with respect to the probability of the forward path. We can say that the time-reversed entropy per unit time characterizes the dynamical randomness of the time-reversed paths in the forward process of the NESS.

Our purpose in the following sections is to prove that the entropy production $\Delta_{\mathrm{i}}^{\tau} S$ over a time interval τ in the stationary state of a Markovian random process is related to the difference between the time-reversed and standard dynamical entropies (5) and (2) according to the central result

$$\frac{1}{\tau}\Delta_{\mathrm{i}}^{\tau} S = h^{\mathrm{R}}(\mathcal{P}) - h(\mathcal{P}) \geqslant 0. \tag{6}$$

The nonnegativity of the entropy production is an immediate consequence of the fact that the difference $h^{\mathrm{R}} - h$ between Eqs. (5) and (2) is a relative entropy per unit time which is known to be nonnegative.(14)

3. TIME-DISCRETE MARKOV CHAINS

Here, we suppose that the NESS is described by a Markov chain of probability transitions $P(\omega|\omega')$ between the coarse-grained states ω and ω', with

$$\sum_{\omega'} P(\omega|\omega') = 1. \tag{7}$$

The probabilities $p_t(\omega)$ of the coarse-grained states ω evolve in time $t \in \mathbb{Z}$ according to the evolution equation

$$\sum_{\omega} p_t(\omega) P(\omega|\omega') = p_{t+1}(\omega'). \tag{8}$$

Typically, the probabilities $p_t(\omega)$ undergo a relaxation toward a stationary state such as a NESS or the equilibrium state where the stationary probabilities denoted by $p(\omega)$ satisfy

$$\sum_{\omega} p(\omega) P(\omega|\omega') = p(\omega'). \tag{9}$$

In the stationary state, the probability of the path $\boldsymbol{\omega} = \omega_0\omega_1 \ldots \omega_{n-1}$ of the Markov chain is given by

$$p(\boldsymbol{\omega}) = p(\omega_0\omega_1 \ldots \omega_{n-1}) = p(\omega_0) P(\omega_0|\omega_1) P(\omega_1|\omega_2) \cdots P(\omega_{n-2}|\omega_{n-1}) \tag{10}$$

because of the Markovian property, whereupon the entropy of this path over a time t is given by

$$\begin{aligned} H_t &\equiv -\sum_{\boldsymbol{\omega}} p(\boldsymbol{\omega}) \ln\, p(\boldsymbol{\omega}) && (11) \\ &= -\sum_{\omega} p(\omega) \ln p(\omega) - (n-1) \sum_{\omega\omega'} p(\omega) P(\omega|\omega') \ln\, P(\omega|\omega') && (12) \end{aligned}$$

and the entropy per unit time by

$$h = \lim_{t\to\infty} \frac{1}{t} H_t = -\sum_{\omega\omega'} p(\omega) P(\omega|\omega') \ln\, P(\omega|\omega') \tag{13}$$

which is the KS entropy of the Markov chain.$^{(11)}$

On the other hand, the time-reversed entropy over the time t is given by

$$H_t^{\rm R} \equiv -\sum_{\boldsymbol{\omega}} p(\boldsymbol{\omega}) \ln\, p(\boldsymbol{\omega}^{\rm R}) \tag{14}$$

$$= -\sum_{\omega} p(\omega) \ln p(\omega) - (n-1) \sum_{\omega\omega'} p(\omega) P(\omega|\omega') \ln\, P(\omega'|\omega) \tag{15}$$

and the time-reversed entropy per unit time of the Markov chain by

$$h^{\rm R} = \lim_{t\to\infty} \frac{1}{t} H_t^{\rm R} = -\sum_{\omega\omega'} p(\omega) P(\omega|\omega') \ln\, P(\omega'|\omega), \tag{16}$$

which differs from the KS entropy (13) by the permutation of the indices ω and ω' in the transition probability appearing in the logarithm.

The difference between both entropies per unit time (16) and (13) is equal to

$$h^{\rm R} - h = \frac{1}{2} \sum_{\omega\omega'} \left[p(\omega) P(\omega|\omega') - p(\omega') P(\omega'|\omega) \right] \ln \frac{p(\omega) P(\omega|\omega')}{p(\omega') P(\omega'|\omega)} \geqslant 0, \tag{17}$$

which is nonnegative.

In order to identify the right-hand member of Eq. (17) as the entropy production of the Markov chain over one time step, we introduce the entropy of the probability distribution $\{p_t(\omega)\}$ of the coarse-grained states

$$S_t \equiv -\sum_{\omega} p_t(\omega) \ln\, p_t(\omega). \tag{18}$$

The time evolution of the entropy is ruled by Eq. (8) which can be rewritten in the following form by using the condition (7) for the conservation of probability:

$$p_{t+1}(\omega') - p_t(\omega') = \sum_{\omega} \left[p_t(\omega) P(\omega|\omega') - p_t(\omega') P(\omega'|\omega) \right]. \tag{19}$$

Accordingly, the time variation of the entropy (18) can be split as

$$\Delta S_t \equiv S_{t+1} - S_t = \Delta_{\mathrm{e}} S_t + \Delta_{\mathrm{i}} S_t \tag{20}$$

into the *entropy flow*

$$\Delta_{\mathrm{e}} S_t \equiv -\sum_{\omega\omega'} p_t(\omega) P(\omega|\omega') \ln \frac{p_{t+1}(\omega) P(\omega|\omega')}{p_t(\omega) P(\omega'|\omega)} \tag{21}$$

and the *entropy production*

$$\Delta_{\mathrm{i}} S_t \equiv \frac{1}{2} \sum_{\omega\omega'} \left[p_t(\omega) P(\omega|\omega') - p_t(\omega') P(\omega'|\omega) \right] \ln \frac{p_t(\omega) P(\omega|\omega')}{p_t(\omega') P(\omega'|\omega)} \geqslant 0. \tag{22}$$

In a stationary state $p_t(\omega) = p(\omega)$, we notice that the entropy production (22) reduces to the expression in the right-hand side of Eq. (17) which proves our central result

$$\Delta_{\mathrm{i}} S = h^{\mathrm{R}} - h \geqslant 0 \tag{23}$$

for the case of Markov chains where $\tau = 1$.

4. TIME-CONTINUOUS JUMP PROCESSES

In this section, we consider jump processes ruled by the master equation

$$\frac{d}{dt} p_t(\omega') = \sum_{\omega} p_t(\omega) W_{\omega\omega'} \tag{24}$$

for the time-dependent probability $p_t(\omega)$ to find the system in the coarse grained state ω. The master equation conserves the total probability so that the transition rates $W_{\omega\omega'}$ satisfy the condition

$$\sum_{\omega'} W_{\omega\omega'} = 0. \tag{25}$$

Consequently, the master equation (24) can be written in the alternative form

$$\frac{d}{dt} p_t(\omega') = \sum_{\omega} \left[p_t(\omega) W_{\omega\omega'} - p_t(\omega') W_{\omega'\omega} \right]. \tag{26}$$

Examples of such jump processes include birth-and-death processes in stochastic chemical kinetics and population dynamics,(15–18) as well as kinetic processes in quantum field theory(19) and in quantum optics(20) where Eq. (24) is known as Pauli's master equation.(21)

The conditional probability that the system is in the coarse-grained state ω' while it was in the state ω at a time interval τ before is given by

$$P_\tau(\omega|\omega') = \left[e^{\mathsf{W}\tau}\right]_{\omega\omega'}, \tag{27}$$

where W is the matrix of transition rates $W_{\omega\omega'}$. If the time interval is small, we find that

$$P_\tau(\omega|\omega') = \delta_{\omega\omega'} + W_{\omega\omega'}\tau + O(\tau^2). \tag{28}$$

The jump process is Markovian so that the probability of observing the system in the succession of coarse-grained states $\omega_0\omega_1...\omega_{n-1}$ at regular time intervals $t_k = k\tau$ is given by

$$p(\omega_0\omega_1\ldots\omega_{n-1}) = p(\omega_0)P_\tau(\omega_0|\omega_1)P_\tau(\omega_1|\omega_2)\ldots P_\tau(\omega_{n-2}|\omega_{n-1}), \tag{29}$$

where the probabilities $\{p(\omega)\}$ form the stationary solution of the master equation (24)

$$\frac{d}{dt}p(\omega') = \sum_\omega p(\omega)W_{\omega\omega'} = 0. \tag{30}$$

Using Eq. (13), the entropy per unit time is here given by

$$h(\tau) = \left(\ln\frac{\mathrm{e}}{\tau}\right)\sum_{\omega\neq\omega'} p(\omega)W_{\omega\omega'} - \sum_{\omega\neq\omega'} p(\omega)W_{\omega\omega'}\ln W_{\omega\omega'} + O(\tau), \tag{31}$$

which is nothing else than the τ-entropy per unit time characterizing the dynamical randomness of the jump process, as obtained by Gaspard and Wang.(22) Using Eq. (16), we similarly obtain the time-reversed entropy per unit time as

$$h^{\mathrm{R}}(\tau) = \left(\ln\frac{\mathrm{e}}{\tau}\right)\sum_{\omega\neq\omega'} p(\omega)W_{\omega\omega'} - \sum_{\omega\neq\omega'} p(\omega)W_{\omega\omega'}\ln W_{\omega'\omega} + O(\tau), \tag{32}$$

which differs from the τ-entropy per unit time by the permutation of the indices ω and ω' of the transition rate inside the logarithm. The time reversed entropy per unit time also depends on the time interval τ as the τ-entropy per unit time. The reason for the logarithmic increase of these dynamical entropies at small values of τ is that the waiting time between the jumps is a continuous random variable τ which is exponentially distributed. As a consequence, the amount of randomness required to generate the process increases with the time resolution as $\ln(1/\tau)$. Now, the difference between both dynamical entropies (32) and (31) is given by

$$h^{\mathrm{R}}(\tau)-h(\tau)=\frac{1}{2}\sum_{\omega\neq\omega'}\left[p(\omega)W_{\omega\omega'}-p(\omega')W_{\omega'\omega}\right]\ln\frac{p(\omega)W_{\omega\omega'}}{p(\omega')W_{\omega'\omega}}+O(\tau), \tag{33}$$

where τ can be arbitrarily small.

On the other hand, in a NESS, the entropy flow (21) with the conditional probability (28) of the jump process is equal to

$$\frac{1}{\tau}\Delta_{\mathrm{e}}^{\tau}S=-\frac{1}{2}\sum_{\omega\neq\omega'}\left[p(\omega)W_{\omega\omega'}-p(\omega')W_{\omega'\omega}\right]\ln\frac{W_{\omega\omega'}}{W_{\omega'\omega}}+O(\tau) \tag{34}$$

and the entropy production (22) by

$$\frac{1}{\tau}\Delta_{\mathrm{i}}^{\tau}S=\frac{1}{2}\sum_{\omega\neq\omega'}\left[p(\omega)W_{\omega\omega'}-p(\omega')W_{\omega'\omega}\right]\ln\frac{p(\omega)W_{\omega\omega'}}{p(\omega')W_{\omega'\omega}}+O(\tau). \tag{35}$$

Equations (34) and (35) are the known expressions for the entropy flow and the entropy production of jump processes.(18,23)

Therefore, the difference (33) between the dynamical entropies is equal to the entropy production in the NESS

$$\frac{1}{\tau}\Delta_{\mathrm{i}}^{\tau}S=h^{\mathrm{R}}(\tau)-h(\tau)\geqslant 0 \tag{36}$$

in the limit where τ is arbitrarily small. We have thus proved our central result for the case of jump processes.

5. CONNECTION TO THE LEBOWITZ–SPOHN–MAES APPROACH

Recently, Lebowitz and Spohn(9) as well as Maes(10) have emphasized the fact that the probability of a path or history of a random process taking place in space and time is a Gibbsian measure. Gibbsian measures are characterized by an exponential decay of the path probability by increasing the volume of the space-time domain considered. This exponential decay is typically associated with a positive entropy per unit time or a positive entropy per unit time and unit volume.

In this framework, the following identity has been derived between the probabilities of the forward and backward paths

$$p(\boldsymbol{\omega}^{\mathrm{R}}) = e^{-Z_t(\boldsymbol{\omega})} \frac{p(\omega_t)}{p(\omega_0)} p(\boldsymbol{\omega}) \tag{37}$$

in terms of a quantity $Z_t(\boldsymbol{\omega})$ which measures the defect of detailed balance in the NESS.(9,10) For Markovian processes, this quantity is defined as

$$Z_t(\omega_0\omega_1 \ldots \omega_{n-1}) \equiv \ln \frac{P(\omega_0|\omega_1)P(\omega_1|\omega_2)\ldots P(\omega_{n-2}|\omega_{n-1})}{P(\omega_1|\omega_0)P(\omega_2|\omega_1)\ldots P(\omega_{n-1}|\omega_{n-2})}. \tag{38}$$

The statistical average of the quantity (38) grows linearly at a rate given by the entropy production in the NESS

$$\lim_{t\to\infty} \frac{1}{t}\langle Z_t\rangle = \frac{1}{\tau}\Delta_{\mathrm{i}}^{\tau} S. \tag{39}$$

If we take the logarithm of both sides of the identity (37) and average over the path probability of the NESS, we get

$$H_t^{\mathrm{R}} = \langle Z_t\rangle + H_t. \tag{40}$$

If we divide Eq. (40) by the time t and take the limit $t \to \infty$, we recover the identity

$$\frac{1}{\tau}\Delta_{\mathrm{i}}^{\tau} S = h^{\mathrm{R}} - h. \tag{41}$$

This result suggests that the formula (41) could extend to more general random processes.

6. REACTIVE PROCESSES

In this section, we apply the relationship established in the previous sections to nonequilibrium chemical reactions. On nanoscales, reactions are affected by molecular fluctuations, which requires a stochastic description. Reactive nanosystems are described in terms of the numbers of the molecules of the different chemical species involved in the reaction. These numbers undergo random jumps according to some network of reactions $\rho = 1, 2, \ldots, r$:

$$\sum_{i=1}^{a} \nu^i_{<\rho}\, \mathrm{A}^i + \sum_{j=1}^{c} \nu^j_{<\rho}\, \mathrm{X}^j \underset{k_{-\rho}}{\overset{k_{+\rho}}{\rightleftharpoons}} \sum_{i=1}^{a} \nu^i_{>\rho}\, \mathrm{A}^i + \sum_{j=1}^{c} \nu^j_{>\rho}\, \mathrm{X}^j. \tag{42}$$

Besides the intermediate chemical species $\{\mathrm{X}^j\}_{j=1}^{c}$, the chemical species $\{\mathrm{A}^i\}_{i=1}^{a}$ are supplied at constant concentrations by reservoirs, also called chemiostats. We suppose that the reactions take place in a homogeneous and isothermal system such as a continuously stirred tank reactor connected to the chemiostats. At the instant of a reactive event ρ, the numbers of molecules of the intermediate species jump by integer values given by the stoichiometric coefficients

$$\nu^j_\rho \equiv \nu^j_{>\rho} - \nu^j_{<\rho} = -\nu^j_{-\rho} \tag{43}$$

with $j = 1, 2, \ldots, c$. Such a reactive process is thus a particular case of time-continuous jump processes.

The probability $P(\boldsymbol{X}; t)$ that the reactor contains the molecular numbers $\boldsymbol{X}$ at time t is ruled by the master equation

$$\frac{d}{dt} P(\boldsymbol{X}; t) = \sum_{\rho=\pm 1}^{\pm r} \left[P(\boldsymbol{X} - \boldsymbol{\nu}_\rho; t)\, W_\rho(\boldsymbol{X} - \boldsymbol{\nu}_\rho | \boldsymbol{X}) - P(\boldsymbol{X}; t)\, W_{-\rho}(\boldsymbol{X} | \boldsymbol{X} - \boldsymbol{\nu}_\rho) \right]. \tag{44}$$

As proposed by Nicolis and coworkers,$^{(15-17)}$ the transition rates are given in dilute systems according to the mass-action law:

$$W_\rho(\boldsymbol{X} | \boldsymbol{X} + \boldsymbol{\nu}_\rho) = \Omega\, k_\rho \prod_{i=1}^{a} [\mathrm{A}^i]^{\nu^i_{<\rho}} \prod_{j=1}^{c} \frac{X^j}{\Omega} \frac{X^j - 1}{\Omega} \frac{X^j - 2}{\Omega} \cdots \frac{X^j - \nu^j_{<\rho} + 1}{\Omega}, \tag{45}$$

($\rho = \pm 1, \pm 2, \ldots, \pm r$) where Ω is an extensivity parameter proportional to the total number of particles in the reactor, k_ρ is the reaction coefficient, and $[\mathrm{A}^i]$ is the concentration of the species A^i from the chemiostats.

If the system is in the state $\boldsymbol{X}$, the next reaction ρ occurs with the probability

$$P_\rho = \frac{W_\rho(\boldsymbol{X}|\boldsymbol{X}+\boldsymbol{\nu}_\rho)}{\sum_{\rho'=\pm 1}^{\pm r} W_{\rho'}(\boldsymbol{X}|\boldsymbol{X}+\boldsymbol{\nu}_{\rho'})} \tag{46}$$

and the corresponding waiting time has the exponential probability distribution of density

$$\mathcal{P}(T) = \kappa \exp(-\kappa T) \quad \text{with} \quad \kappa = \sum_{\rho'=\pm 1}^{\pm r} W_{\rho'}(\boldsymbol{X}|\boldsymbol{X}+\boldsymbol{\nu}_{\rho'}) \tag{47}$$

which defines Gillespie's algorithm(24,25) for the simulation of the reactive process.

A *path* or *history* of the system is a succession of molecular numbers $\{\boldsymbol{X}_l\}$ and reactive events $\{\rho_l\}$ occurring at random times $\{t_l\}$:

$$\mathcal{X}(t) = \boldsymbol{X}_0 \xrightarrow{\rho_1} \boldsymbol{X}_1 \xrightarrow{\rho_2} \boldsymbol{X}_2 \xrightarrow{\rho_3} \cdots \xrightarrow{\rho_m} \boldsymbol{X}_m. \tag{48}$$

The successive molecular numbers and jump times are related by

$$\begin{aligned} \boldsymbol{X}_l &= \boldsymbol{X}_{l-1} + \boldsymbol{\nu}_{\rho_l}, \\ t_l &= t_{l-1} + T_l \end{aligned} \tag{49}$$

with $l = 1, 2, \ldots, m$, where the waiting times T_l till the next jump are the continuous random variables which are exponentially distributed according to Eq. (47).

Since the path (48) is specified by the molecular numbers $\{\boldsymbol{X}_l\}$ and the reactions $\{\rho_l\}$, the symbols used in the previous sections should be defined as $\omega = \boldsymbol{X} \xrightarrow{\rho} \boldsymbol{X}'$. If the reactive process is stroboscopically observed with the sampling time τ, the probability of the path (48) with $t = n\tau$ is given by

$$\begin{aligned} p(\omega_0\omega_1 \ldots \omega_{n-1}) &= p_{\mathrm{st}}[\mathcal{X}(t)] = P_{\mathrm{st}}(\boldsymbol{X}_0)\, P_\tau(\boldsymbol{X}_0 \xrightarrow{\rho_1} \boldsymbol{X}_1) \\ &\quad \times P_\tau(\boldsymbol{X}_1 \xrightarrow{\rho_2} \boldsymbol{X}_2) \cdots P_\tau(\boldsymbol{X}_{n-1} \xrightarrow{\rho_n} \boldsymbol{X}_n), \end{aligned} \tag{50}$$

where $\rho \in \{0, \pm 1, \pm 2, \ldots, \pm r\}$. Here, we adopt the convention that $\rho = 0$ in the case where no reactive event occurs in the time interval τ. The molecular numbers in the multiple-time probability are now defined by $\boldsymbol{X}_k = \boldsymbol{X}(k\tau)$ with $k = 0, 1, 2, \ldots, n$. The conditional probabilities are given in terms of the transition rates as

$$P_\tau(\boldsymbol{X} \xrightarrow{\rho} \boldsymbol{X}') = \begin{cases} W_\rho(\boldsymbol{X}|\boldsymbol{X}')\,\tau + O(\tau^2) & \text{if } \rho \neq 0, \\ 1 - \sum_{\rho=\pm 1}^{\pm r} W_\rho(\boldsymbol{X}|\boldsymbol{X}')\,\tau + O(\tau^2) & \text{if } \rho = 0. \end{cases} \tag{51}$$

Accordingly, the τ-entropy per unit time (31) is here given by

$$\begin{aligned} h(\tau) = {}& \left(\ln \frac{\mathrm{e}}{\tau}\right) \sum_{\rho \boldsymbol{X} \boldsymbol{X}'} P_{\mathrm{st}}(\boldsymbol{X})\, W_\rho(\boldsymbol{X}|\boldsymbol{X}') \\ & - \sum_{\rho \boldsymbol{X} \boldsymbol{X}'} P_{\mathrm{st}}(\boldsymbol{X})\, W_\rho(\boldsymbol{X}|\boldsymbol{X}') \ln W_\rho(\boldsymbol{X}|\boldsymbol{X}') + O(\tau) \end{aligned} \tag{52}$$

and the time-reversed τ-entropy per unit time (32) by

$$\begin{aligned} h^{\mathrm{R}}(\tau) = {}& \left(\ln \frac{\mathrm{e}}{\tau}\right) \sum_{\rho \boldsymbol{X} \boldsymbol{X}'} P_{\mathrm{st}}(\boldsymbol{X})\, W_\rho(\boldsymbol{X}|\boldsymbol{X}') \\ & - \sum_{\rho \boldsymbol{X} \boldsymbol{X}'} P_{\mathrm{st}}(\boldsymbol{X})\, W_\rho(\boldsymbol{X}|\boldsymbol{X}') \ln W_{-\rho}(\boldsymbol{X}'|\boldsymbol{X}) + O(\tau). \end{aligned} \tag{53}$$

Their difference no longer contains the terms in $\ln(\mathrm{e}/\tau)$:

$$\begin{aligned} h^{\mathrm{R}}(\tau) - h(\tau) = {}& \frac{1}{2} \sum_{\rho \boldsymbol{X} \boldsymbol{X}'} \left[P_{\mathrm{st}}(\boldsymbol{X})\, W_\rho(\boldsymbol{X}|\boldsymbol{X}') - P_{\mathrm{st}}(\boldsymbol{X}')\, W_{-\rho}(\boldsymbol{X}'|\boldsymbol{X})\right] \\ & \times \ln \frac{W_\rho(\boldsymbol{X}|\boldsymbol{X}')}{W_{-\rho}(\boldsymbol{X}'|\boldsymbol{X})} + O(\tau). \end{aligned} \tag{54}$$

In a NESS, the probabilities are constant in time: $(d/dt)P_{\mathrm{st}}(\boldsymbol{X}) = 0$. As a consequence of the master equation (44), we find that

$$\begin{aligned} h^{\mathrm{R}}(\tau) - h(\tau) = {}& \frac{1}{2} \sum_{\rho \boldsymbol{X} \boldsymbol{X}'} \left[P_{\mathrm{st}}(\boldsymbol{X})\, W_\rho(\boldsymbol{X}|\boldsymbol{X}') - P_{\mathrm{st}}(\boldsymbol{X}')\, W_{-\rho}(\boldsymbol{X}'|\boldsymbol{X})\right] \\ & \times \ln \frac{P_{\mathrm{st}}(\boldsymbol{X})\, W_\rho(\boldsymbol{X}|\boldsymbol{X}')}{P_{\mathrm{st}}(\boldsymbol{X}')\, W_{-\rho}(\boldsymbol{X}'|\boldsymbol{X})} + O(\tau) \geqslant 0. \end{aligned} \tag{55}$$

In the limit $\tau \to 0$, the right-hand side is thus equal to the known expression for the entropy production for reactive processes,(23) which proves in this case the relationship (6)

$$h^{\mathrm{R}}(\tau) - h(\tau) = \frac{1}{\tau} \Delta_{\mathrm{i}}^{\tau} S \geqslant 0 \tag{56}$$

between the entropies per unit time and the entropy production of chemical reactions.

7. DISCUSSION

The purpose of this section is to comment on the formula (6) between the entropy production and the direct and time-reversed entropies per unit time and its possible further applications.

At the microscopic level of description, the entropies per unit time are quantities of the order of magnitude of the sum of positive Lyapunov exponents as suggested by Pesin's theorem.(13) Therefore, the entropies per unit time are typically of the order of the inverse of a kinetic time scale multiplied by the Avogadro number. Taking the *difference* between two such large numbers as done in Eq. (6) allows us to obtain a quantity having the order of magnitude of the inverse of a hydrodynamic time scale as it is the case for the entropy production. In this regard, the relationship (6) is similar to the escape-rate formulae, which relate the transport coefficients to the difference between the sum of positive Lyapunov exponents and the Kolmogorov–Sinai entropy per unit time in open systems with absorbing boundary conditions.(2,4,5) The formula (6) thus belongs to the same family of large-deviation relationships as the escape-rate formulae of refs. 2, 4, 5.

Furthermore, the formula (6) can also be applied to deterministic thermostated models of particles moving in external fields.(26–30) In these models, a nonHamiltonian force is added to compensate the heating effect of the external fields so that the system can reach a nonequilibrium steady-state. The nonHamiltonian force preserves the time-reversal symmetry but violates Liouville's theorem of phase-space volume conservation, as a consequence of which there is a nonvanishing mean contraction rate of the phase-space volumes in the nonequilibrium steady-state of these models. In some models such as the Gaussian thermostated Lorentz gas,(26,27) the mean contraction rate has been identified with the entropy production in the nonequilibrium steady-state. In such dynamical systems, the nonequilibrium steady-state is described by a SRB invariant probability measure.(29,30) For a partition into arbitrarily small phase-space cells, the entropy per unit time becomes equal to the KS entropy which is given by the sum of positive Lyapunov exponents according to Pesin's theorem

$$h = \sum_{\lambda_i > 0} \lambda_i . \tag{57}$$

On the other hand, the time-reversed entropy per unit time is given according to Eq. (5) by the decay of the multiple-time probability along a path running backward in time. For a partition into arbitrarily small phase-space cells, the rate of this decay is equal to the sum of the absolute values of the negative Lyapunov exponents

$$h^{\mathrm{R}} = \sum_{\lambda_i < 0} |\lambda_i| = - \sum_{\lambda_i < 0} \lambda_i . \tag{58}$$

The formula (6) shows that the entropy production is then equal to minus the sum of all the Lyapunov exponents and, thus, to the mean phase-space contraction rate

$$\frac{1}{\tau} \Delta_{\mathrm{i}}^{\tau} S = h^{\mathrm{R}} - h = - \sum_{\lambda_i < 0} \lambda_i - \sum_{\lambda_i > 0} \lambda_i = - \sum_{i} \lambda_i \tag{59}$$

as expected. It should here be noticed that systems exist in which the entropy production may not be identified with a phase-space contraction rate. This includes the systems with stochastic thermostats,(31) as well as the systems thermostated by deterministic scattering.(32,33) The formula (6) can be useful to extend the previously known relationship (59) to such more general systems.

A further example of application is to the process of erasure of a computer memory.(34,35) We suppose that the computer memory contains a long arbitrary sequence of bits 0 or 1 and that the erasing device successively deletes them at a rate of one bit per unit time. This erasing process is without production of information and its entropy per unit time is thus vanishing: $h = 0$. In contrast, the time-reversed process produces information at a rate of one new bit per unit time so that the time-reversed entropy per unit time is equal to $h^{\mathrm{R}} = \ln 2$. According to Eq. (6), the entropy production of the erasing process is equal to $\Delta_{\mathrm{i}} S = h^{\mathrm{R}} - h = \ln 2$ per bit in agreement with Landauer's and Bennett's conclusion.(34,35)

The formula (6) can be applied to very general situations because the entropies per unit time can be defined for broad classes of nonequilibrium processes.

8. CONCLUSIONS

In this paper, we have introduced the concept of time-reversed entropy per unit time in analogy with the entropy per unit time known since the work by Shannon,(6) Kolmogorov,(7) and Sinai.(8) Thanks to this new concept, we have shown that, in Markovian random processes, the entropy production is equal to the difference between the time-reversed and the standard entropies per unit time.

The standard entropy per unit time is known to characterize the dynamical randomness of the forward paths or histories of a stochastic process. On the other hand, the time-reversed entropy per unit time characterizes the dynamical randomness of the backward paths or histories with respect to their corresponding forward paths. We have here shown that, out of equilibrium, the difference between the dynamical randomnesses of the forward and backward paths or histories turns out to be directly related to the entropy production. Since the difference between both entropies per unit time is a relative entropy (per unit time) which is a quantity known to be positive,(14) our result is in agreement with the second law of thermodynamics. Our result provides an interpretation of the entropy production as a manifestation of the time-reversal symmetry breaking on the dynamical randomness of the microscopic process. The time-reversal symmetry breaking is caused by the flux boundary conditions imposed by the nonequilibrium constraints at the borders of the system. These nonequilibrium boundary conditions select trajectories with a probability weight and a dynamical randomness which are not time-reversal symmetric so that there is a positive entropy production in the NESS.

We notice that the identity (6) has been obtained for Markovian stochastic processes, which leaves open the question of its status with respect to the underlying microscopic dynamics. To answer such a question, we would need to define the nonequilibrium steady state at the microscopic level of description as already done for simple models such as the multibaker map and the Lorentz gases in refs. 1 and 2. Furthermore, we should use a definition of entropy and entropy production which is appropriate for nonequilibrium steady states of volume-preserving deterministic dynamics.(36,37) We hope to report on this issue in a future publication.

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