

Three faces of the second law. I. Master equation formulation

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We propose a formulation of stochastic thermodynamics for systems subjected to nonequilibrium constraints (i.e. broken detailed balance at steady state) and furthermore driven by external time-dependent forces. A splitting of the second law occurs in this description leading to three second-law-like relations. The general results are illustrated on specific solvable models. The present paper uses a master equation based approach.

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I. INTRODUCTION

The second law of thermodynamics specifies that the total entropy of an isolated macroscopic system cannot decrease in time. This statement applies to the stages of the evolution in which the entropy is well defined. For example, for a system in equilibrium at initial and final times, the final entropy will be larger than the initial one, even though the entropy may not be well defined during the intermediate evolution. However, it is often a very good approximation to assume that the system is in a state of local equilibrium, so that the entropy is well defined at any stage of the process. For example, linear irreversible thermodynamics is built on such an assumption, allowing the use of the Gibbs relation to define entropy locally in terms of the slow conserved quantities (for example, momentum, energy, and concentration of the constituents) [1–3]. The second law can then be reformulated as the non-negativity of the irreversible entropy production (EP) $\dot{S}_i(t) \geq 0$ [4,5],

$$\dot{S}(t) = \dot{S}_e(t) + \dot{S}_i(t), \quad (1)$$

where $\dot{S}(t)$ is the entropy change of the considered subpart and $\dot{S}_e(t)$ is the entropy flow to the environment. In some cases, the environment is idealized as being one or more reservoirs without internal dissipation, so that their entropy change is equal to minus the exchange term: $\dot{S}_r(t) = -\dot{S}_e(t)$. For a single heat reservoir, this entropy exchange is given by the energy inflow divided by its temperature. In the sequel, we will be mainly interested in this situation, with the subsystem of interest, henceforth called the system, in contact with an environment consisting of one or more ideal reservoirs. The irreversible EP in this system is then equal to the total EP $\dot{S}_{tot}(t) \equiv \dot{S}_i(t) \geq 0$.

In more recent developments [6–33], it has been realized that one can formulate thermodynamics for small systems incorporating the effect of the fluctuations. These developments can be seen as the continuation of the pioneering work started by Onsager and co-workers [34–37], with as intermediate steps the fluctuation-dissipation theorem [38], the theory of Gaussian stochastic processes and linear response [39,40], and Green-Kubo relations [41,42]. The essential in-

redient is to guarantee the consistency of the statistical irreversible laws on the system dynamics with the reversibility of the equilibrium reservoirs statistics. In this new thermodynamics, also called stochastic thermodynamics [43,44], the system is described by a probability distribution p_m evolving according to a Markovian master equation. The exchange of energy (heat) or particles with the environment and the other thermodynamic quantities associated to the system states m become stochastic variables. The rates associated to each reservoir satisfy the property of local detailed balance reminiscent of the fact that they always remain at equilibrium. The system entropy is defined using the Shannon expression $S = -\sum_m p_m \ln p_m$ and entropy balance equations of the usual form can be derived via the identification of a non-negative EP consistent with macroscopic nonequilibrium thermodynamics. A minimum EP theorem can also be proved [6,8,43,45–47].

More recently, it was realized that one can study stochastic trajectory-dependent quantities. This is obviously the case for the energy, which is a well-defined mechanical quantity even for single trajectories. For example, an explicit formulation of the first law, conservation of total energy, was given for the stochastic trajectory of a Langevin equation by Sekimoto [7] (see also [48]). The stochastic exchange of energy with idealized reservoirs also allows us to identify the stochastic entropy flow into these reservoirs and to study its statistical properties. This led to the discovery of the celebrated fluctuation theorem: the probability distribution for the cumulated change in stochastic reservoir entropy Δs_r for a nonequilibrium steady state obeys the symmetry relation $P(\Delta s_r)/P(-\Delta s_r) \sim \exp(\Delta s_r)$ for asymptotically large times. We will use henceforth the notation lowercase s for entropic contributions associated to a given stochastic trajectory, in contrast to ensemble average entropies denoted by a capital letter S . This result was first proven for thermostated systems (the main trust of this work is however the development of equilibriumlike statistical-mechanical concepts for dissipative systems [9–12]), followed by derivations for Langevin and master equations [15,17], and for Hamiltonian dynamics [23,24]. The asymptotic nature of the result was linked to the large deviation properties of the characteristic function, and in particular to those of the currents. Implications include Onsager symmetry and beyond [49] and universal features of

efficiency of thermal machines at maximum power [50,51]. Very much in the spirit of the fluctuation theorem, Jarzynski [13,14] and Crooks [16,20,21] obtained the work theorem (see also [52–54]). They found that the probability distribution for the work w performed on a driven system, initially in canonical equilibrium at a specific inverse temperature β^{-1} , obeys the relation $P(w)/\bar{P}(-w)=\exp\{\beta(w-\Delta F)\}$. The overbar corresponds to the probability distribution for the time-reversed experiment. If one assumes that, at the end of the driving, the system relaxes back to equilibrium (at inverse temperature β^{-1}) then $\beta(w-\Delta F)$, the so-called dissipated heat, is equal to the change in total entropy Δs_{tot} of system plus reservoir, so that the work theorem becomes a fluctuation theorem for the change in total entropy Δs_{tot} , $P(\Delta s_{tot})/\bar{P}(-\Delta s_{tot})=\exp(\Delta s_{tot})$ [23,25]. Note that this result is valid for all times. The previous asymptotic fluctuation theorem can in fact be seen as a special case if one assumes that, aside from an initial transient, the steady state can be maintained for long enough times by appropriate driving, so that $\Delta s_{tot}=\Delta s+\Delta s_r\approx\Delta s_r$. The focus on the asymptotic form and the accent on large deviation properties are in our opinion a somewhat misleading representation of the fluctuation theorem. This form arises from the neglect of the system's entropy (the so-called boundary term), for which no readily acceptable interpretation was deemed to exist at the time of the first formulations of the fluctuation theorem. Furthermore, the validity of the theorem is typically compromised for a system with unbounded energy [55–59], which is of course more of the rule rather than the exception. We note however that current fluctuation theorems [27,28] do require the long-time limit since currents are related to the Δs_r part of the entropy.

A further advance consisted of the formulation of the equivalence of the second law at the stochastic level. This required the identification of a trajectory-dependent system entropy. Even though the idea is well known in information theory, where $-\ln p_m$ is the surprise at observing outcome m when its probability is p_m , it took some time before Seifert [25] identified this quantity as the appropriate stochastic system entropy, $s(t)=-\ln p_{m(t)}(t)$. Note that it depends on the actual state $m(t)$ of the considered trajectory at the considered time, as well as on the probability for this state, which itself is in general time dependent. By taking this term into account, the asymptotic fluctuation theorem could be replaced with a fluctuation theorem for the total entropy, which is valid for all times, just as the work theorem of Jarzynski and Crooks. For driven systems in contact with a single reservoir and subjected to a nonconservative force keeping the steady states out of equilibrium, Oono and Paniconi [60] discussed an alternative way of splitting the EP by introducing the excess entropy and housekeeping heat. This led to the formulation of two other fluctuation theorems, namely, the one derived by Hatano and Sasa [22] (for system entropy plus excess entropy) and the other one derived by Speck and Seifert [61] (for the housekeeping heat). While both assume single reservoirs, the former is further restricted to transitions between nonequilibrium steady states.

To close this introductory discussion, we turn to a recent development [33] (see also [29–31,62,63]), which provides a

clarifying and unifying approach of the various fluctuation and work theorems. The total stochastic EP Δs_{tot} is the sum of two constitutive parts, namely, a so-called adiabatic Δs_a and a nonadiabatic Δs_{na} contribution. Each of these contributions corresponds to the two basic ways that a system can be brought out of equilibrium: by applying steady nonequilibrium constraints (adiabatic contribution) or by driving (nonadiabatic contribution). Note that the term “adiabatic” is used here, not in its meaning referring to the absence of heat exchange, but in the meaning of instantaneous relaxation to the steady state. The crucial point is the observation that each of these contributions obeys a separate fluctuation relation, namely [33],

$$\frac{P(\Delta s_{tot})}{\bar{P}(-\Delta s_{tot})}=e^{\Delta s_{tot}}, \quad (2)$$

$$\frac{P(\Delta s_{na})}{\bar{P}^+(-\Delta s_{na})}=e^{\Delta s_{na}}, \quad \frac{P(\Delta s_a)}{P^+(-\Delta s_a)}=e^{\Delta s_a}. \quad (3)$$

The superscript + refers to the adjoint dynamics (also called dual or reversal [21,62]). The aforementioned fluctuation theorems of Hatano and Sasa and of Speck and Seifert are special cases of the fluctuation theorem for Δs_{na} and Δs_a , respectively, when single reservoirs and transitions between steady states are considered. To stress the special status of these theorems, we notice that they arise because of the two available operations to gauge the amount of time-symmetry breaking, namely, time reversal of the driving (overbar: $-$) and the time reversal of the nonequilibrium boundary conditions (superscript: $+$). Applying each of them separately, or both, leads to the three different contributions for the EP.

The above fluctuation theorems imply that the total, adiabatic, and nonadiabatic entropy changes have to be non-negative, each taken separately,

$$\Delta S_{tot}=\langle\Delta s_{tot}\rangle\geq 0, \quad (4)$$

$$\Delta S_{na}=\langle\Delta s_{na}\rangle\geq 0, \quad \Delta S_a=\langle\Delta s_a\rangle\geq 0. \quad (5)$$

This suggests that the second law can in fact be split in two. There are thus three faces to the second law: the increase in the average total entropy, the increase in the average adiabatic entropy, and the increase in the average nonadiabatic entropy. Our purpose here is to clarify and document further the physical properties and the meaning of this remarkable result. In this paper we will focus on the implications for a description in terms of a master equation. The next paper [64] deals with the corresponding results for Langevin and Fokker-Planck dynamics.

II. MASTER EQUATION

A. Entropy balance

We first review and extend the entropy balance equation derived previously for a Markovian process [6,8,29,65]. Our starting point is the following master equation:

$$\dot{p}_m(t) = \sum_{m'} W_{m,m'} p_{m'}(t), \quad (6)$$

where the rate matrix satisfies

$$\sum_m W_{m,m'} = 0. \quad (7)$$

The transitions between states m can be due to different mechanisms ν . Furthermore, these rates can be time dependent via a control variable λ . We thus have

$$W_{m,m'} = W_{m,m'}(\lambda_t) = \sum_\nu W_{m,m'}^{(\nu)}(\lambda_t). \quad (8)$$

When the control variable λ_t changes in time we say that the system is externally driven. For rates that are “frozen” at the values $W_{m,m'}^{(\nu)}(\lambda)$, there is a corresponding stationary distribution, $p_m^{st}(\lambda)$, which we suppose to be unique (i.e., the rate matrix is irreducible) and which will always eventually be reached by the system. It is given by the normalized right eigenvector of zero eigenvalue of the transition matrix,

$$\sum_{m'} W_{m,m'}(\lambda) p_{m'}^{st}(\lambda) = 0. \quad (9)$$

Let us now investigate the time dependence of the system’s Shannon entropy (Boltzmann constant $k_B=1$),

$$S(t) = - \sum_m p_m(t) \ln p_m(t). \quad (10)$$

Using Eqs. (6) and (7) and omitting for compactness of notation the dependences of p_m on t and of W on λ_t , we find

$$\begin{aligned} \dot{S}(t) &= - \sum_m \dot{p}_m \ln p_m \\ &= - \sum_{m,m',\nu} W_{m,m'}^{(\nu)} p_{m'} \ln \frac{p_m}{p_{m'}} \\ &= \frac{1}{2} \sum_{m,m',\nu} \{W_{m,m'}^{(\nu)} p_{m'} - W_{m',m}^{(\nu)} p_m\} \ln \frac{p_{m'}}{p_m} \\ &= \frac{1}{2} \sum_{m,m',\nu} \{W_{m,m'}^{(\nu)} p_{m'} - W_{m',m}^{(\nu)} p_m\} \ln \frac{W_{m,m'}^{(\nu)} p_{m'}}{W_{m',m}^{(\nu)} p_m} \\ &\quad + \frac{1}{2} \sum_{m,m',\nu} \{W_{m,m'}^{(\nu)} p_{m'} - W_{m',m}^{(\nu)} p_m\} \ln \frac{W_{m',m}^{(\nu)}}{W_{m,m'}^{(\nu)}}. \end{aligned} \quad (11)$$

It is revealing to introduce the fluxes $J_{m,m'}^{(\nu)}$, and corresponding forces $X_{m,m'}^{(\nu)}$,

$$J_{m,m'}^{(\nu)}(t) = W_{m,m'}^{(\nu)}(\lambda_t) p_{m'}(t) - W_{m',m}^{(\nu)}(\lambda_t) p_m(t), \quad (12)$$

$$X_{m,m'}^{(\nu)}(t) = \ln \frac{W_{m,m'}^{(\nu)}(\lambda_t) p_{m'}(t)}{W_{m',m}^{(\nu)}(\lambda_t) p_m(t)}. \quad (13)$$

We can rewrite the master equation (6) as

$$\dot{p}_m(t) = \sum_{m',\nu} J_{m,m'}^{(\nu)}(t) = \sum_{m'} J_{m,m'}(t), \quad (14)$$

where we defined

$$J_{m,m'}(t) = \sum_\nu J_{m,m'}^{(\nu)}(t). \quad (15)$$

The system’s EP can thus be rewritten under the familiar form of irreversible thermodynamics,

$$\dot{S}(t) = \dot{S}_e(t) + \dot{S}_i(t). \quad (16)$$

The quantity

$$\begin{aligned} \dot{S}_e(t) &= \frac{1}{2} \sum_{m,m',\nu} J_{m,m'}^{(\nu)}(t) \ln \frac{W_{m',m}^{(\nu)}(\lambda_t)}{W_{m,m'}^{(\nu)}(\lambda_t)} \\ &= \sum_{m,m',\nu} W_{m,m'}^{(\nu)}(\lambda_t) p_{m'}(t) \ln \frac{W_{m',m}^{(\nu)}(\lambda_t)}{W_{m,m'}^{(\nu)}(\lambda_t)} \end{aligned} \quad (17)$$

is the entropy flow and the positive quantity

$$\begin{aligned} \dot{S}_i(t) &= \sum_{m,m',\nu} W_{m,m'}^{(\nu)}(\lambda_t) p_{m'}(t) \ln \frac{W_{m,m'}^{(\nu)}(\lambda_t) p_{m'}(t)}{W_{m',m}^{(\nu)}(\lambda_t) p_m(t)} \\ &= \frac{1}{2} \sum_{m,m',\nu} J_{m,m'}^{(\nu)}(t) X_{m,m'}^{(\nu)}(t) \\ &\geq 0 \end{aligned} \quad (18)$$

is identified as the EP. The latter is zero if and only if the condition of detailed balance is satisfied,

$$W_{m,m'}^{(\nu)}(\lambda) p_{m'} = W_{m',m}^{(\nu)}(\lambda) p_m. \quad (19)$$

We note an important property of the EP. If all the relevant processes ν causing transitions between states m are not correctly identified (for example, if one only identifies a subclass of these processes) the EP will be underestimated. Indeed, using the logarithmic-sum inequality (cf. Theorem 2.7.1 of [66]), it follows that (see also [52–54])

$$\begin{aligned} \dot{S}_i(t) &= \sum_{m,m',\nu} W_{m,m'}^{(\nu)}(\lambda_t) p_{m'}(t) \ln \frac{W_{m,m'}^{(\nu)}(\lambda_t) p_{m'}(t)}{W_{m',m}^{(\nu)}(\lambda_t) p_m(t)} \\ &\geq \sum_{m,m'} W_{m,m'}(\lambda_t) p_{m'}(t) \ln \frac{W_{m,m'}(\lambda_t) p_{m'}(t)}{W_{m',m}(\lambda_t) p_m(t)} \\ &\geq 0. \end{aligned} \quad (20)$$

B. Thermodynamic interpretation

The above derivations and statements can be viewed as purely mathematical in nature and can be applied to any system described by a master equation. The connection with physics is made by associating with each mechanism ν responsible for the transitions between system states a group of variables each separately at its own equilibrium or in other words idealized reservoirs with well-defined thermodynamic

variables (e.g., temperature or chemical potential). The transitions between states m due to different mechanisms ν can, for example, correspond to exchange of heat with different reservoirs or the change in number of particles due to different chemical reactions. As a result the transition rates associated to a given mechanism ν need to obey the condition of local detailed balance,

$$W_{m,m'}^{(\nu)}(\lambda_t) p_{m'}^{eq}(\lambda_t, \nu) = W_{m',m}^{(\nu)}(\lambda_t) p_m^{eq}(\lambda_t, \nu), \quad (21)$$

where the equilibrium distribution $p^{eq}(\lambda_t, \nu)$ is the stationary distribution that would be reached by the system if only a single mechanism ν were present and for the frozen value of the control variable $\lambda = \lambda_t$. In case multiple mechanisms are present, each reservoir tries unsuccessfully to impose its equilibrium distribution on the system resulting in a stationary distribution that does not satisfy the detailed balance condition (19) except if their thermodynamical properties are identical, making the distinction between the various mechanisms useless. As we have seen in Eq. (20), an incorrect identification of the various reservoirs would underestimate the EP and could lead one to believe that a system is at equilibrium while it is not [8]. The assumption that the same expressions for the transition probabilities in Eq. (21) can be used when the control parameter becomes time dependent is based on an assumption that the idealized reservoirs relax infinitely fast to their equilibrium compared to the time scales of the system dynamics.

By an argument of physical consistency, it follows that $\dot{S}_i(t)$ is also equal to the total EP $\dot{S}_{tot}(t)$ in system plus environment. Indeed, since one implicitly assumes that the environment remains at equilibrium at all times using Eq. (21), it does not have an internal EP of its own. Otherwise, the above description in terms of the system alone is not complete, and one needs to include the description of the irreversible processes taking place in the environment. For the same reason, the entropy flow is equal to minus the entropy increase in the reservoir $\dot{S}_e(t) = -\dot{S}_r(t)$. The microscopic origin of these relations has been recently clarified [67].

In order to make the thermodynamic interpretation of the stochastic dynamics transparent, we now explicitly evaluate the various entropies for multiple heat reservoirs satisfying local detailed balance with respect to the canonical equilibrium distribution at the inverse temperature of the corresponding reservoir, i.e., Eq. (21) becomes

$$\frac{W_{m,m'}^{(\nu)}(\lambda)}{W_{m',m}^{(\nu)}(\lambda)} = \exp\{-\beta^{(\nu)}[\epsilon_m(\lambda) - \epsilon_{m'}(\lambda)]\}, \quad (22)$$

where $\epsilon_m(\lambda)$ is the energy of the system when in the state m for the value λ of the control variable. We note that in order to make the connection between the system Shannon entropy (10) and the true thermodynamic entropy, one might have to add a contribution $\sum_m S_m p_m(t)$ to the entropy, where S_m is the entropy of each level m [32,68,69]. However, for simplicity, we now assume that the index m refers to the nondegenerate microscopic state of the system (i.e., $S_m=0$). It immediately follows from Eq. (22) that the entropy flow (17) takes on the familiar thermodynamic form of heat flux over temperature,

$$\dot{S}_e(t) = \sum_{\nu} \beta^{(\nu)} \dot{Q}^{(\nu)}(t), \quad (23)$$

where the heat from the ν reservoir is given by

$$\dot{Q}^{(\nu)}(t) = \sum_{m,m'} J_{m,m'}^{(\nu)}(t) \epsilon_{m'}(\lambda). \quad (24)$$

Since the system energy is obviously given by

$$E(t) = \sum_m \epsilon_m(\lambda) p_m(t), \quad (25)$$

we find from the first principle of thermodynamics (energy conservation),

$$\dot{E}(t) = \dot{W}(t) + \sum_{\nu} \dot{Q}^{(\nu)}(t), \quad (26)$$

that the work is given by

$$\dot{W}(t) = \sum_m \dot{\epsilon}_m(\lambda) p_m. \quad (27)$$

This illustrates that the local detailed balance conditions with the reservoirs (22) lead to a proper formulation of the first [Eq. (26)] and second [Eq. (16)] principles of thermodynamics. We note that it is possible to include particle exchanges with the reservoirs [51]. In the latter case, work can be non-zero even in the absence of driving.

We should finally mention that the system could also be driven out of equilibrium by a nonconservative force instead of different reservoirs. In this case, the local detailed balance condition (21) is not satisfied and even in the presence of a single reservoir, the detailed balance condition (19) will not be satisfied at steady state.

C. Adiabatic and nonadiabatic entropy balance

We next note that the force X (13) can be split in an adiabatic contribution A and a nonadiabatic contribution N ,

$$X_{m,m'}^{(\nu)}(t) = A_{m,m'}^{(\nu)}(\lambda_t) + N_{m,m'}(t), \quad (28)$$

$$A_{m,m'}^{(\nu)}(\lambda_t) = \ln \frac{W_{m,m'}^{(\nu)}(\lambda_t) p_{m'}^{st}(\lambda_t)}{W_{m',m}^{(\nu)}(\lambda_t) p_m^{st}(\lambda_t)}, \quad (29)$$

$$N_{m,m'}(t) = \ln \frac{p_m^{st}(\lambda_t) p_{m'}(t)}{p_{m'}^{st}(\lambda_t) p_m(t)}. \quad (30)$$

The total EP can thus also be split into an adiabatic and a nonadiabatic contribution,

$$\dot{S}_i(t) \equiv \dot{S}_{tot}(t) = \dot{S}_a(t) + \dot{S}_{na}(t), \quad (31)$$

with

$$\begin{aligned} \dot{S}_a(t) &= \frac{1}{2} \sum_{m,m',\nu} J_{m,m'}^{(\nu)}(t) A_{m,m'}^{(\nu)}(\lambda_t) \geq 0 \\ &= \sum_{m,m',\nu} W_{m,m'}^{(\nu)}(\lambda_t) p_{m'}(t) \ln \frac{W_{m,m'}^{(\nu)}(\lambda_t) p_{m'}^{st}(\lambda_t)}{W_{m',m}^{(\nu)}(\lambda_t) p_m^{st}(\lambda_t)}, \end{aligned} \quad (32)$$

$$\begin{aligned}\dot{S}_{na}(t) &= \frac{1}{2} \sum_{m,m'} J_{m,m'}(t) N_{m,m'}(t) \geq 0 \\ &= - \sum_m \dot{p}_m(t) \ln \frac{p_m(t)}{p_m^{st}(\lambda_t)}.\end{aligned}\quad (33)$$

We make a number of remarks. First and most importantly, both $\dot{S}_a(t)$ and $\dot{S}_{na}(t)$ are non-negative EPs. This follows from Jensen's inequality, $-\ln x \geq 1-x$ for $x > 0$, together with Eqs. (7) and (9). The non-negativity of these quantities is in agreement with the fact that the trajectory entropies s_a and s_{na} obey detailed fluctuation theorems [33]. Second, it is clear that the nonadiabatic thermodynamic force, and hence the nonadiabatic EP, is zero in the adiabatic limit $p_m(t) \rightarrow p_m^{st}(\lambda_t)$. This will, for example, be the case when the relaxation to the steady state is extremely fast, and in particular faster than the time scale of the driving λ_t . This observation justifies *a posteriori* the name given to each contribution. Third, we note that one does not need to identify the separate mechanisms ν by which the transition between states takes place for the evaluation of nonadiabatic EP or its corresponding fluxes and forces. It is a function only of the coarse-grained transition probabilities $W = \sum_\nu W^\nu$. Finally, we note that for a system subjected to a nonconservative force and in contact with a single reservoir, the adiabatic EP is the house-keeping heat (divided by the temperature of the reservoir) [22,60,63,70].

The fact that there are two contributions to the total entropy production, which are separately non-negative, suggests that the second law can be "split in two." An elegant way to do so is by the introduction of the so-called excess entropy change [60,22],

$$\dot{S}_{ex}(t) = \frac{1}{2} \sum_{m,m'} J_{m,m'}(t) \ln \frac{p_m^{st}(\lambda_t)}{p_{m'}^{st}(\lambda_t)} = \sum_m \dot{p}_m(t) \ln p_m^{st}(\lambda_t).\quad (34)$$

One easily verifies that

$$\dot{S}(t) = -\dot{S}_{ex}(t) + \dot{S}_{na}(t),\quad (35)$$

$$\dot{S}_r(t) = \dot{S}_{ex}(t) + \dot{S}_a(t).\quad (36)$$

From these two relations, we see that the changes in system and reservoir entropy both have a structure similar to the original second law (16): they consist of the sum of a reversible and an irreversible term if the concept of reversibility is understood with respect to the external driving in the first case (slow external driving implying $\dot{S}_{na}=0$) and with respect to the nonequilibrium constraint exerted by the different reservoirs in the second case (for identical reservoirs $\dot{S}_a=0$). As a result, the excess entropy change can be seen as minus the reversible change of the system entropy change with respect to the driving and as the reversible part of the reservoir entropy changes with respect to the nonequilibrium constraint. By summing these two relations we recover Eq. (31). Relations (31), (35), and (36) thus represent the three faces of the second law.

III. SPECIFIC CLASS OF TRANSFORMATIONS

Additional comments can be made when considering the specific classes of transformation discussed below. To proceed, it is useful to split the nonadiabatic entropy (33) into a "boundary" and a "driving" part [29],

$$\dot{S}_{na}(t) = \dot{S}_b(t) + \dot{S}_d(t),\quad (37)$$

where

$$\dot{S}_b(t) = - \frac{d}{dt} \left(\sum_m p_m(t) \ln \frac{p_m(t)}{p_m^{st}(\lambda_t)} \right),\quad (38)$$

$$\dot{S}_d(t) = - \sum_m \frac{p_m(t)}{p_m^{st}(\lambda_t)} \dot{p}_m^{st}(\lambda_t).\quad (39)$$

The boundary contribution only depends on the initial and final distributions of the considered transformation while the driving part is only nonzero when the control variable evolves in time.

A. Transient relaxation to steady state

The system is supposed to be in an arbitrary state when the external driving is switched off, say at $t=0$. For $t > 0$, we have that $\lambda_t = \lambda$ is time independent, implying $\dot{S}_d(t) = 0$, and therefore

$$\dot{S}_{na}(t) = \dot{S}_b(t) = -\dot{H}(t).\quad (40)$$

Here, $H(t)$ is the relative entropy (or Kullback-Leibler entropy) [66] between the actual and the steady-state distributions,

$$H(t) = D(p(t) \parallel p^{st}(\lambda)) = \sum_m p_m(t) \ln \frac{p_m(t)}{p_m^{st}(\lambda)} \geq 0.\quad (41)$$

We conclude that $H(t)$ is a Lyapunov function, decreasing monotonically in time until the probability distribution reaches its steady-state value. This proof of convergence to the steady state is well known [71], but its connection to the nonadiabatic EP has never been pointed out. The nonadiabatic entropy assumes its minimum value equal to zero at the steady state, but the latter needs not be close to equilibrium.

B. Transitions between steady states

We consider a system that is initially in a steady state $p_m(0) = p_m^{st}(\lambda_{t_i})$. Then somewhere between t_i and t_f the driving variable λ_t changes and after an asymptotically long time T the system has reached its new steady-state distribution $p_m(T) = p_m^{st}(\lambda_{t_f})$. Let us consider the total nonadiabatic entropy change during the time interval T . The boundary term is zero and the driving term is nonzero between t_i and t_f . Relation (35) becomes the second law of steady-state thermodynamics [22,60],

$$\Delta S_{na}(T) = \Delta S_d(T) = \Delta S_{ex}(T) + \Delta S^{st}(T) \geq 0,\quad (42)$$

where $\Delta S^{st}(T)$ is the system entropy change between the initial and final steady states.

C. Time-dependent cycles

We consider a system that is subjected to a time-periodic perturbation with period T . After an initial transient, the probability distribution and the various EP's will also become time-periodic functions with the same period. Because of continuity, we have $p_m(0)=p_m(T)$. Furthermore, $p_m^{st}(\lambda_0)=p_m^{st}(\lambda_T)$. Hence, both the boundary term along a cycle as well as the system entropy change over a period are zero, $\Delta S(T)=\Delta S_b(T)=0$, and relation (35) becomes

$$\Delta S_{na}(T) = \Delta S_{ex}(T) = \Delta S_d(T) \geq 0. \quad (43)$$

We also have, using Eq. (16),

$$\Delta S_{tot}(T) = \Delta S_r(T) = \Delta S_{ex}(T) + \Delta S_d(T) \geq 0. \quad (44)$$

D. Perturbing the steady state

Finally, we investigate how the adiabatic and nonadiabatic EPs change upon applying a perturbation around the steady-state distribution,

$$p_m(t) = p_m^{st}(\lambda) + \delta p_m(t). \quad (45)$$

Clearly, flux (12) can be split as

$$J_{m,m'}^{(v)}(t) = J_{m,m'}^{(v)}(\lambda) + \delta J_{m,m'}^{(v)}(t), \quad (46)$$

where

$$J_{m,m'}^{(v)}(\lambda) = W_{m,m'}^{(v)}(\lambda) p_m^{st}(\lambda) - W_{m',m}^{(v)}(\lambda) p_m^{st}(\lambda), \quad (47)$$

$$\delta J_{m,m'}^{(v)}(t) = W_{m,m'}^{(v)}(\lambda) \delta p_m(t) - W_{m',m}^{(v)}(\lambda) \delta p_m(t). \quad (48)$$

The adiabatic contribution to the EP can be written as the sum of two contributions,

$$\dot{S}_a(t) = \dot{S}_a(\lambda) + \delta \dot{S}_a(t) \geq 0, \quad (49)$$

with

$$\dot{S}_a(\lambda) = \frac{1}{2} \sum_{m,m',v} J_{m,m'}^{(v)}(\lambda) A_{m,m'}^{(v)}(\lambda) \geq 0, \quad (50)$$

$$\delta \dot{S}_a(t) = \frac{1}{2} \sum_{m,m',v} \delta J_{m,m'}^{(v)}(t) A_{m,m'}^{(v)}(\lambda). \quad (51)$$

We now turn to the nonadiabatic EP which using Eqs. (33) and (45) now reads

$$\dot{S}_{na}(t) = - \sum_m \delta \dot{p}_m(t) \ln \frac{p_m(t)}{p_m^{st}(\lambda)} \geq 0. \quad (52)$$

In analogy to the total EP [which can be written in a bilinear form in terms of flux and forces (18)], we can write the nonadiabatic EP as a bilinear form of the nonadiabatic flux and force as

$$\dot{S}_{na}(t) = - \sum_{m,m'} \delta J_{m,m'} N_{m,m'} \geq 0. \quad (53)$$

We conclude that the adiabatic EP has a constant (zero-order) and first-order terms in the deviation δp around the station-

ary state p_m^{st} , while the nonadiabatic EP is of second order. In general, since $\delta \dot{S}_a(t)$ can be negative, we can find situations where $\dot{S}_a(t)$ and even $\dot{S}_i(t)$ are smaller than $\dot{S}_a(\lambda)$. This is the well-known result that the total EP is not necessarily minimum in nonequilibrium steady states. It is however a minimum if the steady states correspond to equilibrium since in this case $A_{m,m'}^{(v)}(\lambda)=0$ [6,8].

IV. APPLICATIONS

A. Two-level system

We consider a system with two levels, $m=1,2$, with p_m as the probability to find the system in level m . Due to conservation of total probability, the master equation (6) can be reduced to a single differential equation for the probability $p=p_2=1-p_1$ to be in level 2,

$$\dot{p}(t) = -\gamma(\lambda_t)p(t) + W_{21}(\lambda_t), \quad (54)$$

with $\gamma(\lambda)=W_{21}(\lambda)+W_{12}(\lambda)$. The steady-state solution is $p^{st}(\lambda)=W_{21}(\lambda)/\gamma(\lambda)$.

We first present the general solution for a periodic perturbation, with a period T , without specifying the form of the rates at this stage. We focus on the long-time regime, where all transients have disappeared, and the time behavior of $p(t)$ itself is periodic with period T . We need to solve Eq. (54) subject to periodic boundary conditions $p(0)=p(T)$. For simplicity, we focus on the case of a piecewise constant perturbation. Hence, the driving period consists of two regimes I and II, namely, $\lambda_t=\lambda_I$ for $0 \leq t < t_I$, and $\lambda_t=\lambda_{II}$ for $t_I \leq t < T$. The solution of Eq. (54) reads $[p_I^{st}=p^{st}(\lambda_I), p_{II}^{st}=p^{st}(\lambda_{II})]$

$$0 \leq t < t_I: p(t) = [p(T) - p_I^{st}]e^{-\gamma t} + p_I^{st}, \quad (55)$$

$$t_I \leq t < T: p(t) = [p(t_I) - p_{II}^{st}]e^{-\gamma_{II}(t-t_I)} + p_{II}^{st}. \quad (56)$$

Using the matching condition (continuity of p) at the transitions between regions I and II, we find that

$$p(t_I) = \frac{p_I^{st}(e^{\gamma t_I} - 1) - p_{II}^{st}(e^{-\gamma_{II}(T-t_I)} - 1)}{e^{\gamma t_I} - e^{-\gamma_{II}(T-t_I)}}, \quad (57)$$

$$p(T) = \frac{p_I^{st}(e^{-\gamma t_I} - 1) - p_{II}^{st}(e^{\gamma_{II}(T-t_I)} - 1)}{e^{-\gamma t_I} - e^{\gamma_{II}(T-t_I)}}. \quad (58)$$

Equations (57) and (58) with Eqs. (55) and (56) provide the exact and explicit long-time solution of Eq. (54) under piecewise constant periodic driving.

We now turn to the entropies. We consider the case of two different reservoirs $\nu=L,R$, with corresponding transition rates $W=\sum_\nu W^{(\nu)}$. Entropies (31)–(33) become

$$\dot{S}_{tot} = \sum_\nu [W_{12}^{(\nu)} p - W_{21}^{(\nu)} (1-p)] \ln \frac{W_{12}^{(\nu)} p}{W_{21}^{(\nu)} (1-p)}, \quad (59)$$

$$\dot{S}_a = \sum_\nu [W_{12}^{(\nu)} p - W_{21}^{(\nu)} (1-p)] \ln \frac{W_{12}^{(\nu)} p^{st}}{W_{21}^{(\nu)} (1-p^{st})}, \quad (60)$$

$$\dot{S}_{na} = \dot{p}(t) \ln \frac{(1-p)p^{st}}{(1-p^{st})p}. \quad (61)$$

As an illustration, we consider two physical models that are described by the above two-level master equation. The first is a single-electron quantum level in contact with a left (L) or a right (R) electronic reservoir ($\nu=L,R$). The level can thus be empty, $1-p$, or filled, p , and transitions between these two states correspond to the exchange of an electron with one of the two reservoirs. The rates are given by the Fermi golden rule rates for each of the reservoirs [72],

$$W_{21}^{(\nu)} = \Gamma f(\lambda_\nu), \quad W_{12}^{(\nu)} = \Gamma [1 - f(\lambda_\nu)], \quad (62)$$

where $f(x) = (\exp\{x\} + 1)^{-1}$ is the Fermi distribution and Γ is the system-reservoir couplings chosen for simplicity identical for the two reservoirs. Physically, the changes in the driving parameter $\lambda_\nu = (\epsilon - \mu_\nu)/T_\nu$ could result from changes in the energy of the level ϵ or in the temperature T_ν and chemical potential μ_ν of the ν reservoir. The thermodynamics of this model has been discussed in Refs. [73,74]. The time dependence of the rates can result from either the external control of the energy of the level (e.g., with an electric field) or the control of the reservoir chemical potentials.

Our second model represents a two-level atom interacting with left (L) and right (R) reservoirs of thermal light. The rates describing the transitions between the levels are then given by

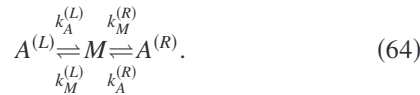
$$W_{21}^{(\nu)} = \Gamma n(\lambda_\nu), \quad W_{12}^{(\nu)} = \Gamma [1 + n(\lambda_\nu)], \quad (63)$$

where $n(x) = (\exp\{x\} - 1)^{-1}$ is the Bose-Einstein distribution and $\lambda_\nu = \epsilon/T_\nu$. The time dependence of the rates can thus come either from an external control of the energy spacing between the levels ϵ or from the control of the temperature of the reservoirs T_ν .

The probability distribution as well as the various entropies around the cycle can be analytically evaluated. For the purpose of illustration, we reproduce the typical behavior in Figs. 1 and 2.

B. Chemical reaction model

Consider the following chemical reaction:



Denoting by m the number of particles of species M and using $\nu=L,R$, we find that the corresponding transition rates are given by

$$W_{m-1,m}^{(\nu)} = k_M^{(\nu)} m, \quad W_{m+1,m}^{(\nu)} = k_A^{(\nu)} A^{(\nu)}(t). \quad (65)$$

The concentrations of $A^{(L)}(t)$ and $A^{(R)}(t)$ are externally controlled in a time-dependent manner. Rescaling time by $k_M^{(L)} + k_M^{(R)}$, we can redefine the rates as

$$W_{m-1,m}^{(\nu)} = \alpha^{(\nu)} m, \quad W_{m+1,m}^{(\nu)} = \lambda_t^{(\nu)}, \quad (66)$$

where we introduced

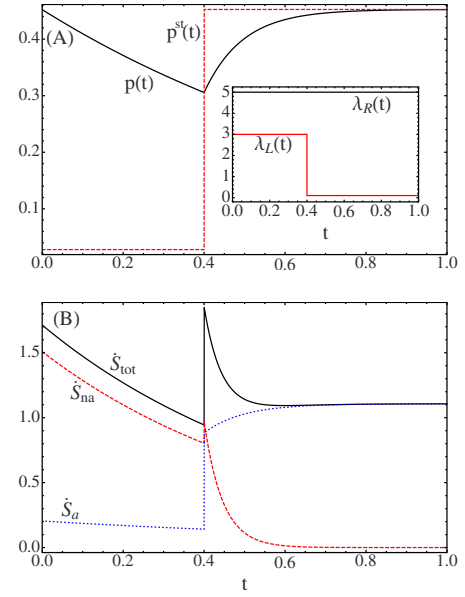


FIG. 1. (Color online) (A) Actual probability distribution along the cycle and stationary solution corresponding to the instantaneous values of the driving displayed in the inset. (B) The total, adiabatic, and nonadiabatic entropy productions along the cycle. The Bose rates (63) are used with $\Gamma=0.5$. Also, $T=1$ and $t_f=0.4$.

$$\alpha^{(\nu)} = \frac{k_M^{(\nu)}}{k_M^{(L)} + k_M^{(R)}}, \quad \lambda_t^{(\nu)} = \frac{k_A^{(\nu)} A^{(\nu)}(t)}{k_M^{(L)} + k_M^{(R)}}. \quad (67)$$

The resulting master equation reads ($m=0,1,\dots$ with convention $p_{-1}=0$) [71]

$$\begin{aligned} \dot{p}_m &= \sum_\nu \{ \alpha^{(\nu)}(m+1)p_{m+1} + \lambda_t^{(\nu)}p_{m-1} - (\lambda_t^{(\nu)} + \alpha^{(\nu)}m)p_m \} \\ &= (m+1)p_{m+1} + \lambda_t p_{m-1} - (\lambda_t + m)p_m. \end{aligned} \quad (68)$$

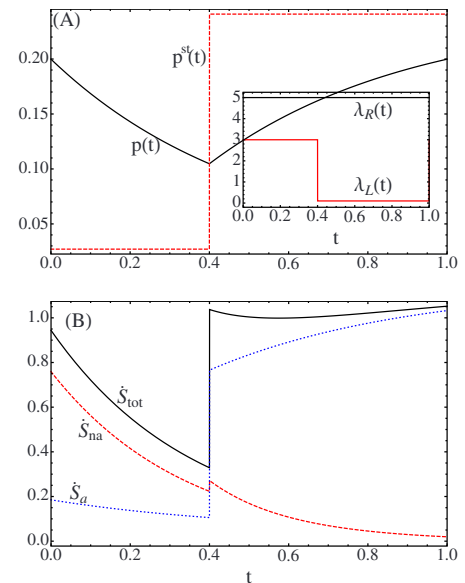


FIG. 2. (Color online) Same as Fig. 1, but using the Fermi rates (62) instead of the Bose rates.

From first to second line, we used $\sum_\nu \lambda_t^{(\nu)} = \lambda_t$ and $\sum_\nu \alpha^{(\nu)} = 1$. Equation (68) can be most easily solved by switching to the generating function

$$F(s, t) = \sum_{m=0}^{\infty} s^m p_m(t). \quad (69)$$

Using Eqs. (68) and (69), one finds

$$\partial_t F(s, t) = (s-1)\lambda_t F(s, t) - (s-1)\partial_s F(s, t). \quad (70)$$

For the purpose of illustration, we focus on a specific time-dependent solution of this equation, for which the explicit analytical expression can be obtained. Indeed, one readily verifies by inspection that

$$F(s, t) = e^{\bar{m}(t)(s-1)} \quad (71)$$

is an exact solution of Eq. (70), propagating in time. As suggested by the notation, $\bar{m}(t)$ is the time-dependent average

$$\bar{m} = \bar{m}(t) = \sum_{m=0}^{\infty} m p_m(t), \quad (72)$$

which obeys the following equation:

$$\dot{\bar{m}}(t) = \lambda_t - \bar{m}(t). \quad (73)$$

Its exact time-dependent solution is given by

$$\bar{m}(t) = e^{-(t-t_0)} \left\{ \bar{m}(t_0) + \int_{t_0}^t d\tau e^{(\tau-t_0)} \lambda_\tau \right\}. \quad (74)$$

We conclude that the propagating Poissonian distribution,

$$p_m(t) = \frac{\bar{m}^m}{m!} e^{-\bar{m}}, \quad (75)$$

with the average given by Eq. (74), is an exact time-dependent solution of the master equation. The corresponding frozen steady states are

$$p_m^{st}(t) = \frac{[\bar{m}^{st}]^m}{m!} e^{-\bar{m}^{st}}, \quad (76)$$

with

$$\bar{m}^{st} = \lambda_t. \quad (77)$$

We note, using Eqs. (66) and (75), that

$$\frac{W_{m+1, m}^{(\nu)} p_m(t)}{W_{m, m+1}^{(\nu)} p_{m+1}(t)} = \frac{\lambda_t^{(\nu)}}{\alpha^{(\nu)} \bar{m}(t)}. \quad (78)$$

We see that at steady state, the detailed balance condition is not in general satisfied. Equilibrium is only attained if $\lambda_t^{(\nu)} = \alpha^{(\nu)} \lambda_t$. We thus have two mechanisms bringing the system out of equilibrium: the breaking of detailed balance by the steady state and the time-dependent driving from $\lambda_t^{(\nu)}$.

Using these analytical results, we can now obtain explicit results for entropies (31)–(33),

$$\dot{S}_{tot}(t) = \sum_\nu (\alpha^{(\nu)} \bar{m} - \lambda_t^{(\nu)}) \ln \frac{\alpha^{(\nu)} \bar{m}}{\lambda_t^{(\nu)}}, \quad (79)$$

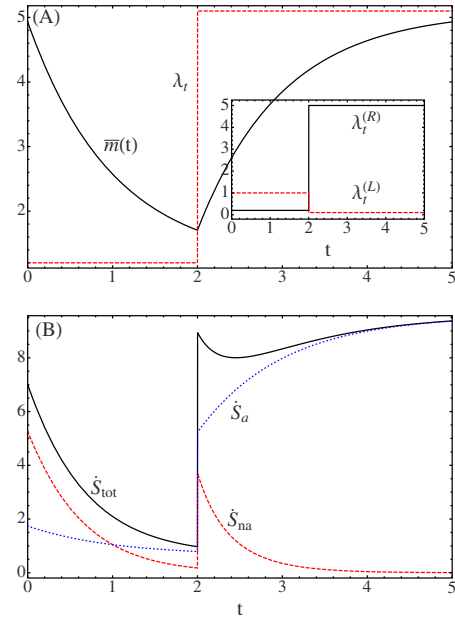


FIG. 3. (Color online) (A) Actual average $\bar{m}(t)$ and stationary average λ_t along the cycle [they uniquely determine the actual and stationary probability distributions (75) and (76)] corresponding to the instantaneous values of the driving displayed in the inset. (B) The total, adiabatic, and nonadiabatic entropy productions along the cycle. Also, $T=5$ and $t_f=2$.

$$\dot{S}_a(t) = \sum_\nu (\alpha^{(\nu)} \bar{m} - \lambda_t^{(\nu)}) \ln \frac{\alpha^{(\nu)} \bar{m}^{st}}{\lambda_t^{(\nu)}}, \quad (80)$$

$$\dot{S}_{na}(t) = -\dot{\bar{m}} \ln \frac{\bar{m}}{\lambda_t} = (\bar{m} - \lambda_t) \ln \frac{\bar{m}}{\lambda_t}, \quad (81)$$

which are all positive. Not surprisingly, the nonadiabatic contribution vanishes in the adiabatic limit $\bar{m} = \lambda_t$. On the other hand, the adiabatic contribution vanishes under the instantaneous detailed balance condition $\lambda_t^{(\nu)} = \alpha^{(\nu)} \lambda_t$ (remembering that $\lambda_t = \bar{m}^{st}$).

To compare the results with the two-level model, we again assume that the system is subjected to a periodic piecewise constant driving of period T . One finds

$$0 \leq t < t_f: \bar{m}(t) = e^{-t} [\bar{m}(T) + \lambda_{I}(e^t - 1)],$$

$$t_f \leq t < T: \bar{m}(t) = e^{-(t-t_0)} [\bar{m}(t_f) + \lambda_{II}(e^{t-t_f} - 1)], \quad (82)$$

where

$$\bar{m}(t_f) = \frac{\lambda_I(e^{-t_f} - 1) + \lambda_{II}(e^{-T} - e^{-t_f})}{e^{-T} - 1}, \quad (83)$$

$$\bar{m}(T) = \frac{\lambda_I(e^{T-t_f} - 1) + \lambda_{II}(e^T - e^{t_f})}{e^T - 1}. \quad (84)$$

The resulting behavior of the probability distribution and the various EPs around the cycle are shown in Fig. 3.

V. CONCLUSIONS

In this paper, we started by showing how to identify entropy and entropy production for a stochastic dynamics described by Markovian master equations with time-dependent rates. The key element is that the entropy production can be “split” into two parts, each satisfying a second-law-like relation. By assuming that the rates satisfy a local detailed balance condition, we have also shown that the dynamics provides a nonequilibrium thermodynamics description of the system. The thermodynamic implications of this splitting re-

main to be properly understood. To progress in this direction we calculated the various entropies on different exactly solvable models. In the companion paper [64], we proceed similarly for a stochastic dynamics described by a Fokker-Planck equation.

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