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Second law for transitions between nonequilibrium steady states

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We show that the system entropy change for the transitions between nonequilibrium steady states arbitrarily far from equilibrium for any constituting process is given by the relative entropy of the distributions of these steady states. This expression is then shown to relate to the dissipation relations of both S. Vaikuntanathan and C. Jarzynski [Europhys. Lett. **87**, 60005 (2009)] and R. Kawai *et al.* [Phys. Rev. Lett. **98**, 080602 (2007)] in the case of energy-conserving driving.

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I. INTRODUCTION

Recently, there have been many novel approaches to understanding physical systems driven away from equilibrium. Among such approaches we emphasize the work theorems of Jarzynski [1] and Crooks [2], steady-state thermodynamics [3,4], and stochastic thermodynamics [5–8]. In this very same context, a new and profound understanding of the second law of thermodynamics has been possible through its relation to the dissipation in phase space [9–11], the relation between dissipation and lag in irreversible processes [12], the Landauer principle and the second law [13], and generalized fluctuation relations [14].

Important progress concerning the second law has recently been made by Esposito and Van den Broeck [15–17], where they have shown that the total entropy production stems from adiabatic and nonadiabatic contributions. Although both of these entropy productions are non-negative, they are very different in nature since these two distinct contributions represent two different manners of driving a system out of equilibrium. The adiabatic entropy production in a physical system occurs when the system is driven through nonequilibrium boundary conditions. It should be noted that this use of the term adiabatic does not refer to the absence of heat exchange but to the instantaneous relaxation to the steady state as remarked in [16]. On the other hand, the nonadiabatic entropy production stems from the external driving with non-energy-conserving dynamics. Esposito and Van den Broeck have further shown that the system entropy production is the nonadiabatic entropy production minus the excess term for the transitions between the nonequilibrium steady states [16].

In a related context, Speck and Seifert [18] have recently shown that the equilibrium form of the fluctuation-dissipation theorem (FDT) can be used for a colloidal particle in a periodic potential if one measures the velocity with respect to the local mean velocity. We also note that a modified fluctuation-dissipation relation for a nonequilibrium steady state has recently been experimentally verified [19]. Speck and Seifert end their discussion by asking whether some other non-velocity-like concepts can be used in their equilibrium form when one studies nonequilibrium steady states.

Considering the colloidal particle in a periodic potential studied by Speck and Seifert [18], we note that this model is particular in that its average excess heat is zero. Motivated by this observation, we aim to show that in this contribution the equilibrium form of the second law can be used for the transitions between the nonequilibrium steady states as Speck and Seifert have shown the restoration of the equilibrium FDT for the same class of transitions. However, it is worth remarking that our treatment is general and not limited only to the Brownian particles in periodic potential.

This paper is organized as follows: In the next section, we derive the formula for the entropy change associated with the transitions between nonequilibrium steady states arbitrarily far from equilibrium. Next, examples are provided to clarify the use of the previously derived main equation. The relation of the present work to the entropy change for the transitions between the equilibrium states and to the previous works derived in the case of energy-conserving dynamics is then discussed. Finally, concluding remarks are presented.

II. THEORY

In stochastic thermodynamics, the entropy of a physical system is given by its time-dependent Shannon entropy,

$$S(t) = -\sum_m p_m(t)\ln p_m(t), \tag{1}$$

where we set the Boltzmann constant equal to unity. The probability to find the system in a state m at time t is denoted by $p_m(t)$, and its time evolution is governed by the following Markovian master equation:

$$\dot{p}_m(t) = \sum_n W_{mn}\, p_n(t), \tag{2}$$

where the rate matrix W_{mn} is responsible for the transitions between the states as a result of different mechanisms ν and time-dependent driving of the control parameter, i.e., $W_{mn} = W_{mn}(\lambda_t) = \sum_\nu W_{mn}^{(\nu)}(\lambda_t)$. The rate matrix has the following property:

$$\sum_m W_{mn}(\lambda_t) = 0. \tag{3}$$

Taking the time derivative of the system entropy in Eq. (1) together with the Markovian master equation (2), one can show

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that the following equation holds:

$$\dot{S}(t) + \dot{S}_r(t) = \dot{S}_{\text{tot}}(t), \tag{4}$$

where the change in total entropy $\dot{S}_{\text{tot}}(t)$ reads

$$\dot{S}_{\text{tot}}(t) = \sum_{m,n,\nu} W_{mn}^{(\nu)}(\lambda_t) p_n(t) \ln \frac{W_{mn}^{(\nu)}(\lambda_t) p_n(t)}{W_{nm}^{(\nu)}(\lambda_t) p_m(t)}, \tag{5}$$

while the entropy change in the reservoirs $\dot{S}_r(t)$ can be given by

$$\dot{S}_r(t) = \sum_{m,n,\nu} W_{mn}^{(\nu)}(\lambda_t) p_n(t) \ln \frac{W_{mn}^{(\nu)}(\lambda_t)}{W_{nm}^{(\nu)}(\lambda_t)}. \tag{6}$$

In order to apply the above formalism to the physical systems attaining nonequilibrium steady states, one further assumes that the rate matrix W_{mn} is irreducible in the sense that there is a unique stationary distribution $p_n^{st}(\lambda)$ eventually reached by the system corresponding to the control parameter set constant in time, i.e., $\sum_n W_{mn}(\lambda) p_n^{st}(\lambda) = 0$. Armed with the irreducibility of the rate matrix, one can show that the change in total entropy can be divided into the adiabatic,

$$\dot{S}_a(t) = \sum_{m,n,\nu} W_{mn}^{(\nu)}(\lambda_t) p_n(t) \ln \frac{W_{mn}^{(\nu)}(\lambda_t) p_n^{st}(\lambda_t)}{W_{nm}^{(\nu)}(\lambda_t) p_m^{st}(\lambda_t)}, \tag{7}$$

and nonadiabatic entropy changes, i.e.,

$$\dot{S}_{na}(t) = -\sum_m \dot{p}_m(t) \ln \frac{p_m(t)}{p_m^{st}(\lambda_t)}, \tag{8}$$

so that $\dot{S}_{\text{tot}}(t) = \dot{S}_a(t) + \dot{S}_{na}(t)$, where the subscripts denote adiabatic and nonadiabatic contributions, respectively. In order to relate the above equations to thermodynamics, the stochastic thermodynamics requires that the transition rates related to a given mechanism ν satisfy the following local detailed balance condition (DBC) [15–17]:

$$W_{mn}^{(\nu)}(\lambda_t) p_n^{eq}(\lambda_t, \nu) = W_{nm}^{(\nu)}(\lambda_t) p_m^{eq}(\lambda_t, \nu). \tag{9}$$

When the system is coupled to a single reservoir for a fixed value of the control parameter λ, the stationary distribution becomes an equilibrium distribution, i.e., $p_m^{st}(\lambda) = p_m^{eq}(\lambda)$. Then, for such a system under the influence of only conservative forces, the adiabatic entropy production vanishes, as can be seen from Eqs. (7) and (9). However, when the system is coupled to multiple reservoirs with different thermodynamic properties, the reservoirs try to impose their respective equilibrium distributions, resulting in an overall stationary distribution. It is worth remarking that the adiabatic entropy production can also be caused by the nonconservative driving in the presence of a single reservoir.

Note that the nonadiabatic entropy production is zero in the adiabatic limit since then we have $p_m(t) \to p_m^{st}(\lambda_t)$, indicating that the physical system moves through a sequence of successive steady states at each time instance [16]. As a result, one has $\dot{S}_{\text{tot}}(t) = \dot{S}_a(t)$. Since the only term surviving in an adiabatic switching is $\dot{S}_a(t)$, it is called the adiabatic entropy change, while the rest of the total entropy contribution is called nonadiabatic.

Focusing now only on the nonadiabatic entropy change, we can further split it into the excess entropy change $\dot{S}_{ex}(t)$, given as

$$\dot{S}_{ex}(t) = \sum_m \dot{p}_m(t) \ln p_m^{st}(\lambda_t), \tag{10}$$

and the change in the system entropy,

$$\dot{S}(t) = -\sum_m \dot{p}_m(t) \ln p_m(t) = \frac{d}{dt}\left(-\sum_m p_m(t) \ln p_m(t)\right), \tag{11}$$

so that

$$\dot{S}_{na}(t) = \dot{S}_{ex}(t) + \dot{S}(t). \tag{12}$$

The excess entropy change is defined as the entropy change caused by the transition between the states, as can be seen from Eq. (10). In fact, if one considers the transitions between the equilibrium states under conservative driving, the excess entropy change multiplied by the temperature becomes the total heat dissipated to the surrounding medium. We from now on consider only the nonadiabatic contribution and the transitions between the nonequilibrium steady states [15–17]. Therefore, a system is initially assumed to be in a normalized steady state $p_m^{st}(0)$ corresponding to the initial value of the control parameter λ_{t_i}. The external driving is represented as usual by the change of the control parameter λ_{t_i} to its final value λ_{t_f}. Assuming that a steady state is formed for fixed values of the control parameter after an asymptotically long time, i.e., the irreducibility of the rate matrix, a new normalized steady-state distribution $p_m^{st}(T)$ is reached after a long time T. For the transitions between the nonequilibrium steady states [16], the change in the system entropy reads

$$\Delta S = -\sum_m p_m^{st}(T) \ln p_m^{st}(T) + \sum_m p_m^{st}(0) \ln p_m^{st}(0), \tag{13}$$

and the following second-law-like relation [16] is satisfied:

$$\Delta S_{na} - \Delta S_{ex} = \Delta S. \tag{14}$$

It is important to note that the expression above obtained by Esposito and Van den Broeck [16] for the transitions between the nonequilibrium steady states is quite general and already includes both the change in the system entropy and the excess entropy change as well. On the other hand, the usual formulations of the second law between the equilibrium states are only focused on the change in the system entropy. Therefore, our main motivation is to write Eq. (14) so that the system entropy change incorporates the excess entropy change within, forming one term only, which can be written as a relative entropy (see below for more on this). This change in the system entropy, including also the excess entropy change within, will be denoted as ΔS^{st} [see, for example, Eq. (17)]. For consistency, ΔS^{st} must naturally be equal to ΔS_{na} in Eq. (14), formerly obtained in Ref. [16].

The average excess entropy change with respect to the final steady state is

$$\Delta S_{ex} = \sum_m \left[p_m^{st}(T) - p_m^{st}(0)\right] \ln p_m^{st}(T). \tag{15}$$

It is worth noting that the equation above for the excess entropy change cannot be obtained from the more general Eq. (10) by a simple integration due to the dependence of the control parameter on time. However, since $p_m^{st}(T)$ is a steady state obtained by keeping the control parameter constant in time for an asymptotically long duration T, it is independent of t, thereby justifying the derivation of Eq. (15). It is seen from Eq. (14) that the system entropy change is not equal to the nonadiabatic entropy change due to the excess entropy contribution. For a Brownian particle in a periodic potential, the excess entropy change is zero since the steady states in this model also correspond to the equilibrium distributions once they are reached [17,18]. However, the excess change is not zero in general. Motivated by the particular model studied by Speck and Seifert [18], we now generally include the excess entropy term in the system entropy change for the transitions between the nonequilibrium steady states. This incorporation is necessary in order to relate our results to the recent formulas derived for the transitions between equilibrium states since the latter are formulated in terms of the system entropy change only. Note that the inclusion of the excess term in the system entropy change also makes the latter equal to the nonadiabatic entropy change, as can be seen from Eq. (14). To include the excess entropy term, we treat as if it is zero and consider the result of this equality as a condition to be satisfied by the system entropy change, which reads

$$\sum_m p_m^{st}(T) \ln p_m^{st}(T) = \sum_m p_m^{st}(0) \ln p_m^{st}(T), \tag{16}$$

as can be easily seen from Eq. (15). Incorporating Eq. (16) into the change of the system entropy given by Eq. (13), we obtain

$$\Delta S^{st} = -\sum_m p_m^{st}(0) \ln p_m^{st}(T) + \sum_m p_m^{st}(0) \ln p_m^{st}(0), \tag{17}$$

which can be rewritten as

$$\Delta S^{st} = \sum_m p_m^{st}(0) \ln \left(\frac{p_m^{st}(0)}{p_m^{st}(T)} \right), \tag{18}$$

where we have denoted the system entropy change ΔS including the excess term by ΔS^{st}. Before proceeding further, one can check whether considering the excess entropy term as zero in the form of a constraint and its inclusion in the system entropy change resulted in any mathematical discrepancies. Note that one has initially the nonadiabatic entropy change equal to $\Delta S_{na} = \sum_m p_m^{st}(0) \ln(\frac{p_m^{st}(0)}{p_m^{st}(T)})$, as can be seen from Eqs. (12)–(14). Since we have obtained exactly the same expression in Eq. (18) for the system entropy change, this implies that the excess term is well incorporated into the system entropy without loss of generality.

We now note that the right-hand side of Eq. (18) is the nonnegative relative entropy expression $D[p^{st}(0) \| p^{st}(T)]$ (also known as Kullback-Leibler distance) between the steady-state distributions [20], i.e.,

$$\Delta S^{st} = D[p^{st}(0) \| p^{st}(T)] \geqslant 0. \tag{19}$$

This is our main result, which relates the system (or, equivalently, nonadiabatic) entropy change due to the transitions between nonequilibrium steady states to the relative entropy of the initial and final steady-state distributions.

It is worth noting the difference between Eq. (19) and the expression $\dot{S}_{na}(t) = -\frac{d}{dt} D[p(t) \| p^{st}(\lambda)]$ obtained in Refs. [16,17]. Apart from a minus sign, the equation found in Refs. [16,17] has a time-dependent probability $p(t)$ as opposed to Eq. (19) since the former expresses how the system relaxes to its new steady state once the control parameter is fixed in time, whereas Eq. (19) is related to what happens between two steady states, each independent of time, i.e., when they are already relaxed but separated from one another by an asymptotically long time interval T.

Our main result, i.e., Eq. (19), shows that the equilibrium form of the second law is preserved if the excess entropy change is incorporated into the system entropy change. This can also be seen by inspecting the second law derived by Hatano and Sasa [4], i.e., $T\Delta S \geqslant -Q_{ex}$. This expression of the second law immediately gives our main result, Eq. (19), once the excess heat Q_{ex}, equal to $T\Delta S_{ex} = Q_{ex}$, is incorporated into the system entropy so that one now has $\Delta S^{st} \geqslant 0$ since $\Delta S + \Delta S_{ex} = \Delta S^{st}$. This is plausible since the Hatano-Sasa form of the second law is derived for a system under nonconservative driving in contact with a single reservoir, and the excess entropy change is the same as the excess heat divided by the temperature of the reservoir under this condition.

It is also worth noting that the system entropy change now possesses all the information of the nonadiabatic entropy change as a result of incorporating the excess entropy change, as can be seen from Eq. (14). It is well known that the nonadiabatic entropy change is related to the system properties and is independent of the constituting process [17]. Therefore, our main result, being exactly at the same level of description as the nonadiabatic entropy change, is also independent of the process, which generates the steady-state conditions, be it through the time-dependent driving or multiple reservoirs with different thermodynamic properties. We also note that Eq. (19) is valid for any kind of transition, slow or not.

Another related issue concerns when the equality holds for the second law given by Eq. (19): valid for arbitrary protocols and independent of the constituting process, the second law written in terms of the system entropy given by Eq. (19) is zero for two cases. (i) The first trivial case is when the steady-state distribution, once reached, remains unchanged despite the presence of the time-dependent driving or when the switching is slow enough not to perturb the steady state. (ii) The second case is nontrivial: the entropy change given by Eq. (19) is zero also when the steady-state distribution does not change its form drastically despite the presence of driving. To understand this, consider a case where $p_m^{st}(0) = (\frac{e^{\alpha}-1}{e^{\alpha}})e^{-\alpha m}$ and $p_m^{st}(T) = (\frac{e^{\delta}-1}{e^{\delta}})e^{-\delta m}$ are initial and final normalized steady-state distributions, respectively. The terms α and δ are constants, which usually depend on the values of friction and diffusion, for example. Enforcing Eq. (16), i.e., incorporating the excess entropy change into the system itself, a simple calculation shows that $\alpha = \delta$, yielding zero system entropy change in Eq. (19). This provides a new insight into the physical meaning of processes regarding the transitions between nonequilibrium steady states. In other words, a transition process yields zero entropy production if the steady distribution does not change its form drastically. One observes no entropy change in the physical system if an initial exponential steady-state distribution is preserved exactly or only changes its argument under the influence of external driving or due to the coupling of the physical system to multiple reservoirs with different thermodynamic properties. However, a transition from an exponential steady-state distribution to a Gaussian one produces a nonzero entropy change, as we will see below for the Van der Pol oscillator under the influence of noise.

One might ask whether our central result, Eq. (19), provides information on the entropy change when the physical system is acted on by an energy-conserving and conservative driving [or, considering the generality of Eq. (19), one can have equilibrium states by keeping the thermodynamic properties of the multiple reservoirs the same], so that the steady states are replaced by the equilibrium states in Eq. (19). In fact, all the steps above can be repeated in their full generality only by noting that the nonequilibrium steady states are replaced by the equilibrium ones, so that one obtains the relation $\Delta S^{eq} = D[p^{eq}(0)\|p^{eq}(T)] \geqslant 0$ as the second law for the transitions between initial and final equilibrium distributions, where the equality is satisfied for quasistatic processes.

In order to see that this is in fact the case, we consider the nonequilibrium Landauer principle in Ref. [13]. This principle in its full generality reads

$$\beta W_{\text{diss}} - D[p(T)\|p^{eq}(T)] + D[p(0)\|p^{eq}(0)] = \Delta S_{\text{tot}}, \tag{20}$$

where β is the inverse temperature. The dissipated work W_{diss} is given by $\langle W\rangle - \Delta F^{eq}$, where $\langle W\rangle$ and ΔF^{eq} stand for the average work and free energy difference between the equilibrium states, respectively. In the equation above, the relative entropy terms are separately zero if the system is both initially and finally at equilibrium [13]. Moreover, ΔS_{tot} is the total entropy change and becomes equal to ΔS_{na} since the adiabatic contribution ΔS_a vanishes for a single reservoir with conservative driving or for multiple reservoirs with the same thermodynamical properties due to the local detailed balance condition [15–17]. Moreover, since the excess entropy change is incorporated into the system entropy in deriving Eq. (19) [see also Eq. (14)], the nonadiabatic entropy change ΔS_{na} is equal to the change in the system entropy ΔS. Under the influence of conservative driving, the steady states now relax to the equilibrium states [see, e.g., the paragraph above Eq. (5) in Ref. [21]], so that we have

$$\beta W_{\text{diss}} = \Delta S^{eq} = D[p^{eq}(0)\|p^{eq}(T)] \geqslant 0. \tag{21}$$

We note that $W_{\text{diss}} \geqslant 0$ is indeed the second law of thermodynamics, and the dissipated work, being explicitly equal to $\langle W\rangle - \Delta F^{eq}$, also relates only two equilibrium states, just like the relative entropy expression $D[p^{eq}(0)\|p^{eq}(T)]$. Moreover, this equality also ensures that the relative entropy formulation of the second law attains zero only for quasistatic, reversible processes since only then does the dissipated work vanish. From Eq. (21), one can further see why our main result, Eq. (19), has been interpreted as preserving the equilibrium form of the second law.

It is worth remarking that one can also derive Eq. (21) directly without using the Landauer principle derived in Ref. [13]. However, before proceeding, it might be important to see how the usual work formulation of the second law is obtained: The first law reads $\langle W\rangle = \Delta U + Q$, where the dissipated heat is negative by sign convention. The work applied to the system either increases the energy U of the system or is dissipated into the surrounding medium in the form of heat, i.e., $Q = T\Delta S_m$. The total entropy change is given by the equation $\Delta S_{\text{tot}} = \Delta S + \Delta S_m$, where ΔS is the change in the system entropy. Therefore, the first law now reads $\langle W\rangle = \Delta U + T\Delta S_{\text{tot}} - T\Delta S$. This last equation can further be written as $(\langle W\rangle - \Delta U + T\Delta S)/T = \Delta S_{\text{tot}} \geqslant 0$, where we have used $\Delta S_{\text{tot}} \geqslant 0$. Remembering the definition of the Helmholtz free energy $F = U - TS$ and assuming both equilibrium states are at the same temperature T, we can obtain the work formulation of the second law as $(\langle W\rangle - \Delta F^{eq})/T = \beta W_{\text{diss}} \geqslant 0$, setting the Boltzmann constant to unity. In accordance with the work formulation of the second law, we now initially couple our system to a thermal reservoir at some temperature β^{-1}, so that the initial equilibrium distribution is given by $p^{eq}(0) = \frac{e^{-\beta H(\Gamma;\lambda_{t_i})}}{Z(\beta^{-1},\lambda_{t_i})}$, with Z being the partition function, corresponding to the initial value of the control parameter λ_{t_i}, such as volume, where Γ denotes the phase space variables. Similar to the transitions between the nonequilibrium steady states, the external conservative driving is represented by the change of the control parameter λ_{t_i} to its final value λ_{t_f}. Having changed the control parameter to its final value λ_{t_f}, we bring the system to another equilibrium state by coupling it to a thermal reservoir at the same temperature β^{-1}, i.e., $p^{eq}(T) = \frac{e^{-\beta H(\Gamma;\lambda_{tf})}}{Z(\beta;\lambda_{tf})}$, where we invoke the concept of an ideal superbath, implying that no work is done through the process of coupling [10]. From Eq. (21), one can directly calculate

$$\begin{aligned} D[p^{eq}(0)\|p^{eq}(T)] = {} & -\beta\big\langle H(\Gamma;\lambda_{t_i})\big\rangle + \beta F\big(\beta;\lambda_{t_i}\big) \\ & - \beta F\big(\beta;\lambda_{t_f}\big) + \beta\sum_m p^{eq}(0) H\big(\Gamma;\lambda_{t_f}\big), \end{aligned} \tag{22}$$

where we have also used the relation $F(\beta;\lambda) = -\beta^{-1}\ln Z(\beta;\lambda)$. Using Eq. (16) now for the equilibrium distributions rather than the nonequilibrium steady states, we obtain the relation $\sum_m p^{eq}(0)H(\Gamma;\lambda_{t_f}) = \sum_m p^{eq}(T)H(\Gamma;\lambda_{t_f}) = \langle H(\Gamma;\lambda_{t_f})\rangle$. By substituting this relation for the last term on the right-hand side of Eq. (22) and also using $\langle W\rangle = \langle H(\Gamma;\lambda_{t_f})\rangle - \langle H(\Gamma;\lambda_{t_i})\rangle$ due to the conservation of total energy, we finally obtain Eq. (21), i.e., $D[p^{eq}(0)\|p^{eq}(T)] = \beta(\langle W\rangle - \Delta F^{eq}) = \beta W_{\text{diss}}$.

As an illustrative example, we consider the free expansion of an ideal gas from a volume $V/2$ to a final volume V, with both states being at equilibrium at temperature β^{-1} in accordance with the scenario above. The Hamiltonian for the free expansion is time independent, i.e., $\langle H(\Gamma;\lambda_{t_i})\rangle = \langle H(\Gamma;\lambda_{t_f})\rangle$ so that $\langle W\rangle = 0$. The relative entropy $D[p^{eq}(0)\|p^{eq}(T)]$ is equal to $\ln(\frac{Z(\beta;\lambda_{tf})}{Z(\beta;\lambda_{t_i})})$, where we have used the time independence of the Hamiltonian and the normalization $\int d\Gamma p^{eq}(0) = 1$. Note that we now use the continuous version of the relative entropy expression. The ratio of the final and initial partition functions can be calculated as

$$\frac{Z(\beta;\lambda_{tf})}{Z\big(\beta;\lambda_{t_i}\big)} = \frac{V\int d^3p\,\exp(-\beta p^2/2m)}{\left(\frac{V}{2}\right)\int d^3p\,\exp(-\beta p^2/2m)} = 2. \tag{23}$$

Therefore the relative entropy $D[p^{eq}(0)\|p^{eq}(T)]$ between the initial and final equilibrium states is then equal to $\ln 2$. Using Eq. (21), we see that the dissipated work $W_{\rm diss}$ is equal to $(\beta^{-1}\ln 2)$, which is greater than zero, as expected, since the process of free expansion is irreversible. The value of the dissipated work can directly be checked through $W_{\rm diss} = \langle W\rangle - \Delta F^{eq}$, noting that the average work $\langle W\rangle$ is zero. Then, $W_{\rm diss}$ is equal to $(-\Delta F^{eq})$, which is again equal to $(\beta^{-1}\ln 2)$. Note that one does not need to use the constraint in Eq. (16) for this particular example owing to the fact that the Hamiltonian is time independent.

Although we have only considered transitions between equilibrium states above, one can use the nonequilibrium Landauer principle [13] to include, for example, the transition from an initial equilibrium state to a final nonequilibrium one. Hence, one can write Eq. (20) as

$$\Delta S^{eq} - D[p(T)\|p^{eq}(T)] = \Delta S_{\rm tot}, \tag{24}$$

where the term $D[p(0)\|p^{eq}(0)]$ is zero since the system is initially at equilibrium. One has to keep the right-hand side of the equation above as $\Delta S_{\rm tot}$ since the final state is not at equilibrium any longer. In other words, one does not consider only the transitions between the equilibrium states, and consequently, boundary terms must be included too [see in particular Eqs. (37)–(39) and (42) in Ref. [16]]. Therefore, $\Delta S_{\rm tot}$ cannot be equal to ΔS^{eq} in general, as we had in Eq. (21). However, the total entropy $\Delta S_{\rm tot}$ is always non-negative [13], i.e., $\Delta S_{\rm tot} \geqslant 0$, implying

$$\Delta S^{eq} \geqslant D[p(T)\|p^{eq}(T)]. \tag{25}$$

This expression was recently obtained by Vaikuntanathan and Jarzynski [12] for the relation between the dissipation and the lag, where they have used $\beta W_{\rm diss}$ instead of its equal ΔS^{eq} [see Eq. (21) above]. Finally, following Ref. [12] [see in particular the section below Eq. (10) in Ref. [12]], one can write Eq. (25) as

$$\Delta S^{eq} \geqslant D[p(T)\|\widetilde{p}^{eq}(0)], \tag{26}$$

where the tilde denotes the reverse process so that the initial state of the system during the reverse process is the final equilibrium state, i.e., $p^{eq}(T) = \widetilde{p}^{eq}(0)$. This last relation was obtained by Kawai *et al.* [9,10] and relates the dissipation to the time reversal asymmetry. Equation (26), on the other hand, relates the change in equilibrium entropies to the time-reversed process.

III. EXAMPLES

Before proceeding, we would like to note that the results of the previous section are valid in the continuous case even though our formalism has been, in general, discrete so far. As an illustrative model, we first consider a driven Brownian particle on a circle [17,18],

$$\dot{x} = u_t + \sqrt{2D}\xi\ , \tag{27}$$

where u_t is the time-dependent periodic drift and D is the time-independent diffusion constant, also assuming $x \in [0,1]$. This model represents a colloidal particle moving in a periodic potential, and it is used to study the violation of the fluctuation-dissipation theorem in nonequilibrium steady states with external driving [18]. Note that the force (and hence the potential) is directly proportional to the periodic drift term in stochastic thermodynamics [see Eq. (15) in Ref. [17]]. The stationary solution for the driven Brownian particle is equal to unity for any value of the control parameter, i.e., $p^{st}(0) = p^{st}(T) = 1$ [17,18]. In other words, once the Brownian particle has relaxed to this steady state with $p^{st} = 1$, it remains so despite any external driving. Our main result, i.e., Eq. (19), yields zero entropy change for this model. Note that this result was also observed in Ref. [17] for the nonadiabatic entropy change using the Fokker-Planck formulation of the stochastic thermodynamics once the steady-state distribution is reached, rendering the excess entropy contribution redundant from there on for the transitions between the nonequilibrium steady states.

A nontrivial example is the Van der Pol oscillator subject to noise. Then the Ito-Langevin type stochastic equation reads

$$\dot{x} = v, \quad \dot{v} + (a + bE)v + x = \eta(t), \tag{28}$$

where a and b are the controllable linear and fixed nonlinear friction coefficients, respectively [22]. The term E denotes, setting the mass and the angular frequency equal to unity for simplicity, the energy of the oscillation, i.e., $E = \frac{1}{2}(v^2 + x^2)$. The random noise is defined to be Gaussian with the noise intensity $\sqrt{2D}$, i.e., $\langle\eta(t)\rangle = 0, \langle\eta(t)\eta(t')\rangle = 2D\delta(t-t')$. We assume that we can control the change in the linear frictional term, i.e., $a = \gamma - \lambda$ and $\gamma \gg \frac{bE}{2}$, where λ denotes the control parameter and γ is the linear friction coefficient by default. The most general stationary solution of the noise-driven Van der Pol oscillator then reads

$$p^{st}(\lambda) = \exp\left(\frac{-aE - \frac{1}{2}bE^2}{D}\right), \tag{29}$$

apart from the appropriate normalization [22]. From here on, we use the energy representation, since it is equivalent to the phase space integration for the simple harmonic oscillator case. We now assume that the physical system initially described by the stationary distribution $p^{st}(0)$ with a zero value of the control parameter evolves into $p^{st}(T)$ with $\lambda_B = \gamma$ through a protocol controlled by an external agent. The initial stationary distribution corresponding to $\lambda = 0$ is given by

$$p^{st}(0) = \frac{\gamma}{D}\exp\left(-\frac{\gamma E}{D}\right), \tag{30}$$

where we have used $\gamma \gg \frac{bE}{2}$. The final steady state with $\lambda = \gamma$ reads

$$p^{st}(T) = \sqrt{\frac{2b}{\pi D}}\exp\left(-\frac{b}{2D}E^2\right). \tag{31}$$

The left-hand side of Eq. (16) can now be calculated as $[\frac{1}{2}\ln(\frac{2b}{\pi D}) - \frac{1}{2}]$, whereas the right-hand side of the same equation yields $[\frac{1}{2}\ln(\frac{2b}{\pi D}) - \frac{Db}{\gamma^2}]$. Therefore, one explicitly obtains from Eq. (16)

$$\frac{\gamma^2}{2Db} = 1\ . \tag{32}$$

Incorporating the relation above into Eq. (19) is tantamount to including the excess entropy change into the system entropy.

Equation (19) by itself explicitly yields

$$\Delta S = \int_0^\infty dE \frac{\gamma}{D} \exp\left(-\frac{\gamma}{D}E\right) \ln\left[\frac{\frac{\gamma}{D}\exp\left(-\frac{\gamma}{D}E\right)}{\sqrt{\frac{2b}{\pi D}}\exp\left(-\frac{b}{2D}E^2\right)}\right], \tag{33}$$

which, after integration, becomes

$$\Delta S = \ln\left(\sqrt{\pi\frac{\gamma^2}{2Db}}\right) - 1 + \frac{Db}{\gamma^2}. \tag{34}$$

Including the relation given by Eq. (32), which is tantamount to including the excess entropy change in the system entropy, we obtain

$$\Delta S^{st} = \ln(\sqrt{\pi}) - 1 + \tfrac{1}{2}, \tag{35}$$

which finally yields

$$\Delta S^{st} = D(p^{st}(0) \parallel p^{st}(T)) \approx 0.07, \tag{36}$$

which is indeed greater than zero, thereby indicating the irreversibility of the transition between these two nonequilibrium steady states. The smallness of this value is expected since the departure from the compared steady state with the zero control parameter is given with respect to the steady state corresponding to $\lambda_B = \gamma$, where γ is itself supposed to be small in all realistic cases.

IV. CONCLUSIONS

To summarize, the system entropy change for the transitions between nonequilibrium steady states arbitrarily far from equilibrium is obtained in terms of the relative entropy of the concomitant steady-state distributions. This result is independent of the constituting process in the sense that steady states can result either due to the nonconservative driving or through the presence of multiple reservoirs with different thermodynamic properties. We also note that the same expression for the transition between nonequilibrium steady states, i.e., Eq. (19), can be used for the transitions between equilibrium states only by replacing the stationary distributions with the corresponding equilibrium ones. Considering only the transitions between the equilibrium states, our result given by Eq. (21) implies the relations obtained in Refs. [9,10,12]. However, these previous relations considered the dissipated work as a measure of the second law, while we have related them to the entropy change between the equilibrium states through relative entropy expression.

It is worth noting that one should not confuse the main result of this paper given by Eq. (19) with the well-known similar expression $D[p(t)\| p^{st}(\lambda)]$ [16]. This expression can be considered as a proof of convergence to steady state and relates the actual and the corresponding steady-state distributions, whereas Eq. (19), on the other hand, relates two distinct steady states. In this context, we also note that a new approach has recently been introduced by defining a novel state function information free energy which also includes the adiabatic term in nonequilibrium thermodynamics [23].

Finally, we remark that the dissipated work formula given by Eq. (21) in this work is obviously restricted to the systems attaining equilibrium at the same temperature after the driving of the control parameter is finalized, and more progress is needed to derive such relations in the case of heat conducting systems [24]. We hope that in the future our results can be experimentally tested, e.g., by using the Van der Pol oscillator studied in this work or a motor protein coupled to an ATP-regenerating system such that the motor protein forms a nonequilibrium steady state [25].

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