Geometrical expression of excess entropy production

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We derive a geometrical expression of the excess entropy production for quasistatic transitions between nonequilibrium steady states of Markovian jump processes, which can be exactly applied to nonlinear and nonequilibrium situations. The obtained expression is geometrical; the excess entropy production depends only on a trajectory in the parameter space, analogous to the Berry phase in quantum mechanics. Our results imply that vector potentials are needed to construct the thermodynamics of nonequilibrium steady states.

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I. INTRODUCTION

The investigation of thermodynamic structures of nonequilibrium steady states (NESSs) has been a topic of active research in nonequilibrium statistical mechanics [1–17]. For example, the extension of the relations in equilibrium thermodynamics, such as the Clausius equality, to NESSs is a great challenge [1–8]. The extended thermodynamics, which is called steady-state thermodynamics (SST) [2], is expected to be useful in analyzing and predicting the dynamical properties of NESSs. However, the complete picture of SST has not been understood.

In equilibrium thermodynamics, the Clausius equality tells us how one can determine thermodynamic potential (entropy) by measuring the heat:

$$\Delta S - \sum_{\nu} \beta^{\nu} Q^{\nu} = 0, \tag{1}$$

which is universally valid for quasistatic transitions between equilibrium states. Here ν is an index of the heat baths, β^{ν} is the inverse temperature of bath ν, Q^{ν} is the heat that the system absorbed from bath ν, and S is the Shannon entropy of the system. The second term on the left-hand side (lhs) of Eq. (1) is called the entropy production in the baths. To generalize the Clausius equality to nonequilibrium situations, it has been proposed [1,2] that heat Q^{ν} needs to be replaced by excess heat $Q^{\nu}_{\rm ex}$, which describes an additional heat induced by a transition between NESSs with time-dependent external control parameters such as the electric field. Correspondingly, the total heat can be decomposed as $Q^{\nu} = Q^{\nu}_{\rm ex} + Q^{\nu}_{\rm hk}$, where the housekeeping heat $Q^{\nu}_{\rm hk}$ describes the steady heat current in a NESS without any parameter change. Quantitative definitions of these quantities will be given later. One may then expect that there exists some thermodynamic potential $S_{\rm SST}$ that characterizes NESSs such that

$$\Delta S_{\rm SST} - \sum_{\nu} \beta^{\nu} Q^{\nu}_{\rm ex} = 0 \tag{2}$$

holds for quasistatic transitions between NESSs, where the second term on the lhs corresponds to the excess part of the entropy production in the baths. Komatsu, Nakagawa, Sasa, and Tasaki (KNST) found that $S_{\rm SST}$ in Eq. (2) is a symmetrized version of the Shannon entropy in the lowest order of nonequilibrium [4,5]. However, the full-order expression of the extended Clausius equality Eq. (2) has been elusive. The fundamental questions arise as to what the nonequilibrium thermodynamic potential $S_{\rm SST}$ in Eq. (2) is in the full-order expression and whether such a potential exists at all.

In this paper we answer these questions and derive a full-order expression of the excess entropy production for Markovian jump processes. We note that driven lattice gases are special cases of our formulation. We have found that an extended Clausius equality in the form of Eq. (2) does not hold in general; the scalar thermodynamic potential $S_{\rm SST}$ should be replaced by a vector potential. In other words, the first term on the lhs of Eq. (2) should be replaced by a geometrical quantity that depends only on trajectories in the parameter space. Our result includes the equilibrium Clausius equality Eq. (1) and KNST's extended Clausius equality as special cases. We will also derive the general condition that there exists a thermodynamic potential $S_{\rm SST}$ such that Eq. (2) holds.

We have used the technique of the full counting statistics [11,18] to prove our main results. In the context of the full counting statistics (and also stochastic ratchets), it has been reported [19–26] that several phenomena in classical stochastic processes are analogous to Berry's geometrical phase in quantum mechanics [27,28]. In this analogy, the above-mentioned vector potential corresponds to the gauge field that induces the Berry phase. Our result can also be regarded as a generalization of these previous studies on the classical Berry phase.

This paper is organized as follows. In Sec. II we formulate the model of our system and define the decomposition of the entropy production into the housekeeping and excess parts based on the full counting statistics. In Sec. III we derive our main results, which consist of the geometrical expressions of the excess parts of the cumulant generating function and the average of the entropy production. In Sec. IV we apply our main results to two special cases: One is equilibrium thermodynamics with the detailed balance and the other is KNST's extended Clausius equality. In Sec. V we discuss a quantum dot as a simple example, where Eq. (2) does not hold in general. In Sec. VI we conclude this paper with a discussion.

II. SETUP

We first formulate our setup and define the decomposition of the cumulant generating function of the entropy production into the excess and housekeeping parts.

A. Dynamics

We consider Markovian jump processes with $N < \infty$ microscopic states. Let p_x be the probability that the system is in state x. The probability distribution of the system is then characterized by the vector $|p\rangle := [p_1, p_2, \ldots, p_N]^T$, where $1,2,\ldots,N$ describe the states and T describes the transpose of the vector. The time evolution of the probability distribution is given by a master equation $|\dot{p}(t)\rangle = R(\boldsymbol{\alpha}(t))|p(t)\rangle$, where $|\dot{p}(t)\rangle$ describes the time derivative of $|p(t)\rangle$ and $R(\boldsymbol{\alpha})$ is an $N \times N$ matrix characterizing the transition rate of the dynamics with external parameters $\boldsymbol{\alpha}$. Here the external parameters correspond, for example, to a potential or a nonconservative force applied to a lattice gas, or the temperatures of the heat baths. We drive the system by changing $\boldsymbol{\alpha}$. For simplicity of notation, we will often omit $\boldsymbol{\alpha}(t)$ or t in the following discussion. We note that $\sum_x R_{xy} = 0$ holds for every y, where R_{xy} is the xy component of R that characterizes the transition rate from state y to x. We assume that R is irreducible such that R has eigenvalue 0 without degeneracy due to the Perron-Frobenius theorem. We write as $\langle 1|$ and $|p^S\rangle$ the left and right eigenvectors of R corresponding to eigenvalue 0 such that $\langle 1|R = 0$ and $R|p^S\rangle = 0$ hold. We note that $\langle 1| = [1,1,\ldots,1]$ holds and that $|p^S\rangle = [p_1^S, p_2^S, \ldots, p_N^S]^T$ is the unique steady distribution of the dynamics with a given $\boldsymbol{\alpha}$. For simplicity, we assume that R is diagonalizable. We also assume that the transition matrix can be decomposed into the contributions from multiple heat baths, labeled by ν, as $R_{xy} = \sum_\nu R_{xy}^\nu$.

We next introduce the entropy production that depends on trajectories of the system. Such a trajectory-dependent entropy production has been studied in terms of nonequilibrium thermodynamics of stochastic systems [13,29–31]. The entropy production in bath ν with transition from y to x is given by

$$\sigma_{xy}^\nu = \begin{cases} \ln \frac{R_{xy}^\nu}{R_{yx}^\nu} = -\beta^\nu Q_{xy}^\nu & \text{if} \quad R_{xy}^\nu \neq 0,\ R_{yx}^\nu \neq 0 \\ 0 & \text{if} \quad R_{xy}^\nu = 0,\ R_{yx}^\nu = 0, \end{cases} \tag{3}$$

where Q_{xy}^ν is the heat that is absorbed in the system from bath ν during the transition from y to x. The equality in Eq. (3) is consistent with the detailed fluctuation theorem [13,29–31]. The integrated entropy production from time 0 to τ is determined by the trajectory of the system's states during the time interval as

$$\sigma = \sum_{t:\ \text{jump}} \sigma_{x(t+0)y(t-0)}^\nu, \tag{4}$$

where the sum is taken over all times at which the system jumps and $y(t-0)$ and $x(t+0)$ are the states immediately before and after the jump at t, respectively. We note that the ensemble average of σ is equivalent to the entropy production in the conventional thermodynamics of macroscopic systems. A reason why we consider the trajectory-dependent entropy production lies in the fact that the entropy production is connected to the heat through Eq. (3) at the level of each trajectory.

B. Full counting statistics

We then discuss the full counting statistics of σ. Let $P(\sigma)$ be the probability of σ. Its cumulant generating function is given by

$$S(i\chi) := \ln \int d\sigma\, e^{i\chi\sigma} P(\sigma), \tag{5}$$

where $\chi \in \mathbb{R}$ is the counting field. Here $S(i\chi)$ leads to the cumulants of σ such as $\langle \sigma \rangle = \partial S(i\chi)/\partial(i\chi)|_{\chi=0}$, where $\langle \cdots \rangle$ describes the statistical average. To calculate $S(i\chi)$, we define the matrix R_χ as $(R_\chi)_{xy} := \sum_\nu R_{xy}^\nu \exp(i\chi\sigma_{xy}^\nu)$ and consider the time evolution of vector $|p_\chi(t)\rangle$ corresponding to

$$|\dot{p}_\chi(t)\rangle = R_\chi(\boldsymbol{\alpha}(t))|p_\chi(t)\rangle, \tag{6}$$

with initial condition $|p_\chi(0)\rangle := |p(0)\rangle$. The formal solution of Eq. (6) is given by $|p_\chi(t)\rangle = T \exp_\leftarrow[\int_0^\tau R_\chi(\boldsymbol{\alpha}(t))dt]|p(0)\rangle$, where $T \exp_\leftarrow$ describes the left-time-ordered exponential. Then we can show that

$$e^{S(i\chi)} = \langle 1|p_\chi(\tau)\rangle \tag{7}$$

holds, where $\langle \cdot|\cdot \rangle$ means the inner product of the left and right vectors.

We write the eigenvalues of R_χ as λ_χ^n, where $n = 0$ corresponds to the eigenvalue with the maximum real part. If $|\chi|$ is sufficiently small, λ_χ^0 is not degenerated and R_χ is diagonalizable. We write as $\langle \lambda_\chi^n|$ and $|\lambda_\chi^n\rangle$ the left and right eigenvectors corresponding to λ_χ^n, which we can normalize as $\langle \lambda_\chi^n|\lambda_\chi^m\rangle = \delta_{nm}$, with δ_{nm} the Kronecker delta. In particular, we write $\langle \lambda_\chi^0| =: \langle 1_\chi|$ and $|\lambda_\chi^0\rangle =: |p_\chi^S\rangle$. We note that if $\chi = 0$, $\langle 1_\chi|$ and $|p_\chi^S\rangle$ reduce to $\langle 1|$ and $|p^S\rangle$, respectively.

C. Decomposition of the entropy production

It is known that $\lambda_\chi^0(\boldsymbol{\alpha})$ is the cumulant generating function of σ in the steady distribution with the parameter $\boldsymbol{\alpha}$. More precisely, $\lambda_\chi^0(\boldsymbol{\alpha})$ satisfies

$$\lambda_\chi^0(\boldsymbol{\alpha}) = \lim_{\tau \to +\infty} \frac{S(i\chi;\boldsymbol{\alpha};\tau)}{\tau}, \tag{8}$$

where $S(i\chi;\boldsymbol{\alpha},\tau)$ is the cumulant generating function of σ from 0 to τ with $\boldsymbol{\alpha}$ fixed.

We then decompose the cumulant generating function into two parts:

$$S(i\chi) = S_{\rm hk}(i\chi) + S_{\rm ex}(i\chi), \tag{9}$$

where $S_{\rm hk}(i\chi)$ is the housekeeping part defined as

$$S_{\rm hk}(i\chi) := \int_0^\tau \lambda_\chi^0(\boldsymbol{\alpha}(t))dt \tag{10}$$

and $S_{\rm ex}(i\chi)$ is the excess part defined as $S_{\rm ex}(i\chi) := S(i\chi) - S_{\rm hk}(i\chi)$. The average of the excess entropy production is given by

$$\langle \sigma \rangle_{\rm ex} = \left. \frac{\partial S_{\rm ex}(i\chi)}{\partial(i\chi)} \right|_{\chi=0}. \tag{11}$$

We note that the above decomposition is consistent with that in Refs. [4,5]. In fact, from Eqs. (8) and (11) we can show

$$\langle \sigma \rangle_{\rm ex} = \langle \sigma \rangle - \int_0^\tau \langle \dot{\sigma} \rangle_{{\rm hk};\boldsymbol{\alpha}(t)} dt, \tag{12}$$

where $\langle\dot\sigma\rangle_{\mathrm{hk};\boldsymbol\alpha} := \partial\lambda^0_\chi(\boldsymbol\alpha)/\partial(i\chi)|_{\chi=0}$ is the long-time average of the entropy production per unit time with $\boldsymbol\alpha$ fixed.

III. MAIN RESULTS

We now discuss the main results of this paper, which we will refer to as Eqs. (16) and (17). First of all, we expand $|p_\chi(t)\rangle$ as

$$|p_\chi(t)\rangle = \sum_n c_n(t)e^{\Lambda^n_\chi(t)}\big|\lambda^n_\chi(\boldsymbol\alpha(t))\big\rangle, \tag{13}$$

where $\Lambda^n_\chi(t) := \int_0^t \lambda^n_\chi(\boldsymbol\alpha(t'))dt'$. We can show that $\dot c_0 = -\sum_n c_n\langle 1_\chi|\dot\lambda^n_\chi\rangle e^{\Lambda^n_\chi-\Lambda^0_\chi}$ and $\langle 1_\chi|\dot\lambda^n_\chi\rangle = \langle 1_\chi|\dot R_\chi|\lambda^n_\chi\rangle/(\lambda^n_\chi - \lambda^0_\chi)$ hold. Therefore, if the speed of the change of the external parameters is much smaller than the relaxation speed of the system, we obtain

$$\dot c_0(t) \simeq -c_0(t)\langle 1_\chi(\boldsymbol\alpha(t))\big|\dot p^S_\chi(\boldsymbol\alpha(t))\big\rangle. \tag{14}$$

Here we have used that the real part of $\Lambda^n_\chi - \Lambda^0_\chi$ is negative for all $n \neq 0$. We note that this result is similar (but not equivalent) to the adiabatic theorem in quantum mechanics.

Assume that we quasistatically change the parameter $\boldsymbol\alpha$ between time 0 and τ along a curve C in the parameter space. The solution of Eq. (14) is given by

$$\begin{aligned} c_0(\tau) &= c_0(0)\exp\left(-\int_0^\tau dt\big\langle 1_\chi(\boldsymbol\alpha(t))\big|\dot p^S_\chi(\boldsymbol\alpha(t))\big\rangle\right) \\ &= c_0(0)\exp\left(-\int_C\langle 1_\chi|d\big|p^S_\chi\rangle\right), \end{aligned}\tag{15}$$

where d on the right-hand side (rhs) means the total differential in terms of $\boldsymbol\alpha$ such that $d|p^S_\chi\rangle := d\boldsymbol\alpha\cdot\frac{\partial}{\partial\boldsymbol\alpha}|p^S_\chi\rangle$. Let the initial distribution be the steady distribution $|p(0)\rangle = |p^S(\boldsymbol\alpha(0))\rangle$, which leads to $c_0(0) = \langle 1_\chi(\boldsymbol\alpha(0))|p^S(\boldsymbol\alpha(0))\rangle$. We then obtain the excess part of the cumulant generating function as

$$\begin{aligned} S_{\mathrm{ex}}(i\chi) = &\int_C\langle 1_\chi|d\big|p^S_\chi\rangle \\ &+\ln\langle 1_\chi(\boldsymbol\alpha(0))|p^S(\boldsymbol\alpha(0))\rangle + \ln\big\langle 1\big|p^S_\chi(\boldsymbol\alpha(\tau))\big\rangle, \end{aligned}\tag{16}$$

where the rhs is geometrical and analogous to the Berry phase in quantum mechanics [27]; it depends only on the trajectory C in the parameter space. More precisely, the rhs of Eq. (16) is analogous to the noncyclic Berry phase [26,28]. We note that $\Lambda^n_\chi(\tau)$ is analogous to the dynamical phase. In this analogy, $|p^S_\chi\rangle$ and R_χ correspond to a state vector and a Hamiltonian, respectively. The equality in Eq. (16) is our first main result.

In the terminology of the Berry phase, $\langle 1_\chi|d|p^S_\chi\rangle$ corresponds to a vector potential or a gauge field whose base space is the parameter space. The second and third terms on the rhs of Eq. (16) confirm the gauge invariance of $S_{\mathrm{ex}}(i\chi)$, as is the case for quantum mechanics [28], where the gauge transformation corresponds to the transformation of the left and right eigenvectors of $R_\chi(\boldsymbol\alpha)$ as $\langle 1_\chi(\boldsymbol\alpha)| \mapsto \langle 1_\chi(\boldsymbol\alpha)|e^{-\theta(\boldsymbol\alpha)}$ and $|p^S_\chi(\boldsymbol\alpha)\rangle \mapsto e^{\theta(\boldsymbol\alpha)}|p^S(\boldsymbol\alpha)\rangle$ with $\theta(\boldsymbol\alpha)$ a scalar. We note that several formulas that are similar to Eq. (16) have been obtained for different setups [20–22,24–26].

By differentiating Eq. (16) in terms of $i\chi$, we obtain a simple expression of the average of the excess entropy production:

$$\int_C\langle 1'|d|p^S\rangle + \langle\sigma\rangle_{\mathrm{ex}} = 0, \tag{17}$$

where $\langle 1'| := \partial\langle 1_\chi|/\partial(i\chi)|_{\chi=0}$. The equality in Eq. (17) is the second main result, which is the full-order expression of the average of the excess entropy production. In contrast to Eq. (2), the first term on the lhs of Eq. (17) is not given by the difference of a scalar potential S_{SST}, but by a geometrical quantity. We also refer to $\langle 1'|d|p^S\rangle$ as a vector potential.

We can explicitly calculate $\langle 1'|$. By differentiating both sides of $\langle 1_\chi|R_\chi = \lambda^0_\chi R_\chi$ in terms of $i\chi$, we have $\langle 1'| = -\langle 1|\partial R_\chi/\partial(i\chi)|_{\chi=0}R^\dagger + k\langle 1|$, where $R^\dagger$ is the Moore-Penrose pseudoinverse of R and k is an unimportant constant. Therefore, we obtain

$$\langle\sigma\rangle_{\mathrm{ex}} = \int_C\sum_{\nu xyz}\sigma^\nu_{xy}R^\nu_{xy}R^\dagger_{yz}dp^S_z. \tag{18}$$

Similar formulas for particle currents have been obtained in Refs. [19,23].

We consider next the condition for the existence of the thermodynamic potential S_{SST} that satisfies Eq. (2). For simplicity, we assume that the parameter space is simply connected, i.e., there is no hole or singularity. The necessary and sufficient condition for the existence of S_{SST} is that the integral in the first term on the lhs of Eq. (17) is always determined only by the initial and final points of C or, equivalently, $\oint_C\langle 1'|d|p^S\rangle = 0$ holds for every closed curve C. In addition, the Stokes theorem states that $\oint_C\langle 1'|d|p^S\rangle = \int_S d(\langle 1'|d|p^S\rangle)$ holds, where S is a surface whose boundary is C and d means the exterior derivative. By using the wedge product, we have

$$\begin{aligned} d(\langle 1'|d|p^S\rangle) = d\langle 1'|\wedge d|p^S\rangle &:= \sum_x d1'_x\wedge dp^S_x \\ &= \sum_{xkl}\frac{\partial 1'_x}{\partial\alpha_k}\frac{\partial p^S_x}{\partial\alpha_l}d\alpha_k\wedge d\alpha_l, \end{aligned}$$

where $1'_x$ means the x component of the vector $\langle 1'|$ and α_k is the k component of $\boldsymbol\alpha$. Therefore, the necessary and sufficient condition is that

$$d\langle 1'|\wedge d|p^S\rangle = 0 \tag{19}$$

holds in every point of the parameter space. Equation (19) is equivalent to

$$\sum_x\left(\frac{\partial 1'_x}{\partial\alpha_k}\frac{\partial p^S_x}{\partial\alpha_l} - \frac{\partial 1'_x}{\partial\alpha_l}\frac{\partial p^S_x}{\partial\alpha_k}\right) = 0 \tag{20}$$

for all (k,l). In the terminology of the gauge theory, $d\langle 1'|\wedge d|p^S\rangle$ corresponds to the strength of the gauge field or the curvature. For the case of the $U(1)$-gauge theory, the curvature is the magnetic field.

In equilibrium thermodynamics, Eq. (19) holds due to the Maxwell relation and $\langle 1'|d|p^S\rangle$ becomes the total differential of the Shannon entropy, as we will see in the following section. In contrast, Eq. (19) does not hold for transitions between NESSs in general. In this sense, the vector potential $\langle 1'|d|p^S\rangle$

plays a fundamental role instead of the scalar thermodynamic potential (i.e., the Shannon entropy) in SST.

IV. SPECIAL CASES

In this section we discuss two special cases in which the first term on the lhs of Eq. (17) reduces to the total differential of a scalar thermodynamic potential.

A. Equilibrium thermodynamics

In general, we can explicitly show that Eq. (17) reduces to the equilibrium Clausius equality if the detailed balance is satisfied. Let E_x be the energy of state x. The transition rate is given by $R_{xy} = e^{\beta(E_y - W_{xy})}$ with $W_{xy} = W_{yx}$, the steady distribution is given by $p_x^S = e^{-\beta E_x}/Z$ with Z the partition function, and the entropy production in a bath is given by $\sigma_{xy} = -\beta(E_x - E_y) = -\beta Q_{xy}$. In the quasistatic limit, the system is in contact with a single heat bath with inverse temperature β at each time, while β can be time dependent. We then obtain

$$\langle 1'|d|p^S\rangle = \sum_x \beta E_x dp_x^S = d\left(-\sum_x p_x^S \ln p_x^S\right), \quad (21)$$

which means that $\langle 1'|d|p^S\rangle$ is the total differential of the Shannon entropy.

B. KNST's extended Clausius equality

We now show that Eq. (17) reduces to KNST's extended Clausius equality [4,5] in the lowest order of nonequilibrium. Here we assume that for every (x,y) there exists at most a single ν that satisfies $R_{xy}^\nu \neq 0$, so that we can remove the index ν. This is the same assumption as in Refs. [4,5]. Moreover, we formally introduce the time reversal of states: The time reversal of the state x, denoted by x^*, is assigned in the phase space. Since we are considering stochastic jump processes that usually do not have any momentum term, we just interpret the correspondence $x \mapsto x^*$ as a formal mathematical map. Correspondingly, we should replace $\ln(R_{xy}^\nu/R_{yx}^\nu)$ in Eq. (3) by $\ln(R_{xy}^\nu/R_{y^*x^*}^\nu)$. Only with this replacement do all of the foregoing arguments remain unchanged in the presence of the time reversal. We also assume that in thermal equilibrium, $p_x^S = p_{x^*}^S$ holds. We define

$$\eta := \sum_{xyz} \ln\left(p_{x^*}^S/p_{y^*}^S\right) R_{xy} R_{yz}^\dagger dp_z^S = \sum_x \left(\ln p_{x^*}^S\right) dp_x^S \quad (22)$$

and $\tilde{R}_{xy} := R_{y^*x^*} p_{x^*}^S / p_{y^*}^S$. Here $\tilde{R}$ is the adjoint of R for the cases of $x = x^*$ [9,12]. We note that $\sum_x \tilde{R}_{xy} = 0$ holds for every y. Since $R = \tilde{R}$ holds if the detailed balance is satisfied, we characterize the nonequilibrium of the dynamics by $\varepsilon := \max_{xy} |(\tilde{R}_{xy} - R_{xy})/R_{xy}|$. We then obtain

$$\begin{aligned}\langle 1'|d|p^S\rangle + \eta &= \sum_{xyz} \ln(\tilde{R}_{xy}/R_{xy}) R_{xy} R_{yz}^\dagger dp_z^S \\ &= \sum_{xyz} (\tilde{R}_{xy} - R_{xy}) R_{yz}^\dagger dp_z^S + O(\varepsilon^2 \Delta) \\ &= O(\varepsilon^2 \Delta), \end{aligned} \quad (23)$$

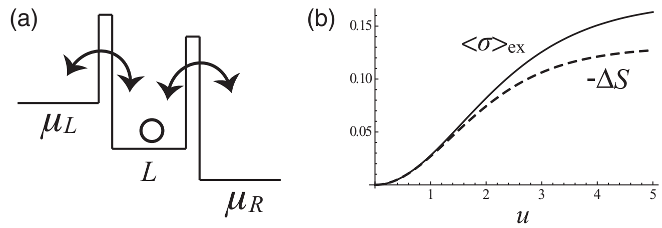

FIG. 1. (a) Schematic of the model of a quantum dot. A single electron is transferred to and from the two heat baths with chemical potentials μ_L and μ_R. (b) $\langle\sigma\rangle_{\rm ex}$ (solid line) and $-\Delta S$ (dashed line) for quasistatic processes. They are coincident with each other up to second order of the nonequilibrium of the final state, which is denoted by u.

where $\Delta := \max_x |dp_x^S|$ characterizes the amount of the infinitesimal change of the steady distribution. In addition,

$$\eta = d\left(\sum_x p_x^S \ln\sqrt{p_x^S p_{x^*}^S}\right) + O(\varepsilon^2\Delta) \quad (24)$$

holds [5]. From Eqs. (23) and (24) we obtain

$$\langle 1'|d|p^S\rangle = d\left(-\sum_x p_x^S \ln\sqrt{p_x^S p_{x^*}^S}\right) + O(\varepsilon^2\Delta), \quad (25)$$

which implies KNST's extended Clausius equality, where the first term on the rhs is the total differential of the symmetrized Shannon entropy. We note that if we gradually change the parameter $\boldsymbol{\alpha}$ from an equilibrium distribution, then KNST's extended Clausius equality is valid up to $O(\varepsilon^2)$ because $\Delta = O(\varepsilon)$ holds.

V. EXAMPLE

As a simple example that illustrates the absence of a scalar thermodynamic potential, we consider a stochastic model of a quantum dot that is in contact with two baths that are labeled by $\nu = L$ and R [see also Fig. 1(a)] [18]. This model describes the stochastic dynamics of the number of electrons in the dot by a classical master equation.

An electron is transferred from the baths to the dot one by one or vice versa. We assume that the states of the dot are $x = 0$ and 1, which respectively denote that the electron is absent and occupies the dot. The probability distribution is described by $|p\rangle = [p_0, p_1]^T$ and the transition rate is given by $R = \sum_{\nu=L,R} R^\nu$ with

$$R^\nu = \begin{bmatrix} -\gamma_\nu f_\nu & \gamma_\nu(1-f_\nu) \\ \gamma_\nu f_\nu & -\gamma_\nu(1-f_\nu) \end{bmatrix}, \quad (26)$$

where γ_ν is the tunneling rate between the dot and bath ν and $f_\nu = (e^{\beta(E-\mu_\nu)}+1)^{-1}$ is the Fermi distribution function with β the inverse temperature of the baths, μ_ν the chemical potential of bath ν, and E the excitation energy of the dot. The entropy production is given by $\sigma_{00}^\nu = \sigma_{11}^\nu = 0$ and $\sigma_{10}^\nu = -\sigma_{01}^\nu = \sigma_\nu$ with $\sigma_\nu := \beta(\mu_\nu - E)$. For simplicity, we set $\gamma_L = \gamma_R =: \gamma$. Without loss of generality, we assume that the control parameters are σ_L and σ_R.

We can explicitly calculate the vector potential as

$$\langle 1'|d|p^S\rangle = -\frac{1}{4}(\sigma_L + \sigma_R)[f_L(1-f_L)d\sigma_L + f_R(1-f_R)d\sigma_R] \tag{27}$$

and the curvature as

$$d\langle 1'| \wedge d|p^S\rangle = \frac{1}{4}[f_L(1-f_L) - f_R(1-f_R)]d\sigma_L \wedge d\sigma_R. \tag{28}$$

Therefore, the curvature vanishes only if $\mu_L = \mu_R$ or $2E = \mu_L + \mu_R$ holds. The former case corresponds to equilibrium thermodynamics. Since the curvature vanishes only on the two lines in the two-dimensional parameter space, any scalar potential cannot be defined on the entire parameter space. We note that the quantities that we have calculated here are different from those in previous research [20–22,24,25].

As a simple illustration, we consider the following situation. The dot is initially in thermal equilibrium with $\sigma_L = \sigma_R = 0$. We then quasistatically change σ_L from 0 to u, while σ_R is not changed. We calculate $\langle\sigma\rangle_{\rm ex} = \int_0^u \sigma_L f_L(1-f_L)d\sigma_L/4$ for this process. For comparison, we also calculate the difference of the Shannon entropy between the initial and final distributions of the dot, denoted as ΔS. Figure 1(b) shows $\langle\sigma\rangle_{\rm ex}$ (solid line) and $-\Delta S$ (dashed line) versus u. They are coincident with each other up to $O(u^2)$, which is consistent with the extended Clausius equality discussed in Sec. IV B with $u = O(\varepsilon) = O(\Delta)$.

VI. CONCLUSION

We have derived the geometrical expressions of the excess entropy production for quasistatic transitions between NESSs: Eq. (16) for $S_{\rm ex}(i\chi)$ and Eq. (17) for $\langle\sigma\rangle_{\rm ex}$. Our results imply that the vector potentials $\langle 1_\chi|d|p_\chi^S\rangle$ and $\langle 1'|d|p^S\rangle$ play important roles in SST. We have also derived the condition Eq. (19) that a scalar thermodynamic potential exists.

We note that the arguments in Secs. II and III are not restricted to the case of entropy production σ_{xy}^ν, but can be formally applied to an arbitrary quantity f_{xy}^ν that satisfies $f_{xx}^\nu = 0$. In fact, even if we replace σ_{xy}^ν by any f_{xy}^ν, the formal expressions of the main results in Sec. III remain unchanged. However, we have explicitly used the properties of σ_{xy}^ν such as Eq. (3) in Sec. IV.

We also note that, as is the case for the gauge theory, we can rephrase our results in Eqs. (15) and (16) in terms of differential geometry [32]. We consider a trivial vector bundle whose base manifold is the parameter space $\{\boldsymbol{\alpha}\}$. The fiber is $\mathbb{C}$ and $c_0(t)$ in Eq. (13) is an element of the fiber. Then $\langle 1_\chi|d|p_\chi^S\rangle$ is a connection form and Eq. (14) describes the parallel displacement of c_0 with the connection along curve C.

In this paper we have assumed that nonequilibrium dynamics is modeled by a Markovian jump process with transition rate R being diagonalizable. The generalization of our results to other models of nonequilibrium dynamics is a future issue. For example, it is worth investigating whether our result can be generalized to Langevin systems. Moreover, the investigation of the usefulness of our results in nonequilibrium thermodynamics is also a future challenge.

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