

Generalized Onsager's reciprocal relations for the master and Fokker-Planck equations

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The Onsager's reciprocal relation plays a fundamental role in the nonequilibrium thermodynamics. However, unfortunately, its classical version is valid only within a narrow region near equilibrium due to the linear regression hypothesis, which largely restricts its usage. In this paper, based on the conservation-dissipation formalism, a generalized version of Onsager's relations for the master equations and Fokker-Planck equations was derived. Nonlinear constitutive relations with nonsymmetric and positively stable operators, which become symmetric under the detailed balance condition, constitute key features of this new generalization. Similar conclusions also hold for many other classical models in physics and chemistry, which in turn make the current study as a benchmark for the application of generalized Onsager's relations in nonequilibrium thermodynamics.

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I. INTRODUCTION

In 1931, L. Onsager published two consecutive papers, "Reciprocal relations in irreversible processes, I and II," in *Physical Review* [1,2]. In these works, based on the time reversibility of microscopic dynamics and the linear regression hypothesis, Onsager established the later well-known "celebrated reciprocal relations," which have been commonly regarded as the beginning of modern nonequilibrium thermodynamics [3]. Onsager's relation pointed out the intrinsic duality of coefficients between nonequilibrium fluxes and forces for different irreversible processes, and thus played a fundamental role in various mechanical, chemical, thermal, and electrical coupling systems [4]. For his distinguished contributions to nonequilibrium thermodynamics, Onsager was awarded in Chemistry in 1968.

Mathematically, Onsager argued that the local entropy production rate σ , which is semipositive according to the second law of thermodynamics, can be written into a bilinear form involving two column vectors, $\mathbf{J} \equiv (J_k)$ and $\mathbf{X} \equiv (X_k)$,

$$\sigma = \mathbf{J} \cdot \mathbf{X} = \sum_k J_k X_k \geq 0, \quad (1)$$

where $J_k(x, t)$ and $X_k(x, t)$ denote the thermodynamic flux and force, which depend on the space and time coordinates (x, t) ($x \in \mathbb{R}^n, t \geq 0$), for the k 'th irreversible process, respectively. Especially, in the region near equilibrium, the thermodynamic fluxes and forces adopt a simple linear constitutive relation:

$$\mathbf{J}(\mathbf{X}) = \mathbf{M} \cdot \mathbf{X}, \quad (2)$$

where \mathbf{M} is a constant matrix. To make sure $\sigma \geq 0$, the matrix \mathbf{M} must be positive semidefinite. Furthermore, according to Onsager's argument, \mathbf{M} is symmetric, too ($\mathbf{M} = \mathbf{M}^T$). Equation (2) with the symmetry requirement is known as the Onsager's reciprocal relation in literature [3,5]. Later,

the Onsager's original derivation was extended to systems including odd variables by Casimir [6].

It is well known that the Onsager's relation is based on the time-reversal invariance of microscopic dynamics and the linear regression hypothesis. For example, the existence of a constant symmetric matrix \mathbf{M} linking the thermodynamic forces and fluxes is closely related to the linear regression hypothesis [1,2], which, to a great pity, is valid only in a narrow region near equilibrium. In order to go far from the equilibrium, nonlinear Onsager's relations have been studied in systems with small fluctuations by Stratonovich [7], in discrete systems by Hurley and Garrod [8], in terms of the master equation and Fokker-Planck equation under a generalized detailed balance symmetry by Hanggi [9], and in quantum systems by Beretta [10]. Hazoglou *et al.* [11] introduced higher-order generalizations of Onsager's relations based on the principle of maximum caliber. See Refs. [12–14] for more details of symmetries among the higher-order transport coefficients. Bertini *et al.* formulated a macroscopic fluctuation theory to calculate the large deviation functional in nonequilibrium steady states, which is regarded as the modern framework of Onsager's regression hypothesis [15,16]. On the other hand, Gabrielli, Jona-Lasinio, and Landim demonstrated that for an interacting particle system the Onsager's relation can be recovered by the large deviation theory without microscopic reversibility [17,18].

More recently, we proposed a novel conservation-dissipation formalism (CDF) for modeling various irreversible processes [19]. In CDF, a key step is the adoption of a nonlinear constitutive relation between thermodynamic forces and fluxes:

$$\mathbf{J} = \mathcal{M}\mathbf{X}, \quad (3)$$

where $\mathbf{X} \in \chi$, χ is a properly defined function space, $\mathcal{M} : \chi \rightarrow \chi$ denotes an operator acting on function \mathbf{X} , such as matrix multiplication for master equations and integral transform for Fokker-Planck equations to be specified later. Notice $\mathcal{M} = \mathcal{M}_{\mathbf{X}}$ is no longer a constant matrix and could depend on thermodynamic forces \mathbf{X} , too. Again, the operator \mathcal{M} should

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be positive semidefinite (or positively stable to be strict) in order to fulfill the second law of thermodynamics. However, the symmetry requirement has to be abandoned since the classical Onsager's relation does not hold in general. In this way, Eq. (3) could be considered as a direct generalization of Onsager's relation in the nonlinear form.

Furthermore, in CDF, we assumed that thermodynamic forces come from entropic contributions in consistent with Onsager:

$$X_k = -\frac{\delta F}{\delta \alpha_k}, \quad (4)$$

where $\alpha_k(x, t)$ denotes either conserved or dissipative variables in an enlarged state variable space in accordance with the spirit of extended irreversible thermodynamics proposed by Muller and Ruggeri [20] and Jou, Lebon, and Casas-Vazquez [5], etc., $F = F(\{\alpha_k\})$ is the relative entropy (or free energy). Meanwhile, thermodynamic fluxes are directly related to the changes of their corresponding state variables in time:

$$J_k = \frac{\partial \alpha_k}{\partial t}. \quad (5)$$

In this way, models for various irreversible processes constructed by CDF could be cast into an elegant unified form—the generalized Onsager's relation.

The generalized Onsager's relation adopted in CDF has been explored and applied in several distinguished areas, including several classical partial differential equations in mathematical physics [21], chemical reactions under detailed balance condition [22], Levermore's hierarchies for the Boltzmann equation [23], etc. In the current paper, we are going to explore two more important examples—the master equation and the Fokker-Planck equation. These two equations have been widely used for modeling various irreversible processes, e.g., in vivo transcription and translation of genes with multiple phenotypic states [24], particles diffusion, permeation and sedimentation in solutions [25], and so on.

By defining thermodynamic forces as the functional derivatives of relative entropy with respect to the probability (or probability density in the continuous case) and thermodynamic fluxes as the probability flow, we proved that these two quantities in the master equation and in the Fokker-Planck equation are closely related to each other through the generalized Onsager's relations in Eq. (3). Especially, when the reference state in the relative entropy is changed from the nonequilibrium steady state (NESS) to the equilibrium state under detailed balance condition, the operator \mathcal{M} becomes symmetric again (though still not necessarily be constant). Our results showed that both the master equation and the Fokker-Planck equation possess an elegant mathematical structure in consistent with the CDF and may serve as a benchmark for the application of generalized Onsager's relation in nonequilibrium thermodynamics in the future.

The generalizations of Onsager's relations are well known in the field of stochastic thermodynamics, where the model equations are the Langevin equation (equivalently, on the deterministic equation side, the Fokker-Planck equation) and master equation, etc. In recent years, there have been extensive notable works concerning the thermodynamics of irreversible stochastic processes [26–38], which can be regarded as the

continuation of Onsager's original work. Gallavotti showed that the fluctuation theorem reduces to the Onsager's relations with zero power input (i.e., near equilibrium) [39]. Afterwards, this type of fluctuation theorem was derived for systems undergoing Kramers-Langevin dynamics by Kurchan [40]. Jarzynski obtained a transient relation for the free energy difference between two states of a system driven by conservative forces [29], which is now widely known as the Jarzynski equality. Later, Jarzynski equality was established for time-dependent Markov processes within the master equation formalism [30]. Seifert showed that the stochastic nonequilibrium dynamics given by Langevin equations and master equations obeyed a fluctuation theorem [33]. Furthermore, it was proved that an integral fluctuation theorem for the housekeeping heat was valid for transitions between steady states [41]. All these works could be interpreted as extensions of the Onsager's relation in the modern theory according to Gallavotti's work.

II. GENERALIZED ONSAGER'S RELATION FOR THE MASTER EQUATION

In the first case, let us consider a finite-state Markov process described by a general type of master equations in the form of

$$\frac{d}{dt} p_i(t) = \sum_{j \neq i} (q_{ij} p_j - q_{ji} p_i), \quad i = 1, \dots, N, \quad (6)$$

where $p_i \geq 0$ is the probability for finding the system in state i and $q_{ij} \geq 0$ ($i \neq j$) denotes the transition rate from state j to state i , $q_{ii} = -\sum_{j \neq i} q_{ji}$. Without loss of generality, the transition rate matrix (q_{ij}) is required to satisfy the irreducibility condition, which claims that, for any states $i_0 \neq i_1$, there is a sequence of indices j_1, j_2, \dots, j_l , such that $i_0 = j_1, i_1 = j_l$ and $q_{j_{m+1} j_m} > 0$ for $1 \leq m \leq l-1$. In other words, between each pair of states i_0 and i_1 , there exists a pathway with all positive transition rates.

If the transition rate matrix satisfies the irreducibility condition, as well as the initial condition satisfies $p_i(0) = p_i^0$ with $0 \leq p_i^0 \leq 1$ and $\sum_i p_i^0 = 1$ for all states i , Schnakenberg has proven that there exists a “unique” NESS with a stationary probability distribution $\{0 < p_i^s < 1\}$ as the long-time solution of the master equation [42], that is, $\sum_j q_{ij} p_j^s = \sum_j q_{ji} p_i^s$. One class of master equations is of particular importance, that is, its stationary probability distribution $\{p_i^e\}$ further satisfies the condition of detailed balance, $q_{ij} p_j^e = q_{ji} p_i^e$.

With respect to the NESS, we can introduce the total internal energy $U = -k_B T \sum_i p_i \ln p_i^s$, entropy $S = -k_B \sum_i p_i \ln p_i$, and relative entropy $F = k_B T \sum_i p_i \ln(p_i/p_i^s)$. Throughout the present work, k_B is the Boltzmann constant and the temperature T is assumed to be constant. According to the Kullback-Leibler divergence [43,44], $F \geq 0$ and $dF/dt \leq 0$. Now the master equation in Eq. (6) can be rewritten into a more compact structure, as stated in the following theorem.

Theorem II.1: Given thermodynamic fluxes $J_i = \frac{dp_i}{dt}$ and thermodynamic forces $X_i = -\frac{\partial F}{\partial p_i}$, the master equation in (6) obeys the generalized Onsager's relation:

$$J_i = -\sum_j M_{ij} \frac{\partial F}{\partial p_j}, \quad (7)$$

with

$$M_{ij} = \begin{cases} -\frac{q_{ij} \exp[\sigma(p_i, p_j)]}{k_B T p_i^s}, & i \neq j, \\ \sum_{j \neq i} \frac{q_{ij} \exp[\sigma(p_i, p_j)]}{k_B T p_i^s}, & i = j. \end{cases} \quad (8)$$

Proof. To see this, we start with

$$\begin{aligned} J_i &= \sum_{j \neq i} (q_{ij} p_j - q_{ji} p_i) = \sum_{j \neq i} q_{ij} (p_j p_i^s - p_i p_j^s) / p_i^s \\ &= \sum_{j \neq i} q_{ij} \{ \exp[\ln(p_j p_i^s)] - \exp[\ln(p_i p_j^s)] \} / p_i^s \\ &= \sum_{j \neq i} q_{ij} \exp[\sigma(p_i, p_j)] [\ln(p_j p_i^s) - \ln(p_i p_j^s)] / p_i^s \\ &= - \sum_{j \neq i} \frac{q_{ij} \exp[\sigma(p_i, p_j)]}{p_i^s} \\ &\quad \times [\ln(p_i / p_i^s) + 1 - \ln(p_j / p_j^s) - 1] \\ &= - \sum_{j \neq i} \frac{q_{ij} \exp[\sigma(p_i, p_j)]}{k_B T p_i^s} \left(\frac{\partial F}{\partial p_i} - \frac{\partial F}{\partial p_j} \right) \\ &= - \sum_j M_{ij} \frac{\partial F}{\partial p_j}. \end{aligned}$$

The second equality dues to the definition of NESS, $\sum_j q_{ij} p_j^s = \sum_j q_{ji} p_i^s$; while the fourth one is by the mean-value theorem, where $\sigma(p_i, p_j) = \sigma(p_j, p_i)$ takes values between $\ln(p_j p_i^s)$ and $\ln(p_i p_j^s)$. ■

In Ref. [45], Kikuchi formalized a variational approach to derive the steady state of Markovian irreversible processes. His variational approach was adapted and improved to solve a stationary dynamical problem by Pelizzola [46] and then extended to the nonstationary regime by Domínguez *et al.* recently [47]. Roughly speaking, these studies [45,47] aim to construct a variational principle for solving Markovian dynamical equations, while our work utilizes the variational calculus as a tool to rewrite the master equations into the conservation-dissipation structure.

Note here the operator \mathcal{M} given in Eq. (3) is just an ordinary matrix multiplication. The coefficient matrix \mathbf{M} above has a novel feature with all diagonal elements being positive while all off-diagonal elements being negative. And the sum of each row is exactly zero. This kind of matrix has very nice mathematical properties, e.g., all of its nonzero eigenvalues have strictly positive real part (positively stable). Therefore, except for single zero mode in correspondence to the conservation of total probability, the system modeled by the master equation is dissipative and evolves towards the NESS according to the second law of thermodynamics. Furthermore, if the transition rate matrix meets the requirement of detailed balance, then oscillatory modes will disappear and the matrix \mathbf{M} becomes symmetric again. However, this does not necessarily mean we fall into a region where the linear regression hypothesis applies, since \mathbf{M} can still depend on the probability p . The above argument is summarized in the following theorem.

Theorem II.2: \mathbf{M} defined in Eq. (8) is a positively stable matrix. Zero is single eigenvalue of \mathbf{M} and its right null space is spanned by $(1/\sqrt{N}, \dots, 1/\sqrt{N})$, which is independent of p_i ($i = 1, 2, \dots, N$). Furthermore, \mathbf{M} is symmetric and positive

semidefinite if and only if the condition of detailed balance holds.

Proof. It is easily seen that \mathbf{M} thus defined is a matrix with zero row sum. Then according to the Gershgorin circle theorem, any eigenvalue of \mathbf{M} lays inside the circle $\cup_{i=1}^N G_i$, where $G_i = \{z \in \mathbb{C} | |z - M_{ii}| \leq \sum_{j \neq i} |M_{ij}| = M_{ii}\}$. Thus the nonzero eigenvalues of \mathbf{M} must have strictly positive real parts, which means \mathbf{M} is a positively stable matrix. The Gershgorin circle theorem also excludes pure imaginary eigenvalues. Furthermore, based on the results proved by Yan and Yong [48], 0 is a single eigenvalue of \mathbf{M} , and its right null space is spanned by $(1/\sqrt{N}, \dots, 1/\sqrt{N})$, which is independent of p_i ($i = 1, 2, \dots, N$). The sufficient and necessary condition for \mathbf{M} to be symmetric and positive semidefinite (since \mathbf{M} is a positively stable matrix) is straightforward to be seen by noticing the fact that $\exp[\sigma(p_i, p_j)]$ is symmetric. ■

Based on above generalized Onsager's relation for the master equation, we can readily recover the stronger version of the Clausius inequality discussed by Ge [49], Esposito [35], *et al.*, i.e.,

$$\begin{aligned} \frac{d}{dt} S(t) &= \sum_i \frac{\partial S}{\partial p_i} \frac{dp_i}{dt} \\ &= \frac{1}{T} \sum_{ij} \frac{\partial F}{\partial p_i} M_{ij} \frac{\partial F}{\partial p_j} - \frac{1}{T} \sum_{ij} \frac{\partial U}{\partial p_i} M_{ij} \frac{\partial F}{\partial p_j} \\ &= -\frac{1}{T} \frac{dF}{dt} - \frac{Q_{\text{ex}}}{T}, \end{aligned}$$

where we recognize the excess heat $Q_{\text{ex}} = -dU/dt$ as the heat exchange involved in the spontaneous relaxation of an open system, and $\dot{S}_{\text{na}} = -\frac{1}{T} \frac{dF}{dt}$ as the nonadiabatic entropy production rate [35]. $\dot{S}_{\text{na}} \geq 0$ is easily obtained by the positiveness of \mathbf{M} . To measure how far a system was kept away from the equilibrium state (or detailed balance), a housekeeping heat $Q_{\text{hk}}(t) = \frac{1}{2} k_B T \sum_{i,j} (q_{ij} p_j - q_{ji} p_i) \ln [(q_{ij} p_j^s)/(q_{ji} p_i^s)] \geq 0$ was introduced ($Q_{\text{hk}} = 0$ if and only if under the condition of detailed balance) in literature. This concept was first proposed by Oono and Paniconi [50] inside a purely phenomenological framework for the NESS thermodynamics. Later, Hatano and Sasa [32] combined it with the Langevin dynamics and established a deep connection between the NESS thermodynamics with the Jarzynski equality. According to their theory, a process was irreversible for converting work into excess heat when modulating the housekeeping heat.

In our formulation, the antisymmetric part of matrix \mathbf{M} plays a similar role. We notice that, in the NESS, \mathbf{M} needs not to be symmetric if the NESS does not satisfy the condition of detailed balance. In general, \mathbf{M} can be split into a symmetric part $\mathbf{M}^s = (\mathbf{M} + \mathbf{M}^T)/2$ and an antisymmetric part $\mathbf{M}^a = (\mathbf{M} - \mathbf{M}^T)/2$. The latter can be used as a direct measure of how far a system is kept away from the detailed balance just like the housekeeping heat. However, we think \mathbf{M}^a is more intrinsic than Q_{hk} , since the role of the housekeeping heat on measuring the detailed balance and keeping the Clausius inequality can be readily replaced by non-negative functions of \mathbf{M}^a . For example, we may choose $\bar{Q}_{\text{hk}} = -2(k_B T)^3 \text{tr}(\mathbf{M}^a)^2 = \frac{1}{2} k_B T \sum_{i,j} [(q_{ij} p_j^s - q_{ji} p_i^s) \exp[\sigma(p_i, p_j)] / (p_i^s p_j^s)]^2$, which

is non-negative and vanishes if and only if under the condition of detailed balance.

III. GENERALIZED ONSAGER'S RELATION FOR THE FOKKER-PLANCK EQUATION

In this part, we move to the Fokker-Planck (F-P) equation. The F-P equation is a type of partial differential equation, which has been widely used in the studies of nonequilibrium thermodynamics. It is well known that the F-P equation could be rigorously derived from the master equation by Kramers-Moyal expansion [51]. We further proved that the formulations of NESS thermodynamics separately built on these two equations were consistent with each other in the limit of large system size [52]. Thus, it would be expected that the F-P equation could also be casted into the CDF, so that the Onsager's relation still holds in a generalized version.

Let us begin with a general Fokker-Planck equation,

$$\frac{\partial}{\partial t} p(x, t) = -\nabla \cdot \mathbf{K}(x, t), \quad (9)$$

where $p = p(x, t)$ is the probability density at position $x \in \mathbb{R}^n$ and time $t \geq 0$. The probability flux $\mathbf{K} = (K_1, K_2, \dots, K_n)$ is given by

$$K_i(x, t) = u_i(x)p - \sum_{j=1}^n D_{ij}(x) \frac{\partial p}{\partial x_j}, \quad \forall i = 1, 2, \dots, n. \quad (10)$$

Here $\mathbf{u} = (u_1, u_2, \dots, u_n)$ and $\mathbf{D} = (D_{ij})_{n \times n}$ represent the drift and diffusion coefficients, respectively, which are assumed to be real differentiable functions of position x . Furthermore, $\mathbf{D}(x)$ is a symmetric and positive-definite matrix according to the fluctuation-dissipation theorem [53]. For details of above equations, like the initial and boundary conditions, analytical solutions, and numerical methods, please see Ref. [53].

Again, we define the NESS $0 < p^s(x) < 1, x \in \mathbb{R}^n$ as the solution of $\frac{\partial}{\partial t} p(x, t) = 0$, which also means

$$\nabla \cdot \mathbf{K}^s(x) = 0, \quad \mathbf{K}^s(x) = \mathbf{u}(x)p^s(x) - \mathbf{D}(x)\nabla p^s(x), \quad (11)$$

i.e., the divergence of the probability flux vanishes at the NESS. If a probability density $0 < p^e(x) < 1, x \in \mathbb{R}^n$ further satisfies the vanishing of flux \mathbf{K} itself, that is,

$$\mathbf{u}(x)p^e(x) - \mathbf{D}(x)\nabla p^e(x) = 0, \quad \forall x \in \mathbb{R}^n, \quad (12)$$

we say $p^e(x)$ obeys the condition of detailed balance. The F-P equation in (9) is detailed balanced if and only if there exists a potential energy function $\phi(x)$ such that $\mathbf{D}^{-1}(x)\mathbf{u}(x) = -\frac{\nabla\phi(x)}{k_B T}$. Based on the potential condition, the equilibrium solution of the F-P equation is given by a canonical probability distribution, $p^e(x) = Z^{-1}e^{-\frac{\phi(x)}{k_B T}}$, where $Z = \int_{\mathbb{R}^n} e^{-\frac{\phi(x)}{k_B T}} dx$ is the partition function [54].

With respect to the NESS, we specify the relative entropy for the F-P equation as

$$F_2(t) = \frac{1}{2} \int dx \frac{p(x, t)^2}{p^s(x)} - \frac{1}{2}. \quad (13)$$

It is a particular version of the general Tsallis-type relative entropy

$$F_\alpha(t) = \frac{1}{\alpha(\alpha-1)} \left[\int dx p \left(\frac{p}{p^s} \right)^{\alpha-1} - 1 \right],$$

with the real number $\alpha (\alpha \neq 0, 1)$ known as the parameter of nonextensivity in statistical mechanics. As a generalization of the Boltzmann entropy, the Tsallis entropy was introduced in the framework of nonextensive thermodynamics [55]. It has been widely applied to image processing, magnetic storms, earthquakes, information theory, etc. [56]. Alternative generalizations were introduced by Rényi [57], Grassberger, Procaccia [58], and many others [59–61].

Remark III.1: As $\alpha \rightarrow 1$, the Tsallis-type relative entropy F_α converges to the Boltzmann-type relative entropy F_B as

$$\lim_{\alpha \rightarrow 1} F_\alpha(t) = \int dx p(x, t) \ln \frac{p(x, t)}{p^s(x)} \equiv F_B(t). \quad (14)$$

Similarly to the Boltzmann-type relative entropy, F_α has the following properties:

$$F_\alpha \geq 0, \quad \frac{dF_\alpha}{dt} \leq 0,$$

for the F-P equation [62]. Moreover, $F_\alpha = 0$ and $dF_\alpha/dt = 0$ if and only if the system reaches the NESS. Mathematically, this means that the relative entropy F_α can serve as the Lyapunov function for the F-P equation.

Given the thermodynamic flux $J(x, t) = \frac{\partial p}{\partial t}$ and the thermodynamic force $X(x, t) = -\frac{\delta F_2}{\delta p(x, t)}$, the F-P equation could be rewritten into a more compact mathematical structure.

Theorem III.2: The Fokker-Planck equation in Eq. (9) obeys the generalized Onsager's relation:

$$J(x, t) = - \int dy M(x, y) \frac{\delta F_2}{\delta p(y, t)}, \quad (15)$$

with the kernel function $M(x, y)$ defined as

$$M(x, y) = \nabla_x \cdot [\mathbf{D}(x)p^s(x) \cdot \nabla_y \delta(y-x)] - \mathbf{K}^s(x) \cdot \nabla_y \delta(y-x), \quad (16)$$

where $\delta(y-x)$ is the Dirac's δ function and $\nabla_y \equiv (\frac{\partial}{\partial y_1}, \frac{\partial}{\partial y_2}, \dots, \frac{\partial}{\partial y_n})$.

Proof. Since the functional derivative is calculated as $\frac{\delta F_2}{\delta p(y, t)} = \frac{p(y, t)}{p^s(y)}$, it is direct to verify the following equations:

$$\begin{aligned} & - \int dy M(x, y) \frac{\delta F_2}{\delta p(y, t)} \\ &= \int dy \left\{ -\nabla_x \cdot [\mathbf{D}(x)p^s(x) \cdot \nabla_y \delta(y-x)] \right. \\ & \quad \left. + \mathbf{K}^s(x) \cdot \nabla_y \delta(y-x) \right\} \frac{p(y, t)}{p^s(y)} \\ &= -\nabla_x \cdot \left[\mathbf{D}(x)p^s(x) \cdot \int dy \nabla_y \delta(y-x) \frac{p(y, t)}{p^s(y)} \right] \\ & \quad + \mathbf{K}^s(x) \cdot \int dy \nabla_y \delta(y-x) \frac{p(y, t)}{p^s(y)} \\ &= \nabla_x \cdot \left[\mathbf{D}(x)p^s(x) \cdot \int dy \delta(y-x) \nabla_y \frac{p(y, t)}{p^s(y)} \right] \end{aligned}$$

$$\begin{aligned}
 & -\mathbf{K}^s(x) \cdot \int dy \delta(y-x) \nabla_y \frac{p(y,t)}{p^s(y)} \\
 &= \nabla_x \cdot \left[\mathbf{D}(x) p^s(x) \nabla_x \frac{p(x,t)}{p^s(x)} \right] - \mathbf{K}^s(x) \cdot \nabla_x \frac{p(x,t)}{p^s(x)},
 \end{aligned}$$

where the integration by parts of the Dirac's δ function is used in the third step. Combining above equations with the fact that $\nabla_x \cdot \mathbf{K}^s(x) = 0$, we have

$$\begin{aligned}
 & -\int dy M(x,y) \frac{\delta F_2}{\delta p(y,t)} \\
 &= \nabla_x \cdot \left[\mathbf{D}(x) p^s(x) \nabla_x \frac{p(x,t)}{p^s(x)} - \frac{p(x,t)}{p^s(x)} \mathbf{K}^s(x) \right] \\
 &= -\nabla_x \cdot [\mathbf{u}(x) p(x,t) - \mathbf{D}(x) \nabla p(x,t)] = -\nabla_x \cdot \mathbf{K}(x,t).
 \end{aligned}$$

Based on above result, we can see that for the F-P equation the operator \mathcal{M} in the generalized Onsager's relation (3) becomes an integral transform with the kernel function $M(x,y)$ defined in space $L_2(\mathbb{R}^n)$. The kernel function M can be naturally separated into two parts:

$$\begin{aligned}
 M^s(x,y) &= \nabla_x \cdot [\mathbf{D}(x) p^s(x) \cdot \nabla_y \delta(y-x)], \\
 M^a(x,y) &= -\mathbf{K}^s(x) \cdot \nabla_y \delta(y-x),
 \end{aligned}$$

which correspond to two different types of equations:

$$\begin{aligned}
 \frac{\partial}{\partial t} p(x,t) &= \nabla \cdot \left[\mathbf{D}(x) p^s(x) \nabla \frac{p(x,t)}{p^s(x)} \right] \\
 &= -\nabla \cdot [(\mathbf{D}(x) \nabla \ln p^s(x)) p - \mathbf{D}(x) \nabla p], \quad (17) \\
 \frac{\partial}{\partial t} p(x,t) &= -\nabla \cdot \left[\frac{p(x,t)}{p^s(x)} \mathbf{K}^s(x) \right] \\
 &= \nabla \cdot [(\mathbf{D}(x) \nabla \ln p^s(x)) p - \mathbf{u}(x) p]. \quad (18)
 \end{aligned}$$

Notice the first one is still a F-P equation with drift and diffusion coefficients defined as $[\mathbf{D}(x) \nabla \ln p^s(x)]$ and $\mathbf{D}(x)$, respectively. A nontrivial consequence of the above decomposition is that the system (17) automatically satisfies the condition of detailed balance since

$$[\mathbf{D}(x) \nabla \ln p^s(x)] p^s(x) - \mathbf{D}(x) \nabla p^s(x) = 0, \quad \forall x \in \mathbb{R}^n.$$

In contrast, Eq. (18) is a Liouville equation in the phase space for $\frac{dx}{dt} = \mathbf{u}(x) - \mathbf{D}(x) \nabla \ln p^s(x)$, which is a canonical conserved system [54] since $\nabla \cdot [p^s(\mathbf{u} - \mathbf{D} \nabla \ln p^s)] = 0$.

To see the mathematical properties of $M^s(x,y)$ and $M^a(x,y)$, let us consider the set of real, differentiable, and square-integrable functions from \mathbb{R}^n to \mathbb{R} by \mathcal{C}^1 and an inner product on it $(\xi_1, \xi_2) = \int \xi_1(x) \xi_2(x) dx$ for $\xi_1, \xi_2 \in \mathcal{C}^1$. Then the following statements hold for $M^s(x,y)$:

Theorem III.3: (1) $M^s(x,y)$ is symmetric, that is, for any functions $\xi_1(x), \xi_2(y) \in \mathcal{C}^1$, the following identity holds:

$$\begin{aligned}
 & \iint dx dy \xi_1(x) M^s(x,y) \xi_2(y) \\
 &= \iint dx dy \xi_1(x) M^s(y,x) \xi_2(y). \quad (19)
 \end{aligned}$$

(2) $M^s(x,y)$ is positive definite.

Proof. First, it is direct to calculate the integration for any functions $\xi_1(x)$ and $\xi_2(y)$ in \mathcal{C}^1 ,

$$\begin{aligned}
 & \iint dx dy \xi_1(x) M^s(x,y) \xi_2(y) \\
 &= \iint dx dy \xi_1(x) \nabla_x \cdot [\mathbf{D}(x) p^s(x) \cdot \nabla_y \delta(y-x)] \xi_2(y) \\
 &= -\int dx \nabla_x \xi_1(x) \cdot [\mathbf{D}(x) p^s(x)] \cdot \int dy \xi_2(y) \nabla_y \delta(y-x) \\
 &= \int dx \nabla_x \xi_1(x) \cdot [\mathbf{D}(x) p^s(x)] \cdot \nabla_x \xi_2(x) \\
 &= \int dy \nabla_y \xi_2(y) \cdot [\mathbf{D}(y) p^s(y)] \cdot \nabla_y \xi_1(y) \\
 &= \iint dx dy \xi_1(x) M^s(y,x) \xi_2(y),
 \end{aligned}$$

where the integration by parts is used in the second step, and the boundary terms are neglected. The symmetry of $\mathbf{D}(x)$ guarantees that the fourth step holds. Thus, the function $M^s(x,y)$ is symmetric.

Second, for any function $\xi(x) \in \mathcal{C}^1$,

$$\begin{aligned}
 & \iint dx dy \xi(x) M^s(x,y) \xi(y) \\
 &= \int dx \nabla_x \xi(x) \cdot [\mathbf{D}(x) p^s(x)] \cdot \nabla_x \xi(x) \geq 0,
 \end{aligned}$$

due to the positiveness of the matrix $\mathbf{D}(x)$ and stationary probability density $p^s(x)$. This means $M^s(x,y)$ is positive semidefinite. However, zero is not an eigenvalue of $M^s(x,y)$. To see this point, we look at the null space of $M^s(x,y)$, which is given by $\{\xi \in \mathcal{C}^1 \mid \int M^s(x,y) \xi(y) dy = 0, \xi \neq 0\}$ or

$$\int dy \nabla_x \cdot [\mathbf{D}(x) p^s(x) \cdot \nabla_y \delta(y-x)] \xi(y) = 0.$$

Multiplying $\xi(x)$ and integrating both sides of above equation with respect to x , one has $\int dx \nabla_x \xi(x) \cdot [\mathbf{D}(x) p^s(x)] \cdot \nabla_x \xi(x) = 0$. As $\mathbf{D}(x)$ is positive definite and $p^s(x) > 0$, we have $\nabla_x \xi(x) \equiv 0$, which leads to $\xi(x) \equiv 0$. Thus the null space of $M^s(x,y)$ is empty. This completes the proof. ■

Analogy to the analysis of $M^s(x,y)$, following properties could be established for $M^a(x,y)$.

Theorem III.4: The kernel function $M^a(x,y)$ is antisymmetric, that is, for any functions $\xi_1(x), \xi_2(y) \in \mathcal{C}^1$, the following identity holds:

$$\begin{aligned}
 & \iint dx dy \xi_1(x) M^a(x,y) \xi_2(y) \\
 &= -\iint dx dy \xi_1(x) M^a(y,x) \xi_2(y). \quad (20)
 \end{aligned}$$

Proof. For any functions $\xi_1(x)$ and $\xi_2(y)$ in \mathcal{C}^1 ,

$$\begin{aligned}
 & \iint dx dy \xi_1(x) M^a(x,y) \xi_2(y) \\
 &= -\iint dx dy \xi_1(x) \mathbf{K}^s(x) \cdot \nabla_y \delta(y-x) \xi_2(y) \\
 &= \int dx \xi_1(x) \mathbf{K}^s(x) \cdot \int dy \delta(y-x) \nabla_y \xi_2(y) \\
 &= \int dx \xi_1(x) \mathbf{K}^s(x) \cdot \nabla_x \xi_2(x)
 \end{aligned}$$

$$\begin{aligned}
&= \int dy \xi_1(y) \mathbf{K}^s(y) \cdot \nabla_y \xi_2(y) \\
&= - \int dy \nabla_y \cdot [\xi_1(y) \mathbf{K}^s(y)] \xi_2(y) \\
&= - \int dy \nabla_y \xi_1(y) \cdot \mathbf{K}^s(y) \cdot \xi_2(y) \\
&= - \iint dx dy \xi_1(x) M^a(y, x) \xi_2(y),
\end{aligned}$$

where the relation $\nabla_y \cdot \mathbf{K}^s(y) = 0$ is used in the sixth step. Thus, $M^a(x, y)$ is antisymmetric. This completes the proof. \blacksquare

We conclude the foregoing results in the following corollary.

Corollary III.5: Analogously to the master equation, the right-hand side of the F-P equation $J(x, t) = -\nabla \cdot \mathbf{K}(x, t)$ represents the nonequilibrium flux, and $X(y, t) = -\delta F_2 / \delta p(y, t)$ is the nonequilibrium force. They are related by the generalized Onsager's relation, *i.e.*, $J(x, t) = \mathcal{M}_{(x, y)} X(y, t)$, in which \mathcal{M} is a positively stable integral operator. Furthermore, if the F-P equation satisfies the detailed balance condition, \mathcal{M} becomes symmetric and positive definite, which recovers the classical Onsager's relations.

Referring to the corollary above, the free-energy dissipation rate for the F-P equation is calculated as

$$\begin{aligned}
\frac{dF_2}{dt} &= \left(\frac{\delta F_2}{\delta p(x, t)}, \frac{\partial p(x, t)}{\partial t} \right) \\
&= \left(\frac{\delta F_2}{\delta p(x, t)}, \mathcal{M}_{(x, y)} \left[-\frac{\delta F_2}{\delta p(y, t)} \right] \right) \\
&= - \left(\frac{\delta F_2}{\delta p(x, t)}, \mathcal{M}_{(x, y)}^s \left[\frac{\delta F_2}{\delta p(y, t)} \right] \right) \\
&= - \int dx \nabla_x \left(\frac{p}{p^s} \right) \cdot \mathbf{D}(x) p^s(x) \cdot \nabla_x \left(\frac{p}{p^s} \right) \leq 0,
\end{aligned}$$

where in the third equality, we have used the antisymmetric property of \mathcal{M}^a ,

$$\begin{aligned}
&\left(\frac{\delta F_2}{\delta p(x, t)}, \mathcal{M}_{(x, y)}^a \left[\frac{\delta F_2}{\delta p(y, t)} \right] \right) \\
&= - \left(\frac{\delta F_2}{\delta p(x, t)}, \mathcal{M}_{(x, y)}^a \left[\frac{\delta F_2}{\delta p(y, t)} \right] \right) = 0.
\end{aligned}$$

To measure how far the system is kept away from detailed balance, we introduce the housekeeping heat of the F-P equation [49],

$$Q_{\text{hk}} = \int dx \mathbf{K}^s(x) \cdot \frac{\mathbf{D}^{-1}(x) p(x, t)}{[p^s(x)]^2} \cdot \mathbf{K}^s(x) \geq 0,$$

where \mathbf{D}^{-1} is the inverse of matrix \mathbf{D} , the above equality holds if and only if in the state of detailed balance. We notice that $M^a(x, y) = -\mathbf{K}^s(x) \cdot \nabla_y \delta(y - x)$ plays the same role as Q_{hk} for the F-P equation, since Q_{hk} can be explicitly expressed as functions of M^a ,

$$\begin{aligned}
Q_{\text{hk}} &= \int dx \left[\int dy M^a(x, y) \ln p^s(y) \right] \cdot \frac{\mathbf{D}^{-1}(x) p(x, t)}{[\nabla p^s(x)]^2} \\
&\quad \cdot \left[\int dy M^a(x, y) \ln p^s(y) \right]
\end{aligned}$$

$$\begin{aligned}
&= \int dx \left[\int dy M^a(x, y) p^s(y) \right] \cdot \frac{\mathbf{D}^{-1}(x) p(x, t)}{[p^s(x) \nabla p^s(x)]^2} \\
&\quad \cdot \left[\int dy M^a(x, y) p^s(y) \right].
\end{aligned}$$

The two expressions above are equivalent, which shows that M^a can readily replace the role of Q_{hk} in characterizing the detailed balance condition.

Under the condition of detailed balance, the conservation-dissipation structure specified in Eq. (17) falls into the framework of Onsager's variational principle proposed by M. Doi [25], which was extensively applied to soft matters and complex fluids [63]. However, the generalized Onsager's relation proposed for general F-P equations has an antisymmetric part to measure the distance of a system away from the detailed balance, which was not included in Doi's theory.

In the region near the steady state, the Boltzmann-type relative entropy converges to the Tsallis-type relative entropy, *i.e.*, $F_B(t) = \int dx p \ln \frac{p}{p^s} \approx \int dx p \left(\frac{p}{p^s} - 1 \right) = \int dx \frac{p^2}{p^s} - 1 = 2F_2(t)$. This means the classical Boltzmann-type relative entropy could also be used to characterize the F-P equation near the NESS. However, when far away from the NESS, there is no simple decomposition of the operator $\mathcal{M}_{(x, y)}$ for the F-P equation with respect to the Boltzmann-type relative entropy, which is stated as follows.

Remark III.6: With respect to the Boltzmann-type relative entropy $F_B = \int dx p \ln \frac{p}{p^s}$, all results above for the operator $\tilde{\mathcal{M}}_{(x, y)}$ of the F-P equation could be deduced, except the antisymmetric property. That is,

$$\begin{aligned}
\frac{\partial}{\partial t} p(x, t) &= \tilde{\mathcal{M}}_{(x, y)} \left[-\frac{\delta F_B}{\delta p(y, t)} \right] \\
&= - \int dy [\tilde{M}^s(x, y) + \tilde{M}^a(x, y)] \frac{\delta F_B}{\delta p(y, t)},
\end{aligned}$$

$$\tilde{M}^s(x, y) = \nabla_x \cdot [\mathbf{D}(x) p(x, t) \cdot \nabla_y \delta(y - x)],$$

$$\tilde{M}^a(x, y) = -\frac{p(x, t)}{p^s(x)} \mathbf{K}^s(x) \cdot \nabla_y \delta(y - x).$$

Here $\tilde{M}^s(x, y)$ is symmetric and positive definite, the F-P equation corresponding to $\tilde{M}^s(x, y)$ is detailed balanced, while $\tilde{M}^a(x, y)$ is not antisymmetric in general.

IV. CONCLUSIONS AND DISCUSSIONS

A. Conclusions

In this paper, we have explored the thermodynamic formalism of the master equation and the Fokker-Planck equation. Following the conservation-dissipation structure, a nonlinear constitutive relation between the thermodynamic flux and force was introduced, which generalized the classical Onsager's relation. With respect to the NESS, the operator generally contains a symmetric and positive semidefinite part and an antisymmetric part. Especially, when the steady state further satisfies the detailed balance condition, the antisymmetric part vanishes and the operator becomes symmetric again. Thus, the antisymmetric part of the operator could be used for measuring the deviation of the NESS away from the detailed balance, in place of the housekeeping heat in other formulations. It

is well known that the Onsager's reciprocal relation plays a key role in nonequilibrium thermodynamics. Consequently, the CDF, which adopted in the generalized Onsager's relation as a central element, may be a reasonable mathematical framework for modeling various irreversible processes.

In the formulation of F-P equations, the Tsallis-type relative entropy with parameter $\alpha = 2$ was adopted instead of the classical Boltzmann-type relative entropy in order to maintain the elegant mathematical structure of the operator \mathcal{M} . We suspect the inapplicability of the Boltzmann-type relative entropy was closely related to the convergence rate of the F-P equation towards the NESS. If this was true, then for fractional F-P equations, the Tsallis-type relative entropy with different nonextensive parameter α would be essential for the construction of generalized Onsager's relation. Similar examples also include the nonlinear F-P equations. Related works are ongoing.

B. Relations with the stochastic diffusion processes

Recently, Chetrite and Gawedzki developed a unified approach to different fluctuation relations, which is traced to the application of various time reversals for stochastic diffusion processes [34]. They examined the fluctuation relations of Langevin equations and Fokker-Planck equations, which are particularly relevant to the mathematical rigorousness of the present work.

Consider a stochastic process \mathbf{X}_t in \mathbb{R}^d described by the following differential equation:

$$\dot{x} = \mathbf{M}\nabla H + \zeta, \quad (21)$$

where \mathbf{M} is a constant matrix (not restricted to be symmetric), $H = H_t$ is a time-dependent Hamiltonian, and ζ_t is a d -dimensional white noise with

$$\langle \zeta_t^i \zeta_s^j \rangle = 2\delta(t-s)\beta^{-1}\Gamma^{ij}, \quad (22)$$

where $\beta = (k_B T)^{-1}$. This is a special example of diffusion processes with the deterministic vector field as $\mathbf{M}\nabla H$ and the random vector field as ζ . Furthermore, Eq. (21) describes the Langevin dynamics with the additional force $G_t \equiv 0$ [34].

In general, the matrix \mathbf{M} could be decomposed into a symmetric part \mathbf{M}^s and an antisymmetric part \mathbf{M}^a . According to the canonical choice of the time inversion for the Langevin dynamics [34], we have

$$\mathbf{M}\nabla H = \mathbf{M}^s\nabla H + \mathbf{M}^a\nabla H, \quad (23)$$

where $\mathbf{M}^s\nabla H$ and $\mathbf{M}^a\nabla H$ are loosely termed as the dissipative and conservative parts of the deterministic vector field,

respectively. By combining the dissipative part and the stochastic part together, one has $\dot{x} = \mathbf{M}^s\nabla H + \zeta$, and by the Itô calculus, one deduces the corresponding Fokker-Planck equation

$$\frac{\partial}{\partial t} p = -\nabla \cdot [(\mathbf{M}^s\nabla H)p - \beta^{-1}\Gamma\nabla p]. \quad (24)$$

Similarly, the conservative part corresponds to the following equation:

$$\frac{\partial}{\partial t} p = -\nabla \cdot [(\mathbf{M}^a\nabla H)p]. \quad (25)$$

In parallel to the above splitting of the Langevin equation, the corresponding Fokker-Planck equation $\partial_t p = -\nabla \cdot [(\mathbf{M}\nabla H)p - \beta^{-1}\Gamma\nabla p]$ could be decomposed directly based on our results mentioned in the last section, which gives

$$\begin{aligned} \frac{\partial}{\partial t} p &= -\nabla \cdot [(\beta^{-1}\Gamma\nabla \ln p^s)p - \beta^{-1}\Gamma\nabla p], \\ \frac{\partial}{\partial t} p &= -\nabla \cdot [(\mathbf{M}\nabla H)p - (\beta^{-1}\Gamma\nabla \ln p^s)p], \end{aligned} \quad (26)$$

where $p^s = p^s(x)$ denotes the steady state of the original Fokker-Planck equation. Assuming above decompositions are in agreement with the results of Chetrite and Gawedzki, we have

$$\beta^{-1}\Gamma\nabla \ln p^s = \mathbf{M}^s\nabla H, \quad \mathbf{M}\nabla H = \beta^{-1}\Gamma\nabla \ln p^s + \mathbf{M}^a\nabla H, \quad (27)$$

by comparing the Eqs. (24), (25), and (26). Therefore,

$$\mathbf{M}^s = -\Gamma, \quad p^s(x) = Z^{-1}e^{-\beta H}. \quad (28)$$

Here $\mathbf{M}^s = -\Gamma$ determines the matrix \mathbf{M}^s in terms of the correlation Γ , which is a simple example of the fluctuation-dissipation relation and states that the symmetric part of the general diffusion vector field must be equal to the spatial covariance of its stochastic field. Moreover, notice that the stationary distribution $p^s(x) = Z^{-1}e^{-\beta H}$ satisfies the detailed balance condition. This is the case for the Langevin equation with $\mathbf{M}^a = 0$. In conclusion, the equivalence of decompositions in Eqs. (24), (25), and Eq. (26) recovers the fluctuation-dissipation relation and restricts the Langevin equation to be detailed balanced.

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