

# The Zeroth Law of Thermodynamics and Volume-Preserving Conservative Dynamics with Equilibrium Stochastic Damping

Hong Qian

Department of Applied Mathematics  
University of Washington, Seattle  
WA 98195-2420, U.S.A.

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## Abstract

The zeroth law of thermodynamics states that a system's equilibrium is unaltered whether it encounters or is detached from a heat bath. We generalize this notion mathematically and show that Ao's stochastic process [*J. Phys. A: Math. Gen.* **37**, L25 (2004)] is consistent with a phase-volume preserving conservative dynamical system in equilibrium with a stochastic damping satisfying the zeroth law:  $dq = (\gamma - D\nabla\phi)dt + d\xi(t)$  where  $\nabla \cdot \gamma = 0$ ,  $\langle \xi(t)\xi(t') \rangle = 2D\delta(t - t')$ . As a form of detailed balance, the zeroth law implies stationary density  $u^{ss}(q) = e^{-\phi(q)}$ . We show that a hallmark of such systems is an orthogonality between the gradient of the stationary density and the conservative current in phase space:  $\nabla\phi \cdot \gamma = 0$ . A stochastic thermodynamics based on time reversal  $(t, \phi, \gamma) \rightarrow (-t, \phi, -\gamma)$  yields a novel formula for dissipation  $h_d^*(t) = -\int_{\mathbb{R}^n} \nabla\phi \cdot D\nabla \ln(u(q, t)e^\phi) dq$  and entropy production  $e_p^*(t) = -dF(t)/dt$ : The "generalised free energy"  $F(t)$  never increases. Entropy balance equation  $\frac{dS}{dt} = e_p^* - h_d^*$  is also recovered. The relations among Ao's stochastic process, a Hodge-like potential-flux decomposition, stochastic Hamiltonian system with even and odd variables such as Klein-Kramers equation, and the theory of GENERIC, are discussed. When the  $\phi$  is given, three different types of time reversal leading to different open-subsystem thermodynamics are suggested.

## 1 Introduction

Significant progress has been made in recent years on stochastic dynamics and thermodynamics of mesoscopic systems with a Markovian description. A mathematical theory of

nonequilibrium statistical thermodynamics that encompassing both transient kinetics toward an equilibrium and driven nonequilibrium steady state seems to emerge from Markovian dynamics. See [1, 2, 3, 4, 5, 6] and references cited within. Historically in chemistry and biological sciences, one of the major motivations of stochastic dynamics is overdamped single macromolecule in aqueous solution — the Zimm-Rouse polymer theory [7, 8]. While overdamped stochastic dynamics is extensively studied with wide applications, underdamped systems with stochastic damping [9, 10, 11, 12, 13] have been mainly studied within physics community which includes, for examples, laser physics, electrical circuits, Josephson junctions, nanomechanical resonator, etc. [14, 15, 16]. Many such systems exhibit stochastic resonance phenomena [17, 18, 4].

Outside traditional physical systems, part of the difficulties in formulating a “underdamped stochastic dynamics” is the uncertainty in identifying even and odd dynamic variables [19, 20], analogous to positions and velocities in classical mechanics. Furthermore, because the degenerated nature of the diffusion process represented by Klein-Kramers equation [9, 21, 22, 23], ascertaining the stationary distribution of a stochastic Hamiltonian dynamics can be mathematically delicate.<sup>1</sup>

In the present paper, we approach this problem from a rather different starting point. In the theory of nonlinear dynamics, a conservative system with volume-preserving flow in phase space is the natural generalization of Hamiltonian dynamics [25]. Ordinary differential equation  $\dot{q} = \gamma(q)$  with  $\nabla \cdot \gamma(q) = 0$  can also be represented as flow in phase space  $\partial_t u(q, t) = -\gamma(q) \cdot \nabla u(q, t)$ . When coupled to an stochastic, damping, it is natural to consider a stochastic differential equation (SDE)

$$dq(t) = \gamma(q)dt + \left\{ -D\nabla\phi(q)dt + d\xi(t) \right\} \quad (1)$$

in which the terms inside  $\{\dots\}$ , in the spirit of P. Langevin [26], represent the “friction” and “collision” of a stochastic damping:  $\langle \xi(t)\xi(t') \rangle = 2D\delta(t-t')$ . Now if we generalize the idea of the *zeroth law of thermodynamics* which states that a system’s equilibrium is unaltered whether it encounters or is detached from another with which it is in equilibrium, then we can assume that the stationary density of the system (1),  $u^{ss}(q)$ , has to be the *same*

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<sup>1</sup>I thank Prof. Min Qian of Peking University for extensive discussions on stochastic processes, dynamical systems, and time reversibility. His 1979 paper [23] in Chinese, which had inspired [24], has attempted to introduce a stochastic Hamiltonian system along the line of Klein, Kramers, Wang and Uhlenbeck, and illustrated the importance of fluctuation-dissipation relation in obtaining Gibbs’ canonical ensemble.

as the stationary density of the damping alone:

$$u^{ss}(q) = e^{-\phi(q)}. \quad (2)$$

This generalized notion of the zeroth law shares the same spirit of detailed balance in statistical chemistry and fluctuation-dissipation relation in statistical physics: *If a bath is in equilibrium with a system, then the equilibrium bath is invariant irrespective of whether it is in contact with the system or not.* A nonequilibrium steady state arises when the condition in (2) is violated due to a dis-equilibrium between the bath and the conservative dynamical system [10, 24, 27, 28, 29, 30, 31]: the stochastic bath then constitutes an active driving force [32].

The equilibrium stochastic systems introduced as such have an important orthogonal relation between  $\nabla\phi$  and  $\gamma$ . To show this, we write the Kolmogorov forward equation for the SDE in (1):

$$\frac{\partial u(q, t)}{\partial t} = \nabla \cdot \left[ D\nabla u - \left( \gamma(q) - D\nabla\phi(q) \right) u \right]. \quad (3)$$

Then Eq. 2 implies  $-\nabla \cdot [\gamma(q)u^{ss}] = u^{ss}(q)(\gamma(q) \cdot \nabla\phi) = 0$ . Therefore, for dynamics with  $u^{ss}(q) > 0$ , the equilibrium damping implies the orthogonality. Also, the stationary current is simply  $\gamma(q)u^{ss}(q)$ .

In 2004, P. Ao has proposed a novel form of a stochastic process together with a decomposition scheme that yields stationary probability density and stationary rotational motion, as well as a steady state thermodynamics [33, 34]. This novel stochastic theory has intrigued and mystified many researchers. Ao and his coworkers have further carried out explicit computations for linear stochastic differential equations following the general theory [35]. One of the key features in the linear system is an orthogonality between the gradient of stationary density and the stationary probability current.

In the present work, we show that Ao's stochastic processes [33] is consistent with the stochastic dynamics with volume-preserving flow introduced above, *e.g.*, Eqs. 1 and 2. We shall also clarify the mathematical foundation of Ao's "conservative thermodynamics" in the presence of stationary probability current [34] based on the reversibility under time reversal  $(t, \phi, \gamma) \rightarrow (-t, \phi, -\gamma)$  for Eq. 1 [20]. Under this time reversal, a measure-theoretical entropy production rate  $e_p^*$  is introduced and it in fact equals to the decreasing rate of a generalized free energy functional  $-dF/dt$ , where [34]

$$F[u(q, t)] = \int_{\mathbb{R}^n} u(q, t) \ln \left( u(q, t) e^{\phi(q)} \right) dq. \quad (4)$$

$-dF/dt$ , which is non-negative, has been called free energy dissipation in [36, 37] and non-adiabatic entropy production in [38, 39, 40]. In the stationary state,  $e_p^* \equiv 0$ , and the probability current is analogous to the inertia in mechanics and induction in electrical circuits [14, 15].

The new theory is a synthesis of several known results interwoven into a coherent presentation. To clarify, we shall point out its novel aspects: *(i)* It develops a underdamped stochastic dynamics in the general term of dynamical systems without the need of a Hamiltonian, nor the identification of even and odd variables; *(ii)* generalizes the notion of the zeroth law of thermodynamics in connection to an equilibrium condition; *(iii)* derived an orthogonal relation between  $\nabla\phi$  and  $\gamma$ . Note this orthogonality is not the same as the earlier one studied in [41, 42], where the term corresponding to  $\gamma$  was not a divergence-free current in general. *(iv)* It shows a consistency with the stochastic dynamical equation proposed by Ao in [33]; *(v)* introduced a trajectory-based entropy production formula using the time reversal  $(t, \phi, \gamma) \rightarrow (-t, \phi, -\gamma)$ . This justifies Ao's conservative thermodynamics [34].

## 2 Conservative dynamics with stochastic damping

### 2.1 Ao's stochastic process

Consider a multi-dimensional stochastic process in continuous space with continuous time,  $q(t)$ . The usual stochastic differential equation (SDE) is written as

$$dq(t) = b(q)dt + d\xi(q, t) \quad (5)$$

in which  $\xi(t)$  is a white noise. However in [33] it was suggested that one considers a class of systems in the form

$$[S(q) + A(q)] \frac{dq}{dt} = -\nabla\phi(q) + \zeta(q, t), \quad (6)$$

where

$$\langle \zeta(q, t) \zeta^T(q, t') \rangle = 2S(q) \delta(t - t'). \quad (7)$$

The  $\phi(q)$  is a scalar function, and  $S(q)$  and  $A(q)$  are symmetric and anti-symmetric matrices, respectively.

Without being mathematically rigorous, one can formally establish the relation between Eq. 6 and the conventional SDE (5): Introducing a transformation via an auxiliary matrix inversion  $(S(q) + A(q))^{-1} = G(q)$  one obtains [33]

$$\frac{dq}{dt} = -G(q)\nabla\phi(q) + \xi(q, t), \quad (8)$$

with

$$\begin{aligned} \langle \xi(q, t)\xi^T(q, t') \rangle &= \langle G(q)\zeta(q, t)\zeta^T(q, t')G(q)^T \rangle \\ &= 2G(q)S(q)G^T(q)\delta(t - t'). \end{aligned} \quad (9)$$

Then the associated Kolmogorov partial differential equation in divergence form, following [43, 44], is,

$$\frac{\partial u(q, t)}{\partial t} = \nabla \cdot \left[ G(q)S(q)G^T(q)\nabla u + G(q)\nabla\phi(q)u \right]. \quad (10)$$

One of the key results in [33] is that the stationary density for the stochastic process being  $e^{-\phi(q)}$ . Then the stationary current  $J(q)$  satisfies [45, 37]

$$J(q)e^{\phi(q)} = G(q)S(q)G^T(q)\nabla\phi(q) - G(q)\nabla\phi(q). \quad (11)$$

From Eq. 11 one has

$$\begin{aligned} (\nabla\phi(q))^T \cdot J(q)e^{\phi(q)} &= (\nabla\phi(q))^T \cdot \left[ GSG^T\nabla\phi(q) - G\nabla\phi(q) \right] \\ &= \left( G^T\nabla\phi(q) \right)^T \cdot \left[ -S + G^{-T} \right] \left( G^T\nabla\phi(q) \right) \\ &= \left( G^T\nabla\phi(q) \right)^T \cdot \left[ -S + S + A^T \right] \left( G^T\nabla\phi(q) \right) \\ &= 0. \end{aligned} \quad (12)$$

Since  $e^{\phi(q)} \neq 0$ , Eq. 12 means  $(\nabla\phi(q))^T \cdot J(q) = 0$  is a *necessary condition* for Ao's stochastic processes. Therefore it is a special case of the process introduced in Sec. 1.

**Wang's Hodge-like decomposition.** The orthogonality in Eq. 12 leads to several interesting properties for the stochastic dynamics. First, noting the SDE in (5) and the relation in (11), we have the drift

$$b(q) = -G(q)\nabla\phi(q) = -D\nabla\phi(q) + J(q)e^{\phi(q)}, \quad (13)$$

and  $\langle \xi(t)\xi(t') \rangle = 2D\delta(t-t')$ . Denoting  $\gamma(q) = J(q)e^{\phi(q)}$ , then

$$b(q) = -D\nabla\phi + \gamma, \quad \nabla \cdot \gamma = 0, \quad \nabla\phi \cdot \gamma = 0. \quad (14)$$

The right-hand-side of (13) are Wang's potential and flux landscapes [45, 37] for a general SDE. The orthogonality between the gradient and current terms is an additional feature of Ao's stochastic processes. The first two equations in (14) are a Helmholtz-Hodge-like decomposition with diffusion matrix  $D$  [46]. As far as we know, there is no orthogonality in a Hodge decomposition in general.

**Xing's Hamiltonian representation.** For a Hamiltonian system, the orthogonality is a necessary consequence of a damped Hamiltonian dynamics [10, 23] in equilibrium with detailed-balanced stochastic damping:

$$\frac{d}{dt} \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} \frac{\partial H}{\partial y} + \eta_x(x, y) \\ -\frac{\partial H}{\partial x} + \eta_y(x, y) \end{pmatrix} + \Gamma(x, y) \begin{pmatrix} \frac{dw_x}{dt} \\ \frac{dw_y}{dt} \end{pmatrix}. \quad (15)$$

Its corresponding Kolmogorov forward equation is a generalization of the Klein-Kramers equation

$$\frac{\partial u}{\partial t} = (\nabla_x, \nabla_y) \left[ \frac{1}{2} \begin{pmatrix} \nabla_x \\ \nabla_y \end{pmatrix} \Gamma(x, y) \Gamma^T(x, y) - \begin{pmatrix} \frac{\partial H}{\partial y} + \eta_x \\ -\frac{\partial H}{\partial x} + \eta_y \end{pmatrix} \right] u. \quad (16)$$

It has a reversibility condition for the damping and the noise [47]: There exists an equilibrium between the system and the heat bath:  $u^{eq} = e^H$  such that

$$\left[ \frac{1}{2} \begin{pmatrix} \nabla_x \\ \nabla_y \end{pmatrix} \Gamma(x, y) \Gamma^T(x, y) - \begin{pmatrix} \eta_x(x, y) \\ \eta_y(x, y) \end{pmatrix} \right] u^{eq}(x, y) = 0. \quad (17)$$

Then the stationary distribution to (16) with both Hamiltonian and heat bath parts is again  $u^{eq} = e^{-H}$  with a current in phase space:

$$J(x, y) = - \begin{pmatrix} \frac{\partial H}{\partial y} \\ -\frac{\partial H}{\partial x} \end{pmatrix} u^{eq}(x, y). \quad (18)$$

Indeed,  $\nabla u^{eq} \cdot J = 0$ . Eqs. (16) and (17) are based on Itô's integration. It is easy to see that if another convention for integration is chosen, both equations will have different expressions; but Eq. (18) is invariant.

Eqs. (13), (15), and (18) together suggest that for any SDE (5) with stationary density  $e^{-\phi}$  and flux  $J$ , if  $\nabla\phi \cdot J = 0$ , then the SDE can be re-written as

$$dq(t) = \left\{ -D\nabla\phi(q) + d\xi(t) \right\} + \gamma(q) \quad (19)$$

in which the first two terms in the  $\{\cdot\cdot\cdot\}$  is from the heat bath with detailed balance. They are analogous to the “friction” and “collision” in classical mechanics, defining the notions of dissipation and fluctuation in the general stochastic dynamics. The dynamics described by the  $\gamma(q)$  is a deterministic conservative system [25] with a volume preserving flow in phase space:

$$\frac{d}{dt} \int_{\mathfrak{D}(t)} dq = \oint_{\partial\mathfrak{D}} \gamma(q) \cdot d\vec{S} = \int_{\mathfrak{D}} \nabla \cdot \gamma(q) dq = 0. \quad (20)$$

Indeed, it has been shown that Ao’s process can be mathematically represented as a Hamiltonian system with a stochastic damping corresponding to a harmonic bath [48]. Another Hamiltonian system also emerges from conditional probability and path-integral formalism [49, 50]. The relation between these two remains to be elucidated.

**Grmela-Öttinger’s GENERIC form.** If the  $\gamma(q)$  in Eq. 1 is a Hamiltonian system, then the deterministic part of the system has the GENERIC form proposed by Grmela and Öttinger [51]:

$$\begin{pmatrix} dx \\ dy \end{pmatrix} = \left[ \begin{pmatrix} \frac{\partial H}{\partial y} \\ -\frac{\partial H}{\partial x} \end{pmatrix} - \begin{pmatrix} D_{xx} & D_{xy} \\ D_{yx} & D_{yy} \end{pmatrix} \begin{pmatrix} \frac{\partial \phi}{\partial x} \\ \frac{\partial \phi}{\partial y} \end{pmatrix} \right] dt + \begin{pmatrix} d\xi_x(t) \\ d\xi_y(t) \end{pmatrix}. \quad (21)$$

The orthogonality has also figured prominently in the GENERIC structure which has a rich geometric interpretation.

**Detailed balance in systems with even and odd variables.** There have been extensive discussions on detailed balance in stochastic differential equation with even and odd variables. See earlier work [10, 11, 12, 13], a nice summary in the textbook [19], and more recent papers [24, 27, 28, 29, 30, 31]. Detailed balance for system with position  $\mathbf{x}$  and velocity  $\mathbf{v}$  is defined through a symmetry between the transitions  $(\mathbf{x}, \mathbf{v}, t) \rightarrow (\mathbf{x}', \mathbf{v}', t + \tau)$  and  $(\mathbf{x}', -\mathbf{v}', t) \rightarrow (\mathbf{x}, -\mathbf{v}, t + \tau)$ . The *detailed balance condition* in an even-and-odd system is shown to be sufficient for the probability current  $\mathbf{J} = -\mathbf{J}^-$  where the  $\mathbf{J}^-$  is the stationary current under time reversal ([19], Eq. 5.3.53). Also, for constant diffusion matrix, the cross terms between even and odd variables are necessarily zero. Furthermore, the stationary solution is “solved” in [19] (Eq. 5.3.85). Finally, recognizing the orthogonal condition presented in the present work, their Eq. 5.3.82 can be simplified into  $\sum_i \frac{\partial}{\partial x_i} I_i(\mathbf{x}) = 0$ ; where  $I$  is our  $\gamma$ .

**A generalized Klein-Kramers equation.** As we have already noted, while the choice of the intergration for an SDE with multiplicative noise is not unique, *e.g.*, Itô, Stratonovich,

or Ao's divergence form [44], there is no ambiguity at the partial differential equation level. A conservative dynamics in equilibrium with stochastic damping can be written as, in Itô's form:

$$\frac{\partial u(q, t)}{\partial t} = \nabla \cdot \left[ \left( \nabla (D(q)u(q, t)) - \eta(q)u(q, t) \right) - \gamma(q)u(q, t) \right], \quad (22)$$

with  $\eta(q)$  and  $\phi(q)$  being related via

$$\nabla \left( D(q)e^{-\phi(q)} \right) - \eta(q)e^{-\phi(q)} = 0. \quad (23)$$

Solving  $\eta(q)$  from Eq. (23) and substituting it into (22), we have

$$\frac{\partial u(q, t)}{\partial t} = \nabla \cdot \left[ D(q) \left( \nabla u(q, t) + u(q, t) \nabla \phi(q) \right) - \gamma(q)u(q, t) \right], \quad (24)$$

which is precisely the divergence form Ao advocated. Eqs. 16 and 17 together are a special case of (24). In fact, (17) implies that (16) has the form

$$\frac{\partial u}{\partial t} = (\nabla_x, \nabla_y) \left\{ \frac{1}{2} \Gamma(x, y) \Gamma^T(x, y) \left[ \begin{pmatrix} \nabla_x \\ \nabla_y \end{pmatrix} - \begin{pmatrix} \nabla_x \ln u^{eq} \\ \nabla_y \ln u^{eq} \end{pmatrix} \right] - \begin{pmatrix} \frac{\partial H}{\partial y} \\ -\frac{\partial H}{\partial x} \end{pmatrix} \right\} u.$$

## 2.2 Stochastic thermodynamics

A volume-perserving conservative dynamics  $\dot{q} = \gamma(q)$  is time-reversible in the sense  $t \rightarrow -t$  and  $\gamma \rightarrow -\gamma$  [25]; see Fig. 1. In terms of such a time reversal, let us consider a stochastic path  $\omega_t = \{q(s) | 0 \leq s \leq t\}$  and its time-reversed path  $\omega_t^- = \{q(t-s) | 0 \leq s \leq t\}$  under the probability measures  $\mathbb{P}^{+\gamma}$  and  $\mathbb{P}^{-\gamma}$  defined by SDEs  $dq = (\gamma - D\nabla\phi)dt + d\xi(t)$  and its time-reversal  $dq^- = (-\gamma - D\nabla\phi)dt + d\xi(t)$ , respectively. A sample-path based entropy production can be introduced [40, 47, 52, 54, 55, 56]:

$$e_p^*(t) = E^{\mathbb{P}^{+\gamma}} \left[ \ln \frac{d\mathbb{P}^{+\gamma}(\omega_t)}{d\mathbb{P}^{-\gamma}(\omega_t^-)} \right] \quad (25)$$

$$= - \int_{\mathbb{R}^n} J(q, t) \cdot \nabla \ln \left( \frac{u(q, t)}{u^{eq}(q)} \right) dq, \quad (26)$$

$$= \int_{\mathbb{R}^n} u(q, t) \nabla \ln \left( u(q, t) e^{\phi(q)} \right) \cdot D\nabla \ln \left( u(q, t) e^{\phi(q)} \right) dq \geq 0, \quad (27)$$

where  $J(q, t) = (\gamma - D\nabla\phi)u(q, t) - D\nabla u(q, t)$ , and  $E^{\mathbb{P}^{+\gamma}}[\dots]$  denotes ensemble average with respect to  $\mathbb{P}^{+\gamma}$ . We note that the  $\gamma$  term has disappeared in the final expression: Entropy production is a purely determined by the damping mechanism.



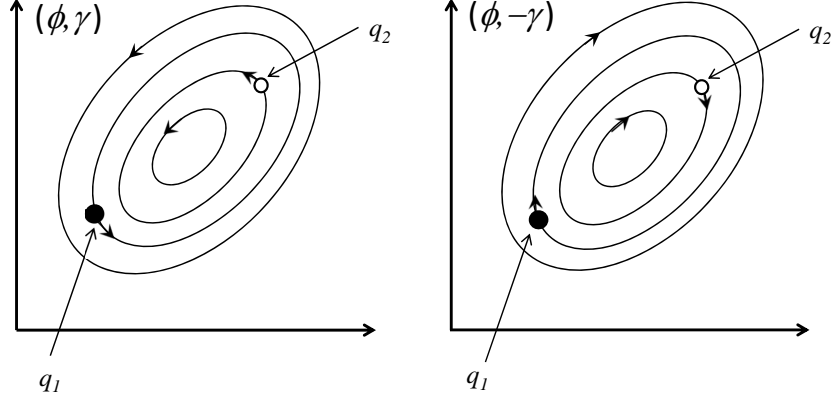


Figure 1: In stationarity with  $\tau \geq t$ , the joint probability distribution  $\Pr \{q(t) = q_1, q(\tau) = q_2\}$  for the diffusion process on the left, according (1) with  $(\phi, \gamma)$ , i.e.,  $dq(t) = (\gamma - D\nabla\phi)dt + d\xi(t)$  and  $\nabla\phi \cdot \gamma = 0$ , is the same as the joint probability distribution  $\Pr \{q^-(t) = q_2; q^-(\tau) = q_1\}$  for the diffusion process on the right,  $q^-(t)$  with  $(\phi, -\gamma)$ , under a time reversals:  $\Pr \{q^-(-t) = q_2; q^-(-\tau) = q_1\} = \Pr \{q^-(\tau - t) = q_2; q^-(0) = q_1\} = \Pr \{q(0) = q_1, q(\tau - t) = q_2\} = \Pr \{q(t) = q_1; q(\tau) = q_2\}$ . The closed cycles in both plots, the contours of  $\phi$ , are the same; the actual velocity along a contour is determined by  $\|\gamma\|$ .

It is important to point out that the  $e_p^*$  introduced in Eq. 25 is different from the standard entropy production for a stochastic diffusion [47, 54, 55, 56]. In the literature,  $e_p^*$  has been called as free energy dissipation or non-adiabatic entropy production [36, 38, 39, 40].

In terms of the  $e_p^*$ , one can define a nonequilibrium, generalized free energy [56],

$$F(t) = \int_{\mathbb{R}^n} u(q, t) \ln \left( \frac{u(q, t)}{u^{eq}(q)} \right) dq. \quad (28)$$

Then its time change, as has been shown in [34]:

$$\frac{dF(t)}{dt} = \int_{\mathbb{R}^n} J(x, t) \cdot \nabla \ln \left( \frac{u(q, t)}{u^{eq}(q)} \right) dx = -e_p^*(t) \leq 0. \quad (29)$$

Eq. 29 should be interpreted as follows: *For Gibbs' canonical ensemble with non-uniform  $u^{eq}(q) = e^{-\phi(q)}$ , the thermodynamic potential is free energy  $F$  whose decreasing rate is the entropy production  $e_p^*$ .*

We also note that the generalized nonequilibrium free energy  $F(t) = U(t) - S(t)$  with

$$U(t) = - \int_{\mathbb{R}^n} u(q, t) \ln u^{eq}(q) dq, \quad S(t) = - \int_{\mathbb{R}^n} u(q, t) \ln u(q, t) dq. \quad (30)$$

They can be interpreted as internal (conservative) energy and entropy, respectively. Furthermore,

$$\frac{d}{dt} \left( \int_{\mathbb{R}^n} u(q, t) \ln u^{eq}(q) dq \right) = - \int_{\mathbb{R}^n} \nabla \phi \cdot D \nabla \ln \left( u(q, t) e^\phi \right) dq. \quad (31)$$

We note again that the  $\gamma$  term has completely disappeared. The right-hand-side of (31) can be interpreted as “heat flux”, analogous to the heat in classical thermodynamics,  $h_d^*(t)$ .

Then,

$$\frac{dS}{dt} = e_p^*(t) - h_d^*(t), \quad h_d^* = - \int_{\mathbb{R}^n} \nabla \phi \cdot D \nabla \ln \left( u(q, t) e^\phi \right) dq, \quad (32)$$

which is known as the entropy balance equation in Dutch school of nonequilibrium thermodynamics [57]:  $\frac{dS}{dt} = \frac{d_i S}{dt} + \frac{d_e S}{dt}$ . See also [10] for a discussion on the meanings of these terms as the system’s entropy change, total entropy production, and heat dissipation.

### 2.3 Three different types of time reversal

We now consider the general SDE in Eq. 5. In [56], we have introduced the notion of a *canonical conservative dynamics* with respect to a differentiable invariant density  $\rho(x)$ :  $\dot{x} = j(x)$  with  $\nabla \cdot (\rho(x)j(x)) = 0$ . The general SDE, when its stationary density is known, can always be re-written as [56, 19]

$$dx(t) = \left( b(x) + D(x) \nabla \phi(x) \right) dt + \left\{ - D(x) \nabla \phi(x) dt + d\xi(t) \right\}, \quad (33)$$

in which  $e^{-\phi(x)} = u^{ss}(x)$  is the stationary density. Then  $j(x) = b(x) + D(x) \nabla \ln \phi(x)$  is a canonical conservative dynamics with respect to  $u^{ss}(x)$ . It has been shown in [56] that under time reversal  $(t, \phi, j) \rightarrow (-t, \phi, -j)$ , the system in (33) has again entropy production  $e_p^*(t) = -dF/dt$ .<sup>2</sup>

One can further decompose the term  $j(x)$  into parallel and perpendicular to  $\nabla \phi(x)$ :  $j(x) = j_{\parallel}(x) + j_{\perp}(x)$ , with

$$j_{\parallel}(x) = \left( \frac{j(x) \cdot \nabla \phi(x)}{\|\nabla \phi(x)\|^2} \right) \nabla \phi(x), \quad j_{\perp}(x) = j(x) - j_{\parallel}(x), \quad (34)$$

where  $\nabla \phi(x) \cdot j_{\perp}(x) = 0$ . Then

$$b(x) = -D(x) \nabla \phi(x) + j_{\perp}(x) + j_{\parallel}(x). \quad (35)$$

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<sup>2</sup>It is intriguing to note that according to D. Ruelle, for a smooth dynamical systems (e.g., Anosov diffeomorphisms), entropy production is always zero if there is an invariant density [58]: It only becomes strictly positive when an invariant measure is singular, i.e, fractal [59].

The last term can also be written as

$$j_{\parallel}(x) = \left( \frac{\nabla \cdot j(x)}{\|\nabla\phi(x)\|^2} \right) \nabla\phi(x). \quad (36)$$

It represents the non-conservative nature of  $j(x)$  [60]. According to time reversal  $(t, \phi, j) \rightarrow (-t, \phi, j)$ , all  $j(x)$  contributes to stationary entropy production [47, 4]; and according to time reversal  $(t, \phi, j) \rightarrow (-t, \phi, -j)$ , there will be no stationary entropy production [56]. The present work and Eq. 35 suggests yet another time reversal:  $(t, \phi, j_{\perp}) \rightarrow (-t, \phi, -j_{\perp})$ , under which stationary dissipation arises from  $j_{\parallel}$ . These three different time reversals reflect assumptions based on over-damped, non-damped or under-damped nature of a stationary dynamics of a subsystem. For systems with overdamped time reversibility, they have a potential condition  $D^{-1}(x)b(x) = \nabla\phi$  and the stationary density is  $e^{-\phi(x)}$  with zero stationary current. For systems with underdamped time reversibility, they have an orthogonal decomposition  $b(x) = D(x)\nabla\phi + \gamma$  with  $\nabla \times \gamma = 0$  and  $\gamma \cdot D(x)\nabla\phi = 0$ . Then the stationary density and current are  $e^{-\phi(x)}$  and  $\gamma(x)e^{-\phi(x)}$ , respectively.

## 3 Discussion

### 3.1 Orthogonality for infinitesimal noise

We now consider a general SDE with an infinitesimal stochastic term:

$$dq(t) = b(q)dt + \sqrt{\epsilon}d\xi(t), \quad \langle \xi(t)\xi(t') \rangle = 2D\delta(t-t'), \quad (37)$$

with Fokker-Planck equation

$$\frac{\partial u(q, t)}{\partial t} = -\nabla \cdot J(q, t), \quad J(q, t) = b(q)u(q, t) - \epsilon D \nabla u(q, t). \quad (38)$$

The large deviation principle suggests that [41, 42, 61, 50]

$$u^{ss}(q) = \exp\left(-\frac{\psi_{\epsilon}(q)}{\epsilon}\right), \quad (39)$$

and thus,  $J^{ss}(q) = u^{ss}(q)(b(q) + D\nabla\psi_{\epsilon}(q))$ . Then  $\nabla \cdot J^{ss}(q) = 0$  implies

$$\epsilon \nabla \cdot \left( b(q) + D\nabla\psi_{\epsilon}(q) \right) = \left( b(q) + D\nabla\psi_{\epsilon}(q) \right) \cdot \nabla\psi_{\epsilon}(q). \quad (40)$$

Reversibility under time reversal  $(t, \phi, \gamma) \rightarrow (-t, \phi, \gamma)$  is equivalent to  $\gamma = b + D\nabla\psi_{\epsilon} = 0$  [47, 4, 5]. This is also known as potential condition [13, 19]. In the present work with time

reversal  $(t, \phi, \gamma) \rightarrow (-t, \phi, -\gamma)$ ,  $\gamma \neq 0$  but  $\nabla \cdot \gamma = \gamma \cdot \nabla \psi_\epsilon = 0$ . One could consider these conditions as more general ‘‘solvability conditions’’ for the steady state of a stochastic dynamics.

Eq. 40 is exact. We now consider the limit of small  $\epsilon$ , and  $\psi_\epsilon(q) = \phi_0(q) + \epsilon\phi_1(q) + \dots$ , where

$$\nabla\phi_0(q) \cdot (D\nabla\phi_0(q) + b(q)) = 0, \quad (41)$$

$$\nabla\phi_1(q) \cdot (2D\nabla\phi_0(q) + b(q)) = \nabla \cdot (D\nabla\phi_0(q) + b(q)), \quad (42)$$

$$\nabla\phi_2(q) \cdot (2D\nabla\phi_0(q) + b(q)) = \nabla \cdot (D\nabla\phi_1(q)) - (\nabla\phi_1(q))D(\nabla\phi_1(q)). \quad (43)$$

We thus have a decomposition that is resemblant to that of Helmholtz-Hodge:

$$b(q) = -D\nabla\phi_0(q) + (b(q) + D\nabla\phi_0(q)), \quad (44)$$

in which the two terms are orthogonal by the definition of  $\phi_0(q)$ , as given in (41). This is a well-known result in the theory of large deviation [41, 50]. However, Eq. 40 indicates that, in the limit of  $\epsilon \rightarrow 0$ ,  $\nabla \cdot (b(q) + D\nabla\phi_0(q))$  is  $\frac{0}{0}$ . In fact, from (42)

$$\nabla \cdot (b(q) + D\nabla\phi_0(q)) = -\nabla\phi_1(q) \cdot (2D\nabla\phi_0(q) + b(q)) \quad (45)$$

is on the order  $O(1)$ . Only when  $\phi_1(q) \equiv$  a constant, the equation in (44) becomes an orthogonal Hodge decomposition in the asymptotic limit of  $\epsilon \rightarrow 0$ . Ao’s stochastic process has all  $\phi_i(q) = 0$  with  $i \geq 1$ .

### 3.2 Boltzmann’s thermodynamic probability and Kolmogorov backward equation

Motivated by Eq. 31, let us introduce  $\Omega(q, t) = u(q, t)e^{\phi(q)}$ . Then

$$\frac{\partial\Omega(q, t)}{\partial t} = \nabla \cdot D\nabla\Omega(q, t) - (\gamma(q) + D\nabla\phi(q)) \cdot \nabla\Omega(q, t). \quad (46)$$

The Kolmogorov backward equation corresponding to (24) is

$$\frac{\partial v(q, t)}{\partial t} = \nabla \cdot D\nabla v(q, t) - (D\nabla\phi(q) - \gamma(q)) \cdot \nabla v(q, t). \quad (47)$$

They differ only by a  $\gamma \rightarrow -\gamma$ . The function  $\Omega(q, t)$  can be interpreted as Boltzmann’s ‘‘thermodynamic probability’’, whose logarithm is a thermodynamic potential (Boltzmann

entropy). Finally, the probability current consists of a “mechanical” force  $\gamma$  and an “entropic” force  $-D\nabla \ln \Omega$ :

$$j(q, t) = \gamma(q) - D\nabla \ln \Omega(q, t). \quad (48)$$

We also note that for both Eqs. 46 and 47, if  $v(q, t) > 0$ , there is an Boltzmann’s H-theorem like relation:

$$\frac{d}{dt} \int_{\mathbb{R}^n} \left( \Omega(q, t) \ln \Omega(q, t) \right) e^{-\phi(q)} dq = - \int_{\mathbb{R}^n} (\nabla \Omega) \cdot (D\nabla \Omega) \left( \frac{e^{-\phi}}{\Omega} \right) dq \leq 0. \quad (49)$$

### 3.3 Conservative and dissipative dynamics

The notions of conservative and dissipative systems are fundamental concepts in mechanics and thermodynamics. They are at the core of I. Prigogine’s challenge to Newton-Laplace’s world view [62, 63, 64]. Entropy production is the key mathematical quantity characterizing dissipation. Since 1980s, it has become increasingly clear that the mathematical foundation of entropy production lies at the notion of *time reversal* [47, 52, 53, 54, 55].

For the dynamics associated with system in (1), classical Newtonian notion of time reversal is  $(t, \phi, \gamma) \rightarrow (-t, \phi, -\gamma)$  which gives rise to an entropy production  $e_p^*$  solely by the non-adiabatic part  $-dF/dt$ . On the other hand, if one chooses time reversal  $(t, \phi, \gamma) \rightarrow (-t, \phi, \gamma)$ , then total entropy production  $e_p$  is the sum of both adiabatic and non-adiabatic entropy productions [36, 40]. The adiabatic part is also known as house-keeping heat [65]: It represents the amount of active energy input to sustain a nonequilibrium steady state [56].

To put the above discussion into sharper contrast, consider the following biophysical experiment on a single motor protein in the presence of given ATP and ADP concentrations in solution. At 100 cycles per second, a motor protein runs for a day with a total  $\sim 10^7$  ATP hydrolysis. However, at a millimolar concentration in a millilitre volume, there are  $10^{17}$  total number of ATP molecules. Hence, with a single motor protein running for a day in such a mesoscopic system, the concentration of ATP changes only 1 part of 10 billion. It is essentially undetectable.

Now consider an experiment on a type II superconducting ring with a current in the presence of a magnet. This system has been considered in condensed matter physics as an equilibrium system. However, according to Newton’s third law, the supercurrent has

to exert a force on the magnet and causing it to slowly demagnetize even though it is essentially undetectable [66].

Newton's first law states that a linear constant motion persists in the absence of a force. A rotational motion, hence, requires a force, even when it does no work. According to Newton's third law and our understanding of the constituents of matter, there is always a *consequence*, à la Lord Kelvin, at the origin of the force field that causes the rotational motion, i.e., a stationary current. The *environment* of an open system, therefore, can not be absolutely time reversible.

Conservative or dissipative description of an open subsystem are mathematical models which depend upon an experimentalist's knowledge and perspective. They are rather theoretical issues; the dynamics is closer to the reality.<sup>3</sup>

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