

Stochastic dynamics, large deviation principle, and nonequilibrium thermodynamics

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By examining the deterministic limit of a general ϵ -dependent generator for Markovian dynamics, which includes the continuous Fokker-Planck equations and discrete chemical master equations as two special cases, the intrinsic connections among mesoscopic stochastic dynamics, deterministic ordinary differential equations or partial differential equations, large deviation rate functions, and macroscopic thermodynamic potentials are established. Our result not only solves the long-lasting question of the origin of the entropy function in classical irreversible thermodynamics, but also reveals an emergent feature that arises automatically during the deterministic limit, through its large deviation rate function, with both time-reversible dynamics equipped with a Hamiltonian function and time-irreversible dynamics equipped with an entropy function.

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I. INTRODUCTION

Statistical equilibrium thermodynamics in terms of the theory of ensembles, as formulated originally by Gibbs, has a more fundamental origin; there is a growing consensus that the description of large deviations from the theory of probability provides a mathematical foundation for the subject [1] (see [2–4] and references therein for some of the recent developments). One of the most important insights from [3] is that one is able to derive nonequilibrium steady-state chemical thermodynamics using the same approach.

Briefly, the large deviation theory says that if a sequence of probability distributions has a deterministic limit, there exists concomitantly a scalar *rate function* for the convergence, which is defined on the entire state space. This rate function provides a variational principle akin to those associated with various thermodynamic potentials for different ensembles [5–8]. The existence of a thermodynamic potential such as entropy, in addition to being justified through the Clausius equality in traditional thermodynamics and the logarithm of thermodynamic *probability* as Boltzmann used in the mechanical theory of heat, could be hidden in the *assumption* of the sequence of probability distributions and its deterministic limit. We recall that, according to Boltzmann's approach, the existence of a thermodynamic potential function, regardless of its specific form, is the only prerequisite for developing thermodynamics: Thermodynamic forces are introduced as conjugate variables, work as “the force times the displacement,” and then automatically become a part of the energy change.

It is well known that the large deviation principle plays a key role in the equilibrium statistical mechanics [1,9]. In this study we are going to show that it also acts as the statistical foundation of nonequilibrium thermodynamics, specifically, the classical irreversible thermodynamics (CIT). Classical irreversible thermodynamics was developed by Onsager, Prigogine, de Groot and Mazur, and others, as a natural generalization of concepts from equilibrium to nonequilibrium thermodynamics by introducing (i) the local equilibrium assumption which secures a spatiotemporal entropy density function and (ii) a linear thermodynamic force-flux relationship [10]. However, so far, a solid and general theoretical foundation of CIT has not been established with a bottom-up approach. In this paper we propose a bridge between the CIT and the application of the large deviation principle in the small-noise limit for a wide class of stochastic dynamics, representing by both diffusion and jump processes.

The existence of a nonequilibrium steady state is essential for our construction and its role cannot be overemphasized. In fact, a key step of our approach is to examine the stationary solution to a Hamilton-Jacobi equation satisfied by the large deviation rate function, which has been rigorously demonstrated for many cases in the limiting process of stochastic to deterministic nonlinear dynamics [11]. The latter is the macroscopic dynamics covered by CIT, for which the stationary large deviation rate function becomes the (relative) entropy function.

The paper is organized as follows. In Sec. II a very general ϵ -dependent generator for Markovian dynamics, which includes the continuous Fokker-Planck equations and discrete chemical master equations as two special cases, is introduced. By examining the macroscopic limit, deterministic nonlinear ordinary differential equation (ODEs) and partial differential equations (PDEs), which are widely used in modeling nonequilibrium processes, are derived from the Markovian

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dynamics as the noise level $\epsilon \rightarrow 0$. Most importantly, during this limit process, stationary large deviation rate functions emerge automatically and serves as the entropy foundation for classical irreversible thermodynamics as shown in Sec. III. This conclusion is further justified through several concrete exactly solvable examples. Since the present paper is a synthesis of several lines of research into a coherent theory for nonequilibrium thermodynamics, in Sec. IV we discuss the relation between previous work and ours. Section V contains a general discussion about entropy, energy, dissipative dynamics, and conservative dynamics.

II. LARGE DEVIATION PRINCIPLE AND STOCHASTIC DYNAMICS

Most stochastic dynamics has a *natural* deterministic limit, which can and should be understood as a form of the law of large numbers (LLN) in the theory of probability. If one uses an ϵ to represent this limiting process and denote the stochastic dynamics by $Y_\epsilon(t)$, one has

$$\lim_{\epsilon \rightarrow 0} Y_\epsilon(t) = y(t), \quad (1)$$

where $y(t)$ represents deterministic dynamics. By envisioning the $y(t)$ as the limit of a sequence of $Y_\epsilon(t)$, there is an emergent variational principle associated with the deterministic $y(t)$: This is the essence of our new thermodynamics. One example of the type of limit theorems in (1) was given by Kurtz. According to [12], for any finite time the volume-averaged trajectories of particle numbers inside a given chemical reaction system, which follows a pure jump Markov process, will converge in probability to the solution of a set of deterministic ODEs in the limit of infinitely large particle number and volume (with the volume per particle being ϵ) while keeping a finite ratio between the two: the concentration. One can find details of this result in the texts by van Kampen [13], Gardiner [14], and Keizer [15].

In general, $Y_\epsilon(t)$ can be either discrete or continuous: For Markov dynamics, it can be a diffusion process driven by a stochastic Wiener process $W(t)$, or an integer-valued continuous-time jump process on the lattice \mathbb{Z}^N driven by a stochastic Poisson process $\Xi(t)$. In the former case, $\sqrt{\epsilon}$ is the amplitude of the $W(t)$; for the latter, the jump size is proportional to ϵ , which means we are taking the continuum limit. For a spatiotemporal dynamics $Y_\epsilon(x, t)$, the well-known examples are the solution to a stochastic partial differential equation (SPDE) with ϵ scaled white noise and interacting particle systems (IPSs) [16]. The corresponding limit law such as in (1) is called the hydrodynamic limit: In this case, the limit $y(x, t)$ usually satisfies a nonlinear PDE [17–19].

A. ϵ -dependent Markov transition probability

Let us now consider the situation that a continuous-time stochastic Markov $Y_\epsilon(t)$ is not given explicitly, but only in terms of a dynamic equation, as its generator:

$$\frac{\partial}{\partial t} \rho_\epsilon(z; t) = \int_{\mathbb{R}^n} T(z|\xi; \epsilon) \rho_\epsilon(\xi; t) d\xi, \quad (2a)$$

$$\rho_\epsilon(z; t) dz = \Pr\{z < Y_\epsilon(t) \leq z + dz\}. \quad (2b)$$

This is a special form of the Chapman-Kolmogorov equation for Markov dynamics, assuming a time-homogeneous rate for the transition probability. Here $\rho_\epsilon(z; t)$ denotes the probability density of the system in state z at time t , with $\epsilon \ll 1$ a small parameter indicating the strength of randomness.

In addition, $T(z|\xi; \epsilon)$ is the transition probability from state ξ to state z , which has the following essential properties: For $z, \xi \in \mathbb{R}^n$ and $\epsilon > 0$, (i)

$$T(z|\xi; \epsilon) \geq 0 \quad \text{for } z \neq \xi,$$

(ii)

$$\int_{\mathbb{R}^n} T(z|\xi; \epsilon) dz = 0,$$

and (iii)

$$\lim_{\epsilon \rightarrow 0} T(z|\xi; \epsilon) = -F(\xi) \delta'(z - \xi).$$

The first two are standard properties for an infinitesimal Markov generator and the third one indicates a deterministic (weak-noise) limit as $\epsilon \rightarrow 0$,

$$\begin{aligned} \frac{\partial \rho(z; t)}{\partial t} &= - \int_{\mathbb{R}^n} [F(\xi) \delta'(z - \xi)] \rho(\xi; t) d\xi \\ &= - \int_{\mathbb{R}^n} \nabla \cdot [F(\xi) \rho(\xi; t)] \delta(z - \xi) d\xi \\ &= - \nabla \cdot [F(z) \rho(z; t)], \end{aligned} \quad (3)$$

which represents a nonlinear ODE

$$\frac{dz(t)}{dt} = F(z). \quad (4)$$

Note that (i) and (ii) imply that $T(z|\xi; \epsilon)$ has a negative signed Dirac δ atomic measure at $z = \xi$. However, for finite ϵ , there could be other positive signed atomic measures at $z - \xi \neq 0$ in the form

$$T(z|\xi; \epsilon) = R(\xi) \left[\frac{\delta(z - \xi + \epsilon v) - \delta(z - \xi)}{\epsilon} \right], \quad (5)$$

in which the amplitude $R(\xi)$ is non-negative and the location v can be positive or negative. We therefore assume the general form for the Markov generator $T(z|\xi; \epsilon)$,¹

$$\begin{aligned} T(z|\xi; \epsilon) &= \sum_{\ell=-m}^m R_\ell(\xi) \left[\frac{\delta(\xi - z + \epsilon v_\ell) - \delta(\xi - z)}{\epsilon} \right] \\ &\quad - A(\xi) \delta'(z - \xi) + \epsilon D(\xi) \delta''(z - \xi), \end{aligned} \quad (6)$$

in which $A, \delta' \in \mathbb{R}^n$ are vectors; $D, \delta'' \in \mathbb{R}^n \times \mathbb{R}^n$, with D a positive definite matrix; and $v_\ell = -v_{-\ell}$. As a concrete example, it is noted that the first term on the right-hand side of (6) is the generator for chemical master equations with ϵ scaled jump size and time, leading to ϵv_ℓ and $\epsilon^{-1} R_\ell$ [22], while the

¹The theory of Lévy processes gives a more rigorous treatment of a Markov process whose probability of increments changes continuously in time [20,21]. Our assumption here amounts to a class of diffusion with jumps in units of ϵ .

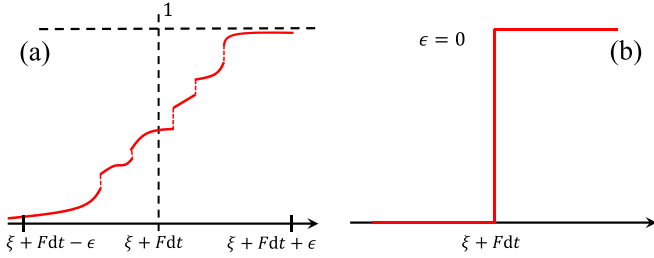


FIG. 1. (a) General, discontinuous transition probability distribution function $P_\epsilon(x|\xi; dt)$ defined in (8) (b) approaches (b) $H[x - \xi - F(\xi)dt]$ as $\epsilon \rightarrow 0$.

last two terms on the right-hand side are those for the drift and ϵ scaled diffusion terms in the Fokker-Planck equation.

It is noted that in the formula (6) the mechanical and chemical contributions to the dynamics (given by A and D and by R , respectively) scale with the same small parameter ϵ . However, as the ϵ from chemical contribution originates from the infinitely large population limit, while the ϵ in the diffusion process represents thermal fluctuations in mechanical movements, they do not have to be the same thing. In general this means that we need to deal with a double-limit problem when studying its asymptotic behaviors (see footnote 1). Here, for simplicity, we just use the same small parameter ϵ for both processes, since in order to have macroscopic chemomechanics they have to be infinitesimals on the same order.

In the limit of $\epsilon \rightarrow 0$, the generator in (6) gives

$$F(z) = A(z) + \sum_{\ell=-m}^m v_\ell R_\ell(z). \quad (7)$$

$$\begin{aligned} \frac{\partial \varphi(z, t)}{\partial t} &= \epsilon \int_{\mathbb{R}^n} e^{[\varphi(z, t) - \varphi(\xi, t)]/\epsilon} \left\{ A(\xi) \delta'(z - \xi) - \epsilon D(\xi) \delta''(z - \xi) - \sum_{\ell=1}^m R_\ell(\xi) \left[\frac{\delta(\xi - z + \epsilon v_\ell) - \delta(\xi - z)}{\epsilon} \right] \right\} d\xi \\ &= -A(z) \nabla \varphi(z, t) - \nabla \varphi(z, t) D(z) \nabla \varphi(z, t) - \sum_{\ell=-m}^m R_\ell(z) [e^{v_\ell \nabla \varphi(z, t)} - 1]. \end{aligned} \quad (11)$$

Notice the subtlety for the following double limit as $\epsilon \rightarrow 0$ and $\epsilon' \rightarrow 0$, which is singular:

$$\begin{aligned} \lim_{\epsilon' \rightarrow 0} \lim_{\epsilon \rightarrow 0} \epsilon' e^{\varphi(z)/\epsilon'} \int_{\mathbb{R}} e^{-\varphi(\xi)/\epsilon'} \left(\frac{\delta(\xi - z + \epsilon v) - \delta(\xi - z)}{\epsilon} \right) d\xi \\ = \lim_{\epsilon' \rightarrow 0} \lim_{\epsilon \rightarrow 0} \frac{\epsilon'}{\epsilon} [e^{-[\varphi(z + \epsilon v) - \varphi(z)]/\epsilon'} - 1] = \begin{cases} \lim_{\epsilon \rightarrow 0} e^{-[\varphi(z + \epsilon v) - \varphi(z)]/\epsilon} - 1 = e^{-v[d\varphi(z)/dz]} - 1, & \epsilon' = \epsilon \\ \lim_{\epsilon' \rightarrow 0} -\frac{v\epsilon'}{\epsilon'} \left[\frac{d\varphi(z)}{dz} \right] = -v \left[\frac{d\varphi(z)}{dz} \right], & \epsilon \rightarrow 0 \text{ first.} \end{cases} \end{aligned}$$

Actually, the limit does not exist if taking $\epsilon' \rightarrow 0$ first.

With respect to the Hamilton-Jacobi equation in (11), it becomes possible to introduce a Hamiltonian function

$$H(z, y) = A(z)y + y^T D(z)y + \sum_{\ell=-m}^m R_\ell(z) [e^{v_\ell y} - 1] \quad (12)$$

and the corresponding Hamiltonian dynamics

$$\frac{dz}{dt} = \frac{\partial H(z, y)}{\partial y} = A(z) + 2D(z)y + \sum_{\ell=-m}^m v_\ell R_\ell(z) e^{v_\ell y}, \quad (13)$$

$$\frac{dy}{dt} = -\frac{\partial H(z, y)}{\partial z} = -A'(z)y - y^T D'(z)y - \sum_{\ell=-m}^m R'_\ell(z) [e^{v_\ell y} - 1]. \quad (14)$$

This provides a unified treatment of the weak-noise limit of continuous diffusion processes as well as Kurtz's limit of jump process. The latter is modeled by a Poisson process $Y(t; \lambda)$ with rate λ to represent the particle number change during each chemical reaction in a stochastic way. As $\epsilon \rightarrow 0$, $\epsilon Y(t; \epsilon^{-1} \lambda) \rightarrow \lambda t$.

Figure 1 illustrates graphically the nature of the assumption in (6) when $z, \xi \in \mathbb{R}$. The corresponding transition probability distribution function in an infinitesimal dt is

$$P_\epsilon(x|\xi; dt) = \int_{-\infty}^x [\delta(z - \xi) + T(z|\xi; \epsilon) dt] dz, \quad (8)$$

which in general contains discontinuous jumps. In the limit of $\epsilon \rightarrow 0$, it converges to the Heaviside step function $H(x - \xi - B(\xi)dt)$.

B. Large deviation principle and Hamiltonian dynamics

Besides the LLN, it is well known that, associated with the probability of Y_ϵ at time t , there exists a large deviation principle

$$-\lim_{\epsilon \rightarrow 0} [\epsilon \ln \Pr\{\eta < Y_\epsilon(t) \leq \eta + d\eta\}] = \varphi(\eta, t), \quad (9)$$

in which non-negative $\varphi(\eta, t)$, called the large deviation rate function, has a global minimum equal to zero when $\eta = y(t)$. Now if one uses the result in (9) as the basis for an assumption like the WKB ansatz

$$\rho_\epsilon(z; t) = \exp\left(-\frac{\varphi(z, t)}{\epsilon}\right) \quad (10)$$

and substitutes this expression into (2a), one has the leading-order terms

Clearly, the above Hamiltonian system accepts the zero-noise dynamics (4) and (7) as a solution when the momentum is equal to zero ($y = 0$). Thus it corresponds to the relaxation dynamics towards an attractor. All other solutions to the Hamiltonian system with $y \neq 0$ correspond to rare events which are impossible in the deterministic dynamics and are only populated in fluctuations.

Meanwhile, according to classical mechanics, we can also construct a variational principle by considering the Lagrangian function

$$L(z, \dot{z}) = [y\dot{z} - H(z, y)]_{y=y(z, \dot{z})}, \quad (15)$$

in which y as a function of z and \dot{z} is obtained from solving the implicit equation (13). Clearly, $H(z, y)$ and $L(z, \dot{z})$ are Legendre transforms of each other. In terms of $L(z, \dot{z})$, the conjugate variable $y = \partial L(z, \dot{z}) / \partial \dot{z}$. Consequently, the most probable path consistent with the above Hamiltonian dynamics with given $z(0)$ and $z(T)$ is given through the least action principle

$$\min_{z(s)} \int_0^T L(z(s), \dot{z}(s)) ds. \quad (16)$$

C. $-\varphi^{ss}$ as an entropy functional

We now show that the stationary solution to Eq. (11) is an entropy functional for the nonlinear differential equation (4),

$$\begin{aligned} \frac{d}{dt} \varphi^{ss}[z(t)] &= F(z) \cdot \nabla_z \varphi^{ss}(z) \\ &= \left(A(z) + \sum_{\ell=-m}^m \nu_\ell R_\ell(z) \right) \cdot \nabla_z \varphi^{ss}(z), \end{aligned} \quad (17)$$

where $\varphi^{ss}(z)$ satisfies

$$\begin{aligned} A(z) \nabla \varphi^{ss}(z) + \nabla \varphi^{ss}(z) D(z) \nabla \varphi^{ss}(z) \\ + \sum_{\ell=-m}^m R_\ell(z) [e^{\nu_\ell \nabla \varphi^{ss}(z)} - 1] = 0. \end{aligned} \quad (18)$$

From (18) and using the inequality $e^a - 1 - a \geq 0$ for all $a \in \mathbb{R}$,

$$\begin{aligned} -F(z) \nabla \varphi^{ss}(z) &= \nabla \varphi^{ss}(z) D(z) \nabla \varphi^{ss}(z) \\ &+ \sum_{\ell=-m}^m R_\ell(z) [e^{\nu_\ell \nabla \varphi^{ss}(z)} - 1 - \nu_\ell \nabla \varphi^{ss}(z)] \\ &\geq 0. \end{aligned} \quad (19)$$

Therefore, the PDE (11) is the equation one seeks to define an entropy, thus the nonequilibrium thermodynamics of the nonlinear system (4).

It is important to identify $-d\varphi^{ss}/dt$ not as the entropy production rate but rather as the instantaneous rate of entropy

change. Then one has [3,23]

$$\begin{aligned} &\underbrace{-\frac{d}{dt} \varphi^{ss}[z(t)]}_{\text{entropy change}} \\ &= - \left[A(z) + \sum_{\ell=-m}^m \nu_\ell R_\ell(z) \right] \nabla_z \varphi^{ss}(z) \\ &= \underbrace{A(z) D^{-1}(z) A(z) + \sum_{\ell=1}^m [R_\ell(z) - R_{-\ell}(z)] \ln \left(\frac{R_\ell(z)}{R_{-\ell}(z)} \right)}_{\text{entropy production}} \\ &\quad - \underbrace{(A + D \nabla \varphi^{ss}) D^{-1} (A + D \nabla \varphi^{ss})}_{\text{mechanical drive}} \\ &\quad - \underbrace{\sum_{\ell=1}^m (R_\ell - R_{-\ell}) \ln \left[\frac{R_\ell}{R_{-\ell}} e^{\nu_\ell \nabla \varphi^{ss}} \right]}_{\text{chemical drive}} \\ &\quad + \underbrace{(A \nabla \varphi^{ss} + \nabla \varphi^{ss} D \nabla \varphi^{ss})}_{\text{chemomechanical exchange}}. \end{aligned} \quad (20)$$

According to (18), the last term representing chemomechanical exchange can also be expressed as

$$[A(z) + \nabla \varphi^{ss}(z) D(z)] \nabla \varphi^{ss}(z) = - \sum_{\ell=-m}^m R_\ell(z) [e^{\nu_\ell \nabla \varphi^{ss}(z)} - 1].$$

By ‘‘chemomechanics’’ we mean the continuous variables describing mechanical movements and the discrete jump processes representing chemical reactions as discrete events. From the standpoint of all the atoms as point masses in the molecules, the distinction between mechanics and chemistry disappears; the latter is an emergent phenomenon of a very complex particle ‘‘diffusion’’ in a potential force field as first elucidated by Kramers [24].

Let us now consider the specific situation in which both the mechanical and chemical parts are in detailed balance on their own [3,23],

$$A(z) = -D(z) \nabla_z U(z), \quad (21)$$

$$\ln \left(\frac{R_\ell(z)}{R_{-\ell}(z)} \right) = -\nu_\ell \nabla_z G(z), \quad (22)$$

in which $U(z)$ is a mechanical potential function and $G(z)$ is the Gibbs function for a chemical part. Substituting these two potential conditions into (4) and (7), we have

$$\frac{dz(t)}{dt} = - \left[D \nabla_z U + \sum_{\ell=1}^m 2\nu_\ell \hat{R}_\ell \sinh \left(\frac{1}{2} \nu_\ell \nabla_z G \right) \right]. \quad (23)$$

Equation (11) becomes

$$\begin{aligned} \frac{\partial \varphi(z, t)}{\partial t} &= (\nabla U - \nabla \varphi) D \nabla \varphi \\ &\quad - \sum_{\ell=0}^m 2\hat{R}_\ell \left[\cosh \left(\nu_\ell \nabla \varphi - \frac{1}{2} \nu_\ell \nabla G \right) \right. \\ &\quad \left. - \cosh \left(\frac{1}{2} \nu_\ell \nabla G \right) \right], \end{aligned} \quad (24)$$

in which $\hat{R}_\ell(z) = [R_\ell(z)R_{-\ell}(z)]^{1/2}$. In a chemomechanical equilibrium, both thermomechanics described by the continuous variables and thermochemistry represented by the jump processes have to be in their respective equilibrium; furthermore, the chemomechanical energy transduction has to be precisely balanced by mechanochemical energy transduction in the reverse process. Here U and G are actually different views of the same invariant probability measure with detailed balance. As a consequence, a global chemomechanical equilibrium is reached when $U(z) = \varphi^{ss}(z) = G(z)$.

D. PDEs as deterministic limits

Our previous derivations can be formally extended to nonlinear PDEs, which are the most widely used models in nonequilibrium thermodynamics. Partial differential equations originally arose from treating fluid dynamics in terms of Newtonian mechanics; the thermodynamics of the continuum thus naturally follows. There is a long tradition in the physics of nonequilibrium thermodynamics in terms of continuum theory [10] on the one hand and in formulating mathematical theory of PDEs in terms of ideas from thermodynamics [25,26] on the other hand. Ultimately, with a statistical foundation of thermodynamics in mind, a system of PDEs can be understood as the hydrodynamic limit of a SPDE or IPS. For example, nonequilibrium thermodynamics emerges in the asymptotic limit via the law of large deviations in the interaction particle system [27] and generalized Gibbsian chemical thermodynamics emerges in the asymptotic limit of Kurtz's theorem [12] and so does the chemomechanics we outlined in Sec. II above.

To begin with, let us consider a spatiotemporal stochastic process $Y_\epsilon(x, t)$, where $x \in \Omega \subset \mathbb{R}$, whose probability distribution for the entire function of x at a given time t ,

$$\Pr\{z(x) < Y_\epsilon(x, t) \leq z(x) + dz(x)\} = \rho_\epsilon[z(x); t]dz(x), \quad (25)$$

is given by a Chapman-Kolmogorov equation

$$\frac{\partial}{\partial t} \rho_\epsilon[z(x); t] = \int T_\epsilon[z(x)|\xi(x)] \rho_\epsilon[\xi(x); t] d\xi(x), \quad (26)$$

in which $\rho_\epsilon[z(x); t] = \rho_\epsilon[z(x)](t)$ is a functional of $z(x)$, and $z(x)$, $\xi(x)$, and $d\xi(x)$ are all in an appropriate function space. Similarly, the transition probability $T_\epsilon[z(x)|\xi(x)]$ is assumed to take the general form

$$\begin{aligned} T_\epsilon[z(x)|\xi(x)] &= \sum_{\ell=-m}^m R_\ell[\xi(x)] \\ &\times \left[\frac{\delta[\xi(x) - z(x) + \epsilon v_\ell(x)] - \delta[\xi(x) - z(x)]}{\epsilon} \right] \\ &- A[\xi(x)] \delta'[\xi(x) - z(x)] + \epsilon D[\xi(x)] \delta''[\xi(x) - z(x)], \end{aligned} \quad (27)$$

where $R_\ell[\xi(x)]$, $A[\xi(x)]$, and $D[\xi(x)]$ are all functionals of $\xi(x)$. Here $\delta'[\xi(x) - z(x)]$ and $\delta''[\xi(x) - z(x)]$ represent functional (or variational) derivatives of Dirac δ functions defined

as

$$\delta'[z] \equiv \frac{\delta}{\delta z}(\delta[z]) = \lim_{h \rightarrow 0} \frac{\delta[z + hdz] - \delta[z]}{h}. \quad (28)$$

With respect to this generator, in the limit of $\epsilon \rightarrow 0$, we have

$$\lim_{\epsilon \rightarrow 0} T_\epsilon[z(x)|\xi(x)] = -F[\xi(x)] \delta'[z(x) - \xi(x)], \quad (29)$$

with the functional

$$F[z(x)] = A[z(x)] + \sum_{\ell=-m}^m v_\ell(x) R_\ell[z(x)]; \quad (30)$$

therefore,

$$\frac{\partial}{\partial t} \rho_0[z(x); t] = -\frac{\delta}{\delta z} \{F[z(x)] \rho_0[z(x); t]\}. \quad (31)$$

This equation for the functional $\rho_0[z(x); t]$ actually represents a nonlinear partial differential equation

$$\frac{\partial z(x, t)}{\partial t} = F[z(x, t)], \quad (32)$$

in which F maps a function space in which $z(x, t)$ belongs to \mathbb{R} .

E. Conservation dissipation formalism

We now assume a more concrete form for F up to the second-order spatial derivative of $z(x, t)$, $F[z(x, t)] = F(z, z_x, z_{xx}, x)$. This corresponds to a rather broad class of nonlinear PDEs discussed in the literature

$$\frac{\partial z(x, t)}{\partial t} = F(z, z_x, z_{xx}, x), \quad (33)$$

in which z_x denotes $\partial z(x, t)/\partial x$. A PDE in which $F = -\nabla \cdot j(z_x, z, x) + s(x)$ is called a transport equation; F without the z_{xx} term is called hyperbolic and with the z_{xx} term is called parabolic. Further, F without the z is called the Hamilton-Jacobi equation. When F does not contain z_{xx} , the nonlinear first-order PDE can be solved by the method of characteristics [28–30]; for a Hamilton-Jacobi equation this method gives rise to a Hamiltonian system.

In particular, a group of first-order PDEs in the form

$$\partial_t z = - \sum_{j=1}^n \partial_{x_j} J_j(z) + Q(z), \quad (34)$$

where

$$z = \begin{pmatrix} z_s \\ z_d \end{pmatrix}, \quad J_i(z) = \begin{pmatrix} f_i(z) \\ g_i(z) \end{pmatrix}, \quad Q(z) = \begin{pmatrix} 0 \\ q(z) \end{pmatrix},$$

are of great interest in both nonequilibrium thermodynamics and mathematical physics. Here $z = z(x, t)$ is a set of independent variables used for characterizing the system under study. In addition, $J_i(z)$ are fluxes in the x_i direction, while $q(z) \neq 0$ represents nonzero source or sink terms. We notice that terms in $Q(z)$ corresponding to z are all zeros, which means variables z_s obey local conservation laws. The theoretical significance of local conservation laws is that they point out which kind of variables (an integration of z_s in the whole space) do not change with time. In contrast, since the source terms for z_d are nonzero, the spatial integration of z_d is no

longer constant. This gives a natural classification of z_s and z_d variables.

With respect to the above equations, a very general mathematical formulation, the conservation dissipation formalism (CDF) [31], for modeling nonequilibrium processes was constructed. The following are two key assumptions of the formulation.

(i) There is a strictly concave smooth function $\eta = \eta(z)$, called entropy, such that $\eta_{zz} \cdot J_{iz}(z)$ is symmetric for each i and for all $z = (z_s, z_d)$ under consideration.

(ii) There is a positive-definite matrix $M(z)$, called the dissipation matrix, such that $q(z) = M(z) \cdot \eta_{z_d}(z)$.

The first assumption is the famous entropy condition for hyperbolic conservation laws due to, e.g., Godunov [32] and Friedrichs and Lax [33], which ensures the system is globally symmetrizable and hyperbolic. Then the Poincaré lemma implies that there is a function $K_i = K_i(z)$ such that

$$\eta_z \cdot J_{iz} = K_{iz}.$$

The second condition is a nonlinearization of the celebrated Onsager reciprocal relation [34,35], which ensures that the states far away from equilibrium tend to equilibrium in a long time.

Now it is easy to see that, for $F[z(x, t)]$ in (33) which meet the two requirements of the CDF, $-\varphi^{ss}$ turns out to be the desired entropy function. Its corresponding time evolution is given through the balance equation

$$\frac{\partial \varphi^{ss}(z)}{\partial t} = \sum_{j=1}^n \partial_{x_j} K_j(z) - \sigma(z), \quad (35)$$

where $K_i(z)$ is the entropy flux and $\sigma(z) = \frac{\partial \varphi^{ss}(z)}{\partial t} M(z) \frac{\partial \varphi^{ss}(z)}{\partial z} \geq 0$ is the entropy production rate. This result establishes an interesting connection between stochastic thermodynamics, large deviation rate functions, and macroscopic nonequilibrium thermodynamics. As the formulation for the CDF looks similar to what we do for CIT in the next section, no more details will be presented here. Interested readers may work it out by themselves.

III. LARGE DEVIATION PRINCIPLE AND CLASSICAL IRREVERSIBLE THERMODYNAMICS

A. Logical structure of CIT

In contrast to the deterministic limit of stochastic processes discussed in previous sections, which provides a direct linkage between mesoscopic and macroscopic dynamics, there are also other schools, such as classical irreversible thermodynamics, trying to derive the governing equations for macroscopic deterministic dynamics directly from a thermodynamic point of view. The mathematics of macroscopic classical irreversible thermodynamics, such as presented in [10], has a very elegant and clear logical structure, which we summarize here.

(i) First, one considers the macroscopic system to be locally fully specified by several quantities, say, \mathbf{u}_i , \mathbf{v}_i , and \mathbf{w}_i , $i \in \mathfrak{S}$, which are called state variables. For example, in classical hydrodynamics, the fluid density ρ , velocity v , and total energy e are the most often used ones. This assumption is generally referred to as the local equilibrium hypothesis

in the literature, which allows the application of concepts and methodology in equilibrium thermodynamics directly to nonequilibrium systems. In CIT, another remarkable feature of state variables is that each of them satisfies a system of conservation laws of its own, which means $\mathbf{u}(t) = \{u_i(t), i \in \mathfrak{S}\}$ follows

$$\frac{du_i(t)}{dt} = \sum_{j \in \mathfrak{S}} (J_{ji}^{(u)} - J_{ij}^{(u)}), \quad (36)$$

where $J_{ij}^{(u)} \geq 0$ is a one-way flux.

(ii) The local equilibrium hypothesis also guarantees the existence of a local strictly convex entropy function $s_i \equiv S(u_i, v_i, w_i)$. Then, by differential calculus (or the Gibbs relation in thermodynamics) one has

$$\begin{aligned} \frac{ds_i}{dt} &= \left(\frac{\partial s_i}{\partial u_i} \right) \left[\frac{du_i(t)}{dt} \right] + \left(\frac{\partial s_i}{\partial v_i} \right) \left[\frac{dv_i(t)}{dt} \right] \\ &\quad + \left(\frac{\partial s_i}{\partial w_i} \right) \left[\frac{dw_i(t)}{dt} \right] \\ &= \sum_{\xi=u,v,w} \left(\frac{\partial s_i}{\partial \xi_i} \right) \sum_{j \in \mathfrak{S}} (J_{ji}^{(\xi)} - J_{ij}^{(\xi)}) \end{aligned} \quad (37a)$$

$$\begin{aligned} &= \underbrace{\sum_{\xi=u,v,w} \sum_{j \in \mathfrak{S}} \frac{1}{2} \left[\frac{\partial s_i}{\partial \xi_i} - \frac{\partial s_j}{\partial \xi_j} \right] (J_{ji}^{(\xi)} - J_{ij}^{(\xi)})}_{\text{local entropy production rate = force} \times \text{flux}} \\ &\quad + \underbrace{\sum_{\xi=u,v,w} \sum_{j \in \mathfrak{S}} J_{ji}^{(S,\xi)}}_{\text{entropy exchange flux}}, \end{aligned} \quad (37b)$$

in which the net entropy flux due to transport of ξ ,

$$J_{ij}^{(S,\xi)} = \frac{1}{2} \left[\frac{\partial s_i}{\partial \xi_i} + \frac{\partial s_j}{\partial \xi_j} \right] (J_{ij}^{(\xi)} - J_{ji}^{(\xi)}) = -J_{ji}^{(S,\xi)}. \quad (37c)$$

Equation (37) has established a *local* entropy balance law in the form given by (35). If ξ represents the energy, volume, or concentration of a chemical species, then $\partial s_i / \partial \xi_i \equiv (\partial S / \partial \xi)_i$, $i \in \mathfrak{S}$, will be $1/T_i$, p_i/T_i , and μ_i/T_i respectively, with T_i , p_i , and μ_i the local temperature, pressure, and chemical potential. Then the corresponding *thermodynamic forces* between states i and j are $1/T_i - 1/T_j$, $p_i/T_i - p_j/T_j$, and $\mu_i/T_i - \mu_j/T_j$.

(iii) Equation (37b), which splits (37a) into symmetric and antisymmetric terms, is actually a discrete version of the integration by parts in differential calculus, which is employed in the third step of CIT based on continuous variables. We recognize $\sum_{j \in \mathfrak{S}} (J_{ij} - J_{ji})$ as a discrete analog of a divergence term, in which $J_{ij} \geq 0$ is a one-way flux. Thus we have

$$\begin{aligned} \left(\frac{\partial s_i}{\partial \xi_i} \right) \sum_{j \in \mathfrak{S}} (J_{ij} - J_{ji}) &= - \sum_{j \in \mathfrak{S}} \left[\left(\frac{\partial s_j}{\partial \xi_j} \right) - \left(\frac{\partial s_i}{\partial \xi_i} \right) \right] J_{ji} \\ &\quad + \sum_{j \in \mathfrak{S}} \left[\left(\frac{\partial s_j}{\partial \xi_j} \right) J_{ji} - \left(\frac{\partial s_i}{\partial \xi_i} \right) J_{ij} \right]. \end{aligned} \quad (38)$$

The last term is again a divergence term, which is determined by only boundary values when summed over a set of i 's.

Interestingly, if we identify $s_j/\xi_j - s_i/\xi_i$ as a thermodynamic force between states i and j , the term $(s_j/\xi_j - s_i/\xi_i)J_{ji}$ is not consistent with Onsager's entropy production rate: According to his theory, a thermodynamics flux is the net flux $J_{ij} - J_{ji}$, not the one-way flux [36]. This observation suggests that instead of Eq. (38), we should make J_{ij} and J_{ji} symmetric:

$$\begin{aligned} & \left(\frac{\partial s_i}{\partial \xi_i} \right) \sum_{j \in \mathfrak{S}} (J_{ij} - J_{ji}) \\ &= \left(\frac{\partial s_i}{\partial \xi_i} \right) \sum_{j \in \mathfrak{S}} \left[\left(\frac{J_{ij} - J_{ji}}{2} \right) - \left(\frac{J_{ji} - J_{ij}}{2} \right) \right] \\ &= -\frac{1}{2} \sum_{j \in \mathfrak{S}} \left[\left(\frac{\partial s_j}{\partial \xi_j} \right) - \left(\frac{\partial s_i}{\partial \xi_i} \right) \right] (J_{ji} - J_{ij}) \\ &+ \frac{1}{2} \sum_{j \in \mathfrak{S}} \left[\left(\frac{\partial s_i}{\partial \xi_i} \right) + \left(\frac{\partial s_j}{\partial \xi_j} \right) \right] (J_{ji} - J_{ij}). \end{aligned} \quad (39)$$

This is precisely Eq. (37b).

(iv) The fourth step in CIT is to introduce a thermodynamic force-flux relationship

$$\begin{bmatrix} J_{ij}^{(u)} - J_{ji}^{(u)} \\ J_{ij}^{(v)} - J_{ji}^{(v)} \\ J_{ij}^{(w)} - J_{ji}^{(w)} \end{bmatrix} = -\mathbf{M}_{ij}(\mathbf{u}, \mathbf{v}, \mathbf{w}) \begin{bmatrix} \frac{\partial s_i}{\partial u_i} - \frac{\partial s_j}{\partial u_j} \\ \frac{\partial s_i}{\partial v_i} - \frac{\partial s_j}{\partial v_j} \\ \frac{\partial s_i}{\partial w_i} - \frac{\partial s_j}{\partial w_j} \end{bmatrix}, \quad (40)$$

where \mathbf{M}_{ij} is a 3×3 positive-definite symmetric matrix. With this assumption, the local entropy production rate in (37) is strictly positive except all forces and fluxes are zero. When $\mathbf{M}_{ij}(\mathbf{u}, \mathbf{v}, \mathbf{w})$ is evaluated at an equilibrium ($J_{ij} = J_{ji}$), it becomes a constant matrix. In that case, Eq. (40) is called Onsager's near-equilibrium linear force-flux relationship, which can be derived from the principle of detailed balance.

The force-flux relation does not need to be linear. Another well-known example is

$$\begin{bmatrix} \ln(J_{ij}^{(u)}/J_{ji}^{(u)}) \\ \ln(J_{ij}^{(v)}/J_{ji}^{(v)}) \\ \ln(J_{ij}^{(w)}/J_{ji}^{(w)}) \end{bmatrix} = -\mathbf{M}_{ij} \begin{bmatrix} \frac{\partial s_i}{\partial u_i} - \frac{\partial s_j}{\partial u_j} \\ \frac{\partial s_i}{\partial v_i} - \frac{\partial s_j}{\partial v_j} \\ \frac{\partial s_i}{\partial w_i} - \frac{\partial s_j}{\partial w_j} \end{bmatrix}. \quad (41)$$

This is the Gibbs chemical affinity-flux relationship. It implies that, for each and every set of cyclic indices $i_0, i_1, \dots, i_n, i_{n+1} = i_0$ in the state space \mathfrak{S} ,

$$\sum_{k=0}^n \mathbf{M}_{i_k k+1}^{-1} \begin{bmatrix} \ln(J_{i_k k+1}^{(u)}/J_{i_{k+1} i_k}^{(u)}) \\ \ln(J_{i_k k+1}^{(v)}/J_{i_{k+1} i_k}^{(v)}) \\ \ln(J_{i_k k+1}^{(w)}/J_{i_{k+1} i_k}^{(w)}) \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}, \quad (42)$$

which is known as chemical detailed balance. The three zeros in (42) imply that there exist three potential functions on the state space \mathfrak{S} . With (41) the local entropy production rate in (37) is non-negative and it is equal to zero if and only if $J_{ij}^{(\xi)} = J_{ji}^{(\xi)}$ for all $i, j \in \mathfrak{S}$ and $\xi = u, v, w$.

B. CIT for master equations

Let us now follow the same steps (i)–(iv) for a master equation which conserves the probability

$$\frac{dp_i(t)}{dt} = \sum_{j \in \mathfrak{S}} (J_{ji} - J_{ij}), \quad J_{ij} = p_i(t)q_{ij} \geq 0. \quad (43)$$

Introducing a local entropy function $s_i = -p_i \ln p_i$, then

$$\begin{aligned} \frac{ds_i}{dt} &= -(\ln p_i + 1) \frac{dp_i(t)}{dt} \\ &= \frac{1}{2} \sum_{j \in \mathfrak{S}} (p_i q_{ij} - p_j q_{ji}) \ln \left(\frac{p_i}{p_j} \right) \\ &+ \frac{1}{2} \sum_{j \in \mathfrak{S}} (p_i q_{ij} - p_j q_{ji}) [\ln(p_i p_j) + 2]. \end{aligned} \quad (44)$$

Now introducing an affinity-flux relationship $\ln(p_i/p_j) = M_{ij}(p_i q_{ij} - p_j q_{ji})$, where

$$M_{ij}(p_i, p_j) = \frac{\ln p_i - \ln p_j}{p_i q_{ij} - p_j q_{ji}}, \quad (45)$$

it is easy to show that each element of M is strictly positive if and only if $q_{ij} = q_{ji}$.

When $q_{ij} \neq q_{ji}$, the above simple entropy function that is independent of $\{q_{ij}\}$ can no longer be a valid choice. Rather, a proper entropy function has to be informed by the dynamics in (43). One of the best known examples is to consider the stationary probability distribution to (43), $\{\pi_i\}$: $\tilde{s}_i = -p_i \ln(p_i/\pi_i)$. This is the fundamental idea of free energy. Instead of (44) one then has

$$\begin{aligned} \frac{d\tilde{s}_i(t)}{dt} &= \frac{1}{2} \sum_{j \in \mathfrak{S}} (p_i q_{ij} - p_j q_{ji}) \ln \left(\frac{p_i \pi_j}{p_j \pi_i} \right) \\ &+ \frac{1}{2} \sum_{j \in \mathfrak{S}} (p_i q_{ij} - p_j q_{ji}) \left[\ln \left(\frac{p_i p_j}{\pi_i \pi_j} \right) + 2 \right]. \end{aligned} \quad (46)$$

One therefore has an affinity-flux relationship $\ln(p_i \pi_j / p_j \pi_i) = \tilde{M}_{ij}(p_i q_{ij} - p_j q_{ji})$, with

$$\tilde{M}_{ij}(p_i, p_j) = \frac{\ln(p_i/\pi_i) - \ln(p_j/\pi_j)}{p_i q_{ij} - p_j q_{ji}}. \quad (47)$$

The matrix \tilde{M} is symmetric and semipositive definite if and only if the detailed balance condition holds $\pi_i q_{ij} = \pi_j q_{ji}$ (see, e.g., Ref. [37] for a rigorous proof).

C. φ^{ss} as the statistical foundation of CIT

The entropy function plays a key role during the formulation of CIT; however, its origin is a mystery in macroscopic thermodynamics and CIT does not provide an answer to it. Interestingly, the large deviation rate function obtained from the limit process of mesoscopic stochastic dynamics turns out to be the desired entropy function for the macroscopic thermodynamic modeling and thus it provides a solid statistical foundation for CIT.

To make this point clear, we start with the stationary large deviation function (or the free energy function in this case)

and examine its full time derivative in accordance with CIT,

$$\begin{aligned} \frac{d\varphi^{ss}[z(x, t)]}{dt} &= \frac{dz(x, t)}{dt} \frac{\delta\varphi^{ss}[z(x, t)]}{\delta z} \\ &= - \sum_{l=-m}^m R_l[z] [e^{v_l \delta\varphi^{ss}[z]/\delta z} - 1] - A[z] \frac{\delta\varphi^{ss}[z]}{\delta z} - \frac{\delta\varphi^{ss}[z]}{\delta z} D[z] \frac{\delta\varphi^{ss}[z]}{\delta z} + \frac{dz}{dt} \frac{\delta\varphi^{ss}[z]}{\delta z} \\ &= - \sum_{l=-m}^m R_l[z] \left[e^{v_l \delta\varphi^{ss}[z]/\delta z} - v_l \frac{\delta\varphi^{ss}[z]}{\delta z} - 1 \right] + \left[\frac{dz}{dt} - \sum_{l=-m}^m v_l R_l[z] - A[z] - \frac{\delta\varphi^{ss}[z]}{\delta z} D[z] \right] \frac{\delta\varphi^{ss}[z]}{\delta z} \\ &= -\sigma_1 - \sigma_2. \end{aligned} \tag{48}$$

It can be seen that $\sigma_1 \geq 0$ by Bernoulli's inequality. To keep $\sigma_2 \geq 2$ in accordance with the second law of thermodynamics, CIT suggests taking

$$\frac{dz}{dt} - \sum_{l=-m}^m v_l R_l[z] - A[z] = \frac{\delta\varphi^{ss}[z(x, t)]}{\delta z} (D[z] - M[z]), \tag{49}$$

where $M[z] \geq 0$ must be semipositive definite. In particular, if we choose $M[z] = D[z]$, the macroscopic equation in (32) is recovered. Comparing to the original equation, we see that models derived from CIT are not completely specified unless the entropy production rate is given too (which means $M[z]$ is given). This ambiguity arises from the fact that a dissipative process is not fully specified by the entropy function, but also by its dissipation rate.

D. Exactly solvable models

Finally, we look at several examples, which could be explicitly solved, to illustrate the intrinsic relation between mesoscopic stochastic dynamics, macroscopic deterministic dynamics, large deviation rate functions, classical irreversible thermodynamics, Hamiltonian dynamics, and so on (see Fig. 2).

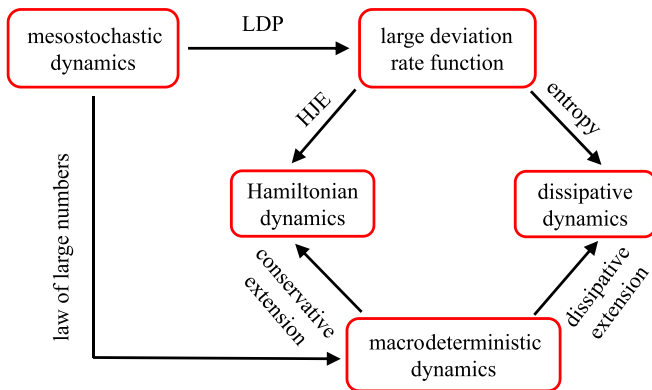


FIG. 2. Relation between stochastic dynamics, macroscopic limit, large deviation theory, etc. Here LDP denotes large deviation principle and HJE Hamilton-Jacobi equation.

1. Fokker-Planck equations for the Ornstein-Uhlenbeck process

By taking $R(\xi) = 0$, $A(\xi) = -az$, and $D(\xi) = D$ in the generator in (6), we arrive at the famous Fokker-Planck equation

$$\frac{\partial p_\epsilon(z, t)}{\partial t} = \frac{\partial}{\partial z} \cdot \left[\epsilon D \frac{\partial}{\partial z} p_\epsilon(z, t) + az p_\epsilon(z, t) \right]. \tag{50}$$

It corresponds to the Ornstein-Uhlenbeck process, a particular realization of the general Langevin dynamics, which reads

$$dz(t) = -azdt + \sqrt{2\epsilon D} dB(t), \tag{51}$$

under the meaning of Itô's calculus. In this case, the distribution function could be exactly solved as

$$p_\epsilon(z, t) = \left[\frac{a}{2\pi\epsilon D(1 - e^{-2at})} \right]^{1/2} \exp \left[-\frac{az^2}{2\epsilon D(1 - e^{-2at})} \right], \tag{52}$$

with respect to the initial condition $p_\epsilon(z, 0) = \delta(z)$.

It is straightforward to show the large deviation rate function $\varphi(z, t) = az^2/2D(1 - e^{-2at})$ and its stationary solution $\varphi^{ss}(z) = az^2/2D$. With respect to these formulas, we can repeat previous derivations of CIT. It is easy to check that the relation $dz/dt = -az$ guarantees a positive entropy production. On the other hand, as suggested by the large deviation principle, we can also introduce a Hamiltonian dynamics

$$\frac{dz}{dt} = 2Dy - az, \tag{53}$$

$$\frac{dy}{dt} = ay, \tag{54}$$

with a Hamiltonian function $H(z, y) = Dy^2 - azy$, which is equivalent to a Lagrangian dynamics

$$\ddot{z} - a^2z = 0 \tag{55}$$

given by the Lagrangian function $L(z, \dot{z}) = (\dot{z} + az)^2/4D$. Noticeably, both dynamics are time-reversible generalizations of $dz/dt = -az$.

2. Chemical reactions under complex balance conditions

In the next example, we consider a discrete generator with $A(\xi) = 0$ and $D(\xi) = 0$. In this case, the chemical master equations are obtained, whose deterministic limit gives usual

ODEs

$$\frac{dz(t)}{dt} = \sum_{\ell=1}^m \nu_{\ell} \cdot [R_{\ell}(z) - R_{-\ell}(z)] \quad (56)$$

for m chemical reactions with general rate functions $R_{\ell}(z)$. Here $z = (z_1, z_2, \dots, z_n)$ are the concentrations of the n species, and stoichiometric coefficients $\nu_{\ell} = (\nu_{\ell 1}, \nu_{\ell 2}, \dots, \nu_{\ell n})$.

Due to the condition of complex balance, a concept first introduced by Horn and Jackson [38] for a class of chemical reactions with laws of mass action, it can be shown that the kinetic equation above has a unique stationary solution z^{ss} [39], and the stationary large deviation rate function [3]

$$\varphi^{ss}(z) = \sum_{i=1}^n z_i \ln \left(\frac{z_i}{z_i^{ss}} \right) - z_i + z_i^{ss} \quad (57)$$

is a solution to

$$\sum_{\ell=1}^m R_{\ell}(z) [e^{\nu_{\ell} \nabla \varphi^{ss}(z)} - 1] + R_{-\ell}(z) [e^{-\nu_{\ell} \nabla \varphi^{ss}(z)} - 1] = 0. \quad (58)$$

Then, according to CIT, a possible dissipative extension of (56) is

$$\frac{dz}{dt} = \sum_{\ell=1}^m \nu_{\ell} \cdot [R_{\ell}(z) - R_{-\ell}(z)] - M(z) \ln \left(\frac{z_i}{z_i^{ss}} \right), \quad (59)$$

which, however, requires prior knowledge of the stationary solution z^{ss} and is nearly impossible for real applications. In contrast, the conservative extension does not require such information. With respect to the Hamiltonian function $H(z, y) = \sum_{\ell=1}^m \{R_{\ell}(z)[e^{\nu_{\ell} y} - 1] + R_{-\ell}(z)[e^{-\nu_{\ell} y} - 1]\}$, the derivation of corresponding Hamiltonian dynamics is straightforward, i.e.,

$$\frac{dz}{dt} = \sum_{\ell=1}^m \nu_{\ell} [R_{\ell}(z)e^{\nu_{\ell} y} - R_{-\ell}(z)e^{-\nu_{\ell} y}], \quad (60)$$

$$\frac{dy}{dt} = - \sum_{\ell=1}^m \{R'_{\ell}(z)[e^{\nu_{\ell} y} - 1] + R'_{-\ell}(z)[e^{-\nu_{\ell} y} - 1]\}. \quad (61)$$

It is noted that when the momentum $y = 0$, we recover the original kinetic equation in (56), which is in fact dissipative and time irreversible in nature.

3. Slow chemomechanical coupling near equilibrium

Compared to purely diffusive or purely chemical processes, the nontrivial chemomechanical coupling is far more interesting. In this case, we need to solve the stationary Hamilton-Jacobi equation in the full form

$$\begin{aligned} & [A(z) + \nabla \varphi^{ss}(z) D(z)] \nabla \varphi^{ss}(z) \\ & = \sum_{\ell=1}^m R_{\ell}(z) [1 - e^{\nu_{\ell} \nabla \varphi^{ss}(z)}] + R_{-\ell}(z) [1 - e^{-\nu_{\ell} \nabla \varphi^{ss}(z)}], \end{aligned} \quad (62)$$

which for most situations can only be solved numerically.

We now consider the problem in which both the mechanical and chemical parts are in rapid equilibrium, e.g., detailed

balance, on their own,

$$A(z) = -D(z) \nabla U(z), \quad \ln \left(\frac{R_{\ell}(z)}{R_{-\ell}(z)} \right) = -\nu_{\ell} \nabla G(z),$$

but the chemomechanical conversion is slow and is not yet in equilibrium and thus $U(z) \neq G(z)$; then $\varphi^{ss}(z)$ is equal to neither. Substituting these two into (62), we have

$$\begin{aligned} & \nabla \varphi^{ss}(z) D(z) \nabla [\varphi^{ss}(z) - U(z)] \\ & = \sum_{\ell=1}^m [e^{\nu_{\ell} \nabla \varphi^{ss}(z)} - 1] R_{\ell}(z) [e^{\nu_{\ell} \nabla [G(z) - \varphi^{ss}(z)]} - 1]. \end{aligned} \quad (63)$$

The terms $\nabla(\varphi^{ss} - U)$ and $\nabla(\varphi^{ss} - G)$ are the thermomechanical force and thermochemical force, respectively. A true equilibrium has both being zero. We see that if $\nabla(U - \varphi^{ss}) > 0$, then $\nabla(G - \varphi^{ss}) < 0$. This implies a net mechanical to chemical energy conversion.

Near equilibrium, the last factor on the right-hand side of (63) can be approximated by Taylor expansion. In the special case of $D(z) = \sum_{\ell=1}^m \frac{R_{\ell}(z) - R_{-\ell}(z)}{\ln R_{\ell}(z) - \ln R_{-\ell}(z)} \nu_{\ell} \otimes \nu_{\ell}$ (called biochemical conductance in stoichiometric network theory), where \otimes denotes the direct product of vectors, Eq. (63) can be solved explicitly. In this case, the thermomechanical force and thermochemical force are equal and opposite and are given by the difference between chemical potential and mechanical potential, i.e., $\nabla(\varphi^{ss} - U) = -\nabla(\varphi^{ss} - G) = \nabla(G - U)/2$.

For chemical reactions with the mass-action law in equilibrium, an explicit formula for $G(z)$ is known, that is, $G(z) = \sum_{i=1}^n z_i \ln(z_i/z_i^{ss}) - z_i + z_i^{ss}$ (see the second example above). As a consequence, $U(z) = \sum_{i=1}^n z_i \ln(z_i/z_i^{ss}) - z_i + z_i^{ss}$ and $A(z) = -D(z) \ln(z/z^{ss})$. It is worth noting that the term $\sum_{i=1}^n z_i \ln z_i$, which appears in both $G(z)$ and $U(z)$, has different interpretations in chemistry and in mechanics: The former is caused by chemical affinities, while the latter, according to Flory and Huggins, is an entropic effect reflecting the tendency of particle mixing.

IV. RELATION TO PREVIOUS WORK

There are three lines of research that are highly relevant and with respect to which the present work is seeking a synthesis.

(i) The statistical behavior of a stochastic system, its fluctuations and its entropy productions has been investigated. The classical theory of e.g., Einstein, Landau, Onsager, and Machlup for equilibrium fluctuations with detailed balance, Keizer's theory for nonequilibrium steady-state fluctuations [15], and the recently developed stochastic thermodynamics of finite trajectories [40] are well-known landmarks (see [41] for a recent development).

(ii) The study of large deviations beyond (i) for a *sequence* of stochastic systems with a LLN focuses on securing the existence of a rate function and deriving its particular form. Mathematical work tends to focus on the former and physics literature on the latter. For the mathematical method we refer interested readers to the comprehensive reviews written for physicists [5–9]. The traditional Gaussian fluctuation theory is simply the local Hessian structure near the global minimum of the rate function.

Along this direction, the weak-noise limit of Markovian dynamics, e.g., $\epsilon \rightarrow 0$ discussed in Sec. II, has been dis-

cussed many times in the past, both rigorously and applied. We mention in particular the extensive studies carried out by Graham and Tél [42,43] for the Fokker-Planck equation and by Hu [44], Dykman *et al.* [45], and Agazzi *et al.* [46] for the chemical master equation.

(iii) The parallel work for the spatiotemporal infinite-dimensional stochastic system is technically much more demanding. The demonstration of a deterministic limit and its form, usually a nonlinear PDE, is already a challenging task. There is a large literature on obtaining the hydrodynamic limit. Its history dates back to the pioneering works of Liggett [16], Guo *et al.* [17], and many others. On the discrete IPS, the exact results on the asymmetric simple exclusion process is particularly worth mentioning [47] (see [48] for a more recent study). A closely related approach is the reaction diffusion master equation in continuous time (see the earlier work of Keizer [15] on the fluctuating Boltzmann equation, that of Vance and Ross [49] on fluctuating Turing patterns, and the more recent work [50] in connection to numerical computations). On continuous space-time SPDEs, Graham and Tél also investigated the Ginzburg-Landau equation with weak noise [51]; Gonçalves and Jara studied the nonequilibrium fluctuations of the Kardar-Parisi-Zhang equation in terms of an Einstein relation [52]. With the LLN in hand, a systematic treatment of the fluctuations of hydrodynamic equations was carried out in macroscopic fluctuation theory [53,54]. Results on large deviations followed [27,55,56].

In contradistinction to the above-mentioned research areas (i)–(iii), our present work is a part of the recent development on setting the large deviation structure, being a limiting law for a sequence of Markov processes, as the mathematical foundation for nonequilibrium stochastic thermodynamics, beyond the studies of a Markov process. This type of limit law is to thermodynamic behavior what the central limit theorem is to the Gaussian fluctuation theory. The focus is on the mathematical origin of thermodynamic behavior itself: Here we combine all these results together, by using an ϵ -dependent Markov generator, in providing a unified mathematical physics in which the large deviation theory serves the statistical foundation of general nonequilibrium thermodynamics, like CIT and CDF. This synthesis is missing from most of the previous studies. One exception is the macroscopic fluctuation theory, developed by Bertini *et al.*, in which thermodynamic relationships among force, work, and quasipotential as energy were discussed; another is a study from us on extended irreversible thermodynamics [57].

Because of the nature of synthesis, in Sec. II D we discussed how to derive PDEs as the deterministic limits from a spatiotemporal stochastic process, in order to incorporate the general theory of CDF which includes both time and space. The work in (iii) above provides the more advanced, in-depth materials for this section. We merely give a heuristic coverage

before moving toward the main purpose of our present work: going beyond the law of large numbers, e.g., the proper hydrodynamic limit, and focusing on the entropy structure on top of those hydrodynamic equations.

V. CONCLUSION

The macroscopic limit of mesoscopic stochastic dynamics, especially the Markovian dynamics with either continuous or discrete state space, has been well understood since the pioneering works of Kurtz, Guo *et al.*, and many others. On the other hand, the fact that the large deviation principle, which emerges concomitantly during the limit process and provides the entropy as a macroscopic potential function of nonequilibrium thermodynamics, was not fully appreciated in the past. In the present study, by examining the deterministic limit of a general ϵ -dependent generator for Markovian dynamics, which includes the continuous Fokker-Planck equations and discrete chemical master equations as two special cases, the intrinsic connections between mesoscopic stochastic dynamics, its macroscopic limit, large deviation rate functions, and classical irreversible thermodynamics and its potential have been established. To provide concrete examples on our construction, the purely linear Ornstein-Uhlenbeck process, chemical reactions under the complex balance condition, and nontrivial slow chemomechanical coupling near equilibrium were solved explicitly. The investigation of more interesting chemical-mechanical coupled systems is left to future studies. In conclusion, our result not only solves the long-lasting question on the origin of entropy function in CIT, but also suggests a more general principle for emergent phenomena.

In our study, an amazing observation is that both the dissipative dynamics equipped with a (relative) entropy function and the conservative dynamics equipped with a Hamiltonian function arise automatically from the large deviation principle of mesoscopic stochastic dynamics. This emergent phenomenon not only highlights the inseparable nature of the first law and the second law of thermodynamics, which state the essential roles of energy and entropy in a thermodynamical view of dynamics, but also provides a practical way for constructing either conservative or dissipative dynamics of any given deterministic dynamics by considering its stochastic correspondence.

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