The statistical foundation of entropy in extended irreversible thermodynamics

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Abstract

In the theory of extended irreversible thermodynamics (EIT), the flux-dependent entropy function plays a key role; it is a fundamental distinction between EIT and the usual flux-independent entropy function adopted by classical irreversible thermodynamics (CIT). However, its existence, as a prerequisite for EIT, and its statistical origin have never been justified. In this work, by studying the macroscopic limit of an $\epsilon$-dependent Langevin dynamics, which admits a large deviations (LD) principle, we show that the stationary LD rate functions of probability density $p_\epsilon(x,t)$ and joint probability density $p_\epsilon(x,\dot{x},t)$ actually turn out to be the desired flux-independent entropy function in CIT and flux-dependent entropy function in EIT respectively. The difference of the two entropy functions is determined by the time resolution for Brownian motions times a Lagrangian, the latter arises from the LD Hamilton–Jacobi equation and can be used for constructing conserved Lagrangian/Hamiltonian dynamics.

Keywords: large deviations rate function, flux-dependent entropy function, Lagrangian, extended irreversible thermodynamics

1. Introduction

Classical irreversible, nonequilibrium thermodynamics for macroscopic systems championed by the so called Belgian–Dutch school, based on the double foundation of a nonequilibrium entropy function and thermodynamic force-flux relationships, developed by Onsager et al and many other authors, is based on the local equilibrium hypothesis [1]. The supposition guarantees the existence of an entropy function $S(u)$ of the macroscopic state variable $u$, which itself can be a function of space $x$ and time $t$ in a system with irreversible transport [2]. To go beyond the local equilibrium hypothesis, extended irreversible thermodynamics (EIT) assumes

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the existence of a new type of entropy functions $S(u, q)$ where variable $q$ is a flux that represents the rates of transport processes $[3, 4]$. In classical thermodynamics, the very existence of a ‘thermodynamic potential function’, as a principle, is sufficient for deriving a collection of mathematical relations that encompass the physics of thermodynamics.

To provide the abstractly introduced entropy function with a mechanistic basis, Helmholtz and Boltzmann advanced the mechanical theory of heat which firmly established that the concept of entropy in thermodynamics has a statistical foundation in terms of the dynamics of the constituents of a macroscopic system. They were able to mathematically derive the Gibbs’ equation $dE = TdS - pdV$ for mechanical systems in thermodynamic equilibrium based on (a) identifying a thermodynamic state as an entire level set of a Hamiltonian function $H(x, p)$; and (b) Boltzmann’s entropy $S(E) = k_B \ln \Omega(E)$, where $\Omega(E)$ is the Lebesgue volume of $\{(x, p)| E < H(x, p) \leq E + dE\}$ $[5]$.

In recent years, replacing the deterministic Hamiltonian description by a stochastic Markov dynamics and identifying the Gibbs–Shannon entropy as a mesoscopic counterpart of entropy in a system with fluctuations, a rather complete nonequilibrium thermodynamics in a state space has been formulated $[6, 7]$. This theory exhibits four novel features:

(a) It represents all transport phenomena universally as the probabilistic flux in the state space; then entropy production $\equiv$ entropic force $\times$ probabilistic flux.

(b) It removes the need for the local equilibrium assumption; in fact it shows that the assumption is only a part of developing Markovian models for real world processes as engineering.

(c) It proves a ‘law of entropy balance’ $[1]$ as a theorem, providing the notions of entropy production and entropy exchange with a stochastic dynamic representation.

(d) If the Markov process has detailed balance, then the entropy exchange becomes the rate of a mean potential energy change.

In the light of this development, one naturally asks ‘what is the statistical foundation of the $S(u, q)$ in EIT?’ In the present work, we extend the stochastic, Markov formulation of irreversible thermodynamics depicted above to address this important question. There should be no doubt that the statistical foundation of the $S(u, q)$ has to reside in a stochastic dynamics of the constituents of a mesoscopic system.

2. Mesoscopic stochastic dynamics and its macroscopic limit

The material in this section is not new in mathematical literature $[8–10]$. However, focusing a discussion on the transport of probability in a general continuous state space $\mathbb{R}^n$, and discussing large deviations rate function (LDRF) as the foundation of thermodynamic potentials, in parallel to thermodynamic limit of irreversible processes and the theory of stochastic entropy production rates, provides a necessary background for the new development in section 3. Furthermore, though the equations in this section as well as the ideas behind them can be found from place to place, a clarification on the intrinsic connection between the LDRF of dynamical systems under small random perturbations and classical irreversible thermodynamics (CIT) deserves a particular emphasis, especially in the context of nonequilibrium steady state.

2.1. Mesoscopic stochastic dynamics

By mesoscopic, we mean a dynamic description of a system in terms of a stochastic mathematical representation, with either discrete or continuous state space and time. In the present
work, we consider only the continuous time. We give the general formulation in a continuous state space \( \mathbb{R}^n \), which in fact covers discrete, integer-valued \( \mathbb{Z}^n \) using Dirac-\( \delta \) function. However, to clearly illustrate our ideas and reduce the burden of mathematical manipulations, more involved computations in the second half of the paper are carried out in terms of a discrete state space.

To be specific, let us consider a continuous-time, stochastic Markov dynamics in a state space \( \mathcal{S} \), which are completely specified by two mathematical objects: a probability distribution \( p(\mathbf{x}, 0) \), as an initial condition, and a transition rate function for the probability \( T(\mathbf{x}, t + \Delta t| \mathbf{x}', t) \). All information concerning transport processes in the state space \( \mathcal{S} \) is coded in the function \( T \colon \mathcal{S} \rightarrow \mathcal{S} \), and

\[
p(\mathbf{x}, t + \Delta t) = \int_{\mathcal{S}} T(\mathbf{x}, t + \Delta t| \mathbf{x}', t) p(\mathbf{x}', t) d\mathbf{x}'.
\]

(1)

Equation (1) is known as Chapman–Kolmogorov equation. It is the foundational equation for Markov dynamics. In terms of this mathematical representation, Gibbs entropy in statistical thermodynamics has been identified as a functional of the \( p(\mathbf{x}, t) \):

\[
S^{\text{CIT}}[p(\mathbf{x}, t)] = - \int_{\mathcal{S}} p(\mathbf{x}, t) \ln p(\mathbf{x}, t) d\mathbf{x}.
\]

(2)

A rather complete CIT, without the local equilibrium hypothesis, has been developed based on equation (2) [11–13]. One significant success of this theory is the unification between discrete stochastic chemical kinetics and Gibbsian equilibrium chemical thermodynamics for heterogeneous substances [14, 15], and the extension of the latter to open, living biochemical systems [16–18].

How does the \( q \) variable enter this stochastic formalism? All information concerning \( q \) is contained in the \( T \). But it cannot be the rate of transition probability per se since \( q \) is necessarily zero in an equilibrium. One naturally considers the ‘net probability flux’ from \( \mathbf{x} \rightarrow \mathbf{x}' \)

\[
J(\mathbf{x}', t + \Delta t| \mathbf{x}, t) = p(\mathbf{x}, t) T(\mathbf{x}', t + \Delta t| \mathbf{x}, t) - p(\mathbf{x}', t) T(\mathbf{x}, t + \Delta t| \mathbf{x}', t),
\]

(3)

which is zero if and only if a stochastic dynamical system reaches equilibrium state with detailed balance. For a mesoscopic system, thus conceptually one expects the EIT entropy is a function of both \( p(\mathbf{x}, t) \) and \( J(\mathbf{x}', t + \Delta t| \mathbf{x}, t) \), the two key characteristics of a nonequilibrium system [19]. The \( p(\mathbf{x}, t) T(\mathbf{x}', t + \Delta t| \mathbf{x}, t) \) is called the one-way flux from \( \mathbf{x} \) to \( \mathbf{x}' \), and the \( J \) in (3) is called the net flux from states \( \mathbf{x} \) to \( \mathbf{x}' \) [20].

To address this issue, let us consider a stochastic process \( \mathbf{x}(t) \) given by the Langevin dynamics

\[
d\mathbf{x}(t) = \mathbf{b}(\mathbf{x}) dt + \sqrt{2\epsilon \mathbf{D}(\mathbf{x})} d\mathbf{B}(t),
\]

(4)

with drift \( \mathbf{b}(\mathbf{x}) \) and the diffusion coefficient \( \mathbf{D}(\mathbf{x}) \) that is symmetric and positive definite, \( \epsilon \ll 1 \) is a small parameter indicating the level of stochasticity. As \( \epsilon \to 0 \), the Langevin dynamics approaches to a deterministic dynamics \( d\mathbf{x}/dt = \mathbf{b}(\mathbf{x}) \). According to Itô’s calculus, it is well-known that the instantaneous probability density function \( p(\mathbf{x}, t) \) and transition probability

---

3 For finite state space, this functional is also known as Shannon entropy, which emerges from the asymptotic behavior of the frequency distribution of \( n \) identical, independently distributed (i.i.d.) random events, as \( n \to \infty \).
According to the milestone work of Freidlin–Wentzell and Donsker–Varadhan [8–10], the large deviations theory supports a WKB ansatz, allowing the introduction of a Hamiltonian function 

\[ H(x, y) = y^T D(x)y + y^T b(x), \]  

where \( y = \partial \varphi(x, t) / \partial x \), and the corresponding Hamiltonian dynamics

\[
\frac{dx}{dt} = \frac{\partial H(x, y)}{\partial y} = 2D(x)y + b(x),
\]

\[
\frac{dy}{dt} = -\frac{\partial H(x, y)}{\partial x} = -y^T \frac{\partial D(x)}{\partial x} y - y^T \frac{\partial b(x)}{\partial x} .
\]

The Hamiltonian dynamics is a generalization of the deterministic dynamics \( dx/dt = b(x) \), in which \( y \) can be regarded as fluctuations in ‘a momentum space’. If \( y(0) = 0 \), then \( y(t) = 0 \) for all \( t > 0 \) and \( x(t) \) follows the \( dx/dt = b(x) \). A very dramatic feature of this generalization is the ‘conservative nature’ of \((x, y)(t)\) dynamics.

If a diffusion process satisfies \( b(x) = -D(x) \nabla \varphi^{eq}(x) \), then it is sufficient and necessary that the diffusion is non-driven. The emergent Hamiltonian for a non-driven stochastic system can be transformed, via a canonical transformation, into a form which is an even function of the momentum variable \( p \), signifying time reversibility:

\[
H(x, y) = y^T D(x)y + y^T b(x),
\]

\[
= y^T D(x) \left( y - \nabla \varphi^{eq}(x) \right) = p^T D(q)p + V(q) = \tilde{H}(q, p),
\]

in which \( q = x \) and

\[
p = y - \frac{1}{2} \nabla \varphi^{eq}(x), \quad V(q) = -\frac{1}{4} [\nabla \varphi^{eq}(q)]^T D(q) \nabla \varphi^{eq}(q).
\]

Indeed, the Hamiltonian in (11a) has the Newtonian expression with a separation of a kinetic energy and a potential energy. The matrix \( D(q) \) in the kinetic energy represents a curved space.

To show the transformation is canonical, we note

\[
\{x, y, H(x, y)\} \rightarrow \{x, \tilde{y} = y + f(x), \tilde{H}(x, \tilde{y}) = H(x, \tilde{y} - f(x))\}.
\]
has
\[ \frac{d\mathbf{x}}{dt} = \left( \frac{\partial H}{\partial \mathbf{y}} \right)_{\mathbf{x}} = \left( \frac{\partial \tilde{H}(\mathbf{x}, \mathbf{y})}{\partial \mathbf{y}} \right)_{\mathbf{x}}, \] (13)
\[ \frac{d\mathbf{y}}{dt} = \frac{d\mathbf{y}}{dt} + \mathbf{f}'(\mathbf{x}) \left( \frac{d\mathbf{x}}{dt} \right) = -\left( \frac{\partial H}{\partial \mathbf{x}} \right)_{\mathbf{y}} - \left( \frac{\partial H}{\partial \mathbf{y}} \right)_{\mathbf{x}} \mathbf{f}'(\mathbf{x}) = -\left( \frac{\partial \tilde{H}(\mathbf{x}, \mathbf{y})}{\partial \mathbf{x}} \right)_{\mathbf{y}}. \] (14)

On the other hand, if a diffusion process has \( \mathbf{D}^{-1}(\mathbf{x})\mathbf{b}(\mathbf{x}) \) not being a gradient vector field, then it is easy to show that its corresponding Lagrangian equation
\[ D_{ij}^{-1}(\mathbf{x})\ddot{x}_j = \frac{1}{2} \left[ \frac{\partial b_j(\mathbf{x})D_{jk}^{-1}(\mathbf{x})b_k(\mathbf{x})}{\partial x_i} \right] - \dot{x}_j \frac{\partial D_{ij}^{-1}(\mathbf{x})b_k(\mathbf{x})}{\partial x_i} - x_j \frac{\partial D_{ik}^{-1}(\mathbf{x})b_j(\mathbf{x})}{\partial x_k} - x_k \frac{\partial D_{ij}^{-1}(\mathbf{x})b_k(\mathbf{x})}{\partial x_j}. \] (15a)

It has two Lorentz magnetic force like terms [21], since they makes no contributions to the work (\( \mathbf{x} \times \) Lorentz force = 0). One may also look for alternative time irreversible extensions, which is a central topic in nonequilibrium thermodynamics, by examining the stationary LDRF \( \varphi^{st}(\mathbf{x}(t)) \).
\[ \left[ \frac{\partial \varphi^{st}(\mathbf{x})}{\partial \mathbf{x}} \right]^T \left( \mathbf{D}(\mathbf{x}) \frac{\partial \varphi^{st}(\mathbf{x})}{\partial \mathbf{x}} + \mathbf{b}(\mathbf{x}) \right) = 0. \] (16)

Equation (16) reveals a decomposition of the vector field \( \mathbf{b}(\mathbf{x}) \):
\[ \mathbf{b}(\mathbf{x}) = -\mathbf{D}(\mathbf{x})\nabla \varphi^{st}(\mathbf{x}) + \gamma(\mathbf{x}), \] (17)
in which \( \gamma^T(\mathbf{x}) \cdot \nabla \varphi^{st}(\mathbf{x}) = 0 \) for all \( \mathbf{x} \). The stationary LDRF \( \varphi^{st}(\mathbf{x}) \) can, and should be identified as the free energy function in irreversible thermodynamics, as illustrated below.

CIT as presented by Onsager and others first suggested that any non-driven systems spontaneously approaches to an equilibrium steady state [1, 22]. This corresponds to \( \gamma(\mathbf{x}) = 0 \) in the stochastic dynamics. Then one has
\[ \frac{d\mathbf{x}(t)}{dt} = -\mathbf{D}(\mathbf{x})\nabla \varphi^{st}(\mathbf{x}). \] (18)

This is precisely what has been expected from and discussed in CIT. In fact,
\[ \frac{d}{dt} \varphi^{st}(\mathbf{x}(t)) = \left[ \frac{\partial \varphi^{st}(\mathbf{x})}{\partial \mathbf{x}} \right]^T \frac{d\mathbf{x}(t)}{dt} = -\mathbf{b}^T(\mathbf{x})\mathbf{D}^{-1}(\mathbf{x})\mathbf{b}(\mathbf{x}) \leq 0, \] (19)
which means \( \varphi^{st} \) is the relative entropy for CIT, since it is also positive and convex as fundamental mathematical properties of LDRF. The theory of CIT particularly recognizes a geometric interpretation of \( \mathbf{D}^{-1}(\mathbf{x}) \): it provides an appropriate metric in the tangent space of \( \mathbf{x} \), to which \( \mathbf{b}(\mathbf{x}) \) belongs.
More generally without detailed balance, based on (17) one still has

$$
\frac{d}{dt} \varphi^{ss}(x(t)) = \left[ \frac{\partial \varphi^{ss}(x)}{\partial x} \right]^T b(x) = - \left[ \frac{\partial \varphi^{ss}(x)}{\partial x} \right]^T D(x) \left[ \frac{\partial \varphi^{ss}(x)}{\partial x} \right] \leq 0. \tag{20}
$$

In fact,

$$
\frac{d}{dt} \varphi^{ss}(x(t)) = -b^T(x)D^{-1}(x)b(x) + \gamma^T(x)D^{-1}(x)\gamma(x), \tag{21}
$$

which implies a Pythagorean relation among three entropy productions [23]:

$$
\begin{align*}
\text{total entropy production} & = b^T(x)D^{-1}(x)b(x) \\
\text{free energy dissipation} & = \left[ D(x)\nabla \varphi^{ss} \right]^T D^{-1}(x) \left[ D(x)\nabla \varphi^{ss} \right] \\
\text{house-keeping heat} & = \gamma^T(x)D^{-1}(x)\gamma(x). \tag{22}
\end{align*}
$$

The two terms on the rhs of (22) have been identified as Boltzmann’s thesis and Prigogine’s thesis of irreversibility [24]. Boltzmann’s thesis focuses on transient relaxation kinetics that approaches to an equilibrium in a non-driven system, and Prigogine’s idea articulates driven dissipative phenomena that can exist even in a stationary state. In stochastic thermodynamics, these two origins are represented by free energy dissipation and house-keeping heat, as two distinct parts of the total entropy production [12, 25, 26]. The house-keeping heat has a dual interpretation: as an external driving force to an overdamped thermodynamics or as the inertia effect in a conservative dynamics. The latter interpretation, as we show below, can be further developed in terms of an internal conjugate variable.

A remark is in order: equation (21) is a more legitimate thermodynamic law than the entropy balance equation [1]:

$$
\frac{dS}{dt} = \frac{d_i S}{dt} + \frac{d_f S}{dt}, \tag{23}
$$

in which among the three terms, entropy change ($dS$), entropy production ($d_i S$), and entropy flux ($d_f S$), only the ($d_i S/dt$) has a definite sign. The $\varphi^{ss}$ on the lhs of (21) is a free energy, and each one of the three terms in (21) has a definite sign. As it has been known from equilibrium thermodynamics, free energy is the appropriate thermodynamic potential function of a non-isolated system; not entropy.

### 3. Flux-dependent entropy and irreversible thermodynamics

With the background set in section 2, we shall now move on to the new topic—the statistical foundation of EIT indicated by flux-dependent entropy functions, which is a direct generalization of the CIT.

#### 3.1. Flux-dependent entropy function

For stochastic dynamics without detailed balance, equation (18) no longer holds true. In order to take the nonzero vector field $\gamma(x)$ into consideration, one needs to study not only the state of a system, but also the fluxes between any two given states. Flux of a mesoscopic stochastic dynamics in $\mathcal{S}$, as given in (3), is completely determined by $\rho(x, t)$ and transition probability
\( T(x, t + \Delta t|x', t) \) defined in (5) and (6). For an infinitesimal \( \Delta t \), the transition probability for the diffusion process in (6) has the form

\[
T_t(x, t + \Delta t|x', t) = \frac{1}{\sqrt{(4\pi\epsilon(\Delta t))^n} \det \mathbf{D}(x')}} \times \exp \left[ -\frac{[x - x' - \mathbf{b}(x')\Delta t]^T \mathbf{D}^{-1}(x')[x - x' - \mathbf{b}(x')\Delta t]}{4\epsilon(\Delta t)} \right]. \tag{24}
\]

Then Hill’s net probability flux in (3) \((\Delta x)^{-1}J(x + \Delta x, t + \Delta t|x, t)\) becomes

\[
\lim_{\Delta x \to 0} \frac{1}{[\Delta x]} \left[ p_t(x, t)T_t(x + \Delta x, t + \Delta t|x, t) - p_t(x + \Delta x, t)T_t(x, t + \Delta t|x + \Delta x, t) \right] = \left[ \epsilon \mathbf{D}(x) \right]^{-1} \mathbf{b}(x)p_t(x, t) - \nabla p_t(x, t). \tag{25}
\]

The probability flux in diffusion theory, \( \mathbf{J}_t(x, t) \equiv \mathbf{b}(x)p_t(x, t) - \epsilon \mathbf{D}(x)\nabla p_t(x, t) \) is actually \( \epsilon \mathbf{D}(x) \times \) Hill’s net flux. This result also reveals that while the mesoscopic flux \( \mathbf{J}_t(x, t) \) is completely determined once \( p_t(x, t) \) and the transition probability \( T_t(x, t|x', t) \) are known, in the macroscopic limit, the transport flux \( \mathbf{J}_t(x, t) \) is not determined by \( x(t) \) and vector field \( \mathbf{b}(x) \).

In the macroscopic limit as \( \epsilon \to 0 \), it can be shown that

\[
p_t(x, t) \to \delta(x - \tilde{x}(t)), \tag{26a}
\]

\[
-\epsilon \ln p_t(x, t) \to \varphi(x, t), \tag{26b}
\]

\[
-\epsilon \ln T_t(x + \Delta x, t + \Delta t|x, t) \to L(x, \tilde{x}) \Delta t, \tag{26c}
\]

\[
-\epsilon \ln p_t^{ss}(x) \to \varphi^{ss}(x), \tag{26d}
\]

\[
\frac{\mathbf{J}_t^{ss}(x)}{p_t^{ss}(x)} \to \gamma(x), \tag{26e}
\]

in which \( \tilde{x}(t) \) is the solution to \( \ddot{x} = \mathbf{b}(x) \), \( \gamma(x) \) is defined in (17). The Lagrangian \( L(x, \tilde{x}) = \frac{1}{2}[\tilde{x} - \mathbf{b}(x)]^T \mathbf{D}^{-1}(x)[\tilde{x} - \mathbf{b}(x)] \), with \( \tilde{x} = \Delta x/\Delta t \) as the LDRF for the transition probability over infinitesimal \( \Delta t \). And,

\[
\frac{\mathbf{J}_t(x, t)}{p_t(x, t)} = \mathbf{b}(x) - \epsilon \mathbf{D}(x)\nabla \ln p_t(x, t) \to \mathbf{b}(x) + \mathbf{D}(x)\nabla \varphi(x, t). \tag{27}
\]

With respect to the probability density \( p_t(x, t) \) and transition probability \( T_t(x, t + \Delta t|x', t) \), one natural choice of the flux-dependent entropy function is

\[
S^{\text{meso-ET}}(t; \Delta t) = -\int p_t(x, t)T_t(x', t + \Delta t|x, t) \times \ln[p_t(x, t)T_t(x', t + \Delta t|x, t)]dx dx'. \tag{28}
\]

Then we have
Note that for a continuous distribution, the mathematics in the theory of large deviations, especially in the Lagrangian function and conditional probabilities, becomes more involved. The Lagrangian function and conditional probabilities are given as:

\[ S_{\text{meso-IFT}}(t; \Delta t) = S_{\text{meso-CTT}}(t; \Delta t) - \int_\Theta p_\epsilon(x, t)T_e(x', t + \Delta t|x) \]

\[ \times \ln T_e(x', t + \Delta t|x)dx'd. \] (29)

Considering the Gaussian-form solution of \( T_e(x', t + \Delta t|x) \) given in (24), it is easy to show that the difference between \( S_{\text{meso-IFT}} \) and \( S_{\text{meso-CTT}} \) is a function of \( \Delta t \), which is expected to tend to zero as \( \Delta t \to 0 \). Following the definition, we further have:

\[
\frac{dS_{\text{meso-CTT}}}{dt} = - \int_\Theta \frac{\partial}{\partial x} \left[ e^{D(x)} \frac{\partial p_\epsilon}{\partial x} - b(x)p_\epsilon \right] \ln p_\epsilon dx
\]

\[
= \int_\Theta \left[ e^{D(x)} \frac{\partial p_\epsilon}{\partial x} - b(x)p_\epsilon \right] \frac{\partial}{\partial x} (\ln p_\epsilon) dx
\]

\[
= - \int_\Theta b(x) \frac{\partial p_\epsilon}{\partial x} dx + \int_\Theta \frac{\partial}{\partial x} \left[ e^{D(x)} \right] \frac{\partial p_\epsilon}{\partial x} dx. \] (30)

The last two terms represent entropy flux and entropy production rate respectively. Meanwhile,

\[
\frac{dS_{\text{meso-IFT}}}{dt} - \frac{dS_{\text{meso-CTT}}}{dt}
\]

\[ = - \int_\Theta \left[ \frac{\partial}{\partial t} p_\epsilon(x, t) T_e(x', t + \Delta t|x, t) + p_\epsilon(x, t) \frac{\partial}{\partial t} T_e(x', t + \Delta t|x, t) \right] \]

\[ \times \ln T_e(x', t + \Delta t|x, t)dx'd. \]

### 3.2. Lagrangian function and conditional probabilities

In the theory of large deviations, \( \epsilon \) stands for the level of stochasticity. The large deviations principle then states \( e^{-\varphi(x,t)/\epsilon} \) as the probability density function of \( x(t) \), with the rate function \( \varphi(x,t) \) given as:

\[
\varphi(z, t) = \min_{x(s)} \int_0^t L [x(s), \dot{x}(s)] ds.
\] (31)

\[
x(0) = x_0
\]

\[
x(t) = z
\]

\[ ^4 \text{Note that for a continuous distribution, the mathematics of}
\]

\[
\lim_{\epsilon \to 0} \int_R p_\epsilon(x) \ln p_\epsilon(x) dx
\]

\[ \text{where } p_\epsilon(x) = \delta(x) \text{ as } \epsilon \to 0, \text{ is not necessarily zero? An example is the Gaussian distribution with variance } \epsilon:
\]

\[
- \int_R p_\epsilon(x) \ln p_\epsilon(x) dx = - \int_R p_\epsilon(x) \left[ -\frac{x^2}{2\epsilon} - \frac{1}{2} \ln(2\pi\epsilon) \right] dx = \frac{1}{2} + \frac{1}{2} \ln(2\pi\epsilon).
\]

It is not zero; it does not even converge as \( \epsilon \to 0 \). This is in sharp contrast to a discrete distribution, which has \[ \sum \delta_{i\theta} \ln \delta_{i\theta} = 0. \]
Let us particularly consider $J.\text{Phys. A: Math. Theor.}$ with mean $\langle x(t) \rangle$. The probabilistic significance of which is again a Gaussian distribution, with zero mean and covariance matrix $\epsilon/\Delta t$ in which $\Delta t = t - t'$.

non-differentiable! in the context of ‘certain smooth functions’ while strictly speaking, according to Itô, conditioned at $x(t)$, with the ‘time resolution’ $\Delta t$. Mathematically, this means we consider $x_{t}(t)$ in the context of ‘certain smooth functions’ while strictly speaking, according to Itô, $x_{t}(t)$ is non-differentiable!

Now noting the relation between $y$ and $\dot{x} = b(x) + 2D(x)y$, the conditional probability density for the conjugate variable $y$, or momentum, is

$$p_y(y|\Delta t) = \frac{1}{\sqrt{(4\pi\epsilon/\Delta t)^n}} \exp \left\{ -\frac{\Delta^2 y^2 D^{-1}(x)}{4\epsilon} \right\},$$

which is again a Gaussian distribution, with zero mean and covariance matrix $\epsilon/(2\Delta t)D^{-1}(x)$. It is noted that the covariance matrices for $\dot{x}$ and $y$ are proportional to $D(x)$ and $D^{-1}(x)$ respectively.
It is easy to verify the familiar relationship between Lagrangian $L(x, \dot{x})$ in (34) and Hamiltonian function $H(x, y) = y^T D(x) y + y^T b(x)$:

\[
\begin{align*}
  y &= \left( \frac{\partial L(x, \dot{x})}{\partial \dot{x}} \right)_x = \frac{1}{2} D^{-1}(x) [\dot{x} - b(x)], \\
  \dot{x} &= \left( \frac{\partial H(x, y)}{\partial y} \right)_x = 2D(x)y + b(x), \\
  L(x, \dot{x}) &= \dot{x}^T y - H(x, y).
\end{align*}
\]

From the conditional probability in (33) and (35), we have the joint probability density function for $x$ and $\dot{x}$:

\[
p_r(x, \dot{x}, t; \Delta t) = A_1(\epsilon, t, \Delta t) \exp \left\{ -\frac{1}{\epsilon} [\varphi(x, t) + \Delta t L(x, \dot{x})] \right\},
\]

in which $A_1(\epsilon, t, \Delta t)$ is a normalization factor. Similarly, the joint probability for $x$ and $y$:

\[
p_r(x, y, t; \Delta t) = A_2(\epsilon, t, \Delta t) \exp \left\{ -\frac{1}{\epsilon} [\varphi(x, t) + \Delta t y^T D(x)y] \right\}.
\]

It should be noted that $\Delta t$ stands for the time resolution required for the existence of a normal ‘smooth’ diffusion process. Roughly speaking, as the Brownian motion is non-differentiable, in order to properly define $x$ and $\dot{x}$ in the context of ‘certain smooth functions’, we need to coarse grain the time scale by looking at their averages over a ‘microscopically sufficiently long yet macroscopically sufficiently short’ (due to CIT) time resolution $\Delta t$. The shorter $\Delta t$ is, the larger $\dot{x}$ (or $y$) will be, as a manifestation of certain uncertainty principle we will address in detail later. In this sense, even though $\Delta t \ll 1$, $\Delta t y^T D(x)y$ may still be comparable with $\varphi(x, t)$ and makes a non-negligible contribution to the joint probability.

3.3. LDRF and extended irreversible thermodynamics

To go beyond the so-called local equilibrium hypothesis, Müller and Ruggeri [3], Jou et al [4] have proposed the EIT as a modification of CIT. A major difference of the two theories lays on the choice of state variables. In CIT, only variables used in equilibrium thermodynamics are allowed, while in EIT nonequilibrium variables characterizing the fluxes of transport processes are adopted too. For example, in an EIT formulation of classical hydrodynamics, the fluid density $\rho$, velocity $v$, total energy $E$, stress tensor $P$ and heat flux $q$ are all taken as independent variables. While, in CIT the stress tensor $P$ and heat flux $q$ have to be treated as dependent variables, i.e. $P = P(\rho, v, E)$ and $q = q(\rho, v, E)$. This difference is raised by the fact that only the first three variables appear in the description of equilibrium thermodynamics of fluids, while the latter two are not. Actually, $P$ and $q$ are fluxes relating to the transport of momentum and energy in a nonequilibrium process.

As EIT adopts an enlarged space of state variables, it exhibits greater versatility in dealing with nonequilibrium processes than CIT. One of the first non-trivial successful applications of EIT is the derivation of Cattaneo’s law for heat conduction, which resolves the problem of infinite-speed propagation of thermal signals predicted by the Fourier’s law. Later, EIT has been applied to a range of phenomenology in heat transport, second sound in solids, ultrasound propagation or generalized hydrodynamics, etc [4]. Despite its great success, the origin of flux-dependent entropy function in EIT has never been clarified. Interestingly, as we have shown above, the large derivation function obtained from the limit process of a mesoscopic
stochastic dynamics turns out to be the entropy function for CIT-like modeling theories. We expect in the future a growing set of EIT-like theories under the stochastic framework.

To make this point clear, we look for large derivation functions as a function of both state variable $x$ and its flux in accordance with EIT. Obviously, the conditional probability in (37) meets our requirement, i.e.

$$\varphi(x, y, t; \Delta t) = -\lim_{\epsilon \to 0} \epsilon \ln[p_t(x, y, t; \Delta t)] = \varphi(x, t) + y^T[\Delta yD(x)]y,$$

in which $y = \frac{1}{2}D^{-1}(x)[\dot{x} - b(x)]$. $\varphi(x, y, t; \Delta t)$ can be regarded as a level 1.5 LDRF [27], since the ordinary level 1 LDRF

$$\varphi(x, t) = \min_y \varphi(x, y, t; \Delta t)$$

can be obtained by the contraction principle [9, 10]. Interestingly, it is easy to see that the minimum in the above formula is reached at $y = 0$ or $dx/dt = b(x)$, the determinist dynamics when $\epsilon = 0$.

The stationary large derivation rate function

$$\varphi''(x, y; \Delta t) = \lim_{t \to \infty} \varphi(x, \dot{x}, t; \Delta t) = \varphi''(x) + y^T[\Delta yD(x)]y$$

actually provides the statistical foundation of the flux-dependent entropy function used in the EIT. Its full time derivative obeys the entropy balance law,

$$\frac{d\varphi''(x, y, \Delta t)}{dt} = \left[ \frac{\partial \varphi''(x, \Delta t)}{\partial x} \right]^T \frac{dx}{dt} + \left[ \frac{\partial \varphi''(y, \Delta t)}{\partial y} \right]^T \frac{dy}{dt}$$

$$= \left[ \frac{\partial \varphi''(x)}{\partial x} \right]^T \frac{dx}{dt} + \Delta t \left[ \frac{\partial [y^T D(x)]y}{\partial x} \right]^T \frac{dx}{dt} + 2y^T[\Delta yD(x)]y$$

$$= \left\{ \left[ \frac{\partial \varphi''(x)}{\partial x} \right]^T + \Delta t \left[ \frac{\partial [y^T D(x)]y}{\partial x} \right]^T \right\} [2D(x)y + b(x)] + 2y^T[\Delta yD(x)]y$$

$$= \frac{\partial}{\partial x} \left[ \Delta t \left( y^T D(x)y \right) \right] (2D(x)y + b(x)) + \left[ \frac{\partial \varphi''(x)}{\partial x} \right]^T b(x)$$

$$+ 2\Delta y^T D(x) \left\{ (\Delta t)^{-1} \frac{\partial \varphi''(x)}{\partial x} - \frac{1}{2} \frac{\partial}{\partial x} \left[ 2D(x)y + b(x) \right] y + \frac{dy}{dt} \right\},$$

by inserting the known relation $dx/dt = 2D(x)y + b(x)$ and using integration by parts. In last step, the first term is recognized as the entropy flux. The next two terms are entropy production rates, which must be non-positive and equal to zero if and only if at the stationary state. Actually, it has already been shown in (20) that $[\partial \varphi''(x)/\partial x]^T b(x) \leq 0$ in accordance with CIT, so that we only need to require

$$\frac{dy}{dt} = -(\Delta t)^{-1} \frac{\partial \varphi''(x)}{\partial x} + \frac{1}{2} \frac{\partial}{\partial x} \left[ 2D(x)y + b(x) \right] y - \alpha(x, y)y$$

(42)
where \( \alpha(x, y) \geq 0 \) is a non-negative function. In particular, at the stationary state when \( dy/dt = 0 \), we arrive at the gradient dynamics,

\[
y \propto (\Delta t)^{-1/2} \frac{\partial \varphi^{ss}(x)}{\partial x},
\]

(43)

which happens at the correct time scale of \( (\Delta t)^{-1/2} \) for Brownian motions.

The global minimum of \( \varphi^{ss}(x, y; \Delta t) \) is obtained at

\[
y^* = 0, \quad x^* = \min_x \varphi^{ss}(x).
\]

(44)

For stochastic dynamics with detailed balance, \( b(x) = -D(x)\nabla \varphi^{ss}(x) \). Therefore, at the global minimum of \( \varphi^{ss}(x, y; \Delta t) \), the flux \( \dot{x}_{|_{x=x^*}} = b(x^*) = 0 \). This is the desired property for an equilibrium state. In general, however, if without detailed balance we have \( b(x) = -D(x)\nabla \varphi^{ss}(x) + \gamma(x) \) where \( \gamma(x) \cdot \nabla \varphi^{ss}(x) = 0 \). In this case, the global minimum of \( \varphi^{ss}(x, y; \Delta t) \) implies \( \nabla \varphi^{ss}(x^*) = 0 \) and a non-vanishing flux \( \dot{x}_{|_{x=x^*}} = \gamma(x^*) \); it is a nonequilibrium steady state. Please see figure 1 for an overview on the relations among stochastic dynamics, Hamiltonian dynamics, and dissipative dynamics by CIT and EIT.

### 3.4. Explicit results for the Ornstein–Uhlenbeck process

We now turn our attention to an example—the exactly solvable 1D Ornstein–Uhlenbeck process (OUP) [8, 9]:

\[
dx(t) = -bx(t)dt + \sqrt{2\epsilon}dB(t), \quad b > 0,
\]

with its KFE for the transition probability \( T_\epsilon(x, t|x', t') \),

\[
\frac{\partial T_\epsilon(x, t|x', t')}{\partial t} = \frac{\partial}{\partial x} \left( \epsilon D \frac{\partial T_\epsilon}{\partial x} + bxT_\epsilon \right), \quad T_\epsilon(x, t|x', t')|_{t=t'} = \delta(x - x').
\]

(45)
Equation (45) can be solved exactly to yield
\[
T_{\epsilon}(x,t|y,t') = \left\{ \frac{b}{2\pi \epsilon D} \left[ 1 - e^{-2b(t-t')} \right] \right\}^{1/2} \exp \left\{ -\frac{b}{2\epsilon D} \left[ x - x' e^{-b(t-t')} \right]^2 \right\}.
\]
(46)

More generally, Fokker–Planck equation (FPE) for the OUP is the same linear partial differential equation in (45) with the $T_{\epsilon}$ replaced by a probability density function
\[
p_{\epsilon}(x,t) = \left[ \frac{b}{2\pi \epsilon D(1 - e^{-2bt})} \right]^{1/2} \exp \left[ -\frac{bx^2}{2\epsilon D(1 - e^{-2bt})} \right],
p_{\epsilon}(x,0) = \delta(x),
\]
(47)

that changes with time.

Based on these formulas, we can derive the flux-independent and flux-dependent LDRF explicitly as
\[
\varphi^{sb}(x) = \frac{bx^2}{2D},
\]
(48)
\[
\varphi^{sb}(x,y;\Delta t) = \frac{bx^2}{2D} + (\Delta t D)y^2,
\]
(49)
where $y = (i + bx)/(2D)$. Repeating the same procedure of previous derivations, a natural dissipative dynamics suggested by EIT is
\[
\frac{dx}{dt} = 2Dy - bx,
\]
(50)
\[
\frac{dy}{dt} = -\frac{bx}{\Delta t D} - \frac{by}{2},
\]
(51)
by setting $\alpha(x,y) = 0$. In this case, $\varphi^{sb}(x,y;\Delta t)$ turns to be the relative entropy with the dissipation rate as $(bx)^2/D + \Delta t bDy^2$. Meanwhile, we can also get a Hamiltonian dynamics
\[
\frac{dx}{dt} = 2Dy - bx,
\]
(52)
\[
\frac{dy}{dt} = by,
\]
(53)
with the Hamiltonian function $H(x,y) = Dy^2 - bxy$. It is noted that both dynamical systems are extensions of $dx/dt = -bx$, but their time reversibilities are completely opposite.

### 3.5. Uncertainties in the zero-noise limit

What is the origin of the ‘macroscopic, deterministic thermodynamics?’ The title suggests an answer. This seemingly paradoxical statement is precisely a consequence of the concept of asymptotic limit, which had been considered as a ‘devil’s invention’. Together with Zeno’s paradox and Newton’s fluxion, they are a permanent part of the modern mathematics. Furthermore, in theoretical physics, it is well appreciated that when a limit process is singular, a wide range of counterintuitive subjects can arise; and new theories of reality emerge [28].
Let us again use the OUP to illustrate our idea. Consider
\[ p_\epsilon(x, 0) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-x')^2}{2\sigma^2}}, \]  
(54a)
\[ p'_\epsilon(x, t) = \int_R T_\epsilon(x, t|x''', 0)p_\epsilon(x''', 0)dx'''. \]  
(54b)
Noting the \( p(x, 0) \) in (54a) tending to \( \delta(x-x') \) as \( \sigma \to 0 \). We are particularly interested in the limit of \( \sigma \to 0 \) and the ‘zero-noise limit’ \( \epsilon \to 0 \).

When considering WKB ansatz, we immediately notice that the supposition \( \delta(x-x') = e^{-\frac{b}{2\epsilon^2}(x',0)} \) cannot be valid. In other words, in the asymptotic limit, \( \varphi(x, t) \) in terms of its characteristic lines is not fully defined by \( x = x' \) at \( t = 0 \). Additional information is required. This additional information is precisely in the limit process of \( \sigma \to 0 \). On the other hand, \( p(x, 0) = e^{-\varphi(x,0)/\epsilon} \) implies \( \varphi(x, 0) = -\epsilon \ln p_\epsilon(x, 0) \). Therefore, in the limit of \( \epsilon \to 0 \), the \( \varphi(x, 0) \) corresponding to any proper \( p_\epsilon(x, 0) \) vanishes.

These uncertainty about \( \varphi(x, 0) \) is precisely solved by the conjugate variable \( y \) in the Hamiltonian characteristic lines for the solution of the nonlinear HJE
\[ \frac{\partial \varphi(x, t)}{\partial t} = -D \left( \frac{\partial \varphi}{\partial x} \right)^2 + bx \left( \frac{\partial \varphi}{\partial x} \right). \]  
(55)
The ‘momentum variable’ \( y \) in the Hamiltonian dynamics represents the randomness that gives rise to a rare event in a stochastic dynamics. Comparing the equation
\[ \frac{dx}{dt} = \frac{\partial H(x, y)}{\partial y} = -bx + 2Dy \]  
(56) with the SDE
\[ dx(t) = -bxdt + \xi(t), \quad \xi(t) = \sqrt{2D}dB(t), \]  
(57)
where \( \xi(t) \) is a ‘white noise’, we have
\[ y(t) = \sqrt{\frac{\epsilon}{2D}} \frac{\partial \varphi}{\partial x}(x) \left( \frac{dB(t)}{dt} \right). \]  
(58)
Therefore, in terms of the white noise in (57),
\[ y(t) \cdot \xi(t) = \frac{\epsilon}{\sqrt{\Delta t}}. \]  
(59)
This is a kind of ‘uncertainty principle’ between the variance in \( x \) and in momentum. Therefore, while \( \varphi(x, t) \) emerges as a quantity in the zero-noise limit, \emph{its is neither the asymptotic limit of the solution to FPE with proper initial value, nor an asymptotic limit of the solution to KFE with Dirac-\( \delta \) initial value!} The HJE represents a novel behavior of its own.

We now investigate the double limit \( \epsilon, \sigma \to 0 \) for the function
\[ -\epsilon \ln p_\epsilon(x, t) = \frac{\epsilon(x - \mu(t))^2}{2\Xi(t)} + \frac{\epsilon}{2} \ln(2\pi \Xi(t)), \]  
(60a) in which, from equation (54a), \( \mu(t) = x'e^{-bt} \), which is independent of \( \epsilon \) and \( \sigma^2 \). And,
\[ \theta^2(t) = \frac{D}{b} \left( 1 - e^{-2bt} \right), \quad \Xi(t) = \sigma^2 e^{-2bt} + \theta^2(t). \]  
(60b)
The total Gaussian variance at time $t$, $\Xi(t)$, has two parts, a decreasing contribution from the initial $\sigma^2$ and an increasing Markovian $\partial^2 \theta(t)$. In the limit of $\epsilon \to 0$ and $\sigma \to 0$,

$$- \lim_{\sigma \to 0} \lim_{\epsilon \to 0} \epsilon \ln p^\epsilon(x,t) = 0 \neq - \lim_{\epsilon \to 0} \lim_{\sigma \to 0} \epsilon \ln p^\sigma(x,t)$$

$$= \lim_{\epsilon \to 0} \left( \frac{b(x - x' e^{-bt})^2}{2D (1 - e^{-2bt})} + \epsilon \ln \left[ \frac{2\pi eD}{b} (1 - e^{-2bt}) \right] \right) = \frac{b(x - x' e^{-bt})^2}{2D (1 - e^{-2bt})} \quad (61)$$

The limit is highly singular; we particularly note that in the rhs of (61), there is an uncertainty at $t = 0$, even after taking the limit $\epsilon \to 0$.

4. Discussion

4.1. Diffusion, friction, and mass

The Einstein relation. From a stochastic treatment of mechanical motion, pioneered by Einstein et al more than a century ago, one has for example

$$\frac{d^2x}{dt^2} = -\eta \frac{dx}{dt} - U'(x) + A\xi(t), \quad (62)$$

respectively, in which $\xi(t)$ is a white noise represented by the ‘derivative’ of the non-differentiable Brownian motion, $dB(t)/dt$. Two limiting cases are particularly worth discussion: (i) overdamped limit where $m = 0$ and (ii) spatial translational symmetric $U(x) =$ const. The stationary distributions for (i) and (ii) are

$$f_s(x) = Z_1^{-1} e^{\frac{2m^2}{\eta x^2}} \quad \text{and} \quad f_s(v) = Z_2^{-1} e^{\frac{2m^2}{\eta v^2}} \quad (63)$$

in which $Z_1$ and $Z_2$ are corresponding normalization factors for the two distributions. Comparing (63) with Boltzmann’s law and the Maxwell distribution, one identifies $A^2 = 2\eta k_B T$, where $k_B$ is Boltzmann’s constant and $T$ is temperature in Kelvin. According to the diffusion theory, $\frac{2\pi}{k_B T} = D$ is the diffusion coefficient. Therefore we arrive at the Einstein relation $D\eta = k_B T$, a well known result in statistical mechanics.

Diffusion and mass. In our present work, in the process of providing both entropy in CIT, $-\phi^{\text{BH}}(x)$, and flux-dependent entropy in EIT, $-\phi^{\text{BH}}(x,y;\Delta t)$, with a stochastic dynamic foundation in a broad sense, we have been led to an intriguing relation between the diffusion matrix $D(x)$ defined on the state space and the geometry concept of an Riemannian metric in the tangent space for $\xi$. The relation in (33) suggests an identification of $k_B T[2\pi eD(x)]^{-1}$ with a space-dependent ‘mass’, if $x$ is the Newtonian spatial coordinate. Combining this with the Einstein relation, $\frac{k_B T}{\eta} = \frac{(\Delta x)^2}{2(\Delta t)} = \frac{k_B T}{2\eta m}$. This relation gives an provocative hypothesis that $m \sim \frac{(\Delta x)^2}{k_B T}$.

4.2. Fick’s law as a consequence of Brownian motion

The heat or diffusion equation is obtained traditionally by combining the continuity equation $\partial u/\partial t = -\partial J/\partial x$ with Fick’s law $J = -D(\partial u/\partial x)$. However, derivation as such immediately suggests the possibility of generalizing Fick’s law. But this turns out to be mis-leading. In the context of Brownian motion, the Fick’s law should be understood as ‘an imbalance between the probability flux $J_{A \rightarrow B}$ of a single diffusant, from region $A$ to region $B$, and the $J_{B \rightarrow A}$’. It is not driven by concentration gradient per se; rather it is driven by an ‘entropic force’ $F$.
\[ J = \frac{(F/\eta)u(x,t)}{u(x,t)} \text{ where } \eta \text{ is the frictional coefficient of the diffusant, } F = -k_B T \ln u(x,t)/\partial x, \] and \[ D = \frac{k_B T}{\eta} \text{ is the Einstein relation. Any attempt to improving Fick's law can only be considered as a phenomenological theory; a fundamental approach to the subject has to consider hydrodynamic limit of interacting particle systems [29].} \]

4.3. Parabolic vs hyperbolic dynamics, and EIT

Another key anchoring points of EIT is the parabolic vs hyperbolic dynamic equations [30]. It is well-known that the former, in terms of diffusion, has an infinite velocity for propagating a disturbance: solution to \[ \partial u(x,t)/\partial t = \kappa \partial^2 u/\partial x^2, \] if \( u(x,0) = \delta(x-x_0), u(x,t) \neq 0 \) for all \( x \in \mathbb{R} \) when \( t > 0 \). This diffusive behavior is in sharp contrast to hyperbolic dynamics. Indeed, for many physical phenomena on a short time scales and with high frequencies, inertia plays an important role; the diffusive description becomes unrealistic. We would like to point out, however, that a more fundamental distinction between parabolic vs hyperbolic dynamics is between stochastic and deterministic. The latter emerges in a macroscopic limit.

4.4. Ergodicity and local equilibrium hypothesis

Two fundamental issues deserve further discussions: (i) ergodic hypothesis in connection to statistical mechanics, and (ii) local equilibrium hypothesis in connection to nonequilibrium thermodynamics.

The theory we developed is based on the stochastic, Markovian representation of a complex dynamics. In this context, ergodicity means the existence of a unique, attractive, invariant probability distribution, irrespective of whether the system has detailed balance or not. In the former case the stationary process is an equilibrium steady state with zero flux and no dissipation; and for the latter case the stationary process is a nonequilibrium steady state sustained by continuous energy input, with nonzero transport fluxes and positive entropy production. The ergodicity only became a nagging issue when the dynamical foundation is a deterministic system. In this case, it is now widely accepted that ergodic hypothesis is not a sufficient condition for a physically meaningful invariant distribution; the chaotic hypothesis was put forward to strengthen the foundation [31]. In stochastic dynamics, in addition to ergodicity, chaotic mixing is usually also satisfied [32]. In a view of large deviations from equilibrium and the application of EIT to non-ergodic processes, see the recent [33] for further details.

The local equilibrium hypothesis was introduced into the theory of nonequilibrium thermodynamics in order to secure the existence of a spatiotemporal dependent entropy function that satisfies the Gibbs equation. It was shown that by extending the local equilibrium concept to the mesoscale and introducing entropy as functional of the probability density over the state space of \((x,v)\) (or generalizing the \(p(x,t)\) in equation (2) to \(p(x,v,t)\)), Rubi et al obtained the Kramers equation with both position and velocity variables [34]. This approach to underdamped systems, which was also further developed in recent years in connection to fluctuation theorem [35,36], directly expanded the state space for kinematics. In contrast, our work shows an expansion of the state space, with conjugate variables, as a consequence of stochastic dynamics in the macroscopic limit via LD principle. By the same logic of the present work, one would expect conjugate variables corresponding to both \(x\) and \(v\) following [34]. More studies are required to further resolve these issues. In addition, while our work articulates ‘stochastic dynamics dictates thermodynamics’, [34] derives stochastic dynamics from thermodynamic principles. See [24] for more discussions on their contradistinction.

It has also been made clear recently that local equilibrium hypothesis has a role to play in the engineering applications of the stochastic dynamic theory to real world systems, when one
needs to be able to obtain the rate functions for probabilistic transition [17]. In our stochastic
theory, the nonequilibrium thermodynamics is concerned with transport flux of probability in
a state space; which represents all the different transport phenomena in real work, e.g., mass
transport, heat conduction, ionic movement, diffusion, and chemical reactions.

The above discussion is from a theory perspective. For real world phenomena that involve
slow thermalization, the local equilibrium assumption is no longer valid. Nevertheless, a
metastable nonequilibrium steady state on an appropriate time scale can be formulated as a
stochastic dynamical system. In general, this type of problems can analyzed either as a quasi-
steady-state without external drive or nonequilibrium steady-state with a sustained driven. In
chemical kinetic systems, their corresponding irreversible thermodynamics can be different, as
discussed in [37].

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