Thermodynamics of the General Diffusion Process:
Equilibrium Supercurrent and Nonequilibrium Driven
Circulation with Dissipation

Hong Qian
Department of Applied Mathematics
University of Washington
Seattle, WA 98195-3925, USA

December 19, 2014

Abstract

Unbalanced probability circulation, which yields cyclic motions in phase space, is the defining
characteristics of a stationary diffusion process without detailed balance. In over-damped soft
matter systems, such behavior is a hallmark of the presence of a sustained external driving force
accompanied with dissipations. In an under-damped and strongly correlated system, however,
cyclic motions are often the consequences of a conservative dynamics. In the present paper, we
give a novel interpretation of a class of diffusion processes with stationary circulation in terms
of a Maxwell-Boltzmann equilibrium in which cyclic motions are on the level set of stationary
probability density function thus non-dissipative, e.g., a supercurrent. This implies an orthog-
onality between stationary circulation $J^{ss}(x)$ and the gradient of stationary probability density
$f^{ss}(x) > 0$. A sufficient and necessary condition for the orthogonality is a decomposition of
the drift $b(x) = j(x) + D(x)\nabla \phi(x)$ where $\nabla \cdot j(x) = 0$ and $j(x) \cdot \nabla \phi(x) = 0$. Stationary pro-
cesses with Maxwell-Boltzmann equilibrium has an underlying conservative dynamics $\dot{x} = j(x) \equiv (f^{ss}(x))^{-1} J^{ss}(x)$, and a first integral $\phi(x) \equiv -\ln f^{ss}(x) = \text{const}$, akin to a Hamiltonian system.

At all time, an instantaneous free energy balance equation exists for a given diffusion system; and
an extended energy conservation law among a family of diffusion processes with different parameter $\alpha$ can be established via a Helmholtz theorem. For the general diffusion process without the orthogonality, a nonequilibrium cycle emerges, which consists of external driven $\varphi$-ascending steps and spontaneous $\varphi$-descending movements, alternated with iso-$\varphi$ motions. The theory presented here provides a rich mathematical narrative for complex mesoscopic dynamics.

1 Introduction

P. W. Anderson, J. J. Hopfield, and many other condensed matter physicists have all pointed out that emergent phenomena at each and every different scales actually obey different laws which require research that is just as fundamental in its nature as any other research [1, 2, 3]. The intricate behavior of a complex dynamic is particularly pronounced at a mesoscopic scale which contains too many individual “bodies” from a Newton-Laplacian perspective but not sufficient many, and often too strong an interaction and too heterogeneous, for the universal statistical laws such as central limit theorems and Gaussian processes.

This paper provides a didactic mathematical narrative of the general diffusion process, as a concrete model for complex stochastic nonlinear dynamics, in the light of two very different thermodynamic interpretations. The first one has its root in over-damped soft matters where sustained cyclic motions are considered a driven phenomenon accompanied with dissipation. The second one is motivated by under-damped and strongly correlated systems in which oscillatory motions are often the consequences of a conservative dynamics.

Throughout the paper, classical thermodynamic terminologies are introduced with precise mathematical definitions in the framework of the general diffusion process. They are perfectly consistent with equilibrium statistical mechanics [4, 5] and mostly in accord with known notions in nonequilibrium statistical physics. Their ultimate validity, of course, are judged by the internal logic of the mathematics. Indeed, there is a growing awareness that, in order to fully develop a thermodynamic theory for mesoscopic nonequilibrium systems, its foundation has to be shifted away from the empirical notion of local equilibrium first formulated by the Brussel school, toward a mathematical theory. In the present work, it is the Markov dynamics [6, 7, 8].

As expressed by some high-energy physicists “the rest is chemistry” [1]; one can indeed learn
from chemistry a very powerful perspective on complex systems around us: First, classical chemistry distinguish itself from physics by quantifying a dynamical system in terms of “species”, “individuals”, and the numbers of individuals in a particular species, rather than tracking the detailed particle positions and velocities. This practice is consistent with many-body physics in which Eulerian rather than Lagrangian description of a fluid, and second quantization, are prefered. This was a fundamental insight of Boltzmann who, together with Maxwell, Gibbs, Smoluchowski, Einstein, and Langevin, paved the way to use stochastic mathematics as the proper language for quantifying complex systems.

Second, while nonequilibrium thermodynamics in homogeneous systems usually deals with temperature gradient, nonequilibrium chemical thermodynamics often deals with isothermal systems with all kinds of interesting phenomena, including animated living matters, under chemical potential differences. Chemical equilibrium is actually an isothermal, dynamic concept.

Third, perhaps the most profound insight from chemistry, is the recognition of emerging discrete states, and transitions among them in molecules — each one a nonlinear continuous many-atom system in its own right: Such a state is sufficiently stable against small perturbations of the underlying equations of atomic motion to be identified as a distinct “chemical species”. Such a transition is on an entirely different time scale; it necessarily crosses a barrier chemists called a “transition state”. The rare event can be quantified in terms of an exponentially distributed random time and the notion of a “reaction coordinate” or an “order parameter”. This is a great achievement in multi-scale modeling by separation of time scales.

Finally, and possibly a deep idea from chemistry, is that stationary probability, as an emergent statistical entity, can actually be formulated as a law of force that quantifies collective motion of a system. Entropic force arises from mere probabilistic descriptions; and the concept of “potential of mean force” first articulated by J. G. Kirkwood in the theory of fluid mixtures is the ultimate explanation of equilibrium free energy; and it is actually a conditional probability! Chemical potential difference can do mechanical work; it can power a “Maxwell demon”.

While the chemistry providing a perspective, the mathematical theory of stochastic processes fully developed in the first half of 20th century provides a powerful analytical tool for representing complex dynamics. In fact, many key notions in chemistry echo important concepts in the theory
of probability [10]. In recent years, a nonequilibrium steady state with positive entropy production that is consistent with over-damped soft matters and biochemical systems [11] [12] has been mathematically defined in terms of Markov processes [13] [14] [15]. Stochastic thermodynamics has emerged as a unifying theory of nonequilibrium statistical mechanics [16] [17] [18] [19]. Classical phase transition theory can be understood using elementary chemical master equations and stochastic differential equations with bistability in the limit of both time and system’s size tending to infinities [20] [21].

Indeed, stochastic dynamics, which formalizes rapid stochastic and slower nonlinear dynamics and provides dual descriptions on both individual trajectories and ensemble probability distributions, seems to be a natural match for Anderson’s hierarchical structure of sciences generated by symmetry breakings [20] [22]. Even the Universe has become only one of the individuals of a multiverse [23].

This paper is structured as follows: In Sec. 2, results following the first perspective are summarized [6] [7] [15]. This is the main story line of the theory of stochastic thermodynamics which goes much further to fully explore trajectory-based thermodynamics and fluctuation theorems [16] [17] [18] [19]. Sec. 3 begins with introducing the notion of Maxwell-Boltzmann (MB) equilibrium with non-dissipative supercurrent, and presents the defining characteristics of diffusion processes that possess an MB equilibrium with circulations: (i) an orthogonality between stationary current $J^{ss}$ and the gradient of the stationary potential $\varphi(x) = -\ln f^{ss}(x)$; (ii) a decomposition of $b(x) = j(x) - D(x)\nabla \varphi(x)$ where $\nabla \cdot j(x) = 0$ and $j(x) \cdot \nabla \varphi(x) = 0$. Sec. 4 investigates the emergent divergence-free vector field $j(x, \alpha)$ from a family of diffusion processes with MB equilibrium: $\dot{x} = j(x, \alpha)$ has a first integral $\varphi(x, \alpha)$. The Helmholtz theorem is applied to establish an extended energy conservation law $h = h(\sigma_B, \alpha)$ for the entire family of diffusion processes, among the $\varphi$-level sets of which $h$ is the energy and $\sigma_B$ is the Boltzmann entropy. Sec. 5 studies diffusion processes that do not meet the orthogonality condition. We argue that the stationary process of such a system has both external driving force and dissipation, thus it is a nonequilibrium steady state within the framework of under-damped thermodynamics. Sec. 6 provides some discussions.
2 Diffusion processes with and without circulation

We reconsider a family of stochastic, diffusion process $X_{\alpha\beta}(t)$ with transition probability density function $f_{\alpha\beta}(x, t | y)$ satisfies Fokker-Planck equation

$$\frac{\partial f_{\alpha\beta}(x, t)}{\partial t} = \nabla \cdot \left( \beta^{-1} D(x, \alpha) \nabla f_{\alpha\beta}(x, t) - b(x, \alpha) f_{\alpha\beta}(x, t) \right),$$  \hspace{1cm} (1)

with non-local boundary condition and initial data

$$\int_{\mathbb{R}^n} f_{\alpha\beta}(x, t) dx = 1; \quad f_{\alpha\beta}(x, 0) = \delta(x - y),$$  \hspace{1cm} (2)

in which $x, y, b \in \mathbb{R}^n$, and $D$ is a $n \times n$ positive definite matrix. The $\alpha$ is a continuous parameter defining a family of related diffusion processes; and the $\beta$ is a scaling parameter quantifying the magnitude of the “noise”. We shall assume that a positive, steady state probability density function exists

$$\lim_{t \to \infty} f_{\alpha\beta}(x, t | y) = f_{\alpha\beta}^{ss}(x),$$  \hspace{1cm} (3)

which is independent of $y$ and satisfies the stationary Fokker-Planck equation

$$\beta^{-1} D(x, \alpha) \nabla f_{\alpha\beta}^{ss}(x) - b(x, \alpha) f_{\alpha\beta}^{ss}(x) \equiv -J_{ss}^{ss}(x), \quad \nabla \cdot J_{ss}^{ss}(x) = 0,$$  \hspace{1cm} (4)

under the same conditions in (2). For more discussion on the mathematical setup of this problem, see [6, 15].

The following facts are known under appropriate mathematical conditions. All discussions in Sec. 2 and Sec. 3 assume a fixed value of $\alpha$, which we shall suppress until Sec. 4.

2.1 Diffusion processes with detailed balance

The system (1) is called detailed balanced if $J_{ss}^{ss}(x) = 0 \forall x \in \mathbb{R}^n$. This is true if and only if a $\varphi(x)$ exists such that $D^{-1}(x)b(x) = -\nabla \varphi(x)$. Then $f_{\alpha\beta}^{ss}(x) = Z^{-1}(\beta)e^{-\beta \varphi(x)}$ where $\varphi(x)$ is a potential energy of the system, and $Z(\beta)$ is a normalization factor:

$$Z(\beta) = \int_{\mathbb{R}^n} e^{-\beta \varphi(x)} dx.$$  \hspace{1cm} (5)
Then the quantity

$$F(t) = \frac{1}{\beta} \int_{\mathbb{R}^n} f(x, t) \ln \left( \frac{f(x, t)}{f^{ss}(x)} \right) \, dx$$

$$= \langle \varphi(x) \rangle - \beta^{-1} \left( -\int_{\mathbb{R}^n} f(x, t) \ln f(x, t) \, dx \right) + \beta^{-1} \ln Z(\beta),$$

(6)

in which we introduced notion $\langle \cdot \cdot \cdot \rangle$ as expected value with respect to time-dependent probability distribution $f(x, t)$. The first term in (7) is the mean energy of the system at time $t$, and the term in the parenthesis is Gibbs-Shannon entropy. Therefore, it is natural to indentify the $F(t)$ as an instantaneous, generalized free energy of the dynamical system at time $t$. Actually, $F(t)$ is defined with respect to the equilibrium free energy of the system: $F(t) \geq 0$ and it is zero when $f(x, t) = f^{ss}(x)$. Classical statistical mechanics of inanimate matters uses universal mechanical energy as a reference point; thus the equilibrium free energy is $-\beta^{-1} \ln Z(\beta)$.

As a function of time, it can be mathematically shown that

$$\frac{dF(t)}{dt} = \int_{\mathbb{R}^n} J(x, t) \nabla \mu(x, t) \leq 0,$$

(8)

in which $\mu(x, t) = \varphi(x) + \beta^{-1} \ln f(x, t)$, $J(x, t) = -f(x, t)D(x) \nabla \mu(x, t)$. $\mu(x, t)$ can and should be interpreted as a generalized chemical potential, or thermodynamic force, and $J(x, t)$ as the corresponding thermodynamic flux. $F(t)$ monotonically decreasing until reaching its minimum zero. In fact, $e_p(t) = -\beta \frac{dF(t)}{dt} \geq 0$ is called entropy production rate for the diffusion process [15, 6].

One also has

$$\frac{dS(t)}{dt} \equiv \frac{d}{dt} \left( -\int_{\mathbb{R}^n} f(x, t) \ln f(x, t) \, dx \right) = e_p(t) + \frac{d}{dt} \langle \varphi(x) \rangle,$$

(9)

the right-hand-side of which are entropy production, usually written as $\frac{dS}{dt}$ which is not a total differential, and $\frac{dS}{dt}$ is the heat flux due to exchange with the environment [11]. Nonequilibrium entropy balance equation like (9) was first put forward phenomenologically by the Belgian thermodynamist de Donder, founder of the Brussels School [25, 26]. The shift from using state function

*In classical statistical mechanics, Newtonian mechanical energy is given a priori. Then the potential condition $D^{-1}(x)b(x) = -\nabla \varphi(x)$ becomes the fluctuation-dissipation relation. It is an essential equation completing a phenomenological theory of equilibrium fluctuations in terms of a diffusion process. It has the same nature as the detailed balance condition in discrete-state Markov process models widely used in chemistry [24].
entropy to free energy, and the fact that $e_p(t) \equiv -\beta \frac{dF(t)}{dt}$, reflect Helmhotz’s and Gibbs’ insight: the Second Law is “free energy decreases” for a canonical system, not “entropy increases”; but the origin of decreasing free energy is still the same positive entropy production.

The mathematical theory of stochastic processes offers additional insights for systems with detailed balance: A stationary stochastic trajectory $X(t)$ is time-reversible in a statistical sense [6, 15]. Therefore, anything accomplished through a sequence of events has an equal probability of being undone; nothing can be accomplished in an equilibrium dynamics. The linear operator on the right-hand-side of (1) is self-adjoint; there can be no oscillatory dynamics, only multi-exponential decays.

2.2 Diffusion processes with unbalanced circulation

A diffusion process without detailed balance has $J^{ss}(x) \neq 0$, but $\nabla \cdot J^{ss}(x) = 0$. The system has unbalanced probability circulation in the stationary state as its hallmark. The two mathematical objects: $\varphi_\beta(x) \equiv -\beta^{-1} \ln f^{ss}_\beta(x)$ and $J^{ss}_\beta(x)$ can be understood in analogous to the potential and current in an electrical system. Note that $\varphi_\beta(x)$ is now also a function of $\beta$, and its limit when $\beta \to \infty$ can be highly non-smooth. Still, if one introduces $F(t)$ as in (6), then Eq. (8) becomes

$$\frac{dF(t)}{dt} = E_{in}(t) - e_p(t),$$

(10)

where

$$E_{in}(t) = \int_{\mathbb{R}^n} J(x, t) \left( D^{-1}(x)b(x) - \beta^{-1} \nabla \ln f^{ss}_\beta(x) \right) dx,$$

(11)

$$e_p(t) = \int_{\mathbb{R}^n} J(x, t) \left( D^{-1}(x)b(x) - \beta^{-1} \nabla \ln f(x, t) \right) dx.$$  

(12)

All three quantities have definitive sign [27, 28, 29, 30]:

$$\frac{dF(t)}{dt} \leq 0, \quad E_{in}(t) \geq 0, \quad e_p(t) \geq 0.$$

(13)

Detailed balance holds if and only if $E_{in}(t) = 0$, stationarity holds if and only if $\frac{dF(t)}{dt} = 0$, and $e_p(t) = 0$ implies both. There are two verbal interpretations for Eqs. (10-13). (10) can be read as a generalized nonequilibrium free energy balance equation with instantaneous energy source from its environment $E_{in}(t)$ and dissipation $e_p(t)$ [7, 8]. Alternatively, $e_p(t) = -\frac{dF(t)}{dt} + E_{in}(t)$
can be read as total entropy production has two distinct origins: the spontaneous self-organization into stationary state and the continuous environmental drive that keeps the system away from its equilibrium. The two terms correspond nicely to Boltzmann’s thesis and Prigogine’s thesis on irreversibility, respectively. Quasi-steady state is a conceptual device that bridges these two views [31].

2.3 Diffusion operator decomposition

The right-hand-side of (1) is a second-order linear differential operator,
\[ \mathcal{L}[u] = \nabla \cdot \left( \beta^{-1} \mathbf{D}(x, \alpha) \nabla u(x) - b(x, \alpha) u(x) \right), \] (14)
in an appropriate Hilbert space \( \mathcal{H} \), with inner product
\[ \langle u, v \rangle = \int_{\mathbb{R}} u(x)v(x)(f^{ss}(x))^{-1} \, dx, \quad u, v \in \mathcal{H}. \] (15)

Then \( \mathcal{L} \) is self-adjoint if and only if the diffusion process is detail balanced [6, 15]. Furthermore \( \mathcal{L} = \mathcal{L}_S + \mathcal{L}_A \), where
\[ \langle \mathcal{L}_S[u], v \rangle = \langle u, \mathcal{L}_S[v] \rangle, \quad \langle \mathcal{L}_A[u], v \rangle = -\langle u, \mathcal{L}_A[v] \rangle, \]
\( \forall u, v \in \mathcal{H} \).

A diffusion process with self-adjoint \( \mathcal{L}_S \) has \( E_{in}(t) = 0 \).

A degenerated diffusion with skew symmetric \( \mathcal{L}_A \) has \( \frac{dF(t)}{dt} = 0 \) for all \( t \). It actually has a non-random dynamics whose trajectories follow the ordinary differential equation \( \dot{x} = (f^{ss}_\beta(x))^{-1}J^{ss}_\beta(x) \) [7]. The solution curves of this equation in phase space is identical to \( \dot{x} = J^{ss}_\beta(x), \nabla \cdot J^{ss}_\beta(x) = 0 \).

Paradoxically, such a dynamical system is called “conservative” in classical mechanics.

Because the diffusion with \( \mathcal{L}_A \) is degenerate, both \( E_{in}(t) \) and \( e_p(t) \) in (11) and (12) are infinite thus no longer defined.

3 \( \nabla \phi \perp J^{ss} \): Circulation as a supercurrent in a Maxwell-Boltzmann equilibrium

All the mathematical narrative so far fits established chemical thermodynamics of over-damped molecular systems. In particular, when applied to a molecular motor, the \( E_{in} \) term in (10) is indeed
the amount of ATP hydrolysis free energy, and $e_p$ the heat dissipation.

In physics, however, the notion of a persistent current describes a perpetual electrical current without requiring an external power source. A superconducting current is one example. We now show that an alternative, novel thermodynamic interpretation based on an under-damped dynamic perspective is equally legitimate [3]: $J^{ss}(x) = 0$ is no longer the defining characteristics of an equilibrium. Rather we define a Maxwell-Boltzmann (MB) equilibrium as $J^{ss}(x) \cdot \nabla \varphi(x) = 0$ where $\varphi(x) = -\beta^{-1} \ln f^{ss}_\beta(x)$. Unbalanced circulation on an equal-$\varphi$ level set is considered conservative.

The following facts are known under appropriate mathematical conditions.

### 3.1 $\varphi(x)$ is independent of $\beta$

Assuming when $\beta = 1$ $J^{ss}_1(x) \perp \nabla \varphi_1(x)$. This implies also an orthogonality between $J^{ss}_1(x)$ and $\nabla f^{ss}_1(x) \forall x \in \mathbb{R}^n$. One can decompose vector field $b(x)$ as

$$b(x) = (f^{ss}_1(x))^{-1} J^{ss}_1(x) + D(x) \nabla \ln f^{ss}_1(x),$$

which can be re-written as

$$b(x) = \left( f^{ss}_1(x) \right)^{-\beta} \left( (f^{ss}_1(x))^{-1+\beta} J^{ss}_1(x) \right) + \beta^{-1} D(x) \nabla \ln \left( f^{ss}_1(x) \right)^\beta.$$

Since

$$\nabla \cdot \left( (f^{ss}_1(x))^{-1+\beta} J^{ss}_1(x) \right) = 0,$$

we identify $(f^{ss}_1(x))^{-1+\beta} J^{ss}_1(x) = J^{ss}_\beta(x)$ and $(f^{ss}_1(x))^\beta = f^{ss}_\beta(x)$, which is a solution to (4). Therefore, $f^{ss}_\beta(x) = Z^{-1}(\beta) e^{-\beta \varphi(x)}$. Furthermore, $J^{ss}_\beta(x) = j(x) e^{-\beta \varphi(x)}$ in which $j(x)$ is also independent of $\beta$ and divergence free:

$$\nabla \cdot j(x) = e^{\beta \varphi(x)} \nabla \cdot J^{ss}_\beta(x) + J^{ss}_\beta(x) \cdot \nabla e^{\beta \varphi(x)} = 0.$$

The diffusion process in (1) has an MB equilibrium if and only if

$$b(x) = j(x) - D(x) \nabla \varphi(x), \quad \nabla \cdot j(x) = 0, \quad j(x) \cdot \nabla \varphi(x) = 0.$$

This result generalizes the potential condition in Sec. 2.1 with an additional divergence-free, orthogonal $j(x)$. (18) is a much more restrictive condition on $b(x)$ then $b(x) = (f^{ss}_\beta(x))^{-1} J^{ss}_\beta(x)$ —
$\beta^{-1}D(x)\nabla \ln f_\beta^{ss}(x)$, which is valid for any $f_\beta^{ss}(x)$ with a stationary $f_\beta^{ss}(x)$ \[32, 33\]. In general, when $\beta \rightarrow \infty$, the existence and characterizations of the limits of $\mu_\beta(\omega) = \int_\omega f_\beta^{ss}(x)dx$ and $\varphi_\beta(x) = -\beta^{-1} \ln f_\beta^{ss}(x)$ are highly non-trivial.

### 3.2 Nonlinear dynamics $j(x)$

The unbalanced stationary circulation in a MB equilibrium $J_\beta^{ss}(x) = j(x)e^{\beta \varphi(x)}$ has a clear deterministic, underlying nonlinear dynamics

$$\frac{dx}{dt} = j(x), \quad \nabla \cdot j(x) = 0. \quad (19)$$

Zero divergence of the vector field $j(x)$ means the dynamics is volume preserving in phase space. Furthermore, $\varphi(x)$ is one conserved quantity:

$$\frac{d}{dt} \varphi(x(t)) = \nabla \varphi(x) \cdot \left( \frac{dx}{dt} \right) = \nabla \varphi(x) \cdot j(x) = 0. \quad (20)$$

Therefore, the dynamics in Eq. [19] is akin to a Hamiltonian system. There is an agreement between the stochastic thermodynamics and the nonlinear dynamics. Indeed, the operator decomposition in Sec. 2.3, $\mathcal{L} = \mathcal{L}_S + \mathcal{L}_A$ matches the vector field decomposition $b(x) = j(x) - D(x)\nabla \varphi(x)$:

$$\mathcal{L}_S[u] = \nabla \cdot \left[ \beta^{-1}D\nabla \ln \left( u(x)e^{\beta \varphi(x)} \right) u(x) \right], \quad (21)$$

$$\mathcal{L}_A[u] = -\nabla \cdot \left( j(x)u(x) \right). \quad (22)$$

### 3.3 Entropy production

It has been shown that for a diffusion processes with MB equilibrium, the entropy production rate that is consistent with both known physics and the stochastic trajectory-based mathematical formulation based on time reversl is the free energy decreasing rate, or non-adiabatic entropy production [8]:

$$\frac{dF(t)}{dt} = \int_{\mathbb{R}^n} J(x,t) \left( \nabla \varphi(x) + \beta^{-1} \nabla \ln f(x,t) \right) dx \quad (23)$$

$$= -\int_{\mathbb{R}^n} \nabla \mu(x,t) D(x) \nabla \mu(x,t) f(x,t) dx, \quad (24)$$
in which again \( \mu(x, t) = \varphi(x) + \beta^{-1} \ln f(x, t) \), as in Eq. [8]. We note that even though \( J(x, t) = j(x)f(x, t) - f(x, t)D(x)\nabla \mu(x, t) \) contains the conservative current \( j(x) \), it has completely disappeared in the final entropy production formula (24).

Secondly, the rate of mean energy change:

\[
\frac{d}{dt} \langle \varphi(x) \rangle = \int_{\mathbb{R}^n} J(x, t)\nabla \varphi(x)dx
\]

\[
= \beta^{-2} \int_{\mathbb{R}^n} \nabla (e^{\beta \mu(x, t)}) D(x)\nabla (e^{-\beta \varphi(x)})dx.
\]

(25)

(26)

The meanings of the two quantities \( E_{\text{in}}(t) \) and \( e_p(t) \) are yet to be discovered for the under-damped systems. The mathematical expression for stationary \( E_{\text{in}} \) and \( e_p \) in (11) and (12) now reads

\[
\int_{\mathbb{R}^n} j(x)D^{-1}(x)j(x)e^{-\beta \varphi(x)}dx.
\]

(27)

It has a resemblance to kinetic energy; one should argue that in an under-damped thermal mechanical equilibrium, kinetic energy comes in and heat goes out.

### 3.4 Three examples

We now give three examples of diffusion processes, with increasing generality, that have an MB equilibrium [8].

**Ornstein-Uhlenbeck process.** As a Gaussian Markov process, the Ornstein-Uhlenbeck (OU) process is the most widely used stochastic-process model in science and engineering [34, 35]. Interestingly, its stationary process is always an MB equilibrium. Realizing that stationary OU process is the universal theory for linear stochastic dynamics [36, 37, 38], this result will have far-reaching implications.

An OU process has a constant diffusion matrix \( D \) and a linear \( b(x) = -Bx \). All the eigenvalues of \( B \) are assumed to have positive real parts. The stationary probability density and circulation can be exactly computed in terms of the covariant matrix \( \Xi \) of a Gaussian distribution:

\[
f^{ss}(x) = \frac{1}{(2\pi)^{n/2}} (\det(\Xi))^{-\frac{1}{2}} \exp \left(-\frac{1}{2} x^T \Xi^{-1} x \right),
\]

(28a)

\[
J^{ss}(x) = (B - D\Xi^{-1})xf^{ss}(x),
\]

(28b)

\[
B\Xi + \Xi B^T = 2D.
\]

(28c)
\( J^{ss}(x) = 0 \) if and only if \( BD = DB^T \) [39]. Then \( \Xi = B^{-1}D \). In general, the solution to the Lyapunov matrix equation (28c) has an integral representation

\[
\Xi = 2 \int_0^\infty e^{-B^s}De^{-B^Ts}ds.
\]

Noting that \( \Xi B^T - D = D - B\Xi \) is anti-symmetric [40],

\[
J^{ss}(x) \cdot \nabla f^{ss}(x) = \left( (B - D\Xi^{-1})xf^{ss}(x) \right)^T \cdot \nabla f^{ss}(x)
\]

\[
= -\left( f^{ss}(x) \right)^2 \left( x^T(B - D\Xi^{-1})^T\Xi^{-1}x \right)
\]

\[
= -\left( f^{ss}(x) \right)^2 x^T\Xi^{-1}(\Xi B^T - D)\Xi^{-1}x = 0.
\]

In fact, the linear vector field \(-Bx\), which has a decomposition \((D\Xi^{-1} - B)x - D\Xi^{-1}x\) as in (18), can be further represented as [40]

\[
-Bx = -(A + D)\nabla \left( \frac{1}{2}x^T\Xi^{-1}x \right).
\]

(29)

in which matrix \( A + D \) has a symmetric part \( D \) and an anti-symmetric part \( A = B\Xi - D \). In other words, any linear vector field \( b(x) = -(A + D)\nabla \varphi(x) \) where \( \varphi(x) \) is quadratic.

The corresponding linear stochastic differential equation

\[
dX(t) = -(A + D)\nabla \varphi(x)dt + (2D)^{\frac{1}{2}}dB(t),
\]

then, can be re-written as

\[
M\,dX(t) = -\nabla \varphi(x)dt + \Gamma dB(t),
\]

(30a)

in which \( M = (A + D)^{-1}, \Gamma = M(2D)^{\frac{1}{2}} \), and

\[
\Gamma\Gamma^T = 2MDM^T = M + M^T,
\]

(30b)

which is twice the symmetric part of \( M \). Stochastic differential equations expressed such as (30), which describes a stochastic dynamics without detailed balance but still reaching an MB equilibrium \( e^{-\varphi(x)} \), first appeared in [41].

**Klein-Kramers equation.** The Klein-Kramers equation is the canonical stochastic Newtonian dynamics with a stochastic damping that satisfies fluctuation-dissipation relation, thus a Maxwell-Boltzmann distribution in its stationary state. It has

\[
D = k_BT \begin{pmatrix} 0 & 0 \\ 0 & \eta(x) \end{pmatrix}, \quad b(x,y) = \begin{pmatrix} m^{-1}y \\ -U'(x) - m^{-1}\eta(x)y \end{pmatrix},
\]

(31)
and \( f^{ss}(x, y) = \exp \left( -\frac{H(x, y)}{k_B T} \right) \) where the Hamiltonian function \( H(x, y) \) is the total mechanical energy \( H(x, y) = \frac{y^2}{2m} + U(x) \), (32) and 

\[
J^{ss}(x, y) = \left( \begin{array}{c}
m^{-1} y \\
-U'(x)
\end{array} \right) f^{ss}(x, y), \quad j(x, y) = \left( \begin{array}{c}
\frac{\partial H}{\partial y} \\
-\frac{\partial H}{\partial x}
\end{array} \right).
\]

(33)

\[ \frac{d}{dt} (x, y)^T = j(x, y) \] is indeed the underlying Hamiltonian dynamics. The stationary stochastic circulation \( J^{ss}(x) \) is the Hamiltonian conservative dynamics weighted by the stationary probability \( f^{ss}(x, y) \).

**P. Ao’s stochastic process.** P. Ao and his coworkers have generalized the Eq. 29 and the Kramers-Klein equation to a class of nonlinear diffusion processes \([40, 41, 42, 43]\) with:

\[
D(x) = \frac{1}{2} \left( G(x) + G^T(x) \right), \quad b(x) = -G(x) \nabla \phi(x).
\]

(34)

The stationary probability density and circulation are again readily obtained:

\[
f^{ss}(x) = e^{-\phi(x)}, \quad J^{ss}(x) = \frac{1}{2} \left( G(x) - G^T(x) \right) \nabla f^{ss}(x).
\]

(35)

Obviously, \( J^{ss}(x) \cdot \nabla f^{ss}(x) = 0 \). Two interesting mathematical questions arise from this model:

(i) For any divergence-free vector field \( j(x) \) with a first integral \( \phi(x) \), e.g., \( j(x) \perp \nabla \phi(x) \), whether there always exists an anti-symmetrix \( A(x) \) such that \( j(x) = A(x) \nabla \phi(x) \)? This is true for any Hamiltonian system, with even \( n \), where \( A \) is symplectic. For \( n = 3 \), such a \( j(x) \) is called a gradient conjugate system, whose solution curves are all closed orbits \([44]\).

(ii) For a vector field \( b(x) \) that satisfies the decomposition in \([18]\), what is the relationship between a Sinai-Bowen-Ruelle type invariant measure, when it exists, and the the \( e^{-\beta \phi(x)} \) in the limit of \( \beta^{-1} \to 0 \) \([45]\)?

(iii) For any vector field \( b(x) \), whether there always exists an symmetric matrix \( D(x) \) such that \( b(x) = j(x) - D(x) \nabla \phi(x) \) with divergence-free \( j(x) \) and \( j(x) \perp \nabla \phi(x) \)?

### 4 Helmholtz theorem and Carnot cycle

We now consider the family of diffusion processes in terms of the parameter \( \alpha \) in \([1]\). All the discussions in Sec. \([2]\) and Sec. \([3]\) have been focused on the dynamics and thermodynamics of
one autonomous dynamical system, or time-homogeneous stochastic process, with a single \( \alpha \) value. Particularly, we have noticed that the generalized, nonequilibrium free energy \( F(t) \) in (10) takes its stationary state as the reference point. Classical thermodynamics, however, is a theory of relationships among different stationary states connected through “changing a parameter”. Being able to provide a common energy reference point for diffusion processes with different \( \alpha \), one needs a unique \( \varphi(x, \alpha) \) which can not be obtained unambiguously from the analysis presented so far in Sec. 3.

4.1 Generalizing Helmholtz theorem

One should recognize that the long-time “state” of \( x(t) \) following the equation of motion (19) is not a single point in \( \mathbb{R}^n \); but a bounded orbit confined in a particular level set of \( \varphi \); it is actually “a state of stationary motion” [46]. This distinguishes a microscopic state in classical mechanics from a macroscopic state in classical thermodynamics. In general, \( x(t) \) is not ergodic on the entire level set. However, realizing that \( j(x) \) is only a deterministic representation of the stochastic circulation, one expects a time-scale separation between the intra-\( \varphi \)-level-set motion and motion across level sets [47]. To represent and characterize an entire \( \varphi \) level set, Boltzmann’s idea was to quantify it using some geometric quantities. The volume it contains in \( \mathbb{R}^n \) is one example:

\[
\sigma_B(h, \alpha) = \ln \left( \int_{\varphi(x, \alpha) \leq h} dx \right). \tag{36}
\]

An elementary calculation of probability yields

\[
- \beta^{-1} \ln \int_{h<\varphi(x, \alpha) \leq h+\Delta h} e^{-\beta \varphi(x, \alpha)} dx = \varphi(x, \alpha) - \beta^{-1} \ln \int_{h<\varphi(x, \alpha) \leq h+\Delta h} dx. \tag{37}
\]

Since “free energy is equal to internal energy minus temperature times entropy”, recognizing the last term in (37) as entropy is almost mandatory. Then,

\[
Z_{\alpha}(\beta) = \int_{\mathbb{R}^n} e^{-\beta \varphi(x, \alpha)} dx = \int_{-\infty}^{\infty} e^{-\beta h + \sigma_B(h, \alpha)} \left( \frac{\partial \sigma_B}{\partial h} \right)_{\alpha} dh \tag{38}
\]

\[
= \int_{-\infty}^{\infty} e^{-\beta h} \left( \int_{\varphi(x, \alpha) = h} dS \right)_{\parallel \nabla \varphi(x, \alpha) \parallel} dh. \tag{39}
\]

The term inside the parenthesis in (39) is known as microcanonical partition function [48]. Eq. 39 relates the microcanonical partition function to the canonical partition function \( Z_{\alpha}(\beta) \).
We now apply the Helmholtz theorem [46] for the family of conservative dynamics \( j(x, \alpha) \) with parameter \( \alpha \), which has a conserved quantity \( \varphi(x, \alpha) \) [47]. Note that due to its definition, the vector field \( j(x, \alpha) \) is structurally stable within the framework of the general diffusion process [1].

\( \sigma_B \) in (36) is an increasing function of \( h \), thus implicit function theorem applies to \( \sigma_B(h, \alpha) \).

Thus we have \( h = h(\sigma_B, \alpha) \), and

\[
dh = \left( \frac{\partial h}{\partial \sigma_B} \right)_\alpha \ d\sigma_B + \left( \frac{\partial h}{\partial \alpha} \right)_{\sigma_B} \ d\alpha,
\]

in which

\[
\left( \frac{\partial \sigma_B}{\partial h} \right)_\alpha = \frac{\int_{\varphi(x,\alpha)=h} \ dS}{\int_{\varphi(x,\alpha) \leq h} \ d\mathbf{x} \ |\nabla_x \varphi(x, \alpha)|} = \left[ \frac{\int_{\varphi(x,\alpha)=h} \ x_k \left( \frac{\partial \varphi(x, \alpha)}{\partial x_k} \right)_{x,j \neq k,\alpha} \ dS}{\int_{\varphi(x,\alpha)=h} \ |\nabla_x \varphi(x, \alpha)|} \right]^{-1},
\]

which is the same for all \( k = 1, 2, \ldots, n \). This is known as the virial theorem in classical mechanics. Gauss-Ostrogradsky-Green’s divergence theorem is used to derive (42) from (41).

We shall denote

\[
\theta(h, \alpha) \equiv \left( \frac{\partial \sigma_B}{\partial h} \right)_\alpha^{-1}, \quad F_{\alpha}(h, \alpha) \equiv -\left( \frac{\partial h}{\partial \alpha} \right)_{\sigma_B}.
\]

Then,

\[
\frac{F_{\alpha}}{\theta} = -\left( \frac{\partial h}{\partial \alpha} \right)_{\sigma_B} \left( \frac{\partial \sigma_B}{\partial h} \right)_\alpha = \left( \frac{\partial \sigma_B}{\partial \alpha} \right)_h.
\]

Historically, the significance of the Helmholtz theorem is generalizing mechanical energy conservation to the First Law of Thermodynamics. It provided a mechanical theory of heat [46]. In the present theory, our Eq. 40 has extended conservative \( \varphi(x, \alpha) \) defined for each stochastic dynamical system with a particular \( \alpha \) to a much broader energy conservation law \( h(\sigma_B, \alpha) \) among a family of dynamical systems with different \( \alpha \).

**Free energy and entropy of a Gaussian distribution.** For a \( n \)-dimensional Gaussian distribution with covariance matrix \( \Xi(\alpha) \), the quadratic potential function \( \varphi(x) \) has the form \( \frac{1}{2} \sum_{k=1}^{n} \lambda_k^{-1} x_k^2 \).
under an orthonormal transformation, where $\lambda$ are the eigenvalues of $\Xi$. Then

$$\sigma_B(h) = \ln \left( V_n \prod_{k=1}^{n} \sqrt{2h\lambda_k} \right) = \frac{n}{2} \ln h + \frac{1}{2} \ln \det (\Xi) + \frac{n}{2} \ln 2 + \ln V_n, \quad (45)$$

in which $V_n = \pi^{n/2} \Gamma^{-1}(\frac{n}{2} + 1)$ is the volume of an $n$-dimensional Euclidean ball with radius 1.

Free energy of the same quadratic $\varphi(x)$, according to canonical partition function, is

$$-\beta^{-1} \ln \int_{\mathbb{R}^n} \exp \left( -\frac{\beta}{2} x^T \Xi^{-1} x \right) dx = -\beta^{-1} \left\{ \frac{n}{2} \ln \left( 2\pi \beta^{-1} \right) + \frac{1}{2} \ln \det (\Xi) \right\}. \quad (45)$$

Mean internal energy is $\bar{h} = \frac{n}{2\beta}$, and entropy is

$$\frac{n}{2} \ln \bar{h} + \frac{1}{2} \ln \det (\Xi) + \frac{n}{2} + \frac{n}{2} \ln \left( \frac{4\pi}{n} \right),$$

which agrees with the $\sigma_B(h, \alpha)$ in (45) when $n$ is large, via Stirling’s formula.

If the determinant of $\Xi(\alpha)$ is linearly dependent upon a parameter $\alpha$, then, $(\frac{\partial \sigma_B}{\partial \alpha})_h = (2\alpha)^{-1}$, and $\alpha F_\alpha = \frac{1}{2} \theta$. One could identify $\theta$ with temperature, $\alpha$ as volume, and $F_\alpha$ as pressure, then this relation is the law of ideal gas in classical thermodynamics. Eqs. 43 and 45 also give $\theta = 2h/n$. $h$ being a function of $\theta$ alone is known as Joule’s law, which states that the internal energy of an ideal gas is a function only of its temperature.

Based on these observations, it is not unreasonable to suggest the OU process as a mesoscopic dynamic model for stochastic thermodynamic behavior of an ideal system, such as ideal gases and ideal solutions [49].

$\beta$ as an ensemble average of $\langle (\partial \sigma_B / \partial h)_{\alpha} \rangle$. Note that the right-hand-side of (38) can also be re-written into a different expression:

$$Z_{\alpha}(\beta) = \int_{-\infty}^{\infty} e^{-\beta h + \sigma_B(h, \alpha)} \beta dh, \quad (46)$$

in which $\beta$ plays the role of $(\frac{\partial \sigma_B}{\partial h})_{\alpha}$ in (38). $\beta$, in fact, can be expressed implicitly as an ensemble average of $(\frac{\partial \sigma_B}{\partial h})_{\alpha}$:

$$\beta = \frac{1}{Z_{\alpha}(\beta)} \int_{-\infty}^{\infty} e^{-\beta h + \sigma_B(h, \alpha)} \left( \frac{\partial \sigma_B}{\partial h} \right)_{\alpha} dh. \quad (47)$$
4.2 Carnot cycle in a family of diffusion processes with MB equilibrium

Functional relations among triple quantities such as \((\sigma_B, h, \alpha)\), \((\sigma_B, F_\alpha, \alpha)\), and \((\theta, F_\alpha, \alpha)\) are called “equations of state” in the classical thermodynamics. They are powerful mathematical tools quantifying long-time behavior of a family of conservative dynamics \(j(x, \alpha)\).

A Carnot cycle consists of two iso-\(\theta\) curves and two iso-\(\sigma_B\) curves in \(\alpha\) versus \(F_\alpha\) plane.

Let us again consider the simple model \(\sigma_B(h, \alpha) = \mu \ln h + \nu \ln \alpha\). Then we have equations for iso-\(\theta\) curves and iso-\(\sigma_B\) curves:

\[
\alpha F_\alpha = \nu \theta, \quad \text{and} \quad \alpha^{1+\nu/\mu} F_\alpha = \frac{\nu}{\mu} e^{\alpha_B/\mu}. \tag{48}
\]

5 Externally driven cycle of a diffusion process with dissipative circulation

The foregoing discussion clearly points to two mathematical objects \(J_{ss}(x)\) and \(\varphi(x) = -\ln f_{ss}(x)\) associated with a stationary diffusion process. We shall set \(\beta = 1\) in the following discussion. The steamlines of vector field \(J_{ss}(x)\) and the level sets of \(\varphi(x)\) are perfect matched in a Maxwell-Boltzmann equilibrium with non-dissipative circulation.

If the condition (18) is not met, then a diffusion process has stationary circulation with dissipation. This implies the process also has to be externally driven. Thus, its stationary process is in a nonequilibrium steady state, as illustrated in Fig. 1(A). One can in fact idealize any closed orbit in phase space into four pieces as shown in Fig. 1(B): Movement from \(c \to d\) is a spontaneous relaxation from high \(\varphi\)-level to low \(\varphi\)-level accompanied with dissipation; it is followed by a non-dissipative step from \(d \to a\) confined in the level set \(\varphi(x) = \varphi_2\); then followed by a transition \(a \to b\) from low \(\varphi\)-level to high \(\varphi\)-level, which has to driven by an external force; and finally another non-dissipative move from \(b \to c\) confined in the level set \(\varphi(x) = \varphi_1\).

The the analysis of energetic steps discussed above, and illustrated in Fig. 1 is analogous to a pendulum system with damping and being driven:

\[
m \frac{d^2x}{dt^2} = -k \sin x - \eta \left(\frac{dx}{dt}\right) + \xi(t), \tag{49}
\]

in which \(\xi(t)\) is an oscillatory driving force. In the absence of damping \(-\eta \dot{x}\) and driving force
Figure 1: (A) Diffusion processes that have non-orthogonal $J^{ss}(x)$ and $\nabla \varphi(x)$ have the streamlines of $J^{ss}$ passing through different level sets of $\varphi$. Being a conservative dynamics, the streamlines of vector field $J^{ss}$ have almost closed orbits according to Poincaré recurrence theorem. Any closed orbit can be approximated by portions that are confined in $\varphi$-level sets, and portions that perpendicular to $\varphi$-level sets. (B) An idealized red closed loop $abcd$ consists four steps. Assuming $\varphi_1 > \varphi_2$, then step $ab$ decreases in probability, thus it in general has to be externally driven; steps $bc$ and $da$ are confined in $\varphi$-level sets, thus they are conservative; step $cd$ increases in probability, thus it is spontaneous with dissipation.

$\xi(t)$, the mechanical energy level sets are

$$H(x, \dot{x}) = \frac{m}{2} \dot{x}^2 + k \left( 1 - \cos x \right).$$

Then,

$$\frac{d}{dt} H(x, \dot{x}) = -\eta \dot{x}^2 + \dot{x} \xi(t). \quad (50)$$

When the right-hand-side of (50) is positive, the system gains energy; and when it is negative, the system dissipates energy. Over a complete cycle, these two terms have to balance with each other.

One could argue that the orthogonal relation between $j(x)$ and $\nabla \varphi(x)$, for all $x$, in a system with MB equilibrium is a “local equilibrium condition”. Such a condition provides a mathematical basis for organizing the entire $\mathbb{R}^n$ state space, and the conservative motions, in terms of a single scalar $\varphi(x)$. It has been suggested as a possible mathematical statement of the Zeroth Law of thermodynamics [8]. In contrast, the system in Fig. [1] has its level sets and streamlines “out of equilibrium”.

18
6 Discussion

One interesting implication of the present work, perhaps, is that a linear stochastic dynamics is always consistent with a Maxwell-Boltzmann equilibrium, together with a Hamiltonian system-like conservative dynamics \[40, 8\]. This result completely unifies the stochastic thermodynamic theory and the linear phenomenological approaches to equilibrium fluctuations pioneered by Einstein and Onsager, and extended by many others, e.g., R. Kubo, Landau-Lifshitz, H. B. Callen, M. Lax, and J. Keizer, to name a few.

It is important to realize, therefore, that near a stable dynamic fixed point, one can not determine the nature of equilibrium vs. nonequilibrium fluctuations in a subsystem from the internal data alone. Additional information concerning the external environment is required to uniquely select one of the two possible thermodynamics. In fact, the origin of the entropy production in an overdamped nonequilibrium steady state is outside the subsystem, as the notions of source and sink clearly imply. Therefore, a nonequilibrium steady state of a subsystem can only be “fully understood” by including its environment; and for a universe without an outside, a underdamped thermodynamics with the heat death is the only logic consequence.

We have recently suggested that the mathematical description of stochastic dynamics is an appropriate analytical framework for P. W. Anderson’s hierarchical structure of science \[20\]. The origin of randomness has been widely discussed by many scholars; for example Poincaré has stated in 1908 that \[50\] “A very small cause, which escapes us, determines a considerable effect which we cannot ignore, and we then say that this effect is due to chance.” In the light of \[1, 2, 3\], this might be updated: “A very complex collection of causes, which are not understood by us, determines an un-avoidable consequence which we cannot ignore, and we then say that this effect is due to chance, or our ignorance”.

The stochastic diffusion theory presented in the present work could provide a richer narrative for complex phenomenon which has a stochastic dynamic description, but currently lacks a concrete connection to vocabularies with mechanical and statistical thermodynamic implications, for example behavioral economics. Paraphrasing Montroll and Green \[51\]: The aim of a stochastic thermodynamic theory is to develop a formalism from which one can deduce the collective behavior of complex systems composed of a large number of individuals from a specification of the
component species, the laws of force which govern interactions, and the nature of their surroundings. Since the work of Kirkwood [9], it has become clear that “the laws of force” can themselves emergent properties with statistical (entropic) nature. Indeed, Eq. [40] could be recognized as one of such.

Probability is a force of nature. In the western legal system, this term refers to an event outside of human control for which no one can be held responsible. Still, something no individual, or a small group of individuals, can be held responsible is nevertheless responsible by each and every individual, together. More is different.

References

[1] Anderson P W 1972 More is different: Broken symmetry and the nature of the hierarchical structure of science Science 177 393–396

[2] Hopfield J J 1994 Physics, computation, and why biology looks so different J. Theret. Biol. 171 53–60

[3] Laughlin R B, Pines D, Schmalian J, Stojković B P and Wolynes P G 2000 The middle way Proc. Natl. Acad. Sci. USA 97 32–37

[4] Cox R T 1950 The statistical method of Gibbs in irreversible change Rev. Mod. Phys. 22 238–248

[5] Bergmann P G and Lebowitz J L 1955 New approach to nonequilibrium processes Phys. Rev. 99 578–587

[6] Qian H, Qian M and Tang X 2002 Thermodynamics of the general diffusion process: Time-reversibility and entropy production J. Stat. Phys. 107 1129–1141

[7] Qian H 2013 A decomposition of irreversible diffusion processes without detailed balance J. Math. Phys. 54 053302

[8] Qian H 2014 The zeroth law of thermodynamics and volume-preserving conservative system in equilibrium with stochastic damping Phys. Lett. A 378 609–616
[9] Kirkwood J G 1935 Statistical mechanics of fluid mixtures J. Chem. Phys. 3 300–313

[10] Qian H and Kou S C (2014) Statistics and related topics in single-molecule biophysics Annu. Rev. Stat. Appl. 1 465–492

[11] Nicolis G and Prigogine I 1977 Self-Organization in Nonequilibrium Systems: From Dissipative Structures to Order Through Fluctuations (New York: Wiley)

[12] Hill T L 1977 Free Energy Transduction in Biology: The Steady-State Kinetic and Thermodynamic Formalism (New York: Academic Press)

[13] Zhang X-J, Qian H and Qian M 2012 Stochastic theory of nonequilibrium steady states and its applications (Part I) Phys. Rep. 510 1–86

[14] Ge H, Qian M and Qian H 2012 Stochastic theory of nonequilibrium steady states and its applications (Part II): Applications in chemical biophysics Phys. Rep. 510 87–118

[15] Jiang D-Q, Qian M and Qian M-P 2004 Mathematical Theory of Nonequilibrium Steady States, Lect. Notes Math., vol. 1833 (New York: Springer)

[16] Van den Broeck C and Esposito M 2014 Ensemble and trajectory thermodynamics: A brief introduction Physica A to appear

[17] Ge H 2014 Stochastic theory of nonequilibrium statistical physics Adv. Math. (China) 43 161–174

[18] Seifert U 2012 Stochastic thermodynamics, fluctuation theorems and molecular machines Rep. Prog. Phys. 75 126001

[19] Jarzynski C 2011 Equalities and inequalities: Irreversibility and the second law of thermodynamics at the nanoscale Annu. Rev. Cond. Matt. Phys. 2 329–351

[20] Ao P, Qian H, Tu Y and Wang J 2013 A theory of mesoscopic phenomena: Time scales, emergent unpredictability, symmetry breaking and dynamics across different levels arXiv:1310.5585
[21] Ge H and Qian H 2009 Thermodynamic limit of a nonequilibrium steady-state: Maxwell-type construction for a bistable biochemical system *Phys. Rev. Lett.* 103 148103

[22] Qian H 2013 Stochastic physics, complex systems and biology *Quant. Biol.* 1 50–53

[23] Greene B 2011 *The Hidden Reality: Parallel Universes and the Deep Laws of the Cosmos* (U.K.: Vintage Books)

[24] Lewis G N 1925 A new principle of equilibrium *Proc. Natl. Acad. Sci. USA* 11 179–183

[25] Coveney P V 1988 The second law of thermodynamics: entropy, irreversibility and dynamics *Nature* 333 409–415

[26] Tolman R C and Fine P C 1948 On the irreversible production of entropy *Rev. Mod. Phys.* 20 51–77

[27] Esposito M, Harbola U and Mukamel S 2007 Entropy fluctuation theorems in driven open systems: Application to electron counting statistics *Phys. Rev. E* 76 031132

[28] Ge H 2009 Extended forms of the second law for general time-dependent stochastic processes *Phys. Rev. E* 80 021137

[29] Ge H and Qian H 2010 Physical origins of entropy production, free energy dissipation, and their mathematical representations *Phys. Rev. E* 81 051133

[30] Esposito M and Van den Broeck C 2010 Three detailed fluctuation theorems *Phys. Rev. Lett.* 104 090601

[31] Ge H and Qian H 2013 Heat dissipation and nonequilibrium thermodynamics of quasi-steady states and open driven steady state *Phys. Rev. E* 87 062125

[32] Wang J, Xu L and Wang E 2008 Potential landscape and flux framework of nonequilibrium networks: Robustness, dissipation, and coherence of biochemical oscillations *Proc. Natl. Acad. Sci. USA* 105 12271–12276
[33] Feng H and Wang J 2011 Potential and flux decomposition for dynamical systems and nonequilibrium thermodynamics: Curvature, gauge field, and generalized fluctuation-dissipation theorem J. Chem. Phys. 135 234511

[34] Wax N (ed.) 1954 Selected Papers on Noise and Stochastic Processes (New York: Dover)

[35] Fox R R 1978 Gaussian stochastic processes in physics Phys. Rep. 48 180–283

[36] Cox R T 1952 Brownian motion in the theory of irreversible processes. Rev. Mod. Phys. 24 312–320

[37] Onsager L and Machlup S 1953 Fluctuations and irreversible processes Phys. Rev. 91 1505–1512

[38] Lax M 1960 Fluctuations from the nonequilibrium steady state Rev. Mod. Phys. 32 25–64

[39] Qian H 2001 Mathematical formalism for isothermal linear irreversibility Proc. R. Soc. A. 457 1645–1655

[40] Kwon C, Ao, P and Thouless D J 2005 Structure of stochastic dynamics near fixed points Proc. Natl. Acad. Sci. USA 102 13029–13033

[41] Ao P 2004 Potential in stochastic differential equations: Novel construction J. Phys. A. Math. Gen. 37 L25–L30

[42] Yin L and Ao P 2006 Existence and construction of dynamical potential in nonequilibrium processes without detailed balance J. Phys. A. Math. Gen. 39 8593–8601

[43] Ao P, Kwon C and Qian H 2007 On the existence of potential landscape in the evolution of complex systems Complexity 12 19–27

[44] Zhang J-Y 1984 The total periodicity of 3-dimensional gradient conjugate system Scient. Sinica A 27 42–54

[45] Young L-S 2002 What are SRB measures, and which dynamical systems have them? J. Stat. Phys. 108 733–754.
[46] Gallavotti G 1999 *Statistical Mechanics: A Short Treatise* (Berlin: Springer)

[47] Ma Y and Qian H 2014 The Helmholtz theorem for the Lotka-Volterra equation, the extended conservation relation, and stochastic predator-prey dynamics [arXiv:1405.4311](https://arxiv.org/abs/1405.4311)

[48] Khinchin A I 1949 *Mathematical Foundations of Statistical Mechanics* (New York: Dover)

[49] Ma Y and Qian H 2014 Linear irreversibility, Ornstein-Uhlenbeck process, and the universal stochastic thermodynamic behavior *manuscript in preparation*

[50] Poincaré H 2007 *Science and Method*, Maitland, F. transl., Cosimo Classics, New York.

[51] Montroll E W and Green M S 1954 Statistical mechanics of transport and nonequilibrium processes *Annu. Rev. Phys. Chem.* 5 449–476