Thermodynamic Principles of Stochastic Dynamics: Time Symmetries and Data Infinitum

Ying-Jen Yang

A dissertation
submitted in partial fulfillment of the
requirements for the degree of

Doctor of Philosophy

University of Washington
2022

Reading Committee:
Hong Qian, Chair
Matthew Lorig
Thomas Trogdon

Program Authorized to Offer Degree:
Applied Mathematics

University of Washington

Abstract

Thermodynamic Principles of Stochastic Dynamics: Time Symmetries and Data Infinitum

Ying-Jen Yang

Chair of the Supervisory Committee:

Hong Qian

Department of Applied Mathematics

Dynamical systems theory has played a central role in applied mathematics for nearly a century. Besides providing a geometric understanding for difference and differential equations, it is also the main framework for modeling complex systems including those in biology. Complex systems consist of heterogeneous building blocks that are themselves complex objects. Stochastic dynamical models are thus used to represent, statistically, biochemical species in a cell, cells in a tissue, and organisms in an ecosystem. This common stochastic formalism is the foundation for unifying mathematical models in biology at vastly different levels, from cellular biology to terrestrial ecology. We introduce thermodynamic theories from the common stochastic formalism with the following key results: time symmetries dictate dynamic principles and limit theorems in the data infinitum reveal the driving forces conjugated to observables. Our thermodynamic theory is to Markov dissipative dynamics what mechanics is to Hamiltonian dynamical systems. It arises solely from time symmetries and limit theorems in data infinitum and can thus be applied to a wide spectrum of stochastic models in biology and for general complex systems as well. Models in mathematical biology can be integrated in a single universal thermodynamic theory of life.

I dedicate this thesis to

my father Tso-Chi Yang 楊佐琦 (George),

my mother Hui-Ying Ma 馬慧英 (Jasmine),

my sister Ying-Ju Yang 楊穎如 (Catherine), and

my partner Chia-Chen Ho 何佳臻 (Joyce).

Their endless love and continuous support are what make following my passion possible.

— Ying-Jen Yang 楊穎任 (Peter)

Acknowledgments

I would like to give my deepest gratitude to my mentor, Hong Qian. None of the work shown in this thesis is possible without his continuous support and guidance. His insightful perspectives about math, science, and philosophy really open my mind and help me see the world and the mathematics it fits in a different way. It is truly my privilege to be his student and get to work with him for the past five years and the many years to come.

I am very thankful for the continuous support from my committee members: Matt Lorig, Armita Nourmohammad, and Tom Trogdon. The many feedback and suggestions they gave me were really helpful in formulating this thesis and also in thinking about the potential future directions. Without them, my PhD pursuit would not be so smooth and enjoyable.

I also thank my collaborators, Yu-Chen Cheng and Jeffrey Commons, as well as my colleagues and friends in Hong's group: Erin Angelini, Lowell Thompson, Yue Wang, Cameron Wright, and Felix Xiaofeng Ye. Working and discussing math and science with them are refreshing and incredibly enjoyable. It is wonderful to brainstorm with them, to unfold puzzles in mathematics with them, and to share thrills and excitements of the beauty of math and science.

I am very grateful to have a lovely group of cohorts and friends during my PhD study: Tyler Chen, Jorge Cisneros Paz, Matthew Farkas, Nora Gilbertson, Micah Henson, Roman Levin, Kelly Liu, Yuying Liu, Katherine Owens, Diya Sashidhar, Doris Voina, and Ted Zhao. We went through our journey of PhD together and accomplished so many things. Their delightful (in-person and virtual) company in the past five years makes Seattle feel like home to me.

Finally, I thank Ping Ao, Ken Dill, Ian Ford, Hao Ge, Chris Jarzynski, Geng Li, Hans Öttinger, Matteo Polettini, Édgar Roldán, Dalton Sakthivadivel, Udo Seifert, David Sivak, Zhanchun Tu, and Jin Wang. The many discussions I had with them and their feedback for my work were truly stimulating and helpful.

Preface

Mathematical models are used in science to describe patterns we observed from the world around us and to deduct theoretical predictions[1]. In order to summarize patterns mathematically from the observed data, one can start with a library of candidate models based on assumptions and prior understanding of the systems of interest. Scores can then be assigned to each candidate model to identify a model that best fits the data. This is the basic procedure of *data-driven modeling* and is often an important first step to analyze and summarize the observed data. A classic example is Kepler's seminal work on planetary motion. Nowadays, modern computers and new theoretical developments lead to novel data-driven modeling methods such as those in machine learning (Brunton and Kutz, 2019). These models inferred from data can be improved when more data is acquired or when the library of candidate models is updated based on new understanding of the system of interest. While data-driven models summarize patterns quantitatively in a rather systematic way, we argue that having them for given systems of interest is not yet a "complete" scientific theory. They are often *kinematic* models with few mechanistic interpretations or "mechanisms" identified. From this aspect, data-driven modeling is the crucial first step, but not the full story.

The identification of underlying mechanisms is arguably what "understanding" a system means. Mechanistic models allow scientists to unite models from seemly unrelated systems with universal interpretations, and further guide engineers to apply the theory to more complicated systems as well as produce novel designs in technological applications. A *mechanistic modeling* does not have to start from the mathematical patterns identified from data-driven methods. One can start a mechanistic modeling with assumptions and proposed mechanisms based on one's understanding of the system. Mechanistic modeling often leads to idealized toy models that allow one to gain new understandings, which can be made more realistic later

[1] These two usages of mathematical models are fundamentally different. The former summarizes the data, while the latter applies the summarized mathematical rules to unobserved data in the future. The legitimacy of the latter is an assumption that future data is generated in the same way as the data observed, a symmetry of common underlying principles.

by incorporating more details into the model. Yet, mechanistic modeling is often inspired by data-driven models, *e.g.* Newton's *Principia* was influenced by Kepler's work (Tung, 2007). Data-driven models can inspire mechanistic modeling, and mechanistic models can motive specific libraries of candidate models to be considered in data-driving modeling. The two approaches are really complementary to each other rather than exclusive.

In this thesis, we are interested in general *complex systems* whose building blocks are themselves highly complicated. They are systems we encounter in our daily life: biological systems, traffic data, finance data, *etc.* Following reductionlism (Anderson, 1972; Chibbaro *et al.*, 2014), theoretical studies for such complex systems would begin with their microscopic building blocks and then trying to study macroscopic properties of the systems they constitute: cutting a system into small pieces and then integrate them back, which is the spirit of calculus. However, even if we have a complete understanding of their building blocks, it can be hard to study the emergent phenomena in the macroscopic system due to the nonlinear mutual interactions and heterogeneity of these building blocks. This was, perhaps, the main reason why traditional studies in biology focused on organizing facts and proposing qualitative theories, which are very different from mathematically precise theories such as those in physics. (Hopfield, 1994). With modern theoretical development and numerical computation methods, fields of mathematical biology and biophysics emerge, and more quantitative models for diverse phenomena in different scales are now available (Kaneko, 2006; Murray, 2003, 2007; Kot, 2001). Taking a bird-view of these diverse models instead of a frog-view for specific phenomena (Dyson, 2010), my thesis aims to provide a unifying mechanistic modeling formalism for complex systems and providing universal kinetic mechanisms. Given that classical or quantum mechanical origins of these kinematic models are very removed, our kinetic principles must be *de-mechanised, i.e.* not relying on classical or quantum mechanics. It turns out that symmetry and limit theorems are the keys to achieve such principles for complex systems, as we shall show in this thesis.

Reductionlism guides scientists to study more and more elemental units, from atoms to particles. With the advance of modern theories and technologies, we can now observe microscopic objects in the subatomic levels. In a sense, it is not clear whether the elementary particles in the current theories in physics are the most fundamental building blocks of the universe or not. Is it possible that the Standard Model in physics is just another individual-level theory that we can use to study its corresponding population-level systems, as any middle layers in P. W. Anderson's hierarchy of science? In other words, is it possible that the various particles in the Standard Model are themselves macroscopic, consisting of even smaller and "more

fundamental" unknown elements? This type of thought was put forwarded by Nobelist R. B. Laughlin (2006), and I personally learned this idea from my mentor, Prof. Hong Qian. Recent theoretical results in probability theory actually show that classical-mechanics-like structure (Freidlin and Wentzell, 2012; Ge and Qian, 2012a; Qian, 2021) or even quantum-mechanics-like structure (Commons *et al.*, 2021) can be found in the deterministic limit and the data infinitus limit of general stochastic models. This suggests that the theoretical results in the current thesis might shed light on how and why kinetic principles, such as those in physics, can be developed to explain the world around us.

Contents

I Prologue **1**

1 Introduction **2**

1.1 Stochastic Models of Complex Systems 2

1.2 Statistical Thermodynamics and Data Infinitum 5

1.3 Stationarity and Fluctuation-Dissipation Relation 7

1.4 Irreversibility and Energetics 9

1.5 Summary 15

2 Mathematical Elements of Stochastic Processes **17**

2.1 Probabilistic Model and Stochastic Processes 17

2.2 Time Evolution of Markov Processes 20

2.3 Change of Probability Measure 24

2.4 Summary 28

II Time symmetries dictate dynamic principles **30**

3 Irreversibility of Stochastic Dynamics **31**

3.1 Detailed Balance and Landscape 31

3.2 Irreversibility in Stochastic Dynamics 35

3.3 Adjoint Process and Underlying Equilibrium 40

3.4 Summary and Discussion 43

4 Fluctuation Relations of Irreversibility **46**

4.1 Different Types of Reversal . . . 46
4.2 Irreversibility as Path Relative Entropy . . . 51
4.3 Relative Entropy and Fluctuation Relations . . . 54
4.4 Properties of Irreversibility . . . 59
4.5 Summary and Discussion . . . 62

5 Fundamental Roles of Cycle in Nonequilibrium Dynamics 64

5.1 Cycle Completion and the Landauer-Bennett-Hill Principle . . . 64
5.2 Cycle Flux and Onsager Reciprocality . . . 67
5.3 Bivectorial Cycle Affinity and Cycle Flux in Diffusion . . . 69
5.4 Summary and Discussion . . . 75

6 Thermodynamic Potentials of Continuous Markov Dynamics 77

6.1 Cycle Potential and Dynamic Decomposition . . . 77
6.2 Speed limit of Thermodynamic Rates . . . 80
6.3 Mesoscopic Potential and Macroscopic Potential . . . 85
6.4 Summary and Discussion . . . 90

7 Stationarity and Fluctuation-Dissipation Relations 92

7.1 Doob Decomposition . . . 92
7.2 Generalized Fluctuation-Dissipation Relations . . . 95
7.3 Adjoint Processes and Adjoint Drift . . . 97
7.4 Reversed Decomposition . . . 99
7.5 Summary and Discussion . . . 100

III Data infinitum dictates statistical thermodynamics 102

8 Statistical Thermodynamics and Maximum Entropy Principle 103

8.1 Data Infinitum didtates Statistical Thermodynamics . . . 103
8.2 Maximum Entropy Principle of I.I.D. Sampling . . . 109
8.3 Maximum Entropy Principle in Markov Processes . . . 111

8.4 Summary and Discussion . . . 118

9 Maximum Caliber Principle and the origin of Statistical Thermodynamics 120

9.1 Canonical Posterior and Maximum Caliber Principle . . . 120

9.2 Comparison between Max Entropy and Max Caliber . . . 125

9.3 Measurement-predicted Symmetry Breaking . . . 127

9.4 Thermodynamic Forces and their Statistical Variation . . . 129

9.5 Summary and Discussion . . . 134

IV Epilogue 137

10 Discussion and Future Directions 138

10.1 Applications and Extensions . . . 138

10.2 Cycles in Nonequilibrium Systems . . . 140

10.3 Geometrical Aspects of Thermodynamics . . . 142

10.4 Data Accumulation in Statistical Thermodynamics . . . 144

Appendices 147

Appendix A Bivector Calculus 148

A.1 Differential form and Integration . . . 148

A.2 Bivector and 2-form . . . 150

A.3 Exterior Derivative and the curl of a vector field . . . 151

A.4 Bivector potential of a divergence-free vector field . . . 153

A.5 Geometrical Meaning of Simple Bivectors . . . 155

Appendix B Method of Tilting to obtain Large Deviation Rate Functions 157

B.1 Sanov's Theorem . . . 157

B.2 Method of Tilting . . . 158

B.3 Level-2.5 LDT of Markov Processes . . . 159

Bibliography 165

Part I

Prologue

Chapter 1

Introduction

1.1 Stochastic Models of Complex Systems

Fundamental Importance of Statistical Physics Many systems in our daily life are consist of a large number of microscopic building units, *e.g.* molecules of a gas, cells in a cellular network, and organisms in an ecosystems. Scientific theories in different fields can be arranged in a microscopic-macroscopic order based on the scales at which they apply: theory in a field A is *macroscopic* to field B, which can itself be *macroscopic* w.r.t. another field C[1] (Anderson, 1972; Chibbaro *et al.*, 2014). An important, perhaps the most fundamental (Laughlin, 2006; Qian, 2021), task is thus to have a theory connecting a microscopic theory to a macroscopic one, relatively speaking. As macroscopic systems have a large number of microscopic units, keeping track of the microscopic details for a macroscopic system is not practical, especially for high-dimensional nonlinear systems where chaotic dynamics may occur (Oono, 2013; Strogatz, 2018). A probabilistic theory is employed as a statistical understanding of phenomena that emerge in the macroscopic systems. Such probabilistic approach is pioneered by Boltzmann and Gibbs in the physics of many-body systems and is known as *statistical physics* (Landau and Lifshitz, 1980). As the microscopic dynamics in textbook statistical physics is described by classical or quantum mechanics , the standard statistical physics is also endowed with the name *statistical mechanics* (Huang, 1991).

How to apply statistical physics to complex systems remote to mechanics? While statistical mechnaics has provided successful theoretical understanding of many-body mechanical systems, it is not clear how

[1] Fields of A, B, and C are listed in Anderson's paper. For example, an organism is macroscopic to single cells, whereas single cell is macroscopic to the chemical reactions in a cell.

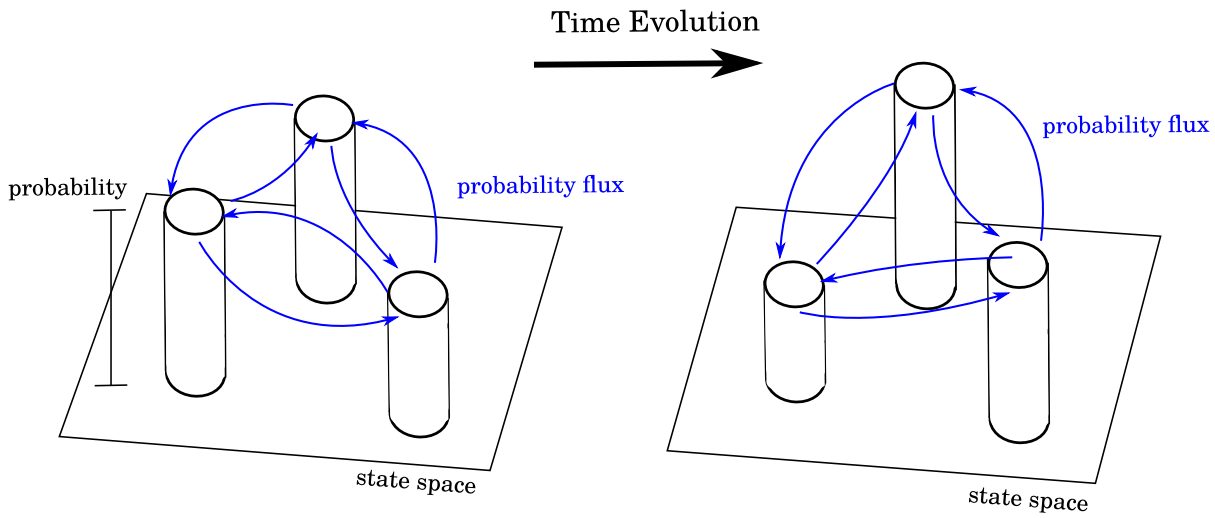


Figure 1.1: In a stochastic formalism, time evolution is described statistically by the re-distribution of probability of state. Dynamics are represented statistically by probability flux in the state space.

such theory can be applied or extended to systems on the higher levels in Anderson's hierarchy. These *mesoscopic systems* are with microscopic units that are themselves complicated and often described by mathematical models rather remote to mechanics (Kaneko, 2006; Murray, 2007). This poses a clear challenge for formulating a *statistical physics* and *thermodynamics* for these *complex systems*. Specifically, it is unclear how thermodynamic concepts such as *energy* and *entropy* could be defined in a complex system without classical or quantum mechanics.

Common probabilistic formalism is the key. The building blocks of complex systems, let alone their intrinsic complexity, are often embedded in a even more complicated environment. Two hemoglobin molecules have their individualism (de Gennes, 1997). Stochastic mathematical models are therefore used to represent these microscopic building blocks such as biochemical species in a cell, cells in a cellular network or organisms in an ecosystem (Prigogine, 1997; Bialek, 2012; Qian *et al.*, 2016a). Phenomena that emerge through the nonlinear interaction between these complex building blocks are thus investigated in a probabilistic manner (Nicolis and Prigogine, 1977; Haken, 1978). Novel phenomena in these stochastic systems are found (Bak, 1996; Zhang *et al.*, 2012). In the stochastic representation of reality in complex systems, all types of events and their dynamics, including physical transport and biochemical reactions, are uniformly described by the probability flux in the phase space (Qian, 2018). See Fig. 1.1 for an illustration. The common proba-

	Kinematics	Kinetics
classical mechanics	ODE	forces and energy
electromagnetism	PDE	E&M fields & potentials
quantum mechanics	linear algebra & Hilbert space	energy
	⋮	
complex systems	stochastic dynamics & their deterministic limits	**thermodynamic principles**

Table 1.1: Kinematics versus Kinetics in physics and in our theory of complex systems. Kinematics of complex systems are described by stochastic dynamics and their deterministic limits. We seek kinetic principles of the stochastic kinematics. The principles we found have thermodynamic interpretations.

bilistic formulation for complex systems can provide a unified understanding of various models in biology at widely different levels, from cells to terrestrial ecology, shedding lights on what life is (Schrödinger/Penrose, 2012). Yet, the common stochastic framework of probabilistic flux is a kinematic description. To have a *statistical physics of complex systems* with unifying understanding for complex systems, we need kinetics as many theories in physics. See, *e.g.*, Table 1.1.

Scope of the this thesis: universal principles In this thesis, instead of investigating methods to formulate stochastic models for complex systems (Lasota and Mackey, 1994; Zwanzig, 2001), we focus on formulating unifying kinetic principles for generic given stochastic models. The principle we formulate has the same formalism as standard thermodynamics and thus have thermodynamic interpretations. In particular, we will

1. identify the thermodynamic notion of *entropic forces* for generic probabilistic models as the driving forces for different statistical properties of a system (Part III) and
2. formulate universal dynamic principles for generic stochastic dynamics from investigating the emergence and the breakdown of symmetries related to time, *e.g.* time-translational symmetry and time-reversal symmetries (Part II).

Our formulation of these thermodynamic principles rely solely on the limit theorems and the symmetries of the stochastic model (Anderson, 1972). The theory is independent from the microscopic details and can thus be applied to any level of Anderson's hierarchy. Probability theory can truly be a new logic of science (Schrödinger, 1944; Prigogine, 1997; Jaynes, 2003; Laughlin, 2006). Limit theorems and time symmetries dictate the governing principles (Yang, 1996).

1.2 Statistical Thermodynamics and Data Infinitum

In the modern probability theory pioneered by Kolmogorov, a probabilistic model consists of a space of atomic events Ω, a space of all possible events $\mathcal{F}$, and a probability measure that describes the probability of events (see Chap. 2.1 for a review). The former two specify a class of systems of interest, and different probability measures lead to different statistical properties for the systems in the class (Qian *et al.*, 2019; Yang and Qian, 2020). In our statistical thermodynamics formulated in Part III, we consider systems with the same $(\Omega, \mathcal{F})$ but different statistical properties as systems in different "*thermodynamic states*".

When we have a system in hand, a fundamental task is thus to identify which thermodynamic state it is in, *i.e.* seeking its underlying probability measure. Such information is revealed by measuring a set of observables of interest $G(\omega) : \Omega \mapsto \mathbb{R}^m$. With a reference probability measure chosen as the *ground state* with a prior probabilistic model $\mathbb{P}$, the measurement of the observables will indicate whether the system is in the ground state or an *excited state* described by a posterior probability $\mathbb{Q}$. The *information* of the measuring G is represented as a change of probability measure (CPM) (Qian *et al.*, 2019; Yang and Qian, 2020) as we will introduce in Sec. 2.3. For independent identically distributed (i.i.d.) and Markov-correlated data, the CPM was carried out by the Gibbs conditioning principle in mathematics (van Campenhout and Cover, 1981; Csiszár *et al.*, 1987; Dembo and Zeitouni, 2009; Chetrite and Touchette, 2013, 2015a) and the Maximum Entropy Principle (MEP) in standard statistical physics (Jaynes, 1957; Touchette, 2009; Chetrite and Touchette, 2015b).

The information from the measuring the observables is only considered to be conclusive in the idealized infinitely large data, *data infinitum*. In fact, the MEP described above is formulated in the data infinitus limit, by using the large deviation theory (LDT) that describes the singular convergence of probabilities in the limit (Touchette, 2009; Dembo and Zeitouni, 2009; Qian and Cheng, 2020). We review this in Secs. 8.2 and 8.3. Importantly, this data infinitus limit, $T \to \infty$, can be considered as a generalization to the classical thermodynamic limit (Lu and Qian, 2022; Commons *et al.*, 2021; Yang and Qian, 2022). A statistical thermodynamics then emerges purely from the limit theorem (Gärtner, 1977; Ellis, 1984) in the LDT of data infinitum. Thermodynamic notions of *entropy*, *free energy*, and *entropic forces* conjugated to the thermodynamic observables are defined by the LDT (Lu and Qian, 2022; Commons *et al.*, 2021; Yang and Qian, 2022). As envisioned by Szilard (1929); Mandelbrot (1964); Hill (2013), a thermodynamic theory can be formulated phenomenologically. Furthermore, our statistical thermodynamic emerge purely from

the data infinitum and does not require mechanics or mechanics-like concept to start. Our theory is thus *de-mechanized* and can be generally applied to any layer in Anderson's hierarchy of scientific theories .

The MEP is motivated from the (asymptotic) equivalence between the Baysesian conditional probability and the conditional average empirical frequency (van Campenhout and Cover, 1981; Csiszár *et al.*, 1987; Dembo and Zeitouni, 2009). It is not the only CPM method that leads to a posterior probabilistic model "consistent" with the measurement of the observable g. Chetrite and Touchette (2013, 2015a) showed that the posterior of the MEP is asymptotically equivalent to the Boltzmann-Gibbs exponentially-tilted posterior. In Sec. 8.1, we demonstrate that our statistical thermodynamics is universal for all posterior probabilistic models consistent with the measurement. Moreover, we conceptually connects the Boltzmann-Gibbs exponentially-tilted posterior discussed by Chetrite and Touchette (2013, 2015a) to the Maximum Caliber Principle (MCP) (Jaynes, 1980; Pressé *et al.*, 2013b). Instead of the axiomatic approach (Shore and Johnson, 1980; Uffink, 1995; Pressé *et al.*, 2013a; Tsallis, 2015; Pressé *et al.*, 2015; Jizba and Korbel, 2019), we provide a novel derivation to the MCP with the "i.i.d. multiverse" concept in Sec. 9.1.1, akin to the many-world interpretation in quantum physics. We further demonstrate that the MCP can be considered as the mesoscopic origin the aforementioned statistical thermodynamics in data infinitum in Sec. 9.1.2.

The asymptotic equivalence between the MEP and the MCP is then revisited, and their conceptual differences are clarified in Sec. 9.2. In our statistical thermodynamics, the ground state is with zero entropic forces and has a probabilistic model equipped with a symmetry of interest. Nonzero entropic forces explain symmetry breaking and parameterized the posterior probability models in the excited states. We discussed two examples of such measurement-predicted symmetry breaking in Sec. 9.3, comparing the emergence of time correlation and breakdown of time reversibility. The former provides a novel decomposition to the entropy in Markov processes; the latter generalizes Onsager's entropy production principle to systems arbitrarily far from equilibrium.

The "canonical" Botlzmann-Gibbs posterior model of the MCP is equipped with more thermodynamic structures. As the posterior of the MEP is asymptotically equivalent to the posterior of the MCP, the additional asymptotic thermodynamic properties from the MCP are shared with the posterior of the MEP. In Sec. 9.4, we use the LDT to derive the Asymptotic Thermodynamic Uncertainty Principle (ATUP) between the statistical fluctuation of the observables g and their conjugated forces $\beta\left(g\right)$ in finite data (Landau and Lifshitz, 1980; Mandelbrot, 1989; Ruppeiner, 1995). The ATUP stems from the reciprocal curvature relation between the entropy and the free energy, providing the reciprocal curvature relation a novel thermodynamic

interpretation. We further identify the mesoscopic origin of them (Schlögl, 1988; Uffink and van Lith, 1999). As a consequence of limit theorems in probability theory, the phenomenological thermodynamics is universal without the need of mechanics.

1.3 Stationarity and Fluctuation-Dissipation Relation

Given a probabilistic model of complex stochastic dynamics, dynamic principles are formulated in Part II. Each step, small or large, of a complex motion can be represented by a "stochastic noise part" and a "deterministic drift part" (Doob, 1990), *cf.* a chance and a necessity (Monod, 1972). Their interplay gives rise to the *fluctuation-dissipation relation* (FDR) in the steady state, a central result in statistical physics (Landau and Lifshitz, 1980; Huang, 1991). From a dynamical systems point of view, a dissipative drift represents a contraction in the state space (many-to-1 in discrete state space) while a stochastic motion implies divergent moves (1-to-many with probabilities). When these two "opposing" tendencies strike a balance and yield a time-translational symmetry in the probability distribution of system's state X_t, the system reaches its steady state and FDR appears.

There are at least two quantitative manifestations of the above physical picture: On the one hand, the classic FDR in linear response theory, following Onsager's regression hypothesis, is a set of relations between a system's relaxation-after-perturbation near an equilibrium and auto-correlation of spontaneous equilibrium fluctuations (Callen and Welton, 1951; Green, 1954; Kubo, 1966; Evans *et al.*, 2005). Extensions of this result to nonequilibrium systems can be found in recent works (Prost *et al.*, 2009; Seifert and Speck, 2010; Altaner *et al.*, 2016). On the other hand, the Einstein relation and the Green-Kubo formula (GKF) are between components with different statistical characteristics, dissipative drift vs. fluctuating "noise", within a stationary process without an external perturbation (Zwanzig, 1965; Elson, 1985). To illustrate, using Langevin's equation for the velocity of a Brownian particle that follows $m(\mathrm{d}V/\mathrm{d}t) = -\eta V + \sqrt{2k_BT\eta}\xi(t)$, $\xi(t)$ being a standard white noise, stationary $\mathbb{E}[\Delta V(t)\Delta V(t+\tau)] = (k_BT/m)e^{-\eta\tau/m}$ where $\Delta V(t) \coloneqq V(t) - \mathbb{E}[V(t)]$. Then,

$$\underbrace{D = \frac{k_BT}{\eta}}_{\text{Einstein relation}} \underbrace{= \int_0^\infty \mathbb{E}[\Delta V(t)\Delta V(t+\tau)]\mathrm{d}\tau}_{\text{Green-Kubo formula}}, \tag{1.1}$$

in which $V(t)$ is a stationary process, and D is the long-time limit of the mean square displacement of $X(t)$, the integration of $V(t)$: $\mathbb{E}\left[(X(t) - X(0))^2\right] \sim 2Dt$. Here, we shall refer relations between noise

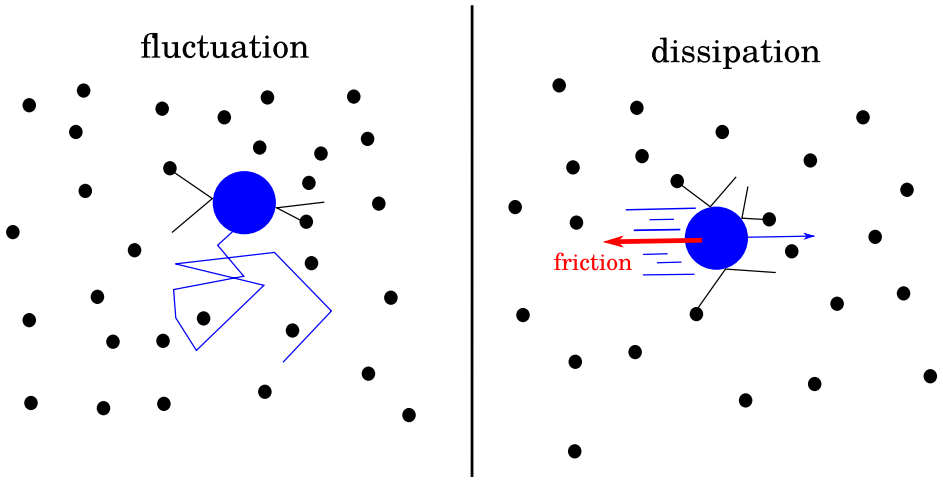


Figure 1.2: The fluctuation of a Brownian particle (characterizing by diffusion) is related to the dissipative friction it experiences (characterized by the friction coefficient). This is the classic fluctuation-dissipation relation in physics.

and drift as generalized Einstein relation (GER) and relations involving time correlation function as the GKF. Extensions of them to the nonequilibrium realm have also been explored: for an n-dimensional linear irreversible Ornstein-Uhlenbeck process, GER takes the form of the Lyapunov matrix equation, connecting to the theory of linear stability and control (Keizer, 1987; Qian, 2001a),

$$2\mathbf{D} = \mathbf{\Xi}\mathbf{B}^{\mathsf{T}} + \mathbf{B}\mathbf{\Xi}, \tag{1.2}$$

where $\mathbf{\Xi}$, $\mathbf{B}$, and $\mathbf{D}$ are matrices of the stationary covariance between states, the linear relaxation, and the diffusion. A nonlinear GKF for nonequilibrium steady state in continuous time Markov processes was also established by Jiang *et al.* (2004); Chen *et al.* (2006):

$$\mathbb{E}\big[D(X_t)\big] = \int_0^\infty \mathbb{E}\big[b(X_t)b(X_{t+\tau})\big]\mathrm{d}\tau, \tag{1.3}$$

where stationary X_t follows a nonlinear stochastic differential equation with drift $b(X_t)$ and diffusion $D(X_t)$.

In Chap. 7, we show that "noise" and "drift" with distinct statistical characteristics can be used as defining properties for a decomposition of general stationary processes, without additional supposition of Markovian, reversibility, linearity, *etc*. In terms of this decomposition, a GER can be formulated. The novel formalism clearly illustrates, actually it defines, the GER as the consequence of stationarity of a process in which the stochasticity is balanced by dissipation. In the past, the stationary Fokker-Planck equation for a Markov process poses a mathematical relation among three: (i) the stationary distribution, (ii) the dissipative

drift, and (iii) the stochastic noise strength. In most applications, one solves (i) based on (ii) and (iii) (Hill, 1989; Jiang *et al.*, 2004). Alternatively, given (i) and (iii), (ii) admits a general decomposition in terms of the other two (Ao, 2004; Wang *et al.*, 2008; Yang and Cheng, 2021) illustrated in Chap. 6. All these previous results are now encompassed in the GER and the GKF in Sec. 7.2, broadly generalizing Eq. (1.2) and Eq. (1.3), respectively.

A key mathematical insight contributing to our result is a general decomposition of stochastic processes discovered by Doob (1990), summarized in Sec. 7.1: a stochastic step can always be written as the sum of a "drift part" that captures the average increment and a "noise part" that captures the stochasticity. The latter parts from all steps constitute a martingale (Grimmett and Stirzaker, 2001; Shreve, 2010; Durrett, 2019), which is a process that has no (conditional) gain or loss on average: a fair game. In the field of stochastic thermodynamics, the theory of martingale has played an important role in studying stopping time statistics and the thermodynamics associated with it (Neri *et al.*, 2017; Chun and Noh, 2019; Manzano *et al.*, 2021). We show in Sec. 7.1 that the martingale increment is uncorrelated to the past, which leads to a clear-cut of two uncorrelated contributions to the fluctuations of the overall stochastic dynamics. For Markov processes with time reversal symmetry, our GER further leads to a new characterization of equilibrium steady state: by considering a process and its adjoint process shown in Sec. 7.3, we show that the covariance matrix between the state and drift is symmetric if the process is reversible. Various forms of the GKF, as corollaries, can be derived for the adjoint drift. In Sec. 7.4, we also identify the 1-to-many and many-to-1 features in the dynamics, representing uncertainties in the future and in the past respectively, with the fluctuations of drift and adjoint drift under Doob decompositions of a process and its adjoint. Time-translational symmetry dictates a generic principle for the balance of the dissipative drift and the fluctuating noise at the steady state.

1.4 Irreversibility and Energetics

Classical thermodynamics describes the energetics of systems in equilibrium or near equilibrium, from mechanical cycles in heat engines to chemical reactions (Onsager, 1931; Landau and Lifshitz, 1980; Callen, 1985; Huang, 1991). With a modern probabilistic approach, such energetics from thermodynamics are extended to systems arbitrarily far from equilibrium in the past decades, known as *stochastic thermodynamics*. See (Seifert, 2012; Yang and Qian, 2020) for recent reviews. The key for such extension is to focus on the

breakdown of time reversal symmetry in a general stochastic process (Chetrite *et al.*, 2021; Yang and Qian, 2020). In fact, as we shall show in this thesis, the energetics can be formulated for generic Markov processes with the consideration of time symmetries alone, without requiring an underlying mechanical theory. The *local equilibrium assumption* required in (Groot and Mazur, 2011) does not enter the stochastic theory *per se* until its application is required for constitutive models of real world processes. Such *de-mechanized* energetics is particularly important for understanding what life is (Schrödinger/Penrose, 2012) as living systems are often described by mathematical models far from mechanics and by definition far from the equilibrium of death. The theory of stochastic thermodynamics has provided a unifying energetic framework for understanding many complex systems recently, *e.g.,* biological functions (Qian, 2007), chemical reactions (Qian and Ge, 2021), and computational functions (Wolpert, 2019) such as prediction (Still *et al.*, 2012), learning (Goldt and Seifert, 2017), and memory (Landauer, 1961; Still, 2020). The energetics of stochastic thermodynamics provides "*common themes for diverse phenomena*" (Jarzynski, 2015).

1.4.1 Irreversibility and Fluctuation Relations

As we will review in Chap. 3, there are three types of irreversibility in a general Markov process with a steady state. These different types of irreversibility are understood as different entropy productions (EPs) in physics (Seifert, 2012). Their statistical properties can be described by comparing their probability distribution functions before and after time reversals, called *fluctuation relations* (FRs) (Jarzynski, 1997; Crooks, 1999; Maes, 2004; Seifert, 2012). For examples, in (Crooks, 1999), Crooks' fluctuation theorem for the total entropy production was introduced for systems with detailed balance and the conditions for it to hold was illustrated; in (Ge and Jiang, 2007), the dissipation function from Evans and Searles (2002) was rigorously shown to generally admit the transient fluctuation theorem (TFT); in (Esposito and Van den Broeck, 2010), a detailed fluctuation theorem related to the involutive property of the change in probability (iDFT) was introduced for total entropy production and non-adiabatic entropy production; in (Seifert, 2012), the generalized Crooks' fluctuation theorem for non-detail balanced systems (rDFT) and TFT for different EPs were discussed thoroughly for diffusion processes, and iDFT was also discussed briefly; in (García-García *et al.*, 2012), rDFT was thoroughly discussed for the three entropy productions but not for the dissipation function.

The diverseness of FRs calls for a unifying formalism to derive all FRs mentioned above in a single formalism, organize their domain of validity comprehensively, and open ways to reveal more properties of

EPs. It is suggested in (Jiang *et al.*, 2004; Ge and Jiang, 2007; Ge, 2009; Wojtkowski, 2009; Shargel, 2010; Chetrite and Gupta, 2011) that measure-theoretic probability theory pioneered by Kolmogorov will do the trick. One key is the understanding that EPs in physics are the *fluctuating relative entropy* for trajectories between the original process and the reversed process, with different EPs given by different reversals or composite of reversals (Crooks, 1998, 1999; Esposito and Van den Broeck, 2010; Seifert, 2012). In the measure-theoretic formalism, EP is thus mathematically expressed as the negative logarithm of the Radon-Nikodym Derivative (RND), which is a re-weighting factor in taking expectation to change a probability measure from the original one to the other as we will introduce in Sec. 2.3. It is this mathematical underpinning that enables us to arrive an organization of FRs and further derive/recover other properties with a deeper understanding of EPs in Chap. 4, *e.g.* their martingale properties (Chetrite and Gupta, 2011; Neri *et al.*, 2017; Chetrite *et al.*, 2019).

Our work serves as a comprehensive overview on how to understand EPs and their statistical properties, primarily FRs, from measure-theoretic probability theory and our change-of-probability-measure (CPM) operator theory. We discuss different time reversals in Sec. 4.1, their associated EPs in physics and chemistry in Sec. 4.2, and derive various FRs from our general and concise approach in Sec. 4.3. By adopting this CPM operator formalism, we can neatly derive many known results in the literature with more rigor and generality, achieve new understanding on EPs and FRs, and reveal more properties of EPs as shown in Sec. 4.4.

1.4.2 Fundamental Roles of Cycles in Nonequilibrium Systems

Nonequilibrium thermodynamics (NET) pioneered by Onsager (1931) is concerned with a diverse array of macroscopic physical and chemical processes: mass transport, heat conduction, chemical reactions, *etc*. A unified treatment in continuous systems was developed in the 1960s (Groot and Mazur, 2011). In recent years, introducing a NET of mesoscopic stochastic dynamics in its phase space has provided a more fundamental formulation in which the different physical and chemical fluxes are all represented by a single probability flux (Qian, 2018). Active transports and reactions in non-equilibrium systems are represented by the nonzero net probability fluxes in the steady state, with broken time-reversal symmetry in these non-equilibrium steady states (NESS) (Jiang *et al.*, 2004).

A steady state in a Markov process requires recurrence of states in time (Grimmett and Stirzaker, 2001), *i.e.* completing cyclic paths in the state space. In fact, it was shown for Markov chains that kinetic cycles

in the state space are the fundamental units for dynamics in the steady state (Schnakenberg, 1976; Hill, 1982; Jiang *et al.*, 2004; Kalpazidou, 2006; Qian *et al.*, 2016b). The system is required to complete a cycle to reveal the breakdown of detailed balance (Hill and Chen, 1975; Yang and Qian, 2021a). This is an important concept that resolved the Maxwell demon "paradox" (Landauer, 1961; Bennett, 2003; Yang and Qian, 2021a) as we shall revisit in Sec. 5.1.

The steady-state probability flux on a transition in Markov chains can be decomposed into the sum of *cycle fluxes* over cycles that contains the transition (Hill, 1989; Jiang *et al.*, 2004). Irreversibility in a NESS, known as the *housekeeping heat*, has a cyclic expression (Qian *et al.*, 2016b; Yang and Qian, 2021a), which shows the origin of the Onsager's reciprocality and symmetry between two transitions in near-equilibrium systems (Hill, 1982; Qian *et al.*, 2016b). In Sec. 5.2, we demonstrate that Onsager's reciprocality is a manifestation of the cyclic dynamics in NESS and can thus be generalized to NESS arbitrarily far from equilibrium (Yang and Qian, 2021a). The near-equilibrium condition is only needed for Onsager's symmetry.

For diffusion in a two-dimensional Euclidean space $\mathbb{R}^2$, with three-dimensional case implied, the roles of kinetic cycles in stochastic dynamics were also studied (Qian, 1998). However, its generalization to diffusion in higher dimensional space $\mathbb{R}^n$, $n > 3$, is highly non-trivial. One of the difficulties is that vector calculus is no longer sufficient for high dimension since vorticity can not be represented by a vector through the right-hand rule: there are more than one dimensions in the "thumb" direction. The key to the generalization to $\mathbb{R}^n$ is to represent an infinitesimal cyclic path by the linear combination of infinitesimal squares described by two vectors (Yang and Qian, 2021a). Quantities defined on an infinitesimal cycle are then described by the mathematical objects called *bivector*s represented by skew-symmetric matrices. See Appendix A for an introduction of the mathematics. Each bivectorial cycle couples two dimensions represented by vectors and gives rise to Onsager's notion of reciprocality in diffusion. In Sec. 5.3, we formulate both cycle affinity and cycle flux as bivectors in $\mathbb{R}^n$ and conclude that cycles are the fundamental elements not just for discrete Markov processes at NESS but also for continuous Markov processes (Yang and Qian, 2021a). The broken time reversal symmetry in NESS is in terms of cycles.

1.4.3 Energy Landscape and Cycle Potential of Markov Dynamics

The potential functions underlying a complex dynamics are fundamental notions in physics *e.g.* the Hamiltonian in classical mechanics and the scalar and vector potentials in electrodynamics. A similar concept of

energy landscape has also been central in understanding the underlying mechanisms of complex biological systems in different levels: from biochemicals (Onuchic *et al.*, 1997; Dill and MacCallum, 2012), cells (Goldberg *et al.*, 2007), organisms (Agozzino *et al.*, 2020), to populations (Nolting and Abbott, 2015). The identification and formulation of these potential functions, however, are challenging for nonequilibrium systems that are remote to mechanics[2]. For the notion of an energy landscape, there are at least three existing mathematical theories to be unified:

1. Freidlin and Wentzell's quasi-potential theory for deterministic dynamical systems as the zero-noise limit of Markov stochastic dynamics (Freidlin and Wentzell, 2012; Nolting and Abbott, 2015; Zhou and Li, 2016),
2. Graham's and Ao's decomposition for stochastic Markov dynamics and deterministic dynamical systems (Graham, 1977a; Ao, 2004; Yin and Ao, 2006; Ding *et al.*, 2020), and
3. the potential-flux theory of stochastic Markov dynamics from stochastic thermodynamics (Wang *et al.*, 2008; Fang *et al.*, 2019).

Although it was understood intuitively that the "nonequilibrium part" in these theory is related to cycles, there is no clear notion of a potential in terms of cycles constituting the nonequilibrium part in continuous processes. We integrate these three lines of work and introduce the cycle potentials complementary to the scalar energy landscape, thus formulating a complete thermodynamic potentials theory for Markov stochastic dynamics and its deterministic limit in Chap. 6 (Qian *et al.*, 2020; Yang and Cheng, 2021).

For equilibrium systems, complex dynamics can be described by a scalar potential function (Yang and Cheng, 2021), known as the energy landscape, as we shall revisit in Sec. 3.1. The energy landscape connects to the stationary distribution of state by the Boltzmann's law. This is the key insight that initiates our work: the time-translation symmetry at the steady state can provide the defining features (potential functions) of dynamics even outside of the steady state. This idea is not foreign to theorists. In mathematics, one can often gain a deeper understanding of an equation when it is expressed in terms of its solutions. While this approach might not sound relevant in engineering, where the goal is to *find* the solution(s), it has been extremely fruitful in theoretical science. A case in point is to re-write the polynomial equation $x^n + a_{n-1}x^{n-1} + \cdots a_1 x + a_0 = 0$ into $(x - x_0)(x - x_1)\cdots(x - x_n) = 0$. In a sense, one could say the set of n roots collectively *defines* the algebraic equation. Indeed, providing the setting for the existence and

[2] For example, it is widely believed that there's no systematic way to find the Lyapunov functions for a nonlinear dynamical system (Strogatz, 2018).

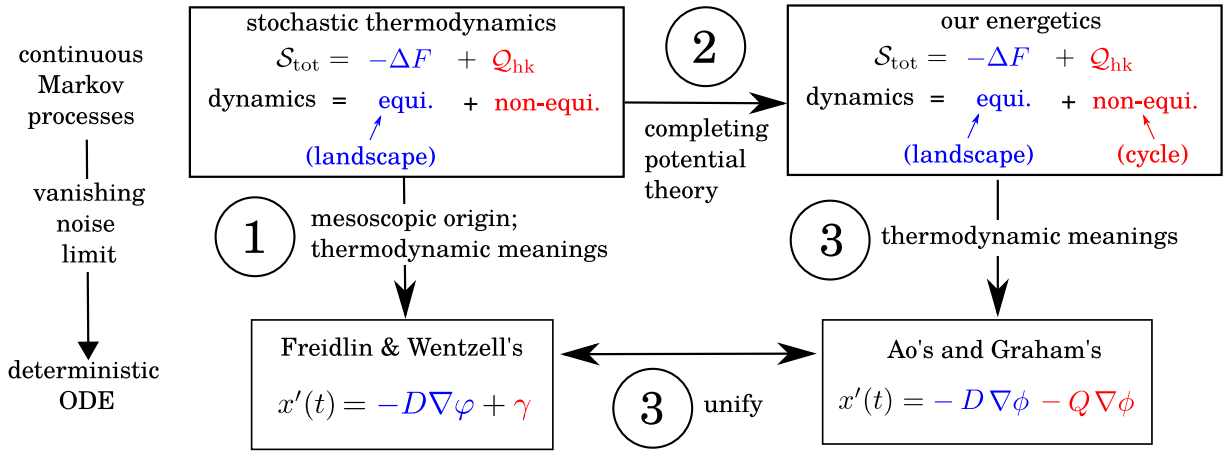


Figure 1.3: Summary of our unifying potentials theory in this chapter. Notations will be introduce in details later throughout the chapter. Step 1 is in (Qian *et al.*, 2020); step 2 is in (Yang and Qian, 2021a); step 3 is in (Yang and Cheng, 2021). Color blue encodes the equilibrium part of the dynamics, and color red represents the non-equilibrium part. Detailed introduction of the various mathematical notions will be provided in later chapters.

uniqueness of such a *re-writing* has become one of the most significant chapters of mathematics (Berlinski, 2008).

For nonequilibrium dynamics, an *energy landscape* Φ can still be introduced as the negative logarithm of π even though the dynamics can not be fully described by any landscape (Kubo *et al.*, 1973; Nicolis and Lefever, 1977; Graham and Schenzle, 1983; Seifert, 2012; Thompson and Qian, 2016; Yang and Cheng, 2021). This was the key to the force-flux decomposition in stochastic thermodynamics (Wang *et al.*, 2008), and this decomposition corresponds to the two disjoint types of irreversibility in stochastic dynamics review in Sec. 3.2 (Seifert, 2012; Yang and Qian, 2020; Ge, 2009; Esposito and Van den Broeck, 2010). By taking the vanishing noise limit, we show in Sec. 6.3 that this decomposition is actually the thermodynamic foundation of Freidlin-Wentzell's theory (Qian *et al.*, 2020; Yang and Cheng, 2021). However, the underlying potential function for the nonequilibrium "flux" component needs to be identified. As this nonequilibrium "flux" component corresponds to the irreversibility at the NESS, our work in Chap. 5 implies that cycles are the fundamental units for such a term. Applying our bivectorial formalism in Sec. 5.3, the cycle potential for the forces and fluxes in nonequilibrium stochastic dynamics is identified in Sec. 6.1. The resulting force decomposition provides thermodynamic meanings to Graham's and Ao's dynamic decomposition (Graham, 1977a; Ao, 2004; Yin and Ao, 2006; Ding *et al.*, 2020), and our probability flux decomposition leads to novel decomposition for the mean rate of thermodynamic quantities as shown in Sec. 6.1. The emergence

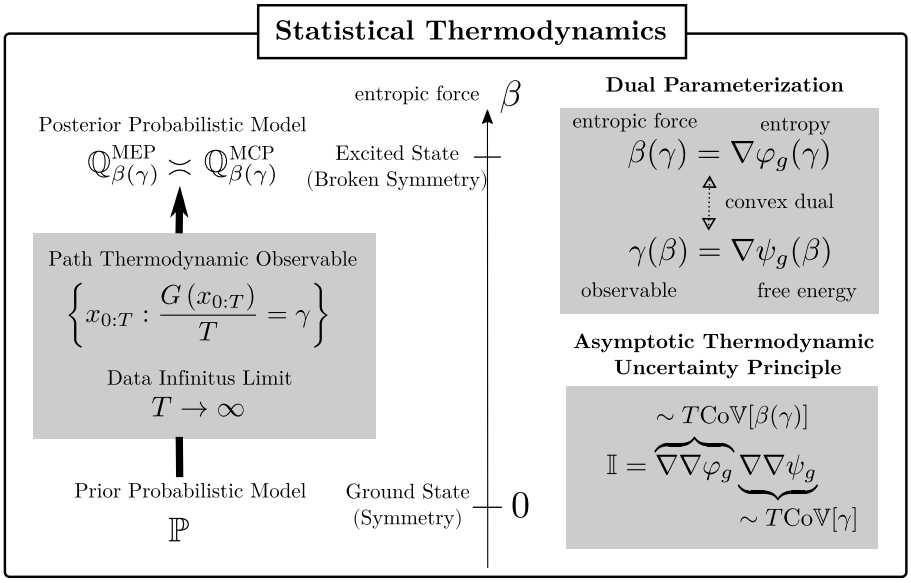


Figure 1.4: Limit theorems in the data infinitum dictate statistical thermodynamics. Thermodynamic concepts such as entropy, free energy, and conjugated variables as entropic forces are introduced in the data infinitus limit. The statistical variations of the observables and of their conjugated forces satisfy an asymptotic thermodynamic uncertainty principle.

of time-translational symmetry dictate the underlying potential functions of complex dynamics, and time irreversibility dissects the potential functions into disjoint sources. See Fig. 1.3 for a summary of how our work unite three theory of potentials for continuous processes.

1.5 Summary

Dynamical systems theory has played a central role in applied mathematics for nearly a century (Strogatz, 2018). Besides providing a geometric understanding for difference and differential equations, it is also the main framework for modeling complex systems such as those in biology (Kot, 2001; Kaneko, 2006; Murray, 2007; Izhikevich, 2010; Gerstner *et al.*, 2014). My thesis proposes a candidate for a unifying theory, both for biological systems and more generally for complex systems. The keys are the unifying stochastic formalism for modeling complex systems (Nicolis and Prigogine, 1977; Haken, 1978) and the focus of symmetries and limit theorems in probability theory (Anderson, 1972; Yang, 1996; Qian *et al.*, 2016a).

Theories in this thesis are summarized schematically in Fig. 1.4 and Fig. 1.5. Our thermodynamic theory is to Markov dissipative dynamics what classical mechanics is to Hamiltonian dynamical systems. The fluctuation-dissipation relations and energetics we develop in Part II arise solely from time symmetries

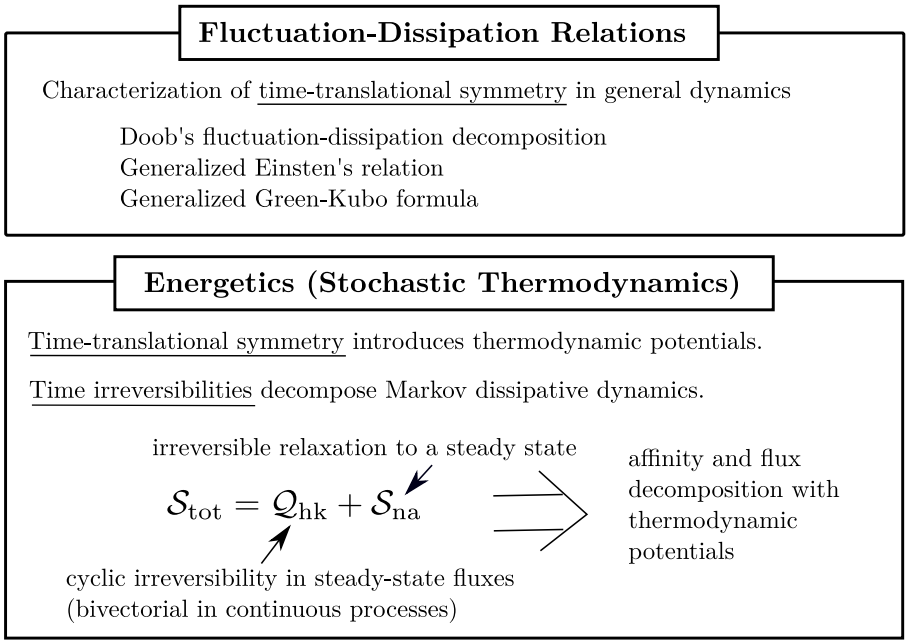


Figure 1.5: Time symmetries dictate dynamic principles. Breakdown of time-reversal symmetry leads to fundamental decomposition of Markov dynamics. Formation of time-translational symmetry is characterized by the fluctuation-dissipation relations.

and can thus be applied to a wide spectrum of stochastic or deterministic models in biology; the statistical thermodynamics we formulate in Part III is purely from limit theorems in data infinitum thereby revealing generic thermodynamic structures between observables and their conjugated forces. Hence, our thermodynamic theory is a theory not only for biological systems but for generic stochastic models for complex systems.

Chapter 2

Mathematical Elements of Stochastic Processes

This chapter introduces preliminary mathematics of probability theory and stochastic process for our thermodynamic theory. Standard mathematical textbooks for Sec. 2.1 and Sec. 2.2 are (Feller, 1991a,b; Grimmett and Stirzaker, 2001; Durrett, 2019; Shreve, 2010). I also benefited a great deal from Professor Matt Lorig's lecture note (Lorig, 2019) when I took Amath 561 & 562, at the University of Washington. For readers with a physics background, (Kampen, 2007; Gardiner, 2009) can also be useful. Sec. 2.3 introduces the notion of change of probability (measure), a key mathematical concept throughout the thesis (Qian *et al.*, 2019; Yang and Qian, 2020, 2022).

2.1 Probabilistic Model and Stochastic Processes

2.1.1 Probability Space and Random Variables

Modern probability theory pioneered by Kolmogorov (2018) starts with formulating a triple: a sample space Ω, the σ-algebra $\mathcal{F}$, and a probability (measure) $\mathbb{P}$, known as the *probability space* $(\Omega, \mathcal{F}, \mathbb{P})$. An outcome ω is a particular result of a random trial. A sample space Ω is the collection of all possible outcomes. We can think of Ω as the *state space* of our system of interest[1]. These outcomes in the state space Ω are the

[1] Here, the sample space as a "state space" is a concept of a "total state" of the system, not to be confused by the state space of a process. For stochastic processes, a "total state" is a path. This will become clear when we introduce stochastic process in Sec. 2.1.2.

atomic event of interest. In general, an event of interest A is a subset of the sample space that we ask the probability of. For example, for a common dice with six faces, the state space is $\{1, 2, 3, 4, 5, 6\}$ and an event can be the even number set $\{2, 4, 6\}$.

The collection of all event of interests of Ω is called a σ-algebra[2], denoted as $\mathcal{F}$. When we are interested in an event, the complement of it, A^c, *i.e.* when A does not happen, is also under our interest. Moreover, if we are already interested in a bunch of events $A_1, A_2^c, \ldots$, then the countable union of them, *i.e.* the event when at least one of it happen, is also interesting to us. Note that with complement and countable union, the countable intersections are automatically included in $\mathcal{F}$. As a result, a σ-algebra of Ω as a collection of all events of interest must have the following three properties in its very definition:

1. containing the empty set $\emptyset$ where nothing happen,
2. being closed under countable union, and
3. being closed under complement.

One main reason to introduce σ-algebra $\mathcal{F}$ along with the sample space Ω is the following. Since we are interested in knowing the probability of every events of interest, which is given by a probability measure $\mathbb{P}$, we need the collection of all events of interest $\mathcal{F}$ to actually define a $\mathbb{P}$ mathematically.

A probability measure $\mathbb{P}$ provides the probability of an event of interest $A \in \mathcal{F}$ by assigning the event $\{\omega : \omega \in A\}$ a real value between 0 and 1,

$$\mathbb{P}\{\omega : \omega \in A\} = \int_A \mathrm{d}\mathbb{P}(\omega) \tag{2.1}$$

where integration is understood in the Lebesgue sense.

A physical observable is a real-valued function that we can measure in practice. It is defined on Ω and is called *random variable* in the theory of probability. In fact, a random variable $X(\omega)$ is a special kind of function from Ω to a real-valued set of possible values $\mathcal{X}$ (state space, *e.g.* $\mathbb{R}$). For $\mathcal{X} \equiv \mathbb{R}$, since we are interested in the statistical properties of $X(\omega)$, we would like to use the probability measure $\mathbb{P}$ defined on the $\mathcal{F}$ of Ω to get the probability of an event such as $\{X(\omega) \in (a, b); a, b \in \mathbb{R}\}$ or for $X(\omega)$ in any countable union/complements of open intervals. The collection of any set that can be formed from open intervals in $\mathbb{R}$, complement of them, and/or countable union of them is called the *Borel sets* of $\mathbb{R}$, denoted as $\mathcal{B}(\mathbb{R})$. The requirement of being able to use a probability measure $\mathbb{P}$ to get that statistical properties of $X(\omega)$ is

[2] It is called σ-algebra because it considers countable union instead of union of a finite number of sets. If the latter case, the set is called an algebra instead of a σ-algebra.

the requirement of *measurability* in measure theory. To be able to compute $\mathbb{P}\{X(\omega) \in B\}$, we need that $\forall B \in \mathcal{B}(\mathbb{R})$, $\{X(\omega) \in B\}$ is a set of ω that is in $\mathcal{F}$. Hence, a random variable is not just a function of Ω but a *measurable function* $X(\omega) : \Omega \mapsto \mathbb{R}$ defined on $(\Omega, \mathcal{F})$ so that $\{X(\omega) \in B\} \in \mathcal{F}, \forall B \in \mathcal{B}(\mathbb{R})$.

The expectation of a random variable is

$$\mathbb{E}\left[X\left(\omega\right)\right] \coloneqq \int_{\Omega} X\left(\omega\right) \mathrm{d}\mathbb{P}\left(\omega\right). \tag{2.2}$$

Since an event $A \in \mathcal{F}$ is a subset of Ω, the probability of an event A can also be represented as an expectation of the indicator function of an event A, $\mathbb{I}_A(\omega)$, *i.e.*

$$\mathbb{P}\left\{\omega : \omega \in A\right\} = \mathbb{E}[\mathbb{I}_A(\omega)] = \int_{\Omega} \mathbb{I}_A\left(\omega\right) \mathrm{d}\mathbb{P}\left(\omega\right) = \int_{A} \mathrm{d}\mathbb{P}\left(\omega\right). \tag{2.3}$$

$\mathbb{I}_A(\omega)$ gives 1 if $\omega \in A$ and 0 otherwise. We will find this expectation expression of $\mathbb{P}\left\{\omega : \omega \in A\right\}$ convenient in many of our later calculations. In the following content, we may suppress the ω in the equations for notation simplicity. We may denote the expectation of $X\left(\omega\right)$ as $\mathbb{E}\left[X\right]$ and the probability of event A as $\mathbb{P}\left\{A\right\}$.

2.1.2 Stochastic Process

A stochastic process is a collection of random variables as state variables X_t labeled by time t, discrete or continuous. The state space $\mathcal{X}$ in a stochastic process is the collection of all possible values of the state variables X_t and is often assumed to be independent of time t. The sample space Ω would be in general a collection of all the paths. For a process with duration T, we have $\Omega = \mathcal{X}^{[0,T]}$. For notation simplicity, let us denote $X_{0:T}$ as the random path from time 0 to time T (inclusive on both ends). A possible realization would be $x_{0:T} \in \Omega$. Here, we consider a stochastic process to be represented by the random "vector" $X_{0:T}$. General physical observables of interest are path observables $G\left(x_{0:T}\right) : \Omega \mapsto \mathbb{R}^m$. The measurable space $(\Omega, \mathcal{F})$, state variables $X_{0:T}$, and path observables of interest $G\left(x_{0:T}\right)$ together specify the system of interest. A probability space $(\Omega, \mathcal{F}, \mathbb{P})$ where $\mathbb{P}$ is the path probability measure specify the statistical properties of the system. Strictly speaking, a stochastic process can be defined without a probability measure (Nutz, 2012). However, here, we are interested in the statistical properties of observables of the process. We consider processes with different statistical properties as different processes or systems in different thermodynamic states as introduced later in Chap. 8.

We are generally interested in how states at different time are related. For a stochastic process, we

would expect the state at time t to be "generated" by the states in the past under certain governing rules that can be applied to generate the full future. Consider a discrete time process, we would consider the joint probability distribution $\mathbb{P}\{X_{0:t}\}$ and also the conditional probability $\mathbb{P}\{X_t|X_{0:t-1}\}$ that tells what the probability distribution of X_t is given a specific past $X_{0:t-1} = x_{0:t-1}$. The marginal probability distribution of X_t would be given by summing over all possible past trajectories $x_{0:t-1}$,

$$P_t(x) \coloneqq \mathbb{P}\{X_t = x\} = \sum_{x_{0:t-1}\in\Omega_{t-1}} \mathbb{P}\{X_t = x|X_{0:t-1} = x_{0:t-1}\}\,\mathbb{P}\{X_{0:t-1} = x_{0:t-1}\}. \tag{2.4}$$

If a process is independent to the whole past once conditioned on the previous time step, then the process is said to be a *Markov process*. In precise mathematical terms, for a Markov process $X_{0:T}$, we have

$$\mathbb{P}\{X_t = x|X_{0:t-1} = x_{0:t-1}\} = \mathbb{P}\{X_t = x|X_{t-1} = x_{t-1}\}. \tag{2.5}$$

It means the state of the system a step before X_{t-1} summarizes the whole past $X_{0:t-1}$ for predicting X_t.

Depending on whether the state space $\mathcal{X}$ and time t are discrete or continuous, there are four common types of Markov processes:

1. Discrete-time Markov chain (DTMC): discrete $\mathcal{X}$ and discrete t
2. Continuous-time Markov chain (CTMC): discrete $\mathcal{X}$ and continuous t
3. Continuous Markov process (diffusion): continuous $\mathcal{X}$ and t (continuous path)
4. Lévy process: a combination of CTMC and diffusion

We will focus on the first three types in this thesis. Intuitively, CTMC could be understood by the continuous time limit of DTMC and diffusion could be understood by the continuous space limit of CTMC. However, the limiting behaviors of them can be mathematically non-trivial, especially with properties associating with another limit such as the zero-noise limit or the infinite-time limit. Discussions on each cases are thus necessary.

2.2 Time Evolution of Markov Processes

We shall now discuss how to describe the time evolution of states X_t in various Markov processes.

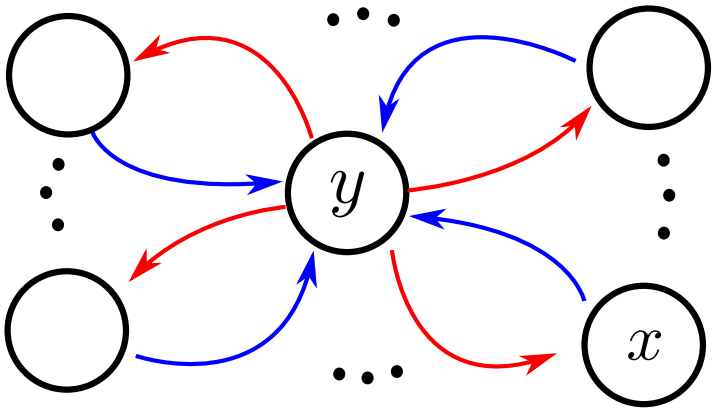


Figure 2.1: Illustration of inward probability flux (blue) and outward probability flux (red) for a state y in the state space.

2.2.1 Time Evolution of Markov Chains

Let us begin with the simplest case: the discrete-time Markov chain (DTMC). In DTMC, a random trajectory of length T is simply $X_{0:T} = X_0 X_1 \cdots X_T$. The probability distribution of X_t, denoted as $P_t(y) \coloneqq \mathbb{P}\{X_t = y\}$, evolves according to the state a step before X_{t-1} and the transition matrix $M_{t|t-1}(y|x) \coloneqq \mathbb{P}\{X_t = y | X_{t-1} = x\}$ at each time,

$$P_t(y) = \sum_{x \in \mathcal{X}} P_{t-1}(x) M_{t|t-1}(y|x). \tag{2.6}$$

Since $\sum_{y \in \mathcal{X}} M_{t|t-1}(y|x) = 1$, we can also rewrite Eq. (2.6) as

$$P_t(y) - P_{t-1}(y) = \underbrace{\sum_{x \in \mathcal{X}; x \neq y} P_{t-1}(x) M_{t|t-1}(y|x)}_{\text{total inward flux}} - \underbrace{\sum_{\eta \in \mathcal{X}; \eta \neq y} P_{t-1}(y) M_{t|t-1}(\eta|y)}_{\text{total outward flux}}. \tag{2.7}$$

The evolution of P_t can thus be understood as the continuity equation of probability: the gain in the probability at position y is equal to the difference between the total inward flux and the total outward flux. The joint probability of a transition pair $P_{t-1,t}(x,y) \coloneqq \mathbb{P}\{X_{t-1} = x, X_t = y\} = P_{t-1}(x) M_{t|t-1}(y|x)$ is thus understood as the *probability flux* in DTMC. See Fig. 2.1 for an illustration.

The probability of a path $x_{0:T}$ is determined by the initial distribution $P_0(\xi)$ and the sequence of transition matrices $M_{t|t-1}(y|x)$ for $t = \{1, 2, \cdots, T\}$,

$$\mathbb{P}\{X_{0:T} = x_{0:T}\} = P_0(x_0) \prod_{t=1}^{T} M_{t|t-1}(x_t|x_{t-1}). \tag{2.8}$$

We call the combinations of P_0 and $M_{t|t-1}$ for $t = \{1, 2, \cdots, T\}$ the *driving protocol* that drives the

DTMC (Yang and Qian, 2020). If the transition matrices are time-independent, then the results above can be greatly simplified. This type of Markov processes is said to be *time-homogeneous* (or *autonomous* in the language of dynamical systems). A stochastic process is said to reach its steady state (assumed it exists) if the probability distribution of state X_t no longer changes in time, denoted as $\pi(x)$. For time-homogeneous DTMC, Eq. (2.6) tells us that $\pi(x)$ satisfies

$$\pi(x) = \sum_{y\in\mathcal{X}} \pi(y) M(x|y), \forall x \in \mathcal{X}; \tag{2.9}$$

The case for continuous-time Markov chain (CTMC) is quite similar to DTMC. A random trajectory is now consist of both jumped state and jumped time. The system stays in state x_0 from $t_0 := 0$ to t_1 and jumped to x_1 at $t_1, \cdots$, and finally stays at x_K since $t_K \leq T$. Intuitively, it can be understood as the continuous time limit of a DTMC with an asymptotic form of transition matrix,

$$M_{t+\mathrm{d}t|t}(y|x) = \delta_{x,y} + Q_t(y|x)\,\mathrm{d}t \tag{2.10}$$

where $\delta_{x,y}$ is the Kronecker delta function and the transition rate matrix $Q_t(y|x)$ tells us the probability to go from state x to y in the time interval $\mathrm{d}t$. Since $\sum_{y\in\mathcal{X}} M_{t+\mathrm{d}t|t}(y|x) = 1$, the diagonal part of $Q_t(y|x)$ is negative and satisfies

$$Q_t(x|x) = -\sum_{y\in\mathcal{X}, y\neq x} Q_t(y|x). \tag{2.11}$$

The term $1 - Q_t(x|x)\,\mathrm{d}t$ is the probability to stay at state x from time t to time $\mathrm{d}t$. In between two consequent jumps, say between time t_{j-1} and t_j, the process has an exponential waiting time with escape rate given by $-\int_{t_{j-1}}^{t_j} Q_t(x|x)\,\mathrm{d}t$ at state x. The local conservation of probability of CTMC can be derived by Eq. (2.7),

$$\frac{\mathrm{d}}{\mathrm{d}t}P_t(x) = \sum_{\xi\in\mathcal{X};\xi\neq x} \left[P_t(\xi)Q_t(x|\xi) - P_t(x)Q_t(\xi|x)\right] \tag{2.12a}$$

$$= \sum_{\xi\in\mathcal{X}} P_t(\xi)Q_t(x|\xi) \tag{2.12b}$$

where $P_t(\xi)Q_t(x|\xi) - P_t(x)Q_t(\xi|x)$ gives the notion of net probability flux in CTMC between state x and state ξ at time t. The path probability of CTMC is

$$\mathbb{P}\{X_{0:T} = x_{0:T}\} = P_0(x_0)\prod_{j=1}^{K} e^{\int_{t_{j-1}}^{t_j} Q_t(x_{j-1}|x_{j-1})\mathrm{d}t} Q_{t_j}(x_j|x_{j-1})\, e^{\int_{t_K}^{T} Q_t(x_K|x_K)\mathrm{d}t}. \tag{2.13}$$

For a time-homogeneous CTMC, the equation for the stationary distribution $\pi(x)$ is

$$0 = \sum_{y\in\mathcal{X}, x\neq y} \left[\pi(y) Q(x|y) - \pi(x) Q(y|x)\right] = \sum_{y\in\mathcal{X}} \pi(y) Q(x|y), \forall x \in \mathcal{X}. \tag{2.14}$$

2.2.2 Time Evolution of Continuous Markov Processes

A continuous time-homogeneous Markov process[3] on $\mathbb{R}^n$ has two quite different representations (Hong *et al.*, 2020). One is based on stochastic continuous trajectories $\mathbf{X}_t$ with its probability measure. The trajectories satisfy a stochastic differential equation (SDE)

$$\mathrm{d}\mathbf{X}_t = \underbrace{[\mathbf{b}(\mathbf{X}_t) + \nabla\cdot\mathbf{D}(\mathbf{X}_t)]\,\mathrm{d}t}_{\text{drift}} + \underbrace{\mathbf{\Gamma}(\mathbf{X}_t)\mathrm{d}\mathbf{W}_t}_{\text{noise}}. \tag{2.15}$$

At each time step from $\mathbf{X}_t$ to $\mathbf{X}_{t+\mathrm{d}t}$, the state evolves with two parts. The "deterministic" part is called the *drift* of the diffusion and $\mathbf{D} \coloneqq \mathbf{\Gamma}\mathbf{\Gamma}^\mathsf{T}/2$ is the diffusion matrix. $(\nabla\cdot\mathbf{D})_j = \sum_{i=1}^n \partial_i \mathbf{D}_{ij}$ with ∂_i denotes partial derivative with respect to $\mathbf{x}_i$. The stochastic part is defined from the n-D Brownian motion $\mathbf{W}_t$. The stochastic increment $\mathrm{d}\mathbf{W}_t$ is an n-D vector of Gaussian-distributed random variable. Components of $\mathrm{d}\mathbf{W}_t$ are independent to each other, independent to $\mathbf{X}_t$, and are all Gaussian-distributed with mean 0 and variance $\mathrm{d}t$.

The other representation is based on the probability density function of state $\mathbf{X}_t$ at time t, denoted as $p(\mathbf{x}, t)$, defined by

$$p(\mathbf{x}, t) \coloneqq \lim_{\mathrm{d}\mathbf{x}\to 0} \frac{\mathbb{P}\{\mathbf{X}_t \in (\mathbf{x}, \mathbf{x}+\mathrm{d}\mathbf{x})\}}{\mathrm{d}\mathbf{x}}. \tag{2.16}$$

Its time evolution is governed by local conservation of probability, also known as the Fokker-Planck equation (FPE),

$$\partial_t p(\mathbf{x}, t) = -\nabla\cdot\left[\mathbf{b}(\mathbf{x})p(\mathbf{x}, t) - \mathbf{D}(\mathbf{x})\nabla p(\mathbf{x}, t)\right]. \tag{2.17}$$

Correspondence between the two representations can be established by Ito's calculus[4]. With Eq. (2.17) as the continuity equation of the probability density p, the (net) probability flux in diffusion is given by the

[3] If the process is time inhomogeneous, our result in this thesis can still be valid as long as the time-dependent $\mathbf{b}$ and $\mathbf{D}$ still gives a unique invariant measure at each moment.

[4] A trajectory $\mathbf{X}_t$ satisfying the SDE has a unique representation of the transitional probability density satisfying the FPE. This was developed by the semigroup approaches (Feller, 1954). However, if we start from the FPE alone and attempt to derive a unique SDE representation from it, we would need the uniqueness of its semigroup solution. The uniqueness requires quite restrictive conditions on the drift and diffusion matrix. See Chap. 3 of (Jiang *et al.*, 2004) for how to relax the conditions, obtain the minimal semigroup solution, and construct the corresponding continuous path $\mathbf{X}_t$.

vector field

$$\mathbf{J}(\mathbf{x},t)=\mathbf{b}(\mathbf{x})p(\mathbf{x},t)-\mathbf{D}(\mathbf{x})\nabla p(\mathbf{x},t) \tag{2.18}$$

described by the vector field $\mathbf{b}$ and the diffusion matrix $\mathbf{D}$. The condition for a diffusion process to reach a steady state $p(\mathbf{x},t)\rightarrow\pi(\mathbf{x})$, according to Eq. (2.17), is a divergence-free requirement for the stationary probability current $\mathbf{J}^{*}(\mathbf{x})\coloneqq\mathbf{b}(\mathbf{x})\pi(\mathbf{x})-\mathbf{D}\nabla\pi(\mathbf{x})$,

$$\nabla\cdot\left[\mathbf{b}(\mathbf{x})\pi(\mathbf{x})-\mathbf{D}\nabla\pi(\mathbf{x})\right]=0. \tag{2.19}$$

With continuous space-time path, the probability of a single path in diffusion is with zero probability (measure). A concept of path probability "density" instead is required. However, path probability density and the path integral formalism are very subtle mathematical notions in continuous Markov processes. The probability "density" of paths near a smooth infinitesimal tube can be described by the Onsager-Machlup function (Onsager and Machlup, 1953). For example, it is shown in (Zeitouni, 1989) that for $\mathrm{d}\mathbf{X}_t=\mathbf{b}(\mathbf{X}_t)\mathrm{d}t+\mathrm{d}\mathbf{W}_t$, the the probability density near a smooth tube $\boldsymbol{\phi}(t)$ has the form of

$$\lim_{\epsilon\rightarrow0}\frac{\mathbb{P}\left\{\left\|\mathbf{X}_t-\boldsymbol{\phi}(t)\right\|<\epsilon\right\}}{\mathbb{P}\left\{\left\|\mathbf{W}_t\right\|<\epsilon\right\}}=e^{-\frac{1}{2}\left[\int_0^T\left(\left|\dot{\boldsymbol{\phi}}(t)-\mathbf{b}(\boldsymbol{\phi}(t))\right|^2\right)\mathrm{d}t+\int_0^T\nabla\cdot\mathbf{b}(\boldsymbol{\phi}(t))\mathrm{d}t\right]} \tag{2.20}$$

where $\|\boldsymbol{\psi}\|\coloneqq\max_{t\in[0.T]}|\boldsymbol{\psi}(t)|$ where $|\cdot|$ is the Euclidean norm in $\mathbb{R}^n$. See (Zeitouni, 1989) and also (Graham, 1977b; Durr and Bach, 1978; Freidlin and Wentzell, 2012) for detailed discussions. It is unclear if such density notion can be rigorously defined by the typical non-smooth path in diffusion. In this thesis, we will not delve into this subtle and intriguing issue. We introduced the concept of path probability in order to compare processes with different statistical properties. For us, the issue of path probability "density" in diffusion can be circumvented by using the Girsanov theorem (Durr and Bach, 1978; Jiang *et al.*, 2004), which we will introduce in the next section.

2.3 Change of Probability Measure

We specify a system of interest by specifying the pair $(\Omega,\mathcal{F})$ and the associated physical observables of interest $X(\omega):\Omega\mapsto\mathcal{X}$ where $\mathcal{X}$ are the set collecting all possible real values X can take. After we have a probability measure $\mathbb{P}$, we have a *probability space* $(\Omega,\mathcal{F},\mathbb{P})$ that introduces (pushes forward) a probability distribution or density function for X, denoted as $P(x)$ or $\rho(x)$ where $x\in\mathcal{X}$. When we observe "two systems" with two different probability distribution functions $P(x)$ and $Q(x)$ (defined on the same state

space $\mathcal{X}$), we can represent such difference in statistical properties either by imagining it was because we have two different observables X and Y, or because we have one observable X but have two probability measures $\mathbb{P}$ and $\mathbb{Q}$ that lead to different statistical properties of X (Qian *et al.*, 2019). This is akin to the dual Heisenberg's and Schrödinger's pictures of quantum physics. In this dissertation, we will be primarily using the latter. We consider a change in the statistical properties of a random variable $X(\omega)$, *i.e.* the difference in its distribution P_X and P_X^ν, is due to the change of probability measure $\mathbb{P} \to \mathbb{P}^\nu$. We introduce general ideas and provide some preliminary examples in this section. More physical applications of this can be found in Chap. 4. And a statistical thermodynamic interpretation will be formulated in Chap. 8.

2.3.1 Radon-Nikodym Derivative

To start, we consider the collection of all possible probability measures on a given measurable space $(\Omega, \mathcal{F})$ forms an affine space of probability measures $\mathcal{P}$ (Hong *et al.*, 2020). With the statistical properties of stochastic systems specified by the probability measures $\mathbb{P} \in \mathcal{P}$, the difference between the statistical properties of two systems is characterized by a change of probability measure (CPM) $\mathbb{P} \to \mathbb{P}^\nu \in \mathcal{P}$, which induces changes in the statistical properties of observables $Y(\omega)$. Such change in statistical properties can be mathematically represented by a random variable called the *Radon-Nikodym Derivative* (RND), denoted as $\frac{\mathrm{d}\mathbb{P}^\nu}{\mathrm{d}\mathbb{P}}(\omega)$ (Qian *et al.*, 2019; Lorig, 2019; Hong *et al.*, 2020). Intuitively, RND serves as a re-weighting factor in taking expectation. For an arbitrary random variable $Y(\omega)$ defined on the measurable space $(\Omega, \mathcal{F})$, it's expectation under $\mathbb{P}^\nu$, denoted as $\mathbb{E}^\nu[Y(\omega)]$, can be expressed by the reweighting factor and the previous expectation $\mathbb{E}[\cdot]$,

$$\mathbb{E}^\nu[Y(\omega)] = \mathbb{E}\left[Y(\omega)\frac{\mathrm{d}\mathbb{P}^\nu}{\mathrm{d}\mathbb{P}}(\omega)\right]. \tag{2.21}$$

To have finite and non-negative $\frac{\mathrm{d}\mathbb{P}^\nu}{\mathrm{d}\mathbb{P}}(\omega)$, we need $\mathbb{P}(A) = 0 \Rightarrow \mathbb{P}^\nu(A) = 0$ for all $A \in \mathcal{F}$ such that $\frac{\mathrm{d}\mathbb{P}^\nu}{\mathrm{d}\mathbb{P}}(\omega)$ is finite. If so, we say that $\mathbb{P}$ is *absolutely continuous* w.r.t. $\mathbb{P}^\nu$, denoted as $\mathbb{P} \gg \mathbb{P}^\nu$. If the two measure are absolutely continuous to each other, we say they are *equivalent* in the theory of probability, often written as $\mathbb{P} \sim \mathbb{P}^\nu$. Essentially, two equivalent measures have non-zero and finite RND, *i.e.* $0 < \frac{\mathrm{d}\mathbb{P}^\nu}{\mathrm{d}\mathbb{P}}(\omega) \leq C < \infty$ with some C.

The concepts of CPM and RND are key concepts throughout this thesis: the theory of fluctuating entropy and entropy production in physics (Qian, 2001b; Seifert, 2005; Qian *et al.*, 2019; Yang and Qian, 2020) presented in Part II and the statistical thermodynamics of data infinitum presented in Part III. To have better

grasp of it, we show how to find the RND for several examples below.

The probability of an event $A \in \mathcal{F}$ in the new probability measure is given by the expectation representation shown in Eq. (2.3),

$$\mathbb{P}^{\nu}\{\omega : \omega \in A\} = \mathbb{E}^{\nu}[\mathbb{I}_A(\omega)] = \mathbb{E}\left[\frac{\mathrm{d}\mathbb{P}^{\nu}}{\mathrm{d}\mathbb{P}}(\omega)\mathbb{I}_A(\omega)\right]. \tag{2.22}$$

For Ω that can be 1-1 labeled by $x \in \mathbb{Z}$, we have the RND reduced to the ratio of probability mass functions

$$\frac{\mathrm{d}\mathbb{P}^{\nu}}{\mathrm{d}\mathbb{P}}(\omega) = \frac{P^{\nu}\left[X\left(\omega\right)\right]}{P\left[X\left(\omega\right)\right]} \tag{2.23}$$

since

$$\mathbb{P}^{\nu}\{x : x \in A\} = \sum_{x\in\mathbb{Z}} \mathbb{I}_A(x)\frac{P^{\nu}(x)}{P(x)}P(x) = \mathbb{E}\left[\mathbb{I}_A(x)\frac{P^{\nu}(x)}{P(x)}\right]. \tag{2.24}$$

For Ω that can be 1-1 labeled by $x \in \mathbb{R}$ such as diffusion processes, we have the RND reduced to the ratio of probability density functions

$$\frac{\mathrm{d}\mathbb{P}^{\nu}}{\mathrm{d}\mathbb{P}}(\omega) = \frac{\rho^{\nu}\left[X\left(\omega\right)\right]}{\rho\left[X\left(\omega\right)\right]} \tag{2.25}$$

since

$$\mathbb{P}^{\nu}\{x : x \in A\} = \int_{\mathbb{R}} \mathbb{I}_A(x)\frac{\rho^{\nu}(x)}{\rho(x)}\rho(x)\mathrm{d}x = \mathbb{E}\left[\mathbb{I}_A(x)\frac{\rho^{\nu}(x)}{\rho(x)}\right]. \tag{2.26}$$

In either cases, the RND is obtained from the ratio, which is defined on the codomain of a random variable, with random variables plugged back in (Qian *et al.*, 2019; Yang and Qian, 2020).

2.3.2 Change of Probability Measure for Markov Processes

With the above concepts, we can derive the RND for Markov chains by using the path probability we derived for DTMC and CTMC in Eq. (2.8) and Eq. (2.13). CPM for Markov chains are carried out by the following RNDs. For DTMC, we have from $\mathbb{P}$ to $\tilde{\mathbb{P}}$, we have

$$\frac{\mathrm{d}\tilde{\mathbb{P}}}{\mathrm{d}\mathbb{P}}\left(\omega\right) = \frac{\tilde{P}_0\left(x_0\right)\prod_{t=1}^{T}\tilde{M}_{t|t-1}\left(x_t|x_{t-1}\right)}{P_0\left(x_0\right)\prod_{t=1}^{T}M_{t|t-1}\left(x_t|x_{t-1}\right)} \tag{2.27}$$

where $\omega = x_{0:T}$ for DTMC and

$$\frac{\mathrm{d}\tilde{\mathbb{P}}}{\mathrm{d}\mathbb{P}}\left(\omega\right) = \frac{\tilde{P}_0\left(x_0\right)\prod_{j=1}^{K} e^{\int_{t_{j-1}}^{t_j}\tilde{Q}_t(x_{j-1}|x_{j-1})\mathrm{d}t}\tilde{Q}_{t_j}\left(x_j|x_{j-1}\right)e^{\int_{t_K}^{T}\tilde{Q}_t(x_K|x_K)\mathrm{d}t}}{P_0\left(x_0\right)\prod_{j=1}^{K} e^{\int_{t_{j-1}}^{t_j}Q_t(x_{j-1}|x_{j-1})\mathrm{d}t}Q_{t_j}\left(x_j|x_{j-1}\right)e^{\int_{t_K}^{T}Q_t(x_K|x_K)\mathrm{d}t}} \tag{2.28}$$

where a trajectory ω in CTMC specifies the jump time $t_1 \cdots t_K$ and the states $x_0 \cdots x_K$. They will serve importance roles in our later discussions of the stochastic thermodynamics of Markov processes.

For continuous Markov processes, we consider the CPM that changes the drift of the process. Consider a continuous Markov process X_t described by the FPE $\partial_t p = -\nabla \cdot [\mathbf{b}p - \mathbf{D}\nabla p]$ under the probability measure $\mathbb{P}$ and by the SDE

$$\mathrm{d}\mathbf{X}_t = [\mathbf{b}(\mathbf{X}_t) + \nabla \cdot \mathbf{D}(\mathbf{X}_t)]\,\mathrm{d}t + \mathbf{\Gamma}(\mathbf{X}_t)\,\mathrm{d}\mathbf{W}_t \tag{2.29}$$

where $\mathbf{W}_t$ is a Wiener process under $\mathbb{P}$. Girsanov theorem (Jiang *et al.*, 2004) tells us that if we define a probability measure $\tilde{\mathbb{P}}$ by the following RND,

$$\frac{\mathrm{d}\tilde{\mathbb{P}}}{\mathrm{d}\mathbb{P}}[\mathbf{x}_{0:T}] = \exp\left\{-\int_0^T \mathbf{\Gamma}^{-1}(\mathbf{x}_t)\,\mathbf{b}(\mathbf{x}_t)\cdot\mathrm{d}\mathbf{W}_t - \frac{1}{4}\int_0^T \mathbf{b}(\mathbf{x}_t)\cdot\mathbf{D}^{-1}(\mathbf{x}_t)\,\mathbf{b}(\mathbf{x}_t)\,\mathrm{d}t\right\} \tag{2.30}$$

for paths $\mathbf{x}_{0:T} \in \mathcal{X}^{[0,T]}$, the process $\mathbf{X}_t$ under the new measure $\tilde{\mathbb{P}}$ have probability density $\tilde{p}(\mathbf{x}, t)$ satisfying $\partial_t \tilde{p} = -\nabla \cdot [\mathbf{D}\nabla\tilde{p}]$ and thus have the same statistical properties as a $\mathbf{Y}_t$ under $\mathbb{P}$ described by

$$\mathrm{d}\mathbf{Y}_t = \nabla \cdot \mathbf{D}(\mathbf{Y}_t)\,\mathrm{d}t + \mathbf{\Gamma}(\mathbf{Y}_t)\,\mathrm{d}\mathbf{W}_t. \tag{2.31}$$

This is another example of the equivalence between change-of-probability measure and change of random variable (Qian *et al.*, 2019; Yang and Qian, 2020).

Later, we will consider the difference between $\frac{\mathrm{d}\tilde{\mathbb{P}}}{\mathrm{d}\mathbb{P}}[\mathbf{x}_{0:T}]$ and $\frac{\mathrm{d}\tilde{\mathbb{P}}}{\mathrm{d}\mathbb{P}}[\mathbf{x}_{T:0}]$. It will then be useful for later purposes that we rewrite Eq. (2.30) into one part that is symmetric under such *trajectory reversal* and the other that is anti-symmetric. By using the SDE of $\mathbf{X}_t$ in Eq. (2.29), we plug in $\mathrm{d}\mathbf{W}_t = \mathbf{\Gamma}^{-1}(\mathbf{X}_t)\cdot[\mathrm{d}\mathbf{X}_t - (\mathbf{b} + \nabla\cdot\mathbf{D})\,\mathrm{d}t]$ and get

$$\ln\frac{\mathrm{d}\tilde{\mathbb{P}}}{\mathrm{d}\mathbb{P}}[\mathbf{x}_{0:T}] = -\frac{1}{2}\int_0^T \mathbf{D}^{-1}\mathbf{b}\cdot\mathrm{d}\mathbf{x}_t + \frac{1}{2}\int_0^T \mathbf{D}^{-1}\mathbf{b}\cdot(\nabla\cdot\mathbf{D})\,\mathrm{d}t + \frac{1}{4}\int_0^T \mathbf{b}\cdot\mathbf{D}^{-1}\mathbf{b}\mathrm{d}t \tag{2.32a}$$

$$= -\frac{1}{2}\int_0^T \mathbf{D}^{-1}\mathbf{b}\circ\mathrm{d}\mathbf{x}_t + \frac{1}{2}\int_0^T \nabla\cdot\mathbf{b}\mathrm{d}t + \frac{1}{4}\int_0^T \mathbf{b}\cdot\mathbf{D}^{-1}\mathbf{b}\mathrm{d}t. \tag{2.32b}$$

where $\boldsymbol{f}(\mathbf{x}_t)\circ\mathrm{d}\mathbf{x}_t$ denotes Stratonovich midpoint integration

$$\boldsymbol{f}(\mathbf{x}_t)\circ\mathrm{d}\mathbf{x}_t \coloneqq \boldsymbol{f}\left(\mathbf{x}_t + \frac{1}{2}\mathrm{d}\mathbf{x}_t\right)\cdot\mathrm{d}\mathbf{x}_t = \boldsymbol{f}(\mathbf{x}_t)\cdot\mathrm{d}\mathbf{x}_t + \mathbf{D}\cdot(\nabla\boldsymbol{f})\,\mathrm{d}t \tag{2.33}$$

where we have used the SDE in Eq. (2.29) for the last equality. If $\mathbf{x}_t$ is Lipschitz continuous, *i.e.* $\mathrm{d}\mathbf{x}_t = O(\mathrm{d}t)$, then $\boldsymbol{f}(\mathbf{x}_t)\circ\mathrm{d}\mathbf{x}_t \equiv \boldsymbol{f}(\mathbf{x}_t)\cdot\mathrm{d}\mathbf{x}_t$. Note that the first term in Eq. (2.32b) is anti-symmetric under trajectory reversal $\mathbf{x}_{0:T} \mapsto \mathbf{x}_{T:0}$ and the rest two terms are both symmetric under trajectory reversal.

Specifically, when the value of the (log) RND is

$$\ln \frac{\mathrm{d}\tilde{\mathbb{P}}}{\mathrm{d}\mathbb{P}}\left[\mathbf{x}_{T:0}\right] = \frac{1}{2}\int_0^T \mathbf{D}^{-1}\mathbf{b}\left(\mathbf{x}_t\right) \circ \mathrm{d}\mathbf{x}_t + \frac{1}{2}\int_0^T \nabla\cdot\mathbf{b}\mathrm{d}t + \frac{1}{4}\int_0^T \mathbf{b}\cdot\mathbf{D}^{-1}\mathbf{b}\mathrm{d}t \tag{2.34}$$

when evaluated at the reversed trajectory.

We note here that there are at least two types of (informal) path integral formulations that are consistent with the Girsanov theorem in Eq. (2.32b) . For a diffusion described by the SDE in Eq. (2.29), the two path functionals are as followed:

$$P_{\mathbf{b}}^{\mathrm{Ito}}\left[\mathbf{X}_{0:T}\right] \coloneqq \mathcal{N}\left(\mathbf{D}\right) e^{-\frac{1}{4}\int_0^T \frac{1}{\mathrm{d}t}\left[\mathrm{d}\mathbf{X}_t - \tilde{\mathbf{b}}(\mathbf{X}_t)\mathrm{d}t\right]\cdot\mathbf{D}^{-1}(\mathbf{X}_t)\left[\mathrm{d}\mathbf{X}_t - \tilde{\mathbf{b}}(\mathbf{X}_t)\mathrm{d}t\right]} \tag{2.35}$$

where we have denoted $\tilde{\mathbf{b}} \coloneqq \mathbf{b} + \nabla\cdot\mathbf{D}$ and

$$P_{\mathbf{b}}^{\mathrm{Mid.}}\left[\mathbf{X}_{0:T}\right] \coloneqq \tilde{\mathcal{N}}\left(\mathbf{D}\right) e^{\left\{-\frac{1}{4}\int_0^T \frac{1}{\mathrm{d}t}\left[\mathrm{d}\mathbf{X}_t - \mathbf{b}\left(\bar{\mathbf{X}}_t\right)\mathrm{d}t\right]\cdot\mathbf{D}^{-1}\left(\bar{\mathbf{X}}_t\right)\left[\mathrm{d}\mathbf{X}_t - \mathbf{b}\left(\bar{\mathbf{X}}_t\right)\mathrm{d}t\right] - \frac{1}{2}\int_0^T \nabla\cdot\mathbf{b}\left(\bar{\mathbf{X}}_t\right)\mathrm{d}t\right\}} \tag{2.36}$$

where $\bar{\mathbf{X}}_t \coloneqq \mathbf{X}_t + \frac{1}{2}\mathrm{d}\mathbf{X}_t$. Then, one can show that

$$\frac{\mathrm{d}\tilde{\mathbb{P}}}{\mathrm{d}\mathbb{P}} = \frac{P_0^{\mathrm{Ito}}\left[\mathbf{X}_{0:T}\right]}{P_{\mathbf{b}}^{\mathrm{Ito}}\left[\mathbf{X}_{0:T}\right]} = \frac{P_0^{\mathrm{Mid.}}\left[\mathbf{X}_{0:T}\right]}{P_{\mathbf{b}}^{\mathrm{Mid.}}\left[\mathbf{X}_{0:T}\right]}, \tag{2.37}$$

i.e. both path integrals are consistent with the Girsanov theorem. Notice the similarity between Eq. (2.36) and the Onsager-Machlup function in Eq. (2.20) (Chernyak *et al.*, 2006). However, the former can take non-smooth paths from diffusion but the latter only takes smooth tube as input. We leave the discussion and comparison of the two aforementioned path functionals to future research.

2.4 Summary

This chapter briefly summarizes the mathematical notions and concepts for a probabilistic model of stochastic processes. The standard notion of the triple $(\Omega, \mathcal{F}, \mathbb{P})$ is introduced together with the notion of random variables as observables/measurable functions in Sec. 2.1. In Sec. 2.2, we introduce three types of Markov processes and the time-evolution equations understood as conservation of probability. The importance concept of *probability flux* is introduced. The notion of a steady state of a process is also introduced: a process reaches its steady state when the distribution of state no longer changes in time, *i.e.* the emergence of a time-translational symmetry. The resulting notion of *stationary distribution* will become essential in throughout Part II of the present thesis. Finally, the notion of *Radon-Nikodym derivative* (RND) that characterizes change of probability measure is introduced in Sec. 2.3. As our theory aims to characterize and compare

different statistical properties of a system, the notion of RND is utmost important and will later be related to the generalized notion of entropy and information.

Part II

Time symmetries dictate dynamic principles

Chapter 3

Irreversibility of Stochastic Dynamics

In this chapter, we provide an in-depth look of stochastic dynamics and introduce energetic concepts from the different types of irreversibility in stochastic dynamics. Definition and properties of equilibrium dynamics are introduced in Sec. 3.1. We then discuss different type of time irreversibility in Sec. 3.2. For an arbitrary nonequilibrium dynamics, its adjoint process and underlying equilibrium process are identified in Sec. 3.3.

3.1 Detailed Balance and Landscape

We will start with a time-homogeneous discrete-time Markov chain (DTMC) as a paradigm to illustrate the concepts. Consider a pair of possible system states x and y. If the transition matrix $M(y|x) \coloneqq \mathbb{P}\{X_{t+1} = y|X_t = x\}$ is bigger than $M(x|y)$, then there's a tendency for the system go from state x to state y. This is a tendency, or rather a time irreversibility, defined on each transition. A natural extension of such tendency to the path level is to compare the conditional probability for a forward path $x_{0:T}$

$$\mathbb{P}\{X_{1:T} = x_{1:T}|X_0 = x_0\} = \prod_{t=1}^{T} M(x_t|x_{t-1}) \tag{3.1}$$

to the one for a backward path $x_{T:0}$,

$$\mathbb{P}\{X_{1:T} = x_{T-1:0}|X_0 = x_T\} = \prod_{t=1}^{T} M(x_{t-1}|x_t)\,. \tag{3.2}$$

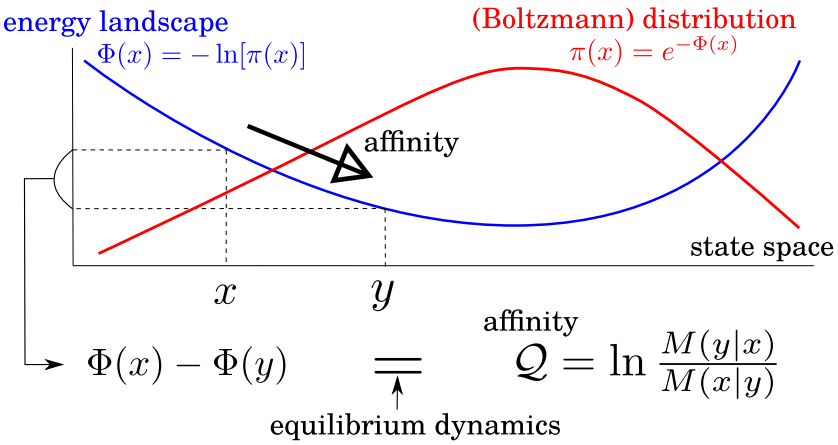


Figure 3.1: Affinity in equilibrium systems is gradient-descending with an energy landscape Φ. In equilibrium systems, the landscape is directly related to the invariant distribution via Boltzmann's law.

Since conditional matrices multiply when expanding in time, the natural quantification of the this conditional time irreversibility is by

$$\mathcal{Q}\left(x_{0:T}\right) := \ln \frac{\mathbb{P}\left\{X_{1:T} = x_{1:T} | X_0 = x_0\right\}}{\mathbb{P}\left\{X_{1:T} = x_{T-1:0} | X_0 = x_T\right\}} = \sum_{t=1}^{T} \ln \frac{M\left(x_t | x_{t-1}\right)}{M\left(x_{t-1} | x_t\right)} = \sum_{t=1}^{T} \mathcal{Q}\left(x_{t-1,t}\right) \tag{3.3}$$

which is additive when connecting time intervals. We shall call this time-additive tendency/time irreversibility as the *affinity*, a term originated from chemistry (Hill, 1977; Nicolis and Prigogine, 1977; Qian *et al.*, 2016b). In overdamped mechanical systems, the affinity corresponds to the entropy production in the environment, which is the heat dissipated by the system divided by the system's temperature (Maes and Netočný, 2003; Sekimoto, 2010; Seifert, 2012). Our theory here is actually not limited to overdamped mechanical systems. We understand the affinity as a conditional time irreversibility, and our theory only relies on time symmetries of stochastic dynamics.

Inspired by the Clausius theorem in thermodynamics (Landau and Lifshitz, 1980; Huang, 1991), we consider whether the nonzero affinity on a pair x and y is solely due to the two states having different "*potential energy*" $\Phi\left(x\right)$ and $\Phi\left(y\right)$ or not. That is, we would like to have $\mathcal{Q}\left(x, y\right) = \Phi\left(x\right) - \Phi\left(y\right)$: if $\Phi\left(x\right) > \Phi\left(y\right)$, then there's a tendency to go from x to y, $\mathcal{Q}\left(x, y\right) > 0$. See Fig. 3.1 for an illustration. However, such "gradient-descending" stochastic dynamics would mean that the affinity of any (closed) cycle

to be zero: for any cyclic path $x_0 x_1 x_2 \cdots x_n x_0$,

$$0 = \ln \frac{M(x_1|x_0) \cdots M(x_n|x_{n-1}) M(x_0|x_n)}{M(x_n|x_0) \cdots M(x_1|x_2) M(x_0|x_1)} \tag{3.4a}$$

$$= [\Phi(x_0) - \Phi(x_1)] + \cdots + [\Phi(x_{n-1}) - \Phi(x_n)] + [\Phi(x_n) - \Phi(x_0)]. \tag{3.4b}$$

This is in fact the Kolmogorov's cycle condition (Kolmogorov, 1936), also known as the Wegscheider condition in chemical kinetics (Wegscheider, 1901; Lewis, 1925) for the concept of *detailed balance*:

$$\pi(x)M(y|x) = \pi(y)M(x|y), \forall x, y \in \mathcal{X} \tag{3.5}$$

where $\pi(x)$ is the stationary distribution (assumed it exists and is unique) of the DTMC. Recall that the invariant distribution π satisfies Eq. (2.9) which can be rewritten as

$$0 = \underbrace{\sum_{y \in \mathcal{X}, y \neq x} \pi(x) M(y|x)}_{\text{total outward flux}} - \underbrace{\sum_{y \in \mathcal{X}, y \neq x} \pi(y) M(x|y)}_{\text{total inward flux}}, \forall x \in \mathcal{X}. \tag{3.6}$$

Since $\pi(x) M(y|x)$ is the probability of a transition from x to y, this equation can be understood as a balance between the total outward probability flux from x, $\sum_{y \in \mathcal{X}, y \neq x} \pi(x) M(y|x)$, and the total inward probability flux, $\sum_{y \in \mathcal{X}, y \neq x} \pi(y) M(x|y)$. Detailed balance condition is saying that the balance is not just on the total level but on every transition. That is, every probability flux on each pair is balanced out, therefore with "detailed" balance. In physics, such steady state with no probability flux is also called *equilibrium* (Landau and Lifshitz, 1980; Huang, 1991). A system with detailed balance steady state is called an equilibrium system.

Eq. (3.5) further implies that, the "potential energy" Φ is actually given by the stochastic entropy (Shannon, 1948; Khinchin, 1957) of the stationary distribution,

$$\ln \frac{M(y|x)}{M(x|y)} = \ln \frac{\pi(y)}{\pi(x)} \Rightarrow \Phi(x) \coloneqq -\ln \pi(x) \tag{3.7}$$

up to irrelevant baseline of the entropy. This is the Boltzmann's law $\pi(x) = e^{-\Phi(x)}$. For equilibrium systems, the affinity $\mathcal{Q}$ is fully described by a scalar function of potential energy as a landscape.

In general, a system will not admit detailed balance. The affinity is no longer solely described by a scalar potential function Φ. Instead, we have, for a general path $x_{0:T}$, a decomposition of the affinity,

$$\mathcal{Q}(x_{0:T}) = \underbrace{[\Phi(x_0) - \Phi(x_T)]}_{\mathcal{Q}_{\text{ex}} = -\Delta\Phi} + \underbrace{\ln \frac{\pi(x_0) \prod_{t=1}^{T} M(x_t|x_{t-1})}{\pi(x_T) \prod_{t=1}^{T} M(x_{t-1}|x_t)}}_{\mathcal{Q}_{\text{hk}}}. \tag{3.8}$$

Following stochastic thermodynamics in physics (Seifert, 2012; Yang and Qian, 2020), the first term that is solely from the landscape is called the *excess heat* (dissipation) $\mathcal{Q}_{\mathrm{ex}}$, and the second term that reflects the breakdown of detailed balance is called the *housekeeping heat* (dissipation) $\mathcal{Q}_{\mathrm{hk}}$. We note that since $\pi(x_0)\prod_{t=1}^{T} M(x_t|x_{t-1})$ is the probability of the path $x_{0:T}$ when the system is at the steady state, the housekeeping heat can be understood as time irreversibility at the steady state

$$\mathcal{Q}_{\mathrm{hk}}[x_{0:T}] = \ln \frac{\mathbb{P}^*\{X_{0:T} = x_{0:T}\}}{\mathbb{P}^*\{X_{0:T} = x_{T:0}\}} \tag{3.9}$$

where probability at the steady state is denoted by $\mathbb{P}^*$. Since $\mathcal{Q}_{\mathrm{hk}} > 0$ implies that the forward path probability is greater than the backward path probability, $\mathbb{P}^*\{X_{0:T} = x_{0:T}\} > \mathbb{P}^*\{X_{0:T} = x_{T:0}\}$, the quantity $\mathcal{Q}_{\mathrm{hk}}$ is thus understood as the energy that is required to break time reversal symmetry of the probability flux at the nonequilibrium steady state (NESS), thus "housekeeping heat".

The probability difference between a forward path and a backward path is crucial for a DTMC to be able perform certain functions in the long term. For example, in many applications in biology and chemistry (Qian, 2007; Qian *et al.*, 2016b), when the system does work and/or causes certain effect in the forward path $x_{0:T}$, *e.g.* march a step for molecular motor, the backward path $x_{T:0}$ will undo the effort. In these cases with $\mathcal{Q}_{\mathrm{hk}} = 0$ for all paths, the system has equal probability to undo any effort. In the long term, no effort can be done on average. It is thus important for a stochastic process to have the non-zero steady state probability flux in NESS to do work in the longer term.

Although $\mathcal{Q}_{\mathrm{hk}}$ as a path observable is in terms of the path probability function at NESS and interpreted as an irreversibility at NESS, it does not mean it is only defined at NESS. From its origin in Eq. (3.8), it gives the extra source in the affinity $\mathcal{Q}$ that is not described by the landscape Φ, no matter the system is in NESS or not. In fact, for nonequilibrium systems, there's always at least one pair of states x and y that has a tendency to go against the landscape Φ, *i.e.* $\mathcal{Q}(x,y) > 0$, $\mathcal{Q}_{\mathrm{hk}}(x,y) > 0$, and $\Phi(x) < \Phi(y)$. It is the housekeeping heat $\mathcal{Q}_{\mathrm{hk}}$ that acts as the energy source, *e.g.* battery, to drive the system to go against the landscape Φ.

3.2 Irreversibility in Stochastic Dynamics

3.2.1 Time-homogeneous Markov Chains

In the last section, we introduced the housekeeping heat $\mathcal{Q}_{\mathrm{hk}}$ which reflects the time-reversal symmetry breaking in terms of the probability flux at the steady state. Specifically, for nonequilibrium systems, the probability flux is nonzero when the system reaches the steady state and the affinity $\mathcal{Q}$ for these systems can not be solely described by a scalar landscape $\Phi \coloneqq -\ln \pi$. For general systems of DTMC that has a steady state described by π, there's yet another obvious breakdown of time-reversal symmetry: the relaxation to steady state. For a system started at a non-stationary distribution $P_0(x) \neq \pi(x)$, the distribution evolves according to the local conservation of probability:

$$P_{t+1}(y) = \sum_{x \in \mathcal{X}} P_t(x) M(y|x). \tag{3.10}$$

The system eventually will reach a steady state $P \to \pi$ in the long term. The deviation from the steady state can be quantified by the stochastic relative entropy (Kullback and Leibler, 1951),

$$F_t(x) = \ln \frac{P_t(x)}{\pi(x)} = \Phi(x) - S_t(x) \tag{3.11}$$

where Φ is the energy and $S_t(x) = -\ln p_t(x)$ is the entropy. For systems with detailed balance, the sum of this fluctuating relative entropy F_t and the standard notion of free energy defined in classical equilibrium thermodynamics was called *nonequilibrium free energy* in (Parrondo *et al.*, 2015). Therefore, the relative entropy F_t got a name *non-steady-state addition* (to free energy) in (Riechers and Crutchfield, 2017). It was also called *exergy* in (Altaner, 2017) and in our previous work (Yang and Qian, 2020). Here, as Qian (2001c) has showed that this relative entropy itself could be understood physically as a "free energy" as well, we will follow Qian (2001c) and call F_t the free energy in this thesis[1].

It can be shown that its expectation approach to zero monotonically

$$\mathbb{E}[\delta F_t] \coloneqq \mathbb{E}[F_{t+1}(X_{t+1}) - F_t(X_t)] \leq 0 \tag{3.12}$$

with equality holds if and only if the system is at steady state $P_{t+1} = P_t = \pi$. The monotonicity of the decay gives "an arrow of time" for the transient dynamics and is termed as "the second law of thermodynamics"

[1] Later, in Part III, there's another notion of "free energy" in the statistical thermodynamics formulated there. These two notions are not the same. Historically, this is because both of these two notions are extensions of the free energy in standard thermodynamics. Let's slightly abuse this term and just keep in mind that the entropy and free energy in stochastic thermodynamics here and in statistical thermodynamics in Part III are different (but related) concepts.

for Markov processes by some (Cover and Thomas, 2006). Interpreting F_t as a free energy, this means that Markov processes always have non-negative average free energy dissipation. However, we note that this irreversibility shows up in both equilibrium and non-equilibrium systems. It is a property of a non-stationary process and is also about the break-down of time translational symmetry in P_t. This "second law" is not the full story as it doesn't include the housekeeping heat $\mathcal{Q}_{\mathrm{hk}}$, which actually is more relevant in the long term.

We now see that a nonequilibrium system has two types of time irreversibility: one is the monotonic relaxation to the steady state quantified by the free energy dissipation $-\Delta F\left(x_{0:T}\right) \coloneqq F_0(x_0) - F_T\left(x_T\right)$ and the other is the nonzero stationary probability flux quantified by the housekeeping heat $\mathcal{Q}_{\mathrm{hk}}$. Beautifully, the sum of the two irreversibility actually composed a notion of total irreversibility as shown in the expression in Eq. (3.13b),

$$\mathcal{S}_{\mathrm{tot}}\left(x_{0:T}\right) = -\Delta F\left(x_{0:T}\right) + \mathcal{Q}_{\mathrm{hk}}\left(x_{0:T}\right) \tag{3.13a}$$

$$= \ln \frac{P_0\left(x_0\right) \prod_{t=1}^{T} M\left(x_t | x_{t-1}\right)}{P_T\left(x_T\right) \prod_{t=1}^{T} M\left(x_{t-1} | x_t\right)} \tag{3.13b}$$

$$= \Delta S\left(x_{0:T}\right) + \mathcal{Q}\left(x_{0:T}\right) \tag{3.13c}$$

where $\Delta S\left(x_{0:T}\right) = S_T\left(x_T\right) - S_0\left(x_0\right) = \left[-\ln p_T\left(x_T\right)\right] - \left[-\ln p_0\left(x_0\right)\right]$. Due to the last expression, this notion of total irreversibility is also understood as the *total entropy production* in physics (Ge, 2009; Esposito and Van den Broeck, 2010; Seifert, 2012). It is the sum of the entropy change in the system ΔS and the dissipated heat $\mathcal{Q}$ understood as the entropy change of the environment. It can be shown that all $\mathcal{S}_{\mathrm{tot}}$, $-\Delta F$, and $\mathcal{Q}_{\mathrm{hk}}$ have non-negative expected values (see Chap. 4). This mathematically shows that $-\Delta F_t$ and $\mathcal{Q}_{\mathrm{hk}}$ represents two disjoint sources of irreversibility of the total $\mathcal{S}_{\mathrm{tot}}$, as we have seen conceptually in our discussion above. Here we note a recent study showing rigorously how the housekeeping heat $\mathcal{Q}_{\mathrm{hk}}$ in a compact, driven process can be mapped to the free energy dissipation of a lifted, detailed-balanced process (Wang and Qian, 2020). It is possible that all $\mathcal{Q}_{\mathrm{hk}}$ could be understood as $-\Delta F$ of some sort, *cf.* conversion between electric field and magnetic field under different coordinates.

3.2.2 Time-inhomogeneous Markov Chains

For time-inhomogeneous processes, the transition matrix changes with time

$$M_t(y|x) \coloneqq P\left(X_t = y | X_{t-1} = x\right). \tag{3.14}$$

Following the same concept as above, the affinity of a path is the sum of the affinity at each time step. We will have, for time-inhomogeneous processes the path affinity as

$$\mathcal{Q}\left(x_{0:T}\right)=\sum_{t=1}^{T}\ln\frac{M_t\left(x_t|x_{t-1}\right)}{M_t\left(x_{t-1}|x_t\right)}. \tag{3.15}$$

From the physics concept of total entropy production $\mathcal{S}_{\mathrm{tot}}$, we have

$$\mathcal{S}_{\mathrm{tot}}\left(x_{0:T}\right)=\Delta S\left(x_{0:T}\right)+\mathcal{Q}\left(x_{0:T}\right)=\ln\frac{p_0\left(x_0\right)\prod_{t=1}^{T}M_t\left(x_t|x_{t-1}\right)}{p_T\left(x_T\right)\prod_{t=1}^{T}M_t\left(x_{t-1}|x_t\right)}. \tag{3.16}$$

The landscape $\Phi:=-\ln\pi_t$ is now time-dependent because M_t is time-dependent. The change in the potential energy landscape of the path $x_{0:T}$ then has two parts

$$\begin{aligned}\Delta\Phi\left(x_{0:T}\right)&=\Phi_T(x_T)-\Phi_0(x_0)\\&=\underbrace{\sum_{t=1}^{T}\left[\Phi_t\left(x_{t-1}\right)-\Phi_{t-1}\left(x_{t-1}\right)\right]}_{\mathcal{W}_{\mathrm{ex}}}+\underbrace{\sum_{t=1}^{T}\left[\Phi_t\left(x_t\right)-\Phi_t\left(x_{t-1}\right)\right]}_{-\mathcal{Q}_{\mathrm{ex}}}.\end{aligned} \tag{3.17}$$

The former term $\mathcal{W}_{\mathrm{ex}}$ is the change in the energy landscape Φ_t due to the change in dynamical rules (the transition matrices), which is often called the *excess work* done on the system. The latter is the same notion of *excess heat* (dissipation) $\mathcal{Q}_{\mathrm{ex}}$ that is the energy change due to the transition of state. Note that the decomposition of affinity $\mathcal{Q}=\mathcal{Q}_{\mathrm{ex}}+\mathcal{Q}_{\mathrm{hk}}$ can be done on each step although M_t is now time-dependent. The path housekeeping heat is simply the sum of housekeeping heat at each step,

$$\mathcal{Q}_{\mathrm{hk}}\left(x_{0:T}\right)=\sum_{t=1}^{T}\ln\frac{\pi_t\left(x_{t-1}\right)M_t\left(x_t|x_{t-1}\right)}{\pi_t\left(x_t\right)M_t\left(x_{t-1}|x_t\right)}. \tag{3.18}$$

The decomposition of $\mathcal{S}_{\mathrm{tot}}$ into two types of irreversibility sources are then

$$\mathcal{S}_{\mathrm{tot}}=\left(\mathcal{W}_{\mathrm{ex}}-\Delta F\right)+\mathcal{Q}_{\mathrm{hk}} \tag{3.19}$$

where $\Delta F=F(x_t,t)-F(x_0,0)=\ln\frac{p_t(x_t)}{\pi_t(x_t)}-\ln\frac{p_0(x_0)}{\pi_0(x_0)}$. The term $\left(\mathcal{W}_{\mathrm{ex}}-\Delta F\right)$ is called the *non-adiabatic entropy production* and denoted as $\mathcal{S}_{\mathrm{na}}$ in stochastic thermodynamics (Esposito and Van den Broeck, 2010). As $\mathcal{Q}_{\mathrm{hk}}=0$ when the system is equilibrium, we will have $\mathcal{S}_{\mathrm{tot}}\equiv\mathcal{S}_{\mathrm{na}}$ if all the M_t admit detailed balance $\forall t$.

3.2.3 Continuous Markov Processes (Diffusion)

The energetics we introduced above for DTMC can be extended to CTMC following the same concepts rather straightforwardly (Ge and Qian, 2010). Here, we instead focus on continuous-time continuous-space Markov processes (diffusion). The notion of affinity in diffusion can be derived in various ways (Lebowitz and Spohn, 1999; Yang and Qian, 2020), here we present the most conceptually straightforward one. Recall that detailed balance condition is zero probability flux at the steady state. For time-homogeneous diffusion, according to Eq. (2.19), this becomes

$$\mathbf{J}^{*}\left(\mathbf{x}\right)=\mathbf{b}\left(\mathbf{x}\right)\pi\left(\mathbf{x}\right)-\mathbf{D}\left(\mathbf{x}\right)\nabla\pi\left(\mathbf{x}\right)=0 \tag{3.20}$$

which tells us that

$$\mathbf{D}^{-1}\mathbf{b}\left(\mathbf{x}\right)=-\nabla\Phi\left(\mathbf{x}\right) \tag{3.21}$$

where $\Phi\left(\mathbf{x}\right)\coloneqq-\ln\pi\left(\mathbf{x}\right)$ is again the potential energy landscape. This tells us that in a diffusion, the affinity of one infinitesimal step $\mathrm{d}\mathbf{x}$ is

$$đ\mathcal{Q}\left(\mathbf{x}\right)=\mathbf{D}^{-1}\mathbf{b}\left(\mathbf{x}\right)\circ\mathrm{d}\mathbf{x}=-\nabla\Phi\left(\mathbf{x}\right)\circ\mathrm{d}\mathbf{x} \tag{3.22}$$

where $\circ$ denotes Stratonovich midpoint integration defined in Eq. (2.33). Note the important distinction between d and $đ$. Infinitesimal change of a function $A(\mathbf{X}_t,t)$ is

$$\mathrm{d}A\left(\mathbf{X}_t,t\right)\coloneqq A(\mathbf{X}_{t+\mathrm{d}t},t+\mathrm{d}t)-A(\mathbf{X}_t,t)=\partial_t A\left(\mathbf{X}_t,t\right)\mathrm{d}t+\nabla A\left(\mathbf{X}_t,t\right)\circ\mathrm{d}\mathbf{X}_t. \tag{3.23}$$

But there is no such a function for a general time-additive work-like quantity $đ\mathcal{B}$. The latter represents work against a non-conservative force, or a "source" term. Any calligraphic letter in the present work is a work-like quantity in this thesis.

For equilibrium systems, the affinity of a path is the sum of all the steps

$$\mathcal{Q}\left(\mathbf{x}_{0:T}\right)=\int_0^T đ\mathcal{Q}=\int_0^T\left(-\nabla\Phi\right)\circ\mathrm{d}\mathbf{x}_t=\int_0^T\mathbf{D}^{-1}\mathbf{b}\left(\mathbf{x}_t\right)\circ\mathrm{d}\mathbf{x}_t=\Phi\left(\mathbf{x}_0\right)-\Phi\left(\mathbf{x}_T\right). \tag{3.24}$$

For nonequilibrium systems, the affinity is still given by (Lebowitz and Spohn, 1999; Yang and Qian, 2020)

$$\mathcal{Q}\left(\mathbf{x}_{0:T}\right)=\int_0^T đ\mathcal{Q}=\int_0^T\mathbf{D}^{-1}\mathbf{b}\left(\mathbf{x}_t\right)\circ\mathrm{d}\mathbf{x}_t. \tag{3.25}$$

Since the steady-state probability flux is nozero $\mathbf{J}^* \neq 0$ for nonequilibrium systems, we have

$$\mathcal{Q}\left(\mathbf{x}_{0:T}\right) = \underbrace{\int_0^T \left(-\nabla\Phi\right) \circ \mathrm{d}\mathbf{x}_t}_{\mathcal{Q}_{\mathrm{ex}}} + \underbrace{\int_0^T \left(\mathbf{D}^{-1}\frac{\mathbf{J}^*}{\pi}\right) \circ \mathrm{d}\mathbf{x}_t}_{\mathcal{Q}_{\mathrm{hk}}}. \tag{3.26}$$

This tells us the notion of $\mathcal{Q}_{\mathrm{ex}}$ and $\mathcal{Q}_{\mathrm{hk}}$ on a diffusion path. Note that since $\mathbf{J}^*$ is stationary probability flux and π is stationary probability, we can introduce a notion of "stationary probability velocity" as

$$\mathbf{v}^* \coloneqq \frac{\mathbf{J}^*}{\pi}. \tag{3.27}$$

The housekeeping heat of a diffusion path is then $\mathcal{Q}_{\mathrm{hk}} = \int_0^T \left(\mathbf{D}^{-1}\frac{\mathbf{J}^*}{\pi}\right) \circ \mathrm{d}\mathbf{x}_t = \int_0^T \left(\mathbf{D}^{-1}\mathbf{v}^*\right) \circ \mathrm{d}\mathbf{x}_t$ which is clearly zero if $\mathbf{J}^* = 0$.

Denoting the stochastic entropy in diffusion as $S\left(\mathbf{x}\right) = -\ln p\left(\mathbf{x}, t\right)$. The total entropy production of a diffusion path is then

$$\begin{aligned}
\mathcal{S}_{\mathrm{tot}} &= \Delta S + \mathcal{Q} && \text{(3.28a)}\\
&= \left[\int_0^T \partial_t S \mathrm{d}t + \int_0^T \nabla S \circ \mathrm{d}\mathbf{x}_t\right] + \int_0^T \mathbf{D}^{-1}\mathbf{b}\left(\mathbf{x}_t\right) \circ \mathrm{d}\mathbf{x}_t && \text{(3.28b)}\\
&= \int_0^T \partial_t S \mathrm{d}t + \int_0^T \mathbf{D}^{-1}\mathbf{v}\left(\mathbf{x}_t, t\right) \circ \mathrm{d}\mathbf{x}_t && \text{(3.28c)}\\
&= -\Delta F + \mathcal{Q}_{\mathrm{hk}} && \text{(3.28d)}
\end{aligned}$$

where the *free energy* F is $\Phi - S$ and the (non-stationary) probability velocity is defined as

$$\mathbf{v}\left(\mathbf{x}_t, t\right) \coloneqq \frac{\mathbf{J}\left(\mathbf{x}, t\right)}{p\left(\mathbf{x}, t\right)} \tag{3.29}$$

with the (non-stationary) probability flux

$$\mathbf{J}\left(\mathbf{x}, t\right) \coloneqq \mathbf{b}\left(\mathbf{x}\right) p\left(\mathbf{x}, t\right) - \mathbf{D}\left(\mathbf{x}\right) \nabla p\left(\mathbf{x}, t\right). \tag{3.30}$$

The irreversibility decomposition of $\mathcal{S}_{\mathrm{tot}} = -\Delta F + \mathcal{Q}_{\mathrm{hk}}$ is directly related to the affinity decomposition $\mathcal{Q} = -\Delta\Phi + \mathcal{Q}_{\mathrm{hk}}$ and thus the vector field decomposition (Wang *et al.*, 2008) as well. From the affinity decomposition $\mathcal{Q} = \mathcal{Q}_{\mathrm{ex}} + \mathcal{Q}_{\mathrm{hk}}$, we have

$$\mathbf{b} = -\mathbf{D}\nabla\Phi + \mathbf{v}^*. \tag{3.31}$$

Moreover, this leads to a less-known probability flux decomposition (Yang and Cheng, 2021)

$$\mathbf{J} = -p\mathbf{D}\nabla F + p\mathbf{v}^*. \tag{3.32}$$

This gives a decomposition of the FPE of diffusion (Qian, 2013, 2014b, 2015; Yang and Cheng, 2021):

$$\partial_t p = -\nabla \cdot (p\mathbf{v}^*) - \nabla \cdot [p\,(-\mathbf{D}\nabla F)]\,. \tag{3.33}$$

The former on the right-hand-side of Eq. (3.33) corresponds to the Liouville equation

$$\partial_t p = -\nabla \cdot (p\mathbf{v}^*) \tag{3.34}$$

of a measure-preserving deterministic dynamical system $\mathbf{x}'(t) = \mathbf{v}^*(\mathbf{x})$ with $e^{-\Phi}$ as an invariant measure. The latter corresponds to a detailed-balanced diffusion process with the same invariant density $e^{-\Phi}$ described by

$$\partial_t p = -\nabla \cdot [p\,(-\mathbf{D}\nabla F)]\,. \tag{3.35}$$

That is, every diffusion process can be regarded as a deterministic dynamical system coupled with the "randomly-damping", detailed-balanced environment (Qian, 2014b, 2015). We note that $e^{-\Phi}$ is the invariant measure *before* and *after* the coupling between Eq. (3.34) and Eq. (3.35). This is considered as a generalization of *the zeroth law of thermodynamics* by Qian (2014b). From a potential theory perspective, for equilibrium systems, both $\mathbf{b}$ and $\mathbf{J}$ are gradient-descending-like, with landscape Φ and F.

3.3 Adjoint Process and Underlying Equilibrium

3.3.1 Continuous Markov Processes

From the decomposition of $\mathbf{b}$ and $\mathbf{J}$ above in Eqs. (3.31) and (3.32), it is clear that $(\mathbf{b}, \mathbf{D}) = (-\mathbf{D}\nabla\Phi, \mathbf{D})$ defines an equilibrium process underlying the nonequilibrium process defined by $(\mathbf{b}, \mathbf{D}) = (-\mathbf{D}\nabla\Phi + \mathbf{v}^*, \mathbf{D})$. The underlying equilibrium process shares the same stationary probability π and potential energy landscape Φ. The RND between the two processes can be found by using the Girsanov theorem shown in Eq. (2.32b), by comparing both of them with the process $(\mathbf{b}, \mathbf{D}) = (\mathbf{0}, \mathbf{D})$. Denoting $\mathbb{P}_{\mathbf{b}}$ as the measure that gives the process $\mathbf{X}_t$ a FPE $\partial_t p = -\nabla \cdot [\mathbf{b}p - \mathbf{D}\nabla p]$, we compute

$$\frac{\mathrm{d}\mathbb{P}_{-\mathbf{D}\nabla\Phi+\mathbf{v}^*}}{\mathrm{d}\mathbb{P}_{-\mathbf{D}\nabla\Phi}} = \frac{\mathrm{d}\mathbb{P}_{-\mathbf{D}\nabla\Phi+\mathbf{v}^*}}{\mathrm{d}\mathbb{P}_{\mathbf{0}}} \frac{\mathrm{d}\mathbb{P}_{\mathbf{0}}}{\mathrm{d}\mathbb{P}_{-\mathbf{D}\nabla\Phi}}. \tag{3.36}$$

For simplicity, let's denote $\mathbf{a} = -\mathbf{D}\nabla\Phi$ and $\mathbf{b} = -\mathbf{D}\nabla\Phi + \mathbf{v}^*$. Recall that in Eq.(2.32b), we had

$$\frac{\mathrm{d}\mathbb{P}_{\mathbf{0}}}{\mathrm{d}\mathbb{P}_{\mathbf{b}}}(\mathbf{x}_{0:T}) = \exp\left\{-\frac{1}{2}\int_0^T \mathbf{D}^{-1}\mathbf{b}\,(\mathbf{x}_t) \circ \mathrm{d}\mathbf{x}_t + \frac{1}{2}\int_0^T \nabla\cdot\mathbf{b}\mathrm{d}t + \frac{1}{4}\int_0^T \mathbf{b}\cdot\mathbf{D}^{-1}\mathbf{b}\mathrm{d}t\right\}. \tag{3.37}$$

This then leads to

$$\frac{\mathrm{d}\mathbb{P}_{\mathbf{b}}}{\mathrm{d}\mathbb{P}_{\mathbf{0}}}\left(\mathbf{x}_{0:T}\right)=\exp\left\{\frac{1}{2}\int_0^T\mathbf{D}^{-1}\mathbf{b}\left(\mathbf{x}_t\right)\circ\mathrm{d}\mathbf{x}_t-\frac{1}{2}\int_0^T\nabla\cdot\mathbf{b}\mathrm{d}t-\frac{1}{4}\int_0^T\mathbf{b}\cdot\mathbf{D}^{-1}\mathbf{b}\mathrm{d}t\right\}. \tag{3.38a}$$

$$\frac{\mathrm{d}\mathbb{P}_{\mathbf{0}}}{\mathrm{d}\mathbb{P}_{\mathbf{a}}}\left(\mathbf{x}_{0:T}\right)=\exp\left\{-\frac{1}{2}\int_0^T\mathbf{D}^{-1}\mathbf{a}\left(\mathbf{x}_t\right)\circ\mathrm{d}\mathbf{x}_t+\frac{1}{2}\int_0^T\nabla\cdot\mathbf{a}\mathrm{d}t+\frac{1}{4}\int_0^T\mathbf{a}\cdot\mathbf{D}^{-1}\mathbf{a}\mathrm{d}t\right\}. \tag{3.38b}$$

then

$$\ln\frac{\mathrm{d}\mathbb{P}_{\mathbf{b}}}{\mathrm{d}\mathbb{P}_{\mathbf{a}}}=\frac{1}{2}\int_0^T\mathbf{D}^{-1}\left(\mathbf{b}-\mathbf{a}\right)\circ\mathrm{d}\mathbf{x}_t-\frac{1}{2}\int_0^T\nabla\cdot\left(\mathbf{b}-\mathbf{a}\right)\mathrm{d}t-\frac{1}{4}\int_0^T\left(\mathbf{b}-\mathbf{a}\right)\cdot\mathbf{D}^{-1}\left(\mathbf{b}+\mathbf{a}\right)\mathrm{d}t. \tag{3.39}$$

Now, using $\mathbf{a}=-\mathbf{D}\nabla\Phi$ and $\mathbf{b}=-\mathbf{D}\nabla\Phi+\mathbf{v}^*$, the above equation simplifies into

$$\ln\frac{\mathrm{d}\mathbb{P}_{\mathbf{b}}}{\mathrm{d}\mathbb{P}_{\mathbf{a}}}=\frac{1}{2}\int_0^T\mathbf{D}^{-1}\mathbf{v}^*\circ\mathrm{d}\mathbf{x}_t-\frac{1}{2}\int_0^T\nabla\cdot\mathbf{v}^*\mathrm{d}t-\frac{1}{4}\int_0^T\mathbf{v}^*\cdot\mathbf{D}^{-1}\left(-2\mathbf{D}\nabla\Phi+\mathbf{v}^*\right)\mathrm{d}t \tag{3.40a}$$

$$=\frac{1}{2}\int_0^T\mathbf{D}^{-1}\mathbf{v}^*\circ\mathrm{d}\mathbf{x}_t+\frac{1}{2}\int_0^T\left(\mathbf{v}^*\cdot\nabla\Phi-\nabla\cdot\mathbf{v}^*\right)\mathrm{d}t-\frac{1}{4}\int_0^T\mathbf{v}^*\cdot\mathbf{D}^{-1}\mathbf{v}^*\mathrm{d}t \tag{3.40b}$$

Since $\nabla\cdot\mathbf{J}^*=0\Rightarrow\nabla\cdot\mathbf{v}^*=\mathbf{v}^*\cdot\nabla\Phi$, we finally arrive

$$\ln\frac{\mathrm{d}\mathbb{P}_{-\mathbf{D}\nabla\Phi+\mathbf{v}^*}}{\mathrm{d}\mathbb{P}_{-\mathbf{D}\nabla\Phi}}\left(\mathbf{x}_{0:T}\right)=\underbrace{\frac{1}{2}\int_0^T\mathbf{D}^{-1}\mathbf{v}^*\circ\mathrm{d}\mathbf{x}_t}_{\mathcal{Q}_{\mathrm{hk}}}-\frac{1}{4}\int_0^T\mathbf{v}^*\cdot\mathbf{D}^{-1}\mathbf{v}^*\mathrm{d}t. \tag{3.41}$$

We note that the logarithm of the RND has an anti-symmetric part given by the housekeeping heat $\mathcal{Q}_{\mathrm{hk}}$ and a symmetric part $\frac{1}{4}\int\mathbf{v}^*\cdot\mathbf{D}^{-1}\mathbf{v}^*\mathrm{d}t$. Baiesi and Maes (2018); Maes (2020) called this symmetric part the *excess of frenesy* and has been advocating the physics of this "symmetric part" as the complementary side of usual stochastic thermodynamics (Seifert, 2012; Yang and Qian, 2020). Informally, this means if we understood $\mathrm{d}\mathbb{P}_{-\mathbf{D}\nabla\Phi+\mathbf{v}^*}\left(\mathbf{x}_{0:T}\right)$ as the path probability of a path $\mathbf{x}_{0:T}$ in the nonequilibrium process $\mathrm{d}\mathbb{P}_{\mathrm{neq}}$, then we have

$$\mathrm{d}\mathbb{P}_{\mathrm{neq}}\left(\mathbf{x}_{0:T}\right)=\mathrm{d}\mathbb{P}_{\mathrm{eq}}\left(\mathbf{x}_{0:T}\right)e^{\frac{1}{2}\mathcal{Q}_{\mathrm{hk}}-\frac{1}{4}\int\mathbf{v}^*\cdot\mathbf{D}^{-1}\mathbf{v}^*\mathrm{d}t} \tag{3.42}$$

where $\mathbb{P}_{\mathrm{neq}}\coloneqq\mathrm{d}\mathbb{P}_{-\mathbf{D}\nabla\Phi+\mathbf{v}^*}$ and $\mathbb{P}_{\mathrm{eq}}\coloneqq\mathbb{P}_{-\mathbf{D}\nabla\Phi}$.

From Eq. (3.41), it is clear that the housekeeping heat $\mathcal{Q}_{\mathrm{hk}}$ can be expressed as a logarithm RND between two probability measures

$$\mathcal{Q}_{\mathrm{hk}}=\ln\frac{\mathrm{d}\mathbb{P}_{-\mathbf{D}\nabla\Phi+\mathbf{v}^*}}{\mathrm{d}\mathbb{P}_{-\mathbf{D}\nabla\Phi-\mathbf{v}^*}}. \tag{3.43}$$

The two processes (the process under the measure $\mathbb{P}_{-\mathbf{D}\nabla\Phi+\mathbf{v}^*}$ and under the measure $\mathbb{P}_{-\mathbf{D}\nabla\Phi-\mathbf{v}^*}$) have reversed net stationary probability flux $\mathbf{J}^*$ and velocity $\mathbf{v}^*$ to each other: they form an adjoint pair. Therefore, the process that has a reversed stationary probability flux to a process is often called the *adjoint process* or the

dual process (Seifert, 2012; Yang and Qian, 2020; Yang and Cheng, 2021). If we denote $\mathbb{P} := \mathbb{P}_{-\mathbf{D}\nabla\Phi+\mathbf{v}^*}$, its adjoint process is represented by the probability measure denoted as $\mathbb{P}^\dagger := \mathbb{P}_{-\mathbf{D}\nabla\Phi-\mathbf{v}^*}$. The housekeeping heat is thus simply denoted as

$$\mathcal{Q}_{\rm hk} = \ln \frac{\mathrm{d}\mathbb{P}}{\mathrm{d}\mathbb{P}^\dagger} \tag{3.44}$$

as a logarithm of path RND, a generalized notion of relative entropy (Kullback and Leibler, 1951; Yang and Qian, 2020). We will actually see in the Sec. 4.2 that the other two types of irreversibility $\mathcal{S}_{\rm tot}$ and $-\Delta F$ (or more generally $\mathcal{S}_{\rm na} = \mathcal{W}_{\rm ex} - \Delta F$ for time-inhomogeneous processes) are also general path relative entropy.

3.3.2 Discrete-time Markov Chain

Note that the underlying equilibrium process $\mathbb{P}_{\rm eq}$ identified above for diffusion processes for both $\mathbb{P}$ and $\mathbb{P}^\dagger$ is given by the algebraic average of probability flux $\mathbf{J} = -p\mathbf{D}\nabla F + p\mathbf{v}^*$ and $\mathbf{J}^\dagger = -p\mathbf{D}\nabla F - p\mathbf{v}^*$,

$$\mathbf{J}_{\rm eq} = \frac{\mathbf{J} + \mathbf{J}^\dagger}{2} = -p\mathbf{D}\nabla F. \tag{3.45}$$

Following the same concept, we can identify the corresponding underlying equilibrium for Markov chains. We first recall the (net) stationary probability flux for DTMC is given by

$$J^*(x,y) = \pi(x) M(y|x) - \pi(y) M(x|y). \tag{3.46}$$

The adjoint process will be given by replacing the transition matrix M with its adjoint

$$M^\dagger(y|x) := \frac{\pi(y)}{\pi(x)} M(x|y). \tag{3.47}$$

One can easily show that $\left(J^\dagger\right)^*(x,y) := \pi(x) M^\dagger(y|x) - \pi(y) M^\dagger(x|y) = -J^*(x,y)$. Then, we can show that the underlying equilibrium process is specified by the probability flux

$$J^*_{\rm eq}(x,y) = \frac{J^*(x,y) + \left(J^\dagger\right)^*(x,y)}{2} \tag{3.48}$$

and thus by the transition matrix

$$M_{\rm eq}(y|x) = \frac{M(y|x) + M^\dagger(y|x)}{2}. \tag{3.49}$$

One can easily check that $\pi(x)$ is still the stationary distribution of the detailed balanced M_{eq}. With the notion of "stationary probability velocity" defined in DTMC as well

$$v^*(x,y) \coloneqq \frac{J^*(x,y)}{\pi(x)} = M(y|x) - M^\dagger(y|x), \tag{3.50}$$

we have the DTMC's version of the decomposition $\mathbf{J} = -p\mathbf{D}\nabla F + p\mathbf{v}^*$ as

$$p(x,t)\, M(y|x) = p(x,t)\, M_{\mathrm{eq}}(y|x) + \frac{1}{2} p(x,t)\, v^*(x,y). \tag{3.51}$$

Moreover, since we have an alternative expression

$$M(y|x) = M_{\mathrm{eq}}(y|x)\, \frac{e^{\mathcal{Q}_{\mathrm{hk}}(x,y)/2}}{\cosh\left(\mathcal{Q}_{\mathrm{hk}}(x,y)/2\right)} \tag{3.52}$$

where $\mathcal{Q}_{\mathrm{hk}}(x,y) = \ln \frac{\pi(x)M(y|x)}{\pi(y)M(x|y)}$ is the housekeeping heat in one step, we have the DTMC's equivalence of Eq. (3.41) as

$$\ln \frac{\mathrm{d}\mathbb{P}_{\mathrm{neq}}}{\mathrm{d}\mathbb{P}_{\mathrm{eq}}} = \ln \frac{P_0(x_0)\prod_{t=1}^T M(x_t|x_{t-1})}{P_0(x_0)\prod_{t=1}^T M_{\mathrm{eq}}(x_t|x_{t-1})} = \frac{1}{2}\mathcal{Q}_{\mathrm{hk}} - \sum_{t=1}^T \ln\cosh\left[\frac{\mathcal{Q}_{\mathrm{hk}}(x_{t-1},x_t)}{2}\right] \tag{3.53}$$

The latter term in Eq. (3.53) corresponds to $\frac{1}{4}\int \mathbf{v}^* \cdot \mathbf{D}^{-1}\mathbf{v}^* \mathrm{d}t$ in diffusion, symmetric under trajectory reversal and under the adjoint process reversal of $\mathbf{v}^*$. We will leave the discussion of its physical meanings to future studies, as discussed in Sec. 10.2.

3.4 Summary and Discussion

In this chapter, we motivate the introduction of thermodynamic notions from considering the time-additive irreversibility of conditional probabilities, known as *affinity* $\mathcal{Q}$. In equilibrium systems, the affinity is fully described by an energy landscape Φ that satisfies the Boltzmann law. In nonequilibrium systems, the housekeeping heat $\mathcal{Q}_{\mathrm{hk}}$ is introduced as the energy needed to sustain the nonzero probability flux in nonequilibrium systems. Together with the irreversible relaxation quantified by the free energy dissipation $-\Delta F_t$, the concept of total irreversibility $\mathcal{S}_{\mathrm{tot}}$ is introduced as the sum of the two disjoint sources of irreversibilities, $\mathcal{Q}_{\mathrm{hk}}$ and $-\Delta F_t$. This irreversibility decomposition leads to thermodynamic meaningful decomposition of the stochastic dynamics. See Fig. 3.2 for a summary. The concept of energy landscape Φ and the housekeeping heat $\mathcal{Q}_{\mathrm{hk}}$ further lead to the adjoint process and the underlying equilibrium process of a general nonequilibrium process, for both Markov chains and diffusion. In our introduction, all of the above notions are introduced naturally by considering time reversal symmetries in a stochastic dynamics. The *local*

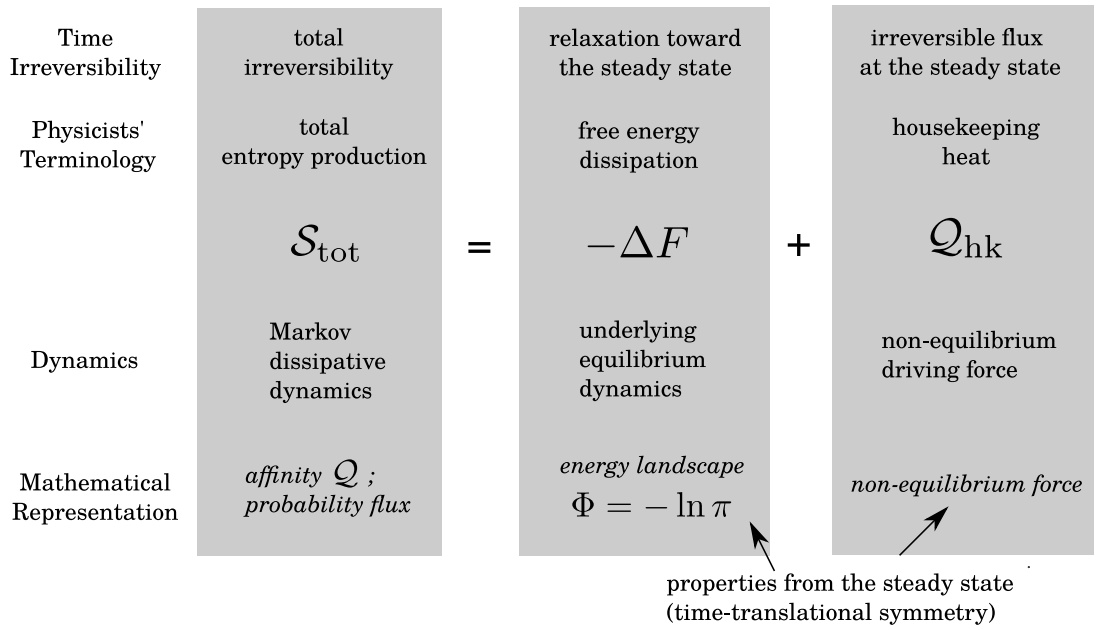


Figure 3.2: Summary of dynamic decomposition indicated by the irreversibility decomposition.

equilibrium assumption (Groot and Mazur, 2011) are not required in the formalism of the general theory. It is only needed when one aims to fit these energetic concepts to a stochastic model of a realistic physical process.

The energetics presented in this chapter is extended below in three ways (Yang and Qian, 2020; Qian *et al.*, 2020; Yang and Qian, 2021a; Yang and Cheng, 2021):

- In Chap. 4, the notions of $\mathcal{S}_{\rm tot}$, $\mathcal{Q}_{\rm hk}$, and $-\Delta F_t$ (or $\mathcal{S}_{\rm na}$ in time-inhomogeneous processes) as different types of irreversibility are formulated clearly as the logarithm of RND between the process and their corresponding time reversals. Statistical properties of them, *e.g.* the celebrated fluctuation relations, are then organized.
- In Chap. 5, we show that nonequilibrium dynamics at NESS are in terms of cyclic trajectories. We revisit, clarify, and extend this concept for Markov chains and develop this concept for general diffusion in $\mathbb{R}^n$. This is an important step for a complete thermodynamic potentials theory of stochastic dynamics as the scalar energy landscape is insufficient to describe nonequilibrium dynamics.
- In Chap. 6, we apply our results in Chap. 5 and introduce the cycle potential that completes the thermodynamic potential theory of Markov stochastic dynamics. With a vanishing noise limit, the theory is then applied to Markov deterministic dynamics and various landscape theories are unified in

our thermodynamic theory.

Chapter 4

Fluctuation Relations of Irreversibility

We have shown in Chap. 3 that the housekeeping heat $\mathcal{Q}_{\rm hk}$ as a quantification of irreversibility in the stationary probability flux can be written as the logarithm of RND between path probability of the original process $\mathbb{P}$ and its adjoint process $\mathbb{P}^\dagger$. We show in this chapter that the other two types of irreversibility are actually also such generalized notion of path relative entropy. We first introduce three types of time reversals in a stochastic dynamics in Sec. 4.1. All three types of irreversibility are then represented as a path relative entropy with corresponding time reversals in Sec. 4.2. The fact that all of them are path relative entropy lead to special statistical properties of them known as the fluctuation relations (FRs) (Jarzynski, 1997; Crooks, 1999; Maes, 2004; Seifert, 2012) organized in Sec. 4.3. Properties of irreversibility are then summarized in Sec. 4.4. In this chapter, we use the term *entropy production* (EP) interchangeably with irreversibility introduced in the last chapter.

4.1 Different Types of Reversal

We first introduce three types of reversal in stochastic dynamics. Again, we use DTMC to illustrate the concepts. Extension to CTMC can be done rather straightforwardly, and see, *e.g.* (Seifert, 2012; Yang and Qian, 2020), for the extension to diffusion.

4.1.1 Adjoint Process

We actually have introduced one type of CPM reversal operator: the adjoint †. For a time-homogeneous DTMC described by $M\left(y|x\right)$, the disjoint process is described by $M^\dagger\left(y|x\right)$ such that the stationary proba-

bility flux is reversed. For a time-inhomogeneous process, we can generalized the disjoint CPM operator to replacing all M with $M^\dagger$, at each time. For a time-inhomogenous DTMC with path probability

$$P_{0:t}(x_{0:t}) = P_0(x_0) \prod_{n=1}^{t} M_n(x_n|x_{n-1}), \tag{4.1}$$

the adjoint process is then

$$P^\dagger_{0:t}(x_{0:t}) = P_0(x_0) \prod_{n=1}^{t} M^\dagger_n(x_n|x_{n-1}). \tag{4.2}$$

This gives the housekeeping heat $\mathcal{Q}_{\rm hk}$ as $\ln \frac{P_{0:t}}{P^\dagger_{0:t}}$ in Sec. 3.2.2.

4.1.2 Trajectory Reversal

The trajectory reversal of a Markov Chain for $n = 0, 1, \cdots, t$ is conventionally defined by a change of random variable

$$X^{\rm T}_n(\omega) \coloneqq X_{t-n}(\omega) \tag{4.3}$$

where we use superscript $\rm T$ to represent time reversal. This definition of $X^{\rm T}_n$ can be treated as the random variable induced by a map on the trajectory space, $r : \Omega \to \Omega$,

$$X^{\rm T}_n(\omega) = X_n(r(\omega)), \tag{4.4}$$

where the map r reverses the order of a trajectory ω, $r(x_{0:t}) = x_{t:0}$. Given a specific trajectory $\omega = x_{0:t}$, the state variable $X_n(\omega)$ is understood as the observed state of the system at time n. We can then clearly see the equivalence between these two definitions,

$$X^{\rm T}_n(x_{0:t}) = X_{t-n}(x_{0:t}) = x_{t-n} = X_n(x_{t:0}). \tag{4.5}$$

By the equivalence between change of random variable and change of probability measure (Qian *et al.*, 2019) as we reviewed in Sec. 2.3, instead of regarding trajectory reversal as a change of random variable, we can also characterize the trajectory reversal as a change of probability measure with a CPM operator $\rm T$. The CPM operator $\rm T$ is realized by the map $r : \Omega \to \Omega$ on the trajectory space. The joint probability after

trajectory reversal is thus given by

$$P^{\mathrm{T}}_{0:t}(x_{0:t}) = \mathbb{P}^{\mathrm{T}}\{X_0(\omega) = x_0, \cdots, X_t(\omega) = x_t\} \tag{4.6a}$$

$$= \mathbb{P}\{X_0(\omega) = x_t, \cdots X_t(\omega) = x_0\} = P_{0:t}(x_{t:0}). \tag{4.6b}$$

We see that the joint probability of finding $x_{0:t}$ in the trajectory reversed process is the same as the joint probability of finding the order-reversed trajectory $x_{t:0}$ in the original process. The assumption that the order-reversed trajectory has a nonzero probability in the original process is the *microscopic reversible* assumption required in (Crooks, 1999).

The equivalence between the change of random variable perspective and the change of probability measure perspective can be seen by the following. The joint probability of the process $X_{0:t}$ under the new measure $\mathbb{P}^{\mathrm{T}}$ is $P^{\mathrm{T}}_{0:t}(x_{0:t})$. The new measure can be realized by the trajectory reversal as shown in Eqs. 4.6 or by the change of random variable by

$$P^{\mathrm{T}}_{0:t}(x_{0:t}) = \mathbb{P}^{\mathrm{T}}\{X_0(\omega) = x_0, \cdots, X_t(\omega) = x_t\} \tag{4.7a}$$

$$= \mathbb{P}\{X^{\mathrm{T}}_0(\omega) = x_0, \cdots, X^{\mathrm{T}}_t(\omega) = x_t\} \tag{4.7b}$$

$$= \mathbb{P}\{X_t(\omega) = x_0, \cdots, X_0(\omega) = x_t\} = P_{t:0}\left(x_{0:t}\right). \tag{4.7c}$$

It is easy to see that the two are equivalent $P_{0:t}(x_{t:0}) = P_{t:0}\left(x_{0:t}\right)$. Conceptually, they are very different. In the change of probability measure perspective, the meaning of X_s is preserved as the state of the s-step after the starting point. The probability distribution of X_s under $\mathbb{P}^{\mathrm{T}}$ is the same as the probability distribution of $X^{\mathrm{T}}_s \coloneqq X_{t-s}$ under $\mathbb{P}$.

From the results above, it can be mathematically shown that the trajectory reversed Markov chain is still Markovian but will be time-inhomogeneous even if the original process is time homogeneous. The Markovian of the trajectory-reversed Markov chain can be shown below. To show Markovian in the reversed process, we would like to show that

$$P^{\mathrm{T}}_{s+1|0:s}\left(x_{s+1}|x_{0:s}\right) \coloneqq \mathbb{P}^{\mathrm{T}}\left\{X_{s+1} = x_{s+1}|X_{0:s} = x_{0:s}\right\} \tag{4.8a}$$

$$= \mathbb{P}^{\mathrm{T}}\left\{X_{s+1} = x_{s+1}|X_s = x_s\right\} = P^{\mathrm{T}}_{s+1|s}\left(x_{s+1}|x_s\right). \tag{4.8b}$$

The left-hand-side can be computed by first computing the joint distribution

$$P^{\mathrm{T}}_{0:s}\left(x_{0:s}\right) = \mathbb{P}^{\mathrm{T}}\left\{X_{0:s} = x_{0:s}\right\} = \sum_{x_{s+1}:x_t} \mathbb{P}^{\mathrm{T}}\left\{X_{0:t} = x_{0:t}\right\} \tag{4.9a}$$

$$= \sum_{x_{s+1}:x_t} P_{t:0}\left(x_{0:t}\right) = \sum_{x_{s+1}:x_t} P_{0:t}\left(x_{t:0}\right) \tag{4.9b}$$

$$= P_{t-s:t}\left(x_{s:0}\right) \tag{4.9c}$$

Denoting $P_s\left(\xi\right) = \sum_{\xi_0:\xi_{s-1}} P_{0:s}\left(\xi_{0:s}\right)$, then we get

$$P^{\mathrm{T}}_{0:s}\left(x_{0:s}\right) = P_{t-s:t}\left(x_{s:0}\right) = P_{t-s}\left(x_s\right) P_{t-s+1|t-s}\left(x_{s-1}|x_s\right) \cdots P_{t|t-1}\left(x_0|x_1\right). \tag{4.10}$$

Therefore,

$$P^{\mathrm{T}}_{s+1|0:s}\left(x_{s+1}|x_{0:s}\right) = \frac{P^{\mathrm{T}}_{0:s+1}\left(x_{0:s+1}\right)}{P^{\mathrm{T}}_{0:s}\left(x_{0:s}\right)} \tag{4.11a}$$

$$= \frac{P_{t-s-1}\left(x_{s+1}\right) P_{t-s|t-s-1}\left(x_s|x_{s+1}\right) \cdots P_{t|t-1}\left(x_0|x_1\right)}{P_{t-s}\left(x_s\right) P_{t-s+1|t-s}\left(x_{s-1}|x_s\right) \cdots P_{t|t-1}\left(x_0|x_1\right)} \tag{4.11b}$$

$$= \frac{P_{t-s-1}\left(x_{s+1}\right)}{P_{t-s}\left(x_s\right)} P_{t-s|t-s-1}\left(x_s|x_{s+1}\right) = P_{t-s-1,t-s}\left(x_{s-1}, x_{s+1}\right) \tag{4.11c}$$

$$= P^{\mathrm{T}}_{s+1|s}\left(x_{s+1}|x_s\right). \tag{4.11d}$$

The reversed process is Markov but time inhomogeneous in general. Note that this reversal is defined only for a given finite-length t, treating the path as a random vector. It tells us that started with the terminal distribution at time t, $P_t\left(\xi\right)$, what is the sequence of the (time-inhomogeneous) transition matrix that restore the same marginal distribution in the reversed order. This time-inhomogeneous driving protocol requires a redefinition for a different length t. Strictly speaking, it is not a process that can evolve for arbitrarily long. This "reversed" process stopped once it restored the initial distribution P_0 at the end of it.

4.1.3 Protocol Reversal

The joint probability of a Markov Chain is determined by the *driving protocol,* P_0 and M_n, $n = 1, 2, \cdots, t$. Thus, we can consider the process where we used the terminal distribution P_t as our new initial distribution and reverse the temporal order of the transition matrices. We shall call this reversal the *protocol reversal* of the process and denote the corresponding CPM operator as R. The new joint distribution is then given by

$$P^{\mathrm{R}}_{0:t}(x_{0:t}) = P_t(x_0) \prod_{n=1}^{t} M_{t+1-n}(x_n|x_{n-1}). \tag{4.12}$$

Compare to the trajectory reversal T which is a "time reversal" at the trajectory level, protocol reversal R is rather a "time reversal" at the population level. On the contrary to the trajectory reversal T ruining time-homogeneity but recovers the initial distribution, the protocol reversal R preserves the time homogeneity if we started with time homogeneous process. However, the marginal distribution at the end of the reversal is usually not the original initial distribution (Yang and Qian, 2020).

The "time reversal" that was considered by most of the previous studies on fluctuation relations (Seifert, 2005; Chernyak *et al.*, 2006; Esposito and Van den Broeck, 2010) is in fact the composition of the two reversals we have just introduced: R and T, denoted as $\mathbb{P}^{\mathrm{RT}}$. The joint distribution is given by

$$\left[P^{\mathrm{R}}_{0:t}\right]^{\mathrm{T}}(x_{0:t}) = P^{\mathrm{R}}_{0:t}(x_{t:0}) = P_t(x_t)\prod_{n=1}^{t} M_{t+1-n}(x_{t-n}|x_{t-n+1}) \tag{4.13}$$

This computation in Equation (4.13) actually gives us a convenient result when working on composite CPMs with time reversal as the last operation, $\mathbb{P} \to \mathbb{P}^{\nu\mathrm{T}}$. The joint probability for such composite operators is given by evaluating at the order-reversed trajectory,

$$P^{\nu\mathrm{T}}_{0:t}(x_{0:t}) = P^{\nu}_{0:t}(x_{t:0}). \tag{4.14}$$

Note that the two operators R and T do not generally commute, $P^{\mathrm{RT}}_{0:t} \neq P^{\mathrm{TR}}_{0:t}$[1].

4.1.4 Involutive Properties of the Reversals

Considering reversals of a process, it is natural to ask whether we can recover the original process by applying the reversal twice or not, *i.e.* in mathematical terms, whether the operator is involutive or not. As we have shown above, the involutive properties of the CPM operator for an EP are the keys for the EP to have FRs.

It is rather straightforward to show that both T and † are involutive. The time reversal T is involutive since the map $r : \Omega \to \Omega$ is involutive. We can verify this by computing

$$P^{\mathrm{TT}}_{0:t}(x_{0:t}) = P^{\mathrm{T}}_{0:t}(x_{t:0}) = P_{0:t}(x_{0:t}). \tag{4.15}$$

[1] From definition, $P^{\mathrm{TR}}_{0:t}(x_{0:t}) = \left[P^{\mathrm{T}}_{0:t}\right]^{\mathrm{R}}(x_{0:t})$ is $P^{\mathrm{T}}_t(x_0)\prod_{n=1}^{t} P^{\mathrm{T}}_{t+1-n|t-n}(x_n|x_{n-1})$. From the fact that T changes the random variable, we get the RHS equals to $P_0(x_0)\prod_{n=1}^{t} P_{n-1|n}(x_n|x_{n-1})$ and becomes $\frac{P_0(x_0)}{P_t(x_t)}\prod_{n=1}^{t}\frac{P_{n-1}(x_n)}{P_n(x_{n-1})}P^{\mathrm{RT}}_{0:t}(x_{0:t})$ by Bayes' rule.

The dual reversal † is involutive by computing

$$P^{\dagger\dagger}_{0:t}(x_{0:t}) = P^{\dagger}_0(x_0)\prod_{n=1}^{t} M^{\dagger\dagger}_n(x_n|x_{n-1}). \tag{4.16}$$

From the joint probability in Equation (4.2), we get $P^{\dagger}_0 = P_0$ and one can show $M^{\dagger\dagger}_n = M_n$ by $\pi^{\dagger}_n = \pi_n$.

Finally, the protocol reversal R is *not* involutive in general. To see this, we start by

$$P^{\mathrm{RR}}_{0:t}(x_{0:t}) = P^{\mathrm{R}}_t(x_0)\prod_{n=1}^{t} M^{\mathrm{R}}_{t+1-n}(x_n|x_{n-1}). \tag{4.17}$$

We thus need to compute P^{R}_t and M^{R}_{t+1-n} from the joint probability given in Equation (4.12). It is straightforward to check that the latter is given simply by

$$M^{\mathrm{R}}_{t+1-n}(j|i) = M_n(j|i). \tag{4.18}$$

However, the terminal distribution of the protocol reversed process is generally not the initial distribution of the original process, $P^{\mathrm{R}}_t \neq P_0$ (Rao and Esposito, 2018). This can be seen by a time homogeneous Markov Chain where P^{R}_t is given by P_t further evolved by t more steps, which gives us P_{2t} not P_0. Thus, we have

$$P^{\mathrm{RR}}_{0:t}(x_{0:t}) = \frac{P^{\mathrm{R}}_t(x_0)}{P_0(x_0)} P_{0:t}(x_{0:t}). \tag{4.19}$$

From this, it is also clear that if $P^{\mathrm{R}}_t = P_0$, then the protocol reversal R becomes involutive[2].

4.2 Irreversibility as Path Relative Entropy

With different reversals and their corresponding CPM operators introduced, we are now ready to consider four different EPs historically defined in physics and chemistry and their fluctuation relations. Specifically, we will introduce a new notion of "irreversibility" called *dissipation function* $\mathcal{S}_{\mathrm{T}}$ and also show that the three types of irreversibility ($\mathcal{S}_{\mathrm{tot}}$, $\mathcal{S}_{\mathrm{na}}$, and $\mathcal{Q}_{\mathrm{hk}}$) introduced in last chapter are all path relative entropy.

[2] An example for an involutive R is to start at $P_0 = \pi_1$ and to fix the driving protocol at M_1 for enough time steps so that the protocol reversed process have enough time to relax back to π_1 by the end of the reversed process.

4.2.1 Dissipation Function $\mathcal{S}_{\mathrm{T}}$

The EP that corresponds to the trajectory reversal T is historically called the *dissipation function* by Evans and Searles (2002), a term goes back to Onsager,

$$\mathcal{S}_{\mathrm{T}}(\omega) \coloneqq \ln \frac{\mathrm{d}\mathbb{P}}{\mathrm{d}\mathbb{P}^{\mathrm{T}}}(\omega) = \ln \frac{P_{0:t}(X_{0:t}(\omega))}{P_{0:t}(X_{t:0}(\omega))}. \tag{4.20}$$

We note that the dissipation function does *not* satisfy additive properties when connecting two time intervals, *i.e.* for $0 < s < t$, we have

$$\mathcal{S}_{\mathrm{T}}(x_{0:t}) \neq \mathcal{S}_{\mathrm{T}}(x_{0:s}) + \mathcal{S}_{\mathrm{T}}(x_{s:t}) \tag{4.21}$$

The dissipation function requires a re-definition every-time we march forward in time. The dissipation function defined here is not really a property of "a stochastic process" but rather a property of "a length-t random vector", *cf.* Markov processes vs. Markov random fields.

4.2.2 Total Entropy Production $\mathcal{S}_{\mathrm{tot}}$

The total entropy production $\mathcal{S}_{\mathrm{tot}}$ we introduced is actually given by composing protocol reversal R and then the trajectory reversal T,

$$\mathcal{S}_{\mathrm{tot}}(x_{0:t}) = \ln \frac{\mathrm{d}\mathbb{P}}{\mathrm{d}\mathbb{P}^{\mathrm{RT}}}(x_{0:t}) = \ln \frac{\mathrm{d}\mathbb{P}}{\mathrm{d}\mathbb{P}^{\mathrm{C}}}(x_{0:t}) = \ln \frac{P_0(x_0)M_1(x_1|x_0)\cdots M_t\left(x_t|x_{t-1}\right)}{P_t(x_t)M_t(x_{t-1}|x_t)\cdots M_1\left(x_0|x_1\right)} \tag{4.22}$$

where we have denoted the composition of R and T as a composite operator C, *i.e.* $\mathbb{P}^{\mathrm{C}} = \left[\mathbb{P}^{\mathrm{R}}\right]^{\mathrm{T}}$. We note that the total entropy production satisfies additive property when connecting two time intervals, *i.e.,* for $0 < s < t$,

$$\mathcal{S}_{\mathrm{tot}}(x_{0:t}) = \mathcal{S}_{\mathrm{tot}}(x_{0:s}) + \mathcal{S}_{\mathrm{tot}}(x_{s:t}). \tag{4.23}$$

This can actually be shown by a more informative expression for $\mathcal{S}_{\mathrm{tot}}$. By noticing that T is involutive, $\mathbb{P}^{TT} = \mathbb{P}$, we have

$$\mathcal{S}_{\mathrm{tot}}(\omega) = \ln \frac{\mathrm{d}\mathbb{P}^{TT}}{\mathrm{d}\mathbb{P}^{RT}}(\omega) = \ln \frac{\mathrm{d}\mathbb{P}^{TT}(\omega)}{\mathrm{d}\mathbb{P}^{RT}(\omega)} = \ln \frac{\mathrm{d}\mathbb{P}^{T}(r\left(\omega\right))}{\mathrm{d}\mathbb{P}^{R}(r\left(\omega\right))} = \ln \frac{\mathrm{d}\mathbb{P}^{T}}{\mathrm{d}\mathbb{P}^{R}}(r(\omega)). \tag{4.24}$$

In DTMC, this becomes

$$\mathcal{S}_{\mathrm{tot}}(x_{0:t}) = \ln \frac{P_t(x_t)P_{t-1|t}\left(x_{t-1}|x_t\right)\cdots P_{0|1}(x_0|x_1)}{P_t(x_t)P_{t|t-1}\left(x_{t-1}|x_t\right)\cdots P_{1|0}(x_0|x_1)} = \sum_{s=1}^{t} \ln \frac{P_{s-1|s}(x_{s-1}|x_s)}{P_{s|s-1}(x_{s-1}|x_s)}. \tag{4.25}$$

This shows us why the total entropy production $\mathcal{S}_{\rm tot}$ is additive in connecting time intervals. When t is extended to $t+1$, the total entropy production is simply given by

$$\mathcal{S}_{\rm tot}(x_{0:t+1}) = \mathcal{S}_{\rm tot}(x_{0:t}) + \ln \frac{P_{t|t+1}(x_t|x_{t+1})}{P_{t+1|t}(x_t|x_{t+1})}. \tag{4.26}$$

We note that the transition matrices $P_{s-1|s}$ for $s = 1, 2, ..., t$ are the ones that recover the initial distribution P_0 at the end of the reversed process. The reversal T can thus be understood as the "ideal" time reversal that "does not loss any information". On the other hand, using the transition matrices $P_{s|s-1}$ with $s = 1, 2, ..., t$ comes from the protocol reversal R, which is the "macroscopic reversal" which is more feasible since it corresponds to a direct reverse of the "driving force". Hence, this expression in Eq. (4.24) states that the total entropy production quantifies the difference between the ideal time reversal T and the more-feasible protocol reversal R.

4.2.3 Non-adiabatic Entropy Production $\mathcal{S}_{\rm na}$

The difference between the free energy dissipation $-\Delta F$ and the excess work done *on* the system $\mathcal{W}_{\rm ex}$ is the *non-adiabatic* EP, $\mathcal{S}_{\rm na}$, defined in (Esposito and Van den Broeck, 2010),

$$\mathcal{S}_{\rm na}(\omega) = \mathcal{W}_{\rm ex}(\omega) - \Delta F(\omega) = \mathcal{Q}_{\rm ex}(\omega) + \Delta S(\omega) = \ln \frac{\mathrm{d}\mathbb{P}}{\mathrm{d}\mathbb{P}^{\mathrm{R}\dagger\mathrm{T}}}(\omega). \tag{4.27}$$

The equivalence between the last equations can be seen by a direct computation of $P_{0:t}^{\mathrm{R}\dagger\mathrm{T}}(x_{0:t})$. Since T is the last CPM operator in the composition, we can directly get $P_{0:t}^{\mathrm{R}\dagger\mathrm{T}}$ by evaluating $P_{0:t}^{\mathrm{R}\dagger}$ at the order-revered trajectory. We thus first compute $P_{0:t}^{\mathrm{R}\dagger}(x_{0:t})$ via

$$P_0^{\mathrm{R}}(x_0) \prod_{n=1}^{t} \left[M_n^{\mathrm{R}}\right]^{\dagger}(x_n|x_{n-1}) = P_0^{\mathrm{R}}(x_0) \prod_{n=1}^{t} M_{t+1-n}^{\dagger}(x_n|x_{n-1}) \tag{4.28}$$

and get that

$$P_{0:t}^{\mathrm{R}\dagger\mathrm{T}}(x_{0:t}) = P_0^{\mathrm{R}}(x_t) \prod_{n=1}^{t} M_{t+1-n}^{\dagger}(x_{t-n}|x_{t+1-n}). \tag{4.29}$$

The equivalence can then be established.

By the definition $\mathcal{W}_{\rm ex}(\omega) - \Delta F(\omega)$, one can see that the non-adiabatic EP is also additive when connecting time interval,

$$\mathcal{S}_{\rm na}(x_{0:t}) = \mathcal{S}_{\rm na}(x_{0:s}) + \mathcal{S}_{\rm na}(x_{s:t}) \tag{4.30}$$

which is obvious from its relation to $\mathcal{W}_{\rm ex}$ and ΔF. Similar to $\mathcal{S}_{\rm tot}$, the non-adiabatic entropy production turns out to be comparing two reversals at the reversed trajectory: the ideal one $\mathbb{P}^T$ and the reversed-order adjoint process $\mathbb{P}^{R\dagger}$ where the irreversibility of flux is imposed:

$$\mathcal{S}_{\rm na}(\omega) = \ln \frac{\mathrm{d}\mathbb{P}^T(r\,(\omega))}{\mathrm{d}\mathbb{P}^{R\dagger}(r\,(\omega))} = \ln \frac{\mathrm{d}\mathbb{P}^T}{\mathrm{d}\mathbb{P}^{R\dagger}}(r(\omega)). \tag{4.31}$$

In DTMC, this becomes

$$\mathcal{S}_{\rm na}(x_{0:t}) = \ln \frac{P_t(x_t)P_{t-1|t}\,(x_{t-1}|x_t)\cdots P_{0|1}(x_0|x_1)}{P_t(x_t)P^\dagger_{t|t-1}\,(x_{t-1}|x_t)\cdots P^\dagger_{1|0}(x_0|x_1)} = \sum_{s=1}^{t} \ln \frac{P_{s-1|s}(x_{s-1}|x_s)}{P^\dagger_{s|s-1}(x_{s-1}|x_s)}. \tag{4.32}$$

Note that $\mathcal{S}_{\rm na}$ reduces to the dissipative work $\mathcal{W}_{\rm d}$ defined in (Jarzynski, 1997; Crooks, 1998) for systems with detailed balance.

4.3 Relative Entropy and Fluctuation Relations

As shown above, all types of irreversibility (EPs) discussed above are *fluctuating* relative entropy corresponding to a CPM operator ν, as the negative natural logarithm of the RND,

$$\mathcal{S}_\nu(\omega) \coloneqq \ln \frac{\mathrm{d}\mathbb{P}}{\mathrm{d}\mathbb{P}^\nu}(\omega), \tag{4.33}$$

which is also a random variable (Qian, 2001b; Seifert, 2005; Ge *et al.*, 2006; Ge and Qian, 2007; Qian *et al.*, 2019). We now show general statistical properties of a fluctuating relative entropy. The advantages of working with S_ν instead of the RND can be seen the time additivity of the types of irreversibility as shown in Eq. (4.23) and Eq. (4.30). We note that S_ν is always finite given our assumption that the probability measure space $\mathcal{P}$ collects $\mathbb{P}$s that are absolute continuous to each other, *i.e.* $0 < \frac{\mathrm{d}\mathbb{P}}{\mathrm{d}\mathbb{P}^\nu}(\omega) < \infty$.

The fluctuating relative entropy $\mathcal{S}_\nu(\omega)$ reflects the difference between the measure $\mathbb{P}$ and the reference probability measure $\mathbb{P}^\nu$. If the stochastic process is symmetric under the operator ν, *i.e.* $\mathbb{P}^\nu = \mathbb{P}$, then $\mathcal{S}_\nu(\omega) = 0, \forall\omega \in \Omega$. With different ν, we find have various different EPs discussed above. It is therefore desirable to find the general statistical properties of a given EP given it's definition in Equation (4.33).

4.3.1 General Statistical Properties

Directly from the definition of EP in Equation (4.33), the following three key statistical properties of S_ν can be derived rather straightforwardly.

1. *Non-negative expectation:* By Jensen's inequality, the expectation of $\mathcal{S}_\nu$ w.r.t $\mathbb{P}$ is non-negative, $\mathbb{E}[\mathcal{S}_\nu] \geq 0$, and equality only holds when $\mathbb{P} = \mathbb{P}^\nu$ due to the strict convexity of negative logarithm. This result for EPs in physical processes extends the classical second law of thermodynamics (Ge, 2009).
2. *Integral Fluctuation Theorem* (IFT) or called Jarzynski's equality (Jarzynski, 1997):

$$\mathbb{E}\left[e^{-\mathcal{S}_\nu}\right] = \mathbb{E}\left[\frac{\mathrm{d}\mathbb{P}^\nu}{\mathrm{d}\mathbb{P}}\right] = \mathbb{E}^\nu[1] = 1. \tag{4.34}$$

3. *General fluctuation relation* (GFR):

$$\mathbb{P}\left\{\mathcal{S}_\nu(\omega) \in \mathrm{d}s\right\} = e^s \mathbb{P}^\nu\left\{\mathcal{S}_\nu(\omega) \in \mathrm{d}s\right\} \tag{4.35}$$

   where $\mathrm{d}s$ is a shorthand for the infinitesimal interval $(s, s + \mathrm{d}s)$. This GFR states for the EP, $\mathcal{S}_\nu = \ln \frac{\mathrm{d}\mathbb{P}}{\mathrm{d}\mathbb{P}^\nu}$, that quantifies the difference between $\mathbb{P}$ and $\mathbb{P}^\nu$, its probability densities under $\mathbb{P}$ and $\mathbb{P}^\nu$ are up to an exponential factor.

GFR can be derived by considering the probability density of $\mathcal{S}_\nu$ under the new measure $\mathbb{P}^\nu$, characterizing the statistical properties of $\mathcal{S}_\nu$ in the ν process:

$$\begin{aligned}
\mathbb{P}^\nu\left\{\mathcal{S}_\nu(\omega) \in \mathrm{d}s\right\} &= \mathbb{E}\left[\frac{\mathrm{d}\mathbb{P}^\nu}{\mathrm{d}\mathbb{P}}(\omega)\, \mathbb{I}_{\{\mathcal{S}_\nu(\omega)\in \mathrm{d}s\}}\right] && \text{(4.36a)}\\
&= \mathbb{E}\left[e^{-\mathcal{S}_\nu(\omega)} \mathbb{I}_{\{\mathcal{S}_\nu(\omega)\in \mathrm{d}s\}}\right] && \text{(4.36b)}\\
&= e^{-s}\mathbb{P}\left\{\mathcal{S}_\nu(\omega) \in \mathrm{d}s\right\}. && \text{(4.36c)}
\end{aligned}$$

We will see below that most fluctuation relations discussed in the literature come directly from this GFR. We remark that the three properties above holds for *any* fluctuating relative entropy defined as the negative logarithm of a RND.

4.3.2 Detailed Fluctuation Theorems

The detailed fluctuation theorems that were considered in the literature (Crooks, 1999; Chernyak *et al.*, 2006; Esposito and Van den Broeck, 2010; Seifert, 2012) have the form of

$$\mathbb{P}\left\{\mathcal{S}_\nu(\omega) \in \mathrm{d}s\right\} = e^s \mathbb{P}^\nu\left\{\hat{\mathcal{S}}_\nu(\omega) \in -\mathrm{d}s\right\} \tag{4.37}$$

where $\hat{\mathcal{S}}_\nu$ can be various different random variables under different considerations. The DFT comes directly from GFR in Equation (4.36c) if there is an odd parity between the original random variable $\mathcal{S}_\nu$ and the new

random variable $\hat{\mathcal{S}}_\nu$ under consideration,

$$\hat{\mathcal{S}}_\nu(\omega) = -\mathcal{S}_\nu(\omega). \tag{4.38}$$

Two choices of $\hat{\mathcal{S}}_\nu$ were discussed in the past, which we will briefly summarize below.

Recall that $\mathcal{S}_\nu$ serves as a random variable that quantifies the effect of the CPM operator ν acting on $(\Omega, \mathcal{F}, \mathbb{P})$. When considering a different process $(\Omega, \mathcal{F}, \mathbb{P}^\eta)$, the EP that does the same for the η process as $\mathcal{S}_\nu$ does for the original process should be given by replacing $\mathbb{P}$ with $\mathbb{P}^\eta$,

$$\mathcal{S}^\eta_{\eta\nu}(\omega) \coloneqq \ln \frac{\mathrm{d}\mathbb{P}^\eta}{\mathrm{d}\mathbb{P}^{\eta\nu}}(\omega) \tag{4.39}$$

where $\mathbb{P}^{\eta\nu} = [\mathbb{P}^\eta]^\nu$ is operating η on $\mathbb{P}$ first and then applying ν on $\mathbb{P}^\eta$. The two $\hat{\mathcal{S}}_\nu$s considered in the past (Esposito and Van den Broeck, 2010; Seifert, 2012) correspond to two different ηs.

A mathematically natural consideration for η is to take η as ν, which will lead to Esposito and Van den Broeck's detailed fluctuation theorem in. In this setting, the odd parity requirement in Equation (4.38) becomes an involutive requirement of the operator ν,

$$\mathcal{S}^\nu_{\nu\nu} = \ln \frac{\mathrm{d}\mathbb{P}^\nu}{\mathrm{d}\mathbb{P}^{\nu\nu}} = -\mathcal{S}_\nu = \ln \frac{\mathrm{d}\mathbb{P}^\nu}{\mathrm{d}\mathbb{P}} \Leftrightarrow \mathbb{P}^{\nu\nu} = \mathbb{P}. \tag{4.40}$$

Denoting $\mathcal{S}^\nu_{\nu\nu}$ as $\tilde{\mathcal{S}}_\nu$, the detailed fluctuation theorem from the involutive property (iDFT) (Esposito and Van den Broeck, 2010) then reads

$$\mathbb{P}\left\{\mathcal{S}_\nu(\omega) \in \mathrm{d}s\right\} = e^s \mathbb{P}^\nu \left\{\tilde{\mathcal{S}}_\nu(\omega) \in -\mathrm{d}s\right\}. \tag{4.41}$$

In a physical process, the driving protocol of the system is determined by macroscopic thermodynamics parameters, and thermodynamics quantities such as heat and work are dependent upon the driving protocol. Therefore, in most of the physics literature, the $\hat{\mathcal{S}}_\nu$ considered was given by first taking η as the macroscopic, protocol reversal R, as we will defined explicitly in Equation (4.12), and then evaluating $\hat{\mathcal{S}}_\nu$ at the order reversed trajectory $r(\omega)$ where r is a map from Ω to Ω that reverses the trajectory $\omega \in \Omega$. By denoting $\bar{\mathcal{S}}_\nu(\omega) \coloneqq \mathcal{S}^{\mathrm{R}}_{\mathrm{R}\nu}(\omega)$ and using $\bar{\mathcal{S}}_\nu(r(\omega))$ for $\hat{\mathcal{S}}(\omega)$, we get the generalized Crooks' fluctuation theorem (Crooks, 1999, 2000; Chernyak *et al.*, 2006; Seifert, 2012; García-García *et al.*, 2012),

$$\mathbb{P}\left\{\mathcal{S}_\nu(\omega) \in \mathrm{d}s\right\} = e^s \mathbb{P}^\nu \left\{\bar{\mathcal{S}}_\nu(r(\omega)) \in -\mathrm{d}s\right\}. \tag{4.42}$$

To fix the terminology, we would refer this detailed fluctuation theorem as the rDFT. The odd parity requirement $\bar{\mathcal{S}}_\nu(r(\omega)) = -\mathcal{S}_\nu(\omega)$ turns out to be an involutive requirement on the operator R for the CPM

operators we are interested in, as shown in Equation (4.48) and (4.51).

To check the validity of iDFT and rDFT, we should check the necessary and sufficient condition: for $\mathcal{S}_\nu$ and $-\hat{\mathcal{S}}_\nu$ to have the same probability density of under $\mathbb{P}^\nu$. The odd parity condition in Equation (4.38) is a stricter condition on $\mathcal{S}_\nu$ and $\hat{\mathcal{S}}_\nu$[3] and only a sufficient condition. To prove a DFT to be valid, we can show this sufficient condition to be true, but to prove a DFT to be invalid, we would need to show a necessary condition of it to be false. For simplicity, we will only check the the sufficient condition in Equation (4.38) for a DFT here. If an EP does not admit this odd-parity condition, we will leave its DFT inconclusive and leave it for future consideration.

4.3.3 Transient Fluctuation Theorem

Only very special operator ν defined on the probability measure space $\mathcal{P}$ can be represented as a result of a map μ from Ω to Ω. In those special cases, the map μ maps an event of interest $A \in \mathcal{F}$ to another, $\mu(A) \in \mathcal{F}$, which is obtained by replacing all the ωs in A by the $\mu(\omega)$s, *e.g.* if $A = \omega_1 \cup \omega_2$, then $\mu(A) = \mu(\omega_1) \cup \mu(\omega_2)$. The new measure is then given by

$$\mathbb{P}^\nu \{A\} = \mathbb{P} \{\mu(A)\} . \tag{4.43}$$

If an operator ν is involutive, *i.e.* $\mathbb{P}^{\nu\nu} = \mathbb{P}$, then we already know that $\mathcal{S}_\nu$ admits iDFT. If the operator ν is further realized by an involutive map $\mu : \Omega \to \Omega$ on the trajectory space as Eq. (4.43), *i.e.* $\mu(\mu(\omega)) = \omega$, we would have $\mathcal{S}_\nu(\mu(\omega)) = \ln \frac{\mathrm{d}\mathbb{P}^\nu}{\mathrm{d}\mathbb{P}^{\nu\nu}}(\omega) = \tilde{\mathcal{S}}_\nu(\omega) = \ln \frac{\mathrm{d}\mathbb{P}^\nu}{\mathrm{d}\mathbb{P}}(\omega) = -\mathcal{S}_\nu(\omega)$. Then, by Equation (4.43), we have $\mathbb{P}^\nu \{\mathcal{S}_\nu(\omega) \in \mathrm{d}s\} = \mathbb{P} \{\mathcal{S}_\nu(\mu(\omega)) \in \mathrm{d}s\}$. With our GFR, we obtain the so-called *transient fluctuation theorem* (TFT) (Evans and Searles, 1994; Searles and Evans, 1999; Evans and Searles, 2002; Jiang *et al.*, 2004; Ge and Jiang, 2007; Seifert, 2012),

$$\mathbb{P} \{\mathcal{S}_\nu(\omega) \in \mathrm{d}s\} = e^s \mathbb{P} \{\mathcal{S}_\nu(\omega) \in -\mathrm{d}s\} . \tag{4.44}$$

TFT is particularly important since it provides explicitly the asymmetry between having a positive and negative EP in the same process. The probability (density) of finding a positive EP is exponentially higher than the probability of finding a negative one.

The validity of TFT is easy to check since involutive property $\mathbb{P}^{\nu\nu} = \mathbb{P}$ is a necessary condition for TFT. If $\mathbb{P}^{\nu\nu} \neq \mathbb{P}$ then $\mathbb{E}[\ln \frac{\mathrm{d}\mathbb{P}}{\mathrm{d}\mathbb{P}^{\nu\nu}}] > 0 \Rightarrow \mathbb{E}[\mathcal{S}_\nu] > \mathbb{E}[-\mathcal{S}^\nu_{\nu\nu}]$ by Jensen's inequality. We then know $\mathcal{S}_\nu$ and $-\mathcal{S}^\nu_{\nu\nu}$

[3] Note that saying two random variables to be the same $X(\omega) = Y(\omega)$ usually means that they return the same value for every $\omega \in \Omega$. This is a stronger statement than saying two random variables $X(\omega)$ and $Y(\omega)$ to have the same probability distribution.

FR	definition	relative entropy	sufficient conditions
GFR	$\frac{\mathbb{P}\{\mathcal{S}_\nu(\omega)\in(s,s+\mathrm{d}s)\}}{\mathbb{P}^\nu\{\mathcal{S}_\nu(\omega)\in(s,s+\mathrm{d}s)\}}=e^s$	$\mathcal{S}_\nu(\omega)=\ln\frac{\mathrm{d}\mathbb{P}}{\mathrm{d}\mathbb{P}^\nu}(\omega)$	generally valid
IFT	$\mathbb{E}\left[e^{-S_\nu}\right]=1$		
rDFT	$\frac{\mathbb{P}\{\mathcal{S}_\nu(\omega)\in(s,s+\mathrm{d}s)\}}{\mathbb{P}^\nu\left\{\bar{\mathcal{S}}_\nu[r(\omega)]\in(-s-\mathrm{d}s,-s)\right\}}=e^s$	$\bar{\mathcal{S}}_\nu(\omega)=\ln\frac{\mathrm{d}\mathbb{P}^R}{\mathrm{d}\mathbb{P}^{R\nu}}(\omega)$	$\bar{\mathcal{S}}_\nu[r(\omega)]=-\mathcal{S}_\nu(\omega)$
iDFT	$\frac{\mathbb{P}\{\mathcal{S}_\nu(\omega)\in(s,s+\mathrm{d}s)\}}{\mathbb{P}^\nu\left\{\tilde{\mathcal{S}}_\nu(\omega)\in(-s-\mathrm{d}s,-s)\right\}}=e^s$	$\tilde{\mathcal{S}}_\nu(\omega)=\ln\frac{\mathrm{d}\mathbb{P}^\nu}{\mathrm{d}\mathbb{P}^{\nu\nu}}(\omega)$	ν involutive on $\mathcal{P}$
TFT	$\frac{\mathbb{P}\{\mathcal{S}_\nu(\omega)\in(s,s+\mathrm{d}s)\}}{\mathbb{P}\{\mathcal{S}_\nu(\omega)\in(-s-\mathrm{d}s,-s)\}}=e^s$	$\mathcal{S}_\nu(\omega)=\ln\frac{\mathrm{d}\mathbb{P}}{\mathrm{d}\mathbb{P}^\nu}(\omega)$	ν realized by an involutive map on Ω

Table 4.1: The five fluctuation relations (FRs) of the relative entropy $\mathcal{S}_\nu$, with the CPM operator ν discussed here. IFT is the integral fluctuation theorem Jarzynski (1997); GFR is the general FR in Equation (4.35); TFT is the transient fluctuation theorem in (Kurchan, 1998; Evans and Searles, 2002; Ge and Qian, 2007; Seifert, 2012), iDFT is the detailed fluctuation theorem in (Esposito and Van den Broeck, 2010), and rDFT is the generalization of Crooks' fluctuation theorem (Seifert, 2005, 2012; Crooks, 1999; Chernyak *et al.*, 2006; García-García *et al.*, 2012) . R and r are time reversals of processes to be introduced in the next chapter. We have shown in the text that TFT implies iDFT. This summarizes the hierarchical structure of the validity of the five FRs. . Table adapted from (Yang and Qian, 2020).

have different probability densities w.r.t. $\mathbb{P}$ $\Rightarrow$ TFT is false. Here, we see that TFT is a sufficient condition for $\mathcal{S}_\nu$ to have iDFT but not necessary. This is because not all involutive operator $\nu:\mathcal{P}\to\mathcal{P}$ can be realized by an involutive map $\mu:\Omega\to\Omega$[4].

4.3.4 Summary

Treating a physical operation on stochastic processes as a CPM operator ν on probability space $\mathcal{P}$, we have characterized the change in the statistical properties of a physical operation via the negative natural logarithm of the RND, which one defines it as the EP $\mathcal{S}_\nu$. In fact, a hierarchy of the validity for FRs in general stochastic processes is revealed from our work as summarized in Table 4.1 :

1. Non-negative expectation, IFT (Jarzynski, 1997; Seifert, 2012), and GFR are generally true from the definition of $\mathcal{S}_\nu$.
2. With $\hat{\mathcal{S}}_\nu(\omega)=-\mathcal{S}_\nu(\omega)$, we have DFTs. In the literature, $\hat{\mathcal{S}}_\nu(\omega)$ was chosen to be $\tilde{\mathcal{S}}_\nu(\omega):=\mathcal{S}^\nu_{\nu\nu}(\omega)$ to get iDFT (Esposito and Van den Broeck, 2010) if the CPM operator ν is involutive, or

[4] Here is an explicit example for an involutive operator $\nu:\mathcal{P}\to\mathcal{P}$ not realized by an involutive map $\mu:\Omega\to\Omega$. Consider two binary random variables X_1 and X_2 that can take values 0 or 1. Suppose the joint probabilities for four possible realizations are $P_{1,2}(0,0)=p, P_{1,2}(0,1)=q, P_{1,2}(1,0)=r, P_{1,2}(1,1)=s$ where $p+q+r+s=1$. The joint probabilities in the new measure $\mathbb{P}^\nu$ is given by $P^\nu_{1,2}(0,0)=\sqrt{(1-r-s)-p^2}, P^\nu_{1,2}(0,1)=(1-r-s)-\sqrt{(1-r-s)-p^2}, P^\nu_{1,2}(1,0)=r, P^\nu_{1,2}(1,1)=s$. One can show that $\mathbb{P}^{\nu\nu}=\mathbb{P}$. And clearly the involutive operator ν can not be realized by an involutive map $\mu:\Omega\to\Omega$.

$\bar{\mathcal{S}}_\nu(r(\omega)) \coloneqq \mathcal{S}^{\mathrm{R}}_{\mathrm{R}\nu}(r(\omega))$ to get rDFT (Crooks, 1999, 2000; Seifert, 2012) if the protocol reversal operator R is involutive (for the ν we considered).

3. Further with the CPM operator ν as an involutive map on the trajectory space, from $\Omega \to \Omega$, we have TFT (Evans and Searles, 2002; Ge and Jiang, 2007; Seifert, 2012).

The results above are true no matter the stochastic process has discrete or continuous state space $\mathcal{X}$, is with discrete or continuous time, is time homogeneous or not, or has any specific initial distribution such as the invariant distribution. The Markovian assumption is not even imposed except the definition of the protocol reversal R. Our derivation only relies on assuming all $\mathbb{P} \in \mathcal{P}$ to be absolute continuous to each other, the notation of CPM operator, the definition of EP, and conditions for more restricted FRs such as DFTs and TFT.

4.4 Properties of Irreversibility

With these general results for fluctuation relations of relative entropy in hand, we are now ready examine the fluctuation relations for $\mathcal{S}_{\mathrm{T}}$, $\mathcal{S}_{\mathrm{tot}}$, $\mathcal{S}_{\mathrm{na}}$, and $\mathcal{Q}_{\mathrm{hk}}$. The key would be to check the involutive properties for the corresponding reversals. Before that, we first note that the three reversals T, R, and † are actually related. By direct computation, one can show that the important decomposition we discussed in Sec. 3.2, $\mathcal{S}_{\mathrm{tot}} = \mathcal{S}_{\mathrm{na}} + \mathcal{Q}_{\mathrm{hk}}$ (Ge, 2009) is from the intriguing property

$$\frac{\mathrm{d}\mathbb{P}}{\mathrm{d}\mathbb{P}^{\mathrm{RT}}} = \frac{\mathrm{d}\mathbb{P}}{\mathrm{d}\mathbb{P}^{\dagger}} \frac{\mathrm{d}\mathbb{P}}{\mathrm{d}\mathbb{P}^{\mathrm{R}\dagger\mathrm{T}}}. \tag{4.45}$$

Since $\mathcal{Q}_{\mathrm{hk}} = 0$ when the system possesses detailed balance, $\mathcal{S}_{\mathrm{tot}} \equiv \mathcal{S}_{\mathrm{na}}$ in detailed balance systems.

4.4.1 Fluctuation relations of Irreversibility

Since the CPM operator T is realized by an involutive map $r : \Omega \to \Omega$. We thus know $\mathcal{S}_{\mathrm{T}}$ admits both TFT and iDFT. The TFT of $\mathcal{S}_{\mathrm{T}}$ has been discussed in (Seifert, 2012; Ge and Jiang, 2007; Evans and Searles, 2002). However, $\mathcal{S}_{\mathrm{T}}$ does not satisfy the odd-parity, sufficient condition for rDFT. We note that the dissipation function $\mathcal{S}_{\mathrm{T}}$ on the protocol reversed process R is given by $\bar{\mathcal{S}}_{\mathrm{T}}(\omega) = \ln \frac{\mathrm{d}\mathbb{P}^{\mathrm{R}}}{\mathrm{d}\mathbb{P}^{\mathrm{RT}}}(\omega)$ which gives

$$\bar{\mathcal{S}}_{\mathrm{T}}(r(\omega)) = \ln \frac{\mathrm{d}\mathbb{P}^{\mathrm{RT}}}{\mathrm{d}\mathbb{P}^{\mathrm{RTT}}}(\omega) = \ln \frac{\mathrm{d}\mathbb{P}^{\mathrm{RT}}}{\mathrm{d}\mathbb{P}^{\mathrm{R}}}(\omega) = -\bar{\mathcal{S}}_{\mathrm{T}}(\omega) \neq -\mathcal{S}_{\mathrm{T}}(\omega). \tag{4.46}$$

Unless pathologically $\bar{\mathcal{S}}_{\mathrm{T}}(r(\omega)) \neq -\mathcal{S}_{\mathrm{T}}(\omega)$ but $\mathbb{P}^{\mathrm{T}}\left\{\bar{\mathcal{S}}_{\mathrm{T}}(r(\omega)) \in -\mathrm{d}s\right\} = \mathbb{P}^{\mathrm{T}}\{\mathcal{S}_{\mathrm{T}}(\omega) \in -\mathrm{d}s\}$, the dissipation function $\mathcal{S}_{\mathrm{T}}$ would not admit rDFT.

The composite operator $\mathrm{C} \coloneqq \mathrm{RT}$ for $\mathcal{S}_{\mathrm{tot}}$ is generally not involutive[5]. Thus, $\mathcal{S}_{\mathrm{tot}}$ does not admit TFT and the odd-parity, sufficient condition for iDFT. For rDFT, we note

$$\bar{\mathcal{S}}_{\mathrm{tot}}(\omega) \coloneqq \ln \frac{\mathrm{d}\mathbb{P}^{\mathrm{R}}}{\mathrm{d}\mathbb{P}^{\mathrm{RC}}}(\omega) = \ln \frac{\mathrm{d}\mathbb{P}^{\mathrm{R}}}{\mathrm{d}\mathbb{P}^{\mathrm{RRT}}}(\omega). \tag{4.47}$$

and thus

$$\bar{\mathcal{S}}_{\mathrm{tot}}(r(\omega)) = \ln \frac{\mathrm{d}\mathbb{P}^{\mathrm{RT}}}{\mathrm{d}\mathbb{P}^{\mathrm{RRTT}}}(\omega) = \ln \frac{\mathrm{d}\mathbb{P}^{\mathrm{RT}}}{\mathrm{d}\mathbb{P}^{\mathrm{RR}}}(\omega) \tag{4.48}$$

which becomes $-\mathcal{S}_{\mathrm{tot}}(\omega)$ if R is involutive, *i.e.* $\mathbb{P}^{\mathrm{RR}} = \mathbb{P}$. Hence, if R is involutive, $\mathcal{S}_{\mathrm{tot}}$ admits rDFT. Recall that the requirement for R to be involutive is the terminal distribution of the protocol reversed process to recover the initial distribution of the original process, *i.e.* $P_t^{\mathrm{R}} = P_0$. This condition was discussed in (Crooks, 1999; Seifert, 2005, 2012).

Similar to the total EP $\mathcal{S}_{\mathrm{tot}}$, the non-adiabatic EP $\mathcal{S}_{\mathrm{na}}$ admit neither the TFT nor the odd-parity, sufficient condition for iDFT since the composite operator $\mathrm{R} \dagger \mathrm{T}$ is not involutive in general. For rDFT, we compute

$$\bar{\mathcal{S}}_{\mathrm{na}}(r(\omega)) = \ln \frac{\mathrm{d}\mathbb{P}^{\mathrm{RT}}}{\mathrm{d}\mathbb{P}^{\mathrm{RR}\dagger}}(\omega) = \ln \frac{P_t(X_t(\omega))}{P_t^{\mathrm{R}}(X_0(\omega))} \prod_{n=1}^{t} \frac{M_n(X_{n-1}(\omega)|X_n(\omega))}{M_n^{\dagger}(X_n(\omega)|X_{n-1}(\omega))} \tag{4.49}$$

where the denominator can be obtained by using Equation (4.19) for $\mathbb{P}^{\mathrm{RR}}$ and apply $\dagger$ on it. Now, since

$$\frac{M_n(X_{n-1}|X_n)}{M_n^{\dagger}(X_n|X_{n-1})} = \frac{\pi_n(X_{n-1})}{\pi_n(X_n)}, \tag{4.50}$$

we get

$$\bar{\mathcal{S}}_{\mathrm{na}}(r(\omega)) = \ln \frac{P_0(X_0(\omega))}{P_t^{\mathrm{R}}(X_0(\omega))} - \mathcal{S}_{\mathrm{na}}(\omega). \tag{4.51}$$

We see that the condition for the odd parity to hold, $\bar{\mathcal{S}}_{\mathrm{na}}(r(\omega)) = -\mathcal{S}_{\mathrm{na}}(\omega)$, is $P_0 = P_t^{\mathrm{R}}$, *i.e.*, R to be involutive! Hence, similar to the total EP $\mathcal{S}_{\mathrm{tot}}$, the non-adiabatic EP $\mathcal{S}_{\mathrm{na}}$ admits rDFT if the CPM operator R is involutive. The rDFT of $\mathcal{S}_{\mathrm{na}}$ is an extension to Crooks' fluctuation theorem (Crooks, 1998, 1999, 2000).

[5] This can be easily seen by considering the case for only one time step. We have $P_{0,1}^{\mathrm{C}}(x_0, x_1) = P_1(x_1)P_{1|0}(x_0|x_1)$ from Equation (4.13). Thus, we have $P_{0,1}^{\mathrm{CC}}(x_0, x_1)$ equal to $P_1^{\mathrm{C}}(x_1)P_{1|0}^{\mathrm{C}}(x_0|x_1)$. With $P_{0,1}^{\mathrm{C}}$ given above, we get $P_1^{\mathrm{C}} = P_1$ and $P_{1|0}^{\mathrm{C}} = P_1(x_0)P_{1|0}(x_1|x_0)/P_0^{\mathrm{C}}(x_1)$. Therefore, $P_{0,1}^{\mathrm{CC}}(x_0, x_1) = P_1(x_1)P_1(x_0)P_{1|0}(x_1|x_0)/P_0^{\mathrm{C}}(x_1)$ which is not $P_{0,1}(x_0, x_1)$ unless all P_0, P_1, and P_0^{C} are the invariant distribution of the transition matrix $P_{1|0}$.

4.4.2 Martingale Properties of Entropy Productions

With our measure-theoretic understanding of EPs, more statistical properties of EPs could be found by revealing more on the mathematical properties of their corresponding RNDs and CPM operators. For example, by recognizing the RND of $\mathcal{Q}_{\rm hk}$, $\exp(-\mathcal{Q}_{\rm hk})$, is a martingale, a statistics of the infimum of $\mathcal{Q}_{\rm hk}$ is introduced in (Chetrite and Gupta, 2011; Neri *et al.*, 2017; Chetrite *et al.*, 2019). Here, we shall discuss the martingale properties of the four EPs and the conditions for the exponential of the negative of them to be a martingale.

In our discrete time Markov chain paradigm, a functional $M(X_{0:t})$ is a martingale if it satisfies

$$\mathbb{E}[M(X_{0:t})|X_{0:s}] = M(X_{0:s}) \tag{4.52}$$

$\forall s \in \{0, 1, \cdots, t\}$. It can be shown rather straightforwardly that since $\mathcal{S}_{\rm T}$ is not additive in time, $\exp(-\mathcal{S}_{\rm T})$ would not generally be a martingale. Thus, in the following discussion, we will focus on $\mathcal{S}_{\rm tot}$, $\mathcal{Q}_{\rm hk}$, and $\mathcal{S}_{\rm na}$.

We note that all of $\mathcal{S}_{\rm tot}$, $\mathcal{Q}_{\rm hk}$, and $\mathcal{S}_{\rm na}$ are additive in time. Therefore, for $\exp(-\mathcal{S}_\nu)$ to be a martingale where $\nu = {\rm RT}, \dagger$,or ${\rm R}\dagger{\rm T}$, we need

$$\mathbb{E}[e^{-\mathcal{S}_\nu(X_{0:t})}|X_{0:s}] = e^{-\mathcal{S}_\nu(X_{0:s})}\mathbb{E}[e^{-S_\nu(X_{s:t})}|X_{0:s}] \tag{4.53a}$$

$$= e^{-\mathcal{S}_\nu(X_{0:s})}\mathbb{E}[e^{-S_\nu(X_{s:t})}|X_s] \stackrel{?}{=} e^{-\mathcal{S}_\nu(X_{0:s})}. \tag{4.53b}$$

We thus want to have $\mathbb{E}[e^{-\mathcal{S}_\nu(X_{s:t})}|X_s] = 1, \forall s \in \{0, 1, \cdots, t\}$. By using the definition for $\nu = {\rm RT}, \dagger$, and ${\rm R}\dagger{\rm T}$, one will find

$$\mathbb{E}[e^{-\mathcal{S}_{\rm tot}(X_{s:t})}|X_s] = \frac{P^{\rm R}_{\rm end}(X_s)}{P_s(X_s)}, \tag{4.54a}$$

$$\mathbb{E}[e^{-\mathcal{Q}_{\rm hk}(X_{s:t})}|X_s] = 1, \text{ and} \tag{4.54b}$$

$$\mathbb{E}[e^{-\mathcal{S}_{\rm na}(X_{s:t})}|X_s] = \frac{P^{{\rm R}\dagger}_{\rm end}(X_s)}{P_s(X_s)} \tag{4.54c}$$

where

$$P^{\rm R}_{\rm end}(x_s) = \sum_{x_{s+1:t}} P_t(x_t) \prod_{n=0}^{t-s-1} M_{t-n}(x_{t-n-1}|x_{t-n}) \tag{4.55a}$$

$$\text{and } P^{{\rm R}\dagger}_{\rm end}(x_s) = \sum_{x_{s+1:t}} P_t(x_t) \prod_{n=0}^{t-s-1} M^\dagger_{t-n}(x_{t-n-1}|x_{t-n}) \tag{4.55b}$$

and are the terminal distributions of the processes R and R$\dagger$ defined on the time interval $s : t$.

This shows that $\exp(-\mathcal{Q}_{\rm hk})$ is always a martingale which implies that $\mathcal{Q}_{\rm hk}$ is a submartingale satisfying

$$\mathbb{E}[\mathcal{Q}_{\rm hk}(X_{0:t})|X_{0:s}] \geq \mathcal{Q}_{\rm hk}(X_{0:s}) \tag{4.56}$$

by the convexity of negative logarithm. Since s is arbitrary in $0:t$, the RHS of Equation (4.54a) and (4.54c) needs to be 1 for all x_s and s. This means that $\exp(-\mathcal{S}_{\rm tot})$ or $\exp(-\mathcal{S}_{\rm na})$ are only martingale when the reversal R or R† recovers all the marginal distributions in a reversed order: $P_t \to P_{t-1} \to \cdots \to P_0$ in the reversed process, which is not generally true. One exception is when the dynamics is time homogeneous and also starts with the invariant distribution such that $P_n = \pi, \forall n \in \{0, 1, \cdots, t\}$.

4.5 Summary and Discussion

In this chapter, we characterize the difference between the statistical properties of the original stochastic process and the one after reversal by a change of probability measure, an analog to Schrödinger's picture on Quantum Mechanics (Qian *et al.*, 2019). A change in statistical properties from a physical operation is represented by an operator ν operating on a probability measure $\mathbb{P}$ in the probability measure space $\mathcal{P}$. With our mathematically more general and concise CPM formalism, we have presented a comprehensive study of the properties of irreversibilites (EPs) including FRs. Sufficient conditions for the FRs of the four EPs are summarized in Table 4.2. Importantly, a hierarchy of the generality for FRs in general stochastic processes can be revealed from our work: both IFT and GFR are generally true; rDFT and iDFT require odd parity symmetry with different $\hat{S}_\nu$ as stated in (Seifert, 2012); and TFT further requires the CPM operator to be realized by an involutive map on the trajectory space Ω. This hierarchical structure of the domain of validity for FRs reveals relation between FRs such as TFT implies iDFT.

We further demonstrate how to obtain other properties of EPs from their logarithm RND definitions such as their martingale properties and distinguish the difference between dissipation function $\mathcal{S}_{\rm T}$ introduced by Evans and Searles (2002) and the total entropy production $\mathcal{S}_{\rm tot}$. The properties of the four EPs (irreversibility) in physics and chemistry including various FRs we have discussed above have been summarized in Table 4.2. The "paradox" that the two EPs have the same entropy production rate but with non-negative difference in expectation for finite time interval in time homogeneous processes is resolved by noting the failure of time additivity for the dissipation function.

It is important to note that throughout this chapter (and this thesis), we have assumed the state variables

	$= 0$ when	$\mathbb{E}[\cdot] \geq 0$, IFT, GFR	TFT	iDFT	rDFT	additive in time	$e^{-[\cdot]}$ a martingale
$\mathcal{S}_T$	EQ	Yes	Yes	Yes	NESS	NESS	NESS
$\mathcal{S}_{\rm tot}$	EQ	Yes	NESS	NESS	if $P_0 = P_t^R$	Yes	NESS
$\mathcal{Q}_{\rm hk}$	TH+DB	Yes	NESS	Yes	Yes	Yes	Yes
$\mathcal{S}_{\rm na}$	NESS	Yes	NESS	NESS	if $P_0 = P_t^R$	Yes	NESS

Table 4.2: Properties of the four path relative entropy for Markov processes. $\mathbb{E}[\cdot]$ denotes the expectation and the non-negative expectation of entropy production is the classical second law of thermodynamics. P_0 is the initial distribution of the original process. P_t^R is the terminal distribution of the protocol reversed process, *i.e.* the distribution one gets by starting with initial distribution P_t and then marching with reversed order of transition proability matrices for t steps. TH stands for time homogeneous; EQ stands for equilibrium (steady state with detailed balance); and NESS means the nonequilibrium steady state. Note that in NESS, we have $\mathcal{S}_{\rm T} \equiv \mathcal{S}_{\rm tot} \equiv \mathcal{Q}_{\rm hk}$ and $\mathcal{S}_{\rm na} = 0$. Table adapted from (Yang and Qian, 2020).

X_n to have even parity under the time reversal, *i.e.* they are position-like physical quantities. One extension to our work is to consider variables that have odd parity under time reversal such as velocity (Spinney and Ford, 2012; Ge, 2014; Li and Tu, 2019). Note that if one transform a system with memory (such as underdamped systems) into a Markov dynamics, the extended state variable in the Markov dynamics will have odd parity dimensions (Zeng and Wang, 2017).

The general theory we presented in Section 4.3 is in fact a general result for *fluctuating relative entropy* and its statistical properties. It can also be applied to entropies defined in information theory (Cover and Thomas, 2006). For example, suppose we have a finite state space $\mathcal{X} \equiv \Omega$, we can choose the reference measure P_X^ν to be the uniform distribution, *i.e.* $\mathbb{P}^\nu$ as the Lebesgue measure, to get an entropy corresponding to the maximum entropy $\ln \|\Omega\|$ minuses the fluctuating Shannon entropy of the system, $H(\omega) = \ln \|\Omega\| - [-\ln P_X(X(\omega))]$ where $\|\Omega\|$ represents the size of the sample space. Another example would be to have $\Omega = \mathcal{X} \otimes \mathcal{Y}$ and consider the fluctuating mutual information between two random variables X and Y, $I(\omega) = \ln \frac{P_{X,Y}(X(\omega),Y(\omega))}{P_X(X(\omega))P_Y(Y(\omega))}$. Our theory immediately implies that both $H(\omega)$ and $I(\omega)$ have non-negative expectation, and admit IFT and GFR.

Chapter 5

Fundamental Roles of Cycle in Nonequilibrium Dynamics

As introduced in Sec. 2.2, a stochastic process reaches its steady state when the total inward and outward probability fluxes balance out at each state. The existence of a steady state requires the system to have recurring states, *i.e.* forming cyclic paths (Durrett, 2019; Jiang *et al.*, 2004). This strongly imply that cyclic paths in the state space have fundamental roles in the dynamics at the steady state. Such fundamental importance of cycles have been discussed widely in Markov chains (Schnakenberg, 1976; Hill, 1982; Jiang *et al.*, 2004; Kalpazidou, 2006; Qian *et al.*, 2016b), as we shall review in Sec. 5.1 and add on in Sec. 5.2. Here we further this idea to continuous-space Markov processes (diffusion), from 2-D and 3-D (Qian, 1998) to dimensions higher than 3. Our work completes the cycle theory for nonequilibrium dynamics (Yang and Qian, 2021a). The extension to diffusion in $\mathbb{R}^n$ requires the mathematics of differential form as we summarize in Appendix A. Our results are summarized in a bi-vector calculus formalism in Sec. 5.3, generalizing vector calculus to bi-vector calculus with anti-symmetric matrices.

5.1 Cycle Completion and the Landauer-Bennett-Hill Principle

Time irreversibility in the standard thermodynamics, *i.e.* the second law of thermodynamics, was always about cyclic (mechanical) processes (Landau and Lifshitz, 1980; Huang, 1991). Recall Clausius's theorem:

in any cyclic process throughout which the temperature is defined, we have

$$\oint \frac{đQ}{T} \leq 0 \tag{5.1}$$

where $đQ$ is the infinitesimal amount of heat the system *absorbed* from the reservoir of temperature T. For two reservoirs if $T_{\mathrm{H}} > T_{\mathrm{L}}$, then $\frac{\delta Q_{\mathrm{L}}}{T_{\mathrm{L}}} \leq -\frac{\delta Q_{\mathrm{H}}}{T_{\mathrm{H}}}$, which is Clausius's statement of the 2nd law. Furthermore, the equality holds when the cyclic process is reversible: $\oint \frac{đQ}{T} = 0$, *i.e.* $\int \frac{đQ}{T}$ is path independent. This means that the quantity $\frac{đQ}{T}$ is an exact differential and can be expressed as the difference between a scalar potential $\mathrm{d}S$ given by the entropy.

Results above have been extended to general Markov processes by considering the affinity $đ\mathcal{Q}$ as discussed in Sec. 3.1. The classic "reversibility" in standard thermodynamics becomes the irreversibility at the steady state of Markov processes, *i.e.* the concept of *detailed balance*. By identifying $đ\mathcal{Q} = đQ/T$ for mechanical systems, the Calusius's theorem is in fact a special case of the Kolmogorov's cycle condition in mathematics (Kolmogorov, 1936) and the Wegscheider condition in chemical kinetics (Wegscheider, 1901; Lewis, 1925). The concept of detailed balance can be summarized by the following four equivalent statements (Jiang *et al.*, 2004):

Theorem 5.1. *For a Markov chain with transition matrix $M_{j|i}$ and a unique invariant distribution π_i, the following statements are equivalent:*

1. *Detailed balance: for any transition i to j, steady-state probability fluxes are balanced*

$$\pi_i M_{j|i} = \pi_j M_{i|j}.$$

2. *Affinity of any path $i_0 i_1 \cdots i_k$ can be expressed as the exact difference of a scalar potential Φ,*

$$\mathcal{Q}\left(i_0 \cdots i_k\right) = \Phi\left(i_k\right) - \Phi\left(i_0\right).$$

3. *No cycle affinity: for all cycles $i_0 i_1 \cdots i_k i_0$,*

$$\mathcal{Q}(i_0 i_1 \cdots i_k i_0) \coloneqq \ln \frac{M_{i_1|i_0} M_{i_2|i_1} \cdots M_{i_0|i_k}}{M_{i_k|i_0} M_{i_{k-1}|i_k} \cdots M_{i_0|i_1}} = 0.$$

4. *The average entropy production in the steady state (average housekeeping heat) is zero:*

$$q_{\mathrm{hk}} = \sum_{i,j} \pi_i M_{j|i} \ln \frac{\pi_i M_{j|i}}{\pi_j M_{i|j}} = 0.$$

While the first condition, $\pi_i M_{j|i} = \pi_j M_{i|j}$, defined on all transitions $i \mapsto j$ is often considered as the

"definition" of detailed balance, we argue that the zero cycle affinity condition is conceptually more "fundamental". We first notice that the "no-net-flux" condition $\pi_i M_{j|i} = \pi_j M_{i|j}$ is not a property locally defined to the transition alone: the stationary distribution π_i is a global property of the whole system. In contrast, the "no-cycle-affinity" condition $\mathcal{Q}(\sigma)$ is locally defined for a cycle $\sigma := i_0 i_1 \cdots i_k i_0$. Furthermore, let's consider the following thought experiment. Suppose we have a discrete-state Markov process and would like to determine whether its stationary process is detailed balanced or not, *i.e.* in equilibrium or not. We run the process with a trajectory $i_0 i_1 \cdots i_k$ and measure the affinity of the path

$$\mathcal{Q}(i_0 i_1 \cdots i_k) = \ln \left(\frac{M_{i_1|i_0} M_{i_2|i_1} \cdots M_{i_k|i_{k-1}}}{M_{i_0|i_1} M_{i_1|i_2} \cdots M_{i_{k-1}|i_k}} \right). \tag{5.2}$$

The "no-cycle-affinity" condition states that the process admits a detailed balanced steady state if and only if $\mathcal{Q}(\sigma) = 0$ for all cycles σ, *e.g.* $i_0 i_1 \cdots i_k i_0$. Therefore, we shall examine $\mathcal{Q}$ everytime the process completes a cycle, and if $\mathcal{Q} = 0$, we continue to run the process for another cycle. We can draw the conclusion either when we encounter a cycle with nonzero $\mathcal{Q}$, signifying detailed balance broken, or we complete all cycles and find that all cycles are reversible with zero dissipation.

In the thought experiment above, we see that it is essential to finish cycles to determine whether a system admits detailed balance or not. We can't gain useful information before the process completes a full cycle. This is because for a trajectory one-step before the completion of a cycle, say $i_0, i_1, \cdots i_k$, with all distinct states, there's always a possibility that the last step balances out the probability difference, *i.e.*

$$\mathcal{Q}(i_0 i_1 \cdots i_k) + \mathcal{Q}(i_k i_0) = 0, \tag{5.3}$$

giving us a reversible cycle with no zero cycle affinity. We shall call this observation the *Landauer-Bennett-Hill (LBH) principle*: in the theory of computation, R. Landauer (1961) applied the second law of thermodynamics to point out the necessary accompanied heat dissipation of "erasing one bit"; C. H. Bennett (2003) then used Landauer's principle to argue that it is the last step of "erasing bits" in a cyclic Maxwell demon that "saves" the second law. Independently in the theory of cycle kinetics driven by chemostatic chemical potential, T. L. Hill introduced the concept of *cycle completion* (Hill and Chen, 1975) and argued that cycles in mesoscopic nonequilibrium thermodynamics (NET) are more fundamental than transitions (Hill, 1977). The notion of "erasing one bit" of Landauer's and Bennett's matches exactly the idea of "completing one cycle".

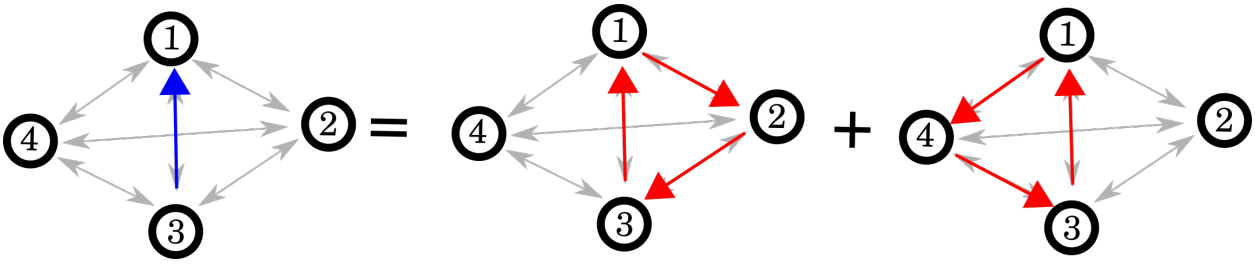


Figure 5.1: Edge flux from state 3 to state 1 (blue) at the steady state is decomposed into the sum of cycle fluxes in (red) cycles that contain the edge $3 \mapsto 1$.

All the discussion above summarizes into one very important concept: the fundamental dynamic units for nonequilibrium steady states (NESS) are cycles. Concepts and properties in NESS should be understood in terms of cycles: including the stationary probability flux, the housekeeping heat, and Onsager's reciprocality (Onsager, 1931). We shall review such understanding the its implications for Markov chains (Jiang *et al.*, 2004; Qian *et al.*, 2016b; Yang and Qian, 2021a) in the next section.

5.2 Cycle Flux and Onsager Reciprocality

One of the most important cyclic understanding of steady state stochastic dynamics is the following. The one-way edge stationary flux actually has an all-cycle decomposition (Qian and Qian, 1979, 1982; Qian and Wang, 1999; Hill, 1989; Jiang *et al.*, 2004),

$$\pi_i p_{j|i} = \sum_{\sigma \in \text{all cycles}} J_\sigma \mathbb{I}_\sigma(i,j) \tag{5.4}$$

where the "cycle flux" J_σ is the occurrence rate of a cycle σ in an infinite-long ergodic trajectory and $\mathbb{I}_\sigma(i,j) = 1$ if edge ij is in cycle σ and $= 0$ otherwise. See Fig. 5.1 for an illustration with a simple example. This result can be intuitively seen by a simple frequentists' understanding of $\pi_i p_{j|i}$ and J_σ. In an infinitely-long ergodic trajectory, the value of $\pi_i p_{j|i}$ is the asymptotic occurrence rate of the transition $i \mapsto j$. The system revisit state i infinite times in an infinitely-long ergodic trajectory. Therefore, each of the transition[1] $i \mapsto j$ belongs to a cycle $ij \cdots i$. This means that the asymptotic occurrence rate of transitions $i \mapsto j$ is equal to the sum of the occurrence rate of all cycles that contains the transition $i \mapsto j$, therefore Eq. (5.4).

With the cycle-flux decomposition of an edge flux, the average housekeeping heat in Theorem 5.1 has a

[1] For a finite path, there may be one possible exception at the end. But that is negligible in an infinitely-long trajectory.

cycle representation:

$$q_{\rm hk} = \sum_{i,j} \pi_i p_{j|i} \ln \frac{\pi_i p_{j|i}}{\pi_j p_{i|j}} = \sum_\sigma J_\sigma \left[\sum_{i,j} \mathbb{I}_\sigma(i,j) \ln \frac{\pi_i p_{j|i}}{\pi_j p_{i|j}} \right] = \sum_\sigma J_\sigma \mathcal{Q}(\sigma). \tag{5.5}$$

Since $\pi_i p_{j|i}$ and J_σ have frequency interpretations as the occurrence rate of transition $i \mapsto j$ and cycle σ in an infinitely long chain, the average housekeeping heat is in fact

$$q_{\rm hk} = \lim_{T\to\infty} \frac{\mathcal{Q}_{\rm hk}\left(x_{0:T}\right)}{T} = \sum_{i,j} \pi_i p_{j|i} \mathcal{Q}_{\rm hk}(ij) \tag{5.6a}$$

$$= \sum_\sigma J_\sigma \mathcal{Q}(\sigma). \tag{5.6b}$$

As $\mathcal{Q}\left(\sigma\right)$ is locally defined on σ, this gives a vivid picture of how $\mathcal{Q}_{\rm hk}\left(x_{0:T}\right)$ accumulates in time in $x_{0:\infty}$: every time the process finishes a cycle σ, the irreversibility $\mathcal{Q}_{\rm hk}$ adds up a cycle affinity $\mathcal{Q}\left(\sigma\right)$. Equilibrium systems with $e_{\rm p} = 0$ is because the occurrence rate of $J_\sigma = J_{\sigma^-}$ so $\mathcal{Q}\left(\sigma\right)$ cancels out with $\mathcal{Q}\left(\sigma^-\right)$ in total.

The cycle flux J_σ actually has an analytic expression for Markov chains (Hill, 1989; Jiang *et al.*, 2004). From it, one can show that

$$\mathcal{Q}(\sigma) = \ln \frac{J_\sigma}{J_{\sigma_-}} \tag{5.7}$$

where σ_- is the cycle with reversed orientation of σ. This means that $\mathcal{Q}(\sigma) = 0$ if and only if $J_\sigma = J_{\sigma_-}$. This is a very important property that relates cycle affinity (force) to cycle flux. Such property is not guaranteed in the other type of cycle-flux decomposition in graph theory where cycles are defined as *fundamental cycle*s (Schnakenberg, 1976).

The net edge flux $\eta = ij$ from state i to state j has the following cycle expression:

$$J_\eta = \pi_i p_{j|i} - \pi_j p_{i|j} = \sum_\sigma \left(J_\sigma - J_{\sigma_-}\right) \mathbb{I}_\sigma(\eta). \tag{5.8}$$

Let's denote the housekeeping heat on the edge $\eta = ij$ as

$$\mathcal{Q}_{\rm hk}\left(ij\right) \coloneqq \ln \frac{\pi_i M_{j|i}}{\pi_j M_{i|j}}. \tag{5.9}$$

Then, with

$$\mathcal{Q}\left(\sigma\right) = \sum_{\eta'} \mathcal{Q}_{\rm hk}\left(\eta'\right) \mathbb{I}_\sigma(\eta') = \ln \frac{J_\sigma}{J_{\sigma^-}}, \tag{5.10}$$

we now have

$$J_\eta = \sum_\sigma \left(e^{\mathcal{Q}(\sigma)} - 1\right) J_{\sigma\_}\mathbb{I}_\sigma(\eta) = \sum_\sigma \left(e^{\sum_{\eta'} \mathcal{Q}_{\rm hk}(\eta')\mathbb{I}_\sigma(\eta')} - 1\right) J_{\sigma\_}\mathbb{I}_\sigma(\eta). \tag{5.11}$$

This couples the "force" on edges η' to the flux on edge η. When the system is near equilibrium, all $\mathcal{Q}_{\rm hk}(\eta')$ are small. One then have

$$J_\eta = \sum_\sigma \left(e^{\sum_{\eta'} \mathcal{Q}_{\rm hk}(\eta')\mathbb{I}_\sigma(\eta')} - 1\right) J_{\sigma\_}\mathbb{I}_\sigma(\eta) \tag{5.12a}$$

$$\approx \sum_\sigma \sum_{\eta'} \mathbb{I}_\sigma(\eta)\mathcal{Q}_{\rm hk}(\eta')\,\mathbb{I}_\sigma(\eta')J_{\sigma\_} \tag{5.12b}$$

$$= \sum_{\eta'} \underbrace{\left[\sum_\sigma \mathbb{I}_\sigma(\eta)J_{\sigma\_}\mathbb{I}_\sigma(\eta')\right]}_{\text{Symmetric Onsager matrix}} \mathcal{Q}_{\rm hk}(\eta'). \tag{5.12c}$$

This is the Onsager's reciprocality and symmetry in Markov chains (Hill, 1982; Qian *et al.*, 2016b). This clearly shows that Onsager's reciprocality and symmetry fundamentally originate from the cycle expression.

Now, from a more careful look at Eq. (5.11), we observe that the reciprocality between η and η' manifests in that the mutual interaction between them are coupled only through cycles that contain both η and η' (Yang and Qian, 2021a): among all cycles, only those which contains η contribute to J_η; among them, only those which contains η' has the effect from η', *i.e.* a $\mathcal{Q}_{\rm hk}(\eta')$ term in $(\cdots)$; and only among these shared cycles does $\mathcal{Q}_{\rm hk}(\eta)$ affect back to $J_{\eta'}$, as illustrated by Fig. 5.2. That is, Onsager's reciprocality in Markov chains are solely due to "cycle coupling" and holds for a system in its NESS arbitrarily far from equilibrium. The symmetry of the reciprocality further requires the system to be near equilibrium in general discrete-systems.

5.3 Bivectorial Cycle Affinity and Cycle Flux in Diffusion

Parallel to the cycle representation of discrete-state Markov processes which we have reviewed above, we now present a cycle representation for the NET of continuous Markovian stochastic dynamics in its phase space, the whole Euclidean $\mathbb{R}^n$, and discuss how the LBH principle comes in. The $n = 2$ (and $n = 3$ implied) case, in which a vector potential arises, has been investigated by Qian (1998). However, the generalization to $n > 3$ systems is nontrivial. One of the difficulties is that, for systems with $n > 3$, vector calculus is no long sufficient since it is not possible to represent vorticity by a vector through the

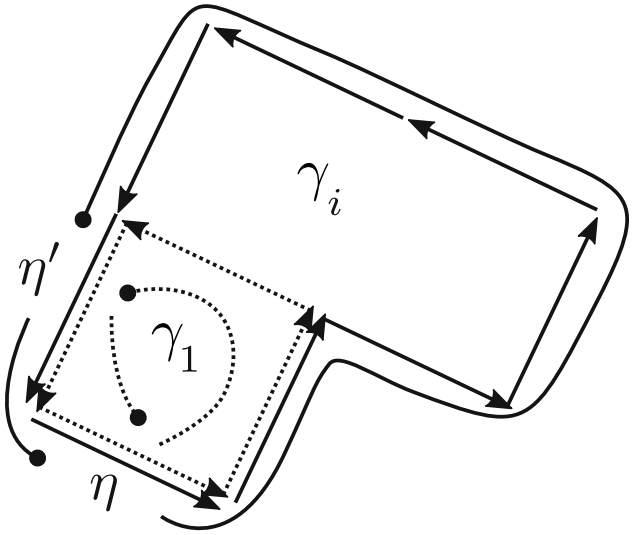


Figure 5.2: Two edges η and η' are coupled through all the cycles γ they are both in. The cycle-coupling is the origin of Onsager's reciprocality. Arrows represent cycle edges, and line with dot at the end represents the driving from force to flux. Dash lines indicate the smallest cycle coupling and solid lines indicate another cycle coupling. This figure is from our work (Yang and Qian, 2021a).

right-hand rule: there are more than one dimensions in the "thumb" direction. It turns out that both the cycle flux and cycle affinity in the continuous system are bivectors (see Appendix A), which can be represented by their skew-symmetric $n \times n$ matrices components.

5.3.1 Cycle Changes of Thermodynamic Quantities

A work-like quantity in diffusion is defined on transitions and is integrated along a path according to the infinitesimal equation

$$đ\mathcal{W}\left(\mathbf{X}_t, t\right) \coloneqq \boldsymbol{f}\left(\mathbf{X}_t, t\right) \circ \mathrm{d}\mathbf{X}_t = \boldsymbol{f}\left(\mathbf{X}_t + \frac{1}{2}\mathrm{d}\mathbf{X}_t, t\right) \circ \mathrm{d}\mathbf{X}_t \tag{5.13}$$

where $\circ$ denotes Strotanovich midpoint integration. By stochastic calculus and the SDE given by Eq. (2.29), it can also be rewritten as

$$đ\mathcal{W}\left(\mathbf{X}_t, t\right) = \boldsymbol{f}\left(\mathbf{X}_t, t\right) \cdot \mathrm{d}\mathbf{X}_t + \frac{1}{2}\mathrm{d}\mathbf{X}_t \cdot \nabla \boldsymbol{f}\left(\mathbf{X}_t, t\right) \mathrm{d}\mathbf{X}_t \tag{5.14a}$$

$$= \left\{\mathbf{b}\left(\mathbf{X}_t\right) \cdot \boldsymbol{f}\left(\mathbf{X}_t, t\right) + \nabla \cdot \left[\mathbf{D}\left(\mathbf{X}_t\right) \boldsymbol{f}\left(\mathbf{X}_t, t\right)\right]\right\} \mathrm{d}t + \boldsymbol{f}\left(\mathbf{X}_t, t\right) \cdot \boldsymbol{\Gamma}\left(\mathbf{X}_t\right) \mathrm{d}\mathbf{W}_t. \tag{5.14b}$$

For a smooth cyclic path $\Gamma : \mathbf{x}(t), 0 \leq t \leq \tau$ where $\mathbf{x}(0) = \mathbf{x}(\tau) = \boldsymbol{\xi}$ in $\mathbb{R}^n$, the cyclic "work" can be rewritten by considering a surface Σ whose boundary is given by the path Γ and using Stoke's theorem (Feng and Wang, 2011).

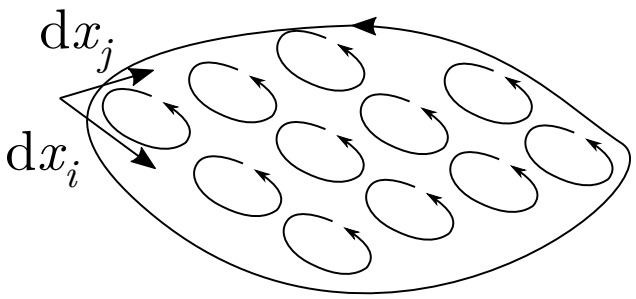


Figure 5.3: Illustration of Stoke's theorem in Eq. (5.15). The total "work" done on a bigger cycle is the sum of the "work" on the smaller constituting cycles.

$$\mathcal{W}(\Gamma) = \oint_\Gamma \boldsymbol{f} \cdot \mathrm{d}\mathbf{x} = \oint_\Gamma \sum_{i=1}^{n} f_i \mathrm{d}x_i \tag{5.15a}$$

$$= \int_\Sigma \sum_{1\le i<j\le n} (\partial_i f_j - \partial_j f_i)\, \mathrm{d}x_i \wedge \mathrm{d}x_j = \int_\Sigma \nabla \wedge \boldsymbol{f} \cdot \mathrm{d}\boldsymbol{\sigma}. \tag{5.15b}$$

In Eq. (5.15), neither $\nabla \wedge \boldsymbol{f}$ nor $\mathrm{d}\boldsymbol{\sigma}$ are vectors in $\mathbb{R}^n$; rather they are bivectors, planary objects that have skew-symmetric matrix components with respect to the orthonormal basis $\{\mathbf{e}_i \wedge \mathbf{e}_j, 1 \le i < j \le n\}$ where $\mathbf{e}_i$ is the unit vector in the ith direction of Cartesian coordinate and $\mathbf{e}_i \wedge \mathbf{e}_j$ is the signed area of the parallelogram spanned by $\mathbf{e}_i$ and $\mathbf{e}_j$. The $\nabla \wedge \boldsymbol{f} = \sum_{i<j}(\partial_i f_j - \partial_j f_i)\mathbf{e}_i \wedge \mathbf{e}_j$ denotes the "curl" of $\boldsymbol{f}$, representing the vorticity of $\boldsymbol{f}$ by a bivector with skew-symmetric matrix components. Here, we understand $\mathrm{d}x_i \wedge \mathrm{d}x_j$ as the (i,j)th components of the infinitesimal plane $\mathrm{d}\boldsymbol{\sigma}$ as a bivector. The dot product in Eq. (5.15) between two bivectors are defined as the half of the Frobenius product between their matrix components. See Appendix A for a more detailed introduction in the language of differential form.

The cyclic changes of the thermodynamic quantities are then given by,

$$\Delta\Phi(\Gamma) = -\mathcal{Q}_{\mathrm{ex}}(\Gamma) = 0 \tag{5.16a}$$

$$\Delta S(\Gamma) = -\Delta F(\Gamma) = S(\boldsymbol{\xi}, \tau) - S(\boldsymbol{\xi}, 0) \tag{5.16b}$$

$$\mathcal{Q}(\Gamma) = \mathcal{Q}_{\mathrm{hk}}(\Gamma) = \int_\Sigma \nabla \wedge \left(\mathbf{D}^{-1}\mathbf{b}\right) \cdot \mathrm{d}\boldsymbol{\sigma} \tag{5.16c}$$

$$\mathcal{S}_{\mathrm{tot}}(\Gamma) = \Delta S(\Gamma) + \mathcal{Q}(\Gamma) \tag{5.16d}$$

where $\boldsymbol{\xi}$ is the starting and ending state of the trajectory Γ. If the path probability of a path Γ in a Markov process starts with the invariant probability as the initial distribution, $\Delta S\left(\Gamma\right) = 0$ for all cycles Γ, over which the total entropy production equals to the heat dissipation:

$$\mathcal{S}^*_{\mathrm{tot}}(\Gamma) = \mathcal{Q}(\Gamma) = \int_\Sigma \nabla \wedge \left(\mathbf{D}^{-1}\mathbf{b}\right) \cdot \mathrm{d}\boldsymbol{\sigma}. \tag{5.17}$$

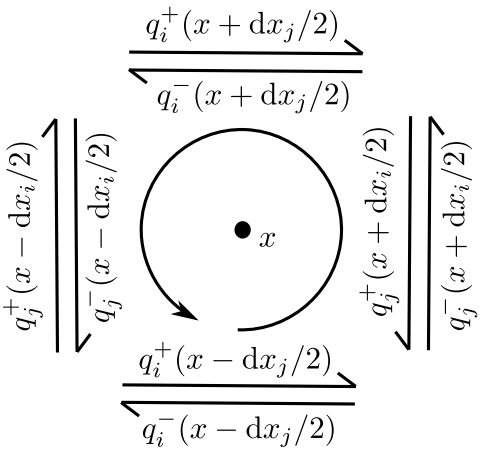


Figure 5.4: Transitions on an infinitesimal square $\mathrm{d}x_i \wedge \mathrm{d}x_j$ in a lattice. The eight transition rates $q_{i \text{ or } j}^{\pm}$ determine the cycle affinity. This explains the physical picture of cycle affinity as shown in Eq. (5.18). This figure is adapted from (Yang and Qian, 2021a).

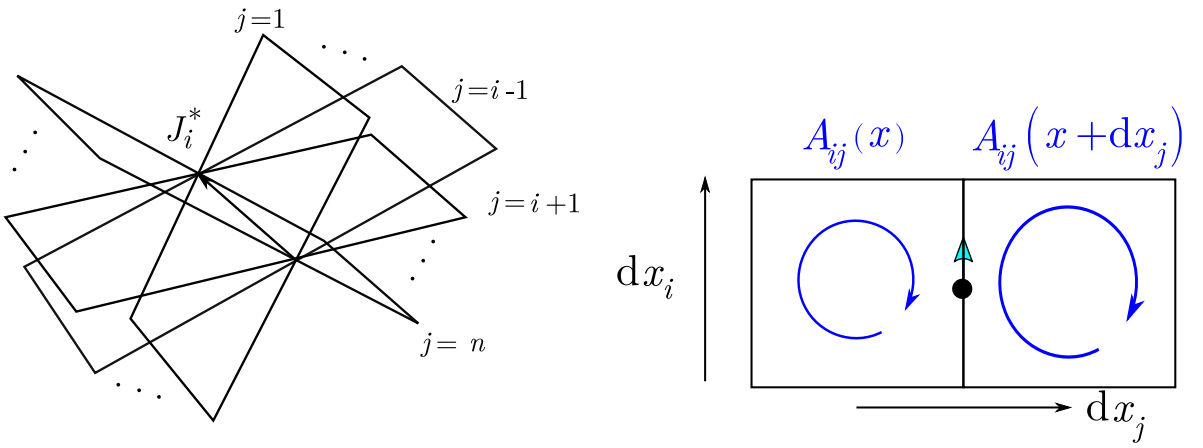
S and Φ are state functions, but $\mathcal{Q}$ and $\mathcal{S}_{\text{tot}}^*$ are not. In fact, Eq. (5.17) shows that $\nabla \wedge \left(\mathbf{D}^{-1}\mathbf{b}\right) \cdot \mathrm{d}\boldsymbol{\sigma}$ is the cyclic entropy production of an infinitesimal cycle $\mathrm{d}\boldsymbol{\sigma}$, and the total cyclic entropy production is the integral of all the infinitesimal cycle that tiles the cycle Γ. This implies that the bivector $\nabla \wedge \left(\mathbf{D}^{-1}\mathbf{b}\right)$ can be interpreted as the *cycle affinity* in diffusion, and the Kolmogorov's cycle condition in diffusion for detailed balanced systems becomes a zero cycle affinity condition $\nabla \wedge \left(\mathbf{D}^{-1}\mathbf{b}\right) = \mathbf{0}$. With Poincaré lemma applied on the contractible $\mathbb{R}^n$, this implies that $\mathbf{D}^{-1}\mathbf{b}$ is curl-free if and only if it is a gradient field, with a scalar potential given by Φ.

The physical picture of cycle affinity is clear in the discrete lattice picture as shown in Fig. 5.4. Focusing on the infinitesimal square of $\mathrm{d}x_i \wedge \mathrm{d}x_j$ at $\mathbf{x}$, the cycle affinity of the counterclockwise cycle is given by

$$\mathcal{Q}_{ij}\left(\mathbf{x}\right) = \ln \frac{q_i^+(\mathbf{x}-\frac{\mathrm{d}x_j}{2})q_j^+(\mathbf{x}+\frac{\mathrm{d}x_i}{2})q_i^-(\mathbf{x}+\frac{\mathrm{d}x_j}{2})q_i^-(\mathbf{x}-\frac{\mathrm{d}x_i}{2})}{q_i^-(\mathbf{x}-\frac{\mathrm{d}x_j}{2})q_j^-(\mathbf{x}+\frac{\mathrm{d}x_i}{2})q_i^+(\mathbf{x}+\frac{\mathrm{d}x_j}{2})q_i^+(\mathbf{x}-\frac{\mathrm{d}x_i}{2})} \tag{5.18a}$$

$$\sim \left[\partial_i\left(\frac{1}{\mathrm{d}x_j}\ln\frac{q_j^+(\mathbf{x})}{q_j^-(\mathbf{x})}\right) - \partial_j\left(\frac{1}{\mathrm{d}x_i}\ln\frac{q_i^+(\mathbf{x})}{q_i^-(\mathbf{x})}\right)\right]\mathrm{d}x_i\mathrm{d}x_j. \tag{5.18b}$$

where $\frac{1}{\mathrm{d}x_j}\ln\frac{q_j^+}{q_j^-}$ becomes $\left(\mathbf{D}^{-1}\mathbf{b}\right)_j$ from the theory of diffusion. We see that the particular order of $\partial_i\left(\mathbf{D}^{-1}\mathbf{b}\right)_j - \partial_j\left(\mathbf{D}^{-1}\mathbf{b}\right)_i$ is because the increment of q_j^+/q_j^- in the i-th direction flavors the counterclockwise rotation whereas the increment of q_i^+/q_i^- in the j-th direction hinders it. Their net contribution gives the force on the cycle, the cycle affinity.



(a) (b)

Figure 5.5: **(a)** For each unit vector $\hat{x}_i$ at a lattice point, there are $(n-1)$ number of $\hat{x}_j$ with which $\hat{x}_i \wedge \hat{x}_j$ forms a bivector, an oriented planar element. A_{ij} is the cycle flux around the element. **(b)** Bivector potential A_{ij} and its derivative $\partial_j A_{ij}$ in a discrete lattice system. $A_{ij}(n) - A_{ij}(n-1)$ contributes to the edge flux along $\hat{x}_i$. A similar $A_{ik}(m) - A_{ik}(m-1)$ also contributes to the same edge flux. This is the geometric meaning of Eq. (5.19).

5.3.2 Cycle Representation of Kinematic Stationary Probability Flux

The divergence-free stationary flux $\mathbf{J}^*$ can be expressed in terms of a *bivector potential* $\mathbf{A}(\mathbf{x})$ for diffusion on $\mathbb{R}^n$, $\nabla \times \mathbf{A} = \mathbf{J}^*$ according to Poicaré's lemma (See Appendix A). Note that $\mathbf{A}$ is also not a vector in $\mathbb{R}^n$ in general; rather it is a bivector whose components A_{ij} satisfy

$$J_i^*(\mathbf{x}) = (\nabla \times \mathbf{A})_i(\mathbf{x}) = \sum_{j=1}^{n} \partial_j A_{ij}(\mathbf{x}). \tag{5.19}$$

It is straightforward to verify that $\nabla \cdot (\nabla \times \mathbf{A}) = 0$. See Appendix for the derivation. Throughout this thesis, we fix the $\times$ notation in $\nabla \times \mathbf{A}$ to denote the vector from a bivector potential $\mathbf{A}$, $(\nabla \times \mathbf{A})_i \coloneqq \sum_{j=1}^{n} \partial_j A_{ij}$, and the $\wedge$ notation in $\nabla \wedge \mathbf{u}$ to map a vector $\mathbf{u}$ to a bivector: $(\nabla \wedge \mathbf{u})_{ij} \coloneqq \partial_i u_j - \partial_j u_i$.

The physical meaning of Eq. (5.19) is as followed. For every infinitesimal change $\mathrm{d}x_i$ in the x_i direction at the point $\mathbf{x} \equiv (x_1, \cdots, x_n) \in \mathbb{R}^n$, there are $(n-1)$ orthogonal directions $\mathrm{d}x_j$, $j \neq i$, and $\mathrm{d}x_i \wedge \mathrm{d}x_j$ corresponds to a bivector, an infinitesimal planar element in the ij-th plane, as shown in Fig. 5.5a. Here, we give the bivector potential $A_{ij}(\mathbf{x})$ a physical interpretation as the *stationary cycle flux* around the oriented infinitesimal planar element $\mathrm{d}x_i \wedge \mathrm{d}x_j$ at $\mathbf{x}$. The ith component of $\mathbf{J}^*$, J_i^*, is determined from all the neighboring infinitesimal planes $\mathrm{d}x_i \wedge \mathrm{d}x_j$, $j \neq i$. $\partial_j A_{ij}$ contributes a net edge flux along x_i due to the pair of A_{ij} at $(x_1, \cdots, x_j, \cdots, x_n)$, and at $(x_1, \cdots, x_j - \mathrm{d}x_j, \cdots, x_n)$ as shown in Fig. 5.5b.

An increasing A_{ij} in the jth direction leads to a positive net flow $\partial_j A_{ij}$ in the x_i direction. In a word,

Eq. (5.19) gives a cycle representation of the steady state fluxes J_i^* along the edges in terms of the cycle fluxes around the planar elements. An earlier discussion for 3-D cases can be found in Qian (1998). $\mathbf{A}(\mathbf{x})$ is a potential of $\mathbf{J}^*(\mathbf{x})$ in terms of vorticity componenets at $\mathbf{x}$.

5.3.3 Landauer-Bennettt-Hill principle in diffusion

The average rate of $\mathcal{W}$ is then given by

$$\dot{\mathcal{W}} := \frac{\mathbb{E}\left[\mathrm{d}\mathcal{W}\right]}{\mathrm{d}t} = \int \left(\mathbf{b}\cdot\boldsymbol{f} + \nabla\cdot(\mathbf{D}\boldsymbol{f})\right) p\mathrm{d}V = \int \mathbf{J}\cdot\boldsymbol{f}\mathrm{d}V = \mathbb{E}\left[\mathbf{v}\cdot\boldsymbol{f}\right]. \tag{5.20}$$

where $\mathrm{d}V = \prod_{i=1}^n \mathrm{d}x_i$ is the volume of an n-dimensional infinitesimal cube, $\mathbf{J}$ is the probability flux identified in Eq. (2.18) and $\mathbb{E}\left[\cdot\right]$ denotes expectation. In NESS, the $\mathbf{J}(\mathbf{x},t)$ in Eq. (5.20) is replaced by the divergence-free stationary flux $\mathbf{J}^*(\mathbf{x})$. With our bivector potential, the mean rate of $\mathcal{W}$ in Eq. (5.13) with corresponding force $\boldsymbol{f}$ can be rewritten by integration by part,

$$\dot{\mathcal{W}}^* = \int_{\mathbb{R}^n} \mathbf{J}^*\cdot\boldsymbol{f}\mathrm{d}V = \int_{\mathbb{R}^n} (\nabla\times\mathbf{A})\cdot\boldsymbol{f}\mathrm{d}V \tag{5.21a}$$

$$= \int_{\mathbb{R}^n} \mathbf{A}\cdot(\nabla\wedge\boldsymbol{f})\,\mathrm{d}V \tag{5.21b}$$

where the scalar product in Eq. (5.21a) is between two vectors whereas the scalar product in Eq. (5.21b) is between two bivectors, defined as the half Frobenius product of their antisymmetric matrix components . Importantly, Eq. (5.21b) gives the mean rate of $\mathcal{W}$ at NESS a new cyclic representation: it is the average of vorticity $\nabla\wedge\boldsymbol{f}$, weighted by the cycle flux $\mathbf{A}$. This immediately implies that thermodynamic quantities with a gradient force $-\nabla U$ would have zero mean rate in NESS since $\nabla\wedge(-\nabla U) = 0$. That includes all the functions Φ, S, and F, implying that the mean rates of $\mathcal{S}_{\mathrm{tot}}$, $\mathcal{Q}$, and $\mathcal{Q}_{\mathrm{hk}}$ are all identical at NESS, $\dot{\mathcal{S}}^*_{\mathrm{tot}} = \dot{\mathcal{Q}}^* = \dot{\mathcal{Q}}^*_{\mathrm{hk}}$. This has been termed as a "gauge freedom" (Feng and Wang, 2011; Polettini, 2012).

Thus, the average total entropy production rate at NESS can be written as

$$\dot{\mathcal{S}}^*_{\mathrm{tot}} = \int_{\mathbb{R}^n} \mathbf{A}\cdot\left[\nabla\wedge(\mathbf{D}^{-1}\mathbf{b})\right]\mathrm{d}V. \tag{5.22}$$

The stationary cycle flux $\mathbf{A}$ is a purely kinematic concept that doesn't have any thermodynamic content. A closed loop Γ in $\mathbb{R}^n$ contains a surface Σ which can be tiled by an array of tiny oriented infinitesimal planar elements at $\mathbf{x}$, for all $\mathbf{x}\in\Sigma$. $\mathbf{A}(\mathbf{x})$ then decomposes $\mathbf{J}^*(\mathbf{x})$, following Kirchhoff's law, in terms of the occurrence rate of these tiny oriented elements along the infinitely long, ergodic path $\mathbf{X}_t$. As a vorticity description of the NESS, $\mathbf{A}$ is ***nonlocally*** determined.

On the other hand, as hinted by Eq. (5.17) and further by Eq. (5.22), the *cycle affinity* (Qian *et al.*, 2016b), as the Onsager's thermodynamic force corresponding to the cycle flux, is ***locally*** determined through $\nabla\wedge\left(\mathbf{D}^{-1}\mathbf{b}\right)$. $\mathbf{D}^{-1}\mathbf{b}$ should be identified as the vector potential of the cycle affinity. This is in sharp contrast to the standard expression $\dot{\mathcal{S}}^*_{\rm tot}=\int_{\mathbb{R}^n}\mathbf{J}^*\cdot\mathbf{D}^{-1}\mathbf{v}^*\mathrm{d}V$ where the thermodynamic force corresponding to the edge flux $\mathbf{J}^*$is nonlocally defined by $\mathbf{D}^{-1}\mathbf{v}^*$. Note that the cycle affinity has components

$$\left[\nabla\wedge\left(\mathbf{D}^{-1}\mathbf{b}\right)\right]_{ij}=\partial_i(\mathbf{D}^{-1}\mathbf{b})_j-\partial_j(\mathbf{D}^{-1}\mathbf{b})_i, \tag{5.23}$$

representing how the *two* dimensions x_i and x_j are coupled.

This constitutes the LBH principle for diffusion processes: Entropy production in NESS is characterized by the locally-defined cycle affinity as a bivector; entropy production of a bigger loop is the integral of the cycle affinity of infinitesimal cycles as shown in Eq. (5.17); and the average entropy production rate is the average cycle affinity, weighted by the cycle flux of infinitesimal cycles as shown in Eq. (5.22). The fundamental unit of NESS is the non-detailed-balanced kinetic cycle (Hill, 1977), in terms of bivectors.

5.4 Summary and Discussion

Results in this chapter clearly point to the importance of *cycle representation* for mesoscopic nonequilibrium thermodynamics (NET) in terms of cycle flux $\mathbf{A}$ and cycle affinity $\nabla\wedge\left(\mathbf{D}^{-1}\mathbf{b}\right)$. The former is a pure kinematic concept and the latter contains all the fundamental information on NET. We show that the cycle flux and cycle affinity are not simple vectors in $\mathbb{R}^n$; rather they are bivectors, which can be represented by skew-symmetric matrices. The cycle flux is the bivector potential of the conventional NESS flux; and the cycle affinity has a vector potential $\mathbf{D}^{-1}(\mathbf{x})\mathbf{b}(\mathbf{x})$ which is obtained *locally*.

Some of the mathematics in the present work is contained in the diffusion process on a manifold (Qian and Wang, 1999) and the gauge field formulations of NET (Feng and Wang, 2011; Polettini, 2012). The present work provides a clearer physics of NET in phase space as a formulation of Onsager's general principle for entropy production. We identify the bivector nature of the cycle representation in terms of a local cycle affinity and a nonlocal kinematic cycle flux; and reveal a unified Landauer-Bennett-Hill thermodynamic principle for stationary nonequilibrium systems.

We noted a parallel between quantum mechanical phase giving a reality to the "indeterminate" vector potential in electromagnetism (Wu and Yang, 2006) and our stochastic formulation giving a vorticity inter-

pretation to the bivector $\mathbf{A}$ in stochastic thermodynamics: Steady state flux $\mathbf{J}^*$ turns out to be a derivative.

A diffusion process in $\mathbb{R}^n$ always has its NESS thermodynamic force $\mathbf{D}^{-1}\mathbf{v}^*$ linearly related to transport flux $\mathbf{J}^*$, $\left(\mathbf{D}^{-1}\mathbf{v}^*\right)_i = e^{\Phi}\sum_{j=1}^n D_{ij}^{-1}J_j^*$. Many previous studies have explored this unique feature (Qian, 2001b; Reguera *et al.*, 2005). In the bivectorial representation there is a further linear affinity-vorticity relationship

$$\nabla \wedge \left(\mathbf{D}^{-1}\mathbf{b}\right)(\mathbf{x}) = \mathcal{O}\mathbf{A}(\mathbf{x}). \tag{5.24}$$

where $\mathcal{O} = \nabla \wedge \left(e^{\Phi}\mathbf{D}^{-1}\nabla\times\right)$. We shall call the operator $\mathcal{O}$ the *Onsager operator*. It linearly relates the cycle flux bivector to the cycle affinity bivector. As an example for the Onsager operator superimposing different $\mathbf{A}$ from different processes, we note that $(\Phi, \mathbf{A}, \mathbf{D})$ together specify a diffusion process on $\mathbb{R}^n$ with Φ and $\mathbf{A}$ as the scalar and bivector potentials of $\mathbf{b}$. Therefore, for a family of systems with fixed Φ and $\mathbf{D}$, different bivector potential $\mathbf{A}$ gives us different processes. With $\mathcal{O}$ fixed in a family, a third process in this family with $\mathbf{A}_3 = \mathbf{A}_1 + \mathbf{A}_2$ will have cycle affinity $\mathcal{O}\mathbf{A}_3 = \mathcal{O}(\mathbf{A}_1 + \mathbf{A}_2) = \mathcal{O}\mathbf{A}_1 + \mathcal{O}\mathbf{A}_2$. With in this family, $(\Phi, \mathbf{0}, \mathbf{D})$ is a reversible process; and $(\Phi, -\mathbf{A}, \mathbf{D})$ is the adjoint process.

The bivectorial cycles in diffusion processes demonstrates vividly the reciprocality between two dimensions. How treating a diffusion process as a discrete-state Markov process on infinitesimal lattice system could reveal the fundamental origin of the general force-flux linearity and the symmetry in the Onsager's reciprocality for systems even far away from equilibrium remain to be ellucinated in future works. We note that the mean NESS entropy production rate has a simple bilinear form:

$$\dot{\mathcal{S}}_{\text{tot}}^* = \int_{\mathbb{R}^n} \mathbf{A}\cdot\mathcal{O}\mathbf{A}\mathrm{d}V. \tag{5.25}$$

Incidentally, Onsager also considered tiny vortices "who wanted to play" as the fundamental objects in hydrodynamic turbulent flow (Eyink and Sreenivasan, 2006).

Chapter 6

Thermodynamic Potentials of Continuous Markov Dynamics

In this chapter, the dynamic decomposition from irreversibility introduced in Chap. 3 is extended by the novel cyclic understanding of nonequilibrium dynamics in Chap. 5. In Sec. 6.1, the bivectorial cyclic potential introduced in Chap. 5 is introduced to derive a further cycle decomposition of dynamics in diffusion. This further decomposition completes the thermodynamic potential theories of nonequilibrium stochastic dynamics, in terms of scalar energy landscape for the underlying equilibrium dynamics and in term of cycles for the nonequilibrium fluxes. Decomposition of mean rates of thermodynamics are discussed in Sec. 6.1 and their speed limits are discussed in Sec. 6.2. By taking the zero-noise limit, our thermodynamic potential theory further units the two existing landscape theories of deterministic dynamics from Graham (1977a); Ao (2004), and from Freidlin and Wentzell (2012) in Sec. 6.3.

6.1 Cycle Potential and Dynamic Decomposition

6.1.1 Bivectorial Decomposition with Cycle Velocity

The divergent-free stationary current $\mathbf{J}^*$ can be furthered expressed as the n-D "curl" of a *bivector* $\mathbf{A}$, an anti-symmetric matrix that represents *cycle flux* as shown in Sec. 5.3,

$$\mathbf{J}^* = \nabla \times \mathbf{A} \tag{6.1}$$

where $(\nabla \times \mathbf{A})_i = \sum_{j=1}^{n} \partial_j A_{ij}$. While solving an explicit form of $\mathbf{A}$ requires a non-trivial calculation on solving Eq. (6.1), this expression actually allows us to reveal more structure of the system as shown below. The stationary probability velocity $\mathbf{v}^*$ can then be expressed as

$$\mathbf{v}^* = e^{\Phi} \nabla \times \mathbf{A} = \nabla \times \left(e^{\Phi} \mathbf{A}\right) - \mathbf{A} \nabla e^{\Phi}. \tag{6.2}$$

We then introduce the notion of *cycle velocity*

$$\mathbf{Q} = \frac{1}{\pi} \mathbf{A} = e^{\Phi} \mathbf{A}, \tag{6.3}$$

which is also a *bivector*. The stationary velocity $\mathbf{v}^*$ then has the decomposition

$$\mathbf{v}^* = -\mathbf{Q} \nabla \Phi + \nabla \times \mathbf{Q} \tag{6.4}$$

where the former is perpendicular to $\nabla \Phi$ and the latter is divergence-free. This type of rewriting was first proposed mathematically by Graham (1977a) and recently by Ding *et al.* (2020). Our introduction here provides probabilistic and thermodynamic interpretations of Eq. 6.4 (Yang and Cheng, 2021). The vector field $\mathbf{b}$ now has a decomposition in terms of Φ, $\mathbf{Q}$, and $\mathbf{D}$,

$$\mathbf{b} = -\mathbf{D} \nabla \Phi - \mathbf{Q} \nabla \Phi + \nabla \times \mathbf{Q}, \tag{6.5}$$

This decomposition has been extensively discussed by P. Ao *el. al.* in the past decades (Ao, 2004; Yin and Ao, 2006; Shi *et al.*, 2012). Here, we show its generality and reveal a novel probabilistic origin with a cycle interpretation. We can further derive the following novel decomposition of the probability flux

$$\mathbf{J} = p\mathbf{v} = -p\mathbf{D} \nabla F - p\mathbf{Q} \nabla F + \nabla \times (p\mathbf{Q}) \,. \tag{6.6}$$

In a word, $(\Phi, \mathbf{Q})$ are the scalar and bivector potentials of the vector field $\mathbf{b}$, and $(F, p\mathbf{Q})$ are the scalar and bivector potentials of the flux $\mathbf{J}$.

6.1.2 Mean Rate Decomposition of Thermodynamic Quantities

The above probability flux decomposition in Eq. (6.6) leads to a new understanding on the mean rates of various thermodynamic quantities. By stochastic calculus, recall that the average rate of work-like quantity $đ\mathcal{W} = \boldsymbol{f}\left(\mathbf{X}_t, t\right) \circ \mathrm{d}\mathbf{X}_t$ is given by Eq. (5.20):

$$\dot{\mathcal{W}} \coloneqq \frac{\mathbb{E}\left[đ\mathcal{W}\right]}{\mathrm{d}t} = \int \mathbf{J} \cdot \boldsymbol{f} \mathrm{d}\mathbf{x} = \mathbb{E}\left[\mathbf{v} \cdot \boldsymbol{f}\right]. \tag{6.7}$$

where $\mathbb{E}[\cdot]$ denotes expectation with respect to $p(\mathbf{x},t)$. With $\mathbf{v}=\mathbf{v}^*-\mathbf{D}\nabla F$, we further have

$$\dot{\mathcal{W}}=\frac{\mathbb{E}[đ\mathcal{W}]}{\mathrm{d}t}=\mathbb{E}\left[(-\mathbf{D}\nabla F)\cdot\boldsymbol{f}\right]+\mathbb{E}\left[\mathbf{v}^*\cdot\boldsymbol{f}\right]. \tag{6.8}$$

The second term, by integration by part, can be rewritten as

$$\mathbb{E}\left[\mathbf{v}^*\cdot\boldsymbol{f}\right]=\mathbb{E}\left[\mathbf{Q}\cdot\nabla\wedge\boldsymbol{f}\right]+\mathbb{E}\left[\mathbf{Q}\cdot\boldsymbol{f}\wedge(-\nabla F)\right]. \tag{6.9}$$

Both wedge terms are bivectors with components $(\mathbf{u}\wedge\mathbf{w})_{ij}=u_iw_j-u_jw_i$ for $1\le i<j\le n$. The scalar products in Eq. (6.9) between two bivectors are the half of the Frobenius products between matrices, $\mathbf{A}\cdot\mathbf{B}=\sum_{i<j}A_{ij}B_{ij}=\frac{1}{2}\sum_{i,j}A_{ij}B_{ij}$. Since $\|\mathbf{u}\wedge\mathbf{w}\|=\sqrt{(\mathbf{u}\wedge\mathbf{w})\cdot(\mathbf{u}\wedge\mathbf{w})}$ is the area of the parallelogram of $\mathbf{u}$ and $\mathbf{w}$ in $\mathbb{R}^n$, a (simple) bivector $\mathbf{u}\wedge\mathbf{w}$ can be understood as a generalized "signed" area of in $\mathbb{R}^n$. See Appendix A for a brief introduction. We note that the notion of curl in $\mathbb{R}^3$ is generalized to $\mathbb{R}^n$ by two different operations: $\nabla\times$ and $\nabla\wedge$ as discussed in Sec. 5.3. The former maps a bivector to a divergence free vector field as shown in Eq. (6.1), while the latter maps a vector field $\boldsymbol{f}$ to a bivector $\nabla\wedge\boldsymbol{f}$ representing the vorticity of the vector field.

The decomposition in Eq. (6.9) shows the fundamental roles of cycles in nonequilibrium thermodynamics with nonzero $\mathbf{v}^*$. Both terms in Eq. (6.9) are cyclic averages of bivectors, both averaged over the "cycle flux" pQ_{ij} in each infinitesimal plane $\mathrm{d}x_i\wedge\mathrm{d}x_j$. This is an extension to results in Chap. 5 where cycle flux $\mathbf{A}=\pi\mathbf{Q}$ was first introduced in NESS (Yang and Qian, 2021a). We note that as the system approaches NESS as $t\to\infty$, the term $\mathbb{E}\left[\mathbf{Q}\cdot\nabla\wedge\boldsymbol{f}\right]$ persists whereas $\mathbb{E}\left[\mathbf{Q}\cdot\boldsymbol{f}\wedge(-\nabla F)\right]\to 0$ since $F\to 0$.

The two terms in Eq. (6.9) have the following physical interpretations. With $\nabla\wedge\boldsymbol{f}$ being the n-D "curl" of vectors, its cyclic average $\mathbb{E}\left[\mathbf{Q}\cdot\nabla\wedge\boldsymbol{f}\right]$ is the mean circulation of the force $\boldsymbol{f}$. Hence, if a force is a gradient vector field $\boldsymbol{f}=-\nabla U$, then $\nabla\wedge(-\nabla U)=\mathbf{0}$. This implies $\mathbb{E}\left[\mathbf{Q}\cdot\nabla\wedge\boldsymbol{f}\right]$ would be zero in the mean rate of state observables: S, Φ, and F. On the other hand, the wedge product $\boldsymbol{f}\wedge(-\nabla F)$ is the generalized "signed" area spanned by the two vectors $\boldsymbol{f}$ and $-\nabla F$. $\mathbb{E}\left[\mathbf{Q}\cdot\boldsymbol{f}\wedge(-\nabla F)\right]$ is thus a "torque-like" quantity representing the mean area between the force $\boldsymbol{f}$ and $-\nabla F$ averaged over all its planar components. It would be zero when $\boldsymbol{f}$ is parallel to $-\nabla F$.

Eq. (6.9) shows us that the average orthogonality between ∇F and $\mathbf{v}^*$,

$$\mathbb{E}\left[(-\nabla F)\cdot\mathbf{v}^*\right]=0 \tag{6.10}$$

previously shown in Qian *et al.* (2020) and Yang and Qian (2021a) is due to both ∇F being a gradient field

and parallel to $-\nabla F$. The mean rate of free energy then has the expression

$$\dot{F} = \mathbb{E}\left[-\left(\nabla F\right)\cdot\mathbf{D}\nabla F\right] \leq 0. \tag{6.11}$$

It is a purely "gradient-descending" term with no cyclic contribution, reflecting the detailed-balanced dynamics of Eq. (3.35) hidden behind. The housekeeping heat dissipation rate, on the other hand, has the following new expression

$$\dot{\mathcal{Q}}_{\mathrm{hk}} = \ \mathbb{E}\left[\mathbf{Q}\cdot\nabla\wedge\left(\mathbf{D}^{-1}\mathbf{b}\right)\right] - \mathbb{E}\left[\mathbf{Q}\cdot\left(\mathbf{D}^{-1}\mathbf{v}^{*}\right)\wedge\nabla F\right] \tag{6.12}$$

where the first term is the average cycle affinity. Eq. (6.12) is purely cyclic, reflecting the measure-preserving deterministic dynamics of Eq. (3.34) hidden behind, as discussed in Sec. 3.2.3.

The mean rates of entropy and mesoscopic potential now have the following new expressions:

$$\dot{S} = \ +\underbrace{\mathbb{E}\left[\nabla S\cdot\mathbf{D}\nabla S\right]}_{\geq 0} - r + w \tag{6.13a}$$

$$\dot{\Phi} = \ -\underbrace{\mathbb{E}\left[\nabla\Phi\cdot\mathbf{D}\nabla\Phi\right]}_{\geq 0} + r + w \tag{6.13b}$$

where $w = \mathbb{E}\left[\mathbf{Q}\cdot\left(\nabla\Phi\wedge\nabla S\right)\right]$ denotes a wedge product term and $r = \mathbb{E}\left[\nabla S\cdot\mathbf{D}\nabla\Phi\right]$ denotes a scalar product term. Besides the source/sink terms, the two rates have two common contributions: a "curl" w measuring the perpendicularity between $\nabla\Phi$ and ∇S and an inner product r. As the system approaches NESS, $S\to\Phi$ and the wedge product term $w\to 0$. Both $\mathbb{E}\left[\nabla S\cdot\mathbf{D}\nabla S\right]$ and r converge to $\mathbb{E}\left[\nabla\Phi\cdot\mathbf{D}\nabla\Phi\right]$, canceling each other out.

6.2 Speed limit of Thermodynamic Rates

In a time-inhomogeneous diffusion, the infinitesimal changes of thermodynamics quantities are the three scalar functions

$$\mathrm{d}\Phi = \underbrace{\partial_t\Phi\mathrm{d}t}_{\mathcal{W}_{\mathrm{ex}}} + \underbrace{\nabla\Phi\circ\mathrm{d}\mathbf{X}_t}_{-\mathcal{Q}_{\mathrm{ex}}}, \tag{6.14a}$$

$$\mathrm{d}S = \partial_t S\mathrm{d}t + \nabla S\circ\mathrm{d}\mathbf{X}_t, \tag{6.14b}$$

$$\mathrm{d}F = \partial_t F\mathrm{d}t + \nabla F\circ\mathrm{d}\mathbf{X}_t, \tag{6.14c}$$

and the various heat dissipation and entropy production

$$đ\mathcal{Q}_{\rm hk} = \mathbf{D}^{-1}\mathbf{v}^* \circ \mathrm{d}\mathbf{X}_t, \tag{6.15a}$$

$$đ\mathcal{Q} = \mathbf{D}^{-1}\mathbf{b} \circ \mathrm{d}\mathbf{X}_t = đ\mathcal{Q}_{\rm hk} + đ\mathcal{Q}_{\rm ex}, \tag{6.15b}$$

$$đ\mathcal{S}_{\rm tot} = \mathrm{d}S + đ\mathcal{Q} = \partial_t S \mathrm{d}t + \mathbf{D}^{-1}\mathbf{v} \circ \mathrm{d}\mathbf{X}_t, \tag{6.15c}$$

$$đ\mathcal{S}_{\rm na} = \mathcal{W}_{\rm ex} - \mathrm{d}F = \partial_t S \mathrm{d}t - \nabla F \circ \mathrm{d}\mathbf{X}_t. \tag{6.15d}$$

The excess work $\mathcal{W}_{\rm ex}$ is the "work" absorbed to change the landscape Φ whereas the excess heat $\mathcal{Q}_{\rm ex}$ is the "heat" dissipated by the system from the landscape. Here, we discuss briefly how the total irreversibility $\mathcal{S}_{\rm tot}$ imposes speed limit to the mean production of scalar and work-like quantities.

6.2.1 Entropic Bound on the Fano Factor of Infinitesimal Changes

Since $\mathbb{E}\left[\partial_t S\right] = 0$, the mean rate of the main thermodynamics quantities defined in Eqs. (6.14) are given by

$$\dot{\mathcal{S}}_{\rm tot} = \mathbb{E}\left[\mathbf{v} \cdot \mathbf{D}^{-1}\mathbf{v}\right],\ \dot{\mathcal{Q}}_{\rm hk} = \mathbb{E}\left[\mathbf{v} \cdot \mathbf{D}^{-1}\mathbf{v}^*\right], \tag{6.16a}$$

$$\dot{\mathcal{S}}_{\rm na} = \mathbb{E}\left[\mathbf{v} \cdot (-\nabla F)\right],\ \dot{\mathcal{Q}}_{\rm ex} = \mathbb{E}\left[\mathbf{v} \cdot (\nabla \Phi)\right], \tag{6.16b}$$

$$\dot{S} = \mathbb{E}\left[\mathbf{v} \cdot (\nabla S)\right],\ \dot{\mathcal{Q}} = \mathbb{E}\left[\mathbf{v} \cdot \mathbf{D}^{-1}\mathbf{b}\right]. \tag{6.16c}$$

With Eq. (6.10), the mean rates of housekeeping heat and non-adiabatic entropy production can thus be rewritten as

$$\dot{\mathcal{Q}}_{\rm hk} = \mathbb{E}\left[\mathbf{v}^* \cdot \mathbf{D}^{-1}\mathbf{v}^*\right] \text{ and } \dot{\mathcal{S}}_{\rm na} = \mathbb{E}\left[\nabla F \cdot \mathbf{D}\nabla F\right] \tag{6.17}$$

which shows that they are both positive.

By defining the inner product $\langle \mathbf{u}, \mathbf{w} \rangle := \mathbb{E}\left[\mathbf{u} \cdot \mathbf{D}^{-1}\mathbf{w}\right]$, Eq. (6.7) then becomes $\mathbb{E}\left[đ\mathcal{W}\right] = \langle \mathbf{v}, \mathbf{D}\boldsymbol{f} \rangle \mathrm{d}t$. By applying Cauchy-Schwarz inequality, we then have

$$\left|\langle \mathbf{v}, \mathbf{D}\boldsymbol{f} \rangle\right|^2 \leq \langle \mathbf{v}, \mathbf{v} \rangle \langle \mathbf{D}\boldsymbol{f}, \mathbf{D}\boldsymbol{f} \rangle. \tag{6.18}$$

Eq. (6.18) can be applied to the mean rate of $\mathcal{Q}_{\rm hk}$, $\mathcal{S}_{\rm na}, \mathcal{Q}_{\rm ex}, S$ and $\mathcal{Q}$ by choosing the corresponding thermodynamic force: $\boldsymbol{f} = \mathbf{D}^{-1}\mathbf{v}^*, (-\nabla F), \nabla\Phi, \nabla S$, and $\mathbf{D}^{-1}\mathbf{b}$. While the inequality for the two entropy production $\mathcal{Q}_{\rm hk}$ and $\mathcal{S}_{\rm na}$ leads to known relations $\mathbb{E}\left[đ\mathcal{Q}_{\rm hk}\right] \leq \mathbb{E}\left[đ\mathcal{S}_{\rm tot}\right]$ and $\mathbb{E}\left[đ\mathcal{S}_{\rm na}\right] \leq \mathbb{E}\left[đ\mathcal{S}_{\rm tot}\right]$. The other

leads to speed limit on the production of $\mathcal{Q}_{\rm ex}$, S, and $\mathcal{Q}$:

$$|\langle \mathbf{v}, \mathbf{D}\nabla\Phi\rangle|^2 \leq \langle \mathbf{v},\mathbf{v}\rangle \langle \mathbf{D}\nabla\Phi, \mathbf{D}\nabla\Phi\rangle \Rightarrow \left(\dot{\mathcal{Q}}_{\rm ex}\right)^2 \leq \dot{\mathcal{S}}_{\rm tot}\mathbb{E}\left[\nabla\Phi\cdot\mathbf{D}\nabla\Phi\right] \tag{6.19a}$$

$$|\langle \mathbf{v}, \mathbf{D}\nabla S\rangle|^2 \leq \langle \mathbf{v},\mathbf{v}\rangle \langle \mathbf{D}\nabla S, \mathbf{D}\nabla S\rangle \Rightarrow \left(\dot{S}\right)^2 \leq \dot{\mathcal{S}}_{\rm tot}\mathbb{E}\left[\nabla S\cdot\mathbf{D}\nabla S\right] \tag{6.19b}$$

$$|\langle \mathbf{v}, \mathbf{b}\rangle|^2 \leq \langle \mathbf{v},\mathbf{v}\rangle \langle \mathbf{b}, \mathbf{b}\rangle \Rightarrow \left(\dot{\mathcal{Q}}\right)^2 \leq \dot{\mathcal{S}}_{\rm tot}\mathbb{E}\left[\mathbf{b}\cdot\mathbf{D}^{-1}\mathbf{b}\right]. \tag{6.19c}$$

Some of these results were reported by Dechant and Sasa (2018b). We derived these results independently.

If we consider the variance of the infinitesimal change $đ\mathcal{W}$, we get

$$\mathbb{V}\left[đ\mathcal{W}\right] = \mathbb{E}\left[\left(đ\mathcal{W}\right)^2\right] - \left(\mathbb{E}\left[đ\mathcal{W}\right]\right)^2 \tag{6.20a}$$

$$= \mathbb{E}\left[\left(đ\mathcal{W}\right)^2\right] - \left(\mathbb{E}\left[\mathbf{b}\cdot\boldsymbol{f} + \nabla\cdot\left(\mathbf{D}\boldsymbol{f}\right)\right]\mathrm{d}t\right)^2 \tag{6.20b}$$

$$= 2\mathbb{E}\left[\boldsymbol{f}\cdot\mathbf{D}\boldsymbol{f}\right]\mathrm{d}t + O(\mathrm{d}t^2). \tag{6.20c}$$

Applying this to $\mathcal{Q}_{\rm ex}$, S and $\mathcal{Q}$, we get a nicer form of the above inequalities in terms of the Fano factor for instantaneous changes

$$\frac{\mathbb{V}\left[đ\mathcal{Q}_{\rm ex}\right]}{\mathbb{E}\left[đ\mathcal{Q}_{\rm ex}\right]^2} \geq \frac{2}{\mathbb{E}\left[đ\mathcal{S}_{\rm tot}\right]}, \frac{\mathbb{V}\left[\mathrm{d}S\right]}{\mathbb{E}\left[\mathrm{d}S\right]^2} \geq \frac{2}{\mathbb{E}\left[đ\mathcal{S}_{\rm tot}\right]}, \text{ and } \frac{\mathbb{V}\left[đ\mathcal{Q}\right]}{\mathbb{E}\left[đ\mathcal{Q}\right]^2} \geq \frac{2}{\mathbb{E}\left[đ\mathcal{S}_{\rm tot}\right]}. \tag{6.21}$$

This is the instantaneous version of the recently-obtained thermodynamic uncertainty relation for work-like quantities (Barato and Seifert, 2015)

$$\frac{\mathbb{V}\left[\mathcal{W}_{0\sim T}\right]}{\left(\mathbb{E}\left[\mathcal{W}_{0\sim T}\right]\right)^2} \geq \frac{2}{\mathbb{E}\left[\mathcal{S}_{\rm tot}\right]}. \tag{6.22}$$

See (Horowitz and Gingrich, 2020) and the references within for an overview. Extension of Eq. (6.21) to the finite time interval result in Eq. (6.22) is nontrivial since time steps are correlated. Doob's h-transform may be needed as shown by Pigolotti *et al.* (2017) where a similar calculation was carried out. We note that Dechant and Sasa (2018a) formally proved Eq. (6.22) in time-inhomogeneous diffusion by bounding the generating function in a path integral formalism.

6.2.2 Fisher Information of Time and Thermodynamic Speed Limit

Consider an arbitrary scalar observable $f(\mathbf{X}_t, t)$ of the diffusion process $\mathbf{X}_t$ satisfying the SDE in Eq. (2.29):

$$\mathrm{d}\mathbf{X}_t = \left[\mathbf{b}\left(\mathbf{X}_t\right) + \nabla\cdot\mathbf{D}\left(\mathbf{X}_t\right)\right]\mathrm{d}t + \boldsymbol{\Gamma}\left(\mathbf{X}_t\right)\mathrm{d}\mathbf{W}_t, \tag{6.23}$$

the rate of its average value is given by

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbb{E}[f(\mathbf{X}_t,t)] = \int_{\mathcal{X}} p(\mathbf{x},t)\,\partial_t f(\mathbf{x},t)\,\mathrm{d}\mathbf{x} + \int_{\mathcal{X}} f(\mathbf{x},t)\,\partial_t p(\mathbf{x},t)\,\mathrm{d}\mathbf{x} \tag{6.24a}$$

$$= \mathbb{E}[\partial_t f] - \mathbb{E}[f\partial_t S] \tag{6.24b}$$

where $S \coloneqq -\ln p$ is the Gibbs-Shannon (stochastic) entropy. Now, since $\mathbb{E}[\partial_t S] = 0$, the second term of Eq. (6.24a) can be further rewritten as a covariance,

$$\mathbb{E}[f\partial_t S] = \int_{\mathcal{X}} (f - \mathbb{E}[f])(\partial_t S - \mathbb{E}[\partial_t S])\,p\mathrm{d}\mathbf{x} = \mathrm{Co}\mathbb{V}(f, \partial_t S). \tag{6.25}$$

This leads to a continuous-time Price equation (Price, 1970) in terms of the Gibbs-Shannon entropy,

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbb{E}[f] = \mathbb{E}[\partial_t f] + \mathrm{Co}\mathbb{V}(f, -\partial_t S). \tag{6.26}$$

Specifically, if $f = \partial_t S$, it leads to a relation between second time (partial) derivative of S and the variance of $\partial_t S$,

$$I(t) \coloneqq \mathbb{E}\left[\partial_t^2 S\right] = \mathbb{V}[\partial_t S] \geq 0. \tag{6.27}$$

This positive quantity is the Fisher information with respect to the time parameter t. It plays significant role in population dynamics (Fisher, 2000; Price, 1970; Lessard, 1997; Qian, 2014a) and, as we shall see below, in stochastic thermodynamics as well (Crooks, 2007; Ito, 2018; Nicholson *et al.*, 2018; Ito and Dechant, 2020; Nicholson *et al.*, 2020).

By Cauchy-Schwarz inequality and the Price equation, we get

$$\mathbb{V}[f]\cdot\mathbb{V}[\partial_t S] = \mathbb{V}[f]\cdot I(t) \geq [\mathrm{Co}\mathbb{V}(f,\partial_t S)]^2 = \left\{\frac{\mathrm{d}}{\mathrm{d}t}\mathbb{E}[f] - \mathbb{E}\left[\frac{\partial f}{\partial t}\right]\right\}^2. \tag{6.28}$$

This is in fact an extended form of Cramér-Rao inequality in statistics. Now, by stochastic calculus, we get

$$\mathrm{d}f(\mathbf{X}_t,t) = (\partial_t f + \mathcal{A}f)\,\mathrm{d}t + \nabla f\cdot\mathbf{\Gamma}\mathrm{d}\mathbf{W}_t \tag{6.29}$$

where $\mathcal{A}[h] \coloneqq \mathbf{b}\cdot\nabla h + \nabla\cdot\mathbf{D}\nabla h$ is the generator in Komolgorov backward equation (Grimmett and Stirzaker, 2001; Durrett, 2019). With this, one get

$$\frac{\mathbb{E}[\mathrm{d}f]}{\mathrm{d}t} = \mathbb{E}[\partial_t f] + \int_{\mathcal{X}} p\mathcal{A}f\mathrm{d}\mathbf{x} = \mathbb{E}[\partial_t f] + \int_{\mathcal{X}} (\mathcal{A}^* p)\,f\mathrm{d}\mathbf{x} \tag{6.30a}$$

$$= \int_{\mathcal{X}} p(\partial_t f)\,\mathrm{d}\mathbf{x} + \int_{\mathcal{X}} (\partial_t p)\,f\mathrm{d}\mathbf{x} = \frac{\mathrm{d}}{\mathrm{d}t}\mathbb{E}[f(\mathbf{X}_t,t)] \tag{6.30b}$$

where $\mathcal{A}^*[h] \coloneqq -\nabla\cdot[\mathbf{b}h - \mathbf{D}\nabla h]$, the adjoint of $\mathcal{A}$, is the generator in Komolgorov forward equation

(Grimmett and Stirzaker, 2001; Durrett, 2019). Therefore, the term in $\{\cdots\}$ on the right-hand-side of Eq. (6.28) can be rewritten as

$$\frac{\mathbb{E}\left[\mathrm{d}f - \partial_t f \mathrm{d}t\right]}{\mathrm{d}t} = \frac{\mathbb{E}\left[\nabla f \circ \mathrm{d}\mathbf{X}_t\right]}{\mathrm{d}t} = \mathbb{E}\left[\mathcal{A}f\right]. \tag{6.31}$$

In stochastic thermodynamics, three scalar functions are of prominent importance. If we set f to be the energy landscape $\Phi(\mathbf{X}_t, t)$, then Eq. (6.28), together with the rewriting in Eq. (6.31), leads to an inequality of mean rate of the excess heat $đ\mathcal{Q}_{\mathrm{ex}} = \nabla\Phi \circ \mathrm{d}\mathbf{X}_t$ (Ito and Dechant, 2020; Nicholson *et al.*, 2020),

$$\left(\frac{\mathbb{E}\left[đ\mathcal{Q}_{\mathrm{ex}}\right]}{\mathrm{d}t}\right)^2 \leq \mathbb{V}\left[\Phi\right] I(t). \tag{6.32}$$

Now with $\mathbb{E}\left[\partial_t S\right] = 0$, we get that $\mathbb{E}\left[\mathrm{d}S\right] = \mathbb{E}\left[\nabla S \circ \mathrm{d}\mathbf{X}_t\right]$. Therefore, Eq. (6.28) also leads to an inequality of the mean entropy rate with $f = S$ (Nicholson *et al.*, 2020),

$$\left(\frac{\mathbb{E}\left[\mathrm{d}S\right]}{\mathrm{d}t}\right)^2 \leq \mathbb{V}\left[S\right] I(t). \tag{6.33}$$

Lastly, we note that $đ\mathcal{S}_{\mathrm{na}} = \partial_t\Phi \mathrm{d}t - \mathrm{d}F = \partial_t S \mathrm{d}t - \nabla F \circ \mathrm{d}\mathbf{X}_t$. Therefore, $\mathbb{E}\left[đ\mathcal{S}_{\mathrm{na}}\right] = \mathbb{E}\left[-\nabla F \circ \mathrm{d}\mathbf{X}_t\right]$. Then using Eq. (6.28) gives us an inequality of the non-adiabatic entropy production rate

$$\left(\frac{\mathbb{E}\left[đ\mathcal{S}_{\mathrm{na}}\right]}{\mathrm{d}t}\right)^2 \leq \mathbb{V}\left[F\right] I(t). \tag{6.34}$$

Eq. (6.18) actually leads to a relation between $I(t)$ and the total entropy production (Ito and Dechant, 2020). We note that treating $\partial_t S$ as a function of $\mathbf{X}_t$ and t, we have the infinitesimal change of it as,

$$\mathrm{d}\left(\partial_t S\right) = \partial_t^2 S \mathrm{d}t + \nabla\left(\partial_t S\right) \circ \mathrm{d}\mathbf{X}_t. \tag{6.35}$$

Since, again, $\frac{\mathrm{d}}{\mathrm{d}t}\mathbb{E}[f(X_t,t)] = \frac{\mathbb{E}[\mathrm{d}f]}{\mathrm{d}t}$, we have that

$$\mathbb{E}\left[\mathrm{d}\left(\partial_t S\right)\right] = \mathrm{d}\mathbb{E}\left[\partial_t S\right] = 0 = \mathbb{E}\left[\partial_t^2 S\right] \mathrm{d}t + \mathbb{E}\left[\nabla\left(\partial_t S\right) \circ \mathrm{d}\mathbf{X}_t\right] \tag{6.36}$$

Therefore, we have an alternative expression for $I(t)$ as

$$I(t) = \mathbb{E}\left[\partial_t^2 S\right] = -\frac{\mathbb{E}\left[\nabla\left(\partial_t S\right) \circ \mathrm{d}\mathbf{X}_t\right]}{\mathrm{d}t} = -\mathbb{E}\left[\mathcal{A}\partial_t S\right]. \tag{6.37}$$

Therefore, using $\boldsymbol{f} = -\nabla\left(\partial_t S\right)$ and applying Eq. (6.18), we arrive

$$\left[I(t)\right]^2 \leq \dot{\mathcal{S}}_{\mathrm{tot}} \mathbb{E}\left[\nabla\left(\partial_t S\right) \cdot \mathbf{D}\nabla\left(\partial_t S\right)\right]. \tag{6.38}$$

Therefore, zero mean total entropy production implies zero Fisher information. The converse is also true

when the system admits detailed balance since $I = 0$ when the system reaches its steady state.

6.3 Mesoscopic Potential and Macroscopic Potential

6.3.1 Mesoscopic Potential and Maxwell-Boltzmann Equilibrium

We have referred the scalar $\Phi := -\ln \pi$ in Eq. (6.5) as the scalar potential or the energy landscape for Markov processes. This identification actually is central in stochastic thermodynamic (Thompson and Qian, 2016; Huang *et al.*, 2017). The potential goes by many names as reviewed by Thompson and Qian (2016). In this section, we shall refer it as the *mesoscopic potential* to later distinguish it with the macroscopic, emergent potential in the thermodynamic zero-noise limit. In systems with detailed balance, the mesoscopic potential Φ is the scalar potential for the affinity $\mathcal{Q}$ defined from irreversibility as shown in Eq. (3.7) and Eq. (3.3), and it is also the Lyapunov function for deterministic dynamics $\mathbf{x}'(t) = \mathbf{b}(\mathbf{x})$ underlying a diffusion process with detailed balance (Yang and Cheng, 2021). Physically, it can also be understood as the potential of mean force (Kirkwood, 1935; Thompson and Qian, 2016).

For general nonequilibrium time-homogeneous systems, the stationary distribution is still in the form of the Boltzmann distribution $\pi = e^{-\Phi}$ based on our definition of Φ. However, the Lyapunov property for the underlying deterministic dynamics is no longer true in general (Yang and Cheng, 2021):

$$\frac{\mathrm{d}}{\mathrm{d}t}\Phi(\mathbf{x}) = \nabla\Phi(\mathbf{x}) \cdot \mathbf{b}(\mathbf{x}) = \underbrace{-\nabla\Phi \cdot \mathbf{D}\nabla\Phi}_{\leq 0} + \nabla\Phi \cdot \mathbf{v}^*. \tag{6.39}$$

The condition for the Lyapunov property is

$$\nabla\Phi \cdot \mathbf{v}^* \leq \nabla\Phi \cdot \mathbf{D}\nabla\Phi \tag{6.40}$$

which can be rewritten as

$$\nabla \cdot \mathbf{v}^* \leq \nabla\Phi \cdot \mathbf{D}\nabla\Phi \tag{6.41}$$

according to the stationary FPE equation $\nabla \cdot \mathbf{J}^* = 0 = \nabla \cdot (\pi\mathbf{v}^*) \Leftrightarrow \nabla\Phi \cdot \mathbf{v}^* = \nabla \cdot \mathbf{v}^*$. A sufficient condition for the Lyapunov property is thus

$$\nabla \cdot \mathbf{v}^* = \mathbf{v}^* \cdot \nabla\Phi = 0 \tag{6.42}$$

which states that the stationary velocity $\mathbf{v}^*$ is divergence-free and at the same time perpendicular to the gradient of the potential. $\mathbf{v}^*$ is like a superconducting current in this case (Qian, 2015).

Nonequilibrium system satisfying Eq. (6.42) is said to admit *Maxwell-Boltzmann (M-B) equilibrium* by Qian (2015). In such systems, Φ is a Lyapunov function of $\mathbf{x}'(t) = \mathbf{b}(\mathbf{x})$, and the vector field $\mathbf{b}$ can be decomposed into a generalized gradient term $-\mathbf{D}\nabla\Phi$ and a divergent-free term $\mathbf{v}^*$, akin to the Helmholtz decomposition in $\mathbb{R}^3$. Furthermore, with M-B equilibrium, the deterministic dynamics $\mathbf{x}'(t) = \mathbf{v}^*(\mathbf{x})$ corresponding to the Liouville equation in Eq. (3.34) has a divergent-free vector field $\nabla \cdot \mathbf{v}^* = 0$ and a conserved quantity $\Phi(\mathbf{x})$. It is a generalization of Hamiltonian systems with energy Φ (Qian, 2014b, 2015). We note that according to our cycle velocity decomposition of $\mathbf{v}^*$ in Eq. (6.4), the condition for M-B equilibrium becomes the perpendicularity between the divergence-free part and the gradient of Φ,

$$(\nabla \times \mathbf{Q}) \cdot \nabla\Phi = 0 \tag{6.43}$$

since $-\mathbf{Q}\nabla\Phi$ is perpendicular to Φ.

6.3.2 Random Perturbations and the Emergent Macroscopic Potential

Although the Lyapunov property of the mesoscopic potential Φ for $\mathbf{x}' = \mathbf{b}(\mathbf{x})$ cannot be guaranteed in nonequilibrium mesoscopic systems, its emergent, macroscopic potential in the thermodynamic zero-noise limit is guaranteed to have Lyapunov property locally (Qian *et al.*, 2020). To see this, we shall introduce a parameter ϵ to characterize the thermodynamic zero-noise limit of diffusion with $\epsilon \to 0$. In general, both the drift force $\mathbf{b}_\epsilon$ and the diffusion matrix $\mathbf{D}_\epsilon$ may depend on the parameter, resulting both the mesoscopic potential Φ_ϵ and cycle velocity $\mathbf{Q}_\epsilon$ to be ϵ-dependent as well. Here, we are interested in the case where $\mathbf{b}_\epsilon \to \mathbf{b}_0$ and $\mathbf{D}_\epsilon \to \mathbf{D}_0 = \mathbf{0}$ such that the diffusion converges to a deterministic dynamics $\mathbf{x}'(t) = \mathbf{b}_0(\mathbf{x})$, *i.e.* for small ϵ, the diffusion is a random perturbation to the deterministic dynamics.

To begin, let us consider the (thermodynamic) limiting process where the drift is ϵ-independent, $\mathbf{b}$, and the diffusion matrix is proportional to ϵ, $\mathbf{D}_\epsilon = \epsilon\mathbf{D}$ (Qian *et al.*, 2020). The diffusion is then governed by the FPE

$$\partial_t p(\mathbf{x}, t) = -\nabla \cdot [\mathbf{b}(\mathbf{x}) p(\mathbf{x}, t) - \epsilon \mathbf{D}(\mathbf{x}) \nabla p(\mathbf{x}, t)] \tag{6.44}$$

or equivalently by the SDE

$$\mathrm{d}\mathbf{X}_t = [\mathbf{b}(\mathbf{X}_t) + \epsilon\nabla \cdot \mathbf{D}(\mathbf{X}_t)]\,\mathrm{d}t + \mathbf{\Gamma}(\mathbf{X}_t)\,\mathrm{d}\mathbf{W}_t \tag{6.45}$$

where $\epsilon\mathbf{D} = \mathbf{\Gamma}\mathbf{\Gamma}^\mathsf{T}/2$. By imposing an WKB ansatz on the invariant density π_ϵ, we can get an asymptotic

series of the mesoscopic potential Φ_ϵ (Qian *et al.*, 2020),

$$\Phi_\epsilon(\mathbf{x}) = \frac{\varphi(\mathbf{x})}{\epsilon} - \ln\omega(\mathbf{x}) - a\ln\epsilon + O(\epsilon). \tag{6.46}$$

Equations for φ and ω can then be obtained by plugging this back to the stationary FPE $\nabla\cdot\mathbf{J}_\epsilon^* = 0$:

$$0 = -\boldsymbol{\gamma}\cdot\nabla\varphi \tag{6.47a}$$

$$\nabla\cdot(\omega\boldsymbol{\gamma}) = -\nabla\varphi\cdot\mathbf{D}\nabla\omega \tag{6.47b}$$

where $\boldsymbol{\gamma}(\mathbf{x}) = \mathbf{b}(\mathbf{x}) + \mathbf{D}(\mathbf{x})\nabla\varphi(\mathbf{x})$. We thus have an orthogonal decomposition of the drift vector field (Freidlin and Wentzell, 2012)

$$\mathbf{b}(\mathbf{x}) = -\mathbf{D}(\mathbf{x})\nabla\varphi(\mathbf{x}) + \boldsymbol{\gamma}(\mathbf{x}). \tag{6.48}$$

More importantly, since $\boldsymbol{\gamma}$ is perpendicular to $\nabla\varphi$ according to Eq. (6.47a), φ is the Lyapunov function of the macroscopic deterministic dynamics $\mathbf{x}'(t) = \mathbf{b}(\mathbf{x})$ in the thermodynamic limit.

Furthermore, it is further shown by Qian *et al.* (2020) that the above decomposition can be directly linked to the irreversibility decomposition. Denoting $\mathrm{e_p}$, q_{hk}, and f_{d} as the mean rate of the total entropy production, housekeeping heat, and free energy dissipation. It is shown by Qian *et al.* (2020) that $\epsilon\mathrm{e_p} \to \left[\mathbf{b}\cdot\mathbf{D}^{-1}\mathbf{b}\right]_{\mathbf{x}=\hat{\mathbf{x}}}$, $\epsilon q_{\mathrm{hk}} \to \left[\boldsymbol{\gamma}\cdot\mathbf{D}^{-1}\boldsymbol{\gamma}\right]_{\mathbf{x}=\hat{\mathbf{x}}}$ and $\epsilon f_{\mathrm{d}} \to \left[\nabla\varphi\cdot\mathbf{D}\nabla\varphi\right]_{\mathbf{x}=\hat{\mathbf{x}}}$ where $\hat{\mathbf{x}}$ is a solution of $\mathbf{x}'(t) = \mathbf{b}(\mathbf{x})$. This further leads to a Pythogorean-like relation,

$$\|\mathbf{D}\nabla\varphi\|^2 + \|\boldsymbol{\gamma}\|^2 = \|\mathbf{b}\|^2 \tag{6.49}$$

where the norm is given by $\|\mathbf{u}\|^2 = \langle\mathbf{u},\mathbf{u}\rangle$ with inner product $\langle\mathbf{u},\mathbf{v}\rangle = \mathbf{u}\cdot\mathbf{D}^{-1}\mathbf{v}$. Eq. (6.48) thus gives the dissipation of the macroscopic potential φ of the dynamical system $\mathbf{x}'(t) = \mathbf{b}(\mathbf{x})$ a physical meaningful decomposition

$$\frac{\mathrm{d}}{\mathrm{d}t}\varphi(\mathbf{x}) = \mathbf{b}(\mathbf{x})\cdot\nabla\varphi(\mathbf{x}) = \underbrace{\boldsymbol{\gamma}(\mathbf{x})\cdot\mathbf{D}^{-1}(\mathbf{x})\,\boldsymbol{\gamma}(\mathbf{x})}_{\text{non-conservative pump}} - \underbrace{\mathbf{b}(\mathbf{x})\cdot\mathbf{D}^{-1}(\mathbf{x})\,\mathbf{b}(\mathbf{x})}_{\text{total energy dissipation}} \leq 0. \tag{6.50}$$

In the random perturbation considered here, we have ϵ-independent $\mathbf{b}$ and an ϵ-dependent $\epsilon\mathbf{D}$. With our cycle velocity decomposition of $\mathbf{b}$ in Eq. (6.5), at finite ϵ, we have

$$\mathbf{b} = -\epsilon\mathbf{D}\nabla\Phi_\epsilon - \mathbf{Q}_\epsilon\nabla\Phi_\epsilon + \nabla\times\mathbf{Q}_\epsilon \tag{6.51}$$

where the left-hand-side is ϵ-independent. With the WKB ansatz of Φ_ϵ in Eq. (6.46), we get

$$\mathbf{b} = -\mathbf{D}\nabla\varphi + \epsilon\left[-\mathbf{D}\nabla\left(\ln\omega\right)\right] - \frac{\mathbf{Q}_\epsilon}{\epsilon}\nabla\varphi - \mathbf{Q}_\epsilon\nabla\left(\ln\omega\right) + \nabla\times\mathbf{Q}_\epsilon. \tag{6.52}$$

Now, since by taking $\epsilon\to 0$, the right-hand-side should be $O(1)$, this would mean

$$\mathbf{Q}_\epsilon = \epsilon\mathbf{Q} + \epsilon^2\mathbf{Q}_2 + O(\epsilon^3). \tag{6.53}$$

Then, by matching Eq. (6.52) order-by-order, we get

$$\mathbf{b} = -\mathbf{D}\nabla\varphi - \mathbf{Q}\nabla\varphi \tag{6.54a}$$

$$0 = -\mathbf{D}\nabla\left(\ln\omega\right) - \mathbf{Q}_2\nabla\varphi - \mathbf{Q}\nabla\left(\ln\omega\right) + \nabla\times\mathbf{Q}. \tag{6.54b}$$

This further shows that

$$\boldsymbol{\gamma} = -\mathbf{Q}\nabla\varphi \tag{6.55}$$

where $\mathbf{Q}$ is the leading order of $\mathbf{Q}_\epsilon$.

Our work shows that any deterministic dissipative dynamics $\mathbf{x}'(t) = \mathbf{b}\left(\mathbf{x}\right)$, as the deterministic limit of stochastic dynamics with a steady state, can have he form

$$\mathbf{x}'(t) = \mathbf{b}(\mathbf{x}) = -\left[\mathbf{D}\left(\mathbf{x}\right) + \mathbf{Q}\left(\mathbf{x}\right)\right]\nabla\varphi\left(\mathbf{x}\right). \tag{6.56}$$

Note that this does not preclude the deterministic dynamics to have attractors with nonzero velocity, *e.g.* limit cycle or strange attractor. Our derivation shows that while $\nabla\varphi = 0$ on the attractor, $\mathbf{Q}$ actually diverges on the attractor such that $-\mathbf{Q}\nabla\varphi = \mathbf{x}'(t) = O(1)$. This is shown by taking $\epsilon\to 0$ of Eq. (6.45) to arrive at $\boldsymbol{\gamma} = -\mathbf{Q}\nabla\varphi$ with $\mathbf{Q} < \infty$ and $\nabla\varphi > 0$ in a deleted neighborhood of the attractor, and then using the continuity of $\boldsymbol{\gamma} = \mathbf{b} + \mathbf{D}\nabla\varphi$ near the attractor to draw the conclusion. See Zhu *et al.* (2006) for a concrete example. Here we provide a proof with the method of random perturbation based on the bivectorial formalism we introduced. We also note that the macroscopic potential $\varphi(\mathbf{x})$ is in general only locally smooth. For nonequilibrium dynamics, φ can be non-smooth on the separatrix of basins of attractions (Ge and Qian, 2012b). However, the dynamics on the separatrix is usually the least relevant for the deterministic dynamics.

6.3.3 Random Perturbation in Ao *et al.*

Yin and Ao (2006) considered the deterministic dynamical system $\mathbf{x}'(t) = \mathbf{b}\left(\mathbf{x}\right)$ to be the zero-mass limit of

a second-order Klein-Kramers equation. That is, they started from the Klein-Kramers equations with linear friction, gradient force, and small white noise, and took the zero-mass limit (first) and arrived a random perturbation with a specific scaling $\Phi_\epsilon = \phi/\epsilon, \mathbf{D}_\epsilon = \epsilon\mathbf{D}$, and $\mathbf{Q}_\epsilon = \epsilon\mathbf{Q}$ with ϵ representing the noise strength. The underlying deterministic equation of this kind of "mechanics-based" random perturbation takes the form

$$\mathbf{x}'(t) = -\mathbf{D}\nabla\phi - \mathbf{Q}\nabla\phi. \tag{6.57}$$

We note that compared to φ, which is only locally smooth in general, the macroscopic potential ϕ here is globally smooth as given in the Klein-Kramers equation and is also the Lyapunov function of the deterministic dynamics in Eq. (6.57). However, the random perturbation here needs an underlying Klein-Kramers equation. Whether all dynamical systems $\mathbf{x}'(t) = \mathbf{b}(\mathbf{x})$ can be represented as the zero-mass limit of a Klein-Kramers equations or not remains to be elucidated (Zhu *et al.*, 2006; Ao *et al.*, 2007; Shi *et al.*, 2012).

A natural question that follows is how to compare the two aforementioned random perturbations if they have the same deterministic dynamics. With the the drift decomposition with cycle velocity shown in Eq. (6.5), we see that the two random perturbations differ at the ϵ-dependence of the drift $\mathbf{b}_\epsilon$. Specifically, they correspond to different next-order term $\mathbf{b}_1$ in $\mathbf{b}_\epsilon = \mathbf{b}_0 + \epsilon\mathbf{b}_1$. The $\mathbf{b}_1 = \mathbf{0}$ in (Qian *et al.*, 2020) and $\mathbf{b}_1 = \nabla \times \mathbf{Q}$ in (Yin and Ao, 2006). For general $\mathbf{b}_1$, the equations for φ and ω in the asymptotic series of Φ_ϵ satisfies

$$0 = -\boldsymbol{\gamma} \cdot \nabla\varphi \tag{6.58a}$$

$$\nabla \cdot (\omega\boldsymbol{\gamma}) = -\nabla\varphi \cdot [\mathbf{D}\nabla\omega - \mathbf{b}_1]. \tag{6.58b}$$

We see that the (Hamilton-Jacobi) equation of φ in Eq. (6.58a) is independent to $\mathbf{b}_1$ but the equations for the next-order term ω differs. This means that the decomposition we had for $\mathbf{b}_0 = -(\mathbf{D} + \mathbf{Q})\nabla\varphi$ is general for any $\mathbf{b}_\epsilon$. To see this, simply replace the $\mathbf{b}$ in Eq. (6.52) with $\mathbf{b}_\epsilon = \mathbf{b}_0 + \epsilon\mathbf{b}_1$. Furthermore, the two macroscopic potentials from the two aforementioned random perturbations both satisfies Eq. (6.58a) and the difference in Φ_ϵ lies in the ω term (Yang and Cheng, 2021). In fact, the unique orthogonal decomposition theorem from Freidlin and Wentzell (2012) further guarantee the two macroscopic potentials to have the same shape in the domain where φ is continuously differentiable and with nonzero gradient.

Lastly, we note that the macroscopic potential ϕ from (Yin and Ao, 2006) is a Lyapunov function for $\mathbf{x}'(t) = \mathbf{b}_0(\mathbf{x}) = -\mathbf{D}\nabla\phi - \mathbf{Q}\nabla\phi$ but is generally not for $\mathbf{x}'(t) = \mathbf{b}_\epsilon(\mathbf{x}) = -\mathbf{D}\nabla\phi - \mathbf{Q}\nabla\phi + \epsilon\nabla \times \mathbf{Q}$

unless

$$\epsilon \left(\nabla \times \mathbf{Q}\right) \cdot \nabla\phi \leq \nabla\phi \cdot \mathbf{D}\nabla\phi. \tag{6.59}$$

The domain for Eq. (6.59) to hold can be enlarged with smaller ϵ, and will be the whole space if the random perturbation has a Maxwell-Boltzmann equilibrium such that $\left(\nabla \times \mathbf{Q}\right) \cdot \nabla\phi = 0$. In fact, any systems with constant cycle velocity $\mathbf{Q}$ admits Maxwell-Boltzmann equilibrium, *e.g.* the Ornstein-Uhlenbeck process as shown by Kwon *et al.* (2005).

6.4 Summary and Discussion

In this chapter, we extend the decomposition of continuous Markov process associated with the total entropy production decomposition (Wang *et al.*, 2008) by introducing the bivectorial cycle velocity (Yang and Cheng, 2021). Hidden structures in the mean rate of thermodynamic quantities are revealed. Further in the small noise thermodynamic limit, the emergent dynamical system is shown to admit a generalized gradient form. Differences among three random perturbations are further discussed with the bivectorial formalism. We unite landscape theories from Graham (1977a) and Ao (2004), and from Freidlin and Wentzell (2012) with our thermodynamic theory (Yang and Cheng, 2021). See Fig. 6.1 for a summary of the result in this chapter. This theory can be applied to many biological systems. See Sec. 10.1 for a discussion on the possible future applications and extensions inspired by several possible applications.

Our thermodynamic potential theory requires

1. one identifies the stochastic origin of a deterministic Markov dynamic model and
2. the Markov stochastic dynamics has a steady state.

The scalar potential Φ and bivectorial cycle potential $\mathbf{Q}$ are both identified from properties at the steady state. Systems with a steady state is characterized by the fluctuation-dissipation relations we will discuss in the next Chap. 7. In short, the time-translation symmetry at the steady state dictates the drift to be *dissipative* in order to balance the fluctuating noise. Our thermodynamic potential theory is for Markov dissipative systems.

The introduction of cycle velocity organizes the two notions of equilibrium in thermodynamics:

1. Equilibrium in classical thermodynamics is detailed balanced with zero stationary velocity $\mathbf{v}^* = \mathbf{0}$ and zero housekeeping heat dissipation $\mathcal{Q}_{\rm hk} = 0$. The cycle velocity satisfies $\nabla \times \mathbf{Q} = \mathbf{Q}\nabla\Phi$ in equilibrium.

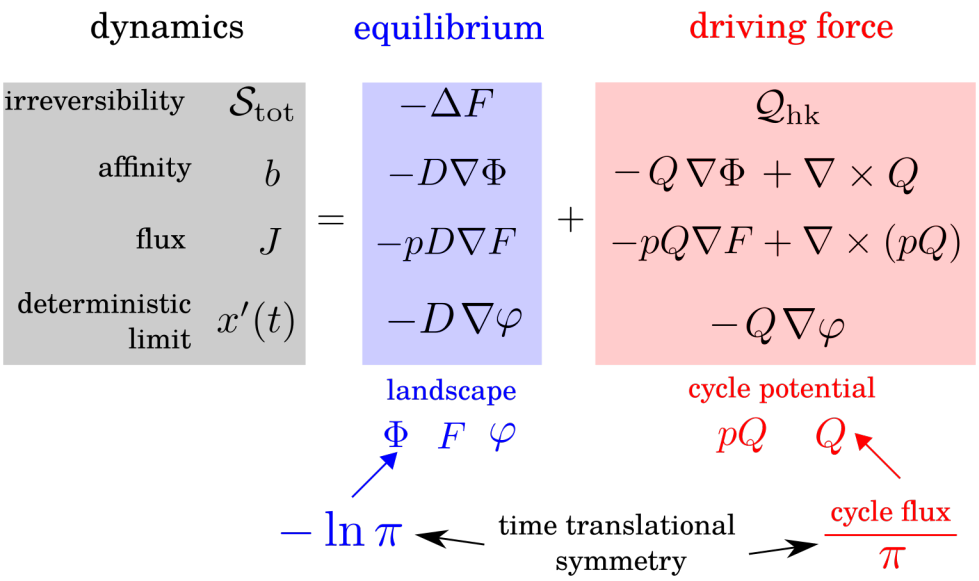


Figure 6.1: Summary of the dynamic decomposition for continuous Markov processes and their deterministic limit presented in this chapter. Irreversibility decomposition allows one to decompose a Markov dissipative dynamics into its underlying equilibrium and the nonequilibrium driving forces. The underlying landscape and cycle potential describing the two parts respectively are both revealed from the steady state of system, *i.e.* when the system has time translational symmetry.

2. The notation of M-B equilibrium introduced by Qian (2014b, 2015) is an extension of the notion of equilibrium, from $\mathbf{v}^* = \mathbf{0}$ to $\mathbf{v}^* \perp \nabla\Phi$. The orthoganality $\mathbf{v}^* \perp \nabla\Phi$ is equivalent to $(\nabla\times\mathbf{Q})\perp\nabla\Phi$ in the bivectorial formalism since $\nabla\Phi\cdot\mathbf{Q}\nabla\Phi = 0$.

Therefore, all systems with constant cycle velocity $\mathbf{Q}$ are in M-B equilibrium, *e.g.* the Ornstein-Uhlenbeck process (Kwon *et al.*, 2005). For systems with M-B equilibrium, the potential Φ is the Lyapunov function of $\mathbf{x}'(t) = \mathbf{b}(\mathbf{x})$.

The thermodynamic potential theory presented in this chapter is for Markov processes with continuous space and time (diffusion). A similar theory can actually be formulated for the discrete-space Markov chains as well, with the same energy landscape $\Phi = -\ln\pi$ and the cycle flux J_σ in Markov chains discussed in Sec. 5.2. The decomposition and implications are more complicated due to the arbitrary topology a Markov chain can have. See Sec. 10.2 for a discussion for this future direction.

Chapter 7

Stationarity and Fluctuation-Dissipation Relations

The energetics we present from Chap. 3 to 6 for both Markov stochastic dynamics and their deterministic limits are revealed from both time-reversal symmetry and time-translational symmetry. With concepts from the steady state, *i.e.* energy landscape and cycles, we have a fundamental decomposition of Markov dynamics based on the irreversibility decomposition. In this chapter, we show that the time-translational symmetry alone can decree a standard result in statistical physics, *i.e.* the *fluctuation-dissipation relation* (FDR) (Zwanzig, 1965; Elson, 1985; Keizer, 1987; Qian, 2001a; Jiang *et al.*, 2004; Chen *et al.*, 2006). In Sec. 7.1, we introduce the key mathematical result of Doob's drift-noise decomposition in our discussion of FDR. Generalized FDRs are then presented in Sec. 7.2. By discussing the FDR in the adjoint process, we arrive a novel characterization of equilibrium system in Sec. 7.3. The drift-noise decomposition in the adjoint process is further connected to a more generalized reversed decomposition in Sec. 7.4.

7.1 Doob Decomposition

Here we consider a general discrete time n-dimensional (n-D) stochastic process, not necessarily Markovian, $\mathbf{X}_t \in \mathbb{R}^n$, $t \in \mathbb{N}$. Continuous time processes can be discussed by considering the infinitesimal $\mathrm{d}t$ and taking the continuous time limit[1]. As before, we use $\mathbf{X}_{0:t}$ to denote the entire stochastic trajectory from time 0 to time t. The change of the value of the state of the system from time t to $t+1$ has a natural decomposition

[1] Doob-Meyer decomposition theorem should be considered for continuous time processes (Meyer, 1962, 1963)

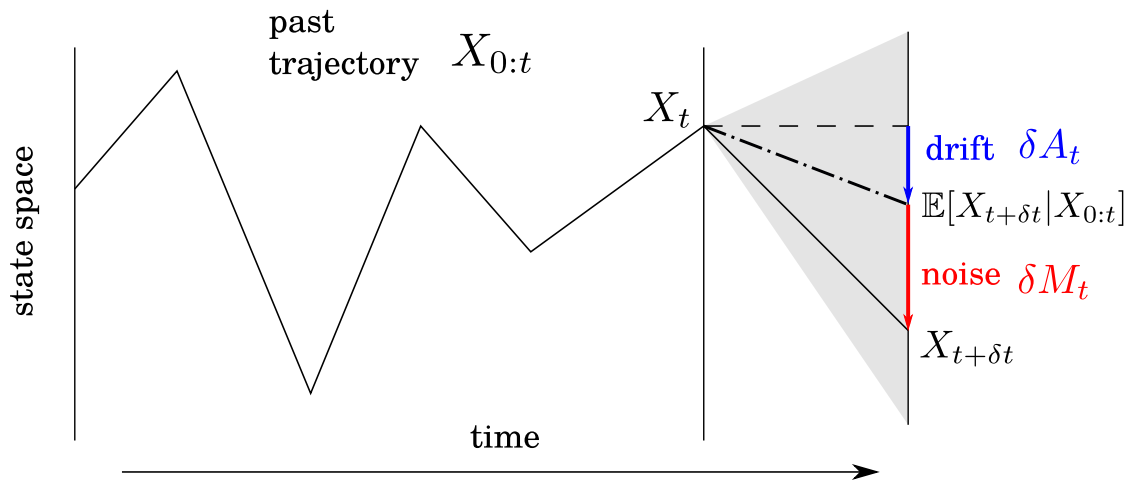


Figure 7.1: Illustration for Doob decomposition. The change in one step is decomposed into the conditional expected change, drift, and the deviation from it, the noise.

by the conditional expectation:

$$\delta \mathbf{X}_t \coloneqq \mathbf{X}_{t+1} - \mathbf{X}_t = \delta \mathbf{A}_t \left(\mathbf{X}_{0:t}\right) + \delta \mathbf{M}_t \left(\mathbf{X}_{0:t+1}\right) \tag{7.1}$$

where

$$\delta \mathbf{A}_t \left(\mathbf{X}_{0:t}\right) \coloneqq \mathbb{E}\left[\mathbf{X}_{t+1} | \mathbf{X}_{0:t}\right] - \mathbf{X}_t \tag{7.2a}$$

$$\delta \mathbf{M}_t \left(\mathbf{X}_{0:t+1}\right) \coloneqq \mathbf{X}_{t+1} - \mathbb{E}\left[\mathbf{X}_{t+1} | \mathbf{X}_{0:t}\right]. \tag{7.2b}$$

See Fig. 7.1 for an illustration. The first term $\delta \mathbf{A}_t$ in the decomposition is the conditional average change of $\mathbf{X}_t$, a function of entire, non-Markovian $\mathbf{X}_{0:t}$, that captures the average dynamics of $\mathbf{X}_t$, $\mathbb{E}\left[\delta \mathbf{X}_t | \mathbf{X}_{0:t}\right] = \delta \mathbf{A}_t$. Hence, the increment $\delta \mathbf{A}_t$ is referred as the *drift* of $\mathbf{X}_t$. The second term $\delta \mathbf{M}_t$ captures the 1-to-many randomness in the change of $\mathbf{X}_t$, it has a zero (conditional) mean:

$$\mathbb{E}\left[\delta \mathbf{M}_t | \mathbf{X}_{0:t}\right] = 0 \text{ and } \mathbb{E}\left[\delta \mathbf{M}_t\right] = 0. \tag{7.3}$$

The existence of this decomposition of a general process in Eq. (7.1) into the sum of two processes is known as the *Doob decomposition theorem* (Doob, 1990; Grimmett and Stirzaker, 2001).

The decomposed process $\mathbf{M}_t = \sum_{k=0}^{t-1} \delta \mathbf{M}_t$ satisfies

$$\mathbb{E}\left[\mathbf{M}_t | \mathbf{X}_{0:s}\right] = \mathbf{M}_s, \text{ for all } 0 \leq s \leq t \tag{7.4}$$

due to the zero conditional gain in every increment. In the theory of probability, such a process is called a

martingale (Grimmett and Stirzaker, 2001; Shreve, 2010). Typical examples of martingales are an unbiased random walk in discrete time and a Brownian motion in the continuous time.

The zero (conditional) mean properties of the martingale increment in Eq. (7.3) implies that $\delta\mathbf{M}_t$ is an increment uncorrelated to the past (but not necessarily independent): for an arbitrary path scalar variable of $\mathbf{X}_{0:t}$, $f\left(\mathbf{X}_{0:t}, t\right)$, the covariance between f and any component of $\delta\mathbf{M}_t$, say the ith one denoted as $\delta M_t^{(i)}$, is zero:

$$\mathrm{CoV}\left[f\left(\mathbf{X}_{0:t}, t\right), \delta M_t^{(i)}\right] = 0. \tag{7.5}$$

This leads to the following two important results. To present them in a more concise way, we will use $[\![\mathbf{u}, \mathbf{w}]\!]$ to denote the covariance matrix between two vector random variables $\mathbf{u}$ and $\mathbf{w}$ in this chapter. Specifically, the i, j component of $[\![\mathbf{u}, \mathbf{w}]\!]$ is $\mathrm{CoV}\left[u_i, w_j\right]$.

First, the martingale increments at different times are uncorrelated $[\![\delta\mathbf{M}_t, \delta\mathbf{M}_s]\!] = \mathbf{0}$. This leads to the fact that a martingale has an ever-increasing, additive fluctuation,

$$[\![\mathbf{M}_t, \mathbf{M}_t]\!] = \sum_{k=0}^{t-1} [\![\delta\mathbf{M}_k, \delta\mathbf{M}_k]\!]. \tag{7.6}$$

The scalar version of this, the variance of M_t satisfies $\mathbb{V}\left[M_t\right] = \sum_{k=0}^{t-1} \mathbb{V}\left[\delta M_k\right]$ as a discrete-time analogue of Itô isometry (Shreve, 2010) and is, in a sense, more general than Itô isometry since the martingale in Itô isometry is the Brownian motion which has independent increments whereas Eq. (7.6) doesn't require independency in the increments.

Second, the uncertainty of increment $\delta\mathbf{X}_t$ actually has two uncorrelated sources identified by the Doob decomposition in Eq. (7.1),

$$[\![\delta\mathbf{X}_t, \delta\mathbf{X}_t]\!] = [\![\delta\mathbf{A}_t, \delta\mathbf{A}_t]\!] + [\![\delta\mathbf{M}_t, \delta\mathbf{M}_t]\!]. \tag{7.7}$$

The two sources of the uncertainty in $\delta\mathbf{X}_t$ are rather disjoint conceptually. Since $\delta\mathbf{A}_t$ is a function of the past path $\mathbf{X}_{0:t}$, the fluctuation of $\delta\mathbf{A}_t$ is really about the uncertainty of the past. On the contrary, the uncertainty of $\delta\mathbf{M}_t$ is about the fluctuation in the conditional mapping from $\mathbf{X}_t$ to $\mathbf{X}_{t+1}$. If the conditional mapping is deterministic, then $\delta\mathbf{M}_t = 0$ but $[\![\delta\mathbf{A}_t, \delta\mathbf{A}_t]\!]$ could still be nonzero if there is uncertainty in the initial condition and/or the past state.

The two results shown above are valid for general processes. Assumptions such as Markovian, stationarity, or detailed balance (as we will introduce later) are not needed. In fact, the Doob decomposition can also

be applied to an arbitrary path variable $\mathcal{U}_t(\mathbf{X}_{0:t})$. The decomposition then becomes $\delta\mathcal{U}_t = \delta A_{\mathcal{U}_t} + \delta M_{\mathcal{U}_t}$ where $\delta A_{\mathcal{U}_t} \coloneqq \mathbb{E}[\mathcal{U}_{t+1}|\mathbf{X}_{0:t}] - \mathcal{U}_t$ and $\delta M_{\mathcal{U}_t} \coloneqq \mathcal{U}_{t+1} - \mathbb{E}[\mathcal{U}_{t+1}|\mathbf{X}_{0:t}]$. The results presented above still hold.

7.2 Generalized Fluctuation-Dissipation Relations

7.2.1 Generalized Einstein Relation

If the process $\mathbf{X}_t$ reaches a steady state, the probability distribution of state no longer changes in time. For those stationary $\mathbf{X}_t$, all its cumulants will be fixed in time. The average state of $\mathbf{X}_t$ would be constant in time, meaning that the average drift of the observable would be zero at the steady state $\mathbb{E}_*[\delta\mathbf{A}_t] = 0$ where $\mathbb{E}_*[\cdot]$ means expectation for the stationary process. For the evolution of the covariance matrix, we have

$$\begin{aligned}\delta[\![\mathbf{X}_t, \mathbf{X}_t]\!] &\coloneqq [\![\mathbf{X}_{t+1}, \mathbf{X}_{t+1}]\!] - [\![\mathbf{X}_t, \mathbf{X}_t]\!] \\ &= [\![\delta\mathbf{A}_t, \mathbf{X}_t]\!] + [\![\delta\mathbf{A}_t, \mathbf{X}_t]\!]^{\mathsf{T}} + [\![\delta\mathbf{X}_t, \delta\mathbf{X}_t]\!]\end{aligned} \tag{7.8}$$

where T denotes the transpose of a matrix. This shows that the covariance of states always have a source given by the fluctuation of transitions. Stationarity of $\mathbf{X}_t$ is achieved by the balance between the drift and the fluctuation such that $\delta[\![\mathbf{X}_t, \mathbf{X}_t]\!] = \mathbf{0}$,

$$[\![\delta\mathbf{A}_t, \mathbf{X}_t]\!]_* + [\![\delta\mathbf{A}_t, \mathbf{X}_t]\!]_*^{\mathsf{T}} = -[\![\delta\mathbf{X}_t, \delta\mathbf{X}_t]\!]_* \tag{7.9}$$

where $[\![\mathbf{u}, \mathbf{w}]\!]_*$ denotes covariance matrix of $\mathbf{u}$ and $\mathbf{w}$ when the process is stationary. This shows that the symmetric part of $[\![\delta\mathbf{A}_t, \mathbf{X}_t]\!]_*$ is negative-definite. In physics, the drift $\delta\mathbf{A}_t$ in a stable process is considered as the dissipation of the dynamics. Eq. (7.9) is thus a generally-valid *Einstein relation* (GER) implied by stationarity. In a scalar process, Eq. (7.9) reduces to $2\mathrm{Co}\mathbb{V}_*(\delta A_t, X_t) = -\mathbb{V}_*[\delta X_t]$ which shows that the drift δA_t, on average, has an opposite sign of the value of X_t as a "dissipation" to X_t. In fact, the result can be extended to arbitrary observable of the process, $U_t(\mathbf{X}_t)$, *e.g.* the energy of the system. The Doob decomposition of its dynamics becomes $\delta U_t = \delta A_{U_t} + \delta M_{U_t}$ where $\delta A_{U_t} \coloneqq \mathbb{E}[U_{t+1}|\mathbf{X}_{0:t}] - U_t$ and $\delta M_{U_t} \coloneqq U_{t+1} - \mathbb{E}[U_{t+1}|\mathbf{X}_{0:t}]$. The GER then becomes $2\mathrm{Co}\mathbb{V}_*(\delta A_{U_t}, U_t) = -\mathbb{V}_*[\delta U_t]$ which clearly portraits a relation between fluctuation $\mathbb{V}_*[\delta U_t]$ and the energy dissipation δA_{U_t}. See Fig. 7.2 for an illustration for the GER.

In Ornstein-Uhlenbeck (OU) processes described by the stochastic differential equation $\mathrm{d}\mathbf{X}_t = -\mathbf{B}\mathbf{X}_t\mathrm{d}t +$

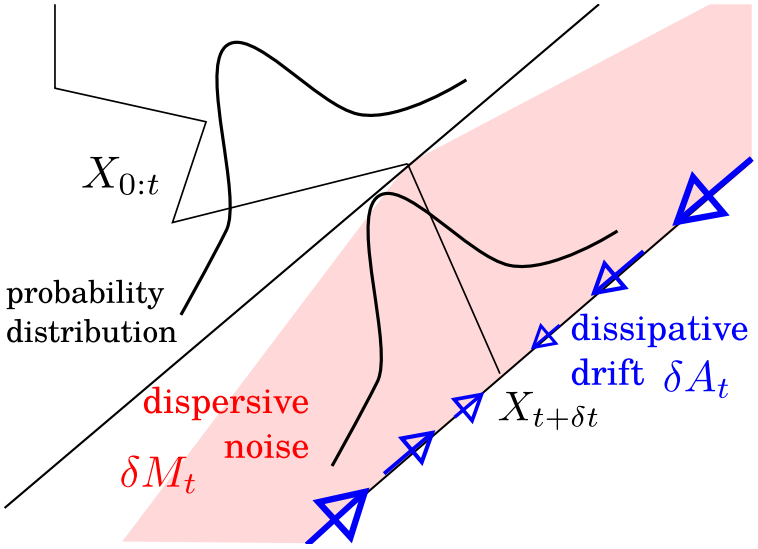


Figure 7.2: Fluctuation-dissipation relations emerge as the balance between dissipative drift and dispersive noise necessary for a time-translational symmetry in the probability distribution of state in stationary processes.

$\mathbf{\Gamma} \mathrm{d}\mathbf{W}_t$ where $\mathbf{W}_t$ is the n-D Brownian motion, we have $\delta \mathbf{A}_t = -\mathbf{B}\mathbf{X}_t \mathrm{d}t$ and $[\![\mathrm{d}\mathbf{X}_t, \mathrm{d}\mathbf{X}_t]\!]_* = 2\mathbf{D}\mathrm{d}t$ where $\mathbf{D} = \mathbf{\Gamma}\mathbf{\Gamma}^\mathsf{T}/2$ is the diffusion matrix. Eq. (7.9) then reduces to the Einstein relation for linear systems given by the Lyapunov matrix equation in Eq. (1.2) (Qian, 2001a). The GER in Eq. (7.9) is valid for any stationary processes. Conditions such as Markovian or detailed balance are not needed. It is a necessary condition for the stationarity of fluctuation and covariance. We note that the stationarity of $\mathbf{X}_t$ actually requires all of its cumulants to be fixed in time. Thus, any martingale, supermartingale, or submartingale will not satisfy the GER since a martingale has an ever-increasing variance and both supermartingale and submartingale have a monotonic drift.

7.2.2 Generalized Green-Kubo Formula

Eqs. (7.8) and (7.9) further allow us to derive a general Green-Kubo formula (GKF) for a stationary processes (Kubo, 1966; Jiang *et al.*, 2004; Chen *et al.*, 2006). We note that for $t \geq 0$, we have

$$[\![\delta \mathbf{A}_t, \delta \mathbf{A}_0]\!] = [\![\mathbf{X}_{t+1}, \delta \mathbf{A}_0]\!] - [\![\mathbf{X}_t, \delta \mathbf{A}_0]\!] . \tag{7.10}$$

Therefore,

$$\sum_{k=0}^{\infty} [\![\delta \mathbf{A}_k, \delta \mathbf{A}_0]\!] = [\![\mathbf{X}_\infty, \delta \mathbf{A}_0]\!] - [\![\mathbf{X}_0, \delta \mathbf{A}_0]\!] . \tag{7.11}$$

Assuming that $\mathbf{X}_t$ has a finite correlation time, the first term is zero. Then, by applying Eq. (7.9) to the above equation, we get a general GKF that relates auto-correlation of the dissipative drift $\delta\mathbf{A}_t$ to the fluctuation of $\delta\mathbf{M}_t$ at steady state,

$$[\![\delta\mathbf{X}_t, \delta\mathbf{X}_t]\!]_* = \sum_{k=0}^{\infty} \left\{ [\![\delta\mathbf{A}_k, \delta\mathbf{A}_0]\!]_* + [\![\delta\mathbf{A}_k, \delta\mathbf{A}_0]\!]_*^{\mathsf{T}} \right\} \tag{7.12}$$

which becomes

$$[\![\delta\mathbf{M}_t, \delta\mathbf{M}_t]\!]_* = \sum_{k=-\infty}^{\infty} [\![\delta\mathbf{A}_k, \delta\mathbf{A}_0]\!]_* \tag{7.13}$$

by using Eq. (7.7) and stationarity. Eq. (7.13) shows that the GKF is really a relation between the drift $\delta\mathbf{A}_t$ and the martingale increment $\delta\mathbf{M}_t$. The results for continuous time processes derived in the past (Jiang *et al.*, 2004; Chen *et al.*, 2006) lost this important insight since in the continuous time processes considered have $\delta\mathbf{A}_t = O(\mathrm{d}t)$ and $\delta\mathbf{M}_t = O(\sqrt{\mathrm{d}t})$, which makes the covariance of the drift higher order.

7.3 Adjoint Processes and Adjoint Drift

The Doob decomposition shown in Eq. (7.1) is with respect to the forward probability measure $\mathbb{P}$. In Markov processes with steady states, we can consider the Doob decomposition given by the adjoint probability measure $\mathbb{P}^\dagger$ (*i.e.,* the decomposition in the adjoint process) where the transition probability is given by

$$\mathbb{P}^\dagger \{\mathbf{X}_{t+1} = \mathbf{y} | \mathbf{X}_t = \mathbf{x}\} = \frac{\pi(\mathbf{y})}{\pi(\mathbf{x})} \mathbb{P}\{\mathbf{X}_{t+1} = \mathbf{x} | \mathbf{X}_t = \mathbf{y}\} \tag{7.14}$$

where π is the invariant distribution. The adjont Doob decomposition is then

$$\delta\mathbf{X}_t = \delta\mathbf{A}_t^\dagger + \delta\mathbf{M}_t^\dagger \tag{7.15}$$

with $\delta\mathbf{A}_t^\dagger \coloneqq \mathbb{E}^\dagger[\mathbf{X}_{t+1}|\mathbf{X}_t] - \mathbf{X}_t$ and $\delta\mathbf{M}_t^\dagger \coloneqq \mathbf{X}_{t+1} - \mathbb{E}^\dagger[\mathbf{X}_{t+1}|\mathbf{X}_t]$. The covariance between $\mathbf{X}_t$ and $\delta\mathbf{A}_t$ and the covariance between $\mathbf{X}_t$ and $\delta\mathbf{A}_t^\dagger$ are only subject to a transpose at steady state,

$$[\![\mathbf{X}_t, \delta\mathbf{A}_t]\!]_* = \left[\!\!\left[\mathbf{X}_t, \delta\mathbf{A}_t^\dagger\right]\!\!\right]_*^{\mathsf{T}}. \tag{7.16}$$

This gives us a neater expression of the GER in Eq. (7.9),

$$\left[\!\!\left[\mathbf{X}_t, \delta\mathbf{A}_t + \delta\mathbf{A}_t^\dagger\right]\!\!\right]_* = -[\![\delta\mathbf{X}_t, \delta\mathbf{X}_t]\!]_*. \tag{7.17}$$

This allows one to show that for reversible (detailed balanced) systems where the forward and the adjoint processes are the same, we have $\delta\mathbf{A}_t = \delta\mathbf{A}_t^\dagger$ and thus

$$[\![\mathbf{X}_t, \delta\mathbf{A}_t]\!]_* = -\frac{1}{2}[\![\delta\mathbf{X}_t, \delta\mathbf{X}_t]\!]_* \tag{7.18}$$

which shows that the covariance matrix $[\![\mathbf{X}_t, \delta\mathbf{A}_t]\!]_*$ is symmetric and negative-definite. This gives yet another characterization of detailed balance and is the generalization of $\mathbf{B\Xi}$ being symmetric for reversible OU processes (Qian, 2001a). We note that the GKF also have two sibling expressions in terms of the adjoint drift for continuous time Markov chain (Chen *et al.*, 2006). One can derive

$$[\![\delta\mathbf{X}_t, \delta\mathbf{X}_t]\!]_* = \sum_{k=0}^{\infty}\left[\!\left[\delta\mathbf{A}_k, \delta\mathbf{A}_0^\dagger\right]\!\right]_* + \left[\!\left[\delta\mathbf{A}_k, \delta\mathbf{A}_0^\dagger\right]\!\right]_*^{\mathsf{T}} \tag{7.19a}$$

$$= \sum_{k=0}^{\infty}\left[\!\left[\delta\mathbf{A}_k^\dagger, \delta\mathbf{A}_0^\dagger\right]\!\right]_* + \left[\!\left[\delta\mathbf{A}_k^\dagger, \delta\mathbf{A}_0^\dagger\right]\!\right]_*^{\mathsf{T}} \tag{7.19b}$$

by a similar approach [2].

In a continuous process described by stochastic differential equations,

$$\mathrm{d}\mathbf{X}_t = (\mathbf{b} + \nabla\cdot\mathbf{D})\,\mathrm{d}t + \mathbf{\Gamma}\mathrm{d}\mathbf{W}_t, \tag{7.20}$$

where $\mathbf{D} = \mathbf{\Gamma}\mathbf{\Gamma}^{\mathsf{T}}/2$ is the diffusion matrix and $\mathbf{W}_t$ is the Brownian motion, we have $\delta\mathbf{A}_t = (\mathbf{b} + \nabla\cdot\mathbf{D})\,\mathrm{d}t$ and $\delta\mathbf{M}_t = \mathbf{\Gamma}\mathrm{d}\mathbf{W}_t$. The vector field decomposition $\mathbf{b} = -\mathbf{D}\nabla\Phi - \mathbf{Q}\nabla\Phi + \nabla\times\mathbf{Q}$ discussed in (Yang and Cheng, 2021) provides an alternative proof for the GER in continuous processes. By using integration by part, $\mathbf{Q} = -\mathbf{Q}^{\mathsf{T}}$ and $\mathbf{D} = \mathbf{D}^{\mathsf{T}}$, the covariance $[\![\mathbf{X}_t, \delta\mathbf{A}_t]\!]_* = [\![\mathbf{X}_t, \mathbf{b} + \nabla\cdot\mathbf{D}]\!]_*\,\mathrm{d}t$ can be further rewritten as

$$[\![\mathbf{X}_t, \delta\mathbf{A}_t]\!]_* = \mathbb{E}_*\left[\mathbf{Q} - \mathbf{D}\right]\mathrm{d}t. \tag{7.21}$$

This shows that $[\![\mathbf{X}_t, \delta\mathbf{A}_t]\!]_* + [\![\mathbf{X}_t, \delta\mathbf{A}_t]\!]_*^{\mathsf{T}} = \mathbb{E}_*\left[\mathbf{Q} - \mathbf{D}\right]\mathrm{d}t + \mathbb{E}_*\left[-\mathbf{Q} - \mathbf{D}\right]\mathrm{d}t = -2\mathbb{E}_*\left[\mathbf{D}\right]\mathrm{d}t$, which is exactly the continuous-time version of Eq. (7.12). With $\mathbf{Q}$ understood as the cycle velocity in continuous processes (Yang and Qian, 2021a; Yang and Cheng, 2021), Eq. (7.21) actually presents an interesting relation between average cycle velocity $\mathbb{E}_*\left[\mathbf{Q}\right]$, average diffusion matrix $\mathbb{E}_*\left[\mathbf{D}\right]$, and covariance between

[2] The derivation is by formulating the drift of an arbitrary function of the process $f(\mathbf{X}_t)$ as an operator $\mathcal{A}$ operating on f: $\mathcal{A}f(\mathbf{X}_t) \coloneqq \mathbb{E}\left[f(\mathbf{X}_{t+1})|\mathbf{X}_{0:t}\right] - f(\mathbf{X}_t)$. The adjoint drift is $\mathcal{A}^\dagger f(\mathbf{X}_t) \coloneqq \mathbb{E}^\dagger\left[f(\mathbf{X}_{t+1})|\mathbf{X}_t\right] - f(\mathbf{X}_t)$. A generalization to Eq. (7.10) is $[\![\mathcal{A}f(\mathbf{X}_t), g(\mathbf{X}_0)]\!] = [\![f(\mathbf{X}_{t+1}), g(\mathbf{X}_0)]\!] - [\![f(\mathbf{X}_t), g(\mathbf{X}_0)]\!]$. One can then prove Eq. (7.12) by using $f = X_t^{(i)}$ and $g = \delta A_0^{(j)}$, prove Eq. (7.19a) by using $f = X_t^{(i)}$ and $g = \delta A_0^{\dagger,(j)}$ for Markov processes, and prove Eq. (7.19b) by using $f = \delta A_0^{\dagger,(j)}$ and $g = X_0^{(j)}$ for Markov processes and $\mathbb{E}_*\left[f(\mathbf{X}_t)\,\mathcal{A}g(\mathbf{X}_t)\right] = \mathbb{E}_*\left[g(\mathbf{X}_t)\,\mathcal{A}^\dagger f(\mathbf{X}_t)\right]$. All three relations rely on the asymptotic independence between $\mathbf{X}_\infty$ and $\mathbf{X}_0$.

system state and its conditional drift velocity $\left[\!\left[\mathbf{X}_t, \frac{\delta \mathbf{A}_t}{\mathrm{d}t}\right]\!\right]_*$. We note that $\mathbf{Q} = \mathbf{0}$ corresponds to detailed balanced systems. This again implies the covariance $\left[\!\left[\mathbf{X}_t, \delta\mathbf{A}_t\right]\!\right]_*$ is a symmetric and negative-definite matrix in detailed balanced systems.

7.4 Reversed Decomposition

The Doob decomposition decomposes the dynamics $\delta\mathbf{X}_t$ into a drift part $\delta\mathbf{A}_t$ and a martingale part $\delta\mathbf{M}_t$. One of our key results is that the uncertainty of the dynamics has a resulting uncorrelated decomposition into the fluctuation of the past and the fluctuation of the 1-to-many mapping marching toward the future as shown in Eq. (7.7). Here, we show another decomposition that relates the fluctuation of the dynamics to the many-to-1 uncertainty in the dynamics.

We can decompose $\delta\mathbf{X}_t$ by conditioning on the state one step in the future,

$$\delta\mathbf{X}_t = \delta\mathbf{R}_t + \delta\mathbf{N}_t \tag{7.22}$$

where

$$\delta\mathbf{R}_t = \mathbf{X}_{t+1} - \mathbb{E}\left[\mathbf{X}_t | \mathbf{X}_{t+1}\right] \tag{7.23a}$$

$$\delta\mathbf{N}_t = \mathbb{E}\left[\mathbf{X}_t | \mathbf{X}_{t+1}\right] - \mathbf{X}_t. \tag{7.23b}$$

This is also an uncorrelated decomposition, $\left[\!\left[\delta\mathbf{R}_t, \delta\mathbf{N}_t\right]\!\right] = \mathbf{0}$, which leads us to another fluctuation decomposition,

$$\left[\!\left[\delta\mathbf{X}_t, \delta\mathbf{X}_t\right]\!\right] = \left[\!\left[\delta\mathbf{R}_t, \delta\mathbf{R}_t\right]\!\right] + \left[\!\left[\delta\mathbf{N}_t, \delta\mathbf{N}_t\right]\!\right]. \tag{7.24}$$

$\delta\mathbf{R}_t$ can be thought of as the backward drift and $\delta\mathbf{N}_t$ is a quantification of the many-to-1 uncertainty in the dynamics. Therefore, Eq. (7.24) and Eq. (7.7) together link the many-to-1 uncertainty and 1-to-many uncertainty with forward and backward drift,

$$\left[\!\left[\delta\mathbf{X}_t, \delta\mathbf{X}_t\right]\!\right] = \left[\!\left[\delta\mathbf{A}_t, \delta\mathbf{A}_t\right]\!\right] + \left[\!\left[\delta\mathbf{M}_t, \delta\mathbf{M}_t\right]\!\right] \tag{7.25a}$$

$$= \left[\!\left[\delta\mathbf{R}_t, \delta\mathbf{R}_t\right]\!\right] + \left[\!\left[\delta\mathbf{N}_t, \delta\mathbf{N}_t\right]\!\right]. \tag{7.25b}$$

For Markov processes, the backward drift becomes the adjoint drift at steady state, $\delta\mathbf{R}_t = -\delta\mathbf{A}_t^\dagger$. In fact, the decomposition in Eq. (7.22) is actually from the Doob decomposition of the reversed process $\mathbf{Z}_t = \mathbf{X}_{-t}$. The past and the future is conditionally independent if conditioned on the present in Markov

processes,

$$P_{\mathbf{X}_{0:t}|\mathbf{X}_{t+1:\infty}}\left(\mathbf{x}_{0:t}|\mathbf{x}_{t+1:\infty}\right) = P_{\mathbf{X}_{0:t}|\mathbf{X}_{t+1}}\left(\mathbf{x}_{0:t}|\mathbf{x}_{t+1}\right). \tag{7.26}$$

This means that the conditional expectation $\mathbb{E}\left[\mathbf{X}_t|\mathbf{X}_{t+1}\right]$ in Eq. (7.22) is the same as conditioning the whole future, $\mathbb{E}\left[\mathbf{X}_t|\mathbf{X}_{t+1:\infty}\right]$. The decomposed process is thus

$$\mathbf{N}_t = \sum_{k=0}^{t-1} \delta\mathbf{N}_k = \sum_{k=0}^{t-1} \left(\mathbb{E}\left[\mathbf{X}_t|\mathbf{X}_{t+1:\infty}\right] - \mathbf{X}_t\right), \tag{7.27}$$

a *reversed martingale*, or called *backward martingale* in mathematics (Grimmett and Stirzaker, 2001), for Markov processes.

7.5 Summary and Discussion

In this chapter, we summarize and extend the Einstein relation and the Green-Kubo formula to non-equilibrium, non-linear and non-Markovian systems in a covariance formalism. Two underlying mechanisms contributing to a stochastic change of a system's state were identified: a "deterministic" drift summarizing the past and a noise representing the stochasticity of one-step toward the future. Stationarity of the process requires a dissipative drift to balance out the fluctuation generated by noise, which is the origin of our general fluctuation-dissipation relations. Reversibility and Markovian are not needed but can impose a further symmetry in the covariance between the state and the drift. General relations between the fluctuation and the drift of sweeping dynamics remains to be investigated. Generally speaking, a symmetry is needed to dictate a fluctuation-drift relation.

The GER discussed above is for general stationary processes. It, however, excludes any martingale, submartingale, and supermartingale. Here, we present that a specific type of submartingale in continuous processes actually have a fluctuation-drift relation. We consider a process $\mathcal{E}_t$ whose exponentiation $e^{-\mathcal{E}_t}$ becomes a martingale. Stochastic calculus tells us that the drift μ_t and the fluctuation level σ_t in the stochastic differential equation of $\mathcal{E}_t$, $\mathrm{d}\mathcal{E}_t = \mu_t \mathrm{d}t + \sigma_t \mathrm{d}W_t$, is related by

$$2\mu_t = \sigma_t^2. \tag{7.28}$$

This shows that the process $\mathcal{E}_t$ is a submartingale and has a fluctuation-drift relation induced by the requirement of being a martingale after exponentiation. A famous example for $\mathcal{E}_t$ in stochastic thermodynamics is the housekeeping heat $\mathcal{Q}_{\mathrm{hk}}$ (Pigolotti *et al.*, 2017; Chetrite *et al.*, 2019). Another example can be found in

probability theory (Lorig, 2019). A *Radon-Nikodym derivative process* Z_t is defined as $Z_t \coloneqq \mathbb{E}\left[Z|X_{0:t}\right]$ where Z is a (path) random variable satisfying $\mathbb{E}\left[Z\right] = 1$ and $Z > 0$. The random variable Z can be used to define a RND of the process $Z = \frac{\mathrm{d}\tilde{\mathbb{P}}}{\mathrm{d}\mathbb{P}}$. The corresponding general path entropy $\mathcal{S}_t \coloneqq -\ln Z_t$ (Yang and Qian, 2020) is an example of $\mathcal{E}_t$ since $Z_t = e^{-\mathcal{S}_t}$ is a martingale. The relation in Eq. (7.28) was in fact implicitly in Girsanov's theorem in Eq. (2.30).

If the process $\mathcal{E}_t$ is also work-like, *i.e.* $\mathrm{d}\mathcal{E}_t$ can be expressed as $\boldsymbol{f}\circ\mathrm{d}\mathbf{X}_t$ where $\circ$ denotes Stratonovich mid-point integration, it satisfies a Cauchy-Schwarz inequality given the inner product $\langle \mathbf{u}, \mathbf{w}\rangle \coloneqq \mathbb{E}\left[\mathbf{u}\cdot\mathbf{D}^{-1}\mathbf{w}\right]$[3],

$$\left(\mathbb{E}\left[\frac{\mathrm{d}\mathcal{E}_t}{\mathrm{d}t}\right]\right)^2 \leq \mathbb{E}\left[\frac{\mathrm{d}\mathcal{S}_{\mathrm{tot}}}{\mathrm{d}t}\right]\frac{\mathbb{V}\left[\mathrm{d}\mathcal{E}_t\right]}{2\mathrm{d}t,} \tag{7.29}$$

which is an instantaneous version of the recently-celebrated thermodynamic uncertainty relation (Barato and Seifert, 2015; Horowitz and Gingrich, 2020). Then, by Eq. (7.28) and time integration, one gets

$$\mathbb{E}\left[\mathcal{E}_t\right] \leq \mathbb{E}\left[\mathcal{S}_{\mathrm{tot}}\right]. \tag{7.30}$$

The total entropy production is the upper bound of any work-like $\mathcal{E}_t$ process. The force $\boldsymbol{f}$ should satisfy $\boldsymbol{f}\cdot\mathbf{D}\boldsymbol{f} = \mathbf{b}\cdot\boldsymbol{f} + \nabla\cdot(\mathbf{D}\boldsymbol{f})$ for a work-like process to be a martingale after exponentiation. Examples for such a process $\mathcal{E}_t$ include the housekeeping heat $\mathcal{Q}_{\mathrm{hk}}$ and the heat dissipation $\mathcal{Q}$ if the vector field $\mathbf{b}$ is divergence-free.

[3] The proof of this follows quite directly from Dechant and Sasa (2018b); Ito and Dechant (2020). The novel additional step is a recognition that $\mathbb{V}[\mathrm{d}\mathcal{E}_t] = \mathbb{E}[\boldsymbol{f}\cdot\mathbf{D}\boldsymbol{f}]\mathrm{d}t$, as introduced in Sec. 6.2.

Part III

Data infinitum dictates statistical thermodynamics

Chapter 8

Statistical Thermodynamics and Maximum Entropy Principle

In this chapter, we first formulate the statistical thermodynamics emerged in the data infinitus limit and show its universality in Sec. 8.1. We then revisit the probabilistic model from the standard Maximum Entropy Principe for i.i.d. prior and singleton observable in Sec. 8.2. Extensions of the Maximum Entropy Principle to Markov processes are summarized in Sec. 8.3.

8.1 Data Infinitum didtates Statistical Thermodynamics

8.1.1 Data Infinitus Limit as a Generalized Thermodynamic Limit

We consider a general (sampling) process with state space $\mathcal{X}$ that runs discretely or continuously from time 0 to arbitrarily large T. We denote the path space as $\Omega \coloneqq \mathcal{X}^{[0,T]}$. The length-$T$ path is random and denoted as $X_{0:T}$. A realization of the random path is denoted as a lower case $x_{0:T} \in \Omega$. Here, we consider the *data infinitus limit*, or rather the long-term limit, $T \to \infty$ as a generalized thermodynamic limit (Lu and Qian, 2022).

A set of extensive path observables $G\left(x_{0:T}\right) : \mathcal{X}^{[0,T]} \mapsto \mathbb{R}^m$ is considered to be *thermodynamic observables* if its intensive form $g\left(x_{0:T}\right) \coloneqq G\left(x_{0:T}\right)/T$ satisfies a LLN in the data infinitus limit $T \to \infty$ (long term limit of a process):

$$\lim_{T\to\infty} g\left(x_{0:T}\right) = \lim_{T\to\infty} \frac{G\left(x_{0:T}\right)}{T} = \bar{\gamma}. \tag{8.1}$$

When g is the empirical mean value of observables, this is known as ergodicity when empirical mean value is equal to the expected value w.r.t. the invariant probability. More precisely, we require the distribution of the intensive observable g to converge singularly to a delta function with an asymptotic form characterized by an WKB ansatz in the limit $T \to \infty$ (Bender and Orszag, 1999),

$$\mathbb{P}_{\text{true}}\left\{g\left(x_{0:T}\right) \in \mathrm{d}\gamma\right\} = e^{-T\varphi_g^{\text{true}}(\gamma)+O(\ln T)} \tag{8.2}$$

where φ_g^{true} is called the large deviation rate function (LDRF) of g under the (unknown) true underlying probability measure $\mathbb{P}_{\text{true}}$. Here, $\mathbb{P}_{\text{true}}\left\{g\left(x_{0:T}\right) \in \mathrm{d}\gamma\right\}$ is a short-hand for the probability of g to be in an infinitesimal interval $[\gamma, \gamma + \mathrm{d}\gamma)$. In the data infinitus limit $T \to \infty$, the observed event $\left\{g\left(x_{0:T}\right) \in \mathrm{d}\bar{\gamma}\right\} \equiv \left\{G\left(x_{0:T}\right)/T \in \mathrm{d}\bar{\gamma}\right\}$ would be *typical* with all other events $\left\{g\left(x_{0:T}\right) \notin \mathrm{d}\bar{\gamma}\right\}$ exponentially rare under the path probability $\mathbb{P}_{\text{true}}$ of the system. In mathematics, this is expressed as an (exponential) asymptotic equivalence[1],

$$\mathbb{P}_{\text{true}}\left\{g\left(x_{0:T}\right) \in \mathrm{d}\bar{\gamma}\right\} \asymp 1, \tag{8.3}$$

saying that the LDRF under $\mathbb{P}_{\text{true}}$ should be zero at $g = \bar{\gamma}$, $\varphi_g^{\text{true}}\left(\bar{\gamma}\right) = 0$.

When the system has different underlying path probability measure $\mathbb{P}_{\text{true}}$, the values $\bar{\gamma}$ of the intensive thermodynamic observables g vary. We consider these different statistical properties of system as the system in different *thermodynamic states*. The different thermodynamic states can be parameterized by $\bar{\gamma}$. Thus, the values of $\bar{\gamma}$ can be treated as the *thermodynamic parameters*. When we have a system in hand, we don't know which thermodynamic state the system is in. We resort to measuring the thermodynamic observables (the extensive G or the intensive g) to get $\bar{\gamma}$ and infer $\mathbb{P}_{\text{true}}$.

8.1.2 Fundamental Roles of the Entropic Forces

In standard thermodynamics, a system is considered to driven by *entropic force*s to change from one thermodynamic state to the other, *i.e.* having different values of $\bar{\gamma}$. To identify the entropic forces conjugated to the thermodynamic observables, we need a notion of *entropy*. We show below that such notion can be generally define from the LDT in the data infinitus limit.

Among all the possible thermodynamic states, the ground state is the state where the entropic forces are zero. Such state serves as a reference probability measure $\mathbb{P}$ is often "assigned" based on certain symmetries

[1] $f_\epsilon\left(x\right) \asymp g_\epsilon\left(x\right)$ means $\lim_{\epsilon\to 0} \log \frac{f_\epsilon(x)}{g_\epsilon(x)} = 0$.

of interest in physics. The symmetry comes from, for examples, exchangeability between particles, translational symmetry, *etc*. This way, the entropic forces represent the "cause" of symmetry breaking (Anderson, 1972). With respect to the reference probability measure $\mathbb{P}$, the observed event $\{g \in \mathrm{d}\bar{\gamma}\}$ is not necessarily typical under $\mathbb{P}$. If the event is typical $\mathbb{P}$, then we consider that $\mathbb{P}$ is "consistent" with the measurement $\{g \in \mathrm{d}\bar{\gamma}\}$ and the system is in the ground state. However, if the observed event is non-typical under $\mathbb{P}$, the non-typicality translates to having a nonzero LDRF $\varphi_g(\bar{\gamma}) \neq 0$ in the WKB form of the probability distribution of g

$$\mathbb{P}\{g \in \mathrm{d}\gamma\} = e^{-T\varphi_g(\gamma)+o(T)}. \tag{8.4}$$

The measurement $\{g \in \mathrm{d}\bar{\gamma}\}$ then inform us to update from the reference measure $\mathbb{P}$ as a prior to a posterior probability measure $\mathbb{Q}$ such that the observed event is typical under it, *i.e.*

$$\mathbb{Q}\{g \in \mathrm{d}\gamma\} = e^{-T\tilde{\varphi}_g(\gamma)+o(T)} \tag{8.5}$$

and $\tilde{\varphi}_g(\bar{\gamma}) = 0$. This change of probability measure (CPM) is mathematically represented by another observable called the Radon-Nikodym derivative (RND) (Qian *et al.*, 2019; Yang and Qian, 2020), which can be intuitively thought of as the path probability ratio in our discussion here.

Now, it is essential that we realize any RND that change the probability measure can be decomposed into the part tilting the probability of the level set $\{g \in \mathrm{d}\gamma\}$ and the part reweighing the conditional probability for finding a path $x_{0:T}$ in the level set:

$$\frac{\mathrm{d}\mathbb{Q}}{\mathrm{d}\mathbb{P}}(x_{0:T}) = \frac{\mathbb{Q}\{g(x_{0:T})\}\,\mathbb{Q}\{x_{0:T}|g(x_{0:T})\}}{\mathbb{P}\{g(x_{0:T})\}\,\mathbb{P}\{x_{0:T}|g(x_{0:T})\}}. \tag{8.6}$$

The former part changes the statistics of g in the CPM whereas the latter does not. Then, with the WKB form of Eq. (8.4) and Eq. (8.5), we have

$$\ln\frac{\mathrm{d}\mathbb{Q}}{\mathrm{d}\mathbb{P}}(x_{0:T}) = T[\varphi_g(\gamma) - \tilde{\varphi}_g(\gamma)] + o(T) + \ln\frac{\mathbb{Q}\{x_{0:T}|g(x_{0:T})\}}{\mathbb{P}\{x_{0:T}|g(x_{0:T})\}}. \tag{8.7}$$

As $\varphi_g \neq \tilde{\varphi}_g$, this clearly shows that the desired RND in Eq. (8.6) must be an exponential tilting to change the typicality of the thermodynamic observables g. The fundamental reason of representing the information of data, *i.e.* the CPM, as the logarithmic RND is due to the singular convergence of probability in data infinitus limit, *i.e.* by LDT (Bender and Orszag, 1999; Touchette, 2009; Dembo and Zeitouni, 2009).

As the RND should be indicated by the measured value $\bar{\gamma}$, we suppose that the RND is parameterized

by a set of parameters $\theta(\bar{\gamma})$ and denote the essential ingredients in Eq. (8.7) as

$$s_{\theta(\gamma)} \coloneqq \varphi_g(\gamma) - \tilde{\varphi}_g(\gamma) \text{ and} \tag{8.8a}$$

$$c_{\theta(\gamma)} \coloneqq \ln \frac{\mathbb{Q}\{x_{0:T} | g(x_{0:T}) \in \mathrm{d}\gamma\}}{\mathbb{P}\{x_{0:T} | g(x_{0:T}) \in \mathrm{d}\gamma\}}. \tag{8.8b}$$

By the LDT, the typicality conditions $\mathbb{Q}\{g \in \mathrm{d}\bar{\gamma}\} \asymp 1$ are that $\tilde{\varphi}_g(\bar{\gamma}) = 0, \nabla\tilde{\varphi}_g(\bar{\gamma}) = 0$, and $\nabla\nabla\tilde{\varphi}_g(\bar{\gamma}) \succeq 0$, which translate to the following three conditions in terms of φ_g from the prior and $s_{\theta(\bar{\gamma})}$ from the tilting:

$$s_{\theta(\bar{\gamma})}[\bar{\gamma}] = \varphi_g(\bar{\gamma}), \tag{8.9a}$$

$$\nabla s_{\theta(\bar{\gamma})}[\bar{\gamma}] = \nabla\varphi_g(\bar{\gamma}), \text{ and} \tag{8.9b}$$

$$\nabla\nabla s_{\theta(\bar{\gamma})}(\bar{\gamma}) \preceq \nabla\nabla\varphi_g[\bar{\gamma}] \tag{8.9c}$$

As we expect $\tilde{\varphi}_g(\gamma)$ and $\varphi_g(\gamma)$ to be analytic near the observed value $\bar{\gamma}$, we can Taylor expand $s_{\theta(\bar{\gamma})}(\gamma)$ around $\bar{\gamma}$ to get

$$s_{\theta(\bar{\gamma})}(\gamma) = \varphi_g(\bar{\gamma}) + \beta \cdot \delta\gamma + \delta\gamma \cdot A\delta\gamma + O\left(\delta\gamma^3\right) \tag{8.10a}$$

$$= \varphi_g(\bar{\gamma}) - \beta \cdot \bar{\gamma} + \beta \cdot \gamma + O\left(\delta\gamma^2\right) \tag{8.10b}$$

where $\delta\gamma \coloneqq \gamma - \bar{\gamma}$ and both β and A are parameters in the set $\theta(\bar{\gamma})$. The typicality condition in Eq. (8.9b) immediately tells us that the parameter β is determined by

$$\beta = \nabla\varphi_g(\bar{\gamma}) \in \mathbb{R}^m. \tag{8.11}$$

With the LDRF of g,

$$\varphi_g(\gamma) \coloneqq -\lim_{T\to\infty} \frac{1}{T} \ln \mathbb{P}\{g \in \mathrm{d}\gamma\}, \tag{8.12}$$

understood as the *entropy* in our thermodynamic theory, the parameters β are the "*entropic forces*" that tilts the average of g in the posterior $\mathbb{Q}$. This means that "any" CPM must have the entropic forces β in its set of parameters $\theta(\bar{\gamma})$ such that the measured event $\{g \in \mathrm{d}\bar{\gamma}\}$ is typical under the posterior. If the LDRF φ_g is convex (as we shall generally assume in this thesis), then Eq. (8.11) can be inverted by

$$\bar{\gamma} = \nabla\psi_g(\beta) \tag{8.13}$$

where ψ_g is the scaled cumulant generating function (sCGF) (Touchette, 2009; Lu and Qian, 2022):

$$\psi_g(\beta) \coloneqq \lim_{T\to\infty} \frac{1}{T} \ln \mathbb{E}\left[e^{T\beta\cdot g}\right]. \tag{8.14}$$

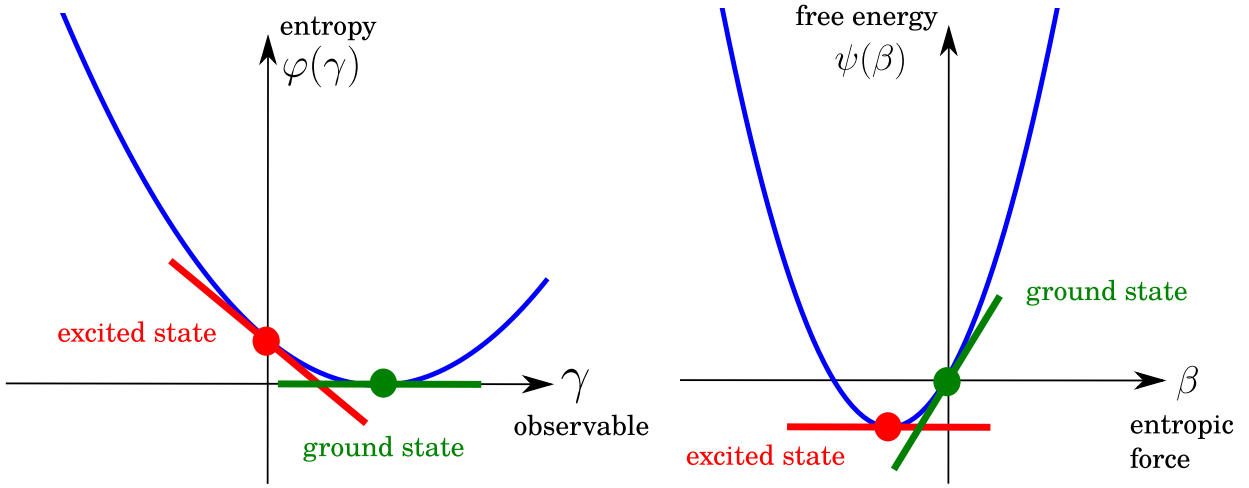


Figure 8.1: A simple Gaussian example for the Legendre convex pair of entropy $\varphi(\gamma)$ and free energy $\psi(\beta)$. Legendre transform is a point-slope transformation. For a dual pair (γ, β), colored green and red, point/slope in one space is the slope/point in the dual space.

Then, β would be the *only* set of parameters in the posterior, *i.e.* all parameters $\theta(\bar{\gamma})$ can be parameterized by the entropic forces β. This explains the fundamental roles of the entropic forces β as the *thermodynamic parameters* that parameterized the *thermodynamic state*.

8.1.3 Thermodynamic Relations

The sCGF ψ_g is understood as the *free energy* in our thermodynamic theory. From its definition in Eq. (8.14), it can always be expressed as the Legendre-Fenchel transform (LFT) of the *entropy* φ_g,

$$\psi_g(\beta) = \sup_{\gamma} [\beta \cdot \gamma - \varphi_g(\gamma)]. \tag{8.15}$$

When ψ_g exists and is differentiable (we will assume this throughout this thesis), the Gätner-Ellis theorem tells us that the *entropy* φ_g can also be expressed as the LFT of the *free energy* ψ_g and is thus strictly convex (Gärtner, 1977; Ellis, 1984; Touchette, 2009),

$$\varphi_g(\gamma) = \sup_{\beta} [\beta \cdot \gamma - \psi_g(\beta)]. \tag{8.16}$$

Convex duality between φ_g and ψ_g then emerges and the LFT can be reduces to the more familiar Legendre transform

$$\varphi_g(\gamma) + \psi_g(\beta) = \beta \cdot \gamma \tag{8.17}$$

with dual coordinates β or γ. See Fig. 8.1 for a pictorial illustration of the convex pair. In particular, γ can

be parameterized by β by

$$\nabla\psi_g(\beta) = \gamma. \tag{8.18}$$

and β can be parameterized by γ by

$$\beta = \nabla\varphi_g(\gamma). \tag{8.19}$$

The Gärtner-Ellis theorem indicates a dual structure, leading to an emergent thermodynamics solely from the LDT in the data infinitus limit (Lu and Qian, 2022; Commons *et al.*, 2021; Yang and Qian, 2022). Notions of "entropy" φ_g and "free energy" ψ_g are defined from the LDT of the data infinitus limit. With $\gamma = \nabla\psi_g(\beta)$ and $\beta = \nabla\varphi_g(\gamma)$, thermodynamic differential relations between the "entropy" φ_g and "free energy" ψ_g in LDT can be written down

$$\mathrm{d}\varphi_g = \beta \cdot \mathrm{d}\gamma \tag{8.20a}$$

$$\mathrm{d}\psi_g = \gamma \cdot \mathrm{d}\beta. \tag{8.20b}$$

We will show later in Sec. 9.1 that this thermodynamic structure has "a mesoscopic origin" from the Maximum Caliber Principle (Pressé *et al.*, 2013b).

We note here that although we have concluded that a thermodynamic state (the posterior $\mathbb{Q}$) is parameterized by entropic force β with a thermodynamic structure, the specific functional form of $\mathbb{Q}_\beta$ is not yet specified. We need a probabilistic model for $\mathbb{Q}_\beta$ based on the prior $\mathbb{P}$, the functional form of the observables g, and the measured values $\bar{\gamma}$ of the observables. In particular, in the general expression

$$\frac{\mathrm{d}\mathbb{Q}}{\mathrm{d}\mathbb{P}}(x_{0:T}) = e^{T\left[\varphi_g(\bar{\gamma})-\beta\cdot\bar{\gamma}+\beta\cdot g(x_{0:T})+O\left(\delta\gamma^2\right)\right]+o(T)}\frac{\mathbb{Q}\left\{x_{0:T}|g\left(x_{0:T}\right)\right\}}{\mathbb{P}\left\{x_{0:T}|g\left(x_{0:T}\right)\right\}}, \tag{8.21}$$

all the terms $O\left(\delta\gamma^2\right)$, $o(T)$, and $\ln\frac{\mathbb{Q}\{x_{0:T}|g(x_{0:T})\}}{\mathbb{P}\{x_{0:T}|g(x_{0:T})\}}$ are parameterized by β but their specific forms needs to be determined. In the following sections and in the next chapter, we introduce the posterior probabilistic models from the Maximum Entropy Principle the Maximum Caliber Principle, motivated by the Bayesian conditional probability and by Boltzmann-Gibbs exponential tilting, respectively.

8.2 Maximum Entropy Principle of I.I.D. Sampling

8.2.1 Gibbs Conditioning Principle

Let's start with the simplest case. We assumean i.i.d. prior $\mathbb{P}\left\{X_{1:T}=x_{1:T}\right\}=\prod_{t=1}^{T}p\left(x_t\right)$. Here, for notation simplicity, we relabel underlying path as $x_{1:T}$ with length T instead of $x_{0:T}$ with length $T+1$. Let's define the *empirical frequency* of all the possible states x in the state space $\mathcal{X}$:

$$\nu_x\left(x_{1:T}\right)\coloneqq\frac{1}{T}\sum_{t=1}^{T}\delta_x\left(x_t\right), \tag{8.22}$$

where $\delta_x\left(x_t\right)$ is a Kronecker delta function which is 1 when $x_t=x$ and is 0 otherwise. We assume that we measure a general singleton-type path observable g that is the empirical mean of an observable $\hat{g}\left(x\right)$ as a functional of the empirical frequency ν:

$$g\left(x_{1:T}\right)\coloneqq\frac{1}{T}\sum_{t=1}^{T}\hat{g}_{x_t}=\sum_{x\in\mathcal{X}}\nu_x\left(x_{1:T}\right)\hat{g}_x. \tag{8.23}$$

With an observation on the event $\left\{g\in\mathrm{d}\gamma\right\}$, a natural posterior would be to compute the Bayesian conditional probability under the prior

$$\mathbb{P}\left\{X_s=\xi\middle|g\left(X_{1:T}\right)\in\mathrm{d}\gamma\right\},\text{for }s=\left\{1,2,\cdots,T\right\}. \tag{8.24}$$

Note that since X_s are i.i.d. and the observable $g\left(x_{1:T}\right)$ is symmetric to any permutation of $X_{1:T}$, we see that the conditional probabilities for different s are in fact identical. Then, for any function $h:\mathcal{X}\mapsto\mathbb{R}$, we have

$$\mathbb{E}\left\{h_{X_s}\middle|g\in\mathrm{d}\gamma\right\}=\mathbb{E}\left\{\frac{1}{T}\sum_{s=1}^{T}h_{X_s}\middle|g\in\mathrm{d}\gamma\right\}=\mathbb{E}\left\{\sum_{x\in\mathcal{X}}\nu_x h_x\middle|g\in\mathrm{d}\gamma\right\}. \tag{8.25}$$

This means that

$$\mathbb{P}\left\{X_s=\xi\middle|g\left(X_{1:T}\right)\in\mathrm{d}\gamma\right\}=\mathbb{E}\left[\nu_\xi\middle|g\left(X_{1:T}\right)\in\mathrm{d}\gamma\right] \tag{8.26}$$

for any $s=\left\{1,2,\cdots,T\right\}$ and any data size T. The conditional probability is identical but not independent due to the constraint (Dembo and Zeitouni, 2009).

8.2.2 Maximum Entropy Principle for i.i.d. sampling

In the data infinitus limit $T\to\infty$, the conditional average empirical frequency on the right-hand side of Eq. (8.26) can be computed. By Sanov's theorem (Sanov, 1958), the distribution of the empirical frequency also

has the WKB form $\mathbb{P}\{\nu \in \mathrm{d}f\} = e^{-T\varphi_\nu(f)+o(T)}$ with its LDRF

$$\varphi_\nu(f) = \sum_{x\in\mathcal{X}} f_x \ln \frac{f_x}{p_x} \tag{8.27}$$

in the relative entropy form (Kullback and Leibler, 1951). Further with $\mathbb{P}\{g \in \mathrm{d}\gamma\} = e^{-T\varphi_g(\gamma)+o(T)}$, we get that

$$\mathbb{P}\left\{\nu \in \mathrm{d}f \middle| g \in \mathrm{d}\gamma\right\} = \frac{\mathbb{P}\{\nu \in \mathrm{d}f\}}{\mathbb{P}\{g \in \mathrm{d}\gamma\}} \delta_{\sum_x f_x \hat{g}_x}(\gamma) \tag{8.28a}$$

$$= e^{-T[\varphi_\nu(f)-\varphi_g(\gamma)]+o(T)} \delta_{\sum_x f_x \hat{g}_x}(\gamma). \tag{8.28b}$$

In the limit $T \to \infty$, this conditional probability concentrates at the q such that $\varphi_\nu(q) = \varphi_g(\gamma)$, which is also the conditional average $q = \mathbb{E}\left[\nu \middle| g(X_{1:T}) \in \mathrm{d}\gamma\right]$ in the limit. By the contraction principle in LDT (Dembo and Zeitouni, 2009; Touchette, 2009), the LDRF of g can be derived from the LDRF of the empirical frequency ν since g is a functional of ν:

$$\varphi_\nu(q) = \varphi_g(\gamma) = \inf_{f:\sum_x f\hat{g}=\gamma} \varphi_\nu(f). \tag{8.29}$$

Therefore, to compute q, we find the **empirical frequency** that minimize the LDRF of the empirical frequency w.r.t. the prior p:

$$q = \arg\inf_f \left\{ \sum_{x\in\mathcal{X}} f_x \ln \frac{f_x}{p_x} - \beta \cdot \left[\sum_{x\in\mathcal{X}} f_x \hat{g}_x - \gamma\right] - \mu\left[\sum_{x\in\mathcal{X}} f_x - 1\right]\right\} \tag{8.30}$$

This is the Gibbs conditioning principle and the Maximum Entropy Principle for i.i.d. sampling (van Campenhout and Cover, 1981; Dembo and Zeitouni, 2009; Cheng *et al.*, 2021). The asymptotic equivalency between the MEP posterior $q(x)$ and the conditional probability $\mathbb{P}\left\{X_s = x | \frac{1}{T}\sum_{t=1}^T \hat{g}_{x_t} \in \mathrm{d}\gamma\right\}$ is known as the equivalence between microcanonical ensemble and canonical ensemble in physics. One can show that withan i.i.d. prior with singleton-type observable g defined as Eq. (8.23), the path posterior is also i.i.d. in the data infinitus limit (Dembo and Zeitouni, 2009):

$$\lim_{T\to\infty} \mathbb{P}\{X_{1:n} = x_{1:n} | g \in \mathrm{d}\gamma\} = \prod_{t=1}^n q_{x_t}, \forall n \in \mathbb{N}. \tag{8.31}$$

Since the LDRF of observable g can be obtained from the LDRF of the empirical frequency ν, the LDT of the empirical mean of path observables g is often called level-1 and the LDT of empirical frequency ν is called level-2 (Barato and Chetrite, 2015). The posterior from MEP in Eq. (8.30) has the Boltzmann-Gibbs

form,

$$q_x = \frac{e^{\beta \cdot \hat{g}_x}}{Z(\beta)} p_x \tag{8.32}$$

where $Z(\beta) = \mathbb{E}\left[e^{\beta \cdot g}\right]$ is known as the partition function in physics or the generating function in mathematics. If the observable $\hat{g}_{x_t}$ is the indicator function itself, $\delta_x(x_t)$, which has the dimension of the state space $\mathcal{X}$, the posterior would have the form of

$$q_x = \frac{e^{u_x}}{\mathbb{E}\left[e^u\right]} p_x \tag{8.33}$$

where the thermodynamic conjugated forces u of empirical frequency become a generalized notion of energy (Commons *et al.*, 2021).

8.3 Maximum Entropy Principle in Markov Processes

The Gibbs Conditioning Principle can be generalized to the case where we assumed Markov processes as a prior and measure transition-type observables (Csiszár *et al.*, 1987; Chetrite and Touchette, 2015a).

8.3.1 Discrete-time Markov Chain

We start with a time-homogeneous DTMC prior specified by the transition matrix $M_{y|x}$ and the initial distribution p_x as a *prior*. The prior path probability of path $x_{0:T}$ is then given by

$$\mathbb{P}\{x_{0:T}\} = p_{x_0} M_{x_1|x_0} \cdots M_{x_T|x_{T-1}}. \tag{8.34}$$

The empirical pair frequency measurement is given by

$$\nu_{i,j}(x_{0:T}) \coloneqq \frac{1}{T} \sum_{t=1}^{T} \delta_{ij}(x_{t-1} x_t). \tag{8.35}$$

When $T \to \infty$, the probability of having a specific empirical frequency has an WKB asymptotic form $\mathbb{P}\{\nu \in \mathrm{d}f\} = e^{-T\varphi_\nu[f] + o(T)}$ and the LDRF is given by (Dembo and Zeitouni, 2009)

$$\varphi_\nu[f] = \sum_{i,j \in \mathcal{X}} f_{ij} \ln \frac{f_{ij}}{\left(\sum_{k \in \mathcal{X}} f_{ik}\right) M_{j|i}}. \tag{8.36}$$

The LDT for empirical pair in a Markov process is often referred to the LDT level 2.5 (Barato and Chetrite, 2015).

We consider a generic transition-type observables:

$$G\left(x_{0:T}\right) \coloneqq \sum_{t=1}^{T} \hat{g}_{x_{t-1},x_t} \in \mathbb{R}^m \tag{8.37}$$

and its intensive form as the empirical mean of $\hat{g}$:

$$g\left(x_{0:T}\right) \coloneqq \frac{G\left(x_{0:T}\right)}{T} = \sum_{x,y\in\mathcal{X}} \nu_{x,y}\left(x_{0:T}\right) \hat{g}_{x,y} \tag{8.38}$$

We are interested in the posterior of the transition matrix M, and we seek the conditional joint probability of $X_{s(T)}$ and $X_{s(T)+1}$:

$$P_T\left(x,y\right) \coloneqq \mathbb{P}\left\{X_s = x, X_{s+1} = y \middle| g\left(x_{0:T}\right) \in \mathrm{d}\gamma\right\} \tag{8.39}$$

where both $s\left(T\right) \to \infty$ and $T - s(T) \to \infty$ as $T \to \infty$ (Csiszár *et al.*, 1987). As the system reaches its steady state as $s(T) \to \infty$, it is intuitively clear from the time-translational symmetry that the conditional probability $P_T\left(x,y\right)$ satisfies

$$\lim_{T\to\infty} P_T\left(x_{s(T)}, x_{s(T)+1}\right) = \lim_{T\to\infty} \mathbb{E}\left[\nu | g \in \mathrm{d}\gamma\right] \tag{8.40}$$

as proven rigorously by Csiszár *et al.* (1987). Csiszár *et al.* further proved that the posterior from conditioning is a time-homogeneous Markov process in the data infinitus limit. Specifically, if we denote $q_{ij} = \lim_{T\to\infty} \mathbb{E}\left[\nu | g \in \mathrm{d}\gamma\right]$, $q_i = \sum_{j\in\mathcal{X}} q_{ij}$, and $q_{j|i} = q_{ij}/q_i$, then, for any n,

$$\lim_{T\to\infty} \mathbb{P}\left\{X_{s(T):s(T)+n} = x_{0:n} \middle| g \in \mathrm{d}\gamma\right\} = q_{x_0} \prod_{t=1}^{n} q_{x_t|x_{t-1}}. \tag{8.41}$$

Similar to the i.i.d. case, the limiting form of the conditional expectation of empirical frequency, *i.e.* q_{ij}, can be computed by the contraction principle (Touchette, 2009) by the LDT of empirical frequencies in DTMC (Dembo and Zeitouni, 2009). Since we have

$$\mathbb{P}\left\{\nu \in \mathrm{d}f | g \in \mathrm{d}\gamma\right\} = e^{-T[\varphi_\nu(f) - \varphi_g(\gamma)] + o(T)} \delta_{\sum_{i,j\in\mathcal{X}} f_{ij}\hat{g}_{i,j}}\left(\gamma\right), \tag{8.42}$$

the contraction principle in the LDT tells us that

$$q = \lim_{T\to\infty} \mathbb{E}\left[\nu | g\left(x_{0:T}\right) \in \mathrm{d}\gamma\right] \tag{8.43a}$$

$$= \arg\inf_f \left\{ \varphi_\nu\left[f\right] - \beta \cdot \left(\sum_{i,j} f_{ij}\hat{g}_{i,j} - \gamma \right) - \sum_i \sigma_i \sum_j \left(f_{ij} - f_{ji}\right) - \mu \left(\sum_{i,j} f_{ij} - 1 \right) \right\}. \tag{8.43b}$$

The limiting form q is the empirical frequency q that maximizes the probability $e^{-T\varphi_\nu[f] + o(T)}$ under the

typicality constraint $\sum_{i,j\in\mathcal{X}} f_{ij}\hat{g}_{i,j} = \gamma$, stationarity constraint

$$\sum_{j\in\mathcal{X}} f_{ij} = \sum_{j\in\mathcal{X}} f_{ji}, \tag{8.44}$$

and the normalization constraint $\sum_{i,j\in\mathcal{X}} f_{ij} = 1$. It is important to notice that the MEP calculation in Markov processes is using the "entropy" given by the LDRF of empirical pair frequencies $\varphi_\nu[f]$ in Eq. (8.36), which is *not* the Kullback-Leibler relative entropy between the prior pair probability and the posterior pair probability. As we will elaborate in Eq. (8.76), $\varphi_\nu[f]$ is in fact a combination of (at least) two relative entropies when one assumesan i.i.d. prior.

Taking the derivative of $\{\cdots\}$ in Eq. (8.43a) w.r.t. f gives us

$$\beta\cdot\hat{g}_{i,j} = \ln\frac{f_{ij}}{\left(\sum_{k\in\mathcal{X}} f_{ik}\right) M_{j|i}} + \sigma_j - \sigma_i - \mu, \tag{8.45}$$

which leads to the posterior transition matrix in the following form:

$$\frac{f_{ij}}{\sum_{k\in\mathcal{X}} f_{ik}} = M_{j|i}\frac{e^{\beta\cdot\hat{g}_{i,j}}e^{-\sigma_j}}{e^{-\mu}e^{-\sigma_i}}. \tag{8.46}$$

All Lagrange multipliers depend on γ. By summing over j on both sides, one gets

$$e^{-\mu}e^{-\sigma_i} = \sum_{j\in\mathcal{X}} M_{j|i}e^{\beta\cdot\hat{g}_{i,j}}e^{-\sigma_j}, \tag{8.47}$$

which implies that $e^{-\mu}$ is an eigenvalue λ of the tilted matrix

$$\tilde{M}_{ij} \coloneqq M_{j|i}e^{\beta\cdot\hat{g}_{i,j}} \tag{8.48}$$

and $e^{-\sigma_i}$ is the corresponding right eigenvector r_i. Thus, σ_i and μ depend on γ through β. The posterior transition matrix then takes the form of

$$\bar{M}_{j|i} = \frac{r_j}{\lambda r_i}M_{j|i}e^{\beta\cdot\hat{g}_{i,j}}. \tag{8.49}$$

The stationary marginal distribution of the posterior Markov chain with transition matrix $\bar{M}_{j|i}$ is $l_i r_i$, where l_i is the left eigenvector. The posterior stationary pair frequency in the nonequilibrium steady state (NESS) is then

$$q_{ij} = l_i(\beta)\frac{\tilde{M}_{ij}}{\lambda(\beta)}r_j(\beta) = l_i(\beta)\frac{M_{j|i}e^{\beta\cdot\hat{g}_{i,j}}}{\lambda(\beta)}r_j(\beta). \tag{8.50}$$

The eigenvalue and eigenvectors here are actually the Perron-Frobenius eigenvalue $\lambda_{\max}$ of the tiled matrix $\tilde{M}$ (Dembo and Zeitouni, 2009; Chetrite and Touchette, 2013, 2015a). An intuitive way to see this

is by plugging the q from different eigenvalues in Eq. (8.50) back into Eq. (8.43a). One would get that for a fixed β, we are finding the q_{ij} from different eigenvalues that minimizes $\beta \cdot \gamma - \ln \lambda(\beta)$, implying that we should choose the largest eigenvalue $\lambda_{\max}$. A more rigorous way is by the following. Notice that the result of the MEP calculation in Eq. (8.43a) is by the contraction principle the LDRF of the path observable $g = G/T$. We can easily see that the LDRF of g can be rewritten as

$$\varphi_g(\gamma) = \varphi_\nu(q) = \sum_{i,j\in\mathcal{X}} q_{ij} \ln \frac{e^{\beta(\gamma)\cdot \hat{g}_{i,j}} r_j}{\lambda_{\max} r_i} \tag{8.51a}$$

$$= \sum_{i,j\in\mathcal{X}} q_{ij} \beta(\gamma) \cdot \hat{g}_{i,j} - \ln \lambda_{\max}[\beta(\gamma)] \tag{8.51b}$$

$$= \beta(\gamma) \cdot \gamma - \ln \lambda_{\max}[\beta(\gamma)]. \tag{8.51c}$$

We now compare this with the process of computing φ_g by the Gärtner-Ellis theorem, as we will review in Sec. 9.1. The LDRF of g can be obtained by

$$\varphi_g(\gamma) = \sup_\beta [\beta \cdot \gamma - \psi_g(\beta)] \tag{8.52}$$

where

$$\psi_g(\beta) = \lim_{T\to\infty} \frac{1}{T} \ln \mathbb{E}\left[e^{\beta\cdot G}\right] \tag{8.53}$$

is the scaled cumulant generating function (sCGF) of g, *i.e.* the leading order of the "free energy" $\Psi(\beta) \coloneqq \ln \mathbb{E}\left[e^{\beta\cdot G}\right] = T\psi_g + o(T)$. Since $G \coloneqq \sum_{t=1}^T \hat{g}_{x_{t-1},x_t}$. We can see that

$$\mathbb{E}\left[e^{\beta\cdot G}\right] = \sum_{x_{0:T}} p_{x_0} \prod_{t=1}^T M_{x_t|x_{t-1}} e^{\sum_{t=1}^T \beta\cdot \hat{g}_{x_{t-1},x_t}} \tag{8.54a}$$

$$= p \cdot \left(M e^{\beta\cdot\hat{g}}\right)^T \mathbf{1} = e^{T\ln\lambda_{\max} + o(T)} \tag{8.54b}$$

where $\mathbf{1} = (1, 1, \cdots, 1)^\mathsf{T}$ is a column vector with all components equal to 1. It then follows that $\psi_g(\beta) = \ln \lambda_{\max}(\beta)$.

8.3.2 Continuous Time Markov Chain

In a continuous time Markov chain (CTMC), a path is described by $(x_0, t_0; x_1, t_1; \cdots; x_K, t_K)$ where the system jumps from x_{k-1} to x_k at time t_k, set $t_0 = 0$ and $t_K \le t_{K+1} = T$. The most informative observables

would be the combination of singleton frequency and transition frequency:

$$f_i = \frac{1}{T}\int_0^T \delta_i\left(x_t\right)\mathrm{d}t, \text{ and } f_{ij} = \frac{1}{T}\sum_{k=1}^{K}\delta_i\left(x_{k-1}\right)\delta_j\left(x_k\right), i \neq j. \tag{8.55}$$

The LDRF of these observables is

$$\varphi_\nu[f] = \sum_{i\neq j} f_{ij}\ln\frac{f_{ij}/f_i}{p_{j|i}} - \sum_{i\neq j} f_{ij} + \sum_{i\neq j} f_i p_{j|i} \tag{8.56}$$

where $p_{j|i}$ is the reference Markov transition rate matrix (Maes and Netočný, 2008). Here and below, $\sum_{i\neq j}$ is a simplified summation notation for summing all transitions $i \in \mathcal{X}$ to $j \in \mathcal{X}$ $(i \neq j)$. The path observable of interest is

$$G\left(x_{0:T}\right) = \int_0^T \hat{h}_{x_t}\mathrm{d}t + \sum_{k=1}^{K}\hat{g}_{x_{k-1},x_k}. \tag{8.57}$$

The MEP is again subject to typicality, normalization and stationarity conditions:

$$\inf_{f_i,f_{ij}}\left\{\varphi_\nu[f] - \beta\cdot\left[\sum_{i\in\mathcal{X}} f_i\hat{h}_i + \sum_{i\neq j} f_{ij}\hat{g}_{i,j} - \gamma\right] - \mu\left[\sum_{i\in\mathcal{X}} f_i - 1\right] - \sum_{i\neq j}\sigma_i\left(f_{ij} - f_{ji}\right)\right\} \tag{8.58}$$

Taking functional derivatives gives us

$$\beta\cdot\hat{h}_i = -\sum_{j(\neq i)}\frac{f_{ij}}{f_i} + \sum_{j(\neq i)} p_{j|i} - \mu \tag{8.59}$$

and

$$\beta\cdot\hat{g}_{i,j} = \ln\frac{f_{ij}}{f_i p_{j|i}} + \sigma_j - \sigma_i, i \neq j. \tag{8.60}$$

Here and below $\sum_{j(\neq i)}$ is a simplified notion of summing all $j \in \mathcal{X}$ except i.

Eq. (8.60) gives us $f_{j|i} = p_{j|i}e^{\beta\cdot\hat{g}_{i,j}}\frac{e^{-\sigma_j}}{e^{-\sigma_i}}$. Plugging this to Eq. (8.59), we then have

$$\sum_{j(\neq i)} p_{j|i}e^{\beta\cdot\hat{g}_{i,j}}e^{-\sigma_j} + \beta\cdot\hat{h}_i e^{-\sigma_i} - \sum_{k(\neq i)} p_{k|i}e^{-\sigma_i} = -\mu e^{-\sigma_i}. \tag{8.61}$$

If we define a tilted matrix

$$\tilde{q}_{ij} = \begin{cases} p_{j|i}e^{\beta\cdot\hat{g}_{i,j}}, & , i \neq j \\ \beta\cdot\hat{h}_i - \sum_{k(\neq i)} p_{k|i} & , i = j \end{cases}, \tag{8.62}$$

then $e^{-\sigma_i}$ is the right-eigenvector of $\tilde{q}$, r_i, with $-\mu$ is the corresponding eigenvalue, λ. Similar to DTMC, one can show that $l_i r_i$ where l_i being the left eigenvector would be the invariant distribution of the posterior

Markov chain described by $\tilde{q}_{ij}$. The posterior transition matrix is

$$q_{j|i} = \begin{cases} p_{j|i} e^{\beta \cdot \hat{g}_{i,j}} \frac{r_j(\beta)}{r_i(\beta)} & , i \neq j \\ -\sum_{k(\neq i)} p_{k|i} + \beta \cdot \hat{h}_i - \lambda_{\max}(\beta) & , i = j \end{cases} \tag{8.63}$$

with posterior stationary singleton distribution $\rho_i = l_i r_i$ and posterior stationary pair distribution $q_{ij} = l_i q_{j|i} e^{\beta \cdot \hat{g}_{i,j}} r_j$. Similar to DTMC, the requirement of $\lambda_{\max}$ being the largest eigenvalue (Chetrite and Touchette, 2013, 2015a) could be intuitively seen by plugging in the posterior $q_i = l_i r_i$ and $q_{ij} = l_i q_{j|i} e^{\beta \cdot \hat{g}_{i,j}} r_j$ into Eq. (8.58).

8.3.3 Diffusion

In continuous time Markov processes (diffusion) in $\mathbb{R}^n$ described by Fokker-Planck equation

$$\partial_t p(x,t) = -\nabla \cdot [b(x) p(x,t) - D(x) \nabla p(x,t)], \tag{8.64}$$

path observables we consider are

$$G(x_{0:T}) = \int_0^T \hat{h}(x_t) \mathrm{d}t + \int_0^T \hat{g}(x_t) \circ \mathrm{d}x_t. \tag{8.65}$$

Generally when the observable is a vector $G \in \mathbb{R}^m$, $\hat{h} \in \mathbb{R}^m$ is a vector and $\hat{g} \in \mathbb{R}^{m^2}$ is a matrix.

The level-2.5 LDT of diffusion process is formulated with empirical singleton frequency ρ and empirical current J:

$$\rho(x) = \frac{1}{T} \int_0^T \delta(x_t - x) \, \mathrm{d}t \text{ and } J(x) = \frac{1}{T} \int_0^T \delta(x_t - x) \circ \mathrm{d}x_t \tag{8.66}$$

with constraints on normalization $\int_{\mathcal{X}} \rho(x) \mathrm{d}x = 1$ and stationarity $\nabla \cdot J = 0$ (Maes *et al.*, 2008; Barato and Chetrite, 2015; Chetrite and Touchette, 2013, 2015a). Note that

$$g(x_{0:T}) \coloneqq \frac{1}{T} G(x_{0:T}) = \int_{\mathcal{X}} \rho(x) \hat{h}(x) \mathrm{d}x + \int_{\mathcal{X}} J(x) \cdot \hat{g}(x) \mathrm{d}x \tag{8.67}$$

is a functional to the empirical singleton frequency ρ and empirical current J. Eq. 8.67 validates the definition of ρ and J in Eq. (8.66). See Sec. B.3.3 for a more detained discussion of J as the notion of the empirical current.

The LDRF of them is often known in the form of

$$\varphi[\rho, J] = \frac{1}{4} \int_{\mathcal{X}} (J - J_\rho) \cdot (\rho D)^{-1} (J - J_\rho) \, \mathrm{d}x \tag{8.68}$$

where $J_\rho \coloneqq \rho b - D\nabla\rho$. Note that J_ρ is in general not divergence-free, a less known but more natural form of φ is actually

$$\varphi\left[\rho, J\right] = \frac{1}{4}\int_{\mathcal{X}} \left(b_{\rho,J} - b\right) \cdot D^{-1} \left(b_{\rho,J} - b\right) \rho \mathrm{d}x \tag{8.69}$$

where $b_{\rho,J} \coloneqq -D\nabla\left(-\ln\rho\right) + J/\rho$ is vector field decomposition from stationary distribution and flux (Wang *et al.*, 2008), note that J is divergence free so $b_{\rho,J}$ can be further rewritten in terms of its bivector potential (Yang and Qian, 2021b; Yang and Cheng, 2021). The alternative form of Eq. (8.69) shows that the tilting due to frequencies measurement is about updating the vector field b, *i.e.* as before, the average behavior.

The MEP for the observable G is then

$$\arg\inf_{\rho,J}\left\{\varphi[\rho,J] - \beta\cdot\left[\int_{\mathcal{X}}\rho\hat{h}\mathrm{d}x + \int_{\mathcal{X}}\hat{g}J\mathrm{d}x - \gamma\right] - \int k\nabla\cdot J\mathrm{d}x - \mu\left[\int\rho\mathrm{d}x - 1\right]\right\}. \tag{8.70}$$

Denoting $u = b_{\rho,J} - b$, functional derivatives w.r.t. ρ and J lead us to

$$\beta\cdot\hat{h} = -\frac{1}{4}u\cdot D^{-1}u - \frac{1}{2}\nabla\cdot u - \frac{1}{2}b\cdot D^{-1}u - \mu \tag{8.71}$$

and

$$\beta\cdot\hat{g} = \frac{1}{2}D^{-1}u - \nabla k. \tag{8.72}$$

Similar to DTMC and CTMC, plugging the latter into the former gives us the eigenvalue problem reported by Chetrite and Touchette (2015a) with linear operator

$$\mathcal{L}_\beta \coloneqq b\cdot\left(\nabla + \beta\cdot\hat{g}\right) + \left(\nabla + \beta\cdot\hat{g}\right)\cdot D\left(\nabla + \beta\cdot\hat{g}\right) + \beta\cdot\hat{h}. \tag{8.73}$$

The equation then shows that $k = \ln r$ where r is the right eigenfunction of $\mathcal{L}_\beta$ with $\lambda = -\mu$ as the corresponding eigenvalue: $\mathcal{L}_\beta\left[r\right] = \lambda r$. The posterior probability current is then $J = \rho b_{\rho,J} - D\nabla\rho$. One can also show from $\nabla\cdot J = 0$ that the stationary singleton distribution is $\rho(x) = l(x)r(x)$ where $l(x)$ is the left eigenfunction of $\mathcal{L}_\beta$ corresponding to λ, satisfying $\mathcal{L}_\beta^*\left[l\right] = \lambda l$ where

$$\mathcal{L}_\beta^* \coloneqq -\left(\nabla - \beta\cdot\hat{g}\right)\cdot b + \left(\nabla - \beta\cdot\hat{g}\right)\cdot D\left(\nabla - \beta\cdot\hat{g}\right) + \beta\cdot\hat{h} \tag{8.74}$$

is the linear operator conjugate to $\mathcal{L}_\beta$ w.r.t. the Lebesgue measure. Plugging in the posterior $\rho = lr$ and $J = \rho b_{\rho,J} + D\nabla\rho$ back to Eq. (8.70) would show that λ should be the largest eigenvalue. The posterior

diffusion process is described by the posterior drift

$$b_{\rho,J} = b + 2D\nabla \ln r + 2D\left(\beta \cdot \hat{g}\right) \tag{8.75}$$

with information of singleton observable h hidden in the right eigenvector r.

8.4 Summary and Discussion

In this chapter, we emphasize an importance concept that the data infinitus limit can be regarded as a generalization to the thermodynamic limit in physics (Lu and Qian, 2022; Commons *et al.*, 2021; Yang and Qian, 2022). In Sec. 8.1, we formulate the statistical thermodynamics purely from the Gärtner-Ellis theorem in the LDT of data infinitus limit. We demonstrate the universality of our statistical thermodynamics from a general discussion and show that all probabilistic models that is consistent with the measurement are parameterized by variables conjugated to the observables, understood as *entropic forces*. The theory is formulated purely phenomenologically and does not require mechanics-like concepts to begin. Our *de-mechanised* statistical thermodynamics can be applied to general stochastic models. The convex duality in the LDT has a thermodynamic interpretation.

As a standard example of probabilistic models that are consistent with the measurement, we revisit the Gibbs conditioning principle and the MEP for singleton observables under i.i.d. prior in Sec. 8.2. The extension to transition-type observables under time-homogeneous Markov process is revisited in Sec. 8.3. It is important to keep in mind that the resulting posterior of a MEP calculation is actually an *empirical frequency* that minimizes the the LDRF for empirical frequency. The posterior is actually the average conditional empirical frequency and also the empirical frequency that is asymptotically the most probable under the prior probability. See Fig. 8.2 for a pictorial summary. It is worth noticing that the entropy (the LDRF) for empirical frequencies in time-homogeneous Markov chains is NOT in the Kullback-Leibler relative entropy form. Derivations of the LDRF of empirical frequencies can be found in Appendix B.

The entropy for empirical frequencies is actually a combination of at least two types of relative entropy. This can be seen by the following consideration. When a pair frequency is measured in a discrete-time Markov chain, the LDRF is given by LDT 2.5, $\varphi_\nu(f) = \sum_{i,j\in\mathcal{X}} f_{ij} \ln \frac{f_{ij}/f_i}{M_{j|i}}$. When we assume the prior process to be i.i.d., *i.e.* $M_{j|i} = p_j$, the time correlation in the posterior will be solely indicated by the measurement. If we measure the empirical joint frequencies $\nu_{ij} = \frac{1}{T}\sum_{t=1}^{T} \delta_{ij}\left(x_{t-1}x_t\right)$, the posterior

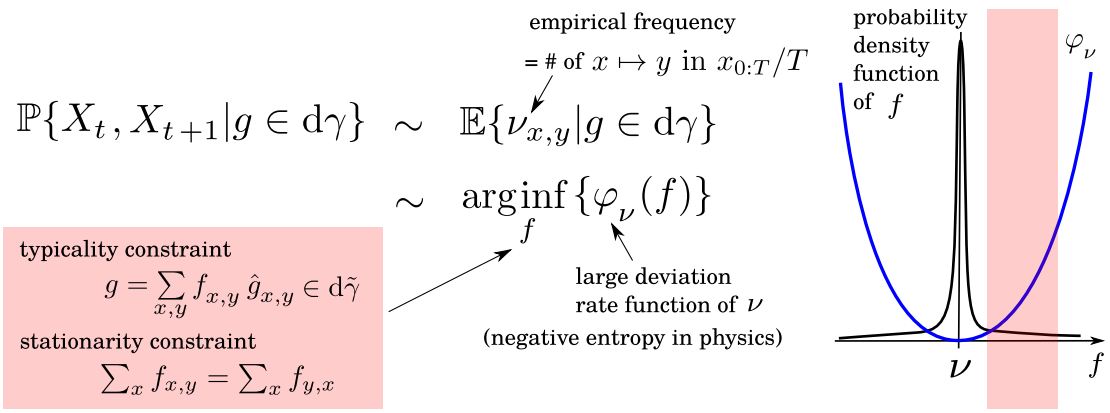


Figure 8.2: Pictorial summary for the Maximum Entropy Principle. Red area represents the frequencies that satisfy the constraints (normalization constraint not listed). Due to the exponential singular convergence of empirical frequency, only the empirical frequency with smallest φ_ν matters, thus Maximum Entropy.

probabilistic model will be a time-homogeneous Markov chain described by the measured values of the empirical frequencies ν_{ij}, say $\nu_{ij} = f_{ij}$. The LDRF of this observed f_{ij} under the prior probability $\mathbb{P}$ is then

$$\sum_{i,j\in\mathcal{X}} f_{ij} \ln \frac{f_{ij}}{f_i p_j} = \sum_{i,j\in\mathcal{X}} f_{ij} \ln \frac{f_{ij}}{f_i f_j} + \sum_{i\in\mathcal{X}} f_i \ln \frac{f_i}{p_i}. \tag{8.76}$$

The entropy for a DTMC is actually the mutual information between the two consequent states and the relative entropy between the empirical distribution and the prior. These two terms should be understood as follows: there are two parts in the model assumption: 1. i.i.d. and 2 the form of the probability distribution. The first term reports the deviation from i.i.d., and the second term gives deviation from the probability distribution. The significance of this result is that these two different kinds of deviations from the model can be quantified by a single âĂIJquantityâĂİ, the entropy (mutual information) of dependence and the entropy of deviation of the distribution are simply added together. We consider this relation a fundamental reason why mutual information is a natural measure of dependence. This result connects the LDT 2.5 for DTMC (Dembo and Zeitouni, 2009) to Sanov's theorem (Sanov, 1958) and information theory (Cover and Thomas, 2006).

Chapter 9

Maximum Caliber Principle and the origin of Statistical Thermodynamics

In this chapter, we first derive the Maximum Caliber Principle with a novel "i.i.d. multiverse" approach in Sec. 9.1. The conceptual differences and asymptotic equivalency between the Maximum Entropy and Maximum Caliber are discussed in Sec. 9.2. In our theory of statistical thermodynamics, the prior is chosen as the reference point of the entropic forces w.r.t. symmetries of interest. Measurement of the observables then infer non-zero entropic forces representing the breakdown of symmetries. We provide two examples of such measurement-inferred symmetry breaking in Sec. 9.3, comparing the breakdown of time independency and time reversibility. In Sec. 9.4, we introduce the Asymptotic Thermodynamic Uncertainty Principle for the statistical variations of the observables and of their conjugated entropic forces, and identify its the mescoscopic origin.

9.1 Canonical Posterior and Maximum Caliber Principle

9.1.1 Formulation of the Maximum Caliber Principle

We now formulate the Maximum Caliber Principle (MCP) with a rather novel derivation different from the axiomatic approach (Shore and Johnson, 1980; Uffink, 1995; Pressé *et al.*, 2013a,b; Jizba and Korbel, 2019; Pressé *et al.*, 2015; Tsallis, 2015). We recall that the intensive form g of the extensive thermodynamic observable $G\left(x_{0:T}\right)$ is assumed to satisfy the LLN. The ideal data infinitum will give us a definite value of

the observable g. Since the measured value is deterministic, any i.i.d. copy of the system will give us the same value of g, although generally with different microscopic path $x_{0:T}$. Hence, if we have many i.i.d. copy of the system (either mentally or physically) and each of them has infinitely long trajectory, then the empirical mean of the path measurements will be exactly the same as the one measured value we had. We can thus use the only one value we had to compute the posterior path measure from these i.i.d. copies by "the MEP for i.i.d. (path) sampling", which is historically called the Maximum Caliber Principle (Jaynes, 1980; Pressé *et al.*, 2013b).

More precisely and more generally, suppose we have n i.i.d. systems, $n \in \mathbb{N}$, with each of the system providing us length-T measurement of an extensive path observable G with value $\Gamma_T^{(i)}$, $G\left(x_{0:T}\right) \in \mathrm{d}\Gamma_T^{(i)}$ where $i \in \{1, 2, \cdots, n\}$. We can then compute the empirical mean of G for these n i.i.d. systems,

$$\bar{\Gamma}_T \coloneqq \frac{1}{n} \sum_{i=1}^{n} \Gamma_T^{(i)}. \tag{9.1}$$

We assume an arbitrary prior path measure $\mathbb{P}$ that can give us path probability from x_0 to x_L, *i.e.* $\mathbb{P}\left\{X_{0:L} = x_{0:L}\right\}$ or in short as $\mathbb{P}\left\{x_{0:L}\right\}$, where $L \geq T$ and L can be arbitrarily large. We now imagine $N - n$ numbers of "imaginative i.i.d. copies of the system", with certain (unknown) $\Gamma_T^{(i)}$ values for $i \in \{n+1, \cdots, N\}$. With the total empirical average of the N copies denoted as

$$\Gamma_T \coloneqq \frac{1}{N} \sum_{i=1}^{N} \Gamma_T^{(i)} = \frac{n}{N} \bar{\Gamma}_T + \frac{1}{N} \sum_{i=n+1}^{N} \Gamma_T^{(i)}, \tag{9.2}$$

the MEP of i.i.d. sampling can give us a posterior by taking the infinite copy limit $N \to \infty$.

Denoting the "empirical frequency of length-L path" as $f\left(x_{0:L}\right)$, we would compute

$$\mathbb{Q}_\beta\left(x_{0:L}\right) = \arg\inf_f \left\{ \sum_{x_{0:L}} f\left(x_{0:L}\right) \ln \frac{f\left(x_{0:L}\right)}{\mathbb{P}\left(x_{0:L}\right)} - \beta \cdot \left[\sum_{x_{0:T}} f\left(x_{0:T}\right) G\left(x_{0:T}\right) - \Gamma_T \right] \right\} \tag{9.3}$$

where f are normalized path measures. Note that since the constraint is only up to time T, we can decompose the optimization of f into the part $f\left(x_{0:T}\right)$ and the part for $f\left(x_{T+1:L}|x_{0:T}\right)$. It can be straightforwardly shown that the optimization for $f\left(x_{T+1:L}|x_{0:T}\right)$ for every given $x_{0:T}$ guarantees that the posterior stays as the prior for $t > T$, *i.e.* $f\left(x_{T+1:L}|x_{0:T}\right) = \mathbb{P}\left(x_{T+1:L}|x_{0:T}\right)$. Only the first length-$T$ of the path probability gets updated.

Now, we don't know the values of $\Gamma_T^{(i)}$, $n < i \leq N$, in our mental i.i.d. copy. We can only "approximate" Γ_T by $\bar{\Gamma}_T$. Yet, we know that when $T \to \infty$, each and every $\Gamma_T^{(i)}/T \to \gamma$. This means that with infinitely long trajectory $T \gg 1$, we can instead compute Eq. (9.3) with Γ_T replaced by its approximation $\bar{\Gamma}_T$. This

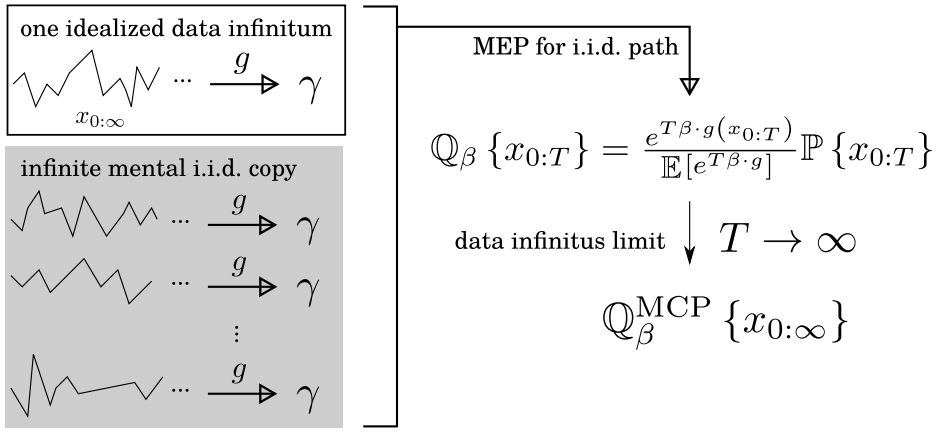


Figure 9.1: Pictorial summary of the Maximum Caliber Principle as the Maximum Entropy of the imaginative i.i.d. mental copy (multiverse) of samples.

approximated calculation leads to the Boltzmann-Gibbs exponential path measure as a posterior becomes exact in the limit $T \to \infty$:

$$\mathbb{Q}_\beta(x_{0:L}) = \frac{e^{\beta\cdot G(x_{0:T})}}{\mathbb{E}\left[e^{\beta\cdot G(x_{0:T})}\right]}\mathbb{P}(x_{0:L}) \tag{9.4}$$

where β is determined by $\bar{\Gamma}_T$. Note that in our derivation, the legitimacy of using the MCP is based on the LLN of the thermodynamic observable G in the data infinitus limit $T \to \infty$. Applying the MCP to finite T is an approximation. The following Fig. 9.1 summarizes pictorially the Maximum Caliber Principle.

9.1.2 Properties of the Maximum Caliber Principle

The MCP formulated above has several nice properties as we summarize them here.

9.1.2.1 Minimum Approach and Sufficient Statistics

From our discussion, the MCP is the minimum, necessary exponential tilting on the path probability to give a posterior such that the measurement is typical under it, *cf.* (Jaynes, 1957; Kullback and Leibler, 1951): the CPM in the MCP is given by a simple linear form,

$$\ln\frac{\mathrm{d}\mathbb{Q}_\beta}{\mathrm{d}\mathbb{P}} = \beta\cdot G - \Psi(\beta) = T[\beta\cdot g - \psi(\beta)] + o(T). \tag{9.5}$$

Compared this to the general tilting in CPM previously shown in Eq. (8.21), all the nonlinear terms $O\left(\delta\gamma^2\right)$ and also $\ln\frac{\mathbb{Q}_\beta\{x_{0:T}|G(x_{0:T})\}}{\mathbb{P}\{x_{0:T}|G(x_{0:T})\}} = 0$ are set to zero in the MCP. The latter, in fact, implies that the RND from

the MCP is a function of path only through the observable G. The condition

$$\mathbb{Q}_\beta \left\{ x_{0:T} | G = \Gamma \right\} = \mathbb{P} \left\{ x_{0:T} | G = \Gamma \right\}, \tag{9.6}$$

means that the conditional probability of an observed event $\{G = \Gamma\}$ is the same for the whole family, independent to the parameters β. When we measure the observable G, we only have information about the level set of G. We do not have any information inside a level set of G, so the posterior distribution inside is kept the same as the prior. In a sense, the fact that $\mathbb{Q}_\beta \left\{ x_{0:T} | G \left(x_{0:T} \right) \in \mathrm{d}\Gamma \right\}$ is independent to β means that the measurement of G have captured a "full information" of β. In statistics, such an observable G is said to be a *sufficient statistic* of the parameters β. The fact that the RND is a functional of G implies that G is a sufficient statistic of β is known as the Fisher-Neyman factorization theorem. The Pitman-Koopman-Darmois theorem in statistics tells us that only the exponential family has a finite-dimensional sufficient statistics when sample size increases, among the families whose range is independent to the parameters (Darmois, 1935; Pitman, 1936; Koopman, 1936).

9.1.2.2 Mesoscopic Origin of the Emergent Thermodynamic Structure

For each path prior $\mathbb{P}$ and a given set of path observables of interest $G \left(x_{0:T} \right)$, the MCP gives an exponential family of potential posterior parameterized by β as the "excited thermodynamic states" with the prior $\mathbb{P}$ as the "ground state" where $\beta = 0$. For a given measurement of $G = \Gamma$, the β in the posterior can be determined. In the calculation of Eq. (9.3), the parameter β as a Lagrange multiplier is determined such that the mean value under the posterior $\mathbb{Q}_\beta$ is the measured value Γ. The mean value of G under $\mathbb{Q}_\beta$ can be obtained by the cumulant generating function (CGF) of G under $\mathbb{P}$:

$$\Psi_T \left(\beta \right) \coloneqq \ln \mathbb{E} \left[e^{\beta \cdot G} \right] \tag{9.7}$$

(assume it exists and is differentiable), which can be understood as the *free energy* in statistical physics. The desired β then satisfies

$$\Gamma = \mathbb{E}_\beta \left[G \right] = \nabla \Psi_T \left(\beta \right) \tag{9.8}$$

where $\mathbb{E}_\beta \left[\cdot \right]$ represents taking expectation under $\mathbb{Q}_\beta$. As Ψ_T is strictly convex, Eq. (9.8) can be inverted to give a uniquely determined parameter

$$\beta \left(\Gamma \right) = \nabla \Phi_T \left(\Gamma \right) \tag{9.9}$$

by $\Phi_T(\Gamma) = \beta(\Gamma)\cdot\Gamma - \Psi_T[\beta(\Gamma)]$ as the Legendre transform of Ψ_T. We also notice that

$$\Phi_T(\Gamma) = \ln \frac{\mathrm{d}\mathbb{Q}_{\beta(\Gamma)}}{\mathrm{d}\mathbb{P}}(\Gamma) \tag{9.10}$$

characterizes the change of measure from $\mathbb{P}$ to the posterior $\mathbb{Q}_{\beta(\gamma)}$ and is thus a generalized notion of entropy (Qian *et al.*, 2019; Yang and Qian, 2020). That is, β is the "entropic force". A pair of "thermodynamic-like" equations for the Φ_T and the Ψ_T can be written down:

$$\mathrm{d}\Phi_T(\Gamma) = \beta(\Gamma)\cdot\mathrm{d}\Gamma \tag{9.11a}$$

$$\mathrm{d}\Psi_T(\beta) = \Gamma(\beta)\cdot\mathrm{d}\beta. \tag{9.11b}$$

Relations above can be done in an "intensive" way. If we define $\gamma \coloneqq \Gamma/T$,

$$\phi_T(\gamma) \coloneqq \Phi_T(T\gamma)/T, \tag{9.12}$$

and $\psi_T(\beta) \coloneqq \Psi_T(\beta)/T$, then the "intensive" parameter has the form of $\beta_i = \frac{\partial\Phi_T(\Gamma)}{\partial\Gamma_i} = \frac{\partial\phi_T(\gamma)}{\partial\gamma_i}$. In the data infinitus limit $T\to\infty$, we have $\phi_T \to \varphi_g$ and $\psi_T \to \psi_g$. Eqs. (9.11) becomes the two fundamental statistical thermodynamic equations shown in Eqs. (8.20). These Eqs. (9.11) from the MCP can be treated as the "mesoscopic" origin of the emergent thermodynamic structure in the data infinitum (Lu and Qian, 2022).

9.1.2.3 Maximum-Likelihood Estimator and the Gärtner-Ellis Theorem

The uniquely determined $\beta(\Gamma)$ is actually the β that maximizes the likelihood of observing the event $\mathbb{Q}_\beta\{G(x_{0:T})\in\mathrm{d}\Gamma\}$ among the exponential family. We have

$$\sup_\beta \mathbb{Q}_\beta\{G\in\mathrm{d}\Gamma\} = \sup_\beta \frac{e^{\beta\cdot\Gamma}}{Z(\beta)}\mathbb{P}\{G\in\mathrm{d}\Gamma\} \tag{9.13a}$$

$$= e^{\sup_\beta[\beta\cdot\Gamma-\Psi_T(\beta)]}\mathbb{P}\{G\in\mathrm{d}\Gamma\}. \tag{9.13b}$$

Therefore, the predicted β from Eq. (9.9) is also the *maximum-likehood estimator* in statistics. We also see that the entropy Φ_T here is actually maximized as the Legendre-Fenchel transform of the CGF Ψ_T,

$$\Phi_T(\Gamma) = \sup_\beta[\beta\cdot\Gamma - \Psi_T(\beta)]. \tag{9.14}$$

Eq. (9.14) clearly gives rise to the Gärtner-Ellis Theorem in Eq. (8.16). The Gärtner-Ellis Theorem in the LDT reflects the existence of the canonical exponentially-tiltied posterior indicated by the MCP. The

shapes of "entropy" $\varphi_g(\gamma)$ and "free energy" $\psi_g(\beta)$ actually implies the asymptotic statistics of g and $\beta(g)$ in the canonical exponential family $\mathbb{Q}_\beta$. We now demonstrate an Asymptotic Thermodynamic Uncertainty Principle between the statistical variance of g and $\beta(g)$ from the curvature relations of in the Sec. 9.4 below.

9.2 Comparison between Max Entropy and Max Caliber

Both the MEP and the MCP introduced above are formulated in the ideal data infinitus limit. They lead to asymptotic equivalent posteriors and the same asymptotic statistics for the observable (Chetrite and Touchette, 2013, 2015a). However, the MEP and the MCP are conceptually very different, and their differences can only be seen when observing transition-type observable or with a Markov prior. Here, we should use the DTMC case as the paradigm to discuss their asymptotic equivalence and conceptual differences here.

In the MEP formulated above, we started with either an i.i.d. prior or a time-homogeneous Markov prior. Then, through Gibbs conditioning principle (van Campenhout and Cover, 1981; Dembo and Zeitouni, 2009) and its Markov extension (Csiszár *et al.*, 1987; Chetrite and Touchette, 2013, 2015a), conditional probabilities are then connected to the conditional average empirical frequencies, specifically in Eq. (8.26) and Eq. (8.40). The LDP then allows one to use the contraction principle in LDT (Touchette, 2009; Qian and Cheng, 2020) to compute the conditional average empirical frequencies by a maximum/minimum entropy computation, with entropy given by the LDRF of empirical frequencies in LDT level 2 (Sanov, 1958) and level 2.5 (Maes and Netočný, 2008; Maes *et al.*, 2008; Barato and Chetrite, 2015). The posterior of the MEP is a time-homogeneous Markov chain with transition matrix given by $\bar{M}_{j|i}$ defined in Eq. (8.49). Note that the MEP is about the dynamics, *i.e.* the transition matrix. The Markov extension of the Gibbs conditioning principle does not tell us the posterior initial distribution (Csiszár *et al.*, 1987). As the information of initial distribution of a Markov process decays in the limit $T \to \infty$, we consider the inference of the initial distribution as an issue separate from the dynamics inference.

On the other hand, the MCP is formulated by assuming that the single measurement of the observable $g(x_{0:\infty}) \coloneqq \lim_{T\to\infty} \frac{G(x_{0:T})}{T} = \gamma$ from the ideal infinite-long trajectory $x_{0:\infty}$ is one sampling of an imagined i.i.d. "multiverse". Since $g(x_{0:\infty})$ is deterministic in the data infinitus limit, the one measurement is enough to infer the imaginative "empirical mean of the i.i.d. multiverse" where we can use a traditional MEP for i.i.d. "sampling". The formulation is to compute the posterior for a given T and then taken the data infinitus limit. The canonical posterior length-L path probability we get from a length-T measurement

$g\left(x_{0:T}\right) \coloneqq G\left(x_{0:T}\right)/T = \gamma_T$ is given by Eq. (9.4). While it is known in Ge *et al.* that a transition-type path observable $G\left(x_{0:T}\right) = \sum_{t=1}^{T} \hat{g}_{x_{t-1},x_t}$ leads to a Markov process (Ge *et al.*, 2012), it is less known that this canonical posterior is actually time-inhomogeneous for $0 \leq t \leq T$ when $T < \infty$ and only becomes time-homogeneous in the data infinitus limit $T \to \infty$, where it converges to a time-homogeneous Markov process with the same transition matrix as the MEP posterior (Chetrite and Touchette, 2015a). We shall briefly review this below by using DTMC as a paradigm.

With a time-homogeneous DTMC prior characterized by initial distribution p_{x_0} and transition matrix $M_{y|x}$ (i.i.d. as a special case when $M_{y|x} = p_y$), the MCP posterior is

$$\mathbb{Q}_\beta\left\{x_{0:L}\right\} = \frac{p_{x_0}}{Z_T} \prod_{t=1}^{T} \tilde{M}_{x_{t-1},x_t} \prod_{t=T+1}^{L} M_{x_t|x_{t-1}} \tag{9.15}$$

where $\tilde{M}$ is the tilted matrix defined in Eq. (8.48) and

$$Z_T = \sum_{x_{0:T} \in \mathcal{X}^{[0,T]}} p_{x_0} \prod_{t=1}^{T} \tilde{M}_{x_{t-1},x_t} = p \cdot \left(M e^{\beta \cdot \hat{g}}\right)^T \mathbf{1} \asymp \lambda_{\max}^T \tag{9.16}$$

where $\lambda_{\max}$ is the largest eigenvalue of $\tilde{M}$. We first show that Eq. (9.15) gives a time-inhomogeneous Markovian structure for $0 \leq t \leq T$. We compute the posterior conditional probability from time $t-1$ to t:

$$\hat{M}^{T-t}_{x_t|x_{t-1}} \coloneqq \mathbb{Q}_\beta\left\{X_t = x_t | X_{t-1} = x_{t-1}\right\} = \frac{v_{x_t}(T-t)}{v_{x_{t-1}}(T-t+1)} \tilde{M}_{x_{t-1},x_t} \tag{9.17}$$

where $v(n) = \tilde{M}^n \mathbf{1}$ is the vector one gets by multiplying the one vector $\mathbf{1}$ with the tilted matrix $\tilde{M}$ for s times. Notation $v_j(s)$ represents the j-th component of the vector v. In general, the ratio $v_{x_t}(T-t)/v_{x_{t-1}}(T-t+1)$ depends on both t and T. The initial distribution from the MCP posterior is given by

$$\hat{q}^T_x \coloneqq \mathbb{Q}_\beta(X_0 = x) = p_x \frac{v_x(T)}{Z_T}. \tag{9.18}$$

The Markov structure of the joint distribution in Eq. (9.15) is thus by the following expression:

$$\mathbb{Q}_\beta\left\{x_{0:L}\right\} = q^T_{x_0} \prod_{s=1}^{T} \hat{M}^{T-s}_{x_s|x_{s-1}} \prod_{t=T+1}^{L} M_{x_t|x_{t-1}}. \tag{9.19}$$

When the data infinitus limit is taken, the "transition matrix" converge to the posterior transition matrix from MEP,

$$\lim_{s\to\infty} \hat{M}^s_{y|x} = \frac{r_y}{\lambda_{\max} r_x} M_{y|x} e^{\beta \cdot \hat{g}_{x,y}} = \bar{M}_{y|x} \tag{9.20}$$

where r is the right eigenvector of $\lambda_{\max}$. Therefore, the posterior path probability from MCP is asymptotic

equivalent to the one from MEP (Chetrite and Touchette, 2013, 2015a). The initial distribution converges to

$$q_x \coloneqq \lim_{T\to\infty} \hat{q}_x^T = \frac{p_x r_x}{\sum_{x\in\mathcal{X}} p_x r_x}. \tag{9.21}$$

The posterior of MCP in the idealized data infinitus limit is then

$$\mathbb{Q}_\beta \{x_{0:\infty}\} = \frac{p_{x_0} r_{x_0}}{\sum_{x\in\mathcal{X}} p_x r_x} \prod_{t=1}^{\infty} \bar{M}_{x_t|x_{t-1}} \tag{9.22}$$

If we follow the standard "thermodynamic" concept of applying the limiting result back to the finite case as a leading order approximation (Anderson, 1972), we would use the measured value γ_T from $g(x_{0:T})$, $T \gg 1$ to get $\beta(\gamma_T)$, $\lambda_{\max}$ and r. Then, use Eq. (9.22) as the posterior of MCP, instead of using Eq. (9.19).

9.3 Measurement-predicted Symmetry Breaking

We now provide two examples of the symmetry-breaking indicated by the measurement.

9.3.1 Pair Frequency Measurement and Time Correlation

With the i.i.d. prior $\mathbb{P}\{x_{0:\infty}\} = \prod_{t=0}^{\infty} p(x_t)$ but transition-type observable g defined in Eq. (8.38). The MEP will give us a posterior transition matrix $\bar{M}_{j|i}$ defined in Eq. (8.49). Moreover, because of the i.i.d. prior, the Bayesian conditional pair probability is the same for any $s = \{1, \cdots, T\}$:

$$\mathbb{P}\{X_{s-1} = x, X_s = y | g \in \mathrm{d}\gamma_T\} = \mathbb{E}[\nu_{x,y} | g \in \mathrm{d}\gamma_T] \tag{9.23}$$

where ν is the empirical pair frequency defined in Eq. (8.35). This means that the posterior initial distribution is given by the posterior stationary distribution $l_x r_x$ of the transition matrix $\bar{M}$. The posterior path probability from the MEP is then

$$\mathbb{Q}_\beta^{\text{driven}} \{x_{0:\infty}\} = l_{x_0} r_{x_0} \prod_{t=1}^{\infty} \bar{M}_{x_t|x_{t-1}} \tag{9.24}$$

On the other hand, the posterior path probability from the MCP, according to Eq. (9.22), is given by

$$\mathbb{Q}_\beta^{\text{cano}} \{x_{0:\infty}\} = \frac{p_{x_0} r_{x_0}}{\sum_{x\in\mathcal{X}} p_x r_x} \prod_{t=1}^{\infty} \bar{M}_{x_t|x_{t-1}}. \tag{9.25}$$

We see that the two posteriors have different posterior initial distributions but are asymptotically equivalent. Both posteriors have a data-induced Markovian structure with the same transition matrix $\bar{M}$. Note that if $g(x_{0:T})$ is actually a singleton observable $\frac{1}{T}\sum_{t=1}^{T} \hat{g}(x_t)$, then the posterior probabilistic model will be i.i.d.

process as considered in Sec. 8.2. Time independence symmetry is broken by the transition-type observable.

9.3.2 Non-Gradient Observable and Irreversibility

For a possibly non-equilibrium Markov process, the natural reference would be a prior with detailed balance (Evans, 2004, 2005). We show here that when a detailed balanced prior is used, we can predict nonequilibrium posterior only when the path observable g is non-symmetric under path reversal. The entropy production at the nonequilibrium steady state (NESS) in the posterior is then shown to be in Onsager's form (Onsager, 1931; Landau and Lifshitz, 1980).

For DTMC, the path observable we measure is

$$g(x_{0:T}) \coloneqq \frac{1}{T}\sum_{t=1}^{T} \hat{g}_{x_{t-1},x_t} \in \mathrm{d}\gamma. \tag{9.26}$$

The posterior pair distribution at NESS was given by $q_{ij} = l_i \frac{M_{j|i}e^{\beta(\gamma)\cdot\hat{g}_{i,j}}}{\lambda} r_j$. With detailed balance $M_{j|i}$, the entropy production at NESS (*a.k.a.* housekeeping heat, see (Yang and Qian, 2020) for a review) would be

$$q_{\mathrm{hk}} \coloneqq \sum_{i,j\in\mathcal{X}} q_{ij} \ln \frac{q_{ij}}{q_{ji}} = \sum_{i,j\in\mathcal{X}} q_{ij} \ln \frac{M_{j|i}e^{\beta(\gamma)\cdot\hat{g}_{i,j}}}{M_{i|j}e^{\beta(\gamma)\cdot\hat{g}_{j,i}}} = \sum_{i,j\in\mathcal{X}} q_{ij}\beta\cdot\left[\hat{g}_{i,j} - \hat{g}_{j,i}\right]. \tag{9.27}$$

We see that only the anti-symmetric part of the matrix $\hat{g}_{i,j}$ contribute to the entropy production. Furthermore, due to the stationarity constraint of q_{ij} in Eq. (8.44), the enetropy production is zero if the pair observable is gradient-like $\hat{g}_{i,j} = u_j - u_i$ (Monthus, 2011; Chetrite and Touchette, 2015a). These tells us that only the measurement from non-symmetric, non-gradient transition observable $\hat{g}_{i,j}$ can lead us to a non-equilibrium posterior DTMC.

For diffusion, we measure the observable vector $g(x_{0:T}) = \frac{1}{T}\int_0^T \hat{h}\left(x_t\right)\mathrm{d}t + \frac{1}{T}\int_0^T \hat{g}\left(x_t\right)\circ\mathrm{d}x_t = \gamma$. For later convenience, let us denote $\gamma_{\hat{g}} \coloneqq \frac{1}{T}\int_0^T \hat{g}\left(x_t\right)\circ\mathrm{d}x_t$. The posterior process is described by $b_{\rho,J} = b + 2D\left(\beta\cdot\hat{g}\right) + 2D\nabla\ln r$ according to Eq. (8.75). If $\gamma_{\hat{g}} = 0$, *i.e.* the measurement is not on the transitions, the posterior is only driven by a generalized gradient force, which lead to equilibrium posterior. The posterior can only be irreversible when $\gamma_{\hat{g}} \neq 0$. Furthermore, suppose we have detailed balanced prior b, the posterior entropy production at NESS is

$$q_{\mathrm{hk}} \coloneqq \int_{\mathcal{X}} J\cdot\left(D^{-1}b_{\rho,J}\right)\mathrm{d}x = 2\beta\int_{\mathcal{X}} J\cdot\hat{g}\mathrm{d}x = 2\beta\left(\gamma\right)\cdot\gamma_{\hat{g}} \tag{9.28}$$

where $J = \rho b_{\rho,J} - D\nabla\rho$ with $\rho(x) = l(x)r(x)$. Since J is divergence-free, q_{hk} can only be non-zero when $\hat{g}$ is non-gradient (Chetrite and Touchette, 2013, 2015a), *i.e.* with nonzero curl (Yang and Cheng, 2021).

Note that the entropy production in posterior Markov processes in both Eq. (9.27) and Eq. (9.28) can be summarized by the following expression in $T \to \infty$:

$$q_{\text{hk}} = \beta(\gamma) \cdot [g(x_{0:T}) - g(x_{T:0})] \tag{9.29}$$

where $x_{T:0}$ is the reversed trajectory of $x_{0:T}$ and γ is the measured value of $g(x_{0:T})$. This is in fact a generalization to Onsager's theory (Onsager, 1931; Landau and Lifshitz, 1980). For arbitrarily nonequilibrium systems, the entropy production is the product of the irreversible part of the path observables g and the thermodynamic conjugated forces β of the whole observables g. The posterior Markov process can only be nonequilibrium if the path observable breaks path reversal symmetry $g(x_{0:T}) \neq g(x_{T:0})$ in the data infinitus limit. The result here gives us a notion of the "underlying" equilibrium process for a non-equilibrium process. We start with an equilibrium prior and the data from measuring the observables g reveal the irreversibility of the process to us. The conjugated variables $\beta(\gamma)$ drive the system from equilibrium to a non-equilibrium posterior process. Generic properties of the conjugated force $\beta(\gamma)$ is further shown in the following section.

9.4 Thermodynamic Forces and their Statistical Variation

The thermodynamic conjugated forces $\beta = \nabla\varphi_g$ parameterize posteriors and are functions of the measured values of the observable g, previously denoted as γ. The definite level of the conjugated forces are revealed when the data is infinite. When the data are large but finite, the values of g fluctuate leading to a fluctuating predicted conjugated force $\beta(g)$. The statistical variations of g and $\beta(g)$ satisfy an uncertainty principle derived by Landau and Lifshitz (1980) from a linear theory of β . We shall call it the *Asymptotic Thermodynamic Uncertainty Principle* (ATUP) here to better distinguish it from the recently-celebrated "thermodynamic uncertainty relation" in stochastic thermodynamics (Barato and Seifert, 2015; Gingrich *et al.*, 2016; Horowitz and Gingrich, 2020). The ATUP lead to debates on whether the temperature of a system (or more generally thermodynamic conjugated variables) actually fluctuates or not. These debates were settled by Mandelbrot (1989) who explained that the aforementioned ATUP was about the "estimation" of temperature one predicted from observation on our isolated system. The estimation, as a function of energy, gives a prediction about the temperature of the reservoir the system once contacted with. Their values fluctuate due to the energy fluctuation in our system when we disconnected our system from the reservoir.

Here, we present the LDT derivation of the ATUP and identify its mesoscopic origin. By doing so, we connect three results associated with the fluctuation of observables and thermodynamic conjugated forces:

1. the LDT formulation of the ATUP of Landau and Lifshitz for finite but large T and its relation to the reciprocal curvatures of LDRF φ and the sCGF ψ;
2. the susceptibility of the statistics of observables due to variation of thermodynamic conjugated forces;
3. Schlögl's uncertainty relation (Schlögl, 1988; Uffink and van Lith, 1999) as the mesoscopic version of the ATUP.

The LDRF of the conjugated forces we derived also allows us to access higher order cumulants of them.

9.4.1 Asymptotic Thermodynamic Uncertainty Principle (ATUP) and Reciprocal Curvatures of Entropy and Free Energy

Suppose that we have known that our system of interest is under $\mathbb{Q}_\alpha$ with thermodynamic conjugated force α. Here, since the posteriors from MEP and from MCP are asymptotically equivalent, we will work with the Botlzmann-Gibbs posterior from MCP in this section. For a finite but large T measurement of g, the values of g fluctuates according to the probability $e^{-T\varphi_{g;\alpha}(\gamma)+O(\ln T)}$, where $\varphi_{g;\alpha}$ is the LDRF of g under $\mathbb{Q}_\alpha$. The LDRF $\varphi_{g;\alpha}$ is related to the LDRF of g under the reference measure $\mathbb{P}$ by the exponential tilting of MCP:

$$\varphi_{g;\alpha}(\gamma) = \varphi_g(\gamma) - [\alpha\cdot\gamma - \psi_g(\alpha)]\,. \tag{9.30}$$

The sCGF of g under $\mathbb{Q}_\alpha$ is

$$\psi_{g;\alpha}(\eta) = \psi_g(\eta+\alpha)\,. \tag{9.31}$$

When $\alpha = 0$, we have $\mathbb{Q}_0 \equiv \mathbb{P}$. The mean and covariance of g under $\mathbb{Q}_\alpha$, in the leading order, would be given by the derivatives of its sCGFs $\psi_{g;\alpha}(\eta)$ with $\eta = 0$ plugged in, *e.g.* $\mathbb{E}_\alpha[g] \sim \nabla\psi_g(\alpha)$ and $T\mathrm{Co}\mathbb{V}_\alpha[g] \sim \nabla\nabla\psi_g(\alpha)$.

Based on the measured value of g, we would predict the thermodynamic conjugated force by[1]

$$\beta(g) = \nabla\varphi_g(g) \tag{9.32}$$

which is also a random variable because g fluctuates. For large T, the most-likely value of β is the correct one $\alpha = \nabla\varphi_g(\gamma_\alpha)$ where $\gamma_\alpha := \mathbb{E}_\alpha[g]$. The fluctuation of $\beta(g)$ under large but finite T can be approximated

[1] The thermodynamic conjugated force is defined with zero point chosen to be the reference measure $\mathbb{P}$ with certain symmetries. It should be always defined by the gradient of the LDRF of g under $\mathbb{P}$, even if our system in-hand is at macrostate $\mathbb{Q}_\beta$.

by the LDRF of $\beta(g)$ under $\mathbb{Q}_\alpha$, again obtained by the contraction principle:

$$\varphi_{\beta;\alpha}(\eta) = \inf_{y:\beta(y)=\eta} \varphi_{g;\alpha}(\eta) = \varphi_{g;\alpha}(\nabla\psi_g(\eta)) = \varphi_{g;\alpha}(\nabla\psi_{g;\alpha}(\delta)). \tag{9.33}$$

For simplicity, we have denoted $\delta = \eta - \alpha$ as the deviation of the predicted thermodynamic conjugated force.

By the convex duality between the LDRF $\varphi_{g;\alpha}(\gamma)$ and the sCGF $\psi_{g;\alpha}(\beta)$, one has the reciprocality between the curvature (Hessian) of the two functions,

$$\mathbf{I} = [\nabla\nabla\varphi_{g;\alpha}(\gamma)]\left[\nabla\nabla\psi_{g;\alpha}(\beta)\big|_{\beta=\nabla\varphi_{g;\alpha}(\gamma)}\right] = \left[\nabla\nabla\varphi_{g;\alpha}(\gamma)\big|_{\gamma=\nabla\psi_{g;\alpha}(\beta)}\right][\nabla\nabla\psi_{g;\alpha}(\beta)] \tag{9.34}$$

where $\mathbf{I}$ is the identify matrix. This allows one to compute the leading-order fluctuation of the thermodynamic forces β from its LDRF, we compute

$$T\mathrm{Co}\mathbb{V}_\alpha[\beta] \sim \nabla\nabla\psi_{\beta;\alpha}(0) = [\nabla\nabla\varphi_{\beta;\alpha}(\nabla\psi_{\beta;\alpha}(0))]^{-1}. \tag{9.35}$$

To continue, we need the derivatives of the LDRF of β under $\mathbb{Q}_\alpha$. We compute

$$\nabla\varphi_{\beta;\alpha}(\eta) = \delta\cdot\nabla\nabla\psi_{g;\alpha}(\delta) \tag{9.36}$$

and

$$\nabla\nabla\varphi_{\beta;\alpha}(\eta) = \nabla\nabla\psi_{g;\alpha}(\delta) + \delta\cdot\nabla\nabla\nabla\psi_{g;\alpha}(\delta). \tag{9.37}$$

Note that based on Eq. (9.35), $\eta := \nabla\psi_{\beta;\alpha}(0)$ takes the value such that $0 = \nabla\varphi_{\beta;\alpha}(\eta)$. With invertible $\nabla\nabla\psi_{g:\alpha}$, this means $\delta = 0$ and thus $\eta = \alpha$. Hence, $\beta(g)$ has a covariance

$$T\mathrm{Co}\mathbb{V}_\alpha[\beta] \sim [\nabla\nabla\psi_{g;\alpha}(0)]^{-1} = \nabla\nabla\varphi_{g;\alpha}(\gamma_\alpha) = [\nabla\nabla\psi_g(\alpha)]^{-1} = \nabla\nabla\varphi_g(\nabla\psi_g(\alpha)) \tag{9.38}$$

This shows that the reciprocality of the two dual functions in Eq. (9.34) reflects the an asymptotic reciprocal relation between g and β under the measure $\mathbb{Q}_\alpha$ as $T\to\infty$,

$$[T\mathrm{Co}\mathbb{V}_\alpha[\beta(g)]][T\mathrm{Co}\mathbb{V}_\alpha(g)] \sim \mathbf{I}. \tag{9.39}$$

The statistically-predicted conjugated force $\beta = \nabla\varphi(g)$ has a small fluctuation if the observable g has big fluctuation, and both are $O(1/T)$. This is the asymptotic "thermodynamic uncertainty principle" between an observable and its conjugated force derived by Landau and Lifshitz (1980) and discussed by Mandelbrot (1989). We provide the unifying LDT derivation here and connect it to the known reciprocal curvature of

φ_g and ψ_g in LDT.

9.4.2 Susceptibility and Fisher Information

Different measured values of $g \coloneqq G/T$ lead to different predicted conjugated forces β, which leads to a different posterior path distribution $\mathbb{Q}_\beta$. We shall see how susceptible the statistics of observables are under variation of β. Here, we use the posterior from MCP, which is an exponential family

$$\mathrm{d}\mathbb{Q}_\beta\left(x_{0:T}\right) = \frac{e^{\beta\cdot G(x_{0:T})}}{Z\left(\beta\right)}\mathrm{d}\mathbb{P}\left(x_{0:T}\right) \tag{9.40}$$

where $Z\left(\beta\right) = \mathbb{E}\left[e^{\beta\cdot G}\right]$ is the "partition function" and $\ln Z\left(\beta\right)$ is the CGF of G.

The Cramér-Rao inequality in statistics, which is an application of Cauchy-Schwarz inequality, gives upper bound for susceptibility of observables. Consider a general vector observable that does not depend on β, say $H\left(x_{0:T}\right)$. The susceptibility of its mean value is then related to the covariance between its value and the value of G:

$$C_{ij} \coloneqq \frac{\partial}{\partial\beta_j}\mathbb{E}_\beta\left[H_i\right] = \mathrm{Co}\mathbb{V}_\beta\left[H_i, G_j\right]. \tag{9.41}$$

There are at least three interesting implications of Eq. (9.41). First, Each components of susceptibility has an upper bound given by the variance:

$$C_{ij}^2 \leq \mathbb{V}_\beta\left[H_i\right]\mathbb{V}_\beta\left[G_j\right] \tag{9.42}$$

This is from the direct use of Cauchy-Schwarz inequality (Cramér-Rao inequality) for scalar.

Second, when $H = G$, the above inequality becomes an equality, implying that the susceptibility matrix is symmetric for G:

$$\frac{\partial\mathbb{E}_\beta\left[G_i\right]}{\partial\beta_j} = \mathrm{Co}\mathbb{V}\left[G_i, G_j\right] = \frac{\partial\mathbb{E}_\beta\left[G_j\right]}{\partial\beta_i}. \tag{9.43}$$

This gives rises to all the Maxwell's relations in our statistical thermodynamics. When $i = j$, Eq. (9.43) further indicates that the value of $\mathbb{E}_\beta\left[G_i\right]$ would increase with increasing β_i with slope given by the fluctuation level $\mathbb{V}_\beta\left[G_i\right] \geq 0$, giving a nice intuition of β_i as the driving force of G_i and why the prediction of β can be unique.

Third, applying the generalized Cauchy-Schwarz inequality (Cramér-Rao inequality) for vectors (Tripathi, 1999), we further gets a "lower bound" for the covariance matrix of H, $\left(\Xi_H\right)_{ij} = \mathrm{Co}\mathbb{V}_\beta\left[H_i, H_j\right]$,

given by the susceptibility matrix:

$$\Xi_H \succeq C\mathcal{I}_\beta^{-1}C^\mathsf{T} \tag{9.44}$$

where the covariance of G is denoted as $(\mathcal{I}_\beta)_{ij} = \mathrm{Co}\mathbb{V}_\beta[G_i, G_j]$ since it is also the *Fisher information* of β and for exponential family $\mathbb{Q}_\beta$ [2]. Eq. (9.44) can be derived by diagonalizing Ξ_H and $\mathcal{I}_\beta$, which can always be done by orthonormal matrices since covariance matrices are symmetric. Below, we show that Eq. (9.44) leads to the mesoscopic origin of the AUR in Eq. (9.39).

9.4.3 Mesoscopic Origin of the ATUP

Consider the stochastic entropy of the observable $g = G/T$, $S_{g;\beta}(\gamma) := -\ln q_{g;\beta}(\gamma)$ where $q_{g;\beta}(\gamma)$ is the probability density of the observable g under $\mathbb{Q}_\beta$ (Qian, 2001b; Seifert, 2005). Here $q_{g;\beta}(\gamma)\,\mathrm{d}\gamma = \frac{e^{T\beta\cdot\gamma}}{Z(\beta)}p(\gamma)\,\mathrm{d}\gamma$ is related to the probability density $p(\gamma)$ of the observable g under $\mathbb{P}$. By choosing $H_i(g) = \frac{\partial S_{g;\beta}}{\partial\gamma_i}\Big|_{\gamma=g}$ (or simply $H_i = \partial_i S_{g;\beta}$) and assuming vanishing boundary conditions of $q_{g;\beta}$, one can show that,

$$\mathrm{Co}\mathbb{V}_\beta[g_i\partial_j S_{g;\beta}] = \delta_{ij}. \tag{9.45}$$

This states that the ith component of the observable g is uncorrelated (but not necessarily independent) to the jth component of the entropic conjugated force $\nabla S_{g;\beta}$.

Eq. (9.42) becomes

$$\mathbb{V}_\beta[g_i]\,\mathbb{V}_\beta[\partial_j S_{g;\beta}] \geq \delta_{ij} \tag{9.46}$$

which is a "thermodynamic uncertainty relation" first obtained by Schlögl (Schlögl, 1988; Uffink and van Lith, 1999). Eq. (9.44) then gives the mesoscopic origin of ATUP,

$$\mathrm{Co}\mathbb{V}_\beta[g]\,\mathrm{Co}\mathbb{V}_\beta[\nabla S_{g;\beta}] \succeq \mathbf{I}. \tag{9.47}$$

This mesoscopic ATUP actually holds for any boundary-vanishing probability density q_g of random variable g: it needs not be exponentially distributed. To see its connection to the ATUP in Eq. (9.39), we note that $\mathrm{Co}\mathbb{V}_\beta[\nabla S_{g;\beta}] \sim T^2\mathrm{Co}\mathbb{V}_\beta[\nabla\varphi_{g;\beta}] = T^2\mathrm{Co}\mathbb{V}_\beta[\nabla\varphi_g]$. The inequality becomes asymptotically an equality in the limit $T\to\infty$ since the leading order of fluctuation is captured by a Gaussian-distributed g (Landau and Lifshitz, 1980).

[2] Denoting $Q_\beta(x_{0:T}) = e^{\beta G(x_{0:T})-\ln Z(\beta)}P(x_{0:T})$ as the path measure, we consider the stochastic entropy $S := -\ln Q_\beta$. The Fisher information is given by $(\mathcal{I}_\beta)_{ij} := \mathbb{E}_\beta[\partial_{\beta_i}\partial_{\beta_j}S] = \mathrm{Co}\mathbb{V}_\beta[(\partial_{\beta_i}S),(\partial_{\beta_j}S)] = \mathrm{Co}\mathbb{V}_\beta[G_i, G_j]$ where the last equality comes from $(\partial_{\beta_i}S) = G_i$.

9.5 Summary and Discussion

Summary In this chapter, we formulate the MCP in a novel and mathematically precise way and show that the MCP is the origin of the emergent thermodynamic structure in Sec. 9.1. We then revisit the asymptotic equivalency and clarify the conceptual differences between the posteriors of the MEP and of the MCP for DTMC in Sec. 9.2. With the ground state chosen with respect to symmetries of interest, we discuss two examples of measurement-predicted symmetry breaking in Sec. 9.3, comparing the emergence of time correlation and the breakdown of time reversal symmetry. For posteriors under nonzero entropic forces, the system is considered to be in its thermodynamic excited state. When data is finite, the statistical variations of the observables and the entropic forces their values predicted satisfy an Asymptotic Thermodynamic Uncertainty Principle (ATUP), which stems from the reciprocal curvature relation between the entropy and the free energy. We derive the ATUP from a LDT formalism in Sec. 9.4 and further identify the mesoscopic origin of the ATUP and the repicrocality.

Compared to the LDT literatures Many mathematical results in Part III have been discussed in the past in the literature on LDT (Ellis, 2005; Touchette, 2009; Dembo and Zeitouni, 2009; Smith, 2011; Chetrite and Touchette, 2013, 2015a,b). However, there are at least three key conceptual differences between our work and those in the past: we emphasize the posterior probability, the thermodynamic conjugated forces that parameterized them, and the emergent statistical thermodynamics. The LDT, as suggested by its name, is about the asymptotic probability of a "rare event" deviated from the mean. However, whether an event is rare or not is actually w.r.t a probability measure. Under a reference measure as a prior $\mathbb{P}$, chosen according to certain symmetries, the observed event in the data infinitus limit could be exponentially rare under $\mathbb{P}$. The mathematics of LDT often carry on the statistical analysis and treat the system as a large deviation from the mean. It is, however, more natural for physicists and applied mathematicians to treat the probability measure as an intrinsic property of the system and consider the "rareness" of the event as an indication that the reference measure is subjected to an update. Hence, we emphasize the posterior probabilities and understand the system as in its "excited state" driven by the notion of thermodynamic conjugated forces β. This is conceptually very different from treating the system as a large deviation.

Comparison to Bayesian's School and Frequentist's School As a LDT-formulated MEP and MCP, our theory dictates a change of probability measure from the reference measure $\mathbb{P}$ as a prior to the posterior

$\mathbb{Q}_\beta$ tilted by the thermodynamic conjugated forces β based on the measurement. Like MEP and MCP, it is a combined approach of the frequentist inference, Bayesian inference, and limit theorems. For example, in the case of measuring the empirical frequencies of states in an i.i.d. sampling, the posterior would be determined exactly as the frequencies one measured in the data infinitus limit, as in the frequentists' school. However, like the Bayesian's school, our theory emphasizes the posterior $\mathbb{Q}_\beta$ and, more importantly, the associated thermodynamic forces β.

Higher-order statistics of the predicted entropic force From the large deviation rate function (LDRF) of the predicted $\beta(g)$ under the posterior $\mathbb{Q}_\alpha$ in Eqs. (9.33), we can actually compute the leading order approximation for other cumulants of $\beta(g)$. For example, for a scalar observable g, the skewness of g and $\beta(g)$ can be found. As the third derivative of sCGF is related to the third derivative of the LDRF by

$$\psi'''(y) = -\varphi'''(x(y))\psi''(y), \tag{9.48}$$

we can compute the third derivative of the sCGF of $\beta(g)$ under $\mathbb{Q}_\alpha$, denoted as $\psi'''_{\beta;\alpha}$, by the third derivative of its LDRF under $\mathbb{Q}_\alpha$, $\varphi_{\beta;\alpha}$. A straightforward calculation will tell us that the leading-order skewness of $\beta(g)$ is related to the leading-order skewness of g by

$$\psi'''_{\beta;\alpha}(0) = -\frac{2\psi'''_{g;\alpha}(0)}{\psi''_{g;\alpha}(0)}. \tag{9.49}$$

We leave the comprehensive discussion of β's asymptotic statistics to future studies.

Non-convexity and Phase Transitions Throughout our discussion, we have assumed that the free energy, *i.e.* the scaled cumulant generating function, of the observables exists and is differentiable. Such condition, according to Gärtner-Ellis theorem implies that the entropy is strictly convex. The situation where entropy is non-convex corresponds to non-differentiability in the free energy (Touchette, 2009). This corresponds to the situation of phase transition and criticality in thermodynamics. In these cases, the free energy is still the Legengre-Fenchel transform of the entropy

$$\psi(\beta) = \sup_\gamma \{\beta \cdot \gamma - \varphi(\gamma)\} \tag{9.50}$$

but the Legengre-Fenchel transform of the free energy will lead to the convex envelop of the entropy, denoted as φ^*:

$$\varphi^*(\gamma) = \sup_{\beta} \{\beta \cdot \gamma - \psi(\beta)\}. \tag{9.51}$$

An important next step for our statistical thermodynamics is to re-formulate the theory of phase transitions in the framework of large deviation theory and classify different types of criticality, in analogue to Landau's theory of phase transitions (Landau and Lifshitz, 1980; Huang, 1991).

Synthesis with the Energetics As a general discussion of statistical inference, the statistical thermodynamics presented here could also shed lights on inference mechanisms in biological systems, *e.g.* active prediction in the brain (Dayan *et al.*, 1995; Sajid *et al.*, 2021) and concentration inference of cells (Lang *et al.*, 2014). An interesting future direction would be to study the role of the thermodynamic conjugated entropic forces β in such biological inference machinery and to potentially connect the statistical thermodynamics in the present work with the stochastic thermodynamics of the underlying biochemical signaling networks (Lang *et al.*, 2014).

Thermodynamic Understanding of Large Deviation Theoretic Results The statistical thermodynamic theory we presented in Part III provides the large deviation theory of data infinitus limit a thermodynamic interpretation. We expect similar thermodynamic aspects can be revealed and integrated in future studies for the large deviation theory of the zero-noise limit of continuous Markov processes (Freidlin and Wentzell, 2012; Ge and Qian, 2012a; Hong and Qian, 2021) and even the large deviation spectral theory of random matrices (Breuer *et al.*, 2016).

Part IV

Epilogue

Chapter 10

Discussion and Future Directions

The thermodynamic principles we synthesize in this thesis consists of the generalization to three key results in the standard thermodynamics and statistical physics (Landau and Lifshitz, 1980; Huang, 1991): the *fluctuation-dissipation relations* (Yang and Qian, 2021b), the *stochastic thermodynamics* that reveals the energetics of processes (Yang and Qian, 2020; Qian *et al.*, 2020; Yang and Qian, 2021a; Yang and Cheng, 2021), and the *statistical thermodynamics* that constitutes relations between observables and their conjugated driving forces (Commons *et al.*, 2021; Yang and Qian, 2022). All these thermodynamic principles are integrated in a single generic principle: symmetries and limit theorems dictate principles (Anderson, 1972; Yang, 1996). In this chapter, we discuss several future directions to enrich, extend, and complete the current theory. In Sec. 10.1, potential application to neuroscience is discussed and several directions of extension are introduced to apply the current theory to evolutionary dynamics, quantum dynamics, and spatiotemporal dynamics. In Sec. 10.2, we discuss future directions to understand nonequilibrium systems such as living systems by our theory of cycles. In Sec. 10.3, we introduce three geometrical aspects of our thermodynamic principles that are worth further investigation. Finally, in Sec. 10.4, we discuss how the Maximum Entropy and the Maximum Caliber principles can be applied to finite data.

10.1 Applications and Extensions

As stochastic thermodynamics and statistical thermodynamics are the two main directions statistical physics are extended to apply to complex systems, there are extensive applications of them in the literature. See (Seifert, 2019; Qian and Ge, 2021) and (Pressé *et al.*, 2013b; Ghosh *et al.*, 2020) for recent reviews. Here, we

discuss potential applications to neuroscience, evolutionary dynamics, quantum systems, and spatiotemporal patterns.

Neuroscience In the search of principles of neural computation, theorists have proposed that neural systems may operate nearly optimally with respect to the physical limits drawn by theories such as information theory (Bialek *et al.*, 2007; Friston, 2010; Denéve *et al.*, 2017; Chalk *et al.*, 2018). With the energetic theory we formulated in Part II, we can go beyond information theoretic bounds and consider the irreversibility/energy consumption of neural computation such as prediction and learning. A potential future direction is then to find relations between irreversibility and the functional performance of neural computation, study how a neural network could approach the thermodynamic limits, and connect them to existing theories (Kinouchi and Copelli, 2006; Beggs and Timme, 2012; Tkačik *et al.*, 2015; Denéve and Machens, 2016; Denéve *et al.*, 2017; Muñoz, 2018). One could start with simple models such as the minimum anticipatory dynamics equipped with short-term memory of periodic stimulus reported by Yang *et al.* (2015). The ternary trade-off of irreversibility, adaptation speed, and prediction accuracy in such adaptive excitable system would be interesting, and our thermodynamic potential theory in Chap. 6 would provide insights of how optimal performance could be achieved. Typical examples for how concepts of cyclic feedback and landscape could help understanding neural systems can be found in (Hopfield, 1982; Lan *et al.*, 2012; Yan *et al.*, 2013).

Evolution When our dynamic principles in Part II is applied to evolutionary biology (Chalub and Rodrigues, 2011; Qian, 2014a), the evolutionary dynamics is formulated as open-ended, continuous progressing processes without a "steady state". This is in sharp contrast to dynamics with a steady state, to which the current theory applies. Actually, such kind of dynamics that sweeps to infinity is mathematically complementary according to Foguel alternative theorem (Lasota and Mackey, 1994), *i.e.* long term behavior is either recurring to form unique steady state or sweeping to infinity. The extension of our dynamic principles to sweeping dynamics would "complete" our theory as a thermodynamic theory of dynamics in complex systems. Primitive work shows that similar energetic descriptions can be obtained for sweeping dynamics if one consider stationary non-normalized measure instead of stationary probability measure. Yet, the stationary measure is non-unique and related to "the boundary condition at infinity". How to determine the conditions for specific application and how it could provide a possible notion of fitness landscape, and/or

fitness flux (Mustonen and Lässig, 2010), remain to be investigated.

Quantum Probability Our thermodynamic principles study the entropic causes of stochastic dynamics under the formulation of classical probability theory. As quantum probability is fundamentally different from the classical one (Nagasawa, 2000; Milz and Modi, 2021; Landi and Paternostro, 2021). How to extend the principles formulated in the present thesis to the quantum realm is a non-trivial and essential issue (Esposito *et al.*, 2009). If such advancement is established, the extended theory would give us a rigorous thermodynamics of information processing in quantum systems and provide insights to the design of quantum computers. Such quantum thermodynamics might have biological significance as well (Lambert *et al.*, 2013).

Random Field Spatiotemporal patterns are a significant chapter in understanding biological systems (Murray, 2003). The extension of our thermodynamic principles to spatiotemporal fields could be formally done by considering a lattice model (Rodríguez *et al.*, 2021). However, as many of results in our thermodynamic principles require properties at the long term limit or even the vanishing noise limit, the exchangeability of the two limits makes the application to spatiotemporal problem mathematically non-trivial. How to extend our dynamic principles to stochastic partial differential equation as a field theory (Calzetta and Hu, 2008; Hairer, 2009; Kamenev, 2011) is thus an important theoretical issue remained to be answered. Such theory, should it be successfully extended, could provide the energetics of spatiotemporal patterns in dissipative systems such as Turing patterns in reaction-diffusion systems and trade-off results such as the energy-speed trade-off of traveling wave and energy-regularity trade-off for spatial patterns.

10.2 Cycles in Nonequilibrium Systems

Cycle Decomposition in Markov Chains In Chap. 6, we decomposed the probability flux $\mathbf{J}(x,t)$ in diffusion into an "equilibrium" part in terms of its scalar potential F and a "nonequilibrium" part in terms of cycles

$$\mathbf{J}(x,t) = \underbrace{-p(x,t)\,\mathbf{D}(x)\,\nabla F(x,t)}_{\text{equilibrium}} \underbrace{-p(x,t)\,\mathbf{Q}(x)\,\nabla F(x,t) + \nabla \times [p(x,t)\,\mathbf{Q}(x)]}_{\text{nonequilibrium}} \tag{10.1}$$

A similar equilibrium-nonequilibrium decomposition was established in Eq. (3.51) for Markov chains:

$$p(x,t)\,M(y|x) = \underbrace{p(x,t)\,M_{\rm eq}(y|x)}_{\text{equilibrium}} + \underbrace{\frac{1}{2}p(x,t)\,v^*(x,y)}_{\text{nonequilibrium}} \tag{10.2}$$

where $M_{\rm eq} = \left(M + M^\dagger\right)/2$ specifies the underlying equilibrium process of the Markov chain, *e.g.* mean rate decompositions. With the cycle flux decomposition introduced in Eq. (5.4), the "nonequilibrium" part, $\frac{1}{2}p(x,t)\,v^*(x,y)$, can also be expressed in terms of cycles:

$$p(x,t)\,M(y|x) = p(x,t)\,M_{\rm eq}(y|x) + \frac{1}{2}p(x,t)\,v^*(x,y) \tag{10.3a}$$

$$= p(x,t)\,M_{\rm eq}(y|x) + \frac{1}{2}\frac{p(x,t)}{\pi(x)}J^*(x,y) \tag{10.3b}$$

$$= p(x,t)\,M_{\rm eq}(y|x) + \frac{1}{2}\frac{p(x,t)}{\pi(x)}\sum_\sigma (J_\sigma - J_{\sigma^-})\,\mathbb{I}_\sigma(x,y). \tag{10.3c}$$

An interesting future direction would be to work out the implications of this further decomposition for Markov chains. We note that Baiesi and Maes (2018); Maes (2020) have been emphasizing importance of the time-symmetric dynamics, which is essentially the underlying equilibrium process in our discussion here.

Cycles and Properties in Nonequilibrium Steady States Our discussion in Chap. 5 clearly portraits the fundamental importance of kinetic cycles for nonequilibrium steady states (NESS). With our theory of cycles, deeper understanding can be established and origins can be identified for properties obtained in NESS, *e.g.* the Onsager's reciprocality and symmetry we discussed in Sec. 5.2. There are at least three important properties for systems at NESS that are worth further investigation:

1. the generalized fluctuation-dissipation relations in Chap. 7 (Yang and Qian, 2021b),
2. large deviations and fluctuation relations for cycle currents (Jiang *et al.*, 2022), and
3. the recently-celebrated thermodynamic uncertainty relations (Barato and Seifert, 2015; Horowitz and Gingrich, 2020; Polettini *et al.*, 2021).

Understanding them in terms of cycles should help revealing the origin of these properties and potentially connect them into a single unifying result.

Cycles and Life In an equilibrium system, there is no net probability flux when the dissipative system arrives its steady state in the long term, as we have reviewed in Sec. 3.1. Any efforts done on the forward

path would be undone by the reverse path with equal probability. It is thus important for a stochastic dissipative system, *e.g.* biological systems, to break detailed balance to have functions in the long term (Nicolis and Prigogine, 1977). Fluxes and transports in NESSs are understood in Part II to be "sustained" by the irreversibility $\mathcal{Q}_{\rm hk}$, thus named housekeeping heat. Hence, this active in-take of "energy", from the point of view from stochastic thermodynamics, is necessary for living systems, and arguably the "definition of being alive", *cf.* Schrödinger/Penrose (2012). Further with the understanding that kinetic cycles in the state space are the fundamental units of NESS, it is natural to try to understand what life is in terms of cycles (Qian *et al.*, 2016b). Here, we notice a comment to various current theories of life in a recent review by Cornish-Bowden and Cárdenas (2020):

> "All of these [theories of life] incorporate the idea of *circularity* to some extent, but all of them fail to take account of mechanisms of metabolic regulation,..."

Our theory in Chap. 5 emphasizes the importance of cycle and its connection to the energy $\mathcal{Q}_{\rm hk}$ required to sustain nonzero cycle flux. It could be the unifying mathematical theory that can integrate all theories of life reviewed in (Cornish-Bowden and Cárdenas, 2020) in a single theory, including the hypercyle theory by Eigen and Schuster (2012) and the "free energy principle" by Friston (2013).

10.3 Geometrical Aspects of Thermodynamics

A geometric understanding of a theory often leads to deeper and more fundamental insights, *e.g.* Einstein's general relativity for gravity. There are at least three possible geometrical aspects of the thermodynamic principles can be discussed in future works.

Information Geometry First, the statistical thermodynamics presented in Part III shows the importance of the exponential family from a prior tilted by conjugated variables. It is the "canonical" posterior from the Maximum Caliber Principle and is the origin of the thermodynamic structures. With the importance of the exponential family identified and the thermodynamic meanings of the parameters identified as *entropic* forces, it is natural and insightful to incorporate information geometry (Amari, 2016; Smith, 2019; Ohga and Ito, 2021) to our statistical thermodynamics (Lu and Qian, 2022; Commons *et al.*, 2021; Yang and Qian, 2022). One key for formulating such geometric theory would be the affine structure of probability measure

space (Hong *et al.*, 2020). A comprehensive discussion of such geometric understanding and how it could be connected to or unified with previous theory (Ruppeiner, 1995) remain to be elucidated.

Nonequilibrium as an internal curvature The break-down of detailed balance could be considered as an internal curvature (Feng and Wang, 2011; Polettini, 2012), akin to the gauge theory in physics. A precise formulation needs the mathematics of fiber bundle, yet the required underlying structural group is not clearly identified in the previous proposal (Feng and Wang, 2011). We expect clues could be found in the gauge freedom of our bivector potential theory (Yang and Qian, 2021a; Yang and Cheng, 2021). Specifically, the bivector potential $\mathbf{A}$ obtained for the divergence-free $\mathbf{J}^*(\mathbf{x}) = \nabla \times \mathbf{A}(\mathbf{x})$ is not unique: it has a gauge freedom with an arbitrary curl-free bivector. The situation has an analogue to that of discrete-state Markov process (Qian and Qian, 1979, 1982), and the vector potential in classical electrodynamics. Interestingly, for discrete-state Markov process, Qian and Qian (1979, 1982) have proven the existence and uniqueness of a gauge with a probabilistic meaning: cycles are not just represented in terms of Kirchhoff decomposition via linearly independent bases (Schnakenberg, 1976); rather the space of *all possible cycles* are considered, on which the unique *probabilistic gauge*, as NESS cycle flux, is the occurrence rate of a given cycle along the infinitely long, ergodic path (Qian and Qian, 1982). Whether such a unique probabilistic gauge also exists for bivector potential $\mathbf{A}$ on $\mathbb{R}^n$, or a more extended space of loops (Jan, 2010), remains to be further investigated.

Diffusion on Manifold In Sec. 6.2, we derived the mean rates of thermodynami quantities

$$\dot{\mathcal{S}}_{\rm tot} = \mathbb{E}\left[\mathbf{v}\cdot\mathbf{D}^{-1}\mathbf{v}\right], \dot{\mathcal{Q}}_{\rm hk} = \mathbb{E}\left[\mathbf{v}^*\cdot\mathbf{D}^{-1}\mathbf{v}^*\right], \tag{10.4a}$$

$$\dot{\mathcal{S}}_{\rm na} = \mathbb{E}\left[\nabla F\cdot\mathbf{D}\nabla F\right], \dot{\mathcal{Q}} = \mathbb{E}\left[\mathbf{v}\cdot\mathbf{D}^{-1}\mathbf{b}\right], \tag{10.4b}$$

$$\dot{S} = \mathbb{E}\left[\nabla S\cdot\mathbf{D}\nabla S\right] - \mathbb{E}\left[\nabla S\cdot\mathbf{D}\nabla\Phi\right] + \mathbb{E}\left[\mathbf{Q}\cdot(\nabla\Phi\wedge\nabla S)\right], \tag{10.4c}$$

$$\dot{\Phi} = -\mathbb{E}\left[\nabla\Phi\cdot\mathbf{D}\nabla\Phi\right] + \mathbb{E}\left[\nabla S\cdot\mathbf{D}\nabla\Phi\right] + \mathbb{E}\left[\mathbf{Q}\cdot(\nabla\Phi\wedge\nabla S)\right]. \tag{10.4d}$$

All the bilinear terms above have the inner production of two gradient vectors are with $\mathbf{D}$ whereas inner product of two "velocities" vectors such as $\mathbf{v}, \mathbf{v}^*$, and $\mathbf{b}$ are with $\mathbf{D}^{-1}$. This strongly implies considering diffusion on a Riemann manifold with $D_{ij}^{-1} = g_{ij}$ as the Riemannian metric tensor and investigate the stochastic thermodynamic structure on it. Such consideration potentially help formulating a rigorous formalism for path integral in diffusion (Takahashi and Watanabe, 1981; Zeitouni, 1989; Capitaine, 2000;

Zhou and Li, 2016). The theory of stochastic thermodynamics (Yang and Cheng, 2021; Jiang *et al.*, 2004) suggests writing the FPE in a symmetric form

$$\frac{\partial p}{\partial t} = -\nabla \cdot (\mathbf{b}p - \mathbf{D}\nabla p) \tag{10.5}$$

so that the vector field $\mathbf{b}$ is directly related to the heat dissipation of the system (Lebowitz and Spohn, 1999). On a Riemann manifold with metric tensor $g^{ij} = D^{ij}$ (which is the i,j th component of $\mathbf{D}$), the generator of the backward equation becomes (Jiang *et al.*, 2004)

$$\mathcal{A} = \frac{1}{2}\Delta + \tilde{b}^i \partial_i \tag{10.6}$$

where $\tilde{b}^i = b^i + \partial_j D^{ij} + D^{jk}\Gamma^i_{jk}$. Γ^i_{jk} is the Christoffel symbols specifying the connection on the Riemann manifold, and Δ is the Laplace-Beltrami operator, a generalization of Laplacian on a manifold. This implies a special connection $\Gamma^i_{jk} = -D_{jk}\partial_l D^{il} = D^{il}\partial_l D_{jk}$ where the original multiplicative-noise stochastic process becomes an additive-noise process on the manifold. Note that the connection here is not the same as the Levi-Civita connection $\Gamma^i_{jk} = \frac{1}{2}D^{im}\left(\partial_l D_{mk} + \partial_k D_{ml} - \partial_m D_{kl}\right)$. Implications of this remain to be investigated. With such generalization developed, many results in stochastic thermodynamics would be greatly simplified. A most notable one is the Pythagorean-like relation shown by Qian *et al.* (2020) for mean entropy production rates

$$\|\mathbf{v}\|^2 = \|\mathbf{v}^*\|^2 + \| - \nabla F\|^2 \tag{10.7}$$

where $\|\mathbf{u}\|^2 = \mathbb{E}\left[u^i g_{ij} u^j\right]$ for cotravariant vectors like $\mathbf{v}$ and $\mathbf{v}^*$ and $\|\mathbf{w}\|^2 = \mathbb{E}\left[w_i g^{ij} w_j\right]$ for covariant vectors such as $-\nabla F$ as indicated by Eqs. (6.16) and (6.17).

10.4 Data Accumulation in Statistical Thermodynamics

Higher-order approximation for finite data in the Statistical Physicists' Approach The probabilistic models from the Maximum Entropy Principle (MEP) and the Maximum Caliber Principle (MCP) are both defined and validated in the idealized data infinitus limit. When they are applied to finite data in practice, direct applications of MEP and MCP are the leading-order approximations on the entropic forces β. Taking transition-type observables $g\left(x_{0:T}\right) = \frac{1}{T}\sum_{t=1}^{T}\hat{g}_{x_{t-1},x_t}$ as an example, data with finite length T, *i.e.* $\{g\left(x_{0:T}\right) = \gamma_T\}$, gives us an approximation for the limiting, deterministic value $\lim_{T\to\infty} g\left(x_{0:T}\right)$. Applying the MEP and the MCP defined in the data infinitus limit back to this finite case means to compute the

largest eigenvalue $\lambda_{\max}$ and the corresponding right eigenvector r of the tilted matrix $\tilde{M}_{ij} = M_{j|i}e^{\beta\cdot\hat{g}_{i,j}}$ where M is the prior transition matrix. The posterior transition matrix from both the MEP and the MCP would be given by

$$\bar{M}_{j|i} = \frac{r_j(\beta)}{\lambda_{\max}(\beta)\, r_i(\beta)} M_{j|i} e^{\beta\cdot\hat{g}_{i,j}}. \tag{10.8}$$

The entropic force β is then approximated by $\beta = \nabla\varphi_g(\gamma_T)$ where φ_g is the large-deviation rate function of the observables g under prior (ground state) probabilistic model specified by the prior initial distribution p_i and the prior transition matrix $M_{j|i}$. Although inferring the initial distribution is generally considered as a separate issue from inferring the transition matrix, the MCP still gives a posterior initial distribution by $p_i r_i(\beta) / \sum_j p_j r_j(\beta)$. This approximation of entropic forces is taken following the standard approach of statistical physicists. If higher-order approximations is desirable, we can go beyond the large deviation and considered the "sub-extensive" part in the WKB form of probability distributions (Hill, 2013; Bedeaux *et al.*, 2020; Lu and Qian, 2022). We leave such extension to future studies.

Extension to incorporate time information When more data is acquired, say we have $g(x_{0:T}) = \gamma_T$ and a newly measured $\hat{g}_{x_T,x_{T+1}} = a$. Then, the most straightforward update of our probabilistic model is by computing

$$\gamma_{T+1} = \frac{T\gamma_T + a}{T+1}. \tag{10.9}$$

This gives us an update on the predicted entropic forces β. It is also clear that no update is needed if $\gamma_T = a$. However, this is "ignoring" the information that $\hat{g}_{x_T,x_{T+1}}$ is observed at the time step from T to $T+1$. This "ignorance" is due to the assumption that the underlying system is time-homogeneous and we should not treat the newly observed data any different from the previous data. In the MEP and the MCP described in Part. III, the observable is an empirical mean of the pair observable $\hat{g}_{i,j}$. No time information is incorporated in the two methods. If we desire to encode time information in our posterior probabilistic model, one would need, *e.g.*, i.i.d. copies of the process such that the transition of a given time can be sampled for multiple times. The MCP we presented in 9.1 is perfect for such extended to incorporate time information since it assumes i.i.d. copies of the process. We leave the development of such extension to future studies.

Bayesian Approach to Finite Data Recall that the MEP is motivated by Bayesian conditional probability. It is connected to the MEP in the data infinitus limit by the Gibbs conditioning principle. For finite data, an

alternative approach is to directly considered the Bayesian conditional probability as a posterior probabilistic model (Hu and Qian, 2022). To establish principles from such approach, the prior probability needs to be "chosen" in a principle way. Our statistical thermodynamics in Part. III, especially our discussion in Sec. 9.3, clearly indicates that the prior probability should be chosen with respect to the symmetry of interest, as the ground state of the entropic forces. We leave the development of this approach and the investigation of how it is potentially connected to the other approaches discussed above to future studies.

Appendices

Appendix A

Bivector Calculus

Here we summarize the mathematics used to derive the results in Chap. 5. In the main text, we used the notion of multivariable calculus and the notion of wedge product without the introduction of differential form for simplicity. However, the concept of differential form and the associated exterior calculus are needed to derive the formula of generalized curl and cross product for dimensions higher than 3 (Arnold, 1997; Fortney, 2018). We shall introduce and use the differential form calculus here. Throughout the text, we will use Cartesian coordinate to describe the entire Euclidean $\mathbb{R}^n$. We first introduce the concept of differential form and how it gives a general notion of integration in Sec. A.1. Then, the concept of bivector and 2-form are introduced in Sec. A.2. Vorticity of a vector, as the first notion of "curl", is then introduced in Sec. A.3. Then, the bivector potential of a divergence-free vector field is introduced with the second notion of "curl" in Sec. A.4. Finally, geometric interpretations are given for simple bivectors in Sec. A.5.

A.1 Differential form and Integration

In vector calculus, the infinitesimal work done by a force $\boldsymbol{f}$ from time t to $t+\delta t$ on a path $\mathbf{y}(t)$ is given by

$$\delta \mathcal{W} = \boldsymbol{f}(\mathbf{y}(t)) \cdot \delta \mathbf{y}(t) = \sum_{j=1}^{n} f_j(\mathbf{y}(t)) \delta y_j(t+\delta t) \tag{A.1}$$

where $\delta \mathbf{y}(t)$ denotes the infinitesimal vector $\mathbf{y}(t+\delta t) - \mathbf{y}(t)$. Usually, to emphasize the infinitesimal limit $\delta t \to 0$, we replace δ with d, leading to a notation $\boldsymbol{f}(\mathbf{y}(t)) \cdot \mathrm{d}\mathbf{y}(t)$. However, in the mathematics of differential form, the operater d is generalized and understood differently. In the main text, we used d as the standard infinitesimal difference operator in calculus. Here, we shall use δ as the infinitesimal operator and

d as the *exterior derivative* of differential form, as we will introduce below.

We first introduce the concept of *1-form*s, which are linear functions that maps a vector to a real number. Notice that the infinitesimal work in Eq. (A.1) actually takes the (tangent) vector $\delta\mathbf{y}(t)$ at a point $\mathbf{y}(t)$ and return us a number. The infinitesimal work is thus generally a differential 1-form at a given point, say $\boldsymbol{\xi}$, associated with a force vector $\boldsymbol{f} = (f_1, f_2, \cdots, f_n)$,

$$\omega_{\boldsymbol{\xi}}(\mathbf{u}) = \sum_{j=1}^{n} f_j(\boldsymbol{\xi})\mathrm{d}x_j(\mathbf{u}). \tag{A.2}$$

It takes an infinitesimal vector $\mathbf{u}$ as an input and gives us the infinitesimal work generated when going from $\boldsymbol{\xi}$ to $\boldsymbol{\xi} + \mathbf{u}$. The basis of an 1-form is $\{\mathrm{d}x_j\}$, which are themselves 1-forms[1]: $\mathrm{d}x_i$ takes a vector $\mathbf{u}$ and gives us its ith component,

$$\mathrm{d}x_i\left(\sum_j u_j\mathbf{e}_j\right) = \mathbf{e}_i \cdot \left(\sum_j u_j\mathbf{e}_j\right) = u_i \tag{A.3}$$

where $\mathbf{e}_i$ is the unit vector in the ith direction. To match up Eq. (A.1) with Eq. (A.2), simply take $\mathbf{u} \coloneqq \delta\mathbf{y}(t)$ and $\boldsymbol{\xi} = \mathbf{y}(t)$. The relation $\mathrm{d}x_i(\square) = \mathbf{e}_i \cdot \square$ is what allows us to write the differential form in a vectorized expression in the main text,

$$\omega_{\boldsymbol{\xi}}(\mathbf{u}) = \sum_i f_i(\boldsymbol{\xi})\mathrm{d}x_i\left(\sum_j u_j\mathbf{e}_j\right) \tag{A.4a}$$

$$= \sum_i f_i(\boldsymbol{\xi})\mathbf{e}_i \cdot \left(\sum_j u_j\mathbf{e}_j\right) = \boldsymbol{f}(\boldsymbol{\xi}) \cdot \mathbf{u}. \tag{A.4b}$$

A differential form is what we can integrate over a manifold. The integral of the work over a path $\Gamma = \{\mathbf{y}(s), 0 \le s \le t\}$ is then

$$\int_\Gamma \omega = \int_\Gamma \sum_{j=1}^{n} f_j\mathrm{d}x_j = \int_0^t \sum_{j=1}^{n} f_j(\mathbf{y}(s))\mathrm{d}x_j(\delta\mathbf{y}(s)) \tag{A.5}$$

where inputs of the differential form are suppressed concisely before the parameterization in the last step. To carry out the computation, one would proceed with $\mathrm{d}x_j(\delta\mathbf{y}(s)) = \delta\mathbf{y}_j(s) = \mathbf{y}_j'(s)\mathrm{d}s$, which makes Eq. (A.5) a usual one dimensional integration w.r.t. s. This identification of differential form turns out to be significant for the general integral of m-form on a general manifold and the generalization of Stoke's theorem.

[1] Here, just treat $\mathrm{d}x_j$ as a notation as the basis of an 1-form.

A.2 Bivector and 2-form

Stokes theorem in $\mathbb{R}^3$ tells us that a line integral of a vector field on a closed loop is equal to the surface integral of the vector field's curl. The intuition behind is that the curl of the vector field gives the vorticity of the vector field of an infinitesimal plane object. When integrating all the infinitesimal planes that tile the surface, neighboring circulation cancels and all the vorticity of the infinitesimal plane combines to give the vorticity on the big loop on the boundary. This intuition is still valid in $\mathbb{R}^n$. To see that, we shall first introduce how the "planary object" is represented in general $\mathbb{R}^n$: it is given by the notion of a (simple) bivector.

Two parameters are needed to parameterize a surface, and a surface can be cut into infinitesimal two dimensional parallelograms with edges given by the two infinitesimal tangent vectors of a point. Moreover, circulation of a vector field over an infinitesimal plane can have two orientations. Putting these together, we use the notion $\mathbf{u} \wedge \mathbf{v}$ to represent an oriented parallelogram object spanned by two vectors $\mathbf{u}$ and $\mathbf{v}$, thus the name *bivector*. The orientation of the object is reflected by the anti-symmetry of the wedge product $\wedge$, $\mathbf{u}\wedge\mathbf{v} = -\mathbf{v}\wedge\mathbf{u}$. The wedge product $\wedge$ is a linear operation satisfying $(c_1\mathbf{u}_1+c_2\mathbf{u}_2)\wedge\mathbf{v} = c_1\mathbf{u}_1\wedge\mathbf{v}+c_2\mathbf{u}_2\wedge\mathbf{v}$ where $c_1, c_2 \in \mathbb{R}$. With these, we can get the component form of the bivector

$$\mathbf{u} \wedge \mathbf{v} = \sum_{1\leq i<j\leq n} (u_i v_j - u_j v_i)\mathbf{e}_i \wedge \mathbf{e}_j \tag{A.6}$$

with basis $\mathbf{e}_i \wedge \mathbf{e}_j$. Importantly, one can show that the area of the parallelogram, denoted as $\|\mathbf{u}\wedge\mathbf{v}\|$ is given by

$$\|\mathbf{u} \wedge \mathbf{v}\|^2 = \sum_{1\leq i<j\leq n} (u_i v_j - u_j v_i)^2. \tag{A.7}$$

An inner product between two bivectors $\mathbf{A} = \sum_{i<j} A_{ij}\mathbf{e}_i \wedge \mathbf{e}_j$ and $\mathbf{B} = \sum_{i<j} B_{ij}\mathbf{e}_i \wedge \mathbf{e}_j$ is thus naturally defined as

$$\mathbf{A} \cdot \mathbf{B} = \sum_{1\leq i<j\leq n} A_{ij}B_{ij} \tag{A.8}$$

with $(\mathbf{e}_i \wedge \mathbf{e}_j) \cdot (\mathbf{e}_k \wedge \mathbf{e}_l) = \delta_{ik}\delta_{jl}$ for $i < j$ and $k < l$.

We note that, in general, bivectors are objects that can be expressed as $\mathbf{A} = \sum_{i<j} A_{ij}\mathbf{e}_i \wedge \mathbf{e}_j$. Not all bivector can be expressed as the wedge product of two vectors. Such bivectors are called *simple bivector*s, and only simple bivectors can have the geometrical meaning as a parallelogram spanned by two vectors: a general bivector can be the sum of many simple bivectors, superposition of many parallelogram. We

also note that due to the anti-symmetry of the wedge product, the component A_{ij} of a bivector $\mathbf{A}$ can be represented by an anti-symmetric matrix. Then, the inner product between two bivectors, as shown in Eq. (A.8), is the half of the Frobenius product of their anti-symmetric components.

Now, similar to an 1-form taking a vector to a real number, a 2-form takes a bivector to a real number.The basis of a 2-form is given by $\{\mathrm{d}x_i \wedge \mathrm{d}x_j\}$ for $1 \leq i < j \leq n$. Specifically, for $1 \leq i < j \leq n$,

$$\mathrm{d}x_i \wedge \mathrm{d}x_j \left(\sum_{k<l} A_{kl} \mathbf{e}_k \wedge \mathbf{e}_l \right) = (\mathbf{e}_i \wedge \mathbf{e}_j) \cdot \left(\sum_{k<l} A_{kl} \mathbf{e}_k \wedge \mathbf{e}_l \right) = A_{ij}. \tag{A.9}$$

Again, the relation between $\mathrm{d}x_i \wedge \mathrm{d}x_j \, (\mathbf{A}) = (\mathbf{e}_i \wedge \mathbf{e}_j) \cdot \mathbf{A}$ is what allow us to rewrite a differential 2-form in a vectorized form in the main text,

$$\omega(\mathbf{A}) = \sum_{i<j} B_{ij} \mathrm{d}x_i \wedge \mathrm{d}x_j \, (\mathbf{A}) = \sum_{i<j} B_{ij} \, (\mathbf{e}_i \wedge \mathbf{e}_j) \cdot \mathbf{A} \tag{A.10a}$$

$$= \sum_{i<j} B_{ij} A_{ij} = \mathbf{B} \cdot \mathbf{A}. \tag{A.10b}$$

When integration the differential 2-form over a surface, the $\mathbf{A}$ as the input of the 2-form here would be the infinitesimal bivector given by the two infinitesimal tangent vectors at a point, representing the infinitesimal tangent parallelogram at the point.

A.3 Exterior Derivative and the curl of a vector field

The concept of curl in vector calculus is useful because of the Stokes theorem in $\mathbb{R}^3$. We shall thus use the generalized version of the Stokes theorem, the Stoke-Cartan theorem, to motivate the notion of *exterior derivative* and get the general definition of the curl of a vector field in $\mathbb{R}^n$.

The Stokes-Cartan theorem states that the integral of a differential form ω over the boundary of some oriented manifold Ω is equal to the integral of its exterior derivative $\mathrm{d}\omega$ over the whole of Ω:

$$\oint_{\partial\Omega} \omega = \int_{\Omega} \mathrm{d}\omega. \tag{A.11}$$

In a sense, the exterior derivative d is defined so that Eq. (A.11) holds for a general manifold. We shall thus understand it with Stokes-Cartan theorem: the exterior derivative of a differential form ω can be interpreted, geometrically, as the integral over the boundary of an infinitesimal parallelepiped $h\Omega$,

$$\mathrm{d}\omega = \lim_{h \to 0} \frac{1}{\|h\Omega\|} \int_{\partial(h\Omega)} \omega \tag{A.12}$$

where $\|h\Omega\|$ denotes the volume of $h\Omega$. With this, one sees that the twice exterior derivative of any differential form has to be zero, $\mathrm{d}\mathrm{d}\omega = 0$. This is by applying the Stokes-Cartan theorem twice for a form that is itself the exterior derivative of another form $\varphi = \mathrm{d}\omega$ (such form is called *exact*). For an arbitrary compact region Ω, we have

$$\int_\Omega \mathrm{d}\mathrm{d}\omega = \int_\Omega \mathrm{d}\varphi = \int_{\partial\Omega} \varphi = \int_{\partial\Omega} \mathrm{d}\omega = \int_{\partial\partial\Omega} \omega. \tag{A.13}$$

Since $\partial\partial\Omega = \emptyset$ and Ω is arbitrary, we have $\mathrm{d}\mathrm{d}\omega = 0$. A form with zero exterior derivative is said to be *closed*. Therefore, every exact form is closed.

The exterior derivative of a k-form is a $(k+1)$-form. The exterior derivative of a general form $\alpha \wedge \beta$ obeys the product rule: Suppose α is a p-form, then

$$\mathrm{d}\left(\alpha \wedge \beta\right) = \mathrm{d}\alpha \wedge \beta + (-1)^p \left(\alpha \wedge \mathrm{d}\beta\right). \tag{A.14}$$

Applying this and $\mathrm{d}\mathrm{d}\omega = 0$, one can get the exterior derivative of the 1-form in Eq. (A.2),

$$\mathrm{d}\left(\sum_{j=1}^n f_j \mathrm{d}x_j\right) = \sum_{j=1}^n (\mathrm{d}f_j) \wedge \mathrm{d}x_j = \sum_{1\le i,j\le n} \left(\frac{\partial f_j}{\partial x_i}\mathrm{d}x_i\right) \wedge \mathrm{d}x_j \tag{A.15a}$$

$$= \sum_{1\le i<j\le n} \left(\frac{\partial f_j}{\partial x_i} - \frac{\partial f_i}{\partial x_j}\right) \mathrm{d}x_i \wedge \mathrm{d}x_j \tag{A.15b}$$

where $\mathrm{d}x_i \wedge \mathrm{d}x_j = -\mathrm{d}x_j \wedge \mathrm{d}x_i$ is used. By Stokes-Cartan theorem, we the have

$$\oint_{\partial\Omega} \sum_{j=1}^n f_j \mathrm{d}x_j = \int_\Omega \sum_{1\le i<j\le n} \left(\frac{\partial f_i}{\partial x_j} - \frac{\partial f_i}{\partial x_j}\right) \mathrm{d}x_i \wedge \mathrm{d}x_j. \tag{A.16}$$

As introduced in Appendix A.2, we can rewrite Eq. (A.16) in the vectorized form,

$$\oint_{\partial\Omega} \boldsymbol{f} \cdot \mathrm{d}\mathbf{x} = \int_\Omega \nabla \wedge \boldsymbol{f} \cdot \mathrm{d}\boldsymbol{\sigma} \tag{A.17}$$

where inner product between bivectors was introduced in Eq. (A.8). Hence, $\nabla \wedge \boldsymbol{f}$ as a bivector is the curl of the vector field $\boldsymbol{f}$.

Since $\mathrm{d}\mathrm{d}\omega = 0$, a gradient vector field is always curl-free, *i.e.* $\nabla \wedge \nabla U = 0$ where U is a scalar potential. For the converse, we apply Poicaré lemma, which states that every closed form is exact (locally) on a contractible domain. Since we are concern with processes on the entire Euclidean manifold $\mathbb{R}^n$, which is contractible, we can conclude that curl-free vector field is globally a gradient field.

A.4 Bivector potential of a divergence-free vector field

Using exterior derivatives and differential forms, the integral of a vector field $\mathbf{F}(\mathbf{x})$ over an $(n-1)$-dimensional closed surface Σ as flux is

$$\oint_\Sigma \sum_{k=1}^{n} F_k(\mathbf{x})\mathrm{d}\sigma_k = \int_\Omega \mathrm{d}\left(\sum_{k=1}^{n} F_k(\mathbf{x})\mathrm{d}\sigma_k\right) \tag{A.18a}$$

$$= \int_\Omega \sum_{k=1}^{n}\left[\sum_{j=1}^{n}\left(\partial_j F_k\right)\mathrm{d}x_j\right]\wedge \mathrm{d}\sigma_k \tag{A.18b}$$

$$= \int_\Omega \sum_{k,j=1}^{n}\left(\partial_j F_k\right)\mathrm{d}x_j\wedge \mathrm{d}\sigma_k \tag{A.18c}$$

$$= \int_\Omega \sum_{j=1}^{n}\left(\partial_j F_j\right)\mathrm{d}V, \tag{A.18d}$$

where Ω is the n-volume contained by the closed $(n-1)$-surface Σ, and

$$\mathrm{d}\sigma_k = (-1)^{k-1}\mathrm{d}x_1\wedge\mathrm{d}x_2\wedge\cdots\wedge\mathrm{d}x_{k-1}\wedge\mathrm{d}x_{k+1}\wedge\cdots\wedge\mathrm{d}x_n \tag{A.19}$$

with $\mathrm{d}x_k$ missing. The $(-1)^{k-1}$ factor is to ensure $\mathrm{d}x_j\wedge\mathrm{d}\sigma_k = \delta_{jk}\mathrm{d}V$ where

$$\mathrm{d}V = \mathrm{d}x_1\wedge\mathrm{d}x_2\wedge\cdots\wedge\mathrm{d}x_n \tag{A.20}$$

is the infinitesimal n dimensional volume element. The $(n-1)$-form $\mathrm{d}\sigma_i$ is the *Hodge dual* of the 1-form $\mathrm{d}x_i$, often denoted as $\mathrm{d}\sigma_i = \star\mathrm{d}x_i$.

Now if a vector field $\mathbf{F}(\mathbf{x})$ is divergence free, *i.e.* $\sum_{j=1}^{n}\left(\partial_j F_j\right) = 0$, then the $(n-1)$-form has a zero exterior derivative,

$$\mathrm{d}\left(\sum_{k=1}^{n} F_k(\mathbf{x})\mathrm{d}\sigma_k\right) = 0. \tag{A.21}$$

Poicaré lemma then guarantees that on a contractible domain,

$$\sum_{k=1}^{n} F_k(\mathbf{x})\mathrm{d}\sigma_k = \mathrm{d}\omega, \tag{A.22}$$

where ω is expected to be an $(n-2)$-form with the general expression

$$\omega = \sum_{1\le i<j\le n} u_{ij}(\mathbf{x})\mathrm{d}\eta_{ij}, \tag{A.23}$$

in which

$$\mathrm{d}\eta_{ij} = (-1)^{i-1+j-2}\mathrm{d}x_1\cdots\mathrm{d}x_{i-1}\wedge\mathrm{d}x_{i+1}\wedge\cdots\mathrm{d}x_{j-1}\wedge\mathrm{d}x_{j+1}\cdots\mathrm{d}x_n \tag{A.24}$$

with $\mathrm{d}x_i$ and $\mathrm{d}x_j$ missing. The $(-1)^{i-1+j-2}$ factor is to ensure $(\mathrm{d}x_i \wedge \mathrm{d}x_j) \wedge \mathrm{d}\eta_{ij} = \mathrm{d}V$ so that $\mathrm{d}\eta_{ij} = \star(\mathrm{d}x_i \wedge \mathrm{d}x_j)$. Then,

$$\mathrm{d}\omega = \sum_{1\le i<j\le n} \sum_{k=1}^{n} (\partial_k u_{ij})\, \mathrm{d}x_k \wedge \mathrm{d}\eta_{ij} \tag{A.25a}$$

$$= \sum_{1\le i<j\le n} \{(\partial_i u_{ij})\, \mathrm{d}x_i \wedge \mathrm{d}\eta_{ij} + (\partial_j u_{ij})\, \mathrm{d}x_j \wedge \mathrm{d}\eta_{ij}\} \tag{A.25b}$$

$$= \sum_{1\le i<j\le n} (-1)\, (\partial_i u_{ij})\, \mathrm{d}\sigma_j + \sum_{1\le i<j\le n} (\partial_j u_{ij})\, \mathrm{d}\sigma_i \tag{A.25c}$$

$$= \sum_{1\le j<i\le n} (-1)\, (\partial_j u_{ji})\, \mathrm{d}\sigma_i + \sum_{1\le i<j\le n} (\partial_j u_{ij})\, \mathrm{d}\sigma_i \tag{A.25d}$$

$$= \sum_{i=1}^{n} \sum_{j=1}^{n} (\partial_j A_{ij})\, \mathrm{d}\sigma_i. \tag{A.25e}$$

In the last step we have introduced $A_{ij}(\mathbf{x}) = u_{ij}(\mathbf{x})$ for $i < j$, $A_{ij}(\mathbf{x}) = -A_{ji}(\mathbf{x})$ for $i > j$ and $A_{ii}(\mathbf{x}) = 0$. It is easy to verify that

$$F_i(\mathbf{x}) = \sum_{j=1}^{n} (\partial_j A_{ij}(\mathbf{x})) \tag{A.26}$$

is a divergence free vector field:

$$\nabla \cdot \mathbf{F}(\mathbf{x}) = \sum_{i=1}^{n} \partial_i F_i(\mathbf{x}) = \sum_{i,j=1}^{n} (\partial_i \partial_j A_{ij}(\mathbf{x})) = 0. \tag{A.27}$$

The vector potential $\mathbf{A}(\mathbf{x})$ of a divergence-free field is a bivector with anti-symmetric matrix components. Since we consider diffusion on the whole $\mathbb{R}^n$, which is contractible. Eq. (A.22) and so Eq. (A.26) are thus globally valid.

In $\mathbb{R}^3$, a divergence free vector field has a vector potential through the same curl differential operator as the one we used to compute the vorticity of a vector field. For general $\mathbb{R}^n$, this is no longer true. To distinguish the two in general, we have used $\nabla\wedge$ as the curl operator that maps a vector field to its vorticity bivector, with $\wedge$ reminding us the result is a bivector. Here, we use $\nabla\times$ to denote the differential operator that links a divergence-free vector field to its bivector potential. Eq. (A.26) is then expressed as

$$\mathbf{F}(\mathbf{x}) = \nabla \times \mathbf{A}(\mathbf{x}). \tag{A.28}$$

The close relation between them can be seen by integration by part: For a divergence-free vector field

$\mathbf{F} = \nabla \times \mathbf{A}$, we have

$$\int_{\mathbb{R}^n} (\nabla \times \mathbf{A}) \cdot \mathbf{u} \, \mathrm{d}V = \int_{\mathbb{R}^n} \sum_{i,j} \partial_j A_{ij} u_i \mathrm{d}V \tag{A.29a}$$

$$= \int_{\mathbb{R}^n} \sum_{i<j} A_{ij} \left(\partial_i u_j - \partial_j u_i\right) \mathrm{d}V = \int_{\mathbb{R}^n} \mathbf{A} \cdot (\nabla \wedge \mathbf{u}) \, \mathrm{d}V. \tag{A.29b}$$

A.5 Geometrical Meaning of Simple Bivectors

In 3-D, we have the notion of a signed area spanned by two vectors $\mathbf{u}$ and $\mathbf{v}$ as a vector by using the right-hand rule, conventionally denoted as $\mathbf{u} \times \mathbf{v}$. This notion of a signed area can be generalized to general n-dimension with the notion of a wedge product $\wedge$ in geometrical algebra. The new object $\mathbf{u} \wedge \mathbf{v}$ is called a *simple bivector*. In 3-D, a simple bivector can be represented by a vector. For dimension higher than three, that is no longer possible. The fundamental reason is when assigning a "direction" for a bivector by using the right-hand rule in dimension higher than 3, there is more than one dimension that is perpendicular to the plane spanned by $\mathbf{u} \wedge \mathbf{v}$. Even though we can not represent it as a vector, we can still think of it as a planar object.

The linear combination of simple bivector is a bivector. In dimension smaller than three (including three), all bivectors are simple. That is, all bivector can be represented by the wedge product of two vectors. For dimension higher than 3, that is no longer true. There are bivectors that can not be represented by a simple wedge product of two vectors. The geometric meaning we presented here is only for simple bivectors.

The wedge product from it's definition have several properties. For example, for two vectors in $\mathbb{R}^n$, we have $\mathbf{u} \wedge \mathbf{v} = -\mathbf{v} \wedge \mathbf{u}$; $\alpha\mathbf{u} \wedge \beta\mathbf{v} = \alpha\beta\mathbf{u} \wedge \mathbf{v}$ where $\alpha, \beta \in \mathbb{R}$ are scalars; $\mathbf{u} \wedge \mathbf{u} = \mathbf{0}$; and $(\mathbf{u} + \alpha\mathbf{v}) \wedge \mathbf{v} = \mathbf{u} \wedge \mathbf{v}$. Besides these rather straightforward one, we also have the nontrivial distributive property

$$(\mathbf{u} + \mathbf{v}) \wedge \mathbf{w} = \mathbf{u} \wedge \mathbf{w} + \mathbf{v} \wedge \mathbf{w}. \tag{A.30}$$

This very property leads to an anti-symmetric matrix representation of bivector and also a Pythogorean theorem for perpendicular $\mathbf{u}$, $\mathbf{v}$, and $\mathbf{w}$.

First, let us show that area actually satisfies Pythogorean theorem. Let us denote $\|\mathbf{u} \wedge \mathbf{v}\|$ as the area indicated by the bivector $\mathbf{u} \wedge \mathbf{v}$. Then, from basic geometry, we have

$$\|\mathbf{u} \wedge \mathbf{v}\|^2 = \|\mathbf{u}\|^2 \|\mathbf{v}\|^2 - (\mathbf{u} \cdot \mathbf{v})^2 . \tag{A.31}$$

Now, applying this to $\| (\mathbf{u}+\mathbf{v}) \wedge \mathbf{w}\|^2$ for perpendicular vectors: $\mathbf{u}\perp\mathbf{v}$, $\mathbf{v}\perp\mathbf{w}$, and $\mathbf{u}\perp\mathbf{w}$, we get

$$\| (\mathbf{u}+\mathbf{v}) \wedge \mathbf{w}\|^2 = \|\mathbf{u}+\mathbf{v}\|^2\|\mathbf{w}\|^2 - [(\mathbf{u}+\mathbf{v})\cdot\mathbf{w}]^2 \tag{A.32a}$$

$$= \left(\|\mathbf{u}\|^2 + \|\mathbf{v}\|^2\right)\|\mathbf{w}\|^2 = \|\mathbf{u}\wedge\mathbf{w}\|^2 + \|\mathbf{v}\wedge\mathbf{w}\|^2. \tag{A.32b}$$

This can be used to derive, *e.g.*, the area of a triangle with three apexes $(a,0,0)$, $(0,b,0)$, and $(0,0,c)$. By applying the Pythagorean theorem twice, one gets that the triangular area is $\sqrt{\left(\frac{ab}{2}\right)^2 + \left(\frac{bc}{2}\right)^2 + \left(\frac{ca}{2}\right)^2}$.

With the distributive property, the simple bivector $\mathbf{u}\wedge\mathbf{v}$ spanned by the two general vectors $\mathbf{u}$ and $\mathbf{v}$ in $\mathbb{R}^n$ has an orthogonal decomposition into $n(n-1)/2$ orthogonal unit signed area $\mathbf{e}_i\wedge\mathbf{e}_j$ and corresponding components $(u_iv_j - u_jv_i)$,

$$\mathbf{u}\wedge\mathbf{v} \;= \left(\textstyle\sum_{i=1}^n u_i\mathbf{e}_i\right)\wedge\left(\sum_{j=1}^n v_j\mathbf{e}_j\right) = \sum_{i<j}(u_iv_j - u_jv_i)\,\mathbf{e}_i\wedge\mathbf{e}_j. \tag{A.33}$$

This shows that $\mathbf{u}\wedge\mathbf{v}$ can be represented by an *anti-symmetric matrix* with components $(u_iv_j - u_jv_i)$.

It can be shown that $\|\mathbf{u}\wedge\mathbf{v}\|^2 = (\mathbf{u}\cdot\mathbf{u})(\mathbf{v}\cdot\mathbf{v}) - (\mathbf{u}\cdot\mathbf{v})^2 = \sum_{i<j}(u_iv_j - u_jv_i)^2$. This implies that the inner product between two bivectors $\mathbf{A}$ and $\mathbf{B}$, which can be represented by anti-symmetric matrices, is just half of the Frobenius product of two matrices, $\mathbf{A}\cdot\mathbf{B} = \sum_{i<j}A_{ij}B_{ij} = \frac{1}{2}\sum_{i,j}A_{ij}B_{ij}$. It is the sum of all the $n(n-1)/2$ multiplied components

The inner product can tell us whether two simple bivectors are "perpendicular" or not. Two perpendicular areas are only defined with a shared edge. Geometrically, we would expect $\mathbf{u}\perp\mathbf{v} = 0 \Leftrightarrow (\mathbf{u}\wedge\mathbf{w})\cdot(\mathbf{v}\wedge\mathbf{w}) = 0$. This can be seen by the computation below,

$$(\mathbf{u}\wedge\mathbf{w})\cdot(\mathbf{v}\wedge\mathbf{w}) = \sum_{i<j}(u_iw_j - u_jw_i)(v_iw_j - v_jw_i) \tag{A.34a}$$

$$= \frac{1}{2}\sum_{i,j}(u_iw_j - u_jw_i)(v_iw_j - v_jw_i) \tag{A.34b}$$

$$= \frac{1}{2}\sum_{i,j}\left[u_iv_iw_j^2 + u_jv_jw_i^2 - (u_iv_j - u_jv_i)w_iw_j\right] = \left(\sum_i u_iv_i\right)\sum_j w_j^2. \tag{A.34c}$$

Appendix B

Method of Tilting to obtain Large Deviation Rate Functions

We introduce the method of tilting to derive Sanov's theorem in level-2 LDT and the level-2.5 LDT of empirical frequencies based on (Barato and Chetrite, 2015). The LDT level 2 and 2.5 of empirical frequencies are essential in the Maximum Entropy Principle in Chap. 8. We start with the motivating calculation to derive Sanov's theorem in Sec. B.1. The general method is then introduced in Sec. B.2. Finally, the LDT 2.5 of discrete-time Markov chains, continuous-time Markov chains, and diffusion are presented as three examples in Sec. B.3. The LDT level 2.5 for discrete-time Markov chains are well-known in mathematics (Dembo and Zeitouni, 2009). For continuous-time processes, see (Maes and Netočný, 2008; Maes *et al.*, 2008) for physicists' approaches and (Bertini *et al.*, 2015b,a) for more mathematical discussions.

B.1 Sanov's Theorem

For an i.i.d. sequence, $X_{1:L} = X_1 X_2 \cdots X_L$. The probability of a specific trajectory $x_{1:L}$ is given by $P(x_{1:L}) = \prod_{i=1}^{L} p(x_i)$. We would like to compute the probability for getting a particular sampled distribution $q(x)$. Note that obtaining a sampled distribution q is typical under the measure $Q(x_{1:L}) = \prod_{i=1}^{L} q(x_i)$. The RND between the two is given by

$$\frac{\mathrm{d}P}{\mathrm{d}Q}(x_{1:L}) = \prod_{i=1}^{L} \frac{p(x_i)}{q(x_i)} \tag{B.1}$$

The probability for obtaining the sampled distribution $q_{\omega_L}(x) = q(x)$ is given by summing over all the

length L trajectory ω_L that gives us q,

$$\mathbb{P}\left(q_{\omega_L}=q\right)=\int \mathbb{I}_{q_{\omega_L}=q}\mathrm{d}P(\omega_L) \tag{B.2a}$$

$$=\int \mathbb{I}_{q_{\omega_L}=q}\frac{\mathrm{d}P(\omega_L)}{\mathrm{d}Q\left(\omega_L\right)}\mathrm{d}Q(\omega_L). \tag{B.2b}$$

Now, the trajectory ω_L we summed over are those $q_{\omega_L}=q$. This tells us that there are $Lq(x)$ number of times the system is at state x. Therefore, we have

$$\left.\frac{\mathrm{d}P(\omega_L)}{\mathrm{d}Q\left(\omega_L\right)}\right|_{q_{\omega_L}=q}=\prod_{i=1}^{L}\frac{p\left(x_i\right)}{q\left(x_i\right)}=\prod_{x\in\mathcal{X}}\left(\frac{p(x)}{q(x)}\right)^{Lq(x)} \tag{B.3}$$

where $\mathcal{X}$ is the state space. Also, in the large L limit, $q_{\omega_L}=q$ is a typical event under the measure Q,

$$\int \mathbb{I}_{q_{\omega_L}=q}dQ(\omega_\infty)\asymp 1. \tag{B.4}$$

Therefore,

$$\mathbb{P}\left(q_{\omega_L}=q\right)=\left.\frac{dP(\omega_L)}{dQ\left(\omega_L\right)}\right|_{q_{\omega_L}=q}\int \mathbb{I}_{q_{\omega_L}=q}dQ(\omega_L)\asymp\prod_{x}\left(\frac{p(x)}{q(x)}\right)^{Lq(x)}. \tag{B.5}$$

Moreover, The LDRF is then

$$\varphi\left(q\right)=-\lim_{L\to\infty}\frac{1}{L}\ln\mathbb{P}\left(q_{\omega_L}=q\right)=\sum_{x}q(x)\ln\frac{q(x)}{p(x)}. \tag{B.6}$$

B.2 Method of Tilting

Tilting is a fast way to get the LDRF (provided that we know how to tilt). There are two conditions to make tilting work (Barato and Chetrite, 2015). Consider a set of sampling observables[1] $\mathbf{g}\left(\omega_T\right)=\left(g_1(\omega_T),g_2(\omega_T),...g_M(\omega_T)\right)$. They are all random variables and a path can be the i.i.d. repetition or Markov process. In either case, there is a path probability measure $\mathrm{d}\mathbb{P}\left(\omega_T\right)$. The goal is to find the LDRF of $\mathbf{g}\left(\omega_T\right)$. Two conditions for tilting to work:

1. There is a tilted measure $\mathbb{P}'\left(\omega_T\right)$ where $\mathbf{g}\left(\omega_T\right)$ is a typical behavior
2. The RND $\frac{\mathrm{d}\mathbb{P}}{\mathrm{d}\mathbb{P}'}\asymp\exp\left(-T\varphi(\mathbf{g})\right)$ under $\mathbb{P}'$ when $T\to\infty$.

In particular, the second condition is why we need to consider a joint empirical frequency in the LDT 2.5 of Markov processes. Tilting shows a reason why the LDRF takes a RND form.

[1] It Cramers theorem, $M=1$ and g_1 is the sampled mean. In Sanov's theorem, $M=1$ (or could be considered as infinite in continuous case) and g_1 is the sampled distribution. At LDT 2.5, $M=2$: g_1 samples state time (distribution) and g_2 samples number of transition.

The intuitive derivation is as followed (Barato and Chetrite, 2015). The probability of the sampled $\mathbf{g}(\omega_T)$ taking a specific value $\boldsymbol{\gamma}$ (or some ball near it for a continuous case) is

$$\mathbb{P}\{\mathbf{g}(\omega_T) = \boldsymbol{\gamma}\} = \int \mathbb{I}_{\{\mathbf{g}(\omega_T)=\boldsymbol{\gamma}\}} \mathrm{d}\mathbb{P}(\omega_T) = \int \mathbb{I}_{\{\mathbf{g}(\omega_T)=\boldsymbol{\gamma}\}} \frac{\mathrm{d}\mathbb{P}}{\mathrm{d}\mathbb{P}'}(\omega_T)\, \mathrm{d}\mathbb{P}'(\omega_T) \tag{B.7a}$$

$$\asymp \int \mathbb{I}_{\{\mathbf{g}(\omega_T)=\boldsymbol{\gamma}\}} \exp\left(-T\varphi(\mathbf{g})\right) \mathrm{d}\mathbb{P}'(\omega_T) \tag{B.7b}$$

$$= \exp\left(-T\varphi(\boldsymbol{\gamma})\right) \int \mathbb{I}_{\{\mathbf{g}(\omega_T)=\boldsymbol{\gamma}\}} \mathrm{d}\mathbb{P}'(\omega_T) \asymp \exp\left(-T\varphi(\boldsymbol{\gamma})\right) \tag{B.7c}$$

where the last equality followed from $\{\mathbf{g}(\omega_T) = \boldsymbol{\gamma}\}$ being typical. Below, let us apply tilting to understand Cramer's theorem, Sanov's theorem, and LDT 2.5 for Markov processes. From a computational point of view, we find the asymptotic value of $\frac{1}{T}\ln\frac{\mathrm{d}\mathbb{P}'}{\mathrm{d}\mathbb{P}}(\omega_T)$ under the measure $\mathbb{P}'$ in the large T limit, which will give us $\varphi(\mathbf{g})$.

B.3 Level-2.5 LDT of Markov Processes

B.3.1 Discrete time Markov Chain

We follow a similar route for discrete time. The path probability is

$$P(x_{0:T}) = \pi(x_0) M(x_1|x_0) \cdots M(x_T|x_{T-1}). \tag{B.8}$$

Then,

$$\frac{d\mathbb{P}}{d\tilde{\mathbb{P}}}(x_{0:T}) = \frac{\pi(x_0) M(x_1|x_0) \cdots M(x_T|x_{T-1})}{\tilde{p}(x_0) \tilde{M}(x_1|x_0) \cdots \tilde{M}(x_T|x_{T-1})} = \frac{p(x_0)}{\tilde{p}(x_0)} \prod_{t=1}^{T} \frac{M(x_t|x_{t-1})}{\tilde{M}(x_t|x_{t-1})} \tag{B.9}$$

Now, suppose we measure the number of transitions $x \mapsto y$, $\forall x, y \in \mathcal{X}$ and denote them as N_{xy}. This gives us the sampled pair probability $N_{xy}/T \to P_{X_t, X_{t+1}}(x, y)$. We note that

$$\frac{N_x}{T} \coloneqq \frac{\sum_y N_{xy}}{T} \to \pi(x) \tag{B.10}$$

We compute

$$\mathbb{P}\{N_{xy}(\omega) = n_{xy}\} = \int \mathbb{I}_{\{N_{xy}(\omega)=n_{xy}\}} \mathrm{d}\mathbb{P}(\omega) = \int \mathbb{I}_{\{N_{xy}(\omega)=n_{xy}\}} \frac{\mathrm{d}\mathbb{P}(\omega)}{\mathrm{d}\tilde{\mathbb{P}}(\omega)} \mathrm{d}\tilde{\mathbb{P}}(\omega). \tag{B.11}$$

Now, for the $\omega = x_{0:T}$ such that $N_{xy}(\omega) = n_{xy}$,

$$\frac{\mathrm{d}\mathbb{P}}{\mathrm{d}\tilde{\mathbb{P}}}(x_{0:T}) = \frac{p(x_0)}{n_{x_0}/T}\prod_{t=1}^{T}\frac{M(x_t|x_{t-1})}{n_{x_{t-1}x_t}/n_{x_{t-1}}} = \frac{p(x_0)}{n_{x_0}/T}\prod_{x,y}\left[\frac{M(y|x)}{n_{xy}/n_x}\right]^{n_{xy}} \tag{B.12a}$$

$$= \exp\left[\ln\frac{p(x_0)}{n_{x_0}/T} + \sum_{x,y} n_{xy}\ln\frac{M(y|x)}{n_{xy}/n_x}\right] \tag{B.12b}$$

Therefore, we have

$$\varphi(N_{xy} = n_{xy}) = \lim_{T\to\infty}\frac{1}{T}\ln\frac{\mathrm{d}\tilde{\mathbb{P}}}{\mathrm{d}\mathbb{P}} = \sum_{x,y}\frac{n_{xy}}{T}\ln\frac{n_{xy}/n_x}{M(y|x)} \tag{B.13a}$$

$$\varphi\left(\frac{N_{xy}}{T} = \tilde{p}(x,y)\right) = \sum_{x,y}\tilde{p}(x,y)\ln\frac{\tilde{p}(x,y)}{\tilde{p}(x)M(y|x)} \tag{B.13b}$$

where $\tilde{p}(x,y) = n_{xy}/T$ and $\tilde{p}(x) = n_x/T$.

Now, note that

$$\mathbb{P}\{N_{xx} = n_{xx}\ \&\ N_{xy} = n_{xy}\ (y \neq x)\} = \mathbb{P}\left\{N_{xx} = n_x - \sum_{y\neq x} n_{xy}\ \&\ N_{xy} = n_{xy}\ (y \neq x)\right\} \tag{B.14a}$$

$$= \mathbb{P}\left\{\frac{N_x}{T} = \frac{n_x}{T}\ \&\ \frac{N_{xy}}{T} = \frac{n_{xy}}{T}\ (y \neq x)\right\} \tag{B.14b}$$

Therefore, instead of measuring all possible transitions, one could also measure the exit transitions $x \mapsto y$ $(y \neq x)$ together with the empirical distribution (number of times the system hits state x) The LDRF is just

$$\varphi\left(\frac{N_x}{T} = \tilde{p}(x), \frac{N_{xy}}{T} = \tilde{p}(x,y)\ (x \neq y)\right)$$

$$= \sum_{x\neq y}\tilde{p}(x,y)\ln\frac{\tilde{p}(x,y)}{\tilde{p}(x)M(y|x)} + \sum_{x}\tilde{p}(x,x)\ln\frac{\tilde{p}(x,x)}{\tilde{p}(x)M(x|x)} \tag{B.15a}$$

$$= \sum_{x\neq y}\tilde{p}(x,y)\ln\frac{\tilde{p}(x,y)}{\tilde{p}(x)M(y|x)} + \sum_{x}\left[\tilde{p}(x) - \sum_{y(\neq x)}\tilde{p}(x,y)\right]\ln\frac{\tilde{p}(x) - \sum_{y(\neq x)}\tilde{p}(x,y)}{\tilde{p}(x)M(x|x)}. \tag{B.15b}$$

This is the LDT 2.5 result.

B.3.2 Continuous time Markov Chain

For a continuous time Markov chain, a length T trajectory $\omega_{0\sim T}$ (ignore subscript from now on) is defined by all the transition times $\{t_1, ..., t_n\}$ and states $\{x_0, x_1, ..., x_n\}$ it has for $t \in [0, T]$. Suppose the steady state probability distribution is $p(x)$ and the transition rate is given by $k(x,y)$. Then, the path probability at

NESS is given by

$$\mathbb{P}(\omega) = p(x_0)\left[e^{-r(x_0)t_1}\mathrm{d}t_1\right]k(x_0,x_1)\left[e^{-r(x_1)(t_2-t_1)}\mathrm{d}t_2\right]\cdots k(x_{n-1},x_n)\left[e^{-r(x_n)(T-t_n)}\right] \tag{B.16}$$

where $r(x) = \sum_{y\neq x} k(x,y)$. Now, suppose we have a different $\tilde{p}(x)$ and $\tilde{k}(x,y)$. Then, this gives a new path probability

$$\tilde{\mathbb{P}}(\omega) = \tilde{p}(x_0)e^{-\tilde{r}(x_0)t_1}\mathrm{d}t_1\tilde{k}(x_0,x_1)e^{-\tilde{r}(x_1)(t_2-t_1)}\mathrm{d}t_2\cdots\tilde{k}(x_{n-1},x_n)e^{-\tilde{r}(x_n)(T-t_n)}. \tag{B.17}$$

The RND between the two measures are given by

$$\frac{\mathrm{d}\mathbb{P}}{\mathrm{d}\tilde{\mathbb{P}}}(\omega) = \frac{p(x_0)}{\tilde{p}(x_0)}\prod_{i=1}^{n}\frac{k\left(x_{i-1},x_i\right)}{\tilde{k}\left(x_{i-1},x_i\right)}e^{-\sum_{i=0}^{n}[r(x_i)-\tilde{r}(x_i)](t_{i+1}-t_i)} \tag{B.18}$$

where $\tilde{k} = \tilde{P}/\tilde{p}$ where $t_{n+1} \coloneqq T$ and $t_0 \coloneqq 0$.

Now, for any given ω, we can compute a sampled joint distribution of sampled distribution ρ_ω and transition rate κ_ω:

$$\rho_\omega(i) = \frac{1}{T}\int_0^T \delta_i(x_t)\,\mathrm{d}t, \text{ and } \kappa_\omega(ij) = \frac{1}{T}\sum_{k=1}^{K}\delta_i(x_{k-1})\,\delta_j(x_k), i\neq j. \tag{B.19}$$

The produced ρ_ω and κ_ω are themselves random, depending on ω. To get the probability of having a specific sampled distribution ρ and transition rate κ, we sum all the path that leads to them

$$\mathbb{P}\left\{\rho_\omega = \rho, \kappa_\omega = \kappa\right\} = \int \mathbb{I}_{\rho_\omega=\rho,\kappa_\omega=\kappa}\mathrm{d}\mathbb{P}(\omega). \tag{B.20}$$

Now, the specific distribution actually gives us a RND by $\tilde{p} = \rho$ and $\tilde{k} = \kappa$. We can rewrite the desired probability as

$$\mathbb{P}\left\{\rho_\omega = \rho, \kappa_\omega = \kappa\right\} = \int \mathbb{I}_{\rho_\omega=\rho,\kappa_\omega=\kappa}\frac{\mathrm{d}\mathbb{P}}{\mathrm{d}\mathbb{P}_{\rho,\kappa}}\mathrm{d}\mathbb{P}_{\rho,\kappa}(\omega). \tag{B.21}$$

In $T\to\infty$, $\{\omega : \rho_\omega = \rho, \kappa_\omega = \kappa\}$ becomes typical events under the $\mathbb{P}_{\rho,\kappa}$ measure (this is tilting), that is $\int \mathbb{I}_{\rho_\omega=\rho,\kappa_\omega=\kappa}\mathrm{d}\mathbb{P}_{\rho,\kappa}(\omega) \simeq 1$. Therefore, $\mathbb{P}\left\{\rho_\omega = \rho, \kappa_\omega = \kappa\right\}$ becomes a first order estimation of the RND.

Roughly speaking, one would have $T\rho(x)\kappa(x,y)$ number of transition $x\mapsto y$ and the time the process stayed at x is given by $T\rho(x)$ (for the $P_{\rho,\kappa}$ process). The former point is less straightforward. We know that the total time in x is roughly $T\rho(x)$. And the average length for each stay is $1/r(x)$ (it is a Poisson process). Therefore, there are $T\rho(x)r(x)$ number of exit from x. Among those, a fraction of $\frac{\kappa(x,y)}{r(x)}$ goes to state y. Therefore, in the infinite long T trajectory, $T\rho(x)r(x)\frac{\kappa(x,y)}{r(x)} = T\rho(x)\kappa(x,y)$ number of transition $x\to y$.

Therefore, the integral in Eq. (B.21) becomes

$$P\left\{\rho_\omega=\rho,\kappa_\omega=\kappa\right\}=\lim_{T\to\infty}\frac{p(x_0)}{\rho(x_0)}\prod_{i=1}^{n(T)}\frac{k\left(x_{i-1},x_i\right)}{\kappa\left(x_{i-1},x_i\right)}e^{-\sum_{i=0}^{n}[r(x_i)-r_\kappa(x_i)](t_{i+1}-t_i)}. \tag{B.22}$$

The term

$$\frac{1}{T}\sum_{i=0}^{n(T)}\left[r\left(x_i\right)-r_\kappa\left(x_i\right)\right]\left(t_{i+1}-t_i\right)=\sum_x\rho(x)\left[r(x)-r_\kappa(x)\right] \tag{B.23a}$$

$$=\sum_x\rho(x)\left[\sum_{y\neq x}k(x,y)-\sum_{y\neq x}\kappa(x,y)\right] \tag{B.23b}$$

Also, there are $T\rho(x)\kappa(x,y)$ number of pair x,y, which means

$$\prod_{i=1}^{n(T)}\frac{k\left(x_{i-1},x_i\right)}{\kappa\left(x_{i-1},x_i\right)}\delta_{x_{i-1},x}\delta_{x_i,y}=\left(\prod_{x,y}\left[\frac{k\left(x,y\right)}{\kappa\left(x,y\right)}\right]^{\rho(x)\kappa(x,y)}\right)^T. \tag{B.24}$$

Therefore,

$$\lim_{T\to\infty}\frac{1}{T}\ln P=\ln\prod_{x,y}\left[\frac{k\left(x,y\right)}{\kappa\left(x,y\right)}\right]^{\rho(x)\kappa(x,y)}+\sum_x\rho(x)\left[\sum_{y\neq x}k(x,y)-\sum_{y\neq x}\kappa(x,y)\right] \tag{B.25}$$

The LDRF of the joint ρ,κ is then

$$\varphi\left(\rho,\mathcal{P}\right)=\sum_{x,y\in\mathcal{X},x\neq y}\mathcal{P}\left(x,y\right)\ln\frac{\mathcal{P}\left(x,y\right)}{\rho(x)k(x,y)}-\mathcal{P}\left(x,y\right)+\rho(x)k(x,y). \tag{B.26}$$

Interestingly, $\varphi\left(\rho,\mathcal{P}\right)$ is the *generalized KL divergence* which is a Bregman divergence (Amari, 2016)

$$D_F\left(\mathcal{P},\rho k\right)=F(\mathcal{P})-F(\rho k)-\left\langle\nabla F(\rho k),\mathcal{P}-\rho k\right\rangle \tag{B.27}$$

generated by the negative entropy $F(p)=\sum_z p(z)\log p(z)$, where z in the transition space.

B.3.3 Diffusion

For diffusion, the sampled density is simply

$$\rho_T\left(x\right)=\frac{1}{T}\int_0^T\delta\left(X_t-t\right)\mathrm{d}t. \tag{B.28}$$

The notion of sampled current in diffusion is less trivial. The notion $\frac{1}{T}\int_0^T\delta\left(X_t-x\right)\left(\mathrm{d}X_t\right)_i$ would converge to the average drift in the steady state, $\mathbb{E}^*\left[b_i+\left(\nabla\cdot D\right)_i\right]$, in diffusion. Instead, the sampled current at

point x is formally given by

$$[j_T(x)]_i = \frac{1}{T}\int_0^T \sum_{j=1}^n \delta\left(X_t - x\right)\delta_{ij} \circ \left(\mathrm{d}X_t\right)_j = \frac{1}{T}\int_0^T \delta\left(X_t - x\right) \circ \left(\mathrm{d}X_t\right)_i . \tag{B.29}$$

Intuitively, focus on a ball near x, computing the average $\mathrm{d}X_t$ that passed through it at time $t + \mathrm{d}t/2$ per unit time. How to show $j_T \to J$ as $T \to \infty$? Recall that for a work-like quantity defined on a transition $đ\mathcal{W}_i = \sum_{j=1}^n f_{ij}\left(X_t\right) \circ \left(\mathrm{d}X_t\right)_j$, its mean rate is

$$\mathbb{E}\left[\frac{đ\mathcal{W}_i}{\mathrm{d}t}\right] = \int_{\mathcal{X}} \sum_{j=1}^n J_j(y) f_{ij}(y) \mathrm{d}y. \tag{B.30}$$

Now, if $f_{ij} = \delta\left(X_t - x\right)\delta_{ij}$, then

$$\mathbb{E}\left[\delta\left(X_t - x\right) \circ \frac{\left(\mathrm{d}X_t\right)_i}{\mathrm{d}t}\right] = \int_{\mathcal{X}} \sum_{j=1}^n J_j(y) f_{ij}(y) \mathrm{d}y = \int_{\mathcal{X}} \sum_{j=1}^n J_j(y)\delta(y-x)\delta_{ij}\mathrm{d}y = J_i(x). \tag{B.31}$$

So,

$$\mathbb{E}\left[\left[j_T(x)\right]_i\right] = \frac{1}{T}\int_0^T \mathbb{E}\left[\delta\left(X_t - x\right) \circ \frac{\left(\mathrm{d}X_t\right)_i}{\mathrm{d}t}\right]\mathrm{d}t = J_i. \tag{B.32}$$

Now, with a given ρ_T and j_T, we need to find the RND between a process with ρ_T and j_T as stationary density and current and the original process with p and J. Note that a process with drift b and diffusion matrix D has

$$J_p = bp - D\nabla p \Rightarrow b = -D\nabla \ln p + \frac{J}{p}. \tag{B.33}$$

The diffusion with ρ_T and j_T is then with drift $\beta = -D\nabla \ln \rho_T + \frac{j_T}{\rho_T}$ and the same diffusion matrix. Girsanov theorem, as reviewed in Sec. 2.3, can then be used to compute the RND between them. In Eq. (2.32b), we had

$$\frac{\mathrm{d}\mathbb{P}_b}{\mathrm{d}\mathbb{P}_0} = \exp\left[\frac{1}{2}\int_0^t D^{-1}b \circ \mathrm{d}X_s - \frac{1}{2}\int_0^t \nabla \cdot b \mathrm{d}s - \frac{1}{4}\int_0^t b \cdot D^{-1} b \mathrm{d}s\right] \tag{B.34}$$

where a process $\mathbf{X}_t$ has a FPE $\partial_t p = -\nabla \cdot (bp - D\nabla p)$ under $\mathbb{P}_b$ and has a FPE $\partial_t p = -\nabla \cdot (D\nabla p)$ under $\mathbb{P}_0$. Note that the first time is anti-symmetric in terms of trajectory reversal. It is related to the action functional. Maes *et al.* (2008) called the rest of the time-symmetric parts, *traffic* . Then, we had in Eq. 3.39 that

$$\frac{\mathrm{d}\mathbb{P}_\beta}{\mathrm{d}\mathbb{P}_b} = e^{\frac{1}{2}\int_0^T D^{-1}(\beta-b)\circ \mathrm{d}X_s - \frac{1}{2}\int_0^T \nabla\cdot(\beta-b)\mathrm{d}s - \frac{1}{4}\int_0^T \beta\cdot D^{-1}\beta \mathrm{d}s + \frac{1}{4}\int_0^T b\cdot D^{-1} b \mathrm{d}s}. \tag{B.35}$$

Then, denoting $\delta = \beta - b$, we have

$$\frac{1}{T}\ln\frac{\mathrm{d}\mathbb{P}_\beta}{\mathrm{d}\mathbb{P}_b} = \frac{1}{T}\int_0^T \frac{1}{2}D^{-1}\delta \circ \mathrm{d}X_t + \frac{1}{T}\int_0^T \left[-\frac{1}{2}\nabla\cdot\delta - \frac{1}{4}\beta\cdot D^{-1}\beta + \frac{1}{4}b\cdot D^{-1}b\right]\mathrm{d}t \tag{B.36a}$$

$$= \frac{1}{2}\left[\int j\cdot\left[D^{-1}\delta\right]\mathrm{d}x - \int \rho\nabla\cdot\delta\mathrm{d}x - \frac{1}{2}\int \rho\left(\beta\cdot D^{-1}\beta - b\cdot D^{-1}b\right)\mathrm{d}x\right]. \tag{B.36b}$$

The LDRF is then

$$\varphi(\rho, j) = \frac{1}{4}\int \rho\frac{(j-J_\rho)}{\rho}\cdot D^{-1}\frac{(j-J_\rho)}{\rho}\mathrm{d}x \tag{B.37a}$$

$$= \frac{1}{4}\int \rho(\beta - b)\cdot D^{-1}(\beta - b)\,\mathrm{d}x \tag{B.37b}$$

where $\beta = -D\nabla\ln\rho + \frac{j}{\rho}$ is the "sampled drift". Note that the LDRF has a quadratic form.

Bibliography

Agozzino, L., Balázsi, G., Wang, J., and Dill, K. A. (2020), "How Do Cells Adapt? Stories Told in Landscapes," Annu Rev Chem Biomol Eng **11** (1), 155–182.

Altaner, B. (2017), "Nonequilibrium thermodynamics and information theory: basic concepts and relaxing dynamics," J. Phys. A: Math. Theor. **50** (45), 454001.

Altaner, B., Polettini, M., and Esposito, M. (2016), "Fluctuation-Dissipation Relations Far from Equilibrium," Phys. Rev. Lett. **117** (18), 180601.

Amari, S.-i. (2016), *Information Geometry and Its Applications*, Applied Mathematical Sciences (Springer Japan).

Anderson, P. W. (1972), "More Is Different," Science **177** (4047), 393–396.

Ao, P. (2004), "Potential in stochastic differential equations: novel construction," J. Phys. A: Math. Gen. **37** (3), L25–L30.

Ao, P., Kwon, C., and Qian, H. (2007), "On the existence of potential landscape in the evolution of complex systems," Complexity **12** (4), 19–27.

Arnold, V. I. (1997), *Mathematical Methods of Classical Mechanics*, 2nd ed. (Springer, New York).

Baiesi, M., and Maes, C. (2018), "Life efficiency does not always increase with the dissipation rate," J. Phys. Commun. **2** (4), 045017.

Bak, P. (1996), *How Nature Works: The Science of Self-organized Criticality* (Copernicus, New York, NY, USA).

Barato, A. C., and Chetrite, R. (2015), "A Formal View on Level 2.5 Large Deviations and Fluctuation Relations," J Stat Phys **160** (5), 1154–1172.

Barato, A. C., and Seifert, U. (2015), "Thermodynamic Uncertainty Relation for Biomolecular Processes," Phys. Rev. Lett. **114** (15), 158101.

Bedeaux, D., Kjelstrup, S., and Schnell, S. (2020), *Nanothermodynamics: General Theory*.

Beggs, J. M., and Timme, N. (2012), "Being Critical of Criticality in the Brain," Front. Physiol. **3**.

Bender, C. M., and Orszag, S. A. (1999), *Advanced Mathematical Methods for Scientists and Engineers: Asymptotic Methods and Perturbation Theory*, 1999th ed. (Springer, New York).

Bennett, C. H. (2003), "Notes on Landauer's principle, reversible computation, and Maxwell's Demon," Stud. Hist. Philos. Sci. B **34** (3), 501–510.

Berlinski, D. (2008), *Infinite Ascent: A Short History of Mathematics*, reprint edition ed. (Modern Library, New York, NY).

Bertini, L., Faggionato, A., and Gabrielli, D. (2015a), "Flows, currents, and cycles for Markov chains: Large deviation asymptotics," Stoch Process Their Appl **125** (7), 2786–2819.

Bertini, L., Faggionato, A., and Gabrielli, D. (2015b), "Large deviations of the empirical flow for continuous time Markov chains," Ann. Inst. H. Poincaré Probab. Statist. **51** (3), 867–900.

Bialek, W. (2012), *Biophysics: Searching for Principles* (Princeton University Press, Princeton, NJ).

Bialek, W., van Steveninck, R. R. d. R., and Tishby, N. (2007), "Efficient representation as a design principle for neural coding and computation," arXiv:0712.4381 .

Breuer, J., Simon, B., and Zeitouni, O. (2016), *Large Deviations and Sum Rules for Spectral Theory - A Pedagogical Approach*, Tech. Rep. arXiv:1608.01467 (arXiv).

Brunton, S. L., and Kutz, J. N. (2019), *Data-Driven Science and Engineering: Machine Learning, Dynamical Systems, and Control*, 1st ed. (Cambridge University Press, Cambridge).

Callen, H. B. (1985), *Thermodynamics and an Introduction to Thermostatistics*, 2nd ed. (Wiley, New York).

Callen, H. B., and Welton, T. A. (1951), "Irreversibility and Generalized Noise," Phys. Rev. **83** (1), 34–40.

Calzetta, E. A., and Hu, B.-L. B. (2008), *Nonequilibrium Quantum Field Theory* (Cambridge University Press, Cambridge, UK ; New York).

van Campenhout, J., and Cover, T. (1981), "Maximum entropy and conditional probability," IEEE Trans. Inform. Theory **27** (4), 483–489.

Capitaine, M. (2000), "On the Onsager-Machlup functional for elliptic diffusion processes," in *Séminaire de Probabilités XXXIV*, Vol. 1729, edited by J. Azéma, M. Ledoux, M. Émery, and M. Yor (Springer Berlin Heidelberg, Berlin, Heidelberg) pp. 313–328.

Chalk, M., Marre, O., and Tkačik, G. (2018), "Toward a unified theory of efficient, predictive, and sparse coding," Proc. Natl. Acad. Sci. U.S.A. **115** (1), 186–191.

Chalub, F. A. C. C., and Rodrigues, J. F., Eds. (2011), *The Mathematics of Darwin's Legacy*, 2011th ed. (Birkhäuser, Basel).

Chen, Y., Chen, X., and Qian, M.-P. (2006), "The Green-Kubo formula, autocorrelation function and fluctuation spectrum for finite Markov chains with continuous time," J. Phys. A: Math. Gen. **39** (11), 2539–2550.

Cheng, Y.-C., Qian, H., and Zhu, Y. (2021), "Asymptotic Behavior of a Sequence of Conditional Probability Distributions and the Canonical Ensemble," Ann. Henri Poincaré **22** (5), 1561–1627.

Chernyak, V. Y., Chertkov, M., and Jarzynski, C. (2006), "Path-integral analysis of fluctuation theorems for general Langevin processes," J. Stat. Mech. **2006** (08), P08001–P08001.

Chetrite, R., and Gupta, S. (2011), "Two Refreshing Views of Fluctuation Theorems Through Kinematics Elements and Exponential Martingale," J Stat Phys **143** (3), 543.

Chetrite, R., Gupta, S., Neri, I., and Roldán, E. (2019), "Martingale theory for housekeeping heat," EPL **124** (6), 60006.

Chetrite, R., Muratore-Ginanneschi, P., and Schwieger, K. (2021), "E. Schrödinger's 1931 paper "On the Reversal of the Laws of Nature" ["über dieUmkehrung der Naturgesetze",Sitzungsberichte der preussischen Akademie der Wissenschaften, physikalische mathematische Klasse, 8 N9 144-153]," arXiv:2105.12617 .

Chetrite, R., and Touchette, H. (2013), "Nonequilibrium Microcanonical and Canonical Ensembles and Their Equivalence," Phys. Rev. Lett. **111** (12), 120601.

Chetrite, R., and Touchette, H. (2015a), "Nonequilibrium Markov Processes Conditioned on Large Deviations," Ann. Henri Poincaré **16** (9), 2005–2057.

Chetrite, R., and Touchette, H. (2015b), "Variational and optimal control representations of conditioned and driven processes," J. Stat. Mech. **2015** (12), P12001.

Chibbaro, S., Rondoni, L., and Vulpiani, A. (2014), *Reductionism, Emergence and Levels of Reality: The Importance of Being Borderline* (Springer International Publishing).

Chun, H.-M., and Noh, J. D. (2019), "Universal property of the housekeeping entropy production," Phys. Rev. E **99** (1), 012136.

Commons, J., Yang, Y.-J., and Qian, H. (2021), "Duality Symmetry, Two Entropy Functions, and an Eigenvalue Problem in Gibbs' Theory," arXiv:2108.08948 .

Cornish-Bowden, A., and Cárdenas, M. L. (2020), "Contrasting theories of life: Historical context, current theories. In search of an ideal theory," Biosystems **188**, 104063.

Cover, T. M., and Thomas, J. A. (2006), *Elements of Information Theory*, 2nd ed. (Wiley-Interscience, Hoboken, N.J).

Crooks, G. E. (1998), "Nonequilibrium Measurements of Free Energy Differences for Microscopically Reversible Markovian Systems," J. Stat. Phys. **90** (5-6), 1481–1487.

Crooks, G. E. (1999), "Entropy production fluctuation theorem and the nonequilibrium work relation for free energy differences," Phys. Rev. E **60** (3), 2721–2726.

Crooks, G. E. (2000), "Path-ensemble averages in systems driven far from equilibrium," Phys. Rev. E **61** (3), 2361–2366.

Crooks, G. E. (2007), "Measuring Thermodynamic Length," Phys. Rev. Lett. **99** (10), 100602.

Csiszár, I., Cover, T., and Byoung-Seon Choi, (1987), "Conditional limit theorems under Markov conditioning," IEEE Trans. Inform. Theory **33** (6), 788–801.

Darmois, G. (1935), "Sur les lois de probabilites a estimation exhaustive," C. R. Acad. Sci. Paris **200**, 1265–1266, (in French).

Dayan, P., Hinton, G. E., Neal, R. M., and Zemel, R. S. (1995), "The Helmholtz Machine," Neural Comput. **7** (5), 889–904.

Dechant, A., and Sasa, S.-i. (2018a), "Current fluctuations and transport efficiency for general Langevin systems," J. Stat. Mech. **2018** (6), 063209.

Dechant, A., and Sasa, S.-i. (2018b), "Entropic bounds on currents in Langevin systems," Phys. Rev. E **97** (6), 062101.

Dembo, A., and Zeitouni, O. (2009), *Large Deviations Techniques and Applications*, 2nd ed. (Springer, Berlin Heidelberg).

Denéve, S., Alemi, A., and Bourdoukan, R. (2017), "The Brain as an Efficient and Robust Adaptive Learner," Neuron **94** (5), 969–977.

Denéve, S., and Machens, C. K. (2016), "Efficient codes and balanced networks," Nat Neurosci **19** (3), 375–382.

Dill, K. A., and MacCallum, J. L. (2012), "The Protein-Folding Problem, 50 Years On," Science **338** (6110), 1042–1046.

Ding, M., Tu, Z., and Xing, X. (2020), "Covariant formulation of nonlinear Langevin theory with multiplicative Gaussian white noises," Phys. Rev. Research **2** (3), 033381.

Doob, J. L. (1990), *Stochastic Processes*, revised edition ed. (Wiley-Interscience, New York, NY).

Durr, D., and Bach, A. (1978), "The Onsager-Machlup function as Lagrangian for the most probable path of a diffusion process | SpringerLink," Commun. Math. Phys. **60** (2), 153–170.

Durrett, R. (2019), *Probability: Theory and Examples*, 5th ed. (Cambridge University Press).

Dyson, F. J. (2010), "Birds and frogs in mathematics and physics," Phys.-Usp. **53** (8), 825.

Eigen, M., and Schuster, P. (2012), *The Hypercycle: A Principle of Natural Self-Organization* (Springer Science & Business Media).

Ellis, R. S. (1984), "Large Deviations for a General Class of Random Vectors," Ann. Probab. **12** (1), 1–12.

Ellis, R. S. (2005), *Entropy, Large Deviations, and Statistical Mechanics*, 2006th ed. (Springer, Leipzig).

Elson, E. L. (1985), "Fluorescence Correlation Spectroscopy and Photobleaching Recovery," Annu. Rev. Phys. Chem. **36** (1), 379–406.

Esposito, M., and Van den Broeck, C. (2010), "Three Detailed Fluctuation Theorems," Phys. Rev. Lett. **104** (9).

Esposito, M., Harbola, U., and Mukamel, S. (2009), "Nonequilibrium fluctuations, fluctuation theorems, and counting statistics in quantum systems," Rev. Mod. Phys. **81** (4), 1665–1702.

Evans, D. J., and Searles, D. J. (1994), "Equilibrium microstates which generate second law violating steady states," Phys. Rev. E **50** (2), 1645–1648.

Evans, D. J., and Searles, D. J. (2002), "The Fluctuation Theorem," Adv. Phys. **51** (7), 1529–1585.

Evans, D. J., Searles, D. J., and Rondoni, L. (2005), "Application of the Gallavotti-Cohen fluctuation relation to thermostated steady states near equilibrium," Phys. Rev. E **71** (5), 056120.

Evans, R. M. L. (2004), "Rules for Transition Rates in Nonequilibrium Steady States," Phys. Rev. Lett. **92** (15), 150601.

Evans, R. M. L. (2005), "Detailed balance has a counterpart in non-equilibrium steady states," J. Phys. A: Math. Gen. **38** (2), 293–313.

Eyink, G. L., and Sreenivasan, K. R. (2006), "Onsager and the theory of hydrodynamic turbulence," Rev. Mod. Phys. **78** (1), 87–135.

Fang, X., Kruse, K., Lu, T., and Wang, J. (2019), "Nonequilibrium physics in biology," Rev. Mod. Phys. **91** (4), 045004.

Feller, W. (1954), "The General Diffusion Operator and Positivity Preserving Semi-Groups in One Dimension," ANN MATH **60** (3), 417–436.

Feller, W. (1991a), *An Introduction to Probability Theory and Its Applications, Vol. 1*, 3rd ed. (Wiley, S.l.).

Feller, W. (1991b), *An Introduction to Probability Theory and Its Applications, Vol. 2*, 2nd ed. (John Wiley & Sons, Inc., New York).

Feng, H., and Wang, J. (2011), "Potential and flux decomposition for dynamical systems and non-equilibrium thermodynamics: Curvature, gauge field, and generalized fluctuation-dissipation theorem," J. Chem. Phys. **135** (23), 234511.

Fisher, R. A. (2000), *The Genetical Theory of Natural Selection: A Complete Variorum Edition* (Oxford University Press, Oxford, New York).

Fortney, J. P. (2018), *A Visual Introduction to Differential Forms and Calculus on Manifolds* (Birkhäuser Basel).

Freidlin, M. I., and Wentzell, A. D. (2012), *Random Perturbations of Dynamical Systems*, 3rd ed., Grundlehren der mathematischen Wissenschaften (Springer-Verlag, Berlin Heidelberg).

Friston, K. (2010), "The free-energy principle: a unified brain theory?" Nat Rev Neurosci **11** (2), 127–138.

Friston, K. (2013), "Life as we know it," J. R. Soc. Interface **10** (86), 20130475.

García-García, R., Lecomte, V., Kolton, A. B., and Domínguez, D. (2012), "Joint probability distributions and fluctuation theorems," J. Stat. Mech. **2012** (02), P02009.

Gardiner, C. (2009), *Stochastic Methods: A Handbook for the Natural and Social Sciences*, 4th ed., Springer Series in Synergetics (Springer-Verlag, Berlin Heidelberg).

Gärtner, J. (1977), "On Large Deviations from the Invariant Measure," Theory Probab. Appl. **22** (1), 24–39.

Ge, H. (2009), "Extended forms of the second law for general time-dependent stochastic processes," Phys. Rev. E **80** (2), 021137.

Ge, H. (2014), "Time reversibility and nonequilibrium thermodynamics of second-order stochastic processes," Phys. Rev. E **89** (2), 022127.

Ge, H., and Jiang, D.-Q. (2007), "The transient fluctuation theorem of sample entropy production for general stochastic processes," J. Phys. A: Math. Theor. **40** (30), F713–F723.

Ge, H., Jiang, D.-Q., and Qian, M. (2006), "Reversibility and Entropy Production of Inhomogeneous Markov Chains," J. Appl. Probab. **43** (4), 1028–1043.

Ge, H., Pressé, S., Ghosh, K., and Dill, K. A. (2012), "Markov processes follow from the principle of maximum caliber," J. Chem. Phys **136** (6), 064108.

Ge, H., and Qian, H. (2010), "Physical origins of entropy production, free energy dissipation, and their mathematical representations," Phys. Rev. E **81** (5), 051133.

Ge, H., and Qian, H. (2012a), "Analytical mechanics in stochastic dynamics: most probable path, large-deviation rate function and hamilton-jacobi equation," Int. J. Mod. Phys. B **26** (24), 1230012.

Ge, H., and Qian, H. (2012b), "Landscapes of non-gradient dynamics without detailed balance: Stable limit cycles and multiple attractors," Chaos **22** (2), 023140.

Ge, H., and Qian, M. (2007), "Generalized Jarzynski equality in inhomogeneous Markov chains," J. Math. Phys. **48** (5), 053302.

de Gennes, P. G. (1997), "Molecular Individualism," Science **276** (5321), 1999–1999.

Gerstner, W., Kistler, W. M., Naud, R., and Paninski, L. (2014), *Neuronal Dynamics: From Single Neurons to Networks and Models of Cognition*, 1st ed. (Cambridge University Press).

Ghosh, K., Dixit, P. D., Agozzino, L., and Dill, K. A. (2020), "The Maximum Caliber Variational Principle for Nonequilibria," Annu. Rev. Phys. Chem. **71** (1), 213–238.

Gingrich, T. R., Horowitz, J. M., Perunov, N., and England, J. L. (2016), "Dissipation Bounds All Steady-State Current Fluctuations," Phys. Rev. Lett. **116** (12), 120601.

Goldberg, A. D., Allis, C. D., and Bernstein, E. (2007), "Epigenetics: A Landscape Takes Shape," Cell **128** (4), 635–638.

Goldt, S., and Seifert, U. (2017), "Stochastic Thermodynamics of Learning," Phys. Rev. Lett. **118** (1), 010601.

Graham, R. (1977a), "Covariant formulation of non-equilibrium statistical thermodynamics," Z Physik B **26** (4), 397–405.

Graham, R. (1977b), "Path integral formulation of general diffusion processes," Z Physik B **26** (3), 281–290.

Graham, R., and Schenzle, A. (1983), "Non-equilibrium potentials and stationary probability distributions of some dissipative models without manifest detailed balance," Z. Physik B **52** (1), 61–68.

Green, M. S. (1954), "Markoff Random Processes and the Statistical Mechanics of Time-Dependent Phenomena. II. Irreversible Processes in Fluids," J. Chem. Phys. **22** (3), 398–413.

Grimmett, G. R., and Stirzaker, D. R. (2001), *Probability and Random Processes*, 3rd ed. (Oxford University Press, Oxford ; New York).

Groot, S. R. D., and Mazur, P. (2011), *Non-Equilibrium Thermodynamics*, dover ed edition ed. (Dover Publications, New York).

Hairer, M. (2009), "An Introduction to Stochastic PDEs," arXiv:0907.4178 [math] .

Haken, H. (1978), *Synergetics: An Introduction Nonequilibrium Phase Transitions and Self-Organization in Physics, Chemistry and Biology*, 2nd ed., Springer Series in Synergetics (Springer-Verlag, Berlin Heidelberg).

Hill, T. L. (1977), *Free Energy Transduction in Biology: The Steady-State Kinetic and Thermodynamic Formalism* (Academic Press).

Hill, T. L. (1982), "The linear Onsager coefficients for biochemical kinetic diagrams as equilibrium one-way cycle fluxes," Nature **299** (5878), 84.

Hill, T. L. (1989), *Free Energy Transduction and Biochemical Cycle Kinetics* (Springer-Verlag, New York).

Hill, T. L. (2013), *Thermodynamics of Small Systems, Parts I & II* (Dover Publications, Mineola, New York).

Hill, T. L., and Chen, Y. D. (1975), "Stochastics of cycle completions (fluxes) in biochemical kinetic diagrams," Proc. Natl. Acad. Sci. U.S.A. **72** (4), 1291–1295.

Hong, L., and Qian, H. (2021), "Stochastic dynamics, large deviation principle, and nonequilibrium thermodynamics," Phys. Rev. E **104** (4), 044113.

Hong, L., Qian, H., and Thompson, L. F. (2020), "Representations and divergences in the space of probability measures and stochastic thermodynamics," J Comput Appl Math **376**, 112842.

Hopfield, J. J. (1982), "Neural networks and physical systems with emergent collective computational abilities," Proc. Natl. Acad. Sci. U.S.A. **79** (8), 2554–2558.

Hopfield, J. J. (1994), "Physics, Computation, and Why Biology Looks so Different," J. Theor. Biol. **171** (1), 53–60.

Horowitz, J. M., and Gingrich, T. R. (2020), "Thermodynamic uncertainty relations constrain non-equilibrium fluctuations," Nat Phys **16** (1), 15–20.

Hu, W., and Qian, H. (2022), "On the Posterior Distribution of a Random Process Conditioned on Empirical Frequencies of a Finite Path: the i.i.d and finite Markov chain case," arXiv:2202.11780 .

Huang, K. (1991), *Statistical Mechanics*, 2nd ed. (Wiley, New York).

Huang, S., Li, F., Zhou, J. X., and Qian, H. (2017), "Processes on the emergent landscapes of biochemical reaction networks and heterogeneous cell population dynamics: differentiation in living matters," J R Soc Interface **14** (130), 10.1098/rsif.2017.0097.

Ito, S. (2018), "Stochastic Thermodynamic Interpretation of Information Geometry," Phys. Rev. Lett. **121** (3), 030605.

Ito, S., and Dechant, A. (2020), "Stochastic Time Evolution, Information Geometry, and the Cramer-Rao Bound," Phys. Rev. X **10** (2), 021056.

Izhikevich, E. M. (2010), *Dynamical Systems in Neuroscience: The Geometry of Excitability and Bursting* (The MIT Press).

Jan, Y. L. (2010), "Markov loops and renormalization," Ann. Probab. **38** (3), 1280–1319.

Jarzynski, C. (1997), "Nonequilibrium Equality for Free Energy Differences," Phys. Rev. Lett. **78** (14), 2690–2693.

Jarzynski, C. (2015), "Diverse phenomena, common themes," Nat Phys **11** (2), 105–107.

Jaynes, E. T. (1957), "Information Theory and Statistical Mechanics," Phys. Rev. **106** (4), 620–630.

Jaynes, E. T. (1980), "The Minimum Entropy Production Principle," Annu. Rev. Phys. Chem. **31** (1), 579–601.

Jaynes, E. T. (2003), *Probability Theory: The Logic of Science*, 1st ed. (Cambridge University Press, Cambridge, UK ; New York, NY).

Jiang, D.-Q., Qian, M., and Qian, M.-P. (2004), *Mathematical Theory of Nonequilibrium Steady States: On the Frontier of Probability and Dynamical Systems*, 2004th ed. (Springer, Berlin ; New York).

Jiang, Y., Wu, B., and Jia, C. (2022), "Large deviations and fluctuation theorems for cycle currents defined in the loop-erased and spanning tree manners: a comparative study," arXiv:2204.01948 .

Jizba, P., and Korbel, J. (2019), "Maximum Entropy Principle in Statistical Inference: Case for Non-Shannonian Entropies," Phys. Rev. Lett. **122** (12), 120601.

Kalpazidou, S. L. (2006), *Cycle Representations of Markov Processes*, 2nd ed. (Springer, New York).

Kamenev, A. (2011), *Field Theory of Non-Equilibrium Systems*, illustrated edition ed. (Cambridge University Press, Cambridge ; New York).

Kampen, N. G. V. (2007), *Stochastic Processes in Physics and Chemistry*, 3rd ed. (North Holland, Amsterdam ; Boston).

Kaneko, K. (2006), *Life: An Introduction to Complex Systems Biology*, 2006th ed. (Springer, Berlin ; New York).

Keizer, J. (1987), *Statistical Thermodynamics of Nonequilibrium Processes* (Springer-Verlag, New York).

Khinchin, A. Y. (1957), *Mathematical Foundations of Information Theory*, 1st ed. (Dover Publications, Mineola, N.Y).

Kinouchi, O., and Copelli, M. (2006), "Optimal dynamical range of excitable networks at criticality," Nat Phys **2** (5), 348–351.

Kirkwood, J. G. (1935), "Statistical Mechanics of Fluid Mixtures," J. Chem. Phys **3** (5), 300–313.

Kolmogorov, A. (1936), "Zur Theorie der Markoffschen Ketten," Math. Ann. **112** (1), 155–160, (In German).

Kolmogorov, A. N. (2018), *Foundations of the Theory of Probability*, 2nd ed. (Dover Publications, Muneola, New York).

Koopman, B. O. (1936), "On distributions admitting a sufficient statistic," Trans. Amer. Math. Soc. **39** (3), 399–409.

Kot, M. (2001), *Elements of Mathematical Ecology*, 1st ed. (Cambridge University Press, Cambridge ; New York, NY).

Kubo, R. (1966), "The fluctuation-dissipation theorem," Rep. Prog. Phys. **29** (1), 255–284.

Kubo, R., Matsuo, K., and Kitahara, K. (1973), "Fluctuation and relaxation of macrovariables," J Stat Phys **9** (1), 51–96.

Kullback, S., and Leibler, R. A. (1951), "On Information and Sufficiency," Ann. Math. Stat. **22** (1), 79–86.

Kurchan, J. (1998), "Fluctuation theorem for stochastic dynamics," J. Phys. A: Math. Gen. **31** (16), 3719–3729.

Kwon, C., Ao, P., and Thouless, D. J. (2005), "Structure of stochastic dynamics near fixed points," Proc. Natl. Acad. Sci. U.S.A. **102** (37), 13029–13033.

Lambert, N., Chen, Y.-N., Cheng, Y.-C., Li, C.-M., Chen, G.-Y., and Nori, F. (2013), "Quantum biology," Nat Phys **9** (1), 10–18.

Lan, G., Sartori, P., Neumann, S., Sourjik, V., and Tu, Y. (2012), "The energy-speed-accuracy tradeoff in sensory adaptation," Nat Phys **8** (5), 422–428.

Landau, L. D., and Lifshitz, E. M. (1980), *Statistical Physics, Third Edition, Part 1: Volume 5*, 3rd ed. (Butterworth-Heinemann, Amsterdam u.a).

Landauer, R. (1961), "Irreversibility and Heat Generation in the Computing Process," IBM J Res Dev **5** (3), 183–191.

Landi, G. T., and Paternostro, M. (2021), "Irreversible entropy production: From classical to quantum," Rev. Mod. Phys. **93** (3), 035008.

Lang, A. H., Fisher, C. K., Mora, T., and Mehta, P. (2014), "Thermodynamics of Statistical Inference by Cells," Phys. Rev. Lett. **113** (14), 148103.

Lasota, A., and Mackey, M. C. (1994), *Chaos, Fractals, and Noise: Stochastic Aspects of Dynamics*, 2nd ed., Applied Mathematical Sciences (Springer-Verlag, New York).

Laughlin, R. B. (2006), *A Different Universe: Reinventing Physics from the Bottom Down* (Basic Books, New York, NY).

Lebowitz, J. L., and Spohn, H. (1999), "A Gallavotti-Cohen-Type Symmetry in the Large Deviation Functional for Stochastic Dynamics," J Stat Phys **95** (1), 333–365.

Lessard, S. (1997), "Fisher's Fundamental Theorem of Natural Selection Revisited," Theor. Popul. Biol. **52** (2), 119–136.

Lewis, G. N. (1925), "A New Principle of Equilibrium," Proc. Natl. Acad. Sci. U.S.A. **11** (3), 179–183.

Li, G., and Tu, Z. C. (2019), "Stochastic thermodynamics with odd controlling parameters," Phys. Rev. E **100** (1), 012127.

Lorig, M. (2019), *Introduction to Probability and Stochastic Processes*, lecture Note for Amath 561 and 562 at University of Washington.

Lu, Z., and Qian, H. (2022), "Emergence and Breaking of Duality Symmetry in Generalized Fundamental Thermodynamic Relations," Phys. Rev. Lett. **128** (15), 150603.

Maes, C. (2004), "On the Origin and the Use of Fluctuation Relations for the Entropy," in *Poincare Seminar 2003*, Progress in Mathematical Physics, Vol. 38 (Birkhäuser Verlag) p. 145.

Maes, C. (2020), "Frenesy: Time-symmetric dynamical activity in nonequilibria," Phys. Rep. **850**, 1–33.

Maes, C., and Netočný, K. (2003), "Time-Reversal and Entropy," J. Stat. Phys. **110** (1), 269–310.

Maes, C., and Netočný, K. (2008), "Canonical structure of dynamical fluctuations in mesoscopic nonequilibrium steady states," EPL **82** (3), 30003.

Maes, C., Netočný, K., and Wynants, B. (2008), "Steady state statistics of driven diffusions," Physica A **387** (12), 2675–2689.

Mandelbrot, B. (1964), "On the Derivation of Statistical Thermodynamics from Purely Phenomenological Principles," J. Math. Phys. **5** (2), 164–171.

Mandelbrot, B. B. (1989), "Temperature Fluctuation: A Well-Defined and Unavoidable Notion," Phys. Today **42** (1), 71.

Manzano, G., Subero, D., Maillet, O., Fazio, R., Pekola, J. P., and Roldán, E. (2021), "Thermodynamics of Gambling Demons," Phys. Rev. Lett. **126** (8), 080603.

Meyer, P. A. (1962), "A decomposition theorem for supermartingales," Ill. J. Math. **6** (2), 193–205.

Meyer, P. A. (1963), "Decomposition of supermartingales: The uniqueness theorem," Ill. J. Math. **7** (1), 1–17.

Milz, S., and Modi, K. (2021), "Quantum Stochastic Processes and Quantum non-Markovian Phenomena," PRX Quantum **2** (3), 030201.

Monod, J. (1972), *Chance and Necessity: An Essay on the Natural Philosophy of Modern Biology*, no additional printings listed edition ed. (Vintage Books, New York).

Monthus, C. (2011), "Non-equilibrium steady states: maximization of the Shannon entropy associated with the distribution of dynamical trajectories in the presence of constraints," J. Stat. Mech. **2011** (03), P03008.

Muñoz, M. A. (2018), "Colloquium: Criticality and dynamical scaling in living systems," Rev. Mod. Phys. **90** (3), 031001.

Murray, J. D. (2003), *Mathematical Biology II: Spatial Models and Biomedical Applications*, 3rd ed. (Springer, New York).

Murray, J. D. (2007), *Mathematical Biology: I. An Introduction*, 3rd ed. (Springer, New York).

Mustonen, V., and Lässig, M. (2010), "Fitness flux and ubiquity of adaptive evolution," Proc. Natl. Acad. Sci. U.S.A. **107** (9), 4248–4253.

Nagasawa, M. (2000), *Stochastic Processes in Quantum Physics*, Monographs in Mathematics (Birkhäuser Basel).

Neri, I., Roldán, E., and Jülicher, F. (2017), "Statistics of Infima and Stopping Times of Entropy Production and Applications to Active Molecular Processes," Phys. Rev. X **7** (1), 011019.

Nicholson, S. B., del Campo, A., and Green, J. R. (2018), "Nonequilibrium uncertainty principle from information geometry," Phys. Rev. E **98** (3), 032106.

Nicholson, S. B., García-Pintos, L. P., del Campo, A., and Green, J. R. (2020), "Time-information uncertainty relations in thermodynamics," Nat Phys , 1–5.

Nicolis, G., and Lefever, R. (1977), "Comment on the kinetic potential and the maxwell construction in non-equilibrium chemical phase transitions," Phys. Lett. A **62** (7), 469–471.

Nicolis, G., and Prigogine, I. (1977), *Self-Organization in Nonequilibrium Systems: From Dissipative Structures to Order through Fluctuations*, 1st ed. (Wiley, New York).

Nolting, B. C., and Abbott, K. C. (2015), "Balls, cups, and quasi-potentials: quantifying stability in stochastic systems," Ecology , 15–1047.1.

Nutz, M. (2012), "Pathwise construction of stochastic integrals," Electron. Commun. Probab. **17**, 10.1214/ECP.v17-2099.

Ohga, N., and Ito, S. (2021), "Information-geometric Legendre duality in stochastic thermodynamics," arXiv:2112.11008 .

Onsager, L. (1931), "Reciprocal Relations in Irreversible Processes. I." Phys. Rev. **37** (4), 405–426.

Onsager, L., and Machlup, S. (1953), "Fluctuations and Irreversible Processes," Phys. Rev. **91** (6), 1505–1512.

Onuchic, J. N., Luthey-Schulten, Z., and Wolynes, P. G. (1997), "Theory of protein folding: the energy landscape perspective," Annu. Rev. Phys. Chem. **48** (1), 545–600.

Oono, Y. (2013), *The Nonlinear World: Conceptual Analysis and Phenomenology*, Springer Series in Synergetics (Springer Japan).

Parrondo, J. M. R., Horowitz, J. M., and Sagawa, T. (2015), "Thermodynamics of information," Nat Phys **11** (2), 131–139.

Pigolotti, S., Neri, I., Roldán, E., and Jülicher, F. (2017), "Generic Properties of Stochastic Entropy Production," Phys. Rev. Lett. **119** (14), 140604.

Pitman, E. J. G. (1936), "Sufficient statistics and intrinsic accuracy," Math. Proc. Camb. Philos. Soc. **32** (4), 567–579.

Polettini, M. (2012), "Nonequilibrium thermodynamics as a gauge theory," EPL **97** (3), 30003.

Polettini, M., Falasco, G., and Esposito, M. (2021), "Tight uncertainty relations for cycle currents," arXiv:2106.00425 .

Pressé, S., Ghosh, K., Lee, J., and Dill, K. A. (2013a), "Nonadditive Entropies Yield Probability Distributions with Biases not Warranted by the Data," Phys. Rev. Lett. **111** (18), 180604.

Pressé, S., Ghosh, K., Lee, J., and Dill, K. A. (2013b), "Principles of maximum entropy and maximum caliber in statistical physics," Rev. Mod. Phys. **85** (3), 1115–1141.

Pressé, S., Ghosh, K., Lee, J., and Dill, K. A. (2015), "Reply to C. Tsallis' "Conceptual Inadequacy of the Shore and Johnson Axioms for Wide Classes of Complex Systems"," Entropy **17** (7), 5043–5046.

Price, G. R. (1970), "Selection and Covariance," Nature **227** (5257), 520–521.

Prigogine, I. (1997), *The End of Certainty*, 1st ed. (Free Press, New York).

Prost, J., Joanny, J.-F., and Parrondo, J. M. R. (2009), "Generalized Fluctuation-Dissipation Theorem for Steady-State Systems," Phys. Rev. Lett. **103** (9), 090601.

Qian, H. (1998), "Vector Field Formalism and Analysis for a Class of Thermal Ratchets," Phys. Rev. Lett. **81** (15), 3063–3066.

Qian, H. (2001a), "Mathematical formalism for isothermal linear irreversibility," Proc. Math. Phys. Eng. Sci. **457** (2011), 1645–1655.

Qian, H. (2001b), "Mesoscopic nonequilibrium thermodynamics of single macromolecules and dynamic entropy-energy compensation," Phys. Rev. E **65** (1), 016102.

Qian, H. (2001c), "Relative entropy: Free energy associated with equilibrium fluctuations and nonequilibrium deviations," Phys. Rev. E **63** (4), 042103.

Qian, H. (2007), "Phosphorylation Energy Hypothesis: Open Chemical Systems and Their Biological Functions," Annu. Rev. Phys. Chem. **58** (1), 113–142.

Qian, H. (2013), "A decomposition of irreversible diffusion processes without detailed balance," J. Math. Phys. **54** (5), 053302.

Qian, H. (2014a), "Fitness and entropy production in a cell population dynamics with epigenetic phenotype switching," Quant Biol **2** (1), 47–53.

Qian, H. (2014b), "The zeroth law of thermodynamics and volume-preserving conservative system in equilibrium with stochastic damping," Phys. Lett. A **378** (7), 609–616.

Qian, H. (2015), "Thermodynamics of the general diffusion process: Equilibrium supercurrent and nonequilibrium driven circulation with dissipation," Eur. Phys. J. Spec. Top. **224** (5), 781–799.

Qian, H. (2018), "Chemical reaction kinetic perspective with mesoscopic nonequilibrium thermodynamics," in *Complexity Science* (WORLD SCIENTIFIC) pp. 347–373.

Qian, H. (2021), "Thermodynamic Behavior of Statistical Event Counting in Time: Independent and Correlated Measurements," arXiv:2109.12806 .

Qian, H., Ao, P., Tu, Y., and Wang, J. (2016a), "A framework towards understanding mesoscopic phenomena: Emergent unpredictability, symmetry breaking and dynamics across scales," Chem. Phys. Lett. **665**, 153–161.

Qian, H., and Cheng, Y.-C. (2020), "Counting single cells and computing their heterogeneity: from phenotypic frequencies to mean value of a quantitative biomarker," Quant Biol **8** (2), 172–176.

Qian, H., Cheng, Y.-C., and Thompson, L. F. (2019), "Ternary Representation of Stochastic Change and the Origin of Entropy and Its Fluctuations," arXiv:1902.09536 .

Qian, H., Cheng, Y.-C., and Yang, Y.-J. (2020), "Kinematic basis of emergent energetics of complex dynamics," EPL **131** (5), 50002.

Qian, H., and Ge, H. (2021), *Stochastic Chemical Reaction Systems in Biology*, 1st ed. (Springer, Switzerland, Cham).

Qian, H., Kjelstrup, S., Kolomeisky, A. B., and Bedeaux, D. (2016b), "Entropy production in mesoscopic stochastic thermodynamics: nonequilibrium kinetic cycles driven by chemical potentials, temperatures, and mechanical forces," J. Phys.: Condens. Matter **28** (15), 153004.

Qian, M., and Wang, Z.-d. (1999), "The Entropy Production of Diffusion Processes on Manifolds and Its Circulation Decompositions," Commun. Math. Phys. **206**, 429–445.

Qian, M.-P., and Qian, M. (1979), "The decomposition into a detailed balance part and a circulation part of an irreversible stationary Markov chain." Sci. Sinica Special Issue II on Math , 69–79.

Qian, M.-P., and Qian, M. (1982), "Circulation for recurrent markov chains," Z. Wahrscheinlichkeitstheorie verw Gebiete **59** (2), 203–210.

Rao, R., and Esposito, M. (2018), "Detailed Fluctuation Theorems: A Unifying Perspective," Entropy **20** (9), 635.

Reguera, D., Rubí, J. M., and Vilar, J. M. G. (2005), "The Mesoscopic Dynamics of Thermodynamic Systems," J. Phys. Chem. B **109** (46), 21502–21515.

Riechers, P. M., and Crutchfield, J. P. (2017), "Fluctuations When Driving Between Nonequilibrium Steady States," J Stat Phys **168** (4), 873–918.

Rodríguez, M. A., Gallego, R., and Wio, H. S. (2021), "Stochastic entropies and fluctuation theorems for a generic 1D KPZ system: Internal and external dynamics," EPL **136** (5), 58005.

Ruppeiner, G. (1995), "Riemannian geometry in thermodynamic fluctuation theory," Rev. Mod. Phys. **67** (3), 605–659.

Sajid, N., Ball, P. J., Parr, T., and Friston, K. J. (2021), "Active Inference: Demystified and Compared," Neural Comput. **33** (3), 674–712.

Sanov, I. N. (1958), "On the probability of large deviations of random variables," Mat. Sbornik 1, **42** (84), 11–44.

Schlögl, F. (1988), "Thermodynamic uncertainty relation," J. Phys. Chem. Solids **49** (6), 679–683.

Schnakenberg, J. (1976), "Network theory of microscopic and macroscopic behavior of master equation systems," Rev. Mod. Phys. **48** (4), 571–585.

Schrödinger, E. (1944), "The Statistical Law in Nature," Nature **153** (3893), 704–705.

Schrödinger/Penrose, E. (2012), *What is Life?: With Mind and Matter and Autobiographical Sketches*, reprint edition ed. (Cambridge University Press, Cambridge ; New York).

Searles, D. J., and Evans, D. J. (1999), "Fluctuation theorem for stochastic systems," Phys. Rev. E **60** (1), 159–164.

Seifert, U. (2005), "Entropy Production along a Stochastic Trajectory and an Integral Fluctuation Theorem," Phys. Rev. Lett. **95** (4), 040602.

Seifert, U. (2012), "Stochastic thermodynamics, fluctuation theorems and molecular machines," Rep. Prog. Phys. **75** (12), 126001.

Seifert, U. (2019), "From Stochastic Thermodynamics to Thermodynamic Inference," Annu. Rev. Condens. Matter Phys. **10** (1), 171–192.

Seifert, U., and Speck, T. (2010), "Fluctuation-dissipation theorem in nonequilibrium steady states," EPL **89** (1), 10007.

Sekimoto, K. (2010), *Stochastic Energetics*, 2010th ed. (Springer, Heidelberg ; New York).

Shannon, C. E. (1948), "A Mathematical Theory of Communication," Bell Syst. Tech. **27** (3), 379–423.

Shargel, B. H. (2010), "The measure-theoretic identity underlying transient fluctuation theorems," J. Phys. A: Math. Theor. **43** (13), 135002.

Shi, J., Chen, T., Yuan, R., Yuan, B., and Ao, P. (2012), "Relation of a New Interpretation of Stochastic Differential Equations to Ito Process," J Stat Phys **148** (3), 579–590.

Shore, J., and Johnson, R. (1980), "Axiomatic derivation of the principle of maximum entropy and the principle of minimum cross-entropy," IEEE Trans. Inf. Theor. **26** (1), 26–37.

Shreve, S. (2010), *Stochastic Calculus for Finance II: Continuous-Time Models* (Springer, New York, NY).

Smith, E. (2011), "Large-deviation principles, stochastic effective actions, path entropies, and the structure and meaning of thermodynamic descriptions," Rep. Prog. Phys. **74** (4), 046601.

Smith, E. (2019), "The information geometry of 2-field functional integrals," arXiv:1906.09312 .

Spinney, R. E., and Ford, I. J. (2012), "Nonequilibrium Thermodynamics of Stochastic Systems with Odd and Even Variables," Phys. Rev. Lett. **108** (17), 170603.

Still, S. (2020), "Thermodynamic Cost and Benefit of Memory," Phys. Rev. Lett. **124** (5), 050601.

Still, S., Sivak, D. A., Bell, A. J., and Crooks, G. E. (2012), "Thermodynamics of Prediction," Phys. Rev. Lett. **109** (12), 120604.

Strogatz, S. H. (2018), *Nonlinear Dynamics and Chaos: With Applications to Physics, Biology, Chemistry, and Engineering* (CRC Press).

Szilard, L. (1929), "Über die Ausdehnung der phanomenologischen Thermodynamik auf die Schewankungserscheinungen," Z. Phys. **32**, 840–856.

Takahashi, Y., and Watanabe, S. (1981), "The probability functionals (Onsager-machlup functions) of diffusion processes," in *Stochastic Integrals*, Lecture Notes in Mathematics, edited by D. Williams (Springer, Berlin, Heidelberg) pp. 433–463.

Thompson, L. F., and Qian, H. (2016), "Nonlinear Stochastic Dynamics of Complex Systems, II: Potential of Entropic Force in Markov Systems with Nonequilibrium Steady State, Generalized Gibbs Function and Criticality," Entropy **18** (8), 309.

Tkačik, G., Mora, T., Marre, O., Amodei, D., Palmer, S. E., Berry, M. J., and Bialek, W. (2015), "Thermodynamics and signatures of criticality in a network of neurons," Proc. Natl. Acad. Sci. U.S.A. **112** (37), 11508–11513.

Touchette, H. (2009), "The large deviation approach to statistical mechanics," Phys. Rep. **478** (1), 1–69.

Tripathi, G. (1999), "A matrix extension of the Cauchy-Schwarz inequality," Econ. Lett. **63** (1), 1–3.

Tsallis, C. (2015), "Conceptual Inadequacy of the Shore and Johnson Axioms for Wide Classes of Complex Systems," Entropy **17** (5), 2853–2861.

Tung, K. K. (2007), *Topics in Mathematical Modeling*, 1st ed. (Princeton University Press, Princeton, N.J).

Uffink, J. (1995), "Can the maximum entropy principle be explained as a consistency requirement?" Stud. Hist. Philos. Sci. B **26** (3), 223–261.

Uffink, J., and van Lith, J. (1999), "Thermodynamic Uncertainty Relations," Found. Phys. **29** (5), 655–692.

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. U.S.A. **105** (34), 12271–12276.

Wang, Y., and Qian, H. (2020), "Mathematical Representation of Clausius' and Kelvin's Statements of the Second Law and Irreversibility," J Stat Phys **179** (3), 808–837.

Wegscheider, R. (1901), "Über simultane Gleichgewichte und die Beziehungen zwischen Thermodynamik und Reactionskinetik homogener Systeme," Monatsh. Chem. **22** (8), 849–906.

Wojtkowski, M. P. (2009), "Abstract fluctuation theorem," Ergod. Th. Dynam. Sys. **29** (1), 273–279.

Wolpert, D. H. (2019), "The stochastic thermodynamics of computation," J. Phys. A: Math. Theor. **52** (19), 193001.

Wu, A. C. T., and Yang, C. N. (2006), "Evolution of the concept of the vector potential in the description of fundamental interactions," Int. J. Mod. Phys. A **21** (16), 3235–3277.

Yan, H., Zhao, L., Hu, L., Wang, X., Wang, E., and Wang, J. (2013), "Nonequilibrium landscape theory of neural networks," Proc. Natl. Acad. Sci. U.S.A. **110** (45), E4185–E4194.

Yang, C. N. (1996), "Symmetry and Physics," Proc Am Philos Soc **140** (3), 267–288.

Yang, Y.-J., Chen, C.-C., Lai, P.-Y., and Chan, C. K. (2015), "Adaptive synchronization and anticipatory dynamical systems," Phys. Rev. E **92** (3), 030701.

Yang, Y.-J., and Cheng, Y.-C. (2021), "Potentials of continuous Markov processes and random perturbations," J. Phys. A: Math. Theor. **54** (19), 195001.

Yang, Y.-J., and Qian, H. (2020), "Unified formalism for entropy production and fluctuation relations," Phys. Rev. E **101** (2), 022129.

Yang, Y.-J., and Qian, H. (2021a), "Bivectorial Nonequilibrium Thermodynamics: Cycle Affinity, Vorticity Potential, and Onsager's Principle," J Stat Phys **182** (3), 46.

Yang, Y.-J., and Qian, H. (2021b), "Nonequilibrium Stationary Process and Fluctuation-Dissipation Relations," arXiv:2106.13374 .

Yang, Y.-J., and Qian, H. (2022), "Statistical Thermodynamics and Data Infinitum: Conjugate Variables as Forces, and their Statistical Variations," arXiv:2205.09321 .

Yin, L., and Ao, P. (2006), "Existence and construction of dynamical potential in nonequilibrium processes without detailed balance," J. Phys. A: Math. Gen. **39** (27), 8593–8601.

Zeitouni, O. (1989), "On the Onsager-Machlup Functional of Diffusion Processes Around Non C2 Curves," Ann. Probab. **17** (3), 1037–1054.

Zeng, Q., and Wang, J. (2017), "Information Landscape and Flux, Mutual Information Rate Decomposition and Connections to Entropy Production," Entropy **19** (12), 678.

Zhang, X.-J., Qian, H., and Qian, M. (2012), "Stochastic theory of nonequilibrium steady states and its applications. Part I," Phys. Rep. **510** (1-2), 1–86.

Zhou, P., and Li, T. (2016), "Construction of the landscape for multi-stable systems: Potential landscape, quasi-potential, A-type integral and beyond," J. Chem. Phys. **144** (9), 094109.

Zhu, X.-M., Yin, L., and Ao, P. (2006), "Limit cycle and conserved dynamics," Int. J. Mod. Phys. B **20** (07), 817–827.

Zwanzig, R. (1965), "Time-Correlation Functions and Transport Coefficients in Statistical Mechanics," Annu. Rev. Phys. Chem. **16** (1), 67–102.

Zwanzig, R. (2001), *Nonequilibrium Statistical Mechanics*, illustrated edition ed. (Oxford University Press, Oxford ; New York).