Doctoral Dissertation
博士論文

Universal geometric structure in nonequilibrium thermodynamics
（非平衡系の熱力学理論において普遍的に現れる幾何学構造の研究）

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Abstract

Equilibrium thermodynamics is a universal theory that applies to every macroscopic system in equilibrium. Although there have been nonequilibrium analogues to various classes of systems, ranging from classical to quantum and mesoscopic to macroscopic, unifying viewpoints are still missing. In this thesis, we explore a general characterization of some aspects of nonequilibrium thermodynamics. We develop a general framework that especially features the entropy production and reveal its physical consequences. The framework, which we call the force-current structure, is composed of three relations that relate dynamics and entropy production. Employing it, we derive two important results generically: the geometric housekeeping-excess decomposition of entropy production and thermodynamic trade-off relations. The housekeeping-excess decomposition provides a precise understanding of irreversibility evaluated by entropy production by splitting it into two contributions from two distinct aspects in nonequilibrium processes. The geometric nature of the force-current structure enables us to formulate the decomposition by the projection of thermodynamic forces, which exhibits higher generality than conventional methods. We also derive thermodynamic trade-off relations, which are inequalities tightening the second law of thermodynamics and reveal that the entropy production is a fundamental cost in nonequilibrium processes. We especially discuss trade-offs between the entropy production and accuracy or speed. The framework and its consequences are applicable to various kinds of systems with local equilibrium; in this thesis, we deal with overdamped Langevin systems, Markov jump processes, chemical reaction networks, hydrodynamic systems, and Markovian open quantum systems.

List of publications

This thesis is based on the following published papers and preprints.

1. Kohei Yoshimura, Yoh Maekawa, Ryuna Nagayama, and Sosuke Ito, “Force-current structure in Markovian open quantum systems and its applications: geometric housekeeping-excess decomposition and thermodynamic trade-off relations” (arXiv:2410.22628)

2. Kohei Yoshimura and Sosuke Ito, “Two applications of stochastic thermodynamic to hydrodynamics”, Physical Review Research **6**(2), L022057 (2024)

3. Kohei Yoshimura, Artemy Kolchinsky, Andreas Dechant, and Sosuke Ito, “Housekeeping and excess entropy production for general nonlinear dynamics”, Physical Review Research **5**(1), 013017 (2023)

The following papers are related but not claimed in this thesis.

1. Ryuna Nagayama, Kohei Yoshimura, Artemy Kolchinsky, and Sosuke Ito, “Geometric thermodynamics of reaction–diffusion systems: Thermodynamic trade-off relations and optimal transport for pattern formation” (arXiv:2311.16569)

2. Masahiro Hoshino, Ryuna Nagayama, Kohei Yoshimura, Jumpei F. Yamagishi, and Sosuke Ito, “Geometric speed limit for acceleration by natural selection in evolutionary processes”, Physical Review Research **5**(2), 023127 (2023)

3. Artemy Kolchinsky, Andreas Dechant, Kohei Yoshimura, and Sosuke Ito, “Information geometry of excess and housekeeping entropy production” (arXiv:2206.14599)

4. Kohei Yoshimura and Sosuke Ito, “Thermodynamic uncertainty relation and thermodynamic speed limit in deterministic chemical reaction networks”, Physical Review Letters **127**, 160601 (2021)

5. Kohei Yoshimura and Sosuke Ito, “Information geometric inequalities of chemical thermodynamics”, Physical Review Research **3**(1), 013175 (2021)

Contents

Part I

Foundations

Chapter 1

Introduction

Thermodynamics tells us what we can do and cannot do in a universal way. Classical equilibrium thermodynamics describes systems in equilibrium states and quantifies the irreversibility of transisions between equilibrium states with entropy. Researchers have explored a universal theory like the equilibrium thermodynamics for a century, and have partially succeeded in establishing it in systems out of equilibrium; one example is chemical thermodynamics. In general, a chemical reaction system can be out of chemical equilibrium, that is, forward and backward reactions are not necessarily balanced. In this sense, the system is nonequilibrium. Nonetheless, chemical thermodynamics has proven that we can discuss irreversibility with thermodynamic concepts such as free energy [1–3]. This owes to the surrounding environment (solvent), which can be regarded as always staying in an equilibrium state. As a result, we can define thermodynamic quantities and find relationship between the phenomenological dynamics of chemical reactions and thermodynamics.

The situation is similar in a state-of-the-art theory of mesoscopic systems, called *stochastic thermodynamics* [4–9]. For example, when we put colloidal particles at a single point in water, the ensemble of the system (in the sense of statistical mechanics) is out of equilibrium. After a long time, the particles diffuse and the system reaches an equilibrium ensemble. In stochastic thermodynamics, we can discuss mesoscopic nonequilibrium processes like this diffusive example in terms of thermodynamics, owing to the environment (water), which is in equilibrium.

In addition to the above two examples, there are several classes of physical systems to which the thermodynamic framework can be established because of the environment relaxing to the equilibrium much faster than the system we focus on. We use the term *nonequilibrium thermodynamics* to refer to the thermodynamic framework applied to such phenomenological dynamics. It is one of the merits of nonequilibrium thermodynamics that we can discuss irreversibility in various nonequilibrium phenomena from a universal viewpoint, based on thermodynamic relations such as the second law.

The scope of nonequilibrium thermodynamics can be historically and physically classified into two groups. The first one consists of macroscopic systems, such as chemical reaction systems and hydrodynamic systems, studied in *irreversible thermodynamics* since the middle of the last century [10–12]. On the other hand, stochastic thermodynamics, which has achieved a significant development in this century, covers the second class, including mesoscopic stochastic processes [4–9] and open quantum systems [13–16]. Nevertheless, they share the defining property, namely, the phenomenological dynamical description of nonequilibrium processes underpinned by environmental equilibrium. Therefore, there should be a unified method to understand and study these systems.

The purpose of this thesis is to provide a framework that enables us to discuss nonequilibrium thermodynamic systems in a unified manner. We have studied nonequilibrium thermodynamics of macroscopic systems [17–20] and mesoscopic classical and quantum systems [19, 21] in the author's PhD course. After studying the variety of systems, we discovered that there is a unifying framework of nonequilibrium thermodynamics and it is useful to understand thermodynamic restrictions in nonequilibrium systems. In this thesis, we present the framework and its implications and show how it includes the specific nonequilibrium systems. Because the framework is characterized by two concepts, thermodynamic force and irreversible current, we call it the *force-current structure*.

The force-current structure can be outlined as follows (Fig. 1.1 summarizes the discussion in the following five paragraphs): Irreversible current (current, in short hereafter) determines the phenomenological time evolution via the continuity equation with an appropriate “divergence” operator. The entropy production rate in the dynamics is provided by the product between the current and thermodynamic force; in other words, thermodynamic force represents the entropy production per each elementary process. The thermodynamic force and the current are connected by a positive-definite and symmetric operator, which assures the nonnegativity of the entropy production rate and, in addition, enables a geometric interpretation.

The structure yields several physical consequences. First, we can show that the dynamical system possesses an equilibrium (detailed balanced) state if and only if the thermodynamic force is conservative (the conservativeness is characterized by “gradient” operator adjoint to the “divergence”). Moreover, the geometric interpretation enables to derive and understand generically two crucial results found in stochastic thermodynamics: housekeeping-excess decomposition and thermodynamic trade-off relations (inequalities).

The housekeeping-excess decomposition offers a precise understanding of the dissipation [5, 6, 22–27]. In a nonequilibrium system, entropy production is incurred by two sources of nonequilibrium effects: breaking of detailed balance and nonstationarity. The housekeeping and the excess contributions of entropy production respectively address these two aspects. Recently, a geometric aspect of the decomposition was pointed out in Ref. [28, 29]. After that, we revealed that the connection is so universal that we can generally define the decomposition by focusing on the geometry of forces even in systems where conventional methods are not applicable [19–21, 30]. In this thesis, we discuss the decomposition generally by using the force-current structure.

We also consider the relationship between the force-current structure and thermodynamic trade-off relations. Thermodynamic trade-off relations refer to inequalities involving the entropy production (rate) and other costs, such as the variance of an observable (which measures how uncertain the observable is) or the time required to change a state from one to another, i.e., the speed of a change. The inequalities involving uncertainty are called thermodynamic uncertainty relations [18, 30–40] and those dealing with speed called thermodynamic speed limits [18, 30, 39, 41–47]. Thermodynamic speed limits often measure states’ distance by using a sophisticated measure called Wasserstein distances [19, 30, 39, 45, 46], developed in optimal transport theory, a branch of mathematics [48]. In this thesis, we derive one kind of thermodynamic uncertainty relation and thermodynamic speed limits utilizing a discrete analogue of the Wasserstein distance, based on our papers [18–21].

To accomplish the goals of providing a framework and deriving physical results, this dissertation is organized as follows: The next chapter, Chapter 2, considers stochastic dynamics of continuous degrees of freedom, such as the Brownian particle, called the Langevin dynamics, which serve as a prototype for understanding the general force-current structure. We explain the dynamics and how thermodynamics is introduced to them. The concept of being conservative, which plays a crucial role in this thesis, is introduced via the standard definition of conservative mechanical forces.

Chapter 3 develops the general theory of the force-current structure. We establish the framework and prove several facts related to the conservativeness.

Chapter 4 deals with the housekeeping-excess decomposition of entropy production. We review the background of the method and general statements derived from the force-current structure. In particular, the conservativeness distinguishes “essentially” equilibrium systems and nonequilibrium ones and defines the housekeeping entropy production by how far the system is from the “equilibriumness.”

Chapter 5 is dedicated to thermodynamic trade-off relations. The understanding of this topic has significantly been deepened in the last decade; we do not review all of the results, but focus on those derived from the force-current structure. Our emphasis is put on short-time thermodynamic uncertainty relations and thermodynamic speed limits using the Wasserstein distance. We provide a review of these results by the Langevin dynamics, and then give general proof via the force-curernt structure.

The latter part of this thesis (chapters 6 to 9) considers specific systems, each of which is based on our papers [19–21] (Ref. [19] includes the results of chapters 6 and 7). All the chapters have a common outline: we first describe the phenomenological dynamics and explain how they can be (re)written in the form of continuity equation. Then, we install thermodynamics by making an assumption that represents equilibrium environment, which is often called the local equilibrium assumption [12], and obtain the entropy production rate and the thermodynamic force. We prove the system possesses the force-current structure and derive and examine the results implied by the structure concretely.

The continuous-time dynamics between discrete mesostates, called the Markov jump processes, are the subject of Chapter 6. While they are one of the most well-studied classes of systems in stochastic thermodynamics, few studies focus on the continuity-equation representation of the phenomenological equation of motion, the

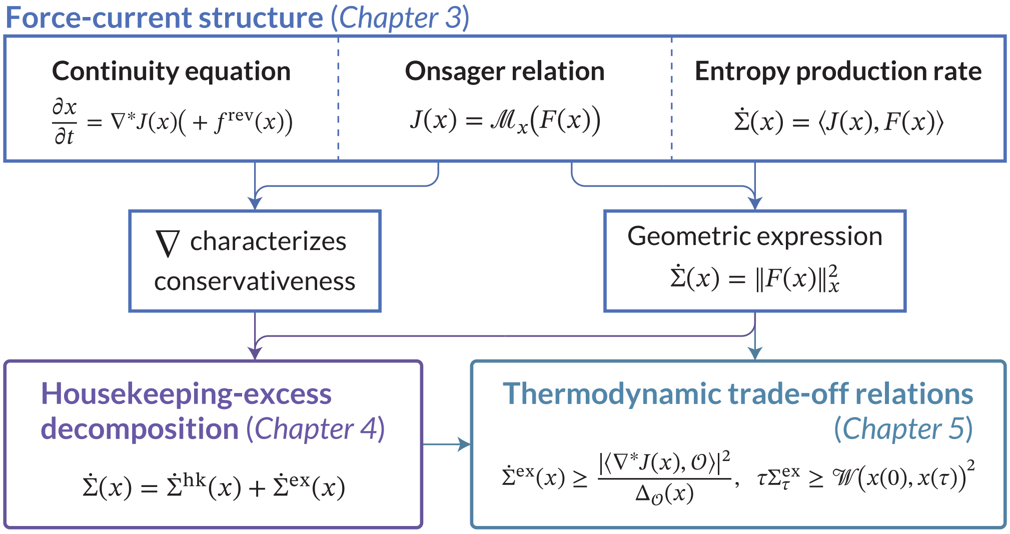

Figure 1.1: Schematics of the general results developed in Part I. Arrows indicate that the statements at the tail jointly lead to that at the head.

master equation. Still, the master equation is written as a continuity equation, where the divergence operator is given by a matrix that is associated with the graph of the mesostates. Cycles of state transitions are represented by null vectors of this matrix.

Chapter 7 discusses chemical reaction networks, assemblies of chemical reactions. They have such a similar framework to Markov jump processes that we can regard them as a generalization of Markov jump processes. In addition to demonstrating the general force-current structure in chemical reaction networks, we also consider how we can establish nonequilibrium thermodynamics in non-ideal chemical systems by examining ideal chemical systems.

We consider hydrodynamic systems described by the Navier–Stokes equation in Chapter 8. In this and next section, we encounter "reversible terms" in phenomenological dynamics, which makes the connection between dynamics and thermodynamics complicated; however, it is still possible to find the force-current structure. Although there are little studies on the housekeeping-excess decomposition in hydrodynamic systems, the general framework successfully offers it. Moreover, our decomposition is revealed to have a connection to Helmholtz' nineteenth century work on minimum dissipation.

The subject of Chapter 9 is open quantum systems. We consider Markovian dynamics expressed by an ordinary differential equation for the density operator, called the quantum master equation. At the beginning, we need to find appropriate definition of thermodynamic forces and currents. According to our latest study [21], we can obtain the force-current structure that is purely quantum, not depending on any specific basis.

We finish the main part with the conclusion in Chapter 10. In this chapter, we provide a table of the key objects of the force-current structure in specific systems.

Appendix A is dedicated to optimal transport theory [48], which provides the aforementioned sophisticated distance measure, the Wasserstein distance. In optimal transport theory, the distance between two states is measured by the transportation cost. The transporation cost has a close connection to the entropy production, leading to a trade-off relation between speed and dissipation. We explain the optimal transport theory between continuous probability distributions, and an extension to discrete systems.

Chapter 2

Warm-up through Langevin system

Before we proceed to the general framework, we outline it through a system that is well studied in nonequilibrium thermodynamics, the Langevin systems. After reviewing its dynamics and thermodynamics, we consider their connections. We expect this section serves as a guide for understanding the abstract discussion in Chapter 3.

2.1 Langevin system

2.1.1 Langevin equation

The Langevin dynamics is a Markovian model that describes stochastic motion under thermal noise, e.g., the trajectory of a colloidal particle in water [49, 50]. The scale separation between the system (e.g., a colloidal particle) and the environmental media (water molecules) rationalizes the Markovian modeling of the dynamics [4].

Let $\boldsymbol{X} \in \mathbb{R}^N$ denote the coordinates of the system (when the number of particles is one and the spatial dimension is three, $N = 3$). We consider the case where the particles are exerted mechanical forces $\boldsymbol{f}$ in a medium having mobility μ and diffusion coefficient D. Then, the Langevin equation is given as [4]

$$\frac{d\boldsymbol{X}}{dt} = \mu \boldsymbol{f}(\boldsymbol{X}) + \sqrt{2D}\boldsymbol{\xi}, \tag{2.1}$$

where $\boldsymbol{\xi}$ is the white Gaussian noise, which satisfies

$$\langle \xi_i(t) \rangle = 0, \quad \langle \xi_i(t)\xi_j(t') \rangle = \delta_{ij}\delta(t-t'). \tag{2.2}$$

Here, $\langle \cdot \rangle$ indicates the ensemble average [1] and δ_{ij} and $\delta(\cdot)$ are the Kronecker delta and the delta function. When the medium's inverse temperature is β, the constants satisfy the fluctuation-dissipation relation [51]

$$\mu = \beta D. \tag{2.3}$$

Equation (2.1) is sometimes referred to as the overdamped Langevin equation because it is derived by ignoring the inertia in the more detailed description of the stochastic dynamics called the underdamped Langevin equation.

2.1.2 Fokker–Planck equation

At the trajectory level, i.e., if we track a time evolution of individual $\boldsymbol{X}$, there is randomness due to the noise $\boldsymbol{\xi}$. However, at the ensemble level, that is, if we consider the probability distribution $P(\boldsymbol{X})$, it evolves deterministically; especially, the Langevin equation (2.1) is known to be equivalent to the Fokker–Planck equation for probability distributions [52]

$$\frac{\partial}{\partial t}P(\boldsymbol{X}) = -\boldsymbol{\nabla} \cdot \big(\mu \boldsymbol{f}(\boldsymbol{X})P(\boldsymbol{X})\big) + \boldsymbol{\nabla} \cdot \big(D\boldsymbol{\nabla}P(\boldsymbol{X})\big). \tag{2.4}$$

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[1] When the coordinate variable $\boldsymbol{X}$ exists in the bracket, we also take the average regarding $\boldsymbol{X}$ over a suitable probability distribution.

Here, $\boldsymbol{\nabla}$ is the differential operator with respect to $\boldsymbol{X}$. If we define the probability current $\boldsymbol{J}_P$ by

$$\boldsymbol{J}_P(\boldsymbol{X}) := \mu \boldsymbol{f}(\boldsymbol{X}) P(\boldsymbol{X}) - D\boldsymbol{\nabla} P(\boldsymbol{X}), \tag{2.5}$$

equation (2.4) turns into the continuity equation

$$\frac{\partial}{\partial t} P(\boldsymbol{X}) = -\boldsymbol{\nabla} \cdot \boldsymbol{J}_P(\boldsymbol{X}). \tag{2.6}$$

When we consider Langevin systems, we assume both the probability distribution and the probability current vanish when $|\boldsymbol{X}| \to \infty$.

We call P^{ss} a steady-state distribution or a steady state in short if it satisfies

$$\boldsymbol{\nabla} \cdot \boldsymbol{J}_{P^{\mathrm{ss}}}(\boldsymbol{X}) = 0. \tag{2.7}$$

Then, the distribution no longer changes and the system becomes stationary. Moreover, the current is called detailed balanced if it vanishes; this is stronger than the steady-state condition. We define the system to be detailed balanced if there is a probability distribution π where the current is detailed balanced. A steady state can depend on time if the mechanical force is time-dependent. We call the steady state corresponding to the mechanical force at the moment the instantaneous steady state.

2.1.3 Ito product and Stratonovich product

In addition to the physical aspects, we here explain some important mathematical properties of the Langevin equation [50]. Formally, the white Gaussian noise $\boldsymbol{\xi}$ should be interpreted as the Wiener process. For a time interval dt, $d\boldsymbol{W} := \boldsymbol{\xi} dt$ becomes a Gaussian random variable that satisfies

$$\langle dW_i \rangle = 0, \quad \langle dW_i dW_j \rangle = \delta_{ij} dt. \tag{2.8}$$

Although this holds for any time interval $dt > 0$, we assume hereafter dt is sufficiently small and neglect terms of the order smaller than dt. If dt is so small, we can regard $dW_i dW_j$ as $\delta_{ij} dt$ without taking average [50].

The product between a function of $\boldsymbol{X}$ and increments that include $d\boldsymbol{W}$, such as $d\boldsymbol{X} = \boldsymbol{X}(t+dt) - \boldsymbol{X}(t)$, must be treated carefully. For a given vector-valued function $\mathbf{g}$, the following two products yield different results:

$$\mathbf{g}(\boldsymbol{X}) \cdot d\boldsymbol{X} := \sum_i g_i(\boldsymbol{X}) dX_i, \tag{2.9}$$

$$\mathbf{g}(\boldsymbol{X}) \circ d\boldsymbol{X} := \sum_i g_i(\boldsymbol{X} + d\boldsymbol{X}/2) dX_i. \tag{2.10}$$

The former one is called the Ito product, while the latter the Stratonovich product [50]. They are different because

$$g_i(\boldsymbol{X} + d\boldsymbol{X}/2) dX_i = g_i(\boldsymbol{X}) dX_i + \frac{1}{2} \sum_j \frac{\partial g_i}{\partial X_j}(\boldsymbol{X}) dX_i dX_j \tag{2.11}$$

and $dX_i dX_j$ will be of the non-negligible order dt.

The advantage of the Ito product is that we can calculate the average easily since we have

$$\begin{aligned}
\langle \mathbf{g}(\boldsymbol{X}) \cdot d\boldsymbol{X} \rangle &= \mu \langle \mathbf{g}(\boldsymbol{X}) \cdot \boldsymbol{f}(\boldsymbol{X}) \rangle dt + \sqrt{2D} \langle \mathbf{g}(\boldsymbol{X}) \cdot d\boldsymbol{W} \rangle \\
&= \mu \langle \mathbf{g}(\boldsymbol{X}) \cdot \boldsymbol{f}(\boldsymbol{X}) \rangle dt + \sqrt{2D} \langle \mathbf{g}(\boldsymbol{X}) \rangle \langle d\boldsymbol{W} \rangle \\
&= \mu \langle \mathbf{g}(\boldsymbol{X}) \cdot \boldsymbol{f}(\boldsymbol{X}) \rangle dt,
\end{aligned}$$

where the second line follows from the fact that $d\boldsymbol{W}$ is independent of $\boldsymbol{X}$. On the other hand, the Stratonovich product aligns with the chain rule

$$dh(\boldsymbol{X}) := h(\boldsymbol{X} + d\boldsymbol{X}) - h(\boldsymbol{X}) = \boldsymbol{\nabla} h(\boldsymbol{X}) \circ d\boldsymbol{X} \tag{2.12}$$

because

$$h(\boldsymbol{X} + d\boldsymbol{X}/2 \pm d\boldsymbol{X}/2) = h(\boldsymbol{X} + d\boldsymbol{X}/2) \pm \nabla h(\boldsymbol{X} + d\boldsymbol{X}/2) \cdot \frac{d\boldsymbol{X}}{2}.$$

Moreover, the expectation value of $\mathbf{g}(\boldsymbol{X}) \circ d\boldsymbol{X}$ can be computed by

$$\langle \mathbf{g}(\boldsymbol{X}) \circ d\boldsymbol{X} \rangle = dt \int \mathbf{g}(\boldsymbol{X}) \cdot \boldsymbol{J}_P(\boldsymbol{X}) dX. \tag{2.13}$$

It is proved as follows:

$$\begin{aligned}
\langle \mathbf{g}(\boldsymbol{X}) \circ d\boldsymbol{X} \rangle &= \langle \mathbf{g}(\boldsymbol{X}) \cdot d\boldsymbol{X} \rangle + \frac{1}{2} \sum_{i,j} \left\langle \frac{\partial g_i}{\partial X_j}(\boldsymbol{X}) dX_i dX_j \right\rangle \\
&= \mu \langle \mathbf{g}(\boldsymbol{X}) \cdot \boldsymbol{f}(\boldsymbol{X}) \rangle dt + \frac{1}{2} \sum_{i,j} \left\langle \frac{\partial g_i}{\partial X_j}(\boldsymbol{X}) (2D dW_i dW_j) \right\rangle \\
&= \mu \langle \mathbf{g}(\boldsymbol{X}) \cdot \boldsymbol{f}(\boldsymbol{X}) \rangle dt + D \langle \nabla \cdot \mathbf{g}(\boldsymbol{X}) \rangle dt \\
&= dt \int \Big(\mathbf{g}(\boldsymbol{X}) \cdot (\mu \boldsymbol{f}(\boldsymbol{X})) + D \nabla \cdot \mathbf{g}(\boldsymbol{X}) \Big) P(\boldsymbol{X}) dX \\
&= dt \int \mathbf{g}(\boldsymbol{X}) \cdot \big(\mu \boldsymbol{f}(\boldsymbol{X}) P(\boldsymbol{X}) - D \nabla P(\boldsymbol{X}) \big) dX,
\end{aligned}$$

where we used the Langevin equation in the second line, the Gaussian property of $d\boldsymbol{W}$ in the third line, and performed integration by parts in the last line.

2.2 Thermodynamics

Owing to the scale separation, we may assume that the environment is always in equilibrium [4]. This is often referred to as the local equilibrium assumption [12]. The fluctuation-dissipation relation (2.3) is nothing but a consequence of the assumption. Then, we can consider thermodynamics of the Langevin dynamics, i.e., the first and second laws. The thermodynamic theory of stochatic systems is called stochastic thermodynamics [4, 7]. In addition to the Langevin dynamics, which involves continuous degrees of freedom, there is a discrete segment in stochastic thermodynamics, which will be explained in Chapter 6.

2.2.1 First law

We first consider the first law in the Langevin system. We need to consider exchange of energy between the particles and the bath (hereafter, we refer to the medium (environment) by the bath or the heat bath, emphasizing its role as a heat reservoir). Sekimoto proposed to define the heat emitted to the bath during a short time interval dt by [4, 53]

$$d\hat{q} = \boldsymbol{f}(\boldsymbol{X}) \circ d\boldsymbol{X}. \tag{2.14}$$

From Eq. (2.13), its expectation value is obtained as

$$\langle d\hat{q} \rangle = dt \int \boldsymbol{f}(\boldsymbol{X}) \cdot \boldsymbol{J}_P(\boldsymbol{X}) dX. \tag{2.15}$$

Assume we have a potential function $U(\boldsymbol{X}; \boldsymbol{a})$ with external parameters $\boldsymbol{a}$. Then, the mechanical force is decomposable into the conservative force $-\nabla U$ and an external force $\boldsymbol{f}^{\mathrm{ext}}$ as $\boldsymbol{f} = -\nabla U + \boldsymbol{f}^{\mathrm{ext}}$. We can influence the system via the parameter $\boldsymbol{a}$ and the external force $\boldsymbol{f}^{\mathrm{ext}}$. By defining the work by $d\hat{w} := \partial_{\boldsymbol{a}} U(\boldsymbol{X}; \boldsymbol{a}) \cdot d\boldsymbol{a} + \boldsymbol{f}^{\mathrm{ext}}(\boldsymbol{X}) \circ d\boldsymbol{X}$, the first law of thermodynamics is established as

$$dU(\boldsymbol{X}; \boldsymbol{a}) = d\hat{w} - d\hat{q} \tag{2.16}$$

at the trajectory level.

2.2.2 Second law

The second law of thermodynamics can also be discussed. Assume the entropy of the system is provided by the Shannon entropy times the Boltzmann constant k_{B} [7]

$$s(\boldsymbol{X}) = -k_{\mathrm{B}} \ln P(\boldsymbol{X}). \tag{2.17}$$

Its average is given by

$$S = \langle s(\boldsymbol{X}) \rangle = -k_{\mathrm{B}} \int P(\boldsymbol{X}) \ln P(\boldsymbol{X}) dX. \tag{2.18}$$

Thus, the rate of entropy change is provided by

$$\begin{aligned} \frac{dS}{dt} &= -k_{\mathrm{B}} \int \frac{\partial P}{\partial t}(\boldsymbol{X}) \ln P(\boldsymbol{X}) dX \\ &= k_{\mathrm{B}} \int \boldsymbol{\nabla} \cdot \boldsymbol{J}_P(\boldsymbol{X}) \ln P(\boldsymbol{X}) dX \\ &= -k_{\mathrm{B}} \int \left(\boldsymbol{\nabla} \ln P(\boldsymbol{X})\right) \cdot \boldsymbol{J}_P(\boldsymbol{X}) dX, \end{aligned} \tag{2.19}$$

where we used the fact that the derivative of $\ln P(\boldsymbol{X})$ will lead to the vanishing term $(d/dt) \int P(\boldsymbol{X}) dX = 0$ and conducted integration by parts in the last line. Note that the equality of the form $(d/dt) \int P \ln P = \int (dP/dt) \ln P$ will be used again and again in this thesis, without explicit explanation.

On the other hand, we also need to consider the entropy change in the environment. We assume that the environment is always in the thermal equilibrium at inverse temperature $\beta = 1/(k_{\mathrm{B}} T)$. Then, the entropy change will be

$$\frac{dS_{\mathrm{env}}}{dt} = k_{\mathrm{B}} \beta \frac{\langle d\hat{q} \rangle}{dt} = k_{\mathrm{B}} \beta \int \boldsymbol{f}(\boldsymbol{X}) \cdot \boldsymbol{J}_P(\boldsymbol{X}) dX. \tag{2.20}$$

Combining the entropy changes of the system and the environment, we finally obtain the total entropy change

$$\dot{\Sigma}_P := \frac{dS}{dt} + \frac{dS_{\mathrm{env}}}{dt} = \int \boldsymbol{J}_P(\boldsymbol{X}) \cdot \left[k_{\mathrm{B}} \beta \boldsymbol{f}(\boldsymbol{X}) - k_{\mathrm{B}} \boldsymbol{\nabla} \ln P(\boldsymbol{X}) \right] dX, \tag{2.21}$$

which we call the entropy production rate (EPR).

The second law of thermodynamics claims $\dot{\Sigma}_P$ is always non-negative; in fact, we can prove this statement, owing to the local equilibrium assumption. Looking at Eq. (2.21), we think of defining thermodynamic force $\boldsymbol{F}_P$ by

$$\boldsymbol{F}_P(\boldsymbol{X}) := k_{\mathrm{B}} \beta \boldsymbol{f}(\boldsymbol{X}) - k_{\mathrm{B}} \boldsymbol{\nabla} \ln P(\boldsymbol{X}). \tag{2.22}$$

Then, we realize that the thermodynamic force is connected to the probability current $\boldsymbol{J}_P$ by

$$\boldsymbol{J}_P(\boldsymbol{X}) = \frac{D P(\boldsymbol{X})}{k_{\mathrm{B}}} \boldsymbol{F}_P(\boldsymbol{X}) = \mu T P(\boldsymbol{X}) \boldsymbol{F}_P(\boldsymbol{X}), \tag{2.23}$$

by comparing Eqs. (2.5) and (2.22) and using the fluctuation-dissipation relation (2.3). This relation can be regarded as a kind of the linear relation given in linear response theory [10, 11]. The EPR now reads

$$\dot{\Sigma}_P = \int \boldsymbol{J}_P(\boldsymbol{X}) \cdot \boldsymbol{F}_P(\boldsymbol{X}) dX = \mu T \int |\boldsymbol{F}_P(\boldsymbol{X})|^2 P(\boldsymbol{X}) dX \tag{2.24}$$

and it is non-negative as μT and $P(\boldsymbol{X})$ are always non-negative. It is worth noting that Eq. (2.24) is the squared norm of the thermodynamic force with $\mu T P(\boldsymbol{X})$ being the metric.

We define P to be equilibrium if the EPR vanishes there. From Eq. (2.24), an equilibrium state must satisfy $\boldsymbol{F}_P(\boldsymbol{X}) = 0$. Furthermore, Eq. (2.23) shows that being equilibrium is equivalent to the detailed balance $\boldsymbol{J}_P(\boldsymbol{X}) = 0$.

Although the thermodynamic force has "force" in its name, it has the dimension of entropy density and provides the entropy production on the movement from $\boldsymbol{X}$ to $\boldsymbol{X}+d\boldsymbol{X}$. This is evident once realizing the relation

$$ds + k_{\mathrm{B}}\beta d\hat{q} = \boldsymbol{F}_P(\boldsymbol{X}) \circ d\boldsymbol{X}, \tag{2.25}$$

where $ds = s(\boldsymbol{X}+d\boldsymbol{X}) - s(\boldsymbol{X})$.

2.3 Conservativeness and detailed balance

2.3.1 Conservative force

When there are no external forces, the mechanical force is provided by a potential function as $\boldsymbol{f} = -\boldsymbol{\nabla} U$ and the thermodynamic force becomes

$$\boldsymbol{F}_P(\boldsymbol{X}) = -\boldsymbol{\nabla}\phi_P(\boldsymbol{X}), \quad \text{with} \quad \phi_P(\boldsymbol{X}) = k_{\mathrm{B}}[\ln P(\boldsymbol{X}) + \beta U(\boldsymbol{X})]. \tag{2.26}$$

We define a thermodynamic force $\boldsymbol{F}$ to be *conservative* if it is given as the gradient of a potential. We say a system is conservative if $\boldsymbol{F}_P$ is conservative for every P.

This terminology is consistent with mechanics. Note that the thermodynamic force can be separated as

$$\boldsymbol{F}_P(\boldsymbol{X}) = \boldsymbol{F}_0(\boldsymbol{X}) - \boldsymbol{\nabla}(k_{\mathrm{B}} \ln P(\boldsymbol{X})) \tag{2.27}$$

with $\boldsymbol{F}_0(\boldsymbol{X}) \coloneqq k_{\mathrm{B}}\beta \boldsymbol{f}(\boldsymbol{X})$. Therefore, the system is conservative if and only if the mechanical force is conservative in the sense of mechanics.

With the canonical distribution

$$P^{\mathrm{can}}(\boldsymbol{X}) \coloneqq \frac{e^{-\beta U(\boldsymbol{X})}}{Z_\beta}, \quad Z_\beta = \int e^{-\beta U(\boldsymbol{X})} dX, \tag{2.28}$$

the potential ϕ_P is rewritten as

$$\phi_P(\boldsymbol{X}) = k_{\mathrm{B}} \ln \frac{P(\boldsymbol{X})}{P^{\mathrm{can}}(\boldsymbol{X})} - k_{\mathrm{B}} \ln Z_\beta. \tag{2.29}$$

Since $\ln Z_\beta$ does not depend on $\boldsymbol{X}$, the potential

$$\tilde{\phi}_P(\boldsymbol{X}) = k_{\mathrm{B}} \ln \frac{P(\boldsymbol{X})}{P^{\mathrm{can}}(\boldsymbol{X})} \tag{2.30}$$

also provides the same thermodynamic force,

$$\boldsymbol{F}_P(\boldsymbol{X}) = -\boldsymbol{\nabla}\tilde{\phi}_P(\boldsymbol{X}). \tag{2.31}$$

From this formula, it is evident that the thermodynamic force vanishes when $P = P^{\mathrm{can}}$. Since the probability current is connected to the thermodynamic force via Eq. (2.23), it also vanishes then. That is, the detailed balance holds at $P = P^{\mathrm{can}}$.

When the system is conservative, the EPR is reformed into

$$\dot{\Sigma}_P = -k_{\mathrm{B}} \frac{\partial}{\partial t} D(P(t) \| P^{\mathrm{can}}(s))\Big|_{s=t}, \tag{2.32}$$

where $P^{\mathrm{can}}(s)$ is the instantaneous canonical distribution defined by the potential U at time s, and D is the Kullback–Leibler divergence

$$D(P\|Q) \coloneqq \int P(\boldsymbol{X}) \ln \frac{P(\boldsymbol{X})}{Q(\boldsymbol{X})} dX. \tag{2.33}$$

This is because

$$\begin{aligned} k_{\mathrm{B}}\frac{\partial}{\partial t}D(P(t)\|P^{\mathrm{can}}(s))\Big|_{s=t} &= \int \frac{\partial P}{\partial t}(\boldsymbol{X})\tilde{\phi}_P(\boldsymbol{X})dX \\ &= -\int (\boldsymbol{\nabla}\cdot\boldsymbol{J}_P(\boldsymbol{X}))\tilde{\phi}_P(\boldsymbol{X})dX \\ &= \int \boldsymbol{J}_P(\boldsymbol{X})\cdot\boldsymbol{\nabla}\tilde{\phi}_P(\boldsymbol{X})dX \\ &= -\int \boldsymbol{J}_P(\boldsymbol{X})\cdot\boldsymbol{F}_P(\boldsymbol{X})dX = -\dot{\Sigma}_P, \end{aligned}$$

where we used the fact that the derivative of $\ln P$ results in 0 in the first line, and did integration by parts in the third line.

If the system is autonomous (i.e., U does not change in time), Eq. (2.32) becomes

$$\dot{\Sigma}_P = -k_{\mathrm{B}}\frac{d}{dt}D(P\|P^{\mathrm{can}}). \tag{2.34}$$

As the EPR is always non-negative, we see the convergence to the canonical state. The ERP vanishes at the canonical distribution, which means that P^{can} is the equilibrium state.

2.3.2 Equivalence

We can reorganize the above discussion more formally; we can prove that the following two statements are equivalent:

(1) There exists a potential ψ such that

$$\boldsymbol{F}_0(\boldsymbol{X}) = -\boldsymbol{\nabla}\psi(\boldsymbol{X}). \tag{2.35}$$

(2) There exists a probability distribution π where the detailed balance holds

$$\boldsymbol{J}_\pi(\boldsymbol{X}) = 0. \tag{2.36}$$

Let us first prove that (1) leads to (2). We can choose π as

$$\pi(\boldsymbol{X}) = \frac{1}{Z}e^{-\psi(\boldsymbol{X})/k_{\mathrm{B}}} \quad \text{with} \quad Z = \int e^{-\psi(\boldsymbol{X})/k_{\mathrm{B}}}dX, \tag{2.37}$$

which is a probability distribution because it is positive and satisfies the normalization $\int \pi(\boldsymbol{X})dX = 1$. The force vanishes at $P = \pi$ because

$$\begin{aligned} \boldsymbol{F}_\pi(\boldsymbol{X}) &= \boldsymbol{F}_0(\boldsymbol{X}) - k_{\mathrm{B}}\boldsymbol{\nabla}\ln\pi(\boldsymbol{X}) \\ &= \boldsymbol{F}_0(\boldsymbol{X}) + \boldsymbol{\nabla}\psi(\boldsymbol{X}) = 0. \end{aligned}$$

Again, the linear relation (2.23) concludes that $\boldsymbol{J}_\pi(\boldsymbol{X}) = 0$.

The converse is also shown with the linear relation (2.23). From it, we find $\boldsymbol{F}_\pi(\boldsymbol{X}) = 0$, that is,

$$\boldsymbol{F}_0(\boldsymbol{X}) - \boldsymbol{\nabla}(k_{\mathrm{B}}\ln\pi(\boldsymbol{X})) = 0,$$

which shows $\psi(\boldsymbol{X}) = -k_{\mathrm{B}}\ln\pi(\boldsymbol{X})$ provides $\boldsymbol{F}_0(\boldsymbol{X})$ in the form of Eq. (2.35).

The equivalence indicates that the system possesses an equilibrium state if and only if it is conservative; while the equilibrium was defined in terms of the steady-state property, detailed balance, now we have another characterization with a thermodynamic notion, namely, the thermodynamic force. We can judge whether the system is an "equilibrium system", by just looking at the thermodynamic force, without knowing whether the detailed balance holds in steady states.

The thermodynamic force becomes nonconseravtive if the mechanical force has a nonconservative contribution (in the sense of mechanics), such as an external stir. Alternatively, while now we assume β, μ and D are constant, their anisotropy can make the thermodynamic force nonconservative [54]. They can prevent the system from relaxing to the equilibrium and incurr dissipation even in the steady state.

2.4 Cycle and breaking of detalied balance

While the detailed balance is characterized by the gradient, we can also quantitatively discuss its breaking by using the adjoint, the divergence. In a steady state, the current satisfies

$$\nabla \cdot \boldsymbol{J}_{P\mathrm{ss}}(\boldsymbol{X}) = 0. \tag{2.38}$$

If the detailed balance holds, we have $\boldsymbol{J}_{P\mathrm{ss}}(\boldsymbol{X}) = 0$; however, it does not in general. Still, if we assume thatthe dimension N is 3, we can obtain

$$\boldsymbol{J}_{P\mathrm{ss}}(\boldsymbol{X}) = \nabla \times \boldsymbol{A}(\boldsymbol{X}) \tag{2.39}$$

with a vector field $\boldsymbol{A}$, where × indicates the cross product. That is, the steady-state condition (2.38) generally implies that the current becomes a rotation.

This is physically natural; if the system is conservative, the system relaxes to a detailed-balanced steady state, and there are no net current and dissipation. On the other hand, if there is an external driving that forces the steady state to be nonequilibrium, there should be some cyclic motion that does not change the system in total but causes certain dissipation. Such a cyclic contribution is represented by the rotation form in Eq. (2.39), or more generally, the kernel of the divergence. This point of view was introduced by Qian in Ref. [55] to discuss the nonequilibrium thermodynamics of molecular motors and generalized to higher-dimensional systems in Ref. [56].

Correspondingly to Eq. (2.39), we may define a cyclic force by

$$\boldsymbol{B}(\boldsymbol{X}) \coloneqq \nabla \times \boldsymbol{F}_{P\mathrm{ss}}(\boldsymbol{X}). \tag{2.40}$$

As a result, we get the formula

$$\dot{\Sigma}_{P\mathrm{ss}} = \int \boldsymbol{A}(\boldsymbol{X}) \cdot \boldsymbol{B}(\boldsymbol{X}) dX \tag{2.41}$$

because

$$\begin{aligned}
\int \boldsymbol{J}_{P\mathrm{ss}}(\boldsymbol{X}) \cdot \boldsymbol{F}_{P\mathrm{ss}}(\boldsymbol{X}) dX &= \int [\nabla \times \boldsymbol{A}(\boldsymbol{X})] \cdot \boldsymbol{F}_P(\boldsymbol{X}) dX \\
&= \sum_{i,j,k} \int \epsilon_{ijk} \partial_j A_k(\boldsymbol{X}) [\boldsymbol{F}_P(\boldsymbol{X})]_i dX \\
&= -\sum_{i,j,k} \int \epsilon_{ijk} A_k(\boldsymbol{X}) \partial_j [\boldsymbol{F}_P(\boldsymbol{X})]_i dX \\
&= -\sum_{i,j,k} \int (-\epsilon_{kji}) A_k(\boldsymbol{X}) \partial_j [\boldsymbol{F}_P(\boldsymbol{X})]_i dX \\
&= \int \boldsymbol{A}(\boldsymbol{X}) \cdot [\nabla \times \boldsymbol{F}(\boldsymbol{X})] dX,
\end{aligned}$$

where ϵ_{ijk} is the Levi–Civita symbol, and we conducted integration by parts in the third line.

Even though the interpretation of Eq. (2.41) is not apparent for the Langevin dynamics, its discrete counterpart, discussed in later sections, is a renowned formula found by Schnakenberg [57] and easily interpreted as the decomposition of the total dissipation into the contributions from each “cycles.”

Chapter 3

General framework of force-current structure

This section aims to establish a general framework that includes the author's research spreading over several kinds of systems. We have studied nonequilibrium thermodynamics of classicalstochastic systems, chemical systems, hydrodynamic systems and quantum systems. In particular, we have explored an underlying common geometric structure of thermodynamic forces and insights it provides to nonequilibrium thermodynamics. Although systems that we can consider are diverse, the important concepts have already appeared in the previous section: continuity equation, current, thermodynamic force, and their close connection.

3.1 Dynamics and current

3.1.1 Mathematical structure

We always consider the dynamics of an open system coupled to a single or multiple environment(s). The system can exchange energy or particles with the environments. Let us prepare a mathematical ground to treat such a dynamics.

We assume the state of the system is described by a variable x that resides in a subset $\mathcal{S}$ of a linear space $\mathcal{S}_0$. We call $\mathcal{S}_0$ the state space. If the system's dynamics are stochastic, we will choose a variable that represents the ensemble, while if it is deterministic, we will take macroscopic quantities, e.g., concentrations in chemical systems.

In the Langevin dynamics, x is the probability distribution and $\mathcal{S}_0$ is a suitable functional space. There is arbitrariness in choosing $\mathcal{S}$. Naively, $\mathcal{S}$ would be the set of normalized positive distributions, but we can impose only the positivity condition of the distributions. We can regard the normalization property as a consequence of the equation of motion, rather than what is intrinsic to the system (discussed later).

In addition to the state space $\mathcal{S}_0$, we introduce another linear space for variables such as forces and currents, $\mathcal{F}$, which we call the force space. We regard each dimension of $\mathcal{F}$ corresponds to an elementary process in the dynamics. Remember that $[\boldsymbol{F}_P(\boldsymbol{X})]_i$ provides the entropy production by the movement dX_i in the Langevin dynamics. That is, the vector-valued function $\boldsymbol{F}_P$ stores every possible value of entropy production when the system's state is given by P. Similarly, we will introduce a thermodynamic force as a map from $x \in \mathcal{S}$ to an element in $\mathcal{F}$ that stores the information of entropy production.

These spaces are equipped with inner products; we simply write them as $\langle \cdot, \cdot \rangle$ for both spaces. The spaces can be real or complex linear spaces, but we conduct general discussion as if they are real for simplicity. It is not difficult to verify the discussion in the complex case. The spaces should be called the Hilbert spaces rather than just linear spaces; yet, we do not need to stick to mathematical rigorousness in this point and roughly use the terminology.

3.1.2 Dynamics

We assume that we can model the dynamics by the following equation of motion

$$\frac{\partial x}{\partial t} = f^{\mathrm{rev}}(x) + \nabla^* J(x). \tag{3.1}$$

First, $f^{\mathrm{rev}}(x)$ is a reversible term, which comes from the system's internal dynamics and not influenced by the environment. While it does not exist in the overdamped Langevin dynamics, the underdamped version has a reversible term [49]. Another example is the unitary term in the open quantum systems (see Chapter 9). Generally, the reversible term does not cause any dissipation and has little to do with thermodynamics. However, it is crucial for time evolution, so we need to care about it when considering connections between thermodynamics and dynamics.

Next, J is a current. It is a map from $\mathcal{S}$ to $\mathcal{F}$ and provides the occurrence rates of the elementary processes. For example, the elements of the probability current $[\boldsymbol{J}_P(\boldsymbol{X})]_i dt$ can be regarded as the averaging weight corresponding to dX_i as in Eq. (2.13).

Finally, we have the gradient operator ∇, which is a linear map from $\mathcal{S}_0$ to $\mathcal{F}$. Its adjoint ∇^*, the divergence operator is defined by

$$\langle \nabla^* J, \phi \rangle = \langle J, \nabla \phi \rangle \tag{3.2}$$

for any $J \in \mathcal{F}$ and $\phi \in \mathcal{S}_0$. When ∇ is the differential operator $\boldsymbol{\nabla}$, its adjoint will be $-\boldsymbol{\nabla}\cdot$, where the dot indicates that it takes a vector-valued function and returns a dot product.

The divergence operator and the current constitute the continuity-equation part of the dynamics. If there is no reversible term, which is often the case with systems without inertia, the equation of motion becomes purely a continuity equation as

$$\frac{\partial x}{\partial t} = \nabla^* J(x). \tag{3.3}$$

We say x^{ss} is a steady state if it satisfies $f^{\mathrm{rev}}(x^{\mathrm{ss}}) + \nabla^* J(x^{\mathrm{ss}}) = 0$. When $J(x^{\mathrm{ss}}) = 0$ holds, the current is said to be detailed balanced. Althogh being detailed balanced does not mean being a steady state in the most general sense, if the system does not have a reversible term, the detailed balance guarantees a steady state. As is often the case with systems with discrete degrees of freedom, the current J can be expressed by the difference between a forward and a backward contribution as $J = J^+ - J^-$. Then, the detailed balance can be understood as the balance between J^+ and J^-. When the detailed balance is violated in the steady state, it can be called a nonequilibrium steady state, or in short, NESS.

3.1.3 Conservation laws

The gradient operator usually has a nontrivial kernel (null space). For the differential operator $\boldsymbol{\nabla}$, a constant function that returns a constant for any $\boldsymbol{X}$ vanishes when multiplied by $\boldsymbol{\nabla}$.

We call a vector $\lambda \in \mathcal{S}_0$ a conservation law if it satisfies

$$\langle \lambda, f^{\mathrm{rev}}(x) \rangle = 0 \quad \forall x \in \mathcal{S}, \tag{3.4}$$

$$\nabla \lambda = 0. \tag{3.5}$$

This is because then $\langle \lambda, x \rangle$ is conserved:

$$\frac{d}{dt}\langle \lambda^{(i)}, x \rangle = \left\langle \lambda^{(i)}, \frac{\partial x}{\partial t} \right\rangle = \langle \lambda^{(i)}, f^{\mathrm{rev}} \rangle + \langle \nabla \lambda^{(i)}, J(x) \rangle = 0.$$

When there is no reversible term, every null vector of ∇ becomes a conservation law. In the Langevin case, constant function $\lambda_c : \boldsymbol{X} \mapsto c \in \mathbb{R}$ is a conservation law as mentioned. It provides a conservative quantity

$$\langle \lambda_c, P \rangle = \int cP(\boldsymbol{X})dX = c\int P(\boldsymbol{X})dX. \tag{3.6}$$

Therefore, we can regard the normalization $\int P(\boldsymbol{X})dX = 1$ as a conservation law emerging from the equation of motion, instead of an assumption on the system.

We assume that there are a finite number of linearly independent conservation laws and write them as $\{\lambda^{(i)}\}_{i=1,\ldots,n}$.

3.2 Thermodynamics and thermodynamic force

3.2.1 Local equilibrium assumption

Next, we consider thermodynamics. To this end, we postulate the local equilibrium assumption [12, 58]. That is, we assume that the degrees of freedom other than those we focus on relax to the thermal equilibrium very fast. As a consequence, we expect that there is a consistency between the (remained) phenomenological dynamics of the system and thermodynamics and thermodynamic functions are well defined with the system's variable and a few thermodynamic parameters, such as the environment's temperature. This assumption is equivalent to assuming the scale separation between the system and the environment.

3.2.2 Thermodynamic force and entropy production

We assume that we have a thermodynamic force $F : \mathcal{S} \to \mathcal{F}$ that quantifies the entropy production in each elementary process. It is equivalent to saying that entropy production rate (EPR) $\dot{\Sigma}(x)$ is given by

$$\dot{\Sigma}(x) = \langle J(x), F(x) \rangle. \tag{3.7}$$

Similarly to the continuity-equation form (3.1) being an assumption, Eq. (3.7) is also an assumption. In concrete systems, we will obtain Eq. (3.7) by evaluating the entropy change in the system dS/dt and the environmental entropy change $\dot{S}_{\mathrm{env}}$ as we did in Chapter 2. In defining the entropy and calculating $\dot{S}_{\mathrm{env}}$, local equilibrium will be required.

The second law of thermodynamics claims that the entropy never decreases. Thus, the EPR given in Eq. (3.7) must be non-negative; but it is not derived from what we have discussed. We need some relation between the thermodynamic force and current.

We assume that there is a symmetric and positive linear map $\mathcal{M}_x : \mathcal{F} \to \mathcal{F}$, which may depend on x, that satisfies

$$\mathcal{M}_x\big(F(x)\big) = J(x). \tag{3.8}$$

Here, the symmetric and positive property means that $\langle F', \mathcal{M}_x(F'') \rangle = \langle \mathcal{M}_x(F'), F'' \rangle$ for any $F', F'' \in \mathcal{F}$ and $\langle F', \mathcal{M}_x(F') \rangle > 0$ for any $F' \in \mathcal{F}$ such that $F' \neq 0$. The positivity implies that $\mathcal{M}_x(F') = 0$ only if $F' = 0$ because otherwise $\langle F', \mathcal{M}_x(F') \rangle = 0$ even though $F' \neq 0$. The symmetry and positivity naturally lead to an inner product

$$\langle F', F'' \rangle_x \coloneqq \langle F', \mathcal{M}_x(F'') \rangle \tag{3.9}$$

and the induced norm $\|F'\|_x \coloneqq \sqrt{\langle F', F' \rangle_x}$. The existence of $\mathcal{M}_x$ ensures the non-negativity of the EPR; we can rewrite Eq. (3.7) as

$$\dot{\Sigma}(x) = \|F(x)\|_x^2, \tag{3.10}$$

which is obviously non-negative. This expression will be the starting point of the discussion in Chapter 4. For convenience, we call Eq. (3.8) the Onsager relation, as it generalizes a similar relationship in linear response theory found in Onsager's papers [10, 11].

We call x^{eq} an equilibrium state when $\dot{\Sigma}(x^{\mathrm{eq}}) = 0$ holds. It is obvious that x^{eq} is an equilibrium state if the current is detailed balanced $J(x^{\mathrm{eq}}) = 0$. The converse is ensured by the Onsager relation: $\dot{\Sigma}(x^{\mathrm{eq}}) = 0$ implies $F(x^{\mathrm{eq}}) = 0$ because of Eq. (3.10), which further means $J(x) = 0$ due to the Onsager relation (3.8).

In the Langevin dynamics, the current and the thermodynamic force are acutally connected as in Eq. (2.23), where $\mathcal{M}_x$ is the multiplication of $\mu T P(\boldsymbol{X})$, which is provided by $x = P(\boldsymbol{X})$ and the environment's parameters, μ and T. In general, $\mathcal{M}_x$ is expressed by x and some parameters associated with the local equilibrium property of the environment.

Equation (3.8) usually follows from the local equilibrium assumption. In particular, it leads to a connection between kinetics and thermodynamics, often referred to as a local detailed balance. It takes various forms; the fluctuation-dissipation relation (2.3) can be seen as a kind of local detailed balance.

We call the above structure involving dynamics and thermodynamics the *force-curernt structure*. We provide the summary below.

Force-current structure

1. Equation of motion is written with current and gradient

$$\frac{\partial x}{\partial t} = f^{\mathrm{rev}}(x) + \nabla^* J(x) \quad \text{or} \quad \frac{\partial x}{\partial t} = \nabla^* J(x) \qquad (3.1)\,/\,(3.3)$$

2. Thermodynamic force gives entropy production rate as

$$\dot{\Sigma}(x) = \langle J(x), F(x) \rangle \qquad (3.7)$$

3. Positive and symmetric linear map connects force and current

$$\mathcal{M}_x\big(F(x)\big) = J(x) \qquad (3.8)$$

3.2.3 Alternative of the force-current relation

We make an advanced remark about the Onsager relation (3.8). Now, the thermodynamic force is mapped to the current by a linear map, which enables us to write the EPR as a squared norm. However, we can choose a *nonlinear* map, which then provides the EPR by the *divergence* between forces. Such a method has proven useful in systems with discrete degrees of freedom [59, 60], but we do not discuss these results in this thesis.

3.3 Conservativeness and detailed balance

As in the Langevin dynamics, we can discuss the connection between conservativeness of thermodynamic forces and detailed balance. However, deducing a general result like the equivalence between conservativeness and detailed balance on the most general ground is challenging. Still, additional (technical) assumptions enable us to reproduce the proof in general. This point was loosely treated in our previous studies [20, 21], so here we try to rigorously identify the conditions to generally obtain the equivalence.

3.3.1 Assumptions

Here, we make two assumptions:

Assumption C1. Thermodynamic forces are always written in the form

$$F(x) = F_0 - \nabla \varphi(x) \qquad (3.11)$$

where $F_0 \in \mathcal{F}$ is independent of x and $\varphi : \mathcal{S} \to \mathcal{S}_0$ is bijective.

Assumption C2. For any $\psi \in \mathcal{S}_0$ and $x \in \mathcal{S}$, there is a solution $\mu \in \mathbb{R}^n$ to the equations

$$g_i(\mu; \psi) := \left\langle \lambda^{(i)}, \varphi^{-1}\Big(\psi - \sum_{i=1}^{n} \mu_i \lambda^{(i)}\Big) \right\rangle = \langle \lambda^{(i)}, x \rangle. \qquad (3.12)$$

The first assumption, C1, is realized with $F_0 = k_{\mathrm{B}}\beta \boldsymbol{f}(\boldsymbol{X})$ and $\varphi(x) = k_{\mathrm{B}} \ln P(\boldsymbol{X})$ in the Langevin dynamics (note that here the probability distribution $P(\boldsymbol{X})$ plays the role of x). The bijectivity is guaranteed because now $\mathcal{S}$ is all the positive distributions rather than normalized positive distributions.

The second condition means we can find a state of the form $\varphi^{-1}(\psi - \sum_{i=1}^{n} \mu_i \lambda^{(i)})$ that satisfies the conservation laws. To the best of our knowledge, this condition cannot be reasonably loosened and we need to check if it holds in each case. In the Langevin dynamics, this equation reads

$$g(\mu;\psi) = \int e^{[\psi(X)-\mu]/k_{\mathrm{B}}} dX = 1 \tag{3.13}$$

for μ, and it is solved by

$$\mu = k_{\mathrm{B}} \ln \int e^{\psi(X)/k_{\mathrm{B}}} dX. \tag{3.14}$$

With this μ, $e^{[\psi(X)-\mu]/k_{\mathrm{B}}}$ becomes a normalized probability distribution. More nontrivial examples are provided in later sections (specifically, in Sec. 6.3.4, Sec.7.2.4, and Sec. 9.2.4, and in an example in Sec. 9.5.2).

3.3.2 Equivalence

We define a thermodynamic force to be conservative if it is provided by

$$F = -\nabla\phi \tag{3.15}$$

with a potential $\phi \in \mathcal{S}$. A system is said to be conservative if for any $x \in \mathcal{S}$, there is a potential $\phi(x)$ such that $F(x) = -\nabla\phi(x)$. Given assumptions C1 and C2, we can prove that the following statements are equivalent:

(1) There is a potential $\psi \in \mathcal{S}_0$ such that $F_0 = -\nabla\psi$.

(2) For any $x \in \mathcal{S}$, there exists $\pi \in \mathcal{S}$ such that $J(\pi) = 0$ and $\langle \lambda^{(i)}, \pi\rangle = \langle \lambda^{(i)}, x\rangle$ for all i.

Let us show (1) ⇒ (2). We choose π as

$$\pi = \varphi^{-1}\Big(\psi + \sum_i \mu_i \lambda^{(i)}\Big), \tag{3.16}$$

where μ is the solution to

$$g_i(\mu;\psi) = \langle \lambda^{(i)}, x\rangle, \tag{3.17}$$

which exists due to the second assumption. Then, we have

$$F(\pi) = F_0 - \nabla\varphi(\pi) = F_0 - \nabla\psi = 0,$$

where we used $\nabla\lambda^{(i)} = 0$ in the second equality. Therefore, we find $J(\pi) = 0$ because of the Onsager relation.

The converse is immediately proved as follows: $J(\pi) = 0$ implies $F(\pi) = 0$ because of the positivity of $\mathcal{M}_\pi$ as already discussed. Then, we find

$$F_0 = \nabla\varphi(\pi)$$

since $F(\pi) = F_0 - \nabla\varphi(\pi)$.

If assumption C2 is not satisfied, we can only prove that (1) is equivalent to

(2') There exists $\pi \in \mathcal{S}$ such that $J(\pi) = 0$.

That is, for a given initial state, it will no longer be guaranteed that there is an equilibrium state that has the same values of the conserved quantities.

The implication of the equivalence does not change from the Langevin case: whether the system is an equilibrium system can be judged not only from the dynamical point of view, but also by the thermodynamic criterion, i.e., whether the thermodynamic force is conservative or not. In concrete systems discussed in the following, the equivalence is obtaiend once we prove that the two assumptions are satisfied.

3.4 Cycle and breaking of detailed balance

Finally, we generically define cycles by the kernel of ∇^*. A current $J \in \mathcal{F}$ is defined to be a cycle if it satisfies $\nabla^* J = 0$. For example, a steady-state current becomes a cycle when there is no reversible term. Cycles correspond to currents that break the detailed balance and represent motions that do not cause any change in total but incurs certain dissipation.

Since the kernel of ∇^* is a linear space, it can be expressed as the image of another operator $\mathcal{T}$ that maps some space into $\mathcal{F}$ and identically satisfies $\nabla^*\mathcal{T} = 0$. Let a steady-state current $J(x^{\mathrm{ss}})$ be written as $\mathcal{T}(j_c)$. Physically, j_c is interpreted as providing the occurence rate of each cyclic motion. Then, if we define the thermodynamic force on cycles as

$$f_c \coloneqq \mathcal{T}^*(F(x^{\mathrm{ss}})) \tag{3.18}$$

with the adjoint $\mathcal{T}^*$, the EPR reads

$$\dot{\Sigma}(x^{\mathrm{ss}}) = \langle j_c, f_c \rangle. \tag{3.19}$$

As explained later, this is the generalization of the formula given by Schnakenberg [57].

Chapter 4

Housekeeping-excess decomposition

The geometric housekeeping-excess decomposition is one of the most crucial consequences of the general framework presented in the preceding section. In this chapter, we provide a brief introduction to the housekeeping-excess decomposition and reveal its intimate connection to the force-current structure and conservativeness.

4.1 Review

In this section, we review the history of the housekeeping-excess decomposition of EPR. We describe the motivation of the decomposition and two famous formulations: the Hatano–Sasa and the Maes–Netočný decomposition.

4.1.1 Breaking and recovery of the second law

For equilibrium states A and B, we can obtain the entropy difference by measuring heat quasistatically

$$\Delta S := S(B) - S(A) = \lim_{\tau\to\infty} \int_0^\tau \frac{\dot{q}}{T} dt, \tag{4.1}$$

where $\dot{q}$ is the heat flux into the system per time and T is the bath temperature [61]. For a finite-time protocol, we have instead the Clausius inequality

$$\Delta S \geq \int_0^\tau \frac{\dot{q}}{T} dt, \tag{4.2}$$

which is a form of the second law of thermodynamics.

On the other hand, if the system is externally driven to be out of equilibrium and there is a heat flux even if the system is in a steady state, the quasistatic limit causes divergence

$$\int_0^\tau \frac{\dot{q}}{T} dt \to \infty \tag{4.3}$$

and we cannot measure the entropy difference.

In Ref. [22], Oono and Paniconi proposed to subtract the *housekeeping heat* $\dot{q}^{\mathrm{hk}}$ from $\dot{q}$ to obtain the *excess heat* $\dot{q}^{\mathrm{ex}}$ and recover the formula (4.1) as

$$\Delta S = \lim_{\tau\to\infty} \int_0^\tau \frac{\dot{q}^{\mathrm{ex}}}{T} dt. \tag{4.4}$$

In general, we can expect the generalized Clausius inequality

$$\Delta S \geq \int_0^\tau \frac{\dot{q}^{\mathrm{ex}}}{T} dt \tag{4.5}$$

and the steady-state version of the Clausius inequality for the housekeeping heat

$$-\frac{q^{\mathrm{hk}}}{T} \geq 0. \tag{4.6}$$

4.1.2 Hatano–Sasa decomposition in Langevin dynamics

The first concrete atempt to define the housekeeping and excess heats was provided by Hatano and Sasa in the overdamped Langevin dynamics [23]. At the trajectory level, they define the housekeeping heat flux as

$$\dot{q}^{\mathrm{hk,HS}}dt = -T\boldsymbol{F}_{P^{\mathrm{ss}}}(\boldsymbol{X}) \circ d\boldsymbol{X}, \tag{4.7}$$

where HS stands for Hatano–Sasa and P^{ss} is the instantenous steady state. Remembering the definition of the thermodynamic force (2.22), we can rewrite it into

$$\dot{q}^{\mathrm{hk,HS}}dt = -\boldsymbol{f}(\boldsymbol{X}) \circ d\boldsymbol{X} + \beta^{-1}\boldsymbol{\nabla} \ln P^{\mathrm{ss}}(\boldsymbol{X}) \circ d\boldsymbol{X}. \tag{4.8}$$

Given the definition of heat (2.14) (note that there the sign of heat is opposite), we obtain the excess heat

$$\dot{q}^{\mathrm{ex,HS}}dt = -\beta^{-1}\boldsymbol{\nabla} \ln P^{\mathrm{ss}}(\boldsymbol{X}) \circ d\boldsymbol{X}. \tag{4.9}$$

For the Langevin dynamics, we can prove the inequalities in Eqs. (4.5) and (4.6) at the ensemble level. Let us check Eq. (4.6) first. This proof is given in Ref. [29]. By taking the average, the housekeeping heat becomes

$$\langle \dot{q}^{\mathrm{hk,HS}} \rangle = -T \int \boldsymbol{F}_{P^{\mathrm{ss}}}(\boldsymbol{X}) \cdot \boldsymbol{J}_P(\boldsymbol{X}) dX. \tag{4.10}$$

Equation (4.6) is proved if we can rewrite this equality into

$$\langle \dot{q}^{\mathrm{hk,HS}} \rangle = -\mu T^2 \int P(\boldsymbol{X}) |\boldsymbol{F}_{P^{\mathrm{ss}}}(\boldsymbol{X})|^2 dX. \tag{4.11}$$

This is proved as follows: first, we have

$$\int P(\boldsymbol{X}) \boldsymbol{F}_{P^{\mathrm{ss}}}(\boldsymbol{X}) \cdot (\boldsymbol{F}_P(\boldsymbol{X}) - \boldsymbol{F}_{P^{\mathrm{ss}}}(\boldsymbol{X})) dX = 0 \tag{4.12}$$

because

$$\boldsymbol{F}_P(\boldsymbol{X}) - \boldsymbol{F}_{P^{\mathrm{ss}}}(\boldsymbol{X}) = -k_{\mathrm{B}} \boldsymbol{\nabla} \ln \frac{P(\boldsymbol{X})}{P^{\mathrm{ss}}(\boldsymbol{X})} = -k_{\mathrm{B}} \frac{P^{\mathrm{ss}}(\boldsymbol{X})}{P(\boldsymbol{X})} \boldsymbol{\nabla}\left(\frac{P(\boldsymbol{X})}{P^{\mathrm{ss}}(\boldsymbol{X})} \right)$$

and

$$\begin{aligned}
\int P(\boldsymbol{X}) \boldsymbol{F}_{P^{\mathrm{ss}}}(\boldsymbol{X}) \cdot (\boldsymbol{F}_P(\boldsymbol{X}) - \boldsymbol{F}_{P^{\mathrm{ss}}}(\boldsymbol{X})) dX &= -k_{\mathrm{B}} \int P^{\mathrm{ss}}(\boldsymbol{X}) \boldsymbol{F}_{P^{\mathrm{ss}}}(\boldsymbol{X}) \cdot \boldsymbol{\nabla}\left(\frac{P(\boldsymbol{X})}{P^{\mathrm{ss}}(\boldsymbol{X})} \right) dX \\
&= -\frac{k_{\mathrm{B}}}{\mu T} \int \boldsymbol{J}_{P^{\mathrm{ss}}}(\boldsymbol{X}) \cdot \boldsymbol{\nabla}\left(\frac{P(\boldsymbol{X})}{P^{\mathrm{ss}}(\boldsymbol{X})} \right) dX \\
&= \frac{k_{\mathrm{B}}}{\mu T} \int [\boldsymbol{\nabla} \cdot \boldsymbol{J}_{P^{\mathrm{ss}}}(\boldsymbol{X})] \frac{P(\boldsymbol{X})}{P^{\mathrm{ss}}(\boldsymbol{X})} dX = 0,
\end{aligned}$$

where we used integration by parts in the last line. Then, Eq. (4.11) follows from the calculation

$$\begin{aligned}
T \int \boldsymbol{F}_{P^{\mathrm{ss}}}(\boldsymbol{X}) \cdot \boldsymbol{J}_P(\boldsymbol{X}) dX &= \mu T^2 \int P(\boldsymbol{X}) \boldsymbol{F}_{P^{\mathrm{ss}}}(\boldsymbol{X}) \cdot \boldsymbol{F}_P(\boldsymbol{X}) dX \\
&= \mu T^2 \int P(\boldsymbol{X}) \boldsymbol{F}_{P^{\mathrm{ss}}}(\boldsymbol{X}) \cdot \Big(\boldsymbol{F}_{P^{\mathrm{ss}}}(\boldsymbol{X}) + \boldsymbol{F}_P(\boldsymbol{X}) - \boldsymbol{F}_{P^{\mathrm{ss}}}(\boldsymbol{X}) \Big) dX \\
&= \mu T^2 \int P(\boldsymbol{X}) |\boldsymbol{F}_{P^{\mathrm{ss}}}(\boldsymbol{X})|^2 dX.
\end{aligned}$$

Next, we consider the generalized Clausius inequality (4.5). The averaged excess heat is given by

$$\begin{aligned}
\langle \dot{q}^{\mathrm{ex,HS}} \rangle &= -\beta^{-1} \int [\boldsymbol{\nabla} \ln P^{\mathrm{ss}}(\boldsymbol{X})] \cdot \boldsymbol{J}_P(\boldsymbol{X}) dX \\
&= \beta^{-1} \int \ln P^{\mathrm{ss}}(\boldsymbol{X}) \boldsymbol{\nabla} \cdot \boldsymbol{J}_P(\boldsymbol{X}) dX,
\end{aligned}$$

where the second line is obtained by integration by parts. Since the time derivative of the Shannon entropy is provided as (see Eq. (2.19))

$$\frac{dS}{dt} = -k_{\mathrm{B}} \int \big(\boldsymbol{\nabla} \ln P(\boldsymbol{X})\big) \cdot \boldsymbol{J}_P(\boldsymbol{X}) dX,$$

we have

$$\begin{aligned}\frac{dS}{dt} - \frac{\langle \dot{q}^{\mathrm{ex,HS}} \rangle}{T} &= -k_{\mathrm{B}} \int \left[\boldsymbol{\nabla} \ln \frac{P(\boldsymbol{X})}{P^{\mathrm{ss}}(\boldsymbol{X})}\right] \cdot \boldsymbol{J}_P(\boldsymbol{X}) dX \\ &= \int [\boldsymbol{F}_P(\boldsymbol{X}) - \boldsymbol{F}_{P^{\mathrm{ss}}}(\boldsymbol{X})] \cdot \boldsymbol{J}_P(\boldsymbol{X}) dX.\end{aligned}$$

From Eqs. (2.23) and (4.12), we further obtain

$$\frac{dS}{dt} - \frac{\langle \dot{q}^{\mathrm{ex,HS}} \rangle}{T} = \mu T \int P(\boldsymbol{X}) |\boldsymbol{F}_P(\boldsymbol{X}) - \boldsymbol{F}_{P^{\mathrm{ss}}}(\boldsymbol{X})|^2 dX, \tag{4.13}$$

which shows that Eq. (4.5) holds at every moment.

In summary, we have two non-negative quantities

$$-\frac{\langle \dot{q}^{\mathrm{hk,HS}} \rangle}{T} = \int \boldsymbol{F}_{P^{\mathrm{ss}}}(\boldsymbol{X}) \cdot \boldsymbol{J}_P(\boldsymbol{X}) dX, \tag{4.14}$$

$$\frac{dS}{dt} - \frac{\langle \dot{q}^{\mathrm{ex,HS}} \rangle}{T} = \int [\boldsymbol{F}_P(\boldsymbol{X}) - \boldsymbol{F}_{P^{\mathrm{ss}}}(\boldsymbol{X})] \cdot \boldsymbol{J}_P(\boldsymbol{X}) dX, \tag{4.15}$$

and they sum up to the total EPR as

$$\dot{\Sigma}_P = -\frac{\langle \dot{q}^{\mathrm{hk,HS}} \rangle}{T} + \left[\frac{dS}{dt} - \frac{\langle \dot{q}^{\mathrm{ex,HS}} \rangle}{T}\right]. \tag{4.16}$$

Therefore, it is reasonable to define the housekeeping and excess EPRs as

$$\dot{\Sigma}_P^{\mathrm{hk,HS}} := \int \boldsymbol{F}_{P^{\mathrm{ss}}}(\boldsymbol{X}) \cdot \boldsymbol{J}_P(\boldsymbol{X}) dX \tag{4.17}$$

$$\dot{\Sigma}_P^{\mathrm{ex,HS}} := \int [\boldsymbol{F}_P(\boldsymbol{X}) - \boldsymbol{F}_{P^{\mathrm{ss}}}(\boldsymbol{X})] \cdot \boldsymbol{J}_P(\boldsymbol{X}) dX. \tag{4.18}$$

We call the decomposition $\dot{\Sigma}_P = \dot{\Sigma}_P^{\mathrm{hk,HS}} + \dot{\Sigma}_P^{\mathrm{ex,HS}}$ the Hatano–Sasa (HS) decomposition. Since the HS excess EPR vanishes when the system changes adiabatically following the steady state closely, it is sometimes called the non-adiabatic EPR [5, 6]. They are defined solely with the current, thermodynamic force, and the steady state, so we can generalize them to the general force-current structure.

It is worth noting that the definition (4.18) can recover the formula (2.32) without detailed balance; the HS excess EPR is provided as

$$\dot{\Sigma}_P^{\mathrm{ex,HS}} = -k_{\mathrm{B}} \frac{\partial}{\partial t} D(P(t) \| P^{\mathrm{ss}}(s))\Big|_{s=t}. \tag{4.19}$$

It is easily proved as

$$\begin{aligned}-k_{\mathrm{B}} \frac{\partial}{\partial t} D(P(t) \| P^{\mathrm{ss}}(s))\Big|_{s=t} &= -k_{\mathrm{B}} \int \frac{\partial P}{\partial t}(\boldsymbol{X}) \ln \frac{P(\boldsymbol{X})}{P^{\mathrm{ss}}(\boldsymbol{X})} dX = k_{\mathrm{B}} \int \boldsymbol{\nabla} \cdot \boldsymbol{J}_P(\boldsymbol{X}) \ln \frac{P(\boldsymbol{X})}{P^{\mathrm{ss}}(\boldsymbol{X})} dX \\ &= -k_{\mathrm{B}} \int \boldsymbol{J}_P(\boldsymbol{X}) \cdot \boldsymbol{\nabla} \ln \frac{P(\boldsymbol{X})}{P^{\mathrm{ss}}(\boldsymbol{X})} dX = k_{\mathrm{B}} \int \boldsymbol{J}_P(\boldsymbol{X}) \cdot [\boldsymbol{F}_P(\boldsymbol{X}) - \boldsymbol{F}_{P^{\mathrm{ss}}}(\boldsymbol{X})] dX.\end{aligned}$$

Equation (4.19) implies not only the convergence to the (instantaneous) steady state but also the limitation of the Hatano–Sasa decomposition as discussed in Sec. 4.2.

4.1.3 Maes–Netočný decomposition as an alternative

Another proposal of decomposition was given by Maes and Netočný (MN) thirteen years after the Hatano–Sasa decomposition [25] in relation to the so-called minimum entropy production principle [62]. They define the MN housekeeping EPR as

$$\dot{\Sigma}_P^{\mathrm{hk,MN}} := \inf_{\psi} \mu T \int |\boldsymbol{F}_P(\boldsymbol{X}) - (-\boldsymbol{\nabla}\psi(\boldsymbol{X}))|^2 P(\boldsymbol{X}) dX. \tag{4.20}$$

It is easy to see that $\dot{\Sigma}_P^{\mathrm{hk,MN}}$ is non-negative and not bigger than $\dot{\Sigma}_P$; thus, the MN excess EPR $\dot{\Sigma}_P^{\mathrm{ex,MN}}$ is defined by

$$\dot{\Sigma}_P^{\mathrm{ex,MN}} := \dot{\Sigma}_P - \dot{\Sigma}_P^{\mathrm{hk,MN}} \tag{4.21}$$

and becomes non-negative. They also show that the excess EPR follows

$$\dot{\Sigma}_P^{\mathrm{ex,MN}} = \inf_{\psi} \mu T \int |\boldsymbol{\nabla}\psi(\boldsymbol{X})|^2 P(\boldsymbol{X}) dX \quad \text{s.t.} \quad \mu T \boldsymbol{\nabla} \cdot (P(\boldsymbol{X}) \boldsymbol{\nabla}\psi(\boldsymbol{X})) = \boldsymbol{\nabla} \cdot \boldsymbol{J}_P(\boldsymbol{X}). \tag{4.22}$$

Therefore, the MN excess EPR can be interpreted as the minimum EPR to induce the time evolution by conservative force.

We can relate them to the Clausius inequality as follows. Let ψ^* be the optimizer of Eq. (4.22). We first confirm the relaion

$$\dot{\Sigma}_P^{\mathrm{ex,MN}} = -\int \psi^*(\boldsymbol{X}) \boldsymbol{\nabla} \cdot \boldsymbol{J}_P(\boldsymbol{X}) dX. \tag{4.23}$$

This is because

$$\begin{aligned} \mu T \int |\boldsymbol{\nabla}\psi^*(\boldsymbol{X})|^2 P(\boldsymbol{X}) dX &= -\mu T \int \psi^*(\boldsymbol{X}) \boldsymbol{\nabla} \cdot [P(\boldsymbol{X}) \boldsymbol{\nabla}\psi^*(\boldsymbol{X})] dX \\ &= -\int \psi^*(\boldsymbol{X}) \boldsymbol{\nabla} \cdot \boldsymbol{J}_P(\boldsymbol{X}) dX, \end{aligned}$$

where the second line comes from the condition in Eq. (4.22). Then, we define the pseudo-canonical distribution P^{pc} by

$$P^{\mathrm{pc}}(\boldsymbol{X}) := \frac{P(\boldsymbol{X}) e^{-\psi^*(\boldsymbol{X})/k_{\mathrm{B}}}}{Z}, \quad Z := \int P(\boldsymbol{X}) e^{-\psi^*(\boldsymbol{X})/k_{\mathrm{B}}} dX, \tag{4.24}$$

to rewrite the potential into

$$\psi^*(\boldsymbol{X})/k_{\mathrm{B}} = \ln P(\boldsymbol{X}) - \ln P^{\mathrm{pc}}(\boldsymbol{X}) - \ln Z. \tag{4.25}$$

If we define the stochastic MN excess heat by

$$\dot{q}^{\mathrm{ex,MN}} dt := -\beta^{-1} \boldsymbol{\nabla} \ln P^{\mathrm{pc}}(\boldsymbol{X}) \circ d\boldsymbol{X} \tag{4.26}$$

similarly to Eq. (4.9), we get

$$\frac{\langle \dot{q}^{\mathrm{ex,MN}} \rangle}{T} = -k_{\mathrm{B}} \int \boldsymbol{\nabla} \ln P^{\mathrm{pc}}(\boldsymbol{X}) \cdot \boldsymbol{J}_P(\boldsymbol{X}) dX. \tag{4.27}$$

Therefore, we obtain

$$\dot{\Sigma}_P^{\mathrm{ex,MN}} = \frac{dS}{dt} - \frac{\langle \dot{q}^{\mathrm{ex,MN}} \rangle}{T} \tag{4.28}$$

because

$$
\begin{aligned}
\frac{dS}{dt} - \frac{\langle \dot{q}^{\mathrm{ex,MN}} \rangle}{T} &= -k_{\mathrm{B}} \int \boldsymbol{\nabla} \ln \frac{P(\boldsymbol{X})}{P^{\mathrm{pc}}(\boldsymbol{X})} \cdot \boldsymbol{J}_P(\boldsymbol{X}) dX \\
&= \int \boldsymbol{\nabla} \psi^*(\boldsymbol{X}) \cdot \boldsymbol{J}_P(\boldsymbol{X}) dX \\
&= -\int \psi^*(\boldsymbol{X}) \boldsymbol{\nabla} \cdot \boldsymbol{J}_P(\boldsymbol{X}) dX
\end{aligned}
$$

and the last line provides the MN excess EPR as in Eq. (4.23). Finally, we see that the inequality

$$
\dot{\Sigma}_P^{\mathrm{ex,MN}} \geq 0, \tag{4.29}
$$

which is always valid by definition, provides an extention of the Clausius inequality with the definition of excess heat as in Eq. (4.26).

At this point, defining the housekeeping and excess EPRs is only to provide the generalized Clausius inequlaity in a concise form. In this sense, the HS and MN decompositions are not so different. However, as discussed in the next section, decomposing EPR has another aspect; the decomposed portions can be seen as the contributions from distinct aspects in the whole dynamics. That is, the housekeeping EPR stems from the external driving that brings the system away from equilibrium, while the excess represents the minimum dissipation without futile cyclic motion. This point of view is no longer associated with any steady states and captured much better by the MN decomposition.

4.2 Geometric decomposition from the force-current structure

The two definitions can be extended to various systems based on the force-current structure. Essentially, the generalization of the HS decomposition has been done by 2010's; on the other hand, the generalizability of the MN decomposition had not been realized until we and another group found it independently [19, 59].

4.2.1 Drawback of the HS decomposition

Although it is not so obvious which expression of the HS excess and housekeeping EPRs in the Langevin system to refer to when generalizing it, they are usually generalized based on the expression in Eqs. (4.17) and (4.18) as [5, 6, 24, 26, 27, 63, 64]

$$
\dot{\Sigma}^{\mathrm{hk,HS}}(x) := \langle J(x), F(x^{\mathrm{ss}}) \rangle, \tag{4.30}
$$

$$
\dot{\Sigma}^{\mathrm{ex,HS}}(x) := \langle J(x), F(x) - F(x^{\mathrm{ss}}) \rangle. \tag{4.31}
$$

They obviously divide the total EPR (defined in Eq. (3.7)) as

$$
\dot{\Sigma}(x) = \dot{\Sigma}^{\mathrm{hk,HS}}(x) + \dot{\Sigma}^{\mathrm{ex,HS}}(x), \tag{4.32}
$$

which is the generalized HS decomposition.

Although this definition has been widely adopted in various types of dynamics such as Markov jump processes [5], chemical reaction networks [26, 27], and open quantum systems [24, 63], their positivity is not guaranteed by the force-current structure. In fact, the HS excess EPR can be negative even if there is a stable steady state [59, 64]. As discussed in Chapters 7 and 9, the steady state in the definition should satisfy some conditions, which requires the steady state to be similar to equilibrium states.

In addition, the definition explicitly depends on the steady state; this has two problems. First, in nonlinear systems, we may have multiple (locally) stable steady states [65, 66], or may not have meaningful steady states due to limit cycles and turbulence [66–70]. Hence, the HS decomposition does not work in these physically important systems. In addition, the HS decomposition and related decompositions [71, 72] involve steady states, or in other words, long-time behavior. In this sense, the decomposition is not “local in time.” This can make the HS decomposition less competent for analyzing the rate of dissipation.

4.2.2 Geometric decomposition

We can avert these problems by generalizing the MN decomposition. The generalization presented below was studied in our series of papers [19–21]. We first developed a geometric decomposition that generalizes the MN decomposition to Markov jump processes and chemical reaction networks in Ref. [19]. Another group also found a similar generalization at almost the same time independently [59]. We then moved to hydrodynamic systems [20] and Markovian open quantum systems [21] and established the geometric decomposition there. In the following, we explain the geometric decomposition based on the force-current strucute. We argue concrete realizations in later chapters.

We can think of a geometric decomposition by comparing Eq. (4.20) with the geometric expression (2.24). We define the housekeeping EPR by

$$\dot{\Sigma}^{\mathrm{hk}}(x) := \inf_{F' \in \mathscr{C}} \|F(x) - F'\|_x^2. \tag{4.33}$$

Here, $\mathscr{C}$ is the space of the conservative forces, defined by

$$\mathscr{C} = \{-\nabla\psi \mid \psi \in \mathcal{S}_0\} \subset \mathscr{F}. \tag{4.34}$$

As discussed in Sec. 3.3, if the thermodynamic force is conservative, the system is an equilibrium system. Equation (4.33) provides the squared distance between the actual thermodynamic force and the conservative spaces, hence it quantifies how nonequilibrium the system is. In other words, the housekeeping EPR is the dissipation due to the breaking of detailed balance. If the system is detailed balanced, there is no houskeeeping dissipation.

The housekeeping EPR is always non-negative by definition and never larger than the total EPR as $F' = 0$, which returns $\dot{\Sigma}(x)$, falls into the feasible set of minimization. Thus, defining the excess EPR by

$$\dot{\Sigma}^{\mathrm{ex}}(x) := \dot{\Sigma}(x) - \dot{\Sigma}^{\mathrm{hk}}(x), \tag{4.35}$$

we obtain a non-negative decomposition of the EPR,

$$\dot{\Sigma}(x) = \dot{\Sigma}^{\mathrm{hk}}(x) + \dot{\Sigma}^{\mathrm{ex}}(x), \tag{4.36}$$

which we call the geometric decomposition. The geometric decomposition overcomes the problems of the HS decomposition as the excess EPR is also always non-negative and the decomposition does not rely on the existence of steady states. All it needs is the force-current structure.

Next, we prove the equality

$$\dot{\Sigma}^{\mathrm{ex}}(x) = \inf_{F' \in \mathscr{F}} \|F'\|_x^2 \quad \text{s.t.} \quad \nabla^* \mathscr{M}_x(F') = \nabla^* J(x), \tag{4.37}$$

which generalizes Eq. (4.22). From this expression, we can learn an important meaning of the excess EPR. It can be rewritten in terms of current as

$$\dot{\Sigma}^{\mathrm{ex}}(x) = \inf_{J' \in \mathscr{F}} \langle J', \mathscr{M}_x^{-1}(J') \rangle \quad \text{s.t.} \quad \nabla^* J' = \nabla^* J(x), \tag{4.38}$$

where $\mathscr{M}_x^{-1}$ is the inverse of $\mathscr{M}_x$. That is, the excess EPR generally characterizes the dissipation that is required to induce the irreversible part of the dynamics, $\nabla^* J(x)$. If there is no reversible part in the equation of motion, it is connected to the whole dynamics, and consequently, vanishes in a steady state,

$$\dot{\Sigma}^{\mathrm{ex}}(x^{\mathrm{ss}}) = 0, \tag{4.39}$$

which is realized by $J' = 0$ in Eq. (4.38). This corresponds to the equality in the generalized Clausius inequality and is always valid in the HS decomposition. On the other hand, if we have a reversible part, the connection to the stationarity becomes subtle; we will not generally obtain such an equality. It can be seen as another deviation from the original idea by Oono and Paniconi, which does not exist in the HS decomposition; nevertheless, the excess EPR of the geometric decomposition never becomes negative to hold much wider range of application. Moreover, it has richer connections to other fields such as thermodynamic trade-off relations and optimal transport theory, as discussed in later chapters.

Before proving Eq. (4.37), we consider the orthogonal complement of $\mathscr{C}$ regarding the inner product (3.9). If a vector F' belongs to the orthogonal complement $\mathscr{C}^{\perp}$, it satisfies

$$0 = \langle F', \nabla\psi\rangle_x = \langle\psi, \nabla^*\mathscr{M}_x(F')\rangle \tag{4.40}$$

for any $\psi \in \mathscr{S}_0$. Thus, the orthogonal complement is given by

$$\mathscr{C}^{\perp} = \{F' \in \mathscr{F} \mid \nabla^*\mathscr{M}_x(F') = 0\}. \tag{4.41}$$

In terms of the corresponding current $J' = \mathscr{M}_x(F')$, we can interpret this space as the forces that induce cyclic currents, which satisfy

$$\nabla^* J' = 0. \tag{4.42}$$

Additionally, we define the affine space

$$F(x) + \mathscr{C}^{\perp} = \{F' \in \mathscr{F} \mid \nabla^*\mathscr{M}_x(F' - F(x)) = 0\}. \tag{4.43}$$

If a vector F'' belongs to this space, the corresponding current $J'' = \mathscr{M}_x(F'')$ satisfies

$$\nabla^* J'' = \nabla^* J(x), \tag{4.44}$$

which indicates that the two currents lead to the same dynamical result and that we can get one by adding or subtracting cyclic currents to/from the other.

We show Eq. (4.37). Let F^* be the minimizer of Eq. (4.33) (see also Fig. 4.1, where $F_c(x)$ corresponds to F^*). It is the unique minimizer because Eq. (4.37) is a strictly convex optimization. It also possesses these properties

1. $F^* \in F(x) + \mathscr{C}^{\perp}$.
2. F^* is the unique intersection between $\mathscr{C}$ and $F(x) + \mathscr{C}^{\perp}$.
3. $F^* = \arg\min_{F' \in F(x)+\mathscr{C}^{\perp}} \|F'\|_x^2$.

Once they are confirmed, Eq. (4.37) is soon verified: By definition of $\mathscr{C}^{\perp}$, the right-hand side is rewritten as

$$\inf_{F' \in F(x)+\mathscr{C}^{\perp}} \|F'\|_x^2, \tag{4.45}$$

which is solved by F^* from property 3. It is actually the excess EPR because the total EPR is transformed as

$$\begin{aligned}\dot{\Sigma}(x) = \|F(x)\|_x^2 &= \|F(x) - F^* + F^*\|_x^2 \\ &= \|F(x) - F^*\|_x^2 + \|F^*\|_x^2 + 2\langle F(x) - F^*, F^*\rangle_x \\ &= \|F(x) - F^*\|_x^2 + \|F^*\|_x^2\end{aligned}$$

and $\|F(x) - F^*\|_x^2$ is the housekeeping EPR. Here, we used $F(x) - F^* \in \mathscr{C}^{\perp}$ and $F^* \in \mathscr{C}$.

Although the properties are standard results of linear algebra and functional analysis, here we provide rough proof (if you are convinced by looking at Fig. 4.1, you can skip the following proof and jump to the last paragraph). Let us show the first property, i.e., that it satisfies

$$\langle F(x) - F^*, F'\rangle_x = 0 \tag{4.46}$$

for any $F' \in \mathscr{C}$. Otherwise,

$$\|F(x) - F^* - \alpha F'\|_x^2 = \|F(x) - F^*\|_x^2 + \|F'\|_x^2\alpha\left(\alpha - \frac{\langle F(x) - F^*, F'\rangle_x}{\|F'\|_x^2}\right) \tag{4.47}$$

can be smaller than $\|F(x) - F^*\|_x^2$ by setting

$$\alpha = \frac{\langle F(x) - F^*, F'\rangle_x}{2\|F'\|_x^2} \tag{4.48}$$

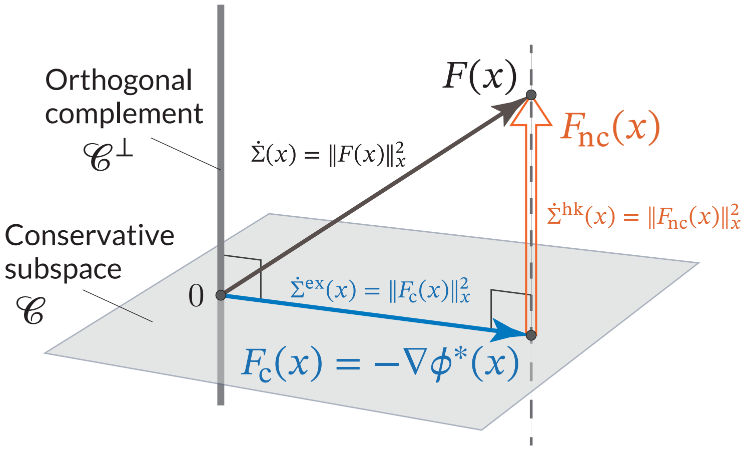

Figure 4.1: Schematic diagram of the geometric decomposition. On the one hand, we can see that the thermodynamic force is orthogonally projected to the conservative subspace $\mathscr{C}$. The projected (conservative) force $F_{\mathrm{c}}(x) = -\nabla\phi^*(x)$ provides the excess EPR. The difference (nonconservative force) $F_{\mathrm{nc}}(x)$ leads to the housekeeping EPR. On the other hand, the nonconservative force $F_{\mathrm{nc}}(x)$ can be regarded as providing the distance between the origin (zero force) 0 and the affine space $F(x) + \mathscr{C}^{\perp}$. This interpretation corresponds to Eq. (4.37). This figure is adapted from Ref. [21].

because then

$$\|F(x) - F^* - \alpha F'\|_x^2 = \|F(x) - F^*\|_x^2 - \frac{(\langle F(x) - F^*, F'\rangle_x)^2}{4\|F'\|_x^2} < \|F(x) - F^*\|_x^2, \tag{4.49}$$

which contradicts the minimization property of F^*.

To show the second property, the uniqueness, we assume there exists F' that also belongs to the intersection $\mathscr{C} \cap (F(x) + \mathscr{C}^{\perp})$. Then, $F' - F^* \in \mathscr{C} \cap \mathscr{C}^{\perp}$. Therefore, $\|F' - F^*\|_x^2 = \langle F' - F^*, F' - F^*\rangle_x = 0$, which concludes $F' = F^*$. Thus, F^* must be the unique intersection of $\mathscr{C}$ and $F(x) + \mathscr{C}^{\perp}$.

We finally show the third property. Take $F' \in F(x) + \mathscr{C}^{\perp}$. Then, because $F^* \in \mathscr{C}$ and $F' - F^* \in \mathscr{C}^{\perp}$, we get

$$\|F'\|_x^2 = \|F' - F^* + F^*\|_x^2 \tag{4.50}$$
$$= \|F' - F^*\|_x^2 + \|F^*\|_x^2 + 2\langle F' - F^*, F^*\rangle_x \tag{4.51}$$
$$= \|F' - F^*\|_x^2 + \|F^*\|_x^2. \tag{4.52}$$

Therefore, $\|F'\|_x^2$ is bigger than $\|F^*\|_x^2$ as long as $F' \neq F^*$; thus, F^* is the unique optimizer of the minimization $\inf_{F' \in F(x) + \mathscr{C}^{\perp}} \|F'\|_x^2$.

In summary, the geometric decomposition divides the total EPR into the housekeeping and excess EPRs provided by minimizations as in Eqs. (4.33) and (4.37), which provide orthogonal projection of the thermodynamic force. Those minimizations are accomplished by a unique optimizer. The situation is depicted schematically as in Fig. 4.1, which roughly shows the validity of the three mathematical properties. Hereafter, we write the optimizer as $F_{\mathrm{c}}(x)$ since it belongs to the conservative subspace $\mathscr{C}$. We also let $F_{\mathrm{nc}}(x)$ denote the difference $F(x) - F_{\mathrm{c}}(x)$ (nc stands for "nonconservative"). As a result, we obtain the explicit representations of the decomposition

$$\dot{\Sigma}^{\mathrm{hk}}(x) = \|F_{\mathrm{nc}}(x)\|_x^2, \tag{4.53}$$
$$\dot{\Sigma}^{\mathrm{ex}}(x) = \|F_{\mathrm{c}}(x)\|_x^2. \tag{4.54}$$

The induced currents $J_{\mathrm{c}}(x) = \mathscr{M}_x(F_{\mathrm{c}}(x))$ and $J_{\mathrm{nc}}(x) = \mathscr{M}_x(F_{\mathrm{nc}}(x))$ satisfy

$$\nabla^* J_{\mathrm{c}}(x) = \nabla J(x), \quad \nabla^* J_{\mathrm{nc}}(x) = 0 \tag{4.55}$$

because $F_{\mathrm{nc}}(x) \in \mathscr{C}^{\perp}$. The conservative force has a potential $\phi^*(x)$ such that $F_{\mathrm{c}}(x) = -\nabla\phi^*(x)$. Combining it with the first equation in Eq. (4.55), we find

$$\nabla^* \mathscr{M}_x\big(\nabla\phi^*(x)\big) = -\nabla J(x) = -\frac{\partial x}{\partial t} + f^{\mathrm{rev}}(x). \tag{4.56}$$

In practice, this equation can be used to obtain the decomposition directly. Up to the null space of ∇, $\nabla^*\mathscr{M}_x\nabla$ tends to be an invertible operator, and we can derive an explicit expression

$$\phi^*(x) = -(\nabla^*\mathscr{M}_x\nabla)^+\big(\nabla J(x)\big), \tag{4.57}$$

where $+$ indicates a kind of generalized inverse.

4.2.3 Maximization formula

In addition to the minimization representations, the geometric decomposition also has maximization expressions:

$$\dot{\Sigma}^{\mathrm{hk}}(x) = \sup_{F' \in \mathscr{C}^{\perp}} \frac{|\langle F(x), F' \rangle_x|^2}{\|F'\|_x^2}, \tag{4.58}$$

$$\dot{\Sigma}^{\mathrm{ex}}(x) = \sup_{F' \in \mathscr{C}} \frac{|\langle F(x), F' \rangle_x|^2}{\|F'\|_x^2}. \tag{4.59}$$

The total EPR can also be given similarly as

$$\dot{\Sigma}(x) = \sup_{F' \in \mathscr{F}} \frac{|\langle F(x), F' \rangle_x|^2}{\|F'\|_x^2}. \tag{4.60}$$

Those formulas are proved by the Cauchy–Schwarz inequality. We first show Eq. (4.60). For any $F' \in \mathscr{F}$, we have

$$|\langle F(x), F' \rangle_x|^2 \leq \|F'\|_x^2 \|F(x)\|_x^2 \tag{4.61}$$

and the equality is acheived by $F' = F(x)$. By dividing both sides by $\|F'\|_x^2$ and considering the maximization regarding F', we obtain Eq. (4.60).

If F' is restricted to $\mathscr{C}$, since $\langle F_{\mathrm{nc}}(x), F' \rangle_x = 0$, we have

$$|\langle F(x), F' \rangle_x|^2 = |\langle F_{\mathrm{c}}(x), F' \rangle_x|^2 \leq \|F'\|_x^2 \|F_{\mathrm{c}}(x)\|_x^2 \tag{4.62}$$

and the equality can be acheived by $F' = F_{\mathrm{c}}(x)$, which implies Eq. (4.59) because $\dot{\Sigma}^{\mathrm{ex}}(x) = \|F_{\mathrm{c}}(x)\|_x^2$. Equation (4.58) is also given in the same way by restricting F' to $\mathscr{C}^{\perp}$.

4.2.4 Schnakenberg formula

In section 3.4, we proved Eq. (3.19) for steady states. It was key that the steady-state current is expressed by an operator $\mathcal{T}$ that characterizes the cycles. Now, the nonconservative current $J_{\mathrm{nc}}(x) = \mathscr{M}_x(F_{\mathrm{nc}}(x))$ also satisfies

$$\nabla^* J_{\mathrm{nc}}(x) = 0. \tag{4.63}$$

Therefore, there is $j_c^{\dagger}$ such that $J_{\mathrm{nc}}(x) = \mathcal{T}(j_c^{\dagger})$. We also define

$$f_c^{\dagger} = \mathcal{T}^*(F_{\mathrm{nc}}(x)) \tag{4.64}$$

to obtain the generalization of the Schnakenberg formula (3.19)

$$\dot{\Sigma}^{\mathrm{hk}}(x) = \langle j_c^{\dagger}, f_c^{\dagger} \rangle. \tag{4.65}$$

While the original equality is only available in a steady state, Eq. (4.65) holds in any state. This is because the housekeeping EPR reflects the nonequilibrium aspect of the system at the moment.

We expect the formula for the housekeeping EPR can be useful for analyzing nonequilibrium nonstationary states, as the cyclic point of view provided by the original Schnakenberg formula has offered insights into nonequilibrium steady states [73–76].

Chapter 5

Thermodynamic trade-off relations

Arguably, various thermodynamic trade-off relations are one of the biggest achievements of modern stochastic thermodynamics [7, 9]. It reveals universal trade-offs between the entropy production, the fundamental "cost" in physics, and other costs like accuracy or speed.

In this chapter, we illustrate general ideas by reviewing relevant results in Langevin systems, and explain that the force-current structure can be used to generally discuss them.

5.1 Review

5.1.1 Overview

The second law of thermodynamics is generally stated as

$$\dot{\Sigma}(x) \geq 0. \tag{5.1}$$

The inequality expresses that the total entropy of the universe must not decrease at every instance. Importantly, it provides a universal restriction to any physical processes.

The equailty is achieved when we manipulate the system very slowly, i.e., quasi-statistically. On the other hand, one cannot deduce any information about finite speed processes other than the inequality, which becomes looser as the process gets faster. Moreover, as discussed in the last chapter, if there are external effects that break detailed balance, the equality will never be achieved. Still, we can tighten the inequality by the housekeeping-excess decomposition as we have seen.

There is another direction. In the last decade, stochastic thermodynamics has found several universal bounds that generalize the second law of thermodynamics. For example, the thermodynamic uncertainty relation (TUR) is a lower bound on the EPR, typically provided as

$$\dot{\Sigma}(x) \geq \frac{j^2}{D} \tag{5.2}$$

with a flow j and a diffusivity or fluctuation measure D. The inequality quantitatively shows that the dissipation is inevitable when (1) we want to gain a flow j and (2) we want to reduce fluctuations D.

It was first proposed in a simple model of stochastic reaction in a steady state [31, 36], and later proved for general Markov jump processes in steady states [32, 77]. Following these findings, the TUR is extended in several directions, including inequalities for processes starting form arbitrary initial states during an arbitrary time interval, in both classical and quantum systems [19, 28, 29, 34, 35, 37, 39, 40, 60, 77–90]. We proposed its generalization in deterministic chemical reaction networks [18].

The TUR can be practically useful: First, it leads to trade-offs between power and efficiency [91, 92]. These results go beyond Carnot's bound on the efficiency of heat engines [61]. Moreover, it can be used to estimate the value of EPR, which is difficult to directly measure [37, 85, 93, 94].

Another type of trade-off is the thermodynamic speed limit (TSL); it is typically given by

$$\tau\Sigma_\tau = \tau \int_0^\tau \dot{\Sigma}(x_t)dt \geq \mathcal{D}(x(0), x(\tau))^2, \tag{5.3}$$

where τ is a time interval and $\mathcal{D}(x(0), x(\tau))$ is a length between states. It indicates that to change a state into another one distant from it by $\mathcal{D}(x(0), x(\tau))$, we cannot simultaneously decrease the time and EPR.

A general speed limit involving entropy production was first given in Ref. [41], which used the total variation as the distance measure. Similar bounds were derived in open quantum systems [43], chemical reaction networks [18], and evolutionary processes [95]. After that, it has been realized that we can utilize a more sophisticated distance, called the Wasserstein distance [19, 28, 29, 39, 44–46, 60, 96–99] (earlier applications to stochastic thermodynamics can be found in Refs. [100–102]). The Wasserstein distance is studied in optimal transport theory, a branch of mathematics [48]. These bounds are sometimes called classical speed limits in comparison with the quantum speed limit [103–106] or speed limit theorems [107], but we call them thermodynamic speed limits to emphasize that they involve the fundamental thermodynamic cost, entropy production.

In this section, we review these relations more concretely via the Langevin dynamics. Then, we will reveal how they can be derived from the force-current structure.

5.1.2 Thermodynamic uncertainty relation

Let us consider an observable $\mathcal{O}(\boldsymbol{X})$ and its expectation value

$$\langle \mathcal{O} \rangle = \int \mathcal{O}(\boldsymbol{X}) P(\boldsymbol{X}) dX. \tag{5.4}$$

In an infinitesimal time interval dt, the observable changes as

$$d\mathcal{O} = \mathcal{O}(\boldsymbol{X} + d\boldsymbol{X}) - \mathcal{O}(\boldsymbol{X}) = \boldsymbol{\nabla}\mathcal{O}(\boldsymbol{X}) \circ d\boldsymbol{X}, \tag{5.5}$$

where we used the chain rule (2.12) to obtain the last equality. We also have

$$\langle (d\mathcal{O})^2 \rangle = 2D\langle |\boldsymbol{\nabla}\mathcal{O}(\boldsymbol{X})|^2 \rangle dt \tag{5.6}$$

up to the leading order (hereafter we neglect terms of order smaller than dt). Therefore, the average and variance of the change are given by

$$\langle d\mathcal{O} \rangle = dt \int \boldsymbol{\nabla}\mathcal{O}(\boldsymbol{X}) \cdot \boldsymbol{J}_P(\boldsymbol{X}) dX, \tag{5.7}$$

$$\mathrm{Var}(d\mathcal{O}) = dt\, 2D \int |\boldsymbol{\nabla}\mathcal{O}(\boldsymbol{X})|^2 P(\boldsymbol{X}) dX, \tag{5.8}$$

where Var is the variance and defined by $\langle d\mathcal{O}^2 \rangle - \langle d\mathcal{O} \rangle^2$. We find that $\langle d\mathcal{O} \rangle / dt$ corresponds to the time derivative of $\langle \mathcal{O} \rangle$:

$$\begin{aligned} \frac{d}{dt}\langle \mathcal{O} \rangle &= \int \mathcal{O}(\boldsymbol{X}) \frac{\partial P}{\partial t}(\boldsymbol{X}) dX = -\int \mathcal{O}(\boldsymbol{X}) \boldsymbol{\nabla} \cdot \boldsymbol{J}_P(\boldsymbol{X}) dX \\ &= \int \boldsymbol{\nabla}\mathcal{O}(\boldsymbol{X}) \cdot \boldsymbol{J}_P(\boldsymbol{X}) dX. \end{aligned} \tag{5.9}$$

We also define the diffusivity $D_{\mathcal{O}}$ by

$$D_{\mathcal{O}} := \lim_{dt \to 0} \frac{\mathrm{Var}(d\mathcal{O})}{2dt} = D \int |\boldsymbol{\nabla}\mathcal{O}(\boldsymbol{X})|^2 P(\boldsymbol{X}) dX. \tag{5.10}$$

If $\mathcal{O} = X_i$, D_{X_i} becomes the diffusion constant D. In general, $D_{\mathcal{O}}$ quantifies how easily the observable diffuses, i.e., becomes uncertain.

The changing rate $d_t\langle \mathcal{O} \rangle = d\langle \mathcal{O} \rangle / dt$ and the diffusivity yield the lower bound on the EPR [80]

$$\dot{\Sigma}_P \geq k_{\mathrm{B}} \frac{(d_t \langle \mathcal{O} \rangle)^2}{D_{\mathcal{O}}}. \tag{5.11}$$

We call this kind of lower bounds on the EPR short-time TURs. The short-time TUR indicates a univeral trade-off between the dissipation $\dot{\Sigma}_P$ and the diffusivity relative to the changing rate; i.e., if we want to keep the dynamics accurate, we need dissipation.

The short-time TUR is proved by just applying the Cauchy–Schwarz inequality to $d_t\langle\mathcal{O}\rangle$:

$$\begin{aligned}(d_t\langle\mathcal{O}\rangle)^2 &= \left(\int \boldsymbol{\nabla}\mathcal{O}(\boldsymbol{X})\cdot\boldsymbol{J}_P(\boldsymbol{X})dX\right)^2\\ &\leq \int |\boldsymbol{\nabla}\mathcal{O}(\boldsymbol{X})|^2 DP(\boldsymbol{X})dX \int \frac{|\boldsymbol{J}_P(\boldsymbol{X})|^2}{DP(\boldsymbol{X})}dX\\ &= D_{\mathcal{O}}\int \frac{1}{k_{\mathrm{B}}}\boldsymbol{J}_P(\boldsymbol{X})\cdot\boldsymbol{F}_P(\boldsymbol{X})dX = \frac{1}{k_{\mathrm{B}}}D_{\mathcal{O}}\dot{\Sigma}_P,\end{aligned}$$

where we used Eq. (2.23) in the third line.

In the Langevin dynamics, we can extend the short-time TUR in two ways. First, the observable can depend on the trajectory rather than the instantaneous state. We consider a current-like observable with weight $\boldsymbol{w}$ defined by

$$d\mathcal{J}_{\boldsymbol{w}} = \boldsymbol{w}(\boldsymbol{X})\circ d\boldsymbol{X}. \tag{5.12}$$

By replacing $\boldsymbol{\nabla}\mathcal{O}$ in the above proof with $\boldsymbol{w}$, we can generalize the inequality to current-like observables as

$$\dot{\Sigma}_P \geq k_{\mathrm{B}}\frac{\langle\mathcal{J}_{\boldsymbol{w}}\rangle^2}{D_{\mathcal{J}_{\boldsymbol{w}}}}, \tag{5.13}$$

where

$$\langle\mathcal{J}_{\boldsymbol{w}}\rangle := \lim_{dt\to 0}\frac{\langle d\mathcal{J}_{\boldsymbol{w}}\rangle}{dt} = \int \boldsymbol{w}(\boldsymbol{X})\cdot\boldsymbol{J}_P(\boldsymbol{X})dX, \tag{5.14}$$

$$D_{\mathcal{J}_{\boldsymbol{w}}} := \lim_{dt\to 0}\frac{\mathrm{Var}(d\mathcal{J}_{\boldsymbol{w}})}{2dt} = D\int |\boldsymbol{w}(\boldsymbol{X})|^2 P(\boldsymbol{X})dX. \tag{5.15}$$

The short-time TUR for the state-dependent observable $\mathcal{O}$ is derived by setting $\boldsymbol{w} = \boldsymbol{\nabla}\mathcal{O}$. Thus, the lower bound in Eq. (5.13) is more general than that in Eq. (5.11). However, we should be aware that to measure the current-like observable experimentally, we need to obtain two-point statistics, which is harder to know than the moments of observables that are determined by the instantaneous state.

Second, the EPR can be replaced by the excess EPR as

$$\dot{\Sigma}_P^{\mathrm{ex}} \geq k_{\mathrm{B}}\frac{(d_t\langle\mathcal{O}\rangle)^2}{D_{\mathcal{O}}}. \tag{5.16}$$

Let ψ^* be the potential that provides the excess EPR (Sec. 4.1.3). Since it satisfies $\boldsymbol{\nabla}\cdot\boldsymbol{J}_P(\boldsymbol{X}) = -\mu T\boldsymbol{\nabla}\cdot(P(\boldsymbol{X})\boldsymbol{\nabla}\psi^*(\boldsymbol{X}))$, the proof of the short-time TUR can be recast as

$$\begin{aligned}(d_t\langle\mathcal{O}\rangle)^2 &= \left(-\int \mathcal{O}(\boldsymbol{X})\boldsymbol{\nabla}\cdot\boldsymbol{J}_P(\boldsymbol{X})dX\right)^2\\ &= \left(\mu T\int \mathcal{O}(\boldsymbol{X})\boldsymbol{\nabla}\cdot(P(\boldsymbol{X})\boldsymbol{\nabla}\psi^*(\boldsymbol{X}))dX\right)^2\\ &= \left(-\int(\mu TP(\boldsymbol{X}))\boldsymbol{\nabla}\mathcal{O}(\boldsymbol{X})\cdot\boldsymbol{\nabla}\psi^*(\boldsymbol{X})dX\right)^2\\ &\leq \int \mu TP(\boldsymbol{X})|\boldsymbol{\nabla}\mathcal{O}(\boldsymbol{X})|^2dX\int \mu TP(\boldsymbol{X})|\boldsymbol{\nabla}\psi^*(\boldsymbol{X})|^2dX\\ &= \frac{1}{k_{\mathrm{B}}}D_{\mathcal{O}}\dot{\Sigma}_P^{\mathrm{ex}},\end{aligned}$$

where we used the Cauchy–Schwarz inequality with $\mu TP(\boldsymbol{X})$ being the metric in the fourth line. Because the excess EPR is never larger than the total EPR, Eq. (5.16) also tightens the short-time TUR (5.11).

5.1.3 Thermodynamic speed limit

Next, we consider transforming an ensemble $P_a(\boldsymbol{X})$ to $P_b(\boldsymbol{X})$. Optimal transport theory provides us with a distance function, called the Wasserstein distance, in terms of transportation as [48]

$$\mathscr{W}(P_a, P_b) = \inf_{\Pi} \sqrt{\int \int |\boldsymbol{X} - \boldsymbol{Y}|^2 \Pi(\boldsymbol{X}, \boldsymbol{Y}) dX dY}, \tag{5.17}$$

where Π must connect the two distributions as

$$\int \Pi(\boldsymbol{X}, \boldsymbol{Y}) dY = P_a(\boldsymbol{X}), \quad \int \Pi(\boldsymbol{X}, \boldsymbol{Y}) dX = P_b(\boldsymbol{Y}). \tag{5.18}$$

We will provide a detailed introduction to optimal transport theory in Appendix. A. One key point of the Wasserstein distance is the following expression called the Benamou–Brenier formula [48, 108]:

$$\mathscr{W}(P_a, P_b) = \inf_{p,\psi} \sqrt{\tau \int_0^\tau \int p(t, \boldsymbol{X}) |\boldsymbol{\nabla} \psi(t, \boldsymbol{X})|^2 dX dt} \tag{5.19}$$

with conditions

$$p(0) = P_a, \quad p(\tau) = P_b, \quad \frac{\partial p}{\partial t}(t, \boldsymbol{X}) = -\boldsymbol{\nabla} \cdot (p(t, \boldsymbol{X}) \boldsymbol{\nabla} \psi(t, \boldsymbol{X})). \tag{5.20}$$

Note that the time evolution of the actual distribution $P(t)$ can satisfy these conditions when we set $P_a = P(0)$ and $P_b = P(\tau)$; we can use the potential ψ^* that provides the excess EPR (Sec. 4.1.3) because it satisfies

$$\frac{\partial P}{\partial t}(\boldsymbol{X}) = -\mu T \boldsymbol{\nabla} \cdot (P(\boldsymbol{X}) \boldsymbol{\nabla} \psi^*(\boldsymbol{X})). \tag{5.21}$$

With the actual trajectory of the distribution and the potential ψ^*, we get the upper bound of the Wasserstein distance

$$\mathscr{W}(P(0), P(\tau)) \leq \sqrt{\tau (\mu T)^2 \int_0^\tau \int P(t, \boldsymbol{X}) |\boldsymbol{\nabla} \psi^*(t, \boldsymbol{X})|^2 dX dt}. \tag{5.22}$$

Here, remember that the potential provided the excess EPR as

$$\dot{\Sigma}_P^{\mathrm{ex}} = \mu T \int P(\boldsymbol{X}) |\boldsymbol{\nabla} \psi^*(\boldsymbol{X})|^2 dX. \tag{5.23}$$

Therefore, the inequality turns into a lower bound on the excess entropy production (EP)

$$\Sigma_\tau^{\mathrm{ex}} = \int_0^\tau \dot{\Sigma}_P^{\mathrm{ex}} dt \geq \frac{\mathscr{W}(P(0), P(\tau))^2}{\mu T \tau}. \tag{5.24}$$

The equality is satisfied when the time evolution is optimal, i.e., it provides the Wasserstein distance:

$$\mathscr{W}(P(0), P(\tau)) = \sqrt{\tau \int_0^\tau \int P^*(t, \boldsymbol{X}) |\boldsymbol{\nabla} \psi^*(t, \boldsymbol{X})|^2 dX dt}, \tag{5.25}$$

where $P^*(t)$ gives the optimal time evolution. This condition is a finite-time extension of the quasistatic process, and the lower bound is achieved in a finite-speed protocol. According to the optimal transport theory, the optimal solution satisfies the constant-speed property [48]

$$\int P^*(t, \boldsymbol{X}) |\boldsymbol{\nabla} \psi^*(t, \boldsymbol{X})|^2 dX = \text{const.} \tag{5.26}$$

Equation (5.24) can be rearranged into the TSL [29]

$$\tau \Sigma_\tau^{\mathrm{ex}} \geq \frac{\mathscr{W}(P(0), P(\tau))^2}{\mu T}. \tag{5.27}$$

From this inequality, we can see that if one wants to change the system's state from $P(0)$ into $P(\tau)$, the time interval and the excess EPR cannot be reduced simultaneously.

Of course, the excess EPR is not larger than the total EPR, we also have the weaker inequality [45]

$$\tau\Sigma_\tau \geq \frac{\mathscr{W}(P(0), P(\tau))^2}{\mu T}. \tag{5.28}$$

However, it is natural that we obtained the stronger one (5.27), which involves the excess EPR, because the excess EPR ideally provides the minimum EPR to cause the dynamics. It represents the inevitable dissipation in the state change, which conflicts with the required time.

5.2 Thermodynamic trade-off relations from the force-current structure

5.2.1 Thermodynamic uncertainty relation

From the force-current structure, we can derive the short-time-TUR-like inequality

$$\dot{\Sigma}^{\mathrm{ex}}(x) \geq \frac{|\langle \nabla^* J(x), \mathcal{O}\rangle|^2}{\Delta_{\mathcal{O}}(x)}, \tag{5.29}$$

where we define

$$\Delta_{\mathcal{O}}(x) := \|\nabla\mathcal{O}\|_x^2 = \langle \nabla\mathcal{O}, \mathscr{M}_x(\nabla\mathcal{O})\rangle. \tag{5.30}$$

In the Langevin dynamics, the map $\mathscr{M}_x$ is identified with the multiplication of $\mu TP(\boldsymbol{X})$, so we find

$$\Delta_{\mathcal{O}}(x) = \langle \boldsymbol{\nabla}\mathcal{O}, \mu TP\boldsymbol{\nabla}\mathcal{O}\rangle = \frac{D}{k_{\mathrm{B}}}\int |\boldsymbol{\nabla}\mathcal{O}(\boldsymbol{X})|^2 P(\boldsymbol{X}) dX = \frac{1}{k_{\mathrm{B}}} D_{\mathcal{O}}. \tag{5.31}$$

Moreover, since there is no reversible term, we have

$$\langle \nabla^* J(x), \mathcal{O}\rangle = \langle \partial x/\partial t, \mathcal{O}\rangle = d_t\langle x, \mathcal{O}\rangle. \tag{5.32}$$

Therefore, Eq. (5.29) generalizes Eq. (5.16).

In general, however, $\Delta_{\mathcal{O}}(x)$ defined in Eq. (5.30) is not necessarily physically interpretable, unlike in the Langevin case. Nonetheless, $\Delta_{\mathcal{O}}(x)$ is usually upper bounded by what can be naturally understood as a measure of fluctuations. With the upper bound on $\Delta_{\mathcal{O}}(x)$ denoted by $\mathcal{D}_{\mathcal{O}}(x)$, we can rewrite Eq. (5.29) into the generalized short-time TUR

$$\dot{\Sigma}^{\mathrm{ex}}(x) \geq \frac{|\langle J(x), \nabla\mathcal{O}\rangle|^2}{\mathcal{D}_{\mathcal{O}}(x)}. \tag{5.33}$$

Again, if there is no reversible term, the numerator reads $(d_t\langle x, \mathcal{O}\rangle)^2$ and we get

$$\dot{\Sigma}^{\mathrm{ex}}(x) \geq \frac{|d_t\langle x, \mathcal{O}\rangle|^2}{\mathcal{D}_{\mathcal{O}}(x)}. \tag{5.34}$$

Let us prove Eq. (5.29). Remember that the conservative current $J_{\mathrm{c}}(x)$ satisfies $\nabla^* J_{\mathrm{c}}(x) = \nabla^* J(x)$. Thus, we have

$$\langle \nabla^* J(x), \mathcal{O}\rangle = \langle \nabla^* J_{\mathrm{c}}(x), \mathcal{O}\rangle. \tag{5.35}$$

We apply the Cauchy–Schwarz inequality to this quantity to get

$$\begin{aligned} |\langle \nabla^* J(x), \mathcal{O}\rangle|^2 &= |\langle \nabla^* J_{\mathrm{c}}(x), \mathcal{O}\rangle|^2 = |\langle J_{\mathrm{c}}(x), \nabla\mathcal{O}\rangle|^2 \\ &= |\langle \mathscr{M}_x(F_{\mathrm{c}}(x)), \nabla\mathcal{O}\rangle|^2 = |\langle F_{\mathrm{c}}(x), \nabla\mathcal{O}\rangle_x|^2 \\ &\leq \|F_{\mathrm{c}}(x)\|_x^2 \|\nabla\mathcal{O}\|_x^2 = \dot{\Sigma}^{\mathrm{ex}}(x)\Delta_{\mathcal{O}}(x), \end{aligned}$$

which shows Eq. (5.29).

5.2.2 Thermodynamic speed limit

We can define a generalized Wasserstein distance via the Benamou–Brenier formula:

$$\mathcal{W}(x_a, x_b) := \inf_{\xi,\psi} \sqrt{\tau \int_0^\tau \|\nabla\psi(t)\|_{\xi(t)}^2 dt}, \tag{5.36}$$

where ξ and ψ must satisfy

$$\xi(0) = x_a, \quad \xi(\tau) = x_b, \quad \frac{\partial \xi}{\partial t} = -\nabla^* \mathcal{M}_\xi(\nabla\psi). \tag{5.37}$$

This definition reproduces the Wasserstein distance in the Langevin dynamics multiplied by a constant:

$$\mathcal{W}(x_a, x_b) = \mu T \mathcal{W}(P_a, P_b). \tag{5.38}$$

Here, μT appears because the norm $\|\cdot\|_x$ involves $\mathcal{M}_x$, which becomes $\mu T P(\boldsymbol{X})$ in Langevin systems. Although whether Eq. (5.36) gives a mathematically proper distance depends on the situation, it has been proven true for several cases [19, 30, 109, 110].

If we do not have a reversible term, the time evolution $x(t)$ satisfies these conditions and TSLs will be derived. First, note that the conservative force $F_c(x)$ satisfies

$$\frac{\partial x}{\partial t} = \nabla^* J(x) = \nabla^* \mathcal{M}_x(F_c(x)). \tag{5.39}$$

In addition, it has a potential such that $F_c(x) = -\nabla\phi^*(x)$; i.e., we have

$$\frac{\partial x}{\partial t} = -\nabla^* \mathcal{M}_\xi(\nabla\phi^*(x)). \tag{5.40}$$

Therefore, the pair (x, ϕ^*) falls into the feasible set of the minimization (5.36).

As a consequence, we obtain the inequality

$$\mathcal{W}(x(0), x(\tau))^2 \leq \tau \int_0^\tau \|F_c(x(t))\|_{x(t)}^2 dt = \tau \Sigma_\tau^{\mathrm{ex}}. \tag{5.41}$$

First, this inequality can be seen as a lower bound on the excess EP

$$\Sigma_\tau^{\mathrm{ex}} \geq \frac{\mathcal{W}(x(0), x(\tau))^2}{\tau}. \tag{5.42}$$

By rearranging the equation, we also obtain the TSL

$$\tau \Sigma_\tau^{\mathrm{ex}} \geq \mathcal{W}(x(0), x(\tau))^2, \tag{5.43}$$

which shows a universal trade-off between dissipation and time. Here, we should be aware that the generalized Wasserstein distance may involve information of the dynamics because $\mathcal{M}_x$ is contained in the definition. Thus, from the operational viewpoint, what we can manipulate in minimizing the excess dissipation becomes subtle. Even though, fixing the distance $\mathcal{W}(x(0), x(\tau))$, which implies restrictions on the manipulation of the system, we cannot reduce the dissipation and the time required for the change arbitrarily.

5.2.3 Related literature

Here, we mention a few related results.

In Sec. 5.2.1, we derived a short-time and quadratic TUR (5.33); but there are other types of TURs. First, TURs for a finite-time interval exist [34, 35, 84, 89]. They require the notion of joint distribution, which is elusive in deterministic systems, so they have only been obtained in stochastic systems. Finite-time TURs involving the geometric decomposition are discussed in Refs. [19, 28, 29].

In addition, there have recently been found nonlinear (non-quadratic) bounds [39, 60, 88, 90]. They involve nonlinear functions, such as the inverse of $x \tanh x$, which generalize the quadratic function x^2. As a result, we can get restrictions tighter than the conventional inequalites. It is an interesting direction to discuss such nonlinear bounds in terms of the nonlinear Onsager relation mentioned in Sec. 3.2.3.

Finally, we point out that while we used the geometric excess EPR to provide the thermodynamic trade-off relations, the HS excess EPR can also be employed [41, 88, 90, 111, 112]. Nonetheless, the result will only be valid in systems that have special steady states. Moreover, in talking about short-time TURs, the "local-in-time" nature would make the geometric excess EPR more preferrable. Furthermore, existing research has shown that the geometric decomposition fits much better to the optimal transport theory [19, 28–30, 46, 60].

Part II

Zoo of nonequilibrium systems

Chapter 6

Markov jump processes

From this section, we consider various types of physical systems as concrete examples of the general theory developed in the preceding sections. In this section, we deal with stochastic processes with discrete degrees of freedom, called Markov jump processes. They are one of the two main models studied in stochastic thermodynamics, along with the Langevin systems.

6.1 Notation

In this and the next chapter, we consider several quantities with discrete labels, such as probabilities p_i. We use vector notation like $\vec{a}$ to represent a column vector, $(a_1, a_2, \dots, a_n)^{\mathrm{T}}$, where T indicates transposition. We also define the log and exponential of a vector by

$$\ln \vec{a} \coloneqq (\ln a_1, \dots, \ln a_n)^{\mathrm{T}}, \quad \exp \vec{a} \coloneqq (e^{a_1}, \dots, e^{a_n}). \tag{6.1}$$

6.2 Dynamics

6.2.1 Setup

Consider a system with N discrete microstates. We take the occupation probability distribution $\vec{p} = (p_i)_{i=1}^N$ as the fundamental variable x. Thus, the state space is $\mathcal{S}_0 = \mathbb{R}^N$ and the subset is the positive orthant $\mathcal{S} = \mathbb{R}^N_{>0}$. A probability distribution satisfies the normalization $\sum_i p_i = 1$, which we consider as a conservation law $\vec{\lambda}_{\mathrm{prob}} = (1, \dots, 1)^{\mathrm{T}} \in \mathcal{S}$.

In a Markov jump process (MJP), the system in microstate i at time t jumps to j at probability $R^\nu_{ji}(t)dt$ after infinitesimal time interval dt. Here, ν indicates the "route" used in the jump. Physically, ν designates the noise source that induces the jump, like a thermal bath. We define $R_{ij}(t) \coloneqq \sum_\nu R^\nu_{ij}(t)$. Then, the probability distribution is updated by

$$p_i(t+dt) = p_i(t) - \sum_{j(\neq i)} R_{ji}(t)p_i(t)dt + \sum_{j(\neq i)} R_{ij}(t)p_j(t)dt, \tag{6.2}$$

where the second and third terms respectively represent the outflow from state i and the inflow into it. Therefore, $\vec{p}$ obeys the master equation

$$\frac{dp_i}{dt} = \sum_{j(\neq i)} (R_{ij}(t)p_j(t) - R_{ji}(t)p_i(t)). \tag{6.3}$$

Since $j = i$ does not matter in the summation, it can also be written as

$$\frac{dp_i}{dt} = \sum_j (R_{ij}(t)p_j(t) - R_{ji}(t)p_i(t)). \tag{6.4}$$

regardless of the definition of $R_{ii}(t)$. If we define $R_{ii}(t)$ by

$$R_{ii}(t) \coloneqq - \sum_{j(\neq i)} R_{ji}(t), \tag{6.5}$$

Eq. (6.3) is rewritten into

$$\frac{dp_i}{dt} = \sum_j R_{ij}(t)p_j(t). \tag{6.6}$$

With a matrix $R(t) = (R_{ij}(t))$, it further reads

$$\frac{d\vec{p}}{dt} = R(t)\vec{p}(t). \tag{6.7}$$

By defining $R^\nu(t) = (R^\nu_{ij}(t))$, it is disassembled as

$$\frac{d\vec{p}}{dt} = \sum_\nu R^\nu(t)\vec{p}(t). \tag{6.8}$$

Hereafter, we make the time dependence implicit for simplicity.

In order to discuss thermodynamics, we need to assume microscopic reversibility. That is, we assume that if $R^\nu_{ij} > 0$, then $R^\nu_{ji} > 0$. On the other hand, we do not necessarily assume that MJPs are irreducible, i.e., every state can be reached from any state after certain time at finite probability. Suppose the microstates are separated into two groups, A and B, which are respectively irreducible and cannot reach each other. Then, the probabilities are respectively conserved;

$$P_A = \sum_{i\in A} p_i, \quad P_B = \sum_{i\in B} p_i \tag{6.9}$$

are constant and satisfy $P_A + P_B = 1$. These equalities can be captured by the conservation laws

$$\lambda^A_i = \begin{cases} 1 & \text{if } i \in A \\ 0 & \text{if } i \in B \end{cases}, \quad \lambda^B_i = \begin{cases} 0 & \text{if } i \in A \\ 1 & \text{if } i \in B \end{cases} \tag{6.10}$$

because then we have

$$\langle \vec{\lambda}^A, \vec{p}\rangle = P_A, \quad \langle \vec{\lambda}^B, \vec{p}\rangle = P_B. \tag{6.11}$$

Note that the conservation of the total probability $\vec{\lambda}_{\mathrm{prob}} = (1, \dots, 1)^{\mathrm{T}}$ is not linearly independent of those two vectors.

6.2.2 Continuity equation

At this stage, the master equation (6.7) does not have the form of continuity equation. To find the gradient operator in MJPs, we need to refer to a branch of mathematics called algebraic graph theory [113].

Consider a directed graph that has nodes $V = \{1, 2, \dots, N\}$ and directed edges E, which connect nodes. While each node is identified as a discrete state, edges are supposed to represent the connectivity between states; we have either of edges $e = (i, j; \nu)$ and $-e = (j, i; \nu)$ in E when $R^\nu_{ij} > 0$. Here, $e = (i, j; \nu)$ represents the jump from i to j mediated by ν, and $-e$ indicates the reversed jump. For convenience, we assume that if $e \in E$ then $-e \notin E$. The staring node of e is denoted by $s(e)$, while the terminal node $t(e)$. We also write the mediating bath as $\nu(e)$. Thus, R_e indicates $R^{\nu(e)}_{t(e)s(e)}$. We say a graph is connected if there are series of edges that connect any two nodes, regardless of the direction.

The structure of the directed graph can be encoded in a matrix called the incidence matrix [113]. It is a $|V| \times |E|$ matrix defined by

$$B_{ie} := \delta_{t(e)i} - \delta_{s(e)i}. \tag{6.12}$$

That is, B_{ie} is 1 if i is the terminal node of e, $B_{ie} = -1$ if $i = s(e)$, and otherwise zero. We also introduce the probability current $\vec{J}(\vec{p}) \in \mathbb{R}^{|E|}$ by

$$J_e(\vec{p}) := R_e p_{s(e)} - R_{-e} p_{t(e)}. \tag{6.13}$$

The probability fluxes $R_e p_{s(e)}$ and $R_{-e} p_{t(e)}$ provide the average occurence rates of jumps e and $-e$, and the current $J_e(\vec{p})$ gives the net frequency of the reversible process. With these quantities, Eq. (6.3) is rewritten as

$$\frac{dp_i}{dt} = \sum_{e \in E} B_{ie} J_e(\vec{p}) \tag{6.14}$$

because

$$\begin{aligned}\sum_{e\in E} B_{ie} J_e(\vec{p}) &= \sum_{e\in E} (\delta_{t(e)i} - \delta_{s(e)i}) J_e(\vec{p}) \\ &= \sum_{\nu} \sum_{j(\neq i)|(j,i;\nu)\in E} (R^{\nu}_{ij} p_j - R^{\nu}_{ji} p_i) - \sum_{\nu} \sum_{j(\neq i)|(i,j;\nu)\in E} (R^{\nu}_{ji} p_i - R^{\nu}_{ij} p_j) \\ &= \sum_{\nu} \sum_{j(\neq i)} (R^{\nu}_{ij} p_j - R^{\nu}_{ji} p_i).\end{aligned}$$

Now that, we can set $\mathcal{F} = \mathbb{R}^{|E|}$ and define the gradient operator $\nabla : \mathcal{S}_0 \to \mathcal{F}$ by

$$\nabla_{ei} = B_{ie}. \tag{6.15}$$

Since the adjoint is just the transposition $\nabla^* = \nabla^{\mathrm{T}}$, we can rewrite the master equation (6.3) into a continuity equation as

$$\frac{d\vec{p}}{dt} = \nabla^{\mathrm{T}} \vec{J}(\vec{p}), \tag{6.16}$$

which is the MJP version of Eq. (3.3). We call $\vec{p}^{\mathrm{ss}}$ a steady state if it satisfies $\nabla^{\mathrm{T}} \vec{J}(\vec{p}^{\mathrm{ss}}) = 0$.

The legitimacy of ∇ as the gradient operator can also be checked by the fact

$$\nabla \vec{\lambda}_{\mathrm{prob}} = 0, \tag{6.17}$$

which is proved as

$$[\nabla \vec{\lambda}_{\mathrm{prob}}]_e = \sum_i (\delta_{t(e)i} - \delta_{s(e)i}) = 1 - 1 = 0.$$

Therefore, conservation law $\vec{\lambda}_{\mathrm{prob}}$ is a null vector of ∇.

6.3 Thermodynamics

6.3.1 Local equilibrium assumption

We introduce thermodynamics by considering the relation between the transition rates and thermodynamic quantities. Consider the case where the system is connected to a single heat bath at inverse temperature β. Then, we can expect that the system will relax to the equilibrium distribution

$$p^{\mathrm{eq}}_i = \frac{e^{-\beta\epsilon_i}}{Z_\beta}, \quad Z_\beta = \sum_i e^{-\beta\epsilon_i} \tag{6.18}$$

and detailed balance holds

$$R_{ji} p^{\mathrm{eq}}_i = R_{ij} p^{\mathrm{eq}}_j, \tag{6.19}$$

where ϵ_i is the energy of ith state. This can be rearranged into

$$\ln \frac{R_{ji}}{R_{ij}} = \beta(\epsilon_i - \epsilon_j). \tag{6.20}$$

Note that, in the jump $i \to j$, $\epsilon_i - \epsilon_j$ is the energy flux into the bath and $k_{\mathrm{B}}\beta(\epsilon_i - \epsilon_j)$ provides the entropy change.

Generalizing Eq. (6.20), we assume the relation

$$\ln \frac{R_e}{R_{-e}} = \Delta s_e^{\mathrm{env}}/k_{\mathrm{B}}, \tag{6.21}$$

where Δs_e denotes the entropy change in the bath in jump e. Equation (6.21) is often referred to as the local detailed balance; we can also regard it as the local equilibrium assumption in the MJP because it implicitly supposes the existence of the thermodynamic structure in the environment. It is essentially a manifestation of the so-called fluctuation theorem [114–116]. As a result, the entropy change in the environment per unit time is given by

$$\dot{S}^{\mathrm{env}} = \sum_e J_e(\vec{p})\Delta s_e^{\mathrm{env}} = k_{\mathrm{B}} \sum_e J_e(\vec{p}) \ln \frac{R_e}{R_{-e}}. \tag{6.22}$$

6.3.2 Thermodynamic force

We define the entropy of the system by the Shannon entropy as

$$s_i = -k_{\mathrm{B}} \ln p_i. \tag{6.23}$$

On average, the system entropy is given by

$$S(\vec{p}) = -k_{\mathrm{B}} \sum_i p_i \ln p_i \tag{6.24}$$

and its changing rate reads

$$\begin{aligned} \frac{dS}{dt} &= -k_{\mathrm{B}} \sum_i \frac{dp_i}{dt} \ln p_i \\ &= -k_{\mathrm{B}} \sum_e J_e(\vec{p}) \sum_i \nabla_{ei} \ln p_i \\ &= k_{\mathrm{B}} \sum_e J_e(\vec{p}) \ln \frac{p_{s(e)}}{p_{t(e)}}, \end{aligned} \tag{6.25}$$

where we used $\sum_i dp_i/dt = 0$ in the first line.

Combining Eqs. (6.22) and (6.25), we find that the total EPR is given by

$$\dot{\Sigma}(\vec{p}) = \frac{dS}{dt} + \dot{S}^{\mathrm{env}} = k_{\mathrm{B}} \sum_e J_e(\vec{p}) \ln \frac{R_e p_{s(e)}}{R_{-e} p_{t(e)}}. \tag{6.26}$$

Therefore, we define the thermodynamic force $\vec{F}(\vec{p}) \in \mathcal{F} = \mathbb{R}^{|E|}$ by

$$F_e(\vec{p}) := k_{\mathrm{B}} \ln \frac{R_e p_{s(e)}}{R_{-e} p_{t(e)}} \tag{6.27}$$

and obtain the expression

$$\dot{\Sigma}(\vec{p}) = \langle \vec{J}(\vec{p}), \vec{F}(\vec{p}) \rangle, \tag{6.28}$$

which provides the counterpart of Eq. (3.7) in MJPs.

6.3.3 Force-current structure

To bridge the thermodynamic force and the current, we define an $|E| \times |E|$ matrix $\mathsf{L}(\vec{p})$ by

$$\mathsf{L}_{ee'}(\vec{p}) := k_{\mathrm{B}}^{-1} \Lambda(R_e p_{s(e)}, R_{-e} p_{t(e)}) \delta_{ee'}, \tag{6.29}$$

where Λ is the logarithmic mean defined for positive numbers x and y by

$$\Lambda(x, y) := \frac{x - y}{\ln(x/y)}. \tag{6.30}$$

We call this matrix the Onsager matrix as it satisfies

$$\vec{J}(\vec{p}) = \mathsf{L}(\vec{p})\vec{F}(\vec{p}), \tag{6.31}$$

which is the MJP version of Eq. (3.8) and completes the force-current structure in MJPs. We note that this log mean form appears in a paper published in 1983 [117]. Recently, it was rediscovered in the context of stochastic thermodynamics [19, 39, 44].

Let us see several properties of the log mean and the Onsager matrix. First, it is between the geometric mean and the arithmetic mean:

$$\sqrt{xy} \leq \Lambda(x,y) \leq \frac{x+y}{2}. \tag{6.32}$$

Therefore, we find that it is always positive as long as $x, y > 0$ and satisfies

$$\Lambda(x,x) = x. \tag{6.33}$$

Thus, L is a positive-definite matrix and the equality

$$k_{\mathrm{B}}\mathsf{L}_{ee}(\vec{p}^{\mathrm{eq}}) = R_e p^{\mathrm{eq}}_{s(e)} = R_{-e} p^{\mathrm{eq}}_{t(e)} \tag{6.34}$$

holds in the equilibrium state, which is defined by $\vec{J}(\vec{p}^{\mathrm{eq}}) = 0$.

The inequalities in Eq. (6.32) are proved as follows: first, note that for any $f(s) > 0$ and $r > 0$, the Cauchy–Schwarz inequality proves

$$\left(\int_1^r f(s)ds\right)^2 = \left(\int_1^r \sqrt{\frac{f(s)}{s}}\sqrt{sf(s)}ds\right)^2 \leq \int_1^r \frac{f(s)}{s}ds \int_1^r sf(s)ds. \tag{6.35}$$

If we choose $f(s) = 1$, the inequality reads

$$(r-1)^2 \leq \ln r \frac{r^2-1}{2} \Leftrightarrow \frac{r-1}{\ln r} \leq \frac{r+1}{2}, \tag{6.36}$$

which, with $r = x/y$, leads to the second inequality in Eq. (6.32). The first one is also obtained by setting $f(s) = 1/s$; then, we get

$$(\ln r)^2 \leq \left(1 - \frac{1}{r}\right)(r-1) \Leftrightarrow r \leq \left(\frac{r-1}{\ln r}\right)^2, \tag{6.37}$$

which results in

$$\sqrt{\frac{x}{y}} \leq \frac{x/y - 1}{\ln(x/y)}. \tag{6.38}$$

Since $y > 0$, multiplying y provides the desired inequality.

The positive-definiteness of the Onsager matrix allows us to trace arguments in preceding sections. For example, we can define an inner product on $\mathcal{F}$ by

$$\langle \vec{F}', \vec{F}'' \rangle_p := \langle \vec{F}', \mathsf{L}(\vec{p})\vec{F}'' \rangle. \tag{6.39}$$

It also induces norm $\|\vec{F}'\|_p := \sqrt{\langle \vec{F}', \vec{F}' \rangle_p}$ and gives the EPR with the geometric expression

$$\dot{\Sigma}(\vec{p}) = \|\vec{F}(\vec{p})\|_p^2. \tag{6.40}$$

When the states' graph is an n-dimensional lattice, i corresponds to a point in the n-dimensional space. Each jump e should be interpreted as a jump from $s(e)$ to an adjacent site $t(e)$ in direction $d = t(e) - s(e)$. We assume the expansion [6, 39]

$$R_e = \frac{D_d(s(e))}{\Delta^2} + \frac{f_d(s(e))}{\Delta} + O(1) \tag{6.41}$$

with the spatial separation between nearest nodes Δ and diffusive and balistic contributions such that $D_{-d}(i) = D_d(i)$ and $f_{-d}(i) = -f_d(i)$. Then, the thermodynamic force and the current will be expanded by

$$
\begin{aligned}
J_e(\vec{p}) &= \left(\frac{D_d(s(e))}{\Delta^2} + \frac{f_d(s(e))}{\Delta}\right)p_{s(e)} - \left(\frac{D_{-d}(t(e))}{\Delta^2} + \frac{f_{-d}(t(e))}{\Delta}\right)p_{t(e)} + O(1) \\
&= \frac{2f_d(s(e))p_{s(e)} - \partial_d\big(D_d(s(e))p_{s(e)}\big)}{\Delta} + O(1), \\
F_e(\vec{p}) &= k_{\mathrm{B}} \ln \frac{\big[D_d(s(e)) + \Delta f_d(s(e))\big]p_{s(e)}}{\big[D_{-d}(t(e)) + \Delta f_{-d}(t(e))\big]p_{t(e)}} + O(\Delta^2) \\
&= k_{\mathrm{B}} \ln\left(1 + \frac{\Delta f_d(s(e))p_{s(e)}}{D_d(s(e))p_{s(e)}}\right) - \ln\left(1 + \frac{\Delta\big[\partial_d(D_d(s(e))p_{s(e)}) - f_d(s(e))p_{s(e)}\big]}{D_d(s(e))p_{s(e)}}\right) + O(\Delta^2) \\
&= k_{\mathrm{B}}\Delta \frac{2f_d(s(e))p_{s(e)} - \partial_d\big(D_d(s(e))p_{s(e)}\big)}{D_d(s(e))p_{s(e)}} + O(\Delta^2),
\end{aligned}
$$

where we used

$$
\begin{aligned}
D_{-d}(t(e))p_{t(e)} &= D_d(s(e) + d)p_{s(e)+d} = D_d(s(e))p_{s(e)} + \Delta\partial_d(D_d(s(e))p_{s(e)}) + O(\Delta^2), \\
f_{-d}(t(e))p_{t(e)} &= -f_d(s(e) + d)p_{s(e)+d} = -f_d(s(e))p_{s(e)} - \Delta\partial_d(f_d(s(e))p_{s(e)}) + O(\Delta^2)
\end{aligned}
$$

and ∂_d is defined like $\partial_d g(s(e)) := [g(s(e) + d) - g(s(e))]/\Delta$. Consequently, the Onsager matrix becomes

$$
\mathsf{L}_{ee}(\vec{p}) = \frac{1}{\Delta^2}\frac{D_e(s(e))}{k_{\mathrm{B}}}p_{s(e)} + O(\Delta^{-1}), \tag{6.42}
$$

which reproduces the Onsager relation in the Langevin system (2.23).

6.3.4 Conservativeness and detailed balance

Let us confirm that MJPs satisfy assumptions C1 and C2, discussed in Sec. 3.3. First, the thermodynamic force satisfies assumption C1 because

$$
\vec{F}(\vec{p}) = \vec{F}_0 - \nabla\vec{\varphi}(\vec{p}) \tag{6.43}
$$

with

$$
F_{0,e} = k_{\mathrm{B}} \ln \frac{R_e}{R_{-e}}, \quad \vec{\varphi}(\vec{p}) = k_{\mathrm{B}} \ln \vec{p}. \tag{6.44}
$$

The function $\vec{\varphi} : \mathbb{R}^N_{>0} \mapsto \mathbb{R}^N$ is actually a bijection.

Assumption C2 can also be verified in important cases. When the system is irreducible and there is only a single conservation law, $\vec{\lambda}_{\mathrm{prob}}$, which represents the conservation of probability, Eq. (3.12) reads

$$
\sum_i e^{\psi_i - \mu} = 1, \tag{6.45}
$$

which is solved by $\mu = \ln \sum_i e^{\psi_i}$. A more nontrivial example is when the system is reducible, and we have two conservation laws as in Eq. (6.10). Then, Eq. (3.12) provides the two equations

$$
\sum_{i\in A} e^{\psi_i - \mu_A} = P_A, \quad \sum_{i\in B} e^{\psi_i - \mu_B} = P_B, \tag{6.46}
$$

where note that now the argument in Eq. (3.12) becomes $\vec{\psi} - \mu_A\vec{\lambda}^A - \mu_B\vec{\lambda}^B$. These equations are also easily solved by $\mu_A = \ln\big(P_A^{-1}\sum_{i\in A} e^{\psi_i}\big)$ and $\mu_B = \ln\big(P_B^{-1}\sum_{i\in B} e^{\psi_i}\big)$.

Therefore, we obtain the equivalence for an irreducible MJP without any non-trivial conservation law, as a consequence of the general discussion; the following two statements are equivalent:

(1) There is a potential $\vec{\psi} \in \mathbb{R}^N$ such that

$$
F_{0,e} = k_{\mathrm{B}} \ln \frac{R_e}{R_{-e}} = \psi_{s(e)} - \psi_{t(e)}. \tag{6.47}
$$

(2) There exists $\vec{\pi} \in \mathbb{R}^N_{>0}$ such that $\vec{J}(\vec{\pi}) = 0$ and $\sum_i \pi_i = 1$.

In detailed balanced systems, condition (1) is satisfied with $\psi_i = k_\mathrm{B}\beta\epsilon_i$ as in Eq. (6.20).

When there are multiple heat baths and jump $i \to j$ is mediated by ν and ν', the local detailed balance (6.20) is generalized to

$$\ln \frac{R^\nu_{ji}}{R^\nu_{ij}} = \beta_\nu(\epsilon_i - \epsilon_j), \tag{6.48}$$

$$\ln \frac{R^{\nu'}_{ji}}{R^{\nu'}_{ij}} = \beta_{\nu'}(\epsilon_i - \epsilon_j). \tag{6.49}$$

On the other hand, conservativeness (6.47) requires

$$\beta_\nu(\epsilon_i - \epsilon_j) = \beta_{\nu'}(\epsilon_i - \epsilon_j). \tag{6.50}$$

Therefore, condition (1) implies that all bath temperathres are the same.

According to the discussion in Sec. 3.3, the detailed-balanced state $\vec{\pi}$ in (2) is obtained as (cf. Eq. (3.16))

$$\vec{\pi} = \vec{\varphi}^{-1}\Big(\vec{\psi} + \mu\vec{\lambda}_\mathrm{prob}\Big), \tag{6.51}$$

which is written down as

$$\pi_i = e^{-(\psi_i+\mu)/k_\mathrm{B}}, \tag{6.52}$$

where μ is determined by $\sum_i \pi_i = 1$; i.e., $\mu = \ln \sum_i e^{-\psi_i/k_\mathrm{B}}$. When the system is connected to a single heat bath, because $\psi_i/k_\mathrm{B} = \beta\epsilon_i$, we finally find

$$\pi_i = \frac{e^{-\beta\epsilon_i}}{Z_\beta}, \quad Z_\beta = \sum_i e^{-\beta\epsilon_i} \tag{6.53}$$

which is nothing but the thermal equilibrium state.

6.3.5 Cycles and breaking of detailed balance

While cycles were introduced abstractly in Sec. 3.4, the kernel of ∇^T can charactrize them as actual cycles on the graph [113]. A cycle C on a graph is just a cyclic collection of edges $\{e_m\}_{m=1,\dots,M}$; then, the edges connect the same number of nodes $\{i_m\}$ where $(i_m, i_{m+1}) = (s(e_m), t(e_m))$ or $(i_m, i_{m+1}) = (t(e_m), s(e_m))$ holds for each m, where the cycle can go through a node more than once, but we assume edges are used at most once. If we define the corresponding vector $\vec{C} \in \mathbb{R}^{|E|}$ by

$$C_e = \begin{cases} 1 & \exists m,\ e = e_m \ \&\ i_m = s(e_m) \\ -1 & \exists m,\ e = e_m \ \&\ i_m = t(e_m) \\ 0 & \text{otherwise} \end{cases}, \tag{6.54}$$

it satisfies $\nabla^\mathrm{T}\vec{C} = 0$ because

$$\begin{aligned} [\nabla^\mathrm{T}\vec{C}]_i &= \sum_e (\delta_{it(e)} - \delta_{is(e)})C_e \\ &= \sum_{m|i_m=i} \Big[\underbrace{\delta_{i_m t(e_{m-1})}}_{\Rightarrow C_{e_{m-1}}=1} - \underbrace{\delta_{i_m s(e_{m-1})}}_{\Rightarrow C_{e_{m-1}}=-1}\Big]C_{e_{m-1}} + \Big[\underbrace{\delta_{i_m t(e_m)}}_{\Rightarrow C_{e_m}=-1} - \underbrace{\delta_{i_m s(e_m)}}_{\Rightarrow C_{e_m}=1}\Big]C_{e_m} \\ &= \sum_{m|i_m=i} (1-1) = 0, \end{aligned}$$

where in the third line, we focus on pairs of jumps (e_{m-1}, e_m) that cross $i_m = i$. For example, if $i_m = t(e_{m-1})$, e_{m-1} is aligned with the direction of the cycle, so $C_{e_{m-1}}$ becomes one. Therefore, we find $\vec{C} \in \ker \nabla^\mathrm{T}$.

We can also show the converse, i.e., $\ker \nabla^{\mathrm{T}}$ is spanned by vectors corresponding to cycles on the graph. To show that, we consider a way to construct an independent set of cycles, focusing on connected graphs (i.e., irreducible MJPs). A spanning tree is a connected subset of the graph that includes all the nodes and no cycles; i.e., every pair of nodes is connected by a unique path. We can easily see that a spanning tree has $N-1$ edges (thus, $|E|-N+1$ edges are eliminated when creating a spanning tree). If we add an edge that exists in the original graph but not in the spanning tree, the newly connected nodes are connected in two ways, by the unique path in the spanning tree and the added edge; thus, we can create a single cycle. In this way, we can make $|E|-N+1$ cycles, which we write $\{C^\mu\}_{\mu=1,\ldots,|E|-N+1}$. The corresponding vectors $\{\vec{C}^\mu\}$ are linearly independent because $C^\mu_{e_{\mu'}} = \delta_{\mu\mu'}$ holds with e_μ being the edge added to make cycle C^μ.

We can further show that $\{\vec{C}^\mu\}$ spans the kernel of ∇^{T}. When the graph is connected, the rank of ∇ becomes $N-1$. In fact, taking $\vec{\phi} \in \mathbb{R}^N$ such that $\nabla\vec{\phi} = 0$, we have

$$\sum_i \nabla_{ei}\phi_i = \nabla_{es(e)}\phi_{s(e)} + \nabla_{et(e)}\phi_{t(e)} = 0, \tag{6.55}$$

which is only satisfied when $\phi_i = \text{const.}$ for any i. Thus, the dimension of $\ker\nabla$ is one, and since ∇ is an $N \times |E|$ matrix, we see that $\operatorname{rank}\nabla = N-1$ (this reveals the fact that an irreducible MJP has only one conservation law, corresponding to the probability conservation). On the other hand, the rank-nullity theorem tells

$$\operatorname{rank}\nabla + \dim\ker\nabla^{\mathrm{T}} = |E|. \tag{6.56}$$

Therefore, we obtain

$$\dim\ker\nabla^{\mathrm{T}} = |E| - N + 1, \tag{6.57}$$

which concludes that $\{\vec{C}^\mu\}$ is a basis of $\ker\nabla^{\mathrm{T}}$.

Consequently, we can identify $\mathcal{T}$ in Sec. 3.4 as the operator

$$\mathcal{T} : \mathbb{R}^{|E|-N+1} \ni (q_\mu) \mapsto \sum_\mu q_\mu \vec{C}^\mu \in \ker\nabla^{\mathrm{T}} \subset \mathbb{R}^{|E|}, \tag{6.58}$$

with its adjoint

$$\mathcal{T}^* : \mathbb{R}^{|E|} \ni \vec{K} \mapsto \left(\langle \vec{C}^\mu, \vec{K}\rangle\right) \in \mathbb{R}^{|E|-N+1}. \tag{6.59}$$

The adjoint operator provides the influence of $\vec{K}$ on each cycle as

$$\langle \vec{C}^\mu, \vec{K}\rangle = \sum_{e\in E|e\in C^\mu} K_e - \sum_{e\in E|-e\in C^\mu} K_e. \tag{6.60}$$

Following the general result, the steady-state dissipation can be expressed by

$$\dot{\Sigma}(\vec{p}^{\mathrm{ss}}) = \sum_\mu j_\mu f_\mu \tag{6.61}$$

with

$$\vec{J}(\vec{p}^{\mathrm{ss}}) = \sum_\mu j_\mu \vec{C}^\mu, \quad f_\mu = \langle \vec{C}^\mu, \vec{F}(\vec{p}^{\mathrm{ss}})\rangle. \tag{6.62}$$

This decomposition into cycles is first obtained by Schnakenberg in Ref. [57]. It represents that the steady-state dissipation is incurred by cyclic motions which do not affect the system's dynamics.

6.4 Housekeeping-excess decomposition

We can obtain the geometric housekeeping-excess decomposition by applying the general framework provided in Sec. 4.2. Here, we do not review every single result, but explain several selected crucial results in addition to some remarks specific to MJPs. More detailed analysis on what follows in this chapter can be found in Ref. [19].

We define the conservative subspace by

$$\mathscr{C} := \operatorname{im}\nabla = \{-\nabla\vec{\phi} \mid \vec{\phi} \in \mathbb{R}^N\} \tag{6.63}$$

and give the housekeeping EPR by

$$\dot{\Sigma}^{\mathrm{hk}}(\vec{p}) = \min_{\vec{F}' \in \mathscr{C}} \|\vec{F}(\vec{p}) - \vec{F}'\|_{\vec{p}}^2. \tag{6.64}$$

The conservative subspace is actually a space of "equilibrium" forces as discussed in Sec. 6.3.4. The potential $\vec{\phi}^*(\vec{p})$ that provides the projected conservative force, $\vec{F}_{\mathrm{c}}(\vec{p}) = -\nabla\vec{\phi}^*(\vec{p})$, solves the equation (cf. Eq. (4.56))

$$\nabla^{\mathsf{T}}\mathsf{L}(\vec{p})\nabla\vec{\phi} = -\frac{d\vec{p}}{dt}. \tag{6.65}$$

By using a pseudo inverse of $\nabla^{\mathsf{T}}\mathsf{L}(\vec{p})\nabla$, we can explicitly describe the potential as

$$\vec{\phi}^*(\vec{p}) = -(\nabla^{\mathsf{T}}\mathsf{L}(\vec{p})\nabla)^{+}\frac{d\vec{p}}{dt}, \tag{6.66}$$

where $+$ denotes the Moore–Penrose inverse.

Matrix $\nabla^{\mathsf{T}}\nabla$ is called the Laplacian matrix [113] and $\nabla^{\mathsf{T}}\mathsf{L}(\vec{p})\nabla$ is the weighted one. Since $\mathsf{L}(\vec{p})$ is full-rank, $\nabla^{\mathsf{T}}\mathsf{L}(\vec{p})\nabla$ has rank $N-1$. Its elements are given by

$$[\nabla^{\mathsf{T}}\mathsf{L}(\vec{p})\nabla]_{ij} = \begin{cases} \sum_{e|i=s(e)\,\mathrm{or}\,t(e)} \mathsf{L}_{ee}(\vec{p}) & \text{if} \quad i = j \\ -\sum_{e|(i,j)=(s(e),t(e))\,\mathrm{or}\,(t(e),s(e))} \mathsf{L}_{ee}(\vec{p}) & \text{if} \quad i \neq j \end{cases}. \tag{6.67}$$

It is the discrete version of the operator

$$\mu T \boldsymbol{\nabla} \cdot P(\boldsymbol{X})\boldsymbol{\nabla}, \tag{6.68}$$

which appears in Langevin systems.

The excess EPR is also given by (cf. Eq. (4.37))

$$\dot{\Sigma}^{\mathrm{ex}}(\vec{p}) = \min_{\vec{F}'}\|\vec{F}'\|_{\vec{p}}^2 \quad \text{s.t.} \quad \nabla^{\mathsf{T}}\mathsf{L}(\vec{p})\vec{F}' = \nabla^{\mathsf{T}}\vec{J}(\vec{p}). \tag{6.69}$$

We also have the alternative expression (cf. Eq. (4.38))

$$\dot{\Sigma}^{\mathrm{ex}}(\vec{p}) = \min_{\vec{J}'}\langle\vec{J}', \mathsf{L}(\vec{p})^{-1}\vec{J}'\rangle \quad \text{s.t.} \quad \nabla^{\mathsf{T}}\vec{J}' = \nabla^{\mathsf{T}}\vec{J}(\vec{p}), \tag{6.70}$$

which suggests that the excess EPR is the minimum EPR with the Onsager matrix $\mathsf{L}(\vec{p})$ fixed.

The nonconservative force $\vec{F}_{\mathrm{nc}}(\vec{p})$ and the corresponding current $\vec{J}_{\mathrm{nc}}(\vec{p}) = \mathsf{L}(\vec{p})\vec{F}_{\mathrm{nc}}(\vec{p})$ give the non-stationary extension of the Schnakenberg formula (6.61) since $\vec{J}_{\mathrm{nc}}(\vec{p}) \in \ker\nabla^{\mathsf{T}}$. We have

$$\dot{\Sigma}^{\mathrm{hk}}(\vec{p}) = \sum_{\mu} j_{\mu}^{\dagger} f_{\mu}^{\dagger} \tag{6.71}$$

with

$$\vec{J}_{\mathrm{nc}}(\vec{p}) = \sum_{\mu} j_{\mu}^{\dagger}\vec{C}^{\mu}, \quad f_{\mu}^{\dagger} = \langle\vec{C}^{\mu}, \vec{F}_{\mathrm{nc}}(\vec{p})\rangle. \tag{6.72}$$

6.5 Thermodynamic trade-off

6.5.1 Thermodynamic uncertainty relation

The TUR in Eq. (5.29) reads

$$\dot{\Sigma}^{\mathrm{ex}}(\vec{p}) \geq \frac{|d_t\langle\mathcal{O}\rangle|^2}{\Delta_{\mathcal{O}}(\vec{p})}, \tag{6.73}$$

where

$$d_t\langle\mathcal{O}\rangle = \frac{d}{dt}\sum_i \mathcal{O}_i p_i = \langle\vec{J}(\vec{p}), \nabla^{\mathrm{T}}\vec{\mathcal{O}}\rangle \tag{6.74}$$

is the changing rate of the expectation value of random variable $\mathcal{O}$ ($\vec{\mathcal{O}} = (\mathcal{O}_i) \in \mathbb{R}^N$) and

$$\Delta_{\mathcal{O}}(\vec{p}) = \|\vec{\mathcal{O}}\|_p^2. \tag{6.75}$$

Because of the inequality (6.32),

$$\|\vec{\mathcal{O}}\|_p^2 = \sum_e L_{ee}(\vec{p})[\nabla^{\mathrm{T}}\vec{\mathcal{O}}]_e^2 \le \frac{1}{2k_{\mathrm{B}}}\sum_e (R_e p_{s(e)} + R_{-e}p_{t(e)})[\nabla^{\mathrm{T}}\vec{\mathcal{O}}]_e^2. \tag{6.76}$$

This quantity can further be rewritten as

$$\sum_e (R_e p_{s(e)} + R_{-e}p_{t(e)})[\nabla^{\mathrm{T}}\vec{\mathcal{O}}]_e^2 = \lim_{dt\to 0}\frac{\mathrm{Var}(d\mathcal{O})}{dt}. \tag{6.77}$$

This is proved as follows: first, in infinitesimal interval dt, jump e occurs at probability $R_e p_{s(e)}dt$. Thus, the change in $\mathcal{O}$, $d\mathcal{O}$, has moments

$$\begin{aligned}\langle d\mathcal{O}^k\rangle &= dt\Bigg(\sum_{e\in E}(\mathcal{O}_{t(e)} - \mathcal{O}_{s(e)})^k R_e p_{s(e)} + \sum_{-e\in E}(\mathcal{O}_{t(e)} - \mathcal{O}_{s(e)})^k R_e p_{s(e)}\Bigg)\\ &= dt\Bigg(\sum_{e\in E}[\nabla^{\mathrm{T}}\vec{\mathcal{O}}]_e^k R_e p_{s(e)} + \sum_{-e\in E}[-\nabla^{\mathrm{T}}\vec{\mathcal{O}}]_{-e}^k R_e p_{s(e)}\Bigg).\end{aligned}$$

Therefore, the variance is given by

$$\begin{aligned}\mathrm{Var}(d\mathcal{O}) &= \langle d\mathcal{O}^2\rangle - \langle d\mathcal{O}\rangle^2\\ &= dt\Bigg(\sum_{e\in E}[\nabla^{\mathrm{T}}\vec{\mathcal{O}}]_e^2 R_e p_{s(e)} + \sum_{-e\in E}[-\nabla^{\mathrm{T}}\vec{\mathcal{O}}]_{-e}^2 R_e p_{s(e)}\Bigg) + o(dt)\\ &= dt\sum_{e\in E}[\nabla^{\mathrm{T}}\vec{\mathcal{O}}]_e^2(R_e p_{s(e)} + R_{-e}p_{t(e)}) + o(dt),\end{aligned}$$

which completes the proof. We define

$$\mathcal{D}_{\mathcal{O}}(\vec{p}) := \frac{1}{2}\sum_e (R_e p_{s(e)} + R_{-e}p_{t(e)})[\nabla^{\mathrm{T}}\vec{\mathcal{O}}]_e^2, \tag{6.78}$$

which can be understood as the short-time variance of observable $\mathcal{O}$ and the discrete extention of the diffusivity in Langevin systems (Eq. (5.10)). As a result, we obtain the TUR

$$\dot{\Sigma}^{\mathrm{ex}}(\vec{p}) \ge k_{\mathrm{B}}\frac{|d_t\langle\mathcal{O}\rangle|^2}{\mathcal{D}_{\mathcal{O}}(\vec{p})}. \tag{6.79}$$

6.5.2 Thermodynamic speed limit

The general description regarding the generalized Wasserstein distance (Eq. (5.36)) suits best MJPs and chemical reaction networks, discussed in the next chapter. It was Maas who proposed to define the Wasserstein distance in MJPs [109] by

$$\mathcal{W}(\vec{p}^a, \vec{p}^b) = \inf_{\vec{p},\vec{\psi}}\sqrt{\tau\int_0^\tau \|\nabla\vec{\psi}(t)\|_{p(t)}^2 dt} \tag{6.80}$$

with conditions

$$\vec{p}(0) = \vec{p}^a, \quad \vec{p}(\tau) = \vec{p}^b, \quad \frac{d\vec{p}}{dt} = \nabla^{\mathrm{T}}\mathsf{L}(\vec{p}(t))\nabla\vec{\psi}(t). \tag{6.81}$$

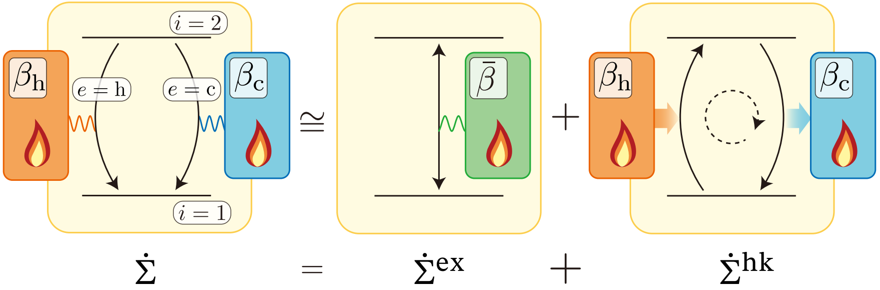

Figure 6.1: (Adapted from Ref. [19]) Schematics of the two-level system. Total EPR $\dot{\Sigma}$ is divided into excess EPR $\dot{\Sigma}^\mathrm{ex}$ and housekeeping EPR $\dot{\Sigma}^\mathrm{hk}$. We can interpret $\dot{\Sigma}^\mathrm{ex}$ as stemming from a relaxation caused by a fictitious single reservoir at the "mean" temperature $\bar{\beta}$, while $\dot{\Sigma}^\mathrm{hk}$ is attributed to heat transfer that does not change the state.

As proved in Ref. [109], it works as a distance between probability distributions (see also Ref. [19]). However, since the definition includes the kinetic information in $\mathsf{L}(\vec{p}(t))$, its interpretation tends to be formal. Nonetheless, the correspondence to the original version of the Benamou–Brenier formula (5.19) is clear by the relation (6.42). For more details, see Appendix A.

As deduced in the general framework, the Wasserstein distance provides a lower bound on the excess EP by

$$\Sigma^\mathrm{ex} = \int_0^\tau \dot{\Sigma}^\mathrm{ex}(\vec{p}(t))dt \geq \frac{\mathcal{W}(\vec{p}(0), \vec{p}(\tau))^2}{\tau}, \tag{6.82}$$

which can be rearranged to result in the TSL

$$\tau\Sigma^\mathrm{ex} \geq \mathcal{W}(\vec{p}(0), \vec{p}(\tau))^2. \tag{6.83}$$

6.6 Example

Here, we illustrate the decomposition and the TUR in a simple two-level stochastic system. Consider a two-level system coupled to two heat baths at inverse temperature β_h and β_c ($\beta_\mathrm{h} < \beta_\mathrm{c}$). For this system, we can analytically obtain the excess and housekeeping EPRs. Let the energy of state i be ϵ_i for $i = 1, 2$ and $\epsilon_2 > \epsilon_1$. There are two kinds of transition associated with the distinct reservoirs, labeled by $e = \mathrm{h}$ and c (which are abbreviated forms of $(2, 1; \mathrm{h})$ and $(2, 1; \mathrm{c})$). Transition e is mediated by the bath at β_e. The system is depicted in Fig. 6.1.

The incidence matrix is then given by

$$B = \begin{pmatrix} 1 & 1 \\ -1 & -1 \end{pmatrix}. \tag{6.84}$$

The matrix $\nabla^\mathsf{T}\mathsf{L}(\vec{p})\nabla$ reads

$$\nabla^\mathsf{T}\mathsf{L}(\vec{p})\nabla = (\ell_\mathrm{h} + \ell_\mathrm{c})\begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \tag{6.85}$$

and its Moore–Penrose inverse

$$(\nabla^\mathsf{T}\mathsf{L}(\vec{p})\nabla)^+ = \frac{1}{4(\ell_\mathrm{h} + \ell_\mathrm{c})}\begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}, \tag{6.86}$$

where

$$\ell_\mathrm{c} = \Lambda(R_\mathrm{c} p_2, R_{-\mathrm{c}} p_1). \tag{6.87}$$

Thus, according to Eq. (6.66), a potential that gives the conservative force is obtained as

$$\begin{aligned}\phi^*(\vec{p}) &= -(\nabla^{\mathsf{T}}\mathsf{L}(\vec{p})\nabla)^{+}\nabla^{\mathsf{T}}\mathsf{L}(\vec{p})\vec{F}(\vec{p}) \\ &= -\frac{1}{4(\ell_{\mathrm{h}}+\ell_{\mathrm{c}})}\begin{pmatrix}1 & -1\\ -1 & 1\end{pmatrix}\begin{pmatrix}1 & 1\\ -1 & -1\end{pmatrix}\begin{pmatrix}\ell_{\mathrm{h}} & 0\\ 0 & \ell_{\mathrm{c}}\end{pmatrix}\begin{pmatrix}F_{\mathrm{h}}\\ F_{\mathrm{c}}\end{pmatrix} \\ &= \frac{\ell_{\mathrm{h}}F_{\mathrm{h}}+\ell_{\mathrm{c}}F_{\mathrm{c}}}{\ell_{\mathrm{h}}+\ell_{\mathrm{c}}}\begin{pmatrix}-1/2\\ 1/2\end{pmatrix}.\end{aligned} \tag{6.88}$$

Since F_{h} and F_{c} are given as

$$F_{\mathrm{h}} = k_{\mathrm{B}}\beta_{\mathrm{h}}(\epsilon_2-\epsilon_1)+k_{\mathrm{B}}(\ln p_2-\ln p_1), \tag{6.89}$$

$$F_{\mathrm{c}} = k_{\mathrm{B}}\beta_{\mathrm{c}}(\epsilon_2-\epsilon_1)+k_{\mathrm{B}}(\ln p_2-\ln p_1), \tag{6.90}$$

the conservative force reads

$$\begin{aligned}\vec{F}_{\mathrm{c}}(\vec{p}) = -\nabla\phi^*(\vec{p}) &= \frac{\ell_{\mathrm{h}}F_{\mathrm{h}}+\ell_{\mathrm{c}}F_{\mathrm{c}}}{\ell_{\mathrm{h}}+\ell_{\mathrm{c}}}\begin{pmatrix}1\\ 1\end{pmatrix} \\ &= \left(k_{\mathrm{B}}\bar{\beta}(\epsilon_2-\epsilon_1)+k_{\mathrm{B}}(\ln p_2-\ln p_1)\right)\begin{pmatrix}1\\ 1\end{pmatrix},\end{aligned} \tag{6.91}$$

where we defined

$$\bar{\beta} := \frac{\ell_{\mathrm{h}}\beta_{\mathrm{h}}+\ell_{\mathrm{c}}\beta_{\mathrm{c}}}{\ell_{\mathrm{h}}+\ell_{\mathrm{c}}}. \tag{6.92}$$

This expression means the conservative force can be attributed to a relaxation mode mediated by a fictitious heat bath at temperature $\bar{\beta}$ (see Fig. 6.1).

On the other hand, the nonconservative current is obtained by

$$\vec{J}_{\mathrm{nc}}(\vec{p}) = \mathsf{L}(\vec{p})(\vec{F}(\vec{p})-\vec{F}_{\mathrm{c}}(\vec{p})) = \frac{\ell_{\mathrm{h}}\ell_{\mathrm{c}}}{\ell_{\mathrm{h}}+\ell_{\mathrm{c}}}(\epsilon_2-\epsilon_1)(\beta_{\mathrm{c}}-\beta_{\mathrm{h}})\begin{pmatrix}1\\ -1\end{pmatrix}. \tag{6.93}$$

The fact that $[J_{\mathrm{nc}}]_{\mathrm{h}} = -[J_{\mathrm{nc}}]_{\mathrm{c}}$ indicates that the nonconservative current does not affect the dynamics, just representing cyclic motion, as depicted in Fig. 6.1. Moreover, the housekeeping EPR now becomes

$$\dot{\Sigma}^{\mathrm{hk}}(\vec{p}) = \frac{k_{\mathrm{B}}\ell_{\mathrm{h}}\ell_{\mathrm{c}}}{\ell_{\mathrm{h}}+\ell_{\mathrm{c}}}(\epsilon_2-\epsilon_1)^2(\beta_{\mathrm{c}}-\beta_{\mathrm{h}})^2, \tag{6.94}$$

which shows that the housekeeping dissipation occurs due to the temperature difference between the two heat baths $\beta_{\mathrm{c}}-\beta_{\mathrm{h}}$.

We also numerically validate the TUR (6.79). The simulation is done with parameters $\beta_{\mathrm{h}}=1, \beta_{\mathrm{c}}=2, \epsilon_2-\epsilon_1=1$, and $R_{-\mathrm{h}}=R_{-\mathrm{c}}=1$, and initial condition $p_0(0)/p_1(0)=10^3$. R_{h} and R_{c} are determined by the local detailed balance. The result is presented in Fig. 6.2. We plot the ratios

$$\eta = \frac{k_{\mathrm{B}}|d_t\langle\mathcal{O}\rangle|^2}{\dot{\Sigma}(\vec{p})\mathcal{D}_{\mathcal{O}}(\vec{p})}, \quad \eta^{\mathrm{ex}} = \frac{k_{\mathrm{B}}|d_t\langle\mathcal{O}\rangle|^2}{\dot{\Sigma}^{\mathrm{ex}}(\vec{p})\mathcal{D}_{\mathcal{O}}(\vec{p})}, \tag{6.95}$$

which satisfy $\eta \le \eta^{\mathrm{ex}}$. We can also confirm the TUR $\eta^{\mathrm{ex}} \le 1$ from the figure. As long as $\mathcal{O}$ is not a null vector of ∇, these ratios are independent of the choice of $\mathcal{O}$. This is because the state space is now two dimensional and ∇ has a one-dimensional kernel.

In the inset of Fig. 6.2, we compare the geometric housekeeping-excess decomposition with the Hatano–Sasa decomposition by using the definition given in Eqs. (4.30) and (4.31). They behave quite similarly in this case.

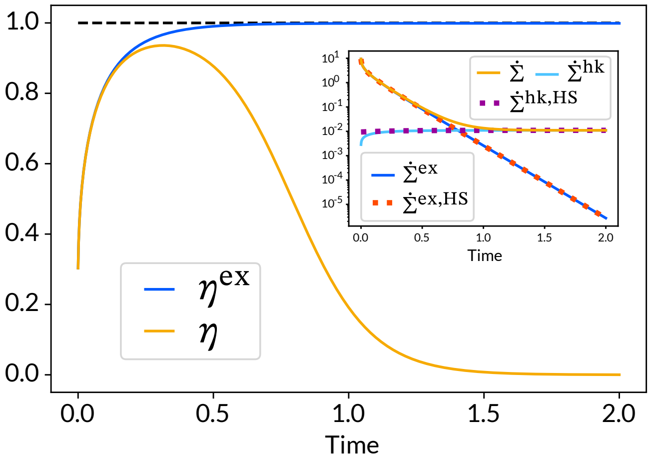

Figure 6.2: (Adapted from Ref. [19]) Verification of the short-time TUR (6.79). The ratios η and η^{ex} between the lower bound $k_{\mathrm{B}}|d_t\langle\mathcal{O}\rangle|^2/\mathcal{D}_{\mathcal{O}}(\vec{p})$ vs. EPR $\dot{\Sigma}$ and excess EPR $\dot{\Sigma}^{\mathrm{ex}}$ are shown. As the system approaches the steady state, η^{ex} becomes close to one, while η vanishes, which is because the total EPR remains finite even in the steady state. In the inset, we compare our decomposition with the HS decomposition. In this example, where a stable steady state exists, they behave in almost the same way.

Chapter 7

Chemical reaction networks

The formal structure of chemical reaction networks is similar to that of Markov jump processes. The force-current structure finally obtained will completely include what was discussed in the preceding chapter. However, the physical objects they describe are completely different. One of the main purposes of this chapter is to understand the similarity and difference between chemical systems and Markov jump processes.

7.1 Dynamics

7.1.1 Setup

A chemical reaction network (CRN) is an assemble of chemical species and reactions between them [3, 118]. Chemical species, like the oxigen molecule or an enzyme, are labeled by $\alpha \in A = \{1, \dots, N\}$. We assume the system is in a well-stirred reaction vessel with a fixed temperature T and pressure. The abundance is measured by the concentrations $\vec{c} = (c_\alpha) \in \mathbb{R}^N_{>0}$. Thus, the state space $\mathcal{S}_0$ and the restricted space $\mathcal{S}$ are given by $\mathbb{R}^N$ and $\mathbb{R}^N_{>0}$.

A reaction, labeled by $e \in E = \{1, \dots, |E|\}$ is designated by how many molecules are involved in it. We write the number of species α that join reaction e as $\nu_{\alpha e} \in \mathbb{Z}_{\geq 0}$, and those produced as $\nu'_{\alpha e} \in \mathbb{Z}_{\geq 0}$. For example, in reaction

$$X_1 + X_2 \xrightarrow{e} 2X_3, \tag{7.1}$$

we have

$$\nu_{1e} = \nu_{2e} = 1, \quad \nu_{3e} = 0, \tag{7.2}$$

$$\nu'_{1e} = \nu'_{2e} = 0, \quad \nu'_{3e} = 2. \tag{7.3}$$

We assume every reaction is reversible; i.e., there are $|E|$ pairs of reversible reactions and $2|E|$ individual reactions. Let $-e$ denote the backward reaction of e; e.g., for the above reaction, backward reaction is given by

$$2X_3 \xrightarrow{-e} X_1 + X_2, \tag{7.4}$$

and the pair is denoted as

$$X_1 + X_2 \overset{e}{\rightleftharpoons} 2X_3 \tag{7.5}$$

and labeled by e. We further define an $N \times |E|$ matrix S, called the stoichiometric matrix, by

$$\mathsf{S}_{\alpha e} := \nu'_{\alpha e} - \nu_{\alpha e}, \tag{7.6}$$

which indicates the net increase of α in reaction e.

7.1.2 Continuity equation

We write the occurrence rate of reaction e (reaction rate) by $J_e(\vec{c})$, where $\vec{c}$ indicates the concentration dependence of the reaction rate. Because each reaction has a forward and a backward reaction, the reaction rate can be split into positive contributions from them as

$$J_e(\vec{c}) = J_e^+(\vec{c}) - J_e^-(\vec{c}), \tag{7.7}$$

where $J_e^\pm(\vec{c}) > 0$ is the occurrence rate of the forward/backward reaction. We can regard each reaction as an elementary step; so we have $\mathscr{F} = \mathbb{R}^{|E|}$ [3]. The reaction rates are given as a vector, $\vec{J}(\vec{c}) = (J_e(\vec{c})) \in \mathscr{F}$.

A typical form of reaction rates is the mass action kinetics:

$$J_e^+(\vec{c}) = k_e^+ \prod_\alpha c_\alpha^{\nu_{\alpha e}}, \quad J_e^-(\vec{c}) = k_e^- \prod_\alpha c_\alpha^{\nu'_{\alpha e}}, \tag{7.8}$$

where $k_e^\pm$ are constants called the rate constants. It was found by Waage and Guldberg in 1867 [119] and is widely believe to hold in ideal (dilute) systems. However, it can be violated in non-ideal (thick or ionic) solutions [120]; so we do not necessarily assume this form unless otherwise stated.

Combining the stoichiometric matrix and the reaction rates, the time evolution of the concentrations is given by

$$\frac{dc_\alpha}{dt} = \sum_e \mathsf{S}_{\alpha e} J_e(\vec{c}), \tag{7.9}$$

or equivalently,

$$\frac{d\vec{c}}{dt} = \mathsf{S}\vec{J}(\vec{c}). \tag{7.10}$$

Therefore, it is natural to introduce the gradient operator $\nabla : \mathscr{S} \to \mathscr{F}$ by

$$\nabla := \mathsf{S}^\mathsf{T}. \tag{7.11}$$

Then, Eq. (7.10) reads

$$\frac{d\vec{c}}{dt} = \nabla^\mathsf{T}\vec{J}(\vec{c}), \tag{7.12}$$

which is the CRN counterpart of Eq. (3.3). We may call the continuity equation the rate equation. Concentration $\vec{c}^{\mathrm{ss}}$ is called a steady-state distribution or a steady state if it satisfies $\nabla\vec{J}(\vec{c}^{\mathrm{ss}}) = 0$. Detailed balance is defined by $\vec{J}(\vec{c}) = 0$, which is stronger than the steady-state condition. Up to here, we are intentionally ignoring external effects on the dynamics, such as exchange of molecules. As discussed in the next section, we consider closed and open systems whose dynamics are described by Eq. (7.10).

The gradient operator defines conservation laws. For example, if the system is substantially closed (i.e., it does not exchange any molecules with outer systems), the total mass is conserved. It is expressed by the vector $\vec{m} \in \mathbb{R}^N_{>0}$ that represents the mass of the chemical species; then, we expect the mass conservation

$$\nabla\vec{m} = 0, \tag{7.13}$$

so that $d_t\langle\vec{m}, \vec{c}\rangle = 0$. CRNs can have other non-trivial conservation laws related to characteristic segments in molecules that are preserved in reactions, called moiety [27]. On the other hand, open CRNs can break conservation laws of closed CRNs [121, 122].

The region that $\vec{c}$ can reach is restricted due to the conservation laws. We define the stoichiometic manifold by [118]

$$\mathcal{M}(\vec{c}_0) := \{\vec{c} \in \mathscr{S} \mid \vec{c} - \vec{c}_0 \in \operatorname{im} \nabla^\mathsf{T}\}. \tag{7.14}$$

Given an appropriate set of conservation laws $\{\lambda^{(i)}\}$, that is, a basis of $\ker \nabla$, it can be written as

$$\mathcal{M}(\vec{c}_0) = \{\vec{c} \in \mathscr{S} \mid \langle\lambda^{(i)}, \vec{c}\rangle = \langle\lambda^{(i)}, \vec{c}_0\rangle, \ \forall i\}. \tag{7.15}$$

Every time course starting from $\vec{c}_0$ is trapped in the stoichiometric manifold.

7.1.3 Closed systems, open systems

Equation (7.12) can be invalid when there are external flux of chemical species from chemostats, i.e., when the system is open. Let the set of exchangeable species be A_{ext} and distinguish it from internal chemical species A, which cannot go out of the vessel. Now, we have $|A| + |A_{\text{ext}}|$ kinds of chemical species. If the chemostatted species A_{ext} are externally injected at rate I_α, their rate equations should read

$$\frac{dc_\alpha}{dt} = \sum_e \nabla_{e\alpha} J_e\Big(\{c_\beta\}_{\beta\in A}, \{c_\gamma\}_{\gamma\in A_{\text{ext}}}\Big) + I_\alpha \quad (\alpha \in A_{\text{ext}}). \tag{7.16}$$

For convenience, we assume that the concentrations of exchangeable species are always maintained by external control [27], i.e., we assume

$$c_\alpha = \text{const.} \quad (\alpha \in A_{\text{ext}}). \tag{7.17}$$

We refer to these controled species as chemostatted species. Consequently, the chemostatted species are effectively eliminated from the dynamical description and we can concentrate on the rate equation (7.12) for the internal species. The vector $\vec{c}$ is understood as representing the internal species concentrations $(c_\alpha)_{\alpha\in A}$.

Nonetheless, the information of chemostatted species is still embedded in the reaction rates $\vec{J}(\vec{c})$. For example, in the mass action kinetics, the reaction rates are given like

$$J_e^+(\vec{c}) = k_e^+ \prod_{\alpha\in A} c_\alpha^{\nu_{\alpha e}} \quad \text{with} \quad k_e^+ = \kappa_e^+ \prod_{\alpha\in A_{\text{ext}}} c_\alpha^{\nu_{\alpha e}}, \tag{7.18}$$

where κ_e^+ should be understood as the genuine rate constant and k_e^+ is the apparent (effective) rate constant given by the genuine one and the constant concentrations $\{c_\alpha\}_{\alpha\in A_{\text{ext}}}$.

As we effectively forget chemostatted species, we may have reactions such as

$$\varnothing \overset{e}{\rightleftharpoons} X_\alpha, \tag{7.19}$$

where $\varnothing$ represents vacancy where there were some chemical species if we did not ignore chemostatted species. Apparently, this reaction breaks the conservation of mass, which often occurs in open CRNs described in this way. Then, the reaction rate turns into

$$J_e(\vec{c}) = k_e^+ - J_e^-(c_\alpha) \tag{7.20}$$

with a constant k_e^+.

In open systems, Eq. (7.12) may not have a unique stable steady-state solution. Due to the nonlinearlity of the reaction rates, it may have multiple steady states [65], or exhibit more non-trivial behavior such as limit cycles [68] or chaos [67, 123]. A limit cycle is a stable cyclic motion that does not stop [66]. Physically, the continuous motion is realized by constant supply of chemostatted molecules from the chemostats.

Finally, be aware of the difference between the stoichiometric matrix and the gradient operator. The gradient operator matters only in the effective dynamics of the internal species. Thus, $\nabla_{e\alpha}$ is only defined for $\alpha \in A$. On the other hand, as a matter of fact, chemostatted species also commit reactions, hence, we can define their stoichiometry and $\mathsf{S}_{\alpha e}$ can be defined for $\alpha \in A_{\text{ext}}$. Therefore, the stoichiometric matrix is separated as

$$\mathsf{S} = \begin{pmatrix} \nabla^{\mathrm{T}} \\ \mathsf{S}^{\text{ext}} \end{pmatrix} \begin{matrix} \} \ \alpha \in A \\ \} \ \alpha \in A_{\text{ext}} \end{matrix}, \tag{7.21}$$

where $\mathsf{S}^{\text{ext}}_{\alpha e} = \mathsf{S}_{\alpha e}$ for $\alpha \in A_{\text{ext}}$.

7.1.4 Graph theory and complex balance

A CRN cannot be regarded as a graph with nodes A and edges E because $e \in E$ can bridge more than one species. Instead, we define complexes as objects that include chemical species and are connected by edges: a complex is designated by $\vec{\xi} \in \mathbb{Z}^N_{\geq 0}$ that satisfies

$$\exists e \in E,\ \forall \alpha \in A, \quad \xi_\alpha = \nu_{\alpha e}. \tag{7.22}$$

That is, a complex is the reactant or the product of a reaction. Let $P = \{1, \dots, |P|\}$ be the labels of complexes. A CRN can be seen as a graph with nodes P and edges E.

Let us consider the following CRN, called the Brusselator model [68, 124]:

$$\varnothing \overset{1}{\rightleftharpoons} X_1, \quad X_1 \overset{2}{\rightleftharpoons} X_2 \quad 2X_1 + X_2 \overset{3}{\rightleftharpoons} 3X_1. \tag{7.23}$$

It has two chemical species $A = \{X_1, X_2\}$ and three reactions. In addition, there are five complexes

$$\varnothing, \quad X_1, \quad X_2, \quad 2X_1 + X_2, \quad 3X_1, \tag{7.24}$$

which are represented by the vectors

$$\begin{pmatrix} 0 \\ 0 \end{pmatrix}, \quad \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad \begin{pmatrix} 2 \\ 1 \end{pmatrix}, \quad \begin{pmatrix} 3 \\ 0 \end{pmatrix}. \tag{7.25}$$

Aligning them, we get the matrix

$$\mathsf{n} = \begin{pmatrix} 0 & 1 & 0 & 2 & 3 \\ 0 & 0 & 1 & 1 & 0 \end{pmatrix}, \tag{7.26}$$

which is sometimes refered to as the composition matrix [27, 125, 126]. On the other hand, as the reactions bridge the complexes to constitute a graph, the corresponding incidence matrix is given by

$$B = \begin{pmatrix} -1 & 0 & 0 \\ 1 & -1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \\ 0 & 0 & 1 \end{pmatrix}. \tag{7.27}$$

Multiplying these matrices, we obtain the stoichiometic matrix

$$\mathsf{n}B = \mathsf{S} = \begin{pmatrix} 1 & -1 & 1 \\ 0 & 1 & -1 \end{pmatrix}. \tag{7.28}$$

The relation $\mathsf{S} = \mathsf{n}B$ holds generally by definition. As a result, we can consider an intermediate steady-state condition, characteristic to CRNs: we define $\vec{c}^{\mathrm{cb}}$ to be complex balanced if it satisfies

$$B\vec{J}(\vec{c}^{\mathrm{cb}}) = 0, \tag{7.29}$$

which is weaker than detailed balance but stronger than the steady-state condition. It is known that, given the mass action kinetics, a CRN equipped with a complex-balanced steady state is globally stable [118, 127]; therefore, condition (7.29) is so strong that it eliminates the non-trivial behaviors due to nonlinearity, although complex balanced CRNs hold various theoretically nice properties [125, 126, 128, 129]. On the other hand, the steady-state condition $\nabla^{\mathsf{T}}\vec{J}(\vec{c}) = 0$ does not mean stable steady states and allows limit cycles and chaotic behavior.

7.2 Thermodynamics

7.2.1 Local detailed balance

The thermodynamic force, also known as the chemical affinity [2, 3], is defined by

$$F_e(\vec{c}) = -\frac{1}{T} \sum_{\alpha \in A \cup A_{\mathrm{ext}}} \mathsf{S}_{\alpha e} \mu_\alpha(\vec{c}; \vec{c}^{\mathrm{ext}}), \tag{7.30}$$

where μ_α is the chemical potential of α and $\vec{c}^{\mathrm{ext}} = (c_\alpha)_{\alpha \in A_{\mathrm{ext}}}$. It means that the thermynamic force is the chemical potential difference between the reactants and the products. Thermodynamics, especially the second law, is installed by the assumption that the thermodynamic forces $\vec{F}(\vec{c}) \in \mathbb{R}^{|E|}$ are given by

$$F_e(\vec{c}) = R \ln \frac{J_e^+(\vec{c})}{J_e^-(\vec{c})}, \tag{7.31}$$

which we call the local detailed balance in CRNs. Here, R is the gas constant, defined by the Boltzmann constant times the Avogadro number. We explain where this relation comes from and why it can be regarded as the local detailed balance in the next section by considering the so-called ideal solutions.

Equation (7.31) yields the EPR of the form

$$\dot{\Sigma}(\vec{c}) = \langle \vec{J}(\vec{c}), \vec{F}(\vec{c}) \rangle = R \sum_e \left(J_e^+(\vec{c}) - J_e^-(\vec{c}) \right) \ln \frac{J_e^+(\vec{c})}{J_e^-(\vec{c})}. \tag{7.32}$$

Once we admit the assumption in Eq. (7.31), the non-negativity of EPR $\dot{\Sigma}(\vec{c}) \geq 0$ is obvious since $J_e^+(\vec{c}) - J_e^-(\vec{c})$ and $\ln\left(J_e^+(\vec{c})/J_e^-(\vec{c})\right)$ have the same sign. We define an equilibrium state $\vec{c}^{\rm eq}$ by $\dot{\Sigma}(\vec{c}^{\rm eq}) = 0$; then, $\vec{c}$ is an equilibrium state if and only if detailed balance $\vec{J}^+(\vec{c}) = \vec{J}^-(\vec{c})$ holds.

At this point, the second property of the force-current structure (Eq. (3.7)) is provided as an assumption in CRNs; however, this assumption is “proved” from a more physical postulate in ideal systems, as descibed in the next section.

7.2.2 Ideal dilute solution

Equation (7.31) can be proved by a more specific assumption between constants in ideal dilute solutions. A solution is defined to be dilute if the chemical potentials of the solutes are given by

$$\mu_\alpha(\vec{c}; \vec{c}^{\rm ext}) = \mu_\alpha^\circ + RT \ln c_\alpha \quad (\alpha \in A \cup A_{\rm ext}). \tag{7.33}$$

In dilute solutions, the partial pressures of the solutes (resp. solvent) obey the Henry (resp. Raoult) law, i.e., become proportional to the concenrations. Since the chemical potential of ideal gas has the form $\mu = \mu^* + RT \ln p$ with a constant μ^* and the partial pressure p, the vapor-liquid equilibrium concludes Eq. (7.33). The Gibbs free energy is then given by

$$G(\vec{c}; \vec{c}^{\rm ext}) = \sum_{\alpha \in A \cup A_{\rm ext}} c_\alpha (\mu_\alpha^\circ - RT \ln c_\alpha) + RT \sum_{\alpha \in A \cup A_{\rm ext}} c_\alpha, \tag{7.34}$$

where the last term reflects the abundance of the solvent [27].

The constant μ° is called the standard chemical potential and composed of the standard enthalpy of production h_α° and the standard entropy s_α° as $\mu_\alpha^\circ = h_\alpha^\circ - T s_\alpha^\circ$ [120]. Then, we can regard h_α° and $s_\alpha^\circ + R \ln c_\alpha$ as the enthalpy and entropy of a unit amount of chemical species α. The Gibbs free energy is split into the enthalpy H and entropy S as

$$\begin{aligned} &G = H - TS \quad \text{with} \\ &H(\vec{c}; \vec{c}^{\rm ext}) = \sum_{\alpha \in A \cup A_{\rm ext}} h_\alpha^\circ c_\alpha, \quad S(\vec{c}; \vec{c}^{\rm ext}) = \sum_{\alpha \in A \cup A_{\rm ext}} c_\alpha (s_\alpha^\circ + R \ln c_\alpha - R). \end{aligned} \tag{7.35}$$

The time derivative of the system entropy becomes

$$\frac{dS}{dt} = \sum_{\alpha \in A} \frac{dc_\alpha}{dt} (s_\alpha^\circ + R \ln c_\alpha). \tag{7.36}$$

The entropy flux to the environment has two contributions: heat exchange and entropy transport. The heat produced in reaction e is given by

$$Q_e = \sum_{\alpha \in A \cup A_{\rm ext}} \nu_{\alpha e} h_\alpha^\circ - \sum_{\alpha \in A \cup A_{\rm ext}} \nu'_{\alpha e} h_\alpha^\circ. \tag{7.37}$$

Thus, the entropy flux is obtained as

$$\dot{S}_{\rm env} = \sum_e J_e(\vec{c}) Q_e - \sum_{\alpha \in A_{\rm ext}} (s_\alpha^\circ + R \ln c_\alpha) I_\alpha = -\frac{1}{T} \sum_e J_e(\vec{c}) \mathsf{S}_{\alpha e} h_\alpha^\circ - \sum_{\alpha \in A_{\rm ext}} (s_\alpha^\circ + R \ln c_\alpha) I_\alpha, \tag{7.38}$$

where the second term expresses the entropy delivered to the chemostat. Combining Eqs. (7.36) and (7.38), we obtain

$$\dot{\Sigma}(\vec{c}) = \frac{dS}{dt} + \dot{S}_{\rm env} = -\frac{1}{T} \sum_e J_e(\vec{c}) \sum_{\alpha \in A \cup A_{\rm ext}} \mathsf{S}_{\alpha e} \mu_\alpha(\vec{c}; \vec{c}^{\rm ext}). \tag{7.39}$$

This is why the thermodynamic force was defined as in Eq. (7.30). The notion of affinity was found by De Donder in 1920's [2, 130]. For simplicity, we make the dependence of $\dot{\Sigma}$, $\vec{J}$, and $\vec{F}$ on $\vec{c}^{\mathrm{ext}}$ implicit.

The positivity of Eq. (7.39) is proved if we assume the mass action kinetics and the following relationship between constants:

$$RT\ln\frac{\kappa_e^+}{\kappa_e^-} = -\sum_{\alpha\in A\cup A_{\mathrm{ext}}} \mathsf{S}_{\alpha e}\mu_\alpha^\circ, \tag{7.40}$$

where $\kappa_e^\pm$ are the "genuine" rate constants, introduced in Sec. 7.1.3. Equation (7.40) is also referred to as the local detailed balance as it resembles the local detailed balance in MJPs (6.20) [27]. With that relation, we can rewrite the thermodynamic force defined in Eq. (7.30) as

$$F_e(\vec{c}) = -\frac{1}{T}\sum_{\alpha\in A\cup A_{\mathrm{ext}}} \mathsf{S}_{\alpha e}\mu_\alpha^\circ + R\ln\frac{\prod_{\alpha\in A\cup A_{\mathrm{ext}}} c_\alpha^{\nu_{\alpha e}}}{\prod_{\alpha\in A\cup A_{\mathrm{ext}}} c_\alpha^{\nu'_{\alpha e}}} \tag{7.41}$$

$$= R\ln\frac{\kappa_e^+}{\kappa_e^-} + R\ln\frac{\prod_{\alpha\in A\cup A_{\mathrm{ext}}} c_\alpha^{\nu_{\alpha e}}}{\prod_{\alpha\in A\cup A_{\mathrm{ext}}} c_\alpha^{\nu'_{\alpha e}}} = R\ln\frac{J_e^+(\vec{c})}{J_e^-(\vec{c})}. \tag{7.42}$$

Thus, we can prove "assumption" (7.31) in ideal solutions by the more specific assumption between parameters (7.40). The nonnegativity of the EPR immediately follows as discussed.

We can consider the importance of the local detailed balance between constants (7.40) from another point of view. Assume there is no chemostatted species. Then, the relationship enables us to prove that $\vec{J}(\vec{c}) = 0$ if and only if the EPR as defined in Eq. (7.39) vanishes. The "only if" part immediately follows from Eq. (7.39). To discuss the "if" part, we rearrange a term in Eq. (7.39) as

$$\sum_{\alpha\in A}\mathsf{S}_{\alpha e}\mu_\alpha(\vec{c}) = \sum_{\alpha\in A}\mathsf{S}_{\alpha e}\mu_\alpha^\circ + RT\ln\Bigl(\prod_{\alpha\in A} c_\alpha^{\mathsf{S}_{\alpha e}}\Bigr) = \sum_{\alpha\in A}\mathsf{S}_{\alpha e}\mu_\alpha^\circ - RT\ln\frac{\prod_{\alpha\in A} c_\alpha^{\nu_{\alpha e}}}{\prod_{\alpha\in A} c_\alpha^{\nu'_{\alpha e}}}.$$

The mass action kinetics further transforms this as

$$\sum_{\alpha\in A}\mathsf{S}_{\alpha e}\mu_\alpha^\circ - RT\ln\frac{\prod_{\alpha\in A} c_\alpha^{\nu_{\alpha e}}}{\prod_{\alpha\in A} c_\alpha^{\nu'_{\alpha e}}} = \sum_{\alpha\in A}\mathsf{S}_{\alpha e}\mu_\alpha^\circ + RT\ln\frac{k_e^+}{k_e^-} - RT\ln\frac{J_e^+(\vec{c})}{J_e^-(\vec{c})}.$$

Thus, we obtain

$$\dot{\Sigma}(\vec{c}) = -\frac{1}{T}\sum_e J_e(\vec{c})\Bigl[\sum_{\alpha\in A}\mathsf{S}_{\alpha e}\mu_\alpha^\circ + RT\ln\frac{k_e^+}{k_e^-}\Bigr] + R\sum_e J_e(\vec{c})\ln\frac{J_e^+(\vec{c})}{J_e^-(\vec{c})}.$$

The second term is positive unless $\vec{J}(\vec{c}) = 0$. If we want to claim that $\dot{\Sigma}(\vec{c}) = 0$ implies $\vec{J}(\vec{c}) = 0$, it is natural to assume

$$\sum_{\alpha\in A}\mathsf{S}_{\alpha e}\mu_\alpha^\circ + RT\ln\frac{k_e^+}{k_e^-} = 0. \tag{7.43}$$

That is, Eq. (7.40) naturally emerges between the two notions, detailed balance and thermodynamic equilibrium.

However, when the diluteness is not assured, Eq. (7.40) will lose its meaning because the mass action kinetics and the expression (7.33) are no longer valid. One solution is to make the rate constants dependent on concentrations and replace $\ln c_\alpha$ in Eq. (7.33) with $\ln[\gamma_\alpha(\vec{c})c_\alpha]$, where $\gamma_\alpha(\vec{c})$ is the so-called activity coefficient [120]. Then, Eq. (7.40) is recovered with the concentration dependent rate constants and the activity coefficients. However, the concentration dependence of these quantities are elusive in general situations (one interesting approach is the Debye–Hückel theory [131, 132], which involves several parameters). Instead of introducing those quantities, we simply put Eq. (7.31) as an assumption to consider the nonequilibrium thermodynamics of CRNs. Still, it should be verified in the future whether the relation actually holds, analytically, computationally, or experimentally. It is worthnoting that a recent paper [133] proved that we can derive Eq. (7.31) by assuming the local detailed balance in non-ideal *stochastic* CRNs (i.e., described mesoscopically [134]) and a consistency between such a mesoscopic and the macroscopic description.

7.2.3 Force-current structure

As in MJPs, the thermodynamic force and the current are connected by the Onsager matrix (cf. Eq. (6.29))

$$\mathsf{L}_{ee'}(\vec{c}) = R^{-1}\Lambda\big(J_e^+(\vec{c}), J_e^-(\vec{c})\big)\delta_{ee'}, \tag{7.44}$$

which leads to

$$\vec{J}(\vec{c}) = \mathsf{L}(\vec{c})\vec{F}(\vec{c}), \tag{7.45}$$

the CRN analog of Eq. (3.8). Due to the properties of log mean Λ, described in Sec. 6.3.3, we can define an inner product and a norm as

$$\langle \vec{F}', \vec{F}'' \rangle_c := \langle \vec{F}', \mathsf{L}(\vec{c})\vec{F}'' \rangle, \quad \|\vec{F}'\|_c^2 := \sqrt{\langle \vec{F}', \vec{F}' \rangle_c}. \tag{7.46}$$

The EPR is given by the geometric expression

$$\dot{\Sigma}(\vec{c}) = \|\vec{F}(\vec{c})\|_c^2. \tag{7.47}$$

7.2.4 Conservativeness and detailed balance

Conservative forces are defined as those provided by ∇; for example, the thermodynamic force of a closed ideal solution is conservative because Eq. (7.30) is rewritten as

$$\vec{F}(\vec{c}) = -\nabla(\vec{\mu}(\vec{c})/T), \tag{7.48}$$

where $\vec{\mu}(\vec{c}) = (\mu_\alpha(\vec{c}))_{\alpha\in A}$. Although conservativeness is independent of the ideal property, we focus on ideal systems in this section to discuss the equivalence between conservativeness and detailed balance.

Since ∇ only takes the internal species into account, as discussed, Eq. (7.30) does not imply conservative force unless A_{ext} is an empty set. Rather, we generally have

$$F_e(\vec{c}) = -\frac{1}{T}\sum_{\alpha\in A_{\mathrm{ext}}} \mathsf{S}_{\alpha e}\mu_\alpha(\vec{c}^{\,\mathrm{ext}}) - [\nabla(\vec{\mu}(\vec{c})/T)]_e \tag{7.49}$$

for ideal solutions. By using the apparent rate constant $k_e^\pm$ and the relationship (7.40), it is further rearranged as

$$\vec{F}(\vec{c}) = \vec{F}_0 - \nabla\vec{\varphi}(\vec{c}) \quad \text{with} \quad F_{0,e} = R\ln\frac{k_e^+}{k_e^-}, \quad \vec{\varphi}(\vec{c}) = R\ln\vec{c}.$$

Therefore, ideal solutions satisfy assumption C1 in Sec. 3.3 with $\varphi(\vec{c}) = R\ln\vec{c}$. Thus, the general discussion reveals that the following are equivalent:

(1) There exists a potential $\vec{\psi} \in \mathbb{R}^N$ such that

$$\vec{F}_0 = -\nabla\vec{\psi}. \tag{7.50}$$

(2') There exists $\vec{\pi} \in \mathbb{R}_{>0}^N$ such that $\vec{J}(\vec{\pi}) = 0$.

Condition (1) can be stated differently: for any $\vec{C} \in \mathbb{R}^{|E|}$ such that $\nabla^{\mathsf{T}}\vec{C} = 0$, the rate constants satisfy

$$\prod_e (k_e^+)^{C_e} = \prod_e (k_e^-)^{C_e}, \tag{7.51}$$

which is called the Wegscheider condition [135]. Since Eq. (7.51) is equivalent to $\langle \vec{C}, \vec{F}_0 \rangle = 0$, this statement means $\vec{F}_0 \in \operatorname{im}\nabla$, i.e., condition (1).

Let us confirm assumption C2 through a concrete CRN. We consider the following CRN:

$$\varnothing \overset{1}{\rightleftharpoons} X_1, \quad X_1 + X_4 \overset{2}{\rightleftharpoons} X_2, \quad X_2 \overset{3}{\rightleftharpoons} X_3 + X_4, \quad X_3 \overset{4}{\rightleftharpoons} \varnothing. \tag{7.52}$$

The gradient operator is given by

$$\nabla^{\mathrm{T}} = \begin{pmatrix} 1 & -1 & 0 & 0 \\ 0 & 1 & -1 & 0 \\ 0 & 0 & 1 & -1 \\ 0 & -1 & 1 & 0 \end{pmatrix}. \tag{7.53}$$

It has a conservation law

$$\vec{\lambda} = (0, 1, 0, 1)^{\mathrm{T}}, \tag{7.54}$$

which represents the conservation of moiety X_4, which is included in X_2 and X_4. Then, Eq. (3.12) reads

$$e^{\psi_2 - \mu} + e^{\psi_4 - \mu} = c_2 + c_4 \tag{7.55}$$

and solved by

$$\mu = \ln \frac{e^{\psi_2} + e^{\psi_4}}{c_2 + c_4}. \tag{7.56}$$

Therefore, in this CRN, condition (1) is equivalent to the statement

(2) For any concentration $\vec{c} \in \mathbb{R}^4_{>0}$, there exists $\vec{\pi} \in \mathbb{R}^4_{>0}$ such that $\vec{J}(\vec{\pi}) = 0$ and $\pi_2 + \pi_4 = x_2 + x_4$.

Generally speaking, condition (2) means the existence of an equilibrium state in the stoichiometric manifold $\mathcal{M}(\vec{c})$, as is evident from the expression (7.15).

7.2.5 Cycle and breaking of detailed balance

Unlike the MJP case, cycles as defined by ker ∇^{T} are not always interpreted as a cycle on a graph. Let us take the Brusselator (7.23) as an example. In this CRN, ker ∇^{T} is a one-dimensional space spanned by

$$\vec{C} = (0, 1, 1)^{\mathrm{T}}. \tag{7.57}$$

While this vanishes when multiplied by $\nabla^{\mathrm{T}} = \mathrm{n}B$, it cannot be canceled solely by B. That is, although the chain of reactions, $e = 2$ then 3, leaves the total concentration unchanged, it cannot be understood as a cycle on the graph of complexes.

The discrepancy between ker ∇^{T} and ker B is called the deficiency [136],

$$\delta \coloneqq \dim\ker \nabla^{\mathrm{T}} - \dim\ker B. \tag{7.58}$$

It can be proved that the deficiency is also given as

$$\delta = |P| - L - \dim \mathrm{im}\, \nabla^{\mathrm{T}}. \tag{7.59}$$

The deficiency-zero theorem shows that when the mass action kinetics is assumed, $\delta = 0$ if and only if the CRN has a complex-balanced steady state for any value of rate constants as long as it is weakly reversible [118, 136]. Here, a CRN is defined to be weakly reversible if there is a directed chain of reactions with positive rates between any two complexes. As already mentioned, the existence of a complex-balanced steady state implies the global stability of the CRN; thus, $\delta > 0$ is required for the CRN to exhibit nonlinear behavior. For example, the Brusselator model has $\delta = 1$, so it can show a limit cycle, as shown in Example 7.5.

7.2.6 Comparison with MJPs

An MJP can be regarded as a CRN with unimolecular reactions. Let us consider a CRN with species $i \in \{1, \dots, N\}$ and reactions involving just one molecule,

$$X_i \rightleftharpoons X_j. \tag{7.60}$$

In this CRN, the total concenration $\sum_i c_i$ is conserved. Then, there are N complexes, each of which is composed of a single molecule, and matrix n can be the identity. The reaction rates are given as

$$J_e(\vec{c}) = k_e c_{\mathrm{r}(e)} - k_{-e} c_{\mathrm{p}(e)}, \tag{7.61}$$

where $\mathrm{r}(e)$ and $\mathrm{p}(e)$ denote the reactant and the product molecule of reaction e. If we define

$$p_i = \frac{c_i}{\sum_i c_i}, \tag{7.62}$$

the rate equation it obeys reads

$$\frac{dp_i}{dt} = \sum_e B_{ie}(k_e p_{\mathrm{r}(e)} - k_{-e} p_{\mathrm{p}(e)}), \tag{7.63}$$

which is nothing but the master equation of an MJP with transition rates $R_{\pm e} = k_e^{\pm}$.

If k_{B} and R are equated, the thermodynamics of MJPs coincides with that of ideal dilute solutions. The local detailed balance between constants (7.40), which includes entropic contribution coming from the internal degrees of freedom of molecules, looks similar but slightly different from Eq. (6.20), the local detailed balance in MJPs; however, such a contribution is sometimes taken into account in MJPs when the mesoscopic states have internal degrees of freedom [73], but is usually neglected for simplicity.

7.3 Housekeeping-excess decomposition

The geometric housekeeping-excess decomposition can be performed perfectly in the same way as in MJPs. Section 6.4 explains the geometric housekeeping-excess decomposition in CRNs by replacing $\vec{p}$ with $\vec{c}$. In this section, instead, we review the problem of the Hatano–Sasa decomposition in CRNs, which will be overcome by the geometric decomposition.

The HS decomposition is defined for CRNs by [26, 27]

$$\dot{\Sigma}^{\mathrm{hk,HS}}(\vec{c}) := \langle \vec{J}(\vec{c}), \vec{F}(\vec{c}^{\mathrm{ss}}) \rangle, \tag{7.64}$$

$$\dot{\Sigma}^{\mathrm{ex,HS}}(\vec{c}) := \langle \vec{J}(\vec{c}), \vec{F}(\vec{c}) - \vec{F}(\vec{c}^{\mathrm{ss}}) \rangle. \tag{7.65}$$

When $\vec{J}^{\pm}$ is provided by the mass action kinetics, we can show that (cf. Eq. (4.19))

$$\dot{\Sigma}^{\mathrm{ex,HS}}(\vec{c}) = -R \frac{\partial}{\partial t} D(\vec{c}(t) \| \vec{c}^{\mathrm{ss}}(s))\big|_{s=t}, \tag{7.66}$$

where $D(\vec{c} \| \vec{c}') = \sum_\alpha c_\alpha \ln(c_\alpha / c'_\alpha) - c_\alpha + c'_\alpha$ is the generalized KL divergence and $\vec{c}^{\mathrm{ss}}(s)$ is the instantaneous steady state. This is proved as

$$\frac{\partial}{\partial t} D(\vec{c}(t) \| \vec{c}^{\mathrm{ss}}(s))\big|_{s=t} = \sum_\alpha \frac{\partial c_\alpha}{\partial t} \ln \frac{c_\alpha}{c_\alpha^{\mathrm{ss}}} = \sum_e J_e(\vec{c}) \sum_\alpha \nabla_{e\alpha} \ln \frac{c_\alpha}{c_\alpha^{\mathrm{ss}}} = -\frac{1}{R} \sum_e J_e(\vec{c})(F_e(\vec{c}) - F_e(\vec{c}^{\mathrm{ss}})),$$

where the last equality follows from Eq. (7.50). The positivity of the HS excess EPR can be proved if $\vec{c}^{\mathrm{ss}}$ is complex balanced, $B\vec{J}(\vec{c}^{\mathrm{ss}}) = 0$ [26, 27]. However, if the complex balance is violated in the steady state, which is often the case with CRNs with non-zero deficiency, the HS excess EPR becomes negative [59].

On the other hand, the geometric excess (and housekeeping) EPR is always non-negative, as is obvious from the definition

$$\dot{\Sigma}^{\mathrm{hk}}(\vec{c}) = \min_{\vec{F}' \in \mathscr{C}} \|\vec{F}(\vec{c}) - \vec{F}'\|_{\vec{c}}^2 \tag{7.67}$$

$$\dot{\Sigma}^{\mathrm{ex}}(\vec{c}) = \min_{\vec{F}'} \|\vec{F}'\|_{\vec{c}}^2 \quad \text{s.t.} \quad \nabla^{\mathsf{T}} \mathsf{L}(\vec{c}) \vec{F}' = \nabla^{\mathsf{T}} \vec{J}(\vec{c}), \tag{7.68}$$

where $\mathscr{C} = \operatorname{im} \nabla$. Even if there is no stable steady state, we can interpret the excess EPR as the minimum EPR to cause the instantaneous dynamics.

In Ref. [19], we gave this geometric decomposition, which was the first proposal of housekeeping-excess decomposition that applies to general nonlinear systems. Soon later, an independent study [59] and our another paper [60] revealed that we can conduct such a decomposition by using nonlinear relations between forces and currents. While the nonlinear formulations look better than the present definition based on the linear Onsager relation, the situation is not so simple. The method in Ref. [59] needs to first split the total EPR into two convex functions (let us call them 1 and 2), decompose them into houskeeping and excess parts (so we have hk1, ex1, hk2, and ex2), and combine them to define the decomposition (i.e., hk=hk1+hk2, ex=ex1+ex2). This procedure makes it difficult to obtain thermodynamic inequalities. On the other hand, although Ref. [60] leads to nonlinear and thus tight inequalities with a sophisticated definition of decomposition, the diversion to other kinds of system is still elusive. Hence, to clarify the coherent structure among nonequilibrium systems and get trade-off relations, the linear formulation can be the best avenue.

7.4 Thermodynamic trade-off relations

Inequalities similar to the TUR and TSL are proven to be available in our previous study [18], and the general framework can generalize them.

7.4.1 Thermodynamic uncertainty relation

In Ref. [18], we proved the inequality

$$\dot{\Sigma}(\vec{c}) \geq R\frac{(d_t c_\alpha)^2}{\tilde{D}_{\alpha\alpha}(\vec{c})}, \tag{7.69}$$

where

$$\tilde{D}_{\alpha\beta}(\vec{c}) := \frac{1}{2}\sum_e \nabla_{\alpha e}\nabla_{\beta e}(J_e^+(\vec{c}) + J_e^-(\vec{c})) \tag{7.70}$$

is called the scaled diffusion coefficient. When we consider the system-size expansion of the chemical master equation, microscopic description of CRNs, this quantity divided by the volume parameter appears as the diffusion coefficient matrix [137–139]. Thus, we can interpret $\tilde{D}_{\alpha\beta}$ as the measure of the intrinsic fluctuation in the CRN.

On the other hand, the general inequality (5.29) provides

$$\dot{\Sigma}^{\mathrm{ex}}(\vec{c}) \geq \frac{|\langle d_t\vec{c}, \vec{\mathcal{O}}\rangle|^2}{\|\nabla\vec{\mathcal{O}}\|_c^2}. \tag{7.71}$$

As in the MJP case, we can show

$$\|\nabla\vec{\mathcal{O}}\|_c^2 \leq \frac{1}{2R}\sum_e (J_e^+(\vec{c}) + J_e^-(\vec{c}))[\nabla\vec{\mathcal{O}}]_e^2 \tag{7.72}$$

by the hierarchy between means (6.32). We also realize that

$$\frac{1}{2}\sum_e (J_e^+(\vec{c}) + J_e^-(\vec{c}))[\nabla\vec{\mathcal{O}}]_e^2 = \langle\vec{\mathcal{O}}, \tilde{D}(\vec{c})\vec{\mathcal{O}}\rangle =: \tilde{\mathcal{D}}_{\mathcal{O}}(\vec{c}), \tag{7.73}$$

which generalizes the diffusivity in MJPs (6.78) to CRNs. As a result, we obtain the generalized version of TUR

$$\dot{\Sigma}^{\mathrm{ex}}(\vec{c}) \geq R\frac{|\langle d_t\vec{c}, \vec{\mathcal{O}}\rangle|^2}{\tilde{\mathcal{D}}_{\mathcal{O}}(\vec{c})}. \tag{7.74}$$

With $\mathcal{O}_{\alpha'} = \delta_{\alpha'\alpha}$, it leads to Eq. (7.69).

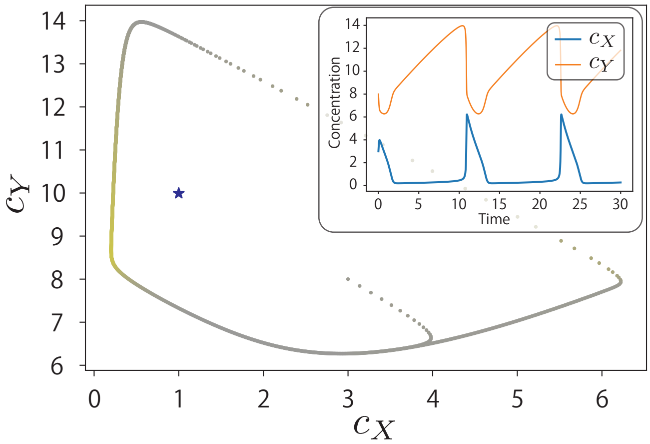

Figure 7.1: (Adapted from Ref. [19]) Time evolution of the concentration in the Brusselator model. The blue star indicates the unstable steady state. On the trajectory, the part colored in yellow indicates high excess EPR.

7.4.2 Thermodynamic speed limit

The generalized Wasserstein defined for MJPs also works in CRNs: it is defined by [19, 110]

$$\mathcal{W}(\vec{c}^a, \vec{c}^b) := \inf_{\vec{c}, \vec{\psi}} \sqrt{\tau \int_0^\tau \|\nabla \vec{\psi}(t)\|^2_{c(t)} dt} \tag{7.75}$$

with conditions

$$\vec{c}(0) = \vec{c}^a, \quad \vec{c}(\tau) = \vec{c}^b, \quad \frac{d\vec{c}}{dt} = \nabla^{\mathsf{T}} \mathsf{L}(\vec{c}(t)) \nabla \vec{\psi}(t). \tag{7.76}$$

The distance is finite only if $\vec{c}^a$ and $\vec{c}^b$ are on the stoichiometric manifold (otherwise, they cannot be connected by the continuity equation). With this quantities, we obtain the TSL [19]

$$\tau \Sigma^{\mathrm{ex}} \geq \mathcal{W}(\vec{c}(0), \vec{c}(\tau))^2. \tag{7.77}$$

7.5 Example

Here, we numerically observe the housekeeping-excess decomposition in a model of chemical oscillation. We adopt the Brusselator model given in Eq. (7.23). We assume the mass action kinetics and set the (apparent) rate constants $k_1 = k_3 = k_{-1} = k_{-3} = 1$, $k_2 = 10$, and $k_{-2} = 0.1$. Then, the time evolution of the concentration distribution $\vec{c} = (c_X, c_Y)^{\mathsf{T}}$ is obtained by solving

$$\begin{aligned} \frac{dc_X}{dt} &= 1 - c_X - 10c_X + 0.1c_Y + c_X^2 c_Y - c_X^3, \\ \frac{dc_Y}{dt} &= 10c_X - 0.1c_Y - c_X^2 c_Y + c_X^3. \end{aligned} \tag{7.78}$$

This CRN has an unstable steady state $\vec{c}^{\mathrm{ss}} = (1, 10)^{\mathsf{T}}$. The time evolution given by numerical integration is shown in Fig. 7.1. The system shows a limit cycle where concentration oscillation is permanently sustained.

We also compute the housekeeping and the excess EPR (Fig. 7.2). The advantage of the geometric decomposition is that it does not refer to any steady states unlike the HS decomposition. Now, we do not have physically meaningful steady states, so we cannot define the HS decomposition. If we wrongly adopt the unstable steady state, we will obtain physically unreasonable negative values (shown in the lower panel of Fig. 7.2).

The computed EPRs suggest a connection between the excess EPR and the dynamics. In Fig. 7.2, the squared norm of $d\vec{c}/dt$ is plotted in arbitrary units. This quantity and the excess EPR have two peaks at the same time, whereas the EPR and the housekeeping EPR have only one. This correlation is reasonable because the excess EPR gives the minimum dissipation to induce the (apparent) dynamics. The region on the trajectory where the excess EPR becomes large compared to the housekeeping one is colored in yellow in Fig. 7.1.

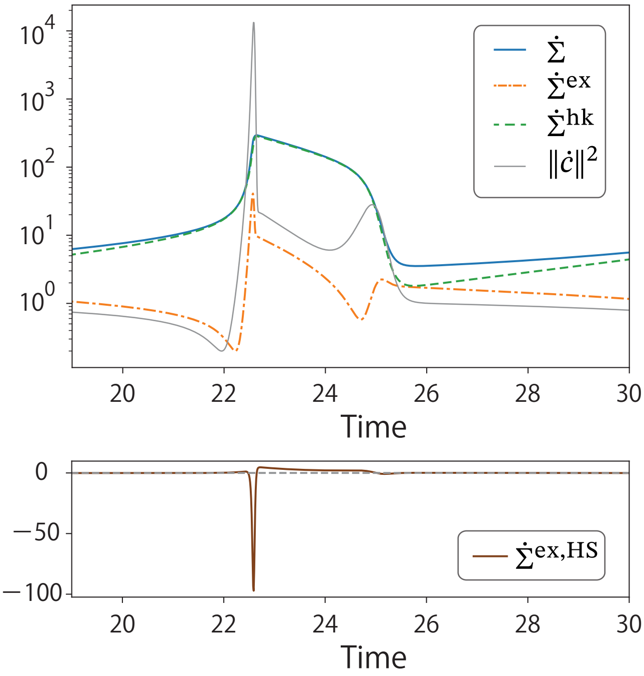

Figure 7.2: (Adapted from Ref. [19]) Decomposed EPRs in one period of oscillation. In the upper panel, we show the time evolution of EPR, housekeeping EPR, and excess EPR. In addition, we plot the squared norm of $d\vec{c}/dt$ in arbitrary units. We can confirm the correlation with the excess EPR. This is consistent with the fact that the excess EPR is supposed to reflects nonstationary aspect of the system. The bottom panel shows the HS excess EPR defined with a wrong stationary state, which exhibits negative values.

Chapter 8

Hydrodynamic systems

In this chapter, we consider macroscopic hydrodynamic systems described by the Navier–Stokes equation. CRNs and hydrodynamic systems are two of the main subjects of the historical field of nonequilibrium thermodynamics called irreversible thermodynamics [12]. We discuss how a force-current structure is established in this system, which recasts not only studies in irreversible thermodynamics but also an older result, the Helmholtz minimum dissipation theorem.

8.1 Notation

For two $d \times d$ matrices A and B, the Hilbert–Schmidt inner product is defined by

$$\mathsf{A} : \mathsf{B} := \sum_{i,j} A_{ij} B_{ij} = \mathrm{tr}(\mathsf{A}^{\mathrm{T}} \mathsf{B}), \tag{8.1}$$

where tr is the trace. The colon indicates dot product over two indices. We write the induced norm $\sqrt{\mathsf{A} : \mathsf{A}}$ simply as $|\mathsf{A}|$.

We can decompose a matrix A into a symmetric and an anti-symmetric part by

$$\mathsf{A}^{\mathrm{s}} = \frac{\mathsf{A} + \mathsf{A}^{\mathrm{T}}}{2}, \quad \mathsf{A}^{\mathrm{a}} = \frac{\mathsf{A} - \mathsf{A}^{\mathrm{T}}}{2}. \tag{8.2}$$

The symmetric part can be split further into the identity part $(\mathrm{tr}\,\mathsf{A})\mathsf{I}/d$ and the traceless part

$$\mathsf{A}^{\mathrm{s,tl}} = \mathsf{A}^{\mathrm{s}} - \frac{1}{d}(\mathrm{tr}\,\mathsf{A})\mathsf{I}, \tag{8.3}$$

where I is the identity matrix. Note that the anti-symmetric matrix is always traceless. It is easy to see that this sepearation leads to the decomposition of the inner product

$$\mathsf{A} : \mathsf{B} = \mathsf{A}^{\mathrm{s}} : \mathsf{B}^{\mathrm{s}} + \mathsf{A}^{\mathrm{a}} : \mathsf{B}^{\mathrm{a}} = \mathsf{A}^{\mathrm{s,tl}} : \mathsf{B}^{\mathrm{s,tl}} + \frac{1}{d}(\mathrm{tr}\,\mathsf{A})(\mathrm{tr}\,\mathsf{B}) + \mathsf{A}^{\mathrm{a}} : \mathsf{B}^{\mathrm{a}}. \tag{8.4}$$

For a vector field $\boldsymbol{u}(\boldsymbol{x})$, we define its gradient $\boldsymbol{\nabla}\boldsymbol{u}(\boldsymbol{x})$ as a tensor field with elements $\partial_i u_j(\boldsymbol{x})$ ($\partial_i := \partial/\partial x_i$). The dot product between tensor field $\mathsf{A}(\boldsymbol{x})$ and the differential operator $\boldsymbol{\nabla}$ gives a vector field with elements $[\boldsymbol{\nabla} \cdot \mathsf{A}(\boldsymbol{x})]_i = \sum_j \partial_j A_{ji}(\boldsymbol{x})$.

8.2 Dynamics

8.2.1 Setup

We consider a compressible Newtonian fluid in a region $\Omega \subset \mathbb{R}^d$ with boundary $\partial\Omega$ [140]. For simplicity, we assume Ω is connected and bounded. We define $\boldsymbol{n}(\boldsymbol{x})$ as the normal vector at $\boldsymbol{x} \in \partial\Omega$ directed to the external region; thus, the Gauss theorem is provided as

$$\int_{\Omega} \boldsymbol{\nabla} \cdot \boldsymbol{u}(\boldsymbol{x}) dV = \int_{\partial\Omega} \boldsymbol{u}(\boldsymbol{x}) \cdot \boldsymbol{n}(\boldsymbol{x}) dS. \tag{8.5}$$

We explain what “compressible” and “Newtonian” mean soon later.

The system is described by the density field $\rho(\boldsymbol{x}) \in \mathbb{R}_{>0}$ and the velocity field $\boldsymbol{v}(\boldsymbol{x}) \in \mathbb{R}^d$ ($\boldsymbol{x} \in \Omega$). We allow the fluid to cross the boundary, so $\boldsymbol{v}(\boldsymbol{x}) \cdot \boldsymbol{n}(\boldsymbol{x})$ may not vanish in general. The dynamics is given by the continuity equation of density

$$\frac{\partial \rho}{\partial t}(\boldsymbol{x}) = -\boldsymbol{\nabla} \cdot (\rho(\boldsymbol{x})\boldsymbol{v}(\boldsymbol{x})) \tag{8.6}$$

and the Navier–Stokes equation [140, 141]

$$\rho(\boldsymbol{x})\frac{D\boldsymbol{v}}{Dt}(\boldsymbol{x}) = \boldsymbol{\nabla} \cdot \sigma_{\rho,\boldsymbol{v}}(\boldsymbol{x}), \tag{8.7}$$

where D/Dt is the material derivative defined by

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + \boldsymbol{v}(\boldsymbol{x}) \cdot \boldsymbol{\nabla}, \tag{8.8}$$

and $\sigma_{\rho,\boldsymbol{v}}$ is the stress tensor. For compressible Newtonian fluids, it reads

$$\sigma_{\rho,\boldsymbol{v}}(\boldsymbol{x}) = -p(\rho(\boldsymbol{x}))\mathbf{I} + \left[\zeta(\rho(\boldsymbol{x})) - \frac{2}{d}\mu(\rho(\boldsymbol{x}))\right](\boldsymbol{\nabla} \cdot \boldsymbol{v}(\boldsymbol{x}))\mathbf{I} + 2\mu(\rho(\boldsymbol{x}))\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{v}(\boldsymbol{x}). \tag{8.9}$$

Here, $p(\rho)$ is the pressure determined by the density, $\zeta(\rho)$ the volume viscosity, $\mu(\rho)$ the shear viscosity, and $\boldsymbol{\nabla}^{\mathrm{S}}$ the symmetric gradient defined by

$$\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{u}(\boldsymbol{x}) := [\boldsymbol{\nabla}\boldsymbol{u}(\boldsymbol{x})]^{s}. \tag{8.10}$$

We define the second viscosity coefficient λ by $\zeta - (2/d)\mu$ to write the stress tensor simply as

$$\sigma_{\rho,\boldsymbol{v}}(\boldsymbol{x}) = -p(\rho(\boldsymbol{x}))\mathbf{I} + \lambda(\rho(\boldsymbol{x}))(\boldsymbol{\nabla} \cdot \boldsymbol{v}(\boldsymbol{x}))\mathbf{I} + 2\mu(\rho(\boldsymbol{x}))\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{v}(\boldsymbol{x}). \tag{8.11}$$

In addition, we note that the stress tensor has another expression

$$\sigma_{\rho,\boldsymbol{v}}(\boldsymbol{x}) = -p(\rho(\boldsymbol{x}))\mathbf{I} + \zeta(\rho(\boldsymbol{x}))(\boldsymbol{\nabla} \cdot \boldsymbol{v}(\boldsymbol{x}))\mathbf{I} + 2\mu(\rho(\boldsymbol{x}))[\boldsymbol{\nabla}\boldsymbol{v}]^{\mathrm{s,tl}}(\boldsymbol{x}). \tag{8.12}$$

Compressibility is defined as being not incompressible, which is defined by the condition $\boldsymbol{\nabla} \cdot \boldsymbol{v}(\boldsymbol{x}) = 0$. As usual, when discussing incompressible fluids, we also assume homogeneity $\boldsymbol{\nabla}\rho(\boldsymbol{x}) = 0$, which results in $\partial_t\rho(\boldsymbol{x}) = -\boldsymbol{\nabla} \cdot (\rho(\boldsymbol{x})\boldsymbol{v}(\boldsymbol{x})) = 0$. Then, ζ and μ become constants[1]. Thus, if the fluid is incompressible, the stress tensor becomes much simpler as

$$\tilde{\sigma}_{\rho,\boldsymbol{v}}(\boldsymbol{x}) = -p(\boldsymbol{x})\mathbf{I} + 2\mu\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{v}(\boldsymbol{x}). \tag{8.13}$$

The condition $\boldsymbol{\nabla} \cdot \boldsymbol{v}(\boldsymbol{x}) = 0$ implies that $\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{v}(\boldsymbol{x})$ is traceless.

Newtonianity means that ζ and μ are independent of the velocity gradients $\boldsymbol{\nabla}\boldsymbol{v}$. It is usually violated in polymeric fluids, where non-Newtonian viscosity arises from the slow relaxation of internal degrees of freedom [142, 143].

We allow the boundary to move. Let $\boldsymbol{v}_w(\boldsymbol{x})$ denote the velocity at $\boldsymbol{x} \in \partial\Omega$. Then, the time derivative of a spatial integral of a time-dependent field $\int_\Omega \phi(\boldsymbol{x})dV$ has two contributions: first, there is a contribution from the integrand,

$$\int_\Omega \frac{\partial \phi}{\partial t}(\boldsymbol{x})dV. \tag{8.14}$$

In addtion, we also have a contribution from the boundary

$$\int_{\partial\Omega} \phi(\boldsymbol{x})\boldsymbol{v}_w(\boldsymbol{x}) \cdot \boldsymbol{n}(\boldsymbol{x})dS. \tag{8.15}$$

---

[1] But p does not. This is because the deviation from the constant value $p(\rho = \text{const.})$ becomes relevant.

Therefore, we find

$$\frac{d}{dt}\int_{\Omega}\phi(\boldsymbol{x})dV = \int_{\Omega}\frac{\partial\phi}{\partial t}(\boldsymbol{x})dV + \int_{\partial\Omega}\phi(\boldsymbol{x})\boldsymbol{v}_w(\boldsymbol{x})\cdot\boldsymbol{n}(\boldsymbol{x})dS. \tag{8.16}$$

This is called the Reynolds transport theorem [144]. If we adopt the no-slip boundary condition, the wall velocity $\boldsymbol{v}_w$ should coincide with $\boldsymbol{v}$. If the region is moving at a constant velocity $-\boldsymbol{V}$, we have $\boldsymbol{v}_w(\boldsymbol{x}) = -\boldsymbol{V}$ at any $\boldsymbol{x} \in \partial\Omega$, e.g., when Ω is the outside of Ω^c and Ω^c is the body of a microswimmer moving at $\boldsymbol{V}$.

When $\phi(\boldsymbol{x})$ is of the form $\rho(\boldsymbol{x})Q(\boldsymbol{x})$, the continuity equation of density (8.6) leads to the formula

$$\frac{d}{dt}\int_{\Omega}\rho(\boldsymbol{x})Q(\boldsymbol{x})dV = \int_{\Omega}\rho(\boldsymbol{x})\frac{DQ}{Dt}(\boldsymbol{x})dV - \int_{\partial\Omega}\rho(\boldsymbol{x})Q(\boldsymbol{x})(\boldsymbol{v}(\boldsymbol{x}) - \boldsymbol{v}_w(\boldsymbol{x}))\cdot\boldsymbol{n}(\boldsymbol{x})dS, \tag{8.17}$$

because

$$\begin{aligned}\int_{\Omega}\frac{\partial(\rho Q)}{\partial t}(\boldsymbol{x})dV &= \int_{\Omega}\rho\frac{\partial Q}{\partial t}dV + \int_{\Omega}\frac{\partial\rho}{\partial t}QdV\\ &= \int_{\Omega}\rho\frac{\partial Q}{\partial t}dV - \int_{\Omega}\boldsymbol{\nabla}\cdot(\rho\boldsymbol{v})QdV\\ &= \int_{\Omega}\rho\left[\frac{\partial Q}{\partial t} + \boldsymbol{v}\cdot\boldsymbol{\nabla}Q\right]dV - \int_{\partial\Omega}\rho Q\boldsymbol{v}\cdot\boldsymbol{n}dS,\end{aligned}$$

where we used the Gauss theorem in the third line. We omitted the spatial dependence in the above calculation, which we also do in the following if there is no risk of misunderstanding.

8.2.2 Continuity equation

Although we have a continuity equation of density (Eq. (8.6)), Equation (8.7) does not possess the form of continuity equation (3.1). It turns into a continuity equation if we define the momentum current by

$$\mathsf{J}_{\rho,\boldsymbol{v}} := \rho\boldsymbol{v}\otimes\boldsymbol{v} - \sigma_{\rho,\boldsymbol{v}}, \tag{8.18}$$

where $[\boldsymbol{v}\otimes\boldsymbol{v}]_{ij} = v_i v_j$. Then, the Navier–Stokes equation is rewritten as

$$\frac{\partial\rho\boldsymbol{v}}{\partial t} = -\boldsymbol{\nabla}\cdot\mathsf{J}_{\rho,\boldsymbol{v}}(\boldsymbol{x}). \tag{8.19}$$

because

$$\begin{aligned}\rho\frac{D\boldsymbol{v}}{Dt} &= \rho\frac{\partial\boldsymbol{v}}{\partial t} + \rho\boldsymbol{v}\cdot\boldsymbol{\nabla}\boldsymbol{v} = \frac{\partial\rho\boldsymbol{v}}{\partial t} - \boldsymbol{v}\frac{\partial\rho}{\partial t} + \rho\boldsymbol{v}\cdot\boldsymbol{\nabla}\boldsymbol{v}\\ &= \frac{\partial\rho\boldsymbol{v}}{\partial t} + \boldsymbol{v}\boldsymbol{\nabla}\cdot(\rho\boldsymbol{v}) + \rho\boldsymbol{v}\cdot\boldsymbol{\nabla}\boldsymbol{v} = \frac{\partial\rho\boldsymbol{v}}{\partial t} + \boldsymbol{\nabla}\cdot(\rho\boldsymbol{v}\otimes\boldsymbol{v}).\end{aligned}$$

Equation (8.19) is valid even if the fluid is incompressible with $\sigma_{\rho,\boldsymbol{v}}$ replaced with $\tilde{\sigma}_{\rho,\boldsymbol{v}}$ (Eq. (8.13)).

Now, we have continuity equations (8.6) and (8.19); however, the currents in these equations do not necessarily provide irreversible contributions. We can judge whether a term in an equation of motion is reversible or not by considering time reversal. For the continuity equation of density (8.6), both terms flip their signs when we perform time reversal $t \to -t$ and $\boldsymbol{v} \to -\boldsymbol{v}$, which means the equation is totally reversible. On the other hand, under that transformation, the terms of the Navier–Stokes equation (8.19) behave as

$$\begin{gathered}\frac{\partial\rho\boldsymbol{v}}{\partial t} \to \frac{\partial\rho\boldsymbol{v}}{\partial t},\\ \rho\boldsymbol{v}\otimes\boldsymbol{v} + p(\rho)\mathsf{I} \to \rho\boldsymbol{v}\otimes\boldsymbol{v} + p(\rho)\mathsf{I},\\ -\lambda(\rho)(\boldsymbol{\nabla}\cdot\boldsymbol{v})\mathsf{I} - 2\mu(\rho)\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{v} \to \lambda(\rho)(\boldsymbol{\nabla}\cdot\boldsymbol{v})\mathsf{I} + 2\mu(\rho)\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{v}.\end{gathered}$$

Therefore, the Navier–Stokes equation includes irreversible terms; the momentum current is split into into the reversible and irreversible parts as

$$\begin{aligned}\mathbf{J}_{\rho,\boldsymbol{v}} &= \mathbf{J}^{\mathrm{rev}}_{\rho,\boldsymbol{v}} + \mathbf{J}^{\mathrm{irr}}_{\rho,\boldsymbol{v}}, &(8.20)\\ \mathbf{J}^{\mathrm{rev}}_{\rho,\boldsymbol{v}} &= \rho\boldsymbol{v}\otimes\boldsymbol{v} + p(\rho)\mathbf{I}, &(8.21)\\ \mathbf{J}^{\mathrm{irr}}_{\rho,\boldsymbol{v}} &= -\lambda(\rho)(\boldsymbol{\nabla}\cdot\boldsymbol{v})\mathbf{I} - 2\mu(\rho)\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{v}. &(8.22)\end{aligned}$$

Finally, the continuity equations turn out to have the same structure as Eq. (3.1) with the correspondence

$$\begin{aligned}x &\leftrightarrow (\rho,\boldsymbol{v}) &(8.23)\\ f^{\mathrm{rev}}(x) &\leftrightarrow \big(-\boldsymbol{\nabla}\cdot(\rho\boldsymbol{v}),\ -\boldsymbol{\nabla}\cdot\mathbf{J}^{\mathrm{rev}}_{\rho,\boldsymbol{v}}\big) &(8.24)\\ \nabla^{*} &\leftrightarrow \big(\varnothing,\ -\boldsymbol{\nabla}\cdot\,\big) &(8.25)\\ J(x) &\leftrightarrow \big(\varnothing,\ \mathbf{J}^{\mathrm{irr}}_{\rho,\boldsymbol{v}}\big). &(8.26)\end{aligned}$$

When the fluid is incompressible, ρ falls into a parameter. The momentum current and its irreversible component are given as

$$\mathbf{J}_{\rho,\boldsymbol{v}} = \mathbf{J}^{\mathrm{rev}}_{\rho,\boldsymbol{v}} + \tilde{\mathbf{J}}^{\mathrm{irr}}_{\rho,\boldsymbol{v}} \quad \text{with} \quad \tilde{\mathbf{J}}^{\mathrm{irr}}_{\rho,\boldsymbol{v}} = -2\mu\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{v}. \tag{8.27}$$

8.2.3 State space, force space, and gradient operator

When considering thermodynamics, $\mathbf{J}^{\mathrm{irr}}_{\rho,\boldsymbol{v}}$ will be the unique source of irreversibility. Because it is only related to the dynamics of the velocity field, we focus on the space of velocity fields and consider the density ρ as given. We set $\mathcal{S}_0$ to a space of vector fields with certain smoothness. As the irreversible current is a symmetric tensor field, we can think of defining $\mathcal{F}$ to be the space of symmetric tensor fields. These spaces are equipped with the usual inner products; for two tensor fields $\mathbf{J}$ and $\mathbf{J}'$, we define

$$\langle\mathbf{J},\mathbf{J}'\rangle := \int_{\Omega}\mathbf{J}(\boldsymbol{x}):\mathbf{J}'(\boldsymbol{x})dV. \tag{8.28}$$

To be more careful, we would need to consider separately the space of currents and that of forces, one of which is the dual space of the other. It is also required to treat $\partial_t(\rho\boldsymbol{v})$ as a linear map $\boldsymbol{u}\mapsto\int_{\Omega}\mathbf{J}:\boldsymbol{\nabla}\boldsymbol{u}\,dV$ rather than just a vector field. However, since such mathematical rigorousness does little good to physics, we do not consider this point except Sec. 8.4.

Having said that, the domain of the gradient operator ∇ does matter. To get the correspondence $\nabla^{*}\leftrightarrow-\boldsymbol{\nabla}\cdot$, we need to define ∇ by

$$\nabla\,:\,\mathcal{S}_{\mathrm{b}}\ni\boldsymbol{w}\mapsto\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{w}\in\mathcal{F} \tag{8.29}$$

with

$$\mathcal{S}_{\mathrm{b}} := \{\boldsymbol{w}\in\mathcal{S}_0 \mid \boldsymbol{w}(\boldsymbol{x}) = 0\ \text{ if}\,\boldsymbol{x}\in\partial\Omega\}. \tag{8.30}$$

Then, for any $\boldsymbol{w}\in\mathcal{S}_{\mathrm{b}}$ and $\mathbf{J}\in\mathcal{F}$, we have

$$\langle\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{w},\mathbf{J}\rangle = \langle\boldsymbol{w},-\boldsymbol{\nabla}\cdot\mathbf{J}\rangle \tag{8.31}$$

because

$$\begin{aligned}\langle\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{w},\mathbf{J}\rangle &= \frac{1}{2}\int_{\Omega}\sum_{i,j}(\partial_i w_j + \partial_j w_i)\mathsf{J}_{ij}dV\\ &= \frac{1}{2}\Big(-\int_{\Omega}\sum_{i,j}w_j\partial_i\mathsf{J}_{ij}dV + \int_{\partial\Omega}\sum_{i,j}w_j\mathsf{J}_{ij}n_i dS\Big) + \frac{1}{2}\Big(-\int_{\Omega}\sum_{i,j}w_i\partial_j\mathsf{J}_{ij}dV + \int_{\partial\Omega}\sum_{i,j}w_i\mathsf{J}_{ij}n_j dS\Big)\\ &= -\int_{\Omega}\sum_{i,j}w_i\partial_j\mathsf{J}_{ij}dV = \langle\boldsymbol{w},-\boldsymbol{\nabla}\cdot\mathbf{J}\rangle,\end{aligned}$$

where we used the Gauss theorem in the second line and the symmetry of $\mathbf{J}$ in the third line. The boudary term is removed because $\boldsymbol{u}\in\mathcal{S}_{\mathrm{b}}$. We note that while the gradient operator is defined on $\mathcal{S}_{\mathrm{b}}$, the adjoint maps $\mathcal{F}$ to a wider space, as is often the case with unbounded operators.

As the domain of ∇ is set to $\mathcal{S}_{\mathrm{b}}$, its kernel becomes trivial; i.e., $\boldsymbol{\nabla}\boldsymbol{u} = 0$ implies $\boldsymbol{u} = 0$. This means that we have no nontrivial conservation law.

8.3 Thermodynamics

8.3.1 Local equilibrium assumption

The Navier–Stokes equation implicitly assumes local equilibrium; it includes pressure that depends on the density, the existence of which is a typical consequence of the local equilibrium assumption [12, 141]. We further suppose that the temperature is homogeneous, which has also been assumed by writing the Navier–Stokes equation as in Eq. (8.7); otherwise, parameters depend on the inhomogeneous temperature, and we need to deal with thermal transport.

The local equilibrium assumption also allows us to define the specific entropy (entropy per unit mass, which we also call entropy density) [12]

$$s(\boldsymbol{x}) = s(u(\boldsymbol{x}), \rho(\boldsymbol{x})) \tag{8.32}$$

by

$$s(U/N, N/V) := S_{\mathrm{TD}}(U, V, N)/N = S_{\mathrm{TD}}(U/N, V/N, 1), \tag{8.33}$$

where $S_{\mathrm{TD}}(U, V, N)$ is the macroscopic entropy function and the second equality follows from the homogeneity of S_{TD}. The internal energy density per unit mass u gives the total energy density by

$$e = u + \frac{1}{2}|\boldsymbol{v}|^2, \tag{8.34}$$

where the second term represents the kinetic energy. The entropy density satisfies the thermodynamic relation

$$ds = \frac{1}{T}du + \frac{p}{T}d\rho^{-1} \tag{8.35}$$

because of the macroscopic relation $TdS = dU + PdV - \mu dN$. From the Lagrangian perspective, it is translated into [140]

$$\frac{Ds}{Dt} = \frac{1}{T}\frac{Du}{Dt} + \frac{p}{T}\frac{D\rho^{-1}}{Dt}. \tag{8.36}$$

8.3.2 Entropy production rate and thermodynamic force

Given the entropy density, we can compute the EPR. First, the system entropy is given by

$$S = \int_{\Omega} \rho(\boldsymbol{x})s(\boldsymbol{x})dV. \tag{8.37}$$

Its time derivative is computed with formula (8.17) as

$$\frac{dS}{dt} = \int_{\Omega} \rho\frac{Ds}{Dt}dV - \int_{\partial\Omega} \rho(\boldsymbol{x})s(\boldsymbol{x})(\boldsymbol{v}(\boldsymbol{x}) - \boldsymbol{v}_w(\boldsymbol{x})) \cdot \boldsymbol{n}(\boldsymbol{x})dS. \tag{8.38}$$

The entropy change in the environment also consists of the boundary entropy outflow from Ω and the local heat dissipation as

$$\dot{S}_{\mathrm{env}} = \int_{\partial\Omega} \rho(\boldsymbol{x})s(\boldsymbol{x})(\boldsymbol{v}(\boldsymbol{x}) - \boldsymbol{v}_w(\boldsymbol{x})) \cdot \boldsymbol{n}(\boldsymbol{x})dS - \frac{1}{T}\int_{\Omega} \dot{q}(\boldsymbol{x})dV, \tag{8.39}$$

where the heat influx $\dot{q}$ is given by the first law of thermodynamics as

$$\dot{q} = \rho\frac{De}{Dt} - \dot{w} \tag{8.40}$$

with work rate $\dot{w}$ due to viscosity

$$\dot{w}(\boldsymbol{x}) = \boldsymbol{\nabla} \cdot (\sigma_{\rho,\boldsymbol{v}}(\boldsymbol{x}) \cdot \boldsymbol{v}(\boldsymbol{x})), \tag{8.41}$$

which yields the total work on the boundary

$$\dot{W} = \int_\Omega \dot{w}(\boldsymbol{x})dV = \int_{\partial\Omega} \boldsymbol{v}(\boldsymbol{x}) \cdot [\sigma_{\rho,\boldsymbol{v}}(\boldsymbol{x}) \cdot \boldsymbol{n}(\boldsymbol{x})]dS. \tag{8.42}$$

Thus, we can define the EPR as

$$\dot{\Sigma}_{\rho,\boldsymbol{v}} := \frac{dS}{dt} + \dot{S}_{\mathrm{env}} = \int_\Omega \rho\left(\frac{Ds}{Dt} - \frac{1}{T}\frac{De}{Dt}\right)dV + \frac{1}{T}\int_{\partial\Omega} \boldsymbol{v}(\boldsymbol{x}) \cdot [\sigma_{\rho,\boldsymbol{v}}(\boldsymbol{x}) \cdot \boldsymbol{n}(\boldsymbol{x})]dS. \tag{8.43}$$

Using the thermodynamic relation (8.36) and the definition of the total energy (8.34), we find the relations

$$\frac{Ds}{Dt} - \frac{1}{T}\frac{De}{Dt} = -\frac{1}{T}\boldsymbol{v} \cdot \frac{D\boldsymbol{v}}{Dt} + \frac{p}{T}\frac{D\rho^{-1}}{Dt}. \tag{8.44}$$

The terms on the right-hand side can be transformed as

$$\rho\boldsymbol{v} \cdot \frac{D\boldsymbol{v}}{Dt} = \boldsymbol{v} \cdot [\boldsymbol{\nabla} \cdot \sigma_{\rho,\boldsymbol{v}}] \tag{8.45}$$

from the Navier–Stokes equation and

$$\rho\frac{D\rho^{-1}}{Dt} = -\frac{1}{\rho}\frac{D\rho}{Dt} = -\frac{1}{\rho}\left(\frac{\partial\rho}{\partial t} + \boldsymbol{v} \cdot \boldsymbol{\nabla}\rho\right) = -\frac{1}{\rho}(-\boldsymbol{\nabla} \cdot (\rho\boldsymbol{v}) + \boldsymbol{v} \cdot \boldsymbol{\nabla}\rho) = \boldsymbol{\nabla} \cdot \boldsymbol{v} \tag{8.46}$$

due to the continuity equation. Thus, we obtain

$$\begin{aligned}
\dot{\Sigma}_{\rho,\boldsymbol{v}} &= \frac{1}{T}\int_\Omega (-\boldsymbol{v} \cdot [\boldsymbol{\nabla} \cdot \sigma_{\rho,\boldsymbol{v}}] + p\boldsymbol{\nabla} \cdot \boldsymbol{v})dV + \frac{1}{T}\int_{\partial\Omega} \boldsymbol{v} \cdot [\sigma_{\rho,\boldsymbol{v}} \cdot \boldsymbol{n}]dS \\
&= \frac{1}{T}\int_\Omega \left(\boldsymbol{\nabla}\boldsymbol{v} : \sigma_{\rho,\boldsymbol{v}} + p\boldsymbol{\nabla} \cdot \boldsymbol{v}\right)dV \\
&= -\frac{1}{T}\int_\Omega \boldsymbol{\nabla}\boldsymbol{v} : \mathbf{J}^{\mathrm{irr}}_{\rho,\boldsymbol{v}}dV,
\end{aligned}$$

where the last line follows from the definition of $\sigma_{\rho,\boldsymbol{v}}$ and $\mathbf{J}^{\mathrm{irr}}_{\rho,\boldsymbol{v}}$. Due to the symmetry of $\mathbf{J}^{\mathrm{irr}}_{\rho,\boldsymbol{v}}$, it can be further written as

$$\dot{\Sigma}_{\rho,\boldsymbol{v}} = -\frac{1}{T}\int_\Omega \boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{v} : \mathbf{J}^{\mathrm{irr}}_{\rho,\boldsymbol{v}}dV. \tag{8.47}$$

Its positivity immediately follows from

$$\begin{aligned}
-\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{v} : \mathbf{J}^{\mathrm{irr}}_{\rho,\boldsymbol{v}} &= \boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{v} : \left[\left[\zeta(\rho) - \frac{2}{d}\mu(\rho)\right](\boldsymbol{\nabla} \cdot \boldsymbol{v})\mathbf{I} + 2\mu(\rho)\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{v}\right] \\
&= \left[(\boldsymbol{\nabla}\boldsymbol{v})^{\mathrm{s,tl}} + \frac{1}{d}(\boldsymbol{\nabla} \cdot \boldsymbol{v})\mathbf{I}\right] : \left[\zeta(\rho)(\boldsymbol{\nabla} \cdot \boldsymbol{v})\mathbf{I} + 2\mu(\rho)(\boldsymbol{\nabla}\boldsymbol{v})^{\mathrm{s,tl}}\right] \\
&= 2\mu(\rho)(\boldsymbol{\nabla}\boldsymbol{v})^{\mathrm{s,tl}} : (\boldsymbol{\nabla}\boldsymbol{v})^{\mathrm{s,tl}} + \zeta(\rho)(\boldsymbol{\nabla} \cdot \boldsymbol{v})^2 \geq 0
\end{aligned}$$

because the viscosity coefficients are positive. Finally, equation (8.47) reveals that the thermodynamic force should be given by

$$\mathbf{F}_{\boldsymbol{v}} = -\frac{1}{T}\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{v}. \tag{8.48}$$

As a consequence, we find the formula (3.7) in hydrodynamics

$$\dot{\Sigma}_{\rho,\boldsymbol{v}} = \langle \mathbf{J}^{\mathrm{irr}}_{\rho,\boldsymbol{v}}, \mathbf{F}_{\boldsymbol{v}} \rangle. \tag{8.49}$$

The thermodynamic force (8.48) is connected to the irreversible current as

$$\mathbf{J}^{\mathrm{irr}}_{\rho,\boldsymbol{v}} = T\lambda(\rho)(\mathrm{tr}\,\mathbf{F}_{\boldsymbol{v}})\mathbf{I} + 2T\mu(\rho)\mathbf{F}_{\boldsymbol{v}}. \tag{8.50}$$

Thus, we can define the Onsager operator by

$$\Pi_\rho \,:\, \mathsf{F}' \mapsto T\lambda(\rho)(\operatorname{tr}\mathsf{F}')\mathsf{I} + 2T\mu(\rho)\mathsf{F}', \tag{8.51}$$

which is positive and symmetric because

$$\langle \mathsf{F}', \Pi_\rho(\mathsf{F}'')\rangle = \frac{1}{T}\int_\Omega \Big[2\mu(\rho)(\mathsf{F}')^{\mathrm{s,tl}} : (\mathsf{F}'')^{\mathrm{s,tl}} + \zeta(\rho)(\operatorname{tr}\mathsf{F}')(\operatorname{tr}\mathsf{F}'')\Big]dV.$$

It establishes the third relation (3.8) of the force-current structure. Consequently, the EPR is given by

$$\dot{\Sigma}_{\rho,\boldsymbol{v}} = \|\mathsf{F}_{\boldsymbol{v}}\|_\rho^2, \tag{8.52}$$

where the norm $\|\cdot\|_\rho$ is induced by the inner product

$$\langle \mathsf{F}', \mathsf{F}''\rangle_\rho := \langle \mathsf{F}', \Pi_\rho(\mathsf{F}'')\rangle. \tag{8.53}$$

The EPR vanishes when $\mathsf{F}_{\boldsymbol{v}} = 0$ holds, which means $\nabla\boldsymbol{v}$ is anti-symmetric:

$$\partial_i v_j = -\partial_j v_i. \tag{8.54}$$

This condition is satisfied, for example, when the system is rotating as a rigid body; Let $d = 2$ and the system rotates around the origin at angular velocity ω. Then, the velocity at $\boldsymbol{x} = (x, y)$ is

$$\boldsymbol{v}(\boldsymbol{x}) = (-\omega y, \omega x). \tag{8.55}$$

Thus, we have $\partial_x v_y = -\partial_y v_x$ and no dissipation occurs.

8.3.3 Incompressible case

Even for the incompressible systems, the ERP is obtained as

$$\dot{\Sigma}_{\rho,\boldsymbol{v}} = -\frac{1}{T}\int_\Omega \nabla^{\mathrm{S}}\boldsymbol{v} : \tilde{\mathsf{J}}^{\mathrm{irr}}_{\rho,\boldsymbol{v}}dV = \frac{2\mu}{T}\int_\Omega \nabla^{\mathrm{S}}\boldsymbol{v} : \nabla^{\mathrm{S}}\boldsymbol{v}dV. \tag{8.56}$$

Thus, the thermodynamic force is defined in the same way, and we find the Onsager relation

$$\tilde{\mathsf{J}}^{\mathrm{irr}}_{\rho,\boldsymbol{v}} = \tilde{\Pi}_\rho(\mathsf{F}_{\boldsymbol{v}}) \quad \text{with} \quad \tilde{\Pi}_\rho \,:\, \mathsf{F}' \mapsto 2T\mu\mathsf{F}'. \tag{8.57}$$

8.3.4 Conservativeness

Consider a situation where $\boldsymbol{v}_w(\boldsymbol{x}) = \boldsymbol{v}(\boldsymbol{x})$ for all $\boldsymbol{x} \in \partial\Omega$ and $\boldsymbol{v}_w(\boldsymbol{x})\cdot\boldsymbol{n}(\boldsymbol{x}) = 0$; i.e., no slip occurs at the boundary and the position and the shape of $\partial\Omega$ do not change. This situation is often discussed in hydrodynamics. Then, take arbitrarily a velocity field $\boldsymbol{v}_0$ such that $\boldsymbol{v}_0(\boldsymbol{x}) = \boldsymbol{v}_w(\boldsymbol{x})$ on $\partial\Omega$. It decomposes the thermodynamic force as

$$\mathsf{F}_{\boldsymbol{v}} = \mathsf{F}_0 - \nabla^{\mathrm{S}}\boldsymbol{\varphi}_{\boldsymbol{v}}, \tag{8.58}$$

where

$$\mathsf{F}_0 = -\frac{1}{T}\nabla^{\mathrm{S}}\boldsymbol{v}_0, \quad \boldsymbol{\varphi}_{\boldsymbol{v}} = \frac{\boldsymbol{v} - \boldsymbol{v}_0}{T}. \tag{8.59}$$

Since $\boldsymbol{v}$ is mapped to $\boldsymbol{\varphi}_{\boldsymbol{v}}$ in a reversible manner, this expression shows that the thermodynamic force can satisfy assumption C1 of Sec. 3.3. Although this is quite a formal discussion based on an arbitrary velocity field $\boldsymbol{v}_0$, following Sec. 3.3, we find that the following statements are equivalent:

(1) There is a velocity field $\boldsymbol{\psi}$ such that $\boldsymbol{\psi}(\boldsymbol{x}) = 0$ on $\partial\Omega$ and $\mathsf{F}_0 = -\nabla^{\mathrm{S}}\boldsymbol{\psi}$.

(2) There exists a velocity field $\boldsymbol{u}$ such that $\mathsf{J}^{\mathrm{irr}}_{\rho,\boldsymbol{u}} = 0$.

8.3.5 Cycles

Formally, we can define "cyclic tensor fields" by

$$\boldsymbol{\nabla} \cdot \mathbf{J}' = 0. \tag{8.60}$$

However, properties of such tensor fields are not yet well understood, and further research is awaited in the future.

8.4 Housekeeping-excess decomposition

8.4.1 General results

Hydrodynamic systems often exhibit turbulence and steady states become hard to obtain [69, 145]; hence, we cannot hope that techniques based on steady states would be useful. On the other hand, the geometric housekeeping-excess decomposition is available even in such cases because it only relies on the force-current structure [20].

The geometric decomposition deals with projection of forces in a linear (functional) space, so we need to choose properly what space to discuss. Not every symmetric tensor has the form $-T\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{u}$, so we need to restrict $\mathscr{F}$ to a narrower space. We re-define the space of forces $\mathscr{F}^*$ by

$$\mathscr{F}^* := \{-\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{\psi} \mid \boldsymbol{\psi} : \Omega \to \mathbb{R}^d\}. \tag{8.61}$$

Then, the conservative subspace $\mathscr{C}$ and its orthogonal complement $\mathscr{C}^\perp$ are defined by

$$\mathscr{C} := \{-\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{\phi} \mid \boldsymbol{\phi}(\boldsymbol{x}) = 0,\ \forall \boldsymbol{x} \in \partial\Omega\}, \tag{8.62}$$

$$\mathscr{C}^\perp = \{\mathbf{F}' \in \mathscr{F}^* \mid \boldsymbol{\nabla} \cdot \Pi_\rho(\mathbf{F}') = 0\}, \tag{8.63}$$

where the condition of $\mathscr{C}^\perp$ is given in this way because

$$\langle -\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{\phi}, \mathbf{F}' \rangle_\rho = \langle \boldsymbol{\phi}, \boldsymbol{\nabla} \cdot \Pi_\rho(\mathbf{F}') \rangle$$

and it becomes zero for any $\boldsymbol{\phi}$ only if $\boldsymbol{\nabla} \cdot \Pi_\rho(\mathbf{F}') = 0$.

The housekeeping EPR is provided by

$$\dot{\Sigma}^{\mathrm{hk}}_{\rho,\boldsymbol{v}} := \inf_{\mathbf{F}' \in \mathscr{C}} \|\mathbf{F}_{\boldsymbol{v}} - \mathbf{F}'\|^2_\rho. \tag{8.64}$$

It vanishes when $\boldsymbol{v}$ satisfies

$$\boldsymbol{\nabla}^{\mathrm{S}}(\boldsymbol{v}/T - \boldsymbol{\phi}) = 0 \tag{8.65}$$

with some $\boldsymbol{\phi}$. Then, there exists a velocity field, $\boldsymbol{u} := \boldsymbol{v} - T\boldsymbol{\phi}$, that satisfies the same boundary condition as $\boldsymbol{v}$ and provides zero dissipation $\dot{\Sigma}_{\rho,\boldsymbol{u}} = 0$ for any ρ. That is, the housekeeping EPR becomes zero if the boundary condition imposed on $\boldsymbol{v}$ allows such an "equilibrium" velocity field. This is prohibited, e.g., when the boundary exerts permanent shear to the system, like in a flow between two plates moving in the opposite directions. Then, the housekeeping EPR becomes finite, evaluating the dissipation due to boundary movements.

If the boundary velocity is zero, or if the system does not have a boundary, like those with the periodic boundary condition, the housekeeping EPR is identically zero. This can be the case, for example, in homogeneous isotropic turbulence [69].

The excess EPR is also given as

$$\dot{\Sigma}^{\mathrm{ex}}_{\rho,\boldsymbol{v}} := \inf_{\mathbf{F}' \in \mathscr{F}^*} \|\mathbf{F}'\|^2_\rho, \quad \text{s.t.} \quad \boldsymbol{\nabla} \cdot \Pi_\rho(\mathbf{F}') = \boldsymbol{\nabla} \cdot \mathbf{J}^{\mathrm{irr}}_{\rho,\boldsymbol{v}}. \tag{8.66}$$

As the condition only involves the irreversible part of the continuity equation, it only means that $\mathbf{F}'$ reproduces the dissipative portion of the total motion. The orthogonal complement of $\mathscr{C}$ provides the excess EPR with another expression

$$\dot{\Sigma}^{\mathrm{ex}}_{\rho,\boldsymbol{v}} = \inf_{\mathbf{F}' \in \mathscr{C}^\perp} \|\mathbf{F}_{\boldsymbol{v}} - \mathbf{F}'\|^2_\rho. \tag{8.67}$$

8.4.2 Incompressible case

When the system is incompressible, the space of forces is changed into

$$\mathscr{F}^* := \{-\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{\psi} \mid \boldsymbol{\psi} : \Omega \to \mathbb{R}^d,\ \boldsymbol{\nabla}\cdot\boldsymbol{\psi} = 0\}. \tag{8.68}$$

Then, the conservative subspace becomes

$$\tilde{\mathscr{C}} := \{-\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{\phi} \mid \boldsymbol{\phi}(\boldsymbol{x}) = 0,\ \forall\boldsymbol{x}\in\partial\Omega;\ \boldsymbol{\nabla}\cdot\boldsymbol{\phi} = 0\}. \tag{8.69}$$

Consequently, the orthogonal complement significantly changes as

$$\tilde{\mathscr{C}}^{\perp} = \{\mathsf{F}' \in \tilde{\mathscr{F}}^* \mid \exists q : \Omega \to \mathbb{R} \text{ s.t. } \boldsymbol{\nabla}\cdot\tilde{\Pi}_\rho(\mathsf{F}') = -\boldsymbol{\nabla} q\} \tag{8.70}$$

because, when $\mathsf{F}' = -\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{\psi}$,

$$\langle \mathsf{F}', -\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{\phi}\rangle_\rho = \langle \boldsymbol{\nabla}\cdot\tilde{\Pi}_\rho(-\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{\psi}), \boldsymbol{\phi}\rangle$$

and it is zero for any $\boldsymbol{\phi}$ satisfying the conditions in Eq. (8.69) if and only if there exists a scalar field q such that $\boldsymbol{\nabla}\cdot\tilde{\Pi}_\rho(-\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{\psi}) = -\boldsymbol{\nabla} q$. In fact, then we have

$$\langle \boldsymbol{\nabla}\cdot\tilde{\Pi}_\rho(-\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{\psi}), \boldsymbol{\phi}\rangle = -\langle \boldsymbol{\nabla} q, \boldsymbol{\phi}\rangle = \langle q, \boldsymbol{\nabla}\cdot\boldsymbol{\phi}\rangle = 0,$$

where the second equality is due to the boundary condition on $\boldsymbol{\phi}$ and the last one due to the incompressibility.

The definitions of the housekeeping and excess EPRs are valid as in Eqs. (8.64) and (8.67). Equation (8.66) can be modified and rewritten as

$$\begin{aligned}\dot{\Sigma}^{\mathrm{ex}}_{\rho,\boldsymbol{v}} &:= \inf_{\mathsf{F}'\in\mathscr{F}^*} \|\mathsf{F}'\|^2_\rho, \quad \text{s.t.} \quad \exists q \text{ s.t. } \boldsymbol{\nabla}\cdot\tilde{\Pi}_\rho(\mathsf{F}') + \boldsymbol{\nabla} q = \boldsymbol{\nabla}\cdot\tilde{\mathbf{J}}^{\mathrm{irr}}_{\rho,\boldsymbol{v}} && (8.71)\\ &= \frac{1}{T^2}\inf_{\boldsymbol{v}'} \|-\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{v}'\|^2_\rho, \quad \text{s.t.} \quad \boldsymbol{\nabla}\cdot\boldsymbol{v}' = 0 \ \&\ \exists q \text{ s.t. } -\mu\boldsymbol{\nabla}^2\boldsymbol{v}' + \boldsymbol{\nabla} q = -\mu\boldsymbol{\nabla}^2\boldsymbol{v}. && (8.72)\end{aligned}$$

8.4.3 Stokes equation

The condition of Eq. (8.70) reduces to the Stokes equation [146, 147]. The Stokes equation is usually stated as a differential equation for $\boldsymbol{v}$ and p as

$$\mu\boldsymbol{\nabla}^2\boldsymbol{v} = \boldsymbol{\nabla} p, \quad \boldsymbol{\nabla}\cdot\boldsymbol{v} = 0. \tag{8.73}$$

It is derived from the Navier–Stokes equation for incompressible fluids

$$\rho\frac{\partial\boldsymbol{v}}{\partial t} = -\boldsymbol{\nabla}\cdot(\rho\boldsymbol{v}\otimes\boldsymbol{v} + p\mathsf{I}) + 2\mu\boldsymbol{\nabla}\cdot(\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{v}). \tag{8.74}$$

By using the incompressibility, the right-hand side can be transformed as

$$-\boldsymbol{\nabla}\cdot(\rho\boldsymbol{v}\otimes\boldsymbol{v} + p\mathsf{I}) + 2\mu\boldsymbol{\nabla}\cdot(\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{v}) = -\rho\boldsymbol{v}\cdot\boldsymbol{\nabla}\boldsymbol{v} - \boldsymbol{\nabla} p + \mu\boldsymbol{\nabla}^2\boldsymbol{v}.$$

Setting $\partial\boldsymbol{v}/\partial t$ to zero and neglecting the convection term $\rho\boldsymbol{v}\cdot\boldsymbol{\nabla}\boldsymbol{v}$, we obtain the Stokes equation (8.73). Neglecting the convection term is justified when the Reynolds number is small[2].

The condition of $\tilde{\mathscr{C}}^{\perp}$ is rearranged into the Stokes equation because

$$-\boldsymbol{\nabla} q = \boldsymbol{\nabla}\cdot\tilde{\Pi}_\rho(-\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{\psi}) = -2\mu T\boldsymbol{\nabla}\cdot(\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{\psi}) = -\mu T\boldsymbol{\nabla}^2\boldsymbol{\psi}, \tag{8.75}$$

where we used the incompressibility of $\boldsymbol{\psi}$ in the last equality.

It is worth noting that pressure p in the Stokes equation is determined by $\boldsymbol{v}$. By taking divergence of the Stokes equation, we find the Poisson equation, $\boldsymbol{\nabla}^2 p = 0$. Given a velocity field $\boldsymbol{v}$, the equation $\mu\boldsymbol{\nabla}^2\boldsymbol{v} = \boldsymbol{\nabla} p$ provides a Neumann boundary condition, with which $\boldsymbol{\nabla}^2 p = 0$ can be solved.

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[2] Reynolds number is defined by the ratio of inertial forces to viscous forces. One important class of low-Reynolds-number systems is microswimmers, such as bacteria moving in water.

Moreover, the solution of the Stokes equation is unique for each boundary condition on $\boldsymbol{v}$. Let a velocity field $\boldsymbol{v}$ satisfy $\boldsymbol{v} = \boldsymbol{v}_w$ on $\partial\Omega$ and $\boldsymbol{v}_\star$ be a solution to the Stokes equation. Then,

$$\begin{aligned}
\mu \int_\Omega |\nabla \boldsymbol{v}|^2 dV &= \mu \int_\Omega |\nabla(\boldsymbol{v} - \boldsymbol{v}_\star) + \nabla \boldsymbol{v}_\star|^2 dV \\
&= \mu \int_\Omega |\nabla(\boldsymbol{v} - \boldsymbol{v}_\star)|^2 dV + \mu \int_\Omega |\nabla \boldsymbol{v}_\star|^2 dV + 2\mu \int_\Omega \nabla(\boldsymbol{v} - \boldsymbol{v}_\star) : \nabla \boldsymbol{v}_\star dV \\
&= \mu \int_\Omega |\nabla(\boldsymbol{v} - \boldsymbol{v}_\star)|^2 dV + \mu \int_\Omega |\nabla \boldsymbol{v}_\star|^2 dV - 2\mu \int_\Omega (\boldsymbol{v} - \boldsymbol{v}_\star) \cdot \nabla \cdot [\nabla \boldsymbol{v}_\star] dV \\
&= \mu \int_\Omega |\nabla(\boldsymbol{v} - \boldsymbol{v}_\star)|^2 dV + \mu \int_\Omega |\nabla \boldsymbol{v}_\star|^2 dV - 2\mu \int_\Omega (\boldsymbol{v} - \boldsymbol{v}_\star) \cdot \nabla^2 \boldsymbol{v}_\star dV \\
&= \mu \int_\Omega |\nabla(\boldsymbol{v} - \boldsymbol{v}_\star)|^2 dV + \mu \int_\Omega |\nabla \boldsymbol{v}_\star|^2 dV - 2\mu \int_\Omega (\boldsymbol{v} - \boldsymbol{v}_\star) \cdot \nabla p dV \\
&= \mu \int_\Omega |\nabla(\boldsymbol{v} - \boldsymbol{v}_\star)|^2 dV + \mu \int_\Omega |\nabla \boldsymbol{v}_\star|^2 dV + 2\mu \int_\Omega \nabla \cdot (\boldsymbol{v} - \boldsymbol{v}_\star) p dV \\
&= \mu \int_\Omega |\nabla(\boldsymbol{v} - \boldsymbol{v}_\star)|^2 dV + \mu \int_\Omega |\nabla \boldsymbol{v}_\star|^2 dV,
\end{aligned}$$

where we used the boundary condition and the Gauss theorem in the third and sixth lines, the incompressibility in the fourth and last lines, and the Stokes equation in the fifth line. Therefore,

$$\mu \int_\Omega |\nabla \boldsymbol{v}|^2 dV \geq \mu \int_\Omega |\nabla \boldsymbol{v}_\star|^2 dV \tag{8.76}$$

and the equality holds only if $\nabla(\boldsymbol{v} - \boldsymbol{v}_\star)$ vanishes everywhere. Because $\boldsymbol{v}$ and $\boldsymbol{v}_\star$ coincide on the boundary, they must be identical; i.e., the solution to the Stokes equation is unique.

The above inequality can be proved if we replace ∇ with ∇^{S}. Thus, we have revealed (cf. Eq. (8.56))

$$\dot{\Sigma}_{\rho,\boldsymbol{v}} \geq \dot{\Sigma}_{\rho,\boldsymbol{v}_\star}. \tag{8.77}$$

That is to say, among incompressible velocity fields with a fixed boundary condition, the solution to the Stokes equation provides the minimum dissipation. This is known as the Helmholtz dissipation theorem [140, 148].

8.4.4 Minimum dissipations

We continute to consider incompressible fluids. In Ref. [20], we have shown that

$$\dot{\Sigma}^{\mathrm{hk}}_{\rho,\boldsymbol{v}} = \dot{\Sigma}_{\rho,\boldsymbol{v}_\star} \tag{8.78}$$

when the fluid is incompressible. This is easily proved by referring to the general property of the orthogonal projection. Let $\mathsf{F}_{\mathrm{c}} = -\nabla \boldsymbol{\phi}^*$ be the conservative force that provides the housekeeping EPR as

$$\dot{\Sigma}^{\mathrm{hk}}_{\rho,\boldsymbol{v}} = \|\mathsf{F}_{\boldsymbol{v}} - \mathsf{F}_{\mathrm{c}}\|^2_\rho. \tag{8.79}$$

The nonconservative force $\mathsf{F}_{\mathrm{nc}} = \mathsf{F}_{\boldsymbol{v}} - \mathsf{F}_{\mathrm{c}}$ is written as $\mathsf{F}_{\boldsymbol{v}^*}$ with

$$\boldsymbol{v}^* := \boldsymbol{v} - \frac{1}{T}\boldsymbol{\phi}^*, \tag{8.80}$$

which allows us to write $\dot{\Sigma}^{\mathrm{hk}}_{\rho,\boldsymbol{v}} = \dot{\Sigma}_{\rho,\boldsymbol{v}^*}$. This velocity field satisfies incompressibility and coincides with $\boldsymbol{v}$ on the boundary because $\boldsymbol{\phi}^* = 0$ there. Moreover, since F_{nc} belongs to $\tilde{\mathscr{C}}^{\perp}$[3], there exists a scalar field q such that

$$\nabla \cdot \tilde{\Pi}_\rho(\nabla^{\mathrm{S}} \boldsymbol{v}^*) = \mu T \nabla^2 \boldsymbol{v}^* = \nabla q. \tag{8.81}$$

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[3] This is a consequence of the orthogonal projection; but we can directly prove $\langle \mathsf{F}', \mathsf{F}_{\mathrm{nc}} \rangle_\rho = 0$ for any $\mathsf{F}' \in \tilde{\mathscr{C}}$.

Therefore, $\boldsymbol{v}^*$ satisfies the Stokes equation. Because the Stokes equation has a unique solution, we see $\boldsymbol{v}^* = \boldsymbol{v}_\star$ and Eq. (8.78) is shown.

Equations (8.77) and (8.78) reveal that the housekeeping EPR we defined provides the minimum dissipation under a fixed boundary condition. On the other hand, neglecting the convection term also enables us to interpret the excess EPR as a genuine minimum EPR. The excess EPR was given as the minimum under a kinetic constraint in Eq. (8.71). If one can always neglect the convection term $\boldsymbol{v} \cdot \nabla \boldsymbol{v}$, Eq. (8.71) turns into

$$\dot{\Sigma}^{\mathrm{ex}}_{\rho,\boldsymbol{v}} = \inf_{\mathsf{F}' \in \mathscr{F}^*} \|\mathsf{F}'\|^2_\rho, \quad \text{s.t.} \quad \exists q \text{ s.t. } \rho \frac{\partial \boldsymbol{v}}{\partial t} = -\nabla q - \nabla \cdot \tilde{\Pi}_\rho(\mathsf{F}') \tag{8.82}$$

because

$$\nabla \cdot \tilde{\mathsf{J}}^{\mathrm{irr}}_{\rho,\boldsymbol{v}} = -\rho \frac{\partial \boldsymbol{v}}{\partial t} - \nabla \cdot (\rho \boldsymbol{v} \otimes \boldsymbol{v} + p\mathsf{I}) = -\rho \frac{\partial \boldsymbol{v}}{\partial t} - \rho \boldsymbol{v} \cdot \nabla \boldsymbol{v} - \nabla p.$$

Pressure gradient ∇p is absorbed in ∇q. Therefore, Eq. (8.82) shows that the excess EPR is the minimum dissipation to induce the dynamics with the aid of a pressure field q.

8.5 Thermodynamic trade-off relations

In hydrodynamic systems, there are few established results on thermodynamic trade-offs except an inequality we found in Ref. [20]. In this section, we explain that result and provide the derivation.

8.5.1 Thermodynamic uncertainty relation

The general result (5.29) provides an inequality for hydrodynamic systems as

$$\dot{\Sigma}^{\mathrm{ex}}_{\rho,\boldsymbol{v}} \geq \frac{\langle -\nabla \cdot \mathsf{J}^{\mathrm{irr}}_{\rho,\boldsymbol{v}}, \boldsymbol{\psi} \rangle^2}{\Delta_\rho(\boldsymbol{\psi})} \quad \text{for any } \boldsymbol{\psi} \text{ s.t. } \boldsymbol{\psi}(\boldsymbol{x}) = 0, \ \forall \boldsymbol{x} \in \partial\Omega, \tag{8.83}$$

where

$$\Delta_\rho(\boldsymbol{\psi}) := \langle \nabla^{\mathrm{S}} \boldsymbol{\psi}, \Pi_\rho(\nabla^{\mathrm{S}} \boldsymbol{\psi}) \rangle. \tag{8.84}$$

The condition that $\boldsymbol{\psi} = 0$ on the boundary is required for $\boldsymbol{\psi}$ to be in the domain of the gradient operator. Formally, Eq. (8.83) is similar to the short-time TURs, but further discussion is required to understand the physical meaning of the quantities.

In Ref. [20], we consider how Eq. (8.83) can be understood as a TUR. If we further assume $\boldsymbol{\psi}$ to be divergence free ($\nabla \cdot \boldsymbol{\psi} = 0$), we can derive the inequality

$$\dot{\Sigma}^{\mathrm{ex}}_{\rho,\boldsymbol{v}} \geq \frac{1}{\mu_{\max} T \|\nabla \boldsymbol{\psi}\|^2} \left(\int_\Omega \left[\frac{\partial}{\partial t} (\rho \boldsymbol{v} \cdot \boldsymbol{\psi}) - \rho \boldsymbol{v} \cdot \frac{D\boldsymbol{\psi}}{Dt} \right] dV \right)^2, \tag{8.85}$$

where $\mu_{\max} = \max_{\boldsymbol{x} \in \Omega} \mu(\rho(\boldsymbol{x}))$ and $\|\nabla \boldsymbol{\psi}\|^2 := \int_\Omega |\nabla \boldsymbol{\psi}(\boldsymbol{x})|^2 dV$. We may interpret the denominator as the quantity of fluctuations by system parameter $\mu_{\max} T$ and the spatial variation $\|\nabla \boldsymbol{\psi}\|$. This interpretation is also supported by the fact that the viscosity coefficient is determined by the Green–Kubo formula [149]. The numerator indicates a kind of changing rate of $\langle \rho \boldsymbol{v}, \boldsymbol{\psi} \rangle$ because

$$\int_\Omega \frac{\partial}{\partial t} (\rho \boldsymbol{v} \cdot \boldsymbol{\psi}) dV = \frac{d}{dt} \int_\Omega (\rho \boldsymbol{v} \cdot \boldsymbol{\psi}) dV \tag{8.86}$$

when the place and shape of Ω do not change ($\boldsymbol{v}_w \cdot \boldsymbol{n} = 0$) due to Eq. (8.16). We have an additional contribution $\rho \boldsymbol{v} \cdot (D\boldsymbol{\psi}/Dt)$, which can be interpreted as subtracting a convectional aspect of the change in $\langle \rho \boldsymbol{v}, \boldsymbol{\psi} \rangle$. This term will vanish if $\boldsymbol{\psi}$ is given as

$$\boldsymbol{\psi}(\boldsymbol{x}, t) = \boldsymbol{a}(\boldsymbol{\Phi}_t^{-1}(\boldsymbol{x})) \tag{8.87}$$

with a vector field $\boldsymbol{a}$ and the so-called pathline $\boldsymbol{\Phi}$. The pathline is defined as the solution to

$$\frac{\partial}{\partial t}\boldsymbol{\Phi}_t(\boldsymbol{x}) = \boldsymbol{v}(\boldsymbol{\Phi}_t(\boldsymbol{x}), t) \tag{8.88}$$

and represents the position of a particle at time t that started from $\boldsymbol{x}$.

First, we prove that when $\boldsymbol{\psi}$ is given as in Eq. (8.87), $\rho\boldsymbol{v}\cdot(D\boldsymbol{\psi}/Dt)$ becomes zero. We can show $D\boldsymbol{\psi}/Dt = 0$. By the chain rule, we have

$$\frac{\partial}{\partial t}\boldsymbol{\psi}(\boldsymbol{x}, t) = \frac{\partial \boldsymbol{\Phi}_t^{-1}(\boldsymbol{x})}{\partial t}\cdot[\boldsymbol{\nabla}\boldsymbol{a}](\boldsymbol{\Phi}_t^{-1}(\boldsymbol{x})). \tag{8.89}$$

The time derivative of $\boldsymbol{\Phi}_t^{-1}(\boldsymbol{x})$ is given by

$$\partial_t\boldsymbol{\Phi}_t^{-1}(\boldsymbol{x}) = -\boldsymbol{v}(\boldsymbol{x}, t)\cdot\boldsymbol{\nabla}\boldsymbol{\Phi}_t^{-1}(\boldsymbol{x}). \tag{8.90}$$

To prove this equality, we first confirm that for any $\boldsymbol{y}$,

$$\boldsymbol{y} = \boldsymbol{\Phi}_t^{-1}(\boldsymbol{\Phi}_t(\boldsymbol{y})).$$

Thus, by taking the time derivative, we get

$$0 = [\partial_t\boldsymbol{\Phi}_t^{-1}](\boldsymbol{\Phi}_t(\boldsymbol{y})) + \partial_t\boldsymbol{\Phi}_t(\boldsymbol{y})\cdot\boldsymbol{\nabla}\boldsymbol{\Phi}_t^{-1}(\boldsymbol{\Phi}_t(\boldsymbol{y})) = [\partial_t\boldsymbol{\Phi}_t^{-1}](\boldsymbol{\Phi}_t(\boldsymbol{y})) + \boldsymbol{v}(\boldsymbol{\Phi}_t(\boldsymbol{y}), t)\cdot\boldsymbol{\nabla}\boldsymbol{\Phi}_t^{-1}(\boldsymbol{\Phi}_t(\boldsymbol{y})).$$

By setting $\boldsymbol{y} = \boldsymbol{\Phi}_t^{-1}(\boldsymbol{x})$, we obtain Eq. (8.90). Therefore, we finally find

$$\frac{D\boldsymbol{\psi}}{Dt} = \partial_t\boldsymbol{\Phi}_t^{-1}(\boldsymbol{x})\cdot\boldsymbol{\nabla}\boldsymbol{a}(\boldsymbol{\Phi}_t^{-1}(\boldsymbol{x})) + \boldsymbol{v}(\boldsymbol{x}, t)\cdot\boldsymbol{\nabla}\boldsymbol{\Phi}_t^{-1}(\boldsymbol{x})\cdot\boldsymbol{\nabla}\boldsymbol{a}(\boldsymbol{\Phi}_t^{-1}(\boldsymbol{x})) = 0,$$

where we used Eq. (8.90) in the last equality.

Next, let us derive Eq. (8.85) from Eq. (8.83) by using the divergence free condition $\boldsymbol{\nabla}\cdot\boldsymbol{\psi} = 0$. The denominator in the right-hand side of Eq. (8.83) becomes

$$\Delta_\rho(\boldsymbol{\psi}) = 2T\int_\Omega \mu(\rho(\boldsymbol{x}))|\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{\psi}(\boldsymbol{x})|^2 dV$$

because $\mathrm{tr}(\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{\psi}) = \boldsymbol{\nabla}\cdot\boldsymbol{\psi} = 0$. By the inequality $\mu(\rho(\boldsymbol{x})) \le \mu_{\max}$, we get

$$\Delta_\rho(\boldsymbol{\psi}) \le 2\mu_{\max}T\int_\Omega |\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{\psi}(\boldsymbol{x})|^2 dV.$$

Further, we find

$$\Delta_\rho(\boldsymbol{\psi}) \le \mu_{\max}T\|\boldsymbol{\nabla}\boldsymbol{\psi}\|^2 \tag{8.91}$$

because

$$\begin{aligned}
\int_\Omega |\boldsymbol{\nabla}^{\mathrm{S}}\psi(\boldsymbol{x})|^2 dV &= \frac{1}{4}\sum_{i,j}\int_\Omega (\partial_i\psi_j + \partial_j\psi_i)^2 dV \\
&= \frac{1}{2}\sum_{i,j}\int_\Omega \partial_i\psi_j(\partial_i\psi_j + \partial_j\psi_i) dV \\
&= -\frac{1}{2}\sum_{i,j}\int_\Omega \psi_j\partial_i^2\psi_j dV \\
&= \frac{1}{2}\sum_{i,j}\int_\Omega (\partial_i\psi_j)^2 dV = \frac{1}{2}\|\boldsymbol{\nabla}\boldsymbol{\psi}\|^2,
\end{aligned}$$

where we used symmetry in the second line and the divergence-free condition and the boundary condition in the third line.

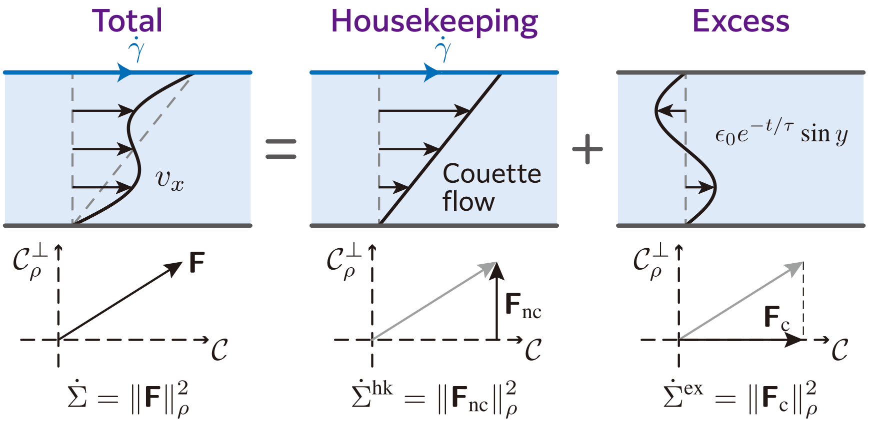

Figure 8.1: (Adapted from Ref. [20]) Decomposition of the dynamics and the EPR in a shear flow. The entire motion is split into the Couette flow, which is a stationary flow, and a perturbative component. This seperation perfectly corresponds to the housekeeping-excess decomposition in this simple solution.

The continuity equation of momentum (8.19) rewrites the numerator as

$$\langle -\nabla \cdot \mathsf{J}^{\mathrm{irr}}_{\rho,\boldsymbol{v}}, \boldsymbol{\psi} \rangle = \langle \partial_t(\rho \boldsymbol{v}) + \nabla \cdot \mathsf{J}^{\mathrm{rev}}_{\rho,\boldsymbol{v}}, \boldsymbol{\psi} \rangle.$$

The term including the reversible current is further reformed as

$$\begin{aligned} \langle \nabla \cdot \mathsf{J}^{\mathrm{rev}}_{\rho,\boldsymbol{v}}, \boldsymbol{\psi} \rangle = -\langle \mathsf{J}^{\mathrm{rev}}_{\rho,\boldsymbol{v}}, \nabla \boldsymbol{\psi} \rangle &= -\int_\Omega (\rho \boldsymbol{v} \otimes \boldsymbol{v} + p(\rho)\mathsf{I}) : \nabla \boldsymbol{\psi} \, dV \\ &= -\int_\Omega \rho \boldsymbol{v} \cdot [(\boldsymbol{v} \cdot \nabla)\boldsymbol{\psi}] dV, \end{aligned}$$

where the second line is proved by using $\mathsf{I} : \nabla \boldsymbol{\psi} = \nabla \cdot \boldsymbol{\psi}$ and considering the summation carefully. Thus, we find

$$\begin{aligned} \langle -\nabla \cdot \mathsf{J}^{\mathrm{irr}}_{\rho,\boldsymbol{v}}, \boldsymbol{\psi} \rangle &= \int_\Omega \left(\frac{\partial \rho \boldsymbol{v}}{\partial t} \cdot \boldsymbol{\psi} - \rho \boldsymbol{v} \cdot [(\boldsymbol{v} \cdot \nabla)\boldsymbol{\psi}] \right) dV \\ &= \int_\Omega \left(\frac{\partial \rho \boldsymbol{v}}{\partial t} \cdot \boldsymbol{\psi} + \rho \boldsymbol{v} \cdot \frac{\partial \boldsymbol{\psi}}{\partial t} - \rho \boldsymbol{v} \cdot \frac{\partial \boldsymbol{\psi}}{\partial t} - \rho \boldsymbol{v} \cdot [(\boldsymbol{v} \cdot \nabla)\boldsymbol{\psi}] \right) dV \\ &= \int_\Omega \left(\frac{\partial}{\partial t}(\rho \boldsymbol{v} \cdot \boldsymbol{\psi}) - \rho \boldsymbol{v} \cdot \frac{D\boldsymbol{\psi}}{Dt} \right) dV. \end{aligned} \tag{8.92}$$

Applying the results in Eqs. (8.91) and (8.92) to Eq. (8.83), we obtain Eq. (8.85).

8.6 Example

We illustrate the decomposition through a toy model of shear flow in $\Omega = S^1 \times [0,1]$ (S^1 is the 1-sphere of length 1. See Fig. 8.1). The boundary is composed of the top and the bottom line, $\partial\Omega = S^1 \times (\{0\} \cup \{1\})$. We fix the bottom $S^1 \times \{0\}$ while letting the top $S^1 \times \{1\}$ move in the x direction at rate $\dot{\gamma}$. We assume the no-slip boundary condition, i.e., every velocity field should satisfy $\boldsymbol{v}(x,0) = (0,0)^{\mathrm{T}}$ and $\boldsymbol{v}(x,1) = (\dot{\gamma},0)^{\mathrm{T}}$. Let the initial density and pressure be uniform and the initial velocity field be the Couette flow $(\dot{\gamma}y,0)^{\mathrm{T}}$ plus the perturbation $(\epsilon_0 \sin(2\pi y), 0)^{\mathrm{T}}$. The ansatz $\rho(t,x,y) = \rho\,(\text{const.})$, $p(t,x,y) = \text{const.}$, and $\boldsymbol{v}(t,x,y) = (\dot{\gamma}y + \epsilon(t)\sin(2\pi y), 0)$ solve the Navier–Stokes equation with $\epsilon(t) = \epsilon_0 e^{-t/\tau}$ ($\tau = \rho/(4\pi^2\mu)$) because the Navier–Stokes equation turns into

$$\dot{\epsilon}(t) = -\frac{4\pi^2\mu}{\rho}\epsilon(t), \tag{8.93}$$

which is because plugging the ansatz leads to

$$\rho\frac{D\boldsymbol{v}}{Dt}=\begin{pmatrix}\rho\dot{\epsilon}(t)\sin(2\pi y)\\0\end{pmatrix}$$

and

$$\boldsymbol{\nabla}\cdot(-p\mathsf{I}+2\mu\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{v})=\mu\boldsymbol{\nabla}^2\boldsymbol{v}=\begin{pmatrix}-(2\pi)^2\mu\epsilon(t)\sin(2\pi y)\\0\end{pmatrix}.$$

Therefore, in this solution, the fluid motion relaxes to the Couette flow. Note that this is just a solution of a partial differential equation, the Navier–Stokes equation, and tells nothing about uniqueness or stability. If the shear is rather fast, the fluid will exihibit turbulence.

For this solution, the thermodynamic force becomes

$$\mathsf{F}_{\rho,\boldsymbol{v}}(t,x,y)=-\frac{\dot{\gamma}+2\pi\epsilon(t)\cos(2\pi y)}{2T}\begin{pmatrix}0&1\\1&0\end{pmatrix}. \tag{8.94}$$

The housekeeping is obtained by the optimization

$$\dot{\Sigma}^{\mathrm{hk}}_{\rho,\boldsymbol{v}}=\inf_{\boldsymbol{u}}\|\mathsf{F}_{\rho,\boldsymbol{v}}-(-\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{u})/T\|^2_{\rho} \tag{8.95}$$

$$=\frac{1}{T}\inf_{\boldsymbol{u}}\int_0^1 dy\int_{S^1}dx\Big[2\mu\{(\partial_x u_x)^2+(\partial_y u_y)^2\}+\lambda(\partial_x u_x+\partial_y u_y)^2+\mu\{\partial_x u_y+\partial_y u_x-\dot{\gamma}-2\pi\epsilon\cos(2\pi y)\}^2\Big], \tag{8.96}$$

where $\boldsymbol{u}$ must vanish on $\partial\Omega$. By taking the functional derivative with respect to u_x and u_y, we find the solution to the optimization must satisfy

$$-2\mu\partial_x^2 u_x-\lambda\partial_x(\partial_x u_x+\partial_y u_y)-\mu\partial_y\{\partial_x u_y+\partial_y u_x-\dot{\gamma}-2\pi\epsilon\cos(2\pi y)\}=0, \tag{8.97}$$

$$-2\mu\partial_y^2 u_y-\lambda\partial_y(\partial_x u_x+\partial_y u_y)-\mu\partial_x\{\partial_x u_y+\partial_y u_x-\dot{\gamma}-2\pi\epsilon\cos(2\pi y)\}=0. \tag{8.98}$$

A solution is given by

$$u_x=\epsilon\sin(2\pi y),\quad u_y=0. \tag{8.99}$$

It is not the unique solution, but the resulting force $-\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{u}/T$ is unique because Eq. (8.95) is strictrly convex regarding $-\boldsymbol{\nabla}^{\mathrm{S}}\boldsymbol{u}/T$. This solution corresponds to the perturbative part in the velocity field. Thus, the conservative force represents the perturbative, decaying component in the whole dynamics, while the nonconservative force is associated with the Couette flow (see Fig 8.1).

As a result, the excess and housekeeping EPRs are given by

$$\dot{\Sigma}^{\mathrm{hk}}_{\rho,\boldsymbol{v}}=\mu\dot{\gamma}^2,\quad \dot{\Sigma}^{\mathrm{ex}}_{\rho,\boldsymbol{v}}=2\pi^2\epsilon_0^2\mu e^{-2t/\tau}. \tag{8.100}$$

As expected from the above discussion, the housekeeping EPR expresses the steady dissipation in the Couette flow. On the other hand, the excess EPR is proportional to the squared perturation, $\epsilon(t)^2$, and approaches zero as the system relaxes to the steady flow.

Chapter 9

Markovian open quantum systems

The final chapter discusses Markovian open quantum systems. Open quantum systems are influenced by environments and evolve not unitarily. Markovian approximation enables us to describe the dynamics by an ordinary differential equation of the density matrix. Assuming thermal relation on the interaction between the system and the environments, thermodynamics can be established in this system.

9.1 Dynamics

9.1.1 Setup

We consider a quantum system with Hilbert space $\mathcal{H}$ attached to single or multiple environments, like a heat bath at inverse temperature β. Let H denote the Hamiltonian of the system. We also write the Hermitian and the anti-Hermitian operators on $\mathcal{H}$ by $\mathrm{herm}(\mathcal{H})$ and $\mathrm{anti}(\mathcal{H})$. The general space of linear operators is written as $\mathrm{opr}(\mathcal{H})$.

We assume the density matrix ρ ($\rho \in \mathrm{herm}(\mathcal{H})$, $\mathrm{tr}\,\rho = 1$, $\rho > 0$[1]) obeys the quantum master equation [13, 150, 151]

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar}[H, \rho] + \mathcal{D}(\rho), \tag{9.1}$$

where $\hbar$ is the reduced Planck constant, $[A, B] = AB - BA$ is the commutator, and $\mathcal{D}(\rho)$ the dissipator defined as

$$\begin{aligned} &\mathcal{D}(\rho) \coloneqq \sum_{k \in K} \mathcal{D}_k(\rho) \\ &\text{with} \quad \mathcal{D}_k(\rho) \coloneqq \gamma_k\Big(L_k \rho L_k^\dagger - \frac{1}{2}\{L_k^\dagger L_k, \rho\}\Big) + \gamma_{-k}\Big(L_{-k} \rho L_{-k}^\dagger - \frac{1}{2}\{L_{-k}^\dagger L_{-k}, \rho\}\Big). \end{aligned} \tag{9.2}$$

Here, $k \in K$ labels jumps, $\{A, B\} = AB + BA$ is the anti-commutator, and $\gamma_k > 0$ and $L_k \in \mathrm{opr}(\mathcal{H})$ are jump rates and jump operators satisfying $L_{-k} = L_k^\dagger$. The last condition represents the reversibility of the jumps, which was assumed in MJPs and CRNs, and is crucial for thermodynamic consideration. We assume the number of jumps $|K|$ is finite. Additionally, we define $K_{\mathrm{all}} \coloneqq K \cup \{-k \mid k \in K\}$. The quantum master equation is also refered to as the Lindblad equation or the Gorini–Kossakowski–Sudarshan–Lindblad equation.

The adjoint of the dissipator is also introduced

$$\begin{aligned} &\mathcal{D}^*(X) \coloneqq \sum_{k \in K} \mathcal{D}_k^*(X) \\ &\text{with} \quad \mathcal{D}_k^*(X) \coloneqq \gamma_k\Big(L_k^\dagger X L_k - \frac{1}{2}\{L_k^\dagger L_k, X\}\Big) + \gamma_{-k}\Big(L_{-k}^\dagger X L_{-k} - \frac{1}{2}\{L_{-k}^\dagger L_{-k}, X\}\Big). \end{aligned} \tag{9.3}$$

It is derived by $\langle X, \mathcal{D}_k(\rho)\rangle = \langle \mathcal{D}_k^*(X), \rho\rangle$, where $\langle A, B\rangle = \mathrm{tr}(A^\dagger B)$ is the Hilbert–Schmidt inner product. It is easily confirmed that $\mathcal{D}_k^*$ satisfies the identity

$$\mathcal{D}_k^*(I_{\mathcal{H}}) = 0. \tag{9.4}$$

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[1] An operator X is positive $X > 0$ if for any vector $|\psi\rangle \neq 0$, it satisfies $\langle\psi|X|\psi\rangle > 0$.

The quantum master equation has two contributions: the unitary term and the dissipation term. We assume the Hamiltonian is time-reversal symmetric and regard the unitary term as the reversible term of Eq. (3.1). Next, we look for a continuity-equation representation of the dissipation term.

9.1.2 Continuity equation

Essentially, the idea to get the continuity-equation representation of the dissipator was provided in Ref. [152]. By using their idea, we derived a continuity equation that is aligned with the context of quantum thermodynamics in Ref. [20]. In this section, we summarize the result according to the terminology of Ref. [20].

First, we introduce an auxiliary space $\mathfrak{h} := \mathbb{C}^{2|K|}$, which is associated with the jumps. We also define operators $\Gamma_k \in \mathrm{herm}(\mathbb{C}^2)$ and $\mathbb{L}_k \in \mathrm{herm}(\mathbb{C}^2 \otimes \mathcal{H})$ by

$$\Gamma_k := \begin{pmatrix} \gamma_k/2 & 0 \\ 0 & \gamma_{-k}/2 \end{pmatrix}, \quad \mathbb{L}_k := \begin{pmatrix} 0 & L_{-k} \\ L_k & 0 \end{pmatrix}. \tag{9.5}$$

The integrated operators $\Gamma \in \mathrm{herm}(\mathfrak{h})$ and $\mathbb{L} \in \mathrm{herm}(\mathfrak{h} \otimes \mathcal{H})$ are given by

$$\Gamma := \bigoplus_{k\in K} \Gamma_k, \quad \mathbb{L} := \bigoplus_{k\in K} \mathbb{L}_k, \tag{9.6}$$

where $\otimes$ and $\oplus$ denote the tensor product and the direct sum.

Then, we can define the current operator $\mathbb{J}(\rho)$ by

$$\mathbb{J}(\rho) := [\mathbb{L}, \Gamma \otimes \rho]. \tag{9.7}$$

It becomes an anti-Hermitian operator on $\mathfrak{h} \otimes \mathcal{H}$. It can be split as

$$\mathbb{J}(\rho) = \bigoplus_{k\in K} \mathbb{J}_k(\rho), \quad \mathbb{J}_k(\rho) := [\mathbb{L}_k, \Gamma_k \otimes \rho], \tag{9.8}$$

which has the further details

$$\mathbb{J}_k(\rho) = \begin{pmatrix} 0 & J_{-k}(\rho) \\ J_k(\rho) & 0 \end{pmatrix}, \quad J_k(\rho) = \frac{1}{2}\gamma_k L_k \rho - \frac{1}{2}\gamma_{-k} \rho L_k. \tag{9.9}$$

As a result, detailed balance, defined by $\mathbb{J}(\rho) = 0$, is characterized by $J_k(\rho) = 0$. Note that we have $J_k(\rho)^\dagger = -J_{-k}(\rho)$ and $\mathbb{J}_k^\dagger(\rho) = -\mathbb{J}_k(\rho)$.

The current operator is accompanied by a gradient super-operator that maps $\mathrm{opr}(\mathcal{H})$ to $\mathrm{opr}(\mathfrak{h} \otimes \mathcal{H})$; we define the gradient super-operator by

$$\nabla_{\mathbb{L}} A := [I_{\mathfrak{h}} \otimes A, \mathbb{L}], \tag{9.10}$$

where $I_{\mathfrak{h}}$ is the identity operator on $\mathfrak{h}$. As $\mathbb{L}$ is Hermitian, $\nabla_{\mathbb{L}}$ maps $\mathrm{herm}(\mathcal{H})$ into $\mathrm{anti}(\mathfrak{h} \otimes \mathcal{H})$. Its adjoint with respect to the Hilbert–Schmidt inner product is given by

$$\nabla_{\mathbb{L}}^* \mathbb{B} = \mathrm{tr}_{\mathfrak{h}}[\mathbb{B}, \mathbb{L}], \tag{9.11}$$

where $\mathrm{tr}_{\mathfrak{h}}$ indicates the partial trace. We call the adjoint $\nabla_{\mathbb{L}}^*$ the divergence super-operator. It also maps $\mathrm{anti}(\mathfrak{h} \otimes \mathcal{H})$ into $\mathrm{herm}(\mathcal{H})$. Equation (9.11) is proved as follows: for any $A \in \mathrm{opr}(\mathcal{H})$ and $\mathbb{B} \in \mathrm{opr}(\mathfrak{h} \otimes \mathcal{H})$,

$$\begin{aligned} \langle \nabla_{\mathbb{L}} A, \mathbb{B} \rangle &= \mathrm{tr}\left([(I_{\mathfrak{h}} \otimes A), \mathbb{L}]^\dagger \mathbb{B} \right) = \mathrm{tr}\left(\mathbb{L}(I_{\mathfrak{h}} \otimes A^\dagger)\mathbb{B} - (I_{\mathfrak{h}} \otimes A^\dagger)\mathbb{L}\mathbb{B} \right) \\ &= \mathrm{tr}\left((I_{\mathfrak{h}} \otimes A^\dagger)(\mathbb{B}\mathbb{L} - \mathbb{L}\mathbb{B}) \right) \\ &= \mathrm{tr}_{\mathcal{H}}(A^\dagger \, \mathrm{tr}_{\mathfrak{h}}[\mathbb{B}, \mathbb{L}]) = \langle A, \mathrm{tr}_{\mathfrak{h}}[\mathbb{B}, \mathbb{L}] \rangle, \end{aligned}$$

where we used the cyclic property of the trace in the second line and $\mathrm{tr}_{\mathcal{H}}$ is the partial trace regarding $\mathcal{H}$. The gradient and divergence super-operators are decomposed as

$$\nabla_{\mathbb{L}} A = \bigoplus_{k\in K} \nabla_{\mathbb{L}_k} A, \quad \nabla_{\mathbb{L}_k} A := [(I_{\mathbb{C}^2} \otimes A), \mathbb{L}_k] = \begin{pmatrix} 0 & [A, L_{-k}] \\ [A, L_k] & 0 \end{pmatrix}, \tag{9.12}$$

$$\nabla_{\mathbb{L}}^* \mathbb{B} = \sum_{k\in K} \nabla_{\mathbb{L}_k}^* \mathbb{B}, \quad \nabla_{\mathbb{L}_k}^* \mathbb{B} := \mathrm{tr}_{\mathbb{C}^2}[\mathbb{B}, \mathbb{L}_k], \tag{9.13}$$

where $I_{\mathbb{C}^2}$ and $\mathrm{tr}_{\mathbb{C}^2}$ are the identity and the partial trace of $\mathbb{C}^2$.

Finally, we can prove

$$\nabla_{\mathbb{L}}^* \mathbb{J}(\rho) = \mathcal{D}(\rho). \tag{9.14}$$

That is, the quantum master equation (9.1) has the form of Eq. (3.1) with reversible term $-(i/\hbar)[H,\rho]$, gradient $\nabla_{\mathbb{L}}$, and current $\mathbb{J}(\rho)$, with the density operator ρ being the fundamental variable. Therefore, the state and the force space can be provided as $\mathcal{S}_0 = \mathrm{herm}(\mathcal{H})$ and $\mathcal{F} = \mathrm{anti}(\mathfrak{h} \otimes \mathcal{H})$. The restricted state space $\mathcal{S}$ is given by imposing positivity.

Let us prove Eq. (9.14). According to Eq. (9.13) and the definition of $\mathcal{D}(\rho)$, it is sufficient to show

$$\mathrm{tr}_{\mathbb{C}^2}[\mathbb{J}_k(\rho), \mathbb{L}_k] = \gamma_k L_k \rho L_k^\dagger - \frac{1}{2}\{L_k^\dagger L_k, \rho\} + \gamma_{-k} L_{-k} \rho L_{-k}^\dagger - \frac{1}{2}\{L_{-k}^\dagger L_{-k}, \rho\}. \tag{9.15}$$

The left-hand side is transformed as

$$[\mathbb{J}_k(\rho), \mathbb{L}_k] = \left[\begin{pmatrix} 0 & J_{-k}(\rho) \\ J_k(\rho) & 0 \end{pmatrix}, \begin{pmatrix} 0 & L_{-k} \\ L_k & 0 \end{pmatrix}\right] = \begin{pmatrix} J_{-k}(\rho)L_k - L_{-k}J_k(\rho) & 0 \\ 0 & J_k(\rho)L_{-k} - L_k J_{-k}(\rho) \end{pmatrix}.$$

Therefore, we find

$$\begin{aligned} \mathrm{tr}_{\mathbb{C}^2}[\mathbb{J}_k(\rho), \mathbb{L}_k] &= J_{-k}(\rho)L_k - L_{-k}J_k(\rho) + J_k(\rho)L_{-k} - L_k J_{-k}(\rho) \\ &= [J_k(\rho), L_{-k}] + \text{h.c.}, \end{aligned}$$

where h.c. indicates the Hermitian conjugate. By the definition of $J_k(\rho)$, we have

$$\begin{aligned} [J_k(\rho), L_{-k}] &= \frac{1}{2}\gamma_k L_k \rho L_{-k} - \frac{1}{2}\gamma_{-k} \rho L_k L_{-k} - \frac{1}{2}\gamma_k L_{-k} L_k \rho + \frac{1}{2}\gamma_{-k} L_{-k} \rho L_k \\ &= \frac{1}{2}\gamma_k L_k \rho L_k^\dagger + \frac{1}{2}\gamma_{-k} L_k^\dagger \rho L_k - \frac{1}{2}\gamma_k L_k^\dagger L_k \rho - \frac{1}{2}\gamma_{-k} \rho L_{-k}^\dagger L_{-k}. \end{aligned}$$

By adding this and the Hermitian conjugate, we can see that Eq. (9.15) holds, so Eq. (9.14) does.

9.1.3 Conservation law

In closed systems, where $K = \varnothing$, an observable $\mathcal{O} \in \mathrm{herm}(\mathcal{H})$ is conserved if it commutes with the Hamiltonian, $[H, \mathcal{O}] = 0$, because then

$$\frac{d}{dt}\langle \mathcal{O} \rangle = -\frac{i}{\hbar}\,\mathrm{tr}(\mathcal{O}[H,\rho]) = \frac{i}{\hbar}\,\mathrm{tr}(\rho[H,\mathcal{O}]) = 0,$$

where $\langle \mathcal{O} \rangle = \mathrm{tr}(\mathcal{O}\rho)$ is the expectation value. The commutativity corresponds to the condition (3.4) in the general framework.

If the system is open ($K \neq \varnothing$), a sufficient condition is given by $\nabla_{\mathbb{L}}$, as in Eq. (3.5); let $\mathcal{O} \in \mathrm{herm}(\mathcal{H})$ be a conserved quantity in the corresponding closed system ($[H, \mathcal{O}] = 0$). Then, if $\mathcal{O}$ satisfies

$$\nabla_{\mathbb{L}} \mathcal{O} = 0, \tag{9.16}$$

$\langle \mathcal{O} \rangle$ is conserved under the quantum master equation because

$$\frac{d}{dt}\langle \mathcal{O} \rangle = -\frac{i}{\hbar}\underbrace{\mathrm{tr}(\mathcal{O}[H,\rho])}_{=0} + \mathrm{tr}(\mathcal{O}\nabla_{\mathbb{L}}^*\mathbb{J}(\rho)) = \mathrm{tr}\left((\nabla_{\mathbb{L}}\mathcal{O})\mathbb{J}(\rho)\right). \tag{9.17}$$

Therefore, we can characterize conservative quantities by two conditions, $[H, \mathcal{O}] = 0$ and $\nabla_{\mathbb{L}} \mathcal{O} = 0$. The most trivial conserved quantity is the identity $I_{\mathcal{H}}$, which indicates the conservation of the trace.

9.2 Thermodynamics

9.2.1 Local equilibrium assumption

The quantum master equation describes dynamics influenced by environments that relax much faster than the bath; thus, it assumes some thermodynamic properties of the environments. We incorporate such an assumption via the local detailed balance [16, 153]

$$k_{\mathrm{B}} \ln \frac{\gamma_k}{\gamma_{-k}} = s_k, \tag{9.18}$$

where s_k indicates the entropy change through jump k in the bath that mediates the jump ($s_{-k} = -s_k$). Equation (9.18) corresponds to the local detailed balance in MJPs (6.21) and CRNs (7.31).

For example, let k involve energy release ω_k with a heat bath at inverse temperature β_k. Then, Eq. (9.18) reads

$$\ln \frac{\gamma_k}{\gamma_{-k}} = \beta_k \omega_k. \tag{9.19}$$

Now, we further assume the thermodynamic consistency relation [13, 16]

$$[L_k, H] = \omega_k L_k. \tag{9.20}$$

If every jump is mediated by a unique heat bath at inverse temperature β and the above two conditions are satisfied, we say that the system is *detailed balanced*. For such systems, we can show that

$$\mathbb{J}(\rho^{\mathrm{eq}}) = 0, \tag{9.21}$$

where $\rho^{\mathrm{eq}} = e^{-\beta H}/Z_\beta$ and $Z_\beta = \mathrm{tr}(e^{-\beta H})$. That is, Eqs. (9.19) and (9.20) are sufficient for the quantum master equation to have the Gibbs state as a detailed balanced steady state (note that $[H, \rho^{\mathrm{eq}}] = 0$).

Equation (9.21) is equivalent to $J_k(\rho^{\mathrm{eq}}) = 0$, which can be confirmed as follows: First, we have

$$J_k(\rho^{\mathrm{eq}}) = \frac{\gamma_k}{2Z_\beta}(L_k e^{-\beta H} - e^{-\beta\omega_k} e^{-\beta H} L_k).$$

We can also show that the commutation relation (9.20) leads to $L_k H^n = (H + \omega_k)^n L_k$: for $n = 1$, it immediately follows from the commutation relation. Assume $L_k H^n = (H + \omega_k)^n L_k$ for certain $n > 1$. Then, we get

$$L_k H^{n+1} = (H + \omega_k)^n L_k H = (H + \omega_k)^n (H + \omega_k) L_k = (H + \omega_k)^{n+1} L_k.$$

By the mathematical induction, $L_k H^n = (H + \omega_k)^n L_k$ is proved. Applying this result to each term of the Taylor expansion of $e^{-\beta H}$, we obtain

$$L_k e^{-\beta H} = \sum_{n=0}^{\infty} \frac{(-\beta)^n}{n!} L_k H^n = \sum_{n=0}^{\infty} \frac{(-\beta)^n}{n!} (H + \omega_k)^n L_k = e^{-\beta(H + \omega_k)} L_k.$$

Therefore, we see $J_k(\rho^{\mathrm{eq}}) = 0$, which implies Eq. (9.21).

9.2.2 Entropy production

The system entropy is defined by the von Neumann entropy [13]

$$S(\rho) = -k_{\mathrm{B}}\, \mathrm{tr}(\rho \ln \rho). \tag{9.22}$$

Its time derivative is given as

$$\begin{aligned}
\frac{dS}{dt} &= -k_{\mathrm{B}}\, \mathrm{tr}\left(\frac{d\rho}{dt} \ln \rho\right) - k_{\mathrm{B}} \underbrace{\mathrm{tr}\left(\frac{d\rho}{dt}\right)}_{=0} \\
&= \underbrace{k_{\mathrm{B}}\, \mathrm{tr}\left(\frac{i}{\hbar}[H, \rho] \ln \rho\right)}_{=0} - k_{\mathrm{B}}\, \mathrm{tr}\left((\nabla_{\mathbb{L}}^* \mathbb{J}(\rho)) \ln \rho\right) \\
&= -k_{\mathrm{B}} \langle \boldsymbol{\nabla}_{\mathbb{L}}^* \mathbb{J}(\rho), \ln \rho \rangle = -k_{\mathrm{B}} \langle \mathbb{J}(\rho), \boldsymbol{\nabla}_{\mathbb{L}} \ln \rho \rangle
\end{aligned} \tag{9.23}$$

where we used $(d/dt)\,\mathrm{tr}(\rho) = 0$ in the second equality and the cyclic property of the trace to obtain the third line.

On the other hand, the enviromnental entropy change is given by [13, 16, 24]

$$\dot{S}_{\mathrm{env}} = \sum_{k\in K} s_k\Big(\gamma_k\,\mathrm{tr}(L_k^\dagger L_k\rho) - \gamma_{-k}\,\mathrm{tr}(L_{-k}^\dagger L_{-k}\rho)\Big), \tag{9.24}$$

where $\gamma_k\,\mathrm{tr}(L_k^\dagger L_k\rho)$ and $\gamma_{-k}\,\mathrm{tr}(L_{-k}^\dagger L_{-k}\rho)$ represent the frequency of the jumps. This can be rewritten as

$$\dot{S}_{\mathrm{env}} = \langle \mathbb{J}(\rho), \mathbb{F}^\circ\rangle, \tag{9.25}$$

where we define $\mathbb{F}^\circ \in \mathrm{anti}(\mathfrak{h}\otimes\mathcal{H})$ by

$$\mathbb{F}^\circ := k_{\mathrm{B}}[\mathbb{L}, \ln\Gamma\otimes I_{\mathcal{H}}], \tag{9.26}$$

which is decomposed as

$$\mathbb{F}^\circ = \bigoplus_{k\in K}\mathbb{F}_k^\circ, \quad \mathbb{F}_k^\circ := k_{\mathrm{B}}[\mathbb{L}_k, \ln\Gamma_k\otimes I_{\mathcal{H}}]. \tag{9.27}$$

Equation (9.25) is proved in three steps: first, we confirm $\langle\mathbb{J}(\rho),\mathbb{F}^\circ\rangle = \sum_{k\in K}\mathrm{tr}(\mathbb{J}_k^\dagger(\rho)\mathbb{F}_k^\circ)$. Next, we have

$$\mathbb{F}_k^\circ = k_{\mathrm{B}}\left[\begin{pmatrix} 0 & L_{-k} \\ L_k & 0\end{pmatrix}\begin{pmatrix} \ln\frac{\gamma_k}{2} I_{\mathcal{H}} & 0 \\ 0 & \ln\frac{\gamma_{-k}}{2} I_{\mathcal{H}}\end{pmatrix}\right] = k_{\mathrm{B}}\ln\frac{\gamma_k}{\gamma_{-k}}\begin{pmatrix} 0 & -L_{-k} \\ L_k & 0\end{pmatrix} = s_k\begin{pmatrix} 0 & -L_{-k} \\ L_k & 0\end{pmatrix}. \tag{9.28}$$

In addition, we get

$$\begin{aligned}
\mathrm{tr}\left(\mathbb{J}_k^\dagger(\rho)\begin{pmatrix} 0 & -L_{-k} \\ L_k & 0\end{pmatrix}\right) &= \mathrm{tr}\left(J_k(\rho)L_{-k} - J_{-k}(\rho)L_k\right) \\
&= \frac{1}{2}\,\mathrm{tr}\left((\gamma_k L_k\rho - \gamma_{-k}\rho L_k)L_{-k} - (\gamma_{-k}L_{-k}\rho - \gamma_k\rho L_{-k})L_k\right) \\
&= \frac{1}{2}\,\mathrm{tr}\left(\gamma_k L_k\rho L_k^\dagger - \gamma_{-k}\rho L_{-k}^\dagger L_{-k} - \gamma_{-k}L_{-k}\rho L_{-k}^\dagger + \gamma_k\rho L_k^\dagger L_k\right) \\
&= \gamma_k\,\mathrm{tr}(L_k^\dagger L_k\rho) - \gamma_{-k}\,\mathrm{tr}(L_{-k}^\dagger L_{-k}\rho).
\end{aligned}$$

Combining these relations, we see that Eq. (9.25) is valid.

Combining Eqs. (9.23) and (9.25), we can provide the EPR as

$$\dot{\Sigma}(\rho) = \frac{dS}{dt} + \dot{S}_{\mathrm{env}} = \langle\mathbb{J}(\rho), \mathbb{F}^\circ - k_{\mathrm{B}}\nabla_{\mathbb{L}}\ln\rho\rangle. \tag{9.29}$$

Therefore, by defining the thermodynamic force as

$$\mathbb{F}(\rho) := \mathbb{F}^\circ - k_{\mathrm{B}}\nabla_{\mathbb{L}}\ln\rho, \tag{9.30}$$

we obtain the quantum counterpart of Eq. (3.7) as [20]

$$\dot{\Sigma}(\rho) = \langle\mathbb{J}(\rho), \mathbb{F}(\rho)\rangle. \tag{9.31}$$

The thermodynamic force is also expressed as

$$\mathbb{F}(\rho) = k_{\mathrm{B}}[\mathbb{L}, \ln(\Gamma\otimes\rho)] \tag{9.32}$$

because

$$\mathbb{F}^\circ - k_{\mathrm{B}}\nabla_{\mathbb{L}}\ln\rho = k_{\mathrm{B}}[\mathbb{L}, \ln\Gamma\otimes I_{\mathcal{H}}] - k_{\mathrm{B}}[I_{\mathfrak{h}}\otimes\ln\rho, \mathbb{L}] = k_{\mathrm{B}}[\mathbb{L}, \ln\Gamma\otimes I_{\mathcal{H}} + I_{\mathfrak{h}}\otimes\ln\rho] = k_{\mathrm{B}}[\mathbb{L}, \ln(\Gamma\otimes\rho)],$$

where in the last equality, we used the property of the log function

$$\ln(X_1\otimes X_2) = \ln X_1\otimes I_{\mathcal{H}_2} + I_{\mathcal{H}_1}\otimes\ln X_2 \tag{9.33}$$

for two Hilbert spaces $\mathcal{H}_1$ and $\mathcal{H}_2$ and $X_i \in \mathrm{herm}(\mathcal{H}_i)$ $(i = 1, 2)$. Again, the thermodynamic force operator can be disassembled as

$$\mathbb{F}(\rho) = \bigoplus_{k\in K} \mathbb{F}_k(\rho), \quad \mathbb{F}_k(\rho) = k_\mathrm{B}[\mathbb{L}_k, \ln(\Gamma_k \otimes \rho)] = \begin{pmatrix} 0 & F_{-k}(\rho) \\ F_k(\rho) & 0 \end{pmatrix}, \quad F_k(\rho) = k_\mathrm{B} \ln \frac{\gamma_k}{\gamma_{-k}} L_k + k_\mathrm{B}[L_k, \ln \rho], \tag{9.34}$$

where the last equality is proved by using Eqs. (9.12) and (9.28).

Due to the separable structure of the operators, we can define partial EPRs by

$$\dot{\Sigma}_k(\rho) \coloneqq \langle \mathbb{J}_k(\rho), \mathbb{F}_k(\rho) \rangle. \tag{9.35}$$

The non-negativity of the total and partial EPRs will be proved simultaneously in the next section.

9.2.3 Force-current structure

Let us consider association between the irreversible dynamics and thermodynamics. To connect the thermodynamic force operator $\mathbb{F}(\rho)$ and the current operator $\mathbb{J}(\rho)$, we introduce a super-operator; let $\mathcal{H}'$ be an arbitrary Hilbert space and $G > 0$ a positive bounded Hermitian operator. We define $\mathcal{M}_G : \mathrm{opr}(\mathcal{H}') \to \mathrm{opr}(\mathcal{H}')$ by

$$\mathcal{M}_G(X) = \frac{1}{k_\mathrm{B}} \int_0^1 G^s X G^{1-s} ds. \tag{9.36}$$

It does not change the hermiticity of the argument; e.g., $\mathcal{M}_G(X)$ is anti-Hermitian if X is. If $\mathcal{H}'$ is finite-dimensional and G has the spectral decomposition

$$G = \sum_i g_i |i\rangle\langle i|, \tag{9.37}$$

the super-operator is explicitly given by

$$\mathcal{M}_G(X) = \frac{1}{k_\mathrm{B}} \sum_{i,j} \Lambda(g_i, g_j) \langle i|X|j\rangle |i\rangle\langle j|, \tag{9.38}$$

where Λ is the log mean (cf. Eq. (6.30)). This is because

$$\begin{aligned} \langle i| \int_0^1 G^s X G^{1-s} ds |j\rangle &= \int_0^1 g_i^s \langle i|X|j\rangle g_j^{1-s} ds = \langle i|X|j\rangle g_j \int_0^1 \left(\frac{g_i}{g_j}\right)^s ds \\ &= \langle i|X|j\rangle g_j \frac{1}{\ln(g_i/g_j)} \left[e^{s \ln(g_i/g_j)} \right]_{s=0}^{s=1} = \frac{g_i - g_j}{\ln(g_i/g_j)} \langle i|X|j\rangle. \end{aligned}$$

Therefore, $\mathcal{M}$ can be understood as a generalization of the multiplication of log mean.

In fact, $\mathcal{M}$ maps $\mathbb{F}(\rho)$ to $\mathbb{J}(\rho)$ if we choose $\mathcal{H}' = \mathfrak{h} \otimes \mathcal{H}$ and $G = \Gamma \otimes \rho$: We have

$$\mathcal{M}_{\Gamma\otimes\rho}(\mathbb{F}(\rho)) = \mathbb{J}(\rho). \tag{9.39}$$

This provides the quantum counterpart of the Onsager relation (3.8). It is proved by referring to expressions (9.7) and (9.32). Given them, we realize that it is sufficient to prove

$$\mathcal{M}_G(k_\mathrm{B}[K, \ln G]) = [K, G] \tag{9.40}$$

for every $G > 0$ and $K \in \mathrm{opr}(\mathcal{H}')$. Since G is positive, there exists Q such that $G = e^Q$. Because of the general relation

$$\frac{d}{ds} e^{sQ} K e^{(1-s)Q} = e^{sQ} Q K e^{(1-s)Q} - e^{sQ} K Q e^{(1-s)Q} = -e^{sQ}[K, Q] e^{(1-s)Q}$$

we can prove the desired equality as

$$\mathcal{M}_G(k_\mathrm{B}[K, \ln G]) = -\int_0^1 e^{sQ}[K, Q] e^{(1-s)Q} ds = -\int_0^1 \frac{d}{ds} e^{sQ} K e^{(1-s)Q} ds = K e^Q - e^Q K = [K, G].$$

The separability shown in Eqs. (9.8) and (9.34) also implies the relation

$$\mathbb{J}_k(\rho) = \mathcal{M}_{\Gamma_k \otimes \rho}(\mathbb{F}_k(\rho)) \tag{9.41}$$

for each k.

Let us call $\mathcal{M}_{\Gamma\otimes\rho}$ the Onsager super-operator. It can be shown to be symmetric and positive definite; thus, it provides an inner product by

$$\langle \mathbb{F}', \mathbb{F}'' \rangle_\rho := \langle \mathbb{F}', \mathcal{M}_{\Gamma\otimes\rho}(\mathbb{F}'') \rangle \tag{9.42}$$

as in Eq. (3.9). We can also obtain a norm,

$$\|\mathbb{F}'\|_\rho := \sqrt{\langle \mathbb{F}', \mathcal{M}_{\Gamma\otimes\rho}(\mathbb{F}') \rangle}, \tag{9.43}$$

and a formula corresponding to Eq. (3.10),

$$\dot{\Sigma}(\rho) = \|\mathbb{F}(\rho)\|_\rho^2, \tag{9.44}$$

which shows the non-negativity of the EPR. Similarly, for $\mathbb{f}', \mathbb{f}'' \in \mathrm{anti}(\mathbb{C}^2 \otimes \mathcal{H})$, we can define

$$\langle \mathbb{f}', \mathbb{f}'' \rangle_\rho^{(k)} := \langle \mathbb{f}', \mathcal{M}_{\Gamma_k\otimes\rho}(\mathbb{f}'') \rangle, \quad \|\mathbb{f}'\|_\rho^{(k)} := \sqrt{\langle \mathbb{f}', \mathbb{f}' \rangle_\rho^{(k)}} \tag{9.45}$$

to obtain

$$\dot{\Sigma}_k(\rho) = \left(\|\mathbb{F}_k(\rho)\|_\rho^{(k)} \right)^2, \tag{9.46}$$

which shows the non-negativity of the partial EPRs. They sum to the total EPR because

$$\sum_{k\in K} \dot{\Sigma}_k(\rho) = \sum_{k\in K} \langle \mathbb{J}_k(\rho), \mathbb{F}_k(\rho) \rangle = \langle \mathbb{J}(\rho), \mathbb{F}(\rho) \rangle = \dot{\Sigma}(\rho),$$

where we used the separable form of $\mathbb{J}(\rho)$ and $\mathbb{F}(\rho)$ to get the second equality.

The symmetric property of $\mathcal{M}_G$ is proved generally as

$$\begin{aligned} &\langle X, \mathcal{M}_G(X') \rangle \\ &= \frac{1}{k_\mathrm{B}} \int_0^1 \mathrm{tr}(X^\dagger G^s X' G^{1-s}) ds = \frac{1}{k_\mathrm{B}} \int_0^1 \mathrm{tr}(G^{1-s} X^\dagger G^s X') ds = \frac{1}{k_\mathrm{B}} \int_0^1 \mathrm{tr}\left((G^s X G^{1-s})^\dagger X' \right) ds \\ &= \langle \mathcal{M}_G(X), X' \rangle. \end{aligned}$$

That is, we have $\mathcal{M}_G^* = \mathcal{M}_G$. We can also show the positive definiteness by using the positive square root F of G, which satisfies $F^2 = G$, $F^\dagger = F$, and $F > 0$ [154]. If $\mathcal{H}$ is finite dimensional, it can be constructed as

$$F = \sum_i \sqrt{g_i} |i\rangle\langle i|.$$

Then, we get

$$\begin{aligned} \langle X, \mathcal{M}_G(X) \rangle &= \frac{1}{k_\mathrm{B}} \int_0^1 \mathrm{tr}(X^\dagger (F^2)^s X (F^2)^{1-s}) ds \\ &= \frac{1}{k_\mathrm{B}} \int_0^1 \mathrm{tr}([F^s X F^{1-s}]^\dagger F^s X F^{1-s}) ds = \frac{1}{k_\mathrm{B}} \int_0^1 |F^s X F^{1-s}|^2 ds \geq 0, \end{aligned}$$

where we used the cyclic property to obtain the second line.

9.2.4 Conservativeness and detailed balance

If we consider a detailed balanced system (cf. Sec. 9.2.1), the thermodynamic force becomes

$$\mathbb{F}(\rho) = -\nabla_{\mathbb{L}}\phi(\rho), \quad \phi(\rho) := k_{\mathrm{B}}(\ln\rho + \beta H). \tag{9.47}$$

That is, detailed balanced systems have conservative forces. On the other hand, if there are multiple baths at different temperatures, the force is no longer conservative.

Equation (9.47) is proved as follows: first, we have

$$k_{\mathrm{B}} \ln \frac{\gamma_k}{\gamma_{-k}} L_k = k_{\mathrm{B}}\beta\omega_k L_k = k_{\mathrm{B}}\beta[L_k, H].$$

Thus, from Eq. (9.34), we see

$$F_k(\rho) = -[\phi(\rho), L_k].$$

On the other hand, Eq. (9.12) shows

$$\nabla_{\mathbb{L}_k}\phi(\rho) = \begin{pmatrix} 0 & [\phi(\rho), L_{-k}] \\ [\phi(\rho), L_k] & 0 \end{pmatrix}.$$

Therefore, considering these equations and Eq. (9.34), we find Eq. (9.47). If the inverse temperature depends on bath, we only have potentials defined for each jump $\phi_k(\rho) = k_{\mathrm{B}}(\ln\rho + \beta_k H)$ with the inverse temperature β_k of the bath mediating jump k and

$$F_k(\rho) = -[\phi_k(\rho), L_k],$$

which does not lead to a conservative thermodynamic force.

As the Onsager super-operator is positive definite, the EPR vanishes when $\mathbb{F}(\rho) = 0$, or equivalently, detailed balance $\mathbb{J}(\rho) = 0$ holds. As mentioned, this occurs in a detailed balanced system when ρ is the Gibbs state ρ^{eq}, as is evident from the expression (9.47). However, it is not the unique state where the EPR vanishes. If $\{Q_i\}$ are the conservation laws, i.e., $[H, Q_i] = 0$ and $\nabla_{\mathbb{L}} Q_i = 0$ holds, then

$$\rho_{\beta,\lambda} := \frac{e^{-\beta H - \sum_i \lambda_i Q_i}}{Z_{\beta,\lambda}} \quad \text{with} \quad \lambda_i \in \mathbb{R}, \;\; Z_{\beta,\lambda} := \mathrm{tr}(e^{-\beta H - \sum_i \lambda_i Q_i}) \tag{9.48}$$

satisfies $\mathbb{F}(\rho_{\beta,\lambda}) = 0$ and $\mathbb{J}(\rho_{\beta,\lambda}) = 0$. Moreover, since $\rho_{\beta,\lambda}$ commutes with H, it becomes a steady state. Equation (9.48) provides the so-called generalized Gibbs ensemble [155]. It is easily proved by using Eq. (9.47) as

$$\mathbb{F}(\rho_{\beta,\lambda}) = -k_{\mathrm{B}}\nabla_{\mathbb{L}}(\ln\rho_{\beta,\lambda} + \beta H) = -k_{\mathrm{B}}\nabla_{\mathbb{L}}(-\sum_i \lambda_i Q_i - \ln Z_{\beta,\lambda} I_{\mathcal{H}}) = 0,$$

where we used $\nabla_{\mathbb{L}} Q_i = 0$ and $\nabla_{\mathbb{L}} I_{\mathcal{H}} = 0$. If we count $Q = I_{\mathcal{H}}$ as a conservation law, the generalized Gibbs ensemble is written as

$$\rho_{\beta,\lambda,\mu} = e^{-\beta H - \sum_i \lambda_i Q_i - \mu Q} = e^{-\beta H - \sum_i \lambda_i Q_i - \mu} \tag{9.49}$$

with $\mu = \ln Z_{\beta,\lambda}$. When the system starts from $\rho(0)$, it would be associated with $\rho_{\beta,\lambda}$ such that

$$q_i := \mathrm{tr}(Q_i\rho(0)) = \mathrm{tr}(Q_i\rho_{\beta,\lambda}). \tag{9.50}$$

Now, let us compare Eqs. (3.11) and (9.30); then, we realize that assumption C1 of Sec. 3.3 is satisfied since

$$\mathbb{F}(\rho) = \mathbb{F}^{\circ} - \nabla_{\mathbb{L}}\varphi(\rho) \tag{9.51}$$

with

$$\varphi(\rho) = k_{\mathrm{B}} \ln\rho. \tag{9.52}$$

Therefore, Eq. (3.12) in assumption C2 reads

$$\operatorname{tr}\left(Q_i e^{(\psi-\sum_i \lambda_i Q_i-\mu)/k_\mathrm{B}}\right) = q_i, \quad \operatorname{tr}\left(e^{(\psi-\sum_i \lambda_i Q_i-\mu)/k_\mathrm{B}}\right) = 1, \tag{9.53}$$

where the latter equation corresponds to $Q = I_{\mathcal{H}}$ and determines $\mu = k_\mathrm{B}^{-1} \ln \operatorname{tr}(e^{(\psi-\sum_i \lambda_i Q_i)/k_\mathrm{B}})$. That is, assumption C2 implies the existence of $\boldsymbol{\lambda}$ such that $q_i = \operatorname{tr}(Q_i \rho_{\beta,\lambda})$ for any q_i and β.

If we assume the existence of such $\boldsymbol{\lambda}$, the general argument in Sec. 3.3 then reveals the equivalence between the two statements:

(1) There exists a potential $\psi \in \operatorname{herm}(\mathcal{H})$ such that $\mathbb{F}^\circ = -\nabla_{\mathbb{L}} \psi$.

(2) For any state ρ, there exists a detailed balanced state $\rho_{\beta,\lambda}$ such that $\operatorname{tr}(Q_i \rho) = \operatorname{tr}(Q_i \rho_{\beta,\lambda})$ for all i.

We define a system to be conservative if it satisfies the first condition. Considering Eqs. (9.12) and (9.28), we find that the first condition is equivalent to the existence of ψ such that

$$s_k L_k = [\psi, L_k]. \tag{9.54}$$

In fact, this condition is satisfied with $\psi = k_\mathrm{B} \beta H$ when the system is detailed balanced.

9.2.5 Cycles

The properties of the cycle as defined by the kernel of $\nabla_{\mathbb{L}}^*$ are yet to be well studied, as in the hydrodynamic case. If we assume that a cyclic operator has the same form as the thermodynamic force and current operators, it reads

$$\mathbb{C} = \oplus_{k\in K} \mathbb{C}_k, \quad \mathbb{C}_k = \begin{pmatrix} 0 & C_{-k} \\ C_k & 0 \end{pmatrix}, \quad C_{-k} = -C_k^\dagger \in \operatorname{opr}(\mathcal{H}). \tag{9.55}$$

For this quantity, $\nabla_{\mathbb{L}}^* \mathbb{C} = 0$ implies

$$\sum_{k\in K} \left([C_{-k}, L_k] + [C_k, L_{-k}]\right) = 0. \tag{9.56}$$

9.2.6 Classical limit

The quantum master equation turns into a classical master equation under some conditions. First, we assume the Hamiltonian H is nondegenerate and eigendecomposed as

$$H = \sum_n \epsilon_n |n\rangle\langle n|. \tag{9.57}$$

The orthonormal basis is assumed to be static. Next, we assume ρ commutes with H,

$$\rho = \sum_n p_n |n\rangle\langle n|, \tag{9.58}$$

which is the "most classical" assumption. Finally, the consistency relation (9.20) is supposed to be satisfied; then, $L_k^\dagger L_k$ commutes with H because

$$[L_k^\dagger L_k, H] = L_k^\dagger [L_k, H] + [L_k^\dagger, H] L_k = \omega_k L_k^\dagger L_k - [L_k, H]^\dagger L_k = \omega_k L_k^\dagger L_k - \omega_k L_k^\dagger L_k = 0. \tag{9.59}$$

Similarly, we get

$$[L_k \rho L_k^\dagger, H] = L_k \rho [L_k^\dagger, H] + [L_k, H] \rho L_k^\dagger = -\omega_k L_k \rho L_k^\dagger + \omega_k L_k \rho L_k^\dagger = 0, \tag{9.60}$$

where we used the identity $[ABC, D] = AB[C, D] + A[B, D]C + [A, D]BC$. Therefore, because we assumed H is nondegenerate, $L_k^\dagger L_k$ and $L_k \rho L_k^\dagger$ are diagonalized by the orthonormal basis $\{|n\rangle\}$.

Now, the matrix elements of the quantum master equation read

$$\begin{aligned}
\langle m|\frac{d\rho}{dt}|l\rangle &= \sum_n \langle m|\Big(\frac{dp_n}{dt}|n\rangle\langle n| + p_n \underbrace{\frac{d|n\rangle}{dt}}_{=0}\langle n| + p_n|n\rangle\underbrace{\frac{d\langle n|}{dt}}_{=0}\Big)|l\rangle = \delta_{ml}\frac{dp_m}{dt},\\
\langle m|\mathcal{D}(\rho)|l\rangle &= \sum_{k\in K_{\mathrm{all}}} \gamma_k \langle m|\Big(L_k\rho L_k^\dagger - \frac{1}{2}\{L_k^\dagger L_k, \rho\}\Big)|l\rangle\\
&= \delta_{ml}\sum_{k\in K_{\mathrm{all}}} \gamma_k\Big(\sum_n p_n |\langle m|L_k|n\rangle|^2 - p_m\langle m|L_k^\dagger L_k|m\rangle\Big)\\
&= \delta_{ml}\sum_{k\in K_{\mathrm{all}}} \gamma_k\Big(\sum_n p_n |\langle m|L_k|n\rangle|^2 - \sum_n p_m|\langle n|L_k|m\rangle|^2\Big),
\end{aligned}$$

where we used the fact that $L_k\rho L_k^\dagger$ and $L_k^\dagger L_k$ are diagonalized by $\{|n\rangle\}$ in the second line and inserted $I_{\mathcal{H}} = \sum_n |n\rangle\langle n|$ in the last line. Therefore, the quantum master equation is equivalent to the classical master equation

$$\frac{dp_m}{dt} = \sum_{n(\neq m)}\sum_{k\in K_{\mathrm{all}}} (R_{mn}^{(k)} p_n - R_{nm}^{(k)} p_m), \tag{9.61}$$

where the transition rates are given by

$$R_{mn}^{(k)} = \gamma_k |\langle m|L_k|n\rangle|^2. \tag{9.62}$$

To obtain the classical local detailed balance (6.21), the backward process of $e = (n \to m; k)$, whose transition rate reads $R_{mn}^{(k)}$, should be $-e = (m \to n; -k)$. Then, we obtain

$$k_{\mathrm{B}} \ln \frac{R_{mn}^{(k)}}{R_{nm}^{(-k)}} = k_{\mathrm{B}} \ln \frac{\gamma_k |\langle m|L_k|n\rangle|^2}{\gamma_{-k}|\langle m|L_k|n\rangle|^2} = s_k, \tag{9.63}$$

where the last equality comes from Eq. (9.18).

9.3 Housekeeping-excess decomposition

Following the general procedure, the housekeeping and the excess EPR are defined for the quantum master equation as [21]

$$\dot{\Sigma}^{\mathrm{hk}}(\rho) := \inf_{\mathbb{F}'\in\mathscr{C}} \|\mathbb{F}(\rho) - \mathbb{F}'\|_\rho^2, \tag{9.64}$$

$$\dot{\Sigma}^{\mathrm{ex}}(\rho) := \inf_{\mathbb{F}'\in\mathscr{C}^\perp} \|\mathbb{F}(\rho) - \mathbb{F}'\|_\rho^2 \tag{9.65}$$

$$= \inf_{\mathbb{F}'\in\mathscr{F}} \|\mathbb{F}'\|_\rho^2 \quad \text{s.t.} \quad \nabla_{\mathbb{L}}^* \mathcal{M}_{\Gamma\otimes\rho}(\mathbb{F}') = \nabla_{\mathbb{L}}^* \mathbb{J}(\rho), \tag{9.66}$$

where the conservative subspace $\mathscr{C}$ and its orthogonal complement $\mathscr{C}^\perp$ are given by

$$\mathscr{C} := \{-\nabla_{\mathbb{L}}\phi \mid \phi \in \mathrm{herm}(\mathcal{H})\}, \tag{9.67}$$

$$\mathscr{C}^\perp = \{\mathbb{F}' \in \mathrm{anti}(\mathfrak{h}\otimes\mathcal{H}) \mid \nabla_{\mathbb{L}}^* \mathcal{M}_{\Gamma\otimes\rho}(\mathbb{F}') = 0\}. \tag{9.68}$$

The housekeeping EPR vanishes when the system is conservative; i.e., $\mathbb{F}^\circ$ is in $\mathscr{C}$, which implies $\mathbb{F}(\rho) \in \mathscr{C}$. The orthogonal complement is derived as follows: for an arbitrary $\phi \in \mathrm{herm}(\mathcal{H})$, $\mathbb{F}' \in \mathscr{C}^\perp$ must satisfy

$$\langle \mathbb{F}', -\nabla_{\mathbb{L}}\phi\rangle_\rho = -\langle \nabla_{\mathbb{L}}^* \mathcal{M}_{\Gamma\otimes\rho}(\mathbb{F}'), \phi\rangle = 0.$$

When $\mathbb{F}'$ is anti-Hermitian, $\nabla_{\mathbb{L}}^* \mathcal{M}_{\Gamma\otimes\rho}(\mathbb{F}')$ becomes Hermitian. Thus, $\nabla_{\mathbb{L}}^* \mathcal{M}_{\Gamma\otimes\rho}(\mathbb{F}')$ must be the zero operator for the equality to hold for any Hermitian ϕ.

If the inverse of the Onsager super-operator $\mathcal{M}_{\Gamma\otimes\rho}^{-1}$ is defined, the excess EPR is given by

$$\dot{\Sigma}^{\mathrm{ex}}(\rho) = \inf_{\mathbb{J}'\in\mathscr{F}} \langle \mathbb{J}', \mathcal{M}_{\Gamma\otimes\rho}^{-1}(\mathbb{J}')\rangle \quad \text{s.t.} \quad \nabla_{\mathbb{L}}^* \mathbb{J}' = \nabla_{\mathbb{L}}^* \mathbb{J}(\rho). \tag{9.69}$$

This representation again suggests the connection between minimum dissipation and the excess EPR.

As discussed generally in Sec. 4.2, there is an optimal potential ϕ_* that provides the EPRs as

$$\dot{\Sigma}^{\mathrm{hk}}(\rho) = \|\mathbb{F}(\rho) - (-\nabla_{\mathbb{L}}\phi_*)\|_\rho^2, \tag{9.70}$$

$$\dot{\Sigma}^{\mathrm{ex}}(\rho) = \|-\nabla_{\mathbb{L}}\phi_*\|_\rho^2. \tag{9.71}$$

In practice, the potential is obtained by performing the optimizations or directly solving the equation

$$-\nabla_{\mathbb{L}}^* \mathcal{M}_{\Gamma\otimes\rho}(\nabla_{\mathbb{L}}\phi) = \mathcal{D}(\rho). \tag{9.72}$$

The Hatano–Sasa decomposition can also be defined for open quantum systems (often referred to as the adiabatic-nonadiabatic decomposition). The HS EPRs are given by [24, 63]

$$\dot{\Sigma}^{\mathrm{hk,HS}}(\rho) := \langle \mathbb{J}(\rho), \mathbb{F}(\rho^{\mathrm{ss}})\rangle, \tag{9.73}$$

$$\dot{\Sigma}^{\mathrm{ex,HS}}(\rho) := \langle \mathbb{J}(\rho), \mathbb{F}(\rho) - \mathbb{F}(\rho^{\mathrm{ss}})\rangle. \tag{9.74}$$

Here, ρ^{ss} is a steady state, where we have $-(i/\hbar)[H,\rho^{\mathrm{ss}}] + \mathcal{D}(\rho^{\mathrm{ss}}) = 0$. The positivity of this decomposition is only assured when the steady state satisfies [64]

$$[L_k, \Phi] = \Delta\phi_k L_k, \tag{9.75}$$

where $\Phi = -\ln\rho^{\mathrm{ss}}$ and $\Delta\phi_k$ is a difference between eigenvalues of Φ. This condition indicates that the jump operators act as creation/annihilation operators regarding the eigenbasis of ρ^{ss}. However, this condition is not always satisfied and the decomposition can fail [64].

9.4 Thermodynamic trade-off relations

9.4.1 Thermodynamic uncertainty relations

The general result provided in Sec. 5.2.1 gives open quantum systems the following inequality [20]

$$\dot{\Sigma}^{\mathrm{ex}}(\rho) \geq \frac{|\langle \nabla_{\mathbb{L}}^*\mathbb{J}(\rho), \mathcal{O}\rangle|^2}{\|\nabla_{\mathbb{L}}\mathcal{O}\|_\rho^2} \tag{9.76}$$

for any observable $\mathcal{O} \in \mathrm{herm}(\mathcal{H})$. The numerator provides the dissipative part of the time derivative of $\langle\mathcal{O}\rangle$ as

$$\frac{d}{dt}\langle\mathcal{O}\rangle = -\frac{i}{\hbar}\,\mathrm{tr}([H,\rho]\mathcal{O}) + \mathrm{tr}(\mathcal{O}\nabla_{\mathbb{L}}^*\mathbb{J}(\rho)) = -\frac{i}{\hbar}\,\mathrm{tr}([H,\rho]\mathcal{O}) + \langle \nabla_{\mathbb{L}}\mathcal{O}, \mathbb{J}(\rho)\rangle, \tag{9.77}$$

and coincides with $(d/dt)\langle\mathcal{O}\rangle$ if $\mathcal{O}$ commutes with H or ρ. As proven later, the denominator is upper bound by $1/k_{\mathrm{B}}$ times the quantity

$$\mathfrak{D}_\rho(\mathcal{O}) := \frac{1}{2}\,\mathrm{tr}\Big(\rho\big(\mathcal{D}^*(\mathcal{O}^2) - \{\mathcal{O}, \mathcal{D}^*(\mathcal{O})\}\big)\Big), \tag{9.78}$$

which we term the quantum diffusivity [20]. We will discuss that this quantity can be interpreted as the diffusivity of $\mathcal{O}$ in the dissipative dynamics. Thus, we obtain the inequality

$$\dot{\Sigma}^{\mathrm{ex}}(\rho) \geq k_{\mathrm{B}}\frac{|\langle \nabla_{\mathbb{L}}^*\mathbb{J}(\rho), \mathcal{O}\rangle|^2}{\mathfrak{D}_\rho(\mathcal{O})} \tag{9.79}$$

and it can be understood as the short-time TUR in open quantum systems. We note that strictly speaking, proving the inequality

$$\|\nabla_{\mathbb{L}}\mathcal{O}\|_\rho^2 \leq \frac{1}{k_{\mathrm{B}}}\mathfrak{D}_\rho(\mathcal{O}) \tag{9.80}$$

requires the Hilbert space to be finte-dimensional because we use the formula (9.38).

Moreover, in a similar way, we can show the TUR for the partial EPRs

$$\dot{\Sigma}_k(\rho) \geq k_{\mathrm{B}} \frac{|\langle \nabla^*_{\mathbb{L}_k} \mathbb{J}_k(\rho), \mathcal{O}\rangle|^2}{\mathfrak{D}^{(k)}_\rho(\mathcal{O})}, \tag{9.81}$$

where

$$\mathfrak{D}^{(k)}_\rho(\mathcal{O}) := \frac{1}{2} \operatorname{tr}\Big(\rho\big(\mathcal{D}^*_k(\mathcal{O}^2) - \{\mathcal{O}, \mathcal{D}^*_k(\mathcal{O})\}\big)\Big). \tag{9.82}$$

It is proved once we admit the inequality

$$\left(\|\nabla_{\mathbb{L}_k}\mathcal{O}\|^{(k)}_\rho\right)^2 \leq \frac{1}{k_{\mathrm{B}}} \mathfrak{D}^{(k)}_\rho(\mathcal{O}). \tag{9.83}$$

Then, the Cauchy–Schwarz inequality proves the inequality as

$$\dot{\Sigma}_k(\rho)\Big(\|\nabla_{\mathbb{L}_k}\mathcal{O}\|^{(k)}_\rho\Big)^2 = \Big(\|\mathbb{F}_k(\rho)\|^{(k)}_\rho\Big)^2\Big(\|\nabla_{\mathbb{L}_k}\mathcal{O}\|^{(k)}_\rho\Big)^2 \geq \Big|\langle \mathbb{F}_k(\rho), \nabla_{\mathbb{L}_k}\mathcal{O}\rangle^{(k)}_\rho\Big|^2 = |\langle \nabla^*_{\mathbb{L}_k}\mathbb{J}_k(\rho), \mathcal{O}\rangle|^2.$$

9.4.2 Quantum diffusivity

We interpret the quantum diffusivity $\mathfrak{D}_\rho(\mathcal{O})$ as a diffusivity because it leads to the classical diffusivity (6.78) when $\mathcal{O}$ commutes with ρ;

$$\mathfrak{D}_\rho(X) = \frac{1}{2} \sum_{n,m(\neq n)} \sum_{k \in K_{\mathrm{all}}} (R^{(k)}_{mn} p_n + R^{(-k)}_{nm} p_m)(\mathcal{O}_m - \mathcal{O}_n)^2, \tag{9.84}$$

where $\mathcal{O}_n := \langle n|\mathcal{O}|n\rangle$ are the eigenvalues of $\mathcal{O}$ and $R^{(k)}_{mn} := \gamma_k |\langle m|L_k|n\rangle|^2$ for $n \neq m$, which can be interpreted as the transition rates in the classical limit considered in Sec. 9.2.6. From Eq. (9.84), we find the quantum diffusivity can provide the classical diffusivity defined in Eq. (6.78) in the classical limit. On the other hand, it is defined regardless of the classicality, so we can consider it as a quantum extension of the classical diffusivity. This is also supported by the fact that the quantity becomes the counterpart of the classical diffusivity in the TUR (9.79) (cf. Eq. (6.79)).

Let us first prove Eq. (9.84). By using the orthonormal basis $\{|n\rangle\}$ that simultaneously diagonalizes $\rho = \sum_n p_n |n\rangle\langle n|$ and $\mathcal{O} = \sum_n \mathcal{O}_n |n\rangle\langle n|$, the definition (9.82) is rewritten as

$$\mathfrak{D}^{(k)}_\rho(\mathcal{O}) = \frac{1}{2} \sum_{n,m} p_n (\mathcal{O}^2_m - 2\mathcal{O}_n\mathcal{O}_m) \langle n|\mathcal{D}^*_k(|m\rangle\langle m|)|n\rangle.$$

From the identity (9.4), which can be stated as $\sum_m \mathcal{D}^*_k(|m\rangle\langle m|) = 0$, we find

$$\sum_{n,m} p_n \mathcal{O}^2_n \langle n|\mathcal{D}^*_k(|m\rangle\langle m|)|n\rangle = 0.$$

Thus, we obtain

$$\mathfrak{D}^{(k)}_\rho(\mathcal{O}) = \frac{1}{2} \sum_{n,m} p_n (\mathcal{O}^2_m - 2\mathcal{O}_n\mathcal{O}_m + \mathcal{O}^2_n) \langle n|\mathcal{D}^*_k(|m\rangle\langle m|)|n\rangle = \frac{1}{2} \sum_{n,m(\neq n)} p_n (\mathcal{O}_m - \mathcal{O}_n)^2 \langle n|\mathcal{D}^*_k(|m\rangle\langle m|)|n\rangle.$$

Moreover, when $m \neq n$, we get

$$\begin{aligned}\langle n|\mathcal{D}^*_k(|m\rangle\langle m|)|n\rangle &= \gamma_k\Big(|\langle m|L_k|n\rangle|^2 - \delta_{nm}\langle n|L^\dagger_k L_k|n\rangle\Big) + \gamma_{-k}\Big(|\langle m|L_{-k}|n\rangle|^2 - \delta_{nm}\langle n|L^\dagger_{-k} L_{-k}|n\rangle\Big)\\ &= R^{(k)}_{mn} + R^{(-k)}_{mn}.\end{aligned}$$

By substituting it to the above expression, we find

$$\mathfrak{D}^{(k)}_\rho(\mathcal{O}) = \frac{1}{2} \sum_{n,m(\neq n)} p_n (\mathcal{O}_m - \mathcal{O}_n)^2 (R^{(k)}_{mn} + R^{(-k)}_{mn}).$$

Rearranging terms soon leads to Eq. (9.84).

Then, two inequalities remain unproven: Eqs. (9.80) and (9.83). We note that Eq. (9.80) is derived from Eq. (9.83) because we have

$$\sum_k \left(\|\nabla_{\mathbb{L}}\mathcal{O}\|_\rho^{(k)}\right)^2 = \|\nabla_{\mathbb{L}}\mathcal{O}\|_\rho^2,$$

which is easily seen from the separable structure of $\nabla_{\mathbb{L}}\mathcal{O}$ (cf. Sec. 9.2.3), and

$$\mathfrak{D}_\rho(\mathcal{O}) = \sum_{k\in K} \mathfrak{D}_\rho^{(k)}(\mathcal{O}),$$

which is obvious from the linearlity of the trace and anti-commutator and the definition of $\mathcal{D}_k^*$.

Proving Eq. (9.82) is accomplished by rewriting

$$\mathfrak{D}_\rho^{(k)}(\mathcal{O}) = \langle \nabla_{\mathbb{L}_k}\mathcal{O}, \mathscr{A}_{\Gamma_k\otimes\rho}(\nabla_{\mathbb{L}_k}\mathcal{O})\rangle, \tag{9.85}$$

where $\mathscr{A}$ is defined by

$$\mathscr{A}_G(X) := \frac{GX + XG}{2}. \tag{9.86}$$

With the eigendecomposition of G, it is given by

$$\mathscr{A}_G(X) = \sum_{i,j} \frac{g_i + g_j}{2}\langle i|X|j\rangle|i\rangle\langle j|. \tag{9.87}$$

We can prove $\langle X, \mathcal{M}_G(X)\rangle \le k_{\mathrm{B}}^{-1}\langle X, \mathscr{A}_G(X)\rangle$ by

$$\langle X, \mathcal{M}_G(X)\rangle = \frac{1}{k_{\mathrm{B}}}\sum_{i,j}\Lambda(g_i, g_j)|\langle i|X|j\rangle|^2 \le \frac{1}{k_{\mathrm{B}}}\sum_{i,j}\frac{g_i+g_j}{2}|\langle i|X|j\rangle|^2 = \frac{1}{k_{\mathrm{B}}}\langle X, \mathscr{A}_G(X)\rangle,$$

where we used the hierarchy between means (6.32). Therefore, once we show Eq. (9.85), Eq. (9.83) immediately follows (here, we assumed that $\Gamma_k \otimes \rho$ has a finite dimension, i.e., that the Hilbert space is finite-dimensional).

Finally, we need to show Eq. (9.85) to derive the TURs (9.79) and (9.81). The right-hand side is rewritten as

$$\begin{aligned}\langle \nabla_{\mathbb{L}_k}\mathcal{O}, \mathscr{A}_{\Gamma_k\otimes\rho}(\nabla_{\mathbb{L}_k}\mathcal{O})\rangle &= \frac{1}{2}\operatorname{tr}\Big((\nabla_{\mathbb{L}_k}\mathcal{O})^\dagger(\Gamma_k\otimes\rho)\nabla_{\mathbb{L}_k}\mathcal{O}\Big) + \frac{1}{2}\operatorname{tr}\Big((\nabla_{\mathbb{L}_k}\mathcal{O})^\dagger\nabla_{\mathbb{L}_k}\mathcal{O}(\Gamma_k\otimes\rho)\Big)\\ &= -\operatorname{tr}\Big((\nabla_{\mathbb{L}_k}\mathcal{O})^2(\Gamma_k\otimes\rho)\Big),\end{aligned}$$

where we used $(\nabla_{\mathbb{L}_k}\mathcal{O})^\dagger = -\nabla_{\mathbb{L}_k}\mathcal{O}$ since $\mathcal{O}$ is Hermitian. Further,

$$-(\nabla_{\mathbb{L}_k}\mathcal{O})^2 = -\begin{pmatrix} 0 & [\mathcal{O}, L_{-k}] \\ [\mathcal{O}, L_k] & 0 \end{pmatrix}^2 = \begin{pmatrix} [L_k^\dagger, \mathcal{O}][\mathcal{O}, L_k] & 0 \\ 0 & [L_{-k}^\dagger, \mathcal{O}][\mathcal{O}, L_{-k}] \end{pmatrix},$$

thus,

$$\langle \nabla_{\mathbb{L}_k}\mathcal{O}, \mathscr{A}_{\Gamma_k\otimes\rho}(\nabla_{\mathbb{L}_k}\mathcal{O})\rangle = \frac{\gamma_k}{2}\operatorname{tr}_{\mathcal{H}}\Big(\rho[L_k^\dagger, \mathcal{O}][\mathcal{O}, L_k]\Big) + \frac{\gamma_{-k}}{2}\operatorname{tr}_{\mathcal{H}}\Big(\rho[L_{-k}^\dagger, \mathcal{O}][\mathcal{O}, L_{-k}]\Big),$$

where we performed the partial trace regarding $\mathfrak{h}$. A straightforward calculation yields the equalities

$$\begin{aligned}[L_k^\dagger, \mathcal{O}][\mathcal{O}, L_k] &= L_k^\dagger\mathcal{O}^2L_k - \frac{1}{2}\{L_k^\dagger L_k, \mathcal{O}^2\} - \Big\{\mathcal{O}, L_k^\dagger\mathcal{O}L_k - \frac{1}{2}\{L_k^\dagger L_k, \mathcal{O}\}\Big\}\\ [L_{-k}^\dagger, \mathcal{O}][\mathcal{O}, L_{-k}] &= L_{-k}^\dagger\mathcal{O}^2L_{-k} - \frac{1}{2}\{L_{-k}^\dagger L_{-k}, \mathcal{O}^2\} - \Big\{\mathcal{O}, L_{-k}^\dagger\mathcal{O}L_{-k} - \frac{1}{2}\{L_{-k}^\dagger L_{-k}, \mathcal{O}\}\Big\},\end{aligned}$$

which finally reveals

$$\langle \nabla_{\mathbb{L}_k}\mathcal{O}, \mathscr{A}_{\Gamma_k\otimes\rho}(\nabla_{\mathbb{L}_k}\mathcal{O})\rangle = \frac{1}{2}\operatorname{tr}_{\mathcal{H}}\Big(\rho\big(\mathcal{D}_k^*(\mathcal{O}^2) - \{\mathcal{O}, \mathcal{D}_k^*(\mathcal{O})\}\big)\Big) = \mathfrak{D}_\rho^{(k)}(\mathcal{O}).$$

In addition, we remark that in terms of the quantum diffisivity, the unitary dynamics is "deterministic." If we replace the dissipator in Eq. (9.78) with the adjoint of the unitary term, we see that it vanishes:

$$\frac{1}{2}\operatorname{tr}\Big(\rho\big(\mathcal{L}^*_{\mathrm{uni}}(\mathcal{O}^2)-\{\mathcal{O},\mathcal{L}^*_{\mathrm{uni}}(\mathcal{O})\}\big)\Big)=0, \tag{9.88}$$

where

$$\mathcal{L}_{\mathrm{uni}}(\rho):=-\frac{i}{\hbar}[H,\rho] \quad \text{and} \quad \mathcal{L}^*_{\mathrm{uni}}(\mathcal{O})=\frac{i}{\hbar}[H,\mathcal{O}]. \tag{9.89}$$

This is because we always have

$$[H,\mathcal{O}^2]-\big\{\mathcal{O},[H,\mathcal{O}]\big\}=H\mathcal{O}^2-\mathcal{O}^2H-(\mathcal{O}H\mathcal{O}-\mathcal{O}^2H+H\mathcal{O}^2-\mathcal{O}H\mathcal{O})=0.$$

Therefore, defining $\mathcal{L}:=\mathcal{L}_{\mathrm{uni}}+\mathcal{D}$, which gives the quantum master equation as $d\rho/dt=\mathcal{L}(\rho)$, we can rewrite the quantum diffisivity into

$$\mathfrak{D}_\rho(\mathcal{O})=\frac{1}{2}\operatorname{tr}\Big(\rho\big(\mathcal{L}^*(\mathcal{O}^2)-\{\mathcal{O},\mathcal{L}^*(\mathcal{O})\}\big)\Big). \tag{9.90}$$

9.4.3 Thermodynamic speed limit

While there have been several studies on the thermodynamic speed limit in open quantum systems [39, 43, 156–158], the Wasserstein distance analogous to the classical definition (6.80) (or more generally, Eq. (5.36)) has been elusive. This is because there is an additional term in the dynamics, namely, the unitary term. One exception is Ref. [44], where the authors nicely avert this problem by focusing on detailed balanced systems.

Another possible direction is to define formally a quantum analogue of the Benamou–Brenier formula by neglecting the unitary term as

$$W(\rho_a,\rho_b):=\inf_{\rho,\phi}\sqrt{\tau\int_0^\tau\|-\nabla_{\mathbb{L}}\phi(t)\|^2_{\rho(t)}dt} \tag{9.91}$$

with conditions

$$\rho(0)=\rho_a,\quad \rho(\tau)=\rho_b,\quad \frac{d\rho}{dt}=-\nabla^*_{\mathbb{L}}\mathcal{M}_{\Gamma\otimes\rho}(\nabla_{\mathbb{L}}\phi(t)). \tag{9.92}$$

The optimization would be accomplished by manipulating the potential $\psi=\phi-k_{\mathrm{B}}\ln\rho$ that gives $\mathbb{F}^\circ$ by $-\nabla_{\mathbb{L}}\psi$.

9.5 Examples

We demonstrate our results in open quantum systems by two examples. One is a two-level system coupled to two heat baths, which is a quantum generalization of the system discussed in Sec. 6.6. In the other example, we consider a model of superradiant systems, where jumps in several qubits simultaneously occur [159, 160].

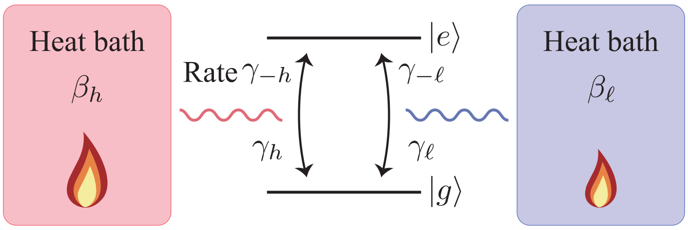
9.5.1 Two-level system attached to two heat baths

First, let us illustrate the general framework and the decomposition through a minimal model of the nonequilibrium quantum system. Consider a two-level system that is equipped with Hamiltonian $H=\hbar\omega|e\rangle\langle e|$ and attached to two heat baths at inverse temperatures β_h and β_ℓ ($\beta_h<\beta_\ell$). The two ways of dissipation induced by the baths are represented by jump operators $L_h=L_\ell=|\mathrm{g}\rangle\langle e|$. The rates obey the local detailed balance

$$\ln\frac{\gamma_h}{\gamma_{-h}}=\beta_h\hbar\omega,\quad \ln\frac{\gamma_\ell}{\gamma_{-\ell}}=\beta_\ell\hbar\omega. \tag{9.93}$$

The system possesses the steady state

$$\rho^{\mathrm{ss}}=\frac{\Gamma_+}{\Gamma_++\Gamma_-}|\mathrm{g}\rangle\langle \mathrm{g}|+\frac{\Gamma_-}{\Gamma_++\Gamma_-}|e\rangle\langle e|, \tag{9.94}$$



$$H = \omega|e\rangle\langle e|, \; L_h = L_\ell = |g\rangle\langle e|$$

Figure 9.1: (Adapted from Ref. [21]) We simulate the dissipative dynamics of a two-level system coupled to two heat baths at different temperatures.

where $\Gamma_\pm = \gamma_{\pm h} + \gamma_{\pm \ell}$. The situation is summarized in Fig. 9.1 (a).

Now, the components of the force and current operators read

$$J_k(\rho) = \frac{\gamma_k \rho_{ee} - \gamma_{-k}\rho_{gg}}{2} L_k + \frac{\rho_{eg}}{2}(\gamma_k |g\rangle\langle g| - \gamma_{-k}|e\rangle\langle e|), \tag{9.95}$$

$$F_k(\rho) = k_{\mathrm{B}}\beta_k \hbar\omega L_k + \left[L_k, k_{\mathrm{B}} \ln \rho\right], \tag{9.96}$$

for $k = h, \ell$. Here, ρ_{ij} denotes the matrix elements of ρ in basis $\{|g\rangle, |e\rangle\}$. We see J_k has a classical component proportional to $\gamma_k \rho_{ee} - \gamma_{-k}\rho_{gg}$ and a non-classical part depending on ρ_{eg}. Since β_k depends on k, F_k cannot be expressed as $[\phi, L_k]$ (thus, the system is non-conservative due to the temperature gap).

To see the relation to the classical example given in Sec. 6.6, we define

$$f_k^{\mathrm{cl}}(\rho) \coloneqq k_{\mathrm{B}}\beta_k\hbar\omega + k_{\mathrm{B}}(\ln \rho_{ee} - \ln \rho_{gg}), \tag{9.97}$$

$$l_k(\rho) \coloneqq \frac{\gamma_k \rho_{ee} - \gamma_{-k}\rho_{gg}}{f_k^{\mathrm{cl}}(\rho)}, \tag{9.98}$$

$$a_k^{\mathrm{cl}}(\rho) \coloneqq \gamma_k \rho_{ee} + \gamma_{-k}\rho_{gg}, \tag{9.99}$$

which are supposed to serve as the classical components of the thermodynamic force, the Onsager operator, and the activity. Then, with a lengthy but straightforward calculation, we can solve Eq. (9.72) to get the relation [21]

$$\phi^*(\rho) = \begin{pmatrix} 0 & 0 \\ 0 & \Delta^{\mathrm{cl}}(\rho) \end{pmatrix} + b_1 \begin{pmatrix} 0 & \rho_{ge} \\ \rho_{eg} & 0 \end{pmatrix} + b_2(\rho) \begin{pmatrix} 0 & 0 \\ 0 & |\rho_{ge}|^2 \end{pmatrix} + o(|\rho_{ge}|^2) \tag{9.100}$$

when the off-diagonal element of ρ is small. Here,

$$\Delta^{\mathrm{cl}}(\rho) = \frac{l_h(\rho) f_h^{\mathrm{cl}}(\rho) + l_\ell(\rho) f_\ell^{\mathrm{cl}}(\rho)}{l_h(\rho) + l_\ell(\rho)} \tag{9.101}$$

provides the classical potential difference as in Eq. (6.88). Moreover, b_1 and $b_2(\rho)$ are coefficients given by

$$b_1 = \frac{a_h^{\mathrm{cl}}(u) + a_\ell^{\mathrm{cl}}(u)}{l_h(u) + l_\ell(u)}, \quad b_2(\rho) = \frac{2(a_h^{\mathrm{cl}}(u) + a_\ell^{\mathrm{cl}}(u))}{\rho_{gg} - \rho_{ee}} \left(\frac{1}{l_h(u) + l_\ell(u)} - \frac{1}{l_h(\rho) + l_\ell(\rho)} \right), \tag{9.102}$$

where $u = I/2$ is the maximally mixed state.

By truncating terms of $o(|\rho_{ge}|^2)$, we can get the approximated value of the excess EPR. We define $\dot{\Sigma}^{\mathrm{ex,app}}(\rho)$ by

$$\begin{aligned} &\dot{\Sigma}^{\mathrm{ex,app}}(\rho) \coloneqq \|-\nabla_{\mathbb{L}} \tilde{\phi}(\rho)\|_\rho^2 \\ &\text{with} \quad \tilde{\phi}(\rho) = \begin{pmatrix} 0 & 0 \\ 0 & \Delta^{\mathrm{cl}}(\rho) \end{pmatrix} + b_1 \begin{pmatrix} 0 & \rho_{ge} \\ \rho_{eg} & 0 \end{pmatrix} + b_2(\rho) \begin{pmatrix} 0 & 0 \\ 0 & |\rho_{ge}|^2 \end{pmatrix}. \end{aligned} \tag{9.103}$$

In Fig. 9.2, we show numerical results of the two-level system demonstrating the accuracy of the approximation. The numerical results here and in the next example are obtained with the Python quantum toolbox, QuTiP [161]. In the time evolution, the system approaches the nonequilibrium steady state where heat flows from the hot bath to the cold bath. At the same time, the total EPR gets closer to the housekeeping EPR, which is almost at a constant value corresponding to the stationary EPR, whereas the excess EPR vanishes. We can see that the excess EPR is well approximated by $\dot{\Sigma}^{\mathrm{ex,app}}(\rho)$ even when ρ is not so close to the steady state.

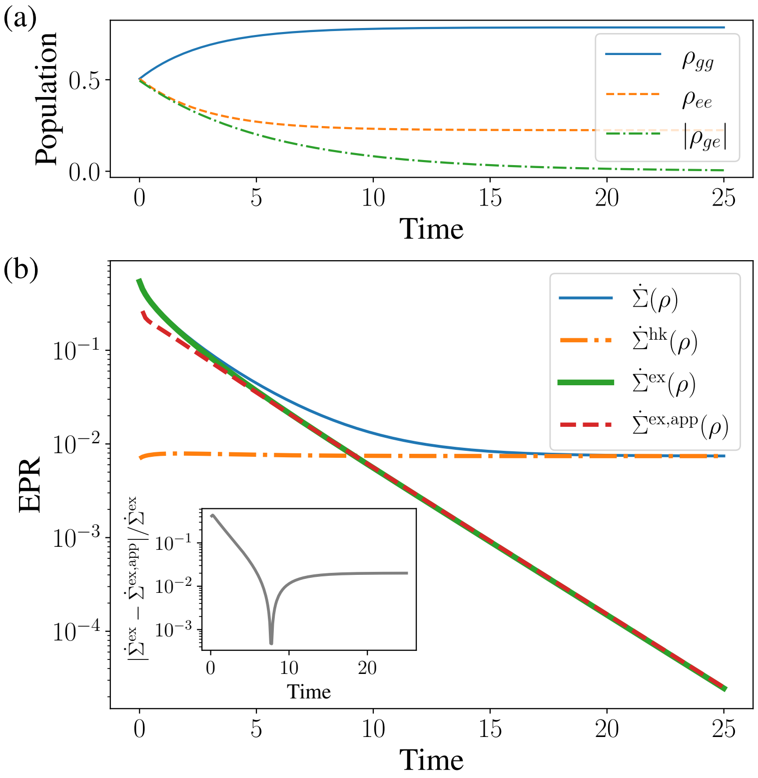


Figure 9.2: (Adapted from Ref. [21]) (a) We begin with a pure state $(|g\rangle + |e\rangle)/\sqrt{2}$ added a small noise to avoid divergence of $\ln\rho$. The coherence ρ_{ge} vanished while the classical population converges to the stationary distribution. We do the simulation with parameters $\hbar\omega = 1$, $k_{\mathrm{B}}\beta_h = 0.58$, $k_{\mathrm{B}}\beta_\ell = 1$, and $\gamma_+ = \gamma_- = 0.1$. (b) We plot the EPRs; as the system relaxes, the total and housekeeping EPRs converge to a single nonzero value, and the excess EPR becomes zero. The approximation formula reproduces the excess EPR well with a small error (shown in the inset).

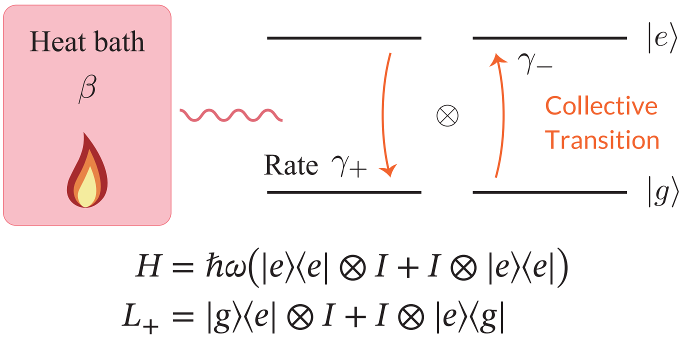


Figure 9.3: (Adapted from Ref. [21]) We consider a model of superradiance, where two two-level systems are simultaneously influenced by a heat bath.

9.5.2 Relaxation of a superradiant system

Next, we discuss the TUR in detail by analyzing the model of superradiance used in Ref. [162]. As depicted in Fig. 9.3, the system consists of two two-level systems with Hamiltonian

$$H = \hbar\omega\big(|e\rangle\langle e| \otimes I + I \otimes |e\rangle\langle e|\big), \tag{9.104}$$

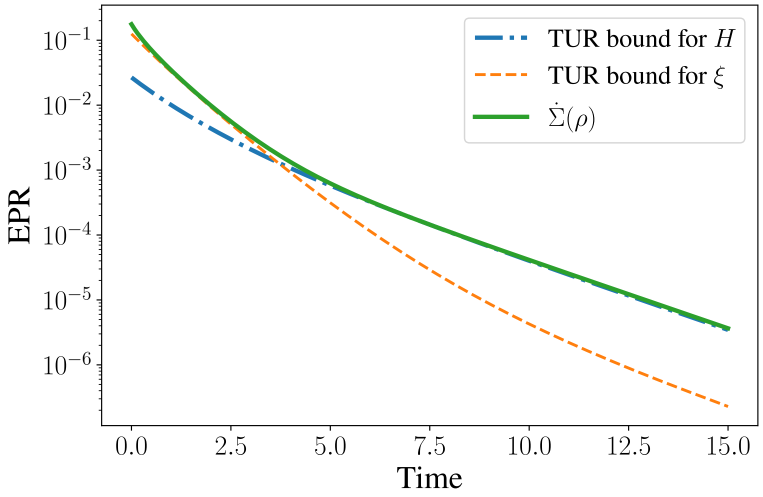


Figure 9.4: (Adapted from Ref. [21]) We simulate the time evolution with parameters $\hbar\omega = 1$, $k_{\mathrm{B}}\beta = 1$, $\gamma_+ = \Gamma(n_{\mathrm{th}} + 1)$ and $\gamma_- = \Gamma n_{\mathrm{th}}$, where $\Gamma = 0.1$ and $n_{\mathrm{th}} = 1/(e^{\beta\hbar\omega} - 1)$. We can observe two stages of relaxation; in the earlier region (before $t \approx 3$), the TUR bound given by $\xi = |ge\rangle\langle eg| + |eg\rangle\langle ge|$ is tighter than that given by H, and the converse holds in the later regime.

which has degeneracy; $|g\rangle|e\rangle$ and $|e\rangle|g\rangle$ both have the eigenvalue ω. We also have a single collective dissipation ($|K| = 1$) represented by

$$L_+ = |g\rangle\langle e| \otimes I + I \otimes |g\rangle\langle e| = L_-^\dagger. \tag{9.105}$$

With the system coupled to a single bath at inverse temperature β, the local detailed balance $\gamma_+/\gamma_- = \exp(\beta\hbar\omega)$ is assumed. The authors of Ref. [162] used this model to exemplify that the coherence between the degenerate states enables the reduction of the dissipation beyond the classical limit.

This system has a nontrivial conservative quantity,

$$Q = \frac{1}{2}\big(|ge\rangle\langle ge| + |eg\rangle\langle eg| - |ge\rangle\langle eg| - |eg\rangle\langle ge|\big). \tag{9.106}$$

It commutes with H and satisfies $\nabla_{\mathbb{L}} Q = 0$ because $L_\pm Q = Q L_\pm = 0$. As discussed in Sec. 9.2.4, then, there is a family of detailed balanced steady states

$$\rho_{\beta,\lambda} = \frac{e^{-\beta H - \lambda Q}}{Z_{\beta,\lambda}}, \quad Z_{\beta,\lambda} = \mathrm{tr}\left(e^{-\beta H - \lambda Q}\right). \tag{9.107}$$

Given an initial state ρ_0 and the initial value $q = \mathrm{tr}(Q\rho_0)$, we can provide a λ such that $q = \mathrm{tr}(Q\rho_{\beta,\lambda})$ by

$$\lambda(\beta, q) = -\ln\left[\frac{q}{1-q}(e^{\beta\hbar\omega} + e^{-\beta\hbar\omega} + 1)\right]. \tag{9.108}$$

It is derived by directly solving $q = \mathrm{tr}(Q\rho_{\beta,\lambda})$ (for details of calculation, see Ref. [21]).

In illustrating the TUR, we choose an initial state so that it has significant coherence between $|ge\rangle$ and $|eg\rangle$ as

$$\rho_0 = \frac{e^{-\beta H}}{\mathrm{tr}(e^{-\beta H})} + \alpha \frac{e^{-\beta\hbar\omega}}{\mathrm{tr}(e^{-\beta H})}\xi \tag{9.109}$$

with $\xi = |ge\rangle\langle eg| + |eg\rangle\langle ge|$. To keep the positivity of ρ_0, $\alpha \in \mathbb{R}$ must satisfy $-1 < \alpha < 1$. We set $\alpha = -0.9$ and plot the time course of the EPR and the TUR bounds (9.79) for $\mathcal{O} = H$ and $\mathcal{O} = \xi$ in Fig. 9.4 with parameter values described in the caption.

In Fig. 9.4, EPR's time evolution shows that there are two regimes of relaxation. We can estimate that the earlier stage is the decay of coherence, and the latter is the usual thermalization. In fact, in the earlier step, the TUR bound for $X = \xi$ is much tighter than that for $X = H$, while H's bound gets closer to the EPR in the later step. Therefore, in the first stage, conflict with the "fluctuation" of ξ is more crucial for the EPR, and later, the TUR associated with the energy will be more important.

Chapter 10

Conclusion

Summary

We have revealed an underlying geometric framework of nonequilibrium thermodynamics, which we call the force-current structure, and shown its physical consequences, the housekeeping-excess decomposition and thermodynamic trade-off relations. We also confirmed that the general results are valid in several nonequilibrium systems. Let us review these results closely.

Part I

Part I was composed of five chapters. After the overall introduction in Chapter 1, we first reviewed the structure of the overdamped Langevin systems in Chapter 2. There, we explained that the Fokker–Planck equation can be written as a continuity equation and we can define the thermodynamic force. The thermodynamic force provides the entropy production rate (EPR) with the current, and the force and the current are connnected by a positive coefficient. This connection provides the EPR with a geometric experssion (2.24), which will later lead to a decomposition of EPR. We also showed that the conservativeness of thermodynamic forces defined by the gradient (differential operator) is consistent with the mechanical concept of conservativeness and implies detailed balance.

Chapter 3 generalized this structure, which we termed the force-current structure. It is composed of the three assumptions: the continuity-equation form of the equation of motion (3.1) (or (3.3)), the product form of the entropy production rate (3.7), and the positive relation between the thermodynamic force and the current (3.8). By using them, we provided the geometric expression of EPR (3.10) and the equivalence between conservativeness and detailed balance. The concrete forms of the abstact concepts discussed in this chapter are summarized in Table 10.1.

Applications of the framework follow: Chapter 4 discussed the geometric housekeeping-excess decomposition of EPR. We reviewed the literature by using the Langevin dynamics such as the conceptualization by Oono

Table 10.1: Key concepts of the force-current structure in various systems

	x	f^{rev}	∇	J	F	$\mathcal{M}$
Langevin dynamics (Ch. 2)	$P(\boldsymbol{X})$	None	$\boldsymbol{\nabla}$	$\boldsymbol{J}_P(\boldsymbol{X})$	$\boldsymbol{F}_P(\boldsymbol{X})$	$\mu T P(\boldsymbol{X})$
Markov jump processes (Ch. 6)	$\vec{p}$	None	B^{T}	$\vec{J}(\vec{p})$	$\vec{F}(\vec{p})$	$\mathsf{L}(\vec{p})$
Chemical reaction networks (Ch. 7)	$\vec{c}$	None	S^{T}	$\vec{J}(\vec{c})$	$\vec{F}(\vec{c})$	$\mathsf{L}(\vec{c})$
Hydrodynamic systems (Ch. 8)	$\rho\boldsymbol{v}$	$-\boldsymbol{\nabla}\cdot\mathbf{J}^{\mathrm{rev}}_{\rho,\boldsymbol{v}}$	$\boldsymbol{\nabla}$	$\mathbf{J}^{\mathrm{irr}}_{\rho,\boldsymbol{v}}$	$\mathbf{F}_{\rho,\boldsymbol{v}}$	$\Pi_\rho(\cdot)$
Open quantum systems (Ch. 9)	ρ	$-(i/\hbar)[H,\rho]$	$\nabla_{\mathbb{L}}$	$\mathbb{J}(\rho)$	$\mathbb{F}(\rho)$	$\mathcal{M}_{\Gamma\otimes\rho}(\cdot)$

and Paniconi, and concrete formulations, one by Hatano and Sasa and the other by Maes and Netočný. We then showed that the Maes–Netočný (MN) decomposition can be generally formulated as a geometric decomposition within the force-current structure given in the preceding chapter. The housekeeping EPR is defined as the dissipation due to the system's deviation from detailed balanced systems. The remainder, which defines the excess EPR, also provides the dissipation stemming purely from dynamical changes. They were provided in a geometrical manner. In addition to the mathematical conciseness, the geometric decomposition possesses more generality than the Hatano–Sasa (HS) decomposition, which is properly defined only systems that have stable steady states. It is applicable to several nonlinear systems, as explained in later chapters.

In Chapter 5, the last chapter of Part I, we derived two kinds of trade-off relations, thermodynamic trade-off relations (TURs) and thermodynamic speed limits (TSLs), from the force-current structure. A thermodynamic trade-off relation refers to a trade-off between reducing entropy production, the thermodynamic cost, and gaining other benefits (reducing other costs). In this thesis, we consider two costs, the short-time fluctuation of an observable, and the time required to change a system's state, corresponding to the TUR and the TSL respectively. We obtained a short-time variant of the TUR, by applying the Cauchy–Schwarz inequality to the geometric representation of the EPR and the excess EPR. The squared-norm representation is also useful in considering the TSLs, which employ the Wasserstein distance, a sophisticated distance measure developed in optimal transport thoery.

The force-current structure

Part II

Part II is a collection of concrete systems where the force-current structure and the accompanying results hold. It begins with Markov jump processess in Chapter 6. We presented the equation of motion, the master equation, as a continuity equation by using graph-theoretical notions. Thermodynamics is also introduced in a standard manner of stochastic theromdynamics. We completed the force-current structure by giving the Onsager operator with the logarithmic means between forward and backward probability fluxes. This chapter is based on Ref. [19].

Chapter 7 considers the force-current structure in chemical reaction networks (CRNs). Although a CRN is a nonlinear system, we revealed that it can be treated similarly to Markov jump processes by focusing on extended graph theoretical concepts. While we reviewed the thermodynamic structure of the ideal solutions, the force-current structure can encompass more general non-ideal CRNs. We note that CRNs are the first system where the geometric method is proved to give properly a decomposition of EPR while the HS decomposition breaks down. It was shown in our work [19].

The third example is hydrodynamic systems, in Chapter 8. We consider the compressible and incompressible Newtonian fluids described by the Navier–Stokes equation. We provided a standard derivation of the EPR and explained that they also fit to the force-current structure. We also proved the housekeeping EPR is equivalent to the minimum dissipation provided by Helmholtz in the nineteenth century when considering incompressible fluids. This chapter's results are first presented in Ref. [20].

Finally, in Chapter 9, we discussed Markovian open quantum systems. We introduced the force-current structure by using an auxiliary Hilbert space to open quantum systems described by the quantum master equation. While preceding work proposed other definitions of thermodynamic forces [24, 43], no further structural discussion was possible. It was in Ref. [21] where we revealed that the thermodynamic force and the current can be defined as anti-Hermitian operators to yield the force-current structure in open quantum systems.

Further perspective

We first consider further applicability of the force-current structure. It has already been applied to reaction-diffusion systems, CRNs with spatial degrees of freedom [30]. In this class of systems, the three requirements are fulfilled and the general consequences can be derived and applied to, for example, pattern formation.

Another possible subject is non-Newtonian fluids. In non-Newtonian fluids, the visocity coefficients can depend on the shear rate (the gradient of the velocity field), so the linear relation between force and current will not be guaranteed [142]. Still, we expect that a recently developed non-Euclidean geometric method similar to the force-current structure [59, 60] would be quite useful in analyzing this system.

In addition, removing the local equilibrium assumption is a challenging but intriguing direction. Currently, the force-current structure is always derived from some assumptions about local equilibrium. However, a recent study, called global thermodynamics, is trying to find a thermodynamic strcuture where the local equilibrium is critically violated [163, 164]. Although the counterpart of the equilibrium thermodynamics is still a subject of ongoing research, we could expect the dynamical theory we provided would be extended to such systems.

Moving away from the structural studies, some concepts could also attract practical interest. For example, the quantum diffusivity can be another interesting research subject. It was introduced naturally from the general result on TUR in Sec. 9.4. Although we have proved that it turns into the classical diffusivity in limited cases, it is still vague in what sense it represents fluctuations. As the diffusivity generally represents short-time fluctuations, we expect that the quantum diffusivity works as a reference point when considering long-time fluctuations.

Acknoledgment

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Appendix A

Introduction to optimal transport theory

In this appendix, we provide some basic results in optimal transport theory [48]. It deals with continuous or discrete distributions, such as probability distributions or concentration distributions. A distance is defined for the distributions, and the infinitesimal structure rewrites the equation of motion into a gradient flow equation. We do not give rigorous proof, so for details, see references such as [48] or [165]. My recent lecture note (written in japanese) would also help physisists understand further details of optimal transport from physical viewpoint [1].

A.1 Continuous systems

A.1.1 Definition

We first consider continuous systems like the Langevin systems discussed in Chapter 2. The *2-Wasserstein distance* is defined for two distributions P and Q by

$$\mathcal{W}(P,Q) \coloneqq \inf_{\Pi} \sqrt{\int\int |\boldsymbol{X}-\boldsymbol{Y}|^2 \Pi(\boldsymbol{X},\boldsymbol{Y}) dX dY}, \tag{A.1}$$

where Π has to satisfy

$$\Pi(\boldsymbol{X},\boldsymbol{Y}) \geq 0, \quad \int \Pi(\boldsymbol{X},\boldsymbol{Y}) dY = P(\boldsymbol{X}), \quad \int \Pi(\boldsymbol{X},\boldsymbol{Y}) dX = Q(\boldsymbol{Y}). \tag{A.2}$$

If Π satisfies this condition, it is called a coupling. The value $\Pi(\boldsymbol{X},\boldsymbol{Y})$ indicates how much mass is transported from $\boldsymbol{X}$ to $\boldsymbol{Y}$. Thus, we sum up over the destinations $\boldsymbol{Y}$, the sum should be the mass at the origin. Also, the final distribution should be accounted by the mass coming from all around the world.

The distance is given by regarding the squared distance $|\boldsymbol{X}-\boldsymbol{Y}|^2$ as the cost per transportation. The minimization is performed over all couplings. It is known that the optimal transportation always exists for the 2-Wasserstein distance [48]. We can choose another function as the transporation cost, such as $|\boldsymbol{X}-\boldsymbol{Y}|^r$ for $r \geq 1$.

A.1.2 Distance

In general, a function $d : X \times X \to \mathbb{R}$ is a distance if it satisfies the following conditions:

$$\begin{aligned}
&\text{1. Nonnegativity} && d(x,y) \geq 0, \\
&\text{2. Nondegeneracy} && d(x,y) = 0 \iff x = y, \\
&\text{3. Symmetry} && d(x,y) = d(y,x), \\
&\text{4. Triangle inequality} && d(x,y) + d(y,z) \geq d(x,z).
\end{aligned} \tag{A.3}$$

Let us confirm that the 2-Wasserstein distance satisfies these conditions.

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[1] Available here https://ykohei.com/files/OT.pdf (PDF).

The nonnegativity is obviously true. The symmetry is also immediately convinced after careful consideration.

The necessity ($\Leftarrow$) in the nondegeneracy is also obvious because if $P = Q$, then no transport is required. The sufficiency is derived as follows: $\mathscr{W}(P, Q) = 0$ indicates Π concentrates $\boldsymbol{X} = \boldsymbol{Y}$, so $\Pi(\boldsymbol{X}, \boldsymbol{Y}) = \pi(\boldsymbol{X})\delta(\boldsymbol{X} - \boldsymbol{Y})$ with some π. Then, we see

$$P(\boldsymbol{X}) = \int \Pi(\boldsymbol{X}, \boldsymbol{Y}) dY = \pi(\boldsymbol{X}), \quad Q(\boldsymbol{X}) = \int \Pi(\boldsymbol{X}, \boldsymbol{Y}) dX = \pi(\boldsymbol{Y}).$$

Therefore, $\mathscr{W}(P, Q) = 0$ implies $P = Q$.

The triangle inequality requires a little technical argument. It means that the following inequality holds for any probability P, Q, R:

$$\mathscr{W}(P, R) + \mathscr{W}(R, Q) \geq \mathscr{W}(P, Q). \tag{A.4}$$

Let Π_1 and Π_2 be the optimal couplings for $\mathscr{W}(P, R)$ and $\mathscr{W}(R, Q)$. Then, we can construct a coupling between P and Q by

$$\Pi_*(\boldsymbol{X}, \boldsymbol{Y}) = \int \frac{\Pi_1(\boldsymbol{X}, \boldsymbol{Z})\Pi_2(\boldsymbol{Z}, \boldsymbol{Y})}{R(\boldsymbol{Z})} dZ. \tag{A.5}$$

Then, by definition, we get

$$\mathscr{W}(P, Q) \leq \sqrt{\int |\boldsymbol{X} - \boldsymbol{Y}|^2 \Pi_*(\boldsymbol{X}, \boldsymbol{Y}) dX dY}.$$

Moreover, the triangle inequality for the Euclidean norm leads to

$$\begin{aligned}\int |\boldsymbol{X} - \boldsymbol{Y}|^2 \Pi_*(\boldsymbol{X}, \boldsymbol{Y}) dX dY &= \int |\boldsymbol{X} - \boldsymbol{Y}|^2 \frac{\Pi_1(\boldsymbol{X}, \boldsymbol{Z})\Pi_2(\boldsymbol{Z}, \boldsymbol{Y})}{R(\boldsymbol{Z})} dX dY dZ \\ &\leq \int (|\boldsymbol{X} - \boldsymbol{Z}| + |\boldsymbol{Z} - \boldsymbol{Y}|)^2 \frac{\Pi_1(\boldsymbol{X}, \boldsymbol{Z})\Pi_2(\boldsymbol{Z}, \boldsymbol{Y})}{R(\boldsymbol{Z})} dX dY dZ,\end{aligned}$$

where we substituted the definition of Π_*. From the Minkowski inequality, we obtain

$$\begin{aligned}&\sqrt{\int (|\boldsymbol{X} - \boldsymbol{Z}| + |\boldsymbol{Z} - \boldsymbol{Y}|)^2 \frac{\Pi_1(\boldsymbol{X}, \boldsymbol{Z})\Pi_2(\boldsymbol{Z}, \boldsymbol{Y})}{R(\boldsymbol{Z})} dX dY dZ} \\ &\leq \sqrt{\int |\boldsymbol{X} - \boldsymbol{Z}|^2 \frac{\Pi_1(\boldsymbol{X}, \boldsymbol{Z})\Pi_2(\boldsymbol{Z}, \boldsymbol{Y})}{R(\boldsymbol{Z})} dX dY dZ} + \sqrt{\int |\boldsymbol{Z} - \boldsymbol{Y}|^2 \frac{\Pi_1(\boldsymbol{X}, \boldsymbol{Z})\Pi_2(\boldsymbol{Z}, \boldsymbol{Y})}{R(\boldsymbol{Z})} dX dY dZ} \\ &= \sqrt{\int |\boldsymbol{X} - \boldsymbol{Z}|^2 \Pi_1(\boldsymbol{X}, \boldsymbol{Z}) dX dZ} + \sqrt{\int |\boldsymbol{Z} - \boldsymbol{Y}|^2 \Pi_2(\boldsymbol{Z}, \boldsymbol{Y}) dY dZ} = \mathscr{W}(P, R) + \mathscr{W}(R, Q),\end{aligned}$$

which finally leads to the triangle inequality.

A.1.3 Monge problem

Another formulation, called the Monge problem, helps us understand the Wasserstein as a transportation cost more intuitively [166]. It is given as

$$\begin{aligned}&\mathscr{W}_M(P, Q) := \inf_{\boldsymbol{T}} \sqrt{C(\boldsymbol{T})}, \\ &\text{with} \quad C(\boldsymbol{T}) := \int |\boldsymbol{X} - T(\boldsymbol{X})|^2 P(\boldsymbol{X}) dX,\end{aligned} \tag{A.6}$$

where $\boldsymbol{T}$ must satisfy

$$Q(\boldsymbol{Y}) = \int P(\boldsymbol{X})\delta(\boldsymbol{Y} - \boldsymbol{T}(\boldsymbol{X})) dX. \tag{A.7}$$

In the Monge problem, $Q(\boldsymbol{Y})$ is accounted by mass $P(\boldsymbol{X})$ of a few places $\boldsymbol{X}$ such that $\boldsymbol{Y} = \boldsymbol{T}(\boldsymbol{X})$. The map $\boldsymbol{T}$ is referred to as a transporation plan. For the 2-Wasserstein distance, if P and Q are not singular, the Monge problem provides the same value as the Wasserstein formulation and the optimal coupling Π is provided by the optimal transporation plan $\boldsymbol{T}$ as $\Pi(\boldsymbol{X}, \boldsymbol{Y}) = P(\boldsymbol{X})\delta(\boldsymbol{Y} - \boldsymbol{T}(\boldsymbol{X}))$ [48].

A.1.4 Benamou–Brenier formula

In addition, the 2-Wasserstein distance can be provided in a kinetic formula.

$$\mathcal{W}(P,Q) = \inf_{p,\boldsymbol{v}} \sqrt{\int_0^1 \int |\boldsymbol{v}(t,\boldsymbol{X})|^2 p(t,\boldsymbol{X}) dX dt}, \tag{A.8}$$

where p, $\boldsymbol{v}$ satisfies

$$p(0,\boldsymbol{X}) = P(\boldsymbol{X}), \quad p(1,\boldsymbol{Y}) = Q(\boldsymbol{Y}), \quad \frac{\partial p}{\partial t}(t,\boldsymbol{X}) = -\boldsymbol{\nabla} \cdot (p(t,\boldsymbol{X})\boldsymbol{v}(t,\boldsymbol{X})). \tag{A.9}$$

As mentioned in Sec. 5.1.3, this is called the Benamou–Brenier formula [48, 108, 165]. The time interval is now $[0,1]$, but it can be rescaled to $[0,\tau]$ $(\tau > 0)$ to yield

$$\mathcal{W}(P,Q) = \inf_{p,\boldsymbol{v}} \sqrt{\tau \int_0^\tau \int |\boldsymbol{v}(t,\boldsymbol{X})|^2 p(t,\boldsymbol{X}) dX dt}. \tag{A.10}$$

Moreover, the velocity field can be replaced by a potential gradient as

$$\mathcal{W}(P,Q) = \inf_{p,\psi} \sqrt{\tau \int_0^\tau \int |\boldsymbol{\nabla}\psi(t,\boldsymbol{X})|^2 p(t,\boldsymbol{X}) dX dt}, \tag{A.11}$$

where the third condition in Eq. (A.9) reads

$$\frac{\partial p}{\partial t}(t,\boldsymbol{X}) = \boldsymbol{\nabla} \cdot (p(t,\boldsymbol{X})\boldsymbol{\nabla}\psi(t,\boldsymbol{X})). \tag{A.12}$$

In fact, the potential that solves Eq. (A.12) is unique up to an additive constant. Intuitively, this is because $\boldsymbol{\nabla} \cdot (p\boldsymbol{\nabla})$ is a nonsingular operator if we neglect the freedom of an additive constant (i.e., the reference point of the potential). Given the unique solution ψ, every velocity field $\boldsymbol{v}$ that satisfies the continuity proves more costly: Let $\boldsymbol{w} \coloneqq \boldsymbol{v} - (-\boldsymbol{\nabla}\psi)$. Then,

$$\begin{aligned}
\int |\boldsymbol{v}|^2 p \, dX &= \int |\boldsymbol{w}|^2 p \, dX + \int |\boldsymbol{\nabla}\psi|^2 p \, dX - 2 \int p\boldsymbol{w} \cdot \boldsymbol{\nabla}\psi \, dX \\
&= \int |\boldsymbol{w}|^2 p \, dX + \int |\boldsymbol{\nabla}\psi|^2 p \, dX + 2 \int \boldsymbol{\nabla} \cdot (p\boldsymbol{w})\psi \, dX \\
&= \int |\boldsymbol{w}|^2 p \, dX + \int |\boldsymbol{\nabla}\psi|^2 p \, dX \geq \int |\boldsymbol{\nabla}\psi|^2 p \, dX,
\end{aligned}$$

where we omit the arguments, performed integration by parts in the second line, and used $\boldsymbol{\nabla} \cdot (p\boldsymbol{w}) = \boldsymbol{\nabla} \cdot (p\boldsymbol{v}) + \boldsymbol{\nabla} \cdot (p\boldsymbol{\nabla}\psi) = 0$ to get the last line.

A.1.5 Gradient flow

The Benamou–Brenier formula suggets that

$$\mathcal{W}(P, P + \dot{P}\Delta t)^2 = \Delta t^2 \int |\boldsymbol{\nabla}\psi(\boldsymbol{X})|^2 P(\boldsymbol{X}) dX \tag{A.13}$$

for a probability distribution P and a "time derivative" $\dot{P}$. Here, ψ is given as the unique solution to the equation

$$\dot{P}(\boldsymbol{X}) = \boldsymbol{\nabla} \cdot (P(\boldsymbol{X})\boldsymbol{\nabla}\psi(\boldsymbol{X})). \tag{A.14}$$

Considering in the opposite direction, we can define a local metric at P by

$$\|\dot{P}\|_P \coloneqq \sqrt{\int |\boldsymbol{\nabla}\psi(\boldsymbol{X})|^2 P(\boldsymbol{X}) dX} \tag{A.15}$$

with the potential ψ uniquely deteremined by P and $\dot{P}$. We can even define an inner product by

$$\langle \dot{P}, \dot{Q} \rangle_P = \int \nabla\psi(\boldsymbol{X}) \cdot \nabla\phi(\boldsymbol{X}) P(\boldsymbol{X}) dX, \tag{A.16}$$

where ϕ is given by P and $\dot{Q}$.

Given that geometry, we can define the Wasserstein gradient of a functional of probability distributions. Let $\mathcal{F}$ map a probability distribution to a real number. Then, we define the gradient by

$$\langle \operatorname{grad} \mathcal{F}, \dot{P} \rangle_P = \frac{d}{dt}\mathcal{F}(P_t)\big|_{t=0} \tag{A.17}$$

for any P_t such that $P_0 = P$ and $\partial P_t/\partial t|_{t=0} = \dot{P}$. For example, for the KL divergence from distribution Q,

$$\mathcal{F}_Q[P] = \int P(\boldsymbol{X}) \ln \frac{P(\boldsymbol{X})}{Q(\boldsymbol{X})} dX, \tag{A.18}$$

the gradient is obtained as

$$\operatorname{grad} \mathcal{F}_Q[P](\boldsymbol{X}) = -\nabla \cdot \left(P(\boldsymbol{X}) \nabla \ln \frac{P(\boldsymbol{X})}{Q(\boldsymbol{X})} \right) \tag{A.19}$$

because

$$\begin{aligned} \frac{d}{dt}\mathcal{F}_Q[P_t] = \int \frac{\partial P}{\partial t}(t, \boldsymbol{X}) \ln \frac{P(t, \boldsymbol{X})}{Q(\boldsymbol{X})} dX &= \int \nabla \cdot (P(t, \boldsymbol{X}) \nabla\psi(t, \boldsymbol{X})) \ln \frac{P(t, \boldsymbol{X})}{Q(\boldsymbol{X})} dX \\ &= -\int P(t, \boldsymbol{X}) \nabla\psi(t, \boldsymbol{X}) \cdot \nabla \ln \frac{P(t, \boldsymbol{X})}{Q(\boldsymbol{X})} dX. \end{aligned}$$

The Fokker–Planck equation (2.4) can be expressed as a gradient flow equation with the Wasserstein gradient. Here, we need to assume $D = 1$ and the mechanical force $\boldsymbol{f}$ is given by a potential U as $\boldsymbol{f} = -\nabla U$. Then, the Fokker–Planck equation reads

$$\frac{\partial P}{\partial t}(\boldsymbol{X}) = \nabla \cdot (\nabla(\beta U(\boldsymbol{X})) P(\boldsymbol{X})) + \nabla^2 P(\boldsymbol{X}), \tag{A.20}$$

where we omitted the time dependence. It can be further rewritten as

$$\frac{\partial P}{\partial t}(\boldsymbol{X}) = \nabla \cdot [P(\boldsymbol{X}) \nabla(\beta U(\boldsymbol{X}) + \ln P(\boldsymbol{X}))]. \tag{A.21}$$

On the other hand, by choosing $\pi(\boldsymbol{X})$ as

$$\pi(\boldsymbol{X}) = \frac{e^{-\beta U(\boldsymbol{X})}}{\int e^{-\beta U(\boldsymbol{X})} dX}, \tag{A.22}$$

we get

$$\operatorname{grad} \mathcal{F}_\pi[P](\boldsymbol{X}) = -\nabla \cdot (P(\boldsymbol{X}) \nabla(\beta U(\boldsymbol{X}) + \ln P(\boldsymbol{X}))). \tag{A.23}$$

Therefore, the Fokker–Planck equation is given as

$$\frac{\partial P}{\partial t}(\boldsymbol{X}) = -\operatorname{grad} \mathcal{F}_\pi[P](\boldsymbol{X}). \tag{A.24}$$

Since $\mathcal{F}_\pi[P]$ is strictly convex, it suggests the convergence to π.

If the diffusion coefficient D is not one, Eq. (A.24) is no longer valid. Still, we can resolve this problem by modifying the Wasserstein distance and the contiunity equation as

$$\mathcal{W}_D(P, Q) = \inf_{p, \psi} \sqrt{\tau \int_0^\tau \int |\nabla\psi(t, \boldsymbol{X})|^2 D p(t, \boldsymbol{X}) dX dt}, \tag{A.25}$$

$$\frac{\partial p}{\partial t}(t, \boldsymbol{X}) = \nabla \cdot (D p(t, \boldsymbol{X}) \nabla\psi(t, \boldsymbol{X})). \tag{A.26}$$

Then, we would recover Eq. (A.24) with modified geometry

$$\langle \dot{P}, \dot{Q} \rangle_{DP} = \int \boldsymbol{\nabla}\psi(\boldsymbol{X}) \cdot \boldsymbol{\nabla}\phi(\boldsymbol{X}) DP(\boldsymbol{X}) dX, \tag{A.27}$$

where ψ and ϕ are determined from $\dot{P} = \boldsymbol{\nabla} \cdot (DP\boldsymbol{\nabla}\psi)$ and $\dot{Q} = \boldsymbol{\nabla} \cdot (DP\boldsymbol{\nabla}\phi)$. For this metric, the gradient of the KL divergence reads

$$\mathrm{grad}_D\, \mathcal{F}_Q[P](\boldsymbol{X}) = -\boldsymbol{\nabla} \cdot \left(DP(\boldsymbol{X}) \boldsymbol{\nabla} \ln \frac{P(\boldsymbol{X})}{Q(\boldsymbol{X})} \right), \tag{A.28}$$

where grad_D indicates that we used the metric that depends on D. Then, the Fokker–Planck equation with a conservative mechanical force will read

$$\frac{\partial P}{\partial t}(\boldsymbol{X}) = -\,\mathrm{grad}_D\, \mathcal{F}_\pi[P](\boldsymbol{X}). \tag{A.29}$$

A.2 Extension to discrete systems

For simplicity, we set $k_\mathrm{B} = 1$ and $R = 1$ in this section.

A mathematical analogues of the Benamou–Brenier formula (A.25) was proposed by mathematicians aiming to express the classical master equation (6.7) as a Wasserstein gradient flow equation [109]. From the physical point of view, it is provided as

$$\mathcal{W}_{\mathsf{L}}(\vec{p}, \vec{q}) = \inf_{\vec{\rho}, \vec{\psi}} \sqrt{\tau \int_0^\tau \|\nabla \vec{\psi}(t)\|^2_{\rho(t)} dt}, \tag{A.30}$$

with the conditions

$$\vec{\rho}(0) = \vec{p}, \quad \vec{\rho}(\tau) = \vec{q}, \quad \frac{d\vec{p}}{dt} = -\nabla^\mathsf{T} \mathsf{L}(\vec{\rho}(t)) \nabla \vec{\psi}(t). \tag{A.31}$$

For notational details, see Chapter 6. From the correspondence between $\mathsf{L}(\vec{p})$ and $DP(\boldsymbol{X})$ discussed in Sec. 6.3.3, it is clear that Eq. (A.30) generalizes Eq. (A.25). Moreover, the normalization is not an essential constraint; we can define the distance also for CRNs by just regarding ∇ in Eq. (A.30) as the transpose of the stoichiometric matrix [19, 110].

The proof of the triangle inequality for these quantity is rather technical and lengthy. It is provided in the original paper [109], which assumes the detailed balance, and our paper [19], not assuming it.

A.2.1 Gradient flow

Similarly to the continuous case, the Wasserstein-like distance yields an inner product between "time derivatives" $\dot{\vec{p}}$ and $\dot{\vec{q}}$ at a probability distribution p by

$$\langle\!\langle \dot{\vec{p}}, \dot{\vec{q}} \rangle\!\rangle_p := \langle \nabla\psi, \nabla\phi \rangle_p \equiv \vec{\psi}^\mathsf{T} \nabla^\mathsf{T} \mathsf{L}(\vec{p}) \nabla \vec{\phi}, \tag{A.32}$$

where $\vec{\psi}$ and $\vec{\phi}$ are obtained by solving $\dot{\vec{p}} = -\nabla^\mathsf{T} \mathsf{L}(\vec{p}) \nabla \vec{\psi}$ and $\dot{\vec{q}} = -\nabla^\mathsf{T} \mathsf{L}(\vec{p}) \nabla \vec{\phi}$. The gradient of the KL divergence,

$$\mathcal{F}_{\vec{q}}[\vec{p}] = \sum_i p_i \ln \frac{p_i}{q_i}, \tag{A.33}$$

is given by

$$\mathrm{grad}\, \mathcal{F}_{\vec{q}}[\vec{p}] = \nabla^\mathsf{T} \mathsf{L}(\vec{p}) \nabla (\ln \vec{p} - \ln \vec{q}) \tag{A.34}$$

in the same way as Eq. (A.28). If the system is detailed balanced, i.e.,

$$\ln \frac{R_e}{R_{-e}} = \beta(\epsilon_{s(e)} - \epsilon_{t(e)}) \tag{A.35}$$

holds, the master equation will be

$$\frac{d\vec{p}}{dt} = -\operatorname{grad}\mathcal{F}_{\vec{p}^{\mathrm{eq}}}[\vec{p}], \tag{A.36}$$

where $p_i^{\mathrm{eq}} \propto e^{-\beta\epsilon_i}$. This is proved as follows: first, note that

$$-\operatorname{grad}\mathcal{F}_{\vec{p}^{\mathrm{eq}}}[\vec{p}] = -\nabla^{\mathrm{T}}\mathsf{L}(\vec{p})\nabla(\ln\vec{p} + \beta\vec{\epsilon})$$

and

$$F_e(\vec{p}) = \ln\frac{R_e p_{s(e)}}{R_{-e}p_{t(e)}} = -[\nabla^{\mathrm{T}}(\ln\vec{p} + \beta\vec{\epsilon})]_e.$$

Therefore, we find

$$-\big[\operatorname{grad}\mathcal{F}_{\vec{p}^{\mathrm{eq}}}[\vec{p}]\big]_i = -\sum_e \nabla_{ei}\frac{J_e(\vec{p})}{F_e(\vec{p})}\big(-F_e(\vec{p})\big) = [\nabla^{\mathrm{T}}\vec{J}(\vec{p})]_i.$$

Similarly, the rate equation (7.12) is given as a Wasserstein gradient flow equation when the detailed balance and the mass action kinetics are assumed [19, 110]. This time, we need to use the generalized KL divergence

$$\mathcal{F}_{\vec{c}'}[\vec{c}] = \sum_\alpha \left(c_\alpha \ln\frac{c_\alpha}{c'_\alpha} - c_\alpha + c'_\alpha\right) \tag{A.37}$$

instead of the KL divergence.

A.2.2 Remark

Although this distance function is difficult to give a transportational meaning such as the Monge problem after all, it reproduces differential geometric properties of the original Wasserstein distance very well [167–169]. It includes some universal inequalities involving the curvature and the convergence speed [48], which can be useful for nonequilibrium thermodynamics [170]. Reference [171] is the only application to nonequilibrium thermodynamics that we could find. The paper provides a lower bound on the EPR by using the so-called logarithmic Sobolev constant, which has much to do with the geometry introduced by the Wasserstein distance [48].

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