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Naoto Shiraishi

An Introduction to Stochastic Thermodynamics

From Basic to Advanced

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Preface

In the past three decades, the field of stochastic thermodynamics has been formulated and highly developed. Stochastic thermodynamics extends the framework of thermodynamics, which is aimed to macroscopic objects, to small fluctuating systems including Brownian particles in the laser trap and molecular motors in living systems. Improvements in experiments enable us to control these small systems accurately, which have pushed further developments of stochastic thermodynamics.

In conventional thermodynamics for macroscopic systems, the entropy is a key quantity, which characterizes the irreversibility of processes. Several relations on entropy and other related quantities are proved in the form of inequalities, such as the second law of thermodynamics. In stochastic thermodynamics, we define entropy production, which characterizes the irreversibility of processes in small systems. Unlike conventional thermodynamics, entropy production satisfies not only inequalities but also equalities in highly nonequilibrium conditions. Celebrated examples are the fluctuation theorem and the Jarzynski equality, taking an impressive exponential forms. These equalities revealed a hidden symmetric structure of entropy, which sheds new light on thermodynamic irreversibility.

Moreover, novel inequalities tighter bounds than the second law of thermodynamics have also been discovered in stochastic thermodynamics. These inequalities supply fresh views on thermodynamic irreversibility in that fundamental thermodynamic constraints exist beyond the second law. In most inequalities, thermodynamic irreversibility is connected to a kind of speed of processes, which is usually out of the scope of conventional thermodynamics.

This textbook aims to provide a comprehensive view of stochastic thermodynamics developed in the last three decades. Important research topics in stochastic thermodynamics including the fluctuation theorem, information thermodynamics, and the thermodynamic uncertainty relation are explained by devoting one or more chapters. This textbook also covers a variety of important universal relations in stochastic thermodynamics, ranging from the stochastic efficiency, waiting time statistics, the Hatano-Sasa relation, the Harada-Sasa relation, to Brownian motors and flashing ratchet, autonomous free energy transducers, efficiency at maximum power, and speed limit inequalities.

Readers are assumed to be familiar with conventional thermodynamics and basic linear algebra, whereas other additional knowledge is not necessary. This textbook is written in a self-contained manner, and we do not require any knowledge on information theory and stochastic processes.

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Chapter 1
Background

1.1 Aims of Stochastic Thermodynamics

Stochastic thermodynamics is an extended form of thermodynamics to small fluctuating systems such as Brownian particles, molecular motors in living systems, and mesoscopic quantum dots. With this framework, novel relations, including the celebrated fluctuation theorem and related relations [1–6] have been discovered, which reveal a hidden symmetric structure of thermodynamic irreversibility in nonequilibrium fluctuations. In the last two decades, stochastic thermodynamics has attracted the interest of many physicists.

Besides them, one basic but important achievement of stochastic thermodynamics is to establish how to define thermodynamic quantities (e.g., heat, work, and entropy) in stochastic fluctuating systems and what relations (e.g., the first and the second law of thermodynamics) hold among them. This is a highly nontrivial task from the standpoint of conventional macroscopic thermodynamics and statistical mechanics. In fact, not so long ago, some people even consider that small stochastic systems may escape from the restriction of conventional macroscopic thermodynamics[1], which can also be seen in many proposals of the perpetual motion machines of the second type. This skeptical view is refuted by the above development of formulations.

We here summarize the significant motivation of stochastic thermodynamics, which is mainly divided into two roots.

The first is based on experimental observations of small fluctuating systems, from biochemical systems to quantum mesoscopic systems. We here take molecular motors in biological systems as prominent examples. From the viewpoint of thermodynamics and statistical mechanics, molecular motors can be regarded as engines converting the chemical potential of resources such as ATP to mechanical force. However, molecular motors apparently differ from conventional heat engines in many aspects: Molecular motors are so small that thermal fluctuation affects them, which sometimes disturbs

[1] For example, Feyerabend [7] states that the Brownian particle can violate the second law of thermodynamics.

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and sometimes helps their motion. This shows clear contrast to conventional heat engines, which do not fluctuate. In addition, molecular motors work autonomously under fluctuation, whereas conventional heat engines are operated externally and deterministically. Interestingly, careful experiments have revealed high efficiency of many molecular motors as F1-ATPase [8, 9], kinesins[2] [11], and myosins [12] compared to our power plants[3]. Therefore, why and how molecular motors achieve high efficiency and what is the significant difference of molecular motors from conventional heat engines are important questions in nonequilibrium statistical mechanics.

The second is motivated by a theoretical interest to understand what structures or fundamental relations exist. One of the central problems in nonequilibrium statistical mechanics is the foundation of thermodynamic irreversibility from a microscopic viewpoint. The problem of how the arrow of time appears from microscopic reversible dynamics[4] has been debated since Boltzmann. Aside from this, several relations in nonequilibrium statistical mechanics rely on both thermodynamics and microscopic dynamics. For example, the fluctuation-dissipation relation was first derived by using the consistency with the second law of thermodynamics [13] and later derived from microscopic dynamics [14, 15]. The original derivation of the Onsager reciprocity theorem [16] employed the combination of thermodynamic phenomenology and reversibility of microscopic dynamics. Although all of these relations are well established, it is a fruitful task to clarify what aspects of thermodynamics and nonequilibrium statistical mechanics are reflected in these relations, which will also help us unveil novel relations. Discovering universal relations in nonequilibriums systems is also important. Unlike equilibrium and near-equilibrium systems, few relations are known in nonequilibrium systems. If we succeed in clarifying universal relations, they might offer clues for the comprehensive characterization of nonequilibrium dynamics, which is an ultimate goal of nonequilibrium statistical physics.

Stochastic thermodynamics has answered these two questions, at least partially.

Regarding the first set of questions, stochastic thermodynamics and stochastic energetics are formulated as a thermodynamic framework for small stochastic systems, ensuring that molecular motors are not different from conventional heat engines from this aspect. In addition, many ratchet models [17] confirm that the unidirectional motion of molecular motors in a stochastic environment is not a surprising phenomenon.

Some researchers, including biophysicists, argued that the specialty of molecular motors is seen in the use of information [18]. Molecular motors consist of several subsystems, and experimental observations [18] suggest that one of the subsystems behaves as if it measures another subsystem and changes its motion depending on the measurement outcome, which is a kind of information processes[5]. This interpre-

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[2] We, however, note that some recent experiments on kinesins reported that the efficiency of kinesins is not so high [10].

[3] The efficiencies of some molecular motors are around 0.7–0.9, whereas those of power plants are usually less than 0.5.

[4] Both Hamilton dynamics and unitary evolution are reversible.

[5] In the case of F1-ATPase, the $\alpha^3\beta^3$ unit surrounds the γ shaft. The $\alpha^3\beta^3$ unit has three main stable states, playing as three different potential landscapes of the γ shaft. The experiment [18]

tation meets the intuitive picture that molecular motors work by harnessing thermal fluctuation. Information thermodynamics serves as a stage to analyze the connection between information and thermodynamic quantities.

Autonomy is also the characteristic of molecular motors, which shows a sharp contrast to conventional externally-controlled engines. Since quasistatic controls cannot be realized in autonomous conditions, the achievability of the Carnot efficiency is nontrivial. Recent studies have revealed the conditions for autonomous systems to achieve the Carnot efficiency.

In addition, recent progress in stochastic thermodynamics elucidate several trade-offs between entropy production and some quantities, including the speed of operations and current fluctuations. These inequalities enable us to define a novel type of efficiency, which may serve as guiding principles of molecular motors in their history of evolution.

Regarding the second set of questions, various universal relations have been derived. In particular, the fluctuation theorem provides a clear understanding of thermodynamic irreversibility. It sheds new light on the importance of time-reversal symmetry and microscopic reversibility. Various relations on entropy production in fact rephrase this symmetry. In addition, known macroscopic laws in thermodynamics and nonequilibrium statistical mechanics, including the second law of thermodynamics, the fluctuation-dissipation theorem, and the Onsager reciprocity theorem, are reproduced by the fluctuation theorem.

It is well known that the second law of thermodynamics and other thermodynamic relations are violated if a process accompanies information processing, which is called the Maxwell's demon problem. Information thermodynamics establishes how to construct a thermodynamic framework for a single subsystem with information processes by introducing the mutual information. From a more abstract viewpoint, information thermodynamics pushes the idea of additive decomposition of entropy production, where we decompose the total entropy production into each small component which individually satisfies thermodynamic relations.

Recently, a number of inequalities, not equalities, have been proposed in stochastic thermodynamics. These inequalities suggest that entropy production also plays the role of the fundamental limitation of the speed of operations in systems. The notion of speed is not fully captured in conventional thermodynamics. The modern framework of stochastic thermodynamics connects two important concepts, the speed of dynamics and the thermodynamic irreversibility.

1.2 Overview of This Textbook

This textbook consists of four parts. Part I is devoted to mathematical foundations and definitions of basic quantities in stochastic thermodynamics. We introduce stochastic

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reports that the $\alpha^3\beta^3$ unit changes its state as if it measured the state of the γ shaft and performs feedback control depending on the measurement outcome.

processes both on discrete states and in continuous space (Langevin systems). In addition to this, we describe how to define thermodynamic quantities (heat, work, and entropy) in small stochastic systems.

In Part II, we present various equalities in stochastic thermodynamics. The most important one is the fluctuation theorem, which unveils an unexpected symmetry in nonequilibrium fluctuations. In fact, most of the equalities shown in stochastic thermodynamic can be regarded as variants of the fluctuation theorem. Another important achievement is information thermodynamics, which combines information theory and stochastic thermodynamics. With this framework, we can analyze the role of information in thermodynamic processes with measurement and feedback operations. In particular, we solve the problem of Maxwell's demon with this framework.

Part III is an exceptional part, where we mainly treat concrete toy models, not universal relations. One-directional transports by external operations and autonomous free energy transducers are two main subjects in this part. We first present numerous toy models showing interesting behaviors, and then seek the general principles behind them.

In Part IV, we present various inequalities in stochastic thermodynamics. One important inequality shown in this part is the thermodynamic uncertainty relation, which connects entropy production and fluctuation around nonequilibrium stationary states. Other inequalities mainly concern the relationship between the entropy production and the speed of dynamics, which elucidates a novel aspect of thermodynamic irreversibility.

1.2.1 Overview of Part I

In Part I, we prepare mathematical tools and explain the basic framework of stochastic thermodynamics. Readers who are familiar with Markov processes, the local detailed-balance condition, and definitions of quantities in stochastic thermodynamics can start from Part II without reading this part.

In Chap. 2, we introduce Markov processes and Markov jump processes on discrete states. In stochastic systems, our main interest is in the probability distribution $\boldsymbol{p}$ on microscopic discrete states, which evolves according to master equation.

$$\frac{d}{dt}\boldsymbol{p}(t) = R\boldsymbol{p}(t),$$

where R is the transition matrix. With some reasonable assumptions on R, the stationary distribution $\boldsymbol{p}^{\mathrm{ss}}$ satisfying $\frac{d}{dt}\boldsymbol{p}^{\mathrm{ss}} = R\boldsymbol{p}^{\mathrm{ss}} = \mathbf{0}$ uniquely exists, and any initial distribution converges to this stationary distribution. We shall prove these results in Sect. 2.3.

We then review the framework of stochastic thermodynamics on discrete states in Chap. 3. We first introduce the Shannon entropy and the stochastic entropy (surprisal) in Sect. 3.1, and then define the heat, work, and entropy production in stochastic systems. The entropy production σ is the most important quantity in stochastic thermodynamics, which quantifies the degree of thermodynamic irreversibility of processes. At the same time, we introduce key ideas; the time-reversal symmetry in equilibrium states and the (local) detailed-balance condition, which are employed in the characterization of heat. At the end of this chapter (Sect. 3.4), we clarify the differences between conventional thermodynamics and stochastic thermodynamics.

In Chap. 4, we treat stochastic processes and stochastic thermodynamics in continuous space. Note that this textbook mainly treats discrete systems and continuous systems appear only in Chap. 11, Sects. 12.1, 17.4.1, and 18.2. Therefore, readers who do not plan to read these sections can skip this chapter.

Unlike the case with discrete states, stochastic processes in continuous space require various careful treatments. A continuous stochastic variable $\hat{x}$ evolves according to the following form of a stochastic differential equation (a general form of Langevin equations):

$$\frac{d\hat{x}}{dt} = a(\hat{x}(t), t) + b(\hat{x}(t), t)\hat{\xi}(t),$$

where $\hat{\xi}(t)$ is the white Gaussian noise satisfying $\langle \hat{\xi}(t) \rangle = 0$ and $\langle \hat{\xi}(t)\hat{\xi}(t') \rangle = \delta(t - t')$. The problem lies in the rule of the product of $b(\hat{x}(t), t)$ and $\hat{\xi}(t)$. In Sect. 4.1.2, we introduce two important rules of products, the Itô product and the Stratonovich product, and explain how the rule of products affects stochastic dynamics. We also introduce the corresponding Fokker-Planck equation, which describes the time evolution of the probability distribution $P(x, t)$. The problem of the rule of products appears in the definition of heat in Langevin systems. As shown in Sect. 4.3, the definition of heat must employ the Stratonovich product to satisfy the first law of thermodynamics. In Sect. 4.6, we demonstrate how to discretize stochastic processes in continuous space into those on discrete states, which allows us to reproduce the results in discrete systems to continuous systems.

1.2.2 Overview of Part II

In Part II, we present various equalities in stochastic thermodynamics. Two important achievements, the fluctuation theorem and the information thermodynamics, are presented in this part.

We introduce and prove the fluctuation theorem and the Jarzynski equality in Chap. 5. The integral fluctuation theorem (IFT) is expressed as

$$\left\langle e^{-\hat{\sigma}} \right\rangle = 1,$$

where $\hat{\sigma}$ is the entropy production and $\langle\cdot\rangle$ represents the ensemble average. Notably, this equality holds in general nonequilibrium processes far from equilibrium. One big advantage of the fluctuation theorem is that it can reproduce known relations in nonequilibrium statistical mechanics. We derive the second law of thermodynamics (Sect. 6.1), the fluctuation-dissipation theorem (Sect. 6.2), and the Onsager reciprocity theorem (Sect. 6.3) from the fluctuation theorem. Not only reproducing existing relations, the fluctuation theorem also produces novel relations. We derive a higher-order fluctuation-dissipation theorem in Sect. 6.2.3. We note that the connection between the IFT and the fluctuation-dissipation theorem can be extended to IFT-type equalities. We present some extensions of the fluctuation-dissipation theorem to nonequilibrium stationary states in Sect. 10.1.

The form of the IFT now becomes a standard form to manifest the existence of a thermodynamic structure because we can withdraw various thermodynamic relations from IFT-type equalities, as mentioned above. We present some important IFT-type equalities in Chap. 7. In Sect. 7.1, we explain a generalized form of the fluctuation theorem, the Hatano-Sasa relation, which serves as a pioneering work for steady state thermodynamics. In Sect. 7.2, we treat systems with coarse-graining of quick variables. While the entropy production is preserved through coarse-graining in equilibrium cases, it generally decreases in nonequilibrium cases. This decrease is characterized by an IFT-type equality.

The fluctuation theorem reflects a hidden symmetric property of entropy production. This symmetric property takes various forms and appears in various situations besides the IFT, which is the subject of Chap. 8. In Sect. 8.2, we see this symmetry in the cumulant generating function. In Sect. 8.3, we consider waiting time statistics of entropy production. In particular, we show that the stochastic variable $e^{-\hat{\sigma}}$ is a martingale in stationary systems. In Sect. 8.3, we introduce stochastic efficiency and show that the least probable stochastic efficiency is the Carnot efficiency. This fact is shown by combining a geometric interpretation of stochastic entropy and the fluctuation theorem.

Chapter 9 is devoted to another important achievement in stochastic thermodynamics, the information thermodynamics. We start from the problem of Maxwell's demon. We review the arguments of Maxwell, Szilard, Brillouin, Landauer, and Bennett in Sect. 9.1. Although some papers and books state that the memory erasure is crucial to understanding Maxwell's demon, we show that this argument is somewhat secondary (which is discussed in Sect. 9.2.3). To clarify this point, we need to formulate the information thermodynamics. We introduce the Sagawa-Ueda relation (Sect. 9.3)

$$\left\langle e^{-\hat{\sigma}+\Delta\hat{I}}\right\rangle = 1,$$

where $\Delta\hat{I}$ is the change in the mutual information between the system of interest and another system (e.g., a memory). Accordingly, we obtain the generalized second law: $\sigma \geq \Delta I$. The Sagawa-Ueda relation reveals that if the exchange in mutual information exists between the system and another system, thermodynamic relations must be modified.

The information thermodynamics is expected to capture the informational aspect of biological systems, including molecular motors. However, the Sagawa-Ueda relation applies only systems with external controls, and autonomous systems such as biological ones are out of the scope. To overcome this problem, we present two extensions of the information thermodynamics to cover general information processes. In Sect. 9.5, we introduce the *partial entropy production* which is a decomposition of entropy production $\hat{\sigma}$ into each possible transition. Notably, the partial entropy production also satisfies an IFT-type equality. Applying this idea to composite systems, we find a generalization of the Sagawa-Ueda relation for general information processes. In Sect. 9.6, we present another type of generalization; relations on causal networks. We introduce the transfer entropy, which is a kind of conditional mutual information, and using this, we show the Ito-Sagawa relation.

In Chap. 10, we investigate relations on response functions around nonequilibrium stationary states. From vast literature seeking the extension of the fluctuation-response relation to nonequilibrium stationary states, we pick up results around nonequilibrium stalling states. In Sect. 10.1, we show that the fluctuation-response relation holds around nonequilibrium stalling states in the same form as the conventional one. As another topic, in Sect. 10.2, we derive some equalities and inequalities on the response of the stationary distribution.

Chapter 11 is an exceptional chapter, where we treat overdamped Langevin systems, not Markov jump processes on discrete states. Thanks to the Gaussian property, we can compute the path probability of overdamped Langevin systems $P(\Gamma)$ in a simple form, which is called the Onsager-Machlup functional (Sect. 11.1.1). Using this expression, in Sect. 11.1.3 we derive the Harada-Sasa relation, which claims that the violation of the fluctuation response relation in the nonequilibrium stationary state is directly related to the stationary heat dissipation. The Harada-Sasa relation is useful in experiments since the stationary heat dissipation is not easy to observe experimentally whereas both the fluctuation and response are measurable. We also present explicit forms of the stationary distribution, the diffusion coefficient, and the mobility in one-dimensional overdamped Langevin systems by employing the techniques of the cumulant generating function (Sect. 11.2).

1.2.3 Overview of Part III

Part. III is an intermission, where we introduce various interesting models. Unlike other parts, most of the arguments in this part (except Sect. 14.4) are model-dependent and not universal.

The subject of Chap. 12 is one-directional transport by external driving. The Curie principle states that if the driving is symmetric, we cannot induce asymmetric, one-directional transport. However, the converse is not always true: some asymmetric driving cannot induce one-directional transport. We first introduce a flashing ratchet, which is a simple model of one-directional transport by switching potential. We then examine the possibility of reversible one-directional transport. One stimulating model, the hidden pump model, realizes (apparently) reversible one-directional transport with finite speed.

In Chap. 13, we see the fact that deciding the direction of transport is not an easy task. We first consider a simple model of Brownian motors in Sect. 13.1. We construct a composite system by rigidly connecting a rectangle object and a wedge-shaped object in baths with different temperatures. This composite object moves steadily in one direction, accompanying heat flow from hot to cold. This model reproduces the adiabatic piston as its limiting case. We present a heuristic and qualitative (partially semi-quantitative) argument to determine the direction of the movement of the composite object. In addition, in Sect. 13.2, a strange composite system called Parrondo's game is analyzed. In this game (system), two subsystems realize transport in the same direction, whereas their composite system realizes transport in the opposite direction.

The subject of Chap. 14 is the behavior of autonomous free energy transducer (stationary cross-transport) from the aspect of maximum efficiency with finite temperature difference (or finite chemical potential difference). We first examine two famous models, Feynman's ratchet and the Büttiker-Landauer model, which convert heat flow to work (Sect. 14.1). Although these models are sometimes claimed to achieve the Carnot efficiency in the quasistatic limits, we show that these models in fact fail to achieve the Carnot efficiency even in the quasistatic limit. The difficulty for autonomous systems to achieve the Carnot efficiency lies in the fact that all variables in autonomous engines inevitably fluctuate, which may cause undesired heat leakage leading and the suppression of efficiency. The attainability of the Carnot efficiency is not expected of all autonomous engines, and in fact we reveal that autonomous engines attain the Carnot efficiency only by satisfying severe conditions. In Sect. 14.2 we briefly review some small autonomous models which attain the Carnot efficiency. In Sect. 14.3 we introduce a model of a macroscopic autonomous engine converting chemical potential difference into mechanical work, whose efficiency is less than the Carnot efficiency in moderate setups, but reaches the Carnot efficiency with singular transition rates. In Sect. 14.4, we derive a general necessary condition for autonomous engines to attain the Carnot efficiency. We show that a certain type of singularity is inevitable to attain the Carnot efficiency, as suggested in the previous section. We then clarify the difference between autonomous engines with finite size and that in the thermodynamic limit by introducing the viewpoint of nonlinear tight-coupling window.

1.2.4 Overview of Part IV

In Part IV, we present various inequalities in stochastic thermodynamics. Particularly important results in this part are the thermodynamic uncertainty relation and some inequalities manifesting the trade-off between the entropy production and the speed of dynamics.

Three chapters, Chaps. 15, 16, and 18, are devoted to investigating the relationship between the entropy production (or related quantities) and the speed of processes (or related quantities) from different perspectives. In Chap. 15, we consider the efficiency at maximum power, which is known to be bounded by the half of the Carnot efficiency in the linear response regime. We derive this result in three different setups, endoreversible thermodynamics, linear irreversible thermodynamics for stationary systems, and a linear expansion of velocity.

In Chap. 16, we prove the trade-off relation between power and efficiency. It is plausible to expect that an engine with large power inevitably accompanies much dissipation, which implies less efficiency. In particular, a heat engine at the Carnot efficiency is expected to have zero power. However, conventional frameworks, thermodynamics and linear irreversible thermodynamics, do not formally prohibit the coexistence of finite power and the Carnot efficiency. To resolve this controversy, we employ the framework of stochastic thermodynamics. In Sect. 16.2, we first derive a trade-off relation between heat current and entropy production $|J^{\mathrm{q}}| \leq \sqrt{\Theta\dot{\sigma}}$ with a coefficient Θ, and applying it we obtain a trade-off inequality between power and efficiency:

$$\frac{W}{\tau} \leq \bar{\Theta}\beta_{\mathrm{L}}\eta(\eta_{\mathrm{C}} - \eta),$$

where $\bar{\Theta}$ is a coefficient (time-average of Θ), β_{L} is the inverse temperature of the cold bath, and η_{C} is the Carnot efficiency. This inequality clearly shows that an engine with high efficiency has lower maximum power, and in particular an engine at the Carnot efficiency has zero power.

In Chap. 17, we present an important inequality in stochastic thermodynamics, the thermodynamic uncertainty relation. The thermodynamic uncertainty relation claims that the entropy production in stationary systems is bounded by any relative fluctuation of current as

$$\frac{\mathrm{Var}(\mathcal{J}_d)}{(\mathcal{J}_d^{\mathrm{ss}})^2}\sigma \geq 2,$$

where $\mathcal{J}_d$ is a cumulative current and $\mathrm{Var}(\cdot)$ represents the variance. The thermodynamic uncertainty relation is now understood as a special case of the generalized Cramèr-rao inequality. We present its proof with this approach in Sect. 17.1.2. Extensions of the thermodynamic uncertainty relation and its optimality are discussed in Sect. 17.2.

We consider speed limit inequalities for classical stochastic systems in Chap. 18. The speed limit inequality is a trade-off relation between the time length of the process (i.e., the speed) and some quantity, which is regarded as the cost of quick state transformation. In the case of both overdamped Langevin systems (Sect. 18.2) and Markov jump processes on discrete states (Sect. 18.3), we find that the entropy production bounds the speed of state transformation. The latter speed limit inequality is expressed as

$$\frac{L(\boldsymbol{p}(0), \boldsymbol{p}(\tau))^2}{2\sigma\overline{A}_\tau} \leq \tau,$$

where $L(\boldsymbol{p}, \boldsymbol{p}')$ is a distance between two probability distributions, A is the activity (average number of jumps), and τ is the time length of the state transformation. Both this chapter and Chap. 16 show that the entropy production, which is a quantifier of thermodynamic irreversibility, is also essential in the argument of the maximum speed of dynamics.

In the final chapter (Chap. 19), we look at variational aspects of entropy production. Variational relations play the role of both equality and inequality: A variational relation is an inequality, and its equality is achievable. We show three variatinoal aspects of entropy production.

1.2.5 How to Read This Textbook?

For readers interested only in Markov jump processes, a course with Chaps. 2 and 3 (basics), Chaps. 5 and 6 (fluctuation theorem), Sect. 7.1 (Hatano-Sasa relation), Sects. 9.2 and 9.3 (basics of information thermodynamics; Sagawa-Ueda relation), Sects. 16.2 and 16.3 (trade-off relation between efficiency and power), Sects. 17.1 and 17.2 (thermodynamic uncertainty relation), Sect. 18.3 (classical speed limit inequality) will provide concise but sound learning. Advanced readers are invited to further reading of Sect. 7.2 (entropy production under coarse-graining), Sect. 8.3 (waiting-time statistics), Sect. 8.4 (stochastic efficiency), Sect. 9.5 (information thermodynamics for general information processes), Sect. 9.6 (Ito-Sagawa relation), Sect. 10.1.1 (fluctuation-dissipation theorem at nonequilibrium stalling state), Sect. 13.1 (Brownian motors), Chap. 15 (efficiency at maximum power), Sects. 19.1 and 19.2 (variational expression of entropy production rate and excess entropy production rate), depending on their interests.

For readers interested in Langevin systems, a short course with Chap.4 (stochastic processes and stochastic thermodynamics in continuous space), Chap. 11 (various results in Langevin systems, which includes the fluctuation theorem), and Sect. 18.2 (a speed limit inequality for Langevin systems) will serve as a brief overview of Langevin systems.

We here classify results in this textbook as with or without the local detailed-balance condition: The following results are proven without requiring the local detailed-balance condition:

- The fluctuation theorem (5.14).
- The Hatano-Sasa relation (7.10).
- The IFT-type equality for hidden entropy production[6] (7.39).
- The Sagawa-Ueda relation (9.28).
- The IFT-type equality for partial entropy production (9.61).
- The trade-off inequality between efficiency and power (16.65).
- The classical speed limit inequality (18.34).

[6] This relation, however, requires some assumptions weaker than the local detailed-balance condition.

- The variational expression of entropy production rate (19.1).
- The Kolchinsky-Wolpert relation (19.41).

Here, the numbers in the bracket represent equation numbers. These relations only use the fact that a system attached to a heat bath relaxes to the equilibrium state (the canonical distribution), and thus these relations have high universality.

In contrast, the following results are proven with requiring the local detailed-balance condition. Although these relations also hold in various systems, the degree of universality is less than the previous ones.

- The Speck-Seifert relation (7.17).
- The martingale property of entropy production (8.47).
- The least probable stochastic efficiency (8.61).
- The fluctuation-dissipation theorem for stalling state (10.5).
- The thermodynamic uncertainty relation (17.4)
- The variational expressions of excess and housekeeping entropy production (19.22) and (19.25).

1.3 Notation, Terminologies and Remarks

Throughout this textbook, we frequently use the following notation, terminologies and setups without any explicit explanation:

Quantities

- A bracket $\langle \cdot \rangle$ represents an ensemble average of a stochastic quantity.
- A quantity with hat $\hat{A}$ means that this quantity is a stochastic variable. A quantity without hat means its ensemble average $A := \langle \hat{A} \rangle$.
- Calligraphic symbols are reserved to represent time-integrated quantities (e.g., $\mathcal{J} := \int_0^\tau dt J(t)$).
- A derivative $\frac{\partial f}{\partial x}$ is also expressed as $\partial_x f$.

States

- We usually use the symbol w to represent a discrete state. The label of a state appears in the subscript[7] as w_i. We frequently use a shorthand notation i to refer to state w_i.
- The probability distribution of state w at time t is denoted by $P(w, t)$. In a vector representation, we write $p_w(t)$. The probability distribution of state w_i is also denoted by $p_i(t)$
- p_w^{eq} represents the equilibrium distribution of state w. p_w^{ss} represents the stationary (steady state) distribution of state w.

[7] Remark that in the systems in continuous space, we use the subscripts to represent the number of steps.

- When we represent a vector, we employ a bold font as $\boldsymbol{p}$.
- $\bar{w}$ represents the time-reversal state of state w, where parity-odd variables (e.g., momentum) are multiplied by -1.

Dynamics (on discrete states)

- We use the word "Markov jump processes" to refer to processes with continuous time. We use the word "Markov chains" to refer to processes with discrete-time. This textbook mainly treats continuous-time Markov jump processes on discrete states otherwise explicitly noted.
- We refer to the matrix R in the master equation for Markov jump processes (Eq. (2.10)) as "transition rate matrix". We refer to the matrix T in the time evolution equation of Markov chains (Eq. (2.4)) as "transition probability matrix".
- In a Markov jump process, a transition rate from a state w to another state w' at time t is written as $P_{w \to w';t}$. The corresponding transition matrix is written as $R_{w'w}$. Since the former symbol is preferable in representing path probabilities, we mainly use the former symbol $P_{w \to w';t}$ in Part II[8] and mainly use the latter symbol $R_{w'w}$ in Part IV.
- The escape rate with a state w at time t is denoted by $e_{w,t}$.
- The transition rate in the time-reversal system (i.e., if there exists a parity-odd field such as a magnetic field in the original system, then we invert its sign in the time-reversal system) is denoted by $P^{\dagger}_{w \to w';t}$.
- The transition rate with tilde as $\tilde{P}_{w \to w';t}$ represents the dual transition rate defined in Eq. (7.2).
- For a transient process, we usually set its time interval as $0 \le t \le \tau$.
- A stochastic trajectory in a Markov jump process is denoted by Γ. In this trajectory, the number of jumps is written as N. The n-th jump occurs at $t = t^n$, and the state is changed from w^{n-1} to w^n. The superscript represents the order of jumps. We write $t^0 = 0$ and $t^{N+1} = \tau$ for convenience.

Langevin systems (in continuous space)

- We usually use the symbol x to represent a state in continuous space.
- When we consider a discretized version of Langevin systems with respect to time, the position (state) and the time at the n-th step are denoted by x_n and t_n, respectively.
- The white Gaussian noise (see Sect. 4.1.1) is denoted by $\hat{\xi}(t)$. Its discretization with time interval Δt is written as $\hat{\xi}_{\Delta t}(t)$.
- The rule of product in stochastic differential equation (see Sect. 4.1.2.1) is denoted by α.
- The Itô, Stratonovich, and anti-Itô product (see Sects. 4.1.2.2 and 4.2.1) are represented by $\cdot$, $\circ$, and $\odot$, respectively.

[8] The exception is Chap. 10, where we use the symbol $R_{w'w}$. In this chapter, we treat response functions in stationary systems with symbols.

Others

- The number of particles is denoted by M. Each particle is labeled with m.
- The number of heat baths is denoted by k. Each bath is labeled with ν.
- The energy of state w is written as E_w.
- The heat current is positive for energy transfer from the system to a bath. Correspondingly, the heat is positive when the heat releases into a bath.
- The entropy production is denoted by σ. The entropy production rate is denoted by $\dot{\sigma}$.
- The inverse temperature is denoted by β.
- We normalize the Boltzmann constant k_B to 1.
- The imaginary unit is denoted by i.
- The density matrix is denoted by ρ.
- The Onsager matrix is denoted by L.
- The work is denoted by W, which is positive when the work is extracted by an external agent.
- The spatial dimension is denoted by D.

We also use the following abbreviations in this textbook:

- CE: Carnot efficiency
- CGACE: coarse-grained autonomous Carnot engine
- DFT: detailed fluctuation theorem
- EMP: efficiency at maximum power
- FDT: fluctuation-dissipation theorem
- FT: fluctuation theorem
- IFT: integral fluctuation theorem
- TUR: thermodynamic uncertainty relation

Part I
Basic Framework

Chapter 2
Stochastic Processes

In this chapter, we introduce a mathematical framework, stochastic processes, which is used to describe small stochastic systems. In most part of this textbook, we consider stochastic processes with discrete states, and this chapter is devoted to such processes. Mathematical foundations of stochastic processes in continuous space are presented in Chap.4.

A stochastic process is a time evolution in a probabilistic manner. The dynamics of a Brownian particle is a celebrated example of stochastic processes, where the movement of the particle is given by the collision of enormous number of small water molecules. Since we do not know the detailed positions and momentums of water molecules, the dynamics of the Brownian particle can be predicted only in a probabilistic form. Another famous toy model of stochastic processes is a random walk on a one-dimensional lattice: A person on the lattice moves left or right by one site with probability half (e.g., by flipping a coin). Various biophysical systems including molecular motors and other elaborated proteins can also be described as stochastic processes.

2.1 Markov Process and Discrete-Time Markov Chain

We here introduce an important class of stochastic processes, a *Markov process*. Roughly speaking, a Markov process is a stochastic process whose dynamics is determined only by its latest state. Although it can be defined in both discrete-time and continuous-time, for simplicity we first explain the Markov property by taking stochastic processes in discrete time steps. Consider a stochastic process in N steps. Through this process, we obtain a stochastic sequence of $N+1$ states, $(w^0, w^1, w^2, \ldots, w^N)$, where w^i is the state at the i-th step.[1] This sequence is regarded as a trajectory of states. We call the transition from the state at the $n-1$-th step to that at the n-th step as the n-th transition or the transition at the n-th step.

[1] We denote the initial state by w^0 for convenience.

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