学位論文

Geometric Approach to Nonequilibrium Statistical Mechanics

（非平衡統計力学への幾何学的アプローチ）

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東京大学大学院理学系研究科
物理学専攻

設樂　智洋

Abstract

In this thesis, we study nonequilibrium statistical mechanics from a geometric perspective. In particular, we (i) examine the relation between quantum information geometry and linear response theory, and (ii) analyze nonequilibrium processes in thermodynamic control and derive a geometric expression for work.

The first original study in this thesis is to understand quantum information geometry based on linear response theory. We show that the quantum Fisher information can be determined by measuring the linear response functions. For that purpose, we generalize the fluctuation-dissipation theorem, and establish the quantitative relation between linear response functions and the generalized covariance, which contains the same amount of information on the quantum state. Based on the generalized fluctuation-dissipation theorem, we can determine the generalized covariance and the quantum Fisher information by measuring linear response functions, such as the dynamical susceptibilities and the complex admittances for all frequencies. We demonstrate that our result is applicable to experimental determination of the skew information, and a validation of skew information-based uncertainty relations.

The second original study is on the analysis of work in thermodynamic control. We extend the thermodynamic metric-based expression for work into two directions. One is to obtain a systematic expansion of the average work from a phenomenological argument, and the other is to obtain an expansion of the work distribution for overdamped Langevin systems. First, we derive a systematic expansion of the work in terms of a small parameter ϵ that characterizes how slowly we control the system. The leading-order contribution is given by the thermodynamic metric expression. The next leading-order contributions to the thermodynamic metric contribution can be detected by comparing the excess work in a forward control and a backward control, and are predicted to scale as $1/T^2$ as a function of the total control time T. Since the expansion is derived without assuming any specific microscopic dynamics, it is valid as long as the perturbation series expansion is valid. Finally, we examine the work distribution in overdamped Langevin systems. We derive the time evolution equation for the moment generating function of the work, and solve it from the lower-order contributions in ϵ. The $O(\epsilon)$ contribution to the generating function reproduces two known facts: the work distribution is Gaussian, and the average work is given by the thermodynamic metric. When we take up to $O(\epsilon^2)$ contributions into account, the work distribution exhibits nonzero skewness, which means that the fluctuation-dissipation relation is violated with scaling $1/T^2$. Furthermore, from the analytic calculation with numerical supports, we conjecture that the nth cumulant of the work scales as $1/T^{n-1}$ for $n \geq 1$.

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Contents

Chapter 1

Introduction

Geometry often deepens our understanding of laws that govern the world, namely, physics: Riemannian geometry in general relativity, differential geometry with affine connections in gauge theory, and topology in condensed matter physics, to name a few. A geometric perspective is also useful in the study of statistical mechanics. The thermodynamic length [1, 2, 3, 4] provides a natural distance between equilibrium states. It has been pointed out [5, 4] that the metric induced by the thermodynamic length is the Fisher metric, which plays an important role in information geometry.

Information geometry [6] treats a differential-geometric structure of statistical manifolds, whose element represents a probability distribution. Historically, information geometry was considered in the theory of statistical inference. The Fisher information, which gives the upper bound on the precision of estimation via the Cramér-Rao inequality [7], is identified as a natural metric on statistical manifolds. Higher-order structures, such as the α-connections, are also closely related to the existence of efficient estimators. The (classical) Fisher information is also characterized as the unique monotone metric, which means that it monotonically decreases under information processing. Since a probability distribution can be interpreted as a (mixed) state in physics, we can safely say that for physicists, information geometry concerns an informationally natural geometric structure on the space of physical states.

If we consider quantum theory, where probability distributions are replaced by density operators, the noncommutativity of operators admits much richer structures than classical information geometry. If we define the quantum Fisher information as a monotone metric on the space of quantum states under information processing, there are infinitely many types of the quantum Fisher information. Recently, the quantum Fisher information has been applied in wide fields of physics, such as quantum information theory [8, 9, 10, 11], condensed matter physics [12, 13, 14], and high energy physics [15]. However, since the noncommutativity is dealt with in a tricky way, the relation between the general quantum Fisher information and observable quantities has been elusive.

In this thesis, we address two aspects of the relation between nonequilibrium statistical mechanics and geometry. First, we establish a quantitative relation between the quantum Fisher information and linear response functions, such as the dynamical susceptibilities and the complex admittances, by generalizing the fluctuation-dissipation theorem. Second, we develop a method of systematically evaluating the work performed on the system when we control the system through external parameters, in both phenomenological and microscopic ways.

This thesis is organized as follows. The main results in this thesis are presented in Chapters 5, 6, and 7.

In Chapter 2, we review the theory of response and relaxation near a thermal equilibrium state. In Sec. 2.1, the linear response function is shown to be quantitatively related to a temporal correlation function at the thermal equilibrium state, as formulated as the Green-Kubo formula and the fluctuation-dissipation theorem. A higher-order generalization of the linear response theory is also discussed in Sec. 2.2.

In Chapter 3, we review some basic materials in thermodynamics. In Sec. 3.1, we review the stochastic thermodynamics, which models thermodynamic properties of microscopic objects surrounded by a thermal bath. In Sec. 3.2, we consider a thermodynamic control of the system. We introduce the thermodynamic metric, which is useful for approximately evaluating the excess work. We also introduce two derivations of this approximate expression, with an emphasis on the separation of time scales between the control and the system dynamics.

In Chapter 4, we review the information geometry. We introduce the classical and quantum Fisher information, and discuss how they are used in estimation theory. There is a one-to-one correspondence between a type of the quantum Fisher information and an operator monotone function. We also introduce the generalized covariance, which also has a one-to-one correspondence to an operator monotone function.

In Chapter 5, we present the first main result of this thesis. We derive the generalized fluctuation-dissipation theorem, which establishes the quantitative relation between the linear response function and the generalized covariance at a thermal equilibrium state. Based on the generalized fluctuation-dissipation theorem, we can determine the generalized covariance by measuring the linear response functions. We also propose an experimental method of determining the quantum Fisher information by measuring the dynamical susceptibilities or the complex admittances for all frequencies.

In Chapters 6 and 7, we present the second main result of this thesis. We examine the average excess work in thermodynamic control in a phenomenological way in Chapter 6. We derive an expansion of the average excess work in terms of a small parameter ϵ that characterizes how slowly we control the system. We discuss the physical picture of the next leading-order terms to the thermodynamic metric term. They can be detected by comparing the excess work in a forward control and a backward control, and they are predicted to scale as $1/T^2$ as a function of the total control time T. Since the expansion is derived without assuming a specific microscopic dynamics, it is valid as long as the perturbation series expansion is valid.

In Chapter 7, we examine the work distribution in overdamped Langevin systems. We derive the time evolution equation for the moment generating function of the work, and solve it from lower-order contributions in ϵ. The $O(\epsilon)$ contribution to the generating function reproduces two known facts: the work distribution is Gaussian, and the average work is given by the thermodynamic metric. When we take up to $O(\epsilon^2)$ contributions into account, the work distribution exhibits nonzero skewness, which means that the fluctuation-dissipation relation is violated with scaling $1/T^2$. Furthermore, from the analytic calculation with numerical supports, we conjecture that the nth cumulant of the work scales as $1/T^{n-1}$ for $n \geq 1$.

Some complicated algebraic manipulations are relegated to Appendices to avoid digressing from the main subject.

Chapter 2

Linear and Nonlinear Response Theory

In this chapter, we review the theory of response and relaxation at thermal equilibrium.

When we apply a magnetic field to paramagnets, the magnetic moment, or the magnetization is induced. Similarly, when we apply an electric field to conductors, an electric current is induced. Such an external force are called a mechanical force in the sense that it can be expressed as a change of the Hamiltonian or the potential of the system. On the other hand, when the temperature gradient or the concentration gradient exists, the heat or diffusion flow is induced. Such a force is called an internal thermal force. Here, we focus on the response to mechanical external forces.

2.1 Linear Response Theory

In this section, we review the linear response theory [16, 17, 18].

In the case of paramagnets or conductors, if the applied field is small, the induced magnetization or current is proportional to the strength of external forces. Below, we consider the deviation from the equilibrium value of general observables against general external forces in this linear response regime.

2.1.1 Phenomenological Theory

In the linear response regime, the value of an observable $A(t)$ at time t deviates from its equilibrium value A^{eq} proportionally to an external force $F(t)$ as

$$A(t) - A^{\mathrm{eq}} = LF(t). \tag{2.1}$$

Here, L is what is called the kinetic coefficient. We generalize this linear relation in the presence of multiple external forces and to the non-Markov case.

Let us consider a case where there are more than one type of external forces labelled by ν. Since we are considering the linear response regime, the whole effect can be expressed as a superposition of the effect of each external force, given by

$$A_\mu(t) - A_\mu^{\mathrm{eq}} = \sum_\nu L_{\mu\nu} F_\nu(t), \tag{2.2}$$

where the label μ denotes the kind of observables that we are interested in.

The relation (2.2) holds true when the changes of external forces are sufficiently slow because it describes the situation where the deviation at time t is determined only by the instantaneous values of external forces $\{F_\nu(t)\}_\nu$. The generalization of this relation to the non-Markov case is expressed as

$$A_\mu(t) - A_\mu^{\mathrm{eq}} = \sum_\nu \chi_{\mu\nu}^\infty F_\nu(t) + \int_0^\infty \mathrm{d}s \sum_\nu \Phi_{\mu\nu}(s) F_\nu(t-s). \tag{2.3}$$

The first term on the right-hand side represents the instantaneous response, while the second term represents the delayed response to the force at time $t-s$. In the latter term, the superposition principle with respect to each time $t-s$ is again employed. The causality imposes that the integration variable s is bounded from below by 0.

The relation between Eqs. (2.2) and (2.3) is explained as follows. It is natural to assume that the effect of an external force vanishes in the long-time limit, $\lim_{s\to\infty} \Phi_{\mu\nu}(s) = 0$, or

$$\Phi_{\mu\nu}(s) \simeq 0 \quad (s \gtrsim \tau), \tag{2.4}$$

where τ is of the order of the relaxation time of the system. When the timescale of the change of external forces $F_\nu(t)$ is larger than τ, i.e.,

$$F_\nu(t-s) \simeq F_\nu(t) \qquad (0 \leq s \lesssim \tau), \tag{2.5}$$

Eq. (2.3) can approximately be simplified as

$$\begin{aligned} A_\mu(t) - A_\mu^{\mathrm{eq}} &\simeq \sum_\nu \chi_{\mu\nu}^\infty F_\nu(t) + \int_0^\tau \mathrm{d}s \sum_\nu \Phi_{\mu\nu}(s) F_\nu(t-s) \\ &\simeq \sum_\nu \chi_{\mu\nu}^\infty F_\nu(t) + \int_0^\tau \mathrm{d}s \sum_\nu \Phi_{\mu\nu}(s) F_\nu(t) \qquad (2.6) \\ &\simeq \sum_\nu \chi_{\mu\nu}^\infty F_\nu(t) + \left(\int_0^\infty \mathrm{d}s \sum_\nu \Phi_{\mu\nu}(s) \right) F_\nu(t). \qquad (2.7) \end{aligned}$$

Therefore, if there is a timescale separation between the system dynamics and the external forces, the non-Markov linear response (2.3) reduces to the Markov one (2.2) with

$$L_{\mu\nu} \simeq \chi_{\mu\nu}^\infty + \int_0^\infty \mathrm{d}s\ \Phi_{\mu\nu}(s). \tag{2.8}$$

Next we consider a relaxation process. Suppose that the κth kind of the external force is applied until time $t = t_1$, and no force is applied after t_1, given as

$$F_\nu(t) = \epsilon\delta_{\nu\kappa}\theta(t_1 - t), \tag{2.9}$$

where the step function is defined as

$$\theta(t) = \begin{cases} 1 & (t \geq 0) \\ 0 & (t < 0). \end{cases} \tag{2.10}$$

Substituting this form of force to the linear response formula (2.3), we obtain

$$\begin{aligned} A_\mu(t) - A_\mu^{\mathrm{eq}} &= \epsilon\chi_{\mu\kappa}^\infty \theta(t_1 - t) + \epsilon \int_{\max[0, t-t_1]}^\infty \mathrm{d}s\ \Phi_{\mu\kappa}(s) & (2.11) \\ &= \epsilon\left(\chi_{\mu\kappa}^\infty \theta(t_1 - t) + \Psi_{\mu\kappa}(\max[0, t - t_1])\right), & (2.12) \end{aligned}$$

where $\Psi_{\mu\kappa}(t)$ is the linear relaxation function defined by

$$\Psi_{\mu\kappa}(t) := \int_t^\infty \mathrm{d}s\ \Phi_{\mu\kappa}(s). \tag{2.13}$$

The linear relaxation function $\Psi_{\mu\kappa}(t)$ quantifies how the value of the observable A_μ approaches to its equilibrium value after the external force F_κ is suddenly switched off. From the definition of the linear relaxation function, the linear response function is obtained by differentiating the linear relaxation function:

$$\Phi_{\mu\nu}(t) = -\frac{\mathrm{d}}{\mathrm{d}t}\Psi_{\mu\nu}(t). \tag{2.14}$$

In this sense, both the response function and the relaxation function have the same amount of information on the system. In the following, we assume that the convergence of the linear response function is sufficiently rapid and the integral (2.13) converges, and therefore

$$\lim_{t\to\infty} \Psi_{\mu\nu}(t) = 0. \tag{2.15}$$

This assumption guarantees that the system approaches an equilibrium state after a sufficiently long time if no external force is applied.

Finally, let us introduce dynamical susceptibilities, or complex admittances. Suppose that the external force is harmonically oscillating, expressed by

$$F_\nu(t) = \mathrm{Re}[F_\nu \mathrm{e}^{i\omega t}]. \tag{2.16}$$

Substituting this to Eq. (2.3), we obtain

$$A_\mu(t) - A_\mu^{\mathrm{eq}} = \sum_\nu \mathrm{Re}[\chi_{\mu\nu}(\omega) F_\nu \mathrm{e}^{i\omega t}], \tag{2.17}$$

where we have defined a dynamical susceptibility (also called a complex admittance) as

$$\chi_{\mu\nu}(\omega) := \chi_{\mu\nu}^{\infty} + \int_0^{\infty} \mathrm{d}t \ \mathrm{e}^{i\omega t}\Phi_{\mu\nu}(t). \tag{2.18}$$

It also describes the linear relation between the Fourier components of external forces and observables as

$$A_{\mu,\omega} = \sum_{\nu} \chi_{\mu\nu}(\omega) F_{\nu,\omega}, \tag{2.19}$$

where

$$F_{\nu}(t) = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi} \mathrm{e}^{-i\omega t} F_{\nu,\omega}, \tag{2.20}$$

$$A_{\mu}(t) - A_{\mu}^{\mathrm{eq}} = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi} \mathrm{e}^{-i\omega t} A_{\mu,\omega}. \tag{2.21}$$

Note that the frequency components are independent of each other because the right-hand side of the linear response relation (2.3) is a convolution of the linear response function and the external force.

2.1.2 Response and Relaxation in a Quantum System

In the previous subsection, we have examined the formal structure of the linear response theory without assuming the underlying microscopic dynamics. In this section, we apply this formalism to a quantum system whose Hamiltonian $\hat{H}(\boldsymbol{\lambda})$ depends on some external control parameters $\boldsymbol{\lambda} = (\lambda_{\nu})$. We control the system through time-dependent external control parameters $\boldsymbol{\lambda}(t)$. We assume that the control parameters take a value near some specific value $\bar{\boldsymbol{\lambda}}$. Then, in the linear response regime, the Hamiltonian can be separated into two parts given as

$$\hat{H}(t) = \hat{H} + \hat{H}_{\mathrm{ext}}(t), \tag{2.22}$$

where each part is defined by

$$\hat{H} := \hat{H}(\bar{\boldsymbol{\lambda}}), \tag{2.23}$$

$$\hat{H}_{\mathrm{ext}}(t) := -\sum_{\nu} F_{\nu}(t) \hat{X}_{\nu}, \tag{2.24}$$

and the time-dependent part of the Hamiltonian $\hat{H}_{\mathrm{ext}}(t)$ is composed of the amplitude of the force $F_{\nu}(t)$ and the corresponding generalized force operator, or the displacement operator, $\hat{X}_{\nu}$, defined by

$$F_{\nu}(t) := \lambda_{\nu}(t) - \bar{\lambda}_{\nu}, \tag{2.25}$$

$$\hat{X}_{\nu} := -\frac{\partial \hat{H}(\boldsymbol{\lambda})}{\partial \lambda_{\nu}}\Big|_{\boldsymbol{\lambda}=\bar{\boldsymbol{\lambda}}}. \tag{2.26}$$

Let us calculate the expectation value of an observable $\hat{A}_\mu$ at time t, namely, $A_\mu(t) = \mathrm{tr}\left[\hat{\rho}(t)\hat{A}_\mu\right]$. The density operator $\hat{\rho}(t)$ evolves according to the von Neumann equation:

$$\frac{\partial \hat{\rho}(t)}{\partial t} = \frac{1}{i\hbar}[\hat{H} + \hat{H}_{\mathrm{ext}}(t), \hat{\rho}(t)]. \tag{2.27}$$

To switch from the Schrödinger picture to the interaction picture, we define the density operator in the interaction picture as

$$\hat{\rho}_{\mathrm{int}}(t) := \mathrm{e}^{i\hat{H}(t-t_0)/\hbar}\hat{\rho}(t)\mathrm{e}^{-i\hat{H}(t-t_0)/\hbar}. \tag{2.28}$$

Note that they coincides with each other at time $t = t_0$, i.e., $\hat{\rho}_{\mathrm{int}}(t_0) = \hat{\rho}(t_0)$. Then, the time evolution of $\hat{\rho}_{\mathrm{int}}(t)$ is calculated as

$$\frac{\partial \hat{\rho}_{\mathrm{int}}(t)}{\partial t} = \frac{1}{i\hbar}[\mathrm{e}^{i\hat{H}(t-t_0)/\hbar}\hat{H}_{\mathrm{ext}}(t)\mathrm{e}^{-i\hat{H}(t-t_0)/\hbar}, \hat{\rho}_{\mathrm{int}}(t)], \tag{2.29}$$

whose solution can formally be written as

$$\hat{\rho}_{\mathrm{int}}(t) = \hat{\rho}_{\mathrm{int}}(t_0) + \int_{t_0}^{t} \mathrm{d}t' \frac{1}{i\hbar}[\mathrm{e}^{i\hat{H}(t'-t_0)/\hbar}\hat{H}_{\mathrm{ext}}(t')\mathrm{e}^{-i\hat{H}(t'-t_0)/\hbar}, \hat{\rho}_{\mathrm{int}}(t')], \tag{2.30}$$

and hence

$$\begin{aligned}\hat{\rho}(t) &= \mathrm{e}^{-i\hat{H}(t-t_0)/\hbar}\hat{\rho}(t_0)\mathrm{e}^{i\hat{H}(t-t_0)/\hbar} \\ &\quad + \int_{t_0}^{t} \mathrm{d}t' \mathrm{e}^{-i\hat{H}(t-t')/\hbar}\frac{1}{i\hbar}[\mathrm{e}^{i\hat{H}(t'-t_0)/\hbar}\hat{H}_{\mathrm{ext}}(t')\mathrm{e}^{-i\hat{H}(t'-t_0)/\hbar}, \hat{\rho}(t')]\mathrm{e}^{i\hat{H}(t-t')/\hbar}.\end{aligned} \tag{2.31}$$

If we consider only the first order with respect to the perturbation, or equivalently, if we use an approximation $\hat{\rho}(t') \simeq \mathrm{e}^{-i\hat{H}(t'-t_0)/\hbar}\hat{\rho}(t_0)\mathrm{e}^{i\hat{H}(t'-t_0)/\hbar}$ in the integrand of Eq. (2.31), we obtain

$$\hat{\rho}(t) \simeq \mathrm{e}^{-i\hat{H}t/\hbar}\hat{\rho}_0\mathrm{e}^{i\hat{H}t/\hbar} + \int_{t_0}^{t} \mathrm{d}t' \mathrm{e}^{-i\hat{H}(t-t')/\hbar}\frac{1}{i\hbar}[\hat{H}_{\mathrm{ext}}(t'), \mathrm{e}^{-i\hat{H}t'/\hbar}\hat{\rho}_0\mathrm{e}^{i\hat{H}t'/\hbar}]\mathrm{e}^{i\hat{H}(t-t')/\hbar}, \tag{2.32}$$

where we have defined $\hat{\rho}_0 := \mathrm{e}^{i\hat{H}t_0/\hbar}\hat{\rho}(t_0)\mathrm{e}^{-i\hat{H}t_0/\hbar}$.

Now let us take the limit of $t_0 \to -\infty$, and assume that the state $\hat{\rho}_0$ is a thermal equilibrium state. This assumption can be justified by the following discussion. The state $\hat{\rho}_0$ is obtained from the initial state $\hat{\rho}(t_0)$ after the time evolution of $-t_0 (> 0)$ under the Hamiltonian $\hat{H}$. If we take the limit of $t_0 \to -\infty$, the state $\hat{\rho}_0$ is expected to be equilibrated, in the sense that the values of observables of our interest coincide with those in the canonical ensemble, irrespective of the initial state $\hat{\rho}(t_0)$. Such a thermalization in isolated quantum systems has been studied well recently [19]. If we also assume that the perturbation exists only after time $t = 0$, then we have

$$\hat{\rho}(t) \simeq \hat{\rho}_{\mathrm{can}} + \int_{-\infty}^{t} \mathrm{d}t' \mathrm{e}^{-i\hat{H}(t-t')/\hbar}\frac{1}{i\hbar}[\hat{H}_{\mathrm{ext}}(t'), \hat{\rho}_{\mathrm{can}}]\mathrm{e}^{i\hat{H}(t-t')/\hbar}, \tag{2.33}$$

where $\hat{\rho}_{\mathrm{can}}$ is the canonical ensemble with the inverse temperature $\beta = 1/k_{\mathrm{B}}T$ defined by $\hat{\rho}_{\mathrm{can}} :=$

$\mathrm{e}^{-\beta \hat{H}}/Z$, and the partition function is defined by $Z = \mathrm{tr}\left[\mathrm{e}^{-\beta \hat{H}}\right]$.

Now we can calculate the expectation value of an observable $\hat{A}_\mu$ at time t. If we define the Heisenberg operator and the equilibrium value of $\hat{A}_\mu$ as $\hat{A}_\mu(t) := \mathrm{e}^{i\hat{H}t/\hbar}\hat{A}_\mu \mathrm{e}^{-i\hat{H}t/\hbar}$ and $A^{\mathrm{eq}}_\mu = \mathrm{tr}\left[\hat{\rho}_{\mathrm{can}}\hat{A}_\mu\right]$, respectively, we obtain

$$\begin{aligned} A_\mu(t) &= A^{\mathrm{eq}}_\mu + \int_{-\infty}^{t} \mathrm{d}t' \frac{1}{i\hbar} \mathrm{tr}\left[[\hat{H}_{\mathrm{ext}}(t'), \hat{\rho}_{\mathrm{can}}]\hat{A}_\mu(t-t')\right] \\ &= A^{\mathrm{eq}}_\mu - \sum_\nu \int_{-\infty}^{t} \mathrm{d}t' \frac{1}{i\hbar} \mathrm{tr}\left[[\hat{X}_\nu, \hat{\rho}_{\mathrm{can}}]\hat{A}_\mu(t-t')\right] F_\nu(t'). \end{aligned} \tag{2.34}$$

By comparing this expression with Eq. (2.3), we obtain an explicit form of the linear response function:

$$\chi^{\infty}_{\mu\nu} = 0, \tag{2.35}$$

$$\Phi_{\mu\nu}(t) = -\frac{1}{i\hbar}\mathrm{tr}\left[[\hat{X}_\nu, \hat{\rho}_{\mathrm{can}}]\hat{A}_\mu(t)\right] \tag{2.36}$$

$$= \frac{1}{i\hbar}\mathrm{tr}\left[\hat{\rho}_{\mathrm{can}}[\hat{X}_\nu, \hat{A}_\mu(t)]\right]. \tag{2.37}$$

Applying the formula (A.1) to Eq. (2.36), we obtain another expression for the linear response function, given by

$$\Phi_{\mu\nu}(t) = \beta \langle\!\langle \dot{\hat{X}}_\nu(0), \hat{A}_\mu(t) \rangle\!\rangle^{\mathrm{canonical}}_{\hat{\rho}_{\mathrm{can}}}, \tag{2.38}$$

where the canonical correlation of two observables is defined by

$$\langle\!\langle \hat{A}, \hat{B} \rangle\!\rangle^{\mathrm{canonical}}_{\hat{\rho}} := \int_0^1 \mathrm{d}\alpha \ \mathrm{tr}\left[\hat{\rho}^{1-\alpha}\hat{A}\hat{\rho}^{\alpha}\hat{B}\right], \tag{2.39}$$

and the time derivative of the Heisenberg operator is defined by $\dot{\hat{X}}_\nu(t) := \mathrm{d}\hat{X}(t)/\mathrm{d}t = (1/i\hbar)[\hat{X}(t), \hat{H}]$. The canonical correlation can be interpreted as one of the extensions of the classical correlation to quantum one. Note that the canonical correlation of two Hermitian operators is symmetric and real:

$$\langle\!\langle \hat{B}, \hat{A} \rangle\!\rangle^{\mathrm{canonical}}_{\hat{\rho}} = \langle\!\langle \hat{A}, \hat{B} \rangle\!\rangle^{\mathrm{canonical}}_{\hat{\rho}}, \tag{2.40}$$

$$(\langle\!\langle \hat{A}, \hat{B} \rangle\!\rangle^{\mathrm{canonical}}_{\hat{\rho}})^* = \langle\!\langle \hat{A}, \hat{B} \rangle\!\rangle^{\mathrm{canonical}}_{\hat{\rho}}. \tag{2.41}$$

If we choose the displacement operator $\hat{X}_\mu(t)$ and the current operator $\hat{J}_\mu(t) := \dot{\hat{X}}_\nu(t) = (1/i\hbar)[\hat{X}(t), \hat{H}]$ as observables to be measured, then the corresponding linear response functions $\phi_{\mu\nu}(t)$ and $\tilde{\phi}_{\mu\nu}(t)$ reduce to the canonical correlations of two temporally separated operators:

$$\phi_{\mu\nu}(t) = \beta \langle\!\langle \hat{X}_\mu(t), \hat{J}_\nu(0) \rangle\!\rangle^{\mathrm{canonical}}_{\hat{\rho}_{\mathrm{can}}}, \tag{2.42}$$

$$\tilde{\phi}_{\mu\nu}(t) = \beta \langle\!\langle \hat{J}_\mu(t), \hat{J}_\nu(0) \rangle\!\rangle^{\mathrm{canonical}}_{\hat{\rho}_{\mathrm{can}}}. \tag{2.43}$$

Equations (2.37), (2.38), and (2.43) are referred to as the Green-Kubo formulae [20, 16, 17].

These formulae show that the linear response function, which describes nonequilibrium processes, is quantitatively related to the time correlation function at thermal equilibrium.

Next we examine a relaxation process where the control parameter takes the form of

$$\boldsymbol{\lambda}(t) = \boldsymbol{\lambda} + \theta(-t)\Delta\boldsymbol{\lambda}. \tag{2.44}$$

Since the control parameter is fixed to be $\boldsymbol{\lambda}(t) = \boldsymbol{\lambda} + \Delta\boldsymbol{\lambda}$ for $t < 0$, the state at time $t = 0$ is described by the canonical ensemble with respect to the control parameter $\boldsymbol{\lambda} + \Delta\boldsymbol{\lambda}$, i.e., $\hat{\rho}(0) = \hat{\rho}_{\mathrm{can}}(\boldsymbol{\lambda} + \Delta\boldsymbol{\lambda})$. Then the system evolves under the Hamiltonian $\hat{H}(\boldsymbol{\lambda})$, and therefore the expectation value of an observable $\hat{A}_\mu$ at time $t > 0$ is given by

$$A_\mu(t) = \mathrm{tr}\left[\hat{\rho}(t)\hat{A}_\mu\right] = \mathrm{tr}\left[\mathrm{e}^{-i\hat{H}(\boldsymbol{\lambda})t/\hbar}\hat{\rho}_{\mathrm{can}}(\boldsymbol{\lambda} + \Delta\boldsymbol{\lambda})\mathrm{e}^{i\hat{H}(\boldsymbol{\lambda})t/\hbar}\hat{A}_\mu\right] = \mathrm{tr}\left[\hat{\rho}_{\mathrm{can}}(\boldsymbol{\lambda} + \Delta\boldsymbol{\lambda})\hat{A}_\mu(t)\right]. \tag{2.45}$$

The linear relaxation function describes the sensitivity to the external force $\Delta\boldsymbol{\lambda}$, and hence given by

$$\begin{aligned}\Psi_{\mu\nu}(t) &= \left.\frac{\partial A_\mu(t)}{\partial(\Delta\lambda_\nu)}\right|_{\Delta\boldsymbol{\lambda}=0} \\ &= \mathrm{tr}\left[\left.\frac{\partial\hat{\rho}_{\mathrm{can}}(\boldsymbol{\lambda} + \Delta\boldsymbol{\lambda})}{\partial(\Delta\lambda_\nu)}\right|_{\Delta\boldsymbol{\lambda}=0}\hat{A}_\mu(t)\right] \\ &= \beta\langle\!\langle\Delta\hat{X}_\nu(0); \hat{A}_\mu(t)\rangle\!\rangle^{\mathrm{canonical}}_{\hat{\rho}_{\mathrm{can}}},\end{aligned} \tag{2.46}$$

where we have used the formula (A.3) to derive the last equality. We can check that the explicit expressions (2.38) and (2.46) indeed satisfy the differential relation (2.14) between the linear response and relaxation functions as follows. From the time translational symmetry, we have

$$\langle\!\langle\Delta\hat{X}_\nu(0); \hat{A}_\mu(t)\rangle\!\rangle^{\mathrm{canonical}}_{\hat{\rho}_{\mathrm{can}}} = \langle\!\langle\Delta\hat{X}_\nu(s); \hat{A}_\mu(t+s)\rangle\!\rangle^{\mathrm{canonical}}_{\hat{\rho}_{\mathrm{can}}} \tag{2.47}$$

for arbitrary s, and hence

$$0 = \langle\!\langle\Delta\dot{\hat{X}}_\nu(0); \hat{A}_\mu(t)\rangle\!\rangle^{\mathrm{canonical}}_{\hat{\rho}_{\mathrm{can}}} + \langle\!\langle\Delta\hat{X}_\nu(0); \dot{\hat{A}}_\mu(t)\rangle\!\rangle^{\mathrm{canonical}}_{\hat{\rho}_{\mathrm{can}}}. \tag{2.48}$$

Therefore, we obtain

$$\begin{aligned}\frac{\mathrm{d}\Psi_{\mu\nu}(t)}{\mathrm{d}t} &= \langle\!\langle\Delta\hat{X}_\nu(0); \dot{\hat{A}}_\mu(t)\rangle\!\rangle^{\mathrm{canonical}}_{\hat{\rho}_{\mathrm{can}}} = -\langle\!\langle\Delta\dot{\hat{X}}_\nu(0); \hat{A}_\mu(t)\rangle\!\rangle^{\mathrm{canonical}}_{\hat{\rho}_{\mathrm{can}}} \\ &= -\langle\!\langle\dot{\hat{X}}_\nu(0); \hat{A}_\mu(t)\rangle\!\rangle^{\mathrm{canonical}}_{\hat{\rho}_{\mathrm{can}}} = -\Phi_{\mu\nu}(t).\end{aligned} \tag{2.49}$$

The linear response function and the relaxation function can be obtained by replacing the commutator with the Poisson bracket and the canonical correlation with the classical correlation.

2.1.3 Fluctuation-Dissipation Theorem

In the previous subsection, we saw that there is a quantitative relation between the linear response and the canonical correlation in thermal equilibrium. Another way of formulating such a relation is the fluctuation-dissipation theorem in the frequency domain, using the symmetrized correlation. Recall that the linear response function of the current operator is given by

$$\tilde{\phi}_{\mu\nu}(t) = \beta \langle\!\langle \hat{J}_\mu(t), \hat{J}_\nu(0) \rangle\!\rangle^{\text{canonical}}_{\hat{\rho}_{\text{can}}}. \tag{2.50}$$

Though the linear response function is physically meaningful only for $t \geq 0$ due to the causality, we formally define the linear response function for $t < 0$ by this equality. The causality is taken into account in Eq. (2.3) by limiting the range of the integral as $s \geq 0$. Next, we define the symmetrized correlation of two current operators by

$$\tilde{C}^{\text{sym}}_{\mu\nu}(t) := \frac{1}{2} \text{tr} \left[\hat{\rho}_{\text{can}} (\hat{J}_\mu(t) \hat{J}_\nu(0) + \hat{J}_\nu(0) \hat{J}_\mu(t)) \right]. \tag{2.51}$$

The Fourier transforms of the linear response function and the symmetrized correlation are defined by

$$\tilde{\phi}_{\mu\nu,\omega} := \int_{-\infty}^{\infty} \mathrm{d}t \; \mathrm{e}^{i\omega t} \tilde{\phi}_{\mu\nu}(t), \tag{2.52}$$

$$\tilde{C}^{\text{sym}}_{\mu\nu,\omega} := \int_{-\infty}^{\infty} \mathrm{d}t \; \mathrm{e}^{i\omega t} \tilde{C}^{\text{sym}}_{\mu\nu}(t), \tag{2.53}$$

respectively.

The fluctuation-dissipation theorem claims the relation between these quantities:

$$\tilde{C}^{\text{sym}}_{\mu\nu,\omega} = \frac{\hbar\omega}{2} \coth\left(\frac{\beta\hbar\omega}{2}\right) \tilde{\phi}_{\mu\nu,\omega}. \tag{2.54}$$

The proof is given at the end of this subsection. It is noteworthy that the coefficient is nothing but the expectation value of energy of a harmonic oscillator with frequency ω in thermal equilibrium. In the classical or high-temperature limit of $\beta\hbar\omega \to 0$, the coefficient approaches to β, which is independent of the frequency.

Though the theorem (2.54) itself is mathematically correct, we need to be careful if we see it as a relation between two independently measurable quantities, that is, the linear response function, which describes nonequilibrium processes, and the time correlation, which describes equilibrium properties. To measure the time correlation, we need to perform a measurement at $t = 0$, and then another measurement at $t = t$. Since the backaction of the first measurement changes the state in general, the operator ordering in the definition of the correlation becomes nontrivial, and depends on how we measure observable in the first measurement. For instance, it is known in quantum optics that the normally ordered correlations and the anti-normally ordered correlations are measured when we measure the electromagnetic field by a photon counter and a quantum counter, respectively [21, 22]. Another study shows that a class of measurements called quasi-classical measurements results in the symmetrized correlation in the thermodynamic limit [23].

Finally we prove the fluctuation-dissipation theorem. Let $\{|E_i\rangle\}$ be the set of eigenstates of the Hamiltonian $\hat{H}$ with eigenenergies $\{E_i\}$, so that the Hamiltonian is decomposed as $\hat{H} = \sum_i E_i |E_i\rangle \langle E_i|$. The canonical ensemble is simultaneously diagonalized as

$$\hat{\rho}_{\mathrm{can}} = \sum_i p_i |E_i\rangle \langle E_i| , \tag{2.55}$$

where the probability distribution is given by $p_i = \mathrm{e}^{-\beta E_i}/Z$. By replacing $\mathrm{tr}\,[\cdot]$ with $\sum_i \langle E_i| \cdot |E_i\rangle$ and inserting a compete set of eigenstates $\sum_j |E_j\rangle \langle E_j|$ in Eq. (2.50), we obtain

$$\begin{aligned}\tilde{\phi}_{\mu\nu}(t) &= \beta \sum_{i,j} p_i \int_0^1 \mathrm{d}\alpha \left(\frac{p_j}{p_i}\right)^{\alpha} \mathrm{e}^{i(E_i - E_j)t/\hbar} \langle E_i|\hat{J}_\mu|E_j\rangle \langle E_j|\hat{J}_\nu|E_i\rangle \\ &= \beta \sum_{i,j} p_i \frac{p_j/p_i - 1}{\log(p_j/p_i)} \mathrm{e}^{i(E_i - E_j)t/\hbar} \langle E_i|\hat{J}_\mu|E_j\rangle \langle E_j|\hat{J}_\nu|E_i\rangle . \end{aligned} \tag{2.56}$$

Then the Fourier transform $\tilde{\phi}_{\mu\nu}(t)$ is given by

$$\begin{aligned}\tilde{\phi}_{\mu\nu,\omega} &= \beta \sum_{i,j} p_i \frac{p_j/p_i - 1}{\log(p_j/p_i)} 2\pi\hbar\delta((E_i - E_j + \hbar\omega)/\hbar) \langle E_i|\hat{J}_\mu|E_j\rangle \langle E_j|\hat{J}_\nu|E_i\rangle \\ &= \frac{1 - \mathrm{e}^{-\beta\hbar\omega}}{\hbar\omega} \sum_{i,j} p_i 2\pi\hbar\delta((E_i - E_j + \hbar\omega)/\hbar) \langle E_i|\hat{J}_\mu|E_j\rangle \langle E_j|\hat{J}_\nu|E_i\rangle . \end{aligned} \tag{2.57}$$

To derive the last line, we have used $p_j/p_i = \mathrm{e}^{-\beta(E_j - E_i)} = \mathrm{e}^{-\beta\hbar\omega}$ owing to the existence of the δ function. The Fourier transform of the symmetrized correlation can be obtained by a similar calculation, leading to

$$\begin{aligned}\tilde{C}^{\mathrm{sym}}_{\mu\nu,\omega} &= \beta \sum_{i,j} p_i \frac{1 + p_j/p_i}{2} 2\pi\hbar\delta((E_i - E_j + \hbar\omega)/\hbar) \langle E_i|\hat{J}_\mu|E_j\rangle \langle E_j|\hat{J}_\nu|E_i\rangle \\ &= \frac{1 + \mathrm{e}^{-\beta\hbar\omega}}{2} \sum_{i,j} p_i 2\pi\hbar\delta((E_i - E_j + \hbar\omega)/\hbar) \langle E_i|\hat{J}_\mu|E_j\rangle \langle E_j|\hat{J}_\nu|E_i\rangle . \end{aligned} \tag{2.58}$$

By comparing the factors before the sums in Eqs. (2.57) and (2.58), we obtain the fluctuation-dissipation theorem (2.54).

2.2 Higher-Order Response Theory

In this section, we review a generalization of the results in the previous section to nonlinear responses.

2.2.1 Phenomenological Approach

We consider the same situation as in the previous section, where the system is applied external forces $F_\nu(t)$ and perturbed from the equilibrium state. A natural generalization of Eq. (2.3) to higher-order responses is given by [24, 25]

$$
\begin{aligned}
A_\mu(t) - A_\mu^{\mathrm{eq}} =& \Delta^{(1)} A_\mu(t) + \Delta^{(2)} A_\mu(t) + \cdots + \Delta^{(n)} A_\mu(t) + \cdots \qquad (2.59)\\
=& \int_0^\infty \mathrm{d}s_1\ \Phi^{(1)}_{\mu\nu_1}(s_1) F_{\nu_1}(t-s_1) \\
&+ \int_0^\infty \mathrm{d}s_1 \int_{s_1}^\infty \mathrm{d}s_2\ \Phi^{(2)}_{\mu\nu_1\nu_2}(s_1,s_2) F_{\nu_1}(t-s_1) F_{\nu_2}(t-s_2) \\
&+ \cdots \\
&+ \int_0^\infty \mathrm{d}s_1 \int_{s_1}^\infty \mathrm{d}s_2 \cdots \int_{s_{n-1}}^\infty \mathrm{d}s_n\ \Phi^{(n)}_{\mu\nu_1\ldots\nu_n}(s_1,\ldots,s_n) F_{\nu_1}(t-s_1)\cdots F_{\nu_n}(t-s_n) \\
&+ \cdots . \qquad (2.60)
\end{aligned}
$$

Here, the first term in the last expression represents the linear response examined in the last section, and the nth term represents the nth order response $\Delta^{(n)} A_\mu(t)$. The instantaneous response is eliminated for simplicity. We note that this expansion does not converge in general and should be interpreted as an asymptotic expansion.

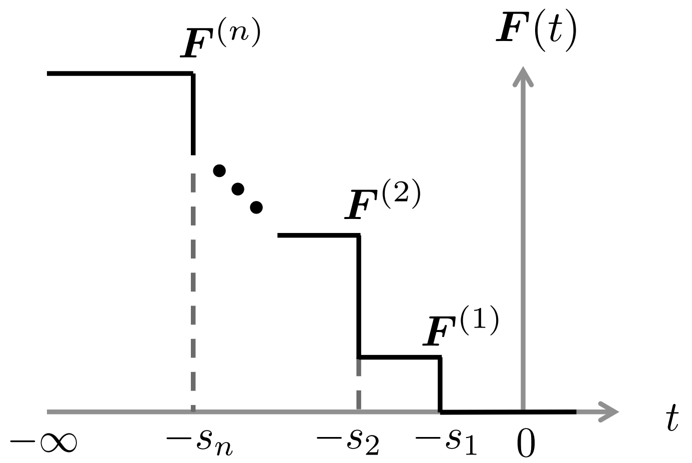

Figure 2.1: Protocol to measure the nth order relaxation function $\Psi^{(n)}_{\mu\nu_1\ldots\nu_n}(s_1,\ldots,s_n)$. The external force is switched off stepwise at $t = -s_n, \ldots, -s_1$.

Next, we consider a generalized relaxation process. Suppose that the external force is switched off stepwise n times at $t = -s_n, \ldots, -s_1$ as

$$
\boldsymbol{F}(t) = \theta(-t-s_n)(\boldsymbol{F}^{(n)} - \boldsymbol{F}^{(n-1)}) + \cdots + \theta(-t-s_2)(\boldsymbol{F}^{(2)} - \boldsymbol{F}^{(1)}) + \theta(-t-s_1)\boldsymbol{F}^{(1)}, \qquad (2.61)
$$

where $0 \le s_1 \le s_2 \le \cdots \le s_n$. We define the nth order relaxation function as the term of the order of $O(F^{(1)}_{\nu_1} F^{(2)}_{\nu_1} \cdots F^{(n)}_{\nu_n})$ in the expansion of $A_\mu(0)$ in this relaxation process:

$$
\Psi^{(n)}_{\mu\nu_1\ldots\nu_n}(s_1,\ldots,s_n) := \left. \frac{\partial^n A_\mu(0)}{\partial F^{(1)}_{\nu_1} \ldots \partial F^{(n)}_{\nu_n}} \right|_{\boldsymbol{F}^{(1)}=\cdots=\boldsymbol{F}^{(n)}=0} . \qquad (2.62)
$$

To see how the relaxation function is related to the response function, we replace the integral variables $s_1, \ldots, s_n$ with $s'_1, \ldots, s'_n$ in Eq. (2.60), and substitute the relaxation protocol (2.61) to it. Then we differentiate both sides with respect to $F^{(1)}_{\nu_1}, \ldots, F^{(n)}_{\nu_n}$ and set $\boldsymbol{F}^{(1)} = \cdots = \boldsymbol{F}^{(n)} = 0$. Almost all terms vanish by this procedure, and the only nonvanishing term in Eq. (2.60) is the nth order response term with $0 \leq s_1 \leq s'_1 \leq s_2 \leq s'_2 \leq \ldots \leq s'_{n-1} \leq s_n \leq s'_n < \infty$. We thereby obtain

$$\Psi^{(n)}_{\mu\nu_1\ldots\nu_n}(s_1, \ldots, s_n) = \int_{s_1}^{s_2} \mathrm{d}s'_1 \int_{s_2}^{s_3} \mathrm{d}s'_2 \cdots \int_{s_n}^{\infty} \mathrm{d}s'_n \Phi^{(n)}_{\mu\nu_1\ldots\nu_n}(s'_1, \ldots, s'_n). \tag{2.63}$$

By applying the fundamental theorem of calculus repeatedly, we obtain

$$\frac{\partial}{\partial s_1}\Psi^{(n)}_{\mu\nu_1\ldots\nu_n}(s_1, \ldots, s_n) = -\int_{s_2}^{s_3} \mathrm{d}s'_2 \cdots \int_{s_n}^{\infty} \mathrm{d}s'_n \Phi^{(n)}_{\mu\nu_1\ldots\nu_n}(s_1, s'_2 \ldots, s'_n), \tag{2.64}$$

$$\frac{\partial}{\partial s_1 \partial s_2}\Psi^{(n)}_{\mu\nu_1\ldots\nu_n}(s_1, \ldots, s_n) = \int_{s_3}^{s_4} \mathrm{d}s'_3 \cdots \int_{s_n}^{\infty} \mathrm{d}s'_n \Phi^{(n)}_{\mu\nu_1\ldots\nu_n}(s_1, s_2, s'_3, \ldots, s_n), \tag{2.65}$$

and finally we obtain

$$\frac{\partial^n}{\partial s_1 \partial s_2 \cdots \partial s_n}\Psi^{(n)}_{\mu\nu_1\ldots\nu_n}(s_1, \ldots, s_n) = (-)^n \Phi^{(n)}_{\mu\nu_1\ldots\nu_n}(s_1, \ldots, s_n). \tag{2.66}$$

Equations (2.63) and (2.66) are the generalization of Eqs. (2.13) and (2.14), respectively. In this sense, not only linear but also higher-order response functions and relaxation functions are related through integration and differentiation.

Similarly to the case of the linear response theory, the system is expected to approach to its equilibrium long time after the external force is removed. Therefore, we assume that the higher-order response functions converge to zero with sufficient rapidity and integrals in Eqs (2.63), (2.64), and (2.65) converge, i.e.,

$$\lim_{s_n \to \infty} \frac{\partial^{k-1}}{\partial s_1 \cdots \partial s_{k-1}} \Psi^{(n)}_{\mu\nu_1\ldots\nu_n}(s_1, \ldots, s_n) = 0 \qquad (k = 1, \ldots, n). \tag{2.67}$$

2.2.2 Response and Relaxation in a Quantum System

In this subsection, we explicitly calculate higher-order response and relaxation functions in a quantum system. We assume that the Hamiltonian has linear dependence on the control parameters as

$$\hat{H}(\boldsymbol{\lambda}(t)) = \hat{H} - \sum_{\nu} \lambda_\nu(t) \hat{X}_\nu, \tag{2.68}$$

and that the control parameter takes a value around zero. The deviation of the expectation value of $\hat{A}$ from its equilibrium value, and hence the nth order response function can be obtained by substituting Eq. (2.31) into itself iteratively. However, here we give another simple derivation of the response function. Suppose that the external force is composed of n pulses given as

$$\boldsymbol{\lambda}(t) = \sum_k \boldsymbol{\epsilon}^{(k)} \Delta(t + s_k), \tag{2.69}$$

where $0 \leq s_1 \leq \cdots \leq s_n$. Then, we can check that the response function is the term $O(\epsilon_{\nu_1}^{(1)} \cdots \epsilon_{\nu_n}^{(n)})$ of the deviation of the value of $\hat{A}_\mu$ under this protocol:

$$\Phi^{(n)}_{\mu\nu_1\ldots\nu_n}(s_1,\ldots,s_n) = \frac{\partial^n}{\partial\epsilon_{\nu_1}^{(1)}\cdots\partial\epsilon_{\nu_n}^{(n)}}\mathrm{tr}\left[\hat{\rho}(0)\hat{A}_\mu\right]\Bigg|_{\boldsymbol{\epsilon}^{(1)}=\cdots=\boldsymbol{\epsilon}^{(n)}=0}. \tag{2.70}$$

The density operator is initially prepared to be the canonical ensemble $\hat{\rho}_{\mathrm{can}}$, and the pulse with magnitude $\boldsymbol{\epsilon}^{(n)}$ is applied at time $t = -s_n$. Then it freely evolves under the Hamiltonian $\hat{H}$ for $-s_n < t < -s_{n-1}$, and another pulse with magnitude $\boldsymbol{\epsilon}^{(n-1)}$ is applied at time $t = -s_{n-1}$. Repeating this process n times, we finally obtain the density operator at $t = 0$ as

$$\begin{aligned}\hat{\rho}(0) =& \mathrm{e}^{-i\hat{H}s_1/\hbar}\mathrm{e}^{i\boldsymbol{\epsilon}^{(1)}\cdot\hat{\boldsymbol{X}}/\hbar}\cdots\mathrm{e}^{-i\hat{H}(s_n-s_{n-1})/\hbar}\mathrm{e}^{i\boldsymbol{\epsilon}^{(n)}\cdot\hat{\boldsymbol{X}}/\hbar}\hat{\rho}_{\mathrm{can}}\mathrm{e}^{-i\boldsymbol{\epsilon}^{(n)}\cdot\hat{\boldsymbol{X}}/\hbar}\mathrm{e}^{i\hat{H}(s_n-s_{n-1})/\hbar}\cdots\mathrm{e}^{-i\boldsymbol{\epsilon}^{(1)}\cdot\hat{\boldsymbol{X}}/\hbar}\mathrm{e}^{i\hat{H}s_1/\hbar}\\ =&\mathrm{e}^{i\boldsymbol{\epsilon}^{(1)}\cdot\hat{\boldsymbol{X}}(-s_1)/\hbar}\cdots\mathrm{e}^{i\boldsymbol{\epsilon}^{(n)}\cdot\hat{\boldsymbol{X}}(-s_n)/\hbar}\hat{\rho}_{\mathrm{can}}\mathrm{e}^{-i\boldsymbol{\epsilon}^{(n)}\cdot\hat{\boldsymbol{X}}(-s_n)/\hbar}\cdots\mathrm{e}^{-i\boldsymbol{\epsilon}^{(1)}\cdot\hat{\boldsymbol{X}}(-s_1)/\hbar},\end{aligned} \tag{2.71}$$

where $\boldsymbol{\epsilon}\cdot\hat{\boldsymbol{X}} := \sum_\nu \epsilon_\nu \hat{X}_\nu$ and the Heisenberg operator is defined as $\hat{X}_\nu(t) := \mathrm{e}^{i\hat{H}t/\hbar}\hat{X}_\nu\mathrm{e}^{-i\hat{H}t/\hbar}$. Therefore, the expectation value of $\hat{A}_\mu$ at $t = 0$ is

$$\begin{aligned}\mathrm{tr}\left[\hat{\rho}(0)\hat{A}_\mu\right] &= \mathrm{tr}\left[\mathrm{e}^{i\boldsymbol{\epsilon}^{(1)}\cdot\hat{\boldsymbol{X}}(-s_1)/\hbar}\cdots\mathrm{e}^{i\boldsymbol{\epsilon}^{(n)}\cdot\hat{\boldsymbol{X}}(-s_n)/\hbar}\hat{\rho}_{\mathrm{can}}\mathrm{e}^{-i\boldsymbol{\epsilon}^{(n)}\cdot\hat{\boldsymbol{X}}(-s_n)/\hbar}\cdots\mathrm{e}^{-i\boldsymbol{\epsilon}^{(1)}\cdot\hat{\boldsymbol{X}}(-s_1)/\hbar}\hat{A}_\mu\right]\\ &= \mathrm{tr}\left[\hat{\rho}_{\mathrm{can}}\mathrm{e}^{-i\boldsymbol{\epsilon}^{(n)}\cdot\hat{\boldsymbol{X}}(-s_n)/\hbar}\cdots\mathrm{e}^{-i\boldsymbol{\epsilon}^{(1)}\cdot\hat{\boldsymbol{X}}(-s_1)/\hbar}\hat{A}_\mu\mathrm{e}^{i\boldsymbol{\epsilon}^{(1)}\cdot\hat{\boldsymbol{X}}(-s_1)/\hbar}\cdots\mathrm{e}^{i\boldsymbol{\epsilon}^{(n)}\cdot\hat{\boldsymbol{X}}(-s_n)/\hbar}\right].\end{aligned} \tag{2.72}$$

To handle many exponentials, we exploit the Baker-Campbell-Hausdorff formula:

$$\mathrm{e}^{\hat{X}}\hat{Y}\mathrm{e}^{-\hat{X}} = \hat{Y} + [\hat{X},\hat{Y}] + \frac{1}{2}[\hat{X},[\hat{X},\hat{Y}]] + \cdots + \frac{1}{n!}[\hat{X},\ldots,[\hat{X},\hat{Y}]\ldots] + \cdots. \tag{2.73}$$

For simplicity of notation, let us introduce a superoperator defined by $\mathrm{ad}_{\hat{X}}(\hat{Y}) := [\hat{X},\hat{Y}]$. The Baker-Campbell-Hausdorff formula can be rewritten as

$$\mathrm{e}^{\hat{X}}\hat{Y}\mathrm{e}^{-\hat{X}} = \sum_{n=0}^{\infty}\frac{[\mathrm{ad}_{\hat{X}}]^n}{n!}(\hat{Y}). \tag{2.74}$$

Using this formula, Eq. (2.72) can be rewritten as

$$\begin{aligned}&\mathrm{tr}\left[\hat{\rho}(0)\hat{A}\right]\\ =&\sum_{m_1,\ldots,m_n=0}^{\infty}\sum_{\nu_1,\ldots,\nu_n}\frac{(-i\epsilon_{\nu_1}^{(1)}/\hbar)^{m_1}\cdots(-i\epsilon_{\nu_n}^{(n)}/\hbar)^{m_n}}{m_1!\cdots m_n!}\mathrm{tr}\left[\hat{\rho}_{\mathrm{can}}[\mathrm{ad}_{\hat{X}_{\nu_1}(-s_1)}]^{m_1}\circ\cdots\circ[\mathrm{ad}_{\hat{X}_{\nu_n}(-s_n)}]^{m_n}(\hat{A}_\mu)\right].\end{aligned} \tag{2.75}$$

Therefore, we obtain the nth order response function as

$$\Phi^{(n)}_{\mu\nu_1\ldots\nu_n}(s_1,\ldots,s_n) = \left(\frac{1}{i\hbar}\right)^n\mathrm{tr}\left[\hat{\rho}_{\mathrm{can}}[\mathrm{ad}_{\hat{X}_{\nu_1}(-s_1)}]\circ\cdots\circ[\mathrm{ad}_{\hat{X}_{\nu_n}(-s_n)}](\hat{A}_\mu)\right], \tag{2.76}$$

or more explicitly,

$$\begin{aligned}&\Phi^{(n)}_{\mu\nu_1\dots\nu_n}(s_1,\dots,s_n)\\&=\left(\frac{1}{i\hbar}\right)^n \mathrm{tr}\left[\hat{\rho}_{\mathrm{can}}\left[\hat{X}_{\lambda_{\nu_n}}(-s_n),\left[\hat{X}_{\lambda_{\nu_{n-1}}}(-s_{n-1}),\dots,\left[\hat{X}_{\lambda_{\nu_2}}(-s_2),\left[\hat{X}_{\lambda_{\nu_1}}(-s_1),\hat{A}_\mu(0)\right]\dots\right]\right]\right].\end{aligned} \tag{2.77}$$

This expression shows that higher-order response functions are given by the expectation value of nested commutators of operators at different times evaluated at equilibrium. This fact means that a nonequilibrium process can be predicted from the equilibrium properties as long as the perturbation expansion is valid in that process. The response function of classical systems can be obtained by replacing commutators with the Poisson brackets in Eq. (2.77).

Finally, combining Eqs. (2.63) and (2.77), we obtain the explicit form of the nth order relaxation function:

$$\begin{aligned}&\Psi^{(n)}_{\mu\nu_1\dots\nu_n}(s_1,\dots,s_n)\\&=\left(\frac{1}{i\hbar}\right)^n \int_{s_1}^{s_2}\mathrm{d}s'_1\cdots\int_{s_n}^{\infty}\mathrm{d}s'_n\mathrm{tr}\left[\hat{\rho}_{\mathrm{can}}\left[\hat{X}_{\lambda_{\nu_n}}(-s'_n),\dots,\left[\hat{X}_{\lambda_{\nu_1}}(-s'_1),\hat{A}_\mu(0)\right]\dots\right]\right].\end{aligned} \tag{2.78}$$

These formulae will be used in later chapters.

Chapter 3

Some Backgrounds on Thermodynamics

3.1 Stochastic Thermodynamics

3.1.1 Langevin Equation and Fokker-Planck Equation

We start form the underdamped Langevin equation

$$m\ddot{x}(t) = -\gamma\dot{x}(t) - \frac{\partial V(x;\boldsymbol{\lambda}(t))}{\partial x}\Big|_{x=x(t)} + \sqrt{\frac{2\gamma}{\beta}}\eta(t). \tag{3.1}$$

The left-hand side represents the inertial term, and m is the mass of a particle. On the right-hand side, the first term represents the friction force with the friction coefficient γ. The second term represents the force experienced by a particle due to an external potential $V(x;\boldsymbol{\lambda}(t))$. We assume that the potential can be changed as a function of time through control parameters $\boldsymbol{\lambda}(t)$. We let $\boldsymbol{\Lambda}$ denote the time dependence of $\boldsymbol{\lambda}(t)$ and call it the protocol. The third term represents the white Gaussian noise term satisfying $\langle\eta(t)\eta(t')\rangle = \delta(t-t')$. The amplitude of the noise is determined from the fluctuation-dissipation theorem of the second kind, so that the canonical ensemble with inverse temperature $\beta = 1/k_BT$ is a steady state.

When the time resolution of the measurement is longer than the time scale m/γ, the inertial term can be neglected, leading to the overdamped Langevin equation

$$\dot{x}(t) = -\frac{1}{\gamma}\frac{\partial V(x;\boldsymbol{\lambda}(t))}{\partial x}\Big|_{x=x(t)} + \sqrt{\frac{2}{\beta\gamma}}\eta(t). \tag{3.2}$$

We focus on the overdamped Langevin equation in the following discussions.

In thermodynamics, the work performed on the system is identified as a change in energy of the system through macroscopic degrees of freedom. Since the control parameter in this Langevin system is $\boldsymbol{\lambda}$, the work is defined by

$$W(\{x(t)\},\boldsymbol{\Lambda}) = \int_0^T \mathrm{d}t\ \dot{\lambda}^\mu(t)\frac{\partial V(x(t);\boldsymbol{\lambda})}{\partial\lambda^\mu}\Big|_{\boldsymbol{\lambda}=\boldsymbol{\lambda}(t)} \tag{3.3}$$

for each realization of the trajectory $\{x(t)\}$.

Remarkably, the distribution of the work satisfy the Jarzynski equality [26, 27, 28]

$$\left\langle \mathrm{e}^{-\beta(W-\Delta F)} \right\rangle = 1, \tag{3.4}$$

where ΔF is the free energy difference $\Delta F = F(\boldsymbol{\lambda}(T)) - F(\boldsymbol{\lambda}(0))$ and $F(\boldsymbol{\lambda}) := -\frac{1}{\beta}\log\int \mathrm{d}x\, \mathrm{e}^{-\beta V(x;\boldsymbol{\lambda})}$. The Jarzynski equality holds for an arbitrary control, even if the system is driven far away from equilibrium during the control. The Jarzynski equality can be used, for example, to determine the free energy from nonequilibrium measurements [29]. From the convexity of the function e^{-x}, we obtain one of the expressions of the second law of thermodynamics

$$\langle W \rangle \geq \Delta F. \tag{3.5}$$

When we are interested only in the average behavior of the system, the density distribution function $\rho(x;t)$ is sufficient to describe the system. To derive the time evolution of the density function, we use Itô's lemma.

Theorem 3.1. (Itô lemma) [30, 31]
For a stochastic process described by $\dot{x}(t) = F(x(t)) + \sigma\eta(t)$ and for a twice differentiable function $f(x)$, the following equality holds:

$$\begin{aligned}
\frac{\mathrm{d}f(x(t))}{\mathrm{d}t} &= \left.\frac{\mathrm{d}f(x)}{\mathrm{d}x}\right|_{x=x(t)} \dot{x}(t) + \frac{1}{2}\sigma^2 \left.\frac{\mathrm{d}^2 f(x)}{\mathrm{d}x^2}\right|_{x=x(t)} \\
&= \left[F(x(t))\left.\frac{\mathrm{d}f(x)}{\mathrm{d}x}\right|_{x=x(t)} + \frac{1}{2}\sigma^2 \left.\frac{\mathrm{d}^2 f(x)}{\mathrm{d}x^2}\right|_{x=x(t)}\right] + \sigma \left.\frac{\mathrm{d}f(x)}{\mathrm{d}x}\right|_{x=x(t)} \eta(t).
\end{aligned} \tag{3.6}$$

By taking the average of the both sides of Eq. (3.6) with respect to the density function $\rho(x;t)$, we obtain

$$\begin{aligned}
&\frac{\partial}{\partial t}\int \mathrm{d}x\ \rho(x;t) f(x) = \int \mathrm{d}x\ \rho(x;t)\left[F(x)\frac{\mathrm{d}f(x)}{\mathrm{d}x} + \frac{1}{2}\sigma^2 \frac{\mathrm{d}^2 f(x)}{\mathrm{d}x^2}\right] \\
\Leftrightarrow &\int \mathrm{d}x\ \frac{\partial \rho(x;t)}{\partial t} f(x) = \int \mathrm{d}x\ \left[-\frac{\partial}{\partial x}\left(\rho(x;t)F(x)\right) + \frac{1}{2}\sigma^2 \frac{\partial^2 \rho(x;t)}{\partial x^2}\right] f(x)
\end{aligned} \tag{3.7}$$

for an arbitrary $f(x)$. Note that the last term in the last line of Eq. (3.6) vanishes after averaging, and that we have integrated by parts to obtain the last equality. Therefore, we have derived the Fokker-Planck equation

$$\frac{\partial \rho(x;t)}{\partial t} = -\frac{\partial}{\partial x}\left(\rho(x;t)F(x)\right) + \frac{1}{2}\sigma^2 \frac{\partial^2 \rho(x;t)}{\partial x^2}. \tag{3.8}$$

For the overdamped Langevin equation (3.2), the Fokker-Planck equation reads

$$\frac{\partial \rho(x;t)}{\partial t} = \frac{1}{\gamma}\frac{\partial}{\partial x}\left(\frac{\partial V(x;\boldsymbol{\lambda}(t))}{\partial x}\rho(x;t) + \frac{1}{\beta}\frac{\partial \rho(x;t)}{\partial x}\right). \tag{3.9}$$

We note that the canonical ensemble $\rho_{\mathrm{can}}^{\boldsymbol{\lambda}}(x)$ is the steady distribution of the Fokker-Planck equation, which justifies the temperature dependence of the amplitude of the noise.

3.1.2 Feynman-Kac formula

In this section, we introduce the Feynman-Kac formulae, which express the solution to a parabolic partial differential equation in terms of an expectation value of an observable with respect to a random process.

Let us consider a stochastic process described by

$$\dot{x}(t) = F(x(t)) + \sigma\eta(t). \tag{3.10}$$

We define two functions by

$$\phi(x;t) := \left\langle \int_0^t \mathrm{d}s\ f(x(s)) \right\rangle_x , \tag{3.11}$$

$$G(x;t) := \left\langle \mathrm{e}^{\int_0^t \mathrm{d}s\ c(x(s))} \right\rangle_x , \tag{3.12}$$

where $f(x)$ and $c(x)$ are arbitrary functions, and the average is taken over a random process (3.10) starting from $x(0) = x$. We will derive the partial differential equations that these functions satisfy. First, as an initial condition, they satisfy $\phi(x; t = 0) = 0$ and $G(x; t = 0) = 1$. Next, we consider a time evolution of $\phi(x;t)$. Let $p(\xi)$ be the probability that the particle moves from x to $x + \xi$ during the time interval from $t = 0$ to $t = \mathrm{d}t$. Then, $\phi(x; t + \mathrm{d}t)$ is evaluated as

$$\begin{aligned} \phi(x;t+\mathrm{d}t) &= f(x)\mathrm{d}t + \left\langle \int_{\mathrm{d}t}^{t+\mathrm{d}t} \mathrm{d}s\ f(x(s)) \right\rangle_x \\ &= f(x)\mathrm{d}t + \int \mathrm{d}\xi\ p(\xi)\phi(x+\xi,t). \end{aligned} \tag{3.13}$$

If we Taylor-expand $\phi(x + \xi, t)$ in terms of ξ up to the second order[1], we obtain

$$\begin{aligned} \phi(x;t+\mathrm{d}t) &= f(x)\mathrm{d}t + \int \mathrm{d}\xi\ p(\xi)\phi(x,t) + \int \mathrm{d}\xi\ p(\xi)\xi\frac{\partial\phi(x,t)}{\partial x} + \frac{1}{2}\int \mathrm{d}\xi\ p(\xi)\xi^2\frac{\partial^2\phi(x,t)}{\partial x^2} \\ &= f(x)\mathrm{d}t + \phi(x,t) + F(x)\frac{\partial\phi(x,t)}{\partial x}\mathrm{d}t + \frac{1}{2}\sigma^2\frac{\partial^2\phi(x,t)}{\partial x^2}\mathrm{d}t, \end{aligned} \tag{3.14}$$

which leads to the partial differential equation

$$\frac{\partial\phi(x;t)}{\partial t} = F(x)\frac{\partial\phi(x;t)}{\partial x} + \frac{1}{2}\sigma\frac{\partial^2\phi(x;t)}{\partial x^2} + f(x). \tag{3.15}$$

In particular, if we take the limit of $t \to \infty$, $\phi(x;t)$ is expected to converge to a stationary distribution $\phi^*(x) = \lim_{t\to\infty}\phi(x;t)$ and the time derivative in Eq. (3.14) vanishes. Therefore, $\phi^*(x)$ is the solution to the ordinary differential equation

$$F(x)\frac{\mathrm{d}\phi^*(x)}{\mathrm{d}x} + \frac{1}{2}\sigma^2\frac{\mathrm{d}^2\phi^*(x)}{\mathrm{d}x^2} = -f(x). \tag{3.16}$$

[1] The higher-order terms vanish since $\int \mathrm{d}\xi\ p(\xi)\xi^n = 0$ $(n \geq 3)$ due to the property of the Gaussian noise.

Similarly, the time evolution of $G(x;t)$ can be calculated as

$$
\begin{aligned}
G(x;t+\mathrm{d}t) &= \mathrm{e}^{c(x)\mathrm{d}t} \left\langle \mathrm{e}^{\int_{\mathrm{d}t}^{t+\mathrm{d}t} \mathrm{d}s\ c(x(s))} \right\rangle_x \\
&= (1+c(x)\mathrm{d}t) \int \mathrm{d}\xi p(\xi) \left(G(x;t) + \xi \frac{\partial G(x;t)}{\partial x} + \frac{1}{2}\xi^2 \frac{\partial^2 G(x;t)}{\partial x^2} \right) \\
&= G(x;t) + c(x)G(x;t)\mathrm{d}t + F(x)\frac{\partial G(x;t)}{\partial x}\mathrm{d}t + \frac{1}{2}\sigma^2 \frac{\partial^2 G(x;t)}{\partial x^2}\mathrm{d}t, \qquad (3.17)
\end{aligned}
$$

which leads to the partial differential equation

$$
\frac{\partial G(x;t)}{\partial t} = F(x)\frac{\partial G(x;t)}{\partial x} + \frac{1}{2}\sigma^2 \frac{\partial^2 G(x;t)}{\partial x^2} + c(x)G(x;t). \qquad (3.18)
$$

To summarize, we have obtain the following theorems.

Theorem 3.2. (Feynman-Kac formula 1)
The solution to the partial differential equation

$$
\frac{\partial \phi(x;t)}{\partial t} = F(x)\frac{\partial \phi(x;t)}{\partial x} + \frac{1}{2}\sigma^2 \frac{\partial^2 \phi(x;t)}{\partial x^2} + f(x) \qquad (3.19)
$$

with an initial condition $\phi(x;t=0)=0$ is given by

$$
\phi(x;t) = \left\langle \int_0^t \mathrm{d}s f(x(s)) \right\rangle_x , \qquad (3.20)
$$

where the average is taken over a random process (3.10) starting from $x(0)=x$. In particular,

$$
\phi^*(x) = \left\langle \int_0^\infty \mathrm{d}s f(x(s)) \right\rangle_x \qquad (3.21)
$$

is the solution to

$$
F(x)\frac{\mathrm{d}\phi^*(x)}{\mathrm{d}x} + \frac{1}{2}\sigma^2 \frac{\mathrm{d}^2\phi^*(x)}{\mathrm{d}x^2} = -f(x). \qquad (3.22)
$$

Theorem 3.3. (Feynman-Kac formula 2)
The solution to the partial differential equation

$$
\frac{\partial G(x;t)}{\partial t} = F(x)\frac{\partial G(x;t)}{\partial x} + \frac{1}{2}\sigma^2 \frac{\partial^2 G(x;t)}{\partial x^2} + c(x)G(x;t) \qquad (3.23)
$$

with an initial condition $G(x;t=0)=1$ is given by

$$
G(x;t) = \left\langle \mathrm{e}^{\int_0^t \mathrm{d}s\ c(x(s))} \right\rangle_x \qquad (3.24)
$$

where the average is taken over a random process (3.10) starting from $x(0)=x$.

We will use these formulae later.

3.2 Thermodynamic Metric

3.2.1 Thermodynamic Metric

In this section, we introduce an effective way to evaluate the work performed on the system during a thermodynamic control. Here, we assume that the control is realized by varying an external potential $V(x; \boldsymbol{\lambda}(t))$ or a Hamiltonian $\hat{H}(\boldsymbol{\lambda}(t))$ as a function of time through m external control parameters $\boldsymbol{\lambda}(t) = (\lambda^\mu(t))_{\mu=1,\ldots,m}$. The time dependence of the control parameters during the control period $0 \leq t \leq T$ is called the protocol, and denoted by $\boldsymbol{\Lambda} = \{\boldsymbol{\lambda}(t)\}_{t\in[0,T]}$. We also assume that the initial state is the canonical ensemble with respect to the initial control parameters $\boldsymbol{\lambda}(0)$ and with the inverse temperature $\beta = 1/k_B T$.

From the second law of thermodynamics, the work performed on the system during the control is equal to or larger than the free-energy difference

$$\langle W(\boldsymbol{\Lambda})\rangle \geq F(\boldsymbol{\lambda}(T)) - F(\boldsymbol{\lambda}(0)) = \Delta F, \tag{3.25}$$

where the free energy is defined by

$$F(\boldsymbol{\lambda}) = -\frac{1}{\beta}\log \mathrm{tr}\left[-\beta \hat{H}(\boldsymbol{\lambda})\right], \tag{3.26}$$

$$F(\boldsymbol{\lambda}) = -\frac{1}{\beta}\log \int \mathrm{d}x\ \mathrm{e}^{-\beta V(x;\boldsymbol{\lambda})}, \tag{3.27}$$

for quantum Hamiltonian systems and overdamped Langevin systems, respectively. The equality is achieved if the control is quasistatic, that is, the speed of control is infinitely slow. For a finite-time control, the inequality (3.25) is strict, and the process is thermodynamically irreversible in general. Then the degree of the irreversibility is quantified by the difference between the work and the free-energy difference, which is called the excess work[2] $\langle W_{\mathrm{ex}}(\boldsymbol{\Lambda})\rangle := \langle W(\boldsymbol{\Lambda})\rangle - \Delta F$. Therefore, evaluation of the excess work in general control processes is an important task.

Under the condition that the state is not driven far away from equilibrium during the control, the excess work can be approximately evaluated as [32, 33]

$$\langle W_{\mathrm{ex}}(\boldsymbol{\Lambda})\rangle \simeq \int_0^T \mathrm{d}t\ \zeta_{\mu\nu}(\boldsymbol{\lambda}(t))\dot{\lambda}^\mu(t)\dot{\lambda}^\nu(t). \tag{3.28}$$

Here and henceforth, the Einstein summation convention is adopted, where the repeated indices are implicitly assumed to be summed. In the approximate expression (3.28), the excess power is quadratic with respect to the velocity of the control parameters. The coefficient $\zeta_{\mu\nu}(\boldsymbol{\lambda})$ is called the thermodynamic metric, and can be expressed as

$$\zeta_{\mu\nu}(\boldsymbol{\lambda}) = \beta\int_0^\infty \mathrm{d}s\, \langle \Delta X_\mu(0;\boldsymbol{\lambda}); \Delta X_\nu(s;\boldsymbol{\lambda})\rangle_{\boldsymbol{\lambda}}^{\mathrm{eq}}. \tag{3.29}$$

Here, the bracket $\langle \Delta X_\mu(0;\boldsymbol{\lambda}); \Delta X_\nu(t;\boldsymbol{\lambda})\rangle_{\boldsymbol{\lambda}}^{\mathrm{eq}}$ denotes the temporal correlation at the equilibrium state with the control parameters $\boldsymbol{\lambda}$ fixed, and $\Delta X_\mu(s;\boldsymbol{\lambda})$ represents the deviation of the general-

[2] Excess work is also called dissipated work, since the excess work is dissipated into the heat bath attached to the system if the final system is in equilibrium.

ized force from its equilibrium value with respect to the parameter λ^μ at time s. More explicitly, for an overdamped Langevin system, the generalized force is defined by $X_\mu(x;\boldsymbol{\lambda}) = -\frac{\partial V(x;\boldsymbol{\lambda})}{\partial \lambda^\mu}$, and $\langle \Delta X_\mu(0;\boldsymbol{\lambda}); \Delta X_\nu(s;\boldsymbol{\lambda})\rangle^{\mathrm{eq}}_{\boldsymbol{\lambda}}$ is interpreted as

$$\langle \Delta X_\mu(x(0);\boldsymbol{\lambda}) \Delta X_\nu(x(s);\boldsymbol{\lambda})\rangle^{\mathrm{eq}}_{\boldsymbol{\lambda}}, \tag{3.30}$$

where the average is taken over the path $\{x(s)\}$ generated by randomly sampling the initial condition $x(0)$ according to the canonical distribution $\propto \mathrm{e}^{-\beta V(x;\boldsymbol{\lambda})}$, and then letting the system evolve in time according to the overdamped Langevin equation. For a quantum system, the generalized force operator is defined by $\hat{X}_\mu(\boldsymbol{\lambda}) = -\frac{\partial \hat{H}(\boldsymbol{\lambda})}{\partial \lambda^\mu}$, and its Heisenberg representation is defined by $\hat{X}_\mu(s;\boldsymbol{\lambda}) = \mathrm{e}^{i\hat{H}(\boldsymbol{\lambda})s/\hbar} \hat{X}_\mu(\boldsymbol{\lambda}) \mathrm{e}^{-i\hat{H}(\boldsymbol{\lambda})s/\hbar}$. Also, the correlation is interpreted as the canonical correlation, and therefore, $\langle \Delta X_\mu(0;\boldsymbol{\lambda}); \Delta X_\nu(s;\boldsymbol{\lambda})\rangle^{\mathrm{eq}}_{\boldsymbol{\lambda}}$ should be interpreted as

$$\langle\!\langle \hat{X}_\mu(0;\boldsymbol{\lambda}), \hat{X}_\nu(s;\boldsymbol{\lambda})\rangle\!\rangle^{\mathrm{can}}_{\hat{\rho}_{\mathrm{can}}(\boldsymbol{\lambda})}. \tag{3.31}$$

We note that only the symmetric part of the thermodynamic metric $\zeta^s_{\mu\nu} := \frac{1}{2}(\zeta_{\mu\nu} + \zeta_{\nu\mu})$ contributes to the excess work in Eq. (3.28). When the generalized force operators have the time reversal symmetry, we can show that the thermodynamic metric is symmetric because

$$\begin{aligned}
\int_0^\infty \mathrm{d}s\, \langle \Delta X_\mu(0;\boldsymbol{\lambda}); \Delta X_\nu(s;\boldsymbol{\lambda})\rangle^{\mathrm{eq}}_{\boldsymbol{\lambda}} &= \int_0^\infty \mathrm{d}s\, \langle \Delta X_\mu(0;\boldsymbol{\lambda}); \Delta X_\nu(-s;\boldsymbol{\lambda})\rangle^{\mathrm{eq}}_{\boldsymbol{\lambda}} \\
&= \int_0^\infty \mathrm{d}s\, \langle \Delta X_\mu(s;\boldsymbol{\lambda}); \Delta X_\nu(0;\boldsymbol{\lambda})\rangle^{\mathrm{eq}}_{\boldsymbol{\lambda}} \\
&= \int_0^\infty \mathrm{d}s\, \langle \Delta X_\nu(0;\boldsymbol{\lambda}); \Delta X_\mu(s;\boldsymbol{\lambda})\rangle^{\mathrm{eq}}_{\boldsymbol{\lambda}},
\end{aligned} \tag{3.32}$$

where we have used the time translational symmetry to obtain the second equality. Since the excess work is positive for any protocol from the second law of thermodynamics, the symmetric part of the thermodynamic metric is positive definite, which ensures that the thermodynamic metric can be interpreted as the metric on the control parameter space.

Based on this approximate expression we can discuss an optimal protocol that requires the smallest excess work among all the protocols that start from $\boldsymbol{\lambda}(0) = \boldsymbol{\lambda}_i$ and end at $\boldsymbol{\lambda}(T) = \boldsymbol{\lambda}_f$ for a fixed control time T. This minimization problem is solved in two steps. First, from the Cauchy-Schwarz inequality, we obtain

$$T \int_0^T \mathrm{d}t \dot{\lambda}^\mu(t)\dot{\lambda}^\nu(t)\zeta_{\mu\nu}(\boldsymbol{\lambda}(t)) \geq \left(\int_0^T \mathrm{d}t \sqrt{\dot{\lambda}^\mu(t)\dot{\lambda}^\nu(t)\zeta_{\mu\nu}(\boldsymbol{\lambda}(t))} \right)^2, \tag{3.33}$$

where the equality is achieved if and only if the excess power $\dot{\lambda}^\mu(t)\dot{\lambda}^\nu(t)\zeta_{\mu\nu}(\boldsymbol{\lambda}(t))$ is constant during the entire protocol $t \in [0, T]$. We note that the right-hand side in Eq. (3.33) is the length of the path on the control parameter space, which is independent of the parametrization and is determined only by the shape of the path. Therefore, once the shape of a path is fixed, the best way to parametrize it, or equivalently, the best time dependence of the control parameter along shape, is to keep the excess power constant. Then, we minimize the length of the path that connects $\boldsymbol{\lambda}_i$ and $\boldsymbol{\lambda}_f$. Such a path is determined by the geodesics equation

$$\ddot{\lambda}^\mu(t) + \dot{\lambda}^\nu(t)\dot{\lambda}^\rho(t)(\Gamma^\mu{}_{\nu\rho})_{\boldsymbol{\lambda}(t)} = 0 \tag{3.34}$$

subject to the boundary conditions $\boldsymbol{\lambda}(0) = \boldsymbol{\lambda}_i$ and $\boldsymbol{\lambda}(T) = \boldsymbol{\lambda}_f$, where $\Gamma^\mu{}_{\nu\rho}$ is the Christffel symbol for the Levi-Civita connection defined by

$$\Gamma^\mu{}_{\nu\rho} = \frac{1}{2}\zeta^{\mu\kappa}\left(\frac{\partial\zeta_{\kappa\rho}}{\partial\lambda^\nu} + \frac{\partial\zeta_{\kappa\nu}}{\partial\lambda^\rho} - \frac{\partial\zeta_{\nu\rho}}{\partial\lambda^\kappa}\right). \tag{3.35}$$

A remarkable feature of the thermodynamic metric expression for the excess work is that the excess power (the integrand in Eq. (3.28)) depends only on $\boldsymbol{\lambda}(t)$ and $\dot{\boldsymbol{\lambda}}(t)$ at time t, even though the value of observables at time t depends on the history of the the parameter $\{\boldsymbol{\lambda}(t')\}_{t'\in[0,t]}$ in general nonequilibrium processes. In this sense, the thermodynamic metric expression (3.28) is local in time, or local in the control space. Owing to the advantages described above, analyses on thermodynamic control based on the thermodynamic metric have been made actively [33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43].

As a historical remark, the expression of the excess work in terms of the thermodynamic metric (3.28) was first derived by Sekimoto and Sasa [32] for overdamped Langevin systems, but the explicit form of the thermodynamic metric was rather complicated, given in terms of the spectral decomposition of the Focker-Planck operator. Later, the simple form of the thermodynamic metric (3.29) in terms of the temporal correlation function in equilibrium was found in Ref. [33] from a phenomenological argument. Rotskoff et al. [43] recently derived the same expression for the thermodynamic metric as Ref. [33] from the overdamped Langevin equation.

In our setting, the system is controlled by a time-dependent Hamiltonian or potential, where driving forces are always conservative. The generalization to steady states in the presense of nonconservative forces is discussed in Ref. [40].

3.2.2 Phenomelogical Derivation

In this section, we review the phenomenological derivation of the thermodynamic metric expression of the excess work (3.28) following Ref. [33], using the linear response theory.

The work performed on the system is given by

$$\langle W(\boldsymbol{\Lambda})\rangle = -\int_0^T \mathrm{d}t\ \dot{\lambda}^\mu(t)\,\langle X_\mu(\boldsymbol{\lambda}(t))\rangle_{\boldsymbol{\Lambda}}\,, \tag{3.36}$$

where $\langle\cdot\rangle_{\boldsymbol{\Lambda}}$ is the average over the nonequilibrium process under the protocol $\boldsymbol{\Lambda}$. By comparing it with the free-energy difference $\Delta F = -\int_0^T \mathrm{d}t\ \dot{\lambda}^\mu(t)\,\langle X_\mu(\boldsymbol{\lambda}(t))\rangle^{\mathrm{eq}}_{\boldsymbol{\lambda}(t)}$, the excess work is expressed as

$$\langle W_{\mathrm{ex}}(\boldsymbol{\Lambda})\rangle = -\int_0^T \mathrm{d}t\ \dot{\lambda}^\mu(t)\,\langle\Delta X_\mu(\boldsymbol{\lambda}(t))\rangle_{\boldsymbol{\Lambda}}\,. \tag{3.37}$$

In the linear response regime, the expectation value of the deviation is given by

$$\begin{aligned}\langle \Delta X_\mu(\boldsymbol{\lambda}(t))\rangle_{\boldsymbol{\Lambda}} &\simeq \int_0^\infty \mathrm{d}s\ \phi_{\mu\nu}(s;\boldsymbol{\lambda}(t))(\lambda^\nu(t-s)-\lambda^\nu(t))\\ &= -\int_0^\infty \mathrm{d}s\ \frac{\mathrm{d}\psi_{\mu\nu}(s;\boldsymbol{\lambda}(t))}{\mathrm{d}s}(\lambda^\nu(t-s)-\lambda^\nu(t)),\end{aligned} \tag{3.38}$$

where $\phi_{\mu\nu}(s)$ and $\psi_{\mu\nu}(s)$ are respectively the linear response and relaxation functions of X_μ against a perturbation X_ν at the equilibirum state with respect to $\boldsymbol{\lambda}(t)$. We have used Eq. (2.14) to obtain the last equality. By integrating Eq. (3.38) by parts, we obtain

$$\begin{aligned}\langle \Delta X_\mu(\boldsymbol{\lambda}(t))\rangle_{\boldsymbol{\Lambda}} \simeq &-\left[\psi_{\mu\nu}(s;\boldsymbol{\lambda}(t))(\lambda^\nu(t-s)-\lambda^\nu(t))\right]_{s=0}^{s=\infty}\\ &-\int_0^\infty \mathrm{d}s\ \psi_{\mu\nu}(s;\boldsymbol{\lambda}(t))\dot{\lambda}^\nu(t-s)\end{aligned} \tag{3.39}$$

The boundary term at $s=0$ vanishes obviously, and the one at $s=\infty$ also vanishes from the assumption (2.15) that the system approaches the equilibrium state eventually when the control parameter is kept fixed. We also assume that the change in the control velocity is sufficiently slow so that

$$\dot{\lambda}^\nu(t-s) \simeq \dot{\lambda}^\nu(t) \tag{3.40}$$

during the time interval where the linear relaxation function $\psi_{\mu\nu}(s;\boldsymbol{\lambda}(t))$ takes effectively nonzero values. We finally obtain the expression of the excess work as

$$\langle W_{\mathrm{ex}}(\boldsymbol{\Lambda})\rangle \simeq \int_0^T \mathrm{d}t\ \dot{\lambda}^\mu(t)\dot{\lambda}^\nu(t)\int_0^\infty \mathrm{d}s\ \psi_{\mu\nu}(s;\boldsymbol{\lambda}(t)). \tag{3.41}$$

The integral over s can be performed independently of the protocol $\boldsymbol{\Lambda}$, giving the thermodynamic metric

$$\int_0^\infty \mathrm{d}s\ \psi_{\mu\nu}(s;\boldsymbol{\lambda}(t)) = \beta\int_0^\infty \mathrm{d}s\ \langle \Delta X_\mu(0;\boldsymbol{\lambda}(t));\Delta X_\nu(s;\boldsymbol{\lambda}(t))\rangle^{\mathrm{eq}}_{\boldsymbol{\lambda}(t)} = \zeta_{\mu\nu}(\boldsymbol{\lambda}(t)). \tag{3.42}$$

In this phenomenological derivation, two approximations are used: linear-response approximation (3.38), and the constant-velocity approximation (3.40). The first approximation is expected to be valid when the control is slow and therefore the system is not driven too far away from equilibrium. However, neither the relation between two approximations nor the quantitative conditions under which these approximations are valid is clear. We will address this issue in Chap. 6

3.2.3 Microscopic Derivation

In this section, we review the microscopic derivation of the expression of excess work in terms of the thermodynamic metric for overdamped Langevin systems, following Ref. [43].

We consider a one-dimensional system described by the overdamped Langevin equation

$$\dot{x}(t) = -\frac{1}{\epsilon\gamma}\frac{\partial V(x;\boldsymbol{\lambda}(t))}{\partial x}\Big|_{x=x(t)} + \sqrt{\frac{2}{\beta\epsilon\gamma}}\eta(t). \tag{3.43}$$

Here, the friction coefficient is given by $\epsilon\gamma$, where ϵ is a positive dimensionless parameter that characterizes the separation of time scales between the system and the control [43]. As ϵ approaches zero, the time-scale separation becomes clearer, which means that the dynamics of the system $x(t)$ is much faster that the change of the control parameters $\boldsymbol{\lambda}(t)$. Though it is difficult to understand intuitively why ϵ characterizes the separation of time scales in this setting, we will show in Chap. 6 that this approach is equivalent to the slow control $\boldsymbol{\Lambda}_\epsilon$ under an overdamped Langevin equation with the friction coefficient fixed. In the following, we expand the excess work in terms of ϵ.

The work performed on the system is defined at the trajectory level as

$$W(\boldsymbol{\Lambda}, \{x(t)\}) = \int_0^T \mathrm{d}t\ \frac{\partial V(x(t);\boldsymbol{\lambda})}{\partial \lambda^\mu}\Bigg|_{\boldsymbol{\lambda}=\boldsymbol{\lambda}(t)}, \tag{3.44}$$

and therefore the the average work is given by

$$\langle W(\boldsymbol{\Lambda})\rangle = \int_0^T \mathrm{d}t\ \dot{\lambda}^\mu(t) \int \mathrm{d}x\ \rho(x;t)\frac{\partial V(x;\boldsymbol{\lambda})}{\partial \lambda^\mu}\Bigg|_{\boldsymbol{\lambda}=\boldsymbol{\lambda}(t)}, \tag{3.45}$$

where $\rho(x;t)$ is the density function at time t. The density function satisfies the Fokker-Planck equation

$$\frac{\partial \rho(x;t)}{\partial t} = \frac{1}{\epsilon\gamma}\frac{\partial}{\partial x}\left(\frac{\partial V(x;\boldsymbol{\lambda}(t))}{\partial x}\rho(x;t) + \frac{1}{\beta}\frac{\partial \rho(x;t)}{\partial x}\right). \tag{3.46}$$

We expand the density function $\rho(x;t)$ in terms of ϵ as

$$\rho(x;t) = \rho_0(x;t)(1 + \epsilon\phi_1(x;t) + \epsilon^2\phi_2(x;t) + \epsilon^3\phi_3(x;t) + \cdots), \tag{3.47}$$

and solve the Fokker-Planck equation (6.26) from lower orders in ϵ. The equations from lower orders read:

$$O(\epsilon^{-1}): \qquad 0 = \frac{\partial}{\partial x}\left(\frac{\partial V(x;\boldsymbol{\lambda}(t))}{\partial x}\rho_0(x;t) + \frac{1}{\beta}\frac{\partial \rho_0(x;t)}{\partial x}\right), \tag{3.48}$$

$$O(\epsilon^0): \qquad \frac{\partial \rho_0(x;t)}{\partial t} = \frac{1}{\gamma}\frac{\partial}{\partial x}\left(\frac{\partial V(x;\boldsymbol{\lambda}(t))}{\partial x}\rho_0(x;t)\phi_1(x;t) + \frac{1}{\beta}\frac{\partial(\rho_0(x;t)\phi_1(x;t))}{\partial x}\right). \tag{3.49}$$

In the lowest order in ϵ, the system is driven in a quasistatic manner, and the state is expected to be in equilibrium. Therefore, we expand the density function $\rho(x;t)$ around the canonical ensemble

$$\rho_0(x;t) = \rho_{\mathrm{can}}^{\boldsymbol{\lambda}(t)}(x) = \frac{\mathrm{e}^{-\beta V(x;\boldsymbol{\lambda}(t))}}{Z(\boldsymbol{\lambda}(t))}, \tag{3.50}$$

which is justified from the fact that the canonical ensemble $\rho_{\rm can}^{\boldsymbol{\lambda}(t)}(x)$ satisfies the $O(\epsilon^{-1})$ equation (3.48). Then, the $O(\epsilon^0)$ contribution to the work gives the free-energy difference $\Delta F = F(\boldsymbol{\lambda}(T)) - F(\boldsymbol{\lambda}(0))$:

$$\langle W(\boldsymbol{\Lambda})\rangle = \int_0^T \mathrm{d}t\ \frac{\mathrm{d}F(\boldsymbol{\lambda}(t))}{\mathrm{d}t} + O(\epsilon) \tag{3.51}$$

$$= \Delta F + O(\epsilon). \tag{3.52}$$

To calculate the excess work, we proceed to the $O(\epsilon)$ contribution to the work. The $O(\epsilon^0)$ equation (3.49) can be rewritten as

$$\frac{1}{\beta\gamma}\frac{\partial^2\phi_1(x;t)}{\partial x^2} - \frac{1}{\gamma}\frac{\partial V(x;\boldsymbol{\lambda}(t))}{\partial x}\frac{\partial\phi_1(x;t)}{\partial x} = \beta\Delta X_\nu(x;\lambda(t))\dot{\lambda}^\nu(t), \tag{3.53}$$

where $X_\nu(x;\boldsymbol{\lambda}) := -\frac{\partial V(x;\boldsymbol{\lambda})}{\partial\lambda^\nu}$ is a generalized force with respect to the control parameter λ^ν, and $\Delta X(x;\boldsymbol{\lambda}) := X(x;\boldsymbol{\lambda}) - \langle X(\,\cdot\,;\boldsymbol{\lambda})\rangle^{\rm eq}_{\boldsymbol{\lambda}}$. Using the Feynman-Kac formula (3.2), the solution to Eq. (3.53) can be expressed as the average value of an observable of a stochastic process as

$$\phi_1(x;t) = -\beta\dot{\lambda}^\nu(t)\int_0^\infty \mathrm{d}\tau\,\langle\Delta X_\nu(x^{\boldsymbol{\lambda}(t)}(\tau),\boldsymbol{\lambda}(t))\rangle_{x,\boldsymbol{\lambda}(t)}\,. \tag{3.54}$$

Here, the bracket $\langle\cdot\rangle_{x,\boldsymbol{\lambda}}$ expresses the expectation value with respect to the random process

$$\frac{\mathrm{d}x^{\boldsymbol{\lambda}}(\tau)}{\mathrm{d}\tau} = -\frac{1}{\gamma}\frac{\partial V(x;\boldsymbol{\lambda})}{\partial x}\Big|_{x=x^{\boldsymbol{\lambda}}(\tau)} + \sqrt{\frac{2}{\beta\gamma}}\eta(\tau) \tag{3.55}$$

with the initial condition$x^\lambda(0) = x$. Combining Eqs. (3.45), (3.47) and (3.54), we obtain the $O(\epsilon)$ contribution to the work, i.e., the lowest contribution to the excess work, given as

$$\begin{aligned}\langle W_{\rm ex}(\boldsymbol{\Lambda})\rangle &= \epsilon\int_0^T \mathrm{d}t\ \dot{\lambda}^\mu(t)\int \mathrm{d}x\ \rho_{\rm can}^{\boldsymbol{\lambda}(t)}(x)\phi_1(x;t)\frac{\partial V(x;\boldsymbol{\lambda}(t))}{\partial\lambda^\mu} + O(\epsilon^2)\\ &= \epsilon\int_0^T \mathrm{d}t\ \dot{\lambda}^\mu(t)\dot{\lambda}^\nu(t)\beta\int_0^\infty \mathrm{d}\tau\int \mathrm{d}x\ \rho_{\rm can}^{\boldsymbol{\lambda}(t)} X_\mu(x;\boldsymbol{\lambda}(t))\,\langle\Delta X_\nu(x^{\boldsymbol{\lambda}(t)}(\tau);\boldsymbol{\lambda}(t))\rangle_{x,\boldsymbol{\lambda}(t)} + O(\epsilon^2),\end{aligned} \tag{3.56}$$

which gives the thermodynamic metric expression for the excess work. The thermodynamic metric is identified as

$$\zeta_{\mu\nu}(\boldsymbol{\lambda}) = \beta\int_0^\infty \mathrm{d}\tau\int \mathrm{d}x\ \rho_{\rm can}^{\boldsymbol{\lambda}} X_\mu(x;\boldsymbol{\lambda})\,\langle\Delta X_\nu(x^{\boldsymbol{\lambda}}(\tau);\boldsymbol{\lambda}(t))\rangle_{x,\boldsymbol{\lambda}}\,. \tag{3.57}$$

Here, the initial condition $x^\lambda(0) = x$ is also sampled from the canonical distribution $\rho_{\rm can}^{\boldsymbol{\lambda}(t)}$, and therefore the thermodynamic metric is rewritten as

$$\zeta_{\mu\nu}(\boldsymbol{\lambda}) = \beta\int_0^\infty \mathrm{d}\tau\,\langle\Delta X_\mu(x^{\boldsymbol{\lambda}}(0);\boldsymbol{\lambda})\Delta X_\nu(x^{\boldsymbol{\lambda}}(\tau);\boldsymbol{\lambda})\rangle^{\rm eq}_{\boldsymbol{\lambda}}\,. \tag{3.58}$$

Therefore, the expression in terms of the thermodynamic metric is given from the lowest-order contribution in the expansion of the excess work in terms of ϵ. Compared with the phenomenological derivation, the physical meaning of the approximation is clearer in this derivation since we have used only one approximation that there is a separation of time scales between the system and the control, which is characterized by a dimensionless small parameter ϵ. This approach admits the possibility of systematically expanding the work in terms of ϵ, which we develop in Chapters 6 and 7.

Chapter 4

Information Geometry

In this chapter, we review a geometric analysis of information theory, especially of estimation theory. We consider a problem of estimation of an unknown probability distribution, and examine the accuracy of estimation. The accuracy of estimation is shown to be closely related to the metric on the space of candidates of the true distribution. In this way, considering a space of probability distributions and introducing a geometrical structure on it provides a useful way to analyze problems in information theory. Such a study is called information geometry [6].

In classical physics, physical states are represented by probability distributions, so that information geometry essentially concerns the geometrical structure on the space of states. We can also consider a quantum generalization of information geometry, where states are represented by density operators instead of probability distributions. In fact, the notion in information geometry has recently been increasingly applied to a variety of fields, such as statistical mechanics [33, 44], condensed-matter physics [12, 13, 45, 46], information theory [8, 9, 47, 48, 10, 11], and high-energy physics [15].

4.1 Classical Information Geometry

4.1.1 Classical Estimation Theory

Let us consider a probability distribution $p = \{p_i\}_{i \in I}$. Here, the symbol I denotes the sample space, or the set of all possible outcomes. We assume that the sample space I is finite[1] ($I = \{1, 2, \dots n\}$ for some $n \in \mathbb{N}$). The probability distribution must satisfy the positivity condition and the normalization condition:

$$p_i \geq 0, \quad {}^{\forall} i \in I, \tag{4.1}$$
$$\sum_{i \in I} p_i = 1. \tag{4.2}$$

Let us consider a family of probability distributions $\{p_{\boldsymbol{\theta}} | \boldsymbol{\theta} \in \Theta\}$ defined on a common sample space I. Each probability distribution is parameterized by an m-dimensional real vector $\boldsymbol{\theta} \in \Theta$,

[1] This assumption is not essential in the estimation theory, but is essential when we prove the uniqueness of the Fisher metric in Čencov's theorem.

where Θ is an open subset of $\mathbb{R}^m$ and is called the parameter space. We assume that $p_{\boldsymbol{\theta},i}$ is sufficiently smooth as a function of the parameter $\boldsymbol{\theta}$ for each $i \in I$. We also assume that all the probability distributions are strictly positive, i.e.,

$$p_{\boldsymbol{\theta},i} > 0, \quad {}^{\forall} i \in I, {}^{\forall} \boldsymbol{\theta} \in \Theta. \tag{4.3}$$

Such an appropriately parameterized family of probability distributions is called a *statistical model*, or a *statistical manifold*.

Suppose that we estimate an unknown parameter $\boldsymbol{\theta}$ from the outcome i. The estimation process is mathematically formulated by a mapping from the sample space to the parameter space, which is called an estimator:

$$\boldsymbol{\theta}^{\mathrm{est}} : I \to \Theta, \tag{4.4}$$

that is, if the outcome is $i \in I$, the estimated value is given by $\boldsymbol{\theta}^{\mathrm{est}}(i)$. Among many possible estimators, we often impose a condition called local unbiasedness, to ensure that the estimator is not so bad.

Definition 4.1. (local unbiasedness)
An estimator $\boldsymbol{\theta}^{\mathrm{est}}$ is called *locally unbiased* at $\boldsymbol{\theta}_0 \in \Theta$ if it satisfies

$$\langle \boldsymbol{\theta}^{\mathrm{est}} \rangle_{\boldsymbol{\theta}_0} = \boldsymbol{\theta}_0, \tag{4.5}$$

$$\frac{\partial}{\partial \theta_a} \langle \theta_b^{\mathrm{est}} \rangle_{\boldsymbol{\theta}} \bigg|_{\boldsymbol{\theta}=\boldsymbol{\theta}_0} = \delta_{ab}, \tag{4.6}$$

where $\langle \bullet \rangle_{\boldsymbol{\theta}} := \sum_i p_{\boldsymbol{\theta},i} \bullet$ is the expectation value of $\bullet$.

The subscripts $a, b, \ldots$ denote the components of a vector in the parameter space. The local-unbiasedness condition requires that the expectation value of the estimator is consistent with a true parameter if it is placed at a particular point $\boldsymbol{\theta}_0$ or its neighbor point $\boldsymbol{\theta}_0 + \mathrm{d}\boldsymbol{\theta}$ up to the first order in $\mathrm{d}\boldsymbol{\theta}$.

Next, we introduce the classical Fisher information, and explain its statistical meaning.

Definition 4.2. (classical Fisher information)
Let $\{p_{\boldsymbol{\theta}} | \boldsymbol{\theta} \in \Theta\}$ be a statistical model on the sample space I. Then, *the classical Fisher information matrix* $J_{\boldsymbol{\theta}}^C$ is a real $m \times m$ matrix whose elements are given as

$$[J_{\boldsymbol{\theta}}^C]_{ab} := \sum_{i \in I} p_{\boldsymbol{\theta},i} \frac{\partial \log p_{\boldsymbol{\theta},i}}{\partial \theta_a} \frac{\partial \log p_{\boldsymbol{\theta},i}}{\partial \theta_b} \tag{4.7}$$

$$= \sum_{i \in I} \frac{1}{p_{\boldsymbol{\theta},i}} \frac{\partial p_{\boldsymbol{\theta},i}}{\partial \theta_a} \frac{\partial p_{\boldsymbol{\theta},i}}{\partial \theta_b}. \tag{4.8}$$

If the local-unbiasedness condition is imposed on estimators, since their expectation value coincides with the accurate parameter, the goodness of the estimator is measured by the variance-covariance matrix[2]:

$$[\mathrm{Var}_{\boldsymbol{\theta}}(\boldsymbol{\theta}^{\mathrm{est}})]_{ab} := \left\langle (\theta^{\mathrm{est}}_a - \left\langle \theta^{\mathrm{est}}_a \right\rangle_{\boldsymbol{\theta}})(\theta^{\mathrm{est}}_b - \left\langle \theta^{\mathrm{est}}_b \right\rangle_{\boldsymbol{\theta}}) \right\rangle_{\boldsymbol{\theta}}. \tag{4.9}$$

An estimator with a small variance is considered to be good. However, the variance of the locally unbiased estimator is bounded from below by the classical Fisher information as stated below.

Theorem 4.3. (classical Cramér-Rao inequality) [7]
For any estimator which is locally unbiased at $\boldsymbol{\theta}$, the following inequality is satisfied:

$$\mathrm{Var}_{\boldsymbol{\theta}}(\boldsymbol{\theta}^{\mathrm{est}}) \geq (J^C_{\boldsymbol{\theta}})^{-1}. \tag{4.10}$$

Proof. Let V and J denote $\mathrm{Var}_{\boldsymbol{\theta}}(\boldsymbol{\theta}^{\mathrm{est}})$ and $J^C_{\boldsymbol{\theta}}$, respectively, as shorthand notations. First we show that for any $\boldsymbol{x}, \boldsymbol{y} \in \mathbb{R}^m$, we have

$$(\boldsymbol{x} \cdot V\boldsymbol{x})(\boldsymbol{y} \cdot J\boldsymbol{y}) \geq (\boldsymbol{x} \cdot \boldsymbol{y})^2. \tag{4.11}$$

By using the local-unbiasedness condition (4.5), we obtain

$$\begin{aligned} \boldsymbol{x} \cdot V\boldsymbol{x} &= \sum_{a,b} x_a \sum_i p_{\boldsymbol{\theta},i}(\theta^{\mathrm{est}}_a(i) - \left\langle \theta^{\mathrm{est}}_a \right\rangle_{\boldsymbol{\theta}})(\theta^{\mathrm{est}}_b(i) - \left\langle \theta^{\mathrm{est}}_b \right\rangle_{\boldsymbol{\theta}}) x_b \\ &= \sum_i \left(\sqrt{p_{\boldsymbol{\theta},i}} \sum_a (\theta^{\mathrm{est}}_a(i) - \theta_a) x_a \right)^2, \end{aligned} \tag{4.12}$$

and we also have

$$\boldsymbol{y} \cdot J\boldsymbol{y} = \sum_i \left(\sqrt{p_{\boldsymbol{\theta},i}} \sum_a \frac{\partial \log p_{\boldsymbol{\theta},i}}{\partial \theta_a} y_a \right)^2. \tag{4.13}$$

Then, by applying the Cauchy-Schwarz inequality, we obtain

$$\begin{aligned} (\boldsymbol{x} \cdot V\boldsymbol{x})(\boldsymbol{y} \cdot J\boldsymbol{y}) &\geq \left(\sum_{a,b} x_a y_b \sum_i p_{\boldsymbol{\theta},i}(\theta^{\mathrm{est}}_a(i) - \theta_a) \frac{\partial \log p_{\boldsymbol{\theta},i}}{\partial \theta_b} \right)^2 \\ &= \left(\sum_{a,b} x_a y_b \sum_i (\theta^{\mathrm{est}}_a(i) - \theta_a) \frac{\partial p_{\boldsymbol{\theta},i}}{\partial \theta_b} \right)^2 \\ &= \left(\sum_{a,b} x_a y_b \left(\frac{\partial}{\partial \theta_b} \langle \theta^{\mathrm{est}}_a \rangle_{\boldsymbol{\theta}} - \theta_a \frac{\partial 1}{\partial \theta_b} \right) \right)^2 \\ &= \left(\sum_{a,b} x_a y_b \delta_{ab} \right)^2 \\ &= (\boldsymbol{x} \cdot \boldsymbol{y})^2, \end{aligned} \tag{4.14}$$

[2] For locally unbiased estimators, the variance-covariance matrix is equal to the mean square error $\left\langle (\theta^{\mathrm{est}}_a(\cdot) - \theta_a)(\theta^{\mathrm{est}}_b(\cdot) - \theta_b) \right\rangle_{\boldsymbol{\theta}}$.

and Eq. (4.11) is proved. Here, we have used the local unbiasedness condition (4.6) in deriving the second last equality.

If we set $\boldsymbol{y} = J^{-1}\boldsymbol{x}$ in inequality (4.11), we obtain

$$(\boldsymbol{x} \cdot V\boldsymbol{x})(\boldsymbol{x} \cdot J^{-1}\boldsymbol{x}) \geq (\boldsymbol{x} \cdot J^{-1}\boldsymbol{x})^2. \tag{4.15}$$

Since J is positive, J^{-1} is also positive, and $\boldsymbol{x} \cdot J^{-1}\boldsymbol{x} \geq 0$. Therefore, we have

$$\boldsymbol{x} \cdot V\boldsymbol{x} \geq \boldsymbol{x} \cdot J^{-1}\boldsymbol{x}, \quad {}^{\forall}\boldsymbol{x} \in \mathbb{R}^m, \tag{4.16}$$

which shows the desired result (4.10). □

In this sense, the classical Fisher information $J^C_{\boldsymbol{\theta}}$ gives the distinguishability of probability distributions around $\boldsymbol{\theta}$.

4.1.2 Monotonicity of the Classical Fisher Metric and Čencov's Theorem

In this section, we discuss another important property of the classical Fisher information, i.e., the monotonicity under information processing.

Information processing can be formulated by a Markov mapping κ. Let $p = \{p_i\}_{i\in I}$ be a probability distribution on a sample space I, and J be another sample space. Then, we can construct a different probability distribution $q = \{q_j\}_{j\in J}$ by

$$q_j := \sum_{i\in I} \kappa(j|i)p_i, \quad {}^{\forall}j \in J. \tag{4.17}$$

To ensure that q is a probability distribution, κ must satisfy

$$\kappa(j|i) \geq 0, \quad {}^{\forall}i \in I, {}^{\forall}j \in J, \tag{4.18}$$

$$\sum_{j\in J} \kappa(j|i) = 1, \quad {}^{\forall}i \in I. \tag{4.19}$$

The matrix element $\kappa(j|i)$ can be interpreted as a conditional probability of obtaining the outcome $j \in J$ given that the original outcome is $i \in I$.

The following theorem gives the precise meaning of the monotonicity of the classical Fisher information under information processing.

Theorem 4.4. (Monotonicity of the classical Fisher information)
Let $\{q_{\boldsymbol{\theta}}\}$ be a statistical model induced from a statistical model $\{p_{\boldsymbol{\theta}}\}$ by a Markov mapping κ. Then, the classical Fisher information monotonically decreases:

$$J^C_{\boldsymbol{\theta}}(\{p_{\boldsymbol{\theta}}\}) \geq J^C_{\boldsymbol{\theta}}(\{q_{\boldsymbol{\theta}}\}). \tag{4.20}$$

Proof. For any $\boldsymbol{x} \in \mathbb{R}^m$, we obtain

$$\begin{aligned}
\boldsymbol{x} \cdot J^C_{\boldsymbol{\theta}}(\{q_{\boldsymbol{\theta}}\})\boldsymbol{x} &= \sum_{a,b} x_a \sum_{j\in J} \frac{1}{q_{\boldsymbol{\theta},j}} \frac{\partial q_{\boldsymbol{\theta},j}}{\partial \theta_a} \frac{\partial q_{\boldsymbol{\theta},j}}{\partial \theta_b} x_b \\
&= \sum_{j\in J} \frac{1}{q_{\boldsymbol{\theta},j}} \left(\sum_a \sum_{i\in I} x_a \frac{\partial p_{\boldsymbol{\theta},i}}{\partial \theta_a} \kappa(j|i) \right)^2 \\
&= \sum_{j\in J} \frac{1}{q_{\boldsymbol{\theta},j}} \left(\sum_a \sum_{i\in I} x_a \frac{\partial \log p_{\boldsymbol{\theta},i}}{\partial \theta_a} p_{\boldsymbol{\theta},i}\kappa(j|i) \right)^2 \\
&= \sum_{j\in J} \frac{1}{q_{\boldsymbol{\theta},j}} \left(\sum_{i\in I} \left(\sum_a x_a \frac{\partial \log p_{\boldsymbol{\theta},i}}{\partial \theta_a} \sqrt{p_{\boldsymbol{\theta},i}\kappa(j|i)} \right) \sqrt{p_{\boldsymbol{\theta},i}\kappa(j|i)} \right)^2 && (4.21) \\
&\leq \sum_{j\in J} \frac{1}{q_{\boldsymbol{\theta},j}} \left(\sum_{i\in I} \left(\sum_a x_a \frac{\partial \log p_{\boldsymbol{\theta},i}}{\partial \theta_a} \right)^2 p_{\boldsymbol{\theta},i}\kappa(j|i) \right) \left(\sum_{i\in I} p_{\boldsymbol{\theta},i}\kappa(j|i) \right) && (4.22) \\
&= \sum_{i\in I, j\in J} \left(\sum_a x_a \frac{\partial \log p_{\boldsymbol{\theta},i}}{\partial \theta_a} \right)^2 p_{\boldsymbol{\theta},i}\kappa(j|i) \\
&= \sum_{a,b} \sum_{i\in I} p_{\boldsymbol{\theta},i} \frac{\partial \log p_{\boldsymbol{\theta},i}}{\partial \theta_a} \frac{\partial \log p_{\boldsymbol{\theta},i}}{\partial \theta_b} x_a x_b = \boldsymbol{x} \cdot J^C_{\boldsymbol{\theta}}(\{p_{\boldsymbol{\theta}}\})\boldsymbol{x}. && (4.23)
\end{aligned}$$

Here, we have used the Cauchy-Schwarz inequality to obtain Eq. (4.22) from Eq. (4.21). □

Theorem 4.4 claims that if we perform information processing, the probability distributions become less distinguishable from each other.

Čencov [49] showed that the classical Fisher information is uniquely determined from the monotonicity. More precisely, the classical Fisher information is characterized as the unique monotone metric on the space of probability distributions.

In the following, we consider a family of all probability distributions defined on the sample space $I_n = \{1, \dots n\}$ ($n \in \mathbb{N}$). Such a family can be expressed as

$$S_{n-1} = \{p \in \mathbb{R}^n | p_i > 0, \sum_i p_i = 1\}. \tag{4.24}$$

We define a monotone metric K by the following conditions.

Definition 4.5. (monotone metric)
Suppose that for every $x, y \in \mathbb{R}^n$, for every $p \in S_{n-1}$, and for every $n \in \mathbb{N}$, a real number $K_p(x, y)$ is defined. Then $K_p(x, y)$ is called a *monotone metric* if the following conditions hold:

(bilinearity) $(x, y) \mapsto K_p(x, y)$ is bilinear.

(positivity) $K_p(x, x) \geq 0$, and the equality holds if and only if $x = 0$.

(continuity) $p \mapsto K_p(x, y)$ is continuous on S_{n-1} for every $x \in \mathbb{R}^n$ and for every $n \in \mathbb{N}$.

(symmetricity) $K_p(x, y) = K_p(y, x)$.

(monotonicity) $K_{\kappa(p)}(\kappa(x), \kappa(x)) \leq K_p(x, x)$ for every Markov mapping $\kappa : \mathbb{R}^n \to \mathbb{R}^m$, for every $p \in S_{n-1}$, for every $x \in \mathbb{R}^n$, and for every $n, m \in \mathbb{N}$.

Here, the bilinearity, positivity, continuity, and symmetricity are imposed so that $K_p(x, y)$ can be interpreted as a metric.

Theorem 4.6. (Čencov's theorem [49])
Let $K_p(\cdot, \cdot)$ be a monotone metric on statistical models whose sample spaces are finite. Then there are constants A and $C > 0$ such that

$$K_p(x, y) = C \sum_i \frac{x_i y_i}{p_i} + A \left(\sum_i x_i \right) \left(\sum_i y_i \right). \tag{4.25}$$

The classical Fisher information of a statistical model $\{p_{\boldsymbol{\theta}}\}$ can be written as

$$K_{p_{\boldsymbol{\theta}}} \left(\frac{\partial p_{\boldsymbol{\theta}}}{\partial \theta_a}, \frac{\partial p_{\boldsymbol{\theta}}}{\partial \theta_b} \right), \tag{4.26}$$

because we have $\sum_i \partial p_{\boldsymbol{\theta},i} / \partial \theta_a = 0$ from the normalization condition and hence the second term in Eq. (4.25) vanishes.

To be precise, the monotonicity is a too strong condition to characterize the classical Fisher metric. If we impose a weaker condition called the invariance, which means that the metric does not change under any reversible Markov mapping, we can show the same result.

4.2 Quantum Information Geometry

4.2.1 Monotonicity of the Quantum Fisher Metric and Petz' Theorem

In the previous section, we have learned that one can naturally introduce a unique metric on the space of probability distributions, namely, the classical Fisher metric. In this section, we discuss the quantum counterpart of the classical Fisher metric. In quantum mechanics, a probability distribution is replaced by a density operator $\hat{\rho}$. The question is whether we can introduce natural metrics on the space of density operators from the viewpoint of the monotonicity under information processing. In fact, due to the noncommutativity of operators, one can introduce infinitely many different types of metrics that satisfy the monotonicity, which are called the quantum Fisher metrics.

To discuss the monotonicity under information processing, we need to know how information processing is formulated. In fact, state changes that can be implemented deterministically by a physical process are characterized by completely positive and trace-preserving (CPTP) mappings [50]. Let $\mathcal{H}_n$ be an n-dimensional Hilbert space, $\mathcal{L}(\mathcal{H}_n)$ be the linear space of all linear operators on $\mathcal{H}_n$, and $\mathcal{S}(\mathcal{H}_n)$ be the set of all density operators on $\mathcal{H}_n$. A linear operator $\mathcal{E} : \mathcal{L}(\mathcal{H}_n) \to \mathcal{L}(\mathcal{H}_m)$ is called completely positive if $\mathcal{E} \otimes \boldsymbol{I}_k : \mathcal{L}(\mathcal{H}_n \otimes \mathcal{H}_k) \to \mathcal{L}(\mathcal{H}_m \otimes \mathcal{H}_k)$ is positive for every $k \in \mathbb{N}$, where $\boldsymbol{I}_k$ is the identity operator on $\mathcal{L}(\mathcal{H}_k)$. Also, a linear operator $\mathcal{E} : \mathcal{L}(\mathcal{H}_n) \to \mathcal{L}(\mathcal{H}_m)$ is called trace-preserving if $\mathrm{tr}\left[\hat{A}\right] = \mathrm{tr}\left[\mathcal{E}(\hat{A})\right]$ for every $\hat{A} \in \mathcal{L}(\mathcal{H}_n)$. These properties guarantee the positivity and the conservation of probability. Note that $\hat{\rho}$ and $\mathcal{E}(\hat{\rho})$ can be operators on different Hilbert spaces.

Definition 4.7. (monotone metric)
Suppose that for every $\hat{A}, \hat{B} \in \mathcal{L}(\mathcal{H}_n)$, for every $\hat{\rho} \in \mathcal{S}(\mathcal{H}_n)$, and for every $n \in \mathbb{N}$, a complex number $K_{\hat{\rho}}(\hat{A}, \hat{B})$ is defined. Then $K_{\cdot}(\cdot, \cdot)$ is called a *monotone metric* if the following four conditions hold:

(sesquilinearity) $(\hat{A}, \hat{B}) \mapsto K_{\hat{\rho}}(\hat{A}, \hat{B})$ is sesquilinear, i.e., conjugate linear with respect to the first argument and linear with respect to the second argument.

(positivity) $K_{\hat{\rho}}(\hat{A}, \hat{A}) \geq 0$, and the equality holds if and only if $\hat{A} = 0$.

(continuity) $\hat{\rho} \mapsto K_{\hat{\rho}}(\hat{A}, \hat{A})$ is continuous on $\mathcal{S}(\mathcal{H}_n)$ for every $\hat{A} \in \mathcal{L}(\mathcal{H}_n)$ and for every $n \in \mathbb{N}$.

(monotonicity) $K_{\mathcal{E}(\hat{\rho})}(\mathcal{E}(\hat{A}), \mathcal{E}(\hat{A})) \leq K_{\hat{\rho}}(\hat{A}, \hat{A})$ for every CPTP mapping $\mathcal{E} : \mathcal{L}(\mathcal{H}_n) \to \mathcal{L}(\mathcal{H}_m)$, for every $\hat{\rho} \in \mathcal{S}(\mathcal{H}_n)$, for every $\hat{A} \in \mathcal{L}(\mathcal{H}_n)$, and for every $n, m \in \mathbb{N}$.

From the Liesz representation theorem [51], the metric can be represented by using superoperator $\boldsymbol{K}_{\hat{\rho}}$ as

$$K_{\hat{\rho}}(\hat{A}, \hat{B}) = \mathrm{tr}\left[\hat{A}^\dagger \boldsymbol{K}_{\hat{\rho}}^{-1}(\hat{B})\right]. \tag{4.27}$$

Petz [52] have shown that there are abundance of monotone metrics on the space of quantum states and are characterized by operator monotone functions. To state the claims by Petz precisely, we need to introduce some definitions. For two Hermitian operators $\hat{A}$ and $\hat{B}$, we denote $\hat{A} \leq \hat{B}$ if and only if $\hat{B} - \hat{A}$ is positive semidefinite. A function $f(x) : (0, \infty) \to (0, \infty)$ is called operator monotone if $0 < \hat{A} \leq \hat{B} \Rightarrow f(\hat{A}) \leq f(\hat{B})$ for every Hermitian operators $\hat{A}$ and $\hat{B}$. We define superoperators $\boldsymbol{L}_{\hat{\rho}}$ and $\boldsymbol{R}_{\hat{\rho}}$ by the following relations:

$$\boldsymbol{L}_{\hat{\rho}}(\hat{A}) = \hat{\rho}\hat{A}, \tag{4.28}$$

$$\boldsymbol{R}_{\hat{\rho}}(\hat{A}) = \hat{A}\hat{\rho}, \tag{4.29}$$

which represent the multiplication of $\hat{\rho}$ from the left and from the right, respectively.

Then, the following theorems hold.

Theorem 4.8. (abundance of monotone metrics) [52]
Let $f(x)$ be an operator monotone function. Then,

$$\boldsymbol{K}_{\hat{\rho}} = \boldsymbol{R}_{\hat{\rho}} f(\boldsymbol{L}_{\hat{\rho}} \boldsymbol{R}_{\hat{\rho}}^{-1}) \tag{4.30}$$

determines a monotone metric in the sense of Def. 4.7.

Theorem 4.9. (characterization of monotone metric) [52]
Let $K_{\hat{\rho}}(\cdot, \cdot)$ be a monotone metric. Then there is an operator monotone function f such that

$$K_{\hat{\rho}}(\hat{A}, \hat{B}) = \mathrm{tr}\left[\hat{A}^\dagger \boldsymbol{K}_{\hat{\rho}}^{-1}(\hat{B})\right], \tag{4.31}$$

Table 4.1: List of the quantum Fisher metrics and the corresponding operator monotone functions $f(x)$.

quantum Fisher metric	$f(x)$
symmetric logarithmic derivative (SLD)	$(x+1)/2$
Bogoliubov-Kubo-Mori (BKM)	$(x-1)/\log x$
right logarithmic derivative (RLD)	x
left logarithmic derivative (LLD)	1
real part of the right logarithmic derivative (real RLD)	$2x/(x+1)$
skew information	$(\sqrt{x}+1)^2/4$

where $\boldsymbol{K}_{\hat{\rho}} := \boldsymbol{R}_{\hat{\rho}} f(\boldsymbol{L}_{\hat{\rho}} \boldsymbol{R}_{\hat{\rho}}^{-1})$.

Theorems 4.8 and 4.9 show that there is a one-to-one correspondence between monotone metrics and operator monotone functions. In the following, we may write $\boldsymbol{K}_{\hat{\rho}}^f$ instead of $\boldsymbol{K}_{\hat{\rho}}$ if we need to express an operator monotone function explicitly. We summarize important instances of the quantum Fisher metrics and the corresponding operator monotone functions in Table. 4.1.

For a quantum-statistical model $\{\hat{\rho}_{\boldsymbol{\theta}}\}$, the matrix whose element is given by the quantum Fisher metric, defined by

$$(J_{\boldsymbol{\theta}}^Q)_{\mu\nu} := \mathrm{tr}\left[\frac{\partial \hat{\rho}_{\boldsymbol{\theta}}}{\partial \theta_\mu} \boldsymbol{K}_{\hat{\rho}_{\boldsymbol{\theta}}}^{-1}\left(\frac{\partial \hat{\rho}_{\boldsymbol{\theta}}}{\partial \theta_\nu}\right)\right], \tag{4.32}$$

is called the quantum Fisher information matrix, or the quantum Fisher information for short. We note that the quantum Fisher information matrix is a Hermitian matrix $(J_{\boldsymbol{\theta}}^Q)_{\mu\nu}^* = (J_{\boldsymbol{\theta}}^Q)_{\nu\mu}$, and therefore it can take complex values for nondiagonal matrix elements. We may write $J_{\boldsymbol{\theta}}^{f,Q}$ instead of $J_{\boldsymbol{\theta}}^Q$ if we need to express an operator monotone function explicitly.

For an operator monotone function $f(x)$, we define the dual of $f(x)$ as

$$\tilde{f}(x) := x f(1/x). \tag{4.33}$$

The quantum Fisher information matrices with respect to $f(x)$ and its dual $\tilde{f}(x)$ are related to each other by

$$(J_{\boldsymbol{\theta}}^{\tilde{f},Q})_{\mu\nu} = (J_{\boldsymbol{\theta}}^{f,Q})_{\nu\mu}. \tag{4.34}$$

If an operator monotone function $f(x)$ is equal to its dual, i.e., $f(x) = \tilde{f}(x)$, it is called symmetric. Then the corresponding quantum Fisher information becomes symmetric and real:

$$(J_{\boldsymbol{\theta}}^{f,Q})_{\mu\nu} = (J_{\boldsymbol{\theta}}^{f,Q})_{\nu\mu} \in \mathbb{R} \tag{4.35}$$

As an example relevant to physics, we consider a statistical model of canonical ensembles [53]. The Hamiltonian is parametrized as $\hat{H}(\boldsymbol{\theta})$, and the canonical ensemble corresponding to $\hat{H}(\boldsymbol{\theta})$

is given by

$$\hat{\rho}_{\boldsymbol{\theta}} = \frac{\mathrm{e}^{-\beta \hat{H}(\boldsymbol{\theta})}}{Z(\boldsymbol{\theta})}, \tag{4.36}$$

where $Z(\boldsymbol{\theta}) = \mathrm{tr}\left[\mathrm{e}^{-\beta \hat{H}(\boldsymbol{\theta})}\right]$ is the partition function. Let us calculate the Bogoliubov-Kubo-Mori (BKM) Fisher information, which corresponds to the choice of $f(x) = (x-1)/\log x = \int_0^1 \mathrm{d}\alpha\, x^\alpha$ as an operator monotone function, of this statistical model. From the identity

$$\frac{\partial \hat{\rho}_{\boldsymbol{\theta}}}{\partial \theta_\mu} = \int_0^1 \mathrm{d}\alpha \hat{\rho}^\alpha \frac{\partial \log \hat{\rho}_{\boldsymbol{\theta}}}{\partial \theta_\mu} \hat{\rho}^{1-\alpha}, \tag{4.37}$$

which can be shown from Eq. (A.3), we obtain $\boldsymbol{K}_{\hat{\rho}_{\boldsymbol{\theta}}}^{-1}(\frac{\partial \hat{\rho}_{\boldsymbol{\theta}}}{\partial \theta_\nu}) = \frac{\partial \log \hat{\rho}_{\boldsymbol{\theta}}}{\partial \theta_\nu}$. Therefore, the BKM Fisher information is calculated as

$$\begin{aligned}
(J_{\boldsymbol{\theta}}^{BKM})_{\mu\nu} &= \mathrm{tr}\left[\frac{\partial \hat{\rho}_{\boldsymbol{\theta}}}{\partial \theta_\mu} \boldsymbol{K}_{\hat{\rho}_{\boldsymbol{\theta}}}^{-1}\left(\frac{\partial \hat{\rho}_{\boldsymbol{\theta}}}{\partial \theta_\nu}\right)\right] \\
&= \int_0^1 \mathrm{d}\alpha\ \mathrm{tr}\left[\hat{\rho}^\alpha \frac{\partial \log \hat{\rho}_{\boldsymbol{\theta}}}{\partial \theta_\mu} \hat{\rho}^{1-\alpha} \frac{\partial \log \hat{\rho}_{\boldsymbol{\theta}}}{\partial \theta_\nu}\right] \\
&= \beta^2 \langle\!\langle \Delta \hat{X}_\mu(\boldsymbol{\theta}), \Delta \hat{X}_\nu(\boldsymbol{\theta}) \rangle\!\rangle_{\hat{\rho}_{\boldsymbol{\theta}}}^{\mathrm{can}},
\end{aligned} \tag{4.38}$$

where $\hat{X}_\mu(\boldsymbol{\theta}) = -\partial \hat{H}(\boldsymbol{\theta})/\partial \theta_\mu$ is the generalized force operator corresponding to θ_μ and $\Delta \hat{X}_\mu(\boldsymbol{\theta}) = \hat{X}_\mu(\boldsymbol{\theta}) - \mathrm{tr}\left[\hat{\rho}_{\boldsymbol{\theta}} \hat{X}_\mu(\boldsymbol{\theta})\right]$ is the deviation from its equilibrium value. The final expression shows that the BKM Fisher information of this statistical model is nothing but the static isothermal susceptibility [18].

Another important example is a one-parameter unitary family model generated by an operator $\hat{A}$, which is defined by

$$\hat{\rho}_\theta = \mathrm{e}^{-i\theta \hat{A}} \hat{\rho} \mathrm{e}^{i\theta \hat{A}}. \tag{4.39}$$

This model is quite frequently considered in the context of quantum metrology [9, 10, 11]. Let us denote by $F^f[\hat{\rho}, \hat{A}]$, the quantum Fisher information of the unitary model (4.39) with respect to an operator monotone function, which can be explicitly expressed as

$$F^f[\hat{\rho}, \hat{A}] := \sum_{i,j} \frac{(p_i - p_j)^2}{p_j f(p_i/p_j)} \left| \langle i|\hat{A}|j\rangle \right|^2, \tag{4.40}$$

where the density operator is diagonalized as $\hat{\rho} = \sum_i p_i |i\rangle \langle i|$. Then, the function $F^f[\hat{\rho}, \hat{A}]$ is convex as a function of a quantum state, as shown in the following theorem.

Theorem 4.10. For arbitrary quantum states $\hat{\rho}_1, \hat{\rho}_2$, an observable $\hat{A}$ and a real number $\lambda \in [0, 1]$, the following inequality holds:

$$F^f[\lambda \hat{\rho}_1 + (1-\lambda)\hat{\rho}_2, \hat{A}] \leq \lambda F^f[\hat{\rho}_1, \hat{A}] + (1-\lambda) F^f[\hat{\rho}_2, \hat{A}]. \tag{4.41}$$

Proof. Let us consider a quantum statistical model defined by

$$\hat{\rho}_\theta = \lambda(\mathrm{e}^{-i\theta\hat{A}}\hat{\rho}_1\mathrm{e}^{i\theta\hat{A}}) \otimes |1\rangle_R \langle 1| + (1-\lambda)(\mathrm{e}^{-i\theta\hat{A}}\hat{\rho}_2\mathrm{e}^{i\theta\hat{A}}) \otimes |2\rangle_R \langle 2| . \tag{4.42}$$

By applying the monotonicity of the quantum Fisher information under a CPTP map defined by

$$\mathcal{E}(\hat{\rho}) := \mathrm{tr}_R[\hat{\rho}], \tag{4.43}$$

we obtain the monotonicity (4.41). □

4.2.2 Quantum State Estimation

The quantum Fisher information was originally introduced in the field of the quantum state estimation [54, 55]. Let us consider a quantum-statistical model $\{\hat{\rho}_{\boldsymbol{\theta}}\}$. Suppose that we estimate the true state by performing a measurement represented by a positive-operator valued measure (POVM) $\{\hat{E}_i\}_{i\in I}$ satisfying the normalization condition $\sum_i \hat{E}_i = \hat{I}$. If the true state is $\hat{\rho}_{\boldsymbol{\theta}}$, the probability of obtaining the outcome i is given by

$$p_{\boldsymbol{\theta},i} = \mathrm{tr}\left[\hat{\rho}_{\boldsymbol{\theta}}\hat{E}_i\right]. \tag{4.44}$$

In this sense, a classical statistical model $\{p_{\boldsymbol{\theta}}\}$ is generated from a pair of a quantum statistical model and one choice of POVM. We define a CPTP map $\mathcal{E}$ that generates a probability distribution by

$$\mathcal{E}(\hat{\rho}) := \sum_{i\in I} \mathrm{tr}\left[\hat{\rho}\hat{E}_i\right] |\phi_i\rangle \langle\phi_i| , \tag{4.45}$$

where $\{|\phi_i\rangle\}_{i\in I}$ is an orthogonal normalized set. From the monotonicity of the quantum Fisher metric, we obtain

$$J^Q_{\boldsymbol{\theta}}(\{\hat{\rho}_{\boldsymbol{\theta}}\}) \geq J^Q_{\boldsymbol{\theta}}(\{\mathcal{E}(\hat{\rho}_{\boldsymbol{\theta}})\}) = J^C_{\boldsymbol{\theta}}(\{p_{\boldsymbol{\theta}}\}). \tag{4.46}$$

By combining this inequality with the classical Cramér-Rao inequality (4.10), we arrive at the following inequality.

Theorem 4.11. (quantum Cramér-Rao inequality)
For any measurement and any estimator which is locally unbiased at $\boldsymbol{\theta}$, the following inequality holds:

$$\mathrm{Var}_{\boldsymbol{\theta}}(\boldsymbol{\theta}^{\mathrm{est}}) \geq (J^Q_{\boldsymbol{\theta}})^{-1}. \tag{4.47}$$

Since the quantum Fisher information is determined only by the quantum-statistical model $\{\hat{\rho}_{\boldsymbol{\theta}}\}$ and independent of the choice of the measurement, the quantum Cramér-Rao inequality gives an absolute upper bound of the accuracy of quantum state estimation. Attainability of the equality in the quantum Cramér-Rao inequality has been discussed well [56, 57, 58], but it is known that we cannot attain the equality in general.

4.2.3 Generalized Covariances

For each quantum Fisher information corresponding to an operator monotone function $f(x)$, we define a generalized covariance [59, 60] of two observables $\hat{A}, \hat{B}$ as

$$\langle\langle \hat{A}, \hat{B} \rangle\rangle_{\hat{\rho}}^{f} := \mathrm{tr}\left[\hat{A}^\dagger \boldsymbol{K}_{\hat{\rho}}^{f} \hat{B}\right]. \tag{4.48}$$

If $\hat{A}, \hat{B}$ and $\hat{\rho}$ are simultaneously diagonalizable as $\hat{A} = \sum_i a_i |\phi_i\rangle \langle\phi_i|, \hat{B} = \sum_i b_i |\phi_i\rangle \langle\phi_i|$, and $\hat{\rho} = \sum_i p_i |\phi_i\rangle \langle\phi_i|$, it reduces to the normal (classical) covariance $\sum_i p_i a_i b_i$. Strictly speaking, we may call it an inner product rather than a covariance, because we need to subtract the product of the expectation value of $\hat{A}$ and $\hat{B}$ to obtain the covariance, but here we follow the definition introduced by Petz [59] and call the quantity defined by Eq. (4.48) the generalized covariance corresponding to an operator monotone $f(x)$. Comparing the generalized covariance with the quantum Fisher metric, the only difference is that the kernel is given by $\boldsymbol{K}_{\hat{\rho}}^{f}$ for the generalized covariance, while $(\boldsymbol{K}_{\hat{\rho}}^{f})^{-1}$ for the quantum Fisher metric.

The generalized covariances include important correlations in the linear response theory, namely, the canonical correlation and the symmetrized correlation. The canonical correlation (2.39), or the Bogoliubov-Kubo-Mori (BKM) inner product, is the generalized covariance with $f(x) = \frac{x-1}{\log x} = \int_0^1 x^\lambda \mathrm{d}\lambda$. Also, when the operator monotone function is given by $f(x) = \frac{1+x}{2}$, the generalized covariance reduces to the symmetrized correlation (2.51)

$$\langle\langle \hat{A}, \hat{B} \rangle\rangle_{\hat{\rho}}^{\mathrm{symm}} = \frac{1}{2}\mathrm{tr}\left[\hat{\rho}(\hat{A}^\dagger \hat{B} + \hat{B}\hat{A}^\dagger)\right]. \tag{4.49}$$

We note that the generalized covariance with an operator monotone function $f(x)$ and that with its dual $\tilde{f}(x) = x f(1/x)$ are related by the relation

$$\langle\langle \hat{A}, \hat{B} \rangle\rangle_{\hat{\rho}}^{\tilde{f}} = \langle\langle \hat{B}^\dagger, \hat{A}^\dagger \rangle\rangle_{\hat{\rho}}^{f} \tag{4.50}$$

If the operator monotone function is symmetric , i.e., $f(x) = \tilde{f}(x)$, the generalized covariance is also symmetric

$$\langle\langle \hat{A}, \hat{B} \rangle\rangle_{\hat{\rho}}^{f} = \langle\langle \hat{B}, \hat{A} \rangle\rangle_{\hat{\rho}}^{f}. \tag{4.51}$$

Here, we give another formulation of the quantum Cramér-Rao inequality using the generalized covariance. For simplicity, we consider a one-parameter model given by

$$\hat{\rho}_\theta = \hat{\rho}_0 + \theta \left.\frac{\partial \hat{\rho}_\theta}{\partial \theta}\right|_{\theta=0} + O(\theta^2) \tag{4.52}$$

$$=: \hat{\rho}_0 + \theta \hat{B} + O(\theta^2). \tag{4.53}$$

Note that $\hat{B}$ is traceless ($\mathrm{tr}\left[\hat{B}\right] = 0$) from the normalization of the density operators $\hat{\rho}_\theta$. Suppose that we estimate θ by performing a projective measurement of $\hat{A}$. Then the local unbiasedness at $\theta = 0$ of this measurement is equivalent to

$$\mathrm{tr}\left[\hat{A}\hat{\rho}_0\right] = 0 \Leftrightarrow \langle\langle \hat{A}, \hat{I} \rangle\rangle^f_{\hat{\rho}_0} = 0, \tag{4.54}$$

$$\left.\frac{\partial}{\partial\theta}\mathrm{tr}\left[\hat{A}\hat{\rho}_\theta\right]\right|_{\theta=0} = 1 \Leftrightarrow \langle\langle \hat{A}, \hat{L} \rangle\rangle^f_{\hat{\rho}_0} = 1, \tag{4.55}$$

where $\hat{L}$ is the logarithmic derivative defined by

$$\hat{L} := (\boldsymbol{K}^f_{\hat{\rho}_0})^{-1}(\hat{B}). \tag{4.56}$$

From the Cauchy-Schwarz inequality, we obtain

$$\langle\langle \hat{A}, \hat{A} \rangle\rangle^f_{\hat{\rho}_0} \langle\langle \hat{L}, \hat{L} \rangle\rangle^f_{\hat{\rho}_0} \geq |\langle\langle \hat{A}, \hat{L} \rangle\rangle^f_{\hat{\rho}_0}|^2 = 1 \tag{4.57}$$

$$\Leftrightarrow \quad \langle\langle \hat{A}, \hat{A} \rangle\rangle^f_{\hat{\rho}_0} \geq \frac{1}{\langle\langle \hat{L}, \hat{L} \rangle\rangle^f_{\hat{\rho}_0}} = \frac{1}{J^Q_{\theta=0}}, \tag{4.58}$$

which is another form of the quantum Cramér-Rao inequality. Note that the leftmost-hand side is the generalized (co)variance of $\hat{A}$, and the denominator in the rightmost-hand side is nothing but the quantum Fisher information. The equality is achieved if

$$\hat{A} = \frac{\hat{L}}{\langle\langle \hat{L}, \hat{L} \rangle\rangle^f_{\hat{\rho}_0}}. \tag{4.59}$$

In this sense, the quantum Fisher information is the inverse of the generalized (co)variance of a proper locally unbiased estimator.

Chapter 5

Determining Quantum Fisher Information from Linear Response Theory

In Chapter 4, we have reviewed, from the viewpoint of the monotonicity under operations, that we can introduce infinitely many types of metrics on the space of quantum states, which are called the quantum Fisher metrics, or the quantum Fisher information, in contrast to the classical case where the classical Fisher metric is determined uniquely. However, operational meanings of the general quantum Fisher information are not fully understood yet, nor even how to determine it experimentally is known, due to the complicated definition.

In this chapter, we propose a protocol of experimentally determining any types of the quantum Fisher information by the use of the similarity between information geometry (statistics) and linear response theory (statistical mechanics) [61]. The central idea is as follows. The quantum Fisher information quantifies the sensitivity, or the response of a quantum state to infinitesimal changes of parameters characterizing it. Therefore, it is quantitatively related to the covariance, or the correlation of the estimated values of the parameters, via the quantum Cramér-Rao inequality. When the state is in thermal equilibrium, such a correlation is also related to the response to external perturbations from the linear response theory. From these two connections, we can determine the quantum Fisher information by measuring linear response functions, or more specifically, dynamical susceptibilities or complex admittances.

First, we establish a close connection between linear response theory and information geometry, by formulating the generalized fluctuation-dissipation theorem in terms of the generalized covariances. Based on the generalized fluctuation-dissipation theorem, we derive a formula that expresses the quantum Fisher information in terms of observable quantities, namely, dynamical susceptibilities or complex admittances. As an application, a possible experimental validation of skew information-based uncertainty relations is discussed. This chapter is based on Ref. [61].

5.1 Generalized Fluctuation-Dissipation Theorem

In this section, we derive the generalized fluctuation-dissipation theorem, which quantitatively connects the generalized covariance and the linear response function. In Chap. 2, we have seen that the response function is quantitatively related to the canonical correlation via the Green-Kubo formulae, and to the symmetrized correlation by the fluctuation-dissipation theorem. Since the generalized covariances are generalizations of correlations of two noncommuting observables including the canonical correlation and the symmetrized correlation, it is expected that the generalized covariances also have the same amount of information about the linear response function. Indeed, such an expectation holds as will be shown below.

Let $\phi_{\mu\nu}(t)$ and $\tilde{\phi}_{\mu\nu}(t)$ be the linear response functions of $\hat{X}_\mu$ and $\hat{J}_\mu$, respectively, to the external perturbation $\hat{H}_{\rm ext}(t) = -\sum_\nu F_\nu(t)\hat{X}_\nu(t)$, as we defined in Chap. 2. The Fourier transforms of these linear response functions are defined by

$$\phi_{\mu\nu,\omega} := \int_{-\infty}^{\infty} {\rm d}t\ {\rm e}^{i\omega t}\phi_{\mu\nu}(t), \tag{5.1}$$

$$\tilde{\phi}_{\mu\nu,\omega} := \int_{-\infty}^{\infty} {\rm d}t\ {\rm e}^{i\omega t}\tilde{\phi}_{\mu\nu}(t). \tag{5.2}$$

We also define the Fourier transforms of the generalized covariance corresponding to an operator monotone function $f(x)$ evaluated at the canonical ensemble $\hat{\rho}_{\rm can} = {\rm e}^{-\beta\hat{H}}/Z$ by

$$C^f_{\mu\nu,\omega} := \int_{-\infty}^{\infty} {\rm d}t\ {\rm e}^{i\omega t}\langle\!\langle \Delta\hat{X}_\mu(t), \Delta\hat{X}_\nu(0)\rangle\!\rangle^f_{\hat{\rho}_{\rm can}}, \tag{5.3}$$

$$\tilde{C}^f_{\mu\nu,\omega} := \int_{-\infty}^{\infty} {\rm d}t\ {\rm e}^{i\omega t}\langle\!\langle \hat{J}_\mu(t), \hat{J}_\nu(0)\rangle\!\rangle^f_{\hat{\rho}_{\rm can}}, \tag{5.4}$$

where $\Delta\hat{X}_\mu(t) := \hat{X}_\mu(t) - X^{\rm eq}_\mu$ is the deviation from the equilibrium value. Then, we can generalize the fluctuation-dissipation theorem as follows.

Theorem 5.1. (Generalized Fluctuation-Dissipation Theorem)
The Fourier transform of the linear response functions and the generalized covariances are quantitatively related through the following equalities:

$$C^f_{\mu\nu,\omega} = -i\hbar\frac{f({\rm e}^{-\beta\hbar\omega})}{1-{\rm e}^{-\beta\hbar\omega}}\phi_{\mu\nu,\omega}. \tag{5.5}$$

$$\tilde{C}^f_{\mu\nu,\omega} = \hbar\omega\frac{f({\rm e}^{-\beta\hbar\omega})}{1-{\rm e}^{-\beta\hbar\omega}}\tilde{\phi}_{\mu\nu,\omega}. \tag{5.6}$$

The proof is provided at the end of this section. This theorem claims that in the frequency domain, not only the symmetrized correlation but any type of the generalized covariance is proportional to the linear response. The choice of an operator monotone function determines the frequency dependence of the coefficient.

Some remarks on the generalized fluctuation-dissipation theorem are in order. First, in the classical limit or the high-temperature limit of $\beta\hbar\omega \to 0$, the coefficients in Eqs. (5.5) and (5.6) become independent of $f(x)$, since the noncommutativity of operators then becomes negligible

Table 5.1: List of the coefficients appearing in the generalized fluctuation-dissipation theorem (5.6) for various quantum Fisher information.

quantum Fisher information	$f(x)$	$f(\mathrm{e}^{-\alpha})/(1-\mathrm{e}^{-\alpha})$
symmetric logarithmic derivative (SLD)	$(x+1)/2$	$(1/2)\cdot\coth(\alpha/2)=\bar{n}+1/2$
Bogoliubov-Kubo-Mori (BKM)	$(x-1)/\log x$	$1/\alpha=(\log(\bar{n}+1)-\log\bar{n})^{-1}$
right logarithmic derivative (RLD)	x	$1/(\mathrm{e}^{\alpha}-1)=\bar{n}$
left logarithmic derivative (LLD)	1	$1/(1-\mathrm{e}^{-\alpha})=\bar{n}+1$
real part of right logarithmic derivative (real RLD)	$2x/(x+1)$	$1/\sinh\alpha=2\bar{n}(\bar{n}+1)/(2\bar{n}+1)$
skew information	$(\sqrt{x}+1)^2/4$	$(1/4)\cdot\coth(\alpha/4)=(2\bar{n}+1+\sqrt{\bar{n}(\bar{n}+1)})/4$

and all types of the generalized covariance reduce to the classical covariance in this limit. Second, this theorem is a generalization of the conventional fluctution-dissipation theorem in the sense that the conventional one (2.54) is reproduced by choosing $f(x)=(1+x)/2$ in Eq. (5.6), which corresponds to the symmetrized correlation and the SLD Fisher information. Finally, the dimensionless factor $f(\mathrm{e}^{-\beta\hbar\omega})/(1-\mathrm{e}^{-\beta\hbar\omega})$ in Eqs. (5.5) and (5.6) can be written in terms of the expectation value of the number operator of the harmonic oscillator in thermal equilibrium, $\bar{n}:=1/(\mathrm{e}^{\alpha}-1)$ with $\alpha:=\beta\hbar\omega$. Indeed, it is equal to a generalized mean [62] of $\bar{n}$ and $\bar{n}+1$, which is defined as $(\bar{n}+1)f(\frac{\bar{n}}{\bar{n}+1})$. For instance, $f(x)=(x+1)/2, \sqrt{x}, 2x/(x+1)$ and $(x-1)/\log x$ correspond to the arithmetic, geometric, harmonic and logarithmic means, respectively. The factor $f(\mathrm{e}^{-\beta\hbar\omega})/(1-\mathrm{e}^{-\beta\hbar\omega})$ for several operator monotone functions corresponding to important types quantum Fisher information are summarized in Table. 5.1.

Finally, we prove the generalized fluctuation-dissipation theorem. Since we assume that the state is the canonical ensemble, the Hamiltonian $\hat{H}$ and the density operator $\hat{\rho}_{\mathrm{can}}$ can be simultaneously diagonalized as

$$\hat{H}=\sum_i E_i\,|E_i\rangle\langle E_i|\,, \tag{5.7}$$

$$\hat{\rho}_{\mathrm{can}}=\sum_i p_i\,|E_i\rangle\langle E_i|\,, \tag{5.8}$$

where $p_i=\mathrm{e}^{-\beta(E_i-F)}$, and $F=-\frac{1}{\beta}\log\mathrm{tr}\left[\mathrm{e}^{-\beta\hat{H}}\right]$ is the free energy. The most important step in deriving Eqs. (5.5) and (5.6) is to write down explicitly the complicated action of the superoperator $\boldsymbol{K}^f_{\hat{\rho}_{\mathrm{can}}}=\boldsymbol{R}_{\hat{\rho}_{\mathrm{can}}}f(\boldsymbol{L}_{\hat{\rho}_{\mathrm{can}}}\boldsymbol{R}^{-1}_{\hat{\rho}_{\mathrm{can}}})$, which appears in the definition of the generalized covariance, by considering the matrix components in the energy eigenbasis $\{|E_i\rangle\}$. If $f(x)=x^k$, we obtain for an arbitrary operator $\hat{A}$,

$$\begin{aligned}\langle E_j|\boldsymbol{K}^{f(x)=x^k}_{\hat{\rho}_{\mathrm{can}}}(\hat{A}_\nu)|E_i\rangle &= \langle E_j|\hat{\rho}^k_{\mathrm{can}}\hat{A}_\nu\hat{\rho}^{1-k}_{\mathrm{can}}|E_i\rangle \\ &= p_i\left(\frac{p_j}{p_i}\right)^k\langle E_j|\hat{A}_\nu|E_i\rangle\,. \end{aligned}\tag{5.9}$$

From the linearity of $\boldsymbol{K}^f_{\hat{\rho}_{\mathrm{can}}}$ with respect to an operator monotone function f, we obtain, for a polynomial $f(x)=\sum_{k=1}^{n} c_k x^k$,

$$\begin{aligned}\langle E_j|\boldsymbol{K}^f_{\hat\rho_{\mathrm{can}}}(\hat A_\nu)|E_i\rangle &= \sum_{k=1}^{n} c_k p_i \left(\frac{p_j}{p_i}\right)^n \langle E_j|\hat A_\nu|E_i\rangle \\ &= p_i f\left(\frac{p_j}{p_i}\right)\langle E_j|\hat A_\nu|E_i\rangle\,. \end{aligned} \tag{5.10}$$

Let m and M be the minimum and maximum of all p_i/p_j's, respectively. Since any operator monotone function $f(x)$ is convex [63] and hence continuous, it can be uniformly approximated by polynomials on the closed interval $[m,M]$ from the Stone-Weierstrass approximation theorem [51], and so can be the superoperator $\boldsymbol{K}^f_{\hat\rho_{\mathrm{can}}}$. Therefore, the relation (5.10) holds for an arbitrary operator monotone function $f(x)$.

Then, the generalized covariance of two displacement operators can be calculated as

$$\begin{aligned}\langle\!\langle \Delta\hat X_\mu(t),\Delta\hat X_\nu(0)\rangle\!\rangle^f_{\hat\rho_{\mathrm{can}}} &= \sum_{i,j}\langle E_i|\Delta\hat X_\mu(t)|E_j\rangle\langle E_j|\Delta\hat X_\nu(0)|E_i\rangle \\ &= \sum_{i,j} p_i f\left(\frac{p_j}{p_i}\right)\mathrm{e}^{i(E_i-E_j)t/\hbar}\langle E_i|\Delta\hat X_\mu|E_j\rangle\langle E_j|\Delta\hat X_\nu|E_i\rangle\,. \end{aligned}\tag{5.11}$$

Therefore, its Fourier transform is given by

$$\begin{aligned}C^f_{\mu\nu,\omega} &= \sum_{i,j} p_i f\left(\frac{p_j}{p_i}\right) 2\pi\hbar\delta(E_i-E_j-\hbar\omega)\langle E_i|\Delta\hat X_\mu|E_j\rangle\langle E_j|\Delta\hat X_\nu|E_i\rangle \\ &= f(\mathrm{e}^{-\beta\hbar\omega})\sum_{i,j} p_i 2\pi\hbar\delta(E_i-E_j-\hbar\omega)\langle E_i|\Delta\hat X_\mu|E_j\rangle\langle E_j|\Delta\hat X_\nu|E_i\rangle\,. \end{aligned}\tag{5.12}$$

Here, we have used the fact that $E_j-E_i=\hbar\omega$ and hence $p_j/p_i=\mathrm{e}^{-\beta\hbar\omega}$ due to the existence of the δ function. By switching from the time domain to the frequency domain, the f-dependent factor becomes independent of the labels i and j, and can be factored out of the sum. A similar calculation leads to the expression of the Fourier transform of the response function $\phi_{\mu\nu,\omega}$ from the Green-Kubo formula (2.37) as

$$\phi_{\mu\nu,\omega} = -\frac{1-\mathrm{e}^{-\beta\hbar\omega}}{i\hbar}\sum_{i,j} p_i 2\pi\hbar\delta(E_i-E_j-\hbar\omega)\langle E_i|\Delta\hat X_\mu|E_j\rangle\langle E_j|\Delta\hat X_\nu|E_i\rangle\,. \tag{5.13}$$

Comparing Eqs. (5.12) and (5.13), we obtain Eq. (5.5).

By a similar calculation to derive Eq. (5.12), we obtain the Fourier transform of the product of two current operators as

$$\tilde C^f_{\mu\nu,\omega} = f(\mathrm{e}^{-\beta\hbar\omega})\sum_{i,j} p_i 2\pi\hbar\delta(E_i-E_j-\hbar\omega)\langle E_i|\hat J_\mu|E_j\rangle\langle E_j|\hat J_\nu|E_i\rangle\,. \tag{5.14}$$

Comparing Eqs. (5.14) and (2.57), we obtain Eq. (5.6), which completes the proof.

5.2 Determining Generalized Covariances

Using the generalized fluctuation-dissipation theorem derived in the previous section, we can reconstruct the generalized covariance from the dynamical susceptibilities and the complex admittance,

$$\chi_{\mu\nu}(\omega) = \int_0^\infty \mathrm{d}t\ \mathrm{e}^{i\omega t}\phi_{\mu\nu}(t), \tag{5.15}$$

$$\tilde{\chi}_{\mu\nu}(\omega) = \int_0^\infty \mathrm{d}t\ \mathrm{e}^{i\omega t}\tilde{\phi}_{\mu\nu}(t), \tag{5.16}$$

which are measurable quantities. By inverse Fourier transforming Eq. (5.5), we obtain

$$\begin{aligned}\langle\!\langle \Delta\hat{X}_\mu(t), \Delta\hat{X}_\nu(0)\rangle\!\rangle^f_{\hat{\rho}} &= \int_{-\infty}^\infty \frac{\mathrm{d}\omega}{2\pi}\mathrm{e}^{-i\omega t}C^f_{\mu\nu,\omega} \\ &= \frac{\hbar}{i}\int_{-\infty}^\infty \frac{\mathrm{d}\omega}{2\pi}\mathrm{e}^{-i\omega t}\frac{f(\mathrm{e}^{-\beta\hbar\omega})}{1-\mathrm{e}^{-\beta\hbar\omega}}\phi_{\mu\nu,\omega},\end{aligned} \tag{5.17}$$

and hence

$$\langle\!\langle \Delta\hat{X}_\mu, \Delta\hat{X}_\nu\rangle\!\rangle^f_{\hat{\rho}} = \frac{\hbar}{i}\int_{-\infty}^\infty \frac{\mathrm{d}\omega}{2\pi}\frac{f(\mathrm{e}^{-\beta\hbar\omega})}{1-\mathrm{e}^{-\beta\hbar\omega}}\phi_{\mu\nu,\omega} \tag{5.18}$$

by setting $t=0$. Noting that $\phi_{\mu\nu,\omega}$ can be expressed in terms of dynamical susceptibilities as $\phi_{\mu\nu,\omega} = \chi_{\mu\nu}(\omega) - \chi_{\nu\mu}(\omega)^*$, we obtain the formula that expresses the generalized covariance in terms of the dynamical susceptibility:

$$\langle\!\langle \Delta\hat{X}_\mu, \Delta\hat{X}_\nu\rangle\!\rangle^f_{\hat{\rho}} = \frac{\hbar}{i}\int_{-\infty}^\infty \frac{\mathrm{d}\omega}{2\pi}\frac{f(\mathrm{e}^{-\beta\hbar\omega})}{1-\mathrm{e}^{-\beta\hbar\omega}}[\chi_{\mu\nu}(\omega) - \chi_{\nu\mu}(\omega)^*]. \tag{5.19}$$

If the operator monotone function is symmetric, i.e., $f(x) = \tilde{f}(x)$, where $\tilde{f}(x) = xf(1/x)$, we can simplify the formula as

$$\langle\!\langle \Delta\hat{X}_\mu, \Delta\hat{X}_\nu\rangle\!\rangle^f_{\hat{\rho}} = \frac{2\hbar}{\pi}\int_0^\infty \mathrm{d}\omega\frac{f(\mathrm{e}^{-\beta\hbar\omega})}{1-\mathrm{e}^{-\beta\hbar\omega}}\mathrm{Im}[\chi^s_{\mu\nu}(\omega)], \tag{5.20}$$

where $\chi^{\mathrm{s}}_{\mu\nu}(\omega) := (\chi_{\mu\nu}(\omega) + \chi_{\nu\mu}(\omega))/2$ is the symmetric part of the dynamical susceptibility matrix. The formulae (5.19) and (5.20) provide a method of experimentally determining an arbitrary type of the generalized covariance. We measure the dynamical susceptibilities, which describe the response to harmonically oscillating external perturbations, for all frequencies $0 < \omega < \infty$, and then integrate out these dynamical susceptibilities with proper weights depending on an operator monotone function $f(x)$.

We can also derive a similar formula for current operators as

$$\langle\!\langle \hat{J}_\mu, \hat{J}_\nu\rangle\!\rangle^f_{\hat{\rho}} = \int_{-\infty}^\infty \frac{\mathrm{d}\omega}{2\pi}\frac{\hbar\omega f(\mathrm{e}^{-\beta\hbar\omega})}{1-\mathrm{e}^{-\beta\hbar\omega}}\tilde{\phi}_{\mu\nu,\omega}. \tag{5.21}$$

A simplified one for a symmetric operator monotone function $f(x)$ is given by

$$\langle\!\langle \hat{J}_\mu, \hat{J}_\nu \rangle\!\rangle_{\hat{\rho}}^f = \frac{2}{\pi}\int_0^\infty \mathrm{d}\omega \frac{\hbar\omega f(\mathrm{e}^{-\beta\hbar\omega})}{1-\mathrm{e}^{-\beta\hbar\omega}} \mathrm{Re}[\tilde{\chi}^{\mathrm{s}}_{\mu\nu}(\omega)]. \tag{5.22}$$

5.3 Determining the Quantum Fisher Information

The quantum Fisher information can also be determined via the equations derived in the previous section ((5.19), (5.20), (5.21), and (5.22)) because it is nothing but the generalized covariance of the logarithmic derivative (4.56).

Here, we explicitly calculate the external perturbation that we need to apply to determine the quantum Fisher information of a specific model. Let us consider a one-parameter unitary model generated by a given operator $\hat{B}$, defined as

$$\hat{\rho}_\theta := \mathrm{e}^{-i\theta\hat{B}}\hat{\rho}\mathrm{e}^{i\theta\hat{B}}. \tag{5.23}$$

The parameter θ is the degree of translation or rotation to be estimated. Suppose, for example, that we want to infer the quantum Fisher information of this model by measuring the complex admittance of current operators $\tilde{\chi}(\omega)$ through Eq. (5.21). Since we are considering a one-parameter model, the indices μ, ν are omitted in the following. In this case, the perturbation $\hat{A}$ must be chosen so that the corresponding current operator $\hat{J}$ may coincide with the logarithmic derivative $\hat{L} := (\boldsymbol{K}^f_{\hat{\rho}})^{-1}(i[\hat{\rho},\hat{B}])$. The matrix element of the perturbation $\hat{X}$ can be obtained by solving the equation $\hat{J} = \hat{L}$, and the solution is

$$\langle E_i|\hat{A}|E_j\rangle = \frac{1-\mathrm{e}^{-\beta(E_i-E_j)}}{(E_i-E_j)f(\mathrm{e}^{-\beta(E_i-E_j)})}\langle E_i|\hat{B}|E_j\rangle\,. \tag{5.24}$$

It is worth noting that the ratio of the matrix elements is equal to the coefficient appearing in Eq. (5.6). However, the correspondence between $\hat{A}$ and $\hat{B}$ is rather complicated. In particular, $\hat{A}$ depends on $f(x)$, so that we need to perform other nonequilibrium measurements to determine other types of the quantum Fisher information.

If we are able to measure the dynamical susceptibility of displacement operators $\chi(\omega)$, we can take the perturbation $\hat{A}$ to be the very generator $\hat{B}$. Indeed, the quantum Fisher information of the unitary model (5.23) corresponding to an operator monotone function $f(x)$ can be expressed in terms of the generalized covariance corresponding to $(x-1)^2/f(x)$:

$$\begin{aligned} J^Q_{\theta=0} &= \sum_{i,j} p_i \frac{(1-p_j/p_i)^2}{f(p_j/p_i)} \left| \langle E_i|\hat{B}|E_j\rangle \right|^2 \\ &= \langle\!\langle \Delta\hat{B}, \Delta\hat{B} \rangle\!\rangle_{\hat{\rho}}^{(x-1)^2/f(x)}. \end{aligned} \tag{5.25}$$

Therefore, we obtain the following formula for a symmetric operator monotone function $f(x)$:

$$J^Q_{\theta=0} = \frac{2\hbar}{\pi}\int_0^\infty \mathrm{d}\omega \frac{1-\mathrm{e}^{-\beta\hbar\omega}}{f(\mathrm{e}^{-\beta\hbar\omega})}\mathrm{Im}[\chi(\omega)], \tag{5.26}$$

where $\chi(\omega)$ is the dynamical susceptibility of $\hat{B}$ against a perturbation $\hat{B}$. We note that Eq. (5.26) reduces to the previous study for the SLD Fisher information [14] if we set $f(x) = (x+1)/2$.

In Sec. 4.2, we have seen that the BKM Fisher information can be determined from the static susceptibility. In contrast, we find that any type of the Fisher information can be determined if we can measure the dynamical susceptibility.

5.4 Application: How to Determine the Skew Information

In this section, we apply our results to the case of determining the skew information, which can be interpreted as one of the quantum Fisher information. Then, we discuss a possible experimental validation of the skew information-based uncertainty relation.

Historically, the skew information was introduced by Wigner and Yanase [64] to quantify the information content contained in the quantum state in the presence of a conserved quantity, and is defined by

$$I_{1/2}(\hat{\rho}, \hat{A}) := -\frac{1}{2}\mathrm{tr}\left[\left([\hat{\rho}^{1/2}, \hat{A}]\right)^2\right], \tag{5.27}$$

where $\hat{A}$ is an arbitrary Hermitian operator. Dyson proposed a one-parameter extension of the skew information

$$I_\alpha(\hat{\rho}, \hat{A}) := -\frac{1}{2}\mathrm{tr}\left[[\hat{\rho}^\alpha, \hat{A}][\hat{\rho}^{1-\alpha}, \hat{A}]\right], \tag{5.28}$$

for $0 < \alpha < 1$, which is called the Wigner-Yanase-Dyson (WYD) skew information. It has been pointed out [65, 66] that the WYD skew information can be interpreted as a special case of the quantum Fisher information of the one-parameter unitary model. Indeed, they are related by the following equality:

$$I_\alpha(\hat{\rho}, \hat{A}) = \frac{\alpha(1-\alpha)}{2} J_{\theta=0}^{f_\alpha, Q}, \tag{5.29}$$

where the operator monotone function of the quantum Fisher information is chosen to be

$$f_\alpha(x) = \alpha(1-\alpha)\frac{(x-1)^2}{(x^\alpha - 1)(x^{1-\alpha} - 1)}. \tag{5.30}$$

Further generalization of the skew information has been made by Hansen [66] based on this observation, which is called the metric adjusted skew information, defined by

$$I_f(\hat{\rho}, \hat{A}) := \frac{f(0)}{2} J_{\theta=0}^{Q}, \tag{5.31}$$

where $f(x)$ is an arbitrary operator monotone function satisfying $f(0) \neq 0$. This is the most general form of the skew information so far. Since the metric adjusted skew information possesses some desired properties such as the convexity as a function of the state [66], it can be interpreted as a quantum part of the fluctuation of the observable $\hat{A}$ at the quantum state $\hat{\rho}$, and applied to the resource theory of asymmetry and coherence in quantum information theory [48], and it can also be applied to uncertainty relations [67, 68, 69, 70, 71]. Here, we focus on the Kennard-Robertson type uncertainty relation [72] between the fluctuations of two noncommuting observables, not on Heisenberg's original uncertainty relation between error and disturbance [73, 74, 75, 76, 77]

The skew information cannot be measured by usual quantum measurements because it includes the term such as $\mathrm{tr}\left[\hat{\rho}^{\alpha}\hat{A}\hat{\rho}^{1-\alpha}\hat{A}\right]$. The methods developed in this chapter gives a way to determine the skew information and hence all the quantities used in various forms of skew information-based uncertainty relations [67, 68, 69, 70, 71]. Indeed, the metric-adjusted skew information can be determined by the formula

$$I_f(\hat{\rho},\hat{A}) = \frac{f(0)\hbar}{\pi}\int_0^{\infty} \mathrm{d}\omega \frac{1-\mathrm{e}^{-\beta\hbar\omega}}{f(\mathrm{e}^{-\beta\hbar\omega})}\mathrm{Im}[\tilde{\chi}(\omega)], \tag{5.32}$$

where $\tilde{\chi}(\omega)$ is the dynamical susceptibility of $\hat{A}$ when the external perturbation $\hat{H}_{\mathrm{ext}}(t) = -F(t)\hat{A}$ is applied.

As an example, we apply our result to a harmonic oscillator system in thermal equilibrium, and demonstrate that the uncertainty relation shown in Ref. [69] can be validated experimentally. We define a quantum fluctuation of the observable $\hat{A}$ at the state $\hat{\rho}$ by

$$U_\alpha(\hat{\rho},\hat{A}) := \sqrt{\langle(\Delta\hat{A})^2\rangle_{\hat{\rho}}^2 - \left(\langle(\Delta\hat{A})^2\rangle_{\hat{\rho}} - I_\alpha(\hat{\rho},\hat{A})\right)^2}. \tag{5.33}$$

Yanagi [69] has shown that the uncertainty relation

$$U_\alpha(\hat{\rho},\hat{A})U_\alpha(\hat{\rho},\hat{B}) \geq \alpha(1-\alpha)\left|\mathrm{tr}\left[\hat{\rho}[\hat{A},\hat{B}]\right]\right|^2 \tag{5.34}$$

holds for any $\alpha \in [0,1]$. We consider a harmonic oscillator in thermal equilibrium:

$$\hat{H} = \frac{1}{2m}\hat{p}^2 + \frac{1}{2}m\omega^2\hat{x}^2. \tag{5.35}$$

We apply an external perturbation corresponding to the position and the momentum operators

$$\hat{A}_\mu := \begin{cases} \hat{x} & (\mu = 1); \\ \hat{p} & (\mu = 2). \end{cases} \tag{5.36}$$

Then, the diagonal components of the dynamical susceptibility are given by

$$\begin{aligned} m\omega\chi_{11}(\omega') =& \frac{1}{m\omega}\chi_{22}(\omega') \\ =& \frac{1}{2}\left(\mathcal{P}\frac{1}{\omega'+\omega} - \mathcal{P}\frac{1}{\omega'-\omega} - i\pi\delta(\omega'+\omega) + i\pi\delta(\omega'-\omega)\right), \end{aligned} \tag{5.37}$$

where $\mathcal{P}$ denotes the principal value. Therefore, from Eqs. (5.30) and (5.32), the WYD skew information is calculated as

$$I_\alpha(\hat{\rho}, \hat{x}) = \frac{\hbar}{2m\omega} \cdot \frac{(1 - \mathrm{e}^{-\alpha\beta\hbar\omega})(1 - \mathrm{e}^{-(1-\alpha)\beta\hbar\omega})}{1 - \mathrm{e}^{-\beta\hbar\omega}}, \tag{5.38}$$

$$I_\alpha(\hat{\rho}, \hat{p}) = \frac{\hbar m\omega}{2} \cdot \frac{(1 - \mathrm{e}^{-\alpha\beta\hbar\omega})(1 - \mathrm{e}^{-(1-\alpha)\beta\hbar\omega})}{1 - \mathrm{e}^{-\beta\hbar\omega}}, \tag{5.39}$$

and the uncertainty relation (5.34) reduces to

$$\frac{(1 - \mathrm{e}^{-2\alpha\beta\hbar\omega})(1 - \mathrm{e}^{-2(1-\alpha)\beta\hbar\omega})}{(1 - \mathrm{e}^{-\beta\hbar\omega})^2} \geq 4\alpha(1-\alpha), \tag{5.40}$$

which can be checked to be true. It is worth noting that the equality in Eq. (5.40) is achieved when $\alpha = 1/2$, even though the state is a mixed state and includes non-minimum uncertainty states.

5.5 Discussion

We discuss the applicability and the efficiency of our proposed method. Our method is applicable in two situations: the Hamiltonian is experimentally given and we want to know the quantum Fisher information of the thermal equilibrium state under that Hamiltonian; the density operator is experimentally given and we want to know the quantum Fisher information of that state. For the latter case, an effective Hamiltonian $\hat{H} = -\frac{1}{\beta}\log\hat{\rho}$ tells us what kind of Hamiltonian we need to engineer. Such a situation seems to be realistic when the system size is relatively small (e.g., a few qubits).

The estimation via the integral (5.19) is efficient for the following reason. The integrand in Eq. (5.19) consists of the δ functions that contribute only if the frequency matches the energy difference of two eigenstates, and hence the integral can be rewritten in terms of a discrete sum. When the system is small, the number of measurement required to estimate the sum is also small. As the size of the system becomes large, the number of the terms in the sum becomes exponentially large. For such a large system, however, the integrand in Eq. (5.19) can be approximated by a continuous function. Therefore, the error of estimation can be controlled by the space of sampling frequencies, and does not depend on the system size.

There are two advantages about our method of determining the quantum Fisher information. First, we can determine the quantum Fisher information without estimating the density operator $\hat{\rho}$ by quantum tomography. Of course, if we can estimate $\hat{\rho}$, we can calculate the quantum Fisher information from the definition itself. However, the estimation of $\hat{\rho}$ requires exponentially many costs of state preparations and measurements, and hence is impractical for a large system. Also, analytical or numerical diagonalization of the Hamiltonian is also a challenge for quantum many-body systems in general. Our method enables us to experimentally determine the information of the complex system for which the theoretical treatment is difficult. Second, in our protocol, the dependence on an operator monotone function appears not in the measurement procedures but in the integration. In other words, once we measure the dynamical susceptibilities for all frequencies, we can determine any type of the generalized covariance or the quantum Fisher information through simple post-processing.

Finally, we discuss possible applications of the results in this chapter. Since the quantum Fisher information quantifies how accurately we can estimate an unknown quantum state, as we have described in Sec. 4.2.2, our method enables us to test whether the equilibrium state, in particular the ground state, of a given Hamiltonian can be a resource for quantum metrology. We can also test whether a state possesses a multipartite entanglement [10, 11] through the quantum Fisher information determined by our method. The advantage of our method compared to Ref. [14] is that it can be applied for any type of the quantum Fisher information. The metric adjusted skew information [66] is the quantum Fisher information of the one-parameter unitary model (5.23), and therefore can be determined experimentally through our method without quantum tomography. Therefore, various forms of skew information-based uncertainty relations [67, 68, 69, 70, 71], which is tighter than the conventional uncertainty relation [72], can be experimentally validated by our method.

Chapter 6

Expansion of Average Excess Work in Thermodynamic Control

In this chapter, we derive an expansion of the average excess work performed on the system during a thermodynamic control by generalizing the phenomenological derivation of the thermodynamic metric expression [33]. Then, we show that the expansion can be interpreted in terms of a single parameter ϵ that characterizes how slowly we control the system, and therefore the expansion is asymptotically correct in the slow-control limit. This chapter is based on the paper 2 in Publication List, which is in preparation.

6.1 Expansion of Average Excess Work

In the phenomenological derivation of the thermodynamic metric expression reviewed in Sec. 3.2.2, two approximations have been used; the linear response and the constant velocity of the control parameters $\dot{\lambda}^\nu(t-s) \simeq \dot{\lambda}^\nu(t)$. To treat these approximations systematically, we replace the linear response with the perturbative expansion (2.60), and the constant velocity approximation with the Taylor expansion

$$\dot{\lambda}^\nu(t-s) = \sum_{k=0}^{\infty} \frac{(-s)^k}{k!} \frac{\mathrm{d}^{k+1}\lambda^\nu(t)}{\mathrm{d}t^{k+1}}. \tag{6.1}$$

To evaluate the average excess work

$$\langle W_{\mathrm{ex}}(\mathbf{\Lambda})\rangle = -\int_0^T \mathrm{d}t\; \dot{\lambda}^\mu(t) \left\langle \Delta X_\mu(\boldsymbol{\lambda}(t))\right\rangle_{\mathbf{\Lambda}}, \tag{6.2}$$

we need to evaluate the expectation value of the deviation of the generalized force from its equilibrium value. From the general theory of the perturbative expansion, it can be expressed as

$$
\begin{aligned}
&\langle \Delta X_\mu(\boldsymbol{\lambda}(t))\rangle_{\boldsymbol{\Lambda}}\\
=&\sum_{n=1}^{\infty}\int_0^\infty \mathrm{d}s_1 \int_{s_1}^\infty \mathrm{d}s_2 \cdots \int_{s_{n-1}}^\infty \mathrm{d}s_n [\lambda^{\nu_1}(t-s_1)-\lambda^{\nu_1}(t)]\cdots[\lambda^{\nu_n}(t-s_n)-\lambda^{\nu_n}(t)]\\
&\qquad\qquad\qquad\qquad\times \phi^{(n)}_{\mu\nu_1\dots\nu_n}(s_1,\dots,s_n;\boldsymbol{\lambda}(t)),
\end{aligned} \tag{6.3}
$$

where $\phi^{(n)}_{\mu\nu_1\dots\nu_n}(s_1,\dots,s_n;\boldsymbol{\lambda})$ denotes the nth order response function of the generalized force $X_\mu(\boldsymbol{\lambda})$ in the equilibrium state with respect to the control parameter $\boldsymbol{\lambda}$.

To change the range of integration in Eq. (6.3), we extend the domain of the response function $\phi^{(n)}_{\mu\nu_1\dots\nu_n}(s_1,\dots,s_n;\boldsymbol{\lambda})$ whose arguments $s_1,\dots,s_n$ are not necessarily ordered in time. For given values of $s_1,\dots,s_n \geq 0$, let σ be a permutation of n elements $\{1,\dots,n\}$ that satisfies $s_{\sigma(1)} \leq s_{\sigma(n)} \leq \cdots \leq s_{\sigma(n)}$. The response function is defined using the permutation σ, given by

$$
\phi^{(n)}_{\mu\nu_1\dots\nu_n}(s_1,\dots,s_n;\boldsymbol{\lambda}) := \phi^{(n)}_{\mu\nu_{\sigma(1)}\dots\nu_{\sigma(n)}}(s_{\sigma(1)},\dots,s_{\sigma(n)};\boldsymbol{\lambda}). \tag{6.4}
$$

Now we can change the range of integration in Eq. (6.3) as

$$
\begin{aligned}
&\int_0^\infty \mathrm{d}s_1 \int_{s_1}^\infty \mathrm{d}s_2 \cdots \int_{s_{n-1}}^\infty \mathrm{d}s_n [\lambda^{\nu_1}(t-s_1)-\lambda^{\nu_1}(t)]\cdots[\lambda^{\nu_n}(t-s_n)-\lambda^{\nu_n}(t)]\phi^{(n)}_{\mu\nu_1\dots\nu_n}(s_1,\dots,s_n;\boldsymbol{\lambda}(t))\\
=&\frac{1}{n!}\int_0^\infty \mathrm{d}s_1 \cdots \int_0^\infty \mathrm{d}s_n [\lambda^{\nu_1}(t-s_1)-\lambda^{\nu_1}(t)]\cdots[\lambda^{\nu_n}(t-s_n)-\lambda^{\nu_n}(t)]\phi^{(n)}_{\mu\nu_1\dots\nu_n}(s_1,\dots,s_n;\boldsymbol{\lambda}),
\end{aligned} \tag{6.5}
$$

which follows from the symmetry of the integrand. Combining Eqs. (6.3), (6.5), and the relation between the response function and the relaxation function (2.66), we can rewrite the nth order contribution to the excess power at time t in Eq. (6.2) can be rewritten as

$$
\begin{aligned}
&P^{(n)}_{\mathrm{ex}}(t)\\
:=&-\dot{\lambda}^\mu(t)\int_0^\infty \mathrm{d}s_1 \int_{s_1}^\infty \mathrm{d}s_2 \cdots \int_{s_{n-1}}^\infty \mathrm{d}s_n [\lambda^{\nu_1}(t-s_1)-\lambda^{\nu_1}(t)]\cdots[\lambda^{\nu_n}(t-s_n)-\lambda^{\nu_n}(t)]\\
&\qquad\qquad\qquad\qquad\times \phi^{(n)}_{\mu\nu_1\dots\nu_n}(s_1,\dots,s_n;\boldsymbol{\lambda}(t))\\
=&\frac{(-)^{n+1}}{n!}\dot{\lambda}^\mu(t)\int_0^\infty \mathrm{d}s_1 \cdots \int_0^\infty \mathrm{d}s_n [\lambda^{\nu_1}(t-s_1)-\lambda^{\nu_1}(t)]\cdots[\lambda^{\nu_n}(t-s_n)-\lambda^{\nu_n}(t)]\\
&\qquad\qquad\qquad\qquad\times \frac{\partial^n}{\partial s_1\cdots\partial s_n}\psi^{(n)}_{\mu\nu_1\dots\nu_n}(s_1,\dots,s_n;\boldsymbol{\lambda}(t)).
\end{aligned} \tag{6.6}
$$

We integrate Eq. (6.6) by parts with respect to $s_1,\dots,s_n$, and obtain

$$
P^{(n)}_{\mathrm{ex}}(t) = \frac{(-)^{n+1}}{n!}\dot{\lambda}^\mu(t)\int_0^\infty \mathrm{d}s_1 \cdots \int_0^\infty \mathrm{d}s_n\ \dot{\lambda}^{\nu_1}(t-s_1)\cdots\dot{\lambda}^{\nu_n}(t-s_n)\psi^{(n)}_{\mu\nu_1\dots\nu_n}(s_1,\dots,s_n;\boldsymbol{\lambda}(t)). \tag{6.7}
$$

The boundary terms vanish if the effect of the perturbation vanishes after a sufficiently long time, as assumed in Eq. (2.67). We further assume that the protocol $\boldsymbol{\Lambda} = \{\boldsymbol{\lambda}(t)\}$ is a sufficiently smooth function and hence can be Taylor-expanded as

$$\dot{\lambda}^{\nu_i}(t-s_i) = \sum_{k_i=0}^{\infty} \frac{(-s_i)^{k_i}}{k_i!} \frac{\mathrm{d}^{k_i+1}\lambda^{\nu_i}(t)}{\mathrm{d}t^{k_i+1}} \qquad (i=1,\ldots,n). \tag{6.8}$$

By substituting the Taylor expansion of the protocol into the nth order contribution to the excess power, we obtain

$$\begin{aligned} &P_{\mathrm{ex}}^{(n)}(t) \\ =&\frac{(-)^{n+k_1+\cdots+k_n+1}}{n!k_1!\cdots k_n!} \sum_{k_1,\ldots,k_n=0}^{\infty} \frac{\mathrm{d}\lambda^{\mu}(t)}{\mathrm{d}t} \frac{\mathrm{d}^{k_1+1}\lambda^{\nu_1}(t)}{\mathrm{d}t^{k_1+1}} \cdots \frac{\mathrm{d}^{k_n+1}\lambda^{\nu_n}(t)}{\mathrm{d}t^{k_n+1}} \\ &\times \int_0^{\infty} \mathrm{d}s_1 \cdots \int_0^{\infty} \mathrm{d}s_n \ s_1^{k_1} \cdots s_n^{k_n} \psi^{(n)}_{\mu\nu_1\ldots\nu_n}(s_1,\ldots,s_n;\boldsymbol{\lambda}(t)), \end{aligned} \tag{6.9}$$

where the protocol-dependent parts are factored out of the integral. Note that the phenomenological derivation of the thermodynamic metric expression of the excess work takes into account only the first term ($n=1, k_1=0$) and neglects all the other terms. If we perform the protocol-independent integration and define the thermodynamic coefficient as

$$\zeta^{(n;k_1\ldots k_n)}_{\mu\nu_1\ldots\nu_n}(\boldsymbol{\lambda}) := \frac{(-)^{n+k_1+\cdots+k_n}}{n!k_1!\ldots k_n!} \int_0^{\infty} \mathrm{d}s_1 \cdots \int_0^{\infty} \mathrm{d}s_n \ s_1^{k_1} \cdots s_n^{k_n} \psi^{(n)}_{\mu\nu_1\ldots\nu_n}(s_1,\ldots,s_n;\boldsymbol{\lambda}), \tag{6.10}$$

we finally obtain the expansion of the excess work as

$$W_{\mathrm{ex}}(\boldsymbol{\Lambda}) = \int_0^T \mathrm{d}t \sum_{n=1}^{\infty} \sum_{k_1,\ldots,k_n=0}^{\infty} \frac{\mathrm{d}\lambda_{\mu}(t)}{\mathrm{d}t} \frac{\mathrm{d}^{k_1+1}\lambda^{\nu_1}(t)}{\mathrm{d}t^{k_1+1}} \cdots \frac{\mathrm{d}^{k_n+1}\lambda^{\nu_n}(t)}{\mathrm{d}t^{k_n+1}} \zeta^{(n;k_1\ldots k_n)}_{\mu\nu_1\ldots\nu_n}(\boldsymbol{\lambda}(t)), \tag{6.11}$$

which is the main result in this chapter. Since the expression (6.11) contains arbitrary higher-order derivatives of $\boldsymbol{\lambda}(t)$, the excess power at time t indeed depends on the history of the control parameters. However, we stress that each term consists of finite-rank derivatives of $\boldsymbol{\lambda}(t)$ and the thermodynamic coefficient at $\boldsymbol{\lambda}(t)$, which is calculated from the information about the equilibrium state $\hat{\rho}_{\mathrm{eq}}(\boldsymbol{\lambda}(t))$. In this sense, Eq. (6.11) provides an approximate expression which is local in the control parameter space when truncated to a finite number of terms.

Since the thermodynamic metric $\zeta^{(1;0)}_{\mu\nu}(\boldsymbol{\lambda})$ behaves like a $(0,2)$ tensor, it is called a metric. However, $\zeta^{(n;k_1\ldots k_n)}_{\mu\nu_1\ldots\nu_n}(\boldsymbol{\lambda})$ does not necessarily behave like tensors, and therefore we call it just a thermodynamic coefficient.

6.2 Physical Meaning of Expansion

To investigate the physical meaning of the expansion of the excess work (6.11), let us introduce a dimensionless parameter $\epsilon > 0$, which characterizes how slowly we control the system. For a protocol $\boldsymbol{\Lambda} = \{\boldsymbol{\lambda}(t)\}_{t\in[0,T]}$, we define an ϵ-modified similar protocol

$$\boldsymbol{\Lambda}_{\epsilon} := \{\boldsymbol{\lambda}(\epsilon t)\}_{t\in[0,T/\epsilon]}, \tag{6.12}$$

which is ϵ times faster than the original protocol $\mathbf{\Lambda}$. We note that the limit $\epsilon \to 0$ corresponds to the quasistatic limit.

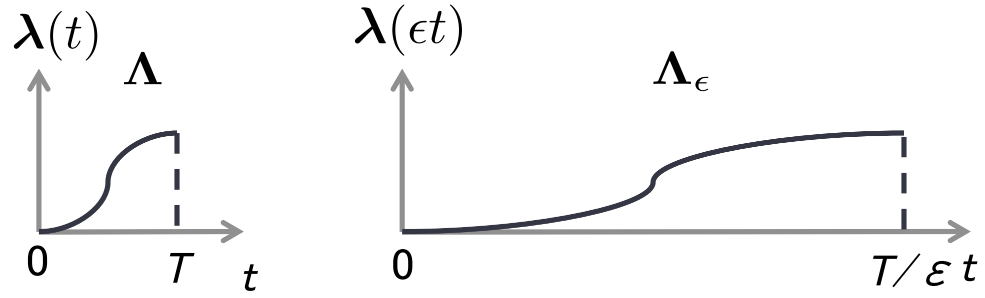

Figure 6.1: The original protocol $\mathbf{\Lambda}$ (left) and the ϵ-modified protocol $\mathbf{\Lambda}_\epsilon$ (right).

Then, the excess work for the protocol $\mathbf{\Lambda}_\epsilon$ is calculated as

$$W_{\mathrm{ex}}(\mathbf{\Lambda}_\epsilon) = \int_0^T \mathrm{d}t \sum_{n=1}^{\infty} \sum_{k_1,\ldots,k_n=0}^{\infty} \epsilon^{n+k_1+\cdots+k_n} \frac{\mathrm{d}\lambda^\mu(t)}{\mathrm{d}t} \frac{\mathrm{d}^{k_1+1}\lambda^{\nu_1}(t)}{\mathrm{d}t^{k_1+1}} \cdots \frac{\mathrm{d}^{k_n+1}\lambda^{\nu_n}(t)}{\mathrm{d}t^{k_n+1}} \zeta^{(n;k_1\ldots k_n)}_{\mu\nu_1\ldots\nu_n}(\boldsymbol{\lambda}(t)) \tag{6.13}$$

$$= \sum_{N=1}^{\infty} \epsilon^N \left(\sum_{\substack{n\geq 1, k_1,\ldots,k_n \geq 0 \\ n+k_1+\cdots+k_n=N}} \int_0^T \mathrm{d}t \frac{\mathrm{d}\lambda^\mu(t)}{\mathrm{d}t} \frac{\mathrm{d}^{k_1+1}\lambda^{\nu_1}(t)}{\mathrm{d}t^{k_1+1}} \cdots \frac{\mathrm{d}^{k_n+1}\lambda^{\nu_n}(t)}{\mathrm{d}t^{k_n+1}} \zeta^{(n;k_1\ldots k_n)}_{\mu\nu_1\ldots\nu_n}(\boldsymbol{\lambda}(t)) \right). \tag{6.14}$$

Therefore, the expansion of excess work (6.14) is essentially the expansion in terms of "slowness" of the control, which is represented by ϵ. The most leading $O(\epsilon)$ term coincides with the thermodynamic metric expression (3.28);

$$W_{\mathrm{ex}}(\mathbf{\Lambda}_\epsilon) = \epsilon \int_0^T \mathrm{d}t\ \dot{\lambda}^\mu(t)\dot{\lambda}^\nu(t)\zeta^{(1;0)}_{\mu\nu}(\boldsymbol{\lambda}(t)) + O(\epsilon^2). \tag{6.15}$$

We will discuss the next leading order terms in the next section.

In the microscopic derivation of the thermodynamic expression of the excess work reviewed in Sec. 3.2.3, a parameter ϵ is introduced in the friction coefficient $\epsilon\gamma$. We show that our expansion in terms of the slowness ϵ, which has a clear physical interpretation, is equivalent to the approach taken in the microscopic derivation [43], by proving that the average work is identical in both ways of introducing a parameter ϵ, namely, by modifying the protocol as $\mathbf{\Lambda}_\epsilon$ and by modifying the friction coefficient as $\epsilon\gamma$ for an overdamped Langevin system. In our approach, the dynamics is fixed as

$$\dot{x}(t) = -\frac{1}{\gamma}\frac{\partial V(x,\lambda(t))}{\partial x}\Big|_{x=x(t)} + \sqrt{\frac{2}{\beta\gamma}}\eta(t), \tag{6.16}$$

while the protocol is modified as

$$\Lambda_\epsilon = \{\lambda_\epsilon(\tau)\}_{\tau\in[0,T/\epsilon]} = \{\lambda(\epsilon\tau)\}_{\tau\in[0,T/\epsilon]}. \tag{6.17}$$

In the approach adopted in Ref. [43], the protocol is fixed to $\mathbf{\Lambda}$, while the dynamics is modified as

$$\dot{x}(t) = -\frac{1}{\epsilon\gamma}\frac{\partial V(x,\lambda(t))}{\partial x}\Big|_{x=x(t)} + \sqrt{\frac{2}{\beta\epsilon\gamma}}\eta(t). \tag{6.18}$$

In the first approach, the density function $\rho(x;\tau)$ satisfies the Fokker-Planck equation

$$\frac{\partial\rho(x;\tau)}{\partial\tau} = \frac{1}{\gamma}\frac{\partial}{\partial x}\left[\frac{\partial V(x;\lambda_\epsilon(\tau))}{\partial x}\rho(x;\tau) + \frac{1}{\beta}\frac{\partial\rho(x;\tau)}{\partial x}\right]. \tag{6.19}$$

By changing the integrating variable from τ to $t = \epsilon\tau$, the average work is expressed as

$$\begin{aligned}\langle W\rangle &= \int_0^{T/\epsilon} \mathrm{d}\tau \int \mathrm{d}x\ \dot{\lambda}_\epsilon(\tau)\frac{\partial V(x;\lambda)}{\partial\lambda}\Big|_{\lambda=\lambda_\epsilon(\tau)}\rho(x;\tau) \\ &= \int_0^{T/\epsilon} \mathrm{d}\tau \int \mathrm{d}x\ \epsilon\dot{\lambda}(\epsilon\tau)\frac{\partial V(x;\lambda)}{\partial\lambda}\Big|_{\lambda=\lambda(\epsilon\tau)}\rho(x;\tau) \\ &= \int_0^{T} \mathrm{d}t\ \int \mathrm{d}x\dot{\lambda}(t)\frac{\partial V(x;\lambda)}{\partial\lambda}\Big|_{\lambda=\lambda(t)}\rho(x;t/\epsilon).\end{aligned} \tag{6.20}$$

On the other hand, in the second approach, the density function $\rho_\epsilon(x,t)$ satisfies the ϵ-modified Fokker-Planck equation

$$\frac{\partial\rho_\epsilon(x;t)}{\partial t} = \frac{1}{\epsilon\gamma}\frac{\partial}{\partial x}\left[\frac{\partial V(x;\lambda(t))}{\partial x}\rho_\epsilon(x;t) + \frac{1}{\beta}\frac{\partial\rho_\epsilon(x;t)}{\partial x}\right]. \tag{6.21}$$

Then the average work is given by

$$\langle W\rangle = \int_0^{T} \mathrm{d}t \int \mathrm{d}x\dot{\lambda}(t)\frac{\partial V(x;\lambda)}{\partial\lambda}\Big|_{\lambda=\lambda(t)}\rho_\epsilon(x;t). \tag{6.22}$$

Comparing Eqs. (6.20) and (6.22), they are identical if

$$\rho(x,t/\epsilon) = \rho_\epsilon(x,t). \tag{6.23}$$

Indeed, Eq. (6.23) holds because $\rho(x,t/\epsilon)$ and $\rho_\epsilon(x,t)$ have the same initial condition (i.e., equilibrium distribution) and the same time evolution as

$$\begin{aligned}\frac{\partial\rho(x;t/\epsilon)}{\partial t} &= \frac{1}{\epsilon}\frac{\partial\rho(x;t/\epsilon)}{\partial(t/\epsilon)} = \frac{1}{\epsilon\gamma}\frac{\partial}{\partial x}\left[\frac{\partial V(x;\lambda_\epsilon(t/\epsilon))}{\partial x}\rho(x;t/\epsilon) + \frac{1}{\beta}\frac{\partial\rho(x;t/\epsilon)}{\partial x}\right] \\ &= \frac{1}{\epsilon\gamma}\frac{\partial}{\partial x}\left[\frac{\partial V(x;\lambda(t))}{\partial x}\rho(x;t/\epsilon) + \frac{1}{\beta}\frac{\partial\rho(x;t/\epsilon)}{\partial x}\right],\end{aligned} \tag{6.24}$$

$$\frac{\partial\rho_\epsilon(x;t)}{\partial t} = \frac{1}{\epsilon\gamma}\frac{\partial}{\partial x}\left[\frac{\partial V(x;\lambda(t))}{\partial x}\rho_\epsilon(x;t) + \frac{1}{\beta}\frac{\partial\rho_\epsilon(x;t)}{\partial x}\right]. \tag{6.25}$$

More explicitly, we can calculate the $O(\epsilon^2)$ contributions to the excess work following the microscopic derivation [43]. For simplicity, we assume that both the system and the control parameter are one-dimensional, but the generalization to higher-dimensional cases is straightforward. The Fokker-Planck equation for this system is given by

$$\frac{\partial \rho_\epsilon(x;t)}{\partial t} = \frac{1}{\epsilon\gamma}\frac{\partial}{\partial x}\left(\frac{\partial V(x;\lambda(t))}{\partial x}\rho_\epsilon(x;t) + \frac{1}{\beta}\frac{\partial \rho_\epsilon(x;t)}{\partial x}\right). \tag{6.26}$$

We expand $\rho_\epsilon(x,t)$ in terms of ϵ as

$$\rho_\epsilon(x;t) = \rho_0(x;t)(1 + \epsilon\phi_1(x;t) + \epsilon^2\phi_2(x;t) + \cdots), \tag{6.27}$$

where $\rho_0(x;t)$ is the Gibbs ensemble for $\lambda(t)$, which is the solution to Eq. (6.26) with $\epsilon = 0$. We substitute Eq. (6.27) into the Fokker-Planck equation (6.26), and obtain the equalities at each order of ϵ as

$$O(\epsilon^{-1}): \qquad 0 = \frac{\partial}{\partial x}\left(\frac{\partial V(x;\lambda(t))}{\partial x}\rho_0(x;t) + \frac{1}{\beta}\frac{\partial \rho_0(x;t)}{\partial x}\right), \tag{6.28}$$

$$O(\epsilon^0): \qquad \frac{\partial \rho_0(x;t)}{\partial t} = \frac{1}{\gamma}\frac{\partial}{\partial x}\left(\frac{\partial V(x;\lambda(t))}{\partial x}\rho_0(x;t)\phi_1(x;t) + \frac{1}{\beta}\frac{\partial(\rho_0(x;t)\phi_1(x;t))}{\partial x}\right), \tag{6.29}$$

$$O(\epsilon^1): \qquad \frac{\partial(\rho_0(x;t)\phi_1(x;t))}{\partial t} = \frac{1}{\gamma}\frac{\partial}{\partial x}\left(\frac{\partial V(x;\lambda(t))}{\partial x}\rho_0(x;t)\phi_2(x;t) + \frac{1}{\beta}\frac{\partial(\rho_0(x;t)\phi_2(x;t))}{\partial x}\right), \tag{6.30}$$

$$O(\epsilon^2): \qquad \frac{\partial(\rho_0(x;t)\phi_2(x;t))}{\partial t} = \frac{1}{\gamma}\frac{\partial}{\partial x}\left(\frac{\partial V(x;\lambda(t))}{\partial x}\rho_0(x;t)\phi_3(x;t) + \frac{1}{\beta}\frac{\partial(\rho_0(x;t)\phi_3(x;t))}{\partial x}\right), \tag{6.31}$$

$$\vdots$$

The $O(\epsilon^{-1})$ equation is satisfied since we expand $\rho_\epsilon(x;t)$ around the Gibbs distribution with respect to $\lambda(t)$. The $O(\epsilon^0)$ equation can be rewritten as

$$\frac{1}{\beta\gamma}\frac{\partial^2\phi_1(x;t)}{\partial x^2} - \frac{1}{\gamma}\frac{\partial V(x;\lambda(t))}{\partial x}\frac{\partial \phi_1(x;t)}{\partial x} = \beta\Delta X(x;\lambda(t))\dot{\lambda}(t), \tag{6.32}$$

where $X(x,\lambda) := -\partial V(x;\lambda)/\partial\lambda$ is a generalized force conjugate to the control parameter λ, and $\Delta X(x;\lambda) := X(x;\lambda) - \langle X(\cdot;\lambda)\rangle_\lambda^{\mathrm{eq}}$. The solution to Eq. (6.32) can be obtained by applying the Feynman-Kac formula (3.2) as

$$\phi_1(x;t) = -\beta\dot{\lambda}(t)\int_0^\infty \mathrm{d}s\,\langle\Delta X(x^{\lambda(t)}(s);\lambda(t))\rangle_{x,\lambda(t)} . \tag{6.33}$$

Here, the bracket $\langle\cdot\rangle_{x,\lambda}$ expresses the expectation value with respect to the random process

$$\frac{\mathrm{d}x^\lambda(s)}{\mathrm{d}s} = -\frac{1}{\gamma}\frac{\partial V(x;\lambda)}{\partial x}\Big|_{x=x^\lambda(s)} + \sqrt{\frac{2}{\beta\gamma}}\eta(s) \tag{6.34}$$

with the initial condition $x^\lambda(0) = x$. Next, the $O(\epsilon^1)$ equation can be rewritten as

$$\frac{1}{\beta\gamma}\frac{\partial^2 \phi_2(x;t)}{\partial x^2} - \frac{1}{\gamma}\frac{\partial V(x;\lambda(t))}{\partial x}\frac{\partial \phi_2(x;t)}{\partial x} = \beta \Delta X(x;\lambda(t))\dot{\lambda}(t)\phi_1(x;t) + \frac{\partial \phi_1(x;t)}{\partial t}\ , \tag{6.35}$$

whose solution can be obtained again from the Feynman-Kac formula (3.2) as

$$\phi_2(x;t) = -\int_0^\infty \mathrm{d}s \left\langle \beta\dot{\lambda}(t)\Delta X(x^{\lambda(t)}(s);\lambda(t))\phi_1(x^{\lambda(t)}(s);t) + \frac{\partial \phi_1(x;t)}{\partial t}\Big|_{x=x^{\lambda(t)}(s}\right\rangle_{x,\lambda(t)} . \tag{6.36}$$

By substituting the explicit form of $\phi_1(x;t)$ into Eq. (6.36), we obtain the $O(\epsilon^2)$ contribution for work as

$$\begin{aligned}
&\int_0^T \mathrm{d}t \int \mathrm{d}x\ (-X(x,\lambda(t)))\dot{\lambda}(t)\rho_0(x;t)\phi_2(x;t) \\
=& -\int_0^T \mathrm{d}t \Bigg\{ \dot{\lambda}(t)\ddot{\lambda}(t)\beta \int_0^\infty \mathrm{d}s\ s \left\langle \Delta X(x^{\lambda(t)}(0),\lambda(t))\Delta X(x^{\lambda(t)}(s),\lambda(t))\right\rangle_{\lambda(t)} \\
&\quad + \dot{\lambda}(t)^3\beta^2 \int_0^\infty \mathrm{d}s \int_0^\infty \mathrm{d}s' \left\langle X(x^{\lambda(t)}(0),\lambda(t))\Delta X(x^{\lambda(t)}(s),\lambda(t))\Delta X(x^{\lambda(t)}(s+s'),\lambda(t))\right\rangle_{\lambda(t)} \\
&\quad + \dot{\lambda}(t)^3\beta^2 \int_0^\infty \mathrm{d}s \int_0^\infty \mathrm{d}s' \left\langle X(x^{\lambda(t)}(0),\lambda(t))\frac{\partial}{\partial \lambda}\left\langle \Delta X(x^\lambda(s'),\lambda)\right\rangle_{x^{\lambda(t)}(s),\lambda}\Big|_{\lambda=\lambda(t)}\right\rangle_{\lambda(t)} \Bigg\} .
\end{aligned} \tag{6.37}$$

This is consistent with our expansion for the $O(\epsilon^2)$ contributions, because there are $\dot{\lambda}(t)^3$ terms and a $\dot{\lambda}(t)\ddot{\lambda}(t)$ term. We note that the coefficient of the $\dot{\lambda}(t)\ddot{\lambda}(t)$ term is the same as ours. By comparing $O(\epsilon^2)$ terms in Eq. (6.14) with the right-hand side of Eq. (6.37), we also find another expression for the $\zeta^{(2;00)}_{\mu\nu_1\nu_2}(\boldsymbol{\lambda})$ as

$$\begin{aligned}
&\zeta^{(2;00)}_{\mu\nu_1\nu_2}(\boldsymbol{\lambda}) \\
=& -\beta^2 \int_0^\infty \mathrm{d}\tau \int_0^\infty \mathrm{d}\tau' \Bigg\{ \left\langle X_\mu(x^{\lambda(t)}(0),\lambda(t))\Delta X_{\nu_1}(x^{\lambda(t)}(\tau),\lambda(t))\Delta X_{\nu_2}(x^{\lambda(t)}(\tau+\tau'),\lambda(t))\right\rangle_{\lambda(t)} \\
&\quad + \left\langle X_\mu(x^{\lambda(t)}(0),\lambda(t))\frac{\partial}{\partial \lambda^{\nu_1}}\left\langle \Delta X_{\nu_2}(x^\lambda(\tau'),\lambda)\right\rangle_{x^{\lambda(t)}(\tau),\lambda}\Big|_{\lambda=\lambda(t)}\right\rangle_{\lambda(t)} \Bigg\}
\end{aligned} \tag{6.38}$$

for an overdamped Langevin system. Furthermore, the higher-order ($O(\epsilon^{n-1})$) equation reads

$$\frac{1}{\beta}\frac{\partial^2 \phi_n(x;t)}{\partial x^2} - \frac{\partial V(x;\lambda(t))}{\partial x}\frac{\partial \phi_n(x;t)}{\partial x} = \beta \Delta X(x;\lambda(t))\dot{\lambda}(t)\phi_{n-1}(x;t) + \frac{\partial \phi_{n-1}(x;t)}{\partial t}. \tag{6.39}$$

Therefore, higher-order corrections can be iteratively obtained by applying the Feynman-Kac formula as

$$\phi_n(x;t) = -\int_0^\infty \mathrm{d}s \left\langle \beta\dot{\lambda}(t)\Delta X(x^{\lambda(t)}(s);\lambda(t))\phi_{n-1}(x^{\lambda(t)}(s);t) + \frac{\partial \phi_{n-1}(x;t)}{\partial t}\Big|_{x=x^{\lambda(t)}(s)}\right\rangle_{x,\lambda(t)} . \tag{6.40}$$

6.3 Next leading order terms

From Eq. (6.14), the excess work is, up to $O(\epsilon^2)$, given by

$$\begin{aligned}W_{\mathrm{ex}}(\mathbf{\Lambda}_\epsilon) =&\epsilon \int_0^T \mathrm{d}t\ \dot{\lambda}_\mu(t)\dot{\lambda}_{\nu_1}(t)\zeta^{(1;0)}_{\mu\nu_1}(\boldsymbol{\lambda}(t)) \\ &+ \epsilon^2 \left(\int_0^T \mathrm{d}t\ \dot{\lambda}_\mu(t)\ddot{\lambda}_{\nu_1}(t)\zeta^{(1;1)}_{\mu\nu_1}(\boldsymbol{\lambda}(t)) + \int_0^T \mathrm{d}t\ \dot{\lambda}_\mu(t)\dot{\lambda}_{\nu_1}(t)\dot{\lambda}_{\nu_2}(t)\zeta^{(2;00)}_{\mu\nu_1\nu_2}(\boldsymbol{\lambda}(t)) \right) + O(\epsilon^3).\end{aligned} \tag{6.41}$$

The $O(\epsilon)$ term is the thermodynamic metric term. The first term in the $O(\epsilon^2)$ contributions is attributed to the non-constant velocity of control parameters, while the second term corresponds to the nonlinear (second order) response to the external perturbation.

6.3.1 Physical Picture

To obtain a physical picture, let us consider a position x of an object in a fluid. When the velocity $\dot{x}$ is small, the fluid around the object forms the laminar flow, resulting in the friction force linear to the velocity as

$$m\ddot{x} = -k_1\dot{x} - V'(x). \tag{6.42}$$

When the velocity is large, the fluid around the object forms the turbulent flow, and the friction force is proportional to the square of the velocity:

$$m\ddot{x} = -k_2\dot{x}^2 - V'(x). \tag{6.43}$$

In our ϵ-expansion of the excess work, the generalized force acting on the system that contributes to the excess work is given by

$$-(\text{force}) = \epsilon\zeta^{(1;0)}\dot{\lambda} + \epsilon^2\zeta^{(2;00)}\dot{\lambda}^2 + \epsilon^2\zeta^{(1;1)}\ddot{\lambda} + O(\epsilon^3), \tag{6.44}$$

when the number of the control parameter is one. In analogy to the above case, by identifying $x \equiv \lambda$, the first, second, and third term can be interpreted as the laminar friction force, the turbulent friction force, and the inertial force, respectively.

6.3.2 Inertial Term

From the definition of the thermodynamic coefficients (6.10), the thermodynamic coefficients $\zeta^{(1;0)}_{\mu\nu}(\boldsymbol{\lambda})$ and $\zeta^{(1;1)}_{\mu\nu}(\boldsymbol{\lambda})$ for a Hamilton system are expressed as

$$\zeta^{(1;0)}_{\mu\nu}(\boldsymbol{\lambda}) = \beta \int_0^\infty \mathrm{d}s \left\langle \Delta\hat{X}_\mu(\boldsymbol{\lambda}), \Delta\hat{X}_\nu(\boldsymbol{\lambda})(s) \right\rangle^{\mathrm{can}}_{\boldsymbol{\lambda}}, \tag{6.45}$$

$$\zeta^{(1;1)}_{\mu\nu}(\boldsymbol{\lambda}) = \beta \int_0^\infty \mathrm{d}s\ s \left\langle \Delta\hat{X}_\mu(\boldsymbol{\lambda}), \Delta\hat{X}_\nu(\boldsymbol{\lambda})(s) \right\rangle^{\mathrm{can}}_{\boldsymbol{\lambda}}, \tag{6.46}$$

where $\langle \cdot, \cdot \rangle_{\boldsymbol{\lambda}}^{\mathrm{can}}$ is the canonical correlation at the equilibrium state corresponding to the control parameter $\boldsymbol{\lambda}$. If the correlation function decays exponentially with the relaxation timescale τ_{rel} as

$$\left\langle \Delta \hat{X}_{\mu}(\boldsymbol{\lambda}), \Delta \hat{X}_{\nu}(\boldsymbol{\lambda})(s) \right\rangle_{\boldsymbol{\lambda}}^{\mathrm{can}} = A \exp\left[-s/\tau_{\mathrm{rel}}\right], \tag{6.47}$$

the thermodynamic coefficients can be calculated as

$$\zeta_{\mu\nu}^{(1;0)}(\boldsymbol{\lambda}) = \beta A \tau_{\mathrm{rel}}, \tag{6.48}$$

$$\zeta_{\mu\nu}^{(1;1)}(\boldsymbol{\lambda}) = \beta A \tau_{\mathrm{rel}}^{2} = \tau_{\mathrm{rel}} \zeta_{\mu\nu}^{(1;0)}(\boldsymbol{\lambda}). \tag{6.49}$$

Therefore, the inertial term is negligible compared with the thermodynamic metric term if the relative change of the control parameter velocity is sufficiently small compared to the relaxation time scale of the system:

$$\frac{\|\ddot{\boldsymbol{\lambda}}(t)\|}{\|\dot{\boldsymbol{\lambda}}(t)\|} \ll \frac{\|\zeta_{\mu\nu}^{(1;0)}(\boldsymbol{\lambda}(t))\|}{\|\zeta_{\mu\nu}^{(1;1)}(\boldsymbol{\lambda}(t))\|} = \frac{1}{\tau_{\mathrm{rel}}}. \tag{6.50}$$

We note that this condition is different from the overdamped approximation, which assumes that the relaxation time scale of momentum is much faster than the time resolution of the observer. Since the leftmost-hand side in Eq. (6.50) scales proportionally to ϵ in the ϵ-modified protocol $\boldsymbol{\Lambda}_{\epsilon}$, this condition is always satisfied in the $\epsilon \to 0$ limit.

6.3.3 Turbulent Friction Term

The turbulent friction term originates from the second-order response to the external perturbations. It is negligible if the speed of the control is sufficiently small compared with the ratio of the laminar/turbulent friction coefficient:

$$\|\dot{\boldsymbol{\lambda}}(t)\| \ll \frac{\|\zeta_{\mu\nu}^{(1;0)}(\boldsymbol{\lambda}(t))\|}{\|\zeta_{\mu\nu_1\nu_2}^{(2;00)}(\boldsymbol{\lambda}(t))\|}. \tag{6.51}$$

Since the left-hand side scales proportionally to ϵ in the ϵ-modified protocol $\boldsymbol{\Lambda}_{\epsilon}$, while the right-hand side is independent of the protocol, this condition is always satisfied in the $\epsilon \to 0$ limit, as in the case of the inertial term.

6.3.4 Detecting $O(\epsilon^2)$ Terms by a Reverse Protocol

We have derived the next-leading-order correction terms to the thermodynamic metric term. They are by definition small compared with the thermodynamic metric term for small ϵ. Then how can we detect such a small correction terms? To answer this question, we consider a reverse protocol. For a given protocol $\boldsymbol{\Lambda} = \{\boldsymbol{\lambda}(t)\}_{t\in[0,T]}$, we define a reverse protocol $\boldsymbol{\Lambda}^{\dagger}$ by

$$\boldsymbol{\Lambda}^{\dagger} := \{\boldsymbol{\lambda}(T-t)\}_{t\in[0,T]}. \tag{6.52}$$

The $O(\epsilon)$ term, which is given by the thermodynamic metric, does not change the sign in

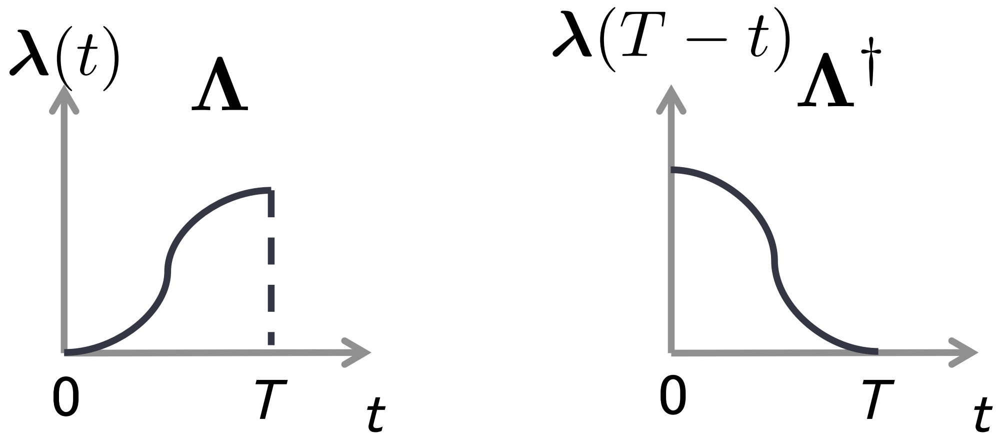

Figure 6.2: Schematic graphs of the forward (left) and backward (right) protocols.

this time-reversed protocol. However, the next leading order terms change the sign in the reverse protocol. More generally, $O(\epsilon^{2k})$ terms change the sign, whereas $O(\epsilon^{2k+1})$ terms do not. Therefore, the $O(\epsilon^2)$ terms become dominant in the difference in the excess work between the forward and reverse protocols as

$$\begin{aligned}\frac{W_{\mathrm{ex}}(\boldsymbol{\Lambda}_\epsilon) - W_{\mathrm{ex}}(\boldsymbol{\Lambda}_\epsilon^\dagger)}{2} =&\epsilon^2 \left(\int_0^T \mathrm{d}t\ \dot{\lambda}_\mu(t)\dot{\lambda}_{\nu_1}(t)\dot{\lambda}_{\nu_2}(t)\zeta^{(2;00)}_{\mu\nu_1\nu_2}(\boldsymbol{\lambda}(t)) + \int_0^T \mathrm{d}t\ \dot{\lambda}_\mu(t)\ddot{\lambda}_{\nu_1}(t)\zeta^{(1;1)}_{\mu\nu_1}(\boldsymbol{\lambda}(t)) \right) \\ &+ O(\epsilon^4), \end{aligned} \tag{6.53}$$

where $O(\epsilon^3)$ terms vanish and hence the next-leading term is $O(\epsilon^4)$. Since the difference is $O(\epsilon^2)$, it is expected to scale as $1/T^2$ as a function of the the total control time. In this sense, these next leading-order $O(\epsilon^2)$ terms characterize the time-reversal symmetry breaking of the excess work in thermodynamic controls.

Chapter 7

Expansion of the Work Distribution in Thermodynamic Control

In the previous chapter, we have calculated the average of excess work and obtained the series expansion in terms of the parameter ϵ that characterizes the slowness of the control. However, the work does not have a definite value even if we control the system through the same protocol, which is not negligible especially in small systems. In this chapter, we calculate the work distribution and derive the expansion in terms of the parameter ϵ. This chapter is based on the paper 3 in Publication List, which is in preparation.

7.1 Setting

To calculate the distribution of the work explicitly, we need to specify the dynamics of the system. Here, we consider a one-dimensional system described by the overdamped Langevin equation

$$\dot{x}(t) = -\frac{1}{\gamma}\frac{\partial V(x;\boldsymbol{\lambda}(t))}{\partial x}\Big|_{x=x(t)} + \sqrt{\frac{2}{\beta\gamma}}\eta(t). \tag{7.1}$$

We control the system by changing the external potential $V(x;\boldsymbol{\lambda})$ as a function of time through control parameters $\boldsymbol{\lambda} = \boldsymbol{\lambda}(t)$. We assume that the potential traps a particle in the sense that $\lim_{|x|\to\infty} V(x;\boldsymbol{\lambda}) = \infty$ for all $\boldsymbol{\lambda}$, and that the initial distribution is the canonical distribution $p_{\mathrm{can}}^{\boldsymbol{\lambda}(0)}(x)$. As in the previous chapter, for a given protocol $\boldsymbol{\Lambda} = \{\boldsymbol{\lambda}(t)\}_{t\in[0,T]}$, we consider an ϵ-modified protocol $\boldsymbol{\Lambda}_\epsilon = \{\boldsymbol{\lambda}_\epsilon(t)\}_{t\in[0,T/\epsilon]} = \{\boldsymbol{\lambda}(\epsilon t)\}_{t\in[0,T/\epsilon]}$. The work under the protocol $\boldsymbol{\Lambda}_\epsilon$ is defined for each trajectory $\{x(t)\}$ as

$$W(\{x(t)\},\boldsymbol{\Lambda}_\epsilon) = \int_0^{T/\epsilon} \mathrm{d}t\ \dot{\lambda}_\epsilon^\mu(t)\frac{\partial V(x(t);\boldsymbol{\lambda})}{\partial \lambda^\mu}\Big|_{\boldsymbol{\lambda}=\boldsymbol{\lambda}_\epsilon(t)}. \tag{7.2}$$

Let $P(\{x(t)\};\boldsymbol{\Lambda}_\epsilon)$ be a probability density function that the trajectory $\{x(t)\}$ is realized under the protocol $\boldsymbol{\Lambda}_\epsilon$. Note that the randomness arises from the initial canonical distribution $p_{\mathrm{can}}^{\boldsymbol{\lambda}(0)}(x)$

and the Gaussian white noise $\eta(t)$. We are interested in the work distribution

$$P(W;\mathbf{\Lambda}_\epsilon)=\int \mathcal{D}x\ P(\{x(t)\};\mathbf{\Lambda}_\epsilon)\delta(W-W(\{x(t)\},\mathbf{\Lambda}_\epsilon)), \tag{7.3}$$

or the cumulant-generating function of work

$$C_W(k;\mathbf{\Lambda}_\epsilon):=\log\int \mathrm{d}W\ \mathrm{e}^{kW}P(W;\mathbf{\Lambda}_\epsilon) \tag{7.4}$$

under the protocol $\mathbf{\Lambda}_\epsilon$. The cumulant-generating function is important in statistical physics because it contains the same information as the rate function through the Gärtner-Ellis theorem in the large-deviation theory [78]. To calculate the cumulant-generating function, we consider the time evolution of the following quantity:

$$G(x,k;t,\mathbf{\Lambda}_\epsilon)=\left\langle\delta(x-x(t))\mathrm{e}^{kW_t}\right\rangle. \tag{7.5}$$

Here, the average $\langle\cdot\rangle$ is taken over the initial canonical distribution and the Gaussian white noise, and W_t denotes the work performed on the system by time t. We also denote $G(x,k;t,\mathbf{\Lambda}_\epsilon)$ as $G(x,k;t)$ when the protocol dependence is clear from the context. Once $G(x,k;t)$ is obtained, we can calculate the cumulant generating function by

$$C_W(k;\mathbf{\Lambda}_\epsilon)=\log\int \mathrm{d}x\ G(x,k;T/\epsilon). \tag{7.6}$$

Previously, the time evolution of the joint probability distribution of x and W, which is defined by

$$P(x,W;\mathbf{\Lambda}_\epsilon)=\int \mathcal{D}x\ P(\{x(t)\};\mathbf{\Lambda}_\epsilon)\delta(x-x(t))\delta(W-W(\{x(t)\},\mathbf{\Lambda}_\epsilon)), \tag{7.7}$$

has been considered to prove that the distribution of the work is Gaussian when the control is slow [79]. As we will show later, to obtain systematically the information about the work distribution and to evaluate the deviation from the Gaussian distribution, it is convenient to consider the generating function $G(x,k;t,\mathbf{\Lambda}_\epsilon)$ rather than the joint distribution function.

To derive the time evolution of $G(x,k;t,\mathbf{\Lambda}_\epsilon)$, we apply stochastic calculus [80]. We rewrite the overdamped Langevin equation in the form of a stochastic differential equation as

$$\mathrm{d}x_t=-\frac{1}{\gamma}\frac{\partial V(x;\boldsymbol{\lambda}_\epsilon(t))}{\partial x}\bigg|_{x=x_t}\mathrm{d}t+\sqrt{\frac{2}{\beta\gamma}}\mathrm{d}w_t, \tag{7.8}$$

where w_t is the Wiener process, which is formally related to the white Gaussian noise as $\eta(t)=$

$\mathrm{d}w_t/\mathrm{d}t$. Then, the increment of $\delta(x-x_t)\mathrm{e}^{kW_t}$ is calculated as

$$\begin{aligned}
&\mathrm{d}(\delta(x-x_t)\mathrm{e}^{kW_t})\\
=&-\delta'(x-x_t)\mathrm{e}^{kW_t}\mathrm{d}x_t+\frac{1}{2}\delta''(x-x_t)\mathrm{e}^{kW_t}\mathrm{d}x_t^2+k\delta(x-x_t)\mathrm{e}^{kW_t}\mathrm{d}W_t+O(\mathrm{d}x_t^3,\mathrm{d}W_t^2)\\
=&-\frac{\partial}{\partial x}[\delta(x-x_t)\mathrm{e}^{kW_t}(-\frac{1}{\gamma}\frac{\partial V(x;\boldsymbol{\lambda}_\epsilon(t))}{\partial x}\mathrm{d}t+\sqrt{\frac{2}{\beta\gamma}}\mathrm{d}w_t)]\\
&+\frac{1}{\beta\gamma}\frac{\partial^2}{\partial x^2}[\delta(x-x_t)\mathrm{e}^{kW_t}\mathrm{d}t]+k\delta(x-x_t)\mathrm{e}^{kW_t}\dot{\lambda}^\mu_\epsilon(t)\frac{\partial V(x;\boldsymbol{\lambda})}{\partial\lambda^\mu}\Big|_{\boldsymbol{\lambda}=\boldsymbol{\lambda}_\epsilon(t)}\mathrm{d}t+o(\mathrm{d}t). \qquad (7.9)
\end{aligned}$$

By taking the average over the Wiener process, we obtain the time evolution equation for $G(x,k;t)$ as

$$\begin{aligned}
\frac{\partial G(x,k;t)}{\partial t}&=\frac{1}{\gamma}\frac{\partial}{\partial x}\left(G(x,k;t)\frac{\partial V(x;\boldsymbol{\lambda}_\epsilon(t))}{\partial x}\right)\\
&\quad+\frac{1}{\beta\gamma}\frac{\partial^2 G(x,k;t)}{\partial x^2}+k\dot{\lambda}^\mu_\epsilon(t)\frac{\partial V(x;\boldsymbol{\lambda})}{\partial\lambda^\mu}\Big|_{\boldsymbol{\lambda}=\boldsymbol{\lambda}_\epsilon(t)}G(x,k;t)\\
\Leftrightarrow\frac{\partial G(x,k;t)}{\partial t}&=\frac{1}{\gamma}\frac{\partial}{\partial x}\left(G(x,k;t)\frac{\partial V(x;\boldsymbol{\lambda}_\epsilon(t))}{\partial x}+\frac{1}{\beta}\frac{\partial G(x,k;t)}{\partial x}\right)-k\dot{\lambda}^\mu_\epsilon(t)X_\mu(x;\boldsymbol{\lambda}_\epsilon(t))G(x,k;t),
\end{aligned} \qquad (7.10)$$

where we have defined the generalized force with respect to the control parameter λ^μ as

$$X_\mu(x;\boldsymbol{\lambda}):=-\frac{\partial V(x;\boldsymbol{\lambda})}{\partial\lambda^\mu}. \qquad (7.11)$$

To express the ϵ-dependence of each term more explicitly, we replace t with t/ϵ in Eq. (7.10), and obtain

$$\begin{aligned}
&\frac{\partial G(x,k;t/\epsilon,\boldsymbol{\Lambda}_\epsilon)}{\partial t}=\frac{1}{\epsilon}\frac{\partial G(x,k;t/\epsilon,\boldsymbol{\Lambda}_\epsilon)}{\partial(t/\epsilon)}\\
=&\frac{1}{\epsilon\gamma}\frac{\partial}{\partial x}\left(G(x,k;t/\epsilon,\boldsymbol{\Lambda}_\epsilon)\frac{\partial V(x;\boldsymbol{\lambda}(t))}{\partial x}+\frac{1}{\beta}\frac{\partial G(x,k;t/\epsilon,\boldsymbol{\Lambda}_\epsilon)}{\partial x}\right)-k\dot{\lambda}^\mu(t)X_\mu(x;\boldsymbol{\lambda}(t))G(x,k;t/\epsilon,\boldsymbol{\Lambda}_\epsilon).
\end{aligned} \qquad (7.12)$$

On the other hand, in the approach adopted in Ref. [43], the protocol $\boldsymbol{\Lambda}$ is fixed, while the friction coefficient γ is modified as $\epsilon\gamma$. Let $G_\epsilon(x,k;t,\boldsymbol{\Lambda})$ be the joint function of the position distribution and the moment generating function of the work at time t under the protocol $\boldsymbol{\Lambda}$ and the overdamped Langevin dynamics whose friction coefficient is $\epsilon\gamma$. Then the time evolution of $G_\epsilon(x,k;t,\boldsymbol{\Lambda})$ is obtained by replacing $\boldsymbol{\lambda}_\epsilon(t)$ with $\boldsymbol{\lambda}(t)$ and γ with $\epsilon\gamma$ in Eq. (7.10), given by

$$\begin{aligned}
&\frac{\partial G_\epsilon(x,k;t,\boldsymbol{\Lambda})}{\partial t}\\
=&\frac{1}{\epsilon\gamma}\frac{\partial}{\partial x}\left(G_\epsilon(x,k;t,\boldsymbol{\Lambda})\frac{\partial V(x;\boldsymbol{\lambda}(t))}{\partial x}+\frac{1}{\beta}\frac{\partial G_\epsilon(x,k;t,\boldsymbol{\Lambda})}{\partial x}\right)-k\dot{\lambda}^\mu(t)X_\mu(x;\boldsymbol{\lambda}(t))G_\epsilon(x,k;t,\boldsymbol{\Lambda}).
\end{aligned} \qquad (7.13)$$

By comparing Eqs. (7.12) and (7.13) and noting that they have the same initial condition as

$$G_\epsilon(x,k;t=0,\mathbf{\Lambda}) = G(x,k;t=0,\mathbf{\Lambda}_\epsilon) = p_{\mathrm{eq}}^{\boldsymbol{\lambda}(0)}(x), \tag{7.14}$$

we obtain

$$G(x,k;t/\epsilon,\mathbf{\Lambda}_\epsilon) = G_\epsilon(x,k;t,\mathbf{\Lambda}). \tag{7.15}$$

Equation (7.15) shows that two ways of introducing a parameter ϵ are equivalent in the sense that they result not only in the same average work (as shown in the previous chapter) but also in the same work distribution.

In the following, we expand $G_\epsilon(x,k;t,\mathbf{\Lambda})(= G(x,k;t/\epsilon,\mathbf{\Lambda}_\epsilon))$ in terms of ϵ, and determine lower-order terms iteratively from the time evolution equation (7.13). For simplicity, we denote $G_\epsilon(x,k;t,\mathbf{\Lambda})$ by $G_\epsilon(x,k;t)$, and expand it as

$$G_\epsilon(x,k;t) = G_0(x,k;t)\{1+\epsilon G_1(x,k;t)+\epsilon^2 G_2(x,k;t)+\cdots\}. \tag{7.16}$$

Then, the time evolution equation (7.13) should be satisfied at each order of ϵ.

7.2 $O(\epsilon^0)$ Contribution to the Generating Function of Work

First, we derive the leading-order term for the generating function. From the $O(\epsilon^{-1})$ equation in Eq. (7.13), we obtain

$$\frac{\partial}{\partial x}\left(G_0(x,k;t)\frac{\partial V(x;\boldsymbol{\lambda}(t))}{\partial x} + \frac{1}{\beta}\frac{\partial G_0(x,k;t)}{\partial x}\right) = 0. \tag{7.17}$$

Since Eq. (7.17) is the differential equation with respect to x only, we can determine only the x-dependence of $G_0(x,k;t)$ as

$$G_0(x,k;t) = f_0(k;t)p_{\mathrm{can}}^{\boldsymbol{\lambda}(t)}(x). \tag{7.18}$$

To determine $f_0(k;t)$, i.e., the k-dependence of $G_0(x,k;t)$, we consider the $O(\epsilon^0)$ equation in Eq. (7.13), given by

$$\begin{aligned}\frac{\partial G_0(x,k;t)}{\partial t} =& \frac{\partial}{\partial x}\left(G_0(x,k;t)G_1(x,k;t)\frac{\partial V(x;\boldsymbol{\lambda}(t))}{\partial x} + \frac{1}{\beta}\frac{\partial (G_0(x,k;t)G_1(x,k;t))}{\partial x}\right) \\ & - k\dot{\lambda}^\mu(t)X_\mu(x;\boldsymbol{\lambda}(t))G_0(x,k;t).\end{aligned} \tag{7.19}$$

Since we assume that the potential is trapping, $G(x,k;t)$ is expected to vanish in the limit of $|x|\to\infty$. Therefore, by integrating Eq. (7.19), we obtain

$$\int_{-\infty}^{\infty} \mathrm{d}x \left(\frac{\partial G_0(x,k;t)}{\partial t} - k\dot{\lambda}^\mu(t) \frac{\partial V(x;\boldsymbol{\lambda})}{\partial \lambda^\mu}\Big|_{\lambda=\lambda(t)} G_0(x,k;t) \right) \tag{7.20}$$

$$= \left[G_0(x,k;t)G_1(x,k;t)\frac{\partial V(x;\boldsymbol{\lambda}(t))}{\partial x} + \frac{1}{\beta}\frac{\partial (G_0(x,k;t)G_1(x,k;t))}{\partial x} \right]_{x=-\infty}^{x=\infty} = 0. \tag{7.21}$$

In the following, we refer to an equation that originates from the boundary condition as the consistency condition. From this $O(\epsilon^0)$ consistency condition, we obtain

$$\begin{aligned} 0 &= \int_{-\infty}^{\infty} \mathrm{d}x \left(\frac{\partial f_0(k;t)}{\partial t} p_{\mathrm{eq}}^{\boldsymbol{\lambda}(t)}(x) + f_0(k;t)\frac{\partial p_{\mathrm{eq}}^{\boldsymbol{\lambda}(t)}(x)}{\partial t} + k\dot{\lambda}^\mu(t) X_\mu(x;\boldsymbol{\lambda}(t)) f_0(k;t) p_{\mathrm{eq}}^{\boldsymbol{\lambda}(t)}(x) \right) \\ &= \frac{\partial f_0(k;t)}{\partial t} + f_0(k;t) k\dot{\lambda}^\mu(t) \int_{-\infty}^{\infty} \mathrm{d}x\ X_\mu(x;\boldsymbol{\lambda}(t)) p_{\mathrm{eq}}^{\boldsymbol{\lambda}(t)}(x). \end{aligned} \tag{7.22}$$

Therefore, we obtain

$$\begin{aligned} \frac{\partial}{\partial t}\log f_0(k;t) &= -k\dot{\lambda}^\mu(t) \int_{-\infty}^{\infty} \mathrm{d}x\ X_\mu(x;\boldsymbol{\lambda}(t)) p_{\mathrm{eq}}^{\boldsymbol{\lambda}(t)}(x) \\ &= k\int_{-\infty}^{\infty} \mathrm{d}x\ \dot{\lambda}^\mu(t) \frac{\partial V(x;\boldsymbol{\lambda})}{\partial \lambda^\mu}\Big|_{\boldsymbol{\lambda}=\boldsymbol{\lambda}(t)} \mathrm{e}^{-\beta(V(x;\boldsymbol{\lambda}(t))-F(\boldsymbol{\lambda}(t)))} \\ &= k\int_{-\infty}^{\infty} \mathrm{d}x\ \mathrm{e}^{F(\boldsymbol{\lambda}(t))} \left(-\frac{1}{\beta}\right) \frac{\partial}{\partial t} \mathrm{e}^{-\beta V(x;\boldsymbol{\lambda}(t))} \\ &= -\frac{k}{\beta}\mathrm{e}^{F(\boldsymbol{\lambda}(t))}\frac{\partial}{\partial t}\int_{-\infty}^{\infty} \mathrm{d}x\ \mathrm{e}^{-\beta V(x;\boldsymbol{\lambda}(t))} \\ &= k\frac{\mathrm{d}F(\boldsymbol{\lambda}(t))}{\mathrm{d}t}, \end{aligned} \tag{7.23}$$

which implies that

$$f_0(k;t) = \tilde{f}_0(k)\exp\left[kF(\boldsymbol{\lambda}(t))\right], \tag{7.24}$$

where $\tilde{f}_0(k)$ is a constant independent of t. From the initial condition (7.14), we obtain $f_0(k;t=0)=1$ and $\tilde{f}_0(k)=\exp\left[-kF(\boldsymbol{\lambda}(0))\right]$, and therefore

$$G_0(x,k;t) = \mathrm{e}^{k(F(\boldsymbol{\lambda}(t))-F(\boldsymbol{\lambda}(0)))} p_{\mathrm{eq}}^{\boldsymbol{\lambda}(t)}(x) = \mathrm{e}^{k\Delta F} p_{\mathrm{eq}}^{\boldsymbol{\lambda}(t)}(x), \tag{7.25}$$

where we have defined the free-energy difference as $\Delta F := F(\boldsymbol{\lambda}(t)) - F(\boldsymbol{\lambda}(0))$. From Eq. (7.25), we see that the assumption that the initial distribution is given by the canonical distribution is needed for the expansion to be consistent. Therefore, we obtain the cumulant-generating function up to the $O(\epsilon^0)$ order as $C_W(k;\boldsymbol{\Lambda}_\epsilon) = k\Delta F + O(\epsilon)$, and

$$\langle W\rangle = \frac{\mathrm{d}\log\langle \mathrm{e}^{kW}\rangle}{\mathrm{d}t}\Big|_{k=0} = \Delta F + O(\epsilon), \tag{7.26}$$

$$\langle (\Delta W)^2\rangle = \frac{\mathrm{d}^2\log\langle \mathrm{e}^{kW}\rangle}{\mathrm{d}t^2}\Big|_{k=0} = 0 + O(\epsilon). \tag{7.27}$$

They reproduce the well-known fact that the work performed on the system is deterministically equal to the free-energy difference in the quasistatic process.

7.3 $O(\epsilon)$ Contribution to the Generating Function of Work

Using the explicit form of $G_0(x,k;t)$ derived in the previous section, let us rewrite the time evolution equation (7.13). We define $\tilde{G}(x,k;t)$ by the relation

$$G(x,k;t) = G_0(x,k;t)\tilde{G}(x,k;t) = \mathrm{e}^{k\Delta F} p_{\mathrm{eq}}^{\boldsymbol{\lambda}(t)}(x)\tilde{G}(x,k;t). \tag{7.28}$$

If we substitute it in Eq. (7.13), we obtain the time evolution equation for $\tilde{G}(x,k;t)$ as

$$\begin{aligned}\frac{\partial \tilde{G}(x,k;t)}{\partial t}\mathrm{e}^{-\beta V(x;\boldsymbol{\lambda}(t))} =& \frac{1}{\beta\epsilon\gamma}\frac{\partial}{\partial x}\left(\frac{\partial \tilde{G}(x,k;t)}{\partial x}\mathrm{e}^{-\beta V(x;\boldsymbol{\lambda}(t))}\right) \\ &- (\beta+k)\dot{\lambda}^\mu(t)\Delta X_\mu(x;\boldsymbol{\lambda}(t))\tilde{G}(x,k;t)\mathrm{e}^{-\beta V(x;\boldsymbol{\lambda}(t))},\end{aligned} \tag{7.29}$$

where $\Delta X_\mu(x;\lambda(t)) := X_\mu(x;\boldsymbol{\lambda}) - \langle X_\mu(\cdot,\boldsymbol{\lambda})\rangle_{\mathrm{eq}}^{\boldsymbol{\lambda}} = X_\mu(x_\mu;\boldsymbol{\lambda}) - \int_{-\infty}^{\infty}\mathrm{d}x\ p_{\mathrm{can}}^{\boldsymbol{\lambda}}(x)X_\mu(x;\boldsymbol{\lambda})$ is the deviation of the generalized force from the equilibrium value. Since $\tilde{G}(x,k;t) = 1+\epsilon G_1(x,k;t)+\epsilon^2 G_2(x,k;t)+\cdots$, we obtain the $O(\epsilon^0)$ equation in Eq. (7.29), given as

$$0 = \frac{1}{\beta}\frac{\partial}{\partial x}\left(\frac{\partial G_1(x,k;t)}{\partial x}\mathrm{e}^{-\beta V(x;\boldsymbol{\lambda}(t))}\right) - \gamma(\beta+k)\dot{\lambda}^\mu(t)\Delta X_\mu(x;\boldsymbol{\lambda}(t))\mathrm{e}^{-\beta V(x;\boldsymbol{\lambda}(t))}. \tag{7.30}$$

By integrating both sides with respect to x, we obtain

$$\begin{aligned}&\frac{\partial G_1(x,k;t)}{\partial x}\mathrm{e}^{-\beta V(x;\boldsymbol{\lambda}(t))} = \beta\gamma(\beta+k)\dot{\lambda}^\mu(t)\int_{-\infty}^{x}\mathrm{d}x'\Delta X_\mu(x';\boldsymbol{\lambda}(t))\mathrm{e}^{-\beta V(x';\boldsymbol{\lambda}(t))} + f_1(k;t) \\ \Leftrightarrow &\frac{\partial G_1(x,k;t)}{\partial x} = \beta\gamma(\beta+k)\dot{\lambda}^\mu(t)\int_{-\infty}^{x}\mathrm{d}x'\Delta X_\mu(x';\boldsymbol{\lambda}(t))\mathrm{e}^{-\beta(V(x';\boldsymbol{\lambda}(t))-V(x;\boldsymbol{\lambda}(t)))} + f_1(k;t)\mathrm{e}^{\beta V(x;\boldsymbol{\lambda}(t))},\end{aligned} \tag{7.31}$$

where $f_1(k;t)$ is a constant independent of x. By integrating both sides with respect to x again, we obtain

$$\begin{aligned}G_1(x,k;t) =& \beta\gamma(\beta+k)\dot{\lambda}^\mu(t)\int_{-\infty}^{x}\mathrm{d}x'\int_{-\infty}^{x'}\mathrm{d}x''\Delta X_\mu(x'';\boldsymbol{\lambda}(t))\mathrm{e}^{-\beta(V(x'';\boldsymbol{\lambda}(t))-V(x';\boldsymbol{\lambda}(t)))} \\ &+ f_1(k;t)\int_{-\infty}^{x}\mathrm{d}x'\mathrm{e}^{\beta V(x';\boldsymbol{\lambda}(t))} + g_1(k;t),\end{aligned} \tag{7.32}$$

where $g_1(k;t)$ is a constant. Since the second term on the right-hand side diverges due to the trapping condition $\lim_{|x|\to\infty} V(x;\boldsymbol{\lambda}) = \infty$, $f_1(k;t)$ should be zero, giving

$$G_1(x,k;t) = \beta\gamma(\beta+k)\dot{\lambda}^\mu(t)\int_{-\infty}^{x}\mathrm{d}x'\int_{-\infty}^{x'}\mathrm{d}x''\Delta X_\mu(x'';\boldsymbol{\lambda}(t))\mathrm{e}^{-\beta(V(x'';\boldsymbol{\lambda}(t))-V(x';\boldsymbol{\lambda}(t)))} + g_1(k;t). \tag{7.33}$$

To determine the k-dependence of $g_1(k;t)$, we consider the $O(\epsilon)$ consistency condition in Eq. (7.29)

$$\int_{-\infty}^{\infty} \mathrm{d}x\ \mathrm{e}^{-\beta V(x;\boldsymbol{\lambda}(t))} \frac{\partial G_1(x,k;t)}{\partial t} + (\beta+k)\dot{\lambda}^\mu(t) \int_{-\infty}^{\infty} \mathrm{d}x\ \mathrm{e}^{-\beta V(x;\boldsymbol{\lambda}(t))} G_1(x,k;t) \Delta X_\mu(x;\boldsymbol{\lambda}(t)) = 0. \tag{7.34}$$

If we substitute Eq. (7.33) in Eq. (7.34), we obtain

$$\begin{aligned}
&\frac{\partial g_1(k;t)}{\partial t} \\
=& -\beta\gamma(\beta+k)\ddot{\lambda}^\mu(t) \int \mathrm{d}^3x\ \Delta X_\mu(x'';\boldsymbol{\lambda}(t)) \frac{\mathrm{e}^{-\beta(V(x;\boldsymbol{\lambda}(t)) - V(x';\boldsymbol{\lambda}(t)) + V(x'';\boldsymbol{\lambda}(t)))}}{Z[\boldsymbol{\lambda}(t)]} \\
&- \beta\gamma(\beta+k)\dot{\lambda}^\mu(t)\dot{\lambda}^\nu(t) \int \mathrm{d}^3x\ \frac{\mathrm{e}^{-\beta V(x;\boldsymbol{\lambda}(t))}}{Z[\boldsymbol{\lambda}(t)]} \frac{\partial}{\partial \lambda^\mu} \left(\Delta X_\nu(x'';\boldsymbol{\lambda}) \mathrm{e}^{-\beta(V(x'';\boldsymbol{\lambda}) - V(x';\boldsymbol{\lambda}))} \right) \Bigg|_{\boldsymbol{\lambda}=\boldsymbol{\lambda}(t)} \\
&- \beta\gamma(\beta+k)^2 \dot{\lambda}^\mu(t)\dot{\lambda}^\nu(t) \int \mathrm{d}^3x\ \Delta X_\mu(x;\boldsymbol{\lambda}(t)) \Delta X_\nu(x'';\boldsymbol{\lambda}(t)) \frac{\mathrm{e}^{-\beta(V(x;\boldsymbol{\lambda}(t)) - V(x';\boldsymbol{\lambda}(t)) + V(x'';\boldsymbol{\lambda}(t)))}}{Z[\boldsymbol{\lambda}(t)]},
\end{aligned} \tag{7.35}$$

where we have introduced a simplified notation

$$\int \mathrm{d}^3x\ \cdot := \int_{-\infty}^{\infty} \mathrm{d}x \int_{-\infty}^{x} \mathrm{d}x' \int_{-\infty}^{x'} \mathrm{d}x''\ \ \cdot\, . \tag{7.36}$$

By substituting $t = 0$ and $x = -\infty$ in Eq. (7.33), we obtain $g_1(k;t=0) = 0$. Therefore, by integrating both sides of Eq. (7.35), we obtain

$$\begin{aligned}
&g_1(k;t) \\
=& -\beta\gamma(\beta+k) \int_0^t \mathrm{d}t' \ddot{\lambda}^\mu(t') \int \mathrm{d}^3x\ \Delta X_\mu(x'';\boldsymbol{\lambda}(t')) \frac{\mathrm{e}^{-\beta(V(x;\boldsymbol{\lambda}(t')) - V(x';\boldsymbol{\lambda}(t')) + V(x'';\boldsymbol{\lambda}(t')))}}{Z[\boldsymbol{\lambda}(t')]} \\
&- \beta\gamma(\beta+k) \int_0^t \mathrm{d}t' \dot{\lambda}^\mu(t')\dot{\lambda}^\nu(t') \int \mathrm{d}^3x\ \frac{\mathrm{e}^{-\beta V(x;\boldsymbol{\lambda}(t'))}}{Z[\boldsymbol{\lambda}(t')]} \frac{\partial}{\partial \lambda^\mu} \left(\Delta X_\nu(x'';\boldsymbol{\lambda}) \mathrm{e}^{-\beta(V(x'';\boldsymbol{\lambda}) - V(x';\boldsymbol{\lambda}))} \right) \Bigg|_{\lambda=\lambda(t')} \\
&- \beta\gamma(\beta+k)^2 \int_0^t \mathrm{d}t' \dot{\lambda}^\mu(t')\dot{\lambda}^\nu(t') \int \mathrm{d}^3x\ \Delta X_\mu(x;\boldsymbol{\lambda}(t')) \Delta X_\nu(x'';\boldsymbol{\lambda}(t')) \\
&\qquad\qquad \times \frac{\mathrm{e}^{-\beta(V(x;\boldsymbol{\lambda}(t')) - V(x';\boldsymbol{\lambda}(t')) + V(x'';\boldsymbol{\lambda}(t')))}}{Z[\boldsymbol{\lambda}(t')]}.
\end{aligned} \tag{7.37}$$

Furthermore, if we assume that the initial velocity of the control parameter is zero, i.e., $\dot{\boldsymbol{\lambda}}(0) = 0$, we can integrate the first term by parts, and obtain

$$
\begin{aligned}
&g_1(k;t) \\
=& -\beta\gamma(\beta+k)\dot{\lambda}^\mu(t)\int \mathrm{d}^3x\ \Delta X_\mu(x'';\boldsymbol{\lambda}(t))\frac{\mathrm{e}^{-\beta(V(x;\boldsymbol{\lambda}(t))-V(x';\boldsymbol{\lambda}(t))+V(x'';\boldsymbol{\lambda}(t)))}}{Z[\boldsymbol{\lambda}(t)]} \\
&-\beta\gamma k(\beta+k)\int_0^t \mathrm{d}t'\dot{\lambda}^\mu(t')\dot{\lambda}^\nu(t')\int \mathrm{d}^3x\ \Delta X_\mu(x;\boldsymbol{\lambda}(t'))\Delta X_\nu(x'';\boldsymbol{\lambda}(t')) \\
&\qquad\qquad\qquad\qquad\qquad\qquad\times\frac{\mathrm{e}^{-\beta(V(x;\boldsymbol{\lambda}(t'))-V(x';\boldsymbol{\lambda}(t'))+V(x'';\boldsymbol{\lambda}(t')))}}{Z[\boldsymbol{\lambda}(t')]},
\end{aligned}
\tag{7.38}
$$

and hence

$$
\begin{aligned}
&G_1(x,k;t) \\
=&\beta\gamma(\beta+k)\dot{\lambda}^\mu(t)\int_{-\infty}^{x}\mathrm{d}x'\int_{-\infty}^{x'}\mathrm{d}x''\Delta X_\mu(x'';\boldsymbol{\lambda}(t))\mathrm{e}^{-\beta(V(x'';\boldsymbol{\lambda}(t))-V(x';\boldsymbol{\lambda}(t)))} \\
&-\beta\gamma(\beta+k)\dot{\lambda}^\mu(t)\int \mathrm{d}^3x\ \Delta X_\mu(x'';\boldsymbol{\lambda}(t))\frac{\mathrm{e}^{-\beta(V(x;\boldsymbol{\lambda}(t))-V(x';\boldsymbol{\lambda}(t))+V(x'';\boldsymbol{\lambda}(t)))}}{Z[\boldsymbol{\lambda}(t)]} \\
&-\beta\gamma k(\beta+k)\int_0^t \mathrm{d}t'\dot{\lambda}^\mu(t')\dot{\lambda}^\nu(t')\int \mathrm{d}^3x\ \Delta X_\mu(x;\boldsymbol{\lambda}(t'))\Delta X_\nu(x'';\boldsymbol{\lambda}(t')) \\
&\qquad\qquad\qquad\qquad\qquad\qquad\times\frac{\mathrm{e}^{-\beta(V(x;\boldsymbol{\lambda}(t'))-V(x';\boldsymbol{\lambda}(t'))+V(x'';\boldsymbol{\lambda}(t')))}}{Z[\boldsymbol{\lambda}(t')]}.
\end{aligned}
\tag{7.39}
$$

We note that the assumption that $\dot{\boldsymbol{\lambda}}(0) = 0$ is indeed needed for the expansion to be consistent, since we have assumed that the initial condition is given by the canonical distribution and therefore $G_1(x,k;t=0) = 0$. From Eqs. (7.6), (7.16) and (7.39), we obtain the cumulant-generating function up to the $O(\epsilon^0)$ order as

$$
C_W(k;\boldsymbol{\Lambda}_\epsilon) = k\Delta F + \epsilon\frac{k(\beta+k)}{\beta}\int_0^T \mathrm{d}t\ \dot{\lambda}^\mu(t)\dot{\lambda}^\nu(t)\zeta^{(1;0)}_{\mu\nu}(\boldsymbol{\lambda}(t)) + O(\epsilon^2),
\tag{7.40}
$$

where we have defined the thermodynamic metric $\zeta^{(1;0)}_{\mu\nu}(\boldsymbol{\lambda})$ as

$$
\zeta^{(1;0)}_{\mu\nu}(\boldsymbol{\lambda}) = -\beta^2\gamma\int \mathrm{d}^3x\ \Delta X_\mu(x;\boldsymbol{\lambda})\Delta X_\nu(x'';\boldsymbol{\lambda})\frac{\mathrm{e}^{-\beta(V(x;\boldsymbol{\lambda})-V(x';\boldsymbol{\lambda})+V(x'';\boldsymbol{\lambda}))}}{Z[\boldsymbol{\lambda}]}.
\tag{7.41}
$$

Here, the iterated integral $\int \mathrm{d}^3x$ is defined as $\int_{-\infty}^{\infty}\mathrm{d}x\int_{-\infty}^{x}\mathrm{d}x'\int_{-\infty}^{x'}\mathrm{d}x''$. We remark that the second integral $\int_{-\infty}^{x}\mathrm{d}x'$ does not converge in general, due to the exponentially large factor $\mathrm{e}^{\beta V(x';\boldsymbol{\lambda})}$. To avoid the divergence, we exchange the order of integrals as

$$
\int_{-\infty}^{\infty}\mathrm{d}x\int_{-\infty}^{x}\mathrm{d}x'\int_{-\infty}^{x'}\mathrm{d}x'' \to \int_{-\infty}^{\infty}\mathrm{d}x'\int_{x'}^{\infty}\mathrm{d}x\int_{-\infty}^{x'}\mathrm{d}x''.
\tag{7.42}
$$

Then, the thermodynamic metric $\zeta^{(1;0)}_{\mu\nu}(\boldsymbol{\lambda})$ is redefined as

$$
\begin{aligned}
&\zeta^{(1;0)}_{\mu\nu}(\boldsymbol{\lambda}) \\
=&-\beta^2\gamma\int_{-\infty}^{\infty}\mathrm{d}x'\frac{\mathrm{e}^{\beta V(x';\boldsymbol{\lambda})}}{Z[\boldsymbol{\lambda}]}\left(\int_{x'}^{\infty}\mathrm{d}x\ \mathrm{e}^{-\beta V(x;\boldsymbol{\lambda})}\Delta X_\mu(x;\boldsymbol{\lambda})\right)\left(\int_{-\infty}^{x'}\mathrm{d}x''\mathrm{e}^{-\beta V(x'';\boldsymbol{\lambda})}\Delta X_\mu(x'';\boldsymbol{\lambda})\right) \\
=&\beta^2\gamma\int_{-\infty}^{\infty}\mathrm{d}x'\frac{\mathrm{e}^{\beta V(x';\boldsymbol{\lambda})}}{Z(\boldsymbol{\lambda})}\left(\int_{x'}^{\infty}\mathrm{d}x\ \mathrm{e}^{-\beta V(x;\boldsymbol{\lambda})}\Delta X_\mu(x;\boldsymbol{\lambda})\right)\left(\int_{x'}^{\infty}\mathrm{d}x''\mathrm{e}^{-\beta V(x'';\boldsymbol{\lambda})}\Delta X_\nu(x'';\boldsymbol{\lambda})\right).
\end{aligned}
\tag{7.43}
$$

We cannot mathematically justify this exchange of the order of integrals since the multiple integral does not converge absolutely and hence the Fubini-Tonelli theorem [51] is not applicable to it. However, we can verify that the redefined thermodynamic metric (7.43) coincides with the original definition of the thermodynamic metric in terms of the temporal correlations for the harmonic potential case. When the external potential is given by

$$V(x;\boldsymbol{\lambda})=\frac{\lambda^1}{2}(x-\lambda^2)^2, \tag{7.44}$$

the thermodynamic metric is calculated from Eq. (7.43) as

$$\zeta^{(1;0)}_{\mu\nu}(\boldsymbol{\lambda})=\begin{pmatrix}\frac{\gamma}{4\beta(\lambda^1)^2} & 0\\ 0 & \gamma\end{pmatrix}, \tag{7.45}$$

which agrees with the previous study [33].

We note that the cumulant-generating function is the second-order polynomial in k up to $O(\epsilon)$. This fact indicates that the work distribution is Gaussian, which is consistent with the previous study [79]. Furthermore, the fluctuation-dissipation relation holds up to $O(\epsilon)$, that is,

$$\langle W-\Delta F\rangle=\frac{\beta}{2}\left\langle(\Delta W)^2\right\rangle+O(\epsilon^2). \tag{7.46}$$

The Jarzynski equality is also satisfied up to $O(\epsilon)$ because

$$\left\langle \mathrm{e}^{-\beta(W-\Delta F)}\right\rangle=1\Leftrightarrow C_W(k=-\beta;\boldsymbol{\Lambda}_\epsilon)=0. \tag{7.47}$$

In fact, the fluctuation-dissipation relation is closely related to the Gaussian distribution of the work and the Jarzynski equality. Let c_n be the nth order cumulant of the work. The cumulants are related to the cumulant-generating function $C_W(k)=\log\int\mathrm{d}W\ P(W)\mathrm{e}^{kW}$ through

$$C_W(k)=\sum_{n=1}^{\infty}c_n\frac{k^n}{n!}. \tag{7.48}$$

If we rewrite the Jarzynski equality in terms of the cumulants, we obtain

$$\langle W\rangle-\Delta F-\frac{\beta}{2}\left\langle(\Delta W)^2\right\rangle=\sum_{n=3}^{\infty}c_n\frac{(-\beta)^n}{n!}. \tag{7.49}$$

Since the work distribution is Gaussian, the higher-order cumulant c_n vanishes for $n \geq 3$, which corresponds to the fact that the cumulant generating function is the second-order polynomial in k. Therefore, the right-hand side in Eq. (7.49) vanishes and the fluctuation-dissipation relation holds. In other words, the violation of the fluctuation-dissipation relation can be detected by the deviation of the work distribution from Gaussian, or the existence of higher-order cumulants, as we will investigate in the next section.

To summarize, the calculation of the cumulant generating function up to $O(\epsilon)$ reproduces the two fundamental facts, namely, the average excess work is expressed in terms of the thermodynamic metric [33, 43] and the work distribution is Gaussian [79].

7.4 $O(\epsilon^2)$ Contribution to the Generating Function of Work

In the previous section, we have seen that two well-known results are reproduced by calculating the cumulant-generating function up to $O(\epsilon)$. To understand how the distribution deviates from Gaussian and how the fluctuation-dissipation relation is violated, we calculate the next leading-order $O(\epsilon^2)$ contribution to the cumulant-generating function.

We can calculate the $O(\epsilon^2)$ contribution to the cumulant-generating function in the same way as the calculation of the $O(\epsilon)$ contribution, and obtain

$$
\begin{aligned}
&C_W(k;\boldsymbol{\Lambda}_\epsilon) = \log\langle \mathrm{e}^{kW}\rangle \\
=&k\Delta F \\
&+\epsilon\cdot\frac{k(\beta+k)}{\beta}\int_0^T \mathrm{d}t\ \dot{\lambda}^\mu(t)\dot{\lambda}^\nu(t)\zeta^{(1;0)}_{\mu\nu}(\boldsymbol{\lambda}(t)) \\
&+\epsilon^2\Bigg[-(\beta\gamma)^2k(\beta+k)\int_0^T \mathrm{d}t\ \dot{\lambda}^\mu(t)\ddot{\lambda}^\nu(t)\left(\int \mathrm{d}^5x\ \Delta X_\mu(x)\Delta X_\nu(x'''')\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x'')-V(x''')+V(x''''))}}{Z}\right) \\
&\qquad -(\beta\gamma)^2k(\beta+k)\int_0^T \mathrm{d}t\ \dot{\lambda}^\mu(t)\dot{\lambda}^\nu(t)\dot{\lambda}^\rho(t) \\
&\qquad\qquad\times\left(\int \mathrm{d}^5x\ \Delta X_\mu(x)\frac{\partial}{\partial\lambda^\nu}\left(\Delta X_\rho(x'''')\mathrm{e}^{-\beta(V(x'''')-V(x'''))}\right)\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z}\right) \\
&\qquad +(\beta\gamma)^2k(\beta+k)\int_0^T \mathrm{d}t\ \dot{\lambda}^\mu(t)\ddot{\lambda}^\nu(t)\left(\int \mathrm{d}^3x\ \Delta X_\mu(x)\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z}\right) \\
&\qquad\qquad\times\left(\int \mathrm{d}^3x\ \Delta X_\nu(x'')\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z}\right) \\
&\qquad +(\beta\gamma)^2k(\beta+k)\int_0^T \mathrm{d}t\ \dot{\lambda}^\mu(t)\dot{\lambda}^\nu(t)\dot{\lambda}^\rho(t)\left(\int \mathrm{d}^3x\ \Delta X_\mu(x)\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z}\right) \\
&\qquad\qquad\times\left(\int \mathrm{d}^3x\ \frac{\partial}{\partial\lambda^\nu}\left(\Delta X_\rho(x'')\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z}\right)\right) \\
&\qquad +(\beta\gamma)^2k^2(\beta+k)\int_0^T \mathrm{d}t\ \dot{\lambda}^\mu(t)\dot{\lambda}^\nu(t)\dot{\lambda}^\rho(t)\left(\int \mathrm{d}^3x\ \Delta X_\mu(x)\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z}\right) \\
&\qquad\qquad\times\left(\int \mathrm{d}^3x\ \Delta X_\nu(x)\Delta X_\rho(x'')\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z}\right) \\
&\qquad -(\beta\gamma)^2k(\beta+k)^2\int_0^T \mathrm{d}t\ \dot{\lambda}^\mu(t)\dot{\lambda}^\nu(t)\dot{\lambda}^\rho(t) \\
&\qquad\qquad\times\left(\int \mathrm{d}^5x\ \Delta X_\mu(x)\Delta X_\nu(x'')\Delta X_\rho(x'''')\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x'')-V(x''')+V(x''''))}}{Z}\right) \\
&\qquad +(\beta\gamma)^2k(\beta+k)^2\int_0^T \mathrm{d}t\ \dot{\lambda}^\mu(t)\dot{\lambda}^\nu(t)\dot{\lambda}^\rho(t)\left(\int \mathrm{d}^3x\ \Delta X_\mu(x'')\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z}\right) \\
&\qquad\qquad\times\left(\int \mathrm{d}^3x\ \Delta X_\nu(x)\Delta X_\rho(x'')\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z}\right)\Bigg] \\
&+O(\epsilon^3).
\end{aligned}
\tag{7.50}
$$

The detail of the calculation is described in Appendix B. Here, the multiple integrals are interpreted as

$$\int \mathrm{d}^3x \cdot := \int_{-\infty}^{\infty} \mathrm{d}x' \int_{x'}^{\infty} \mathrm{d}x \int_{-\infty}^{x'} \mathrm{d}x'' \cdot \tag{7.51}$$

$$\int \mathrm{d}^5x \cdot := \int_{-\infty}^{\infty} \mathrm{d}x' \int_{-\infty}^{x'} \mathrm{d}x''' \int_{x'}^{\infty} \mathrm{d}x \int_{x'''}^{x'} \mathrm{d}x'' \int_{-\infty}^{x'''} \mathrm{d}x'''' \cdot, \tag{7.52}$$

and the abbreviated control parameters in the generalized force $\Delta X_\mu(x)$, the external force $V(x)$, and the partition function Z should be identified with $\boldsymbol{\lambda}(t)$. This result is consistent with the $O(\epsilon^2)$ contribution to the average excess work derived in the previous chapter, since both of them are composed of two types of integrals $\int_0^T \mathrm{d}t\ \dot{\lambda}^\mu(t)\dot{\lambda}^\nu(t)\dot{\lambda}^\rho(t) \cdot$ and $\int_0^T \mathrm{d}t\ \dot{\lambda}^\mu(t)\ddot{\lambda}^\nu(t) \cdot$.

We note that Eq. (7.50) is invariant under the coordinate transformation. Since $\dot{\lambda}^\mu$ and ΔX_μ are contravariant and covariant, respectively, the contracted quantity is a scalar, which is invariant. The terms which are not apparently scalar are

$$\begin{aligned}
&\int_0^T \mathrm{d}t\ \dot{\lambda}^\mu(t) \left(\int \mathrm{d}^3x\ \Delta X_\mu(x) \frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z} \right) \\
&\qquad\qquad \times \int \mathrm{d}^3x\ \frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z} \left(\ddot{\lambda}^\nu(t)\Delta X_\nu(x'') + \dot{\lambda}^\nu(t)\dot{\lambda}^\rho(t)\frac{\partial \Delta X_\nu(x'')}{\partial \lambda^\rho} \right) \\
&- \int_0^T \mathrm{d}t\dot{\lambda}^\mu(t) \int \mathrm{d}^5x\ \Delta X_\mu(x) \frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x'')-V(x''')+V(x''''))}}{Z} \\
&\qquad\qquad \times \left(\ddot{\lambda}^\nu(t)\Delta X_\nu(x'') + \dot{\lambda}^\nu(t)\dot{\lambda}^\rho(t)\frac{\partial \Delta X_\nu(x'')}{\partial \lambda^\rho} \right).
\end{aligned} \tag{7.53}$$

Therefore, we need to show that the factor

$$\ddot{\lambda}^\nu(t)\Delta X_\nu(x'') + \dot{\lambda}^\nu(t)\dot{\lambda}^\rho(t)\frac{\partial \Delta X_\nu(x'')}{\partial \lambda^\rho} \tag{7.54}$$

is invariant. Indeed, it can be rewritten as

$$\ddot{\lambda}^\nu(t)\Delta X_\nu(x'') + \dot{\lambda}^\nu(t)\dot{\lambda}^\rho(t)\frac{\partial \Delta X_\nu(x'')}{\partial \lambda^\rho} = \frac{\mathrm{d}}{\mathrm{d}t}\left(\dot{\lambda}^\nu(t)\Delta X_\nu(x'') \right), \tag{7.55}$$

which is the time derivative of a scalar. Therefore, though each term that composess the cumulant generating function is not necessarily a scalar, the cumulant generating function as a whole is a scalar. Furthermore, the expression of the cumulant generating function is local in time in the sense that each term is written in terms of the time integral and the integrand is a function of $\boldsymbol{\lambda}(t), \dot{\boldsymbol{\lambda}}(t)$, and $\ddot{\boldsymbol{\lambda}}(t)$. In this sense, we have derived the geometric expression of the work distribution on the control parameter space.

We also note that the cumulant-generating function (7.50) up to the $O(\epsilon^2)$ order is the third polynomial in k and satisfies the Jarzynski equality. From Eq. (7.48), the former fact indicates that the work distribution deviates from the Gaussian distribution in such a way that the third cumulant c_3 becomes nonzero, while higher-order cumulants $c_n (n \geq 4)$ are zero up to the $O(\epsilon^2)$

order:

$$c_3 = O(\epsilon^2), \tag{7.56}$$

$$c_n = o(\epsilon^2) \qquad (n \geq 4). \tag{7.57}$$

Strictly speaking, any cumulant-generating function cannot be a polynomial of degree greater than two [81, 31], and therefore all the higher-order cumulants should have nonzero values if the third cumulant has a nonzero value.

Based on these facts, we can discuss how the fluctuation-dissipation relation is violated in finite-time control. From the Jarzynski equality (7.49) and Eqs. (7.56) and (7.57), the violation of the fluctuation-dissipation relation can be quantifies as

$$\langle W\rangle - \Delta F - \frac{\beta}{2}\left\langle(\Delta W)^2\right\rangle = \sum_{n=3}^{\infty} c_n \frac{(-\beta)^n}{n!} = -\frac{\beta^2}{6}c_3 + o(\epsilon^2). \tag{7.58}$$

Equation (7.58) implies that the violation of the fluctuation-dissipation relation scales as ϵ^2, or $1/T^2$ as a function of the total control time.

7.5 Numerical Experiment

To demonstrate the results obtained in this chapter, we perform a numerical experiment. We consider a cusped trapping potential given by

$$V(x;\lambda) = x^2 + \lambda|x|. \tag{7.59}$$

We control the sharpness at the origin through the absolute function $\lambda|x|$ from $\lambda(0) = 0$ to $\lambda(T) = 2$ smoothly, given as

$$\lambda(t) = \begin{cases} \left(\frac{t}{T/2}\right)^3 & (0 \leq t \leq T/2), \\ 2 - \left(\frac{T-t}{T/2}\right)^3 & (T/2 \leq t \leq T). \end{cases} \tag{7.60}$$

We simulate the overdamped Langevin equation with the time-dependent external potental

$$\dot{x}(t) = -\frac{1}{\gamma}\frac{\partial V(x;\lambda(t))}{\partial x}\Big|_{x=x(t)} + \sqrt{\frac{2}{\beta\gamma}}\eta(t), \tag{7.61}$$

with physical constants $\gamma = \beta = 1$, the discretized time-step length $\Delta t = 10^{-4}$, and the initial condition $p_{\mathrm{can}}^{\lambda=0}$. We repeat the simulation 5×10^6 times and calculate the empirical cumulants of the excess work $W_{\mathrm{ex}} = W - \Delta F$ for each total control time $T = 0.25, 0.5, \ldots, 64, 128$. The free energies can be analytically calculated as

$$F(\lambda = 0) = -\frac{1}{2}\log\pi \simeq -0.5723649429, \tag{7.62}$$

$$F(\lambda = 2) = -\log\left(\mathrm{e}\sqrt{\pi}\cdot\mathrm{erfc}(1)\right) \simeq 0.2772405670, \tag{7.63}$$

where the complementary error function is defined as

$$\mathrm{erfc}(x) := \frac{2}{\sqrt{\pi}} \int_x^{\infty} \mathrm{d}t\ \mathrm{e}^{-t^2}. \tag{7.64}$$

The T-dependences of the first, second, and third cumulants are shown in Fig. 7.1. The first, and second cumulants scale as $1/T$ for large T, corresponding to the fact that the cumulant-generating function is a second-order polynomial in k up to $O(\epsilon)$. The third cumulant scales as $1/T^2$ for large T, corresponding to the fact that the the cumulant-generating function is the third polynomial in k up to $O(\epsilon^2)$.

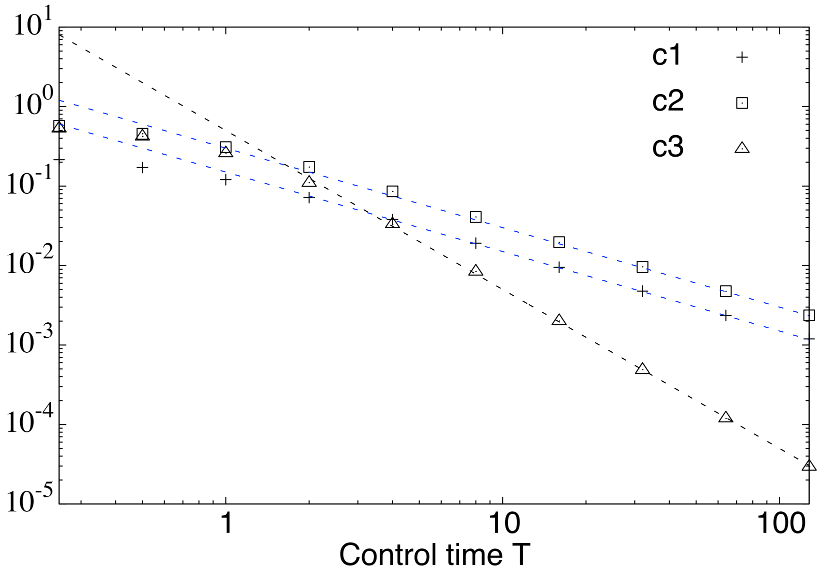

Figure 7.1: The first (cross), second (square), and third (triangle) cumulants of the excess work plotted against the entire control time T. The blue and black dashed lines are the guides to the eye corresponding to the scaling $1/T$ and $1/T^2$, respectively.

We also calculate the degree of violation of the fluctuation-dissipation relation, quantified by

$$-\frac{6}{\beta^2}\left(\langle W\rangle - \Delta F - \frac{\beta}{2}\langle(\Delta W)^2\rangle\right), \tag{7.65}$$

which is shown in Fig. 7.2. It scales as $1/T^2$ for large T and coincides with the third cumulant within the margin of statistical error, which verifies Eq. (7.58).

We further calculate the fourth and fifth cumulants as shown in Fig. 7.3. The fourth cumulant scales as $1/T^3$ for large T, while the fifth cumulant scales as $1/T^4$. Therefore, the coefficient of k^4 in the cumulant-generating function is of the order of ϵ^3, while that of k^5 is of the order of ϵ^4. Equivalently, the $O(\epsilon^3)$ contribution to the cumulant-generating function is a fourth-order polynomial in k, and the $O(\epsilon^4)$ contribution is at least a fifth-order polynomial in k.

So far, we have analytically shown that the $O(\epsilon^n)$ contribution to the cumulant-generating function $C_W(k;\mathbf{\Lambda}_\epsilon)$ is an $(n+1)$th-order polynomial in k for $n = 0, 1, 2$. Also, the numerical simulation suggests that the $O(\epsilon^3)$ contribution to the cumulant-generating function is a fourth-

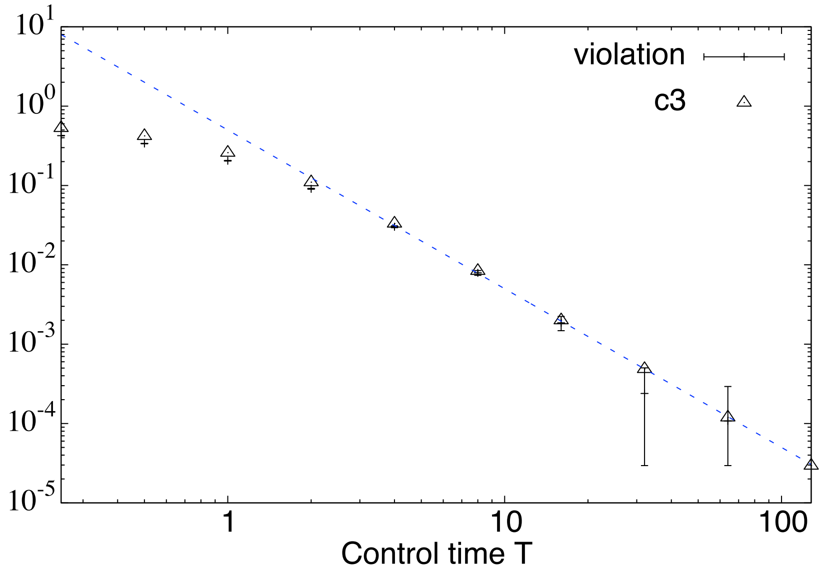

Figure 7.2: The violation of fluctuation-dissipation relation (Eq. (7.65), cross) and the third cumulant of the excess work (triangle) plotted against the entire control time T. The blue dashed lines is the guide to the eye corresponding to the scaling T^{-2}.

order polynomial in k, and the $O(\epsilon^4)$ contribution is at least a fifth-order polynomial in k. From the analytical calculation and the numerical simulation done in this chapter, it is expected that the deviation of the work from the Gaussian distribution arises in such a way that the higher-order cumulants vanish more rapidly as the control approaches the quasistatic limit. More precisely, we conjecture that the $O(\epsilon^n)$ contribution to the cumulant-generating function of the work is an $(n+1)$th-order polynomial in k, and that the nth cumulant c_n of the work scales as $1/T^{n-1}$ for $n \geq 1$.

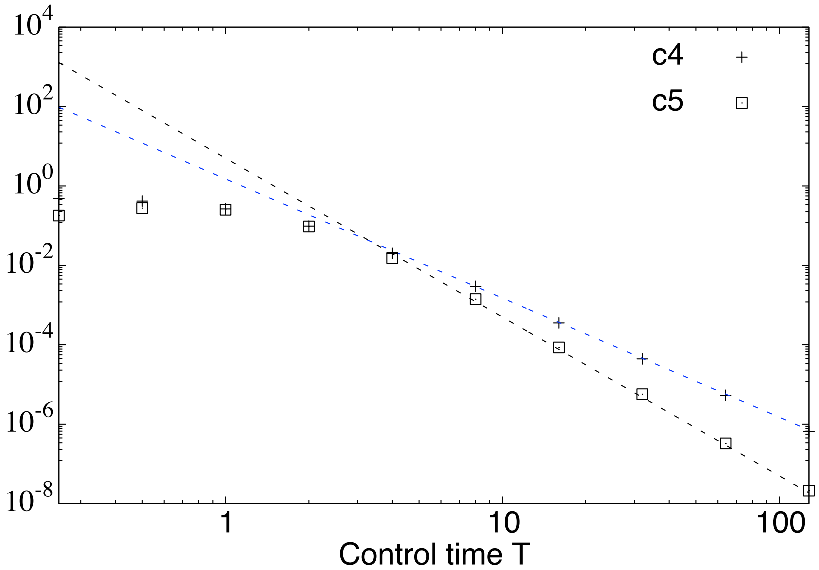

Figure 7.3: The fourth (square) and fifth (triangle) cumulants of the excess work plotted against the entire control time T. The blue and black dotted lines are the guides to the eye corresponding to the scaling T^{-3} and T^{-4}, respectively.

Chapter 8

Conclusion

In this thesis, we have studied nonequilibrium statistical mechanics from a geometric perspective. In particular, we have (i) examined the relation between quantum information geometry and linear response theory and (ii) analyzed nonequilibrium processes in thermodynamic control and derived a geometric expression for work.

In Chapter 2, we have reviewed the theory of response and relaxation near the thermal equilibrium state. We have seen that the linear response function and the linear relaxation function are quantitatively related via integration and differentiation. Such a relation also holds for higher-order response functions and relaxation functions. We have also given an explicit form of response functions in quantum Hamiltonian system, which are expressed as expectation values of some observables at thermal equilibrium. In particular, the linear response function, which describes nonequilibrium phenomena, are quantitatively related to the temporal correlation at thermal equilibrium, which is formulated as the Green-Kubo formula and the fluctuation-dissipation theorem.

In Chapter 3, we have briefly reviewed thermodynamics, especially the stochastic thermodynamics that provides a framework for discussing thermodynamic properties of microscopic system surrounded by a thermal bath. We have also introduced the thermodynamic metric, on which our latter main results are based. The excess work in a thermodynamic control can be approximated as a squared length of the contour in the control parameter space measured with the thermodynamic metric. There are two derivations for this expression: the phenomenological one assuming the linear response, and the microscopic one in overdamped Langevin systems assuming the separation in timescale between the system and the control.

In Chapter 4, we have reviewed the information geometry. In information geometry, we consider a differential-geometrical structure on the space of probability distributions. The Fisher information plays an important role as a metric on that space. In classical information geometry, the classical Fisher metric is shown to be a unique metric that monotonically decreases under information processing. In contrast, in quantum information geometry, where probability distributions are replaced by density operators, there are infinitely many types of monotone metrics due to the noncommutativity of operators, which are called the quantum Fisher metrics or the quantum Fisher information. There is a one-to-one correspondence between the quantum Fisher metric and an operator monotone function. We have also introduced the generalized covariance of two noncommuting observables, which is also defined for each operator monotone function. The quantum Fisher metric and the generalized covariance contain the same amount of information on the geometric structure around the state.

In Chapter 5, we have presented the former main results (i) of this thesis. We have generalized the fluctuation-dissipation theorem, which establishes the quantitative relation between the linear response function and the generalized covariance in the thermal equilibrium state. Based on the generalized fluctuation-dissipation theorem, we can infer the generalized covariance by measuring the linear response functions. We have also proposed the experimental method of determining the quantum Fisher information by measuring the dynamical susceptibilities or the complex admittances for all frequencies. Our method allows us to determine an arbitrary type of the quantum Fisher information, once the linear response functions are measured. One of the advantages of our method is that we can determine the quantum Fisher information without quantum state tomography, and therefore can avoid an exponentially large number of measurements even for large systems.

The relation derived in this chapter is valid only for the thermal equilibrium state. It is an outstanding issue to extend our result to other states, such as nonequilibrium steady states. Measuring a temporal correlation in quantum systems is a nontrivial problem due to the backaction of the measurement. Our result bypasses this problem by showing that the temporal correlation can be indirectly determined by measuring the linear response function, which needs only one measurement and does not suffer from the measurement backaction. However, to understand the noncommutative nature of quantum theory, the direct relation between the generalized covariance and the correlation measurement is also an outstanding issue.

In Chapters 6 and 7, we have presented the latter main result (ii) of this thesis. We have examined the average excess work in thermodynamic control in a phenomenological way in Chapter 6. We have derived an expansion of the excess work in terms of a small parameter ϵ that characterizes how slowly we control the system. We have discussed the physical picture of the next leading-order contributions to the thermodynamic metric term. They can be detected by comparing the excess work in a forward control and a backward control, and are predicted to scale as $1/T^2$ as a function of the entire control time T. Since the expansion is derived without assuming the microscopic dynamics, it is valid as long as the perturbation series expansion is valid. We have obtained the more accurate expression for the excess work than that in terms of the thermodynamic metric. A natural question arising here is, how the optimal protocol that minimizes the excess work is modified from the geodesics determined from the thermodynamic metric in finite-time control.

In Chapter 7, we have examined the work distribution in overdamped Langevin systems. We have derived the time evolution equation for the moment generating function of the work, and solved it from lower-order contributions in ϵ. The $O(\epsilon)$ contribution to the generating function reproduces two known facts: the work distribution is Gaussian, and the average work is given by the thermodynamic metric. When we take up to $O(\epsilon^2)$ contributions into account, the work distribution has nonzero skewness, which means that the fluctuation-dissipation relation is violated with scaling $1/T^2$. Furthermore, from the analytic calculation with numerical supports, we have conjectured that the nth cumulant of the work scales as $1/T^{n-1}$ for $n \geq 1$. Relating global structures such as an f-divergence [82] to thermodynamic quantities is left as a future problem.

We have obtained scalings of many quantities in transient nonequilibrium processes such as cumulants and the difference in excess work between forward and back protocol. Such scalings can be experimentally verified by measuring the work for different total protocol time, in various systems. Possible candidates are biomolcules such as DNA, RNA and proteins [29, 83], a brownian particle in an optical trap [84, 85, 86], a defect center in diamond [87, 83], and an electric circuit [88, 89, 90].

Appendix A

Miscellaneous

A.1 Useful Formulas

$$[\hat{\rho}_{\mathrm{can}}, \hat{A}] = \beta \int_0^1 \mathrm{d}\alpha \; \hat{\rho}_{\mathrm{can}}^{1-\alpha} [\hat{A}, \hat{H}] \hat{\rho}_{\mathrm{can}}^{\alpha}, \tag{A.1}$$

$$\mathrm{e}^{-\beta(\hat{A}+\hat{B})} = \mathrm{e}^{\beta \hat{A}} \left(1 - \int_0^\beta \mathrm{d}\alpha \; \mathrm{e}^{-\alpha \hat{A}} \hat{B} \mathrm{e}^{-\alpha(\hat{A}+\hat{B})} \right), \tag{A.2}$$

$$\frac{\partial \hat{\rho}_{\mathrm{can}}(\boldsymbol{\lambda})}{\partial \lambda_\nu} = \beta \int_0^1 d\alpha \hat{\rho}_{\mathrm{can}}(\boldsymbol{\lambda})^{1-\alpha} \Delta \hat{X}_\nu \hat{\rho}_{\mathrm{can}}(\boldsymbol{\lambda})^{\alpha}. \tag{A.3}$$

Equation (A.1) can be checked by comparing matrix components in the energy eigenbasis [16].

We can show Eq. (A.2) by multplying $\mathrm{e}^{-\beta\hat{A}}$ from the left to both sides and then differentiating them with respect to β [18]. Equation (A.3) immediately follows from Eq. (A.2).

Appendix B

Calculation of the $O(\epsilon^2)$ Contributions to the Generating Function of Work

In this chapter, we calculate the $O(\epsilon^2)$ contribution to the cumulant generating function $C_W(k;\mathbf{\Lambda}_\epsilon)$. From the $O(\epsilon)$ equation for Eq. (7.29), we obtain

$$\begin{aligned}&\frac{\partial}{\partial x}\left(\frac{\partial G_2(x,k;t)}{\partial x}\mathrm{e}^{-\beta V(x;\boldsymbol{\lambda}(t))}\right)\\&=\beta\gamma\left(\frac{\partial G_1(x,k;t)}{\partial t}\mathrm{e}^{-\beta V(x;\boldsymbol{\lambda}(t))}+(\beta+k)\dot{\lambda}^\mu(t)\Delta X_\mu(x;\boldsymbol{\lambda}(t))G_1(x,k;t)\mathrm{e}^{-\beta V(x;\boldsymbol{\lambda}(t))}\right).\end{aligned} \tag{B.1}$$

We perform the integration twice and obtain

$$\begin{aligned}G_2(x,k;t)=&\beta\gamma\int_{-\infty}^{x}\mathrm{d}x'\int_{\infty}^{x'}\mathrm{d}x''\frac{\partial G_1(x'',k;t)}{\partial t}\mathrm{e}^{-\beta(V(x'';\boldsymbol{\lambda}(t))-V(x';\boldsymbol{\lambda}(t)))}\\&+\beta\gamma(\beta+k)\dot{\lambda}_\mu(t)\int_{-\infty}^{x}\mathrm{d}x'\int_{\infty}^{x'}\mathrm{d}x''\Delta X_\mu(x'';\boldsymbol{\lambda}(t))G_1(x'',k;t)\mathrm{e}^{-\beta(V(x'';\boldsymbol{\lambda}(t))-V(x';\boldsymbol{\lambda}(t)))}\\&+g_2(k;t),\end{aligned} \tag{B.2}$$

where $g_2(k;t)$ is a constant independent of x. To determine the k-dependence of $G_2(x,k;t)$, we consider the $O(\epsilon^2)$ consistency condition

$$\int_{-\infty}^{\infty}\mathrm{d}x\left(\frac{\partial G_2(x,k;t)}{\partial t}\mathrm{e}^{-\beta V(x;\boldsymbol{\lambda}(t))}+(\beta+k)\dot{\lambda}^\mu(t)\Delta X_\mu(x;\boldsymbol{\lambda}(t))G_2(x,k;t)\mathrm{e}^{-\beta V(x;\boldsymbol{\lambda}(t))}\right)=0. \tag{B.3}$$

If we substitute Eq. (B.2) for Eq. (B.3), we obtain

$$
\begin{aligned}
0 =&\beta\gamma \int \mathrm{d}^3x \ \frac{\partial^2 G_1(x'')}{\partial t^2}\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))} \\
&+ \beta\gamma\dot{\lambda}^\mu(t) \int \mathrm{d}^3x \ \frac{\partial G_1(x'')}{\partial t}\mathrm{e}^{-\beta V(x)}\frac{\partial}{\partial \lambda^\mu}\left(\mathrm{e}^{-\beta(V(x'')-V(x'))}\right) \\
&+ \beta\gamma(\beta+k)\ddot{\lambda}^\mu(t) \int \mathrm{d}^3x \ G_1(x'')\Delta X_\mu(x'')\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))} \\
&+ \beta\gamma(\beta+k)\dot{\lambda}^\mu(t) \int \mathrm{d}^3x \ \frac{\partial G_1(x'')}{\partial t}\Delta X_\mu(x'')\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))} \\
&+ \beta\gamma(\beta+k)\dot{\lambda}^\mu(t)\dot{\lambda}^\nu(t) \int \mathrm{d}^3x \ G_1(x'')\mathrm{e}^{-\beta V(x)}\frac{\partial}{\partial \lambda^\mu}\left(\Delta X_\nu(x'')\mathrm{e}^{-\beta(V(x'')-V(x'))}\right) \\
&+ Z\frac{\partial g_2(k;t)}{\partial t} \\
&+ \beta\gamma(\beta+k)\dot{\lambda}^\mu(t) \int \mathrm{d}^3x \ \frac{\partial G_1(x'')}{\partial t}\Delta X_\mu(x)\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))} \\
&+ \beta\gamma(\beta+k)^2\dot{\lambda}^\mu(t)\dot{\lambda}^\nu(t) \int \mathrm{d}^3x \ G_1(x'')\Delta X_\mu(x)\Delta X_\nu(x'')\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))},
\end{aligned}
\tag{B.4}
$$

where the variables k and $\boldsymbol{\lambda}$ are abbreviated for simplicity. Noting that $g_2(k;t=0)=0$, we can perform the integration with respect to t in Eq. (B.4) and obtain

$$
\begin{aligned}
g_2(k;t) =& -\beta\gamma\int_0^t \mathrm{d}t' \int \mathrm{d}^3x \ \frac{\partial^2 G_1(x'')}{\partial t'^2}\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z} \\
&-\beta\gamma\int_0^t \mathrm{d}t'\dot{\lambda}^\mu(t') \int \mathrm{d}^3x \ \frac{\partial G_1(x'')}{\partial t'}\frac{\mathrm{e}^{-\beta V(x)}}{Z}\frac{\partial}{\partial \lambda^\mu}\left(\mathrm{e}^{-\beta(V(x'')-V(x'))}\right) \\
&-\beta\gamma(\beta+k)\int_0^t \mathrm{d}t'\ddot{\lambda}^\mu(t') \int \mathrm{d}^3x \ G_1(x'')\Delta X_\mu(x'')\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z} \\
&-\beta\gamma(\beta+k)\int_0^t \mathrm{d}t'\dot{\lambda}^\mu(t') \int \mathrm{d}^3x \ \frac{\partial G_1(x'')}{\partial t'}\Delta X_\mu(x'')\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z} \\
&-\beta\gamma(\beta+k)\int_0^t \mathrm{d}t'\dot{\lambda}^\mu(t')\dot{\lambda}^\nu(t') \int \mathrm{d}^3x \ G_1(x'')\frac{\mathrm{e}^{-\beta V(x)}}{Z}\frac{\partial}{\partial \lambda^\mu}\left(\Delta X_\nu(x'')\mathrm{e}^{-\beta(V(x'')-V(x'))}\right) \\
&-\beta\gamma(\beta+k)\int_0^t \mathrm{d}t'\dot{\lambda}^\mu(t') \int \mathrm{d}^3x \ \frac{\partial G_1(x'')}{\partial t'}\Delta X_\mu(x)\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z} \\
&-\beta\gamma(\beta+k)^2\int_0^t \mathrm{d}t'\dot{\lambda}^\mu(t')\dot{\lambda}^\nu(t') \int \mathrm{d}^3x \ G_1(x'')\Delta X_\mu(x)\Delta X_\nu(x'')\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z}.
\end{aligned}
\tag{B.5}
$$

Therefore, from Eqs. (B.2) and (B.5), we obtain

$$
\begin{aligned}
&G_2(x,k;t)\\
=&\beta\gamma\int_{-\infty}^{x}\mathrm{d}x'\int_{\infty}^{x'}\mathrm{d}x''\frac{\partial G_1(x'',k;t)}{\partial t}\mathrm{e}^{-\beta(V(x'';\boldsymbol{\lambda}(t))-V(x';\boldsymbol{\lambda}(t)))}\\
&+\beta\gamma(\beta+k)\dot{\lambda}_\mu(t)\int_{-\infty}^{x}\mathrm{d}x'\int_{\infty}^{x'}\mathrm{d}x''\Delta X_\mu(x'';\boldsymbol{\lambda}(t))G_1(x'',k;t)\mathrm{e}^{-\beta(V(x'';\boldsymbol{\lambda}(t))-V(x';\boldsymbol{\lambda}(t)))}\\
&-\beta\gamma\int_0^t\mathrm{d}t'\int\mathrm{d}^3x\ \frac{\partial^2 G_1(x'',k;t')}{\partial t'^2}\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z}\\
&-\beta\gamma\int_0^t\mathrm{d}t'\dot{\lambda}^\mu(t')\int\mathrm{d}^3x\ \frac{\partial G_1(x'',k;t')}{\partial t'}\frac{\mathrm{e}^{-\beta V(x)}}{Z}\frac{\partial}{\partial\lambda^\mu}\left(\mathrm{e}^{-\beta(V(x'')-V(x'))}\right)\\
&-\beta\gamma(\beta+k)\int_0^t\mathrm{d}t'\ddot{\lambda}^\mu(t')\int\mathrm{d}^3x\ G_1(x'',k;t')\Delta X_\mu(x'')\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z}\\
&-\beta\gamma(\beta+k)\int_0^t\mathrm{d}t'\dot{\lambda}^\mu(t')\int\mathrm{d}^3x\ \frac{\partial G_1(x'',k;t')}{\partial t'}\Delta X_\mu(x'')\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z}\\
&-\beta\gamma(\beta+k)\int_0^t\mathrm{d}t'\dot{\lambda}^\mu(t')\dot{\lambda}^\nu(t')\int\mathrm{d}^3x\ G_1(x'',k;t')\frac{\mathrm{e}^{-\beta V(x)}}{Z}\frac{\partial}{\partial\lambda^\mu}\left(\Delta X_\nu(x'')\mathrm{e}^{-\beta(V(x'')-V(x'))}\right)\\
&-\beta\gamma(\beta+k)\int_0^t\mathrm{d}t'\dot{\lambda}^\mu(t')\int\mathrm{d}^3x\ \frac{\partial G_1(x'',k;t')}{\partial t'}\Delta X_\mu(x)\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z}\\
&-\beta\gamma(\beta+k)^2\int_0^t\mathrm{d}t'\dot{\lambda}^\mu(t')\dot{\lambda}^\nu(t')\int\mathrm{d}^3x\ G_1(x'',k;t')\Delta X_\mu(x)\Delta X_\nu(x'')\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z}.
\end{aligned}
\tag{B.6}
$$

Then, we can calculate the $O(\epsilon^2)$ contribution to the moment generating function as

$$
\begin{aligned}
&\int \mathrm{d}x\ p_{\mathrm{eq}}^{\boldsymbol{\lambda}(t)}(x) G_2(x,k;t) \\
=&\beta\gamma \int \mathrm{d}^3x\ \frac{\partial G_1(x'',k;t)}{\partial t} \frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z} \\
&+ \beta\gamma(\beta+k)\dot{\lambda}_\mu(t) \int \mathrm{d}^3x\ \Delta X_\mu(x'';\boldsymbol{\lambda}(t)) G_1(x'',k;t) \frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z} \\
&- \beta\gamma \int_0^t \mathrm{d}t' \int \mathrm{d}^3x\ \frac{\partial^2 G_1(x'',k;t')}{\partial t'^2} \frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z} \\
&- \beta\gamma \int_0^t \mathrm{d}t' \dot{\lambda}^\mu(t') \int \mathrm{d}^3x\ \frac{\partial G_1(x'',k;t')}{\partial t'} \frac{\mathrm{e}^{-\beta V(x)}}{Z} \frac{\partial}{\partial \lambda^\mu} \left(\mathrm{e}^{-\beta(V(x'')-V(x'))} \right) \\
&- \beta\gamma(\beta+k) \int_0^t \mathrm{d}t' \ddot{\lambda}^\mu(t') \int \mathrm{d}^3x\ G_1(x'',k;t') \Delta X_\mu(x'') \frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z} \\
&- \beta\gamma(\beta+k) \int_0^t \mathrm{d}t' \dot{\lambda}^\mu(t') \int \mathrm{d}^3x\ \frac{\partial G_1(x'',k;t')}{\partial t'} \Delta X_\mu(x'') \frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z} \\
&- \beta\gamma(\beta+k) \int_0^t \mathrm{d}t' \dot{\lambda}^\mu(t') \dot{\lambda}^\nu(t') \int \mathrm{d}^3x\ G_1(x'',k;t') \frac{\mathrm{e}^{-\beta V(x)}}{Z} \frac{\partial}{\partial \lambda^\mu} \left(\Delta X_\nu(x'') \mathrm{e}^{-\beta(V(x'')-V(x'))} \right) \\
&- \beta\gamma(\beta+k) \int_0^t \mathrm{d}t' \dot{\lambda}^\mu(t') \int \mathrm{d}^3x\ \frac{\partial G_1(x'',k;t')}{\partial t'} \Delta X_\mu(x) \frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z} \\
&- \beta\gamma(\beta+k)^2 \int_0^t \mathrm{d}t' \dot{\lambda}^\mu(t') \dot{\lambda}^\nu(t') \int \mathrm{d}^3x\ G_1(x'',k;t') \Delta X_\mu(x) \Delta X_\nu(x'') \frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z}.
\end{aligned}
\tag{B.7}
$$

If we integrate the third and fifth terms by parts, we obtain

$$
\begin{aligned}
&\int \mathrm{d}x\ p_{\mathrm{eq}}^{\boldsymbol{\lambda}(t)}(x) G_2(x,k;t) \\
=&- \beta\gamma k \int_0^t \mathrm{d}t' \dot{\lambda}^\mu(t') \int \mathrm{d}^3x\ \frac{\partial G_1(x'',k;t')}{\partial t'} \Delta X_\mu(x'') \frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z} \\
&- \beta\gamma k(\beta+k) \int_0^t \mathrm{d}t' \dot{\lambda}^\mu(t') \dot{\lambda}^\nu(t') \int \mathrm{d}^3x\ G_1(x'',k;t') \Delta X_\mu(x) \Delta X_\nu(x'') \frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z}.
\end{aligned}
\tag{B.8}
$$

If we substitute the explicit form of $G_1(x,k;t)$ in Eq. (7.39) and its derivative

$$
\begin{aligned}
&\frac{\partial G_1(x'',k;t')}{\partial t'}\\
=&\beta\gamma(\beta+k)\ddot{\lambda}^{\mu}(t')\int_{-\infty}^{x''}\mathrm{d}x'''\int_{-\infty}^{x'''}\mathrm{d}x''''\Delta X_{\mu}(x'''';\boldsymbol{\lambda}(t'))\mathrm{e}^{-\beta(V(x'''';\boldsymbol{\lambda}(t'))-V(x''';\boldsymbol{\lambda}(t')))}\\
&+\beta\gamma(\beta+k)\dot{\lambda}^{\mu}(t)\dot{\lambda}^{\nu}(t)\int_{-\infty}^{x''}\mathrm{d}x'''\int_{-\infty}^{x'''}\mathrm{d}x''''\frac{\partial}{\partial\lambda^{\mu}}\left(\Delta X_{\nu}(x'''';\boldsymbol{\lambda}(t'))\mathrm{e}^{-\beta(V(x'''';\boldsymbol{\lambda}(t'))-V(x''';\boldsymbol{\lambda}(t')))}\right)\\
&-\beta\gamma(\beta+k)\ddot{\lambda}^{\mu}(t')\left(\int\mathrm{d}^3x\;\Delta X_{\mu}(x'';\boldsymbol{\lambda}(t'))\frac{\mathrm{e}^{-\beta(V(x;\boldsymbol{\lambda}(t))-V(x';\boldsymbol{\lambda}(t'))+V(x'';\boldsymbol{\lambda}(t')))}}{Z[\boldsymbol{\lambda}(t')]}\right)\\
&-\beta\gamma(\beta+k)\dot{\lambda}^{\mu}(t')\dot{\lambda}^{\nu}(t')\left(\int\mathrm{d}^3x\;\frac{\partial}{\partial\lambda^{\mu}}\left(\Delta X_{\mu}(x'';\boldsymbol{\lambda}(t'))\frac{\mathrm{e}^{-\beta(V(x;\boldsymbol{\lambda}(t'))-V(x';\boldsymbol{\lambda}(t'))+V(x'';\boldsymbol{\lambda}(t')))}}{Z[\boldsymbol{\lambda}(t')]}\right)\right)\\
&-\beta\gamma k(\beta+k)\dot{\lambda}^{\mu}(t')\dot{\lambda}^{\nu}(t')\left(\int\mathrm{d}^3x\;\Delta X_{\mu}(x;\boldsymbol{\lambda}(t'))\Delta X_{\nu}(x'';\boldsymbol{\lambda}(t'))\frac{\mathrm{e}^{-\beta(V(x;\boldsymbol{\lambda}(t'))-V(x';\boldsymbol{\lambda}(t'))+V(x'';\boldsymbol{\lambda}(t')))}}{Z[\boldsymbol{\lambda}(t')]}\right)
\end{aligned}
\tag{B.9}
$$

for Eq. (B.8), we obtain

$$
\begin{aligned}
&\int \mathrm{d}x\ p_{\mathrm{eq}}^{\boldsymbol{\lambda}(t)}(x) G_2(x,k;t) \\
=&-(\beta\gamma)^2 k(\beta+k)\int_0^t \mathrm{d}t'\dot{\lambda}^\mu(t')\ddot{\lambda}^\nu(t')\left(\int \mathrm{d}^5x\ \Delta X_\mu(x)\Delta X_\nu(x'''')\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x'')-V(x''')+V(x''''))}}{Z}\right) \\
&-(\beta\gamma)^2 k(\beta+k)\int_0^t \mathrm{d}t'\dot{\lambda}^\mu(t')\dot{\lambda}^\nu(t')\dot{\lambda}^\rho(t') \\
&\qquad\qquad\times\left(\int \mathrm{d}^5x\ \Delta X_\mu(x)\frac{\partial}{\partial\lambda^\nu}\left(\Delta X_\rho(x'''')\mathrm{e}^{-\beta(V(x'''')-V(x'''))}\right)\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z}\right) \\
&+(\beta\gamma)^2 k(\beta+k)\int_0^t \mathrm{d}t'\dot{\lambda}^\mu(t')\ddot{\lambda}^\nu(t')\left(\int \mathrm{d}^3x\ \Delta X_\mu(x)\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z}\right) \\
&\qquad\qquad\qquad\qquad\times\left(\int \mathrm{d}^3x\ \Delta X_\nu(x'')\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z}\right) \\
&+(\beta\gamma)^2 k(\beta+k)\int_0^t \mathrm{d}t'\dot{\lambda}^\mu(t')\dot{\lambda}^\nu(t')\dot{\lambda}^\rho(t')\left(\int \mathrm{d}^3x\ \Delta X_\mu(x)\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z}\right) \\
&\qquad\qquad\qquad\qquad\times\left(\int \mathrm{d}^3x\ \frac{\partial}{\partial\lambda^\nu}\left(\Delta X_\rho(x'')\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z}\right)\right) \\
&+(\beta\gamma)^2 k^2(\beta+k)\int_0^t \mathrm{d}t'\dot{\lambda}^\mu(t')\dot{\lambda}^\nu(t')\dot{\lambda}^\rho(t')\left(\int \mathrm{d}^3x\ \Delta X_\mu(x)\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z}\right) \\
&\qquad\qquad\qquad\qquad\times\left(\int \mathrm{d}^3x\ \Delta X_\nu(x)\Delta X_\rho(x'')\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z}\right) \\
&-(\beta\gamma)^2 k(\beta+k)^2\int_0^t \mathrm{d}t'\dot{\lambda}^\mu(t')\dot{\lambda}^\nu(t')\dot{\lambda}^\rho(t') \\
&\qquad\qquad\times\left(\int \mathrm{d}^5x\ \Delta X_\mu(x)\Delta X_\nu(x'')\Delta X_\rho(x'''')\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x'')-V(x''')+V(x''''))}}{Z}\right) \\
&+(\beta\gamma)^2 k(\beta+k)^2\int_0^t \mathrm{d}t'\dot{\lambda}^\mu(t')\dot{\lambda}^\nu(t')\dot{\lambda}^\rho(t')\left(\int \mathrm{d}^3x\ \Delta X_\mu(x'')\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z}\right) \\
&\qquad\qquad\times\left(\int \mathrm{d}^3x\ \Delta X_\nu(x)\Delta X_\rho(x'')\frac{\mathrm{e}^{-\beta(V(x)-V(x')+V(x''))}}{Z}\right) \\
&+\left(\frac{k(\beta+k)}{\beta}\right)^2\int_0^t \mathrm{d}t'\dot{\lambda}^\mu(t')\dot{\lambda}^\nu(t')\zeta^{(1;0)}_{\mu\nu}(\boldsymbol{\lambda}(t'))\int_0^{t'}\mathrm{d}t''\dot{\lambda}^\rho(t'')\dot{\lambda}^\sigma(t'')\zeta^{(1;0)}_{\rho\sigma}(\boldsymbol{\lambda}(t'')),
\end{aligned}
\tag{B.10}
$$

where the multiple integrals are interpreted as

$$
\int \mathrm{d}^3x\ \cdot := \int_{-\infty}^{\infty}\mathrm{d}x'\int_{x'}^{\infty}\mathrm{d}x\int_{-\infty}^{x'}\mathrm{d}x''\ \cdot \tag{B.11}
$$

$$
\int \mathrm{d}^5x\ \cdot := \int_{-\infty}^{\infty}\mathrm{d}x'\int_{-\infty}^{x'}\mathrm{d}x'''\int_{x'}^{\infty}\mathrm{d}x\int_{x'''}^{x'}\mathrm{d}x''\int_{-\infty}^{x'''}\mathrm{d}x''''\ \cdot . \tag{B.12}
$$

When the moment generating function is give by

$$\langle \mathrm{e}^{kW} \rangle = \mathrm{e}^{k\Delta F}(1 + \epsilon a_1 + \epsilon^2 a_2 + O(\epsilon^3)), \tag{B.13}$$

then the cumulant generating function can be calculated as

$$\log \langle \mathrm{e}^{kW} \rangle = k\Delta F + \epsilon a_1 + \epsilon^2 (a_2 - \frac{1}{2}{a_1}^2) + O(\epsilon^3). \tag{B.14}$$

From Eqs. (B.10) and (B.14), we finally obtain the cumulant generating function up to $O(\epsilon^2)$ as shown in Eq. (7.50).

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