Thermodynamic quantities and fluctuation theorems in open quantum systems

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Abstract

We study fluctuation theorems for open quantum systems using the approach of quantum master equations, and examine the thermodynamic quantities that appear in those fluctuation theorems. The approach of Markovian quantum master equations to the fluctuation theorems was developed by Esposito and Mukamel [Phys. Rev. E **73**, 046129 (2006)]. We show that their discussion can be formally generalized to the case of a non-Markovian heat bath in the case where the local system is linearly connected to the Gaussian heat bath with the spectrum distribution of the Drude form. However, we found that the thermodynamic quantities that appear in those fluctuation theorems can be ill-defined or inconsistent with each other by numerically simulating the spin-boson model.

Contents

4

Chapter 1

Introduction

The research of non-equilibrium statistical physics has been energetically developed for the last decade in the context of fluctuation theorems and the Jarzynski equality. The fluctuation theorem is a symmetry relation with respect to the time reversal of a process and is characterized in terms of the entropy production. The Jarzynski equality is a relation that connects a non-equilibrium quantity and an equilibrium quantity; it relates the average of the non-equilibrium work between two states and their free energy difference. The Jarzynski equality can be derived from the fluctuation theorem and we will briefly explain the derivation below.

The fluctuation theorem was originally found in classical systems and studied both in stochastic [8, 9] and deterministic approaches [20, 25]. The fluctuation theorem for a quantum system was first discussed for an essentially isolated system [21, 33]; the case of open quantum systems is of great interest in recent years [6, 10–12, 23, 27, 29]. Kurchan [21] considered the scheme called the *two-measurement scheme* and it has become a standard approach to the fluctuation theorem of quantum systems.

The two-measurement scheme in an isolated quantum system is as follows:

1. Prepare the system in the canonical equilibrium state;

2. Measure the energy of the system by projecting the system to the nth energy eigenstate $|n\rangle$;

3. Let the system evolve for the time interval $\tau \in (0, T]$ under some external fields manipulated according to the control parameter $\lambda(\tau)$;

4. Measure the energy of the system again and project the state to the mth energy eigenstate $|m\rangle$ at the end of the process.

Let us show the quantum fluctuation theorem for an isolated system by the two-measurement scheme, following Talkner et al. [28, 29]. Even though the system is isolated, because of the control parameter $\lambda(\tau)$ and the fact that the measurement is dissipative, the energy change occurs. Since no heat is produced in an isolated system, the difference of the measured energy is regarded as the work done on the system: $W = E_m - E_n$. The probability to obtain the work W during the interval $(0, T]$ is given by

$$p_{T,0}^{\mathrm{F}}(W) = \sum_{n,m} \delta(W - (E_m - E_n)) \langle m|\hat{U}_{\mathrm{F}}(T,0)|n\rangle \frac{\mathrm{e}^{-\beta E_n}}{Z(0)} \langle n|\hat{U}_{\mathrm{F}}^{\dagger}(T,0)|m\rangle \qquad (1.1)$$

and its characteristic function reads

$$G_{T,0}^{\mathrm{F}}(u) \equiv \int dW\, \mathrm{e}^{iuW} p_{T,0}^{\mathrm{F}}(W)$$

$$= \int dW\, \mathrm{e}^{iuW} \sum_{n,m} \delta(W - (E_m - E_n)) \langle m|\hat{U}_{\mathrm{F}}(T,0)|n\rangle \frac{\mathrm{e}^{-\beta E_n}}{Z(0)} \langle n|\hat{U}_{\mathrm{F}}^{\dagger}(T,0)|m\rangle$$

$$= \sum_{n,m} \mathrm{e}^{iu(E_m - E_n)} \langle m|\hat{U}_{\mathrm{F}}(T,0)|n\rangle \frac{\mathrm{e}^{-\beta E_n}}{Z(0)} \langle n|\hat{U}_{\mathrm{F}}^{\dagger}(T,0)|m\rangle$$

$$= \frac{1}{Z(0)} \mathrm{Tr}\, \mathrm{e}^{iu\hat{H}(T)} \hat{U}_{\mathrm{F}}(T,0) \mathrm{e}^{-(iu+\beta)\hat{H}(0)} \hat{U}_{\mathrm{F}}^{\dagger}(T,0), \tag{1.2}$$

where $\hat{H}(\tau)$ is the Hamiltonian in the Schrödinger picture with explicit time dependence because of the control parameter $\lambda(\tau)$, $\hat{U}_{\mathrm{F}}(T,0)$ is the time evolution operator from $\tau = 0$ to $\tau = T$, and $Z(\tau)$ is the partition function at time τ with the inverse temperature β, i.e. $Z(\tau) = \mathrm{Tr}\exp[-\beta\hat{H}(\tau)]$. The subscript and superscript F stands for the forward process under the forward protocol.

Next we set $v := -u + i\beta$. Since $G_{T,0}^{\mathrm{F}}(u)$ is analytic in the region $S = \{u|0 \leq \mathrm{Im}\,u \leq \beta, -\infty < \mathrm{Re}\,u < \infty\}$, $G_{T,0}^{\mathrm{F}}(v)$ is also analytic. Using v, we have

$$Z(0)G_{T,0}^{\mathrm{F}}(u) = \mathrm{Tr}\, \mathrm{e}^{-(iv+\beta)\hat{H}(T)} \hat{U}_{\mathrm{F}}(T,0) \mathrm{e}^{iv\hat{H}(0)} \hat{U}_{\mathrm{F}}^{\dagger}(T,0)$$

$$= \mathrm{Tr}\, \mathrm{e}^{iv\hat{H}(0)} \hat{U}_{\mathrm{F}}^{\dagger}(T,0) \mathrm{e}^{-(iv+\beta)\hat{H}(T)} \hat{U}_{\mathrm{F}}(T,0). \tag{1.3}$$

Let us now consider the reversed process $\hat{\Theta}|m\rangle \to \hat{\Theta}|n\rangle$ with the backward protocol, where $\hat{\Theta}$ is a time-reversal operator. We denote the quantities for the reversed process under the backward protocol with the subscript and superscript R. The Schrödinger equation for the time evolution operator $\hat{U}_{\mathrm{R}}(\tau,0)$ with the backward protocol reads

$$i\hbar\frac{d}{d\tau}\hat{U}_{\mathrm{R}}(\tau,0) = \hat{H}(T-\tau)\hat{U}_{\mathrm{R}}(\tau,0), \tag{1.4}$$

and the solution $\hat{U}_{\mathrm{R}}(T,0)$ can be written in terms of the forward evolution operator $\hat{U}_{\mathrm{F}}(T,0)$ as [2,3]

$$\hat{U}_{\mathrm{R}}(T,0) = \hat{\Theta}\hat{U}_{\mathrm{F}}^{\dagger}(T,0)\hat{\Theta}. \tag{1.5}$$

The probability to obtain the work W along the reversed processes under the backward protocol during the interval $(0,T]$ is given by

$$p_{T,0}^{\mathrm{R}}(W) = \sum_{\hat{\Theta}n,\hat{\Theta}m} \delta(W - (E_n - E_m)) \langle \hat{\Theta}n|\hat{U}_{\mathrm{R}}(T,0)|\hat{\Theta}m\rangle \frac{\mathrm{e}^{-\beta E_m}}{Z(T)} \langle \hat{\Theta}m|\hat{U}_{\mathrm{R}}^{\dagger}(T,0)|\hat{\Theta}n\rangle$$

$$= \sum_{n,m} \delta(W - (E_n - E_m)) \langle n|\hat{U}_{\mathrm{F}}^{\dagger}(T,0)|m\rangle \frac{\mathrm{e}^{-\beta E_m}}{Z(T)} \langle m|\hat{U}_{\mathrm{F}}(T,0)|n\rangle. \tag{1.6}$$

Then, the characteristic function of $p_{T,0}^{\mathrm{R}}(W)$ reads

$$G_{T,0}^{\mathrm{R}}(u) \equiv \int dW\, \mathrm{e}^{iuW} p_{T,0}^{\mathrm{R}}(W) = \frac{1}{Z(T)} \mathrm{Tr}\, \mathrm{e}^{iu\hat{H}(0)} \hat{U}_{\mathrm{F}}^{\dagger}(T,0) \mathrm{e}^{-(iu+\beta)\hat{H}(T)} \hat{U}_{\mathrm{F}}(T,0). \tag{1.7}$$

Comparing (1.7) with (1.3), we have

$$Z(0)G_{T,0}^{\mathrm{F}}(u) = Z(T)G_{T,0}^{\mathrm{R}}(v) = Z(T)G_{T,0}^{\mathrm{R}}(-u + i\beta), \qquad (1.8)$$

or applying the inverse Fourier transform,

$$p_{T,0}^{\mathrm{F}}(W) = \frac{Z(T)}{Z(0)}\mathrm{e}^{\beta W}p_{T,0}^{\mathrm{R}}(-W) = \mathrm{e}^{-\beta(\Delta F - W)}p_{T,0}^{\mathrm{R}}(-W). \qquad (1.9)$$

This is called the Tasaki-Crooks fluctuation theorem. Taking the sum over all the possible values of W, we have

$$\mathrm{e}^{\beta\Delta F}\sum_{W} p_{T,0}^{\mathrm{F}}(W)\mathrm{e}^{-\beta W} = \sum_{W} p_{T,0}^{\mathrm{R}}(-W) = 1, \qquad (1.10)$$

$$\langle \mathrm{e}^{-\beta W}\rangle = \mathrm{e}^{-\beta\Delta F}. \qquad (1.11)$$

The angular bracket is the average over W of the forward process. This relation is called the quantum Jarzynski equality. It states that the free energy difference can be obtained by calculating the non-equilibrium average $\langle \mathrm{e}^{-\beta W}\rangle$.

The reason why we can formulate such a beautiful relation, written in terms of the thermodynamic quantities, is due to the fact that the initial state is prepared as the canonical equilibrium state and due to the unitary time evolution.

When we discuss the fluctuation theorem in open quantum systems, these nice properties are lost in general unless we directly solve the total isolated system of a local system and its environment. First, we cannot calculate the heat that flows out of the local system under the two-measurement scheme, unless we explicitly measure the energy change of the environment. Second, a local system is not precisely in the canonical equilibrium state in an environment, because it is the total system that is in the canonical equilibrium state. Third, the evolution of the system in an environment is not unitary. The total system evolves unitarily, but the reduced system effectively obeys non-unitary evolution due to dissipation.

In order to overcome the first problem, the approach of the quantum master equation was developed by Esposito and Mukamel instead of the two-measurement scheme. The present Thesis is based on this approach, which we will explain in detail below. One usually assumes a weak coupling between the system and the environment, and then the second problem resolves. For the third problem, approximations such as the Born-Markov approximation and the rotating-wave approximation give a simple equation of motion for the reduced density matrix, and hence they are widely used in order to treat the non-unitary evolution of the open quantum system. The discussion by Esposito and Mukamel is based on these assumption and approximations.

The basic strategy of the approach of the quantum master equation is to write down the dynamics of the density matrix of the system in the reservoir in a form of a birth-death master equation. Then we define the thermodynamic quantities and derive the fluctuation theorems by the analogy with the classical stochastic processes; see Appendix A for the detail. The definitions (2.53) and (2.57) of the heat $\widetilde{q}_{m',m}(\tau)$ and the work $\widetilde{w}_{m',m}(\tau)$ in the discussion by Esposito and Mukamel are analogous to the ones of the heat in (A.2) and the work (A.3) for the classical stochastic process. Note, however, that the definitions of $\widetilde{q}_{m',m}(\tau)$ and $\widetilde{w}_{m',m}(\tau)$ are only hypothetical and their validity should be

examined (Sections 2.3 and 3.1.4). The same goes for the "transition rate" $W_\tau(m', m)$ or $W_{\tau_j}(n_j, n_{j-1}; \{\hat{\sigma}(\tau_j)\})$ that appears in the birth-death master equation (2.16) or (3.16). What truly exists is the evolution of the density matrix $\hat{\rho}(\tau)$ in quantum systems; it is by no mean obvious whether the complete analogy with the classical Markovian stochastic process exists.

The aim of the present Thesis is to answer the following question: *Is the approach by Esposito and Mukamel valid in general, including the region where none of the above assumption or approximations are inappropriate?*

The plan of the present Thesis is as follows. We first review the fluctuation theorem for Markovian quantum master equations developed by Esposito and Mukamel in 2006 in Chapter 2. In Chapter 3, we show that the discussion by Esposito and Mukamel can be formally generalized to the fluctuation theorem *without approximations* for a system linearly connected to a Gaussian heat bath. We then examine whether the thermodynamic quantities that we defined there have the correct properties. We numerically examined the behavior of the dynamics of the spin-boson model, and found that some of those thermodynamic quantities can be ill-defined or inconsistent with each other if we do not use the approximations.

Chapter 2

Fluctuation theorems for Markovian quantum master equations

In the present chapter, we review the fluctuation theorem for Markovian master equations given by Esposito and Mukamel [12].

We consider a system in an environment, and possibly some external fields are applied on the system. Hence, the Hamiltonian of the total system consists of the following:

$$\hat{H}_{\text{tot}}(t) = \hat{H}_{\text{S}}(t) + \hat{H}_{\text{env}} + \hat{H}_{\text{int}}, \tag{2.1}$$

$$\hat{H}_{\text{S}}(t) := \hat{H}_{\text{S}} + \hat{H}_{\text{ext}}(t). \tag{2.2}$$

We then trace out the environmental degrees of freedom and consider the time evolution of the system. In paper by Esposito and Mukamel, the dynamics is not specified for the quantum master equation.

2.1 Quantum trajectory and the birth-death master equation

2.1.1 Quantum trajectory

They assume the situation where the Markovian approximation is good, so that the evolution of the reduced density matrix $|\hat{\rho}(\tau)\rangle\!\rangle$ of the system is described by a Lindblad-type quantum master equation,

$$\frac{d}{d\tau}|\hat{\rho}(\tau)\rangle\!\rangle = \hat{\hat{K}}(\tau)|\hat{\rho}(\tau)\rangle\!\rangle, \tag{2.3}$$

where we used the following notation:

$$|a, b\rangle\!\rangle \equiv |a\rangle\langle b|, \tag{2.4}$$

$$\langle\!\langle a, b|c, d\rangle\!\rangle \equiv \langle a|c\rangle\langle d|b\rangle. \tag{2.5}$$

In (2.3), $\hat{\hat{K}}$ is a dynamical semi-group acting on the Liouville space.

The evolution of the density matrix does not directly lead to the fluctuation theorem. In order to investigate the fluctuation theorem analogously to classical stochastic

processes, they constructed the "quantum trajectory" for the dynamics and discussed the forward and backward probabilities on the trajectory.

Let us consider the event that the jumps between states occur N times during the interval $[0, t]$, and refer to those times as $\tau_1, \ldots, \tau_N$. We denote $\tau_0 = 0$ and $\tau_{N+1} = t$. Note that we are not discretizing the dynamics. The original dynamics is continuous in time and we are merely labeling the transitions. For the set of times $\{\tau_j\}$ when the transitions take place, we obtain a set of $N + 2$ reduced density matrices by solving the quantum master equation:

$$\{\hat{\rho}(0), \hat{\rho}(\tau_1), ..., \hat{\rho}(\tau_N), \hat{\rho}(t)\}. \tag{2.6}$$

The crucial point of the discussion by Esposito and Mukamel is to introduce the time-dependent basis which diagonalizes the reduced density matrix at each time (i.e. eigenvectors), and represent the reduced density matrices as

$$\langle m'_\tau | \hat{\rho}(\tau) | m_\tau \rangle = \langle\!\langle m'_\tau m_\tau | \hat{\rho}(\tau) \rangle\!\rangle = P_\tau(m) \delta_{m'm},$$
$$|\hat{\rho}(\tau)\rangle\!\rangle = \sum_m |m_\tau\rangle P_\tau(m)\langle m_\tau|, \tag{2.7}$$

where we suppressed the subscript τ for m_τ and m'_τ on the right-hand side. Then we can regard the basis $\{|m_\tau\rangle\}$ as a set of states with probability $\{P_\tau(m)\}$ at time τ. We label the elements of the basis $|m_\tau\rangle$ in the non-decreasing order of eigenvalues of $\hat{\rho}(\tau)$. By connecting these states, we are now able to construct a quantum trajectory (Fig. 2.1):

$$n(\tau) = n_0 \rightarrow n_1 \rightarrow n_2 \cdots \rightarrow n_N, \tag{2.8}$$

where n_j represents the state after the jth transition at time τ_j. Hence, $n(\tau) = n_j$ for $\tau_j \leq \tau < \tau_{j+1}$ when $j < N$, and $n(\tau) = n_N$ for $\tau_N \leq \tau \leq t$.

2.1.2 Equation of motion in the mapped space

The evolution in the Liouville space is thereby mapped to the evolution in the discretized space. The master equation for the distribution $P_\tau(m)$ on the mapped space can be obtained from (2.3) as follows:

$$\langle\!\langle m_\tau m_\tau | \frac{d}{d\tau}\hat{\rho}(\tau)\rangle\!\rangle = \sum_{m'} \langle\!\langle m_\tau m_\tau | \hat{\hat{K}}(\tau) | m'_\tau m'_\tau\rangle\!\rangle\langle\!\langle m'_\tau m'_\tau | \hat{\rho}(\tau)\rangle\!\rangle, \tag{2.9}$$

where we used the completeness relation on the diagonalizing basis,

$$\sum_{m'} |m'_\tau m'_\tau\rangle\!\rangle\langle\!\langle m'_\tau m'_\tau | \hat{\rho}(\tau)\rangle\!\rangle = \sum_{m'} |m'_\tau\rangle\langle m'_\tau | \hat{\rho}(\tau) | m'_\tau\rangle\langle m'_\tau|$$
$$= \sum_{m'} |m'_\tau\rangle P_\tau(m')\langle m'_\tau|$$
$$= |\hat{\rho}(\tau)\rangle\!\rangle. \tag{2.10}$$
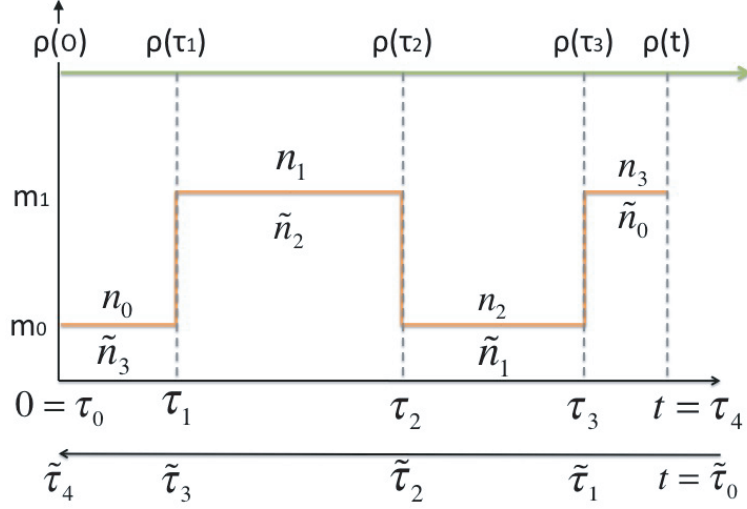
Figure 2.1: A quantum trajectory $n(\tau)$ for $N = 3$ in the case of a two-level system. Precisely speaking, the state m_0 and m_1 are time-dependent, and hence the axis must be dynamically modified, but it is suppressed here for simplicity. The labels with tilder represent the backward process.

The left-hand side of (2.9) can be written as

$$\langle\!\langle m_\tau m_\tau | \frac{d}{d\tau}\hat{\rho}(\tau)\rangle\!\rangle = \langle m_\tau | \frac{d}{d\tau}\hat{\rho}(\tau)|m_\tau\rangle = \frac{d}{d\tau}P_\tau(m) - \langle\frac{d}{d\tau}m_\tau|m_\tau\rangle P_\tau(m) - \langle m_\tau|\frac{d}{d\tau}m_\tau\rangle P_\tau(m)$$

$$= \frac{d}{d\tau}P_\tau(m) - \left(\frac{d}{d\tau}\langle m_\tau|m_\tau\rangle\right)P_\tau(m) = \frac{d}{d\tau}P_\tau(m), \tag{2.11}$$

and thus (2.9) reads

$$\frac{d}{d\tau}P_\tau(m) = \sum_{m'} W_\tau(m, m')P_\tau(m'), \tag{2.12}$$

where

$$W_\tau(m, m') \equiv \langle\!\langle m_\tau m_\tau|\hat{\hat{K}}(\tau)|m'_\tau m'_\tau\rangle\!\rangle. \tag{2.13}$$

The notation of the arguments m and m' in $W_\tau(m, m')$ is opposite to Esposito and Mukamel. We put the state before the transition on the right (m'), and the state after the transition on the left (m). Since the probability is conserved during the evolution as

$$0 = \frac{d}{d\tau}\text{Tr}\,\rho(\tau) = \frac{d}{d\tau}\sum_m P_\tau(m) = \sum_{m'}\left(\sum_m W_\tau(m, m')\right)P_\tau(m'), \tag{2.14}$$

we have

$$\sum_m W_\tau(m, m') = 0, \qquad \text{i.e.} \qquad W_\tau(m', m') = -\sum_{m\neq m'} W_\tau(m, m'). \tag{2.15}$$

11

As a result, we can recast the master equation in the form of a birth-death master equation:

$$\frac{d}{d\tau}P_\tau(m) = \sum_{m'(\neq m)} \left(W_\tau(m,m')P_\tau(m') - W_\tau(m',m)P_\tau(m)\right). \qquad (2.16)$$

Notice, however, that this is constructed from the solution of the original Liouville equation for the density matrix, since the time-dependent basis can be obtained only after we compute the set of density matrices at all times.

2.1.3 Probability of a quantum trajectory

Let us denote the probability that a state never hops from n_j during an interval (τ_j, τ) as $P_{\text{not}}(\tau|\tau_j, n_j)$. We have $P_{\text{not}}(\tau_j|\tau_j, n_j) = 1$ and the equation for $P_{\text{not}}(\tau|\tau_j, n_j)$ is

$$\frac{d}{d\tau}P_{\text{not}}(\tau|\tau_j, n_j) = -\left(\sum_{m\neq n_j} W_\tau(m, n_j)\right) P_{\text{not}}(\tau|\tau_j, n_j). \qquad (2.17)$$

Hence we obtain

$$P_{\text{not}}(\tau|\tau_j, n_j) = \exp\left(-\sum_{m\neq n_j} \int_{\tau_j}^{\tau} d\tau' \, W_{\tau'}(m, n_j)\right). \qquad (2.18)$$

Then the probability $\mu_{\text{F}}[n(\tau)]$ for a given trajectory $n(\tau)$ can be calculated as

$$\mu_{\text{F}}[n(\tau)] = P_0(n_0) \left(\prod_{j=1}^{N} P_{\text{not}}(\tau_j|\tau_{j-1}, n_{j-1})W_{\tau_j}(n_j, n_{j-1})\right) P_{\text{not}}(t|\tau_N, n_N) \qquad (2.19)$$

$$= P_0(n_0) \left[\prod_{j=1}^{N} \exp\left(-\sum_{m\neq n_{j-1}} \int_{\tau_{j-1}}^{\tau_j} d\tau' \, W_{\tau'}(m, n_{j-1})\right) W_{\tau_j}(n_j, n_{j-1})\right]$$

$$\times \exp\left(-\sum_{m\neq n_N} \int_{\tau_N}^{t} d\tau' \, W_{\tau'}(m, n_N)\right), \qquad (2.20)$$

where the subscript F stands for the forward process. Note again that the state n_{j-1} is a function of time: $n_{j-1} = n_{j-1}(\tau')$.

2.1.4 Backward process on a quantum trajectory

Whenever we discuss fluctuation theorems, we must be careful what is meant by "time reversal," because there are basically two kinds of reversal. One of them is the *backward protocol*, which simply reverts the protocol $\widetilde{\lambda}(\tau) = \lambda(t - \tau)$. The other one is the *time-reversed process*, which reverts the protocol and the underlying dynamics (adjoint dynamics). Their difference is discussed in Refs. [7, 18]. In both cases, we compare the forward trajectory and its reversed trajectory. We do not need to choose the initial probability distribution of the *backward protocol* process equal to the final probability distribution of the forward process. When we derive the Crooks-type fluctuation theorem,

we set both of the initial probability distributions of the forward and backward protocol processes as the canonical equilibrium state. In the case of the *time-reversed process*, the initial probability distribution of the reversed dynamics is the same as the final probability distribution of the forward dynamics.

In order to compare the forward quantum trajectory and the backward quantum trajectory, we need to have the same time-dependent basis on both trajectories. However, it is not possible to obtain such an evolution neither by the backward protocol nor the time-reversed process. For instance, if we consider the time-reversed process corresponding to the forward process of the quantum master equation, we have $\widetilde{\tau} = t - \tau$ and

$$\frac{d}{d\widetilde{\tau}} |\widetilde{\rho}(\widetilde{\tau})\rangle\!\rangle = \widetilde{\hat{\hat{K}}}(\widetilde{\tau}) |\widetilde{\rho}(\widetilde{\tau})\rangle\!\rangle. \tag{2.21}$$

In a Markovian quantum master equation, a dissipation term inevitably appears because of the Markov approximation and breaks the time-reversal symmetry:

$$\widetilde{\hat{\hat{K}}}(\widetilde{\tau}) \neq \hat{\hat{K}}(t - \widetilde{\tau}). \tag{2.22}$$

It means that the density matrix does not evolve in the reversed way.

Therefore, let us consider the (hypothetical) *backward process* of the birth-death master equation on the mapped space,

$$\frac{d}{d\widetilde{\tau}} \widetilde{P}_{\widetilde{\tau}}(\widetilde{m}) = \sum_{m'} \widetilde{W}_{\widetilde{\tau}}(\widetilde{m}, \widetilde{m}') \widetilde{P}_{\widetilde{\tau}}(\widetilde{m}'), \tag{2.23}$$

with a property

$$\widetilde{W}_{\widetilde{\tau}}(m, m') = W_{t-\widetilde{\tau}}(m, m'). \tag{2.24}$$

Note that the initial probability of the backward process $\widetilde{P}_{\widetilde{\tau}_0}(m)$ and the final probability of the forward process $P_t(m)$ are not necessarily related. The label of time for the backward trajectory is related to the forward one as $\widetilde{\tau}_j \leftrightarrow \tau_{N-j+1}$ and the value (duration) of the time is related as $\widetilde{\tau}_j = t - \tau_{N-j+1}$. The label of the state is related as $\widetilde{n}_{j-1} = n_{N-j+1}$, so that the trajectory corresponding to $n(\tau)$ is

$$\begin{aligned} \widetilde{n}(\widetilde{\tau}) &= \widetilde{n}_0 \to \widetilde{n}_1 \to \widetilde{n}_2 \cdots \to \widetilde{n}_N \\ &= n_N \to n_{N-1} \to n_{N-2} \cdots \to n_0. \end{aligned} \tag{2.25}$$

The probability of the backward trajectory can be obtained in the same way as the

forward one. We have

$$\mu_{\mathrm{B}}[\widetilde{n}(\widetilde{\tau})]$$

$$= \widetilde{P}_0(n_0) \left[\prod_{j=1}^{N} \exp\left(-\sum_m \int_{\widetilde{\tau}_{j-1}}^{\widetilde{\tau}_j} d\widetilde{\tau}' \, \widetilde{W}_{\widetilde{\tau}'}(\widetilde{m}, \widetilde{n}_{j-1}) \right) \widetilde{W}_{\widetilde{\tau}_j}(\widetilde{n}_j, \widetilde{n}_{j-1}) \right]$$

$$\times \exp\left(-\sum_m \int_{\widetilde{\tau}_N}^{\widetilde{\tau}_{N+1}} d\widetilde{\tau}' \, \widetilde{W}_{\widetilde{\tau}'}(m, \widetilde{n}_N) \right)$$

$$= \widetilde{P}_0(n_0) \left[\prod_{j=1}^{N} \exp\left(-\sum_m \int_{t-\tau_{N-j+2}}^{t-\tau_{N-j+1}} d\widetilde{\tau}' \, W_{t-\widetilde{\tau}'}(m, n_{N-j+1}) \right) W_{\tau_{N-j+1}}(n_{N-j}, n_{N-j+1}) \right]$$

$$\times \exp\left(-\sum_m \int_{t-\tau_1}^{t} d\widetilde{\tau}' \, W_{t-\widetilde{\tau}'}(m, n_0) \right)$$

$$= \widetilde{P}_0(n_0) \left[\prod_{j=1}^{N} \exp\left(-\sum_m \int_{\tau_{N-j+1}}^{\tau_{N-j+2}} d\tau'' \, W_{\tau''}(m, n_{N-j+1}) \right) W_{\tau_{N-j+1}}(n_{N-j}, n_{N-j+1}) \right]$$

$$\times \exp\left(-\sum_m \int_0^{\tau_1} d\tau'' \, W_{\tau''}(m, n_0) \right)$$

$$= \widetilde{P}_0(n_0) \left[\prod_{j=1}^{N} \exp\left(-\sum_m \int_{\tau_j}^{\tau_{j+1}} d\tau'' \, W_{\tau''}(m, n_j) \right) W_{\tau_j}(n_{j-1}, n_j) \right]$$

$$\times \exp\left(-\sum_m \int_0^{\tau_1} d\tau'' \, W_{\tau''}(m, n_0) \right)$$

$$= \widetilde{P}_0(n_0) \left[\prod_{j=1}^{N} \exp\left(-\sum_m \int_{\tau_{j-1}}^{\tau_j} d\tau'' \, W_{\tau''}(m, n_{j-1}) \right) W_{\tau_j}(n_{j-1}, n_j) \right]$$

$$\times \exp\left(-\sum_m \int_{\tau_N}^{t} d\tau'' \, W_{\tau''}(m, n_0) \right). \tag{2.26}$$

The subscript B stands for the backward process. In the second last line, we relabeled the index as $N - j + 1 \to j$.

2.2 The fluctuation theorems

2.2.1 Entropy flow and entropy production

Let us now discuss fluctuation theorems using the probabilities of the forward and backward trajectories. Fluctuation theorems are symmetry relations with respect to the entropy production. Before going to the derivation of the fluctuation theorems, we define the entropy flow and the entropy production in a quantum system.

The entropy of an open system is generally given by the von Neumann entropy

$$S(\tau) \equiv -\mathrm{Tr}\,\hat{\rho}(\tau)\mathrm{ln}\hat{\rho}(\tau) = -\sum_m P_\tau(m)\mathrm{ln}P_\tau(m). \tag{2.27}$$

Using the birth-death master equation (2.16), the time derivative of the entropy reads

$$\dot{S}(\tau) = -\sum_m \dot{P}_\tau(m)\ln P_\tau(m)$$

$$= -\sum_m \sum_{m'(\neq m)} [W_\tau(m,m')P_\tau(m') - W_\tau(m',m)P_\tau(m)]\ln P_\tau(m)$$

$$= -\sum_{m,m'(m\neq m')} [W_\tau(m',m)P_\tau(m)\ln P_\tau(m') - W_\tau(m',m)P_\tau(m)\ln P_\tau(m)]$$

$$= -\sum_{m,m'(m\neq m')} P_\tau(m)W_\tau(m',m)\ln\frac{P_\tau(m')}{P_\tau(m)}. \tag{2.28}$$

From the second line to the third line, we switched the index m and m' of the first term. In analogy with the classical stochastic process [15, 22, 24], we partition this to the entropy flow $\dot{S}_e(\tau)$ and the entropy production $\dot{S}_i(\tau)$:

$$\dot{S}(\tau) = \dot{S}_e(\tau) + \dot{S}_i(\tau), \tag{2.29}$$

$$\dot{S}_e(\tau) \equiv -\sum_{m,m'(m\neq m')} P_\tau(m)W_\tau(m',m)\ln\frac{W_\tau(m',m)}{W_\tau(m,m')}, \tag{2.30}$$

$$\dot{S}_i(\tau) \equiv \sum_{m,m'(m\neq m')} P_\tau(m)W_\tau(m',m)\ln\frac{W_\tau(m',m)P_\tau(m)}{W_\tau(m,m')P_\tau(m')}. \tag{2.31}$$

From the inequality $(C_1 - C_2)\ln(C_1/C_2) \geq 0$ $(C_1 \geq 0, C_2 > 0)$, the second law of thermodynamics

$$\dot{S}_i(\tau) \geq 0 \tag{2.32}$$

is confirmed.

Following the discussion of classical master equations by Seifert [24], we further partition the entropy flow and the entropy production into quantities on a trajectory so that the expectation values over the trajectories may give the above entropies. The entropy along the trajectory $n(\tau)$ is

$$s(\tau; n(\tau)) \equiv -\ln P_\tau(n(\tau)), \tag{2.33}$$

and the derivative reads

$$\dot{s}(\tau; n(\tau)) = -\left.\frac{\dot{P}_\tau(n)}{P_\tau(n)}\right|_{n=n(\tau)} - \sum_{j=1}^{N}\delta(\tau - \tau_j)\ln\frac{P_\tau(n_j)}{P_\tau(n_{j-1})}. \tag{2.34}$$

The first term gives the contribution from the evolution without jumping to the other states. The second term arises from the jumping process at τ_j. This is partitioned as

$$\dot{s}(\tau; n(\tau)) = \dot{s}_e(\tau; n(\tau)) + \dot{s}_i(\tau; n(\tau)), \tag{2.35}$$

$$\dot{s}_e(\tau; n(\tau)) \equiv -\sum_{j=1}^{N}\delta(\tau - \tau_j)\ln\frac{W_\tau(n_j, n_{j-1})}{W_\tau(n_{j-1}, n_j)}, \tag{2.36}$$

$$\dot{s}_i(\tau; n(\tau)) \equiv -\left.\frac{\dot{P}_\tau(n)}{P_\tau(n)}\right|_{n=n(\tau)} - \sum_{j=1}^{N}\delta(\tau - \tau_j)\ln\frac{P_\tau(n_j)W_\tau(n_{j-1}, n_j)}{P_\tau(n_{j-1})W_\tau(n_j, n_{j-1})}. \tag{2.37}$$

Hence, taking the average over the trajectories at time τ, we have

$$\langle \dot{s}(\tau; n(\tau)) \rangle = \dot{S}(\tau), \qquad \langle \dot{s}_{\mathrm{e}}(\tau; n(\tau)) \rangle = \dot{S}_{\mathrm{e}}(\tau), \qquad \langle \dot{s}_{\mathrm{i}}(\tau; n(\tau)) \rangle = \dot{S}_{\mathrm{i}}(\tau), \qquad (2.38)$$

where the average of a quantity $A(\tau; n(\tau))$ over the trajectories is calculated as follows:

$$\langle A(\tau; n(\tau)) \rangle = \sum_{n(\tau)} P_\tau(n(\tau)) A_{\mathrm{cont}}(\tau; n(\tau))$$

$$+ \frac{1}{N} \sum_{j=1}^{N} \int_0^t d\tau'_j \sum_{n'_j, n'_{j-1}(n'_j \neq n'_{j-1})} P_{\tau'_j}(n'_{j-1}) W_{\tau'_j}(n'_j, n'_{j-1}) A_{\mathrm{jump}}^{(\tau'_j)}(\tau; n(\tau')). \quad (2.39)$$

Here $A_{\mathrm{cont}}(\tau; n(\tau'))$ is the term for the process without jumping and $A_{\mathrm{jump}}^{(\tau_j)}(\tau; n(\tau'))$ is the term for the jumping process at time τ_j, e.g. in the case of the derivative of the entropy $\dot{s}(\tau; n(\tau))$,

$$\dot{s}_{\mathrm{cont}}(\tau; n(\tau)) = -\left. \frac{\dot{P}_\tau(n)}{P_\tau(n)} \right|_{n=n(\tau)}, \qquad (2.40)$$

$$\dot{s}_{\mathrm{jump}}^{(\tau_j)}(\tau; n(\tau)) = -\delta(\tau - \tau_j) \ln \frac{P_\tau(n_j)}{P_\tau(n_{j-1})}. \qquad (2.41)$$

In the second term of (2.39), we need the factor $1/N$, because we are over-counting the N identical transitions. Hereafter, we suppress the label $n(\tau)$ for quantities on a single trajectory.

We denote the change of the entropy, the entropy flow, and the entropy production over the interval $[0, t]$ as

$$\Delta S(t) := \int_0^t d\tau\, \dot{S}(\tau), \qquad \Delta S_{\mathrm{e}}(t) := \int_0^t d\tau\, \dot{S}_{\mathrm{e}}(\tau), \qquad \Delta S_{\mathrm{i}}(t) := \int_0^t d\tau\, \dot{S}_{\mathrm{i}}(\tau), \quad (2.42)$$

respectively, and those on a trajectory as

$$\Delta s(t) := \int_0^t d\tau \left(-\left. \frac{\dot{P}_\tau(n)}{P_\tau(n)} \right|_{n(\tau)} - \sum_{j=1}^{N} \delta(\tau - \tau_j) \ln \frac{P_\tau(n_j)}{P_\tau(n_{j-1})} \right)$$

$$= -[\ln P_{\tau_1}(n_0) - \ln P_0(n_0)] - [\ln P_{\tau_1}(n_1) - \ln P_{\tau_1}(n_0)]$$

$$\cdots - [\ln P_{\tau_N}(n_{N-1}) - \ln P_{\tau_{N-1}}(n_{N-1})] - [\ln P_{\tau_N}(n_N) - \ln P_{\tau_N}(n_{N-1})]$$

$$- [\ln P_t(n_N) - \ln P_{\tau_N}(n_N)]$$

$$= \ln P_0(n_0) - \ln P_t(n_N), \qquad (2.43)$$

$$\Delta s_{\mathrm{e}}(t) := -\int_0^t d\tau \sum_{j=1}^{N} \delta(\tau - \tau_j) \ln \frac{W_\tau(n_j, n_{j-1})}{W_\tau(n_{j-1}, n_j)} = -\sum_{j=1}^{N} \ln \frac{W_{\tau_j}(n_j, n_{j-1})}{W_{\tau_j}(n_{j-1}, n_j)}, \qquad (2.44)$$

$$\Delta s_{\mathrm{i}}(t) := \int_0^t d\tau \left(-\left. \frac{\dot{P}_\tau(n)}{P_\tau(n)} \right|_{n(\tau)} - \sum_{j=1}^{N} \delta(\tau - \tau_j) \ln \frac{P_\tau(n_j) W_\tau(n_{j-1}, n_j)}{P_\tau(n_{j-1}) W_\tau(n_j, n_{j-1})} \right)$$

$$= \Delta s(t) - \Delta s_{\mathrm{e}}(t). \qquad (2.45)$$

16

2.2.2 Derivation of the fluctuation theorems

We can now derive the fluctuation theorem in terms of the quantum master equation, using the quantum trajectory and the entropies introduced above.

We set the initial probability of the backward process and the final probability of the forward process are equal, i.e.

$$\widetilde{P}_0(n_N) = P_t(n_N). \tag{2.46}$$

If we define the following function of a trajectory $r_{\mathrm{F}}(t)$, we find that $r_{\mathrm{F}}(t)$ is equal to the entropy production $\Delta s_{\mathrm{i}}(t)$:

$$r_{\mathrm{F}}(t) \equiv \ln\frac{\mu_{\mathrm{F}}[n(\tau)]}{\mu_{\mathrm{B}}[\widetilde{n}(\widetilde{\tau})]} = \ln\frac{P_0(n_0)}{P_t(n_N)} + \sum_{j=1}^{N} \ln\frac{W_{\tau_j}(n_j, n_{j-1})}{W_{\tau_j}(n_{j-1}, n_j)}$$

$$= \Delta s(t) - \Delta s_{\mathrm{e}}(t) = \Delta s_{\mathrm{i}}(t), \tag{2.47}$$

where F stands for the forward process. For the backward process $r_{\mathrm{B}}(t)$, we define

$$r_{\mathrm{B}}(t) \equiv \ln\frac{\mu_{\mathrm{B}}[\widetilde{n}(\widetilde{\tau})]}{\mu_{\mathrm{F}}[n(\tau)]}. \tag{2.48}$$

Using the fact that the summation over all trajectories of the forward paths is equal to the summation over all trajectories of the backward paths, $\sum_{\widetilde{n}(\widetilde{\tau})} = \sum_{n(\tau)}$, we can recast the relation (2.47) in the form of the *integrated fluctuation theorem*,

$$1 = \sum_{\widetilde{n}(\widetilde{\tau})} \mu_{\mathrm{B}}[\widetilde{n}(\widetilde{\tau})] = \sum_{n(\tau)} \mu_{\mathrm{B}}[\widetilde{n}(\widetilde{\tau})] = \sum_{n(\tau)} \mu_{\mathrm{F}}[n(\tau)]e^{-\Delta s_{\mathrm{i}}(t)} =: \left\langle e^{-\Delta s_{\mathrm{i}}(t)} \right\rangle_{\mathrm{F}}. \tag{2.49}$$

Note that in the case of the integrated fluctuation theorem, it does not matter whether the backward process is hypothetical or not, because we do not refer to the backward trajectories. By Jensen's inequality $\langle e^x \rangle \geq e^{\langle x \rangle}$, we confirm $\langle \Delta s_{\mathrm{i}}(t) \rangle = \Delta S_{\mathrm{i}}(t) \geq 0$ analogously to (2.32).

The detailed fluctuation theorem can also be obtained. The probability that $r_{\mathrm{F}}(t)$ becomes equal to $\Delta S_{\mathrm{i}}(t)$ is

$$p_{\mathrm{F}}(\Delta S_{\mathrm{i}}(t)) = \langle \delta(\Delta S_{\mathrm{i}}(t) - r_{\mathrm{F}}(t)) \rangle_{\mathrm{F}}$$

$$= \sum_{n(\tau)} \mu_{\mathrm{F}}[n(\tau)]\delta(\Delta S_{\mathrm{i}}(t) - r_{\mathrm{F}}(t)); \tag{2.50}$$

then (2.47) leads to

$$p_{\mathrm{F}}(\Delta S_{\mathrm{i}}(t)) = \sum_{n(\tau)} \mu_{\mathrm{B}}[\widetilde{n}(\widetilde{\tau})]e^{r_{\mathrm{F}}(t)}\delta(\Delta S_{\mathrm{i}}(t) - r_{\mathrm{F}}(t))$$

$$= e^{\Delta S_{\mathrm{i}}(t)} \sum_{\widetilde{n}(\widetilde{\tau})} \mu_{\mathrm{B}}[\widetilde{n}(\widetilde{\tau})]\delta(\Delta S_{\mathrm{i}}(t) - r_{\mathrm{F}}(t))$$

$$=: e^{\Delta S_{\mathrm{i}}(t)}\langle \delta(\Delta S_{\mathrm{i}}(t) + r_{\mathrm{B}}(t)) \rangle_{\mathrm{B}}$$

$$= e^{\Delta S_{\mathrm{i}}(t)}p_{\mathrm{B}}(-\Delta S_{\mathrm{i}}(t)), \tag{2.51}$$

where we used $\sum_{\widetilde{n}(\widetilde{\tau})} = \sum_{n(\tau)}$ and $r_{\mathrm{B}}(t) = -r_{\mathrm{F}}(t)$ by definition. This is the most familiar form of fluctuation theorems which relates the probability of the entropy production of the forward process to the probability of the entropy production of the backward process.

2.3　Work and heat in open quantum systems

We define the work and the heat for quantum systems that are consistent with the definition of the entropy flow on a quantum trajectory, (2.30), and derive the quantum Jarzynski relation using those thermodynamic quantities. We assume that the microscopic reversibility holds in terms of the heat which we define below (see Appendix A). Because we chose the time-dependent basis to give the entropies on a quantum trajectory, the work and the heat should also be defined in the same manner.

The change of the energy along a trajectory should be the quantity that depends on the initial and the final states only, and thus we define it as

$$\Delta e_{\mathrm{S}}(t) \equiv \langle n_N|\hat{H}_{\mathrm{S}}(t)|n_N\rangle - \langle n_0|\hat{H}_{\mathrm{S}}(0)|n_0\rangle$$
$$= \sum_{j=1}^{N} \left(\langle n_j|\hat{H}_{\mathrm{S}}(\tau_j)|n_j\rangle - \langle n_{j-1}|\hat{H}_{\mathrm{S}}(\tau_{j-1})|n_{j-1}\rangle \right). \tag{2.52}$$

The heat escaped from the system to the heat bath along a trajectory should be defined as

$$\widetilde{q}_{\mathrm{S}}(t) \equiv \sum_{j=1}^{N} \left(\langle n_j|\hat{H}_{\mathrm{S}}(\tau_j)|n_j\rangle - \langle n_{j-1}|\hat{H}_{\mathrm{S}}(\tau_j)|n_{j-1}\rangle \right) =: \sum_{j=1}^{N} \widetilde{q}_{n_j,n_{j-1}}(\tau_j), \tag{2.53}$$

analogously to the heat defined for classical stochastic processes by Crooks [8]. We defined the heat as above because it should be related to the entropy flow along a trajectory $\Delta s_{\mathrm{e}}(t)$ as $\Delta s_{\mathrm{e}}(t) = -\beta \widetilde{q}_{\mathrm{S}}(t)$. If we assume that the microscopic reversibility (which Esposito and Mukamel refers to as the detailed balance) holds in terms of the heat $\widetilde{q}_{m,m'}(\tau)$, i.e.,

$$\frac{W_\tau(m',m)}{W_\tau(m,m')} = \exp\left[\beta\,\widetilde{q}_{m,m'}(\tau)\right] = \exp\left[\beta\left(\langle m_\tau|\hat{H}_{\mathrm{S}}(\tau)|m_\tau\rangle - \langle m'_\tau|\hat{H}_{\mathrm{S}}(\tau)|m'_\tau\rangle\right)\right], \tag{2.54}$$

then, using the birth-death master equation (2.16), we obtain

$$\Delta s_{\mathrm{e}}(t) \equiv -\sum_{j=1}^{N} \ln \frac{W_{\tau_j}(n_j,n_{j-1})}{W_{\tau_j}(n_{j-1},n_j)}$$
$$= -\beta \sum_{j=1}^{N} \left(\langle n_j|\hat{H}_{\mathrm{S}}(\tau_j)|n_j\rangle - \langle n_{j-1}|\hat{H}_{\mathrm{S}}(\tau_j)|n_{j-1}\rangle \right) \tag{2.55}$$
$$= -\beta\,\widetilde{q}_{\mathrm{S}}(t). \tag{2.56}$$

From the first law of thermodynamics, $\Delta e_{\mathrm{S}}(t) = \widetilde{w}_{\mathrm{S}}(t) + \widetilde{q}_{\mathrm{S}}(t)$, the work done on the system along a trajectory should be given as

$$\widetilde{w}_{\mathrm{S}}(t) = \sum_{j=1}^{N} \left(\langle n_{j-1}|\hat{H}_{\mathrm{S}}(\tau_j)|n_{j-1}\rangle - \langle n_{j-1}|\hat{H}_{\mathrm{S}}(\tau_{j-1})|n_{j-1}\rangle \right) =: \sum_{j=1}^{N} \widetilde{w}_{n_j,n_{j-1}}(\tau_j). \tag{2.57}$$

Let us consider the expectation values of these thermodynamic quantities. In the following, the way that we introduce the expectation values differs from the original

paper by Esposito and Mukamel, though the final expressions are the same. We define the expectation value of the heat as the average over the trajectories. Using the birth-death master equation (2.16), we have

$$
\begin{aligned}
\widetilde{Q}_\mathrm{S}(t) &\equiv \langle \widetilde{q}_\mathrm{S}(t) \rangle \\
&= \frac{1}{N} \sum_{j=1}^{N} \int_0^t d\tau'_j \sum_{n'_j, n'_{j-1}(n'_j \neq n'_{j-1})} P_{\tau'_j}(n'_{j-1}) W_{\tau'_j}(n'_j, n'_{j-1}) \\
&\qquad\qquad\qquad\qquad \times \left(\langle n'_j | \hat{H}_\mathrm{S}(\tau'_j) | n'_j \rangle - \langle n'_{j-1} | \hat{H}_\mathrm{S}(\tau'_j) | n'_{j-1} \rangle \right) \\
&= \frac{1}{N} \sum_{j=1}^{N} \int_0^t d\tau'_j \sum_{n'_j} \dot{P}_\tau(n'_j) \langle n'_j | \hat{H}_\mathrm{S}(\tau'_j) | n'_j \rangle \\
&= \int_0^t d\tau \sum_m \dot{P}_\tau(m) \langle m_\tau | \hat{H}_\mathrm{S}(\tau) | m_\tau \rangle.
\end{aligned}
\tag{2.58}
$$

For the expectation value of the change of the energy, we simply take the statistical average over the initial and the final states:

$$
\begin{aligned}
\Delta E_\mathrm{S}(t) = \langle \Delta e_\mathrm{S}(t) \rangle &= \sum_{n_N} P_t(n_N) \langle n_N | \hat{H}_\mathrm{S}(t) | n_N \rangle - \sum_{n_0} P_0(n_0) \langle n_0 | \hat{H}_\mathrm{S}(0) | n_0 \rangle \\
&= \langle H_\mathrm{S}(t) \rangle - \langle H_\mathrm{S}(0) \rangle.
\end{aligned}
\tag{2.59}
$$

This calculation corresponds to the average over the trajectories without any jumps.

By the first law of thermodynamics, the expectation value of the work should be given as

$$
\begin{aligned}
\widetilde{W}_\mathrm{S}(t) &= \Delta E_\mathrm{S}(t) - \widetilde{Q}_\mathrm{S}(t) \\
&= \int_0^t d\tau \sum_m \frac{d}{d\tau} \left[P_\tau(m) \langle m_\tau | \hat{H}_\mathrm{S}(\tau) | m_\tau \rangle \right] - \int_0^t d\tau \sum_m \dot{P}_\tau(m) \langle m_\tau | \hat{H}_\mathrm{S}(\tau) | m_\tau \rangle \\
&= \int_0^t d\tau \sum_m P_\tau(m) \frac{d}{d\tau} \langle m_\tau | \hat{H}_\mathrm{S}(\tau) | m_\tau \rangle.
\end{aligned}
\tag{2.60}
$$

Note that $\langle \widetilde{w}_\mathrm{S}(t) \rangle \neq \widetilde{W}_\mathrm{S}(t)$:

$$
\begin{aligned}
\langle \widetilde{w}_\mathrm{S}(t) \rangle &= \frac{1}{N} \sum_{j=1}^{N} \int_0^t d\tau'_j \sum_{n'_j, n'_{j-1}(n'_j \neq n'_{j-1})} P_{\tau'_j}(n'_{j-1}) W_{\tau'_j}(n'_j, n'_{j-1}) \\
&\qquad\qquad\qquad\qquad \times \left(\langle n'_{j-1} | \hat{H}_\mathrm{S}(\tau'_j) | n'_{j-1} \rangle - \langle n'_{j-1} | \hat{H}_\mathrm{S}(\tau'_{j-1}) | n'_{j-1} \rangle \right) \\
&\neq \frac{1}{N} \sum_{j=1}^{N} \int_0^t d\tau'_j \sum_{n'_{j-1}} P_{\tau'_j}(n'_{j-1}) \frac{d}{d\tau'_j} \langle n'_{j-1} | \hat{H}_\mathrm{S}(n'_{j-1}) | n'_{j-1} \rangle = \widetilde{W}_\mathrm{S}(t).
\end{aligned}
\tag{2.61}
$$

This comes from the fact that the change of the energy is not a trajectory-dependent

quantity:

$$\Delta E_{\mathrm{S}}(t) \neq \frac{1}{N} \sum_{j=1}^{N} \int_0^t d\tau_j' \sum_{n_j', n_{j-1}' (n_j' \neq n_{j-1}')} P_{\tau_j'}(n_{j-1}') W_{\tau_j'}(n_j', n_{j-1}')$$
$$\times \left(\langle n_j' | \hat{H}_{\mathrm{S}}(\tau_j') | n_j' \rangle - \langle n_{j-1}' | \hat{H}_{\mathrm{S}}(\tau_{j-1}') | n_{j-1}' \rangle \right). \quad (2.62)$$

Note that these thermodynamic quantities that we defined here are only quantum analogues of the discussion for the stochastic processes, and thus they are hypothetical quantities. We should examine whether they have the correct properties.

2.3.1 Quantum Jarzynski equality

Finally, we derive the Jarzynski equality in open quantum systems. We set the initial states of the forward and backward evolutions as the equilibrium state. If we assume that the coupling between the system and the bath, $\hat{H}_{\mathrm{int}}$, is weak, we have

$$P_0(n_0) = \frac{\mathrm{e}^{-\beta \langle n_0 | H_{\mathrm{S}}(0) | n_0 \rangle}}{Z(0)}, \qquad\qquad Z(0) = \sum_m \mathrm{e}^{-\beta \langle m | H_{\mathrm{S}}(0) | m \rangle}, \qquad (2.63)$$

$$P_t(n_N) = \frac{\mathrm{e}^{-\beta \langle n_N | H_{\mathrm{S}}(t) | n_N \rangle}}{Z(t)}, \qquad\qquad Z(t) = \sum_m \mathrm{e}^{-\beta \langle m | H_{\mathrm{S}}(t) | m \rangle}. \qquad (2.64)$$

Therefore, the entropy change of the system on a trajectory reads

$$\Delta s(t) = \ln \frac{P_0(n_0)}{P_t(n_N)} = \beta \big(\langle n_N | H_{\mathrm{S}}(t) | n_N \rangle - \langle n_0 | H_{\mathrm{S}}(0) | n_0 \rangle \big) + \ln \frac{Z(t)}{Z(0)}$$
$$= \beta (\Delta e_{\mathrm{S}}(t) - \Delta F(t)), \qquad (2.65)$$

where $\Delta F(t) \equiv -(\ln Z(t) - \ln Z(0))/\beta$ is the free energy difference. The entropy production is expressed as

$$\Delta s_{\mathrm{i}}(t) = \Delta s(t) - \Delta s_{\mathrm{e}}(t) = \beta \big(\Delta e_{\mathrm{S}}(t) - \Delta F(t) - \widetilde{q}_{\mathrm{S}}(t) \big)$$
$$= \beta \big(\widetilde{w}_{\mathrm{S}}(t) - \Delta F(t) \big). \qquad (2.66)$$

Substitution of (2.66) in the integrated fluctuation theorem (2.49) leads to the quantum Jarzynski equality,

$$\langle \exp \left[-\beta (\widetilde{w}_{\mathrm{S}}(t) - \Delta F(t)) \right] \rangle = 1, \qquad (2.67)$$

or

$$\langle \mathrm{e}^{-\beta \widetilde{w}_{\mathrm{S}}(t)} \rangle = \mathrm{e}^{-\beta \Delta F(t)}. \qquad (2.68)$$

Chapter 3

Fluctuation theorems, detailed balance, and microscopic reversibility in a non-Markovian quantum heat bath

The method of the birth-death master equation and the quantum trajectory in Chapter 2 gives a novel way to explore the dynamics of open quantum systems. In the present Chapter, we first generalize the discussion for the Markovian dynamics in the previous Chapter to a dynamics in a non-Markovian heat bath and derive the fluctuation theorem for it (Section 3.1). Then, we numerically investigate the properties of the birth-death master equation in the case of the spin-boson model (Section 3.2) and examine the microscopic reversibility (Section 3.3).

3.1 Generalization to the dynamics in a non-Markovian heat bath

3.1.1 Markovian and non-Markovian heat baths

We use the formalism of the *hierarchy equations of motion* [19, 30–32], which deals with the case of the dynamics of the system in a non-Markovian heat bath.

We refer to it as a Markovian heat bath if its time-scale is much less than the time-scale of the system $\tau_S = 1/\omega_0$. In this case, we obtain a time-local equation of motion for the reduced density matrix. There are two kinds of parameters that determine the time-scale of the heat bath. One is the decay rate γ of the time-correlation function of the heat bath and the other is the Matsubara frequency $\nu_k = 2\pi k/\beta\hbar$ $(k = 1, 2, \cdots)$. Hence we have $\min(\gamma, \nu_1) \gg \omega_0$ for a Markovian heat bath. In the case where the temperature of the heat bath is low, i.e. $\nu_1 \gg \omega_0$ is not satisfied, we refer to it as a non-Markovian heat bath. In this case, we cannot obtain a time-local equation of motion of the system solely in terms of the reduced density matrix even in the limit $\gamma = \infty$, unless we can apply other

kinds of approximations, e.g. the rotating-wave approximation; see the description below (B.31) in Appendix B. In this sense, using a Markovian heat bath as in Chapter 2 is not valid at low temperatures and the treatment in the present Chapter is crucial.

In the formalism of the hierarchy equations of motion, a state of the system is expressed with a set of infinite matrices in an extended space instead of a reduced density matrix. Thereby we can obtain a time-local equation of motion by taking account of the time-correlation of the heat bath as the correlations among the matrices. Then, we can readily extend the discussion in Chapter 2 to the case of a general system as long as the coupling of the system and the bath is linear, and the bath is Gaussian with the spectrum distribution of the Drude form; see Appendix B for the detail.

3.1.2 Notation and the equation of motion for the reduced density matrix

In the formalism of the hierarchy equations of motion, a state is expressed as a set of an infinite number of matrices:

$$\left\{ \hat{\rho}_{j_1,\dots,j_k,\dots}^{(n)}(\tau) \right\} = \hat{\rho}_{0,0,\dots}^{(0)}(\tau),\ \hat{\rho}_{0,0,\dots}^{(1)}(\tau),\ \hat{\rho}_{1,0,\dots}^{(1)}(\tau),\cdots, \tag{3.1}$$

$$\hat{\rho}_{0,0,\dots}^{(0)}(\tau) = \hat{\rho}(\tau), \qquad \hat{\rho}_{0,0,\dots}^{(1)}(\tau),\ \hat{\rho}_{1,0,\dots}^{(1)}(\tau),\cdots =: \{\hat{\sigma}_k(\tau)\}, \tag{3.2}$$

where $\hat{\rho}_{0,0\dots}^{(0)}(\tau)$ is the reduced density matrix in the usual sense and $\{\hat{\sigma}_k(\tau)\}$ are the set of matrices which possess the information of non-Markovian effects. These matrices follow the equation of motion (B.44) – (B.47). The matrices $\{\hat{\sigma}_k(\tau)\}$ are introduced for computational purposes only and possess no physical meaning themselves. The original time correlation of the heat bath is expressed by correlations among the auxiliary matrices. The label n indicates the nth correction with respect to the decay rate of the heat bath γ and the label $\{j_k | k = 1, 2, \dots\}$ indicates the corrections with respect to the temperature, i.e. the Matsubara frequencies ν_k. For simplicity, we denote the set of matrices as

$$\left\{ \hat{\rho}_{j_1,\dots,j_k,\dots}^{(n)}(\tau) \right\} =: |\hat{\rho}_{0,0,\dots}^{(0)}(\tau),\ \hat{\rho}_{0,0\dots}^{(1)}(\tau),\ \hat{\rho}_{1,0\dots}^{(1)}(\tau),\cdots\rangle\!\rangle =: |\hat{\rho}(\tau); \{\hat{\sigma}_k(\tau)\}\rangle\!\rangle. \tag{3.3}$$

We define its inner product as

$$\langle\!\langle \hat{\rho}(\tau); \{\hat{\sigma}_k(\tau)\} | \hat{\rho}'(\tau); \{\hat{\sigma}_k'(\tau)\} \rangle\!\rangle \equiv \mathrm{Tr}\left(\hat{\rho}^\dagger(\tau)\hat{\rho}'(\tau) \right) + \sum_{k=1}^{\infty} \mathrm{Tr}\left(\hat{\sigma}_k^\dagger(\tau)\hat{\sigma}_k'(\tau) \right). \tag{3.4}$$

The following discussion of the quantum trajectory for the hierarchy equations of motion is almost parallel to the one in Chapter 2 except that it is the dynamics with the auxiliary matrices $\{\hat{\sigma}_k(\tau)\}$.

3.1.3 The birth-death master equation for the hierarchy equations of motion

The hierarchy equations of motion can be formally expressed as

$$\frac{d}{d\tau}|\hat{\rho}(\tau); \{\hat{\sigma}_k(\tau)\}\rangle\!\rangle = \hat{\hat{\mathcal{L}}}_{\mathrm{hier}}(\tau)|\hat{\rho}(\tau); \{\hat{\sigma}_k(\tau)\}\rangle\!\rangle. \tag{3.5}$$

Let $\{|m_\tau\rangle\}$ be a basis that diagonalizes $\hat{\rho}(\tau)$. Our purpose is to extract out the equation of motion for the probability $P_\tau(m)$. Taking the inner product with $\langle\!\langle m_\tau m_\tau; \{\hat{0}\}|$ in (3.5), we have

$$\langle\!\langle m_\tau m_\tau; \{\hat{0}\}|\frac{d}{d\tau}|\hat{\rho}(\tau); \{\hat{\sigma}_k(\tau)\}\rangle\!\rangle = \langle\!\langle m_\tau m_\tau; \{\hat{0}\}|\hat{\hat{\mathcal{L}}}_{\text{hier}}(\tau)|\hat{\rho}(\tau); \{\hat{\sigma}_k(\tau)\}\rangle\!\rangle, \qquad (3.6)$$

Next, we decompose $|\hat{\rho}(\tau); \{\hat{\sigma}_k(\tau)\}\rangle\!\rangle$ into the following form:

$$\sum_m |m_\tau m_\tau; \{\hat{\sigma}_k(\tau)\}\rangle\!\rangle\langle\!\langle m_\tau m_\tau; \{\hat{0}\}|\hat{\rho}(\tau); \{\hat{\sigma}_k(\tau)\}\rangle\!\rangle$$

$$= \sum_m \left[(\langle m_\tau|\hat{\rho}(\tau)|m_\tau\rangle) |m_\tau\rangle\langle m_\tau| \otimes \prod_{k=1}^{\infty} \hat{\sigma}_k(\tau) \right]$$

$$= |\hat{\rho}(\tau); \{\hat{\sigma}_k(\tau)\}\rangle\!\rangle, \qquad (3.7)$$

where $\{\hat{0}\} = \{\hat{0}, \hat{0}, \dots\}$ are an infinite set of zero matrices in the space of the auxiliary matrices. In the first equality of (3.7), we used the relation

$$\langle\!\langle m_\tau m_\tau; \{\hat{0}\}|\hat{\rho}(\tau); \{\hat{\sigma}_k(\tau)\}\rangle\!\rangle = \text{Tr}\left(|m_\tau\rangle\langle m_\tau|\hat{\rho}(\tau)\right) + \sum_{k=1}^{\infty} \text{Tr}\left[\hat{0}\,\hat{\sigma}_k(\tau)\right] = \langle m_\tau|\hat{\rho}(\tau)|m_\tau\rangle,$$

$$(3.8)$$

according to the definition of the inner product (3.4) and in the second equality of (3.7), we used the completeness relation for the reduced density matrix ((2.10) in Chapter 2). Applying (3.7) to the right-hand side of (3.6), we have

$$\langle\!\langle m_\tau m_\tau; \{\hat{0}\}|\frac{d}{d\tau}|\hat{\rho}(\tau); \{\hat{\sigma}_k(\tau)\}\rangle\!\rangle$$

$$= \sum_{m'} \langle\!\langle m_\tau m_\tau; \{\hat{0}\}|\hat{\hat{\mathcal{L}}}_{\text{hier}}(\tau)|m'_\tau m'_\tau; \{\hat{\sigma}_k(\tau)\}\rangle\!\rangle\langle\!\langle m'_\tau m'_\tau; \{\hat{0}\}|\hat{\rho}(\tau); \{\hat{\sigma}_k(\tau)\}\rangle\!\rangle. \qquad (3.9)$$

The left-hand side of (3.9) can be also recast as

$$\langle\!\langle m_\tau m_\tau; \{\hat{0}\}|\frac{d}{d\tau}|\hat{\rho}(\tau); \{\hat{\sigma}_k(\tau)\}\rangle\!\rangle$$

$$= \text{Tr}\left(|m_\tau\rangle\langle m_\tau|\frac{d}{d\tau}\hat{\rho}(\tau)\right) + \sum_{k=1}^{\infty} \text{Tr}\left(\hat{0}\frac{d}{d\tau}\hat{\sigma}_k(\tau)\right) = \frac{d}{d\tau}\langle m_\tau|\hat{\rho}(\tau)|m_\tau\rangle$$

$$= \frac{d}{d\tau}\langle\!\langle m_\tau m_\tau; \{\hat{0}\}|\hat{\rho}(\tau); \{\hat{\sigma}_k(\tau)\}\rangle\!\rangle. \qquad (3.10)$$

Then we have

$$\frac{d}{d\tau}\langle\!\langle m_\tau m_\tau; \{\hat{0}\}|\hat{\rho}(\tau); \{\hat{\sigma}_k(\tau)\}\rangle\!\rangle$$

$$= \sum_{m'} \langle\!\langle m_\tau m_\tau; \{\hat{0}\}|\hat{\hat{\mathcal{L}}}_{\text{hier}}(\tau)|m'_\tau m'_\tau; \{\hat{\sigma}_k(\tau)\}\rangle\!\rangle\langle\!\langle m'_\tau m'_\tau; \{\hat{0}\}|\hat{\rho}(\tau); \{\hat{\sigma}_k(\tau)\}\rangle\!\rangle. \qquad (3.11)$$

Defining

$$P_\tau(m) \equiv \langle\!\langle m_\tau m_\tau; \{\hat{0}\} | \hat{\rho}(\tau); \{\hat{\sigma}_k(\tau)\} \rangle\!\rangle, \tag{3.12}$$

$$W_\tau(m, m'; \{\hat{\sigma}_k(\tau)\}) \equiv \langle\!\langle m_\tau m_\tau; \{\hat{0}\} | \hat{\tilde{\mathcal{L}}}_{\mathrm{hier}}(\tau) | m'_\tau m'_\tau; \{\hat{\sigma}_k(\tau)\} \rangle\!\rangle, \tag{3.13}$$

we can rewrite (3.11) as

$$\frac{d}{d\tau} P_\tau(m) = \sum_{m'} W_\tau(m, m'; \{\hat{\sigma}_k(\tau)\}) \, P_\tau(m'). \tag{3.14}$$

Analogously to the discussion in (2.14) in Chapter 2, by the conservation of the probability, we have

$$\sum_m W_\tau(m, m'; \{\hat{\sigma}_k(\tau)\}) = 0, \quad \text{i.e.} \qquad W_\tau(m', m'; \{\hat{\sigma}_k(\tau)\}) = - \sum_{m \neq m'} W_\tau(m, m'; \{\hat{\sigma}_k(\tau)\}). \tag{3.15}$$

We then obtain the birth-death master equation for the hierarchy equations of motion:

$$\frac{d}{d\tau} P_\tau(m) = \sum_{m'(\neq m)} \left[W_\tau(m, m'; \{\hat{\sigma}_k(\tau)\}) P_\tau(m') - W_\tau(m', m; \{\hat{\sigma}_k(\tau)\}) P_\tau(m) \right]. \tag{3.16}$$

3.1.4 The fluctuation theorem

The probabilities for the forward and backward quantum trajectories are obtained just by replacing $W_{\tau_j}(n_j, n_{j-1})$ with $W_{\tau_j}(n_j, n_{j-1}; \{\hat{\sigma}(\tau_j)\})$ in the calculation (2.20) and (2.26):

$$\mu_{\mathrm{F}}[n_{(\tau)}] = P_0(n_0) \left[\prod_{i=1}^N \exp\left(-\sum_m \int_{\tau_{i-1}}^{\tau_i} d\tau' \, W_{\tau'}(m, n_{i-1}; \{\hat{\sigma}(\tau')\}) \right) W_{\tau_j}(n_j, n_{j-1}; \{\hat{\sigma}(\tau_j)\}) \right]$$
$$\times \exp\left(-\sum_m \int_{\tau_N}^t d\tau' \, W_{\tau'}(m, n_N; \{\hat{\sigma}(\tau')\}) \right), \tag{3.17}$$

$$\mu_{\mathrm{B}}[\widetilde{n}_{(\widetilde{\tau})}] = \widetilde{P}_0(\widetilde{n}_0) \left[\prod_{i=1}^N \exp\left(-\sum_{\widetilde{m}} \int_{\widetilde{\tau}_{i-1}}^{\widetilde{\tau}_i} d\tau' \, \widetilde{W}_{\tau'}(\widetilde{m}, \widetilde{n}_{i-1}; \{\widetilde{\hat{\sigma}}(\tau')\}) \right) \widetilde{W}_{\widetilde{\tau}_j}(\widetilde{n}_j, \widetilde{n}_{j-1}; \{\widetilde{\hat{\sigma}}(\widetilde{\tau}_j)\}) \right]$$
$$\times \exp\left(-\sum_{\widetilde{m}} \int_{\widetilde{\tau}_N}^0 d\tau' \, \widetilde{W}_{\tau'}(\widetilde{m}, \widetilde{n}_N; \{\widetilde{\hat{\sigma}}(\tau')\}) \right). \tag{3.18}$$

It is important that the "transition rate" W_τ contains the auxiliary matrices $\{\hat{\sigma}_k(\tau)\}$. We can find an analogy in stochastic processes. In classical non-Markovian stochastic processes, the evolution of a probability distribution without its memory is called the "substitute dynamics" [17, 26]. In the present case, it corresponds to setting the matrices $\{\hat{\sigma}_k(t)\} = \{\hat{0}, \hat{0}, \cdots\}$. It is known that the substitute dynamics gives the correct evolution of the probability, but not the correct transition rate.

In the argument in Chapter 2, the dynamics that gives the backward process was a hypothetical one; the real time-reversed dynamics does not satisfy the relation $\widetilde{W}_{\widetilde{\tau}}(\widetilde{m}, \widetilde{m}') =$

$W_{t-\tilde{\tau}}(\widetilde{m}, \widetilde{m}')$ because the quantum master equation with the Markov approximation breaks the time reversal symmetry. In contrast, the backward process that we consider in (3.18) is truly the process of the time-reversed dynamics because the hierarchy equations of motion formally solve the total system, and does not break the time reversal symmetry. Then we have

$$\widetilde{W}_{\tilde{\tau}}(\widetilde{m}, \widetilde{m}'; \{\widetilde{\hat{\sigma}}(\widetilde{\tau})\}) = W_{t-\tilde{\tau}}(\widetilde{m}, \widetilde{m}'; \{\hat{\sigma}(t - \widetilde{\tau})\}). \tag{3.19}$$

Note that this condition states that the auxiliary matrices $\{\hat{\sigma}(\tau)\}$ also evolve backward because the dynamics of the heat bath must be also reversed. Therefore, the backward process which satisfies (3.19) also becomes a hypothetical one if we truncate the hierarchy, although it would be effectively a real time-reversed process if the the conditions (B.36) and (B.50) are satisfied.

By repeating the same argument as in Chapter 2, we can show the fluctuation theorem for the dynamics in a non-Markovian heat bath. We set the probability of the final state of the forward trajectory equal to the probability of the initial state of the backward trajectory, i.e. $\widetilde{P}_0(\widetilde{n}_0) = P_t(n_N)$, and define the entropy change $\Delta\check{s}(t)$, the entropy flow $\Delta\check{s}_{\mathrm{e}}(t)$, and the entropy production $\Delta\check{s}_{\mathrm{i}}(t)$ as

$$\Delta\check{s}(t) \equiv \ln\frac{P_0(n_0)}{P_t(n_N)}, \tag{3.20}$$

$$\Delta\check{s}_{\mathrm{e}}(t) \equiv -\sum_{j=1}^{N} \ln\frac{W_{\tau_j}(n_j, n_{j-1}; \{\hat{\sigma}(\tau_j)\})}{W_{\tau_j}(n_{j-1}, n_j; \{\hat{\sigma}(\tau_j)\})}, \tag{3.21}$$

$$\Delta\check{s}_{\mathrm{i}}(t) \equiv \Delta\check{s}(t) - \Delta\check{s}_{\mathrm{e}}(t) = \sum_{j=1}^{N} \ln\frac{P_{\tau_j}(n_j)W_{\tau_j}(n_{j-1}, n_j; \{\hat{\sigma}(\tau_j)\})}{P_{\tau_{j-1}}(n_{j-1})W_{\tau_j}(n_j, n_{j-1}; \{\hat{\sigma}(\tau_j)\})}. \tag{3.22}$$

Then $r_{\mathrm{F}}(t)$, the ratio of the probabilities for a forward trajectory and a backward trajectory reads

$$r_{\mathrm{F}}(t) \equiv \ln\frac{\mu_F[n(\tau)]}{\mu_B[\widetilde{n}(\widetilde{\tau})]} = \ln\frac{P_0(n_0)}{P_t(n_N)} - \sum_{j=1}^{N} \ln\frac{W_{\tau_j}(n_{j-1}, n_j; \{\hat{\sigma}(\tau_j)\})}{W_{\tau_j}(n_j, n_{j-1}; \{\hat{\sigma}(\tau_j)\})}$$

$$= \Delta\check{s}(t) - \Delta\check{s}_{\mathrm{e}}(t) = \Delta\check{s}_{\mathrm{i}}(t). \tag{3.23}$$

This relation leads to the integrated fluctuation theorem and the detailed fluctuation theorem:

$$\sum_{n(\tau)} \mu_{\mathrm{F}}[n(\tau)]e^{-\Delta\check{s}_{\mathrm{i}}(t)} =: \left\langle e^{-\Delta\check{s}_{\mathrm{i}}(t)}\right\rangle_{\mathrm{F}} = 1, \tag{3.24}$$

$$p_{\mathrm{F}}(\Delta\check{S}_{\mathrm{i}}(t)) = e^{\Delta\check{S}_{\mathrm{i}}(t)}p_{\mathrm{B}}(-\Delta\check{S}_{\mathrm{i}}(t)), \tag{3.25}$$

where $\Delta\check{S}_{\mathrm{i}}(t) \equiv \langle\Delta\check{s}_{\mathrm{i}}(t)\rangle$. The average $\langle\cdots\rangle_{\mathrm{F}}$ is the average with respect to each of the forward trajectories, whereas the average $\langle\cdots\rangle$ stands for the trajectory average (2.39) with the "transition rate" $W_{\tau_j}(n_j, n_{j-1}; \{\hat{\sigma}(\tau_j)\})$. Even though it is formally the same as the fluctuation theorem for the case in a Markovian heat bath, the "transition rate" W_{τ_j} contains the effect of non-Markovian properties in the auxiliary matrices $\{\hat{\sigma}(\tau_j)\}$.

Unlike other studies of the quantum master equations, our calculation starts from the exact Liouville-von Neumann dynamics of the total system and uses no approximation in principle. Therefore the theorem holds in any parameter region and the simulations that we show below are numerically exact. Our fluctuation theorem is restricted to the system linearly coupled to the Gaussian heat bath with the spectrum distribution of the Drude form. This setting is often assumed when we derive a Markovian quantum master equation microscopically.

It is crucial for a fluctuation theorem whether the quantities $\Delta \check{s}_\mathrm{i}(t)$ and $\Delta \check{s}_\mathrm{e}(t)$ that we defined above are appropriate as the entropy production and the entropy flow, respectively. As a property of the entropy production, we expect it to be zero at equilibrium, i.e.

$$\frac{P_{\tau_j}(n_j)W_{\tau_j}(n_{j-1}, n_j; \{\hat{\sigma}(\tau_j)\})}{P_{\tau_{j-1}}(n_{j-1})W_{\tau_j}(n_j, n_{j-1}; \{\hat{\sigma}(\tau_j)\})} = 1, \tag{3.26}$$

which is nothing but a detailed balance condition. Another requirement of the entropy production is that it is always non-negative. We will show below, however, that there exist some situations where we cannot define the entropy production with (3.22) because the left-hand side of (3.26) becomes negative. As a property of the entropy flow, we expect that it satisfies the following equality:

$$\Delta \check{s}_\mathrm{e}(t) = -\beta \widetilde{q}_\mathrm{S}(t), \tag{3.27}$$

or

$$\frac{W_{\tau_j}(n_{j-1}, n_j; \{\hat{\sigma}(\tau_j)\})}{W_{\tau_j}(n_j, n_{j-1}; \{\hat{\sigma}(\tau_j)\})} = \exp \left[\beta \widetilde{q}(n_j, n_{j-1}, \tau_j) \right], \tag{3.28}$$

where $\widetilde{q}_\mathrm{S}(t) := \sum_{j=1}^{N} \widetilde{q}(n_j, n_{j-1}, \tau_j)$ is the heat that flows out of the system along a trajectory as in the case of the evolution in a Markovian heat bath that is defined in (2.53). The equality (3.28) is what is called the microscopic reversibility, or the local detailed balance.

Note, however, that we can only check the consistency of the entropy flow $\Delta \check{s}_\mathrm{e}(t)$ and the heat $\widetilde{q}(n_j, n_{j-1}, \tau_j)$; while the left-hand side of (3.28) is what we need to examine from the behavior of the birth-death master equation, the heat $\widetilde{q}(n_j, n_{j-1}, \tau_j)$ on the right-hand side is also a hypothetical quantity as we mentioned in Section 2.3.

3.2 Properties of the birth-death master equation

In the present Section, we numerically investigate the properties of the birth-death master equation by simulating the transient dynamics after the system is brought out of the equilibrium state by energy measurement. Specifically, we investigate the deviation from the detailed balance after the energy measurement. It is essential to consider an open system, since we can easily show that the "transition rate" $W_\tau(m, m')$ becomes zero for an isolated system; see Appendix C.

3.2.1 The model for an open quantum system: the spin-boson model

The system that we will consider is the spin-boson model given by the following Hamiltonian:

$$\hat{H} = \hat{H}_{\mathrm{S}}(\hat{\psi}, \hat{\psi}^\dagger) + \hat{H}_{\mathrm{B}}(\hat{b}_\alpha, \hat{b}_\alpha^\dagger) + \hat{H}_{\mathrm{int}}(\hat{\psi}, \hat{\psi}^\dagger, \hat{b}_\alpha, \hat{b}_\alpha^\dagger) + \hat{H}_{\mathrm{counter}}(\hat{\psi}, \hat{\psi}^\dagger), \tag{3.29}$$

$$H_{\mathrm{S}}(\hat{\psi}, \hat{\psi}^\dagger) = \frac{\hbar\omega_0}{2}\hat{\sigma}_z = \frac{\hbar\omega_0}{2}(\hat{\psi}^\dagger\hat{\psi} - \hat{\psi}\hat{\psi}^\dagger), \tag{3.30}$$

$$\hat{H}_{\mathrm{B}}(\hat{b}_\alpha, \hat{b}_\alpha^\dagger) = \sum_\alpha \hbar\omega_\alpha \hat{b}_\alpha^\dagger \hat{b}_\alpha, \tag{3.31}$$

$$\hat{H}_{\mathrm{int}}(\hat{\psi}, \hat{\psi}^\dagger, \hat{b}_\alpha, \hat{b}_\alpha^\dagger) = V(\hat{\psi}, \hat{\psi}^\dagger)\sum_\alpha \widetilde{c}_\alpha \hat{x}_\alpha =: V(\hat{\psi}, \hat{\psi}^\dagger)\sum_\alpha c_\alpha(\hat{b}_\alpha + \hat{b}_\alpha^\dagger), \tag{3.32}$$

$$V(\hat{\psi}, \hat{\psi}^\dagger) = V_1\hat{\sigma}_x + V_2\hat{\sigma}_z = V_1(\hat{\psi}^\dagger + \hat{\psi}) + V_2(\hat{\psi}^\dagger\hat{\psi} - \hat{\psi}\hat{\psi}^\dagger), \tag{3.33}$$

$$\hat{H}_{\mathrm{counter}}(\hat{\psi}, \hat{\psi}^\dagger) = \sum_\alpha \frac{c_\alpha^2 V(\hat{\psi}, \hat{\psi}^\dagger)^2}{2m_\alpha\omega_\alpha^2}. \tag{3.34}$$

The operators $\hat{\sigma}_x$ and $\hat{\sigma}_z$ are the Pauli matrices. The system Hamiltonian $\hat{H}_{\mathrm{S}}(\hat{\psi}, \hat{\psi}^\dagger)$ is the two-level system with its energy difference $\hbar\omega_0$. The heat-bath Hamiltonian $\hat{H}_{\mathrm{B}}(\hat{b}_\alpha, \hat{b}_\alpha^\dagger)$ consists of the harmonic oscillators of many modes. Each mode is labeled by α, and its distribution is of the Drude form; see (B.26) in Appendix B. We omitted the ground-state energy of the harmonic oscillators. The interaction between the system and the heat bath, $\hat{H}_{\mathrm{int}}(\hat{\psi}, \hat{\psi}^\dagger, \hat{b}_\alpha, \hat{b}_\alpha^\dagger)$, is linear in $\hat{x}_\alpha$, and $\widetilde{c}_\alpha = c_\alpha\sqrt{2m_\alpha\omega_\alpha/\hbar}$ represents the coupling strength. We added a counter term $\hat{H}_{\mathrm{counter}}(\hat{\psi}, \hat{\psi}^\dagger)$ to the system Hamiltonian in order to maintain the translation invariance of the system with respect to the heat bath [4, 34]. The total Hamiltonian can be recast as

$$\hat{H} = \frac{\hbar\omega_0}{2}(\hat{\psi}^\dagger\hat{\psi} - \hat{\psi}\hat{\psi}^\dagger) + \sum_\alpha \left[\frac{\hat{p}_\alpha^2}{2m_\alpha} + \frac{1}{2}m_\alpha\omega_\alpha^2 \left(\hat{x} - \frac{c_\alpha V(\hat{\psi}, \hat{\psi}^\dagger)}{m_\alpha\omega_\alpha^2} \right)^2 \right]. \tag{3.35}$$

3.2.2 Thermalization after the energy measurement

General procedure and definitions

We prepare the initial state of the reduced density matrix as

$$\hat{\rho}_{\mathrm{pre}} = \begin{pmatrix} \mathrm{e}^{-\frac{1}{2}\beta\hbar\omega_0} & 0 \\ 0 & \mathrm{e}^{\frac{1}{2}\beta\hbar\omega_0} \end{pmatrix}. \tag{3.36}$$

We let the total system evolve to thermalize without any external fields applied to the system. As long as the coupling between the system and the bath contains a non-vanishing term of V_1, the two-level system exchanges the energy with the bath and relax to a stationary state. Since we are not perturbing the total system with any external fields, we take this stationary state as the equilibrium state. Note that the equilibrium state of the two-level system differs from the canonical state in general; the total system should be in the canonical state at thermal equilibrium, the reduced system is not. After the

thermalization, we measure the energy of the two-level system by projection at time $\tau = 0$ and consider the case where the two-level system is at the ground state. Then we observe the dynamics of the two-level system until it thermalizes again.

The quantity that we observe is the detailed balance condition:

$$\frac{W_\tau(a, b; \{\hat{\sigma}_\tau\})}{W_\tau(b, a; \{\hat{\sigma}_\tau\})} = \frac{\langle a|\hat{\rho}(\tau)|a\rangle}{\langle b|\hat{\rho}(\tau)|b\rangle}, \tag{3.37}$$

where $\{|a\rangle, |b\rangle\}$ is the basis that diagonalizes the reduced density matrix at time τ. We denote the ratio of the "transition rate" between the states a and b (the left-hand side of (3.37)) as

$$\mathrm{DB_L}(\tau) := \frac{W_\tau(a, b; \{\hat{\sigma}_\tau\})}{W_\tau(b, a; \{\hat{\sigma}_\tau\})} \tag{3.38}$$

and the ratio of the probability of the state at time τ (the right-hand side of (3.37)) as

$$\mathrm{DB_R}(\tau) := \frac{\langle a|\hat{\rho}(\tau)|a\rangle}{\langle b|\hat{\rho}(\tau)|b\rangle} = \frac{P_\tau(a)}{P_\tau(b)}. \tag{3.39}$$

We simulate the time evolution of the ratio $\mathrm{DB_L}(\tau)/\mathrm{DB_R}(\tau)$.

In numerical simulation of the hierarchy equations of motion, the set of parameters (N, K) in (B.50) and (B.36) determines the accuracy of the calculation; see Appendix B for the detail. As we take the values of (N, K) larger, the physical quantities converge to a certain value which is numerically exact. We set $\hbar = 1$ below.

Types of the system-bath coupling

We examine the case of σ_x-coupling (i.e. $V_1 = 1$ and $V_2 = 0$) as well as the case of $(\sigma_x + \sigma_z)$-coupling (i.e. $V_1 = V_2 = 1$) to the bath. Figures 3.1a and 3.2a show the time evolution of the ratio $\mathrm{DB_L}(\tau)/\mathrm{DB_R}(\tau)$ for the parameter region where the the Born-Markov approximation and the rotating-wave approximation are relatively appropriate in the case of σ_x-coupling and $(\sigma_x + \sigma_z)$-coupling, respectively.

For the case of σ_x-coupling, the bases are time-independent because no off-diagonal element comes out if the prepared state before the thermalization is diagonal. We can understand this by (B.10) and (B.41) or (B.20) in the Feynman-Vernon theory. Because the coupling is linear in the bath coordinate and the bath is Gaussian, the transition always occurs in even orders of σ_x, and thus it causes no off-diagonal elements. In contrast, the case of the $(\sigma_x + \sigma_z)$-coupling is the one where the basis can be time-dependent. The non-monotonic evolution of $\mathrm{DB_L}(\tau)/\mathrm{DB_R}(\tau)$ in Fig. 3.2a is due to the time evolution of the basis.

We would expect that the Born-Markov approximation and the rotating-wave approximation are appropriate in this region. The deviation from the detailed balance, however, changes drastically as we include more temperature corrections of the hierarchy equations of motion, and thus we conclude that they are still in the non-Markovian region.
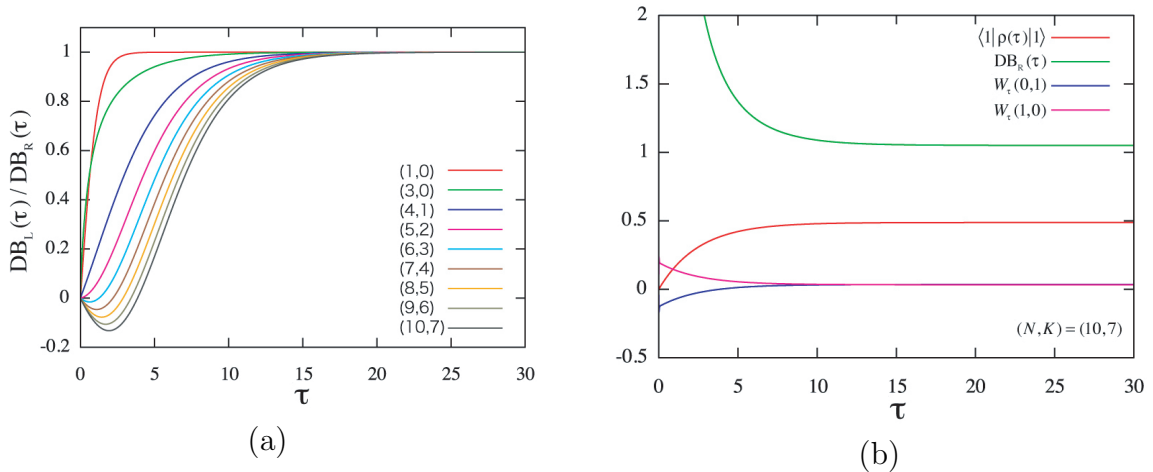
28

Figure 3.1: (a) The evolutions of the ratio $DB_L(\tau)/DB_R(\tau)$ in the case of σ_x-coupling after the energy measurement. The parameter values are $\zeta = 0.005\omega_0$, $\gamma = 100\omega_0$, $\beta = 0.05\omega_0$, the case where we expect the Born-Markov approximation and the rotating-wave approximation to be relatively appropriate. The time step is 10^{-4} in the simulation time. The line $(N, K) = (1, 0)$ corresponds to the case where the heat bath is approximated as Markovian, i.e. $\gamma \to \infty$ and $\beta \to 0$, as assumed in Ref. [5]. The line $(N, K) = (3, 0)$ indicates the case where no corrections with respect to temperature are taken into account. The line converges to the case where an infinite number of auxiliary matrices are taken into account, i.e. the complete correction. (b) The relaxation of the excited-state probability of the system (red line), $DB_R(\tau)$ (green line), the relaxation of the "transition rates" $W_\tau(0, 1)[1/\tau]$ (blue line) and $W_\tau(1, 0)[1/\tau]$ (pink line) in the case of σ_x-coupling. The parameter values are the same as in Fig. 3.1a.

Positivity of the "transition rate"

In the case of the Markovian quantum master equation such as the quantum optical master equation, we can prove that the "transition rate" $W_\tau(m, m')$ is always positive (Appendix D). If we apply the high-temperature approximation to the hierarchy equations of motion, i.e. neglect all the auxiliary matrices with respect to the temperature correction, by putting $K = 0$ in (B.36), we obtain the positive values for $W_\tau(m, m')$ in the region of Fig. 3.2a (the red line). As we can see, however, from the result of the simulation, $W_\tau(m, m')$ can be negative (i.e. $DB_L(\tau)/DB_R(\tau) < 0$) if we include the temperature corrections. Figures 3.3 and 3.4 show the results for the regions where the applicability of the rotating-wave approximation is doubtful. In the case of Fig. 3.3, $W_\tau(m, m')$ gets negative even when we do not include the temperature corrections. Hence we cannot always regard $W_\tau(m, m')$ as the transition rate of the classical birth-death master equation. More importantly, it implies that the entropy production (3.22) can be ill-defined because the argument of the logarithm becomes negative.

Relaxation time of the "transition rate"

We would naively expect that the time for the relaxation of the detailed balance is the same as the relaxation time of the reduced density matrix and the relaxation time of
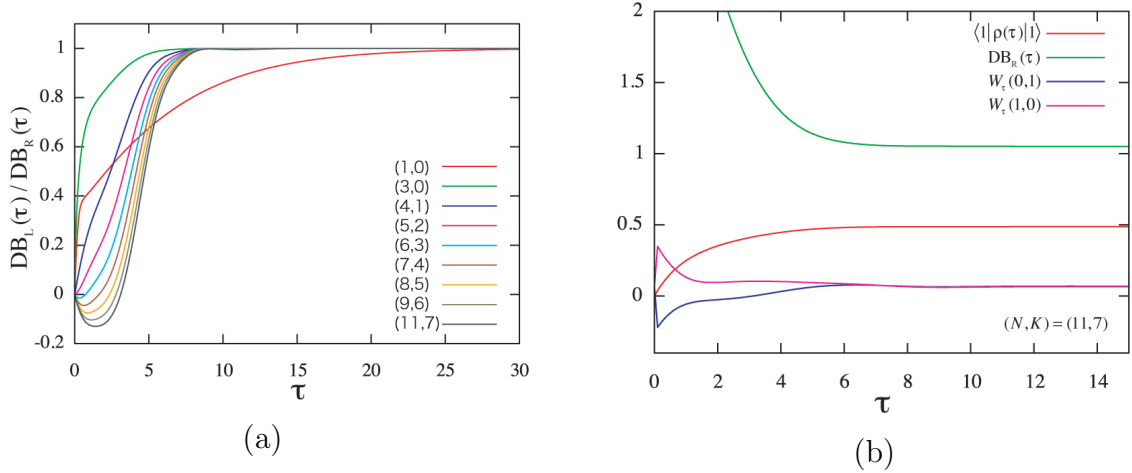
Figure 3.2: (a) The evolutions of the ratio $\mathrm{DB_L}(\tau)/\mathrm{DB_R}(\tau)$ in the case of $(\sigma_x + \sigma_z)$-coupling after the energy measurement. The parameter values are $\zeta = 0.001\omega_0$, $\gamma = 100\omega_0$, $\beta = 0.05\omega_0$, the case where we expect the Born-Markov approximation and the rotating-wave approximation to be relatively appropriate. The time step is 10^{-4} in the simulation time. The line $(N, K) = (1, 0)$ corresponds to the case where the heat bath is approximated as Markovian [5]. The line $(N, K) = (3, 0)$ indicates the case where no corrections with respect to temperature are taken into account. The line converges to the case where infinite number of auxiliary matrices are taken into account, i.e. the complete correction. (b) The relaxation of the excited-state probability of the system (red line), $\mathrm{DB_R}(\tau)$ (green line), the relaxation of the "transition rates" $W_\tau(0, 1)[1/\tau]$ (blue line) and $W_\tau(1, 0)[1/\tau]$ (pink line) in the case of σ_x-coupling. The parameter values are the same as in Fig. 3.2a.

the "transition rates." It is indeed true for the regions of Figs. 3.1 and 3.2. They do not, however, coincide in other parameter regions. Figures 3.3a and 3.3b show that the relaxation of the "transition rates" take shorter time than the relaxation of the detailed balance. Figures 3.4a and 3.4b show that the relaxation of the "transition rates" take longer time than the relaxation of the detailed balance.

Detailed balance in equilibrium

All the results of the simulations show that (3.37) holds whenever the system is in the equilibrium state. The detailed balance is a sufficient condition, but not a necessary condition for the equilibrium state, and is usually discussed in the Markovian region. Therefore, this is a highly nontrivial result; it means that the entropy production that we defined in (3.22) vanishes for infinitely slow processes.
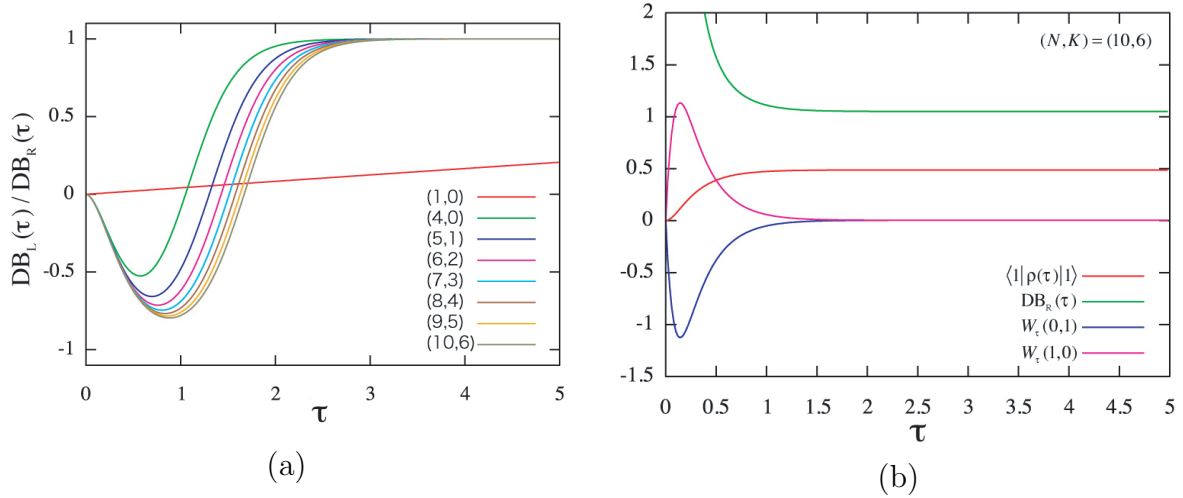
Figure 3.3: The same plots as in Fig. 3.1, but with the parameters $\zeta = 0.05\omega_0$, $\gamma = 10\omega_0$, $\beta = 0.05\omega_0$, the case where the rotating-wave approximation is doubtful.
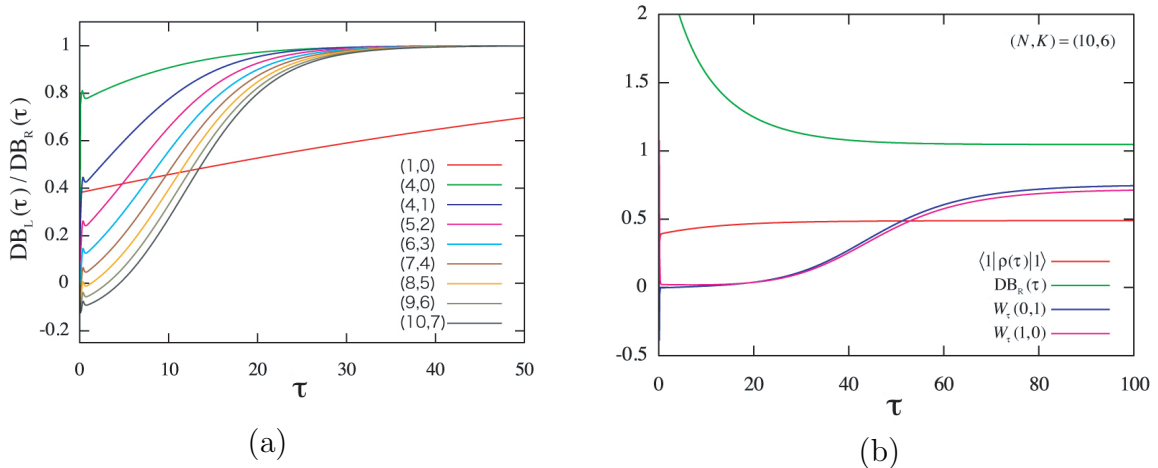

Figure 3.4: The same plots as in Fig. 3.2, but with the parameters $\zeta = 0.1\omega_0$, $\gamma = 100\omega_0$, $\beta = 0.05\omega_0$, the case where the rotating-wave approximation is doubtful.

3.3 Microscopic reversibility: Numerically exact study with the hierarchy equations of motion

The energy measurement of the previous Section was suitable to see the non-equilibrium behavior, but it is difficult to investigate the non-Markovian behavior numerically because the convergence of the hierarchy equations of motion gets extremely slow.

We then consider the following procedure; we prepare the total system in the thermal equilibrium state at time $\tau = 0$, as we did for the transient dynamics, and drive the two-level system by a sinusoidal external field for $\tau \geq 0$. In other words, we add to the Hamiltonian of the total system (3.29), the Hamiltonian of the external field $\hat{H}_{\text{ext}}(\hat{\psi}, \hat{\psi}^\dagger, t)$

$$\hat{H}_{\text{ext}}(\hat{\psi}, \hat{\psi}^\dagger, \tau) = h(\tau)\hat{\sigma}_z = h(\tau)(\hat{\psi}^\dagger\hat{\psi} - \hat{\psi}\hat{\psi}^\dagger) \tag{3.40}$$

with

$$h(\tau) = A\sin(\omega_{\text{ext}}\,\tau). \tag{3.41}$$

Therefore, the system does not go to equilibrium but to a stationary state at best.

In the present Section, we compare the ratio of the "transition rates" $\mathrm{DB}_{\mathrm{L}}(\tau)$ in (3.38) with the following three quantities. First, we compare it with

$$\mathrm{DB}_{\mathrm{R}}^{(\mathrm{eq})}(h(\tau)) := \frac{\langle a'|\hat{\rho}^{\mathrm{eq}}(h(\tau))|a'\rangle}{\langle b'|\hat{\rho}^{\mathrm{eq}}(h(\tau))|b'\rangle}, \tag{3.42}$$

where $\{|a'\rangle, |b'\rangle\}$ is the basis that diagonalizes the equilibrium reduced density matrix $\hat{\rho}^{\mathrm{eq}}(h(\tau))$. Although $\mathrm{DB}_{\mathrm{R}}^{(\mathrm{eq})}(h(\tau))$ looks similar to $\mathrm{DB}_{\mathrm{R}}(\tau)$ in the previous Section, we calculate the ratio of the equilibrium probability with the parameter $h(\tau)$, the fixed value of the external parameter at time τ. When the system is at a quasi-equilibrium state during the evolution, it should satisfy the detailed balance $\mathrm{DB}_{\mathrm{L}}(\tau) = \mathrm{DB}_{\mathrm{R}}^{(\mathrm{eq})}(h(\tau))$ according to the result in Section 3.2.2. Therefore, we can regard that the difference between $\mathrm{DB}_{\mathrm{L}}(\tau)$ and $\mathrm{DB}_{\mathrm{R}}^{(\mathrm{eq})}(h(\tau))$ as an indicator of how close the system is to the thermal equilibrium.

The second quantity that we compare with $\mathrm{DB}_{\mathrm{L}}(\tau)$ is $\exp[-\beta\widetilde{q}(b, a, \tau)]$. The equality $\mathrm{DB}_{\mathrm{L}}(\tau) = \exp[-\beta\widetilde{q}(b, a, \tau)]$ means the microscopic reversibility, from which we can conclude that the definition of $\Delta\check{s}_{\mathrm{e}}(t)$ in (3.21) is correct as the entropy flow, and the definition of $\widetilde{q}(b, a, \tau)$ is also correct as the heat that flows out of the system along a trajectory. If the quantum master equation is expressed as an equation of a quantum dynamical semi-group, and the basis that maps the evolution of the reduced density matrix to the quantum trajectory is time independent, then the "transition rate" $W_\tau(m, m') = \langle\!\langle m, m|\hat{\hat{\mathcal{K}}}(\tau)|m', m'\rangle\!\rangle$ and the heat $\widetilde{q}(b, a, \tau)$ are completely determined by the control parameter of the Hamiltonian of the system, i.e., independent of the state itself. Therefore, under the above assumptions, the microscopic reversibility is always satisfied as long as it is satisfied at equilibrium no matter what protocol we choose. (See Appendix D for the case of the quantum optical master equation.)

The third quantity that we compare with $\mathrm{DB}_{\mathrm{L}}(\tau)$ is $\mathrm{DB}_{\mathrm{R}}(\tau)$, the right-hand side of the detailed balance as we defined in (3.39). The equality $\mathrm{DB}_{\mathrm{L}}(\tau) = \mathrm{DB}_{\mathrm{R}}(\tau)$ means that the detailed balance is satisfied in the non-equilibrium state. Note that one cannot expect the detailed balance to hold out of equilibrium in general.

Among these four quantities that we compare, $\mathrm{DB}_{\mathrm{L}}(\tau)$, $\mathrm{DB}_{\mathrm{R}}^{(\mathrm{eq})}(h(\tau))$, and $\mathrm{DB}_{\mathrm{R}}(\tau)$ are the quantities of the birth-death master equation and $\exp[-\beta\widetilde{q}(b, a, \tau)]$ is the thermodynamic quantity which is suggested by Esposito and Mukamel.

3.3.1   Numerical results

We first consider the case of the $(\sigma_x + \sigma_z)$-coupling to the bath and the parameter region where the Born-Markov approximation and the rotating-wave approximation do not work at all. Although the order of the relaxation time of the reduced density matrix is $\tau_R \sim \mathcal{O}(1)$ (see Figs. 3.5a and 3.5b), because of the difficulty of the numerical simulation of the states that are far from equilibrium, we set the frequency of the external field $\omega_{\mathrm{ext}} \sim \mathcal{O}(10^{-3})$. Thus, we expect that the system might be in a quasi-equilibrium state all the time. Nevertheless, Fig. 3.6 indicates that the deviation of $\mathrm{DB}_{\mathrm{R}}^{(\mathrm{eq})}(h(\tau))$ and $\mathrm{DB}_{\mathrm{L}}(\tau)$ is

the same order as the amplitude of $\mathrm{DB}_{\mathrm{R}}^{(\mathrm{eq})}(h(\tau))$ and thus the system is out of equilibrium significantly. In the present case, $\exp[-\beta \widetilde{q}(b, a, \tau)]$ largely differs from $\mathrm{DB}_{\mathrm{L}}(\tau)$, and thus the microscopic reversibility does not hold in our sense.

In the case of energy measurements, the detailed balance was largely broken while the system is transient. It is interesting that the deviation of $\mathrm{DB}_{\mathrm{R}}(\tau)$ from $\mathrm{DB}_{\mathrm{L}}(\tau)$ is much smaller than that of $\mathrm{DB}_{\mathrm{R}}^{(\mathrm{eq})}(h(\tau))$; even though the system is not in the quasi-equilibrium state, the detailed balance is almost satisfied.

Let us next consider the same driving protocol as the above case in Fig. 3.6 under the parameter region where the Born-Markov approximation and the rotating-wave approximation are relatively appropriate. The result (Fig. 3.7) shows that $\mathrm{DB}_{\mathrm{L}}(\tau) \simeq \mathrm{DB}_{\mathrm{R}}^{(\mathrm{eq})}(h(\tau))$, so that the system is in a quasi-equilibrium state. Figure 3.7 indicates that the break of the microscopic reversibility gets smaller than the case of Fig. 3.6, and thus the definitions of the heat $\widetilde{q}(b, a, \tau)$ and the entropy flow $\Delta \check{s}_{\mathrm{e}}(t)$ become more appropriate. The state almost satisfies the detailed balance as well as in Fig. 3.6.
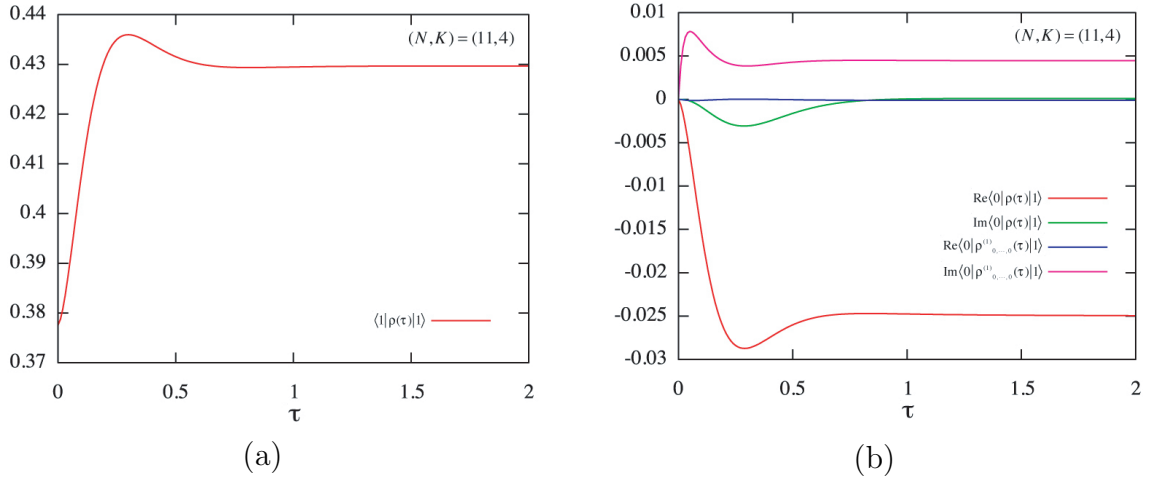

Figure 3.5: (a) The relaxation of the element of the density matrix $\langle 1|\hat{\rho}(\tau)|1\rangle$ to the thermal equilibrium state from the prepared state $\hat{\rho}_{\mathrm{pre}}$ when no external field is applied, where $|1\rangle = (1,0)^T$ and $|0\rangle = (0,1)^T$. It shows that the relaxation time τ_R is $\mathcal{O}(1)$ in the simulation time. The time step is 10^{-4} in the simulation time. (b) The relaxation of the element of the density matrix $\langle 0|\hat{\rho}(\tau)|1\rangle$ and $\langle 0|\hat{\rho}_{0,\ldots,0}^{(1)}(\tau)|1\rangle$ to the thermal equilibrium state from the prepared state $\hat{\rho}_{\mathrm{pre}}$ when no external field is applied. Their relaxation time are also $\mathcal{O}(1)$ in the simulation time.

3.4   Protocols and the non-Markovianity

The dynamics of the local system presumably becomes more non-Markovian for the heat bath with a lower temperature and a longer correlation time. Then, how does *the protocol* of the dynamics affect its non-Markovianity? In order to discuss the effect, let us consider the following three situations of the energy measurement:

(i) The two-level system is in the isolated equilibrium state when it is measured at $\tau = 0$, and is then dumped into the heat bath which is in equilibirum.
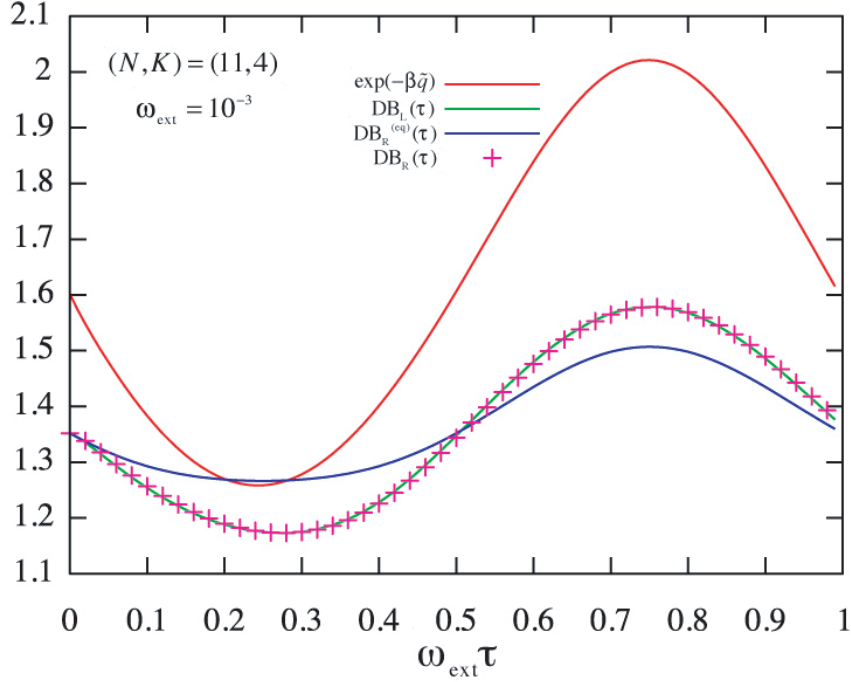
Figure 3.6: The time evolution of $\exp[-\beta\widetilde{q}(b,a,\tau)]$ (red line), $\mathrm{DB_L}(\tau)$ (green line), $\mathrm{DB_R^{(eq)}}(h(\tau))$ (blue line), $\mathrm{DB_R}(\tau)$ (pink points) for $A = 0.25\omega_0$ and $\omega_{\mathrm{ext}} = 10^{-3}$. The time step is 10^{-4} in the simulation time. The horizontal axis is scaled as $\omega_{\mathrm{ext}}\tau$. The parameter values are $\zeta = \omega_0$, $\gamma = 5\omega_0$, and $\beta = 0.5\omega_0$, the case where the Born-Markov approximation and the rotating-wave approximation are inappropriate.

(ii) The two-level system is in the equilibrium state with the heat bath when it is measured at $\tau = 0$, and is then thermalized. (The same procedure as in Section 3.2.2)

(iii) The two-level system is driven by the sinusoidal external field in the heat bath for $t = 2\pi/\omega_{\mathrm{ext}}$ as in Section 3.3. Then we measure the two-level system at $\tau = 0$, and let it thermalize.

Note that the projection by the measurement acts only on the reduced density matrix; the auxiliary matrices are not affected. If the dynamics is Markovian, these three would behave exactly the same. In the representation of the density matrix of the total system, the difference of the auxiliary matrices would appear as a slight deviation of the state of the heat bath from the equilibrium state. However, this slight deviation for the heat bath could be significant for the two-level system. Therefore, these three can behave differently depending on the history before the measurement.

Since we set the initial state of the total system to be a direct product of the canonical states of the local system and the heat bath in the Feynman-Vernon theory, the situation of (i) can be achieved by setting zero matrices for the auxiliary matrices at $\tau = 0$. For (ii) and (iii), we have nonzero matrices for the auxiliary matrices.
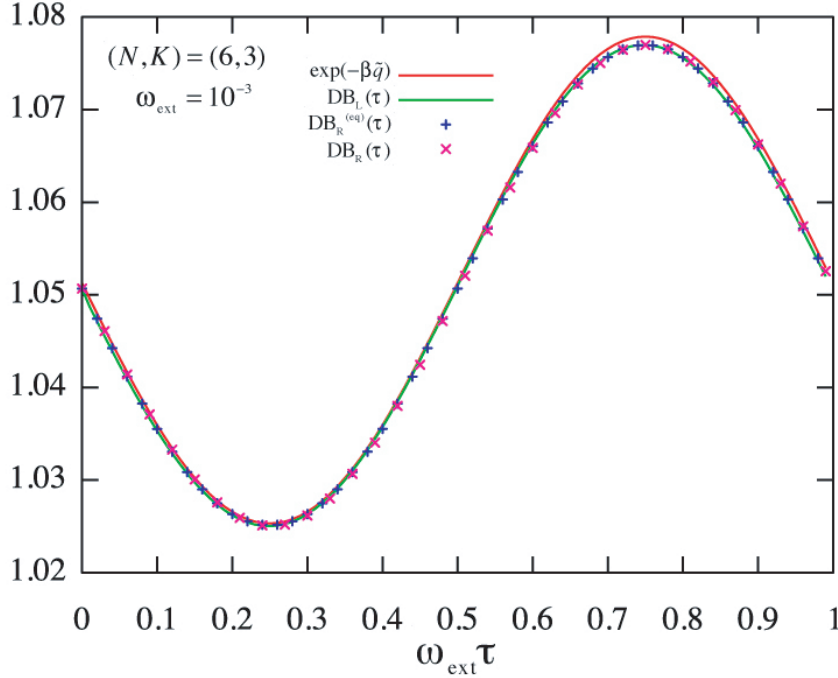
Figure 3.7: The time evolution of $\exp[-\beta\widetilde{q}(b,a,\tau)]$ (red line), $\mathrm{DB_L}(\tau)$ (green line), $\mathrm{DB_R^{(eq)}}(h(\tau))$ (blue points), $\mathrm{DB_R}(\tau)$ (pink points) for $A = 0.25\omega_0$ and $\omega_{\mathrm{ext}} = 10^{-3}$. The time step is 10^{-3} in the simulation time. The horizontal axis is scaled as $\omega_{\mathrm{ext}}\tau$. The parameter values are $\zeta = 0.01\omega_0$, $\gamma = 100\omega_0$, and $\beta = 0.05\omega_0$, the case where the Born-Markov approximation and the rotating-wave approximation are appropriate.

The result of the simulation for the evolution of the ratio $\mathrm{DB_L}(\tau)/\mathrm{DB_R}(\tau)$ is Fig. E.1(a), and that of an element of the reduced density matrix is Fig. E.1(b). They show that the three situations do not cause a drastic difference in spite of the global change of the system and the correction of the hierarchy equations of motion. The difference between (i) and (ii) is even negligible, and thus we can regard that the memory of the equilibrium state is wiped out by the measurement. We obtained the result of (ii) very close to (i) not because the auxiliary matrices are extremely small. Some elements of the auxiliary matrices of (ii) can be larger than (iii).

3.5   Conclusion

We found that the fluctuation theorems for the Markovian quantum master equation can be formally generalized to the case of the master equation in a non-Markovian heat bath. Since these fluctuation theorems are based on the analogy with the classical stochastic processes, we numerically investigated the properties of the dynamics on the quantum trajectory in the case of a system linearly coupled to a Gaussian heat bath with the spectrum distribution of the Drude form.

As the most fundamental property, we found that the detailed balance holds in equilibrium even in the case where the dynamics of the system cannot be regarded as Markovian.
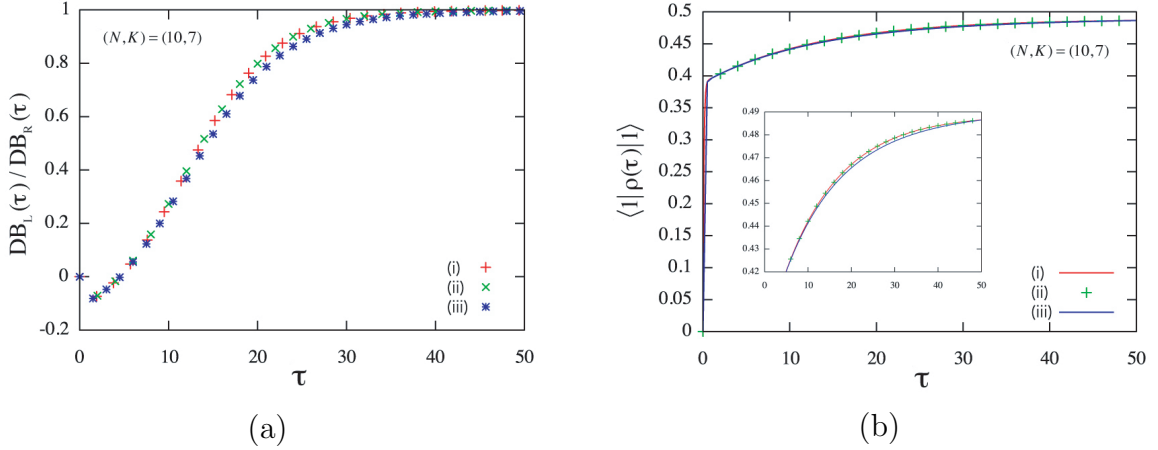
Figure 3.8: (a) The evolutions of the ratio $\mathrm{DB_L}(\tau)/\mathrm{DB_R}(\tau)$ in the case of $(\sigma_x+\sigma_z)$-coupling after the energy measurement with the procedures (i), (ii), and (iii). The parameter values are the same as in Fig. 3.4. We set $(N,K)=(10,7)$. The time step is 10^{-4} in the simulation time. (b) The evolutions of $\langle 1|\hat{\rho}(\tau)|1\rangle$ after the measurement with the same setting as (a).

From the transient dynamics after the energy measurement, we found the following:

- The "transition rate" on the quantum trajectory can be negative, and thus we cannot regard it as the transition rate in the sense of the classical stochastic processes. In this case, the entropy production (3.22) becomes ill-defined.

- The relaxation time of the "transition rates" does not always coincide with the relaxation time of the detailed balance or of the reduced density matrix.

- The memory that the two-level system has been in equilibrium state before the measurement is wiped off when we follow the thermalization after the measurement.

From the dynamics of the system that is driven by a sinusoidal external field in the parameter region which is out of the Markovian limit, we found a case where the microscopic reversibility does not hold. Assuming that the definition of the entropy flow $\Delta \check{s}_\mathrm{e}(t)$ is correct, we can interpret this result as follows; the microscopic reversibility may or may not be satisfied, but the definition of the heat $\widetilde{q}(b,a,\tau)$ is inappropriate in the region where the Born-Markov approximation and the rotating-wave approximation do not work at all. Other possibilities are readily denied. For instance, we cannot imagine the situation where the definition of the heat $\widetilde{q}(b,a,\tau)$ and the entropy flow $\Delta \check{s}_\mathrm{e}(t)$ are both correct, but the microscopic reversibility is simply broken, since the microscopic reversibility directly means the relation $\dot{\check{s}}_\mathrm{e}(t) = -\beta \widetilde{q}(b,a,\tau)$ under the present definitions. If the definition of the entropy flow $\Delta \check{s}_\mathrm{e}(t)$ is inappropriate, there is no point to investigate the microscopic reversibility, and the fluctuation theorems that we considered here lose the physical meaning. Therefore we conclude that the heat $\widetilde{q}(b,a,\tau)$ that we defined above do not have the properties that they suppose to have in general. Only in the Markovian limit, they might be the correct definitions as the thermodynamic quantities.

It is difficult to investigate a state very far from equilibrium numerically, because we require a large set of (N,K) in order to make the result converge. Hence, we need a

more efficient methodology to explore the properties of the dynamics on the quantum trajectory beyond the parameter region that we computed here.

Appendix A

Microscopic reversibility

Let us consider a classical system in a reservoir and suppose that the dynamics of the system is given as a Markovian stochastic process, so that the system possesses no memory of its past. The system is driven by an external field according to a certain protocol with the control parameter $\lambda(\tau)$. We refer to the transition rate of a physical state jumping from m to m' during $[\tau, \tau + \delta\tau]$ as $W_\tau(m, m'; \delta\tau)$.

The microscopic reversibility states that the transition rates $W_\tau(m, m'; \delta\tau)$ and $W_\tau(m', m; \delta\tau)$ are related by

$$\frac{W_\tau(m, m'; \delta\tau)}{W_\tau(m', m; \delta\tau)} = \mathrm{e}^{-\beta q(m', m, \tau; \delta\tau)}, \qquad (A.1)$$

where $q(m', m, \tau; \delta\tau)$ is the heat that flows out of the system to the reservoir during the transition from m to m' during $[\tau, \tau + \delta\tau]$. In terms of the quantities of the system, the heat is given as the change of the energy of the system when the transition has occurred while the control parameter $\lambda(\tau)$ is fixed. If we denote the energy of the state m with the control parameter $\lambda(\tau)$ as $E_m(\lambda(\tau))$, the heat $q(m', m, \tau; \delta\tau)$ should be given as

$$q(m', m, \tau; \delta\tau) \equiv E_{m'}(\lambda(\tau)) - E_m(\lambda(\tau)). \qquad (A.2)$$

On the other hand, if we define the work done on the system as the change of the energy of the system when the control parameter has developed from $\lambda(\tau)$ to $\lambda(\tau + \delta\tau)$ while the state is fixed at m', i.e.

$$w(m', m, \tau; \delta\tau) \equiv E_{m'}(\lambda(\tau + \delta\tau)) - E_{m'}(\lambda(\tau)), \qquad (A.3)$$

then the first law of thermodynamics is satisfied for an interval $\delta\tau$:

$$\Delta e(m', m, \tau; \delta\tau) \equiv E_{m'}(\lambda(\tau + \delta\tau)) - E_m(\lambda(\tau)) = w(m', m, \tau; \delta\tau) + q(m', m, \tau; \delta\tau). \qquad (A.4)$$

The relation (A.1) is called by different names; some people call it the microscopic reversibility and others call it the detailed balance. We use the name the microscopic reversibility throughout the present Thesis. The relation (A.1) is anyway often assumed, or given as the rule of a toy model of a stochastic process.

Appendix B

Hierarchy equations of motion

In this Appendix, we review the formulation of the hierarchy equations of motion. We first review the Feynman-Vernon theory, on which the method of the hierarchy equations of motion is based. We describe the formulation in the case of the spin-boson model, which we explained in Section 3.2.1, though it is essentially the same for the Caldeira-Leggett model.

B.1 The Feynman-Vernon theory

In this Section, we review the Feynman-Vernon theory [14], following Ref. [34]. The aim of the Feynman-Vernon theory is to express the time evolution of the density matrix of the system in a heat bath.

B.1.1 Path-integral representation

We will formally express the reduced density matrix (the system density matrix) in the path-integral representation by integrating out the degrees of freedom of the bath from the total density matrix. For this purpose, we first express the element of the density matrix of the total system in terms of path integral. The density matrix of the total system reads, in the Heisenberg representation,

$$\hat{\rho}_{\text{tot}}(t) = e^{-\frac{i}{\hbar}\hat{H}t}\hat{\rho}_{\text{tot}}(0)e^{\frac{i}{\hbar}\hat{H}t}, \tag{B.1}$$

where $\hat{H}$ is the Hamiltonian of the total system in (3.29) or (3.35). We express the system that we are interested in, i.e. a two-level system, with the basis of coherent states $|\psi(t)\rangle$; we denote the initial state as $|\psi_{\text{i}}\rangle$, and the final state as $|\psi_{\text{f}}\rangle$. We express the degrees of freedom of the bath, i.e. the harmonic oscillators with many modes, with the bases of coordinates; $|\vec{x}_{\text{i}}\rangle := |x_{\alpha_{1,\text{i}}}, x_{\alpha_{2,\text{i}}}, \ldots\rangle$ for the initial state and $|\vec{x}_{\text{f}}\rangle := |x_{\alpha_{1,\text{f}}}, x_{\alpha_{2,\text{f}}}, \ldots\rangle$ for the final state, where α_j are the labels of the modes. Under these notation, the element of

the density matrix of the total system at time t reads

$$
\begin{aligned}
&\langle \psi_{\mathrm{f}}, \vec{x}_{\mathrm{f}} | \hat{\rho}_{\mathrm{tot}}(t) | \psi'_{\mathrm{f}}, \vec{x}'_{\mathrm{f}} \rangle \\
&= \int d\overline{\psi}_{\mathrm{i}} d\psi_{\mathrm{i}} d\vec{x}_{\mathrm{i}} \int d\overline{\psi'}_{\mathrm{i}} d\psi'_{\mathrm{i}} d\vec{x}'_{\mathrm{i}} \\
&\qquad \langle \psi_{\mathrm{f}}, \vec{x}_{\mathrm{f}} | e^{-\frac{i}{\hbar}\hat{H}t} | \psi_{\mathrm{i}}, \vec{x}_{\mathrm{i}} \rangle e^{-\overline{\psi}_{\mathrm{i}}\psi_{\mathrm{i}}} \langle \psi_{\mathrm{i}}, \vec{x}_{\mathrm{i}} | \hat{\rho}_{\mathrm{tot}}(0) | \psi'_{\mathrm{i}}, \vec{x}'_{\mathrm{i}} \rangle e^{-\overline{\psi'}_{\mathrm{i}}\psi'_{\mathrm{i}}} \langle \psi'_{\mathrm{i}}, \vec{x}'_{\mathrm{i}} | e^{\frac{i}{\hbar}\hat{H}t} | \psi'_{\mathrm{f}}, \vec{x}'_{\mathrm{f}} \rangle \\
&=: \int_{\overline{\psi}(0)=\overline{\psi}_{\mathrm{i}},\psi(0)=\psi_{\mathrm{i}},\vec{x}(0)=\vec{x}_{\mathrm{i}}}^{\overline{\psi}(t)=\overline{\psi}_{\mathrm{f}},\psi(t)=\psi_{\mathrm{f}},\vec{x}(t)=\vec{x}_{\mathrm{f}}} D\overline{\psi}\, D\psi\, D\vec{x} \int_{\overline{\psi'}(0)=\overline{\psi'}_{\mathrm{i}},\psi'(0)=\psi'_{\mathrm{i}},\vec{x}'(0)=\vec{x}'_{\mathrm{i}}}^{\overline{\psi'}(t)=\overline{\psi'}_{\mathrm{f}},\psi'(t)=\psi'_{\mathrm{f}},\vec{x}'(t)=\vec{x}'_{\mathrm{f}}} D\overline{\psi'}\, D\psi'\, D\vec{x}' \\
&\qquad e^{\frac{i}{\hbar}S[\overline{\psi},\psi,\vec{x}]} \rho_{\mathrm{tot}}(\overline{\psi}_{\mathrm{i}}, \vec{x}_{\mathrm{i}}; \psi'_{\mathrm{i}}, \vec{x}'_{\mathrm{i}})\, e^{-\frac{i}{\hbar}S[\overline{\psi'},\psi',\vec{x}']},
\end{aligned} \tag{B.2}
$$

where S is the action of the total system,

$$
S = S_{\mathrm{S}} + S_{\mathrm{B}} + S_{\mathrm{I}} = \int_0^t ds\, \big(\mathcal{L}_{\mathrm{S}}(s) + \mathcal{L}_{\mathrm{B}}(s) + \mathcal{L}_{\mathrm{int+counter}}(s) \big), \tag{B.3}
$$

with

$$
\mathcal{L}_{\mathrm{S}}(t) =: i\overline{\psi}(t)\partial_t \psi(t) - \frac{\hbar\omega_0}{2} \big(\overline{\psi}(t)\psi(t) - \psi(t)\overline{\psi}(t) \big) :, \tag{B.4}
$$

$$
\mathcal{L}_{\mathrm{B}}(t) = \frac{1}{2} \sum_\alpha m_\alpha \big[\dot{x}_\alpha^2(t) - \omega_\alpha^2 x_\alpha^2(t) \big], \tag{B.5}
$$

$$
\mathcal{L}_{\mathrm{int+counter}}(t) \equiv \mathcal{L}_{\mathrm{I}}(t) = \sum_\alpha \left(c_\alpha x_\alpha(t) V[\psi(t)] - \frac{1}{2}\frac{c_\alpha^2}{m_\alpha \omega_\alpha^2} V[\psi(t)]^2 \right). \tag{B.6}
$$

The symbol $:\quad:$ in (B.4) stands for the normal ordering.

B.1.2 Product initial state

For simplicity, we assume that the system and the bath are decoupled at $t = 0$, i.e. the total state is written as the direct product. We consider the situation where the heat bath is in equilibrium at $t = 0$, and thus the heat bath is initially in the canonical state:

$$
\hat{\rho}_{\mathrm{tot}}(0) = \hat{\rho}(0) \otimes \frac{1}{Z_{\mathrm{B}}} e^{-\beta \hat{H}_{\mathrm{B}}}, \tag{B.7}
$$

$$
\hat{\rho}_{\mathrm{B}} = \frac{1}{Z_{\mathrm{B}}} e^{-\beta \hat{H}_{\mathrm{B}}}, \qquad Z_{\mathrm{B}} = \mathrm{Tr}_{\mathrm{B}}\, e^{-\beta \hat{H}_{\mathrm{B}}}, \tag{B.8}
$$

$$
\begin{aligned}
\rho_{\mathrm{tot}}(\overline{\psi}_{\mathrm{i}}, \vec{x}_{\mathrm{i}}, \psi'_{\mathrm{i}}, \vec{x}'_{\mathrm{i}}, 0) &= \langle \psi_{\mathrm{i}}, \vec{x}_{\mathrm{i}} | \hat{\rho}_{\mathrm{tot}}(0) | \psi'_{\mathrm{i}}, \vec{x}'_{\mathrm{i}} \rangle \\
&= \langle \psi_{\mathrm{i}} | \hat{\rho}(0) | \psi'_{\mathrm{i}} \rangle \frac{1}{Z_{\mathrm{B}}} \langle \vec{x}_{\mathrm{i}} | e^{-\beta \hat{H}_{\mathrm{B}}} | \vec{x}'_{\mathrm{i}} \rangle \\
&=: \rho(\overline{\psi}_{\mathrm{i}}, \psi'_{\mathrm{i}}, 0) \otimes \rho_{\mathrm{B}}(\vec{x}_{\mathrm{i}}, \vec{x}'_{\mathrm{i}}, 0).
\end{aligned} \tag{B.9}
$$

B.1.3 Time evolution of the reduced density matrix

What we are interested in is the evolution of the system, i.e. the reduced density matrix. It can be obtained by tracing out the degrees of freedom of the bath from the density

matrix of the total system. Under the assumption of the product initial state, we have

$$
\rho(\overline{\psi}_{\mathrm{f}}, \psi'_{\mathrm{f}}, t) = \int d\vec{x}_{\mathrm{f}} \langle \psi_{\mathrm{f}}, \vec{x}_{\mathrm{f}} | \hat{\rho}_{\mathrm{tot}}(t) | \psi'_{\mathrm{f}}, \vec{x}_{\mathrm{f}} \rangle
$$

$$
= \int_{\overline{\psi}(0)=\overline{\psi}_{\mathrm{i}}, \psi(0)=\psi_{\mathrm{i}}, \vec{x}(0)=\vec{x}_{\mathrm{i}}}^{\overline{\psi}(t)=\overline{\psi}_{\mathrm{f}}, \psi(t)=\psi_{\mathrm{f}}, \vec{x}(t)=\vec{x}_{\mathrm{f}}} D\overline{\psi} D\psi\, D\vec{x} \int_{\overline{\psi'}(0)=\overline{\psi'}_{\mathrm{i}}, \psi'(0)=\psi'_{\mathrm{i}}, \vec{x}'(0)=\vec{x}'_{\mathrm{i}}}^{\overline{\psi'}(t)=\overline{\psi'}_{\mathrm{f}}, \psi'(t)=\psi'_{\mathrm{f}}, \vec{x}'(t)=\vec{x}'_{\mathrm{f}}} D\overline{\psi'} D\psi' D\vec{x}'
$$

$$
\mathrm{e}^{\frac{i}{\hbar}(S_{\mathrm{S}}+S_{\mathrm{B}}+S_{\mathrm{I}})} \left(\rho(\overline{\psi}_{\mathrm{i}}, \psi'_{\mathrm{i}}, 0) \otimes \rho_{\mathrm{B}}(\vec{x}_{\mathrm{i}}, \vec{x}'_{\mathrm{i}}; 0) \right) \mathrm{e}^{-\frac{i}{\hbar}(S'_{\mathrm{S}}+S'_{\mathrm{B}}+S'_{\mathrm{I}})}
$$

$$
=: \int D\overline{\psi} D\psi D\overline{\psi'} D\psi'\, \mathrm{e}^{\frac{i}{\hbar}(S_{\mathrm{S}}[\overline{\psi},\psi]-S_{\mathrm{S}}[\overline{\psi'},\psi'])} \mathcal{F}_{\mathrm{FV}}[\overline{\psi}, \psi, \overline{\psi'}, \psi'] \rho(\overline{\psi}_{\mathrm{i}}, \psi'_{\mathrm{i}}, 0). \quad \text{(B.10)}
$$

This functional $\mathcal{F}_{\mathrm{FV}}[\overline{\psi}, \psi, \overline{\psi'}, \psi']$ is what is called the Feynman-Vernon influence functional; all the effect of the bath is packed in here:

$$
\mathcal{F}_{\mathrm{FV}}[\overline{\psi}, \psi, \overline{\psi'}, \psi'] = \int d\vec{x}_{\mathrm{f}} d\vec{x}_{\mathrm{i}} d\vec{x}'_{\mathrm{i}}\, \rho_{\mathrm{B}}(\vec{x}_{\mathrm{i}}, \vec{x}'_{\mathrm{i}}) \int_{\vec{x}(0)=\vec{x}_{\mathrm{i}}}^{\vec{x}(t)=\vec{x}_{\mathrm{f}}} Dx \int_{\vec{x}'(0)=\vec{x}'_{\mathrm{i}}}^{\vec{x}'(t)=\vec{x}_{\mathrm{f}}} D\vec{x}'
$$

$$
\times \exp\left[\frac{i}{\hbar} \left(S_{\mathrm{B}}[\vec{x}] + S_{\mathrm{I}}[\vec{x}, \overline{\psi}, \psi] - S_{\mathrm{B}}[\vec{x}'] - S_{\mathrm{I}}[\vec{x}', \overline{\psi'}, \psi'] \right) \right]
$$

$$
=: \int d\vec{x}_{\mathrm{f}} d\vec{x}_{\mathrm{i}} d\vec{x}'_{\mathrm{i}}\, \rho_{\mathrm{B}}(\vec{x}_{\mathrm{i}}, \vec{x}'_{\mathrm{i}}) F(\overline{\psi}, \psi; \vec{x}_{\mathrm{f}}, \vec{x}_{\mathrm{i}}) F^*(\overline{\psi'}, \psi'; \vec{x}_{\mathrm{f}}, \vec{x}'_{\mathrm{i}}), \quad \text{(B.11)}
$$

where

$$
F(\overline{\psi}, \psi; \vec{x}_{\mathrm{f}}, \vec{x}'_{\mathrm{i}}) = \int_{\vec{x}(0)=\vec{x}_{\mathrm{i}}}^{\vec{x}(t)=\vec{x}_{\mathrm{f}}} Dx \exp\left[\frac{i}{\hbar} \left(S_{\mathrm{B}}[\vec{x}] + S_{\mathrm{I}}[\vec{x}, \overline{\psi}, \psi] \right) \right]. \quad \text{(B.12)}
$$

The influence functional can be calculated explicitly thanks to the fact that the bath is Gaussian (i.e. the ensemble of harmonic oscillators) and that the coupling of the system and the bath is linear.

After some calculation, we find each element of the influence functional as follows [13, 16]:

$$
\rho_{\mathrm{B}}(\vec{x}_{\mathrm{i}}, \vec{x}'_{\mathrm{i}}) = \prod_{\alpha=1}^{N} \rho_{\mathrm{B}}^{(\alpha)}(x_{i,\alpha}, x'_{i,\alpha}), \quad \text{(B.13)}
$$

$$
F(\overline{\psi}, \psi; \vec{x}_{\mathrm{f}}, \vec{x}'_{\mathrm{i}}) = \prod_{\alpha=1}^{N} F^{(\alpha)}(\overline{\psi}, \psi; x_{f,\alpha}, x'_{i,\alpha}), \quad \text{(B.14)}
$$

where

$$
\rho_{\mathrm{B}}^{(\alpha)}(x_{i,\alpha}, x'_{i,\alpha}) = \frac{1}{Z_{\mathrm{B}}} \langle x_{i,\alpha} | \mathrm{e}^{-\beta \hat{H}_{\mathrm{B}}} | x'_{i,\alpha} \rangle
$$

$$
= \left(\frac{m_\alpha \omega_\alpha}{2\pi\hbar \sinh(\beta\hbar\omega_\alpha)} \right)^{\frac{1}{2}} \frac{1}{Z_R^\alpha}
$$

$$
\times \exp\left\{ -\frac{m_\alpha \omega_\alpha}{2\hbar \sinh(\beta\hbar\omega_\alpha)} [(x_{i,\alpha}^2 + x_{i,\alpha}'^2)\cosh(\beta\hbar\omega_\alpha) - 2x_{i,\alpha} x'_{i,\alpha}] \right\},
$$

$$
\text{(B.15)}
$$

$$F_\alpha = \left(\frac{m_\alpha \omega_\alpha}{2\pi i \hbar \sin(\omega_\alpha t)} \right)^{\frac{1}{2}} \exp\left(\frac{i}{\hbar} \phi_\alpha[\overline{\psi}, \psi; x_{f,\alpha}, x_{i,\alpha}] \right), \tag{B.16}$$

with

$$\phi_\alpha[\overline{\psi}, \psi; x_{f,\alpha}, x_{i,\alpha}] = \frac{m_\alpha \omega_\alpha}{2\sin(\omega_\alpha t)}[(x_{i,\alpha}^2 + x_{f,\alpha}^2)\cos(\omega_\alpha t) - 2x_{i,\alpha}\, x_{f,\alpha}]$$

$$+ \frac{x_{i,\alpha} c_\alpha}{\sin(\omega_\alpha t)} \int_0^t dt' \sin\left[\omega_\alpha(t - t')\right] V(t')$$

$$+ \frac{x_{f,\alpha} c_\alpha}{\sin(\omega_\alpha t)} \int_0^t dt' \sin\left[\omega_\alpha t'\right] V(t')$$

$$- \frac{c_\alpha^2}{2\, m_\alpha \omega_\alpha^2} \int_0^t dt'\, V^2(t')$$

$$- \frac{c_\alpha^2}{m_\alpha \omega_\alpha \sin(\omega_\alpha t)} \int_0^t dt' \int_0^{t'} dt'' \sin[\omega_\alpha(t - t')] \sin(\omega_\alpha t'')\, V(t')\, V(t''). \tag{B.17}$$

Substituting these elements into the influence functional, we have

$$\mathcal{F}_{\mathrm{FV}}[\overline{\psi}, \psi, \overline{\psi}', \psi']$$

$$= \int d\vec{x}_{\mathrm{f}} d\vec{x}_{\mathrm{i}} d\vec{x}_{\mathrm{i}}'\, \rho_{\mathrm{B}}(\vec{x}_{\mathrm{i}}, \vec{x}_{\mathrm{i}}') F(\overline{\psi}, \psi; \vec{x}_{\mathrm{f}}, \vec{x}_{\mathrm{i}}) F^*(\overline{\psi}', \psi'; \vec{x}_{\mathrm{f}}, \vec{x}_{\mathrm{i}}')$$

$$= \prod_\alpha \left(\frac{m_\alpha \omega_\alpha}{2\pi \hbar \sinh(\beta \hbar \omega_\alpha)} \right)^{\frac{1}{2}} \frac{1}{Z_R^\alpha} \left(\frac{m_\alpha \omega_\alpha}{2\pi i \hbar \sin(\omega_\alpha t)} \right)^{\frac{1}{2}}$$

$$\times \int d\vec{x}_{\mathrm{f}} d\vec{x}_{\mathrm{i}} d\vec{x}_{\mathrm{i}}'\, \rho_{\mathrm{B}}^{(\alpha)}(\vec{x}_{\mathrm{i}}, \vec{x}_{\mathrm{i}}') F^{(\alpha)}(\overline{\psi}, \psi; \vec{x}_{\mathrm{f}}, \vec{x}_{\mathrm{i}}) F^{(\alpha)*}(\overline{\psi}', \psi'; \vec{x}_{\mathrm{f}}, \vec{x}_{\mathrm{i}}')$$

$$= \prod_\alpha \left(\frac{m_\alpha \omega_\alpha}{2\pi \hbar \sinh(\beta \hbar \omega_\alpha)} \right)^{\frac{1}{2}} \frac{1}{Z_R^\alpha} \left(\frac{m_\alpha \omega_\alpha}{2\pi \hbar \sin(\omega_\alpha t)} \right)^{\frac{1}{2}}$$

$$\times \int d\vec{x}_{\mathrm{f}} d\vec{x}_{\mathrm{i}} d\vec{x}_{\mathrm{i}}' \exp\Bigg\{ -\frac{m_\alpha \omega_\alpha}{2\hbar \sinh(\beta \hbar \omega_\alpha)}[(x_{i,\alpha}^2 + x_{i,\alpha}'^2)\cosh(\beta \hbar \omega_\alpha) - 2x_{i,\alpha}\, x_{i,\alpha}']$$

$$+ \left[\frac{i}{\hbar} \left(\frac{m_\alpha \omega_\alpha}{2\sin(\omega_\alpha t)}[(x_{i,\alpha}^2 + x_{f,\alpha}^2)\cos(\omega_\alpha t) - 2x_{i,\alpha}\, x_{f,\alpha}] \right. \right.$$

$$+ \frac{x_{i,\alpha} c_\alpha}{\sin(\omega_\alpha t)} \int_0^t dt' \sin\left[\omega_\alpha(t - t')\right] V[\overline{\psi}(t'), \psi(t')]$$

$$+ \frac{x_{f,\alpha} c_\alpha}{\sin(\omega_\alpha t)} \int_0^t dt' \sin\left[\omega_\alpha t'\right] V[\overline{\psi}(t'), \psi(t')]$$

$$- \frac{c_\alpha^2}{2\, m_\alpha \omega_\alpha^2} \int_0^t dt'\, V^2[\overline{\psi}(t'), \psi(t')]$$

$$\left. - \frac{c_\alpha^2}{m_\alpha \omega_\alpha \sin(\omega_\alpha t)} \int_0^t dt' \int_0^{t'} dt'' \sin[\omega_\alpha(t - t')] \sin(\omega_\alpha t'')\, V[\overline{\psi}(t'), \psi(t')]\, V[\overline{\psi}(t''), \psi(t'')] \right)$$

$$\left. \left. + \mathrm{c.c.}(\overline{\psi} \to \overline{\psi}', \psi \to \psi', x_\alpha \to x_\alpha') \right] \right\}. \tag{B.18}$$

The term $-\frac{ic_\alpha^2}{2m_\alpha\omega_\alpha^2\hbar}\int_0^t dt'\left(V^2[\overline{\psi}(t'),\psi(t')]-V^2[\overline{\psi'}(t'),\psi'(t')]\right)$ is due to the counter term (B.6) in the Lagrangian. After further calculation, we arrive at

$$\mathcal{F}_{\mathrm{FV}}[\overline{\psi},\psi,\overline{\psi'},\psi']$$
$$=\exp\left[\left(-\frac{i}{\hbar}\right)^2\int_0^t d\tau\,V^\times(\tau)\left(\frac{\partial}{\partial\tau}\int_0^\tau d\tau'\,i\bar{L}_1(\tau-\tau')V^\circ(\tau')+\int_0^\tau d\tau'\,L_2(\tau-\tau')V^\times(\tau')\right)\right]$$
$$\times\exp\left(-\frac{i}{\hbar^2}\int_0^\infty d\omega\,\frac{J(\omega)}{\omega}\int_0^t d\tau\,V^\circ(\tau)V^\times(\tau)\right)\qquad\text{(B.19)}$$
$$=\exp\left\{-\frac{1}{\hbar^2}\int_0^\infty d\omega\int_0^t d\tau\,V^\times(\tau)\left[-i\int_0^\tau d\tau'\,J(\omega)\sin[\omega(\tau-\tau')]V^\circ(\tau')\right.\right.$$
$$\left.\left.+\int_0^\tau d\tau'\,J(\omega)\cos[\omega(\tau-\tau')]\coth\left(\frac{\beta\hbar\omega}{2}\right)V^\times(\tau')\right]\right\}$$
$$\times\exp\left(-\frac{i}{\hbar^2}\int_0^\infty d\omega\,\frac{J(\omega)}{\omega}\int_0^t d\tau\,V^\circ(\tau)V^\times(\tau)\right),\qquad\text{(B.20)}$$

where

$$\bar{L}_1(t)=\int_0^\infty d\omega\,\frac{J(\omega)}{\omega}\cos(\omega t),\qquad\qquad\text{(B.21)}$$

$$L_2(t)=\int_0^\infty d\omega\,J(\omega)\cos(\omega t)\coth\left(\frac{\beta\hbar\omega}{2}\right),\qquad\text{(B.22)}$$

$$J(\omega)=\sum_\alpha\frac{c_\alpha^2\hbar}{2m_\alpha\omega_\alpha}\delta(\omega-\omega_\alpha),\qquad\qquad\text{(B.23)}$$

$$V^\times(\tau):=V^\times(\overline{\psi},\psi,\overline{\psi'},\psi';\tau)\equiv V(\overline{\psi},\psi,\tau)-V(\overline{\psi'},\psi',\tau),\qquad\text{(B.24)}$$

$$V^\circ(\tau):=V^\circ(\overline{\psi},\psi,\overline{\psi'},\psi';\tau)\equiv V(\overline{\psi},\psi,\tau)+V(\overline{\psi'},\psi',\tau).\qquad\text{(B.25)}$$

B.2 The hierarchy equations of motion

It was found by Tanimura et al. [19, 30–32] that the equation of motion for the reduced density matrix can be obtained in non-perturbative manner. This is the method without the Born-Markov approximation nor the rotating wave approximation.

B.2.1 Rewriting the influence functional

We rewrite the expression (B.20) of the Feynman-Vernon theory so that we can clarify the hierarchy structure with respect to the time scale. Here we derive the hierarchy equations of motion with the low-temperature correction, following Ref. [19].

We assume a nearly Gaussian-Markovian heat bath, i.e. the distribution of the harmonic oscillators $J(\omega)$ is Ohmic, but with a Lorentzian cutoff (namely the Drude form):

$$J(\omega)=\frac{\hbar^2\zeta}{\pi\omega_0}\frac{\gamma^2\omega}{\omega^2+\gamma^2}.\qquad\qquad\text{(B.26)}$$

The symbol ζ is the quantity related to the system-bath coupling strength and γ gives the decay rate of the time correlation function of the heat bath. The spectrum becomes Ohmic in the limit $\gamma \to \infty$.

Substituting (B.26) into (B.21) and (B.22), we have

$$\mathcal{F}_{\text{FV}}[\overline{\psi}, \psi, \overline{\psi}', \psi'] = \exp\left\{ -\frac{\zeta\gamma^2}{\pi\omega_0} \int_0^t d\tau\, V^\times(\tau) \int_0^\tau d\tau' \left[\int_0^\infty d\omega \frac{-i\omega}{\omega^2 + \gamma^2} \sin[\omega(\tau - \tau')] V^\circ(\tau') \right.\right.$$

$$\left.\left. + \int_0^\infty d\omega \frac{\omega}{\omega^2 + \gamma^2} \cos[\omega(\tau - \tau')] \coth\left(\frac{\beta\hbar\omega}{2}\right) V^\times(\tau') \right] \right\}$$

$$\times \exp\left(-\frac{i\zeta\gamma}{2\omega_0} \int_0^t d\tau\, V^\circ(\tau) V^\times(\tau) \right). \quad \text{(B.27)}$$

For the first term in the rectangular parentheses

$$\frac{i\zeta\gamma^2}{\pi\omega_0} \int_0^\infty d\omega \frac{\omega}{\omega^2 + \gamma^2} \sin[\omega(\tau - \tau')]$$

$$= \frac{i\zeta\gamma^2}{2\pi\omega_0} \int_{-\infty}^\infty d\omega \frac{\omega}{(\omega + i\gamma)(\omega - i\gamma)} \frac{e^{\omega(\tau-\tau')} - e^{-\omega(\tau-\tau')}}{2i}$$

$$= \frac{i\zeta\gamma^2}{2\omega_0} e^{-\gamma(\tau-\tau')}$$

$$= i\frac{i\zeta}{\beta\hbar\omega_0}\left(-i\frac{\beta\hbar\gamma}{2}\right) \gamma e^{-\gamma(\tau-\tau')}, \quad \text{(B.28)}$$

and for the second term in the rectangular parentheses

$$-\frac{\zeta\gamma^2}{\pi\omega_0} \int_0^\infty d\omega \frac{\omega}{\omega^2 + \gamma^2} \coth\left(\frac{\beta\hbar\omega}{2}\right) \cos[\omega(\tau - \tau')]$$

$$= -\frac{\zeta\gamma^2}{2\pi\omega_0} \int_{-\infty}^\infty d\omega \frac{\omega}{\omega^2 + \gamma^2} \frac{e^{\frac{\beta\hbar\omega}{2}} + e^{-\frac{\beta\hbar\omega}{2}}}{e^{\frac{\beta\hbar\omega}{2}} - e^{-\frac{\beta\hbar\omega}{2}}} \frac{e^{\omega(\tau-\tau')} + e^{-\omega(\tau-\tau')}}{2}$$

$$= -\frac{\zeta\gamma^2}{2\omega_0} \cot\left(\frac{\beta\hbar\omega}{2}\right) e^{-\gamma(\tau-\tau')} - \frac{\zeta\gamma^2}{\beta\hbar\omega_0} \sum_{k=1}^\infty \frac{2\nu_k}{\nu_k^2 - \gamma^2} e^{-\nu_k(\tau-\tau')}, \quad \text{(B.29)}$$

where $\nu_k = 2\pi k/\beta\hbar$ is the Matsubara frequency. We used the fact

$$\text{Res}\{\coth z\} = \lim_{z \to ni\pi} \left[(z - ni\pi) \frac{e^z + e^{-z}}{e^z - e^{-z}}\right] = 1. \quad \text{(B.30)}$$

Thus we have

$$
\mathcal{F}_{\mathrm{FV}}[\overline{\psi}, \psi, \overline{\psi'}, \psi']
$$

$$
= \exp\left\{\int_0^t d\tau \int_0^\tau d\tau' V^\times(\tau) \left[\frac{i\zeta\gamma^2}{2\omega_0} \mathrm{e}^{-\gamma(\tau-\tau')}\right] V^\circ(\tau')\right\}
$$

$$
\times \exp\left\{\int_0^t d\tau \int_0^\tau d\tau' V^\times(\tau) \right.
$$

$$
\left. \times \left[-\frac{\zeta\gamma^2}{2\omega_0} \cot\left(\frac{\beta\hbar\omega}{2}\right) \mathrm{e}^{-\gamma(\tau-\tau')} - \frac{\zeta\gamma^2}{\beta\hbar\omega_0} \sum_{k=1}^\infty \frac{2\nu_k}{\nu_k^2 - \gamma^2} \mathrm{e}^{-\nu_k(\tau-\tau')}\right] V^\times(\tau')\right\}
$$

$$
\times \exp\left(-\frac{i\zeta\gamma}{2\omega_0} \int_0^t d\tau \, V^\circ(\tau) V^\times(\tau)\right). \qquad (\mathrm{B.31})
$$

For the first exponential (which is responsible for the fluctuation), the inside of the rectangular parentheses can be approximated as the δ-function when the time-scale of the system $\tau_{\mathrm{S}} = 1/\omega_0$ is much less than γ. The inside of the rectangular parentheses of the second exponential (which is responsible for the dissipation), however, cannot be approximated as the δ-function no matter how large γ is as long as the Matsubara frequencies $\nu_k = 2\pi k/\beta\hbar$ are not large compared to ω_0. In this case, the influence functional and the reduced density matrix cannot be local in time. Therefore, we classify heat baths as follows:

Markovian heat bath The temperature is high ($\nu_1 \gg \omega_0$) and the decay rate of its time-correlation function is large ($\gamma \gg \omega_0$), so that we can obtain a time-local equation of motion for the reduced density matrix.

non-Markovian heat bath The temperature is low ($\nu_1 \gg \omega_0$ is not satisfied), so that we cannot obtain a time-local equation of motion solely in terms of the reduced density matrix even when the decay rate of its time-correlation function is infinity ($\gamma = \infty$) unless other kinds of approximations, e.g. the rotating-wave approximation, are applicable.

Let us rewrite (B.31) in the following form:

$$
\mathcal{F}_{\mathrm{FV}}[\overline{\psi}, \psi, \overline{\psi'}, \psi'] = \exp\left[\int_0^t d\tau \int_0^\tau d\tau' \Phi(\tau)\Theta(\tau')\gamma \, \mathrm{e}^{-\gamma(\tau-\tau')}\right]
$$

$$
\times \prod_{k=1}^\infty \exp\left[\int_0^t d\tau \int_0^\tau d\tau' \Phi(\tau)\Psi_k(\tau')\nu_k \, \mathrm{e}^{-\nu_k(\tau-\tau')}\right]
$$

$$
\times \exp\left\{-\frac{i\zeta\gamma}{2\omega_0} \int_0^t d\tau \, V^\circ(\tau) V^\times(\tau)\right\}, \qquad (\mathrm{B.32})
$$

$$
\Phi(t) = iV^\times(t), \qquad (\mathrm{B.33})
$$

$$
\Theta(t) = \frac{i\zeta}{\beta\hbar\omega_0}\left[-i\frac{\beta\hbar\gamma}{2}V^\circ(t) + \frac{\beta\hbar\gamma}{2}\cot\left(\frac{\beta\hbar\gamma}{2}\right)V^\times(t)\right], \qquad (\mathrm{B.34})
$$

$$
\Psi_k(t) = \frac{i\zeta}{\beta\hbar\omega_0}\frac{2\gamma^2}{\nu_k^2 - \gamma^2}V^\times(t). \qquad (\mathrm{B.35})
$$

In the form (B.32) of the influence functional, the time scale of each element is now clear. Hence, for $k\ (\geq K+1)$ that satisfies $\nu_k \gg \omega_0$, we may approximate

$$\nu_k\, \mathrm{e}^{-\nu_k(\tau-\tau')} \simeq \delta(\tau-\tau') \qquad (k \geq K+1). \tag{B.36}$$

In other words, the Markovian approximation is valid in the levels $k \geq K+1$, but not in the lower levels. Then (B.32) reads

$$
\begin{aligned}
\mathcal{F}_{\mathrm{FV}}[\overline{\psi},\psi,\overline{\psi}',\psi'] \simeq {}& \exp\left[-\int_0^t d\tau\, \Phi(\tau)\mathrm{e}^{-\gamma\tau}\left(-\int_0^\tau d\tau'\, \gamma\Theta(\tau')\mathrm{e}^{\gamma\tau'}\right)\right] \\
& \times \prod_{k=1}^{K} \exp\left[-\int_0^t d\tau\, \Phi(\tau)\mathrm{e}^{-\nu_k\tau}\left(-\int_0^\tau d\tau'\, \nu_k\Psi_k(\tau')\mathrm{e}^{\nu_k\tau'}\right)\right] \\
& \times \prod_{k=K+1}^{\infty} \exp\left(\int_0^t d\tau\, \Phi(\tau)\Psi_k(\tau)\right) \\
& \times \exp\left(-\frac{i\zeta\gamma}{2\omega_0}\int_0^t d\tau\, V^{\circ}(\tau)V^{\times}(\tau)\right) \\
= {}& \exp\left[-\int_0^t d\tau\, \Phi(\tau)\mathrm{e}^{-\gamma\tau}\left(-\int_0^\tau d\tau'\, \gamma\Theta(\tau')\mathrm{e}^{\gamma\tau'}\right)\right] \\
& \times \prod_{k=1}^{K} \exp\left\{-\int_0^t d\tau\left[\Phi(\tau)\mathrm{e}^{-\nu_k\tau}\left(-\int_0^\tau d\tau'\, \nu_k\Psi_k(\tau')\mathrm{e}^{\nu_k\tau'}\right) + \Phi(\tau)\Psi_k(\tau)\right]\right\} \\
& \times \prod_{k=1}^{\infty} \exp\left(\int_0^t d\tau\, \Phi(\tau)\Psi_k(\tau)\right) \\
& \times \exp\left(-\frac{i\zeta\gamma}{2\omega_0}\int_0^t d\tau\, V^{\circ}(\tau)V^{\times}(\tau)\right).
\end{aligned}
$$

(B.37)

(B.38)

Furthermore, using the formula

$$1 - x\cot x = \sum_{k=1}^{\infty} \frac{2x^2}{\pi^2 k^2 - x^2}, \qquad (0 < |x| < \pi), \tag{B.39}$$

we rewrite the third line of (B.38) as follows:

$$
\begin{aligned}
\prod_{k=1}^{\infty} \exp\left(\int_0^t d\tau\, \Phi(\tau)\Psi_k(\tau)\right) &= \exp\left(-\frac{\zeta}{\beta\hbar\omega_0}\int_0^t d\tau\, \sum_{k=1}^{\infty} \frac{2\gamma^2}{\nu_k-\gamma^2}V^{\times}(\tau)V^{\times}(\tau)\right) \\
&= \exp\left\{-\frac{\zeta}{\beta\hbar\omega_0}\int_0^t d\tau\left[1 - \frac{\beta\hbar\gamma}{2}\cot\left(\frac{\beta\hbar\gamma}{2}\right)\right]V^{\times}(\tau)V^{\times}(\tau)\right\}.
\end{aligned}
$$

(B.40)

Then we arrive at

$$\mathcal{F}_{\mathrm{FV}}[\overline{\psi}, \psi, \overline{\psi}', \psi']$$

$$= \exp\left\{-\int_0^t d\tau \left[\Phi(\tau)\mathrm{e}^{-\gamma\tau}\left(-\int_0^\tau d\tau'\, \gamma\Theta(\tau')\mathrm{e}^{\gamma\tau'}\right) + \Xi(\tau)\right]\right\}$$

$$\times \prod_{k=1}^K \exp\left\{-\int_0^t d\tau \left[\Phi(\tau)\mathrm{e}^{-\nu_k\tau}\left(-\int_0^\tau d\tau'\, \nu_k\Psi_k(\tau')\mathrm{e}^{\nu_k\tau'}\right) + \Phi(\tau)\Psi_k(\tau)\right]\right\},$$

$$\text{(B.41)}$$

where we defined

$$\Xi(\tau) \equiv \frac{\zeta}{\beta\hbar\omega_0}\left[1 - \frac{\beta\hbar\gamma}{2}\cot\left(\frac{\beta\hbar\gamma}{2}\right)\right]V^\times(\tau)V^\times(\tau) + i\frac{\zeta}{\beta\hbar\omega_0}\frac{\beta\hbar\gamma}{2}V^\circ(\tau)V^\times(\tau). \quad \text{(B.42)}$$

B.2.2 Equation of motion for the reduced density matrix

If we take the time derivative of (B.10) with the influence functional (B.37), we can obtain the equation of motion for the reduced density matrix. Nevertheless, before doing that, let us introduce the following auxiliary matrices:

$$\hat{\rho}^{(n)}_{j_1,\ldots,j_K}(\overline{\psi}_{\mathrm{f}}, \psi'_{\mathrm{f}}, t) = \int D\overline{\psi}D\psi \int D\overline{\psi}'D\psi'\, \rho(\overline{\psi}_{\mathrm{i}}, \psi'_{\mathrm{i}}, 0)$$

$$\times \left[\mathrm{e}^{-\gamma\tau}\left(-\int_0^\tau d\tau'\, \gamma\Theta(\tau')\mathrm{e}^{\gamma\tau'}\right)\right]^n$$

$$\times \left[\mathrm{e}^{-\nu_k\tau}\left(-\int_0^\tau d\tau'\, \nu_k\Psi_k(\tau')\mathrm{e}^{\nu_k\tau'}\right)\right]^{j_k}$$

$$\times \mathrm{e}^{\frac{i}{\hbar}S_{\mathrm{S}}[\overline{\psi}, \psi]}\, \mathcal{F}_{\mathrm{FV}}[\overline{\psi}, \psi, \overline{\psi}', \psi']\mathrm{e}^{-\frac{i}{\hbar}S_{\mathrm{S}}[\overline{\psi}', \psi']}. \quad \text{(B.43)}$$

The element $(n, j_1, \ldots, j_K) = (0, 0, \ldots, 0)$ represents the original reduced density matrix. Hereafter, we omit the subscript f for the final state. We can express the derivative of the influence functional in terms of these matrices, and thus we are able to clarify the hierarchy structure of the equation:

$$\frac{\partial}{\partial t}\hat{\rho}_{0,\ldots,0}^{(0)}(\overline{\psi},\psi';t) = -\left(i\hat{\mathcal{L}} + \sum_{k=1}^{K}\hat{\Phi}\hat{\Psi}_k + \hat{\Xi}\right)\hat{\rho}_{0,\ldots,0}^{(0)}(\overline{\psi},\psi';t)$$
$$-\hat{\Phi}\hat{\rho}_{0,\ldots,0}^{(1)}(\overline{\psi},\psi';t) - \sum_{k=1}^{K}\hat{\Phi}\hat{\rho}_{0,\ldots,1,\ldots,0}^{(0)}(\overline{\psi},\psi';t), \qquad \text{(B.44)}$$

$$\frac{\partial}{\partial t}\hat{\rho}_{0,\ldots,0}^{(1)}(\overline{\psi},\psi';t) = -\left(i\hat{\mathcal{L}} + \gamma + \sum_{k=1}^{K}\hat{\Phi}\hat{\Psi}_k + \hat{\Xi}\right)\hat{\rho}_{0,\ldots,0}^{(1)}(\overline{\psi},\psi';t)$$
$$-\hat{\Phi}\hat{\rho}_{0,\ldots,0}^{(2)}(\overline{\psi},\psi';t) - \gamma\hat{\Theta}\hat{\rho}_{0,\ldots,0}^{(0)}(\overline{\psi},\psi';t)$$
$$-\sum_{k=1}^{K}\hat{\Phi}\hat{\rho}_{0,\ldots,1,\ldots,0}^{(1)}(\overline{\psi},\psi';t), \qquad \text{(B.45)}$$

$$\frac{\partial}{\partial t}\hat{\rho}_{1,0,\ldots,0}^{(0)}(\overline{\psi},\psi';t) = -\left(i\hat{\mathcal{L}} + \nu_1 + \sum_{k=1}^{K}\hat{\Phi}\hat{\Psi}_k + \hat{\Xi}\right)\hat{\rho}_{1,0\ldots,0}^{(0)}(\overline{\psi},\psi';t)$$
$$-\hat{\Phi}\hat{\rho}_{1,0,\ldots,0}^{(1)}(\overline{\psi},\psi';t) - \sum_{k=1}^{K}\hat{\Phi}\hat{\rho}_{1,0,\ldots,1,\ldots,0}^{(0)}(\overline{\psi},\psi';t)$$
$$-\nu_1\hat{\Psi}_1\hat{\rho}_{0,\ldots,0}^{(0)}(\overline{\psi},\psi';t), \qquad \text{(B.46)}$$
$$\vdots$$

$$\frac{\partial}{\partial t}\hat{\rho}_{j_1,\ldots,j_K}^{(n)}(\overline{\psi},\psi';t) = -\left[i\hat{\mathcal{L}} + n\gamma + \sum_{k=1}^{K}(j_k\nu_k + \hat{\Phi}\hat{\Psi}_k) + \hat{\Xi}\right]\hat{\rho}_{j_1,\ldots,j_K}^{(n)}(\overline{\psi},\psi';t)$$
$$-\hat{\Phi}\hat{\rho}_{j_1,\ldots,j_K}^{(n+1)}(\overline{\psi},\psi';t) - n\gamma\hat{\Theta}\hat{\rho}_{j_1,\ldots,j_K}^{(n-1)}(\overline{\psi},\psi';t)$$
$$-\sum_{k=1}^{K}\hat{\Phi}\hat{\rho}_{j_1,\ldots,j_k+1,\ldots,j_K}^{(n)}(\overline{\psi},\psi';t)$$
$$-\sum_{k=1}^{K}j_k\nu_k\hat{\Psi}_k\hat{\rho}_{j_1,\ldots,j_k-1,\ldots,j_K}^{(n)}(\overline{\psi},\psi';t). \qquad \text{(B.47)}$$

In the above equations, $\hat{\Phi}, \hat{\Theta}, \hat{\Psi}_k$, and $\hat{\Xi}$ are given in (B.33), (B.34), (B.35), and (B.42) with the replacement $V^\times(t) \to \hat{V}^\times$ and $V^\circ(t) \to \hat{V}^\circ$, where $\hat{V}^\times f \equiv Vf - fV$ and $\hat{V}^\circ f \equiv Vf + fV$.

B.2.3   Terminators

In principle, the set of above equations contains the hierarchy that continues infinitely. Nevertheless, as we will see, the hierarchy elements at a deep enough level can be safely truncated because the Markovian approximation is appropriate for those elements as was

shown in (B.36). Formally solving (B.47), we have

$$
\hat{\rho}_{j_1,\dots,j_K}^{(n)}(\overline{\psi},\psi';t) = \int_0^t ds\, e^{-\left[i\hat{\mathcal{L}}+n\gamma+\sum_{k=1}^K (j_k\nu_k+\Phi\Psi_k)+\Xi\right](t-s)}
$$
$$
\times\left(-\Phi\hat{\rho}_{j_1,\dots,j_K}^{(n+1)}(\overline{\psi},\psi';t) - n\gamma\Theta\hat{\rho}_{j_1,\dots,j_K}^{(n-1)}(\overline{\psi},\psi';t)\right.
$$
$$
-\sum_{k=1}^K \Phi\hat{\rho}_{j_1,\dots,j_k+1,\dots,j_K}^{(n)}(\overline{\psi},\psi';t)
$$
$$
\left.-\sum_{k=1}^K j_k\nu_k\Psi_k\hat{\rho}_{j_1,\dots,j_k-1,\dots,j_K}^{(n)}(\overline{\psi},\psi';t)\right). \tag{B.48}
$$

For $n, j_1, j_2, \cdots j_K$ that satisfy

$$
n\gamma + \sum_{k=1}^K j_k\nu_k \gg \omega_0, \tag{B.49}
$$

we can approximate

$$
\left(n\gamma + \sum_{k=1}^K j_k\nu_k\right) e^{(n\gamma+\sum_{k=1}^K j_k\nu_k)(t-s)} \simeq \delta(t-s), \tag{B.50}
$$

and then

$$
\hat{\rho}_{j_1,\dots,j_K}^{(n)}(\overline{\psi},\psi';t) \simeq \left(n\gamma + \sum_{k=1}^K j_k\nu_k\right)^{-1}\left(-\Phi\hat{\rho}_{j_1,\dots,j_K}^{(n+1)}(\overline{\psi},\psi';t) - n\gamma\Theta\hat{\rho}_{j_1,\dots,j_K}^{(n-1)}(\overline{\psi},\psi';t)\right.
$$
$$
-\sum_{k=1}^K \Phi\hat{\rho}_{j_1,\dots,j_k+1,\dots,j_K}^{(n)}(\overline{\psi},\psi';t)
$$
$$
\left.-\sum_{k=1}^K j_k\nu_k\Psi_k\hat{\rho}_{j_1,\dots,j_k-1,\dots,j_K}^{(n)}(\overline{\psi},\psi';t)\right). \tag{B.51}
$$

Hence the substitution of (B.51) back into (B.47) leads to

$$
\frac{\partial}{\partial t}\hat{\rho}_{j_1,\dots,j_K}^{(n)}(\overline{\psi},\psi';t) \simeq -\left(i\hat{\mathcal{L}} + \sum_{k=1}^K \Phi\Psi_k + \Xi\right)\hat{\rho}_{j_1,\dots,j_K}^{(n)}(\overline{\psi},\psi';t). \tag{B.52}
$$

This is written solely in terms of the matrix with $(n, j_1, \dots, j_K)$, and thus the hierarchy gets truncated here. The matrices which obey (B.52) are called the terminators.

For the numerical calculation, we set

$$
N \equiv n + \sum_{k=1}^K j_k \gg \frac{\omega_0}{\min(\gamma, \nu_1)} \tag{B.53}
$$

as a number that satisfies (B.50).

We obtained the set of closed equations for the matrices; the matrices which do not satisfy (B.36) and (B.50) obey (B.47), and the rest obey (B.52).

51

B.2.4   Numerical implementation

Analytical calculation of the hierarchy equations of motion turns out to be much difficult in most cases, and thus it is usual to obtain the result with numerical simulations. In the above formulation, we can obtain the exact result if we take N in (B.53) and K in (B.36) infinite so that the approximations in (B.50) and (B.36) become exact. We cannot, however, implement this because it requires an infinite set of equations to solve. Hence we simulate with finite (N, K), which produces of course an approximate result. Nevertheless, if we increase the numbers of N and K, the physical quantity that we are calculating converges to a certain value. We can regard this value as the numerically exact result since the simulations with the higher set of (N, K) would only give negligible differences.

The numerical simulations in the present Thesis is based on the program *nonMarkovian09* which is distributed on the website of Yoshitaka Tanimura [1]. We set $\hbar = 1$ there.

Appendix C

Isolated system

In the case of an isolated quantum system, the system obeys the Liouville-von Neumann equation

$$\frac{d}{dt}|\rho(t)\rangle\rangle = \hat{\hat{\mathcal{L}}}|\rho(t)\rangle\rangle = -i[H(t), \rho(t)], \tag{C.1}$$

and the corresponding "transition rate" is

$$
\begin{aligned}
W_t(m, m') &\equiv \langle\langle m_t|\hat{\hat{\mathcal{L}}}|m'_t\rangle\rangle \\
&= -i\Big(\langle m_t|\,[H, |m'_t\rangle\langle m'_t|]\,|m_t\rangle\Big) \\
&= -i\Big(\langle m_t|H|m'_t\rangle\langle m'_t|m_t\rangle - (\langle m_t|H|m'_t\rangle\langle m'_t|m_t\rangle)^*\Big) \\
&= 0. \tag{C.2}
\end{aligned}
$$

Thus, no transitions take place. The picture of the quantum trajectory appears obviously due to the interaction with the reservoir.

Appendix D

Microscopic reversibility of the quantum optical master equation

We show an example where the microscopic reversibility holds when we applied the Born-Markov approximation and the rotating-wave approximation. The equation of motion for the reduced density matrix of the spin-boson model with these approximation is called the quantum optical master equation. We consider the case of the external field which alters the diagonal elements of the reduced system, e.g. the Zeeman magnetic field on a spin:

$$
\hat{H}_{\mathrm{S}}(t) = \begin{pmatrix} \hbar\omega(t) & 0 \\ 0 & -\hbar\omega(t) \end{pmatrix}, \qquad \hbar\omega(t) = \frac{\hbar\omega_0}{2} + h(t). \tag{D.1}
$$

As the region where the Born-Markov approximation and the rotating-wave approximation are appropriate, we consider the case where

$$
\min\left[\gamma, \frac{2\pi}{\beta}\right] \gg \zeta, \qquad\qquad \omega_0 \gg \zeta, \tag{D.2}
$$

with γ the decay rate of the heat bath and ζ the quantity related to the system-bath coupling strength; see (B.23) and (B.26). In this limit, the Lindblad-type quantum master equation can be obtained. In the following calculation, we neglect the contribution of the Lamb-Stark shift, but it does not affect the result.

Let us first solve the time evolution of the reduced density matrix $\hat{\rho}_{\mathrm{S}}(t)$. Expressing operators in the interaction pictures with the superscript (I), we have [4]

$$
\frac{d}{dt}\hat{\rho}_{\mathrm{S}}^{(\mathrm{I})}(t) = \gamma_0(N+1)\left(\sigma_-\hat{\rho}_{\mathrm{S}}^{(\mathrm{I})}(t)\sigma_+ - \frac{1}{2}\sigma_+\sigma_-\hat{\rho}_{\mathrm{S}}^{(\mathrm{I})}(t) - \frac{1}{2}\hat{\rho}_{\mathrm{S}}^{(\mathrm{I})}(t)\sigma_+\sigma_-\right)
$$
$$
+ \gamma_0 N\left(\sigma_+\hat{\rho}_{\mathrm{S}}^{(\mathrm{I})}(t)\sigma_- - \frac{1}{2}\sigma_-\sigma_+\hat{\rho}_{\mathrm{S}}^{(\mathrm{I})}(t) - \frac{1}{2}\hat{\rho}_{\mathrm{S}}^{(\mathrm{I})}(t)\sigma_-\sigma_+\right) \tag{D.3}
$$
$$
=: \mathcal{D}^{(\mathrm{I})}\,\hat{\rho}_{\mathrm{S}}^{(\mathrm{I})}(t), \tag{D.4}
$$

where

$$
\sigma_+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \qquad\qquad \sigma_- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}, \tag{D.5}
$$

and

$$\gamma_0 = \frac{4\omega(t)^3|\vec{d}|^2}{3\hbar c^3}, \qquad\qquad N := N(\omega(t)) = \frac{1}{\exp\big(\beta\hbar\omega(t)\big) - 1}. \qquad (D.6)$$

The vector $\vec{d}$ is the off-diagonal element of the dipole operator,

$$\vec{D}^{(I)}(t) = \vec{d}\sigma_- e^{-i\omega_0 t} + \vec{d}^* \sigma_+ e^{i\omega_0 t}. \qquad (D.7)$$

The general solution of the density matrix is expressed as

$$\hat{\rho}_S^{(I)}(t) = \frac{1}{2}(1 + \langle\vec{\sigma}(t)\rangle \cdot \vec{\sigma}) = \begin{pmatrix} \frac{1}{2}(1 + \langle\sigma_3(t)\rangle) & \langle\sigma_-(t)\rangle \\ \langle\sigma_+(t)\rangle & \frac{1}{2}(1 - \langle\sigma_3(t)\rangle) \end{pmatrix}, \qquad (D.8)$$

which evolves as

$$\frac{d}{dt}\langle\sigma_1(t)\rangle = -\frac{\gamma_0(t)[2N+1]}{2}\langle\sigma_1(t)\rangle, \qquad (D.9)$$

$$\frac{d}{dt}\langle\sigma_2(t)\rangle = -\frac{\gamma_0(t)[2N+1]}{2}\langle\sigma_2(t)\rangle, \qquad (D.10)$$

$$\frac{d}{dt}\langle\sigma_3(t)\rangle = -\gamma_0(t)[2N+1]\langle\sigma_3(t)\rangle - \gamma_0(t). \qquad (D.11)$$

However, since the coupling is weak, the initial equilibrium state is well approximated as

$$\hat{\rho}_S^{(I)}(0) = \begin{pmatrix} e^{-\frac{1}{2}\beta\omega_0} & 0 \\ 0 & e^{\frac{1}{2}\beta\omega_0} \end{pmatrix}. \qquad (D.12)$$

Thus, the density matrix in the interaction picture is a diagonal matrix all the time.

In order to discuss the microscopic reversibility, we need to express the reduced density matrix $\hat{\rho}_S^{(I)}(t)$ and the dissipator $\mathcal{D}^{(I)}(t)$ in the Schrödinger picture. The time evolution operator of the total system reads

$$\hat{U}_0(t) \equiv \exp[-\frac{i}{\hbar}\int dt\, \hat{H}_S(t)] \otimes \exp[-\frac{i}{\hbar}\hat{H}_B t]$$
$$= \begin{pmatrix} \exp[-\frac{i}{2\hbar}\int dt\, \omega(t)] & 0 \\ 0 & \exp[\frac{i}{2\hbar}\int dt\, \omega(t)] \end{pmatrix} \otimes \exp[-\frac{i}{\hbar}\hat{H}_B t]. \qquad (D.13)$$

Since the density matrix has no off-diagonal elements, we have

$$\hat{\rho}_S^{(S)}(t) = \hat{U}_0(t)\hat{\rho}_S^{(I)}(t)\hat{U}_0^\dagger(t) = \hat{\rho}_S^{(I)}(t), \qquad (D.14)$$

where $\hat{\rho}_S^{(S)}(t)$ is the reduced density matrix in the Schrödinger picture. Therefore, the time-dependent basis $\{|a_t\rangle, |b_t\rangle\}$ is time independent in the current case:

$$|a_t\rangle = \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad\qquad |b_t\rangle = \begin{pmatrix} b_1 \\ b_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \qquad (D.15)$$

For the dissipator, using the fact that σ_+ and σ_- translate as

$$\hat{U}_0(t)\sigma_+\hat{U}_0^\dagger(t) = \sigma_+ \exp[-\frac{i}{2\hbar}\int dt\,\omega(t)], \tag{D.16}$$

$$\hat{U}_0(t)\sigma_-\hat{U}_0^\dagger(t) = \sigma_- \exp[\frac{i}{2\hbar}\int dt\,\omega(t)], \tag{D.17}$$

we have

$$\hat{\hat{\mathcal{D}}}^{(S)}(t) = \hat{\hat{U}}_0(t)\hat{\hat{\mathcal{D}}}^{(I)}(t)\hat{\hat{U}}_0^\dagger(t) = \hat{\hat{\mathcal{D}}}^{(I)}(t). \tag{D.18}$$

We are now ready to calculate the ratio of the "transition rate" $W_t(b_t, a_t)$:

$$W_t(b_t, a_t) \equiv \langle\langle b_t|\hat{\hat{\mathcal{D}}}^{(S)}|a_t\rangle\rangle \tag{D.19}$$

$$= \gamma_0 N\left(|a_1|^2|b_2|^2 + |a_2|^2|b_1|^2\right) + \gamma_0|a_2|^2|b_1|^2. \tag{D.20}$$

The second term is the asymmetric part with respect to the process reversal $a_t \leftrightarrow b_t$. We also see that the "transition rate" $W_t(b_t, a_t)$ is real and positive. Substituting the specific form $N = (e^{\beta\omega_0} - 1)^{-1}$, the left-hand side of the microscopic reversibility becomes

$$\frac{W_t(a, b)}{W_t(b, a)} = \frac{e^{\beta\omega_0}|a_2|^2|b_1|^2 + |a_1|^2|b_2|^2}{e^{\beta\omega_0}|a_1|^2|b_2|^2 + |a_2|^2|b_1|^2} = e^{-\beta\hbar\omega(t)}. \tag{D.21}$$

The right-hand side of the microscopic reversibility reads

$$\langle b_t|H_S(t)|b_t\rangle = -\frac{\hbar\omega(t)}{2}, \qquad \langle a_t|H_S(t)|a_t\rangle = \frac{\hbar\omega(t)}{2}, \tag{D.22}$$

$$\exp(\beta[\langle b|H_S(t)|b\rangle - \langle a|H_S(t)|a\rangle]) = e^{-\beta\hbar\omega(t)}, \tag{D.23}$$

and thereby we see that the microscopic reversibility holds in the case where the system is driven by the Zeeman magnetic field.

Appendix E

Convergence of the Hierarchy equation of motion

Although the numerical results of Figs. 3.1, 3.2, 3.3, and 3.4 are not fully converged, we confirmed that those results would eventually converge to the numerically exact values for the larger set of (N, K)'s.
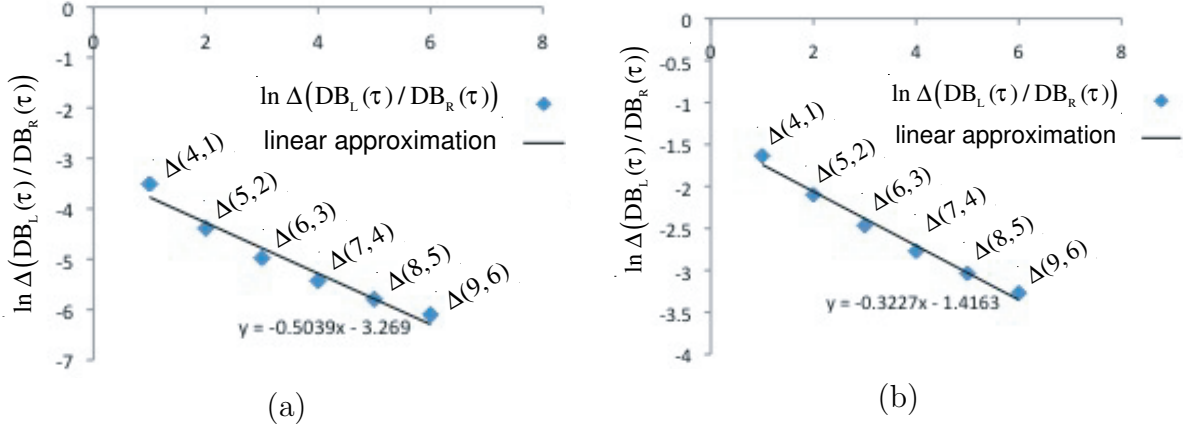

Figure E.1: (a) The evolutions of the ratio $DB_L(\tau)/DB_R(\tau)$ in the case of $(\sigma_x + \sigma_z)$-coupling after the energy measurement with the procedures (i), (ii), and (iii). The parameter values are the same as in Fig. 3.4. We set $(N, K) = (10, 7)$. The time step is 10^{-4} in the simulation time. (b) The evolutions of $\langle 1|\hat{\rho}(\tau)|1\rangle$ after the measurement with the same setting as (a).

Acknowledgements

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