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On the non-equilibrium thermodynamics of quantum systems

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Introduction

This thesis deals with the extension of the laws of thermodynamics to a non-equilibrium setting and in a regime where quantum effects cannot be neglected.

Thermodynamics is a phenomenological theory born in the nineteenth century which studies transformations between equilibrium states of macroscopic systems. This kind of investigation was initially motivated by the necessity to build efficient heat engines, namely machines capable of transforming thermal energy into useful mechanical work, with the result of fostering the second industrial revolution. On top of that, it rapidly became one of the most appreciated physical theories for its generality and still is considered one of the pillars of our understanding of nature.

The fundamental assumption of thermodynamics is that any macroscopic physical system eventually relaxes to an equilibrium state, which is completely characterized by a set of few state-variables, like volume, temperature, energy, pressure, that are related by means of the so-called thermodynamic potentials. While this set of variables depends on the system of interest and is fixed experimentally, the mathematical structure of the theory is nevertheless very general. Aim of thermodynamics is then to predict which equilibrium state a physical system will reach after removing external/internal constraints. This is done according to some physical laws, notably the first and second law of thermodynamics.

The first law regards the conservation of energy that can be exchanged in a transformation between two equilibrium states in the form of heat or in the form of work. The distinction between these two forms of energy exchange can be operatively provided assuming the existence of adiabatic walls, namely assuming that is possible to thermally isolate a physical system. Indeed, heat can be defined comparing two different processes, one of them performed adiabatically, relating the same initial and final equilibrium states. Since it is possible to measure the amount of work exchanged by mechanical tools, and in the adiabatic process work corresponds to the whole energy variation depending only on the initial and final equilibrium states, one obtains the heat exchanged in the second process by difference.

The second law can be expressed in different formulations. The traditional ones are attributed to Kelvin and Clausius and are easily proven to be equivalent. The Kelvin formulation states that it is not possible to extract work from a single heat source at a fixed temperature in a cyclic process, while the Clausius statement is about the impossibility of spontaneous flow of heat from a cold source to a hot source. These statements imply the existence of a state function called entropy that cannot decrease for an isolated system during a thermodynamic transformation. One has to stress that the whole formalism gives information on the final equilibrium state

only, depending on the initial equilibrium state and a set of constraints. In particular, nothing can be concluded for the intermediate steps of the process, unless considering the ideal case of quasi-static transformations, where the system undergoing the thermodynamic process is assumed to be in equilibrium at each instant of time. In this respect, the name thermodynamics is quite misleading, because there is no dynamics (the parameter time does not enter in the description of actual processes).

The theoretical structure of equilibrium thermodynamics, which is very well summarized in [1], was considered completely settled in the first half of the twentieth century, notable exceptions being [2, 3], when the focus of research shifted to possible generalizations in non-equilibrium scenarios.

The first possible generalization of thermodynamics, nowadays known as the theory of Classical Irreversible Thermodynamics [4], has been pioneered by Lars Onsager [5, 6] and further developed by Ilya Prigogine. Global equilibrium is dismissed as a fundamental ingredient of the theory in favor of the less demanding local equilibrium. In other words, thermodynamic variables become functions of the spatial coordinates and of time, maintaining the same relations among themselves through the thermodynamic potentials. The time-evolution is described by means of the so-called constitutive equations, relating the fluxes with the thermodynamic forces or affinities, which are assumed to be the gradients of the thermodynamic variables.

In Classical Irreversible Thermodynamics the constitutive equations are assumed to be linear, thus implicitly restricting to close-to-equilibrium situations. However, such a feature is general enough to include a lot of previous empirical laws used in the description of different physical systems, *e.g.* the Fourier's law for the heat conduction, the Ohm's law for the electrical current and the Fick's law for the matter diffusion. In this framework, very important results as the Onsager relations, describing the interplay between coupled thermodynamic fluxes, can be proved using linear response theory. Linear response thus made it possible to theoretically explain known empirical facts such as, for instance, the phenomenological relations between the Peltier effect (heat flow caused by a voltage difference) and the Seebeck effect (electrical current due to a temperature gradient).

More recently, other phenomenological approaches to the thermodynamics of systems out of equilibrium have been proposed, in situations when Classical irreversible Thermodynamics cannot be applied. For instance, Extended Irreversible Thermodynamics [7] has provided new insight into the physics of systems far from equilibrium, explicitly including the fluxes as independent thermodynamic variables. A paradigmatic example of the phenomenology captured by this theory is the finite speed of heat conduction described by the Cattaneo heat equation [8]. It is worth mentioning also the approach of GENERIC [9–11] (General Equation for Non-Equilibrium Reversible-Irreversible Coupling), that is a further option to study thermodynamics in a non-standard scenario by postulating a certain structure for the evolution equation while maintaining freedom in the choice of thermodynamic variables. Interestingly, GENERIC can be used to connect different levels of description of the same physical system, thus providing a unified picture of many non-equilibrium phenomena [12–14].

Another field of research which generalizes equilibrium thermodynamics deals with the relaxation of the thermodynamic limit. The thermodynamics of small systems, or nanothermodynamics, initiated by Terrell Hill [15] aims at extending the thermodynamic formalism to en-

sembles of systems far from the macroscopic limit. At this level the equivalence of statistical ensembles is lost and the external constraints become essential in the description of physical properties. This theory has wide applications in biochemistry and molecular biology, because it is particularly suited to study the behavior of polymers and colloidal particles [16, 17].

Concerning the statistical justification of the thermodynamic behaviour, the approach called Stochastic Thermodynamics relies on associating definite thermodynamic quantities like heat or work to single trajectories in phase space; then, the probability distribution of these stochastic variables is obtained considering all the possible realizations of the same process (corresponding to different trajectories). Standard thermodynamics arises in this picture through looking at the averages of thermodynamic quantities with respect to their probability distributions, while in principle all statistical moments are accessible as well. Such a theory generalizes equilibrium statistical mechanics because it is well suited for non-equilibrium situations and small sized systems and is currently the subject of intense research. In this framework, Jarzynski and Crooks proved very general and important results known as work fluctuation theorems [18, 19], relating the full non-linear response to an external perturbation of a closed system with an equilibrium thermodynamic quantity, the free energy. These and many other results are summarized in [20].

Apparently, there are many different approaches to generalize the thermodynamics and statistical mechanics of classical systems, namely by considering systems out of equilibrium, or far from the thermodynamic limit or both [21, 22]. However, a unified picture is still lacking because none of them is free from drawbacks and one has to decide what is the most suitable approach depending on the system in question. As a result, part of the scientific community is currently working on such issues.

None of the previously mentioned theories make use of quantum mechanics. However, below a certain size and at very low temperatures quantum effects are expected to become important and in the last decades many efforts have been devoted to extend the theory of non-equilibrium thermodynamics in the quantum domain [23–26]. From a theoretical point of view, it is interesting to understand how the laws of standard thermodynamics emerge from the underlying quantum dynamics. On the other hand, generalizing the laws of thermodynamics for small scale quantum devices could allow to develop a new generation of efficient heat engines operating in the quantum realm.

The renewed interest in the foundations of thermodynamics has been fostered by the high level of accuracy and control in many experimental setups, like ultracold atoms [27], trapped ions [28], optomechanical systems [29] just to mention a few, that allow to investigate the tradeoff between dynamics and thermodynamics in unexplored regimes.

One of the core issues in quantum thermodynamics is the description of equilibration and thermalization in closed quantum systems. Despite being still an open problem, in the last years many important results started to emerge [30–37]. In particular, it has been shown that under very general conditions and for a large class of observables the quantum averages of a physical system become stationary after a certain equilibration time and remain close to the equilibrium value for almost all the time. The main open question in this direction remains the estimate of the equilibration time.

Another interesting problem is the formulation of the first and second law of thermodynamics for small quantum systems out of equilibrium. In this respect, a complete framework was

developed in the late seventies for Markovian open quantum systems evolving in time through master equations in Lindblad form [38, 39]. An open quantum system is a system interacting with another quantum system usually called environment or reservoir, such that its time evolution is essentially different from the Schrödinger one, and non-standard effects like dissipation and decoherence appear. Under suitable assumptions like system and environment being weakly coupled and absence of memory effects (Markov approximation) the dynamics is well described by a master equation in Lindblad form that has a particular mathematical structure [40, 41]. The solution is a one-parameter (time) semigroup of completely positive and trace preserving maps, a so-called quantum dynamical semigroup [42].

The aim of this thesis is the investigation of the non-equilibrium thermodynamics of quantum systems in more general situations, for instance when the Markov approximation is not justified and the evolution is described by non-Markovian dynamical maps. The study of these more general dynamics for an open quantum system has been the subject of intensive research in the last decade [43–45]. Since the behavior in time of most condensed matter quantum devices is described by non-Markovian dynamics, a thorough investigation of the relation between thermodynamics and non-Markovianity is certainly not only of theoretical interest.

Concerning the first law, we propose a way to distinguish heat and work contributions to the variation of energy in a generic bipartite quantum system, namely when the environment is not treated in the thermodynamic limit and remains of finite size so that, in principle, one need deal with both systems without tracing out any of them. This is done using an effective Hamiltonian for both subsystems that contains correction terms due to the interaction between the two of them.

Concerning the second law, we analyze the entropy production, defined as in the standard formalism, in the context of non-Markovian dynamical maps. We show that in general this quantity can be negative for physically legitimate dynamics. However, we argue that in these cases a proper formulation of the second law of thermodynamics requires to consider both system and environment explicitly in the entropy balance. Indeed, one can prove that if the system and environment are initially uncorrelated, the sum of the finite entropy variations in both subsystems is always nonnegative.

Moreover, we comment on the quantum version of the fluctuation theorems, proposing a way to test experimentally the Jarzynski equality. These results generalize the thermodynamic formalism to study fluctuations of arbitrary order, thus containing the full non-equilibrium information about the system.

In all the thesis we adopt the usual perspective taken in the theory of open quantum systems, namely, system and environment together form a closed quantum system evolving according to the Schrödinger equation and the reduced dynamics of each subsystem is dissipative due to the averaging of the degrees of freedom pertaining to the other one. It is worth to mention a different perspective, that is to consider quantum dynamics more general than Schrödinger for closed quantum systems, in such a way that thermodynamics is not derived from quantum mechanics but instead complements it. This is the formulation known as IQT (Intrinsic Quantum Thermodynamics) pushed forward by G. P. Beretta and M. R. von Spakovsky [46–50]. Another interesting point of view deserving to be mentioned is the so-called resource theory of quantum thermodynamics [51–54]. A comprehensive review of the topic, that is complementary to the

present work, can be found in [55].

The thesis is structured as follows. In Chapter 1 we give a brief introduction to the theory of open quantum systems, in particular to the Markovian description by means of quantum dynamical semigroups. We comment on the importance of the property of complete positivity and the possibility to consider time-dependent generators leading to two-parameter semigroups. Then we present the standard description of the non-equilibrium thermodynamics of open quantum systems, as formulated in the seventies in analogy with Classical Irreversible Thermodynamics, with emphasis on the concept of entropy production and on the proof of its positivity. After that, two examples are discussed in which the entropy production is found to be negative, analyzing in what respect these models do not fulfill the requirements of the theory.

More general dynamics of open quantum systems are discussed in Chapter 2. In particular, we review and compare some different options to define non-Markovianity in the quantum domain. The study of thermodynamics in these kind of systems is still at the beginning and aim of the present thesis is to contribute a possible new perspective in addressing the problem. The lack of Markovianity can lead to a transient negative entropy production, as explicitly shown in an example. Moreover, it is known that an asymptotic state for the dynamics is not invariant at finite times when the semigroup property does not hold. This fact is used in another example to show that even the integrated entropy production can become negative. It is then argued that in order to properly describe the thermodynamics of a non-Markovian open quantum system one should explicitly consider the environment in the balance of energy and entropy.

In Chapter 3 we address the question of how to properly formulate the laws of thermodynamics for a generic bipartite quantum system. This can allow to understand what is the more general scenario in which thermodynamics makes sense and then to reduce to the known theory in particular limits. The first issue to solve is a meaningful definition of heat and work in presence of strong coupling between the subsystems. This is done by means of a suitable effective Hamiltonian motivated by physical criteria. It is found that part of the energy is stored in the correlations between the subsystems that can be exchanged between the two parts in the form of heat. Concerning the second law, a very general statement can be proven if the initial state is uncorrelated, namely that the sum of the finite variations of the entropy in system and environment is always nonnegative. This of course does not mean that this quantity is monotonically increasing; indeed it is well known that in quantum systems with finite degrees of freedom recurrences happen [56]. Moreover, this statement does not relate entropy with heat and temperature, the latter not being even defined. We then try to elaborate on a possible definition of temperature in this more general scenario, analyzing two different proposals.

The previous formalism, which contains great part of the original material of this thesis, is then illustrated by means of two examples. Part of the Chapter is also dedicated to the comparison with other proposed formulations in the quantum domain and to the classical counterpart of our theory.

In Chapter 4 we discuss quantum fluctuation theorems, that extend the thermodynamic analysis beyond the study of average values. We distinguish between closed and open quantum systems. In the first case, the theoretical framework is fully settled [57] and we propose a way to test experimentally the quantum Jarzynski equality. In the case of open systems the situation is more complicated. We present the existing results for transient fluctuation theorems in the case

of unital time-evolutions and we comment on the possibility to study the statistics of work and heat considering system and bath explicitly.

The thesis is concluded in Chapter 5 summarizing the key points of the present work. A perspective for possible future work is given, mainly regarding the problem of heat transport in composite quantum systems and the formulation of a unified framework for the fluctuations of heat and work in driven open quantum systems.

Chapter 1

Markovian master equations

In this Chapter the standard formulation of the non-equilibrium thermodynamics of quantum systems, based on the theory of open quantum systems, is reviewed.

An open quantum system is a quantum system S interacting with an external environment or bath B. Even though the dynamics of system and environment together is described by the Schrödinger equation, the system S alone exhibits a richer phenomenology and experiences non-standard effects like dissipation and loss of quantum coherence. Among the many different approaches used to study the dynamics of an open quantum system the most appealing one is to solve the dynamics of system and environment together first, and then compute the exact dynamics of the system alone by averaging over the environmental degrees of freedom. This solution, however, is often impractical and some approximations are required in order to get a theoretical model for the time-evolution of S alone. Another possibility is to assume from the beginning an effective evolution equation based on physically motivated mathematical constraints. This approach is commonly used in the framework of open quantum systems and it will be discussed in Section 1.1.

The usual formulation of non-equilibrium thermodynamics for open quantum systems, which dates back to the late seventies, is based on Markovian master equations, namely evolution equations with no memory effects. This description will be presented in Section 1.2. Particular emphasis will be put on the inequality related to the second law of thermodynamics and on the features of the dynamics that allow to prove such a result. Indeed, the discussion is preparatory for the next Chapter, where more general effective dynamics will be considered, challenging the validity of the inequality.

1.1   Open system dynamics

The dynamics of an open quantum system is essentially different from that of a closed system. Indeed, even though system and environment together evolve unitarily according to the Schrödinger equation, the time-evolution of the system alone experiences non-standard effects like decoherence and dissipation. As a consequence, pure states can be transformed into statistical mixtures during the time-evolution so that the description of quantum states as normalized vectors in a suitable Hilbert space $\mathcal{H}$ is not sufficient and the density matrix formalism must be

adopted. A density matrix ϱ is a convex combination of projectors onto Hilbert space vectors $|\psi_j\rangle$

$$\varrho = \sum_j \lambda_j |\psi_j\rangle\langle\psi_j|, \quad 0 \leq \lambda_j \leq 1, \quad \sum_j \lambda_j = 1. \tag{1.1}$$

If the vectors are orthogonal, thus distinguishable, the weights λ_j can be interpreted as probabilities of being in the pure state $|\psi_j\rangle$. Equivalently, the density matrix is represented by a linear, positive, trace-class operator $\varrho \in \mathcal{T}(\mathcal{H})$ ($\mathcal{T}(\mathcal{H})$ is the set of operators acting on $\mathcal{H}$ with finite trace) with $\mathrm{Tr}(\varrho) = 1$.

The average value of an observable O, described by a bounded ($O \in B(\mathcal{H})$) self-adjoint ($O = O^\dagger$) operator, is computed given the state ϱ of the system as follows

$$\langle O \rangle = \mathrm{Tr}\,(\varrho O) = \sum_j \lambda_j \langle\psi_j|O|\psi_j\rangle. \tag{1.2}$$

Therefore, the average $\langle O \rangle$ is the weighted average in each pure state $|\psi_j\rangle$ with weights λ_j.

Consider the dynamics of the compound quantum system which consists of the open system of interest S and its environment. Its Hilbert space is $\mathcal{H}_{\mathrm{tot}} = \mathcal{H} \otimes \mathcal{H}_B$ and its state is a density matrix $\varrho \in \mathcal{H}_{\mathrm{tot}}$. Given the Hamiltonian, the dynamics of this system is described by the Liouville-von Neumann equation,

$$\partial_t \varrho_t = -i[H, \varrho_t], \tag{1.3}$$

which is the equivalent expression of the Schrödinger equation in the formalism of density matrices, as it is easily seen from the equations below

$$\partial_t |\psi_j(t)\rangle = -iH|\psi_j(t)\rangle, \quad \partial_t \langle\psi_j(t)| = i\langle\psi_j(t)|H, \tag{1.4}$$

using linearity. The solution of equation (1.3), is the density matrix at time t which is related to the density matrix at the initial time through a one-parameter group of linear maps $\mathcal{U}_t : B(\mathcal{H}_{\mathrm{tot}}) \to B(\mathcal{H}_{\mathrm{tot}})$

$$\varrho_t = \mathcal{U}_t[\varrho_0] = U_t \varrho_0 U_t^\dagger, \tag{1.5}$$

where $U_t = \mathrm{e}^{-iHt}$ is a unitary operator. As a consequence, it is easy to check that the time-evolution $\mathcal{U}_t$ preserves the purity of quantum states

$$\mathrm{Tr}[\varrho_t^2] = \mathrm{Tr}[U_t \varrho_0 U_t^\dagger U_t \varrho_0 U_t^\dagger] = \mathrm{Tr}[U_t \varrho_0^2 U_t^\dagger] = \mathrm{Tr}[\varrho_0^2]. \tag{1.6}$$

In order to extract the relevant information for the system of interest one can use the partial trace over the environmental degrees of freedom $\mathrm{Tr}_B(\cdot)$. Indeed, the average of any observable pertaining only to the system S, namely of the form $O_S \otimes \mathbb{1}_B$, can be computed as follows

$$\langle O_S \rangle = \mathrm{Tr}[\varrho\, O_S \otimes \mathbb{1}_B] = \mathrm{Tr}_S[O_S \mathrm{Tr}_B[\varrho]] = \mathrm{Tr}_S[O_S \varrho_S], \tag{1.7}$$

where $\varrho_S = \mathrm{Tr}_B[\varrho]$ is the reduced density matrix of the system which contains all necessary information relative to the system of interest.

Assuming an initially factorized state between system and environment,

$$\varrho_0 = \varrho_S(0) \otimes \varrho_B(0), \tag{1.8}$$

the dynamics of S can be described by a one-parameter family of linear maps Λ_t

$$\varrho_S(0) = \mathrm{Tr}_B\left[\mathcal{U}_t[\varrho_S(0) \otimes \varrho_B(0)]\right] = \sum_{j,k} W_{jk}(t)\varrho_S(0)W_{jk}^\dagger(t) =: \Lambda_t[\varrho_S(0)], \tag{1.9}$$

where $W_{jk}(t) = \sqrt{\lambda_k}\langle E_j|U_t|E_k\rangle \in B(\mathcal{H}_S)$, and $\lambda_k, |E_k\rangle$ are the eigenvalues and eigenvectors of $\varrho_B(0)$. The dynamics Λ_t no longer preserves the purity of quantum states and does not obey a group composition law. In general, it is very difficult to derive the exact dynamics Λ_t starting from the global Scrödinger evolution of SB, so that either some approximations are made or a phenomenological model is introduced from the beginning.

A typical approach to study the dynamics of an open quantum system is to provide a phenomenological master equation that effectively accounts for the interaction with the environment, without explicitly considering the latter. This master equation is written in the form

$$\partial_t \varrho_t = \mathcal{L}\varrho_t, \tag{1.10}$$

where the generator $\mathcal{L} : M_n(\mathbb{C}) \to M_n(\mathbb{C})$ is a linear map satisfying a number of mathematical requirements that correspond to physical constraints. In particular, the solution of the master equation has to preserve the positivity of the density matrix and its trace in order to be consistent with the probabilistic interpretation of the density matrix eigenvalues. Therefore, necessary conditions for the generator are

- $(\mathcal{L}A)^* = \mathcal{L}A^*, \forall A \in M_n(\mathbb{C})$ (hermiticity preservation),

- $\mathrm{Tr}(\mathcal{L}A) = 0, \forall A \in M_n(\mathbb{C})$ (trace preservation).

The following important Lemma has been proved in [40]

Lemma 1.1.1. *Let $(F_j)j = 1,..n^2$ be an orthonormal basis in $M_n(\mathbb{C})$ with respect to the Hilbert-Schmidt scalar product $(A, B) = \mathrm{Tr}\left(A^\dagger B\right)$, with $F_{n^2} = \mathbb{1}/\sqrt{n}$, and let $\mathcal{L} : M_n(\mathbb{C}) \to M_n(\mathbb{C})$ be a linear map such that $(\mathcal{L}A)^* = \mathcal{L}A^*$ and $\mathrm{Tr}(\mathcal{L}A) = 0, \forall A \in M_n(\mathbb{C})$. Then $\mathcal{L}$ can be uniquely written in the form*

$$\mathcal{L}A = -i[H, A] + \sum_{j,k=1}^{n^2-1} h_{jk}\left(F_j A F_k^\dagger - \frac{1}{2}\left\{F_k^\dagger F_j, A\right\}\right), \tag{1.11}$$

where $H = H^*, \mathrm{Tr}(H) = 0$ and $h_{ij} = h_{ji}^*$.

Therefore, the solution of (1.10) with a generator in the form (1.11) is a semigroup of trace-preserving and hermiticity-preserving maps $\Lambda_t = e^{t\mathcal{L}}$. Still, this is not sufficient for a physically meaningful dynamics, which has to preserve the positivity of density matrices.

1.1.1 Positivity and Complete Positivity

In order to preserve positivity further constraints are needed on the matrix $h = (h_{jk})$. Up to now, no general condition is available for the characterization of the generator of positive dynamics. However, the problem is solved if one argues that a stronger condition has to be fulfilled for the physical consistency of the dynamics, namely complete positivity [58].

Definition 1.1. *A linear map* $\Lambda : M_n(\mathbb{C}) \to M_n(\mathbb{C})$ *is called completely positive if* $\Lambda \otimes \mathrm{id}_m$, *where* id_m *is the identity map on* $M_m(\mathbb{C})$, *is positive on* $M_n(\mathbb{C}) \otimes M_m(\mathbb{C})$ *for all* $m \geq 1$.

The physical interpretation of this property goes as follows. Suppose that the system is initially entangled with an inert m-dimensional ancilla, so that, given the dynamics of the system Λ_t, the time-evolution of the compound system and ancilla is $\Lambda_t \otimes \mathrm{id}_m$. The positivity of the compound dynamics is ensured by the complete positivity of Λ_t. The following example clarifies the difference between complete positivity and simple positivity.

Example 1.1. *Consider the transposition map* $\mathbb{T}_2$ *in* $M_2(\mathbb{C})$ *defined as follows*

$$\mathbb{T}_2 : \begin{pmatrix} a & b \\ c & d \end{pmatrix} \to \begin{pmatrix} a & c \\ b & d \end{pmatrix}, \tag{1.12}$$

that preserves the spectrum of matrices, thus being positive. Let $|0\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ *and* $|1\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ *be an orthonormal basis in* $\mathbb{C}^2$ *and define the vector*

$$|\psi\rangle = \frac{1}{\sqrt{2}} \left(|0\rangle \otimes |0\rangle + |1\rangle \otimes |1\rangle \right).$$

The corresponding projector $P = |\psi\rangle\langle\psi|$ *has eigenvalues* $0, 1$ *and is transformed by* $\mathbb{T}_2 \otimes \mathrm{id}_2$ *into*

$$\mathbb{T}_2 \otimes \mathrm{id}_2[P] = \frac{1}{2} \Big(|0\rangle\langle 0| \otimes |0\rangle\langle 0| + |1\rangle\langle 1| \otimes |1\rangle\langle 1| +$$
$$+ |1\rangle\langle 0| \otimes |0\rangle\langle 1| + |0\rangle\langle 1| \otimes |1\rangle\langle 0| \Big)$$
$$= \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

that has eigenvalues $\frac{1}{2}$ *and* $-\frac{1}{2}$. *The negative eigenvalue implies that the transposition* $\mathbb{T}_2$ *is not completely positive despite being positive.*

Contrary to simple positivity, a number of elegant mathematical results are related to complete positivity. In particular, a well-known and celebrated theorem, due to Gorini, Kossakowski and Sudarshan [40], states that

Theorem 1.1.2. *A linear map* $\mathcal{L} : M_n(\mathbb{C}) \to M_n(\mathbb{C})$ *is the generator of a completely positive dynamical semigroup of* $M_n(\mathbb{C})$ *if and only if it can be expressed in the form*

$$\mathcal{L}\varrho = -i[H, \varrho] + \sum_{j,k=1}^{n^2-1} h_{jk} \left(F_j \varrho F_k^\dagger - \frac{1}{2} \left\{ F_k^\dagger F_j, \varrho \right\} \right), \quad \varrho \in M_n(\mathbb{C}) \qquad (1.13)$$

where $H = H^*, \mathrm{Tr}[H] = 0, \mathrm{Tr}[F_i], \mathrm{Tr}[F_i^* F_j] = 0$ *and* (h_{ij}) *is a complex positive matrix. For a given* $\mathcal{L}$, *the so-called Kossakowski matrix* (h_{ij}) *is uniquely determined by the choice of the* F_i's *and the operator* H *is uniquely determined by the condition* $\mathrm{Tr}[H] = 0$.

Remark 1. *A related theorem has been published independently by Lindblad in [41] dealing with the case of a generic separable Hilbert space and a bounded generator. In particular, it is proved that the most general bounded generator of completely positive semigroups has the form* (1.13). *As a matter of fact, many generators of completely positive semigroups used in literature are written in this form but with unbounded operators. In this case, however, there is no guarantee that this is the only possibility. For a recent discussion on this issue see [59].*

Using the previous theorem, one can postulate an effective evolution equation for the open quantum system of interest which respects all the mathematical requirements necessary for the physical consistency of the model. However, sometimes it is useful to complement this approach with a suitable approximation scheme of the global dynamics of SB if a model of the latter is available. In the following we discuss one of these techniques.

1.1.2 Nakajima-Zwanzig method

A possible way to derive approximate master equations for open quantum systems is the so-called Nakajima-Zwanzig projection operator technique [60–62]. Consider a bipartite quantum system with Hamiltonian $H = H_S + H_B + H_{SB}$ whose initial state is factorized $\varrho(t_0) = \varrho_S \otimes \varrho_B$. First of all, define the projectors P and Q as follows:

$$P\varrho(t) = \mathrm{Tr}_B(\varrho(t)) \otimes \overline{\varrho}_B, \quad Q = 1 - P, \qquad (1.14)$$

where $\overline{\varrho}_B$ is a reference state for the bath. For later convenience one chooses the initial state of the environment as reference state, *i.e.* $\overline{\varrho}_B = \varrho_B$. Consider then the Liouville-von Neumann equation

$$\partial_t \varrho(t) = L\varrho(t), \qquad (1.15)$$

where $L[\cdot] = -i[H, \cdot]$, that induces the two equations

$$\partial_t Q\varrho(t) = QLQ\varrho(t) + QLP\varrho(t), \qquad (1.16)$$

$$\partial_t P\varrho(t) = PLP\varrho(t) + PLQ\varrho(t). \qquad (1.17)$$

One can solve formally the first one (1.16)

$$Q\varrho(t) = \mathrm{e}^{QL(t-t_0)} Q\varrho(t_0) + \mathrm{e}^{QLt} \int_{t_0}^t \mathrm{d}s \, \mathrm{e}^{-QLs} QLP\varrho(s), \qquad (1.18)$$

and substitute the result in (1.17)

$$\partial_t P\varrho(t) = PLP\varrho(t) + PLe^{QL(t-t_0)}Q\varrho(t_0) + PLe^{QLt}\int_{t_0}^t e^{-QLs}QLP\varrho(s)\,\mathrm{d}s. \qquad (1.19)$$

Since the initial state is factorized, the second term $PLe^{QL(t-t_0)}Q\varrho(t_0)$ vanishes and the equation becomes

$$\partial_t P\varrho(t) = PLP\varrho(t) + PLe^{QLt}\int_{t_0}^t e^{-QLs}QLP\varrho(s)\,\mathrm{d}s. \qquad (1.20)$$

It turns out that the previous equation is of the form

$$\partial_t \varrho(t) = PLP\varrho(t) + \int_{t_0}^t K(t-s)\varrho(s)\mathrm{d}s, \qquad (1.21)$$

where the memory kernel $K(t-s)$ has been defined as follows

$$K(t-s) := PLe^{QL(t-s)}QLP. \qquad (1.22)$$

Using the fact that $L = L_S + L_B + \lambda\widetilde{L}'$ where

$$L_S[\cdot] = -i[H_S, \cdot], \quad L_B[\cdot] = -i[H_B, \cdot], \quad \widetilde{L}'[\cdot] = -i[\widetilde{H}', \cdot], \qquad (1.23)$$

and $\widetilde{H}' = \sum_j S_j \otimes \widetilde{B}_j$, one can always rewrite the interaction term with centered bath operators $B_j = \widetilde{B}_j - \mathrm{Tr}[\varrho_B\widetilde{B}_j]$ by means of a correction to H_S

$$H_S^\lambda = H_S + \lambda\sum_j S_j\mathrm{Tr}[\varrho_B\widetilde{B}_j], \quad H' = \sum_j S_j \otimes B_j, \quad \mathrm{Tr}[\varrho_B B_j] = 0. \qquad (1.24)$$

Assuming also that the initial state of the bath is stationary with respect to the free evolution $[H_B, \varrho_B]$, it turns out that P, Q commute with both L_S^λ and L_B, and, as a consequence of (1.24), one has

$$P \circ L' \circ P = 0, \quad Q \circ L'[\varrho_S \otimes \varrho_B] = L'[\varrho_S \otimes \varrho_B]. \qquad (1.25)$$

Finally, using all these properties and taking the partial trace over the environmental degrees of freedom, the master equation (1.20) can be rewritten as

$$\partial_t \varrho_S(t) = L_S^\lambda[\varrho_S(t)] + \lambda^2\int_{t_0}^t \mathrm{d}s\,\mathrm{Tr}_B\left(L' \circ e^{(t-s)L^{QQ}} \circ L'[\varrho_S(s) \otimes \varrho_B]\right). \qquad (1.26)$$

This equation is still exact and its solution is often inaccessible. Therefore different approximation schemes have been developed. In the following for sake of simplicity, we consider $t_0 = 0$.

The first approach is to formally integrate Eq. (1.26)

$$\varrho_S(t) = e^{tL_S^\lambda}\varrho_S(0) - \lambda^2\int_0^t \mathrm{d}v \int_0^v \mathrm{d}u\,e^{(t-v)L_S^\lambda}\times$$
$$\times \mathrm{Tr}_B\left(\left[H', e^{(v-u)L^{QQ}}\left[H', \varrho_S(u) \otimes \varrho_B\right]\right]\right). \qquad (1.27)$$

Then, by changing the integration order

$$\int_0^t dv \int_0^v du = \int_0^t du \int_u^t dv \qquad (1.28)$$

and with a suitable change of variable $v \to w = v - u$ one obtains

$$\varrho_S(t) = e^{(t)L_S^\lambda} \varrho_S(0) - \lambda^2 \int_0^t du\, e^{(t-u)L_S^\lambda} \int_0^{t-u} dw\, e^{(-w)L_S^\lambda} \times$$
$$\times \mathrm{Tr}_B \left(\left[H', e^{wL^{QQ}} \left[H', \varrho_S(u) \otimes \varrho_B \right] \right] \right). \qquad (1.29)$$

The approximation consists in substituting τ/λ^2 for t and then take the limit $\lambda \to 0$ in the integral

$$\varrho_S(t) = e^{tL_S^\lambda} \varrho_S(0) - \lambda^2 \int_0^t du\, e^{(t-u)L_S^\lambda} \int_0^\infty dw\, e^{(-w)L_S} \times$$
$$\times \mathrm{Tr}_B \left(\left[H', e^{w(L_S+L_B)} \left[H', \varrho_S(u) \otimes \varrho_B \right] \right] \right). \qquad (1.30)$$

The previous expression is the solution of the following master equation, known as Redfield equation,

$$\partial_t \varrho_S(t) = -i[H_S + \lambda H_S^{(1)}, \varrho_S(t)] + \lambda^2 D_{\mathrm{Red}}[\varrho_S(t)], \qquad (1.31)$$

where

$$D_{\mathrm{Red}}[\varrho] = - \int_0^\infty dw\, e^{(-w)L_S} \mathrm{Tr}_B \left(\left[H', e^{w(L_S+L_B)} \left[H', \varrho \otimes \varrho_B \right] \right] \right). \qquad (1.32)$$

As shown in [63] Redfield master equations generate dynamics which fail to be completely positive, and they are often not even positive.

A better approximation scheme has been suggested by Davies [64–66]. One formally integrates the Redfield equation

$$\varrho_S(t) = e^{tL_S^\lambda} \varrho_S(0) + \lambda^2 \int_0^t du\, e^{(t-u)L_S^\lambda} D_{\mathrm{Red}} \left[\varrho_S(u) \right] \qquad (1.33)$$

and then switch to the interaction picture

$$e^{-tL_S^\lambda} e^{t(L_S^\lambda + \lambda^2 D_{\mathrm{Red}})} \varrho_S(0) = \varrho_S(0) + \lambda^2 \int_0^t du\, e^{-uL_S^\lambda} D_{\mathrm{Red}} e^{uL_S^\lambda} e^{-uL_S^\lambda} e^{u(L_S^\lambda + \lambda^2 D_{\mathrm{Red}})} \varrho_S(0). \qquad (1.34)$$

Davies showed that the term $e^{-uL_S^\lambda} D_{\mathrm{Red}} e^{uL_S^\lambda}$ can be substituted by its ergodic average

$$D_{\mathrm{Dav}}[\varrho] = \lim_{T \to \infty} \frac{1}{2T} \int_{-T}^T ds\, e^{-sL_S^\lambda} D_{\mathrm{Red}} e^{sL_S^\lambda} \varrho. \qquad (1.35)$$

Therefore, coming back to the Schrödinger picture, the following master equation emerges

$$\partial_t \varrho_S(t) = (L_S + \lambda^2 D_{\mathrm{Dav}}) \varrho_S(t), \qquad (1.36)$$

where the generator can be proved to be in the GKSL form. The difference between the generators D_{Red} and D_{Dav} has some important consequences when discussing the thermodynamics of open quantum systems as we will see in the next Section.

Remark 2. *In the derivation of the weak-coupling-limit generators from the Hamiltonian model of system and bath one could also consider a renormalized (physical) Hamiltonian for the system, containing corrections in λ, instead of the bare one. This allows to recover the correct Gibbs state (with respect to the physical Hamiltonian) asymptotically in time as mentioned for instance in [67].*

1.1.3   Time-dependent generator

For a master equation involving a time-dependent generator the previous characterization given in Lemma 1.1.1 can be used at any time with the same basis of orthonormal matrices F_j. As a consequence, the time-dependence is completely encoded in the matrix $h(t) = (h_{jk})(t)$ and in the Hamiltonian H_t, while the overall structure is preserved. In particular, when the matrix is time-dependent and positive semi-definite at any time a corollary of Theorem 1.1.2 states that the solution of Eq. (1.11) is a two-parameter family of trace-preserving completely positive maps satisfying the generalized semigroup composition law [42]

$$\gamma_{t,0} = \gamma_{t,s}\gamma_{s,0}, \quad \gamma_{t,s} = \mathcal{T}e^{\int_s^t \mathrm{d}u\mathcal{L}_u}, \quad t \geq s \geq 0. \tag{1.37}$$

In the following, in order to present the standard framework for the thermodynamics of open quantum systems this kind of dynamics is considered.

One has to mention that in some cases time-dependent generators of two-parameter semi-groups can be derived from microscopic models using a procedure similar to the one discussed before [68]. Indeed, all the approximations remain physically justified for slowly varying external fields; more precisely, they are consistent when the external driving is slow with respect to the bath relaxation time [39].

The situation is more complicated for fast external driving. However, a possible treatment is provided in the case of fast periodic driving by means of the so-called Markov-Floquet formalism [67, 69]. This is a combination of the well-known Floquet theory for periodic Hamiltonians and the theory of quantum Markov semigroups that has been discussed before. In particular, it is assumed that the physical system Hamiltonian is periodic $H_S(t) = H_S(t + T)$ and one defines a constant effective Hamiltonian $\hat{H}_S$ using the spectrum of the propagator at time T, $U(T, 0)$, as follows:

$$U(t,0) := \mathcal{T}e^{-i\int_0^t \mathrm{d}sH_S(s)}, \quad U(T,0) = \sum_k e^{-i\epsilon_k T}|k\rangle\langle k| = e^{-i\hat{H}_S T}, \quad \hat{H}_S = \sum_k \epsilon_k|k\rangle\langle k|. \tag{1.38}$$

The Floquet theory allows to split the propagator $U(t, 0)$ into a periodic unitary $U_P(t) = U_P(t+T)$ and a term related to the constant Hamiltonian $\hat{H}_S$

$$U(t,0) = U_P(t)e^{-i\hat{H}_S t}, \quad U_P(0) = \mathbb{1}; \tag{1.39}$$

this fact in turn simplifies the derivation of the approximate generator, that can be achieved proceeding in a similar fashion as in the time-independent case. As a result, the master equation in Schrödinger picture reads

$$\partial_t \varrho_S(t) = -i[H_S(t), \varrho_S(t)] + \mathcal{L}(t)[\varrho_S(t)], \tag{1.40}$$

where the time-dependent dissipator $\mathcal{L}(t)$ is obtained as a composition of unitaries with a time-independent one

$$\mathcal{L}(t) = \mathcal{L}(t+T) = \mathcal{U}(t,0)\mathcal{L}\mathcal{U}^\dagger(t,0), \quad \mathcal{U}(t,0)[\cdot] = U(t,0)\cdot U^\dagger(t,0). \tag{1.41}$$

Therefore, the solution can be conveniently written as

$$\varrho_S(t) = \mathcal{U}(t,0)\mathrm{e}^{\mathcal{L}t}\varrho_S(0) \tag{1.42}$$

and it is easy to see that any state $\widetilde{\varrho}_S$ such that $\mathcal{L}[\widetilde{\varrho}_S] = 0$ defines a periodic steady state $\widetilde{\varrho}_S(t) = \mathcal{U}(t,0)[\widetilde{\varrho}_S] = \widetilde{\varrho}_S(t+T)$. Typically, in the long-time limit the dissipator $\mathcal{L}$ forces the system to one of these states $\widetilde{\varrho}_S$ producing a so-called limit-cycle.

1.2 Standard thermodynamic description

The thermodynamics of open quantum systems, that is the study of the exchange in time of energy and entropy between the system and its environment, has been studied since the late seventies by means of the theory of quantum dynamical semigroups. In the following, the basic features of this standard description are summarized.

Consider a (possibly driven) open quantum system with (a possibly time-dependent) Hamiltonian H_t described by a finite-dimensional Hilbert space $\mathcal{H}$, whose state at time t (where $t \geqslant 0$) is given by ϱ_t. The internal energy is given by

$$\mathbb{U}_t := \mathrm{Tr}\left[\varrho_t H_t\right], \tag{1.43}$$

and one can distinguish the *heat* and *work* contributions to its time variation ($\partial_t \mathbb{U}_t$) as follows [39]:

$$\partial_t \mathbb{W}_t := \mathrm{Tr}\left[\varrho_t\, \partial_t H_t\right], \tag{1.44}$$

$$\partial_t \mathbb{Q}_t := \mathrm{Tr}\left[\partial_t\varrho_t\, H_t\right]. \tag{1.45}$$

This is a reasonable choice since the work power vanishes if the Hamiltonian is time-independent, namely if there is no external driving; whereas the heat flux is zero when the system is isolated from any kind of environment and thus evolves according to the Schrödinger time evolution generated by H_t. In the following, we concentrate for the moment on undriven open quantum systems (where $H_t = H$) exchanging heat with their environment, which is taken to be a heat bath at inverse temperature β.

Concerning the entropy balance, one can use the von Neumann entropy $\mathbb{S}$ to describe the total entropy of the system out of equilibrium and define the entropy production $\boldsymbol{\sigma}_t$ in analogy with classical irreversible thermodynamics [4], as the difference between the total variation of entropy and the heat flux (1.45) multiplied by the inverse temperature

$$\mathbb{S}_t := -\mathrm{Tr}\left[\varrho_t \log \varrho_t\right], \tag{1.46}$$

$$\boldsymbol{\sigma}_t := \partial_t \mathbb{S}_t - \beta\partial_t \mathbb{Q}_t. \tag{1.47}$$

Throughout the thesis the convention $k_{\mathrm{B}} \equiv \hbar \equiv 1$ is assumed. A straightforward calculation shows that, for a time-independent Hamiltonian H, σ_t can be conveniently rewritten in terms of the derivative of the relative entropy between the state ϱ_t and the Gibbs state $\varrho^{(\beta)} = \mathrm{e}^{-\beta H}/\mathrm{Tr}[\mathrm{e}^{-\beta H}]$, *i.e.*,

$$\sigma_t = -\partial_t \mathbb{S}(\varrho_t \| \varrho^{(\beta)}), \tag{1.48}$$

where $\mathbb{S}(\varrho \| \varrho') := \mathrm{Tr}\left[\varrho \log \varrho - \varrho \log \varrho'\right]$. Indeed, it is sufficient to notice that

$$\beta \partial_t \mathbb{Q}_t = \partial_t \mathrm{Tr}\left[\varrho_t \beta H\right] = -\partial_t \mathrm{Tr}\left[\varrho_t \log\left(\mathrm{e}^{-\beta H}\right)\right] = -\partial_t \mathrm{Tr}\left[\varrho_t \log \varrho^{(\beta)}\right], \tag{1.49}$$

where the last equality follows from $\partial_t \mathrm{Tr}\left[\varrho_t\right] = 0$, and using the definition (1.47) one obtains

$$\sigma_t = -\partial_t \mathrm{Tr}\left[\varrho_t \log \varrho_t\right] + \partial_t \mathrm{Tr}\left[\varrho_t \log \varrho^{(\beta)}\right] = -\partial_t \mathrm{Tr}\left[\varrho_t \log \varrho_t - \varrho_t \log \varrho^{(\beta)}\right]. \tag{1.50}$$

Equation (1.48) holds provided that the Hamiltonian is time-independent and that the environment is a heat bath in thermal equilibrium, without other dynamical assumptions.

If the reduced dynamics of the open quantum system is described by a master equation in the Lindblad form with a unique asymptotic state which is a Gibbs thermal state at the heat bath temperature,

$$\partial_t \varrho_t = -i[H, \varrho_t] + \mathcal{L}[\varrho_t], \qquad \lim_{t \to \infty} \varrho_t = \varrho^{(\beta)} = \frac{\mathrm{e}^{-\beta H}}{Z_\beta}, \tag{1.51}$$

$$\mathcal{L}[\varrho_t] = \sum_k \left(V_k \varrho_\tau V_k^\dagger - \frac{1}{2}\{V_k^\dagger V_k, \varrho_t\}\right), \tag{1.52}$$

one can consistently express the second law of thermodynamics through the nonnegativity of the entropy production $\sigma_t \geqslant 0$ [39]. The proof is based on the fact that any asymptotic state is necessarily also an invariant state for the dynamics due to the semigroup property (given $\varrho_t = \Lambda_t[\varrho_0]$, one has $\Lambda_{t+\delta} = \Lambda_t \Lambda_\delta$) and that the relative entropy is decreasing under CP maps [70],

$$\partial_t \mathbb{S}\left(\Lambda_t[\varrho_0] \| \varrho^{(\beta)}\right) = \partial_t \mathbb{S}\left(\Lambda_t[\varrho_0] \| \Lambda_t[\varrho^{(\beta)}]\right) = \tag{1.53}$$

$$= \lim_{\delta \to 0^+} \frac{\mathbb{S}\left(\Lambda_\delta \Lambda_t[\varrho_0] \| \Lambda_\delta \Lambda_t[\varrho^{(\beta)}]\right) - \mathbb{S}\left(\Lambda_t[\varrho_0] \| \Lambda_t[\varrho^{(\beta)}]\right)}{\delta} \leqslant 0. \tag{1.54}$$

If instead the Hamiltonian is explicitly time-dependent the entropy production can be again related to relative entropy through a more complex formula

$$\sigma_t = -\mathrm{Tr}\left[\mathcal{L}_t[\varrho_t]\left(\log(\varrho_t) - \log(\varrho_t^{(\beta)})\right)\right] = -\partial_s \mathbb{S}\left(\mathrm{e}^{s\mathcal{L}_t}[\varrho_t] \| \varrho_t^{(\beta)}\right)\Big|_{s=0}, \tag{1.55}$$

where $\varrho_t^{(\beta)} = \mathrm{e}^{-\beta H_t}/Z_t$. As a consequence, the entropy production can be proved to be positive assuming the property

$$\mathcal{L}_t[\varrho_t^{(\beta)}] = 0, \tag{1.56}$$

that allows to substitute $\varrho_t^{(\beta)}$ with $\mathrm{e}^{s\mathcal{L}_t}[\varrho_t^{(\beta)}]$ in (1.55). This assumption means that the Gibbs state with respect to the Hamiltonian H_t is stationary for the instantaneous generator $\mathcal{L}_t$ and is

a generalization of the stationarity condition in the time-independent case $\mathcal{L}[\varrho^{(\beta)}] = 0$. If the generator is of time-dependent Lindblad form, it turns out that $\sigma_t \geq 0$ because, for any fixed t, the maps $e^{s\mathcal{L}_t}$ are completely positive and form a one-parameter semigroup with respect to the parameter s.

Moreover, the picture above can be further generalized to more thermal baths at different temperatures, provided that the action of each of them is modelled by a time-dependent generator in Lindblad form $\mathcal{L}_t^{(\beta_i)}$ such that

$$\mathcal{L}_t^{(\beta_i)}[\varrho_t^{(\beta_i)}] = 0. \tag{1.57}$$

As pointed out in [71], the possibility to write the total generator as the sum of terms unambigously associated to a single bath is not warranted in general; however, this is a good approximation when correlations between different baths can be neglected. In this case, the heat exchanged between the system and each bath can be computed as

$$\partial_t \mathbb{Q}_t^{(i)} := \mathrm{Tr}\left[\mathcal{L}_t^{(\beta_i)}[\varrho_t] H_t\right], \tag{1.58}$$

and consequently the entropy production is defined as

$$\sigma_t = \partial_t \mathbb{S}_t - \sum_i \beta_i \partial_t \mathbb{Q}_t^{(i)}. \tag{1.59}$$

Again, the expression above (1.59) for the entropy production can be conveniently rewritten in terms of relative entropy

$$\sigma_t = -\sum_i \partial_s \mathbb{S}\big(e^{s\mathcal{L}_t^{(\beta_i)}}[\varrho_t] \| \varrho_t^{(\beta_i)}\big)\Big|_{s=0}. \tag{1.60}$$

Moreover, by means of assumption (1.57) one can substitute $\varrho_t^{(\beta_i)}$ with $e^{s\mathcal{L}_t^{(\beta_i)}}[\varrho_t^{(\beta_i)}]$. Since the right-hand side of the previous equation is the sum of nonnegative elements that cannot vanish together, because the i-th term is zero when $\varrho_t = \varrho_t^{(\beta_i)}$, in this case the entropy production is strictly positive, *i.e.* $\sigma_t > 0$. The table 1.1 summarizes the relation between the entropy production defined on physical grounds, namely as the difference of the total variation of entropy and the entropy exchanged with the bath due to a heat flux, and the relative entropy.

For completeness one has to mention that a similar formulation of quantum thermodynamics has been given recently for periodically driven open quantum systems whose dynamics is derived using the Markov-Floquet theory. For all the details see *e.g.* [67].

In the above approach the dynamics of the open quantum system is dissipative due to the presence of a suitable environment. However, its presence is not explicitly taken into account in the two definitions (1.44) and (1.45). A different perspective is taken in Chapter 3 whereby a formulation is considered of the thermodynamics of two interacting quantum systems none of which can be neglected [72]. In this case, the heat balance relation strongly depends on the correlations between the two parties built up through the interactions.

Despite being a very natural framework for the study of non-equilibrium thermodynamics in Markovian open quantum systems, many physical models commonly used in literature do not satisfy the previously mentioned requirements, thus failing in the description of the right phenomenology. In the following, we present two of these examples, together with the solutions that are already known and allow to describe the correct thermodynamics.

$\mathcal{L}$, 1 bath	$\boldsymbol{\sigma}_t = -\partial_t \mathbb{S}(\varrho_t \| \varrho^{(\beta)})$
$\mathcal{L}$, N baths	$\boldsymbol{\sigma}_t = -\sum_i \partial_s \mathbb{S}\big(\mathrm{e}^{s\mathcal{L}^{(\beta_i)}}[\varrho_t] \| \mathrm{e}^{s\mathcal{L}^{(\beta_i)}}[\varrho^{(\beta_i)}]\big)\big|_{s=0}$
$\mathcal{L}_t$, 1 bath	$\boldsymbol{\sigma}_t = -\partial_s \mathbb{S}\big(\mathrm{e}^{s\mathcal{L}_t}[\varrho_t] \| \mathrm{e}^{s\mathcal{L}_t}[\varrho_t^{(\beta)}]\big)\big|_{s=0}$
$\mathcal{L}_t$, N baths	$\boldsymbol{\sigma}_t = -\sum_i \partial_s \mathbb{S}\big(\mathrm{e}^{s\mathcal{L}_t^{(\beta_i)}}[\varrho_t] \| \mathrm{e}^{s\mathcal{L}_t^{(\beta_i)}}[\varrho_t^{(\beta_i)}]\big)\big|_{s=0}$

Table 1.1: Relation between entropy production and relative entropy in different physical situations, *i.e.* time-independent vs time-dependent generator, single vs multiple baths.

1.2.1   Markovian non-CP dynamics

The property of complete positivity has been often challenged as nonnecessary for the physical consistency of the dynamics. Therefore, master equations in Lindblad form are sometimes dismissed in favor of the most easily obtained Redfield dynamics (see Section 1.1). In a couple of recent papers [73, 74] however, it is argued that for a completely positive dynamics a consistent formulation of the second law of thermodynamics can be given while, in general, Redfield dynamics, as obtained in (1.31) can lead to violations of the second law. As an example, the authors critically revise the study of an open quantum micro-circuit previously presented in [75], where the time-evolution was indeed modelled as the solution of a Redfield master equation.

The solution of equation (1.31) is a semigroup of trace-preserving but non completely positive maps. The semigroup property derives from the time independence of the generator, while the trace is conserved by the structure of the generator. The lack of complete positivity is a consequence of the Kossakowski matrix not being positive semidefinite and this fact produces a negative entropy production as it is shown in [74]. In order to fix the problem a master equation in Lindblad form has been derived for the same system following the procedure proposed in [64] and presented in the previous section (see (1.36)). Such a master equation generates by construction a time-evolution that is a semigroup of completely positive maps and implies a nonnegative entropy production as shown in (1.53). This example is important because such a system could be experimentally implemented and the discrepancy between different models investigated.

In the next Chapter instead, we will encounter completely positive evolutions producing a negative entropy production, due to the lack of the semigroup property.

1.2.2   Local versus global generator

The previous framework is very effective in describing the thermodynamics of open quantum systems, still one has to be careful in coping with some subtleties. When considering open quantum systems composed of subunits interacting locally with different environments one usually models the dynamics through dissipative generators written using local operators. It has been pointed out in a recent paper [76] that this approach is not correct and thermodynamic inconsistencies arise. In the following we discuss this issue in more detail.

Consider a system composed of two harmonic oscillators with Hamiltonians $H_A = \omega_h a^\dagger a$ and $H_B = \omega_c b^\dagger b$, each one interacting with a thermal bath at a certain temperature. The interaction between the oscillators is taken of the form $H_{AB} = \epsilon(a^\dagger b + ab^\dagger)$. The two thermal baths

are modelled through the following local generators in Lindblad form

$$\mathcal{L}_h(\cdot) = \gamma_h \left(a \cdot a^\dagger - \frac{1}{2}\left\{ a^\dagger a, \cdot \right\} + \mathrm{e}^{-\beta_h \omega_h} \left(a^\dagger \cdot a - \frac{1}{2}\left\{ aa^\dagger, \cdot \right\} \right) \right), \qquad (1.61)$$

$$\mathcal{L}_c(\cdot) = \gamma_c \left(b \cdot b^\dagger - \frac{1}{2}\left\{ b^\dagger b, \cdot \right\} + \mathrm{e}^{-\beta_c \omega_c} \left(b^\dagger \cdot b - \frac{1}{2}\left\{ bb^\dagger, \cdot \right\} \right) \right). \qquad (1.62)$$

These generators are chosen because each of them guarantees the thermalization of a harmonic oscillator, at an inverse temperature β_h and β_c respectively. However, the two oscillators are interacting, and the asymptotic state of the overall dynamics is not a thermal state. This is nothing new, since for a system locally interacting with two baths at different temperatures a nonequilibrium steady state is expected to set in. The key point is that, at stationarity, the heat flux from the system to the hot bath can be calculated, as well as the heat flux to the cold bath, using our previously mentioned formulas (1.58). Of course it turns out that the sum of all heat fluxes is vanishing

$$\left(\partial_t \mathbb{Q}_h(t) + \partial_t \mathbb{Q}_c(t) \right)\Big|_{t=\infty} = 0 \qquad (1.63)$$

because the is no energy variation in the system in the stationary state. The entropy production according to (1.59) is then

$$\boldsymbol{\sigma}_\infty = -\beta_h \partial_t \mathbb{Q}_h(t)|_{t=\infty} - \beta_c \partial_t \mathbb{Q}_c(t)|_{t=\infty} = (\beta_c - \beta_h)\partial_t \mathbb{Q}_h(t)|_{t=\infty}, \qquad (1.64)$$

and has to be positive for the Clausius statement of the second law of thermodynamics to be fulfilled, namely heat should flow from the hot to the cold bath:

$$\partial_t \mathbb{Q}_h(t)|_{t=\infty} > 0. \qquad (1.65)$$

However, it is shown in [76] that this is not the case. A more careful analysis reveals that, though very reasonable, the dynamics considered does not satisfy all the requirements used in the proof of the second law. In particular, the condition (1.57)

$$\mathcal{L}_h(\varrho^{\beta_h}) = 0, \quad \mathcal{L}_c(\varrho^{\beta_c}) = 0, \qquad (1.66)$$

where

$$\varrho^{\beta_h} = \frac{\mathrm{e}^{-\beta_h H}}{\mathrm{Tr}[\mathrm{e}^{-\beta_h H}]}, \quad \varrho^{\beta_c} = \frac{\mathrm{e}^{-\beta_c H}}{\mathrm{Tr}[\mathrm{e}^{-\beta_c H}]} \qquad (1.67)$$

are the thermal states of the compound open system (the two oscillators together) with respect to the Hamiltonian $H = H_A + H_B + H_{AB}$, is not verified. Indeed each generator would thermalize a single noninteracting oscillator, but fails in thermalizing the whole open system.

The solution is presented in the same paper where the generators describing the correct phenomenology are provided

$$\mathcal{L}_h(\cdot) = \gamma_h^+ \cos^2(\theta) \left(d_+ \cdot d_+^\dagger - \frac{1}{2}\left\{ d_+^\dagger d_+, \cdot \right\} + \mathrm{e}^{-\beta_h \omega_+} \left(d_+^\dagger \cdot d_+ - \frac{1}{2}\left\{ d_+ d_+^\dagger, \cdot \right\} \right) \right) +$$

$$+ \gamma_h^- \sin^2(\theta) \left(d_- \cdot d_-^\dagger - \frac{1}{2}\left\{ d_-^\dagger d_-, \cdot \right\} + \mathrm{e}^{-\beta_h \omega_-} \left(d_-^\dagger \cdot d_- - \frac{1}{2}\left\{ d_- d_-^\dagger, \cdot \right\} \right) \right),$$

$$(1.68)$$

$$\mathcal{L}_c(\cdot) = \gamma_c^+ \sin^2(\theta) \left(d_+ \cdot d_+^\dagger - \frac{1}{2} \left\{ d_+^\dagger d_+, \cdot \right\} + \mathrm{e}^{-\beta_c \omega_+} \left(d_+^\dagger \cdot d_+ - \frac{1}{2} \left\{ d_+ d_+^\dagger, \cdot \right\} \right) \right) +$$

$$+ \gamma_c^- \cos^2(\theta) \left(d_- \cdot d_-^\dagger - \frac{1}{2} \left\{ d_-^\dagger d_-, \cdot \right\} + \mathrm{e}^{-\beta_c \omega_-} \left(d_-^\dagger \cdot d_- - \frac{1}{2} \left\{ d_- d_-^\dagger, \cdot \right\} \right) \right),$$

$$(1.69)$$

where

$$d_+ = a \cos(\theta) + b \sin(\theta), \quad d_- = b \cos(\theta) - a \sin(\theta), \tag{1.70}$$

$$\cos^2(\theta) = \frac{\omega_h - \omega_-}{\omega_+ - \omega_-}, \quad \omega_\pm = \frac{\omega_h + \omega_c}{2} \pm \sqrt{\left(\frac{\omega_h - \omega_c}{2} \right)^2 + \epsilon^2}. \tag{1.71}$$

These global generators effectively couple the two oscillators such that each of them alone would thermalize the open system at the proper inverse temperature. This situation perfectly fits into the framework described by Spohn and Lebowitz and is consistent with thermodynamics. It can be proved that the rigorous treatment of weak-coupling limit between system and bath (see Davies [64]) always produces generators of the form (1.69) and (1.68), therefore dynamics that describe correctly the heat exchange between the system and the reservoirs.

It should be said, however, that finding the global generator in many-body quantum systems is usually a hard task, so that in many applications the local generator is anyhow preferred. For this reason, a consistent perturbative scheme has been developed in [77] providing corrections to the local generator such that it satisfies the second law at any order. Moreover, it has been recently argued that the local generator can work better than the global one in some parameter regimes [78, 79], thus implying that this topic deserves further investigation.

In this Chapter we analyzed examples of Markovian open quantum systems with a negative entropy production. We will see in the next Chapter that other mechanisms can lead to a violation of the inequality for the entropy production when more general dynamics are considered.

Chapter 2

Non-Markovian master equations

In this Chapter we study the non-equilibrium thermodynamics of open quantum systems evolving in time through master equations more general than those of time-dependent Lindblad form. In particular, we focus on non-Markovian dynamics and the relation between memory effects and the sign of the entropy production defined in analogy with the Markovian case.

Few results are known for the dynamics of open quantum systems when the Born-Markov approximation is not justified and the study of non-equilibrium thermodynamics in this regime is still at the beginning. This kind of analysis is becoming quite important because many physical systems, like photosynthetic complexes [80, 81], opto-mechanical resonators [82] and superconducting qubits [83], just to mention a few, experience non trivial memory effects and strong correlations with their environment. Therefore, in order to exploit them in the realization of efficient quantum technologies, the balance of energy and entropy is of high importance and has to be thoroughly investigated.

In Section 2.1 the question of how to define non-Markovianity in the quantum domain is addressed and many different proposals are presented and compared. The key point will be the characterization of legitimate dynamical maps whose generator is not of a time-dependent Lindblad form. Using further conditions on the stationary and/or asymptotic state, *i.e.* to be a Gibbs thermal state, one can give a reliable thermodynamic interpretation to these time-evolutions. In this framework, the entropy production can be negative, as shown in Section 2.2 with two different examples.

2.1   Quantum non-Markovianity

Recently, the study of non-Markovian quantum dynamical maps has received much attention because of the high degree of control reached in many experimental setups that allows to exploit physical effects not describable by means of quantum dynamical semigroups. Although various approaches exist in the literature, a general formulation of quantum non-Markovianity is still under debate [43–45]. Some approaches are based on the distinguishability of quantum states [84], others rely on the divisibility of dynamical maps [85–87], on the volume of accessible states [88], on the mutual information between system and environment [89], on the capacity of quantum channels [90]. The relation among different definitions of non-Markovian dynamics

is an open issue and some results in this direction can be found in [91, 92]. In the following, some of the various proposals are discussed and compared.

2.1.1 Distinguishability of quantum states

The first proposal in order to quantify the non-Markovianity of a quantum process has been provided in [84], where the authors associated the backflow of information from the environment to the system with the distinguishability of quantum states. Explicitly, the distinguishability of two quantum states ϱ_1 and ϱ_2 can be quantified by means of the trace distance

$$D(\varrho_1, \varrho_2) = \frac{1}{2}||\varrho_1 - \varrho_2||_1 = \frac{1}{2}\mathrm{Tr}|\varrho_1 - \varrho_2|, \quad \varrho_1, \varrho_2 \in \mathcal{S}, \tag{2.1}$$

where $|| \cdot ||_1$ is the trace norm and $|A| = \sqrt{A^\dagger A}$, which is a metric on the space of density matrices $\mathcal{S}$ satisfying the bounds $0 \le D \le 1$.

A fundamental property of the trace distance is that it is contractive for positive maps Φ, namely $D(\Phi[\varrho_1], \Phi[\varrho_2]) \le D(\varrho_1, \varrho_2)$ for all pairs ϱ_1, ϱ_2 [93]. For a given dynamics Λ_t and a pair of initial density matrices $\varrho_1(0), \varrho_2(0)$, such that $\varrho_1(t) = \Lambda_t[\varrho_1(0)]$ and $\varrho_2(t) = \Lambda_t[\varrho_2(0)]$, one can define the rate of change of the trace distance as

$$r(t, \varrho_1(0), \varrho_2(0)) = \partial_t D(\varrho_1(t), \varrho_2(t)) \tag{2.2}$$

and say that the dynamics Λ_t is non-Markovian if there exists a pair of initial states $\varrho_1(0), \varrho_2(0)$ such that $r > 0$ for some t. This is called the Breuer-Laine-Piilo (BLP) criterion.

The relation between (2.1) and the flow of information is usually justified as follows. Consider an open quantum system S interacting with the environment E and define the two quantities $I_{\mathrm{int}}(t)$ and $I_{\mathrm{ext}}(t)$

$$I_{\mathrm{int}}(t) := D(\varrho_S^1(t), \varrho_S^2(t)), \tag{2.3}$$

$$I_{\mathrm{ext}}(t) := D(\varrho_{SE}^1(t), \varrho_{SE}^2(t)) - D(\varrho_S^1(t), \varrho_S^2(t)). \tag{2.4}$$

The distinguishability of two states of the system at time t is given by $I_{\mathrm{int}}(t)$, while $I_{\mathrm{ext}}(t)$ describes the advantage of discriminating between two quantum states by performing measurements on the global system SE. In this sense, $I_{\mathrm{int}}(t)$ corresponds to the amount of information inside the system and $I_{\mathrm{ext}}(t)$ to the information outside the system. Since the compound system SE evolves unitarily and the trace distance is invariant under the action of unitary maps, one has

$$D(\varrho_{SE}^1(t), \varrho_{SE}^2(t)) = D(\varrho_{SE}^1(0), \varrho_{SE}^2(0)) = I_{\mathrm{int}}(t) + I_{\mathrm{ext}}(t) = I_{\mathrm{tot}} \tag{2.5}$$

and consequently

$$\partial_t I_{\mathrm{int}}(t) + \partial_t I_{\mathrm{ext}}(t) = 0. \tag{2.6}$$

Therefore, if the first quantity decreases the second one automatically increases mimicking an exchange of information between the system and its surrounding. In this framework a dynamics is non-Markovian if a pair of density matrices exists such that the information contained in the system $I_{\mathrm{int}}(t)$ increases over some time interval.

However, one has to be careful with this kind of interpretation because it could lead to some counterintuitive outcomes. It is argued that $I_{\text{ext}}(t)$ quantifies the information not accessible from the system only, namely either stored in the environment or in the correlations between system and environment. Therefore, if one considers the amount of information stored in the environment, by analogy with the definition given for the system, as

$$I_E(t) = D(\varrho_E^1(t), \varrho_E^2(t)), \tag{2.7}$$

where $\varrho_E^1(t) = \text{Tr}_S(\varrho_{SE}^1(t))$ and $\varrho_E^2(t) = \text{Tr}_S(\varrho_{SE}^2(t))$, one would expect that it is always

$$I_{\text{int}}(t) + I_E(t) \leq I_{\text{tot}}, \tag{2.8}$$

the difference $I_{\text{ext}}(t) - I_E(t)$ being stored in the correlations. It is shown in [94] that (2.8) is not satisfied in general.

Another counterintuitive outcome goes as follows. Consider two open quantum systems A and B each one coupled to a different environment E_A and E_B, respectively, and noninteracting between themselves such that the evolution in time of the density matrix of the compound system AB is in the form $\Lambda_t \otimes \Lambda_t$:

$$\varrho_{AB}(t) = \Lambda_t \otimes \Lambda_t[\varrho_{AB}(0)]. \tag{2.9}$$

According to the previous discussion, the information content in the system AB is related to the distinguishability of a pair of density matrices $\varrho_{AB}^1(t)$ and $\varrho_{AB}^2(t)$. Analogously, one could relate the information content of the single subsystems, say A, to the distinguishability of the marginals $\varrho_A^1(t)$ and $\varrho_A^2(t)$. Even if the initial state is factorized, so that it remains factorized at any time t due to the particular form of the time evolution, one finds that

$$\begin{aligned} D(\varrho_{AB}^1(t), \varrho_{AB}^2(t)) &= D(\varrho_A^1(t) \otimes \varrho_B^1(t), \varrho_A^2(t) \otimes \varrho_B^2(t)) \\ &\leq D(\varrho_A^1(t), \varrho_A^2(t)) + D(\varrho_B^1(t), \varrho_B^2(t)), \end{aligned} \tag{2.10}$$

for the subadditivity of the trace distance with respect to tensor products, the equality being true only in the case $\varrho_B^1(t) = \varrho_B^2(t)$ (or the same for A). Therefore, the information content is not additive for two uncorrelated systems and, in principle, from the inequality (2.10) one cannot exclude of obtaining no backflow of information when the two systems are treated separately and a backflow of information considering the two systems together:

$$\begin{cases} \partial_t D(\varrho_A^1(t), \varrho_A^2(t)) \leq 0 \\ \partial_t D(\varrho_B^1(t), \varrho_B^2(t)) \leq 0 \end{cases} \not\Rightarrow \partial_t D(\varrho_{AB}^1(t), \varrho_{AB}^2(t)) \leq 0. \tag{2.11}$$

This fact will be further discussed later when talking about the divisibility property of dynamical maps.

Despite lacking a fully consistent physical interpretation in terms of information backflow, the BLP criterion is the most widely used in literature as a non-Markovianity witness. For completeness one has to mention that in [95] a generalized criterion has been proposed to define non-Markovian dynamics in the same spirit of BLP. This is usually called biased BLP and, according to that, a non-Markovian dynamics is such that one can find a pair of density matrices $\varrho_1(t), \varrho_2(t)$ and a pair of real numbers p_1, p_2, with $p_1 + p_2 = 1$, producing

$$\partial_t \|p_1 \varrho_1(t) - p_2 \varrho_2(t)\|_1 > 0. \tag{2.12}$$

The case $p_1 = p_2 = 1/2$ corresponds to the original BLP.

2.1.2 Memory kernel

Another possibility is to associate non-Markovianity with the presence of a memory kernel in the master equation for the reduced density matrix. For instance, using the Nakajima-Zwanzig projection operator technique [60, 61], as shown in the first Chapter, one obtains an equation in the form

$$\partial_t \varrho(t) = \int_{t_0}^t \mathcal{K}(t-u)\varrho(u)\mathrm{d}u, \quad \varrho(t_0) = \varrho, \tag{2.13}$$

where for simplicity we have neglected the free evolution term. Equivalently, the two-parameter family of linear maps $\Lambda(t,t_0) : \varrho \to \varrho(t) = \Lambda(t,t_0)\varrho$ satisfy the same integro-differential equation:

$$\partial_t \Lambda(t,t_0) = \int_{t_0}^t \mathcal{K}(t-u)\Lambda(u,t_0)\mathrm{d}u, \quad \Lambda(t_0,t_0) = \mathrm{id}. \tag{2.14}$$

According to this point of view, the Markovian limit is recovered when the kernel is singular

$$\mathcal{K}(t-u) = 2\mathcal{L}\delta(t-u) \tag{2.15}$$

and the master equation becomes local in time.

By recalling that equation (2.13) has been derived from the evolution of system and bath together, tracing out the environmental degrees of freedom

$$\Lambda(t,t_0)\varrho = \mathrm{Tr}_B[\mathrm{e}^{-iH(t-t_0)}(\varrho \otimes \varrho_B)\mathrm{e}^{iH(t-t_0)}], \tag{2.16}$$

one should expect that Λ in fact depends on $t - t_0$, *i.e.* $\Lambda(t,t_0) = \Lambda(t - t_0)$, as noticed in [96]. This can be easily verified by formal integration of (2.13). Indeed one obtains

$$\varrho(t) = \varrho + \int_{t_0}^t \mathrm{d}s \int_{t_0}^s \mathrm{d}u\, K(s-u)\varrho(u), \tag{2.17}$$

and, in order to get the map $\Lambda(t,t_0)$ such that $\varrho(t) = \Lambda(t,t_0)\varrho$, one can recursively substitute $\varrho(u)$ in (2.17) as follows

$$\varrho(t) = \varrho + \int_{t_0}^t \mathrm{d}s \int_{t_0}^s \mathrm{d}u\, K(s-u)\varrho + \dots. \tag{2.18}$$

It suffices to change variable in the integral (the same applies to higher order terms) to show that $\Lambda(t,t_0)$ is time-homogeneous, *i.e.* $\Lambda(t,t_0) = \Lambda(t-t_0,0)$,

$$\varrho(t) = \varrho + \int_0^{t-t_0} \mathrm{d}s \int_0^s \mathrm{d}u\, K(s-u)\varrho + \dots \tag{2.19}$$

Therefore, whenever the time-evolution is described by an equation of the form (2.13), the dynamical map is time-homogeneous.

In [96] it is also shown that the previous equation (2.13) can be rewritten avoiding to use a memory kernel, provided that the map $\Lambda(\tau), \tau = t - t_0$, is invertible. Indeed, it is possible to recast the master equation using a time-dependent generator that remembers the initial time t_0

$$\partial_t \Lambda(t,t_0) = \mathcal{L}(t-t_0)\Lambda(t,t_0), \quad \Lambda(t_0,t_0) = \mathrm{id}, \tag{2.20}$$

where the generator is defined through the inverse map Λ^{-1} as follows

$$\mathcal{L}(\tau) = \left(\partial_\tau \Lambda(\tau)\right)\Lambda^{-1}(\tau). \tag{2.21}$$

The dependence on the initial time can be interpreted as the feature revealing non-Markovianity (reminiscent of the memory kernel) and distinguishes equation (2.20) from the time-local master equation commonly found in literature:

$$\partial_t \overline{\Lambda}(t, t_0) = \mathcal{L}(t)\overline{\Lambda}(t, t_0), \quad \overline{\Lambda}(t_0, t_0) = \mathrm{id}. \tag{2.22}$$

In order to better understand the difference between the two equations it is convenient to compare the solutions. The solution of (2.22) reads

$$\overline{\Lambda}(t, t_0) = T \exp\left(\int_{t_0}^t \mathcal{L}_u \mathrm{d}u\right), \tag{2.23}$$

and satisfies the inhomogeneous composition law

$$\overline{\Lambda}(t, t_0) = \overline{\Lambda}(t, s)\overline{\Lambda}(s, t_0), \quad t \geq s \geq t_0, \tag{2.24}$$

while the solution of (2.20) is

$$\Lambda(t - t_0) = T \exp\left(\int_0^{t-t_0} \mathcal{L}_u \mathrm{d}u\right), \tag{2.25}$$

and does not satisfy the composition law (2.24). If we choose for simplicity the case $t_0 = 0$ in (2.25), it turns out that $\Lambda(t) = V(t, s)\Lambda(s)$, for $t \geq s \geq 0$, where

$$V(t, s) = \Lambda(t)\Lambda^{-1}(s) \neq \Lambda(t - s). \tag{2.26}$$

This is considered a manifestation of non-Markovianity in [96].

2.1.3 Divisibility of dynamical maps

A different, but somehow related, approach is presented in Ref. [87], where the non-Markovianity is associated with the lack of CP-divisibility of a dynamical map. A (CP and trace-preserving) dynamical map $\Lambda(t)$ is called CP-divisible if one can write

$$\Lambda(t) = V(t, s)\Lambda(s), \qquad 0 \leqslant s \leqslant t, \tag{2.27}$$

such that the intertwining map $V(t, s)$ is CP for all t, s. With respect to the previous discussion, $t_0 = 0$ is assumed here. The quantum dynamical semigroup generated by the Lindblad master equation (1.52) obviously satisfies this property because there we have $V(t, s) = \Lambda(t - s)$. Moreover, the two parameter family of maps satisfying the time-dependent Lindblad master equation also fits with this requirement [96].

When $V(t, s)$ is positive, the map $\Lambda(t)$ is called P-divisible (which is weaker than CP-divisibility). Following Ref. [97], one can call a dynamical map which is not even P-divisible an *essentially* non-Markovian map.

One can show that the biased BLP measure is equivalent to P-divisibility [97], or, in other words, that the definition of non-Markovianity given in [95] corresponds in this framework to essential non-Markovianity. Indeed, the following Theorem is proven in [97]

Theorem 2.1.1. *Consider an invertible dynamical map* $\Lambda(t) : B(\mathcal{H}) \to B(\mathcal{H})$*.* $\Lambda(t)$ *is P-divisible iff*

$$\partial_t ||\Lambda(t)X||_1 \leq 0, \tag{2.28}$$

for any hermitian operator $X \in B(\mathcal{H})$*, while it is CP-divisible iff*

$$\partial_t ||(\mathrm{id} \otimes \Lambda(t))\widetilde{X}||_1 \leq 0, \tag{2.29}$$

for any hermitian operator $\widetilde{X} \in B(\mathcal{H} \otimes \mathcal{H})$*.*

This important result has been recently generalized for any dynamical map, not necessarily invertible [98].

Interestingly, in [99] it is shown that P-divisibility is not stable under tensor product. In particular, considering two non-interacting systems, each one coupled to an environment such that the reduced dynamics of the two systems is of the form $\Lambda(t) \otimes \Lambda(t)$, the following equivalence has been proved

$$\Lambda(t) \otimes \Lambda(t) \, \text{P-divisible} \Leftrightarrow \Lambda(t) \, \text{CP-divisible} \Leftrightarrow \Lambda(t) \otimes \Lambda(t) \, \text{CP-divisible},$$

namely, for a map of the form $\Lambda(t) \otimes \Lambda(t)$ P-divisibilty and CP-divisibility are equivalent and in turn these properties correspond to the CP-divisibility of the map $\Lambda(t)$. As a consequence, $\Lambda(t) \otimes \Lambda(t)$ fails to be P-divisible if the map $\Lambda(t)$ is P-divisible but not CP-divisible, or, equivalently, according to the BLP criterion the tensor product of two Markovian dynamics can be non-Markovian. Recalling the previous discussion on the interpretation of the distinguishability of quantum states as information content, one could say that, even if no information backflow is present for each subsystem, nevertheless a nonvanishing information backflow might appear when considering the compound system.

2.2   Entropy production

In this Section we describe the nonequilibrium thermodynamics of open quantum systems evolving in time under effective non-Markovian dynamics. Concerning the balance of energy there is not much to say, because the distinction between heat and work can be done as in the Markovian case according to the definitions (1.45) and (1.44) once the Hamiltonian of the system is known. Therefore, we concentrate on the balance of entropy. In particular, we analyze the behavior of the entropy production (1.47) in presence of non-Markovian dynamical maps [100], using the characterization of non-Markovianity based on divisibility. In order to have a meaningful thermodynamic interpretation of this kind of dynamics and to compare them with the situation described in the previous Chapter, we restrict to those evolutions that have a Gibbs state $\varrho^{(\beta)}$ as their unique asymptotic state. In this case, one can use β^{-1} as a reference equilibrium temperature and the entropy production σ_t reads as in Eq. (1.48). For a non-Markovian evolution the asymptotic state is not necessarily an invariant state of the dynamics [101], thus we can distinguish two different situations,

(i) $\forall t \quad \Lambda_t[\varrho^{(\beta)}] = \varrho^{(\beta)},$

(ii) $\exists t$ such that $\Lambda_t[\varrho^{(\beta)}] \neq \varrho^{(\beta)}$.

In the first case, since Λ_t is always taken to be CP, the integrated entropy production $\Sigma_t :=$ $\int_0^t \boldsymbol{\sigma}_{t'} \, \mathrm{d}t'$ is always nonnegative. Indeed, by means of Eq. (1.48), one obtains

$$\Sigma_t = \mathbb{S}(\varrho_0\|\varrho^{(\beta)}) - \mathbb{S}(\Lambda_t[\varrho_0]\|\varrho^{(\beta)}) = \mathbb{S}(\varrho_0\|\varrho^{(\beta)}) - \mathbb{S}(\Lambda_t[\varrho_0]\|\Lambda_t[\varrho^{(\beta)}]) \geqslant 0, \qquad (2.30)$$

where we have used that the relative entropy monotonically decreases under completely positive maps and property (i). Note, however, that the rate $\boldsymbol{\sigma}_t$ can become temporarily negative if the dynamics is essentially non-Markovian (*i.e.*, not P-divisible). Instead, it has been recently proved that if Λ_t is at least P-divisible, then $\partial_t \mathbb{S}\left(\Lambda_t[\varrho_1]\|\Lambda_t[\varrho_2]\right) \leqslant 0$, for any pair of density matrices ϱ_1 and ϱ_2 [102]; in which case $\boldsymbol{\sigma}_t \geqslant 0 \ \forall t$. Concerning the lack of P-divisibility, in Example 1, we discuss a dynamics which fulfills property (i) but with $\boldsymbol{\sigma}_t < 0$ in a certain time interval.

In case (ii) the above argument cannot be used to show that $\Sigma_\tau \geqslant 0$ because the necessary substitution $\varrho^{(\beta)} \to \Lambda_\tau[\varrho^{(\beta)}]$ is not allowed. In fact, in Example 2, we show that the inequality in Eq. (2.30) may be violated.

Remark 3. *We argue that in a non-Markovian context a possible negative entropy production is not directly associated with a violation of the second law of thermodynamics. Rather, it indicates that the presence of the environment at the origin of the dissipative dynamics cannot be entirely neglected. This point of view is also supported by the characterization of non-Markovianity in terms of a backflow of information from the environment to the system. Indeed, lack of P-divisibility can make the distinguishability of two states of the system increase in time [44]. One may then relate such a behavior to processes that cause the entropy of the environment to increase. In fact, one of the messages of this thesis is that a proper formulation of the second law of thermodynamics for a non-Markovian open quantum system cannot be based only on its reduced dynamics. In this respect, it seems better to follow the approach of Refs. [72, 103] and consider explicitly the reservoir in the entropy balance.*

2.2.1 Example 1: Non-Markovian thermalizing qubit

As a first example we consider the following master equation [104]

$$\partial_t \varrho_t = -i\left[\frac{\omega}{2}\sigma_z, \varrho_t\right] + \frac{\gamma(t)}{2}\big(n+1\big)\Big(2\sigma_-\varrho_t\sigma_+ - \{\sigma_+\sigma_-, \varrho_t\}\Big) +$$
$$+ \frac{\gamma(t)}{2}\,n\Big(2\sigma_+\varrho_t\sigma_- - \{\sigma_-\sigma_+, \varrho_t\}\Big), \qquad (2.31)$$

where $n = (\mathrm{e}^{\beta\omega} - 1)^{-1}$ and $\gamma(t)$ is a time-dependent damping rate. By choosing a constant damping, we can easily recover the usual Lindblad master equation for a qubit interacting with a thermal bath at inverse temperature β. One can show that Eq. (2.31) generates a completely positive dynamical map Λ_t iff $\int_0^t \gamma(s)\mathrm{d}s \geq 0$. This is a consequence of the GKSL Theorem (see Theorem 3.1 in [105]) and can be deduced also from the CP conditions for a generic qubit master equation derived in [106] (see Appendix A.2). Moreover, Λ_t is both CP-divisible and P-divisible iff $\gamma(t) \geq 0$ [97].

The solution of Eq. (2.31) in terms of the Bloch vector components reads

$$x(t) - iy(t) = e^{-i\omega t}e^{-\Gamma(t)}\left(x(0) - iy(0)\right), \tag{2.32}$$

$$x(t) + iy(t) = e^{i\omega t}e^{-\Gamma(t)}\left(x(0) + iy(0)\right), \tag{2.33}$$

$$z(t) = e^{-2\Gamma(t)}\left(z(0) - z(\infty)\right) + z(\infty), \tag{2.34}$$

where $\Gamma(t) = \frac{\coth(\beta\omega/2)}{2}\int_0^t \gamma(s)\mathrm{d}s$ and $z(\infty) = -\tanh(\beta\omega/2)$. Notice that the Gibbs state is an invariant state of the dynamics and it is also the unique asymptotic state provided that $\lim_{t\to\infty}\Gamma(t) = \infty$. Therefore, the integrated entropy production Σ_t is nonnegative because of (2.30). Nevertheless, we could expect the entropy production rate to become transiently negative when the dynamics fails to be P-divisible, *i.e.* it is essentially non Markovian. This is indeed the case as we show in the following.

The heat flux is easily found to be

$$\partial_t \mathbb{Q}_t = \frac{\omega}{2}\partial_t z(t) = -\frac{\omega}{2}\gamma(t)\coth(\beta\omega/2)e^{-2\Gamma(t)}\left(z(0) + \tanh(\beta\omega/2)\right), \tag{2.35}$$

so that its sign depends both on the initial condition and on the instantaneous rate $\gamma(t)$. The entropy variation is written by means of the eigenvalues $(1 \pm r(t))/2$ of the density matrix

$$\partial_t \mathbb{S}_t = -\frac{1}{2}\log\left(\frac{1+r(t)}{1-r(t)}\right)\partial_t r(t) =$$

$$= \frac{\gamma(t)\coth(\beta\omega/2)}{4r(t)}\log\left(\frac{1+r(t)}{1-r(t)}\right)\left(x^2(t) + y^2(t) + 2z^2(t) + 2z(t)\tanh(\beta\omega/2)\right), \tag{2.36}$$

where $r(t) = \sqrt{x^2(t) + y^2(t) + z^2(t)}$, and its sign again depends on the rate $\gamma(t)$ and on the initial condition, as we can see rewriting the term in the last bracket

$$x^2(t) + y^2(t) + 2z^2(t) + 2z(t)\tanh(\beta\omega/2) =$$

$$e^{-2\Gamma(t)}\left[x^2(0) + y^2(0) + (z(0) - z(\infty))z(\infty)\right] + e^{-4\Gamma(t)}(z(0) - z(\infty))^2. \tag{2.37}$$

The entropy production rate finally reads

$$\sigma_t = \gamma(t)\coth(\beta\omega/2)e^{-2\Gamma(t)}\times$$

$$\left[\left(x^2(0) + y^2(0) + 2e^{-2\Gamma(t)}(z(0) + |z(\infty)|)^2\right)\frac{1}{4r(t)}\log\left(\frac{1+r(t)}{1-r(t)}\right) + \right.$$

$$\left. + (z(0) + |z(\infty)|)\left(\frac{\beta\omega}{2} - \frac{|z(\infty)|}{2r(t)}\log\left(\frac{1+r(t)}{1-r(t)}\right)\right)\right]. \tag{2.38}$$

In the Appendix A.1 it is proved that the expression in square brackets is always positive, so that the sign of σ_t corresponds to the sign of $\gamma(t)$. Whenever the damping rate is negative, so that the dynamics is essentially non-Markovian, the entropy production rate becomes negative too.

Remark 4. *We stress the fact that a physically legitimate dynamics, namely completely positive and trace preserving, can lead to a negative entropy production rate. This property is associated to the lack of P-divisibility, namely it arises in a class of dynamical maps called essentially non Markovian.*

2.2.2 Example 2: Generalized amplitude damping

This second example aims at highlighting the role of an asymptotic non-invariant state with respect to the internal entropy production. Consider a generalized amplitude damping channel $\Phi(\cdot) = \sum_i E_i(\cdot)E_i^\dagger$ described through the following Kraus operators

$$
\begin{aligned}
E_0 &= \sqrt{p}\left(|0\rangle\langle 0| + \sqrt{1-\gamma}|1\rangle\langle 1|\right), \\
E_1 &= \sqrt{p\gamma}|0\rangle\langle 1|, \\
E_2 &= \sqrt{1-p}\left(\sqrt{1-\gamma}|0\rangle\langle 0| + |1\rangle\langle 1|\right), \\
E_3 &= \sqrt{(1-p)\gamma}|1\rangle\langle 0|,
\end{aligned}
\tag{2.39}
$$

where the parameters $p, \gamma \in [0,1]$. Tuning the parameters $p(t)$ and $\gamma(t)$ as suitable functions of time we can construct a physically legitimate dynamics namely a one-parameter family of completely positive and trace preserving maps Φ_t:

$$
\varrho = \frac{1}{2}\left(\mathbb{1} + x\sigma_x + y\sigma_y + z\sigma_z\right) \mapsto
$$

$$
\Phi_t(\varrho) = \sum_{i=0}^{3} E_i(t)\varrho E_i^\dagger(t) = \frac{1}{2}\left(\mathbb{1} + x(t)\sigma_x + y(t)\sigma_y + z(t)\sigma_z\right).
\tag{2.40}
$$

Explicitly, the Bloch vector components of the density matrix at time t read

$$
x(t) - iy(t) = \sqrt{1-\gamma(t)}\,(x(0) - iy(0)),
\tag{2.41}
$$

$$
x(t) + iy(t) = \sqrt{1-\gamma(t)}\,(x(0) + iy(0)),
\tag{2.42}
$$

$$
z(t) = -\gamma(t) + 2p(t)\gamma(t) + z(0)(1-\gamma(t)).
\tag{2.43}
$$

We can impose that a unique asymptotic state exists for this family of dynamical maps by means of the condition $\gamma(\infty) = 1$; moreover, the asymptotic state becomes a Gibbs state

$$
\varrho_\beta = \frac{e^{-\beta\sigma_z}}{\text{Tr}(e^{-\beta\sigma_z})}
\tag{2.44}
$$

if the further condition $2p(\infty) - 1 = -\tanh(\beta)$ is fulfilled. The initial condition instead implies that $\gamma(0) = 0$. We can choose the time dependence of p and γ such that it is compatible with all these constraints. A possibility is to set

$$
2p(t) - 1 = e^{-\epsilon t}\sin^2(\epsilon t) - \tanh(\beta), \quad \gamma(t) = 1 - e^{-2\lambda t},
\tag{2.45}
$$

so that a quantum dynamical semigroup is easily recovered for $\epsilon = 0$. This can be seen from the time-dependent generator of Φ_t

$$
\mathcal{L}_t(\cdot) = a_t\left(\sigma_-(\cdot)\sigma_+ - \frac{1}{2}\{\sigma_+\sigma_-, \cdot\}\right) + b_t\left(\sigma_+(\cdot)\sigma_- - \frac{1}{2}\{\sigma_-\sigma_+, \cdot\}\right),
\tag{2.46}
$$

which has the following coefficients

$$a_t = \left[\frac{1 - p(t)}{4(1 - \gamma(t))} \partial_t \gamma(t) - \frac{\gamma(t)}{4} \partial_t p(t) \right], \tag{2.47}$$

$$b_t = \left[\frac{p(t)}{4(1 - \gamma(t))} \partial_t \gamma(t) + \frac{\gamma(t)}{4} \partial_t p(t) \right], \tag{2.48}$$

and becomes a time-independent Lindbladian in the limit $\epsilon \to 0$.

The quantity of interest is the difference between the relative entropies (2.30)

$$\Sigma_t = S(\varrho_0||\varrho_\beta) - S(\varrho_t||\varrho_\beta) =$$
$$= -\frac{1}{2} \log \left(\frac{1 - r^2(t)}{1 - r^2(0)} \right) - \frac{r(t)}{2} \log \left(\frac{1 + r(t)}{1 - r(t)} \right) +$$
$$+ \frac{r(0)}{2} \log \left(\frac{1 + r(0)}{1 - r(0)} \right) + \beta(z(0) - z(t)), \tag{2.49}$$

where we used $r(t) = \sqrt{x^2(t) + y^2(t) + z^2(t)}$. Consider for simplicity the special case $x(0) = y(0) = z(0) = 0$, implying also $r(t) = |z(t)|$, such that we can rewrite Eq. (2.49) as follows

$$\Sigma_t = -\frac{1 + |z(t)|}{2} \log \left((1 + |z(t)|)e^{\beta z(t)} \right) - \frac{1 - |z(t)|}{2} \log \left((1 - |z(t)|)e^{\beta z(t)} \right). \tag{2.50}$$

A plot of this quantity for $\beta = 0.1$ and $\epsilon = \lambda = 1$ explicitly shows that $\Sigma_t \leq 0$ in a certain time interval.
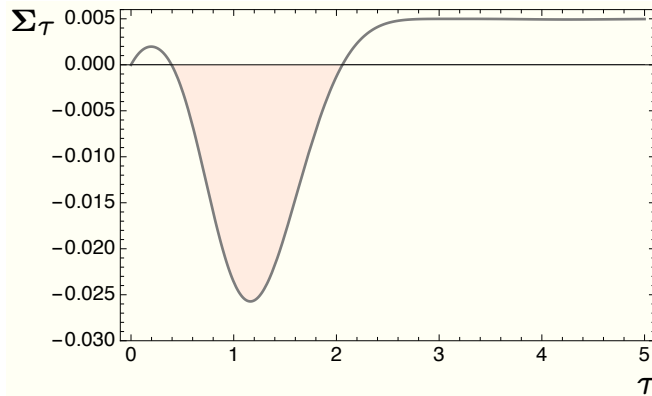

Figure 2.1: Transient negativity of the integrated entropy production Σ_τ.

On the basis of these two examples, one concludes that either the second law of thermodynamics can be violated by physically legitimate dynamical maps or that a more careful formulation of the second law should be given. We choose the latter option, because a very general result has been proven in refs.[72, 103, 107, 108] considering explicitly both system S and bath B in the entropy balance, namely that

$$\Delta \$_S(t) + \Delta \$_B(t) \geq 0. \tag{2.51}$$

This inequality is true provided that the initial state of the composite system $S + B$ is factorized, without particular restrictions on the reduced dynamics of both S and B. In this respect, (2.51) should be considered as the most general formulation of the second law.

Conversely, we have shown that the validity of $\sigma_t \geq 0$ is subject to further dynamical constraints. Heuristically, one can think of obtaining $\sigma_t \geq 0$ as a particular case of (2.51) in three steps. First of all, one has to assume that (2.51) holds true also in a differential form, that is $\partial_t \mathbb{S}_S(t) + \partial_t \mathbb{S}_B(t) \geq 0$. Moreover, since the bath is ususally considered in thermal equilibrium at inverse temperature β one can use the relation $\partial_t \mathbb{S}_B(t) = \beta \partial_t \mathbb{Q}_B(t)$. Finally, the heat flux of the bath is simply related to the heat flux of the system $\partial_t \mathbb{Q}_B(t) = -\partial_t \mathbb{Q}_S(t)$. These hypotheses, though very reasonable, can be violated if system and bath are strongly coupled and correlated, suggesting that one should not consider $\sigma_t \geq 0$ as an a priori valid formulation of the second law. We will come back to this point in the next Chapter, analyzing an exactly solvable model and showing how these three assumptions are violated.

Chapter 3

Thermodynamics of a bipartite quantum system

In the previous Chapters the non-equilibrium thermodynamics of an open quantum system interacting with a large thermal bath has been studied using effective master equations. For Markovian time-evolutions there is a well-established theory which dates back to the seventies [38, 39] whereby the positivity of the entropy production can be proved rigorously. Conversely, in the non-Markovian framework the situation is not yet fully settled. We have shown by means of explicit examples that the entropy production can be transiently negative and we have argued that this outcome should not be interpreted as something unphysical. In the following, we justify this claim attacking the problem from a different perspective.

In order to understand the fate of the laws of thermodynamics when the open system is strongly coupled to an environment consisting of another system, not in general infinite and experiencing a non trivial time-evolution of its own, thus not addressable as an external heat bath in equilibrium, it is necessary to consider explicitly the other system in a global balance of energy and entropy. A possible approach, arguably the most general one, is to treat both systems on the same footing, building a thermodynamic theory valid for a generic bipartite closed quantum system. This would allow to investigate the emergence of the standard thermodynamics under suitable conditions, thus clarifying its limits of validity. Many attempts have been made in this direction in the last decade [23, 103, 109]. In this Thesis we follow the proposal presented in [72] which highlights the role played by correlations between the subsystems.

In Section 3.1 we provide a general formulation of the first law of thermodynamics in a bipartite quantum system. The definitions of heat and work that we use are similar to those presented in Ref. [39]; however, unlike there, we show that, in general, nonequilibrium thermodynamic processes affecting a system A involve work exchange with B without the need for an external driving represented by a time-dependent parameter in the system Hamiltonian, but merely because of the interactions between A and B. Besides, we explicitly show that correlations play an important role in heat transfer between A and B.

As a preliminary and necessary step towards investigating heat and work exchanges between two interacting systems A and B, one needs to unambiguously assign to the two parties a percentage of the interaction energy depending on the state of the compound system. However, due

to AB correlations, there will always be part of the interaction energy that belongs to both A and B together. In thermodynamic terms, extracting this part of the energy would require accessibility of the total system. Thus, we distinguish three contributions to the total internal energy of AB: one accessible only through A, the other one only through B, and the last one only through AB (as a whole) via the AB correlations. We call this latter contribution to the internal energy the *binding energy*. Certainly, although (in the case of time-independent total Hamiltonian) the total internal energy remains constant in time, that of either A or B varies because they interact and thus exchange work and heat.

In Section 3.2 we discuss a general formulation of the second law of thermodynamics based on the only assumption of a factorized initial state for AB. This formulation does not relate entropy with heat or temperature, the latter not being even defined in general. Therefore, we analyze two proposals for defining temperature-like quantities in physical systems out of equilibrium, comparing them by means of two examples reported in Section 3.3. Moreover, we comment on the relation between the general form of the second law and the results described in Chapter 2 for the entropy production under non-Markovian dynamical maps.

The last part of this Chapter is devoted to the comparison with the other proposals in the literature that describe the thermodynamics of a generic bipartite quantum systems. It turns out that our formulation is so far the only one able to pinpoint the thermodynamic role of correlations between the subsystems. The reformulation of the whole machinery in a classical mechanics scenario is also addressed, showing that there is no essential difference with respect to the quantum setting.

3.1 First law of thermodynamics

We consider a closed quantum system AB composed of two interacting subsystems A and B. The Hilbert space dimension of A and B is not constrained; in particular, they can be both finite dimensional such that no proper reservoir is present. The total Hamiltonian is chosen to be time-independent

$$H_{\mathrm{tot}} = H_A + H_B + H_{\mathrm{int}}, \tag{3.1}$$

and the composite system AB, initially described by a factorized density matrix $\varrho_{AB}(0)$, evolves in time according to the Schrödinger equation

$$\partial_t \varrho_{AB}(t) = -i[H_{\mathrm{tot}}, \varrho_{AB}(t)], \qquad \varrho_{AB}(0) = \varrho_A(0) \otimes \varrho_B(0). \tag{3.2}$$

The states of each subsystem are obtained at any time by partial tracing $\varrho_{A,B}(t) = \mathrm{Tr}_{B,A}\left[\varrho_{AB}(t)\right]$; thus from equation (3.2) we have

$$\partial_t \varrho_A(t) = -i[H_A, \varrho_A(t)] - i\mathrm{Tr}_B\left[H_{\mathrm{int}}, \varrho_{AB}(t)\right], \tag{3.3}$$

$$\partial_t \varrho_B(t) = -i[H_B, \varrho_B(t)] - i\mathrm{Tr}_A\left[H_{\mathrm{int}}, \varrho_{AB}(t)\right]. \tag{3.4}$$

In general, systems A and B become correlated in time due to the interaction Hamiltonian, even though they are initially uncorrelated. We can define the operator $\chi(t)$ that describes the correlations (both classical and quantum) between them

$$\chi(t) := \varrho_{AB}(t) - \varrho_A(t) \otimes \varrho_B(t), \tag{3.5}$$

and replacing this expression into equations (3.3) and (3.4) we obtain

$$\partial_t \varrho_A(t) = - i[H'_A(t), \varrho_A(t)] - i\mathrm{Tr}_B\left[H_\mathrm{int}, \chi(t)\right], \tag{3.6}$$

$$\partial_t \varrho_B(t) = - i[H'_B(t), \varrho_B(t)] - i\mathrm{Tr}_A\left[H_\mathrm{int}, \chi(t)\right], \tag{3.7}$$

where a sort of Lamb shift correction has been included in the Hamiltonians

$$H'_{A,B}(t) := H_{A,B} + \mathrm{Tr}_{B,A}\left[\varrho_{B,A}(t)H_\mathrm{int}\right]. \tag{3.8}$$

Therefore, in the evolution equation of each subsystem (3.6),(3.7) we can recognize a Schrödinger-like term, where the time-dependent Hamiltonian $H'_{A,B}(t)$ replaces the free Hamiltonian $H_{A,B}$, and a second dissipative term arising from the correlations established between A and B.

3.1.1 Effective Hamiltonians

The internal energy of the total system is defined as the mean value of the total Hamiltonian with respect to the time-evolving state, namely

$$\mathbb{U}_\mathrm{tot} = \mathrm{Tr}[\varrho_{AB}(t)H_\mathrm{tot}], \tag{3.9}$$

and is constant in time since the dynamics is given by Eq.(3.2).

In order to state the first law of thermodynamics in this setting one has to associate a certain amount of energy to system A and system B and, since they are interacting, it is reasonable to include a contribution from the interaction Hamiltonian to this energy. Therefore, we need to find an effective Hamiltonian for both A and B using physically motivated requirements, such that the internal energy of each subsystem can be unambiguously quantified:

$$\mathbb{U}_A(t) = \mathrm{Tr}[\varrho_A(t)H_A^{(\mathrm{eff})}(t)], \tag{3.10}$$

$$\mathbb{U}_B(t) = \mathrm{Tr}[\varrho_B(t)H_B^{(\mathrm{eff})}(t)]. \tag{3.11}$$

The first condition is a dynamical one: the effective Hamiltonian should drive the unitary part of the evolution equation. With this requirement we can fix $H_{A,B}^{(\mathrm{eff})}(t)$ up to a scalar time-dependent term $\mathcal{C}_{A,B}(t)$ that leaves the dynamical equations (3.6) and (3.7) unaffected

$$H_{A,B}^{(\mathrm{eff})}(t) = H'_{A,B}(t) + \mathcal{C}_{A,B}(t). \tag{3.12}$$

The second condition deals with the interaction Hamiltonian and the local accessibility of energy. Indeed, according to (3.12), an effective interaction Hamiltonian remains defined

$$H_\mathrm{int}^{(\mathrm{eff})}(t) = H_\mathrm{tot} - H_A^{(\mathrm{eff})}(t) - H_B^{(\mathrm{eff})}(t), \tag{3.13}$$

that is a nonlocal operator acting on the Hilbert space of both systems A and B and it cannot be assigned to one of the two. It seems worth rearranging its contribution to the total energy such that it is not accessible by local measurements:

$$\mathrm{Tr}_A[\varrho_A(t)\, H_\mathrm{int}^{(\mathrm{eff})}(t)] = \mathrm{Tr}_B[\varrho_B(t)H_\mathrm{int}^{(\mathrm{eff})}(t)] = 0. \tag{3.14}$$

As a consequence of this second requirement the effective Hamiltonians can be rewritten as follows

$$H_A^{(\text{eff})}(t) = H_A'(t) - \alpha_A \text{Tr}\left[\varrho_A(t) \otimes \varrho_B(t) H_{\text{int}}\right], \tag{3.15}$$

$$H_B^{(\text{eff})}(t) = H_B'(t) - \alpha_B \text{Tr}\left[\varrho_A(t) \otimes \varrho_B(t) H_{\text{int}}\right], \tag{3.16}$$

where the real parameters α_A and α_B are such that $\alpha_A + \alpha_B = 1$.

Remark 5. *Note that one of the real parameters, say α_A, is still undetermined. In general, there is no model-independent condition that fixes this value. This parameter seems like another thermodynamic degree of freedom, whose role should be decided on the basis of the specific physical conditions of the nonequilibrium thermodynamic systems in question.*

Given the internal energies of the constituent systems Eq. (3.10) and the total conserved energy Eq. (3.9), one finds that an energy contribution remains, called *binding* energy $\mathbb{U}_\chi(t)$,

$$\mathbb{U}_\chi(t) := \mathbb{U}_{\text{tot}} - \mathbb{U}_A(t) - \mathbb{U}_B(t), \tag{3.17}$$

which can be interpreted as energy stored in the correlations $\chi(t)$ since it turns out that

$$\mathbb{U}_\chi(t) = \text{Tr}[\chi(t) H_{\text{int}}^{(\text{eff})}(t)]. \tag{3.18}$$

From equation (3.17) it is evident that the internal energy is in general a non additive quantity. Nevertheless, if the contribution stored in the correlations can be neglected, as one assumes in standard statistical mechanics, the energy of the composite system is equal to the sum of the subsystems energies.

3.1.2   Heat and work

In thermodynamics, one usually distinguishes the contributions to the variations of energy into work $\mathbb{W}$ and heat $\mathbb{Q}$. In a quantum system with time-dependent Hamiltonian $H(t)$ this is reasonably done as mentioned in the first Chapter [39, 110]

$$\partial_t \mathbb{Q}(t) = \text{Tr}\left[\partial_t \varrho(t) \, H(t)\right], \tag{3.19}$$

$$\partial_t \mathbb{W}(t) = \text{Tr}\left[\varrho(t) \, \partial_t H(t)\right]. \tag{3.20}$$

First of all, we note that with these definitions, the first law of thermodynamics for the internal energy $\mathbb{U}(t) = \text{Tr}\left[H(t)\varrho(t)\right]$ is identically satisfied:

$$\partial_t \mathbb{U}(t) = \partial_t \mathbb{Q}(t) + \partial_t \mathbb{W}(t). \tag{3.21}$$

Moreover, the work power is vanishing as expected in absence of an external field modelled by a time-dependent potential, while the heat flux is zero for the unitary dynamics generated by $H(t)$, namely in absence of an external interacting quantum system. In our framework we can define

heat flux and work power for both A and B substituting the effective Hamiltonians (3.15),(3.16) in Eqs.(3.19) and (3.20) . As a result, one finds the following expressions

$$\partial_t \mathbb{W}_A(t) = \alpha_B \mathrm{Tr}\left[\varrho_A(t) \otimes \partial_t \varrho_B(t) H_{\mathrm{int}}\right] - \alpha_A \mathrm{Tr}\left[\partial_t \varrho_A(t) \otimes \varrho_B(t) H_{\mathrm{int}}\right] =$$
$$= -\partial_t \mathbb{W}_B(t), \tag{3.22}$$

$$\partial_t \mathbb{Q}_A(t) = -i\mathrm{Tr}\left[\chi(t)\big[H_A^{(\mathrm{eff})}(t), H_{\mathrm{int}}\big]\right], \tag{3.23}$$

$$\partial_t \mathbb{Q}_B(t) = -i\mathrm{Tr}\left[\chi(t)\big[H_B^{(\mathrm{eff})}(t), H_{\mathrm{int}}\big]\right], \tag{3.24}$$

and two separated balances arise

$$\partial_t \mathbb{W}_A(t) + \partial_t \mathbb{W}_B(t) = 0, \tag{3.25}$$

$$\partial_t \mathbb{Q}_A(t) + \partial_t \mathbb{Q}_B(t) = -\partial_t \mathbb{U}_\chi(t). \tag{3.26}$$

Therefore, correlations exchange energy with both subsystems only in the form of heat, because it turns out that the time-dependence of the effective interaction Hamiltonian does not contribute to the variation of the binding energy

$$\partial_t \mathbb{U}_\chi(t) = \mathrm{Tr}[\partial_t \chi(t) H_{\mathrm{int}}^{(\mathrm{eff})}(t)], \qquad \mathrm{Tr}[\chi(t)\partial_t H_{\mathrm{int}}^{(\mathrm{eff})}(t)] = 0. \tag{3.27}$$

This is an interesting result of ref.[72].

Remark 6. *The previous balance equations* (3.25) *and* (3.26) *are not affected by the parameters* $\alpha_{A,B}$. *Moreover, it is shown in equations* (3.22) *and* (3.23) *that work depends on these parameters but not heat. In this respect, the heat flux is fully determined while the work power must be fixed depending on the specific model.*

3.2 Second law of thermodynamics

According to the second law of thermodynamics, the entropy of a macroscopic closed system which is *thermally isolated* (in thermodynamics terminology) can only remain constant or increase in time [111, 112].

In the following we demonstrate the possible emergence of the second law of thermodynamics and the important role of system-bath correlations in this microscopic context.

In the case of a compound system AB, the subadditivity of the von Neumann entropy [70]

$$\mathbb{S}(t) = -\mathrm{Tr}\left[\varrho(t)\log\varrho(t)\right], \tag{3.28}$$

implies that the *mutual information*

$$\mathbb{S}_\chi(t) = \mathbb{S}_A(t) + \mathbb{S}_B(t) - \mathbb{S}_{AB}(t) \tag{3.29}$$

is always nonnegative. Mutual information characterizes the amount of total correlations (both classical and quantum) shared by the two subsystems A and B [113, 114]. Intuitively, if the correlations between A and B increases, $\mathbb{S}_\chi$ becomes larger.

Since we have assumed that the total system AB is closed, it evolves unitarily and its von Neumann entropy $\mathbb{S}_{AB}(t)$ does not change in time (even if its Hamiltonian depends on time). With the assumption that the initial state of AB is uncorrelated (i.e., $\mathbb{S}_\chi(0) = 0$), leads to

$$\Delta\mathbb{S}_A(t) + \Delta\mathbb{S}_B(t) = \mathbb{S}_\chi(t) \geqslant 0, \tag{3.30}$$

where $\Delta\mathbb{S}_A(t) = \mathbb{S}_A(t) - \mathbb{S}_A(0)$ and $\Delta\mathbb{S}_B(t) = \mathbb{S}_B(t) - \mathbb{S}_B(0)$, as obtained in Ref. [115]. This relation states that, as long as one observes subsystems A and B locally and their initial state is without any correlations, the sum of the total variations of the entropies of A and B is always nonnegative. One can consider this property as a form of the second law of thermodynamics for the compound system AB. Notice that such a statement does not rely on the concept of temperature which is not clearly defined in the non-equilibrium setting. In the following, we try to elaborate on that, analyzing two different temperature-like quantities.

3.2.1 Possible definitions of temperature

Unlike in equilibrium thermodynamics, in a general nonequilibrium system "temperature" is not a well-defined quantity (see, e.g., Refs. [116, 117] for some recent discussions). However, given the internal energy $\mathbb{U}(t)$ and the von Neumann entropy $\mathbb{S}(t)$, one can introduce a time-dependent *pseudo-temperature* through the following ratio

$$\frac{1}{T(t)} := \frac{\partial_t\mathbb{S}(t)}{\partial_t\mathbb{U}(t)}, \tag{3.31}$$

which is somewhat reminiscent of the equilibrium definition $1/T = (\partial\mathbb{S}/\partial\mathbb{U})_{N,V}$.

Remark 7. *In generic quantum systems, it is not always clear how to define V and N (or other relevant thermodynamic properties). Additionally, in thermodynamic equilibrium we deal with the partial derivative $(\partial\mathbb{S}/\partial\mathbb{U})_{N,V}$ rather than the ratio of two derivatives $((\partial_t\mathbb{S})/(\partial_t\mathbb{U}))$, which can be different quantities. Noting equations 3.10 and 3.15, the free parameter α_A (and α_B) would also appear in the pseudo-temperature. In general then, one should not expect that the pseudo-temperature necessarily have definite relation with the equilibrium temperature, unless under certain conditions. Later in the examples we show explicitly how in special cases the pseudo-temperature may relate to the equilibrium temperature by appropriately fixing the scalar α_A through thermodynamic properties of the system in question.*

Adopting the concept of pseudo-temperature, one can associate time-dependent pseudo-temperatures $T_{A,B}(t)$ with subsystems A and B and try to construct an entropy production for both subsystems from such a quantity. Using the first law and (3.31), it turns out that

$$\partial_t\mathbb{S}_{A,B}(t) = \frac{\partial_t\mathbb{Q}_{A,B}(t)}{T_{A,B}(t)} + \frac{\partial_t\mathbb{W}_{A,B}(t)}{T_{A,B}(t)}. \tag{3.32}$$

Therefore, formally, a quantity resembling the entropy production can be defined as follows

$$\widetilde{\sigma}_{A,B}(t) := \partial_t\mathbb{S}_{A,B}(t) - \frac{\partial_t\mathbb{Q}_{A,B}(t)}{T_{A,B}(t)} = \frac{\partial_t\mathbb{W}_{A,B}(t)}{T_{A,B}(t)}. \tag{3.33}$$

The quantity $\widetilde{\sigma}$ is analogous to the entropy production as discussed in the previous Chapters, where we have studied the case of an externally driven system A which is weakly coupled to a conservative heat bath B inducing a dissipative dynamics [40, 41, 118, 119]. In that particular context, however, the entropy production is related to the difference between the variation of the entropy $\mathbb{S}_A(t)$ and the entropy flux into or out of the system associated to the heat flux $\partial_t \mathbb{Q}_A(t)$ divided by the temperature of the bath T (rather than $T_A(t)$ as in equation (3.33)).

Notwithstanding these fundamental physical differences, it is still interesting to study to which extent the thermodynamical inequalities $\sigma_t \geq 0$ and (3.30) can be related to the behavior of $\widetilde{\sigma}_{A,B}(t)$ in equation (3.33). It is evident that $\widetilde{\sigma}_{A,B}(t)$ cannot be both strictly positive in general. For example, in the case of the same instantaneous pseudo-temperatures, from (3.33) we obtain $\partial_t \widetilde{\sigma}_A(t) = -\partial_t \widetilde{\sigma}_B(t)$ for $\partial_t \mathbb{W}_A(t) = -\partial_t \mathbb{W}_B(t)$. Moreover, it is not true that the finite variation

$$\widetilde{\Sigma}_A(t) + \widetilde{\Sigma}_B(t) = \int_0^t \mathrm{d}s \, \partial_s \mathbb{W}_A(s) \left(\frac{1}{T_A(s)} - \frac{1}{T_B(s)} \right) \tag{3.34}$$

becomes nonnegative in the absence of initial correlations between A and B, unlike the case for the finite variations of the von Neumann entropies of the reduced states $\varrho_{A,B}(t)$.

One can argue that the quantities $\widetilde{\sigma}_{A,B}(t)$ do not generically behave as expected from true thermodynamic quantities because the instantaneous pseudo-temperatures do not behave themselves as thermodynamic temperatures. This, however, does not exclude that, under certain conditions, proper thermodynamic patterns might emerge.

To alleviate the above situation, we can discern a better motivated notion of temperature by appealing to analogy with standard thermodynamics. In *classical* thermodynamics the relation

$$\mathrm{d}\mathbb{S} = \frac{1}{T} \mathrm{d}\mathbb{Q} \tag{3.35}$$

holds for a system undergoing a quasistatic reversible transformation, whereas for a nonequilibrium process there is an extra term corresponding to the internal entropy production σ,

$$\mathrm{d}\mathbb{S} = \frac{1}{T} \mathrm{d}\mathbb{Q} + \sigma. \tag{3.36}$$

In this case the "temperature" is fixed by the external environment (bath) which is supposed to exchange heat always quasistatically (because of its short relaxation times), *without changing its temperature*. In our formalism, however, we treat the system and bath similarly. Thus we can extend equation (3.36) and identify an *extended* temperature and an entropy production for both system and bath and see how they compare at long times with expected thermodynamic temperatures. One way to do so is to explicitly compute $\partial_t \mathbb{S}(t)$ and $\partial_t \mathbb{Q}(t)$ and next compare them to read an extended temperature $\mathcal{T}$ as

$$\partial_t \mathbb{S}(t) = \frac{1}{\mathcal{T}(t)} \partial_t \mathbb{Q}(t) + \overline{\sigma(t)}. \tag{3.37}$$

Remark 8. *Note that equation (3.37) defines both the extended temperature $\mathcal{T}(t)$ and the generalized entropy production $\overline{\sigma(t)}$. Moreover, unlike the pseudo-temperature $T(t)$, $\mathcal{T}(t)$ is by construction $\alpha_{A,B}$-independent because neither heat nor entropy depends on $\alpha_{A,B}$. In the following examples, we discuss both nonequilibrium temperatures $T(t)$ and $\mathcal{T}(t)$ by comparing them with the equilibrium temperature T (of the bath).*

3.3   Examples

Here we study in detail two examples, in one of which *thermalization* occurs, whereas the other one does not exhibit this feature.

3.3.1   Example 3: Thermalizing qubit

Consider a two-state system (e.g., a spin-1/2 particle or a two-level atom) interacting with a thermal environment, comprised of infinitely many modes at (initial) temperature $T = 1/\beta$, through the Jaynes-Cummings total Hamiltonian $H = H_0 + H_{\text{int}}^{(\lambda)}$, where

$$H_0 = \frac{1}{2}\omega_0\sigma_z + \sum_{k=1}^{\infty}\omega_k a_k^\dagger a_k, \tag{3.38}$$

$$H_{\text{int}}^{(\lambda)} = \lambda\sum_k (f_k^*\sigma_+ \otimes a_k + f_k\sigma_- \otimes a_k^\dagger). \tag{3.39}$$

Here σ_x, σ_y, and $\sigma_z = \text{diag}(1, -1)$ are the Pauli operators, $\sigma_\pm = \sigma_x \pm i\sigma_y$, and a_k is the bosonic annihilation operator for mode k. Although this model is not exactly solvable, we can find the exact states of the system and bath up to any order in λ; see Appendix B for details of $O(\lambda^3)$ calculations. In the following, we label the quantities related to the two-level system with S and the quantities related to the oscillators with B.

In the weak-coupling, long-time, ω-continuum, Markovian limit (where $\lambda \to 0$ and $t \to \infty$ such that $\lambda^2\tau = \text{const.}$ and $\sum_k \to \int_0^\infty \mathrm{d}\omega$), we can find the following Lindblad-type dynamical equation:

$$\begin{aligned}
\partial_t\varrho_S^{(\lambda)}(t) = &-i\big[H_S + H_{\text{LS}}, \varrho_S^{(\lambda)}(t)\big] + \\
&+ \frac{\gamma}{2}\,\overline{n}(\omega_0, \beta)\Big(2\sigma_+\varrho_S^{(\lambda)}(t)\sigma_- - \{\sigma_-\sigma_+, \varrho_S^{(\lambda)}(t)\}\Big) + \\
&+ \frac{\gamma}{2}\big(\overline{n}(\omega_0, \beta) + 1\big)\Big(2\sigma_-\varrho_S^{(\lambda)}(t)\sigma_+ - \{\sigma_+\sigma_-, \varrho_S^{(\lambda)}(t)\}\Big)
\end{aligned} \tag{3.40}$$

where

$$H_{\text{LS}} = 2\lambda^2\mathbb{P}\int_0^\infty \mathrm{d}\omega\,\frac{|f(\omega)|^2}{\omega_0 - \omega}\,(2\,\overline{n}(\omega, \beta) + 1)\,\sigma_z \tag{3.41}$$

$$=: (1/2)\Omega(\lambda^2, \omega_0, \beta)\,\sigma_z, \tag{3.42}$$

is the Lamb-shift Hamiltonian, $\mathbb{P}$ denotes the Cauchy principal value, β is the inverse temperature of the bath,

$$\overline{n}(\omega_0, \beta) = (\mathrm{e}^{\beta\omega_0} - 1)^{-1} \tag{3.43}$$

is the Planck distribution or the mean quanta number in a mode with frequency ω_0, and

$$\gamma = 2\pi\lambda^2|f(\omega_0)|^2 \tag{3.44}$$

is the spontaneous emission rate (see Appendix B). This evolution agrees with the Markovian master equation derived in Ref. [119]. The solution to equation (3.40) is given by

$$\varrho_S^{(\lambda)}(t) = \frac{1}{2} \begin{bmatrix} 1 + z(t) & x(t) - iy(t) \\ x(t) + iy(t) & 1 - z(t) \end{bmatrix}, \tag{3.45}$$

$$x(t) - iy(t) = \big(x(0) - iy(0)\big)\, \mathrm{e}^{-i(\omega_0 + \Omega)t - \widetilde{\gamma}t/2} \tag{3.46}$$

$$x(t) + iy(t) = \big(x(0) + iy(0)\big)\, \mathrm{e}^{i(\omega_0 + \Omega)t - \widetilde{\gamma}t/2} \tag{3.47}$$

$$z(t) = z(0)\mathrm{e}^{-\widetilde{\gamma}t} - \tanh(\beta\omega_0/2)\left(\mathrm{e}^{-\widetilde{\gamma}t} - 1\right) \tag{3.48}$$

where $\widetilde{\gamma} = \gamma \coth(\beta\omega_0/2)$. It is evident from this solution that system S eventually thermalizes,

$$\lim_{t \to \infty} \varrho_S^{(\lambda)}(t) = \varrho_S^{\beta}, \tag{3.49}$$

where $\varrho_S^{\beta} = (1/Z_\beta)\mathrm{e}^{-\beta\omega_0\sigma_z/2}$ is a thermal state in the Gibbs form, in which $Z_\beta = \mathrm{Tr}[\mathrm{e}^{-\beta\omega_0\sigma_z/2}]$ is the partition function.

We can explicitly compute $\partial_t \mathbb{S}_S^{(\lambda)}(t)$ as

$$\partial_t \mathbb{S}_S^{(\lambda)}(t) = -\frac{1}{2} \log \frac{1 + r_S^{(\lambda)}(t)}{1 - r_S^{(\lambda)}(t)}\, \partial_t r_S^{(\lambda)}(t), \tag{3.50}$$

where $r_S^{(\lambda)}(t)$ is the norm of the Bloch vector $\mathbf{r}_S^{(\lambda)} = (x, y, z)$ associated with $\varrho_S^{(\lambda)}(t)$ as $\varrho_S = (1/2)(I + \mathbf{r} \cdot \boldsymbol{\sigma})$ (here $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$), and from equation (3.40) we have

$$\partial_t r_S(t) = \frac{\widetilde{\gamma}[x^2(t) + y^2(t)] - 2\gamma z(t) - 2\widetilde{\gamma}z^2(t)}{2\sqrt{x^2(t) + y^2(t) + z^2(t)}}. \tag{3.51}$$

Additionally, in the Markovian limit, the energy of this system is obtained as

$$\partial_t \mathbb{U}_S^{(\lambda)}(t) = -\frac{\omega_0}{2}\gamma \mathrm{e}^{-\widetilde{\gamma}t}\big(\coth(\beta\omega_0/2)z(0) + 1\big). \tag{3.52}$$

As a result,

$$\lim_{t \to \infty} \frac{1}{T_S^{(\lambda)}(t)} = \beta\left[1 - \frac{\big(x^2(0) + y^2(0)\big)\coth(\beta\omega_0/2)}{2\big(z(0) + \tanh(\beta\omega_0/2)\big)}\right]. \tag{3.53}$$

This pseudo-temperature behaves well, i.e., exhibits thermalization, if there is no initial coherence ($\varrho_{10} = 0$, or equivalently, $x(0) = y(0) = 0$).

In the Markovian regime we consider the thermal bath always in equilibrium (namely, $\varrho_B(\tau) \approx \varrho_B^{\beta}$), and as a consequence the effective energy of S reduces to (see Appendix B)

$$\mathbb{U}_S(t) = \mathrm{Tr}\left[\varrho_S(t)H_S\right], \tag{3.54}$$

and the heat flux reads

$$\partial_t \mathbb{Q}_S(t) = \mathrm{Tr}\left[\partial_t \varrho_S(t)H_S\right] = \frac{\omega_0}{2}\partial_t z(t). \tag{3.55}$$

Comparing equations (3.50) and (3.55) yields

$$\frac{1}{\mathcal{T}_S(t)} = -\frac{1}{\omega_0}\frac{z(t)}{r_S(t)}\log\frac{1+r_S(t)}{1-r_S(t)}, \tag{3.56}$$

$$\overline{\sigma}_S(t) = -\frac{1}{2}\frac{\partial_t r_S(t)}{r_S(t)}\log\frac{1+r_S(t)}{1-r_S(t)}, \tag{3.57}$$

which are both $\alpha_{S,B}$-independent. By substituting the Bloch vector components of the Gibbs state ϱ_S^β, $(x=0, y=0, z=-\tanh(\beta\omega_0/2))$, in equation (3.56), we also see that

$$\lim_{t\to\infty}\mathcal{T}_S(t) = T,$$

which gives the expected equilibrium temperature. Moreover, the sign of $\mathcal{T}_S(t)$ is opposite to the sign of $z(t)$, so that a negative extended temperature points out a population inversion, as for thermal equilibrium.

For the bath thermodynamics, after some algebra (see Appendix B) we find that when $t \to \infty$ (up to $O(\lambda^3)$)

$$\partial_t\mathbb{Q}_B^{(\lambda)}(t) = 4\omega_0\gamma\Big(\big[\big(\overline{n}(\omega_0,\beta)+1\big)\varrho_{00} - \overline{n}(\omega_0,\beta)\varrho_{11}\big] - |\varrho_{10}|^2\Big), \tag{3.58}$$

$$\partial_t\mathbb{U}_B^{(\lambda)}(t) = 4\gamma\omega_0\big[\big(\overline{n}(\omega_0,\beta)+1\big)\varrho_{00} - \overline{n}(\omega_0,\beta)\varrho_{11}\big], \tag{3.59}$$

$$\partial_t\mathbb{S}_B^{(\lambda)}(t) = 4\beta\gamma\omega_0\big[\big(\overline{n}(\omega_0,\beta)+1\big)\varrho_{00} - \overline{n}(\omega_0,\beta)\varrho_{11} - |\varrho_{10}|^2\big], \tag{3.60}$$

whence

$$\lim_{t\to\infty}T_B^{(\lambda)}(t) = \frac{1}{\beta}\Big[1 + \frac{|\varrho_{10}|^2}{\overline{n}(\omega_0,\beta)(\varrho_{00}-\varrho_{11}) + \varrho_{00} - |\varrho_{10}|^2}\Big], \tag{3.61}$$

$$\partial_t\mathbb{S}_B^{(\lambda)}(t) = \beta\,\partial_t\mathbb{Q}_B^{(\lambda)}(t). \tag{3.62}$$

Note that the limit (3.61) is independent of α_B but it depends on the initial state of the system. However, if $\varrho_S(0)$ does not have any coherence, i.e., $\varrho_{10} = 0$, one retrieves the expected value $1/\beta$ for the pseudo-temperature $T_B^{(\lambda)}$. But regardless of the initial state of the system, from equation (3.62), we see that the extended temperature behaves as expected, $\lim_{t\to\infty}\mathcal{T}_B^{(\lambda)}(t) = T$. Besides, the internal entropy production of the bath up to $O(\lambda^3)$ vanishes,

$$\overline{\sigma}_B^{(\lambda)} = 0. \tag{3.63}$$

Remark 9. *Following the discussion in Remark 7, the reason for the difference between the pseudo-temperature and the standard thermodynamic temperature lies in the definition of the former. The entropy of the qubit in this example can be computed using its eigenvalues, which in general depend on the (x, y, z) components of the Bloch vector. From equation (3.54), we can identify the z component with $\mathbb{U}$ (assuming $\omega_0/2 = 1$ for simplicity). Thus we can say that $\mathbb{S}$ is a function of $(x, y, \mathbb{U})$, and we can compute the partial derivative of $\mathbb{S}$ with respect to $\mathbb{U}$ (while keeping x and y fixed),*

$$\left(\frac{\partial\mathbb{S}(x,y,\mathbb{U})}{\partial\mathbb{U}}\right)_{x,y} = -\frac{1}{2}\frac{\mathbb{U}}{\sqrt{x^2+y^2+\mathbb{U}^2}}\log\frac{1+\sqrt{x^2+y^2+\mathbb{U}^2}}{1-\sqrt{x^2+y^2+\mathbb{U}^2}}. \tag{3.64}$$

If we now consider $x(t)$, $y(t)$, and $\mathbb{U}(t)$ evolving according to the dissipative thermalizing dynamics (3.45), we obtain

$$\lim_{t\to\infty}\left(\frac{\partial \mathbb{S}(x,y,\mathbb{U})}{\partial \mathbb{U}}\right)_{x,y} = \beta, \tag{3.65}$$

which agrees with the standard definition of the equilibrium temperature. Rather, the inverse pseudo-temperature $1/T_S^{(\lambda)}(t)$ reads as

$$\frac{\mathrm{d}\mathbb{S}\big(x(t),y(t),z(t)\big)/\mathrm{d}t}{\mathrm{d}\mathbb{U}/\mathrm{d}t}, \tag{3.66}$$

which corresponds to inverting the function $\mathbb{U}(t)$, finding $t(\mathbb{U})$, and computing the total derivative with respect to $\mathbb{U}$,

$$\frac{\mathrm{d}\mathbb{S}}{\mathrm{d}\mathbb{U}}\big(x(\mathbb{U}),y(\mathbb{U}),\mathbb{U}\big) =$$
$$= -\frac{1}{2}\frac{\mathbb{U}+x(\mathbb{U})\frac{\mathrm{d}x}{\mathrm{d}\mathbb{U}}+y(\mathbb{U})\frac{\mathrm{d}y}{\mathrm{d}\mathbb{U}}}{\sqrt{x^2(\mathbb{U})+y^2(\mathbb{U})+\mathbb{U}^2}}\log\frac{1+\sqrt{x^2(\mathbb{U})+y^2(\mathbb{U})+\mathbb{U}^2}}{1-\sqrt{x^2(\mathbb{U})+y^2(\mathbb{U})+\mathbb{U}^2}}. \tag{3.67}$$

In the $t\to\infty$ limit (or $\mathbb{U}\to\mathbb{U}_{\text{thermal}}$) this derivative is different from β because in general

$$x(\mathbb{U})\frac{\mathrm{d}x}{\mathrm{d}\mathbb{U}}+y(\mathbb{U})\frac{\mathrm{d}y}{\mathrm{d}\mathbb{U}} = \frac{x^2(0)+y^2(0)}{2\big(z(0)+\tanh(\beta)\big)} \neq 0. \tag{3.68}$$

The two derivatives coincide only if x and y are fixed during the dynamics, which is the case of vanishing initial coherence.

3.3.2 Example 4: Dephasing qubit

We apply the formalism developed in this Chapter to the exactly solvable model of a qubit in interaction with a thermal bosonic bath [120]. We present this example in order to clarify the final remark in Chapter 2, focusing on the three hypothesis that relate the entropy production σ_t and Eq. (2.51). Consider a total Hamiltonian given by $H_{\text{tot}} = H_S + H_B + H_{\text{int}}$ with

$$H_S = \frac{\omega_0}{2}\sigma_z, \quad H_B = \sum_{k=1}^{\infty}\omega_k \mathrm{a}_k^\dagger \mathrm{a}_k, \quad H_{\text{int}} = \lambda\sigma_z\otimes\sum_{k=1}^{\infty}\big(f_k^* \mathrm{a}_k + f_k \mathrm{a}_k^\dagger\big),$$

where a_k is the bosonic annihilation operator of mode k, satisfying the canonical commutation relations $[\mathrm{a}_k,\mathrm{a}_l^\dagger] = \delta_{kl}$, and the complex parameters f_k are such that $\sum_{k=1}^{\infty}|f_k|^2 < \infty$. We assume that the initial state of the total system can be written as $\varrho_{SB}(0) = \varrho_S(0)\otimes\varrho_B^\beta$, where $\varrho_S(0)$ is the initial state of the qubit and ϱ_B^β is the Gibbs state of the thermal bath at inverse temperature β,

$$\varrho_S(0) = \sum_{\ell,\ell'=0}^{1}\varrho_{\ell\ell'}|\ell\rangle\langle\ell'|, \qquad \sigma_z|\ell\rangle = (-)^\ell|\ell\rangle, \qquad \varrho_B^\beta = \frac{\mathrm{e}^{-\beta\sum_k\omega_k \mathrm{a}_k^\dagger \mathrm{a}_k}}{\mathrm{Tr}\left[\mathrm{e}^{-\beta\sum_k\omega_k \mathrm{a}_k^\dagger \mathrm{a}_k}\right]}. \tag{3.69}$$

In the interaction picture, the Hamiltonian becomes

$$\widetilde{H}_{\mathrm{int}}^{(\lambda)}(t) = U_0^\dagger(t) H_{\mathrm{int}}^{(\lambda)} U_0(t) = \lambda \sigma_z \otimes \left(\mathrm{a}(f_t) + \mathrm{a}^\dagger(f_t) \right), \tag{3.70}$$

where $U_0(t) = \mathrm{e}^{-iH_0 t}$ and f_t is the vector with components $f_k^* \mathrm{e}^{-i\omega_k t}$. The time-ordered exponentiation of $\widetilde{H}_{\mathrm{int}}^{(\lambda)}(t)$ yields

$$\widetilde{U}_\lambda(t) = \mathbb{T}\mathrm{e}^{-i\lambda\sigma_z \otimes \int_0^\tau \mathrm{d}s\, \left(\mathrm{a}(f_s) + \mathrm{a}^\dagger(f_s) \right)} = \mathrm{e}^{-i\lambda^2 \varphi(t)} \mathrm{e}^{-i\lambda\sigma_z \otimes \int_0^\tau \mathrm{d}s\, \left(\mathrm{a}(f_s) + \mathrm{a}^\dagger(f_s) \right)},$$

where the pure phase factor

$$\varphi(t) = \sum_k \frac{|f_k|^2}{\omega_k^2} \left(\omega_k t - \sin(\omega_k t) \right) \tag{3.71}$$

does not contribute to the evolution

$$\varrho_{SB}^{(\lambda)}(t) = U_0(t) \widetilde{U}_\lambda(t) \varrho_{SB}(0) \widetilde{U}_\lambda^\dagger(t) U_0^\dagger(t). \tag{3.72}$$

One can see that

$$\varrho_{SB}^{(\lambda)}(t) = \sum_{\ell,\ell'=0}^{1} \varrho_{\ell\ell'} \mathrm{e}^{-i\omega_0 \zeta_{\ell\ell'} t/2} |\ell\rangle\langle\ell'| \otimes D_\ell(g_t)\, \varrho_B^\beta\, D_{\ell'}^\dagger(g_t), \tag{3.73}$$

where $\zeta_{\ell\ell'} = (-)^\ell - (-)^{\ell'}$, g_τ is the vector with components

$$g_k^*(t) = f_k^* (\mathrm{e}^{-i\omega_k t} - 1)/\omega_k, \tag{3.74}$$

and $D_\alpha(g_t)$ is the displacement operator

$$D_\ell(g_t) = \mathrm{e}^{(-)^\ell \lambda [\mathrm{a}^\dagger(g_t) - \mathrm{a}(g_t)]}, \tag{3.75}$$

whose action can be derived from the canonical commutation relations as

$$D_\ell(g_t)\, \mathrm{a}_k\, D_\ell^\dagger(g_t) = \mathrm{a}_k - (-)^\ell \lambda\, g_k(t) \tag{3.76}$$

$$=: A_k(\ell, \lambda, t). \tag{3.77}$$

From here the reduced density matrices of the two subsystems read as

$$\varrho_S^{(\lambda)}(t) = \varrho_{00}|0\rangle\langle 0| + \varrho_{11}|1\rangle\langle 1| + \mathrm{e}^{-8\lambda^2 \Gamma(t)} \left(\varrho_{10} \mathrm{e}^{i\omega_0 t} |1\rangle\langle 0| + \varrho_{01} \mathrm{e}^{-i\omega_0 t} |0\rangle\langle 1| \right), \tag{3.78}$$

$$\varrho_B^{(\lambda)}(t) = \sum_{\ell=0}^{1} \varrho_{\ell\ell} D_\ell(g_t)\, \varrho_B^\beta\, D_\ell^\dagger(g_t) = \sum_{\ell=0}^{1} \frac{\varrho_{\ell\ell}}{Z_\beta} \mathrm{e}^{-\beta \sum_k \omega_k A_k^\dagger(\ell,\lambda,t)\, A_k(\ell,\lambda,t)}, \tag{3.79}$$

where $\mathrm{Tr}\left[D_\ell(g_t)\, \varrho_B^\beta\, D_{\ell'}^\dagger(g_t) \right] = \mathrm{e}^{-8\lambda^2 \Gamma(t)}$ for $\ell \neq \ell'$, with

$$\Gamma(t) = \sum_k \frac{|f_k|^2}{\omega_k^2} \coth(\beta\omega_k/2) \sin^2(\omega_k t/2). \tag{3.80}$$

Further, denoting the qubit polarization at time $t = 0$ by $\langle\sigma_z\rangle_S$, the effective qubit Hamiltonian takes the form

$$H_S^{(\text{eff})}(t) = \left(\frac{\omega_0}{2} - 4\lambda^2\langle\sigma_z\rangle_S\,\Delta(t)\right)\sigma_z + 4\lambda^2\alpha_S\,\langle\sigma_z\rangle_S^2\,\Delta(t), \tag{3.81}$$

where the explicit time dependence is provided by

$$\begin{aligned}
\Delta(t) &= -\frac{1}{4\lambda\langle\sigma_z\rangle_S}\,\text{Tr}\left[\varrho_B^{(\lambda)}(t)\big(\text{a}(f) + \text{a}^\dagger(f)\big)\right] \\
&= \sum_k \frac{|f_k|^2}{\omega_k}\sin^2(\omega_k t/2).
\end{aligned} \tag{3.82}$$

Similarly, the bath effective Hamiltonian reads as

$$H_B^{(\text{eff})}(t) = \sum_k \omega_k \text{a}_k^\dagger \text{a}_k + \lambda\,\langle\sigma_z\rangle_S\left(\text{a}(f) + \text{a}^\dagger(f)\right) + 4\lambda^2\alpha_B\,\langle\sigma_z\rangle_S^2\,\Delta(t), \tag{3.83}$$

where the time-dependent appears only in the scalar term. From the above relations, the exchanged works between system S and bath B are calculated by using equation (1.44),

$$\partial_t\text{W}_B^{(\lambda)}(t) = 4\lambda^2\alpha_B\,\langle\sigma_z\rangle_S^2\,\partial_t\Delta(t) = -\partial_t\text{W}_S^{(\lambda)}(t), \tag{3.84}$$

where the last equality verifies equation (3.25). In addition, using equation (3.23) and the fact that

$$\begin{aligned}
\left[H_S^{(\text{eff})}(t), H_{\text{int}}\right] &= 0, \\
\left[H_B^{(\text{eff})}(t), H_{\text{int}}\right] &= \lambda\sigma_z \otimes \sum_k \omega_k(f_k\text{a}_k^\dagger - f_k^*\text{a}_k),
\end{aligned}$$

the heat exchanges are given by

$$\partial_t\mathbb{Q}_S^{(\lambda)}(t) = 0, \tag{3.85}$$

$$\partial_t\mathbb{Q}_B^{(\lambda)}(t) = 4\lambda^2\big(1 - \langle\sigma_z\rangle_S^2\big)\,\partial_t\Delta(t). \tag{3.86}$$

The binding energy also becomes

$$\mathbb{U}_\chi^{(\lambda)}(t) = -4\lambda^2\big(1 - \langle\sigma_z\rangle_S^2\big)\,\Delta(t), \tag{3.87}$$

whence $\partial_t\mathbb{Q}_B^{(\lambda)}(t) = -\partial_t\mathbb{U}_\chi^{(\lambda)}(t)$, in agreement with equation (3.26).

Equation (3.85) is physically expected because, with our specific system Hamiltonian ($H_S \propto \sigma_z$) and the interaction Hamiltonian ($H_{\text{int}} \propto \sigma_z \otimes (\text{a} + \text{a}^\dagger)$), we have $[H_S, H_{\text{int}}] = 0$. That is, this interaction with the environment cannot excite or change the *populations* of $\varrho_S(0)$; $\varrho_{00}(t) = \varrho_{00}$ [equation (3.78)]. Thus according to the definition of the heat exchange, we should have $\partial_t\mathbb{Q}_S^{(\lambda)}(t) = \text{Tr}[\partial_t\varrho_S^{(\lambda)}(t)H_S^{(\text{eff})}(t)] = \sum_{\ell=0}^1 \partial_t\varrho_{\ell\ell}(t)q(t)\sigma_{z,\,\ell\ell} = 0$, where we have used the fact that $H_S^{(\text{eff})}(t) = q(t)\sigma_z$ (for some appropriate q read through equation (3.81)).

Furthermore, using equations (3.84) and (3.86), and the fact that $\alpha_S + \alpha_B = 1$, it turns out that, unlike the infinitesimal heat exchanges, the infinitesimal variation of the internal energy of B depends on α_S,

$$\partial_t \mathbb{U}_B^{(\lambda)}(t) = 4\lambda^2 \big(1 - \alpha_S \langle \sigma_z \rangle_S^2 \big) \partial_t \Delta(t). \tag{3.88}$$

One expects the final pseudo-temperature of $T_B^{(\lambda)}(\infty)$, as defined by equation (3.31), to tend to the (initial) bath temperature $T = 1/\beta$ in the limit $\lambda \to 0$ of vanishing coupling between S and B. Indeed, if $\lambda = 0$, the thermal state is time-invariant. Since $\mathrm{Tr}[\partial_t \varrho_B^{(\lambda)}(t)] = 0$, the infinitesimal variation of the von Neumann entropy of B is given by

$$\partial_t \mathbb{S}_B^{(\lambda)}(t) = -\mathrm{Tr}\left[\partial_t \varrho_B^{(\lambda)}(t) \log \varrho_B^{(\lambda)}(t)\right]. \tag{3.89}$$

By expanding equation (3.79) up to $O(\lambda^3)$ one obtains (see Appendix C)

$$\partial_t \mathbb{S}_B^{(\lambda)}(t) = 4\beta\lambda^2 \big(1 - \langle \sigma_z \rangle_S^2\big) \partial_t \Delta(t). \tag{3.90}$$

Now if we use equations (3.84) and (3.86), together with the definition of the pseudo-temperature (3.31), we obtain

$$\lim_{t \to \infty} T_B^{(\lambda)}(t) = \frac{(1 - \alpha_S \langle \sigma_z \rangle_S^2)}{(1 - \langle \sigma_z \rangle_S^2)} T. \tag{3.91}$$

It is evident from this expression that in order to make the pseudo-temperature $T_B^{(\lambda)}$ to be equal to T (in the weak-coupling limit) we need to set $\alpha_S = 1$.

Additionally, we note that by comparing equations (3.86) and (3.90), these quantities are related as

$$\partial_t \mathbb{S}_B^{(\lambda)}(t) = \beta\, \partial_t \mathbb{Q}_B^{(\lambda)}(t). \tag{3.92}$$

Hence, we have $\mathcal{T}_B(t) = T$ and the inverse temperature $\beta = 1/T$ of the bath shows up as the prefactor of the heat flux, as expected in the standard equilibrium thermodynamics (equation (3.36)). Thus up to $O(\lambda^3)$ the internal entropy production in the bath vanishes,

$$\overline{\sigma}_B^{(\lambda)}(t) = 0. \tag{3.93}$$

This is consistent with the classical picture where the bath always exchanges heat quasistatically, see our discussion in the second law of thermodynamics.

Remark 10. *We have verified in two different models that the internal entropy production in a thermal bath vanishes in the weak-coupling limit up to the leading order in λ. This seems to be a general result and is consistent with our expectation from standard, equilibrium thermodynamics.*

Now we consider the pseudo-temperature $T_S^{(\lambda)}(t)$. We first note that, from equations (3.84) and (3.85) and after setting $\alpha_S = 1$, we have

$$\partial_t \mathbb{Q}_S^{(\lambda)}(t) = \partial_t \mathbb{W}_S^{(\lambda)}(t) = 0, \tag{3.94}$$

and thus

$$\partial_t \mathbb{U}_S^{(\lambda)}(t) = 0. \tag{3.95}$$

That is, despite interacting with bath B, system S does not exchange any heat or work (and thus internal energy) with B. Hence, intuitively, we should not expect that its temperature $T_S^{(\lambda)}$ to change; it should remain constant. This is explicitly seen by calculating

$$T_S^{(\lambda)}(t) = \frac{\partial_t \mathbb{U}_S^{(\lambda)}(t)}{\partial_t \mathbb{S}_S^{(\lambda)}(t)} = 0. \tag{3.96}$$

Note that if the system were initially prepared, e.g., in a thermal state with temperature $T_S^{(0)} \neq 0$, in principle its temperature should not change because this system does not thermalize [equation (3.78)]. This fact is captured by our pseudo-temperature as $T_S^{(\lambda)} = 0$. However, we note that $T(t)$ is defined by the given *dynamics* of S and cannot therefore be related to an initial (dynamics-independent) temperature such as an equilibrium temperature assigned by the preparation of the state.

Having calculated the heat and work exchanges by the system, it is also important to see how the von Neumann entropy of the system behaves. Using equation (3.78), the entropy of S can be explicitly calculated from the eigenvalues $\left(1 \pm r_S^{(\lambda)}(t)\right)/2$ of $\varrho_S^{(\lambda)}(t)$, where

$$r_S^{(\lambda)}(t) = \sqrt{1 - 4\left(\varrho_{00}\varrho_{11} - e^{-16\lambda^2\Gamma(t)}|\varrho_{01}|^2\right)}, \tag{3.97}$$

as well as its infinitesimal variation

$$\partial_t \mathbb{S}_S^{(\lambda)}(t) = -\frac{1}{2}\log\frac{1 + r_S^{(\lambda)}(t)}{1 - r_S^{(\lambda)}(t)}\,\partial_t r_S^{(\lambda)}(t) = \lambda^2 b^{(\lambda)}(t)\partial_t\Gamma(t), \tag{3.98}$$

where

$$b^{(\lambda)}(t) = \frac{16|\varrho_{01}|^2}{r_S^{(\lambda)}(t)}e^{-16\lambda^2\Gamma(t)}\log\frac{1 + r_S^{(\lambda)}(t)}{1 - r_S^{(\lambda)}(t)}. \tag{3.99}$$

Note that the quantity $b^{(\lambda)}(t)$ is nonnegative and has a well-defined time-independent limit,

$$b^{(0)} = \frac{16|\varrho_{01}|^2}{r_S^{(0)}(0)}\log\frac{1 + r_S^{(0)}(0)}{1 - r_S^{(0)}(0)}, \tag{3.100}$$

when $\lambda \to 0$. In order to study the time-derivatives $\partial_t\Delta(t)$ and $\partial_t\Gamma(t)$, we consider an *infinite* thermal bath with a *continuum* ω and a regularized Ohmic spectral density given by $f_k \simeq \sqrt{\omega}\,e^{-\omega\epsilon/2}$ (in which $\epsilon \geqslant 0$). Thus we substitute the discrete sums in equations (3.80) and (3.82) with the following integrals:

$$\Delta(t) = \int_0^\infty d\omega\,\sin^2(\omega t/2)\,e^{-\epsilon\omega} = \frac{t^2}{2\epsilon(\epsilon^2 + t^2)}, \tag{3.101}$$

$$\Gamma(t) = \int_0^\infty d\omega\frac{1}{\omega}\coth(\beta\omega/2)\sin^2(\omega t/2)\,e^{-\epsilon\omega}. \tag{3.102}$$

Hence, $\partial_t \Delta(t) = \epsilon t/(t^2 + \epsilon^2)^2$ as well as $\partial_t \Gamma(t) \geqslant 0$, as one can check by changing the variable $\omega t = \widetilde{\omega}$ and taking explicitly the derivative with respect to t. As a result, we see that $\partial_t \mathbb{S}_S^{(\lambda)}(t) \geqslant 0$. Furthermore, as a consequence of equation (3.85), in this regime, the internal entropy production relation (3.33) reduces to

$$\overline{\sigma}_S(t) = \partial_t \mathbb{S}_S^{(\lambda)}(t) \geqslant 0. \tag{3.103}$$

That is, the whole entropy change in the system is entirely due to the internal entropy production, whence the extended temperature $\mathcal{T}_S(t)$ remains undefined because of Remark 8.

Remark 11. *It is an appealing feature of this model that the qubit does not exchange any energy with its environment ($\partial_t \mathbb{U}_S^{(\lambda)}(t) = 0$), whilst its (internal) entropy may change ($\partial_t \mathbb{S}_S^{(\lambda)}(t) \neq 0$) because of its (varying) correlations with the environment ($\partial_t \mathbb{S}_\chi(t) \neq 0$).*

It also may also be interesting to investigate the behavior of the various thermodynamic quantities in the Markovian regime for system S. This is determined by the condition $\beta \ll t$ over the long timescale $1/\lambda^2$ when $\lambda \to 0$. Under these conditions and after removal of the regularization parameter ϵ, one obtains $\Gamma(t) \simeq \pi\tau/(2\beta)$. Thus, the dynamics of system S [equation (3.78)] reads as

$$\varrho_S^{(\lambda)}(t) = \varrho_{00}|0\rangle\langle 0| + \varrho_{11}|1\rangle\langle 1| + e^{-\gamma t}(\varrho_{10}e^{i\omega_0 t}|1\rangle\langle 0| + \varrho_{01}e^{-i\omega_0 t}|0\rangle\langle 1|), \tag{3.104}$$

in which $\gamma = 4\pi\lambda^2/\beta$. This state solves the Lindblad master equation

$$\partial_t \varrho_S^{(\lambda)}(t) = -i\left[\frac{1}{2}\omega_0\sigma_z, \varrho_S^{(\lambda)}(t)\right] + \frac{\gamma}{2}\left(\sigma_z\varrho_S^{(\lambda)}(t)\sigma_z - \varrho_S^{(\lambda)}(t)\right). \tag{3.105}$$

Note that this dynamics has a one-dimensional manifold of fixed points as

$$\lim_{t\to\infty} \varrho_S^{(\lambda)}(t) = \varrho_{00}|0\rangle\langle 0| + \varrho_{11}|1\rangle\langle 1|. \tag{3.106}$$

Thus if we start with the system initially with no coherence (i.e., vanishing off-diagonal elements, $\varrho_{10} = 0$), it will not evolve in time.

Let us now concentrate on the relation between the entropy production and the general statement of the second law (2.51). In particular, it is interesting to check whether the three hypotheses mentioned at the end of Chapter 2 are satisfied or not. In doing that, we allow for a spectral density more general than the Ohmic one.

Remember that $\partial_t \mathbb{Q}_S(t) = 0$ while the entropy of the qubit is given in equation (3.98). Since the quantity $b^{(\lambda)}(t)$ (3.99) is always positive, the sign of $\partial_t \mathbb{S}_S(t)$ corresponds to the sign of $\partial_t \Gamma(t)$, where

$$\Gamma(t) = \int_0^\infty d\omega \frac{|f(\omega)|^2}{\omega^2} \coth(\beta\omega/2) \sin^2(\omega t/2). \tag{3.107}$$

In writing $\Gamma(t)$, the continuum limit has been taken and the sum over the bath modes $\sum_k |f_k|^2$ has been recast into an integral $\int_0^\infty d\omega |f(\omega)|^2$. Concerning the bath quantities, one has

$$\partial_t \mathbb{Q}_B(t) = 4\lambda^2\left(1 - \langle\sigma_z\rangle^2\right)\partial_t\Delta(t), \tag{3.108}$$

$$\partial_t \mathbb{S}_B(t) = 4\beta\lambda^2\left(1 - \langle\sigma_z\rangle^2\right)\partial_t\Delta(t) + o(\lambda^2), \tag{3.109}$$

where

$$\Delta(t) = \int_0^\infty \mathrm{d}\omega \, \frac{|f(\omega)|^2}{\omega} \sin^2(\omega t/2). \tag{3.110}$$

One immediately note that $\partial_t \mathbb{S}_B(t) = \beta \partial_t \mathbb{Q}_B(t)$ up to leading order in the coupling constant, so that the hypothesis of a thermal bath almost in equilibrium seems to be quite robust. Instead, one finds that $\partial_t \mathbb{Q}_S(t) \neq \partial_t \mathbb{Q}_B(t)$ because the first one is identically vanishing while the latter is not. This is possible due to the correlations between the subsystems that can store and exchange energy, effectively acting as a third subsystem [72]. The third hypothesis can be also violated. Indeed, one can show that the following sum

$$\partial_t \mathbb{S}_S(t) + \partial_t \mathbb{S}_B(t), \tag{3.111}$$

possibly becomes negative even though its integral is always positive. The sign of $\partial_t \mathbb{S}_B(t)$ is equal to the sign of $\partial_t \Delta(t)$ while the sign of $\partial_t \mathbb{S}_S(t)$ depends on $\partial_t \Gamma(t)$. One can find $\partial_t \Gamma(t) < 0$, which corresponds to an essentially non Markovian dynamics for S, by choosing a super-Ohmic spectral density

$$|f(\omega)|^2 = \frac{\omega^s}{\omega_c^{s-1}} \, \mathrm{e}^{-\omega/\omega_c}, \tag{3.112}$$

with $s > s_{cr}(\beta)$ (ω_c is a cutoff frequency). The critical ohmicity parameter s_{cr} at zero temperature is 2, while it becomes 3 in the infinite temperature limit [121]. Indeed, for high temperature one can expand the hyperbolic cotangent in $\Gamma(t)$ and

$$\partial_t \Gamma(t) \simeq \frac{1}{2\beta} \widetilde{\Gamma}(s-1) \left[1 + (\omega_c t)^2 \right]^{-\frac{s-1}{2}} \sin[(s-1)\arctan(\omega_c t)], \tag{3.113}$$

where $\widetilde{\Gamma}$ is the Euler gamma function. Moreover, one can find $\partial_t \Delta(t) < 0$ if $s > 1$ because

$$\partial_t \Delta(t) = \frac{\omega_c^2}{2} \widetilde{\Gamma}(s+1) \left[1 + (\omega_c t)^2 \right]^{-\frac{s+1}{2}} \sin[(s+1)\arctan(\omega_c t)]. \tag{3.114}$$

Therefore, for $s = 4$ and at sufficiently high temperature one can find $\partial_t \mathbb{S}_S(t) < 0$ and $\partial_t \mathbb{S}_B(t) < 0$ simultaneously. It happens when $\pi/3 < \arctan(\omega_c t) < \pi/2$.

Remark 12. *This example explicitly shows that the statement* (2.51) *of the second law is not equivalent to* $\sigma_t \geq 0$ *in general. Therefore, a violation of the latter inequality should not be interpreted as something unphysical.*

3.4 Comparison and summary

In this Section we firstly clarify the relation between our analysis of the non-equilibrium thermodynamics of a bipartite quantum system [72] and other approaches adopted in literature. Then we show how the whole formulation can be reproduced using classical mechanics, pointing out that classical correlations in the initial state are sufficient to invalidate the inequality (3.30). In the end we provide a summary of the main results in this Chapter, which is arguably the most relevant part of this Thesis.

3.4.1   Comparison with other formulations

Recently, other proposals appeared whose aim is to study the thermodynamics of a generic bipartite system. In the following we compare these formulations with ours.

In Ref. [109] heat and work are defined for a generic bipartite quantum system using the concept of "local effective measurement basis" (LEMBAS) [122]. More explicitly, they use a procedure similar to ours, arriving at equations (3.6) and (3.7), but at this point they choose to write the modified Hamiltonian H'_S as the sum of two components $\widetilde{H}_S$ and $\overline{H}_S$ such that the first one is commuting with the free Hamiltonian H_S while the other one is not

$$H'_S(t) = \widetilde{H}_S(t) + \overline{H}_S(t), \quad \left[H_S, \widetilde{H}_S(t) \right] = 0, \quad \left[H_S, \overline{H}_S(t) \right] \neq 0. \tag{3.115}$$

Then, only the commuting part is used to compute heat and work

$$\partial_t \mathbb{W}_S(t) = \mathrm{Tr} \left[\varrho_S(t)\, \partial_t \widetilde{H}_S(t) \right], \tag{3.116}$$

$$\partial_t \mathbb{Q}_S(t) = \mathrm{Tr} \left[\partial_t \varrho_S(t)\, \widetilde{H}_S(t) \right]. \tag{3.117}$$

The idea behind this procedure is the following: when the energy is measured locally the basis is fixed by the free Hamiltonian and the only detectable contribution of the interaction consists in a shift of the energy levels. It is worth to say that the role of correlations has not been highlighted in [109], nor the relation between the global balance and the local balances of energy has been studied. In contrast, in our formalism the internal energy associated with each subsystem is defined as the energy which is locally accessible in each individual subsystem by means of arbitrary local measurements and the importance of correlations has been explicitly investigated [72].

Concerning the balance of entropy, the reasoning of Ref. [109] is the same as in Ref. [103]. In particular, it is noticed that when the initial state of the reservoir is in thermal equilibrium at a certain inverse temperature β the variation of von Neumann entropy in the system can be rewritten as

$$\Delta\mathbb{S}(t) = \Delta_i \mathbb{S}(t) + \Delta_e \mathbb{S}(t), \tag{3.118}$$

where

$$\Delta_i \mathbb{S}(t) := \mathbb{S}(\varrho(t) \| \varrho_S(t) \otimes \varrho_B^{(\beta)}), \quad \Delta_e \mathbb{S}(t) := \mathrm{Tr} \left[(\varrho_B(t) - \varrho_B^{(\beta)}) \log \varrho_B^{(\beta)} \right]. \tag{3.119}$$

The term $\Delta_e \mathbb{S}(t)$ is called reversible entropy flow because it can be recast into

$$\Delta_e \mathbb{S}(t) = \beta \mathbb{Q}_B(t), \tag{3.120}$$

where $\mathbb{Q}_B(t) = \mathrm{Tr}[H_B \varrho_B^{(\beta)}] - \mathrm{Tr}[H_B \varrho_B(t)]$, while $\Delta_i \mathbb{S}(t)$ is called irreversible entropy production and is always nonnegative. The difference with respect to our treatment is that the free Hamiltonian of system B is considered in the computation of heat, without corrections due to the interaction.

A similar expression has been also derived in [103] and further discussed in [115]. In particular, the authors found that

$$\Delta\mathbb{S}(t) = \beta \mathbb{Q}_B(t) + \mathbb{S}(\varrho(t) \| \varrho_S(t) \otimes \varrho_B(t)) + \mathbb{S}(\varrho_B(t) \| \varrho_B^{(\beta)}), \tag{3.121}$$

highlighting two different contributions to the irreversible entropy production, namely the variation in time of the state of the environment, pushed out of equilibrium, and the correlations established between the systems.

3.4.2 Classical counterpart

The previously presented approach to defining work and heat exchanges has focused on bipartite quantum systems. However, the very same formulation can be applied to classical bipartite systems SB (where $S; B$ has $n_{S,B}$ degrees of freedom) by considering probability distributions $\varrho(\bar{r})$ over the phase space

$$\mathbb{R}^{2(n_S+n_B)} \ni \bar{r} = (\bar{q}_S, \bar{q}_B; \bar{p}_S, \bar{p}_B)$$

of points with conjugate coordinates $\bar{q} = (\bar{q}_S, \bar{q}_B)$ and $\bar{p} = (\bar{p}_S, \bar{p}_B)$, their Gibbs entropy

$$\mathbb{S}(\varrho) = -\int_{\mathbb{R}^{2(n_S+n_B)}} \mathrm{d}\bar{r}\, \varrho(\bar{r})\, \log \varrho(\bar{r}),$$

and the total time evolution generated by the Poisson brackets with a Hamiltonian function $H_{\mathrm{tot}}(\bar{r})$. In particular, we will show that the sum of the entropy variations can be negative if the initial state is correlated.

Consider two coupled classical oscillators, S and B, with canonical coordinates $\bar{q} = (q_S, q_B)$, $\bar{p} = (p_S, p_B)$, interacting according to the following Hamiltonian function:

$$H(\bar{r}) = \frac{p_S^2}{2} + \frac{p_B^2}{2} + \frac{k}{2}\left(q_S - q_B\right)^2. \tag{3.122}$$

As the initial state of system SB, we take a probability distribution of the form

$$\varrho(\bar{r}) = \frac{\sqrt{1 - \gamma^2}}{4\pi^2} \mathrm{e}^{-(p_S^2 - p_B^2 - q_S^2 - q_B^2 - 2\gamma q_S q_B)/2}, \tag{3.123}$$

where the parameter $-1 < \gamma < 1$ measures the amount of initial correlations between S and B.

The solution of the Liouville equation

$$\partial_t \varrho_t = \partial_{\bar{q}} H\, \partial_{\bar{p}} \varrho_t - \partial_{\bar{q}} \varrho_t\, \partial_{\bar{p}} H \tag{3.124}$$

is given by $\varrho_t(\bar{r}) = \varrho(\bar{r}(-t))$, where $\bar{r}(t)$ solves the Hamilton equations of motion

$$\dot{q}_S = p_S\,, \ \dot{q}_B = p_B\,, \quad \dot{p}_S = -k\left(q_S - q_B\right), \ \dot{p}_B = -k\left(q_B - q_S\right). \tag{3.125}$$

The integration yields

$$\varrho_\tau(\bar{r}) = \frac{\sqrt{1 - \gamma^2}}{4\pi^2} \mathrm{e}^{-(\bar{r}, A_t \bar{r})}, \tag{3.126}$$

where A_t is a 4×4 covariance matrix with entries
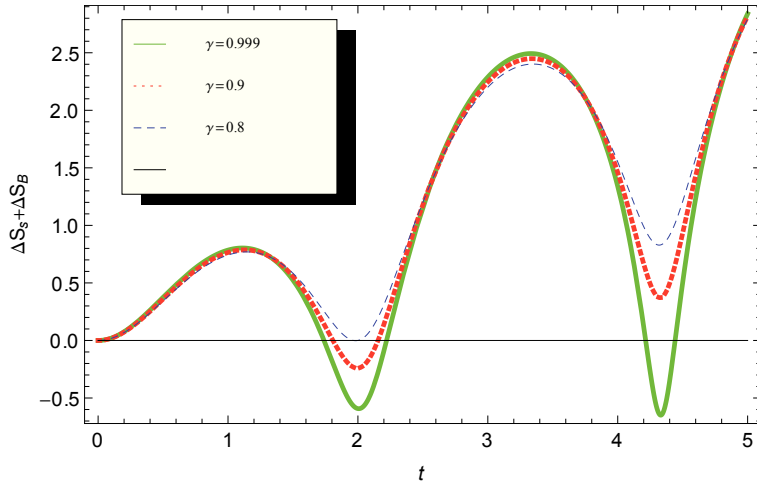
Figure 3.1: $\Delta\mathbb{S}_S(t) + \Delta\mathbb{S}_B(t)$, for $k = 1$ and different values of γ.

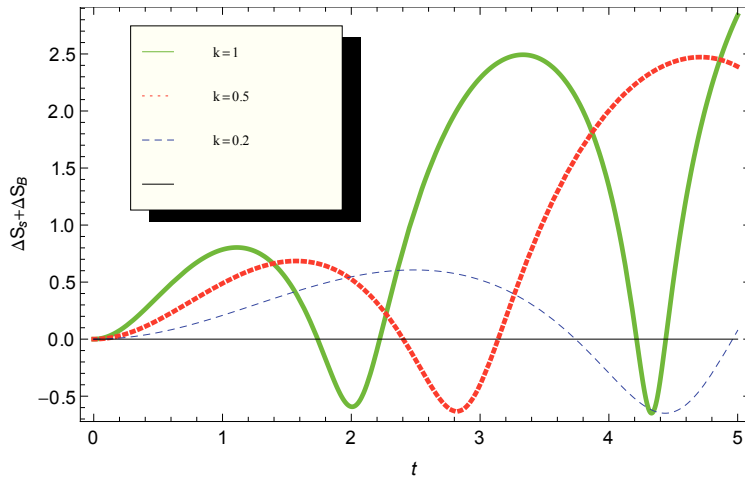Figure 3.2: $\Delta\mathbb{S}_S(t) + \Delta\mathbb{S}_B(t)$, for $\gamma = 0.999$ and different values of k.

$$A_{11} = A_{33} = \frac{1}{4}\left(2 + (2k + \gamma - 1)\sin^2(\sqrt{2k}\,t)\right), \tag{3.127}$$

$$A_{12} = A_{21} = A_{34} = A_{43} = \frac{1}{4}\left(\frac{\sin(2\sqrt{2k}\,t)}{2\sqrt{2k}}(2k + \gamma - 1) - t(1 + \gamma)\right), \tag{3.128}$$

$$A_{13} = A_{31} = \frac{1}{4}\left(2\gamma - (2k + \gamma - 1)\sin^2(\sqrt{2k}\,t)\right), \tag{3.129}$$

$$A_{14} = A_{41} = A_{23} = A_{32} = \frac{1}{4}\left(-\frac{\sin(2\sqrt{2k}\,t)}{2\sqrt{2k}}(2k + \gamma - 1) - t(1 + \gamma)\right), \tag{3.130}$$

$$A_{22} = A_{44} = \frac{1}{4}\left(2 + (1 + \gamma)t^2 - (2k + \gamma - 1)\frac{\sin^2(\sqrt{2k}\,t)}{2k}\right), \tag{3.131}$$

$$A_{24} = A_{42} = \frac{1}{4}\left((\gamma + 1)t^2 + (2k + \gamma - 1)\frac{\sin^2(\sqrt{2k}\,t)}{2k}\right). \tag{3.132}$$

The reduced (or marginal) state of S is then obtained by integrating $\varrho_t(\bar{r})$ over the conjugate coordinates $\bar{r}_B = (q_B, p_B)$ of B,

$$\varrho_t^S(\bar{r}_S) = \int_{-\infty}^{\infty} \mathrm{d}\bar{r}_B\, \varrho_t(\bar{r}). \tag{3.133}$$

It turns out that $\varrho_\tau^S(q_S, p_S)$ is a Gaussian of the form

$$\varrho_t^S(q_S, p_S) = Z(t)\, \mathrm{e}^{-a(\tau)p_S^2 - b(\tau)q_S^2 + c(\tau)p_S q_S}, \tag{3.134}$$

where Z, a, b, and c are the following time-dependent coefficients:

$$Z(t) = \frac{1}{2\pi}\sqrt{4a(t)b(t) - c^2(t)}, \tag{3.135}$$

$$a(t) = \frac{1}{16k\alpha(t)}\Big[1 - \gamma^2 - 2k(-3 + \gamma + 2\tau^2(\gamma^2 - 1)) +$$
$$+ (1 + \gamma)(2k + \gamma - 1)\cos(\sqrt{8k}\,t)\Big], \tag{3.136}$$

$$b(t) = \frac{(1 + \gamma)}{8\alpha(t)}\Big[3(1 - \gamma) + 2k - (2k + \gamma - 1)\cos(\sqrt{8k}\,t)\Big], \tag{3.137}$$

$$c(t) = \frac{(1 + \gamma)}{8\sqrt{k}\,\alpha(t)}\Big[(1 - \gamma)4\sqrt{k}\,t - \sqrt{2}(2k + \gamma - 1)\sin(\sqrt{8k}\,t)\Big], \tag{3.138}$$

$$\alpha(t) = 1 + \frac{(1 - \gamma^2)\,t^2}{4} + (2k + \gamma - 1)\left[\frac{\sin^2(\sqrt{2k}\,t)}{4} +$$
$$+ \frac{(1 + \gamma)}{4}\left((2kt^2 - 1)\frac{\sin^2(\sqrt{2k}\,t)}{2k} + t\frac{\sin(\sqrt{8k}\,t)}{\sqrt{2k}}\right)\right]. \tag{3.139}$$

Because of the $S \leftrightarrow B$ symmetry, $\varrho_t^B(\bar{r}_B)$ has the same functional form in Eq. (3.134) with $\bar{r}_S$ substituted by $\bar{r}_B$.

By means of the reduced states, we can now study the thermodynamic behavior of each subsystem. The entropy of S can be computed as follows:

$$\$_S(t) = -\int_{-\infty}^{\infty} d\bar{r}_S \, \varrho_t^S(\bar{r}_S) \log \varrho_t^S(\bar{r}_S) = \frac{1}{2} \log \left[\frac{(2\pi e)^2}{4a(t)b(t) - c(t)^2} \right], \tag{3.140}$$

so that the difference of the latter with respect to the entropy at time $t = 0$ is given by

$$\Delta\$_S(t) = \frac{1}{2} \log \left[\frac{4a(0)b(0) - c(0)^2}{4a(t)b(t) - c(t)^2} \right] = \frac{1}{2} \log \left[\alpha(t) \right]. \tag{3.141}$$

Depending on the value of γ, $\Delta\$_S(t)$ can become negative in certain time intervals as shown in the figures 3.1 and 3.2. Since $\Delta\$_S(t) = \Delta\$_B(t)$, we find $\delta\$(t) := \Delta\$_S(t) + \Delta\$_B(t) < 0$, namely a violation of the inequality expressed in (3.30) due to initial correlations. Indeed, Fig. 3.1 depicts $\delta\$(t)$ vs. t for three different values of γ at fixed interaction strength $k = 1$, and shows that the transient negativity is suppressed by weakening the initial correlations.

In Fig. 3.2, instead, the amount of initial correlations is fixed and the interaction strength varied; then, the "violations of the second law of thermodynamics" are only delayed in time, but not suppressed, by weakening the interactions. In the case of $k = 0$, $\Delta\$_S(t) = \Delta\$_B(t) = 0$ for each value of $-1 < \gamma < 1$; indeed, the correlations between S and B do not change if the two subsystems do not interact.

Remark 13. *As pointed out in [108], the choice of a special class of initial states (uncorrelated system-bath states in our case) is necessary to derive second law-like inequalities from a global reversible unitary dynamics. In this respect, all the available explanations of the emergence of the second law of thermodynamics from the underlying reversible Schrödinger evolution are not completely satisfactory. We will see another example in the following Chapter when discussing the so-called fluctuation theorems.*

Concerning the heat and work exchanges between S and B, we observe that the effective Hamiltonians of the two subsystems are time-independent. Indeed, the defining quantum expressions in Eq. (3.15), classically becomes

$$H_S^{(\text{eff})}(t) = \frac{p_S^2}{2} + k\frac{q_S^2}{2} + \int_{\mathbb{R}^2} d\bar{r}_B \, \varrho_\tau^B(\bar{r}_B) \, H_{\text{int}}(\bar{r})$$
$$- \alpha_S \int_{\mathbb{R}^4} d\bar{r} \, \varrho_\tau^S(\bar{r}_S) \varrho_\tau^B(\bar{r}_B) \, H_{\text{int}}(\bar{r}), \tag{3.142}$$

with $H_{\text{int}}(\bar{r}) = -kq_S q_B$. The two integrals vanish because H_{int} is an odd function of the single oscillator positions (while the probability distribution is Gaussian). It then follows that work exchanges also vanish so that

$$\partial_t \mathbb{U}_S = \partial_t \mathbb{Q}_S = \partial_t \left[\int_{\mathbb{R}^2} d\bar{r}_S \, \varrho_\tau^S(\bar{r}_S) \left(\frac{p_S^2}{2} + k\frac{q_S^2}{2} \right) \right]$$
$$= k \left(2\tau - \frac{(2k + \gamma - 1)}{(1 - \gamma)} \frac{\sin(\sqrt{8k}\tau)}{\sqrt{8k}} \right), \tag{3.143}$$

and the same holds for system B too. As expected, if the coupling strength k is zero there is no heat flux in the system and the energy of each oscillator is conserved.

Observation 1. *A comment is in order at this point. From the previous discussion one could think that there is no essential difference between classical and quantum mechanics when dealing with the laws of thermodynamics, in particular when dealing with the balance of entropy. This is not completely true and the reason is the following. The complete knowledge of a classical system (the system is described by a single point in phase space) implies the complete knowledge of any subsystem. On the contrary, if a quantum system is in a pure state so that we have complete knowledge of it (zero entropy), its subsystems are in general described by statistical mixtures, due to quantum correlations. Therefore, the inequality (3.30), which in the classical case is due to the experimental uncertainty, in principle eliminable, emerges naturally in quantum mechanics.*

3.4.3 Summary and outlook

This Chapter highlights the role of correlations in the non-equilibrium thermodynamic behavior of generic bipartite interacting quantum systems. In this formulation, interesting relations emerge between correlations, on the one hand, and heat and work exchanges, on the other hand. These relations may enable the extraction of desired thermodynamic properties by partially controlling or manipulating the underlying dynamics of the system. A notion of binding energy has been introduced which only depends on the interaction Hamiltonian and correlations of the total system state, whose variation has been shown to be only of the heat type. In this sense, correlations act as a resource or storage for heat.

Correlations play a fundamental role also in the balance of entropy, where a very general second law-like inequality has been presented, which only depends on the assumption of initial factorized state. We have also defined two notions of nonequilibrium temperatures for the subsystems and consequently two different generalized entropy productions. We have discussed their behavior through two examples: a qubit in interaction with a thermalizing bath and a qubit interacting with a dephasing environment. It turned out that neither of them is completely satisfactory so that the only reliable quantity is the entropy production originally defined by Spohn, Lebowitz and Alicki. Finally, we have shown that the positivity of such a quantity is not equivalent to the positivity of the finite variations of entropy (3.30) and is indeed a much stronger requirement.

Our methodology may provide techniques and tools for employing quantum resources, such as many-body correlations and memory, to engineer thermodynamic processes, for example, to build efficient quantum heat engines, or shed light on our understanding of the role of correlations in biological processes in relation to, e.g., the efficiency of photosynthetic light-harvesting complexes [123].

Chapter 4

Fluctuation theorems

In the previous Chapters a generalization of the standard non-equilibrium thermodynamics of open quantum systems has been presented, dealing with non-Markovian dynamics, finite-size environmental effects and strong coupling. Physical quantities like heat, work and entropy have been consistently defined in this more general scenario and explicitly computed in a number of examples. However, the whole formulation regards average quantities as in the initial formulation of quantum thermodynamics [38, 39] and makes no prediction about fluctuations.

In the following, we discuss a different kind of generalization that has been put forward in the last decade, namely, the study of thermodynamic fluctuations around average values. The starting point was the formulation in 1997 of a very interesting relation, nowadays known as Jarzynski equality [18], between the full non-equilibrium response of a system to an external driving and the free energy difference, an equilibrium property. Such a result has been complemented just one year later by G. Crooks with a so-called fluctuation theorem relating the work done on a system according to some protocol and the work extracted in the time-reversed protocol [19].

The original analysis of Jarzynski and Crooks uses classical mechanics. The quantum fluctuation theorems first appeared in Refs. [124, 125] that boosted a lot of theoretical activity on this issue. An exhaustive summary of the main results obtained up until the last decade is contained in the two reviews [57, 126]. In this Thesis, we will discuss the basic features that are common to all the known approaches to quantum fluctuation relations, analyzing separately the cases of closed and open quantum systems.

In Section 4.1 the definition of work as a stochastic variable is presented and its quantum fluctuation relations are discussed. We make also a proposal in order to test experimentally the quantum Jarzynski equality using molecular vibrations driven by external electric fields. With respect to other experimental tests of the quantum Jarzynski equality [127, 128], the proposal provides a check of the equality in a rather different physical scenario whereby a direct measurement of the free energy difference seems possible.

In Section 4.2 we present some results about fluctuation relations for open quantum systems. In this framework, the situation is less established and still matter of research. A Jarzynski-like equality for heat as a stochastic variable is proven to hold under unital reduced open dynamics [129], namely those dynamics preserving the identity operator. A different approach consists

in describing explicitly the environment. In this scenario, the Jarzynski equality for work can be proved, if the free energy difference is computed according to a modified Hamiltonian, the so-called Hamiltonian of mean force [130]. Some proposals based on measuring the energy of both system and bath at the beginning and at the end is also presented [131].

4.1   Closed quantum systems

In this section we discuss the fluctuation relations for the work performed on a closed quantum system, namely the Jarzynski equality and the Crooks theorem, explaining how the relevant physical quantities are defined and how one could test experimentally these theoretical results.

Consider a closed quantum system driven by an external field, so that the Hamiltonian of the system is time-dependent and its energy is not conserved. The dynamics of a generic quantum state is the unitary evolution determined by the Liouville-von Neumann equation and is thus reversible. According to [132], in this framework, work can be defined by means of a two-measurement protocol. Indeed, for any specific driving, one can measure the energy of the system at the beginning and at the end of the protocol; the difference of the measurement outcomes is a stochastic variable w associated to the work performed on the system. This is a reasonable choice because the entire variation of energy in the system is due to the external driving, so that no heat is dissipated in the process and the energy difference can be safely associated to work. Moreover, the two-measurements are necessary because work, as stated by standard thermodynamics, is not an observable, in the sense that it is not a quantity related to the state but to the process.

In principle, repeating many times this procedure, always with the same driving up to a same final time τ, the full probability distribution $P(w)$ can be accessed experimentally. Explicitly, the probability distribution of work reads [132]

$$P(w) = \sum_{n,m} p_n^0 |\langle E_m^\tau | U(\tau) | E_n^0 \rangle|^2 \, \delta(w - E_m^\tau + E_n^0), \tag{4.1}$$

where E_n^0, E_m^τ are the eigenvalues of $H(0)$, $H(\tau)$ respectively, p_n^0 is the probability of obtaining the outcome E_n^0 in the first measurement, and $U(\tau)$ is the time-evolution operator

$$U(\tau) = \overleftarrow{\mathcal{T}} \mathrm{e}^{-i \int_0^\tau H(s)\mathrm{d}s}. \tag{4.2}$$

This probability distribution, whose analytic computation is very difficult also for relatively simple systems, has been investigated in the case of a quantum harmonic oscillator with time-dependent frequency [133] and small anharmonicity [134], a driven Morse oscillator [135] and a driven oscillator coupled in position/momentum [136].

Proposition 4.1.1. *If the system is initially prepared in a thermal state at inverse temperature β, such that the quantities p_n^0 have the form of a Boltzmann factor*

$$p_n^0 = \frac{\mathrm{e}^{-\beta E_n^0}}{\mathrm{Tr}\left[\mathrm{e}^{-\beta H(0)}\right]}, \tag{4.3}$$

the quantum Jarzynski equality holds true

$$\left\langle e^{-\beta w} \right\rangle = e^{-\beta \Delta F}, \tag{4.4}$$

where the average $\langle \cdot \rangle$ is computed with respect to the probability distribution $P(w)$ and the equilibrium free energy is defined as usual in terms of the partition function Z_t

$$F(t) := -\frac{1}{\beta} \log Z_t, \quad Z_t = \mathrm{Tr}\left[e^{-\beta H(t)} \right]. \tag{4.5}$$

Proof. Given the explicit expression of p_n^0 (4.3), the probability distribution of work (4.1) becomes

$$P(w) = \sum_{n,m} \frac{e^{-\beta E_n^0}}{Z_0} |\langle E_m^\tau | U(\tau) | E_n^0 \rangle|^2 \, \delta(w - E_m^\tau + E_n^0). \tag{4.6}$$

Therefore, a straightforward computation gives

$$\left\langle e^{-\beta w} \right\rangle = \int \mathrm{d}w \, P(w) e^{-\beta w} =$$

$$= \int \mathrm{d}w \sum_{n,m} \frac{e^{-\beta E_n^0}}{Z_0} |\langle E_m^\tau | U(\tau) | E_n^0 \rangle|^2 \, \delta(w - E_m^\tau + E_n^0) e^{-\beta w} =$$

$$= \sum_{n,m} \frac{e^{-\beta E_n^0}}{Z_0} |\langle E_m^\tau | U(\tau) | E_n^0 \rangle|^2 \, e^{\beta(E_n^0 - E_m^\tau)} =$$

$$= \sum_m \frac{e^{-\beta E_m^\tau}}{Z_0} \langle E_m^\tau | U(\tau) \sum_n | E_n^0 \rangle \langle E_n^0 | U^\dagger(\tau) | E_m^\tau \rangle = \frac{Z_\tau}{Z_0} = e^{-\beta \Delta F}$$

$$\square$$

The Jarzynski equality is very important because it relates a quantity that in principle depends on the whole information relative to the driving process, encoded in $P(w)$, with an equilibrium property as the free energy. An immediate consequence of (4.4) is the Kelvin statement of the second law of thermodynamics, namely no work can be extracted in a cyclical process from a system in equilibrium with a single thermal bath. Indeed, applying the Jensen's inequality one finds

$$e^{-\beta \langle w \rangle} \leq \left\langle e^{-\beta w} \right\rangle = e^{-\beta \Delta F}, \tag{4.7}$$

that in turn implies

$$\langle w \rangle \geq \Delta F. \tag{4.8}$$

For a cyclical process $H(\tau) = H(0)$, the free energy difference is vanishing and the result is $\langle w \rangle = 0$, confirming that on average the driving performs work on the system instead of extracting work. This does not mean of course that in a single realization of the protocol the variable w is positive. In a generic process (not cyclic) one can instead say that the so-called irreversible work $\mathcal{W} := \langle w \rangle - \Delta F$ is non negative. This quantity $\mathcal{W}$ measures the difference between the actual average work and the free energy difference, that, at least in standard thermodynamics,

equals the work performed in a isothermal quasi-static process. In the following, we show that this is true also in our setting.

Note that by computing explicitly the average stochastic work $\langle w \rangle$ one has

$$\langle w \rangle = \int \mathrm{d}w P(w) w = \sum_{n,m} p_n^0 |\langle E_m^\tau | U(\tau) | E_n^0 \rangle|^2 (E_m^\tau - E_n^0) =$$
$$= \mathrm{Tr}[H(\tau)\varrho(\tau)] - \mathrm{Tr}[H(0)\varrho(0)] =$$
$$= \int_0^\tau \mathrm{Tr}[\partial_t H(t)\, \varrho(t)] \mathrm{d}t =: \int_0^\tau \partial_t \mathrm{W}(t) \mathrm{d}t, \qquad (4.9)$$

where the last equality follows from the fact that

$$\mathrm{Tr}[H(t)\, \partial_t \varrho(t)] = 0,$$

due to the Schrödinger unitary evolution. Therefore, in a closed quantum system, the definition of work (1.44) given in the previous Chapters is compatible with the other one given in terms of stochastic variables. Moreover, the irreversible work $\mathcal{W}$ (multiplied by a factor β) can be conveniently expressed in general as the difference between two relative entropies

$$\beta\mathcal{W} = \beta\left(\langle w \rangle - \Delta F\right) = \mathbb{S}(\varrho_\tau \| \varrho_\tau^{(\beta)}) - \mathbb{S}(\varrho_0 \| \varrho_0^{(\beta)}), \qquad (4.10)$$

where $\varrho_\tau^{(\beta)} = \mathrm{e}^{-\beta H(\tau)}/Z_\tau$. This is a consequence of the well-known relation [137]

$$\beta\mathrm{Tr}[H(t)\varrho(t)] = \beta F(t) + \mathbb{S}(t) + \mathbb{S}(\varrho_t \| \varrho_t^{(\beta)}), \qquad (4.11)$$

valid for any t, and of the conservation of entropy in a unitary dynamics $\mathbb{S}(\tau) = \mathbb{S}(0)$. The irreversible work (4.10) further reduces to a single relative entropy in the case of an initial thermal state, that is the assumption used to prove the Jarzynski equality

$$\beta\mathcal{W} = \mathbb{S}(\varrho_\tau \| \varrho_\tau^{(\beta)}) \geq 0. \qquad (4.12)$$

This rewriting is also consistent with the interpretation of irreversible work: the farther away is the final state from the Gibbs state corresponding to a quasi-static isothermal process, the greater is $\mathcal{W}$.

Another important result can be obtained in the same framework, by considering also the reversed work protocol or backward protocol. The unitary time evolution $\widetilde{U}(\tau)$ from time 0 to time τ in this second protocol is related as follows with $U(\tau)$

$$\widetilde{U}(\tau) = U^{-1}(\tau) = U^\dagger(\tau). \qquad (4.13)$$

Moreover, it is assumed that the initial state of the backward protocol is $\varrho_\tau^{(\beta)}$, *i.e.* the thermal state at inverse temperature β with respect to the Hamiltonian $H(\tau)$. Therefore, a first measurement of energy is performed projecting the state into an eigenstate $|E_m^\tau\rangle$ of $H(\tau)$ with probability $p_m^\tau = \mathrm{e}^{-\beta E_m^\tau}/Z_\tau$. After that the system evolves with $\widetilde{U}(\tau)$ and a final measurement is performed

at time τ in the basis of $H(0)$. As a consequence, the probability distribution of work in the backward protocol is the following

$$P_B(w) = \sum_{n,m} \frac{\mathrm{e}^{-\beta E_m^\tau}}{Z_\tau} |\langle E_m^\tau | U(\tau) | E_n^0 \rangle|^2 \, \delta(w - E_n^0 + E_m^\tau) \tag{4.14}$$

and by using the properties of the Dirac delta one can find a relation between the backward and the forward probability distributions:

Proposition 4.1.2. *Given the forward probability distribution $P_F(w)$ (4.6) and the backward probability distribution $P_B(w)$ (4.14), the Tasaki-Crooks fluctuation theorem holds true*

$$\frac{P_F(w)}{P_B(-w)} = \mathrm{e}^{\beta(w-\Delta F)}. \tag{4.15}$$

Proof. The result can be proved by a straightforward calculation using the properties of the delta distribution, in particular $f(x)\delta(x-a) = f(a)\delta(x-a)$ and $\delta(x) = \delta(-x)$:

$$P_F(w) = \sum_{n,m} \frac{\mathrm{e}^{-\beta E_n^0}}{Z_0} |\langle E_m^\tau | U(\tau) | E_n^0 \rangle|^2 \, \delta(w - E_m^\tau + E_n^0) =$$

$$= \frac{Z_\tau}{Z_0} \sum_{n,m} \frac{\mathrm{e}^{-\beta(E_m^\tau - w)}}{Z_\tau} |\langle E_m^\tau | U(\tau) | E_n^0 \rangle|^2 \, \delta(w - E_m^\tau + E_n^0) =$$

$$= \mathrm{e}^{\beta(w-\Delta F)} \sum_{n,m} \frac{\mathrm{e}^{-\beta E_m^\tau}}{Z_\tau} |\langle E_m^\tau | U(\tau) | E_n^0 \rangle|^2 \, \delta(-w - E_n^0 + E_m^\tau) =$$

$$= \mathrm{e}^{\beta(w-\Delta F)} P_B(-w)$$

$\square$

In the particular case of a cyclic protocol, $\Delta F = 0$, the theorem states that the probability of performing a certain amount of work on the system is exponentially bigger than the probability of extracting the same amount of work in a reversed protocol. Moreover, one immediately derives the Jarzynski equality from the Crooks relation. This is done by conveniently rewriting Eq. (4.15) as follows

$$P_F(w)\mathrm{e}^{-\beta w} = P_B(-w)\mathrm{e}^{-\beta \Delta F},$$

and then integrating both sides in $\mathrm{d}w$. One uses the fact that $\int \mathrm{d}w P_B(-w) = 1$. As a consequence, the Crooks fluctuation theorem is usually referred to as a detailed fluctuation relation while the Jarzynski equality as an integral fluctuation relation.

The natural question to be answered is which kind of protocol is described by $\widetilde{U}(\tau) = U^\dagger(\tau)$. Introducing the time-reversal operator θ, the following argument is presented in literature [138]: the reversed protocol is related to the transition between the time reversed state $\theta |E_m^\tau\rangle$ and the time reversed state $\theta |E_n^0\rangle$ by means of the evolution operator $U_B(\tau)$,

$$U_B(\tau) = \overleftarrow{\mathcal{T}} \mathrm{e}^{-i \int_0^\tau \theta H(\lambda_B(t))\theta^\dagger \mathrm{d}t}. \tag{4.16}$$

If the forward work protocol is characterized by a time-dependent parameter in the Hamiltonian $\lambda_F(t)$, then the Hamiltonian of the backward protocol is driven in time by the parameter $\lambda_B(t) = \lambda_F(\tau - t)$. As a consequence, one finds the following relation between transition probabilities

$$|\langle E_n^0|\theta^\dagger U_B(\tau)\theta|E_m^\tau\rangle|^2 = |\langle E_n^0|U^\dagger(\tau)|E_m^\tau\rangle|^2 = |\langle E_m^\tau|U(\tau)|E_n^0\rangle|^2, \qquad (4.17)$$

because the so-called microreversibility condition holds true

$$\theta^\dagger U_B(\tau)\theta = U(\tau)^{-1} = U(\tau)^\dagger. \qquad (4.18)$$

This can be seen as follows. Using the properties $\theta\theta^\dagger = \theta^\dagger\theta = 1$ and $\theta i = -i\theta$ one finds

$$\theta^\dagger U_B(\tau)\theta = \overleftarrow{\mathcal{T}} e^{i\int_0^\tau H(\lambda_B(t))\mathrm{d}t}. \qquad (4.19)$$

By looking explicitly at the second order term it turns out that

$$\begin{aligned}
\int_0^\tau \mathrm{d}t \int_0^t \mathrm{d}u\, H(\lambda_B(t))H(\lambda_B(u)) &= \\
= \int_0^\tau \mathrm{d}t \int_0^t \mathrm{d}u\, H(\lambda_F(\tau - t))H(\lambda_F(\tau - u)) &= \\
= \int_0^\tau \mathrm{d}t \int_t^\tau \mathrm{d}u\, H(\lambda_F(t))H(\lambda_F(u)) &= \\
= \int_0^\tau \mathrm{d}u \int_0^u \mathrm{d}t\, H(\lambda_F(t))H(\lambda_F(u)) &
\end{aligned} \qquad (4.20)$$

The analogous treatment can be done on higher order terms so that

$$\overleftarrow{\mathcal{T}} e^{i\int_0^\tau H(\lambda_B(t))\mathrm{d}t} = \overrightarrow{\mathcal{T}} e^{i\int_0^\tau H(\lambda_F(t))\mathrm{d}t} = U(\tau)^\dagger. \qquad (4.21)$$

The statistics of work satisfies other curious relations. In particular, in the following we discuss a further relation with an information theoretic quantity.

4.1.1   Statistics of work

In order to describe the thermodynamics of the driven closed quantum system one could consider equivalently the cumulant generating function

$$\chi(\alpha) = \log\left\langle e^{-\alpha w}\right\rangle = \log\left(\int P(w)e^{-\alpha w}\mathrm{d}w\right), \qquad (4.22)$$

which encodes the same information of $P(w)$, namely the full statistics of work. Indeed, from the cumulant generating function one can extract the nth order cumulant $k(w)_n$ as a derivative

$$k(w)_n = (-1)^n \partial_\alpha^n \chi(\alpha). \qquad (4.23)$$

In the following we will show that $\chi(\alpha)$ is related to the quantum Renyi relative entropy $S_\alpha(\varrho|\sigma)$,

$$S_\alpha(\varrho|\sigma) = \frac{1}{\alpha - 1}\log \mathrm{Tr}[\varrho^\alpha \sigma^{1-\alpha}], \qquad (4.24)$$

between the thermal state $\varrho_\tau^\beta = \mathrm{e}^{-\beta H(\tau)}/Z_\tau$ and the true state of the system at time τ. Indeed, after some algebraic manipulations

$$\left[\sum_{n,m} \frac{\mathrm{e}^{-\beta E_n^0}}{Z_0} \mathrm{e}^{-\alpha(E_m^\tau - E_n^0)} \langle E_m^\tau | U(\tau) | E_n^0 \rangle \langle E_n^0 | U^\dagger(\tau) | E_m^\tau \rangle \right] =$$

$$= \left[\left(\frac{Z_\tau}{Z_0} \right)^{\frac{\alpha}{\beta}} \sum_{n,m} \langle E_m^\tau | \left(\frac{\mathrm{e}^{-\beta E_m^\tau}}{Z_\tau} \right)^{\frac{\alpha}{\beta}} U(\tau) \left(\frac{\mathrm{e}^{-\beta E_n^0}}{Z_0} \right)^{1-\frac{\alpha}{\beta}} | E_n^0 \rangle \langle E_n^0 | U^\dagger(\tau) | E_m^\tau \rangle \right] =$$

$$= \left(\frac{Z_\tau}{Z_0} \right)^{\frac{\alpha}{\beta}} \mathrm{Tr} \left[(\varrho_\tau^\beta)^{\frac{\alpha}{\beta}} U(\tau) (\varrho_0^\beta)^{1-\frac{\alpha}{\beta}} U^\dagger(\tau) \right] =$$

$$= \left(\frac{Z_\tau}{Z_0} \right)^{\frac{\alpha}{\beta}} \mathrm{Tr} \left[(\varrho_\tau^\beta)^{\frac{\alpha}{\beta}} (U(\tau) \varrho_0^\beta U^\dagger(\tau))^{1-\frac{\alpha}{\beta}} \right], \tag{4.25}$$

we get the interesting result

$$\chi(\alpha) = -\alpha \Delta F(\tau) + \left(\frac{\alpha}{\beta} - 1 \right) S_{\frac{\alpha}{\beta}}(\varrho_\tau^\beta | \varrho(\tau)), \tag{4.26}$$

where $\Delta F(\tau) = F(\tau) - F(0) = \frac{1}{\beta}(\log Z_0 - \log Z_\tau)$ is the free energy difference and $\varrho(\tau) = U(\tau) \varrho_0^\beta U^\dagger(\tau)$ is the state at time τ, just before the second measurement is performed. A similar result has been obtained in [139]. As a consistency check, we note that the Jarzynski equality immediately follows from Eq. (4.26) by choosing $\alpha = \beta$:

$$\mathrm{e}^{\chi(\beta)} = \left\langle \mathrm{e}^{-\beta W} \right\rangle = \mathrm{e}^{-\beta \Delta F}. \tag{4.27}$$

Remark 14. *Let be $\mathcal{H} = \mathbb{C}^n$ the Hilbert space of a quantum system and consider two density matrices $\varrho, \sigma \in \mathcal{B}(\mathcal{H})$. The quantum Renyi relative entropy $S_\alpha(\varrho | \sigma)$ is infinite if one of the following statements hold true [140]:*

- *$\mathrm{supp}\, \varrho \nsubseteq \mathrm{supp}\, \sigma$ and $\alpha > 1$,*

- *$\mathrm{supp}\, \varrho \perp \mathrm{supp}\, \sigma$.*

Therefore, the cumulant generating function at finite temperature Eq. (4.26) is never divergent because both ϱ_τ^β and $\varrho(\tau)$ are full rank matrices, i.e. $\mathrm{supp}\, \varrho_\tau^\beta = \mathrm{supp}\, \varrho(\tau) = \mathcal{H}$.

A particular case of work protocol is the so-called quantum quench, where the Hamiltonian of a system is changed instantaneously. Consider now a closed quantum system in its ground state $|E_0^0\rangle$ subjected to a sudden quench $H^0 \to H^1$. By measuring the energy after the quench, one finds the following probability distribution of work

$$P(W) = \sum_n |\langle E_n^1 | E_0^0 \rangle|^2 \, \delta(W - E_n^1 + E_0^0), \tag{4.28}$$

and, as a consequence, the cumulant generating function reads

$$\chi(\alpha) := \log \left\langle \mathrm{e}^{-\alpha W} \right\rangle = \log \left(\langle E_0^0 | \mathrm{e}^{-\alpha H^1} | E_0^0 \rangle \right) + \alpha E_0^0. \tag{4.29}$$

The same results can be obtained directly from Eqs. (4.1) and (4.26), using $U(\tau) = e^{-iH^1\tau}$ and taking the zero temperature limit $(\beta \to \infty)$, such that $e^{-\beta E_n^0}/Z_0 \to \delta_{n,0}$. In this limit the relation with the Renyi divergence is apparently lost.

4.1.2   Isothermal quasi-static process

The opposite case with respect to a quench is a quasi-static process. Consider a driven quantum system initially in equilibrium with an external bath at inverse temperature β. Suppose that the Hamiltonian $H(t)$ changes so slowly that the system remains in equilibrium with the environment at any time, namely its instantaneous state reads

$$\varrho(t) = \frac{e^{-\beta H(t)}}{Z(t)}, \tag{4.30}$$

where $Z(t) = \text{Tr}\left[e^{-\beta H(t)}\right]$. Such a process is isothermal and quasi-static.

Proposition 4.1.3. *For a quasi-static isothermal evolution it turns out that*

$$\partial_t \mathbb{S}(t) = \beta \partial_t \mathbb{Q}(t), \tag{4.31}$$

$$\partial_t \mathbb{F}(t) = \partial_t \mathbb{W}(t), \tag{4.32}$$

where the thermodynamic quantities are defined as usual

$$S(t) := -\text{Tr}\left[\varrho(t)\log\varrho(t)\right], \tag{4.33}$$

$$F(t) := -\frac{1}{\beta}\log Z(t), \tag{4.34}$$

$$\partial_t \mathbb{W}(t) := \text{Tr}\left[\varrho(t)\partial_t H(t)\right], \tag{4.35}$$

$$\partial_t \mathbb{Q}(t) := \text{Tr}\left[\partial_t \varrho(t) H(t)\right]. \tag{4.36}$$

Proof. The proof of Eq. (4.31) is straightforward. Indeed, using the explicit expression of $\varrho(t)$ (4.30) one finds

$$\partial_t \mathbb{S}(t) = -\text{Tr}\left[\partial_t \varrho(t)\log\varrho(t)\right] = \beta\,\text{Tr}\left[\partial_t \varrho(t)H(t)\right] = \beta\partial_t\mathbb{Q}(t).$$

In order to prove Eq. (4.32) we can use the following formula

$$\partial_t(e^{-\beta H(t)}) = \sum_{n=0}^{\infty}\frac{(-\beta)^n}{n!}\,C^n\left(\partial_t H(t)\right)e^{-\beta H(t)},$$

where $C^0 = \text{id}\,$, $C(\cdot) = [H(t), \cdot]$ and $C^n(\cdot)$ involves n nested commutators, which implies

$$\text{Tr}\left[\partial_t(e^{-\beta H(t)})\right] = -\beta\text{Tr}\left[\partial_t H(t)\,e^{-\beta H(t)}\right],$$

due to the ciclicity of the trace. Then

$$\partial_t\mathbb{F}(t) = -\frac{1}{\beta}\partial_t\log Z(t) = -\frac{1}{\beta Z(t)}\text{Tr}\left[\partial_t(e^{-\beta H(t)})\right]$$

$$= \text{Tr}\left[\partial_t H(t)\,\varrho(t)\right] = \partial_t\mathbb{W}(t).$$

$\square$

Remark 15. *Integrating Eq. (4.32) one shows that the free energy difference is related to the work performed during a quasi-static isothermal process. This is consistent with classical thermodynamics.*

Using the operative definition of work, given by the two-measurement protocol, we know how to measure the left-hand side of Eq. (4.4). Thus, in order to verify the Jarzynski equality in experiments, we should estimate independently the right-hand side, that depends on the free energy difference. We have shown that the free energy difference is related to the work performed during a quasi-static isothermal process and this fact could be used in order to test experimentally the equality. This is explained with a simple example.

4.1.3 Example 5: Molecular vibration

We consider a single vibrational mode of a molecule interacting with an external time-dependent electric field. The Hamiltonian of this system is

$$H(t) = \frac{p^2}{2} + \frac{\omega^2 x^2}{2} + \alpha E(t)x = \tag{4.37}$$

$$= \omega \left(a^\dagger a + \frac{1}{2} \right) + \frac{\alpha E(t)}{\sqrt{2\omega}} \left(a^\dagger + a \right), \tag{4.38}$$

where as usual

$$x = \frac{1}{\sqrt{2\omega}} \left(a^\dagger + a \right), \qquad p = i\sqrt{\frac{\omega}{2}} \left(a^\dagger - a \right). \tag{4.39}$$

An equivalent description is given in terms of the displaced ladder operators

$$b(t) = a + \frac{\alpha E(t)}{\omega \sqrt{2\omega}}, \tag{4.40}$$

that allow to rewrite the Hamiltonian as

$$H(t) = \omega \, b^\dagger b(t) + \frac{\omega}{2} - \frac{\alpha^2 E^2(t)}{2\omega^2}. \tag{4.41}$$

From Eq. (4.41) the instantaneous spectrum is easily found to be $\{h_n^t\}_{n=0}^\infty$ with

$$h_n^t = \omega \left(n + \frac{1}{2} \right) - \frac{\alpha^2 E^2(t)}{2\omega^2}. \tag{4.42}$$

Let us study the energy balance in this system during a quasi-static isothermal process. The work is computed as follows:

$$\partial_t W(t) = \frac{\alpha}{\sqrt{2\omega}} \partial_t E(t) \text{Tr} \left[\left(a^\dagger + a \right) \frac{e^{-\beta H(t)}}{Z(t)} \right] =$$

$$= \frac{\alpha}{\sqrt{2\omega}} \partial_t E(t) \text{Tr} \left[\left(b^\dagger(t) + b(t) - \sqrt{\frac{2}{\omega}} \frac{\alpha E(t)}{\omega} \right) \frac{e^{-\beta H(t)}}{Z(t)} \right] =$$

$$= -\frac{\alpha^2}{\omega^2} E(t) \partial_t E(t) = -\frac{\alpha^2}{2\omega^2} \partial_t E^2(t). \tag{4.43}$$

The internal energy is also easily computable

$$U(t) = \text{Tr}\left[\left(\omega\, b^\dagger b(t) + \frac{\omega}{2} - \frac{\alpha^2 E^2(t)}{2\omega^2}\right)\frac{\mathrm{e}^{-\beta H(t)}}{Z(t)}\right] = \frac{\omega}{\mathrm{e}^{\beta\omega} - 1} + \frac{\omega}{2} - \frac{\alpha^2 E^2(t)}{2\omega^2}, \quad (4.44)$$

and taking the time derivative we find

$$\partial_t U(t) = \partial_t W(t), \quad (4.45)$$

which implies a vanishing heat flux. Let's concentrate on this point which seems quite unexpected for a system interacting with the environment. Indeed, for a generic driven system, the thermal states at different times have a different spectrum and, in order to evolve from one to the other, a heat flux between system and bath is needed. In our case instead, it turns out that

$$\text{Sp}\left[\frac{\mathrm{e}^{-\beta H(t)}}{Z(t)}\right] = \left\{\frac{\mathrm{e}^{-\beta h_n^t}}{\sum_m \mathrm{e}^{-\beta h_m^t}}\right\}_{n=0}^\infty = \left\{\frac{\mathrm{e}^{-\beta\omega n}}{\sum_m \mathrm{e}^{-\beta\omega m}}\right\}_{n=0}^\infty = \text{Sp}\left[\frac{\mathrm{e}^{-\beta H(0)}}{Z(0)}\right], \quad (4.46)$$

due to the particular form of the Hamiltonian.

Using this model, the work performed during a quasi-static isothermal protocol can be related to the electric field experimentally tuned. This in turn gives an estimate of the free energy difference needed in the right hand side of the Jarzynski equality. However, one has to say that this outcome is very peculiar and unwarranted in more realistic systems such that the Jarzynski equality is usually tested measuring the left-hand side and computing the free energy according to a theoretical model [127, 128].

4.1.4   Testing Jarzynski equality with Self-Assembled Monolayers

In the following we describe a realistic experimental setting, different from the proposals existing in literature [141–145], in which the quantum Jarzynski equality could be tested. Our approach is not based on interferometric schemes that allow to reconstruct the cumulant generating function, as in [128], while it consists in a direct measurement of the transition probabilities appearing in the work distribution $P(w)$ and in this sense it is similar in spirit to [127]. However, contrary to the work done in [127], we should be able to estimate independently the free energy difference that is the right-hand side of the equality.

Our proposal strongly relies on Self-Assembled Monolayers (SAM) [146] that are structures formed by adsorption of organic molecules on a surface by means of reactive head groups: a paradigmatic example is the adsorption of thiols (carbon chains with a sulfhydryl functional group) onto a gold surface. These organic molecules are also characterized by a tail group that can be used to couple the SAM with other substances [147, 148]. A schematic picture is given in Figure 4.1.

A possibility is to couple two SAMs by means of the tail groups, such that one can construct two surfaces connected via organic chains and a dipole in between. By using the metallic surfaces as the plates of a capacitor, one should be able to apply a varying electric field to the central dipoles. Then, by changing the time-constant of the circuit, different protocols can be
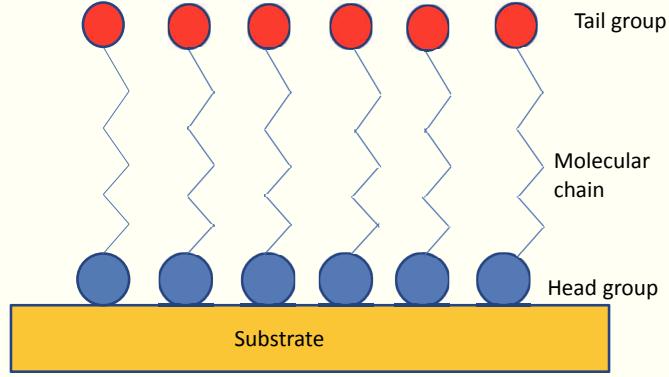
Figure 4.1: Schematic representation of a SAM.

performed always with the same initial and final electric field. The readout of the vibrational occupation at the beginning and at the end is then performed using infrared spectroscopy.

In order to access the transition probabilities one can proceed as follows. The first spectroscopic measurement determines the populations in the initial state. Selecting a sufficiently low temperature all the populations except for the ground state will be negligible. Therefore, the measurement of populations at the end of the protocol give access to the probabilities

$$|\langle E_m^\tau | U(\tau) | E_1^0 \rangle|^2. \tag{4.47}$$

Then, one can repeat the same experiment at a higher temperature, such that also the first excited state $|E_2^0\rangle$ be initially populated. The final populations then give access to

$$|\langle E_m^\tau | U(\tau) | E_1^0 \rangle|^2 + |\langle E_m^\tau | U(\tau) | E_2^0 \rangle|^2 \tag{4.48}$$

where the second term is already known, and so on, one can reconstruct all the transition probabilities. An interesting feature that one should test experimentally is how many energy levels are necessary in order to reproduce the Jarzynski equality, valid when considering the whole spectrum.

Concerning the free energy, this quantity can be independently estimated using EXAFS (extended X-ray absorption fine structure) techniques [149]. Indeed, one has for a generic parametric Hamiltonian $H(\lambda)$

$$F(\Lambda) - F(0) = \int_0^\Lambda d\lambda \, \partial_\lambda F(\lambda) = -\frac{1}{\beta} \int_0^\Lambda d\lambda \, \frac{\partial_\lambda Z(\lambda)}{Z(\lambda)} =$$
$$= -\frac{1}{\beta} \int_0^\Lambda d\lambda \, \mathrm{Tr}[\partial_\lambda H(\lambda) \, \varrho_\lambda^\beta]. \tag{4.49}$$

The EXAFS spectroscopy allows to estimate $\mathrm{Tr}[\partial_\lambda H(\lambda)\,\varrho_\lambda^\beta]$ where λ is, for instance, the distance between atoms. Therefore, this experimental setup would allow to test the Jarzynski equality measuring independently the right-hand side and the left-hand side of the equality, namely the work distribution and the free energy difference.

We are now planning to analyze more quantitatively this experimental scenario by means of numerical simulations. In particular, the Schrödinger equation can be solved numerically for a Morse potential perturbed by an external driving. Through this study one can understand how many transitions are detectable for a certain combination of temperature and electric field and to what extent the Jarzynski equality is satisfied in this non-ideal situation, when only a finite amount of transitions is present.

4.2   Open quantum systems

In the previous section the quantum work fluctuation theorems have been presented in the context of closed quantum systems. In the following, we address the problem of finding similar relations for generic open quantum systems.

The first attempt is to find interesting relations relying on the reduced dynamics of the open system only, exploiting its mathematical properties. It turns out that unital time-evolutions play a special role in this setting and allow to derive a Jarzynski-like fluctuation relation where the total energy difference replaces work. An alternative approach consists in deriving the Crooks fluctuation theorem for the open system as a consequence of the theorem for system and bath together by suitably redefining the free energy [130, 150]. Finally, we present the only way proposed up to now to distinguish the statistics of work and heat, that consists in measuring both the system and the environment at the beginning and at the end of the protocol.

4.2.1   Unital evolutions

The reduced dynamics of an open quantum system up to a certain time τ can be described by a completely positive and trace-preserving map. A particular case is represented by open quantum systems undergoing unital time-evolutions. A quantum dynamical map Λ is called unital if it preserves the identity operator $\Lambda[\mathbb{1}] = \mathbb{1}$. Due to complete positivity the map Λ admits a Kraus decomposition

$$\Lambda[\cdot] = \sum_l A_l(\cdot)A_l^\dagger, \tag{4.50}$$

and the condition of unitality reads $\sum_l A_l A_l^\dagger = \mathbb{1}$. As in the case of closed quantum systems one can access the thermodynamics of the open system by measuring the energy at the beginning and at the end. In general, we can consider a driven open system so that we distinguish the final Hamiltonian $H(\tau)$ and the initial Hamiltonian $H(0)$. The two-measurement protocol therefore goes as follows: a value of the energy E_n^0, which is an eigenvalue of $H(0)$, is detected at the beginning; then the projected state $|E_n^0\rangle\langle E_n^0|$ evolves according to the map Λ up to a certain time τ when the eigenvalue E_m^τ of $H(\tau)$ is measured. As in the previous Section we can define the

probability distribution of the energy difference $P(u)$

$$P(u) = \sum_{l,m,n} p_n^0 \langle E_m^\tau | A_l | E_n^0 \rangle \langle E_n^0 | A_l^\dagger | E_m^\tau \rangle \, \delta(u - E_m^\tau + E_n^0). \tag{4.51}$$

Proposition 4.2.1. *Assuming that the initial state is the thermal state $\varrho_0^{(\beta)}$ one derives the following Jarzynski-like relation*

$$\langle \mathrm{e}^{-\beta(u-\Delta F)} \rangle = \mathrm{Tr}\left[\sum_l A_l A_l^\dagger \varrho_\tau^{(\beta)} \right] = 1, \tag{4.52}$$

where the last equality is due to the unitality condition.

Proof. The proof is a matter of straightforward calculation.

$$\langle \mathrm{e}^{-\beta(u-\Delta F)} \rangle = \int \mathrm{d}u \, P(u) \mathrm{e}^{-\beta(u-\Delta F)} =$$

$$\frac{Z_0}{Z_\tau} \sum_{l,m,n} \frac{\mathrm{e}^{-\beta E_n^0}}{Z_0} \langle E_m^\tau | A_l | E_n^0 \rangle \langle E_n^0 | A_l^\dagger | E_m^\tau \rangle \mathrm{e}^{-\beta(E_m^\tau - E_n^0)} =$$

$$\sum_{l,m} \frac{\mathrm{e}^{-\beta E_m^\tau}}{Z_\tau} \langle E_m^\tau | A_l A_l^\dagger | E_m^\tau \rangle =$$

$$= \mathrm{Tr}\left[\sum_l A_l A_l^\dagger \varrho_\tau^{(\beta)} \right].$$

$\square$

Therefore, if the evolution is unital one has $\sum_l A_l A_l^\dagger = \mathbb{1}$ and a Jarzynski-like equality holds true for the open system, with the total energy difference replacing work. Indeed, when the quantum system is both open and driven, one cannot safely distinguish between work and heat with the two measurement protocol, as can be easily seen calculating $\langle u \rangle$

$$\langle u \rangle = \int \mathrm{d}u \, P(u) u = \sum_{l,m,n} p_n^0 \langle E_m^\tau | A_l | E_n^0 \rangle \langle E_n^0 | A_l^\dagger | E_m^\tau \rangle (E_m^\tau - E_n^0) =$$

$$= \mathrm{Tr}[H(\tau)\varrho(\tau)] - \mathrm{Tr}[H(0)\varrho(0)] =$$

$$= \int_0^\tau \partial_t \mathbb{U}(t) \mathrm{d}t. \tag{4.53}$$

Since the evolution is not unitary $\partial_t \mathbb{U}(t) \neq \partial_t \mathbb{W}(t)$. On the contrary, if we consider the system open but undriven, the energy change can be suitably interpreted as heat, *i.e.* $\partial_t \mathbb{U}(t) = \partial_t \mathbb{Q}(t)$.

In order to derive a Crooks-like relation a sort of reversed protocol is needed. When dealing with unital maps a natural choice is the dual map $\widetilde{\Lambda}$

$$\widetilde{\Lambda}[\cdot] = \sum_l A_l^\dagger (\cdot) A_l, \tag{4.54}$$

whose trace-preservicity is guaranteed by the condition $\sum_l A_l A_l^\dagger$. By defining the dual probability distribution $P_D(u)$

$$P_D(u) = \sum_{l,m,n} p_m^\tau \langle E_n^0 | A_l^\dagger | E_m^\tau \rangle \langle E_m^\tau | A_l | E_n^0 \rangle \, \delta(u - E_n^0 + E_m^\tau), \qquad (4.55)$$

where p_m^τ is the probability to find a value of energy E_m^τ in the first measurement of the reversed protocol, and assuming $p_m^\tau = \mathrm{e}^{-\beta E_m^\tau}/Z_\tau$, one can derive a Crooks-like relation following the same steps as in the unitary case

$$\frac{P(u)}{P_D(-u)} = \mathrm{e}^{-\beta(u-\Delta F)}. \qquad (4.56)$$

Fluctuation theorems for non-unitary dynamical maps were investigated in [151–157] and the peculiarity of unital maps was pointed out in many of them.

4.2.2 System and Bath

An alternative approach is to consider explicitly system and bath and try to derive fluctuation theorems for some thermodynamic quantities of interest.

This is for instance the approach followed in [130, 150] to argue that the Jarzynski relation holds also for generic open driven quantum systems, by suitably redefining the free energy. Indeed, if one considers a driven bipartite quantum system SB evolving in time through the unitary propagator $U(t)$ generated by the total Hamiltonian $H(t) = H_S(t) + H_B + H_{SB}$ (notice the time-dependence only in $H_S(t)$) the Jarzynski equality holds for SB

$$\langle \mathrm{e}^{-\beta w} \rangle = \mathrm{e}^{-\beta \Delta F}, \qquad (4.57)$$

where the free energy difference is the one of the total system

$$\mathrm{e}^{-\beta \Delta F} = \frac{\mathrm{Tr}[\mathrm{e}^{-\beta H(t)}]}{\mathrm{Tr}[\mathrm{e}^{-\beta H(0)}]}. \qquad (4.58)$$

Since the driving acts only on S, the work performed on the whole system is actually performed on S. This can be seen looking at the average $\langle w \rangle$

$$\langle w \rangle = \int_0^\tau \partial_t \mathrm{W}(t) \mathrm{d}t = \int_0^\tau \mathrm{Tr}[\partial_t H(t) \, \varrho(t)] \mathrm{d}t = \int_0^\tau \mathrm{Tr}_S[\partial_t H_S(t) \, \varrho_S(t)] \mathrm{d}t. \qquad (4.59)$$

Moreover, using a reasoning from classical thermodynamics it is argued that the meaningful free energy difference for the system S strongly coupled with B is $\Delta F_S = -1/\beta \log\left(Z_S(t)/Z_S(0)\right)$, where

$$Z_S(t) = \frac{Z(t)}{Z_B} = \frac{\mathrm{Tr}[\mathrm{e}^{-\beta H(t)}]}{\mathrm{Tr}_B[\mathrm{e}^{-\beta H_B}]}. \qquad (4.60)$$

Indeed, the thermodynamic properties derived from the partition function Z_S do not contradict any thermodynamic law [130]. Equivalently, one can say that the free energy of a strongly

coupled open system S is given by the difference between the total free energy $F(t)$ and the bare bath free energy F_B (time-independent) [158]

$$F_S(t) = F(t) - F_B, \quad F_B = -\frac{1}{\beta}\log(Z_B). \tag{4.61}$$

Since the free energy F_B is time-independent, one has $\Delta F(t) = \Delta F_S(t)$ and the Jarzynski equality for the system S is automatically satisfied as a consequence of (4.57)

$$\langle e^{-\beta w}\rangle = e^{-\beta \Delta F_S}. \tag{4.62}$$

The free energy $F_S(t)$ is also considered a reliable thermodynamic quantity because it corresponds to the partition function with respect to the so-called Hamiltonian of mean force

$$H^*(t) = -\frac{1}{\beta}\log\left(\frac{\text{Tr}_B[e^{-\beta H(t)}]}{\text{Tr}_B[e^{-\beta H_B}]}\right), \tag{4.63}$$

which is commonly used for thermodynamic calculations in the classical scenario, for instance in reaction-rate theory [159] and in biomolecular simulations [160], and consists in a modified Hamiltonian for the system of interest that reduces to the bare Hamiltonian in the weak-coupling limit. The relation between this Hamiltonian and the effective Hamiltonian we have defined in Chapter 3 can be matter for future work.

In the same framework, that is a bipartite quantum system SB evolving in time through the unitary propagator $U(t)$ generated by the total Hamiltonian $H = H_S(t) + H_B + H_{SB}$, further investigations have been conducted in order to distinguish the statistics of work from the statistics of heat. In order to do that, it is assumed to have a certain degree of control on the bath. In particular, a double measurement of energy is performed at the beginning and at the end of the process in both system S and bath B. More explicitly, one measures the observable $H_S(0) + H_B$ at the beginning, detecting a value $E_n^0 + E_k^B$ and the observable $H_S(t) + H_B$ at the end, detecting the energy $E_m^\tau + E_l^B$. The stochastic variable representing the variation of energy in the system is $u = E_m^\tau - E_n^0$, that can be associated to the variation of energy in the global system (in the form of work) minus the stochastic variation of the energy in the bath in the form of heat $u_B = E_l^B - E_k^B = -q$. This approach is not valid in case of strong coupling, because the contribution of the interaction Hamiltonian has been neglected in the balance of energy. Following the same argument of the previous Section one can now define a joint probability distribution for u and q, or for $w = u - q$ and q, and access the full statistics of work and heat. This has been done in a series of papers [129, 131, 161–163]. Explicitly, the probability distributions of work and heat read

$$P(w) = \sum_{\substack{m,n,\\\mu,\nu}} p_n^0 p_\nu^B \text{Tr}\left[\Pi_m^\tau \otimes \Pi_\mu^B U(\tau)\Pi_n^0 \otimes \Pi_\nu^B U^\dagger(\tau)\right]\delta(w - E_m^\tau + E_n^0 - E_\nu^B + E_\mu^B), \tag{4.64}$$

$$P(q) = \sum_{\mu,\nu} p_\nu^B \text{Tr}\left[\mathbb{1}_S \otimes \Pi_\mu^B U(\tau)\varrho_S(0) \otimes \Pi_\nu^B U^\dagger(\tau)\right]\delta(q - E_\nu^B + E_\mu^B) \tag{4.65}$$

where $\Pi_m^\tau = |E_m^\tau\rangle\langle E_m^\tau|$, $\Pi_n^0 = |E_n^0\rangle\langle E_n^0|$, $\Pi_\mu^B = |E_\mu^B\rangle\langle E_\mu^B|$ and the initial probabilities are $p_n^0 = \text{Tr}[\Pi_n^0 \varrho_S(0)]$ and $p_\nu^B = \text{Tr}[\Pi_\nu^B \varrho_B(0)]$. A useful concept developed in those works is the so called modified Liouvillian. Indeed it is shown that the work generating function, defined as

$$G_w(s,\tau) = \int \mathrm{d}w P(w) e^{isw} \tag{4.66}$$

can be conveniently rewritten as

$$G_w(s,\tau) = \text{Tr}[e^{isH_S(\tau)} \varrho(\tau,s)], \tag{4.67}$$

where

$$\varrho(\tau,s) = U_{s/2}(\tau)\varrho(0,s)U_{-s/2}^\dagger(\tau), \quad U_s(\tau) = e^{iH_B s}U(\tau)e^{-iH_B s}, \tag{4.68}$$

and the initial condition reads $\varrho(0,s) = e^{-isH_S(0)}\varrho(0)$. On the other hand, the heat generating function reads

$$G_q(s,\tau) = \text{Tr}[\widetilde{\varrho}(\tau,s)], \quad \widetilde{\varrho}(\tau,s) = U_{s/2}(\tau)\varrho(0)U_{-s/2}^\dagger(\tau). \tag{4.69}$$

These relations can be obtained from the definitions of $G_w(s,\tau)$ and $G_q(s,\tau)$ after straightfroward calculations. Note that the auxiliary matrices $\varrho(\tau,s)$ and $\widetilde{\varrho}(\tau,s)$ are not proper density matrices because they fail to be Hermitian. However, despite lacking a physical interpretation, they are a suitable tool to describe the statistics of work and heat. In particular, it has been argued that approximation techniques as the Davies weak-coupling limit can be applied to the dynamics of the auxiliary matrices in order to reconstruct the full statistics of work and heat [131].

For completeness one has to say that a similar perspective, namely the double measurement performed both on the system and on the bath at the beginning and at the end of a protocol, has been recently considered to derive fluctuation theorems for the entropy production [164, 165] under measurement of generic observables and generic processes [138].

Chapter 5

Conclusion and outlook

The nonequilibrium thermodynamics of quantum systems is the subject of current intensive research, both from a theoretical and an applicative point of view. Indeed, on the one hand one is interested in deriving the emergence of the laws of thermodynamics from the microscopic dynamics of quantum systems, and on the other hand one would like to learn how to build efficient quantum devices converting thermal energy into useful work. Moreover, the high degree of control reached in experimental setups like ultracold atoms, optomechanical systems and trapped ions, allows in principle to test the theoretical results in a laboratory.

A complete framework describing the nonequilibrium thermodynamics of open quantum systems in the Markovian scenario, namely when there is a clear separation between the time-scales of system and environment so that memory effects in the dynamics are negligible, was developed in the late seventies by H. Spohn, J. Lebowitz and R. Alicki, in terms of quantum dynamical semigroups. In this setting, a reasonable separation between the heat and work contributions to the variation of energy was introduced. Moreover, the positivity of the entropy production defined in analogy with the theory of Classical Irreversible Thermodynamics could be proved. Aim of this Thesis has been to analyze situations that go beyond such a standard framework.

First of all, we have considered effective dynamics for open quantum systems more general than quantum dynamical semigroups. These dynamics are usually referred to as non-Markovian, because they describe situations in which the system experiences memory effects, *e.g.* a back-flow of information from the environment. We have discussed and compared different definitions of non-Markovianity in the quantum domain because there is no consensus in the scientific community yet and we have studied the laws of thermodynamics, in particular the second law, in this more general scenario. This kind of analysis in not only of theoretical interest because it turns out that the time-evolution of many physical systems is not correctly described by Markovian master equations and non-Markovian models are needed to explain an amount of empirical data.

We have shown that the entropy production, defined in analogy with the Markovian case, can be negative for the class of dynamical maps where the particular property called P-divisibility is not satisfied. Moreover, when the semigroup composition law does not hold, the asymptotic state of the dynamics need not be stationary at finite time. In such a case we have shown that, by choosing an open quantum system that eventually thermalizes at a certain temperature due to the

action of the bath and defining the entropy production by means of this reference temperature, not only this quantity can be negative but the integrated entropy production can be negative too.

We suggested that these outcomes should not be interpreted as a violation of the second law of thermodynamics but as an evidence that in a non-Markovian scenario the contribution of the environment to the balance of entropy must be explicitly taken into account. In order to justify this position and to better understand the thermodynamics of non-Markovian quantum systems we changed perspective and considered a generic bipartite quantum system, where the two subsystems are interacting but initially uncorrelated.

The analysis of the thermodynamics of a generic bipartite quantum system has been performed in order to highlight the role of a non-ideal environment, experiencing non-standard effects due to the finite size and the correlations established between the systems. In this situation the reduced dynamics of the system is typically non-Markovian.

As a first step, we defined a suitable effective Hamiltonian for both systems using physically reasonable requests. Then, by means of this effective Hamiltonian we distinguished between heat and work according to the usual relations proposed already in the seventies, but this time for both system and "bath" (second subsystem). A contribution to the balance of energy remains defined that cannot be associated to a subsystem but can be accessed only by global measurements. We called this contribution, that strongly depends on the correlations established between the systems, binding energy.

Concerning the balance of entropy, we showed that the sum of the entropy variations at finite time in both subsystems is always nonnegative. This could be interpreted as the most general statement of the second law of thermodynamics because it holds provided that the initial state is factorized. However, such a quantity is not monotonically increasing in time. Therefore, we showed that this statement is in general not equivalent to the positivity of the entropy production as defined in the seventies.

We also analyzed in detail two different possible definitions of nonequilibrium temperature. It turns out that none of them is completely satisfactory. The first one, called pseudo-temperature, has been proved not to reduce to the standard equilibrium temperature in a simple example. On the other hand, the so-called extended temperature reproduced correctly the expected phenomenology in the analyzed examples but suffers of an intrinsic arbitrariness in more general situations.

In the last part of the Thesis we concentrated to generalization of the standard thermodynamic description in a different sense. In particular, we have reviewed some results known as fluctuation theorems that extend the analysis of thermodynamics beyond the average values of observables, in principle to fluctuations of any order. They have been first derived using classical mechanics by C. Jarzynski and G. Crooks and then generalized to the quantum domain. The study has been conducted analyzing separately closed quantum systems and open quantum systems. In the first case the theoretical framework is almost settled while the situation is still developing for open systems.

We sketched the proposal of a possible experimental test of the quantum Jarzynski equality in closed quantum systems, specifically in ensembles of diatomic molecules where the vibrational degree of freedom is coupled to an external electric field. In order to get a high degree of control on this physical system we imagined to construct an ordered structure by means of

self-assembled monolayers. We are currently planning to simulate the physical process solving numerically the Schrödinger equation with the Morse potential modified by an external driving, in order to get more precise expectations about the outcome of the experiment. Unlike other experimental tests already performed in different physical systems, our setting should allow to estimate independently both sides of the equality, namely the work distribution and the free energy difference. In particular, the estimate of the free energy can be done using EXAFS techniques.

In the open system scenario we reviewed some important results that could allow further development in the future. In particular, a transient fluctuation theorem exists concerning the fluctuations of heat and entropy under unital dynamics, that are dynamics preserving the identity operator. It is not clear whether similar results could be obtained with other dynamics or for different thermodynamic observables. The experimental investigation of fluctuating thermodynamic quantities in open quantum systems should help in understanding if some more general results can be expected or not. For instance, the protocol proposed in Chapter 4 with self-assembled monolayers could be used to test the Jarzynski equality also in the open system scenario. The hypothesis of performing work on isolated diatomic molecules is due to the electric field varying on a faster time-scale than the typical relaxation time of molecular vibrations. This characteristic time can be modified by increasing the concentration of thiolates in the experimental setup.

Summarizing, in this Thesis the behavior in time of average thermodynamic quantities like heat, work and entropy production has been analyzed in the non-Markovian setting. First of all, we have taken a phenomenological approach, postulating non-Markovian dynamical maps for the system of interest; then we changed perspective and considered explicitly the environment in the balances of energy and entropy. Moreover, a review of the results known as quantum fluctuation theorems has been presented, proposing an experimental test for the quantum Jarzynski equality that, differently from the existing proposals, allows in principle to test both sides of the equality independently. Despite these important achievements, many open questions remain for future work.

A fundamental topic which deserves further investigation is the microscopic description of heat conduction in a chain of interacting particles with boundaries at different temperatures. The framework described in the first Chapter is able to reproduce the direction of heat fluxes from the whole chain to the different baths, satisfying the second law of thermodynamics, but does not account for the local equilibrium and the Fourier law along the chain. This issue is strictly related to the discussion about the differences between the local and global generators that, as already mentioned, is matter of current intensive research.

An open question is how much quantum mechanics enters in the description of thermodynamics. Indeed, as shown in Chapter 3 the definitions of heat and work for a generic bipartite system can be equivalently given in the classical and in the quantum domain. Therefore, a direction for future work could be to understand what is the role of quantum correlations, *e.g.* entanglement, in the thermodynamic balances. More in general one is interested in finding purely quantum effects in quantum thermodynamics.

Another interesting theoretical issue is the description of equilibration and thermalization in closed quantum systems. In particular, despite some recent important results, the estimate of the

thermalization time-scales from the properties of the Hamiltonian is still very challenging. A step forward in this analysis could complement and strengthen the statement of the second law based on the finite variation of entropy in both system and bath.

Some useful hints could arrive from the experiments. Indeed, experimental setups such as ultracold atoms and optomechanical systems can be used to test thermodynamic laws at the microscale and possibly the connection between different scales. The realization of efficient quantum thermal machines should be also based on these systems. An amount of important theoretical results have already been found in this direction but the technological improvement related to efficient quantum devices is still at the beginning. The realization of our proposed experiment with self-assembled monolayers fits into this discussion. Indeed, it could allow to test the Jarzynski fluctuation relation and understand how much the result is robust in the open system scenario so that small quantum systems undergoing nonequilibrium work protocols could be used, for instance, as thermometers. Numerical simulations of this experimental setting would be the preliminary step in this direction.

Appendix A

Example 1

A.1 Sign of the entropy production rate

From Eq. (2.38) it seems that the sign of σ_t depends both on $\gamma(t)$ and on the sign of the expression within square brackets. In this section we prove that the latter is always positive. Let's rewrite the entropy production rate in the convenient way

$$\sigma_t = \gamma(t) \coth(\beta\omega/2) e^{-2\Gamma(t)} \left[A + B + C \right], \tag{A.1}$$

where

$$A = \frac{x^2(0) + y^2(0)}{4r(t)} \log\left(\frac{1 + r(t)}{1 - r(t)} \right), \tag{A.2}$$

$$B = \frac{z(0) + |z(\infty)|}{2} \log\left(\frac{1 + r(\infty)}{1 - r(\infty)} \right), \tag{A.3}$$

$$C = \frac{(z(0) + |z(\infty)|)z(t)}{2r(t)} \log\left(\frac{1 + r(t)}{1 - r(t)} \right). \tag{A.4}$$

Notice that A is always nonnegative while B and C can be either positive or negative. We show in the following that $A + B + C$ is nevertheless positive, distinguishing different situations.

1. If $z(0) + |z(\infty)| \le 0$ then $z(t) \le -|z(\infty)|$ since $z(t) + |z(\infty)| = e^{-2\Gamma(t)}(z(0) + |z(\infty)|)$ and

$$|r(t)| \ge |z(t)| \ge |z(\infty)| = r(\infty). \tag{A.5}$$

Therefore, $B + C \ge 0$ since

$$r(t) \log\left(\frac{1 + r(\infty)}{1 - r(\infty)} \right) - |z(t)| \log\left(\frac{1 + r(t)}{1 - r(t)} \right) \le$$

$$\le r(t) \log\left(\frac{1 + r(\infty)}{1 - r(\infty)} \right) - r(\infty) \log\left(\frac{1 + r(t)}{1 - r(t)} \right) \le 0,$$

where the last inequality holds true because the function

$$f(x) = \frac{1}{x} \log\left(\frac{1 + x}{1 - x} \right),$$

is monotonically increasing for $0 < x < 1$. This can be seen from the first derivative

$$f'(x) = \frac{1}{x^2}\left[\frac{2x}{1-x^2} - \log\left(\frac{1+x}{1-x}\right)\right],$$

that is always positive because

$$\frac{2x}{1-x^2} - |\log(1+x)| - |\log(1-x)| \geq \frac{2x}{1-x^2} - \frac{x}{2}\frac{2+x}{1+x} - \frac{x}{2}\frac{2-x}{1-x} = \frac{x^3}{1-x^2} \geq 0$$

where the following inequalities have been used [166]

$$\frac{2x}{2+x} \leq |\log(1+x)| \leq \frac{x}{2}\frac{2+x}{1+x}, \qquad \frac{2x}{2-x} \leq |\log(1-x)| \leq \frac{x}{2}\frac{2-x}{1-x}.$$

2. In the case $z(0) + |z(\infty)| \geq 0$ we have to distinguish different situations.

   - First of all, if $z(t) \geq 0$ then B and C are both positive.

   - If instead $-|z(\infty)| \leq z(t) \leq 0$ and $r(t) \leq r(\infty)$, then $B + C$ is positive because

$$\log\left(\frac{1+r(\infty)}{1-r(\infty)}\right) - \frac{|z(t)|}{r(t)}\log\left(\frac{1+r(t)}{1-r(t)}\right) \geq$$
$$\geq \log\left(\frac{1+r(\infty)}{1-r(\infty)}\right) - \log\left(\frac{1+r(t)}{1-r(t)}\right) \geq 0.$$

   - The last possibility is $-|z(\infty)| \leq z(t) \leq 0$ and $r(t) \geq r(\infty)$. In this case B is positive and the following inequality holds true

$$x^2(0) + y^2(0) \geq (|z(\infty)| - z(t))(z(0) + |z(\infty)|) \geq 0.$$

As a consequence, $A + C \geq 0$:

$$x^2(0) + y^2(0) - 2|z(t)|(z(0) + |z(\infty)|) \geq$$
$$\geq x^2(0) + y^2(0) - (|z(\infty)| + |z(t)|)(z(0) + |z(\infty)|) \geq 0.$$

Summarizing, the expression in square brackets $A + B + C$ is always nonnegative and the sign of the entropy production rate is only determined by $\gamma(t)$.

A.2   CP conditions

In a recent paper [106] the authors presented the necessary and sufficient conditions characterizing complete positivity for a qubit dynamics of the form:

$$\partial_t \varrho(t) = \mathcal{L}_t[\varrho(t)] = -i\omega(t)[\sigma_z, \varrho(t)] + \frac{\gamma_1(t)}{2}\mathcal{L}_1[\varrho(t)] + \frac{\gamma_2(t)}{2}\mathcal{L}_2[\varrho(t)] + \frac{\gamma_3(t)}{2}\mathcal{L}_3[\varrho(t)], \quad \text{(A.6)}$$

where the following dissipators $\mathcal{L}_i$ are considered

$$\mathcal{L}_1[\varrho(t)] = \sigma_+\varrho(t)\sigma_- - \frac{1}{2}\{\sigma_-\sigma_+, \varrho(t)\}, \tag{A.7}$$

$$\mathcal{L}_2[\varrho(t)] = \sigma_-\varrho(t)\sigma_+ - \frac{1}{2}\{\sigma_+\sigma_-, \varrho(t)\}, \tag{A.8}$$

$$\mathcal{L}_3[\varrho(t)] = \sigma_z\varrho(t)\sigma_z - \varrho(t). \tag{A.9}$$

Explicitly they read

$$0 \leq \mathrm{e}^{-\Gamma(t)}[G(t) + 1] \leq 1 \tag{A.10}$$

$$0 \leq \mathrm{e}^{-\Gamma(t)}G(t) \leq 1 \tag{A.11}$$

$$-\mathrm{e}^{-\Gamma(t)-2\widetilde{\Gamma}(t)}\sin^2\Omega(t) \leq \mathrm{e}^{-\Gamma(t)}G(t)[1 - \mathrm{e}^{-\Gamma(t)}[G(t) + 1]] \tag{A.12}$$

$$\mathrm{e}^{-\Gamma(t)-2\widetilde{\Gamma}(t)}\cos^2\Omega(t) \leq \mathrm{e}^{-\Gamma(t)}[G(t) + 1][1 - \mathrm{e}^{-\Gamma(t)}G(t)], \tag{A.13}$$

where the quantities $\Gamma(t), \widetilde{\Gamma}(t), \Omega(t), G(t)$ are defined as follows

$$\Gamma(t) = \int_0^t \mathrm{d}s\,[\gamma_1(s) + \gamma_2(s)]/2, \tag{A.14}$$

$$\widetilde{\Gamma}(t) = \int_0^t \mathrm{d}s\,\gamma_3(s), \tag{A.15}$$

$$\Omega(t) = \int_0^t \mathrm{d}s\,2\omega(s), \tag{A.16}$$

$$G(t) = \int_0^t \mathrm{d}s\,\mathrm{e}^{\Gamma(s)}\gamma_2(s)/2. \tag{A.17}$$

In our example we consider $\gamma_3 = 0$ and $\gamma_1(t) = c \cdot \gamma_2(t)$ where c is a positive constant. As a consequence it turns out that $\widetilde{\Gamma}(t) = 0$ and

$$\Gamma(t) = \frac{c+1}{2}\int_0^t \mathrm{d}s\,\gamma_2(s),$$

$$G(t) = \frac{1}{c+1}\int_0^t \mathrm{d}s\,\mathrm{e}^{\Gamma(s)}\frac{\mathrm{d}}{\mathrm{d}s}\Gamma(s) = \frac{1}{c+1}\int_0^t \mathrm{d}s\,\frac{\mathrm{d}}{\mathrm{d}s}\mathrm{e}^{\Gamma(s)} = \frac{1}{c+1}[\mathrm{e}^{\Gamma(t)} - 1].$$

Therefore, one can write

$$A(t) = \mathrm{e}^{-\Gamma(t)}[G(t) + 1] = \frac{1}{c+1}[1 - \mathrm{e}^{-\Gamma(t)}] + \mathrm{e}^{-\Gamma(t)} = \frac{c\,\mathrm{e}^{-\Gamma(t)} + 1}{c+1}, \tag{A.18}$$

$$B(t) = \mathrm{e}^{-\Gamma(t)}G(t) = \frac{1 - \mathrm{e}^{-\Gamma(t)}}{c+1}, \tag{A.19}$$

$$C(t) = B(t)[1 - A(t)] = \frac{c[1 - \mathrm{e}^{-\Gamma(t)}]^2}{(c+1)^2}, \tag{A.20}$$

$$D(t) = A(t)[1 - B(t)] = \mathrm{e}^{-\Gamma(t)} + \frac{c[1 - \mathrm{e}^{-\Gamma(t)}]^2}{(c+1)^2}, \tag{A.21}$$

and consequently

$$0 \leq A(t) \leq 1 \Leftrightarrow \Gamma(t) \geq 0, \tag{A.22}$$

$$0 \leq B(t) \leq 1 \Leftrightarrow \Gamma(t) \geq 0, \tag{A.23}$$

$$- \mathrm{e}^{-\Gamma(t)} \sin^2 \Omega(t) \leq 0 \leq C(t), \tag{A.24}$$

$$\mathrm{e}^{-\Gamma(t)} \cos^2 \Omega(t) \leq \mathrm{e}^{-\Gamma(t)} \leq D(t). \tag{A.25}$$

This calculations show that in our example the necessary and sufficient conditions for complete positivity correspond to $\Gamma(t) \geq 0 \, \forall t$.

Appendix B

Thermalizing qubit

B.1 State of the system

Here we obtain the exact state of the total system up to the second order in the interaction coupling λ. After calculating the interaction-picture Hamiltonian $\widetilde{H}_{\text{int}}^{(\lambda)}(\tau) = U_0^\dagger(t)H_{\text{int}}^{(\lambda)}U_0(t)$ and the corresponding evolution operator $\widetilde{U}_\lambda(t) = \mathbb{T}e^{-i\int_0^t \mathrm{d}s\, \widetilde{H}_{\text{int}}^{(\lambda)}(s)}$, one can read the state of the combined system from

$$\varrho_{SB}^{(\lambda)}(t) = U_0(\tau)\widetilde{U}_\lambda(t)\varrho_{SB}(0)\widetilde{U}_\lambda^\dagger(t)U_0^\dagger(t) \tag{B.1}$$

as

$$\begin{aligned}
\varrho_S^{(\lambda)}(t) =\,& \varrho_S^{(0)}(t) + \lambda^2\Big\{ \sigma_+\varrho_S^{(0)}(t)\sigma_- \sum_k |f_k|^2\,|\eta(\omega_0,\omega_k,\tau)|^2\,\overline{n}(\omega_k,\beta) + \\
& + \sigma_-\varrho_S^{(0)}(\tau)\sigma_+ \sum_k |f_k|^2\,|\eta(\omega_0,\omega_k,\tau)|^2\big(\overline{n}(\omega_k,\beta)+1\big) \\
& - \sum_k |f_k|^2\big(\overline{n}(\omega_k,\beta)+1\big)\Big(\xi^*(\omega_0,\omega_k,\omega_k,t)\,\varrho_S^{(0)}(t)\sigma_+\sigma_- + \\
& + \xi(\omega_0,\omega_k,\omega_k,t)\,\sigma_+\sigma_-\,\varrho_S^{(0)}(t)\Big) \\
& - \sum_k |f_k|^2\overline{n}(\omega_k,\beta)\Big(\xi(\omega_0,\omega_k,\omega_k,t)\,\varrho_S^{(0)}(t)\sigma_-\sigma_+ + \\
& + \xi^*(\omega_0,\omega_k,\omega_k,t)\,\sigma_-\sigma_+\,\varrho_S^{(0)}(t)\Big)\Big\} + O(\lambda^3), \tag{B.2}
\end{aligned}$$

and similarly for bath B,

$$
\begin{aligned}
\varrho_B^{(\lambda)}(t) =&\, \varrho_B^\beta + i\lambda\Big(\mathrm{Tr}[\varrho_S(0)\sigma_+]\,\mathrm{e}^{i\omega_0 t}\sum_k f_k^*\,\eta^*(\omega_0,\omega_k,t)\,[\varrho_B^\beta, \mathrm{a}_k] \\
&+ \mathrm{Tr}[\varrho_S(0)\sigma_-]\,\mathrm{e}^{-i\omega_0 t}\sum_k f_k\,\eta(\omega_0,\omega_k,t)\,[\varrho_B^\beta, \mathrm{a}_k^\dagger]\Big) \\
&+ \lambda^2\Big(\mathrm{Tr}[\varrho_S(0)\sigma_-\sigma_+]\sum_{kk'}\Big\{ f_k^* f_{k'}\,\eta^*(\omega_0,\omega_k,t)\eta(\omega_0,\omega_{k'},t)\,\mathrm{a}_k\,\varrho_B^\beta\,\mathrm{a}_{k'}^\dagger \\
&\quad - f_{k'} f_k^* \xi^*(\omega_0,\omega_{k'},\omega_k,t)\,\mathrm{e}^{it(\omega_k-\omega_{k'})}\,\mathrm{a}_{k'}^\dagger \mathrm{a}_k\,\varrho_B^\beta \\
&\quad - f_{k'}^* f_k \xi(\omega_0,\omega_{k'},\omega_k,t)\,\mathrm{e}^{-i(\omega_k-\omega_{k'})t}\,\varrho_B^\beta \mathrm{a}_k^\dagger \mathrm{a}_{k'}\Big\} \\
&+ \mathrm{Tr}[\varrho_S(0)\sigma_+\sigma_-]\sum_{kk'}\Big\{ f_k f_{k'}^*\,\eta(\omega_0,\omega_k,t)\eta^*(\omega_0,\omega_{k'},t)\,\mathrm{a}_k^\dagger\,\varrho_B^\beta\,\mathrm{a}_{k'} \\
&\quad - f_{k'}^* f_k \xi(\omega_0,\omega_{k'},\omega_k,t)\,\mathrm{e}^{-i\tau(\omega_k-\omega_{k'})}\,\mathrm{a}_{k'}\mathrm{a}_k^\dagger\,\varrho_B^\beta \\
&\quad - f_{k'} f_k^* \xi^*(\omega_0,\omega_{k'},\omega_k,t)\,\mathrm{e}^{i(\omega_k-\omega_{k'})t}\,\varrho_B^\beta \mathrm{a}_k\mathrm{a}_{k'}^\dagger\Big\}\Big) + O(\lambda^3),
\end{aligned}
\tag{B.3}
$$

where

$$
\eta(\omega_0,\omega_k,t) = \int_0^t \mathrm{d}s\,\mathrm{e}^{i(\omega_0-\omega_k)s},
\tag{B.4}
$$

$$
\xi(\omega_0,\omega_{k'},\omega_k,t) = \int_0^t \mathrm{d}s_1\,\mathrm{e}^{i(\omega_0-\omega_{k'})s_1}\eta^*(\omega_0,\omega_k,s_1),
\tag{B.5}
$$

$\overline{n}(\omega,\beta)$ shows the Planck distribution or the mean quanta number in a mode with frequency ω [equation (54) of the main text], and $\varrho_S^{(0)}(t) = U_S(t)\varrho_S(0)U_S^\dagger(t)$ is the unperturbed state of S, in which $U_S(t) = \mathrm{e}^{-i\tau H_S}$ (with $H_S = \omega_0\sigma_z/2$) is the free-system evolution.

In the continuum-ω limit, $\sum_k \to \int_0^\infty \mathrm{d}\omega$, we can find the dynamical equation of $\varrho_S^{(\lambda)}(t)$. We differentiate the continuum version of equation (B.2) in which we take $t \to \infty$ in the integrals of the RHS (long-time limit). In the long-time, weak-coupling limit we have $t \to \infty$ and $\lambda \to 0$ such that $\lambda^2 t = \mathrm{const}$. This differentiation yields the Lindblad-type equation of the main text.

B.2   Calculating thermodynamic properties

Using the following notation for the states of the system and the bath:

$$
\varrho_S^{(\lambda)}(t) = \varrho_S^{(0)}(t) + \lambda^2\varrho_S^{(2)}(t) + O(\lambda^3),
\tag{B.6}
$$

$$
\varrho_B^{(\lambda)}(t) = \varrho_B^\beta + \lambda\varrho_B^{(1)}(t) + \lambda^2\varrho_B^{(2)}(t) + O(\lambda^3),
\tag{B.7}
$$

the effective Hamiltonians of S and B can be computed up to $O(\lambda^3)$ as

$$
H_S^{(\mathrm{eff})}(t) = H_S + \lambda\,\mathrm{Tr}_B\left[\varrho_B^{(1)}(t)\,H_{\mathrm{int}}^{(\lambda)}\right] - \lambda\alpha_S\mathrm{Tr}\left[\varrho_S^{(0)}(t) \otimes \varrho_B^{(1)}(t)\,H_{\mathrm{int}}^{(\lambda)}\right],
\tag{B.8}
$$

$$
H_B^{(\mathrm{eff})}(t) = H_B + \mathrm{Tr}_S\left[\varrho_S^{(0)}(t)\,H_{\mathrm{int}}^{(\lambda)}\right] - \lambda\alpha_B\mathrm{Tr}\left[\varrho_S^{(0)}(t) \otimes \varrho_B^{(1)}(t)\,H_{\mathrm{int}}^{(\lambda)}\right].
\tag{B.9}
$$

We obtain

$$\mathrm{Tr}_B\left[\varrho_B^{(1)}(t)\,H_{\mathrm{int}}^{(\lambda)}\right] = 2\lambda\sum_k|f_k|^2\left(i\varrho_{10}\,\sigma_- - \int_0^t\mathrm{d}s\,\mathrm{e}^{i\omega_k t}\mathrm{e}^{i(\omega_0-\omega_k)s} + \mathrm{h.c.}\right),$$

$$\mathrm{Tr}_S\left[\varrho_S^{(0)}(t)\,H_{\mathrm{int}}^{(\lambda)}\right] = 2\lambda\sum_k\left(f_k^*\varrho_{10}\mathrm{e}^{i\omega_0 t}\mathrm{a}_k + \mathrm{h.c.}\right) =: \lambda H_B^{(1)}(t),$$

$$\mathrm{Tr}\left[\varrho_S^{(0)}(t)\otimes\varrho_B^{(1)}(t)\,H_{\mathrm{int}}^{(\lambda)}\right] = 8\lambda|\varrho_{10}|^2\sum_k|f_k|^2\frac{1-\cos[(\omega_0-\omega_k)t]}{(\omega_0-\omega_k)} =: \lambda H_B^{(2)}(t),$$

where "h.c." denotes Hermitian conjugate. The energy of the bath then becomes up to the leading order in λ

$$\mathbb{U}_B^{(\lambda)}(t) = \mathrm{Tr}\left[\varrho_B^{(\lambda)}(t)\,H_B^{(\mathrm{eff})}(t)\right] \simeq$$
$$\simeq \mathbb{U}_B^{(0)} + \lambda^2\left(-\alpha_B\mathrm{Tr}\left[\varrho_B^\beta\,H_B^{(2)}(t)\right] + \mathrm{Tr}\left[\varrho_B^{(1)}(t)\,H_B^{(1)}(t)\right] + \mathrm{Tr}\left[\varrho_B^{(2)}(t)\,H_B\right]\right), \quad \text{(B.10)}$$

which gives

$$\partial_t\mathbb{U}_B^{(\lambda)}(t) = \partial_t\mathbb{Q}_B(t) + \partial_t\mathbb{W}_B(t)$$
$$\simeq \lambda^2\left(\mathrm{Tr}\left[\mathrm{d}\varrho_B^{(2)}(t)\,H_B\right] + \mathrm{Tr}\left[\partial_t\varrho_B^{(1)}(t)\,H_B^{(1)}(t)\right] + \right.$$
$$\left. + \mathrm{Tr}\left[\varrho_B^{(1)}(t)\,\partial_t H_B^{(1)}(t)\right] - \alpha_B\mathrm{Tr}\left[\varrho_B^\beta\,\partial_t H_B^{(2)}(t)\right]\right). \quad \text{(B.11)}$$

After some straightforward algebra we can see that

$$\mathrm{Tr}\left[\partial_t\varrho_B^{(2)}(t)\,H_B\right] = 8\left[\left(\overline{n}(\omega_k,\beta)+1\right)\varrho_{00} - \overline{n}(\omega_k,\beta)\varrho_{11}\right]\times$$
$$\times\sum_k|f_k|^2\frac{\omega_k}{(\omega_0-\omega_k)}\sin[(\omega_0-\omega_k)t], \quad \text{(B.12)}$$

$$\mathrm{Tr}\left[\varrho_B^{(1)}(t)\,\partial_t H_B^{(1)}(t)\right] = 8|\varrho_{10}|^2\sum_k|f_k|^2\frac{\omega_0}{(\omega_0-\omega_k)}\sin[(\omega_0-\omega_k)t], \quad \text{(B.13)}$$

$$\mathrm{Tr}\left[\partial_t\varrho_B^{(1)}(t)\,H_B^{(1)}(t)\right] = -8|\varrho_{10}|^2\sum_k|f_k|^2\frac{\omega_k}{(\omega_0-\omega_k)}\sin[(\omega_0-\omega_k)t], \quad \text{(B.14)}$$

$$\mathrm{Tr}\left[\varrho_B^\beta\,\partial_t H_B^{(2)}(t)\right] = 8|\varrho_{10}|^2\sum_k|f_k|^2\sin[(\omega_0-\omega_k)t]. \quad \text{(B.15)}$$

Hence

$$\partial_t\mathbb{U}_B^{(\lambda)}(t) \simeq 8\lambda^2\sum_k|f_k|^2\sin[(\omega_0-\omega_k)t]\left[|\varrho_{10}|^2(1-\alpha_B)+\right.$$
$$\left.\frac{\omega_k}{(\omega_0-\omega_k)}\left[\left(\overline{n}(\omega_k,\beta)+1\right)\varrho_{00} - \overline{n}(\omega_k,\beta)\varrho_{11}\right]\right]. \quad \text{(B.16)}$$

For the entropy we have

$$\partial_t \mathbb{S}_B^{(\lambda)}(t) = -\text{Tr}\left[\partial_t \varrho_B^{(\lambda)}(t) \log \varrho_B^{\beta}\right] - \text{Tr}\left[\partial_t \varrho_B^{(\lambda)}(t) \left(\log \varrho_B^{(\lambda)}(t) - \log \varrho_B^{\beta}\right)\right], \qquad \text{(B.17)}$$

where the first term has already been computed up to leading order in λ as

$$-\text{Tr}\left[\partial_t \varrho_B^{(\lambda)}(t) \log \varrho_B^{\beta}\right] \simeq \lambda^2 \beta \, \text{Tr}\left[\partial_t \varrho_B^{(2)}(t) H_B\right] =$$
$$\overset{\text{(B.12)}}{=} 8\lambda^2 \beta\left[\left(\overline{n}(\omega_k, \beta) + 1\right)\varrho_{00} - \overline{n}(\omega_k, \beta)\varrho_{11}\right] \sum_k |f_k|^2 \frac{\omega_k}{(\omega_0 - \omega_k)} \sin[(\omega_0 - \omega_k)\tau]. \quad \text{(B.18)}$$

In order to evaluate the second term of equation (B.17) we only need to take care of the contributions of order λ. We use the following integral form for the logarithm of an operator [167]:

$$\log A = \int_0^{\infty} \mathrm{d}x \left[\frac{I}{1+x} - (xI + A)^{-1}\right], \qquad \text{(B.19)}$$

to obtain

$$\log \varrho_B^{(\lambda)}(t) - \log \varrho_B^{\beta} = \int_0^{\infty} \mathrm{d}x \left[\left(xI + \varrho_B^{\beta}\right)^{-1} - \left(xI + \varrho_B^{(\lambda)}(\tau)\right)^{-1}\right]$$
$$= \lambda \int_0^{\infty} \mathrm{d}x \left(xI + \varrho_B^{\beta}\right)^{-1} \varrho_B^{(1)}(t) \left(xI + \varrho_B^{\beta}\right)^{-1} + O(\lambda^2), \qquad \text{(B.20)}$$

where we have used the identity [167]

$$(A + B)^{-1} = A^{-1} - A^{-1}BA^{-1} + A^{-1}BA^{-1}BA^{-1} - O(B^3) \qquad \text{(B.21)}$$

to write

$$\left(xI + \varrho_B^{(\lambda)}(t)\right)^{-1} = \left(xI + \varrho_B^{\beta}\right)^{-1} + \left(xI + \varrho_B^{\beta}\right)^{-1}\left(\varrho_B^{\beta} - \varrho_B^{(\lambda)}(t)\right)\left(xI + \varrho_B^{\beta}\right)^{-1} + O(\lambda^2)$$

and equation (B.7).

To ease notation, we introduce $O_t = \mathrm{a}^{\dagger}(h_t) - \mathrm{a}(h_t)$, with

$$\mathrm{a}(h_t) = i\varrho_{10} \sum_k f_k^* \mathrm{e}^{i\omega_k t} \eta(\omega_0, \omega_k, t) \, \mathrm{a}_k,$$

where we have followed the shorthand introduced in the main text to define the vector $h_t = \{h_k(t)\}$, with $h_k(t) = -i\varrho_{10}^* f_k \mathrm{e}^{-i\omega_k t} \eta^*(\omega_0, \omega_k, t)$. Thus we can rewrite $\varrho_B^{(1)}(t)$ as

$$\varrho_B^{(1)}(t) = [O_t, \varrho_B^{\beta}], \qquad \text{(B.22)}$$

whence

$$-\text{Tr}\left[\partial_t \varrho_B^{(\lambda)}(t) \left(\log \varrho_B^{(\lambda)}(t) - \log \varrho_B^{\beta}\right)\right] =$$
$$-\lambda^2 \int_0^{\infty} \mathrm{d}x \, \text{Tr}\left[[\partial_t O_t, \varrho_B^{\beta}]\left(xI + \varrho_B^{\beta}\right)^{-1}[O_t, \varrho_B^{\beta}]\left(xI + \varrho_B^{\beta}\right)^{-1}\right] + O(\lambda^3). \qquad \text{(B.23)}$$

Considering the spectral decomposition $\varrho_B^\beta = \sum_n r_n |n\rangle\langle n|$, one can see that

$$\mathrm{Tr}\left[[\partial_t O_t\,,\,\varrho_B^\beta]\left(xI+\varrho_B^\beta\right)^{-1}[O_t\,,\,\varrho_B^\beta]\left(xI+\varrho_B^\beta\right)^{-1}\right] =$$
$$= -\sum_{n,m}\langle n|\partial_t O_t|m\rangle\langle m|O_t|n\rangle\frac{(r_n - r_m)^2}{(x+r_n)(x+r_m)}, \tag{B.24}$$

which yields

$$\int_0^\infty \mathrm{d}x\,\mathrm{Tr}\left[[\partial_t O_t\,,\,\varrho_B^\beta]\left(xI+\varrho_B^\beta\right)^{-1}[O_t\,,\,\varrho_B^\beta]\left(xI+\varrho_B^\beta\right)^{-1}\right] =$$
$$= \sum_{n,m}(r_m - r_n)\log\frac{r_n}{r_m}\,\langle n|\partial_t O_t|m\rangle\langle m|O_t|n\rangle \tag{B.25}$$
$$= \mathrm{Tr}\left[\varrho_B^\beta\left(\left[O_t\,,\,\log\varrho_B^\beta\right]\partial_t O_t + \left[\partial_t O_t\,,\,\log\varrho_B^\beta\right]O_t\right)\right]$$
$$= 2\beta\sum_k \omega_k\,\mathrm{Re}\left[h_k(t)\,\partial_t h_k^*(t)\right]$$
$$= 8\beta|\varrho_{10}|^2\sum_k |f_k|^2\frac{\omega_k}{(\omega_0 - \omega_k)}\sin[(\omega_0 - \omega_k)t].$$

Thus, noting equation (B.17), we obtain up to order λ^2

$$\partial_t \mathbb{S}_B^{(\lambda)}(t) = 8\lambda^2\beta\sum_k |f_k|^2\frac{\omega_k\sin[(\omega_0 - \omega_k)t]}{(\omega_0 - \omega_k)}\left[\left(\overline{n}(\omega_k,\beta)+1\right)\varrho_{00} - \overline{n}(\omega_k,\beta)\varrho_{11} - |\varrho_{10}|^2\right]. \tag{B.26}$$

Now, combining equations (B.16) and (B.26), the pseudo-temperature $T_B^{(\lambda)}(t)$ reads as

$$T_B^{(\lambda)}(t) = \frac{\mathrm{d}\mathbb{U}_B^{(\lambda)}(t)}{\mathrm{d}\mathbb{S}_B^{(\lambda)}(t)} =$$
$$= \frac{1}{\beta}\left\{1 + \frac{\sum_k |f_k|^2\frac{\sin[(\omega_0 - \omega_k)t]}{(\omega_0 - \omega_k)}|\varrho_{10}|^2[\alpha_B(\omega_k - \omega_0) + \omega_0]}{\sum_k |f_k|^2\frac{\omega_k\sin[(\omega_0 - \omega_k)t]}{(\omega_0 - \omega_k)}\left[\left(\overline{n}(\omega_k,\beta)+1\right)\varrho_{00} - \overline{n}(\omega_k,\beta)\varrho_{11} - |\varrho_{10}|^2\right]}\right\}. \tag{B.27}$$

If we go to the continuum-ω limit, take the $t\to\infty$ limit, and use the identity

$$\lim_{t\to\infty}\frac{\sin(xt)}{\pi x} = \delta(x), \tag{B.28}$$

we obtain

$$\lim_{t\to\infty}T_B^{(\lambda)}(t) = \frac{1}{\beta}\frac{\left[\left(\overline{n}(\omega_0,\beta)+1\right)\varrho_{00} - \overline{n}(\omega_0,\beta)\varrho_{11}\right]}{\left[\left(\overline{n}(\omega_0,\beta)+1\right)\varrho_{00} - \overline{n}(\omega_0,\beta)\varrho_{11} - |\varrho_{10}|^2\right]}$$
$$= \frac{1}{\beta}\left[1 + \frac{|\varrho_{10}|^2}{\overline{n}(\omega_0,\beta)(\varrho_{00} - \varrho_{11}) + \varrho_{00} - |\varrho_{10}|^2}\right]. \tag{B.29}$$

Let us now study system S. Since we are interested in thermalization we consider the solution to the Lindblad equation (3.40) in Chapter 3, which is given by

$$\varrho_S^{(\lambda)}(t) = \frac{1}{2} \begin{bmatrix} 1 + z(t) & x(t) - iy(t) \\ x(t) + iy(t) & 1 - z(t) \end{bmatrix}, \tag{B.30}$$

$$x(t) - iy(t) = \big(x(0) - iy(0)\big)\, \mathrm{e}^{-i\omega_0 t - \widetilde{\gamma}t/2} \tag{B.31}$$

$$x(t) + iy(t) = \big(x(0) + iy(0)\big)\, \mathrm{e}^{i\omega_0 t - \widetilde{\gamma}t/2} \tag{B.32}$$

$$z(t) = z(0)\mathrm{e}^{-\widetilde{\gamma}t} - \tanh(\beta\omega_0/2)\left(\mathrm{e}^{-\widetilde{\gamma}t} - 1\right) \tag{B.33}$$

where $\widetilde{\gamma} = \gamma \coth(\beta\omega_0/2)$ and $\big(x(0), y(0), z(0)\big)$ are the initial components of the Bloch vector. We can explicitly compute $\partial_t \mathbb{S}_S^{(\lambda)}(t)$ using the eigenvalues of $\varrho_S^{(\lambda)}(t)$, that read $(1/2)\big(1 \pm \sqrt{x^2(t) + y^2(t) + z^2(t)}\big)$, as

$$\partial_t \mathbb{S}_S^{(\lambda)}(t) = -\frac{1}{2} \log\left(\frac{1 + \sqrt{x^2(t) + y^2(t) + z^2(t)}}{1 - \sqrt{x^2(t) + y^2(t) + z^2(t)}}\right) \partial_t \left(\sqrt{x^2(t) + y^2(t) + z^2(t)}\right)$$

$$= -\frac{1}{2} \log\left(\frac{1 + \sqrt{x^2(t) + y^2(t) + z^2(t)}}{1 - \sqrt{x^2(t) + y^2(t) + z^2(t)}}\right) \frac{\frac{\widetilde{\gamma}}{2}\big(x^2(t) + y^2(t)\big) - \gamma z(t) - \widetilde{\gamma}z^2(t)}{\sqrt{x^2(t) + y^2(t) + z^2(t)}}. \tag{B.34}$$

The energy of this system up to order λ^2 is

$$\mathbb{U}_S^{(\lambda)}(t) = \mathrm{Tr}\left[\varrho_S^{(\lambda)}(t) H_S^{(\mathrm{eff})}(t)\right]$$

$$= \frac{\omega_0}{2}\mathrm{Tr}\left[\varrho_S^{(\lambda)}(t)\sigma_z\right] + \lambda(1 - \alpha_S)\left(\mathrm{Tr}\left[\varrho_S^{(\lambda)}(t)\sigma_+\right]\mathrm{Tr}\left[\varrho_B^{(\lambda)}(t)\mathrm{a}(f)\right]\right) +$$

$$+ \lambda(1 - \alpha_S)\left(\mathrm{Tr}\left[\varrho_S^{(\lambda)}(t)\sigma_-\right]\mathrm{Tr}\left[\varrho_B^{(\lambda)}(t)\mathrm{a}^\dagger(f)\right]\right) =$$

$$\simeq \frac{\omega_0}{2}z(t) + 2\lambda^2(1 - \alpha_S)(x^2(0) + y^2(0))\mathrm{e}^{-\widetilde{\gamma}t}\sum_k |f_k|^2 \frac{1 - \cos[(\omega_0 - \omega_k)t]}{(\omega_0 - \omega_k)}, \tag{B.35}$$

where we used equations (B.31) for $\varrho_S^{(\lambda)}(t)$ and $\varrho_B^{(\lambda)}(t) = \varrho_B^\beta + \lambda\varrho_B^{(1)}(t) + O(\lambda^2)$. Recalling equation (3.44) of the main text, the expression above can be differentiated as follows:

$$\partial_t \mathbb{U}_S^{(\lambda)}(t) = -\frac{\omega_0}{2}\gamma\mathrm{e}^{-\widetilde{\gamma}t}\Big(\coth(\beta\omega_0/2)z(0) + 1\Big) +$$

$$+ \frac{\gamma(1 - \alpha_S)}{\pi|f(\omega_0)|^2}(x^2(0) + y^2(0))\mathrm{e}^{-\widetilde{\gamma}t}\sum_k |f_k|^2 \sin[(\omega_0 - \omega_k)t] =$$

$$\overset{\omega-\mathrm{continuum}}{=} -\frac{\omega_0}{2}\gamma\mathrm{e}^{-\widetilde{\gamma}t}\Big(\coth(\beta\omega_0/2)z(0) + 1\Big). \tag{B.36}$$

As a result, the inverse pseudo-temperature becomes

$$
\frac{1}{T_S^{(\lambda)}(t)} = -\frac{1}{2} \log\left(\frac{1 + \sqrt{x^2(t) + y^2(t) + z^2(t)}}{1 - \sqrt{x^2(t) + y^2(t) + z^2(t)}}\right) \times
$$

$$
\times \frac{\frac{1}{2}\coth(\beta\omega_0/2)\big(x^2(0) + y^2(0)\big) + z(t)\Big(\coth(\beta\omega_0/2)z(0) + 1\Big)}{\sqrt{x^2(t) + y^2(t) + z^2(t)}\,(\omega_0/2)\Big(\coth(\beta\omega_0/2)z(0) + 1\Big)}, \qquad \text{(B.37)}
$$

which yields

$$
\lim_{t\to\infty} \frac{1}{T_S^{(\lambda)}(t)} = \beta\left[1 - \frac{\big(x^2(0) + y^2(0)\big)\coth(\beta\omega_0/2)}{2\big(z(0) + \tanh(\beta\omega_0/2)\big)}\right]. \qquad \text{(B.38)}
$$

Thus, similarly to the case of $\lim_{t\to\infty} T_B^{(\lambda)}(t)$, in this case too the pseudo-temperature $T_S^{(\lambda)}(t)$ behaves as expected if there is no initial coherence ($\varrho_{10} = 0$, or equivalently, $x(0) = y(0) = 0$).

Appendix C

Dephasing qubit

If we expand $\varrho_B^{(\lambda)}(t) =: \varrho_B^\beta + \lambda \varrho_B^{(1)}(t) + \lambda^2 \varrho_B^{(2)}(t) + O(\lambda^3)$, we obtain

$$\varrho_B^{(1)}(t) = \langle \sigma_z \rangle_S \Big[\sum_k \big(g_k(t)\mathrm{a}_k^\dagger - g_k^*(t)\mathrm{a}_k\big), \varrho_B^\beta \Big], \tag{C.1}$$

$$\varrho_B^{(2)}(t) = (1/2)\Big\{ \sum_{kk'} \big(g_k(t)\mathrm{a}_k^\dagger - g_k^*(t)\mathrm{a}_k\big)\big(g_{k'}(t)\mathrm{a}_{k'}^\dagger - g_{k'}^*(t)\mathrm{a}_{k'}\big), \varrho_B^\beta \Big\}$$

$$- \sum_k \big(g_k(t)\mathrm{a}_k^\dagger - g_k^*(t)\mathrm{a}_k\big)\varrho_B^\beta \sum_{k'} \big(g_{k'}(t)\mathrm{a}_{k'}^\dagger - g_{k'}^*(t)\mathrm{a}_{k'}\big). \tag{C.2}$$

Since we need to compute the entropy $\mathbb{S}_B^{(\lambda)}(t) = -\mathrm{Tr}[\varrho_B^{(\lambda)}(t) \log \varrho_B^{(\lambda)}(t)]$, we shall need to calculate $\log \varrho_B^{(\lambda)}(t)$ up to $O(\lambda^3)$. In order to do so, we use the following identity [167]:

$$\log(A_0 + \lambda A_1 + \lambda^2 A_2) = \log A_0 + \lambda \int_0^\infty \mathrm{d}x\,(A_0 + xI)^{-1}A_1(A_0 + xI)^{-1}$$

$$- \lambda^2 \int_0^\infty \mathrm{d}x \Big[(A_0 + xI)^{-1}A_1(A_0 + xI)^{-1}A_1(A_0 + xI)^{-1}$$

$$- (A_0 + xI)^{-1}A_2(A_0 + xI)^{-1} \Big] + O(\lambda^3)$$

$$=: L_0 + \lambda L_1 + \lambda^2 L_2 + O(\lambda^3). \tag{C.3}$$

Replacing the terms of $\varrho_B^{(\lambda)}(t)$ in equation (C.3) yields

$$L_0 = \log \varrho_B^\beta, \tag{C.4}$$

$$L_1(t) = \beta \langle \sigma_z \rangle_0 \sum_k \omega_k \big(g_k(t)\mathrm{a}_k^\dagger + g_k^*(t)\mathrm{a}_k\big). \tag{C.5}$$

Hence

$$\mathbb{S}_B^{(\lambda)}(t) = -\mathrm{Tr}\Big[\big(\varrho_B^\beta + \lambda \varrho_B^{(1)}(t) + \lambda^2 \varrho_B^{(2)}(t)\big)\big(L_0 + \lambda L_1(t) + \lambda^2 L_2(t)\big) \Big] + O(\lambda^3)$$

$$= -\mathrm{Tr}[\varrho_B^\beta L_0] - \lambda\Big(\mathrm{Tr}[\varrho_B^\beta L_1(t)] + \mathrm{Tr}[\varrho_B^{(1)}(t)L_0]\Big)$$

$$- \lambda^2\Big(\mathrm{Tr}[\varrho_B^\beta L_2(t)] + \mathrm{Tr}[\varrho_B^{(1)}(t)L_1(t)] + \mathrm{Tr}[\varrho_B^{(2)}(t)L_0]\Big) + O(\lambda^3). \tag{C.6}$$

From this relation we obtain up to order λ^2

$$\partial_t \mathbb{S}_B^{(\lambda)}(t) \simeq -\lambda\Big(\mathrm{Tr}[\varrho_B^\beta\,\partial_t L_1(t)] + \mathrm{Tr}[\partial_t\varrho_B^{(1)}(t)\,L_0]\Big) - \lambda^2\Big(\mathrm{Tr}[\varrho_B^\beta\,\partial_t L_2(t)]$$
$$+ \mathrm{Tr}[\partial_t\varrho_B^{(1)}(t)\,L_1(t)] + \mathrm{Tr}[\varrho_B^{(1)}(t)\,\partial_t L_1(t)] + \mathrm{Tr}[\partial_t\varrho_B^{(2)}(t)\,L_0]\Big). \qquad (C.7)$$

This expression has some irrelevant (i.e., vanishing) terms. This can be seen through the identity $\partial_t \mathbb{S}(t) = -\mathrm{Tr}[\partial_t\varrho \log \varrho]$, from whence

$$\partial_t \mathbb{S}_B^{(\lambda)}(t) \simeq -\lambda\mathrm{Tr}[\partial_t\varrho_B^{(1)}(t)\,L_0] - \lambda^2\Big(\mathrm{Tr}[\partial_t\varrho_B^{(1)}(t)\,L_1(t)] + \mathrm{Tr}[\partial_t\varrho_B^{(2)}(t)\,L_0]\Big). \qquad (C.8)$$

One can see from the identity $\mathrm{Tr}\big[[A, B]f(B)\big] = 0$ (for any A, B, and function f) that here

$$\mathrm{Tr}[\partial_t\varrho_B^{(1)}(t)\,L_0] \overset{(C.1),\ (C.4)}{=} 0. \qquad (C.9)$$

Thus equation (C.8) reduces to

$$\partial_t \mathbb{S}_B^{(\lambda)}(t) \simeq -\lambda^2\Big(\mathrm{Tr}[\partial_t\varrho_B^{(1)}(t)\,L_1(t)] + \mathrm{Tr}[\partial_t\varrho_B^{(2)}(t)\,L_0]\Big),$$
$$= 4\beta\lambda^2(1 - \langle\sigma_z\rangle_S^2)\,\partial_t\Delta(t). \qquad (C.10)$$

Bibliography

[1] H. B. Callen, *Thermodynamics and an introduction to thermostatistics; 2nd ed.* (Wiley, New York, NY, 1985).

[2] E. H. Lieb and J. Yngvason, in *Visions in Mathematics: GAFA 2000 Special Volume, Part I*, edited by N. Alon, J. Bourgain, A. Connes, M. Gromov, and V. Milman (Birkhäuser Basel, Basel, 2010), chap. *The Mathematics of the Second Law of Thermodynamics*, pp. 334–358.

[3] E. H. Lieb and J. Yngvason, "The physics and mathematics of the second law of thermodynamics," *Physics Reports* **310**, 1 (1999).

[4] S. R. De Groot and P. Mazur, *Non-equilibrium thermodynamics* (Dover, New York, NY, 1984).

[5] L. Onsager, "Reciprocal relations in irreversible processes I," *Physical Review* **37**, 405 (1931).

[6] L. Onsager, "Reciprocal relations in irreversible processes II," *Physical Review* **38**, 2265 (1931).

[7] D. Jou, J. Casas-Vázquez, and G. Lebon, *Extended Irreversible Thermodynamics* (Springer Netherlands, Dordrecht, 2010).

[8] C. Cattaneo, "Sulla conduzione del calore," *Atti Sem. Mat. Fis. Univ. Modena* **3**, 83 (1948).

[9] M. Grmela and H. C. Öttinger, "Dynamics and thermodynamics of complex fluids I. Development of a general formalism," *Physical Review E* **56**, 6620 (1997).

[10] H. C. Öttinger and M. Grmela, "Dynamics and thermodynamics of complex fluids II. Illustrations of a general formalism," *Physical Review E* **56**, 6633 (1997).

[11] H. C. Öttinger, *Beyond Equilibrium Thermodynamics* (Wiley, Hoboken, 2005).

[12] M. Grmela, G. Lebon, and C. Dubois, "Multiscale thermodynamics and mechanics of heat," *Physical Review E* **83**, 061134 (2011).

[13] M. Grmela, V. Klika, and M. Pavelka, "Reductions and extensions in mesoscopic dynamics," *Physical Review E* **92**, 032111 (2015).

[14] M. Grmela, "Geometry of multiscale nonequilibrium thermodynamics," *Entropy* **17**, 5938 (2015).

[15] T. L. Hill, *Thermodynamics of small systems: two volumes bound as one* (Dover, New York, NY, 1994).

[16] T. Gilányi, "Small Systems Thermodynamics of Polymer - Surfactant Complex Formation," *The Journal of Physical Chemistry B* **103**, 2085 (1999).

[17] D. G. Hall, "Thermodynamics of ionic surfactant micelle–comments," *Journal of Colloid and Interface Science* **115**, 110 (1987).

[18] C. Jarzynski, "Nonequilibrium equality for free energy differences," *Physical Review Letters* **78**, 2690 (1997).

[19] G. E. Crooks, "Entropy production fluctuation theorem and the nonequilibrium work relation for free energy differences," *Physical Review E* **60**, 2721 (1999).

[20] U. Seifert, "Stochastic thermodynamics, fluctuation theorems and molecular machines," *Reports on Progress in Physics* **75**, 126001 (2012).

[21] D. Jou, J. Casas-Vázquez, and G. Lebon, *Understanding Non-equilibrium Thermodynamics: Foundations, Applications, Frontiers* (Springer, Dordrecht, 2007).

[22] W. Muschik, "Why so many "schools" of thermodynamics?," *Atti della Accademia Peloritana dei Pericolanti - Classe di Scienze Fisiche, Matematiche e Naturali* **86** (2008).

[23] J. Gemmer, M. Michel, and G. Mahler, *Quantum Thermodynamics: Emergence of Thermodynamic Behavior Within Composite Quantum Systems* (Springer, Berlin, Heidelberg, 2009).

[24] S. Vinjanampathy and J. Anders, "Quantum thermodynamics," *Contemporary Physics* **57**, 545 (2016).

[25] J. Millen and A. Xuereb, "Perspective on quantum thermodynamics," *New Journal of Physics* **18**, 011002 (2016).

[26] J. Goold, M. Huber, A. Riera, L. del Rio, and P. Skrzypczyk, "The role of quantum information in thermodynamics – a topical review," *Journal of Physics A: Mathematical and Theoretical* **49**, 143001 (2016).

[27] I. Bloch, J. Dalibard, and W. Zwerger, "Many-body physics with ultracold gases," *Reviews of Modern Physics* **80**, 885 (2008).

[28] D. Leibfried, R. Blatt, C. Monroe, and D. Wineland, "Quantum dynamics of single trapped ions," *Reviews of Modern Physics* **75**, 281 (2003).

[29] M. Aspelmeyer, T. J. Kippenberg, and F. Marquardt, "Cavity optomechanics," *Reviews of Modern Physics* **86**, 1391 (2014).

[30] S. Goldstein, J. L. Lebowitz, R. Tumulka, and N. Zanghì, "Canonical typicality," *Physical Review Letters* **96**, 050403 (2006).

[31] S. Goldstein, J. L. Lebowitz, C. Mastrodonato, R. Tumulka, and N. Zanghì, "Normal typicality and von neumann's quantum ergodic theorem," *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences* **466**, 3203 (2010).

[32] N. Linden, S. Popescu, A. J. Short, and A. Winter, "Quantum mechanical evolution towards thermal equilibrium," *Physical Review E* **79**, 061103 (2009).

[33] V. I. Yukalov, "Equilibration and thermalization in finite quantum systems," *Laser Physics Letters* **8**, 485 (2011).

[34] P. Reimann and M. Kastner, "Equilibration of isolated macroscopic quantum systems," *New Journal of Physics* **14**, 043020 (2012).

[35] C. Gogolin and J. Eisert, "Equilibration, thermalisation, and the emergence of statistical mechanics in closed quantum systems," *Reports on Progress in Physics* **79**, 056001 (2016).

[36] J. Eisert, M. Friesdorf, and C. Gogolin, "Quantum many-body systems out of equilibrium," *Nature Physics* **11**, 124 (2015).

[37] S. Goldstein, D. A. Huse, J. L. Lebowitz, and R. Tumulka, "Macroscopic and microscopic thermal equilibrium," *Annalen der Physik* **529**, 1600301 (2017).

[38] H. Spohn and J. L. Lebowitz, "Irreversible thermodynamics for quantum systems weakly coupled to thermal reservoirs," *Advances in Chemical Physics* **38**, 109 (1978).

[39] R. Alicki, "The quantum open system as a model of the heat engine," *Journal of Physics A: Mathematical and General* **12**, L103 (1979).

[40] V. Gorini, A. Kossakowski, and E. C. G. Sudarshan, "Completely positive dynamical semigroups of N-level systems," *Journal of Mathematical Physics* **17**, 821 (1976).

[41] G. Lindblad, "On the generators of quantum dynamical semigroups," *Communications in Mathematical Physics* **48**, 119 (1976).

[42] R. Alicki and K. Lendi, *Quantum dynamical semigroups and applications* (Springer, Berlin, 2007).

[43] A. Rivas, S. F. Huelga, and M. B. Plenio, "Quantum non-Markovianity: characterization, quantification and detection," *Reports on Progress in Physics* **77**, 094001 (2014).

[44] H.-P. Breuer, E.-M. Laine, J. Piilo, and B. Vacchini, "Colloquium: Non-markovian dynamics in open quantum systems," *Reviews of Modern Physics* **88**, 021002 (2016).

[45] I. de Vega and D. Alonso, "Dynamics of non-Markovian open quantum systems," *Reviews of Modern Physics* **89**, 015001 (2017).

[46] G. P. Beretta, E. P. Gyftopoulos, J. L. Park, and G. N. Hatsopoulos, "Quantum thermodynamics. a new equation of motion for a single constituent of matter," *Il Nuovo Cimento B* **82**, 169 (1984).

[47] G. P. Beretta, E. P. Gyftopoulos, and J. L. Park, "Quantum thermodynamics. a new equation of motion for a general quantum system," *Il Nuovo Cimento B* **87**, 77 (1985).

[48] C. E. Smith and M. R. von Spakovsky, "Comparison of the non-equilibrium predictions of intrinsic quantum thermodynamics at the atomistic level with experimental evidence," *Journal of Physics: Conference Series* **380**, 012015 (2012).

[49] M. R. von Spakovsky and J. Gemmer, "Some trends in quantum thermodynamics," *Entropy* **16**, 3434 (2014).

[50] S. Cano-Andrade, G. P. Beretta, and M. R. von Spakovsky, "Steepest-entropy-ascent quantum thermodynamic modeling of decoherence in two different microscopic composite systems," *Physical Review A* **91**, 013848 (2015).

[51] F. G. S. L. Brandão, M. Horodecki, J. Oppenheim, J. M. Renes, and R. W. Spekkens, "Resource theory of quantum states out of thermal equilibrium," *Physical Review Letters* **111**, 250404 (2013).

[52] F. Brandão, M. Horodecki, N. Ng, J. Oppenheim, and S. Wehner, "The second laws of quantum thermodynamics," *Proceedings of the National Academy of Sciences* **112**, 3275 (2015).

[53] C. Sparaciari, J. Oppenheim, and T. Fritz, "A Resource Theory for Work and Heat," ArXiv e-prints (2016), `1607.01302`.

[54] M. Lostaglio, D. Jennings, and T. Rudolph, "Thermodynamic resource theories, noncommutativity and maximum entropy principles," *New Journal of Physics* **19**, 043008 (2017).

[55] M. Lostaglio, Ph.D. thesis, Imperial College London (2016), https://spiral.imperial.ac.uk/handle/10044/1/43760.

[56] P. Bocchieri and A. Loinger, "Quantum recurrence theorem," *Physical Review* **107**, 337 (1957).

[57] M. Campisi, P. Hänggi, and P. Talkner, "Colloquium: Quantum fluctuation relations: Foundations and applications," *Reviews of Modern Physics* **83**, 771 (2011).

[58] F. Benatti and R. Floreanini, "Open quantum dynamics: Complete positivity and entanglement," *International Journal of Modern Physics B* **19**, 3063 (2005).

[59] I. Siemon, A. S. Holevo, and R. F. Werner, "Unbounded generators of dynamical semi-groups," ArXiv e-prints (2017), `1707.02266`.

[60] S. Nakajima, "On Quantum Theory of Transport Phenomena -Steady Diffusion-," *Progress of Theoretical Physics* **20**, 948 (1958).

[61] R. Zwanzig, "Ensemble method in the theory of irreversibility," *The Journal of Chemical Physics* **33**, 1338 (1960).

[62] E. Fick, G. Sauermann, and W. D. Brewer, *The quantum statistics of dynamic processes* (Springer-Verlag, Berlin, 1990).

[63] R. Dümcke and H. Spohn, "The proper form of the generator in the weak coupling limit," *Zeitschrift für Physik B Condensed Matter* **34**, 419 (1979).

[64] E. B. Davies, "Markovian master equations," *Communications in Mathematical Physics* **39**, 91 (1974).

[65] E. B. Davies, "Markovian master equations III," *Annales de l'I.H.P. Probabilités et statistiques* **11**, 265 (1975).

[66] E. B. Davies, "Markovian master equations. II," *Mathematische Annalen* **219**, 147 (1976).

[67] R. Kosloff, "Quantum Thermodynamics: A Dynamical Viewpoint," *Entropy* **15**, 2100 (2013).

[68] E. B. Davies and H. Spohn, "Open quantum systems with time-dependent hamiltonians and their linear response," *Journal of Statistical Physics* **19**, 511 (1978).

[69] R. Alicki, D. Gelbwaser-Klimovsky, and G. Kurizki, "Periodically driven quantum open systems: Tutorial," ArXiv e-prints (2012), `1205.4552`.

[70] M. A. Nielsen and I. L. Chuang, *Quantum Computation and Quantum Information: 10th Anniversary Edition* (Cambridge University Press, New York, NY, USA, 2011).

[71] M. T. Mitchison and M. B. Plenio, "Non-additive dissipation in open quantum networks out of equilibrium," ArXiv e-prints (2017), `1708.05574`.

[72] S. Alipour, F. Benatti, F. Bakhshinezhad, M. Afsary, S. Marcantoni, and A. T. Rezakhani, "Correlations in quantum thermodynamics: Heat, work, and entropy production," *Scientific Reports* **6**, 35568 (2016).

[73] G. Argentieri, F. Benatti, R. Floreanini, and M. Pezzutto, "Violations of the second law of thermodynamics by a non-completely positive dynamics," *EPL (Europhysics Letters)* **107**, 50007 (2014).

[74] G. Argentieri, F. Benatti, R. Floreanini, and M. Pezzutto, "Complete positivity and thermodynamics in a driven open quantum system," *Journal of Statistical Physics* **159**, 1127 (2015).

[75] F. Pellegrini, C. Negri, F. Pistolesi, N. Manini, G. E. Santoro, and E. Tosatti, "Crossover from adiabatic to antiadiabatic quantum pumping with dissipation," *Physical Review Letters* **107**, 060401 (2011).

[76] A. Levy and R. Kosloff, "The local approach to quantum transport may violate the second law of thermodynamics," *EPL (Europhysics Letters)* **107**, 20004 (2014).

[77] A. S. Trushechkin and I. V. Volovich, "Perturbative treatment of inter-site couplings in the local description of open quantum networks," *EPL (Europhysics Letters)* **113**, 30005 (2016).

[78] P. P. Hofer, M. Perarnau-Llobet, L. D. M. Miranda, G. Haack, R. Silva, J. Bohr Brask, and N. Brunner, "Markovian master equations for quantum thermal machines: local vs global approach," ArXiv e-prints (2017), `1707.09211`.

[79] J. Onam González, L. A. Correa, G. Nocerino, J. P. Palao, D. Alonso, and G. Adesso, "Testing the validity of the local and global GKLS master equations on an exactly solvable model," ArXiv e-prints (2017), `1707.09228`.

[80] P. Rebentrost and A. Aspuru-Guzik, "Communication: Excitonphonon information flow in the energy transfer process of photosynthetic complexes," *The Journal of Chemical Physics* **134**, 101103 (2011).

[81] F. Fassioli, R. Dinshaw, P. C. Arpin, and G. D. Scholes, "Photosynthetic light harvesting: excitons and coherence," *Journal of The Royal Society Interface* **11** (2013).

[82] S. Gröblacher, A. Trubarov, N. Prigge, G. D. Cole, M. Aspelmeyer, and J. Eisert, "Observation of non-Markovian micromechanical brownian motion," *Nature communications* **6** (2015).

[83] M. Malekakhlagh, A. Petrescu, and H. E. Türeci, "Non-Markovian dynamics of a superconducting qubit in an open multimode resonator," *Physical Review A* **94**, 063848 (2016).

[84] H.-P. Breuer, E.-M. Laine, and J. Piilo, "Measure for the degree of Non-Markovian behavior of quantum processes in open systems," *Physical Review Letters* **103**, 210401 (2009).

[85] M. M. Wolf, J. Eisert, T. S. Cubitt, and J. I. Cirac, "Assessing Non-Markovian quantum dynamics," *Physical Review Letters* **101**, 150402 (2008).

[86] M. M. Wolf and J. I. Cirac, "Dividing quantum channels," *Communications in Mathematical Physics* **279**, 147 (2008).

[87] A. Rivas, S. F. Huelga, and M. B. Plenio, "Entanglement and non-markovianity of quantum evolutions," *Physical Review Letters* **105**, 050403 (2010).

[88] S. Lorenzo, F. Plastina, and M. Paternostro, "Geometrical characterization of non-Markovianity," *Physical Review A* **88**, 020102 (2013).

[89] S. Luo, S. Fu, and H. Song, "Quantifying non-markovianity via correlations," *Physical Review A* **86**, 044101 (2012).

[90] B. Bylicka, D. Chruściński, and S. Maniscalco, "Non-Markovianity and reservoir memory of quantum channels: a quantum information theory perspective," *Scientific Reports* **4**, 5720 (2014).

[91] P. Haikka, J. D. Cresser, and S. Maniscalco, "Comparing different non-markovianity measures in a driven qubit system," *Physical Review A* **83**, 012112 (2011).

[92] D. Chruściński, A. Kossakowski, and A. Rivas, "Measures of non-markovianity: Divisibility versus backflow of information," *Physical Review A* **83**, 052128 (2011).

[93] M. B. Ruskai, "Beyond strong subadditivity? Improved bounds on the contraction of generalized relative entropy," *Reviews in Mathematical Physics* **06**, 1147 (1994).

[94] F. A. Wudarski and F. Petruccione, "Exchange of information between system and environment: Facts and myths," *EPL (Europhysics Letters)* **113** (2016).

[95] S. Wißmann, H.-P. Breuer, and B. Vacchini, "Generalized trace-distance measure connecting quantum and classical non-Markovianity," *Physical Review A* **92**, 042108 (2015).

[96] D. Chruściński and A. Kossakowski, "Non-Markovian Quantum Dynamics: Local versus Nonlocal," *Physical Review Letters* **104**, 070406 (2010).

[97] D. Chruściński and S. Maniscalco, "Degree of non-Markovianity of quantum evolution," *Physical Review Letters* **112**, 120404 (2014).

[98] D. Chruściński and Á. Rivas, "Universal equivalence between divisibility and information flow notions of quantum Markovianity," ArXiv e-prints (2017), `1710.06771`.

[99] F. Benatti, D. Chruściński, and S. Filippov, "Tensor power of dynamical maps and positive versus completely positive divisibility," *Physical Review A* **95**, 012112 (2017).

[100] S. Marcantoni, S. Alipour, F. Benatti, R. Floreanini, and A. T. Rezakhani, "Entropy production and non-markovian dynamical maps," *Scientific Reports* **7**, 12447 (2017).

[101] D. Chruściński, A. Kossakowski, and S. Pascazio, "Long-time memory in non-Markovian evolutions," *Physical Review A* **81**, 032101 (2010).

[102] A. Müller-Hermes and D. Reeb, "Monotonicity of the quantum relative entropy under positive maps," *Annales Henri Poincaré* **18**, 1777 (2017).

[103] M. Esposito, K. Lindenberg, and C. Van den Broeck, "Entropy production as correlation between system and reservoir," *New Journal of Physics* **12**, 013013 (2010).

[104] V. Mukherjee, V. Giovannetti, R. Fazio, S. F. Huelga, T. Calarco, and S. Montangero, "Efficiency of quantum controlled non-Markovian thermalization," *New Journal of Physics* **17**, 063031 (2015).

[105] D. Chruściński and A. Kossakowski, "Markovianity criteria for quantum evolution," *Journal of Physics B: Atomic, Molecular and Optical Physics* **45**, 154002 (2012).

[106] J. Lankinen, H. Lyyra, B. Sokolov, J. Teittinen, B. Ziaei, and S. Maniscalco, "Complete positivity, finite-temperature effects, and additivity of noise for time-local qubit dynamics," *Physical Review A* **93**, 052103 (2016).

[107] A. Peres, *Quantum theory : concepts and methods* (Kluwer Academic Publishers, Dordrecht, 1995).

[108] T. Sagawa, in *Lectures on Quantum Computing, Thermodynamics and Statistical Physics*, edited by M. Nakahara and S. Tanaka (World Scientific, Singapore, 2012), chap. *Second law-like Inequalities with quantum relative entropy: an introduction*, pp. 125–190.

[109] H. Hossein-Nejad, E. J. OReilly, and A. Olaya-Castro, "Work, heat and entropy production in bipartite quantum systems," *New Journal of Physics* **17**, 075014 (2015).

[110] R. Balian, *From Microphysics to Macrophysics, vol.1* (Springer-Verlag, Berlin, Heidelberg, 2007).

[111] L. D. Landau and E. M. Lifshitz, *Statistical Physics: V. 5: Course of Theoretical Physics* (Pergamon press, Oxford, 1969).

[112] S. J. Blundell and K. M. Blundell, *Concepts in Thermal Physics* (Oxford University Press, Oxford, 2006).

[113] M. M. Wolf, F. Verstraete, M. B. Hastings, and J. I. Cirac, "Area laws in quantum systems: Mutual information and correlations," *Physical Review Letters* **100**, 070502 (2008).

[114] M. J. W. Hall, "Correlation distance and bounds for mutual information," *Entropy* **15**, 3698 (2013).

[115] D. Reeb and M. M. Wolf, "An improved landauer principle with finite-size corrections," *New Journal of Physics* **16**, 103011 (2014).

[116] J. Casas-Vázquez and D. Jou, "Temperature in non-equilibrium states: a review of open problems and current proposals," *Reports on Progress in Physics* **66**, 1937 (2003).

[117] K. Martens, E. Bertin, and M. Droz, "Dependence of the fluctuation-dissipation temperature on the choice of observable," *Physical Review Letters* **103**, 260602 (2009).

[118] H. P. Breuer and F. Petruccione, *The theory of open quantum systems* (Oxford University Press, Oxford, 2002).

[119] H. Carmichael, *An open systems approach to quantum optics* (Springer, Berlin, 1993).

[120] G. M. Palma, K.-A. Suominen, and A. K. Ekert, "Quantum computers and dissipation," *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences* **452**, 567 (1996).

[121] P. Haikka, T. Johnson, and S. Maniscalco, "Non-markovianity of local dephasing channels and time-invariant discord," *Physical Review A* **87** (2013).

[122] H. Weimer, M. J. Henrich, F. Rempp, H. Schröder, and G. Mahler, "Local effective dynamics of quantum systems: A generalized approach to work and heat," *EPL (Europhysics Letters)* **83**, 30008 (2008).

[123] N. Killoran, S. F. Huelga, and M. B. Plenio, "Enhancing light-harvesting power with coherent vibrational interactions: A quantum heat engine picture," *The Journal of Chemical Physics* **143**, 155102 (2015).

[124] J. Kurchan, "A Quantum Fluctuation Theorem," ArXiv eprints (2000), `cond-mat/0007360`.

[125] H. Tasaki, "Jarzynski Relations for Quantum Systems and Some Applications," ArXiv eprints (2000), `cond-mat/0009244`.

[126] M. Esposito, U. Harbola, and S. Mukamel, "Nonequilibrium fluctuations, fluctuation theorems, and counting statistics in quantum systems," *Reviews of Modern Physics* **81**, 1665 (2009).

[127] S. An, J.-N. Zhang, M. Um, D. Lv, Y. Lu, J. Zhang, Z.-Q. Yin, H. T. Quan, and K. Kim, "Experimental test of the quantum jarzynski equality with a trapped-ion system," *Nature Physics* (2014).

[128] T. B. Batalhão, A. M. Souza, L. Mazzola, R. Auccaise, R. S. Sarthour, I. S. Oliveira, J. Goold, G. De Chiara, M. Paternostro, and R. M. Serra, "Experimental reconstruction of work distribution and study of fluctuation relations in a closed quantum system," *Physical Review Letters* **113**, 140601 (2014).

[129] J. Goold, M. Paternostro, and K. Modi, "Nonequilibrium quantum landauer principle," *Physical Review Letters* **114**, 060602 (2015).

[130] M. Campisi, P. Talkner, and P. Hänggi, "Fluctuation theorem for arbitrary open quantum systems," *Physical Review Letters* **102**, 210401 (2009).

[131] M. Silaev, T. T. Heikkilä, and P. Virtanen, "Lindblad-equation approach for the full counting statistics of work and heat in driven quantum systems," *Physical Review E* **90**, 022103 (2014).

[132] P. Talkner, E. Lutz, and P. Hänggi, "Fluctuation theorems: Work is not an observable," *Physical Review E* **75**, 050102 (2007).

[133] S. Deffner and E. Lutz, "Nonequilibrium work distribution of a quantum harmonic oscillator," *Physical Review E* **77**, 021128 (2008).

[134] S. Deffner, O. Abah, and E. Lutz, "Quantum work statistics of linear and nonlinear parametric oscillators," *Chemical Physics* **375**, 200 (2010).

[135] A. Leonard and S. Deffner, "Quantum work distribution for a driven diatomic molecule," *Chemical Physics* **446**, 18 (2015).

[136] P. Talkner, P. S. Burada, and P. Hänggi, "Statistics of work performed on a forced quantum oscillator," *Physical Review E* **78**, 011115 (2008).

[137] M. J. Donald, "Free energy and the relative entropy," *Journal of Statistical Physics* **49**, 81 (1987).

[138] G. Manzano, J. M. Horowitz, and J. M. R. Parrondo, "Quantum fluctuation theorems for arbitrary environments: adiabatic and non-adiabatic entropy production," ArXiv e-prints (2017), `1710.00054`.

[139] B.-B. Wei and M. B. Plenio, "Relations between dissipated work in non-equilibrium process and the family of rényi divergences," *New Journal of Physics* **19**, 023002 (2017).

[140] M. Mosonyi and F. Hiai, "On the quantum rényi relative entropies and related capacity formulas," *IEEE Transactions on Information Theory* **57**, 2474 (2011).

[141] G. Huber, F. Schmidt-Kaler, S. Deffner, and E. Lutz, "Employing trapped cold ions to verify the quantum jarzynski equality," *Physical Review Letters* **101**, 070403 (2008).

[142] L. Mazzola, G. De Chiara, and M. Paternostro, "Measuring the characteristic function of the work distribution," *Physical Review Letters* **110**, 230602 (2013).

[143] L. Mazzola, G. De Chiara, and M. Paternostro, "Detecting the work statistics through Ramsey-like interferometry," *International Journal of Quantum Information* **12**, 1461007 (2014).

[144] G. De Chiara, A. J. Roncaglia, and J. P. Paz, "Measuring work and heat in ultracold quantum gases," *New Journal of Physics* **17**, 035004 (2015).

[145] S. Gherardini, M. M. Müller, A. Trombettoni, S. Ruffo, and F. Caruso, "Reconstruction of the stochastic quantum entropy production to probe irreversibility and correlations," ArXiv e-prints (2017), `1706.02193`.

[146] C. Vericat, M. E. Vela, G. Corthey, E. Pensa, E. Cortes, M. H. Fonticelli, F. Ibanez, G. E. Benitez, P. Carro, and R. C. Salvarezza, "Self-assembled monolayers of thiolates on metals: a review article on sulfur-metal chemistry and surface structures," *RSC Advances* **4**, 27730 (2014).

[147] M. A. Rampi, O. J. A. Schueller, and G. M. Whitesides, "Alkanethiol self-assembled monolayers as the dielectric of capacitors with nanoscale thickness," *Applied Physics Letters* **72**, 1781 (1998).

[148] O. Zenasni, M. D. Marquez, A. C. Jamison, H. J. Lee, A. Czader, and T. R. Lee, "Inverted surface dipoles in fluorinated Self-Assembled monolayers," *Chemistry of Materials* **27**, 7433 (2015).

[149] D. Norman, "X-ray absorption spectroscopy (exafs and xanes) at surfaces," *Journal of Physics C: Solid State Physics* **19**, 3273 (1986).

[150] M. Campisi, P. Talkner, and P. Hänggi, "Thermodynamics and fluctuation theorems for a strongly coupled open quantum system: an exactly solvable case," *Journal of Physics A: Mathematical and Theoretical* **42**, 392002 (2009).

[151] A. E. Rastegin, "Non-equilibrium equalities with unital quantum channels," *Journal of Statistical Mechanics: Theory and Experiment* **2013**, P06016 (2013).

[152] A. E. Rastegin and K. Życzkowski, "Jarzynski equality for quantum stochastic maps," *Physical Review E* **89**, 012127 (2014).

[153] T. Albash, D. A. Lidar, M. Marvian, and P. Zanardi, "Fluctuation theorems for quantum processes," *Physical Review E* **88**, 032146 (2013).

[154] V. Vedral, "An information - theoretic equality implying the jarzynski relation," *Journal of Physics A: Mathematical and Theoretical* **45**, 272001 (2012).

[155] E. Aurell, J. Zakrzewski, and K. Życzkowski, "Time reversals of irreversible quantum maps," *Journal of Physics A: Mathematical and Theoretical* **48**, 38FT01 (2015).

[156] G. Manzano, J. M. Horowitz, and J. M. R. Parrondo, "Nonequilibrium potential and fluctuation theorems for quantum maps," *Physical Review E* **92**, 032129 (2015).

[157] J. Goold and K. Modi, "Energetic fluctuations in an open quantum process," ArXiv e-prints (2014), `1407.4618`.

[158] G. W. Ford, J. T. Lewis, and R. F. O'Connell, "Quantum oscillator in a blackbody radiation field," *Physical Review Letters* **55**, 2273 (1985).

[159] P. Hänggi, P. Talkner, and M. Borkovec, "Reaction-rate theory: fifty years after Kramers," *Reviews of Modern Physics* **62**, 251 (1990).

[160] B. Roux and T. Simonson, "Implicit solvent models," *Biophysical Chemistry* **78**, 1 (1999).

[161] T. Benoist, M. Fraas, V. Jaksic, and C.-A. Pillet, "Full statistics of erasure processes: Isothermal adiabatic theory and a statistical landauer principle," *Revue Roumaine de Mathématiques pures et appliquées* **62**, 259 (2017).

[162] S. Gasparinetti, P. Solinas, A. Braggio, and M. Sassetti, "Heat-exchange statistics in driven open quantum systems," *New Journal of Physics* **16**, 115001 (2014).

[163] S. Suomela, P. Solinas, J. P. Pekola, J. Ankerhold, and T. Ala-Nissila, "Moments of work in the two-point measurement protocol for a driven open quantum system," *Physical Review B* **90**, 094304 (2014).

[164] S. Pigeon, L. Fusco, A. Xuereb, G. De Chiara, and M. Paternostro, "Thermodynamics of trajectories and local fluctuation theorems for harmonic quantum networks," *New Journal of Physics* **18**, 013009 (2016).

[165] M. Brunelli, A. Xuereb, A. Ferraro, G. De Chiara, N. Kiesel, and M. Paternostro, "Out-of-equilibrium thermodynamics of quantum optomechanical systems," *New Journal of Physics* **17**, 035016 (2015).

[166] F. Topsøe, in *Inequality Theory and Applications*, edited by Y. Cho, J. Kim, and S. Dragomir (Nova Science Publishers, Incorporated, 2007), vol. 4, chap. *Some Bounds for the Logarithmic Function*, pp. 137–151.

[167] F. Hiai and D. Petz, *Introduction to matrix analysis and applications* (Springer Science & Business Media, 2014).