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Quantum fluctuations and correlations in equilibrium and nonequilibrium thermodynamics

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Introduction

This thesis presents and discusses the results I obtained during the three years of my doctoral studies, which I spent between the Department of Physics at the University of Palermo and the Institute of Physics at the University of Freiburg. The main area in which these results are inscribed is the field of research which goes under the name Quantum Thermodynamics. Although the name is self-explanatory, the conceptual motivations and main ideas behind it are so broad - and often not yet fully developed - that almost any quantum phenomenon may in principle be thought as belonging to a quantum thermodynamic framework. Quantum theory is usually regarded as describing strikingly counter-intuitive effects of the microscopic world while, in contrast, thermodynamics is a structure strongly built on everyday life experience. One may then reasonably wonder whether Quantum Thermodynamics is a counter-intuitive microscopic theory of standard thermodynamics or an everyday-life-based theory of quantum effects. The answer is that it is neither the former nor the latter and, as it is usually the case, is built on a subtle interplay between these two extrema. Throughout this thesis I will explore and exploit this interplay to discuss the state of the art of the research on some selected topics of timely interest and to introduce in full details my contribution to them.

Why a quantum view on thermodynamics?

Thermodynamics and quantum theory are both theories of incomplete information. The standard classical thermodynamic description of collective phenomena - such as phase transitions, thermodynamic transformations, macroscopic state functions, etc... - originates from a capitulation: when the physics of a system becomes so complex that, even in principle, its rigorous investigation is beyond reach even for the most skilled researcher, one has to surrender to the impossibility of a detailed microscopic description and introduce the celebrated concept of *subjective lack of knowledge*, which is the core of macroscopic thermodynamics [1, 2]. It postulates the existence of well defined physical properties of each microscopic constituent of a macroscopic sample - properties whose knowledge might be accessible to a perfect observer whose capability of acquiring information is unbounded - but assumes our incapability to uncover them. Thermodynamics is the theory originating from such an incapability, or more precisely is the theory which exploits such an incapability. Despite the limited amount of information available about the microscopic state of a system, indeed, the amount of physical knowledge about a complex many-body sample is astonishingly huge. In this respect thermodynamics represents the archetypical example of the progress of physics, from few everyday life experience observations to general theoretical principles whose validity is supported by uncountable experiments. The lack of knowledge about the microscopic details plays a fundamental role in this process, as it forces the focus on general properties shared by very many model systems, having even strongly different microscopic features but belonging to the same class of macroscopic behaviour. In this spirit concepts, principles and ideas have been developed such as the three laws of thermodynamics, the very concept of ideal gases or the notion of thermal machines, to name but a few.

The existence of a stochastic derivation of the same set of laws does not weaken the strong connection between incomplete knowledge and generality of predictions. On the contrary, it strengthens it. Recurring to a stochastic description of dynamic microscopic processes reflect mathematically, in the use of a probabilistic formulation, the same concept of subjective lack of knowledge and directly leads to the cornerstone of stochastic thermodynamics: the theory of ensembles. The idea of describing what one does *not* know about a system through what one knows about a collection of identical noninteracting systems supplies researchers with an unexpectedly powerful tool to introduce fundamental concepts like temperature (a macroscopic collective property) linking them to microscopic quantities such as the energy characterising the ensemble itself.

On the other hand, nearly one century after the complete formulation of classical thermodynamics, another theory of ensembles has been developed and its physical predictions have been verified over a broad set of different physical scenarios: the quantum theory. In its first formulation, significantly known as quantum mechanics in analogy with the classical mechanics framework, it dealt with the structure and the evolution of isolated systems described by *pure states* - somehow the quantum analogue of a microstate of a classical system, in which the maximum information about the system is encoded. Shortly after, anyway, in order to account for many different effects (some of which are of classical origin, while others are purely quantum features) mostly connected to the unavoidable interaction of any system with their surroundings (generally referred to as *environment*), the need arose for a quantum description of imperfect information about the state of a system. Only partially surprisingly, the same classical idea was introduced to account for the lack of knowledge in quantum realm: the ensemble picture. As much as in the classical case, such a tool turned out to be of fundamental importance to introduce and characterise physical properties for non-classical systems. Temperature, entropy, classical and non-classical correlations, heat, work and so on, were defined starting from the structure and the dynamics of the ensemble state of a quantum system, which goes under the name *density matrix*.

A theoretical and experimental framework accounting for open quantum systems [3] has been developed since then, whose main purpose is to describe static and dynamic effects of various kind of interactions of a quantum system with a structured environment - which in turn may be either classical or quantum. A key concept of this framework is to describe ensemble dynamics by the so-called quantum Master Equation (q-ME or simply ME), which generalises the unitary time evolution of a closed system introducing dissipative effects and decoherence due to the presence of a reservoir. In what follows, and above all in the next chapters, I will rigorously formulate this concept both mathematically and physically. Now I just want to follow the formal analogy between classical stochastic thermodynamics and the theory of open quantum systems, motivated by the fact that both of them fundamentally rely on the concept of ensemble states [4]. As will be clearer throughout this thesis, the structure itself of the q-ME incorporates energy and/or information exchanges between the system of interest and its environment. It therefore describes, often implicitly, the processes which in classical thermodynamics are governed by the first and by the second law of thermodynamics. Moreover, a deeper conceptual question arises proceeding through this analogy: *are classical and quantum lack of information structurally and physically equivalent?* Or, in other words, where does the quantum lack of knowledge originates from? The answer to such a question should take into account two different yet complementary effects: first of all, due to the very structure of quantum theory on complex Hilbert spaces, the existence of physical properties which can not be simultaneously measured - known as non-commuting observables - generates an intrinsic, unavoidable probabilistic behaviour of measurement outcomes even if full information is available about a system or, in other words, even if the system is in a pure state.

The other key factor to be taken into account when exploring the fascinating frontier between thermodynamics and quantum theory is the existence of correlations of non-classical kind [5]: classically, when an interaction between the system and a reservoir is switched on the system evolves non trivially due to several fluxes (heat, entropy) flowing from and to the bath and leading to an additional source of uncertainty about the state of the open system. As an example one may consider the concept of temperature (which is induced by the interaction with a thermal bath), fixing the average energy of the system but spreading its occupation probability in phase space according to a Boltzmann distribution. Such interactions, generally, correlate the system and its environment so that they become statistically dependent. This is even more true in quantum realm, due to the striking existence of quantum correlations (entanglement [5], quantum discord [6]) having no classical analogue and generating a much richer statistical structure of physical properties of the open system even in the case of perfect knowledge about the state of the total one (open system plus environment). This generates, in addition to the previously cited subjective lack of knowledge, an *objective lack of knowledge* which would be present even in the case of perfect, unbounded information acquisition.

This subtle interplay between deep analogies and strong differences generates the branch of physics known as Quantum Thermodynamics [7].

In addition, the ability of having experimental access to mesoscopic and nanoscopic systems [8, 9, 10], whose description necessitates the application of quantum principles [11], stimulated in recent years many different efforts to develop a full description of the interaction of these systems with their surrounding universe, in order to efficiently manipulate them and to protect them from unwanted dissipative effects [12]. The more complex these systems and their environments are, the more interesting and broad becomes the possibility of exploiting their characteristics, and the more a thermodynamic description is needed.

In particular, quantum theory and thermodynamics have to cooperate in the description of systems when, roughly speaking,

- the temperature is very low (how low? This will be specified in details in the following),
- when the spatial dimension of systems is very small (such that the dynamics of these open systems is affected by quantum effects),
- when in general the quantum features of either systems or environments can not be neglected (imagine, for example, to deal with a quantum field state: it manifests peculiar quantum effects such as quantisation of energy or vacuum fluctuations).

Paradigmatic examples of the first class of situations are the so-called Quantum Phase Transitions (QPTs) [13, 14], a collective critical behaviour of many-body systems driven by a sudden change of the scale of *quantum correlations and fluctuations* [15, 16], as opposed to the effect of classical correlations and thermal fluctuations involved in a thermal (i.e., classical) phase transition. More in general, even when the open system does not obey the thermodynamic limit, the interplay between internal and external (i.e., with its bath) quantum correlations and physical, measurable properties of the state of the system attracts a huge deal of attention [17, 18] due to the fundamental role entanglement plays in the theory of quantum information and computation [19], as for example in speeding up computations or in generating secure key distributions in cryptographic protocols. Thermodynamic tools to measure and/or manipulate entanglement are therefore of broad interest.

The second set of systems allows the investigation of the quantum limits of thermodynamics [7]. In other words: to which extent the intrinsic stochastic structure of quantum dynamics can account for the stochasticity of a thermodynamic description of concepts such as heat flux, entropy production, work exchanges, even when the system of interest is far from its thermodynamic limit? These questions are far from being only purely conceptual. There exist indeed classes of laws, valid for classical systems, describing the probabilistic, fluctuating nature of fluxes in and from the system when its state is not an equilibrium state. These laws (second law of thermodynamics, fluctuation dissipation relations [20], fluctuation theorems [21]) and the statistical knowledge they supply are of fundamental importance in characterising what can and what can not be done with, for example, thermodynamic transformations and thermal machines. If and how these laws can be extended, modified and exploited to employ quantum systems in these frameworks is a question of paramount importance.

A partial list of the main lines of research in quantum thermodynamics can be given as follows:

1. First, second and third law of thermodynamics in open quantum systems [22, 23, 24].
2. Equilibrium and nonequilibrium quantum phenomena and fluctuations [25, 26, 27, 28].
3. Quantum extension and generalisation of ensembles structure, dynamics and microstate decomposition [3, 29, 30].

4. Statistical mechanics reformulated exploiting the objectivity in the lack of knowledge about states [4, 31, 32].
5. Quantum critical phenomena and entanglement [13, 14, 15, 16].

This thesis deals mostly with points 2, 4 and 5. It is structured as follows: in Chapter 1 the general physical scenario is introduced and some conceptual and technical tools are given to be exploited in the rest of the work. Chapter 2 is devoted to the presentation of the state of the art on some topics in quantum equilibrium thermodynamics, and is intended as a thematic introduction to part of my results. These results, dealing with the characterisation of a certain class of critical phenomena and the critical review of a widely employed approximation method for quantum many-body physics, are presented and discussed in Chapter 3. The thesis moves then to the state of the art of quantum nonequilibrium thermodynamics, which is presented in Chapter 4, serving as a thematic introduction to the rest of my results, to which Chapter 5 is devoted, about fluctuations and entropy production along quantum nonequilibrium processes. Finally, in Chapter 6 I give some remarks and discuss conclusions and future perspectives of my work.

Chapter 1

Physical scenario

In this Chapter I discuss the physical scenario in which most of the research on quantum thermodynamics moves. Such a scenario is exemplified in the first part of the Chapter by three important phenomena attracting a huge deal of attention in the last decade, namely, quantum critical phenomena, quantum nonequilibirum fluctuations and the quantum origin of equilibrium ensembles. The discussion in this first part is light, intended mostly to introduce questions and themes which will be further developed in the next Chapters.
In the second part of this Chapter some concepts and tools are introduced, which will be useful in the more technical approaches throughout the thesis.

Any theory of thermodynamic phenomena necessitates fundamental ideas to be introduced before the full scenario can be given. Concepts like heat or work, milestones of classical thermodynamics, have however to be carefully introduced in the quantum framework since, apart from some particular limiting cases (as, for example, the weak coupling limit or, in the dynamical case, the so-called rotating wave approximation [3]), there is no clear way to split the internal energy into a heat and a work contribution. Generally speaking, the first law of thermodynamics for a thermalised system in the weak coupling limit, whose Hamiltonian H_S has discrete energy levels E_i, becomes [22]

$$U = \langle H_S \rangle = \sum_i E_i p_i \to \mathrm{d}U = \sum_i \Big(E_i \mathrm{d}p_i + p_i \mathrm{d}E_i \Big). \tag{1.1}$$

For adiabatic variations of the energy levels, and under the weak coupling limit, one can identify the two contributions in (1.1) as, respectively, heat and work exchanges with the environment due to the fact that the variation of energy levels keeping fixed their occupation probabilities p_i does not produce any change in the knowledge about the state of the system - it does not change its entropy - so that

$$\delta W = \sum_i p_i \mathrm{d}E_i, \tag{1.2}$$

$$\delta Q = \sum_i E_i \mathrm{d}p_i. \tag{1.3}$$

This is however not true in general, when the internal energy includes also a non-negligible contribution from the interaction Hamiltonian and when a transformation of the state of a system generates entropy both due to modifications of occupation probabilities and of levels of energy. In out-of-equilibrium contexts, the very definition of entropy production is to be taken carefully, as one may face cases in which a stationary state does not exist and the question arises then about how to quantify of how far from stationarity a system actually is. All these situations offer a very wide field of research, in which almost any standard thermodynamic concept has to undergo, in the best case scenario, deep revisions [33, 34, 35, 36, 37, 38].

In this spirit a number of papers have been published about particular features of quantum processes, leading to somehow surprising results. The second law of thermodynamics still holds on average [23, 39], although temporary violations are not an exotic phenomenon [40, 41, 42] and can be actually measured in not too complicated experimental setups [43, 44]. This is not fully surprising if one refers to the true nature of thermodynamic laws whose validity, also in their classical formulation, fully relies on the extremely low statistical occurrence of processes violating them. This is in turn due to the high number of degrees of freedom of a thermodynamical system and, then, to the statistical occurrence of many microstates resulting in the same macrostate. In most quantum cases, however, the dimension of the Hilbert space of the open system is not too high - it may be, for example, the Hilbert space of a few two-level atoms - resulting in a higher statistical occurrence of violations of thermodynamic laws. The astonishing result of most (if not all) of these works, therefore, is not that standard thermodynamics may be temporary violated during a quantum dynamics, but that it is satisfied on the average, even by small quantum systems. This may not be, a priori, expected since thermodynamic rules have only a statistical origin, as average macroscopic behaviour over very many microscopic ones, while there is no point in differentiating the macroscopic behaviour of an atom from its microscopic one. To a closer look however, as already pointed out before in this thesis, quantum mechanics has two additional sources of stochastic uncertainty: the statistical distribution of measurement outcomes, even in a pure state, and the effect of interaction of the system with a reservoir, or with other parts of the same system, leading to the appearance of non-classical correlations.

It comes clear, then, that a comprehensive study and a full exploitation of quantum thermodynamic behaviour necessitates at least two parallel analyses: of entanglement structure and properties on the one hand, and of the role and effects of measurements of quantities such as energy or information fluxes and other related properties on the other.

1.1 A few important examples: a light discussion

In this Section I will briefly give a slightly more detailed exposition about the main frontiers and the present state of the art of quantum thermodynamics research. The following sections are far from being a comprehensive presentation about subjects of modern research, but are intended to give some technical structure to the previous discussion. In the next sections and chapters, when needed, I will enter in full details about some of these phenomena, focusing the attention on the parts which mostly interested my own research.

1.1.1 Quantum phase transitions: equilibrium fluctuations

To begin with, I analyse one of the most typical equilibrium quantum thermodynamical behaviour, the one associated to a quantum critical point. By equilibrium, in this context, I mean that no dynamical evolution of the open system is involved in the characterisation of the physical properties of the process, such that they do not depend explicitly on time.

Consider then a quantum system whose temperature is kept fixed at absolute zero. This idealisation describes many situations of practical interest in which the system is frozen in its ground state thanks to the fact that the first energy gap is much wider than the average thermal energy [45, 46, 47]. This condition indeed specifies the regime of low temperature I mentioned before in relation to quantum critical behaviour. Under this regime the collective properties of a many-body system only depend on the structure of its ground state [13]. One may wonder however how it is possible to speak about phase transitions when the temperature of the system is effectively vanishing. In particular, the question arises whether it may be possible for a quantum class of systems to show another kind of large-scale order, different from the standard one arising due to thermal fluctuations, which might be responsible for quantum class of phase transitions.

The timescale of the reaction of any system to an external perturbation can be described by means of the characteristic time τ the system itself needs to re-equilibrate. Such a time, close to a thermal critical point, diverges due to the fact that the correlation length becomes infinite. Loosely speaking, calling $\omega = \frac{1}{\tau}$ a characteristic frequency of the system at the transition point, the energy involved in fluctuations at frequency ω of a quantum system is of order of ω.

A classical (thermal) phase transition at the critical temperature T_C can happen as long as the energy scale associated to thermal fluctuation dominates the one associated to quantum fluctuations or, in other words, when

$$k_B T_C > \hbar\omega. \tag{1.4}$$

Since ω vanishes at criticality, thermal fluctuations usually dominate quantum ones for any $T_C \neq 0\,\mathrm{K}$. Incidentally, this is the reason for which thermal phase transitions are said to have a classical origin also for quantum systems.

At zero Kelvin, however, the situation drastically changes since now thermal fluctuations do not hide quantum effects anymore, and a new class of collective critical behaviour of many-body quantum systems is found as a result of zero-point quantum fluctuations [14]. Transitions belonging to such a new class go under the name of Quantum Phase Transitions (QPTs). They are characterised by sudden (I-QPT) or continuous (II-QPT) changes in the structure and properties of the ground state as one or many parameters in the Hamiltonian of the system are changed adiabatically. In the case of a I-QPT, a level crossing between ground state and first excited state is met in the parameters space [48, 49, 50] such that the system suddenly jumps from one state to another one at the quantum critical point (i.e., at the point of the level crossing). In II-QPTs, on the other hand, an avoided level crossing is met in parameter space, whose gap vanishes in the thermodynamic limit giving rise to a smooth change in the properties of the system [51, 52, 53]. In all these cases the collective behaviour responsible for

the phase transition is driven by long-range correlations of quantum origin. Indeed it has been theoretically [54, 55, 56] and experimentally [16, 57] verified that a QPT is always associated to a functional dependence of entanglement on the distance to the quantum critical point formally analogous to the functional dependence of classical correlations on the temperature close to a thermal phase transition: quantum correlations at any scale appear suddenly (I-QPT) or in a continuous way (II-QPT). The typical and most known example of II-QPT is the transition from a Mott insulator to a superfluid phase in a gas of ultracold bosons trapped in an optical lattice [15, 45]. The vast exploitation of these trapped systems is motivated by the precise control one can experimentally exert on almost any feature of the confining potential, allowing physicists to manipulate the sample and to trigger these transitions at will.
Chapter 2 is devoted to a detailed discussion about these phenomena.

1.1.2 Quantum entropy production: out-of-equilibrium fluctuations

As known, the strength of thermodynamic formulation at equilibrium - mostly based on the fact that a many-degrees-of-freedom system is easily described by the use of only a very limited number of macroscopic state variables such as pressure, energy, volume and temperature - is not automatically transferred to the case of out-of-equilibrium processes. Indeed, during a single realisation of a nonequilibrium process the behaviour of a system is fundamentally unpredictable. The fluxes of quantities such as heat or work, flowing from/into the system, undergo strong fluctuations due to microscopic features of the nonequilibrium dynamics. This is true for classical systems, and even more true for quantum systems which have, as discussed before, additional sources of fluctuations and whose dynamics shows particular, characteristic features having no classical analogue thanks to the quantum correlations dynamically built with the bath [3, 58]. However, there exists a class of laws, known as fluctuation theorems (FTs) [21, 26, 27, 59, 60], allowing for a description of the probability distribution for the production of some quantities (such as work, or entropy) along nonequilibrium evolutions. Laws of this kind, linking the stochasticity of microstate evolutions to the stochasticity of macroscopic fluxes, are very well understood in classical frameworks and are known to hold for any classical system. In recent years, the extension of these laws to the quantum realm has attracted a great deal of attention [61, 62, 63, 64, 65] because of the greater and greater importance of nonequilibrium processes of quantum systems embedded in a complex environment for, e.g., technological applications and/or quantum computation procedures [66, 67]. Indeed, a huge part of the branch of physics known as quantum information deals with correlations between quantum systems and information fluxes therefore generated. Such fluxes, as a matter of fact, are very closely related to standard entropy fluxes in a thermodynamic framework, provided of course one introduces when needed some correction terms accounting for the fundamental difference between classical and quantum microscopic dynamics [68, 69, 70].

Classical fluctuation theorems are, for example, the celebrated Jarzynksi equality [59]

$$\langle e^{-\beta W} \rangle = e^{-\beta \Delta F}, \tag{1.5}$$

relating the average value of a function of the classical work needed to drive a system out of equilibrium to the free energy change between initial and final equilibrium states of the process, or its generalisation in terms of entropy production [60] of the form

$$\frac{p_f(\sigma)}{p_b(-\sigma)} = e^{\sigma}, \tag{1.6}$$

relating the probability that entropy σ is produced along a single realisation of the driving protocol acting *forward* (i.e., from the initial to the final ensemble state) to the probability that entropy $-\sigma$ is produced along a single realisation of the driving protocol acting *backward* (i.e., from the final to the initial ensemble state).

The extension of these laws to the general quantum case is tricky for at least two independent factors. On the one hand, as already commented shortly before in this Chapter, the very definition of quantities such as work, heat and entropy production in the quantum case is troublesome and still undergoing a deep conceptual debate. On the other hand, the concept of a single trajectory in phase space can not be applied to quantum evolutions and the characterisation of a single quantum nonequilibrium process can not be given without specifying the way such a process is monitored (or not monitored), the effect and the backaction of measurements in these cases being of fundamental importance [71].

Taking into account both of these issues leads to a number of different FTs, not all of which reproduce the standard result of the classical case. Memory effects in the dynamics, ultimately due to strong quantum correlations created between an open quantum system and its bath, modify for instance the probability distribution of entropy production [72], since they fundamentally affect the information flowing to the environment [41] and the one collected by an external observer [66]. The additional term resulting from such an analysis can be linked to the mutual information shared by system and environment which, in the quantum case, is know to lead to the definition of another measure of non-classical correlations referred to as quantum discord [6].

Another typical quantum deviation from standard FTs is due to the choice of measurement strategy [73] which ultimately generates single quantum trajectories somewhat analogous to phase space classical trajectories [74]. The dependence of quantum evolution on the measuring scheme (meaning how, when and where the total system composed of open system and environment is measured) is strong and non trivial, leading as a consequence to additional fluctuations in physical quantities having purely quantum origins.

A detailed discussion on this class of laws both in classical and quantum systems is given in Chapters 4 and 5 and I therefore postpone any further comment on them.

1.1.3 Origin and structure of quantum ensembles

Last but not least, to conclude this brief review of some concepts of quantum thermodynamics I discuss another example of questions attracting the interest of present research in the field: if and how quantum features can lead to the same stochastic structure of classical ensemble theory. In other words: is one allowed to extend classical ensemble structure to the quantum realm? And in which way? This is a vast and, sometimes, very technical subject of research.

Here, however, I discuss a small part of it which will turn out to be important in understanding part of the exposition of my results in Chapter 3. The results presented in this subsection have been obtained in [31, 32].

To fix ideas, let us consider a total system T on an n-dimensional Hilbert space $\mathcal{H}_T^n$ $(n \gg 1)$, and let us consider a bipartition consisting of a thermal bath B (with Hamiltonian H_B) and an open system S (Hamiltonian H_S). Such a bipartition might be a structural one, due to particular features of the total system under scrutiny (as, for example, a set of atoms interacting with a radiation field), or might also be arbitrarily chosen, provided however that the bath (living in an r-dimensional Hilbert space $\mathcal{H}_B^r$) and the system (d-dimensional Hilbert space $\mathcal{H}_S^d$, where clearly $n = rd$) are only weakly coupled and that $r \gg d$. Under these circumstances it is known that, provided the total system T is prepared in a microcanonical ensemble $\varepsilon_E = \frac{1}{n_E}\mathbb{I}_E$ fixing its energy to the value E (such a microcanonical ensemble corresponds to assigning equal occupation probability $\frac{1}{n_E}$ to any state of T having the same total energy, so that its density operator is proportional to the identity operator $\mathbb{I}_E$ in the subspace $\mathcal{H}_E^{n_E}$ of fixed energy) the state ρ_S of the open system S has, to a very good accuracy, the structure of a Gibbs state [75]. Mathematically

$$\Omega_S \equiv \mathrm{Tr}_B \varepsilon_E \approx \frac{1}{Z} e^{-\beta H_S}, \tag{1.7}$$

where Z is the normalisation of the state known as partition function and Tr_B stands for the trace over the bath degrees of freedom which in turn corresponds to disregarding any detail of the bath and incorporating them in a few parameters (in this case, only the temperature $\frac{1}{k_B\beta}$) characterising the reduced state of the open system. This formulation is valid both in classical and in quantum cases thanks to the already cited analogy between their respective ensemble theories.

The uncertainty about the state of the total system due to the lack of knowledge about its microstate (indeed, the state of the total system is mixed) is passed on to the state of the open system and summed up with the uncertainty due to fact that one neglects bath degrees of freedom. Classically, if one had full knowledge about the microstate of the total system, one would automatically have full information about the microstates of open system and bath making the statistical ensemble approach impossible (and, clearly, useless). In the quantum case this is not true anymore because of (or thanks to) the existence of entanglement between open system and environment, because non-classical correlations prevent one to assign a well defined pure state to an open system alone after tracing out its bath. This is due to the fact that, loosely speaking, part of the information about the open system is contained, thanks to quantum correlations, in the environment and discarding the knowledge about such a state forces one to describe the reduced state of the open system as being mixed. Entanglement generates then a statistical structure somehow analogous to the classical subjective lack of knowledge.

Such an analogy is actually much more than just formal: Popescu *et al.* [31] recently showed that when the total system T is a quantum system, the use of a microcanonical ensemble state becomes unnecessary to obtain a reduced thermal Gibbs state. Indeed one can imagine to prepare the system T in a pure state $|\Psi_E\rangle \in \mathcal{H}_E^{n_E}$ belonging to the standard pure state decomposition of ε_E, so that on the one had the total system has a well defined energy and, on the other, one has full knowledge about its microscopic state. If one performs the same operation as in Eq. (1.7) to obtain the open quantum system state, one gets

$$\mathrm{Tr}_B|\Psi_E\rangle\langle\Psi_E| = \rho_S, \tag{1.8}$$

which once again describes the way an observer sees (i.e., measures) properties of the open system only if he has no information about the state of the bath. In the spirit of what has been said a few lines above, it is not surprising that ρ_S is a mixed state thanks to quantum correlations between S and B. What is probably unexpected is however that

$$\mathrm{Prob}\Big\{\|\rho_S - \Omega_S\| > \epsilon\Big\} < 2e^{-Cn_E\epsilon^2}. \tag{1.9}$$

This equation has to be read as: the probability that, after tracing out the bath degrees of freedom from a total *pure* state of fixed energy, one obtains a reduced state ρ_S which is ϵ-different from the standard thermal Gibbs state Ω_S goes exponentially to zero with the dimension of the energy subshell $\mathcal{H}_E^{n_E}$. C is a positive constant and $\|\rho_1 - \rho_2\|$ is a distance measure of two matrices ρ_1 and ρ_2 in the state space known as Trace Distance [76], which is well known to measure how different two quantum states are with respect to the statistical predictions on any possible measurement outcome on them.

This means that, with a low statistical error, one can associate concepts like temperature and ensemble thermal equilibrium state to an open quantum system even if one has *full knowledge* about the microscopic state of the total system. This, as already commented and as can be shown in details, is due to the existence of entanglement between open system and bath and is therefore a purely quantum effect. As a matter of fact, this means that the *subjective lack of knowledge* characterising classical thermodynamics and originating from the limitedness of the external observer is replaced here by an *objective lack of knowledge* originating from the very structure of quantum correlations and, as such, being an intrinsic feature of quantum thermodynamics which can not be eliminated even by a perfect, limitless external observer.

It is however worth stressing that (1.9) is a probabilistic statement, in which an *a priori* equal distribution of state vectors is assumed. This postulates an a priori particular knowledge of the external observer about the open quantum system.

1.2 Magnifying (and localising) the point of view

Quantum thermodynamics consists of a countless set of different theoretical and experimental research lines. It represents such a multifaceted scenario that a general view on it can not grasp its many fascinating details. On the other hand, a localised view such as the one given in this thesis is far from presenting a full picture of the quantum thermodynamics theory, but magnify the local view on some selected physical phenomena. This Section is therefore a guideline to move between the general delocalised point of view given in the previous Section and the localised point of view which will be found throughout next Chapters.

The interplay between the lack of knowledge due to the many features of open quantum systems and quantum correlations and the underlying probabilistic structure of any thermodynamic theory gives rise to a number of phenomena. In addition to the three examples discussed above, among the most explored problematics stand: the quantum dynamical approach to thermal equilibrium [77, 78, 79] and, possibly, the lack of thermalisation in connection to the structure of the system Hamiltonian and of its dynamics [80, 81]; the extension of macroscopic concepts, like temperature, to the nanoscale [82, 83]; the theory and applicability of quantum thermal machines [23, 38] and quantum feedback protocols [84, 85] in the exploitation of quantum systems to produce certain effects. This still restrictive list shows already how topics of equilibrium and nonequilibrium physics are widely mixed and attracting a comparably big deal of attention of large communities.

The work during my PhD studies, which I extensively present in this thesis, dealt with selected topics both in equilibrium and nonequilibrium thermodynamics. In particular, the results presented in the first part (Chapter 3) belong to the large topic of quantum state characterisation, connecting physical properties of equilibrium thermal states to measures of non-classical correlations. I explored, in producing these results, the structure of low-lying energy level of few-body quantum systems kept at low temperature, moving in the same direction as the research on quantum phase transitions. Consequently, I move along the border of quantum thermodynamic (structure of quantum thermal state) and quantum information (entanglement measures) theories. The second part of the thesis (Chapter 5) presents, on the other hand, results on nonequilibrium thermodynamics. The extension of fluctuation theorems to purely quantum processes and the inclusion of memory effects due to non-Markovian interactions with an environment are the main results of my research in this field. In particular, I managed to derive and characterise corrections to the standard form of fluctuation theorems due to quantum fluctuations and correlations. These results therefore fully belong to the research line exploring how quantum dynamics produce a different kind of stochasticity in the microscopic properties of systems and how such differences can be measured and, in principle, exploited for quantum technology protocols.

1.3 A rigorous quantum view on dynamics, correlations and model systems

Throughout this thesis I will discuss a number of different physical situations, each of which has to be tackled employing a particular set of conceptual and mathematical tools such as, e.g., entanglement measures, Bose-Hubbard models, quantum master equations, non-Markovian processes, etc... Clearly it is not possible to give here a full presentation about all these topics. It is necessary however to supply the reader with some rigorous methods and definitions which will be of help in understanding the rest of this work. This Section aims then at giving some pieces of information about standard models and techniques often used in quantum dynamics and thermodynamics contexts.

1.3.1 Entanglement and its measures

Entanglement [5, 86] is often regarded as one of the most striking features of quantum theory, its importance being both conceptual and practical. From the conceptual point of view, in fact, it discovers one of the main cores of quantum theory, i.e. its underlying non-local structure. Indeed, as much as in the classical case, quantum systems which are non-interacting can still be interdependent, but their correlations are of a striking different nature (they violate, for example, the famous Bell inequalities [19]). More precisely, if two systems exist in an *entangled state*, a measurement on one of them fundamentally affects the structure of the state of the other (i.e., the probability distribution of measurement outcomes on it) despite the fact that these systems may very well be non-interacting (although they must have interacted in the past). Ultimately, this effect can be traced back to two of the main conceptual features of quantum theory: the superposition principle and the collapse postulate.

Rigorously speaking, consider a composite system S divided (formally or physically) into two subsystems S_1 and S_2, each of which lives in its own Hilbert space $\mathcal{H}_1$ and $\mathcal{H}_2$ of dimensions, respectively, d_1 and d_2. A pure separable (non-entangled) state in the composite Hilbert space $\mathcal{H}$ of S has the general form $|\psi_s\rangle = |\varphi_1\rangle \otimes |\phi_2\rangle$, where $|\varphi_1\rangle$ ($|\phi_2\rangle$) is a state of S_1 (S_2). Such a state is, in a sense, classical because a measurement on S_1 has no effect on S_2 since it would project the state $|\psi_s\rangle$ to $|\mu_s\rangle = |a_1\rangle \otimes |\phi_2\rangle$, $|a_1\rangle$ being the state of S_1 after the outcome a_1 has been measured, which is what one would expect from a classical system. Such a structure of a pure state is however not the most general one. It is indeed possible, thanks to the superposition principle, for the system S to be in a state $|\psi_e\rangle = c_1|\psi_s^{(1)}\rangle + c_2|\psi_s^{(2)}\rangle$, where $c_1, c_2 \neq 0$ and $|\psi_s^{(i)}\rangle = |\varphi_1^{(i)}\rangle \otimes |\phi_2^{(i)}\rangle$ ($i = 1, 2$) are separable states, each of which shows a classical behaviour as long as correlations between S_1 and S_2 are concerned. However, if the local states of S_1 and S_2 are such that $|\langle\varphi_1^{(1)}|\varphi_1^{(2)}\rangle|^2 \neq 1$ and $|\langle\phi_1^{(1)}|\phi_1^{(2)}\rangle|^2 \neq 1$, it is not possible to write the state $|\psi_e\rangle$ as a unique separable state. Because of this, it describes a situation in which correlations between S_1 and S_2 exist in a non-classical and non-local way, since the two subsystems may also be separated in space. Imagine in particular that $\langle\varphi_1^{(1)}|\varphi_1^{(2)}\rangle = 0$, and perform a measurement on subsystem S_1 of the observable $|\varphi_1^{(1)}\rangle\langle\varphi_1^{(1)}|$. This generates a collapse of the total system wave function as

$$|\psi_e\rangle = c_1|\varphi_1^{(1)}\rangle \otimes |\phi_2^{(1)}\rangle + c_2|\varphi_1^{(2)}\rangle \otimes |\phi_2^{(2)}\rangle \to |\varphi_1^{(1)}\rangle \otimes |\phi_2^{(1)}\rangle = |\psi_s^{(1)}\rangle. \tag{1.10}$$

A measurement on S_1 alone has then affected also the statistics of S_2, which after the measurement is only due to the structure of $|\phi_2^{(1)}\rangle$ while before the measurement a contribution from $|\phi_2^{(2)}\rangle$ was clearly also present. As remarked previously, these correlations are fundamentally different from the classical case. Countless examples of entangled states have been studied theoretically and produced experimentally [87, 88, 89, 90, 91, 92], and it has been shown that the presence of entanglement makes pure quantum states a powerful tool for protocols such as quantum computation, quantum cryptography, quantum state teleportation, much more suited for these protocols than classical states [19]. In this sense, entanglement is the key quantity of any quantum information framework and the feature which differentiates classical from quantum technologies.

It is important to stress here that two systems being entangled means that some information about a system is contained in the other one. This implies that, if one only looks at the degrees of freedom of, say, S_1 choosing to neglect the degrees of freedom of S_2, one looses a certain amount of information which is available in the knowledge of the full composite state. This means that, starting from an entangled pure state density matrix of the total system S given as $\sigma_e = |\psi_e\rangle\langle\psi_e|$, one obtains for the subsystem S_1

$$\rho_1 = \mathrm{Tr}_2 \sigma_e. \tag{1.11}$$

The state in Eq. (1.11) is called reduced density matrix of the system S_1 and is obtained through a partial trace operation over the degrees of freedom of S_2, which is the mathematical counterpart of neglecting the knowledge about the state of S_2. If the total pure state is entangled, ρ_1 is a mixed state. This reflects the lack of knowledge about S_1, as information about its state is lost by neglecting S_2. As commented before, indeed, entanglement naturally and easily produces mixed quantum states and represents then a precious conceptual tool to introduce ensemble structures in quantum theory. As commented in the previous Section, however, the lack of knowledge producing a reduced mixed state for S_1 is not due to a practical incapability of perfectly measuring its microstate (classical subjective lack of knowledge), but originates from a structural impossibility to access all the information about a system due to its non-classical correlations with another one. That is why in the previous Section I referred to such a mixedness as describing an objective lack of knowledge about the state of a system. Moreover, the more mixed a reduced state is the more information is lost by tracing out part of the total system and therefore the more entangled the total pure state is. Any quantifier of the purity of a reduced state ρ obtained from a pure state $|\psi\rangle$, such as the celebrated von Neumann entropy [93]

$$S_{\mathrm{vN}} = -\mathrm{Tr}\rho \ln \rho, \tag{1.12}$$

measures indeed the pure state entanglement along the bipartition identified by the reduced state itself. A pure reduced state means zero entanglement in the total state, while a maximally mixed reduced state (i.e., a reduced state proportional to the identity operator), is a signature of a pure *maximally entangled* state.

Despite the fact that pure state bipartite entanglement is well understood and easily measured (for example in terms of the well known Schmidt decomposition of the composite state [5]), the same does not hold for bipartite entanglement of mixed states [5, 94]. A general mixed quantum state can be written as a convex sum of pure states such as

$$\rho = \sum_i p_i |\psi_i\rangle\langle\psi_i|. \tag{1.13}$$

The main technical difficulty involved in the few general bipartite entanglement measures available for a state of the form (1.13), such as e.g. the Entanglement of Formation (related to the so-called convex roof extension of von Neumann entropies of reduced states of each pure state in (1.13) [95]), is due to a non-trivial minimisation of a certain functional over any possible pure state decomposition of the same mixed state whose number is always infinite. Despite this, a study of the entanglement inside mixed states is of great interest because of the unavoidable presence, in any situation of practical interest, of the interaction with noise or with a structured environment which usually destroys the purity of the state of the system.

In order to avoid time-consuming minimisations when evaluating bipartite mixed state entanglement, one can resort to two simpler quantities much more easily manageable known as Concurrence and Negativity.

The Concurrence $\mathcal{C}$ [96] is a very simple measure of bipartite entanglement in a mixed total state ρ of 2×2 systems, i.e. when both subsystems have a Hilbert space of dimension 2. In these cases, indeed, the Entanglement of formation is a monotonic function of $\mathcal{C}$. The Concurrence is defined as

$$\mathcal{C} = \mathrm{Max}\{0, \nu\}, \tag{1.14}$$

where $\nu = \sqrt{\mu_1} - \sqrt{\mu_2} - \sqrt{\mu_3} - \sqrt{\mu_4}$. Here the μ_i's are eigenvalues of the matrix $\sqrt{\rho}(\sigma_y \otimes \sigma_y)\rho^*(\sigma_y \otimes \sigma_y)\sqrt{\rho}$, where ρ^* is the complex conjugate of ρ, and $\mu_1 \geq \mu_2 \geq \mu_3 \geq \mu_4$. Although not being evident from the previous definition, the Concurrence is related to the overlap between the mixed state ρ and a mixture of maximally entangled pure states.

The other often used quantity, very attractive thanks to its relative simplicity, is the one called Negativity N [97]. The negativity is an entanglement monotone. Its definition is based on the fact that, as long as the state of a bipartite system is separable, it remains a quantum state even after a partial transposition with respect to the degrees of freedom of only one of its two subsystems. The fact that the spectrum of the matrix obtained after such a partial transposition contains negative eigenvalues is thus a sufficient condition for the non-separability of the state. This condition turns out to be necessary too in the cases of bipartition composed of two two-level systems or by a two- and a three-level system, but in general there exist mixed entangled states having a positive partial transpose spectrum [98]: for this reason such a criterion is not, strictly speaking, a measure of entanglement. When a negative eigenvalue is detected, however, the Negativity quantifies correctly the amount of bipartite mixed state entanglement. It is then common to define Negativity as

$$N = \sum_{\nu} |\lambda_\nu|, \tag{1.15}$$

where the index ν runs over the whole set of negative eigenvalues of the partial transpose of the composite system density matrix. It is well known [99] that equation (1.15), for a bipartition in two subsystems having dimensions d_1 and d_2, is equivalent to

$$N = \frac{\|\rho^{T_1}\| - 1}{d_m - 1}, \tag{1.16}$$

where $d_m = \min\{d_1, d_2\}$, ρ^{T_1} is the matrix obtained from ρ by a partial transposition with respect to the subsystem S_1 and $\|\cdot\|$ is the trace norm [76], defined for a generic operator O as $\|O\| = \mathrm{Tr}\sqrt{O^\dagger O}$.

The quantities in Eqs. (1.14) and (1.16) are the ones I will use in Chapter 3 to characterise the entanglement in thermal states.

1.3.2 Bose-Hubbard model

One of the most studied and investigated models to explore the vast realm of quantum equilibrium (and nonequilibrium) thermodynamics is the so-called Bose-Hubbard model [100], describing the physics of *ultracold* atoms, described as bosons, confined in a structure known as optical lattice [101]. Such a structure, which consists of standing waves created by electromagnetic fields (usually, laser fields), has in the last decades allowed researches to investigate frontiers of physics (such as, for example, a class of quantum phase transitions) which represent one first example of quantum thermodynamic behaviour. In Chapter 3 I will present some results on similar models, and it is therefore useful to exploit this introduction to discuss in few details the physics of a Bose-Hubbard Hamiltonian.

Consider then an optical lattice and a gas of bosons confined inside it [102, 103]. Each atom can be found, when measured, in one of the lattice sites of the crystal. Assume the atom-atom interaction to be short-ranged enough to assume that atoms can interact only through collisions within the same lattice site. In addition, they can move from one site to another one via a tunnelling term. Finally, the energy offset of each site can be tuned resulting in a further single atom Hamiltonian term. Because of the assumption of low temperature, one can suppose the atomic cloud to occupy only the first energetic band in the lattice and, moreover, that interatomic interactions happen only in the form of two-body *s-wave* scatterings with δ-like potentials [45]. This assumption specifies the range of temperature involved. For typical masses of atoms employed in practice, the *l-wave* scattering is frozen for temperatures $T \lesssim m\mathrm{K}$.

The considered atoms being bosons of spin S, the most general state of two of them during interaction (and therefore in the same lattice site) is, in their coupled spin basis,

$$|\Psi_{12}\rangle = \sum_{S_{tot}}^{\text{even}} \sum_{M=-S_{tot}}^{S_{tot}} \Phi_{S_{tot},M} |S_{tot} M\rangle, \tag{1.17}$$

where, to respect bosonic symmetrisation, odd values of the total spin S_{tot} are excluded. Following the physical assumption on the form of the interaction, the scattering potential is

$$V(\mathbf{r}_1 - \mathbf{r}_2) = \delta(\mathbf{r}_1 - \mathbf{r}_2) \sum_{S_{tot}}^{\text{even}} g_{S_{tot}} P_{S_{tot}} \tag{1.18}$$

where $P_{S_{tot}}$ projects the two interacting atoms into state of total spin S_{tot} and $g_{S_{tot}}$ depends on the s-wave scattering parameter of this channel and can therefore be easily tuned by, for example, Feshbach resonance [104]. To simplify the exposition, consider now the case of spin 1 bosons, so that $S_{tot} = 0, 2$ and each atom will be characterised by a spin-1 operator $\mathbf{S}_i$. This is the case I considered in producing some of the results discussed in Chapter 3. If the scattering channels become asymmetric (i.e., if not all the $g_{S_{tot}}$ are equal), such a two-body scattering will contain also a term which can be represented as an effective spin-spin interaction. Indeed, introducing the symmetric and asymmetric scattering amplitudes $\gamma_s = \frac{1}{3}(g_0 + 2g_2)$ and $\gamma_a = \frac{1}{3}(g_2 - g_0)$, Eq. (1.18) can be recast as

$$V(\mathbf{r}_1 - \mathbf{r}_2) = \delta(\mathbf{r}_1 - \mathbf{r}_2)\big(\gamma_s \mathbb{I} + \gamma_a \mathbf{S}_1 \cdot \mathbf{S}_2\big). \tag{1.19}$$

To this term, one adds the kinetic term of each atom and a local potential $V_{\text{loc}}(\mathbf{r})$ characterising the structure of the confinement in the lattice. The N-atom system Hamiltonian is therefore

$$H = \sum_{i=1}^{N} \Big(-\frac{1}{2m}\nabla_i^2 + V_{\text{loc}}(\mathbf{r}_i) \Big) + \frac{1}{2}\sum_{i\neq j} V(\mathbf{r}_i - \mathbf{r}_j). \tag{1.20}$$

One can now employ a second quantisation formalism by introducing the creation and annihilation operators $a^\dagger_{i,m}$, $a_{i,m}$ for an atom in the i-th lattice site in a state with $S_z = m$. Adding to the Hamiltonian in Eq. (1.20) a tunnelling term proportional to a parameter J (which depends, among other things, on the details of the confining potential), accounting for the annihilation of an atom with z-spin m in site i and the simultaneous creation of an atom with the same spin state in the site j, Eq. (1.20) becomes

$$H_{BH} = -J \sum_{<ij>,m} \big(a^\dagger_{i,m} a_{j,m} + a^\dagger_{j,m} a_{i,m} \big) + \epsilon \sum_i \hat{n}_i + \frac{U_0}{2}\sum_i \hat{n}_i(\hat{n}_i - 1) + \sum_i \frac{U_2}{2}\Big((\mathbf{S}^i_{tot})^2 - 2\hat{n}_i \Big), \tag{1.21}$$

where $\hat{n}_i = \sum_{m=-1}^{1} a^\dagger_{i,m} a_{i,m}$ is the number operator of the site i, $U_0 \propto -\lambda_s$ and $U_2 \propto \lambda_a$ are coupling constants accounting for atom-atom interactions, $\mathbf{S}^i_{tot}$ is the sum of all spin operators of atoms in the site i, ϵ is the single atom unperturbed energy at each site and $\sum_{<ij>}$ runs over each pair of neighbouring sites.

The Hamiltonian (1.21) (possibly with U_2=0) is the celebrated Bose-Hubbard Hamiltonian. It has been predicted theoretically and verified experimentally that any system described by such an Hamiltonian undergoes a quantum phase transition from an insulator phase (known as Mott-insulator), where each atom is confined in a well defined lattice site because the interatomic interaction dominates over the tunnelling term, to a superfluid phase in which the atomic cloud is delocalised over the full lattice and the system acts as a superfluid because the tunnelling term dominates over scattering interactions [15, 16, 105, 106].

If one is interested only in the physics of the insulator phase, it is possible to obtain an effective, more manageable Hamiltonian description by performing a second-order perturbative expansion in the tunnel amplitude J [103]. Skipping tedious calculations, the final form of such an effective insulator phase Hamiltonian is

$$H_{\text{eff}} = J_0 + J_1 \sum_{<ij>} \mathbf{S}_i \cdot \mathbf{S}_j + J_2 \sum_{<ij>} \big(\mathbf{S}_i \cdot \mathbf{S}_j \big)^2, \tag{1.22}$$

where J_0, J_1 and J_2 are functions of J^2, U_0 and U_2 and can therefore be externally tuned by changing both the lattice parameters and the scattering amplitudes.

The physics of ultracold gases in the insulating phase is thus mapped onto the physics of an interacting spin system. The analysis of physical properties stemming from this effective description for a few-body system is part of the results presented in Chapter 3.

1.3.3 Quantum master equations, non-Markovianity and unravelling

An open quantum system evolves in a non-unitary way. This is due to the fact that a unitary time evolution can not account for dissipation, decoherence, fluxes of information inside the system etc..., situations which normally characterise the interaction of a quantum system with a reservoir [107]. Starting from Chapter 4 I will make largely use of a rigorous description of dissipative dynamics in the framework of nonequilibrium thermodynamics, mainly resorting to two tools known as Master Equations and stochastic unravelling of the dynamics.

For a closed system, the time evolution of the state ρ from t_0 to t is generated by a dynamical unitary map $\rho(t) = \Lambda_U(t, t_0)\rho(t_0)$ which preserves, for instance, the purity of the state. In the case of open quantum systems, a (non-unitary) dynamical map $\Lambda(t_0, t)$ can also be defined, which maps reduced states of the open quantum system at t_0 to reduced states at t. This is possible, in general, provided the initial *total* state (system plus environment) at t_0 is factorized in the form $\rho_{\text{tot}} = \rho(t_0) \otimes \rho_E(t_0)$. Under this assumption, a superoperator can be defined which maps quantum states to quantum states preserving their trace (which by normalisation has to be 1) and the positivity of any state under the action of the map $\Lambda \otimes \mathbb{I}$ in any extended Hilbert space. This requirement is known as Complete Positivity. Any dynamical map Λ satisfying the conditions of being Trace preserving and Complete Positive is known as CPT map [3].

To fix ideas, consider here an open quantum system whose state $\rho(t)$ (which is the reduced density matrix describing only open system's degrees of freedom, and is generally mixed because of the interaction with a bath) evolves due to two independent effects: the first one originates from the internal Hamiltonian evolution, generated by the unperturbed system Hamiltonian H_S plus a renormalisation term accounting for the effect, on the bare energy levels of the open system, of an interaction with an environment. Such a renormalisation is described by a Lamb-shift Hamiltonian H_{LS} which commutes with H_S. Introducing the operator $H = H_S + H_{LS}$, the first dynamical effect is described by a unitary evolution term of the form

$$\left.\frac{\mathrm{d}\rho(t)}{\mathrm{d}t}\right|_{\text{Unitary}} = -i\left[H(t), \rho(t)\right], \tag{1.23}$$

where a time dependence in H has been introduced to work in full generality. Eq. (1.23) is the usual von Neumann equation describing Hamiltonian evolution of a closed quantum system.
In addition to this, the state of an open system evolves also because of dissipative and decoherence processes describing two different quantities which may flow into the environment: energy and information. Briefly, dissipation describes the irreversible exchange of energy of an open system and is a key feature, for instance, of many thermalisation processes and exists also in a classical equivalent. Decoherence [108], on the other hand, is a purely quantum effect or, more precisely, is the effect responsive for a loss of "quantumness" of an open system. Coherence, indeed, is a purely quantum feature originating from state superposition and, similarly to entanglement, describes how two state in a quantum superposition generate a stochastic behaviour of measurement outcomes which can not be accounted for by a classical description. As information flows into the environment, the probabilistic features of the open systems become more and more classical and the system evolves towards a mixed state. Decoherence is thus one of

the main obstacles to the full exploitation of quantum effects in, e.g., quantum computation protocols [109] and a huge deal of efforts has been devoted to study ways how to protect an open system against such an effect [110, 111]. These two phenomena may happen through many different physical effects, and may be generated by very different reservoirs. Despite this, however, it is possible to show [3, 112] that their effect on the evolution of $\rho(t)$ can be accounted for by a very simple formalism. Indeed

$$\left.\frac{\mathrm{d}\rho(t)}{\mathrm{d}t}\right|_{\text{Dissipation}}^{\text{Decoherence}} = \sum_i \gamma_i(t)\left[A_i(t)\rho(t)A_i^\dagger(t) - \frac{1}{2}\left\{A_i^\dagger(t)A_i(t), \rho(t)\right\}\right], \tag{1.24}$$

where the non-Hermitian operators $A_i(t)$ are known as Lindblad operators [113] and describe all the physical processes by which the open quantum system exchanges energy and/or information with its environment (and, as such, clearly depend on the particular system under scrutiny) and $\gamma_i(t)$ are relaxation rates associated to the i-th physical dissipative or decoherence process (referred to as *channel*).

The total evolution of the reduced state is therefore given as the sum of Eqs. (1.23) and (1.24) as

$$\frac{\mathrm{d}}{\mathrm{d}t}\rho(t) = -i\left[H(t), \rho(t)\right] + \sum_i \gamma_i(t)\left[A_i(t)\rho(t)A_i^\dagger(t) - \frac{1}{2}\left\{A_i^\dagger(t)A_i(t), \rho(t)\right\}\right]. \tag{1.25}$$

Eq. (1.25) is the master equation for an open quantum system, whose solution represents the time evolution of the ensemble state. It describes how the knowledge about the state of a system evolves in the case measurement are neither performed on it nor on its environment. It can be shown [114, 115] that any CPT map generates a master equation which can be cast in this local-in-time or time convolutionless (TCL) form, which means that the time derivative of the state at time t depends on the action of certain class of operators on the state of the system at the same time instant t. Depending on how the Lindblad operators $A_i(t)$ and the relaxation rates $\gamma_i(t)$ depend on time, one identifies three classes of possible dynamics of an open quantum system, i.e. Markovian, time-dependent Markovian and non-Markovian processes.

A Markovian, or memoryless, dynamics is characterised by having time independent Lindblad operators and rates, and $\gamma_i > 0\ \forall i$. It originates, roughly speaking, from a coarse graining operation in time and assumes the typical timescale of environment self-correlations to be much shorter than the timescale characterising the evolution of the open system [3, 113]. This means that the system, on a coarse grained timescale, does not feel any modification in the state of the environment which is indeed assumed not to evolve in time. In the dynamics thus generated, the open system has no memory of his past history and approaches monotonically one of its possible stationary states. The set of dynamical maps $\Lambda(t)$ (one for each time instant $t \geq 0$) associated to a Markovian process forms a semigroup.

In a time-dependent Markovian process [116] both Lindblad operators and relaxation rates depend on time, but such that $\gamma_i(t) \geq 0\ \forall i, t$. At each fixed time instant, then, Eq. (1.25) has a standard Markovian structure and the system keeps having no memory of his past history.

It therefore evolves, at any fixed time t^*, approaching the stationary state associated to the set of fixed operators $A_i(t^*)$ and rates $\gamma_i(t^*)$. Since such a set, however, depends on time, the evolution of the system is not simply a monotonic approach to a unique state but, instead, the system follows the evolution of the instantaneous stationary state determined each time by the instantaneous Markovian form of the master equation, going instantaneously towards stationarity. The set of dynamical maps $\Lambda(t)$ is, in this case, not anymore a semigroup.

Finally, a non-Markovian dynamics is characterised by memory effects [117]. Both Lindblad operators and rates depend on time, and in addition there exists *at least* one channel i_- and a finite time interval $[t_1, t_2]$ such that $\gamma_{i_-}(t) < 0 \;\; \forall t \in (t_1, t_2)$. According to the way one decides to characterise non-Markovianity in the quantum case, such a condition may be or not be sufficient. It is however always necessary. The timescale of environment self-correlations becomes in this case at least comparable to the timescale of dynamical evolution of the open system, which then feels at each step the modifications it induces on the environment itself. Memory comes therefore into play and an instantaneous stationary state (which may even not exist), is in the best case scenario not monotonically approached, i.e. the state of the open system may increase its distance from the set of instantaneous stationary states during the time intervals in which at least one relaxation rate is negative. This is due to information which is given *back* from the environment to the system thanks to their strong dynamically built correlations. There exist many ways to quantify these memory effects [41, 118, 119, 120], each of which exploits a particular physical consequence of the violation of Markovian structure. The presentation of the full picture of non-Markovianity measures is beyond the scope of this Section. Here I only discuss the general features of one of them [41], which is the one most closely related to our definition of non-Markovian fluctuations given in Chapter 5.

One of the possible deviations from the Markovian behaviour is, as discussed, the fact that instantaneously the system does not approach stationarity. Since however an (even instantaneous) stationary state may not exist for non-Markovian dynamics, one has to find a better way to quantify the effect of these backflows of information from environment to the system. Consider then two different states $\rho_1(t_0)$ and $\rho_2(t_0)$, and let them evolve under the action of the same dynamical map $\Lambda(t, t_0)$. If the dynamics was (time-dependent) Markovian, these two states at each time instant would evolve towards the same instantaneous stationary state and their distance would decrease monotonically in time. A deviation from this behaviour can therefore be investigated by analysing the time dependence of their distance, as quantified by means of any valid metric in state space. In particular, in the standard approach [41] one uses the trace distance between states [76] defined as $D_T(\rho_1(t), \rho_2(t)) = \mathrm{Tr}\big|\Lambda(\mathrm{t}, \mathrm{t_0})\rho_1(\mathrm{t_0}) - \Lambda(\mathrm{t}, \mathrm{t_0})\rho_2(\mathrm{t_0})\big|$: the higher is this distance, the more different the two states are with respect to outcomes of measurements performed on them. Clearly a Markovian dynamics is characterised by $\frac{\mathrm{d}D_T(\rho_1(t), \rho_2(t))}{\mathrm{d}t} < 0 \;\; \forall \rho_1, \rho_2$. The non-Markovianity of a certain dynamics has to be a function of the map Λ only and not of the particular pair of initial states chosen. This is achieved by quantifying it as

$$\mathcal{N} = \max_{\{\rho_1, \rho_2\}} \int_{>0} \mathrm{d}t \frac{\mathrm{d}D_T(\rho_1(t), \rho_2(t))}{\mathrm{d}t}, \tag{1.26}$$

where $\int_{>0}$ stands for an integral over every time intervals in which $\frac{\mathrm{d}D_T(\rho_1(t), \rho_2(t))}{\mathrm{d}t} > 0$ and the maximisation is performed over any possible pair of initial states of the open quantum system.

It has moreover been shown [121] that the same result is obtained when such a maximisation is performed only over one state, keeping the other one fixed.

The onset of non-Markovianity, which can be tuned for example by modifying the system-environment interaction strength, has been experimentally observed in a number of situations [43, 44] and, in addition to being a core topic in quantum information science, has been shown to supply a way to probe features of a complex environment by performing measurements on open systems only [122, 123].

Finally, I conclude this technical section by providing a very brief sketch of the method known as unravelling of a dynamics. The mathematical details of this method are given and discussed in Section 5.2 in order to facilitate the interpretation of the results presented there. Here I introduce its general ideas and discuss its conceptual sides. One can think about the procedure of unravelling an ensemble dynamics as being equivalent to going, classically, from a macroscopic thermodynamic view in terms of evolution of ensemble properties to a stochastic thermodynamics formalism which describes the dynamics of a system as a mean value of trajectories of microstates in phase space. In the quantum case, the time evolution of a density matrix (ensemble state) can be obtained by averaging over a high number of stochastic pure state trajectories (the equivalent of phase space trajectories), which are generated accordingly to a number of different methods [71, 124, 125].

Clearly, as measuring the state of a quantum system fundamentally affects its evolution, one has to carefully comment on the physical realizability of single quantum trajectories. Among the existing methods, one in particular is employed in Chapter 5 to study features of nonequilibrum fluctuations and it is therefore worth introducing it here. It goes under the name of stochastic wave function method [74, 126, 127], and describes the situation in which the dynamics of a system is continuously monitored by performing measurements on its environment. Intuitively, this is the "less invasive" way of measuring the time evolution of a single system [128]. Information about its state is extracted from the reservoir by measuring a certain set of effects of system-bath interaction. Imagine, for instance, the open system to be a two-level atom interacting with a radiation field acting as reservoir. The atom-field interaction is mediated by emission or absorption of single photons (which I refer to as transition photons), which can be experimentally detected in the field by performing almost-continuous measurements (i.e., a discrete set of measurements separated in time by a very small time interval δt) on it. A result of a single measurement can either be the detection of a transition photon (absorbed or emitted), or no detection of transition photons. In the first case, one registers the pure state of the atom to have performed a transition (for example, from its excited state to its ground state in the case of emission), while in the second case the pure state evolves in a deterministic (although not unitary) way. Since one has no *a priori* information about the result of measurements, there is no way of predicting the behaviour of the system wave function which becomes then a stochastic variable. The sequence of pure states the system follows conditioned on a set of measurement records is known as quantum trajectory. I refer the reader to Chapter 5 for further discussions and a rigorous formalisation of the method.

Here, to conclude, it is worth stressing that by generating an ensemble of (a high number of) trajectories of this kind and considering average values of physical quantities characterising them, one perfectly recovers the full information available in the master equation formalism [71].

Chapter 2

Quantum equilibrium thermodynamics

Equilibrium thermodynamics encompasses a vast landscape of phenomena, ranging from the definition of macroscopic equilibrium states and quantities characterising them, to the theory of reversible transformations and the one of phase transitions and further to certain formulations of the laws of thermodynamics, not to mention the formalisation of quantum statistics stemming from the spin-statistics theorem and their consequences on the structure of ensemble states of identical particles.

Two main conceptual areas can roughly be identified when one tries to sort out all these different topics, which may be referred to as stationary phenomena and adiabatic transformations. The first area deals with the physical characterisation of properties which do not change in time, neither due to the interaction with an environment nor to the action of an external force tuning some parameters of a system. To this class belong the theory of equilibrium states, of stationary fluxes, and of quantum equilibrium statistics. The second area, on the other hand, deals with those phenomena generated by an adiabatic tuning of some properties of a system. A typical example is the huge class of so-called reversible transformations, in which the system is, at each time instant, very close to an equilibrium state and moves therefore along an (ensemble) equilibrium trajectory. The celebrated Carnot cycle is probably the most famous example of phenomena of this kind.

But there is also another topic of extremely huge interest belonging to this kind of adiabatic transformations, i.e. the physics of a system at a phase transition. When one tunes a certain set of parameters characterising the initial equilibrium state of a system, in such a way that the evolution thus generated is adiabatic (i.e., analogously to reversible transformations, the system follows an ensemble path such that, at each time instant, it is found in an equilibrium state characterised by the instantaneous value of the tuned parameters), a critical point can be met and the system undergoes a phase transition. In this case, the system shows a collective behaviour which is surprisingly the same for large collections of microscopically different models. These sets of collective behaviours are known as universality classes [129]. Clearly, everyone is familiar with the notion of thermal phase transition thanks also to everyday life experiences. There exists, however, a different kind of critical phenomena which shares the same set of universality classes with the thermal transitions but originates from a different physical effect. Such phenomena for a system in its thermodynamic limit are known as quantum phase transitions [14].

The first part of my results, presented and discussed in Chapter 3, deals with some special issues in quantum equilibrium thermodynamics mainly related to the vast topic of quantum phase transitions and of state entanglement characterisation. Therefore, before proceeding to them, I will give in this Chapter some pieces of information on the state of the art of these two interesting research lines.

2.1 Quantum phase transitions

In view of the previous discussion, consider then a system with Hamiltonian $H(\lambda)$ depending on a parameter λ which can be tuned at will [13]. Such a parameter, in the most common cases, is for example a coupling constant describing some internal or external interaction of the system. Suppose that one can modify the value of such a parameter adiabatically. This generates a class of Hamiltonian spectra, each of which is characterised by its ground state with a well-defined energy. One can then look at this set as a parameter-dependent ground state $|g(\lambda)\rangle = |\psi_1(\lambda)\rangle$ (suppose for simplicity the ground state energy to be non-degenerate), a piecewise continuous function of λ, which describes the "thermal" state of the system when the parameter is changed adiabatically at zero temperature. Indeed, along the adiabatic path the system stays always infinitely close to the instantaneous zero temperature thermal equilibrium state, i.e. follows adiabatically the modifications of its ground state. The structure of the state $|\psi_1(\lambda)\rangle$ may or may not change with λ, but assume here that at least some of its physical properties stay unchanged: these properties define the quantum phase of the system and are usually referred to as order parameters.

As a simple example, imagine that at a critical value λ_c the ground state changes from $|\psi_1(\lambda_c - \delta\lambda)\rangle$ to $|\psi_2(\lambda_c + \delta\lambda)\rangle$ because of a level crossing in the ground state energy. What happens physically is that, calling $E_{1(2)}(\lambda)$ the energy associated to $|\psi_{1(2)}(\lambda)\rangle$, one has

$$\begin{aligned} E_1(\lambda) &< E_2(\lambda) \text{ for } \lambda < \lambda_c, \\ E_1(\lambda_c) &= E_2(\lambda_c), \\ E_1(\lambda) &> E_2(\lambda) \text{ for } \lambda > \lambda_c, \end{aligned} \tag{2.1}$$

so that the ground state energy $E_g(\lambda)$ is

$$E_g(\lambda) = \Theta(\lambda_c - \lambda)E_1(\lambda) + \Theta(\lambda - \lambda_c)E_2(\lambda), \tag{2.2}$$

$\Theta(x)$ being the Heaviside step function. Eq. (2.2) defines a *ground state level crossing.* In this situation, for $\lambda = \lambda_c - \delta\lambda$ the system occupies the ground state $|\psi_1\rangle$. After crossing the critical point, the system thermalises again to a zero-temperature Gibbs state and is found in the ground state $|\psi_2\rangle$. If now $|\psi_1\rangle$ and $|\psi_2\rangle$ are characterised by different values of order parameters, the system undergoes a transition between two well-defined phases. In this example, the transition is sharp and may happen for finite as well as for infinite systems and one usually refers to it as a first order quantum phase transition or I-QPT, characterised by a sudden jump in the value of the order parameter. Another possibility, known as second order quantum phase transition or II-QPT (and much more common in the thermodynamic limit), happens when the level crossing discussed above is obtained as a limit of an avoided level crossing whose width tends to zero with the number of components of the system. In this second case the transition is smooth, and the order parameter changes continuously growing, after the critical point is crossed, from zero to a value characterising the new phase. This transition can clearly happen only in the thermodynamic limit. In both cases, anyway, the critical point in parameter space is characterised as being a non-analytical point of the ground state energy [55], in which either its first derivative or one of its higher order derivatives with respect to λ does not exist.

There are at least two very famous examples of QPTs. The first one is detected in a chain of spin 1/2 particles, each of which interacts with its first neighbours and with an external magnetic field applied along a direction which is orthogonal to the spin-spin coupling direction [130]. The Hamiltonian of such a system is, for example, of the form

$$H_{\mathrm{Is}} = -h \sum_i \sigma_i^z - \kappa \sum_{<ij>} \sigma_i^x \sigma_j^x, \tag{2.3}$$

where $\sigma_i^{(z,x)}$ are Pauli matrices of the spin at chain site i, $h > 0$ is the coupling of each spin to the local magnetic field (assumed to be uniform) applied in the z direction and $\kappa > 0$ is a spin-spin interaction parameter. The Hamiltonian (2.3) describes the famous Ising model in a transverse field, widely employed in classical and quantum thermodynamic contexts since it represents one of the few analytical solvable models of experimental interest [131].

As it comes clear just by looking at the structure of Eq. (2.3), two competing effects characterise the features of the ground state. On the one hand, when $h \gg \kappa$, the magnetic effect dominates and in the ground state all the spins tend to be aligned along the z direction so that their magnetic energy is minimised. The ground state is therefore of the form $|g\rangle_h = \prod_i |+_z\rangle_i$, where $|+_z\rangle_i$ is the eigenstate of σ_i^z corresponding to the eigenvalue +1. There is no correlation between the magnetisation at each site and the system behaves as a paramagnet. On the other hand, in the opposite limit $\kappa \gg h$ the mutual spin-spin interaction tends to align them along the x direction such that each spin is parallel to its neighbours. The ground state is degenerate, being $|g\rangle_\kappa^\pm = \prod_i |\pm_x\rangle_i$, having defined $|\pm_x\rangle_i$ as the eigenstates of σ_i^x corresponding to the eigenvalues ± 1. Clearly, for both of the possible ground states in this phase there is a long-range correlation of the single site magnetisation such that the system as a whole shows a spontaneous macroscopic magnetisation and behaves as a ferromagnet. This II-QPT between the quantum paramagnetic and the quantum ferromagnetic phase happens, by tuning h or κ, at the critical point $h = \kappa$.

The second model of interest, already discussed in the previous Chapter, is the Bose-Hubbard model [45, 100]. As anticipated when commenting on the physics of cold atoms in optical lattices, the Hamiltonian (1.21) comprises two opposite effects, i.e. the tunnelling term and the onsite interaction. These two contributions tend to generate very different properties in the ground state of the system: indeed, when the tunnelling term dominates ($J \gg U_0, U_2$) the atomic wave function is delocalised over the full lattice and the system behaves as a superfluid; on the other hand, if the intra-site interaction is much stronger than the site-site coupling ($U_0, U_2 \gg J$), the less energetic configuration is the one in which each atomic wave function is localised in a potential well and the system as a whole behaves as an insulator. Once again, a quantum transition connects these two phases, at a critical point which depends among other things also on the atomic chemical potential and on the average occupancy number of atoms in each lattice site [105, 106].

There exists a strong connection between quantum and thermal critical behaviour: indeed, a quantum phase transition of a d-dimensional system can be mapped onto a thermal phase transition of a fictitious $(d+z)$-dimensional system, where z is the dynamic critical exponent characteristic of the universality class the particular transition belongs to. Moreover, in many cases a quantum critical point can be seen as the limit at $T \to 0\,\mathrm{K}$ of a thermal critical line in the (T, λ)-space. In this section I do not want to give a comprehensive treatment of this fascinating, yet very vast topic. A number of beautiful review works [13, 14] on the field have been published in recent years and I therefore refer to them for further details.

Strictly speaking, a QPT is a transition between ground states and happens therefore at zero Kelvin. This is the most striking difference between classical and quantum transitions, as a classical system has no fluctuations when frozen at absolute zero and therefore can show no critical behaviour. This is not the case for a quantum system, whose features generate even strong fluctuations also in pure states. Although then, at a first glance, a quantum critical point may seem unphysical (after all, phenomena happening only at zero Kelvin are not within experimental reach), their existence leaves signatures on the behaviour of a system in their vicinity at low but non-zero temperatures, thanks to the fact that in most cases quantum features are not immediately suppressed by thermal fluctuations and there is a wide area where an interplay between them can be witnessed. Since Chapter 3 deals with systems having discrete energy spectra, I will analyse here this case in slightly more details.

For a system with a discrete spectrum in a Gibbs equilibrium state, thermal fluctuations originate from the statistical occupancy of all its energy eigenstates according to the usual Boltzmann distribution. The more excited states are significantly occupied, the less the structure of the ground state only affects the physics of the system and the less, therefore, one can witness consequences of a quantum critical point at finite temperatures. Consider indeed equation (1.4) which specifies the regime where one may expect thermal fluctuations to dominate over quantum ones. In the case under scrutiny, the characteristic frequency ω, at low temperature, is related to the energy gap Δ between ground and first excited state roughly as $\hbar\omega = \Delta$. In the vicinity of a ground state level crossing at $\lambda = \lambda_c$, then, depending on how fast Δ vanishes approaching λ_c, there may exist a range of temperature of experimental interest at which

$$k_B T < \Delta, \tag{2.4}$$

such that quantum effects still dominate thermal ones in this whole non-zero temperature range. Physically, this means that the populations of the system's first excited states are, in this range of temperatures, negligible compared to the population of the ground state, whose structure drives then the behaviour of the Gibbs state. Incidentally, note that the interplay between the average energy $k_B T$ absorbed from a bath and gaps in the Hamiltonian spectrum characterises the quantity known as heat capacity C_V, which might then be expected to be a good probe for a quantum critical point at non-zero temperature. In Chapter 3 I will show that this is indeed the case.

As briefly commented in Chapter 1, moreover, a QPT is always associated to a singularity in some entanglement quantifiers (I-QPT) or in one of their derivatives (II-QPT) [54, 55, 56, 57], highlighting how the long range correlations responsible for the transition between two quantum phases are of non-classical origin. All these features motivate part of the research I performed, which is the subject of Chapter 3 and links critical points in parameter space to a sudden jump in bipartite internal entanglement and to some general behaviour of measurable thermal quantities for some simple few-body systems.

2.2 Entanglement and mixedness

In view of the previous discussion, a quantum criticality at finite temperature can be detected when there is a competition between quantum features inside a system and thermal fluctuations induced by a coupling with a bath. Exploiting the results of [31], discussed in Chapter 1 and showing how the structure itself of a thermal equilibrium state can be seen as originating from the system and its thermal bath being in an entangled total pure state, such a competition can be traced back to an interplay between internal (i.e., between two subsystems) and external (i.e., with an environment) non-classical correlations shown by a quantum system. For this reason, such an interplay is described here in some details.

In addition to the structure of thermal states and thermal properties, the link between internal entanglement and the mixedness (i.e., how far the system is from being in a pure state) of a quantum state, which can always be thought as originating from external entanglement with an environment, is of paramount importance in the framework of quantum information and quantum computation, since entanglement is one of - if not the - most important tools to overcome, e.g., classical computation limits. Studies about the influence of external reservoirs on internal non-classical correlations, and schemes to protect these correlations from unwanted effects, such as decoherence, due to the presence of structured environments are of huge conceptual and practical interest [108, 109, 110, 132]. The concept here is simple: the more mixed the state of a system is, the stronger the perturbation exerted by an environment is, and the less information can be encoded within the system in the form of internal correlations [133, 134]. This feature can be rephrased as: the more system and environment are correlated, the less two parts of the system can correlate due to the so-called monogamy of entanglement [135]. A number of analytical and numerical results are available, describing and exemplifying such a behaviour.

Probably the most famous example of results connecting bipartite entanglement and mixedness is the so-called *absolute separability of the Kuś-Życzkowski ball* [133]. Consider a quantum system S whose state ρ lives in a d-dimensional Hilbert space. One can wonder whether it is always possible to choose appropriately two subsystems of S such that ρ, with respect to such a bipartition, is entangled. If this is not possible for any bipartition, the state is said to be absolutely separable. It can be shown that absolutely separable states always exist: the typical example of this class of states is the maximally mixed state $\frac{1}{d}\mathbb{I}$ which, being proportional to the identity, assumes always the same uncorrelated structure in any possible basis in the Hilbert space and whose purity is $\frac{1}{d}$. The result by Kuś and Życzkowski shows that all the states belonging to the hypersphere centred on the maximally mixed state, and whose surface is composed of states having purity $P_c = \frac{1}{d-1}$, are absolutely separable. As a consequence, there is an upper threshold to the mixedness of a state, over which no information in the form of bipartite entanglement can be encoded in a quantum state.

Since, however, one often can not avoid the system of interest to be correlated with an environment, it is of great interest to characterise the maximal amount of entanglement a state can sustain at fixed mixedness. Mixed states having, across an appropriate bipartition, this maximum entanglement are referred to as Maximally Entangled Mixed States (MEMS) [136] and their characterisation is one of the most active researches in the field. Although the exact structure of MEMS is not known in the general case, a number of upper and lower bounds of entanglement and mixedness are known [134] and widely used in, e.g., experimental entanglement estimation through purity measurements. As an example, consider the entanglement quantifier known as Negativity N introduced in Eq. (1.16), and the simplest quantifier of mixedness $P_E(\rho) = 1 - \mathrm{Tr}\rho^2$. Since partial transposition does not modify the eigenvalues of a matrix, the mixedness can be evaluated also on the matrix ρ^{T_1} involved in the definition of N. In terms of its eigenvalues $\{\mu_i\}$, therefore, Negativity and mixedness are given as

$$N = \frac{\sum_i |\mu_i| - 1}{d_m - 1}, \tag{2.5}$$

$$P_E(\rho) = P_E(\rho^{T_1}) = 1 - \sum_i |\mu_i|^2. \tag{2.6}$$

It comes clear from the comparison of Eqs. (2.5) and (2.6) that these two quantities are not independent. Indeed, a simple bound can be obtained by employing the so-called Chebyshev sum inequality $\left(\sum_i^d |a_i|\right)^2 \leq d\sum_i |a_i|^2$. One straightforwardly gets

$$N \leq \frac{1}{d_m - 1}\big(\sqrt{d}\sqrt{1 - P_E} - 1\big), \tag{2.7}$$

bounding the entanglement across any bipartition (at least, the one detectable by the positive partial transpose criterion) by means of a simple mixedness measure, which incidentally can be also experimentally accessed.

The connection of entanglement to the purity of a state is of great interest in the context of quantum equilibrium thermodynamics: in the case of a Gibbs thermal state, the purity measures how strong thermal fluctuations are with respect to the ones characterising the ground state and is then related to the structure and behaviour of standard thermal quantities.

2.3 Gaussian approximation for many-body systems

As a last section of this thematic introduction to equilibrium thermodynamics, I discuss an approximation which is often used in studying thermodynamic properties of many-body systems. This is necessary in view of a full understanding of Chapter 3, where some of my results on this approximation are presented clarifying its limits and highlighting its range of applicability.

The thermodynamics of most everyday-scale phenomena, e.g phase transitions, often reflects the underlying existence of a complex microscopic many-body dynamics which is approachable, generally speaking, in statistical terms only. Understanding the collective behaviour of physical systems comprising a myriad of interacting or not, classical or quantum particles constitute indeed an endless challenge. Experimental and technological successes in recent years do indeed open new problems on a variety of many-body systems [11, 131], to be dealt with by making recourse to the ideas and methods of statistical physics. The correspondent theoretical task is to contrive simple enough but well addressed microscopic models as well as to develop, within the Gibbs framework, widely applicable mathematical/numerical tools leading to predictions of experimental interest.

Recently an interesting approach based on a generalised version of the Central Limit Theorem (CLT) has been proposed by Hartmann, Mahler and Hess [139] and, at least for some specific class of problems, it turns out to be a simple yet powerful predictive tool. Such a method relies on a Gaussian approximation (GA) for the distribution of physical properties of quantum systems. Here I briefly review this Gaussian method, originally presented in [139] and based on a mathematical theorem proven in [140]. The method applies to any linear system whose Hamiltonian can be written as a sum of single site or single block terms, which is often the case for many models of interest [82, 141].

Consider then a many-body system consisting of an N_b-block quantum linear chain with Hamiltonian $H = \sum_{\mu=1}^{N_b} \mathcal{H}_\mu$, where $\mathcal{H}_\mu$ is an operator composed of the block self-Hamiltonian and the interaction $I_{\mu,\mu+1}$ between blocks μ and $\mu+1$, reading

$$\mathcal{H}_\mu = \mathbb{I}^{\otimes(\mu-1)} H_\mu \mathbb{I}^{\otimes(N_b-\mu)} + \mathbb{I}^{\otimes(\mu-1)} I_{\mu,\mu+1} \mathbb{I}^{\otimes(N_b-\mu-1)}, \tag{2.8}$$

$\mathbb{I}$ being the identity operator in the single-block Hilbert space. Each block is described by a finite-dimensional Hilbert space with dimensionality d, the dimension of the total Hilbert space thus being d^{N_b}. It may consist, e.g., of one or several neighbouring spins. Given a total Hamiltonian H, one may define the partitioning into blocks in many different ways. It is worth stressing, however, that the GA applies as long as the dimension of the Hilbert space of each block stays finite.

Define now two bases of the total Hilbert space of the system. The first one, whose vectors will be written as $|\phi\rangle$, is composed of eigenstates of H such that $H|\phi\rangle = E_\phi|\phi\rangle$. The second basis is made up of factorized vectors, written as $|a\rangle = \prod_\mu |a_\mu\rangle$, where each $|a_\mu\rangle$ is a local basis state of block μ. Finally, the two Gaussian parameters are defined as

$$\begin{aligned}\overline{E_a} &= \langle a|H|a\rangle, && (2.9)\\ \Delta_a^2 &= \langle a|H^2|a\rangle - \langle a|H|a\rangle^2. && (2.10)\end{aligned}$$

Note that, thanks to the structure (2.8), the evaluation of the mean values in Eqs. (2.9) and (2.10) does not usually involve technical problems. To calculate the free energy and other thermodynamic quantities within the Gaussian Approximation, one needs know only these two parameters and the ground state energy, and for this reason the Gaussian method is more appealing than other, much more sophisticated methods. From the definitions given above, it is possible to build the operator

$$\zeta = \frac{H - \overline{E_a}}{\Delta_a} \tag{2.11}$$

with eigenvalues z_ϕ. It was shown in [140] with the use of a Central Limit Theorem, that under the condition that a constant $C > 0$ exists such that $\Delta_a^2 \geq N_b C$, the following limit strictly holds:

$$\lim_{N_b \to \infty} \mathrm{P}_a(z_\phi \in [z_1, z_2]) = \int_{z_1}^{z_2} \frac{e^{-\frac{z^2}{2}}}{\sqrt{2\pi}} dz, \tag{2.12}$$

where $\mathrm{P}_a(z_\phi \in [z_1, z_2]) \equiv \sum_{\{|\phi\rangle : z_1 \leq z_\phi \leq z_2\}} |\langle a|\phi\rangle|^2$.

If one naively applies these results to the calculation of the density of states $\eta_G(E)$ and of the partition function Z_G, one readily obtains the following expressions [139], which constitute the core of the GA method:

$$\begin{aligned}\eta_G(E) &= \sum_{\{|a\rangle\}} \frac{e^{\frac{(E-\overline{E_a})^2}{2\Delta_a^2}}}{\Delta_a\sqrt{2\pi}}, && (2.13)\\ Z_G &= \int_{E_g}^{+\infty} \eta_G(E) e^{-\beta E} dE = \sum_{\{|a\rangle\}} \frac{1}{2} e^{-\beta\overline{E_a} + \frac{\beta^2\Delta_a^2}{2}} \mathrm{erfc}\Big(\frac{E_g - \overline{E_a} + \beta\Delta_a^2}{\Delta_a\sqrt{2}}\Big), && (2.14)\end{aligned}$$

where E_g is the ground state energy of the system, the summation is extended over the whole factorized basis $\{|a\rangle\}$ and $\mathrm{erfc}(x)$ is the conjugate Gaussian error function. Here β is the inverse temperature in units of k_B. Note that the evaluation of Eqs. (2.13) and (2.14) requires only the knowledge of the two Gaussian parameters $\overline{E_a}$ and Δ_a^2 (not hard to calculate following Eqs. (2.9) and (2.10)) and of the ground state energy, which can usually be obtained through, e.g., numerical methods.

It should however be emphasized that, rigorously speaking, Eq. (2.12) does not imply Eqs. (2.13) and (2.14), since the number of terms in the latter equations grows exponentially with the number of blocks N_b while $\mathrm{P}_a(z_\phi \in [z_1, z_2])$ converges to (2.12) as $\frac{1}{\sqrt{N_b}}$ [139]. As indeed stated in [139], the reason is that the convergence of the distribution $\mathrm{P}_a(z_\phi \in [z_1, z_2])$ is too weak to justify the summation of a large (infinite, in the limiting case) number of terms appearing in Eqs. (2.13) and (2.14). Thus these equations must be considered as an approximation motivated by a Central Limit Theorem, whose domain of validity should be carefully established. This has been the subject of part of my research discussed in the next Chapter.

Chapter 3

Results on quantum equilibrium thermodynamics

This Chapter deals with the results about quantum equilibrium thermodynamics I obtained during my PhD studies [142, 143, 144, 145]. It is divided into two sections in order to single out the main conceptual areas in which these results are inscribed: the first section concerns the connection between entanglement, thermal quantities and quantum critical points, while in the second the applicability and the limits of the previously presented Gaussian Approximation to many-body quantum systems is discussed.

3.1 Entanglement and thermal properties

This Section deals with the influence entanglement has on thermal equilibrium properties and, in parallel, the way physical quantities characterising a Gibbs state can probe the presence of low-lying level crossings in the energetic spectrum of quantum systems. The crossings are known to generate a sudden jump of quantum correlations, characterising what has been referred to as first order quantum phase transitions. In this section, then, critical phenomena are always meant to be I-QPTs. These results, published in [142, 143, 144], have been obtained by me [142], working together with Dr. A. Napoli and Prof. A. Messina [143] and also with Prof. H. Nakazato [144].

3.1.1 The general picture

I discuss now the general part of my results, which shows a universal connection between the heat capacity of a system and the existence of a quantum critical point. The heat capacity will also turn out to be connected with the possibility for the system itself of forming bipartite quantum correlations. The results discussed in this part have been published in [142].

In view of what has been said in Chapter 1 about the origin and structure of thermal equilibrium states [31], consider a $d-$dimensional system with a discrete (possibly degenerate) spectrum Hamiltonian

$$H_S|i\rangle = E_i|i\rangle. \tag{3.1}$$

The Gibbs equilibrium state of such a system has the form

$$\rho = \frac{1}{Z}\sum_{i=1}^{d} e^{-\beta E_i}|i\rangle\langle i|, \tag{3.2}$$

where Z is the partition function of the open system, while the state of the total system (open system plus bath) can be assumed to be in the pure state $\rho_{\text{tot}} = |\Psi\rangle\langle\Psi|$, an eigenstate of the total Hamiltonian H_{tot}. This state being pure, the purity of ρ in Eq. (3.2) measures the entanglement of the open system with its environment. In particular, the already introduced mixedness parameter $P_E = 1 - \text{Tr}\rho^2$ assumes in this case the form

$$P_E = \frac{Z^2 - \sum_i e^{-2\beta E_i}}{Z^2} = \sum_{i\neq j} P_E^{ij}, \tag{3.3}$$

having defined $P_E^{ij} = \frac{e^{-\beta(E_i+E_j)}}{Z^2}$. One sees then that the mixedness of a thermal state originates from individual contributions from every couple of (different) energy eigenvalues. The correlations with a thermal bath, as evident in Eq. (3.3), originate from an exchange of energy whose main effect is to populate all the Hamiltonian eigenvalues of the open system. This effect, as commented in the previous Chapter, tends to hide the effect of a quantum critical point in the Hamiltonian parameters space and this interplay is at the core of the results presented in this Section. Having this in mind, it is of interest to analyse the way a change in temperature modifies the statistical occupancy of energy levels and, as a consequence, the system-environment correlations. This is investigated by the study of the quantity known as heat capacity, defined as $C_V = -\beta^2\frac{\partial U}{\partial\beta} = \beta^2\left(\langle H_S^2\rangle - \langle H_S\rangle^2\right)$, U being the internal energy of the system. It is nothing but the variance of the Hamiltonian operator compared to the mean thermal energy and, in the formalism used here, reads

$$C_V = \beta^2\sum_{i\neq j} P_E^{ij}\Delta_{ij}^2, \tag{3.4}$$

with $\Delta_{ij}^2 = \frac{(E_i-E_j)^2}{2}$.

There is thus a close connection between the expression of the parameter P_E and the form of C_V . Indeed, they both are expressed as a sum over $i \neq j$ of terms depending on each possible couple of energy levels of the open system. A closer look at Eq. (3.4) shows that each of these contributions to $C_V = \sum_{i\neq j} C_V^{ij}$ has the form

$$C_V^{ij} = P_E^{ij}\frac{(E_i - E_j)^2}{2T^2}, \tag{3.5}$$

highlighting how the heat capacity resembles the mixedness of the state if viewed in terms of its energy content. In this sense purity and heat capacity are closely related, both measuring how mixed a state is: the former from a statistical point of view and the latter from an energetic point of view. One can identify two different contributions in the expression for each C_V^{ij}: the first one, P_E^{ij}, is related to how much the pair of levels E_i, E_j contributes to the mixedness of the state ρ in (3.2). The second one, $\frac{(E_i-E_j)^2}{2T^2}$, depends on how distinguishable the energies of two states are with respect to the mean thermal energy: a couple of degenerate energy levels gives no contribution to heat capacity.

The key step now is to turn the attention to the meaning of the parameter P_E in a quantum context. Indeed, as already pointed out, this parameter measures the entanglement between the d-dimensional open thermalised system and its thermal bath. In particular, when $P_E = P_{\max} = \frac{d-1}{d}$, the bath and the system are maximally entangled, while when $P_E = 0$ the total state $|\Psi\rangle$ is factorized with respect to such a bipartition. Since by definition $P_E^{ij} \geq 0\ \forall i \neq j$, the only way to obtain a vanishing P_E is having $P_E^{ij} \sim 0\ \forall i \neq j$, thus implying also $C_V^{ij} \sim 0$. One concludes that

$$P_E = 0 \Rightarrow C_V = 0. \tag{3.6}$$

From a physical point of view this means that when a thermal state of a system is pure, it necessarily consists of one of the Hamiltonian eigenstates, resulting therefore in no energy uncertainty and leading to a zero heat capacity. The next step is now to link the mixedness of the state to the entanglement the open system exhibits with respect to a possible bipartition into subsystems S_1 and S_2. It is indeed to be expected such a link to be fairly strong thanks to the property of entanglement known as monogamy [135] which ensures that, as long as system and bath are entangled, maximal bipartite entanglement inside the open system can not exist. Vice versa, when a bipartition of the system is maximally entangled, the system and the bath have to be in a separable state. Calling $e_{1,2}$ any bipartite entanglement measure on the open system, it follows that

$$e_{1,2} = \max \Rightarrow P_E = 0 \Rightarrow C_V = 0, \tag{3.7}$$

which is then a general feature of any system having discrete energy levels and of any bipartite entanglement measure on it. Note that the use of heat capacity or internal energy as entanglement witnesses has been put forward, with different results, already in [17, 18].

Let us now analyse more closely the structure of the heat capacity. Introducing the energy gaps of each excited level E_n to the ground state E_g as $\Delta_n = E_n - E_g$, Eq. (3.4) can be cast as

$$C_V = \frac{\beta^2}{2} \frac{\sum_{l,n} e^{-\beta(\Delta_l+\Delta_n)}(\Delta_l - \Delta_n)^2}{\left(\sum_n e^{-\beta\Delta_n}\right)^2}. \tag{3.8}$$

Consider now the case, which is of interest in the context of quantum critical phenomena, of a low temperature thermal state. The leading term in Eq. (3.8) is, in this limit, the one involving only the fundamental gap $\Delta_1 = E_1 - E_g$ between the ground state and the first excited level. This is reasonable since, for low enough temperatures, a thermalised system occupies with statistically relevant probability only these two energetic levels. Therefore

$$C_V \simeq C_V^{(1)} = \frac{\beta^2 \Delta_1^2 e^{-\beta\Delta_1}}{\left(1 + e^{-\beta\Delta_1}\right)^2}, \tag{3.9}$$

where Δ_1 is the energy gap between ground state and first excited level. In the framework of quantum phase transitions, since the Hamiltonian is supposed to depend on a parameter λ, this gap itself depends on such a non-thermal parameter whose variation tunes the transition, which happens when $\Delta_1 \to 0$. Eq. (3.9) in the vicinity of the point $\Delta_1 = 0$ (being nothing but the quantum critical point) describes then a characteristic behaviour of a measurable thermal quantity which can be used to probe, at non-zero temperatures, the existence of a quantum critical phenomenon. Clearly, as temperature rises, more and more gaps are involved in the expression for heat capacity and such a behaviour gets hidden. This characteristic feature of C_V as a function of Δ_1 consists of a structure with two maxima and a central minimum exactly at the critical point, closely related to the so-called Schottky anomaly[1]. Such a feature is shown in Fig. 3.1 where $C_V^{(1)}$ in Eq. (3.9) is plotted against the parameter λ on which the fundamental gap Δ_1 is assumed to depend, and which crosses a critical value λ_c.

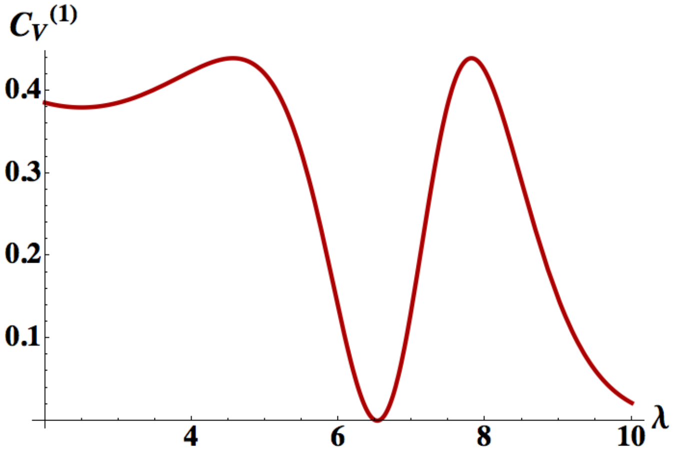

Figure 3.1: $C_V^{(1)}$ for $\beta = 1$ (arbitrary units), versus the parameter λ on which Δ_1 depends as $\Delta_1(\lambda) = 0.2\lambda^2 - \lambda - 2$. A critical point is met when $\Delta_1(\lambda_c) = 0$ and, in the vicinity of this point the heat capacity shows the two characteristic bumps (maxima) predicted by Eq. (3.9). The critical point corresponds to the central minimum.

Eq. (3.9) is completely general, only relying on the assumption of discreteness of energy levels. It describes therefore the general response of any low-temperature thermal state to quantum criticality in its parameters space.

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[1] A Schottky anomaly (also known as Schottky heat capacity) is the behaviour of heat capacity versus temperature, typical of a two level system, characterised by a maximum followed by an asymptotic decreasing toward zero [2]; the difference in the case analysed in this thesis is that temperature is fixed and the only parameter being varied is λ.

3.1.2 Two-atom Bose-Hubbard model

In the rest of this section I discuss two simple yet exemplary models in order to analyse the consequences of Eqs. (3.7) and (3.9) on their physics: a two-atom Bose-Hubbard model discussed here and a two-qubit system discussed further on. Both of these models, despite being clearly away from their thermodynamic limit, show ground state level crossing when some of their Hamiltonian parameters are tuned and therefore, as commented previously, they obey a universal behaviour which also characterises transitions in many-body systems. The results presented here on the two-atom Bose-Hubbard model have been published in [143].

3.1.2.1 Hamiltonian Model

The physics of cold atoms in an optical lattice [45], leading to the Bose-Hubbard Hamiltonian in Eq. (1.21) [100], has already been discussed in Chapter 1 showing how Eq. (1.21) takes into account tunnelling between lattice sites and atom-atom interactions within each site. Systems described by such a Hamiltonian can exist in two different phases: an insulator phase when the atom-atom interaction dominates over the tunnelling term, and a superfluid phase in the opposite limit. These two phases are connected by a II-QPT [105].

Here I am however interested in studying properties of the system in its insulating phase. I will therefore not discuss the II-QPT characterising the Hamiltonian (1.21), but focus instead on possible level crossings in the effective Hamiltonian of the insulator phase [102, 103], which in Chapter 1 was given the form of Eq. (1.22). Here an external magnetic field $\widetilde{\omega}$ is applied to the system, so that the insulating phase Hamiltonian reads

$$H_t^e = \widetilde{\omega} J_z + K_0 + K_1 \sum_{<ij>} (\mathbf{S}_i \cdot \mathbf{S}_j) + K_2 \sum_{<ij>} (\mathbf{S}_i \cdot \mathbf{S}_j)^2, \tag{3.10}$$

where again $\mathbf{S}_i$ represents the total spin operator in the i-th site and $\mathbf{J} = \sum_i \mathbf{S}_i$. The effective coupling constants K_0, K_1, K_2 are related to the parameters t, U_0 and U_2 entering the microscopic Hamiltonian (1.21) [102, 103] as

$$\begin{aligned} K_0 &= \frac{4t^2}{3(U_0+U_2)} - \frac{4t^2}{3(U_0-2U_2)}, \\ K_1 &= \frac{2t^2}{U_0+U_2}, \\ K_2 &= \frac{2t^2}{3(U_0+U_2)} + \frac{4t^2}{3(U_0-2U_2)}, \end{aligned} \tag{3.11}$$

and satisfy the simple equation $K_0 = K_1 - K_2$. In the deep Mott-insulator phase, where (3.10) holds, the tunnelling amplitude t is usually of the order of some kHz but can be also made as small as a few Hz [146]. Measuring the energy in units of t, H_t^e in the case of two atoms only can be cast in the following form

$$\frac{H_t^e}{t} \equiv H = \omega J_z + \tau(\mathbf{S}_1 \cdot \mathbf{S}_2) + \gamma(\mathbf{S}_1 \cdot \mathbf{S}_2)^2 + r\mathbb{I}, \tag{3.12}$$

where

$$\tau = \frac{K_1}{t}, \quad \gamma = \frac{K_2}{t}, \quad \omega = \frac{\widetilde{\omega}}{t}, \quad r = \tau - \gamma, \tag{3.13}$$

and $\mathbb{I}$ is the identity operator in the 9-dimensional Hilbert space of the system. The term proportional to identity in Eq. (3.12) can not be neglected if one wants to investigate the system in its full parameters space.

It is worth noting, in connection with the simplicity of the Hamiltonian model, that such a kind of two-atom models has recently attracted interest in the context, e.g., of the study of tunnelling phenomena [147], mostly connected to Josephson tunnelling between spin condensates [148]. It is moreover appropriate to underline that the physical analysis relies on arguments which are fully general and might thus be useful in the interpretation of analogous physical properties related to more complex physical scenarios (many-atom Bose-Hubbard models, central spin systems, spin chains, etc).

3.1.2.2 Thermal entanglement

The Hamiltonian in Eq. (3.12) can be rewritten, introducing the total spin operator $\mathbf{J} = \mathbf{S}_1 + \mathbf{S}_2$, as

$$H = \omega J_z + \frac{\tau}{2}(J^2 - 4\mathbb{I}) + \frac{\gamma}{4}(J^2 - 4\mathbb{I})^2 + r\mathbb{I}, \tag{3.14}$$

and is therefore diagonal in the coupled basis $|jM\rangle$ of common eigenstates of J^2 and J_z with associated eigenvalues equal to $j(j+1)$ and M respectively. Its energy eigenvalues are

$$E_{jM} = \omega M + \frac{\tau}{2}\big(j(j+1) - 4\big) + \frac{\gamma}{4}\left[\big(j(j+1) - 4\big)^2 - 4\right] \tag{3.15}$$

Let us suppose that the system is in a thermal state at inverse temperature β. The density matrix describing the two spin-1 atoms in the optical lattice is then

$$\rho = \frac{1}{Z} e^{-\beta H}, \tag{3.16}$$

where Z has the expression

$$Z = e^{-\beta\tau}\Big[2\cosh\beta\tau\big(1 + 2\cosh\beta\omega\big) + e^{-\beta(3\gamma - 2\tau)} + 2e^{-\beta\tau}\cosh 2\beta\omega\Big]. \tag{3.17}$$

In order to quantify the thermal entanglement in the state (3.16) one can use the previously introduced Negativity N (being aware of its limitations, discussed in Chapter 1) defined as [97]

$$N = \frac{1}{2}\Big(\sum_{i=1}^{9} |\mu_i| - 1\Big), \tag{3.18}$$

where μ_i's are the eigenvalues of the matrix σ, the partial transpose of ρ with respect to one of the two spins. Writing ρ in the ordered factorized basis $\Big\{|-11\rangle, |1-1\rangle, |-10\rangle, |01\rangle, |0-$

$1\rangle, |10\rangle, |-1-1\rangle, |00\rangle, |11\rangle\Big\}$, and transposing with respect to the spin labeled as 1 leads to

$$\sigma = \begin{pmatrix} R_+ & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & R_+ & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & P_- & Q_- & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & Q_- & P_+ & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & P_- & Q_- & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & Q_- & P_+ & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & L_- & M_- & R_- \\ 0 & 0 & 0 & 0 & 0 & 0 & M_- & Q_+ & M_+ \\ 0 & 0 & 0 & 0 & 0 & 0 & R_- & M_+ & L_+ \end{pmatrix} \tag{3.19}$$

with

$$\begin{aligned} L_\pm &= \frac{1}{Z} e^{-2\beta(\tau \pm \omega)}, \\ M_\pm &= -\frac{1}{Z} e^{-\beta(\tau \pm \omega)} \sinh(\beta\tau), \\ P_\pm &= \frac{1}{Z} e^{-\beta(\tau \pm \omega)} \cosh \beta\tau, \\ R_\pm &= \frac{1}{6Z} e^{-\beta\tau} \big(e^{-\beta\tau} \pm 3e^{\beta\tau} + 2e^{-\beta(3\gamma - 2\tau)} \big), \\ Q_\pm &= \frac{1}{3Z} e^{-\beta\tau} \Big(\frac{3 \pm 1}{2} e^{-\beta\tau} \pm e^{-\beta(3\gamma - 2\tau)} \Big). \end{aligned} \tag{3.20}$$

Six of the nine eigenvalues can be written in the form

$$\begin{aligned} \mu_1 = \mu_2 &= \frac{1}{2}\Big(P_+ + P_- - \sqrt{\left(P_+ - P_-\right)^2 + 4Q_-^2} \Big), \\ \mu_3 = \mu_4 &= R_+, \\ \mu_5 = \mu_6 &= \frac{1}{2}\Big(P_+ + P_- + \sqrt{\left(P_+ - P_-\right)^2 + 4Q_-^2} \Big), \end{aligned} \tag{3.21}$$

while the last three eigenvalues can be obtained solving the secular equation associated to the 3×3 block

$$B = \begin{pmatrix} L_- & M_- & R_- \\ M_- & Q_+ & M_+ \\ R_- & M_+ & L_+ \end{pmatrix}. \tag{3.22}$$

Since the algebraic expression of these last three eigenvalues of σ is quite involved and does not exhibit features deserving special attention, I do not report them explicitly. The knowledge of the eigenvalues μ_i, functions of both temperature and the three model parameters, allows one to investigate, at a given temperature, the behaviour of entanglement in the parameters space. The effect of the nonlinear effective coupling between the two atoms on the thermal entanglement has already been qualitatively investigated in the past [149]. It has been found that the quadratic interaction term favours the existence of thermal entanglement which, however, can survive only for absolute values of the quadratic parameter $\gamma < 0$ larger than a critical value γ_c. In the presence of an external magnetic field ($\omega \neq 0$) the system shows two different phases, one corresponding to $N = 1$ and the other one to $N = 0$, and the value of γ_c at which the transition takes place is dependent on ω. These results have anyway been obtained neglecting from the very beginning the linear interaction term whose intensity is measured by τ in the Hamiltonian model (3.12). I investigated the role played by the linear term in competition with the quadratic and magnetic ones.

3.1.2.3 Results

The negativity N against the linear interaction parameter τ, for ω and γ fixed (and equal to t), is depicted in Fig. 3.2 in correspondence to the three values of average thermal energy $T = 0.05$, $T = 0.6$ and $T = 1$ (in units of k_B and t). The addition of the term proportional to τ to this model is at the origin of an intermediate phase (plateau of the negativity $N = \frac{1}{2}$), so that N undergoes two transitions (vertical lines) differently from what happens when $\tau = 0$ where only one transition is present as shown in Fig. 2 of Ref. [149] and in Fig. 3.3 of this Chapter.

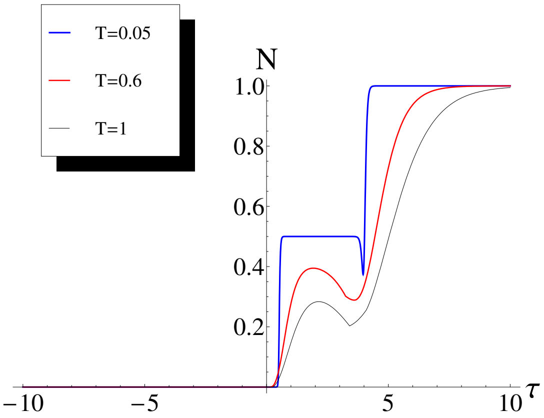

Figure 3.2: Negativity of the system, plotted against τ when $\gamma = \omega = 1$. Energy is measured in units of t and $k_B = 1$.

It is easy to interpret the occurrence of the intermediate phase at $N = \frac{1}{2}$ as originating from the magnetic-field-assisted competition between the quadratic term and the linear one when both γ and τ are positive. To appreciate this point it is enough to note that the two-atom system, due to a positive linear interaction, tends to minimise its total energy assuming $j = 0$ (maximally entangled state), whilst it tends to maximise both j and $|M|$ (factorized state) because of the effect of a positive quadratic interaction in the presence of a magnetic field.

Figure 3.2 shows that the two transitions become sharper for lower temperature T. Investigating the behaviour of the negativity N when the temperature T goes toward zero, it is possible to demonstrate that the smooth transitions shown in Fig. 3.2 become indeed discontinuities. In view of what has been said previously about the connection which exists between the entanglement, thermal properties and the energy spectrum, one may wonder whether this behaviour reflects the existence of level crossings in the ground state of the system. This is indeed the case since, in correspondence to the two transition points of the function N, the ground state

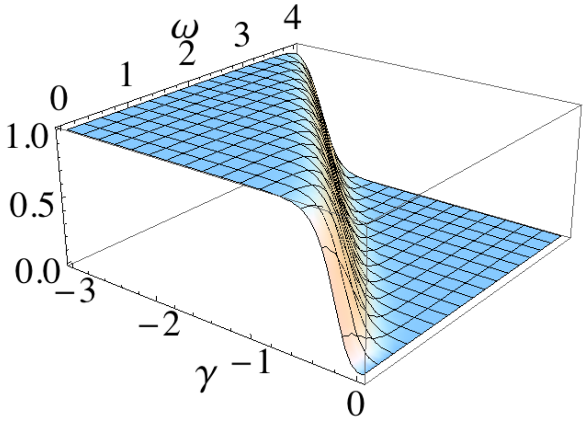

Figure 3.3: Negativity of the system, plotted against γ and ω when $\tau = 0$. Energy is measured in units of t and $k_B = 1$. Only two phases are present corresponding to $N = 0$ and $N = 1$. This plot is analogous to the one depicted in Fig. 2 of G.-F. Zhang and S.-S. Li, Optics Communications **260**, 347 (2006).

energy undergoes two level crossings. One may thus conclude that the results so far obtained for the negativity N in correspondence to low, but nonzero, values of T stem from the existence of critical points in the space of the parameters characterising the Hamiltonian of the system. Indeed, as reported in Fig. 3.4 (where, in order to realise a wider intermediate plateau, γ has been fixed to a value greater than 1 such that the transition to the upper phase occurs at a higher value of τ), the structure of the low-lying energy states of Hamiltonian (3.12) shows two ground state level crossings in **A** and **B**.

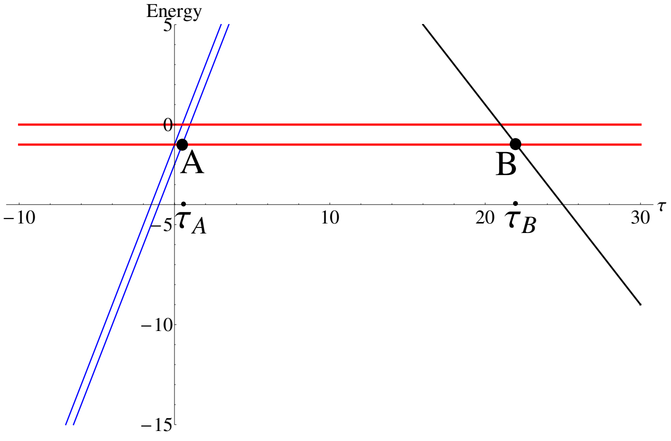

Figure 3.4: Low-lying energy levels of H (in units of t) versus τ when $\gamma = 7$ and $\omega = 1$. Each line corresponds to an energy level, and the different colours describe different groups of Hamiltonian eigenstates split by Zeeman effect. Two crossing points, **A** and **B** in the figure, are clearly visible in correspondence to the values $\tau_A = \frac{1}{2}$ and $\tau_B = 22$.

The presence of these points, where the derivative of the ground state energy clearly un-

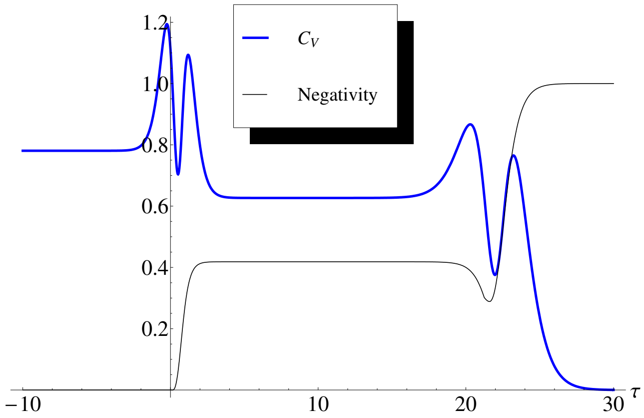

Figure 3.5: Heat capacity and system negativity plotted against τ when $T = 0.6$, $\gamma = 7$ and $\omega = 1$.

dergoes a finite jump, explains why τ_A and τ_B play the roles of analogues of quantum critical points (although, once again, the system is not in the thermodynamic limit), detected by the behaviour of the negativity. In approaching them, the gaps between low-lying energy levels exhibit structural changes going to zero and then rapidly increasing again. This behaviour does not depend on the particular choice for the parameters γ and ω: it stays qualitatively the same at whatever these two parameters are kept fixed.

One can now move to the analysis of the heat capacity of the system in the thermal state. Figure 3.5 reports the dependence of C_V on τ, straightforwardly obtained exploiting the knowledge of Z in Eq. (3.17). In the same Figure the negativity is also plotted. The fixed value of temperature T in these plots is 0.6 and has been chosen taking into account the fact that a temperature close enough to zero always gives a flat, almost vanishing C_V, while a high enough temperature would destroy thermal entanglement, making unsuccessful any attempt to compare it to the heat capacity.

Figure 3.5 exemplifies the two general predictions of Eqs. (3.7) and (3.9) and, in general, of the analysis performed in the previous Section. It demonstrates indeed the existence of a strong similarity between the behaviours of the heat capacity of the system and the one of negativity against τ. Alike the negativity function, also the heat capacity is characterised by three plateaus each of which corresponds to a well defined constant value. Moreover, the higher is the entanglement the lower is the heat capacity and vice versa and, in the maximally entangled phase with $N = 1$ the heat capacity vanishes as predicted by Eq. (3.7). Finally, in correspondence to each transition point the heat capacity shows a peculiar oscillatory behaviour with two maxima and a central minimum exactly at the critical point, which is perfectly described by Eq. (3.9) (when taking into account the explicit dependence of Δ_1 on τ, cf. with Figure 3.1) and which shows how in the vicinity of level crossings the system behaves effectively as a two-level one. These characteristic oscillations in the heat capacity are a measurable signature of a first order quantum critical point (i.e., of a quantum critical point leading to a I-QPT). It is worth noting that such a result is a general property that is independent on the limited region of the parameter space (τ, γ, ω) analysed here for simplicity.

3.1.3 A two-qubit system

The analysis performed on the two-atom Bose-Hubbard model confirms the general predictions of Eqs. (3.7) and (3.9). It is also possible, for some particular models, to go even beyond these general links between entanglement and heat capacity, and to use measurements of heat capacity to effectively quantify the entanglement in, for example, a two-qubit thermal state. This has been the subject of part of my research, whose results are published in [142, 144].

Since the knowledge of the Hamiltonian spectrum and the partition function is of great importance for the study of Eqs. (3.7) and (3.9) and, more generally, of any direct or indirect link between thermal entanglement and thermodynamic quantities, and since the physics at any first order quantum critical point is, at low temperature, fundamentally a two-level system physics, I considered a two-qubit quantum Ising model (whose Hamiltonian has been already given and commented in Eq. (2.3)), thermalised by the presence of a bath. For practical reasons, I introduce here also a y-y spin-spin interaction with the same coupling constant as the x-x term. The Hamiltonian reads

$$H = -\frac{\lambda}{2}(\sigma_1^x\sigma_2^x + \sigma_1^y\sigma_2^y) - \frac{h}{2}\sigma^z. \tag{3.23}$$

It is easy to show that, with respect to the Hamiltonian (3.23) and in the coupled spin basis, the thermal state of such a system is given by

$$\rho = \frac{1}{Z}\begin{pmatrix} e^{\beta h} & 0 & 0 & 0 \\ 0 & e^{\beta\lambda} & 0 & 0 \\ 0 & 0 & e^{-\beta h} & 0 \\ 0 & 0 & 0 & e^{-\beta\lambda} \end{pmatrix}, \tag{3.24}$$

where the partition function is $Z = 2\cosh(\beta h) + 2\cosh(\beta\lambda)$. The evaluation of the heat capacity is thus straightforward. It reads ($k_B = 1$)

$$\frac{C_V}{\beta^2} = \frac{h^2 + \lambda^2 + \frac{1}{2}(\lambda - h)^2\cosh\big(\beta(\lambda + h)\big) + \frac{1}{2}(\lambda + h)^2\cosh\big(\beta(\lambda - h)\big)}{(\cosh(\beta h) + \cosh(\beta\lambda))^2}. \tag{3.25}$$

At the same time one wants to quantify entanglement between the two qubits in the system. In order to measure the degree of quantum correlation characterising a two-spin system the typical choice is, as previously discussed, the concurrence $\mathcal{C}$. I use here this entanglement quantifier instead of the negativity thanks both to the fact that the concurrence is a true entanglement measure (without the drawbacks of negativity) and to its particularly simple expression in terms of Hamiltonian parameters. It is defined as $\mathcal{C} = \mathrm{Max}\{0, \nu\}$, where $\nu = \sqrt{\mu_1} - \sqrt{\mu_2} - \sqrt{\mu_3} - \sqrt{\mu_4}$. Remember that the μ_i's are eigenvalues of the matrix $\sqrt{\rho}(\sigma_y \otimes \sigma_y)\rho^*(\sigma_y \otimes \sigma_y)\sqrt{\rho}$ and $\mu_1 \geq \mu_2 \geq \mu_3 \geq \mu_4$. Evaluating such a quantity, after some trivial calculations, one obtains

$$\mathcal{C} = \mathrm{Max}\Big\{0, \nu = \frac{2}{Z}(|\sinh\beta\lambda| - 1)\Big\}. \tag{3.26}$$

Notice that, strictly speaking, the system in its thermal state is entangled if and only if $|\lambda| > \frac{1}{\beta}\ln(1+\sqrt{2}) = \widetilde{\lambda}$. One could be surprised noticing that such a value of λ does not depend upon h since a magnetic field is usually expected to uncorrelate single constituents of a magnetic system. Nevertheless, the partition function explicitly depends upon h in such a way that, when $h \gg \lambda$, $\mathcal{C}$ is almost zero even if $\lambda > \widetilde{\lambda}$. Only when $\lambda \gtrsim h$ the concurrence is significantly different from zero. From Eq. (6) one then obtains the concurrence as a function of the three quantities β, λ and h. Since, in most cases, the parameter on which one can exert the most detailed control is the magnetic field h, and since moreover the magnetic field does not affect the sign of ν, it is possible to keep it fixed for each value of temperature and interaction strength λ such that the three-variable function $\mathcal{C}(\beta, \lambda, h)$ can be regarded as a class of two-variable functions $\mathcal{C}_h(\beta, \lambda)$ depending on the externally tuneable parameter h.

This is particularly convenient as it allows for the possibility to invert $\mathcal{C}$ and find an analytical expression for the functions $\lambda_h(\mathcal{C}, \beta)$, valid at least in a range of values of $\mathcal{C}$.

3.1.3.1 Heat Capacity versus Concurrence: analytical results and discussion

Strictly speaking, actually, the best one can do is to find analytical expressions for the functions $\lambda_h(\nu, \beta)$ each of which, as long as $\nu \geq 0$, coincides with $\lambda_h(\mathcal{C}, \beta)$. To this end, write $\mathcal{C}$ as

$$\mathcal{C}_h = \text{Max}\Big\{0, \nu = \frac{1}{\cosh\beta h + \sqrt{1+\sinh^2\beta\lambda}}(|\sinh\beta\lambda| - 1)\Big\}. \tag{3.27}$$

As can be seen from (6), entanglement is an even function of λ. Setting then $x = \sinh\beta\lambda$ and $a = \cosh\beta h$ and limiting the analysis to positive values of λ, results in $\nu = \frac{x-1}{a+\sqrt{1+x^2}}$.

It is then straightforward to obtain

$$\lambda_h(\nu, \beta) = \frac{1}{\beta}\text{ArcSinh}\Big(\frac{a\nu + 1 + \nu\sqrt{(a\nu+1)^2 + 1 - \nu^2}}{1-\nu^2}\Big). \tag{3.28}$$

For each fixed value of temperature and magnetic field, when $\nu \in [0, 1]$ the function (3.28) describes the exact dependence of λ upon the entanglement quantified by $\mathcal{C}$. Nonetheless, as anticipated before, there is a range of values of $\lambda \in \big[0, \frac{1}{\beta}\ln(1+\sqrt{2})\big]$ originating from negative values of ν or, in other words, resulting in zero entanglement: in this range the concurrence is a non-invertible function of λ. When employing ν, however, there is no such an obstacle but one has to be careful when commenting on the results with $\nu < 0$, having in mind that the only physically relevant results can be obtained by looking at the restriction of the functions $\lambda_h(\nu, \beta)$ to the set $\nu \in [0, 1]$, while for negative values of ν there is no link between the interaction strength and the entanglement.

Since C_V is by construction a function of λ, by substituting (3.28) into (3.25) one obtains the set of functions $C_{V_h}(\beta,\nu)$ as

$$\begin{aligned}\frac{C_{V_h}(\beta,\nu)}{\beta^2} &= \frac{1}{(a+\cosh(\beta\lambda_h(\nu,\beta)))^2}\Bigg(h^2+\lambda_h^2(\nu,\beta)+\frac{1}{2}(\lambda_h(\nu,\beta)-h)^2\cosh\big(\beta(\lambda_h(\nu,\beta)+h)\big)+\\ &+ \frac{1}{2}(\lambda_h(\nu,\beta)+h)^2\cosh\big(\beta(\lambda_h(\nu,\beta)-h)\big)\Bigg).\end{aligned} \tag{3.29}$$

For fixed temperature and magnetic field the domain of ν in the function $C_{V_h}(\beta,\nu)$ is given by

$$\mathrm{D}=\left[-\frac{1}{a+1},1\right], \tag{3.30}$$

as can be easily seen from (6) by evaluating the values of ν for $\lambda=0$ and for $\lambda\to\infty$. Once again, there is a part of this domain corresponding to negative values of ν, where heat capacity and entanglement are independent quantities. Note that this range depends on temperature through the β-dependence of a such that, in particular, D tends to the interval $[0,1]$ when $\beta\to\infty$. This means that, when the temperature goes towards zero, all the physics of the system is due to quantum effects and thus the heat capacity is fully characterised by quantum correlations only. On the other hand, for any non-zero temperature, there exist situations in which thermal effects dominate over quantum ones so that the heat capacity is determined by thermal correlations with the bath.

Eq. (3.29) goes beyond Eq. (3.7). It gives indeed a direct analytical expressions of a thermal parameter in terms of an entanglement measure and shows how, once the entanglement in the system is known and different from zero, heat capacity has a well defined value. Unfortunately, the converse is not true.

By measuring all energies in units of h, one obtains the function $C_{V_1}(\beta,\nu)$ whose behaviour is shown in Fig. 3.6 for 9 different values of β. First of all, this figure confirms again the predictions of Eq. (3.7) since the heat capacity always goes to zero for maximally entangled states, irrespectively of the temperature. Another interesting detail worth noticing is that, as expected, lowering temperature results in a narrower range of negative values of ν. This means that in the limit of very low temperature the behaviour of heat capacity fully depends on the entanglement between the two spins in the system. Third, as it is easily seen from Fig. 3.6, heat capacity is never a monotonic function of the concurrence. This is the reason why it is not possible, with just a single measurement of heat capacity, to infer the value of entanglement. Nevertheless, as shown in the next subsection, it is possible to make some precise predictions about the entanglement value by a set of measurements at different temperatures.

3.1.3.2 Concurrence from Heat Capacity: an experimental protocol

Consider, to fix ideas, the function in Eq. (3.29) with $\beta=2$ (see Fig. 3.7). Suppose that one actually measures the heat capacity of a system described by Hamiltonian (3.23) and that

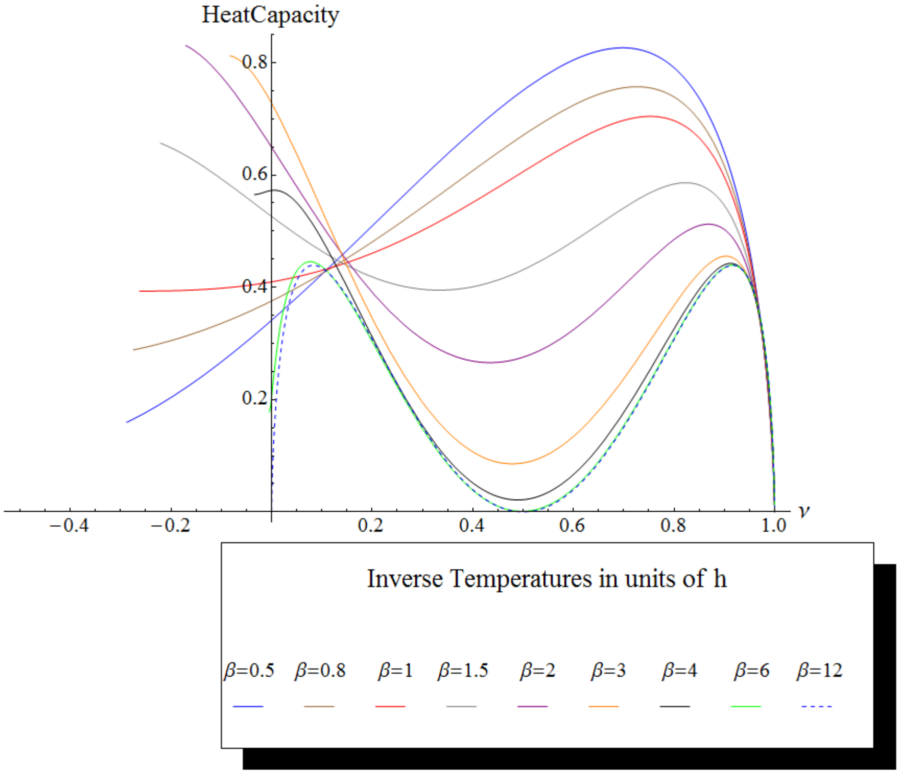

Figure 3.6: Heat Capacity C_V of the system versus Concurrence $\mathcal{C}$ (all energies are measured in units of magnetic field h) for 9 different values of β: $\beta = 0.5$ (blue line), $\beta = 0.8$ (brown line), $\beta = 1$ (red line), $\beta = 1.5$ (gray line), $\beta = 2$ (purple line), $\beta = 3$ (orange line), $\beta = 4$ (black line), $\beta = 6$ (green line) and $\beta = 12$ (blue dashed line).

one can control values of the temperature (by for instance keeping the system in contact with a reservoir) and of the external magnetic field. Since the system is fixed, λ has a constant value which, nevertheless, is not known to the experimentalist. It is interesting to wonder to what extent it might be possible to obtain information about microscopic details of the system (concurrence, entanglement, values of λ) by measuring C_V. Suppose then to measure all energies in units of magnetic field and to fix temperature such that $\beta = 2$. Finally, perform a measurement of heat capacity to get the value C_{meas2} ($C_{meas2} = 0.4$ in the example shown in Fig. 3.7). It is easily seen from Fig. 3.6 that such a value of heat capacity can be associated with up to three different values of concurrence or, which is the same, up to three values of λ since the knowledge of ν directly yields the value of the coupling parameters through Eq. (3.28). Although it is possible to conceive this proposal of experimental protocol in terms of C_V and ν only, I make use here of λ to simplify the notation and the discussion. By a single measurement there is no way to infer which is the one value actually characterising the physical system. These possible values of λ compatible with the measure C_{meas2} can easily be obtained from the function $C_V(\lambda, \beta = 2)$ in Eq. (3.25).

There are thus three possible systems, respectively characterised by values λ_1, λ_2 and λ_3, having

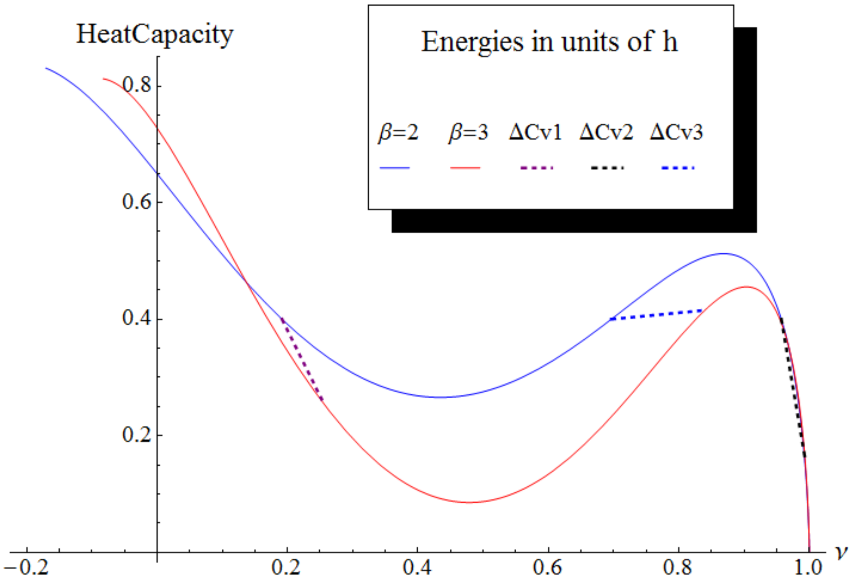

Figure 3.7: Heat Capacity C_V of the system versus parameter ν (all energies are measured in units of magnetic field h) for 2 different values of β: $\beta = 2$ (blue line) and $\beta = 3$ (red line). The Figure also shows, by dashed lines, the changes in heat capacity and concurrence when going from $\beta = 2$ to $\beta = 3$ for the three possible values of λ associated to $C_{meas2} = 0.4$. It should be noted that the changes in heat capacity strongly depend on the starting point on the curve with $\beta = 2$. Heat capacity gaps $C_V(\beta = 2) - C_V(\beta = 3)$ are sensibly different for the three possible values of λ discussed in the text, enabling one to distinguish between the three possible physical systems associated with them.

the same heat capacity. Looking at the example of Fig. 3.7 with $C_{meas2} = 0.4$, these three values are $\lambda_1 \sim 0.76$, $\lambda_2 \sim 1.6$ and $\lambda_3 \sim 2.7$. The question arises whether it is possible or not to identify which one of these three values is the real one.
Suppose now to measure heat capacity for the same system having a different temperature, say $\beta = 3$. I assume here that changing the temperature does not affect the coupling strength λ between spins and, since its value belongs to the set $S_a = \{\lambda_1, \lambda_2, \lambda_3\}$, one can only measure one of the three values $C_V(\lambda_1, \beta = 3)$, $C_V(\lambda_2, \beta = 3)$ or $C_V(\lambda_3, \beta = 3)$. Since these values are in general different from each other, one immediately identifies the original value of λ. Indeed there is a set $S_b = \{\lambda_4, \lambda_5, \lambda_6\}$ of values of λ associated with the measure C_{meas3}, and there must be at least one common element between S_a and S_b. If this common element is unique, one immediately identifies the physical value λ_p of the coupling constant λ. If more than one element in $\{\lambda_1, \lambda_2, \lambda_3\}$ is associated with the measured heat capacity C_{meas3}, one moves forward by measuring C_V for a third temperature, obtaining a new set S_c of possible values of λ and looking for the common element of S_a, S_b and S_c. This procedure can be employed until the physical value of λ is uniquely identified.

Clearly, once λ is known the entanglement can be directly inferred. With simple measurements of the heat capacity of a two-qubit system one is thus able to measure the entanglement (quantified by the concurrence) and any other microscopic property of the system. It is not reasonable to expect this direct link to hold universally. For more complex systems there is in general no easy way to infer entanglement by measurements of simple thermal properties (but of course these measurements yield a great deal of information about first order entanglement critical points as shown by Eq. (3.9)). This simple model however exemplifies how strong such a connection may become in particular cases and that, probably, Eqs. (3.7) and (3.9) are not the full story.

3.2 On the merit of the Gaussian approximation method

The second part of this Chapter is devoted to the exposition of my work about the applicability and the limits of the previously discussed Gaussian Approximation (GA) for many-body systems. This method can be inscribed within the landscape of equilibrium thermodynamics as it allows for an approximate estimation of the two main quantities characterising thermal equilibrium physics: the density of states η and the partition function Z. My work in the field showed that results based on this method have to be taken carefully since, despite its wide range of applicability, the method structurally yields unphysical predictions. These results of mine have been obtained together with Dr. O. Lychkovskiy and with Prof. A. Messina and are published in [145].

In this work, in particular, I studied the physical predictions of the GA and compared them to the exact behaviour of thermodynamic quantities. Such a comparison is performed both in general terms, by investigating the underlying structure of the GA method, and by applying it to some particular model systems.

3.2.1 General investigation

In Chapter 2 I already singled out a possible source of problems intrinsically characterising the GA method due to the speed of convergence of the Central Limit Theorem, on which the method is based, with the number of constituents of the many-body system. To be more specific, Eqs. (2.13) and (2.14), due to their structural dependence on Gaussian parameters and their scaling with the number N_b of blocks, are prime suspects for unphysical behaviour. That is why, in my work, I analysed in detail their physical predictions.

To facilitate the understanding of this Section, I rewrite here Eqs. (2.13) and (2.14) for the density of states and the partition function under the GA:

$$\eta_G(E) = \sum_{\{|a\rangle\}} \frac{e^{\frac{(E-\overline{E_a})^2}{2\Delta_a^2}}}{\Delta_a\sqrt{2\pi}}, \tag{3.31}$$

$$Z_G = \int_{E_g}^{+\infty} \eta_G(E) e^{-\beta E} dE = \sum_{\{|a\rangle\}} \frac{1}{2} e^{(-\beta\overline{E_a}+\frac{\beta^2\Delta_a^2}{2})} \left(\operatorname{erfc}\Big(\frac{E_g-\overline{E_a}+\beta\Delta_a^2}{\Delta_a\sqrt{2}}\Big)\right), \tag{3.32}$$

defined making use of the Gaussian parameters

$$\overline{E_a} = \langle a|H|a\rangle, \tag{3.33}$$

$$\Delta_a^2 = \langle a|H^2|a\rangle - \langle a|H|a\rangle^2. \tag{3.34}$$

3.2.1.1 Error function at large positive and negative arguments

To begin with, a technical issue which is crucial for discussing the GA at large N_b has to be noted. Focus then on the behaviour of the complementary error function which enters Eq. (3.32). It has been shown [141] that its argument grows with the number of blocks as $\sqrt{N_b}$. One indeed expects that

$$\begin{aligned} E_g &= N_b\varepsilon_g\big(1+O(N_b^{-1})\big),\\ \overline{E_a} &= N_b\overline{\varepsilon}_a\big(1+O(N_b^{-1})\big),\\ \Delta_a^2 &= N_b\delta_a^2\big(1+O(N_b^{-1})\big), \end{aligned} \tag{3.35}$$

where ε_g, $\overline{\varepsilon}_a$ and δ_a are quantities defined *per block* and, as such, independent on N_b. The above linear scaling is a generic feature of any modular Hamiltonian like the one in Eq. (2.8) (this will be exemplified by means of specific models further on in this Section). Also note that the linear scaling of Δ_a^2 is in accordance with $\Delta_a^2 \geq N_b C$, which is a necessary condition for the applicability of the method. Therefore, the argument of the complementary error function in Eq. (3.32) can be written as

$$\sqrt{N_b}\frac{\varepsilon_g - \overline{\varepsilon_a} + \beta\delta_a^2}{\delta_a\sqrt{2}} \tag{3.36}$$

which, at large N_b, is a very large number, either positive or negative depending on the sign of $(\varepsilon_g - \overline{\varepsilon_a} + \beta\delta_a^2)$. The complementary error function has a well-known asymptotic behaviour at large arguments:

$$\operatorname{erfc}(x) \sim \begin{cases} 2, & x \to -\infty,\\ e^{-x^2}/(\sqrt{\pi}x), & x \to +\infty. \end{cases} \tag{3.37}$$

One may expect (and I will show later on that such an expectation is met) that this different behaviours produce certain discontinuities in thermal quantities when the temperature is such that $(\varepsilon_g - \overline{\varepsilon_a} + \beta\delta_a^2)$ changes its sign. In addition to its asymptotic form, the complementary error function satisfies also an exact inequality [150] which limits $\operatorname{erfc}(x)$ at $x > 0$ as

$$\operatorname{erfc}(x) < \frac{e^{-x^2}}{\sqrt{\pi}x}. \tag{3.38}$$

3.2.1.2 High temperature limit

As a first comparison, consider the high temperature behaviours of both the exact partition function $Z = \operatorname{Tr}\big(e^{-\beta H}\big)$ and the partition function Z_G obtained from GA and given in Eq. (3.32). Formally expanding the exponential function of H in Z up to the second order in β one straightforwardly gets

$$Z = \operatorname{Tr}\Big(1 - \beta H + \frac{\beta^2}{2}H^2\Big) + O(\beta^3). \tag{3.39}$$

Note now that the trace operation is independent on the basis chosen to evaluate it. One can for example use the factorized basis $\{|a\rangle\}$ defined in the previous Chapter and composed of factorized single-block states. In this way, equation (3.39) can be written as

$$\begin{aligned} Z &= \sum_{\{|a\rangle\}} \Big(1 - \beta\langle a|H|a\rangle + \frac{\beta^2}{2}\langle a|H^2|a\rangle\Big) + O(\beta^3) \\ &= \sum_{\{|a\rangle\}} \Big(1 - \beta\langle a|H|a\rangle + \frac{\beta^2}{2}\langle a|H|a\rangle^2 + \frac{\beta^2}{2}\big(\langle a|H^2|a\rangle - \langle a|H|a\rangle^2\big)\Big) + O(\beta^3). \end{aligned} \tag{3.40}$$

Equation (3.40) does not of course coincide with (3.32). Nevertheless, in the limit of high temperatures such that

$$T > \max_{\{|a\rangle\}} \frac{\delta_a^2}{\overline{\varepsilon_a} - \varepsilon_g}, \tag{3.41}$$

the arguments of *all* error functions in (3.32) are negative and one can use the asymptotic form of $\mathrm{erfc}(x)$ when $x \to -\infty$ (see Eq. (3.37)) to obtain

$$\begin{aligned} Z_G &\simeq \sum_{\{|a\rangle\}} e^{\beta^2 \frac{\Delta_a^2}{2}} e^{-\beta\overline{E_a}} \\ &= \sum_{\{|a\rangle\}} \Big(1 - \beta\langle a|H|a\rangle + \frac{\beta^2}{2}\langle a|H|a\rangle^2 + \frac{\beta^2}{2}\big(\langle a|H^2|a\rangle - \langle a|H|a\rangle^2\big)\Big) + O(\beta^3), \end{aligned} \tag{3.42}$$

which is the same result obtained in (3.40).

This shows that, within the order β^2 in the high temperature limit, any physical prediction stemming from the GA coincides with the exact results since, by exploiting the knowledge of the partition function, one can obtain expressions for every thermodynamical quantities of interest.

3.2.1.3 Low temperature limit

One may wonder now: what about low temperatures? In order to avoid annoying divergences when taking the limit $T \to 0$, in the present subsection (but nowhere else!) I define the Hamiltonian (2.8) in such a way that the non-degenerate ground state energy E_g vanishes. The exact partition function reads

$$Z = 1 + \sum_{i=2}^{d^{N_b}} e^{-\beta E_i} > 1. \tag{3.43}$$

Here, the E_i's are eigenstates of the total Hamiltonian.

On the other hand, at low enough temperatures such that

$$T < \min_{\{|a\rangle\}} \frac{\delta_a^2}{\overline{\varepsilon_a}}, \tag{3.44}$$

one is able to bound the approximate partition function Z_G from above. Indeed at such low temperatures the arguments of *all* error functions in Eq. (3.32) are positive, and exploiting inequality (3.38) one obtains

$$Z_G \leq d^{N_b} \max_{\{|a\rangle\}} \frac{e^{-\bar{\varepsilon}_a^2/(2\delta_a^2)}}{\sqrt{\pi N_b/2}(\beta\delta_a - \bar{\varepsilon}_a/\delta_a)} \to 0 \quad \text{as} \quad T \to 0. \tag{3.45}$$

One thus sees that the approximate partition function can not reproduce the exact result when temperature is low enough. This is a consequence of the fact that the Gaussian Approximation does not hold when the system is very close to being in a single eigenstate of H (in our case, in the ground state). In [139] such a failure in reproducing exact results at $T \approx 0$ was noted in connection with the study of an Ising chain, and it was argued that the GA would in general fail when predicting physical properties at zero temperature.

The analysis performed up to now dealt with limiting forms of GA at high and low temperature regimes revealing that, while at high temperatures this approximation works satisfactory, at low temperatures something goes wrong in the expression of the partition function. Since however, the partition function itself is not a measurable quantity, it would be reasonable to argue that the discrepancies detected between the GA and the exact result may not have physical consequences. This is not the case: to answer this question, in what follows and under specific constraints on Gaussian parameters $\overline{E_a}$ and Δ_a^2, explicit expressions for measurable quantities obtained from Z_G are given in the thermodynamic limit in the *whole range of temperatures*. This analysis allows to elucidate that, contrarily to what happens in the high temperature limit, the GA is unable to reproduce physical results in the range of low and intermediate temperatures.

3.2.2 An analytical expression for the free energy under constant Gaussian parameters

Consider a model in which the Gaussian parameters Δ_a and $\overline{E_a}$ in some factorized basis do not depend on a, such as

$$\begin{aligned} \overline{E_a} &= 0, \\ \Delta_a &= \sqrt{N}\delta > 0 \ \ \forall\ a. \end{aligned} \tag{3.46}$$

Note that the first equation implies the ground state energy to be negative unless the Hamiltonian is identically zero. From equations (3.31) and (3.32) it is then possible to obtain the Gaussian Approximation for the density of states and the partition function in the form

$$\eta_G = \frac{d^{N_b}}{\sqrt{2\pi N_b}\delta} e^{-E^2/(2\delta^2 N_b)}, \tag{3.47}$$

$$Z_G = \frac{d^{N_b}}{2} e^{\frac{\beta^2\delta^2 N_b}{2}} \operatorname{erfc}\left[\sqrt{\frac{N_b}{2}}\left(\frac{\delta}{T} + \frac{\varepsilon_g}{\delta}\right)\right]. \tag{3.48}$$

These quantities, while representing the starting point of any thermodynamical analysis, have an elusive physical meaning since they can not be directly measured. The goal is then to check the physical predictive power of the GA focusing the analysis on other quantities exhibiting operationally clear physical meaning. A typical choice is to calculate the free energy per block, defined as $-N_b^{-1}T\ln Z$. In the GA framework this can easily be obtained from Eq. (3.47) with the use of asymptotic expressions (3.37) for the error function. In the thermodynamic limit it results

$$f_G \equiv \lim_{N_b\to\infty}(-N_b^{-1}T\ln Z_G) = \begin{cases} -T(\ln d - \frac{\varepsilon_g^2}{2\delta^2}) + \varepsilon_g & \text{for} \quad T < -\frac{\delta^2}{\varepsilon_g}, \\ -T\ln d - \frac{\delta^2}{2T} & \text{for} \quad T \geq -\frac{\delta^2}{\varepsilon_g}. \end{cases} \tag{3.49}$$

One can now compare the low-temperature behaviour of the exact free energy f and the approximation f_G. First of all note that, at $T = 0$, $f_G = \varepsilon_g$ as it should. One can easily verify that this happens simply thanks to the choice of ground state energy as a lower limit of integration in Eq. (3.32), which ensures that f_G at zero temperature always equals the ground state energy per spin.

What about the entropy at zero temperature? The GA gives $S_G \equiv \frac{\partial f_G}{\partial T}|_{T=0} = -\ln d + \frac{\varepsilon_g^2}{2\delta^2}$. However, according to the third law of thermodynamics, the entropy goes to zero as $T = 0$ [151].[2] This disagreement shows that the GA is unable to reproduce the exact thermodynamics when temperature is low enough.
Note further that

- f_G and $\frac{\partial f_G}{\partial T}$ are continuous at $T = -\frac{\delta^2}{\varepsilon_g}$. However $\frac{\partial^2 f_G}{\partial T^2}$ and further derivatives are not. Thus the GA predicts a fake thermal phase transition which contradicts the general result that thermal phase transitions do not exist in 1D systems with finite-range interactions [129]. This shows how, even at intermediate temperature, the agreement with exact results is very poor.
- f_G at $T > -\frac{\delta^2}{\varepsilon_g}$ coincides with the first two terms of the high-temperature expansion of f, as expected from (3.42).

3.2.3 A generalised formula for the free energy under weaker constraints on Gaussian parameters

It is also possible to relax one of the two constraints (3.46) imposed on Gaussian parameters and to consider the more general situation in which $\Delta_a = \text{const}$ but $\overline{E_a}$ is not. In performing such an analysis one works in the limit of very high number of blocks, when the number of terms in the sums in (3.31) and (3.32) becomes very large and tends to infinity in the thermodynamic limit. In these situations it is reasonable to exchange the summation over $|a\rangle$ by an integration over energy, introducing a density $\eta_{free}(\overline{E})$ defined as the number of states $|a\rangle$ for which $\overline{E_a} \in [\overline{E}, \overline{E} + d\overline{E}]$. With this definition one can then replace summation with integration as

$$\sum_{|a\rangle} \to \int \eta_{free}(\overline{E})d\overline{E}. \tag{3.50}$$

---

[2] The third law can be violated only for systems whose ground state degeneracy grows exponentially with the number of blocks. Here however no assumption is made on the degeneracy of the ground state.

With the help of (3.50) one can rewrite Eq. (3.31) in the integral form

$$\eta_G(E) = \int \eta_{free}(\overline{E}) \frac{1}{\sqrt{2\pi N_b}\delta} e^{-(E-\overline{E})^2/(2\delta^2 N_b)} d\overline{E}. \tag{3.51}$$

Here the "free" density of states $\eta_{free}(\overline{E})$, introduced in (3.50), has itself the form of a sum $\sum_{\{|a\rangle\}} \delta(\overline{E} - E_a)$. It is often useful to approximate it by some more regular and manageable functions. In what follows the choice to approximate it as a Gaussian function (as often done when dealing with these kind of densities [152]) is made, exploiting a second time the Central Limit Theorem (CLT) on which the GA is based and introducing therefore a further source of error since the Gaussian distribution is unable to exactly reproduce the behaviour of $\eta_{free}(\overline{E})$ at its tails [152]. The approximation thus obtained may be then referred to as double Gaussian Approximation (GGA), stressing the fact that the CLT is applied twice in two different steps of its derivation. Being aware of the further error thus introduced, one can develop the GGA. Assume for simplicity that single-block free Hamiltonians H_μ have the same structure for all μ (the generalisation to the case of different H_μ is straightforward). Consider a basis $\{|a^l_\mu\rangle\}$, $l = 1, 2, ..., d$ in a d-dimensional single-block Hilbert space and, without loss of generality, set $\sum_l \langle a^l_\mu | H_\mu | a^l_\mu \rangle = 0$.

The *statistical* standard deviation of a single-block self-Hamiltonian relative to a specific basis $\{|a^l_\mu\rangle\}$ can be then defined as $\sigma^2 \equiv \frac{1}{d} \sum_l \langle a^l_\mu | H_\mu | a^l_\mu \rangle^2$. From the Central Limit Theorem one thus obtains

$$\eta_{free}(\overline{E}) \simeq \frac{d^{N_b}}{\sqrt{2\pi N_b}\sigma} e^{-\overline{E}^2/(2\sigma^2 N_b)}. \tag{3.52}$$

Note that, as already pointed out, such an approximation does not work properly at the tails of the distribution. Nonetheless, exploiting it, it is possible to apply the GGA to obtain

$$\begin{aligned} \eta_G(E) &\simeq \int_{\varepsilon_1}^{+\infty} d\overline{E} \frac{d^{N_b}}{2\pi N_b \sigma\delta} e^{-(E-\overline{E})^2/(2\delta^2 N_b) - \overline{E}^2/(2\sigma^2 N_b)} \\ &= \frac{d^{N_b} e^{-\varepsilon^2 N_b/(2(\delta^2+\sigma^2))}}{2\sqrt{2\pi N_b(\delta^2+\sigma^2)}} \operatorname{erfc}\left[\sqrt{\frac{N_b}{2}} \sqrt{\delta^{-2}+\sigma^{-2}} \Big(\varepsilon_1 - \frac{\varepsilon}{1+\delta^2/\sigma^2}\Big)\right]. \end{aligned} \tag{3.53}$$

Here $E \equiv N_b \varepsilon$ and $\varepsilon_1 \equiv \min\limits_{\{|a^l_\mu\rangle\}} \langle a^l_\mu | H_\mu | a^l_\mu \rangle$. Note that the case studied in the previous subsection, with $\overline{E_a} = \text{const}$, corresponds to the limit $\sigma \to 0$. In this limit $\operatorname{erfc}(x) \sim 2$ and Eq. (3.53) reduces to the expression given in (3.47), as it should. In the framework of this approximation and using the asymptotic expressions for $\operatorname{erfc}(x)$ one obtains

$$\begin{aligned} Z_G \simeq \theta\Big(\varepsilon_1\Big(1+\frac{\delta^2}{\sigma^2}\Big) - \varepsilon_g\Big) N_b \int_{\varepsilon_g}^{\varepsilon_1\left(1+\frac{\delta^2}{\sigma^2}\right)} &\left[\frac{d^{N_b} e^{-\frac{\varepsilon^2 N_b}{2(\delta^2+\sigma^2)} - \beta\varepsilon N_b}}{2\sqrt{2\pi N_b(\delta^2+\sigma^2)}} \times \right. \\ &\left. \frac{e^{-\frac{N_b}{2}(\delta^{-2}+\sigma^{-2})\left(\varepsilon_1 - \frac{\varepsilon}{1+\frac{\delta^2}{\sigma^2}}\right)^2}}{\sqrt{\frac{\pi N_b}{2}} \sqrt{\delta^{-2}+\sigma^{-2}} \left(\varepsilon_1 - \frac{\varepsilon}{1+\frac{\delta^2}{\sigma^2}}\right)}\right] d\varepsilon + N_b \int_{\varepsilon_m}^{+\infty} \frac{d^{N_b} e^{-\frac{\varepsilon^2 N_b}{(2(\delta^2+\sigma^2))} - \beta\varepsilon N_b}}{\sqrt{2\pi N_b(\delta^2+\sigma^2)}} d\varepsilon, \end{aligned} \tag{3.54}$$

where $\theta(x)$ is the Heaviside step function and $\varepsilon_m \equiv \max\left\{\varepsilon_g, \varepsilon_1\left(1+\frac{\delta^2}{\sigma^2}\right)\right\}$.
The first term corresponds to erfc(x) with positive argument, while the second term corresponds to erfc(x) with negative argument. There are some cases in which the first term can be neglected or equals zero (e.g. in the Ising model). The second term alone gives rise to another complementary error function which closely resembles the one analysed previously in obtaining Eq. (3.49). Following the same steps one then gets

$$f_{GG} = \left\{ \begin{array}{ll} -T(\ln d - \frac{\varepsilon_m^2}{2(\delta^2+\sigma^2)}) + \varepsilon_m & \text{for} \quad T < -\frac{\delta^2+\sigma^2}{\varepsilon_m}, \\ -T\ln d - \frac{\delta^2+\sigma^2}{2T} & \text{for} \quad T \geq -\frac{\delta^2+\sigma^2}{\varepsilon_m}. \end{array} \right. \tag{3.55}$$

Eq. (3.55) shows the same behaviour as (3.49). All comments made for (3.49) are thus valid also in this case. In particular, it still predicts an unphysical thermal phase transition and violates the third law of thermodynamics. It is worth stressing that (3.55) is valid as long as the first term in (3.54) can be neglected or actually equals zero, and within the limits of the additional approximation used to obtain (3.52).

3.2.4 Application to a specific model

The Gaussian method and its intrinsic limitations are analysed here for a quantum Ising chain which, as previously commented, describes a system of interacting qubits embedded in an external transverse magnetic field. Its Hamiltonian was already given in Eq. (2.3) and it is reported again here to simplify the reading of this Section. One has

$$H_{\text{Is}} = -J\sum_{j=1}^{N}\sigma_j^x\sigma_{j+1}^x + h\sum_{j=1}^{N}\sigma_j^z, \tag{3.56}$$

where σ_j^α, $\alpha = x, y, z$ is the α-component of the Pauli matrix vector corresponding to site j, J is the spin-spin interaction parameter and h is the external magnetic field. In what follows I mainly work in the thermodynamic limit, where different boundary conditions are known to yield the same physical results.

Being integrable, this model can be exactly diagonalised via a Jordan-Wigner transformation [153], obtaining in the thermodynamic limit the following expressions for ground state energy and for free energy per spin

$$\begin{aligned} \varepsilon_g^{\text{Is}} &= -\frac{1}{\pi}\int_0^\pi dp\sqrt{J^2+h^2+2hJ\cos p}, \\ f^{\text{Is}} &= -\frac{T}{\pi}\int_0^\pi dp \ln\left[2\cosh\frac{\sqrt{J^2+h^2+2hJ\cos p}}{T}\right]. \end{aligned} \tag{3.57}$$

It is worth noting that the application of the GA to this model has been discussed in [139], where the exact partition function for the Ising model has been compared to the one obtained by means

of Eq. (3.32). However, as previously said, the partition function itself is not measurable and, to grasp the physics of the GA method, one should turn to measurable quantities.
Consider each block to be made of a single spin, and introduce the following notation for the eigenstates of σ^y

$$\sigma^y|y\rangle = |y\rangle, \quad \sigma^y|\tilde{y}\rangle = -|\tilde{y}\rangle, \tag{3.58}$$

and analogously for x and z.

To apply the GA, one can take the factorised states to be made of eigenstates of σ^y, e.g.

$$|a_y\rangle = |yy\tilde{y}\tilde{y}yy\tilde{y}yy...y\rangle, \tag{3.59}$$

thus easily obtaining $\overline{E}_a = 0$ and $\delta^2 = J^2 + h^2$. The formula (3.49) can be straightforwardly applied to obtain f_G^{Is}, which reads

$$f_G^{\text{Is}} = \begin{cases} f_G^{\text{Is}-} & \text{for} \quad T < -\frac{J^2+h^2}{\varepsilon_g^{\text{Is}}}, \\ f_G^{\text{Is}+} & \text{for} \quad T \geq -\frac{J^2+h^2}{\varepsilon_g^{\text{Is}}}, \end{cases} \tag{3.60}$$

where

$$\begin{aligned} f_G^{\text{Is}-} &= -T\ln 2 - \frac{T}{(J^2+h^2)\pi^2}\left(\int_0^\pi dp\sqrt{J^2+h^2+2hJ\cos p}\right)^2 \\ &- \frac{1}{\pi}\int_0^\pi dp\sqrt{J^2+h^2+2hJ\cos p}, \qquad (3.61) \\ f_G^{\text{Is}+} &= -T\ln 2 - \frac{J^2+h^2}{2T}. \qquad (3.62) \end{aligned}$$

As expected, this equation predicts a wrong behaviour of the Ising free energy at low temperatures, which is shown in Fig. 3.8.

3.2.4.1 Gaussian Approximation for the Ising model in a different factorized basis

As stated when discussing the general features of the GA method, the choice of the factorized basis is arbitrary. To show this, consider now as factorized basis the eigenbasis of $H^0 = h\sum_{j=1}^N \sigma_j^z$, which is the same basis used in [139] to numerically evaluate the partition function from equation (3.32). With the same notation introduced in the previous subsection one gets

$$|a_z\rangle = |zz\tilde{z}\tilde{z}zz\tilde{z}...z\rangle. \tag{3.63}$$

This gives

$$\varepsilon_1 = -h, \quad \delta_z = J, \quad \sigma_z = h \tag{3.64}$$

and

$$\overline{E_a} = h(2k - N), \tag{3.65}$$

where k is the number of up spins in the factorized state $|a_z\rangle$ or, which is the same, is the number of z in the state $|a_z\rangle$. $\overline{E_a}$, in this case, depends on a implying the use of the GGA. Equation (3.55) might thus be applied, provided its conditions are met.
One can check numerically that

$$\varepsilon_1(1+\delta_z^2/\sigma_z^2) - \varepsilon_g^{\mathrm{Is}} \leq 0 \tag{3.66}$$

for all values of model parameters J and h. The free energy is then given by Eq. (3.55). However, as can easily be checked, this result exactly coincides with one obtained in the previous subsection employing the y-basis. The reason is that in a y-product basis, as done before, one gets

$$\delta_y = \sqrt{J^2 + h^2} \tag{3.67}$$

and, as a consequence,

$$\delta_y^2 = \delta_z^2 + \sigma_z^2. \tag{3.68}$$

This relation, here shown for the Ising chain, indeed holds for a certain class of systems as expressed by the following

Statement: Consider a model with Hamiltonian (2.8) represented as $H = H^0 + I$, I being an inter-block interaction, and two product bases, $\{|a\rangle\}$ and $\{|\tilde{a}\rangle\}$, such that

1. $\Delta_a = \text{const}$ and $\Delta_{\tilde{a}} = \text{const}$,
2. $\forall a \ \ E_a = 0$,
3. $\forall \tilde{a} \ \ \langle \tilde{a}|I|\tilde{a}\rangle = 0$ and $H^0|\tilde{a}\rangle = E^0_{\tilde{a}}|\tilde{a}\rangle$.

Then

$$\tilde{\delta}^2 + \tilde{\sigma}^2 = \delta^2.$$

The above Statement implies that if conditions 1,2 and 3 are met for a particular system, then equation (3.49) and equation (3.55) actually give the same result and one is entitled to use the simplest one.

To compare then how the choice of different bases affects the results of the method, Fig. 3.8 presents the free energy obtained from the GA in y-basis (identical to the free energy from the GGA in the z-basis) in the thermodynamic limit, to be compared with the free energy obtained from the GA in the z-basis numerically evaluated for 1000 spins in the chain with open boundary conditions. Both of them are further compared to the exact result in the thermodynamic limit, too.

One can notice a very good agreement between both the approximate free energies and the exact one as long as temperature is high enough ($T \gg \frac{-\delta^2}{\varepsilon_g}$), as expected from the high temperature expansion in equation (3.42), but such a good agreement breaks down at intermediate and low temperatures. The GA in y-basis, in particular, gives the worst approximation, while

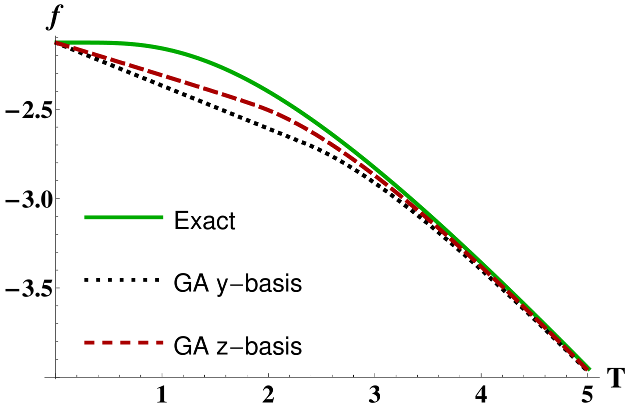

Figure 3.8: Free energy per spin plotted against temperature obtained from the exact formula (3.57) (green solid line), from the GA in the y-basis (obtained both from (3.60) or from the same expression stemming from (3.55), black dotted line) and from the GA in the z-basis (obtained directly with the use of (3.32) in the case of $N_b = 1000$, red dashed line) for an Ising chain when $J = 1$ and $h = 2$. It is possible to notice, as expected, how the high temperature behaviour predicted by the GA closely resembles the exact one, while at low temperature the GA, in both bases, violates the third law of thermodynamics. Nevertheless the agreement with the exact result is better for the GA in the z-basis.

the GA in z-basis is closer to the exact free energy despite still showing all the drawbacks highlighted previously when discussing the intrinsic limitations of the method. Note that the GA in y-basis, which as said coincides with the z-basis GGA for this particular model, is affected by a greater source of error, while GA in z-basis, derived directly from (3.32) (and as such, not in the thermodynamic limit), is more accurate. The difference between the approximate and exact results is even more marked if one considers that many measurable quantities are obtained as derivatives of the free energy with respect to temperature. Note indeed the two features previously highlighted: when the temperature approaches zero the exact free energy is flat, corresponding to a vanishing entropy, while the GA free energies have non-zero derivative (and, thus, entropy) at $T = 0$. Moreover, it can be noticed that the two GA free energies have a second-order non-differentiable point around $T \sim 2.5$, which corresponds to the fake thermal phase transition already commented.

3.2.5 Remarks

One could wonder whether the GA might be more efficiently exploited to get an insight into the physics of statistical models when analysed in their non-thermal parameter space: the possibility of detecting signatures of quantum critical points in the behaviour of thermodynamic functions might be an alternative field of applicability of this method. It is well known that an Ising chain described by (3.56) indeed shows the presence of a QPT when $h = J$, leading to a transition from a ferromagnetic to a paramagnetic phase. Such a transition is a second order QPT, which means it leaves signatures in the critical behaviour of the second derivative of free energy with respect to one of the two Hamiltonian parameters when $T \to 0$. Such a criticality is due to a non-analytical point in the ground state energy (which by definition is the limit of free energy as $T \to 0$) and is thus clearly present, as easily checked, also in the GA which strongly depends on ε_g. Nevertheless, as shown in the previous section and as can be seen from (3.49), the knowledge of ε_g is a *necessary condition* for the application of the GA to any system. This means that in order to calculate f_G one should know in advance ε_g and has therefore access to its whole set of non-analytical points. The GA is then unable to supply further information on QPTs or to extract them more efficiently directly from the Hamiltonian operator. Differently from the argumentation in [139] indeed, the GA could actually be applied to the study of QPTs (when $T = 0$, the free energy given by the GA coincides with the physical one even if, as noticed in [139], the two partition functions strongly differ) but requires the same computational effort as an exact analysis and is thus not useful in simplifying any calculation.

To summarise:

- At high temperature any thermodynamic quantity obtained from the GA coincides with the high-temperature expansion of the exact functions, within the order β^2.
- For systems with Δ_a independent on $|a\rangle$ and for systems with finitely-many blocks, the GA predicts non-zero entropy at $T = 0$ in striking contradiction to the third law of thermodynamics.
- For systems with Δ_a independent on $|a\rangle$ the GA predicts a fake thermal phase transition at an intermediate temperature, in contradiction to the very general result according to which 1-D systems can not show any such transition [129].
- As discussed above, the GA is useless when applied to the analysis of quantum criticality at fixed, vanishing temperature.

In conclusion, any physical prediction obtained from the Gaussian Approximation at low and intermediate temperatures, like for example the one reported in [82], has to be taken cautiously and deserve further analysis with different, more sophisticated tools.

Chapter 4

Quantum nonequilibrium thermodynamics

Nonequilibrium systems are found everywhere in physics. All the theory of transport phenomena [154, 155], most of biological systems of physical interests [155, 156, 157], the research of deep conceptual and practical interest on quantum efficiency [158, 159], classical and quantum thermodynamic machines [1, 23], these are just a few examples of situations whose understanding requires going beyond equilibrium physics.

Despite the paramount importance of nonequilibrium phenomena, a general picture allowing for their analysis is not yet available, since a comprehensive description poses non trivial conceptual and technical problems already in the classical case. This is testified by the existence of only a limited number of laws allowing for some statistical predictions on nonequilibrium properties of complex systems, among which stand the second law of thermodynamics and the celebrated class of theorems known as fluctuation-dissipation relations [160]. The latter, in particular, has been for long time the only structured framework in which nonequilibrium processes could be studied, although under some pretty restrictive assumptions.

A huge step forward has been done, however, in the late nineties when Christopher Jarzynski [59], and Gavin Crooks right after him [60], formulated a set of laws which in a disappointingly simple way account for any kind of nonequilibrium processes, characterising their probability distribution of energy or entropy fluxes. The predictive power of these laws is astonishing, and they have already been experimentally verified over a satisfactory broad range of physical situations [8, 61, 161, 162, 163], always proving themselves as the golden tool to tackle complex, non trivial out-of-equilibrium physics.

Despite the fact that my interest for these laws has been exclusively focused on their quantum validity, to fully grasp their meaning it is useful - if not necessary - to briefly go through their classical counterparts [21, 59, 60, 164]. This, apart from respecting the chronological order at which the theory has been developed, allows ideas to be fixed, concepts to be introduced and the general framework to be specified in a more familiar and controlled context.

4.1 A step backward: classical nonequilibrium thermodynamics

Consider then a classical system whose Hamiltonian $H(\lambda)$ depends on a set of parameters λ, and imagine to be able to exert an external control on these parameters, producing a time variation of their values through a fixed protocol $\lambda(t)$, such that they start from initial values λ_0 before the protocol begins and end up to final values λ_T after time T. All their values in the time interval $[0, T]$ are specified *a priori*. I refer to such a protocol as *driving* throughout this thesis.

4.1.1 Classical fluctuation theorems

Consider now, to fix ideas, the system to be in a thermal equilibrium state at time $t < 0$ before the driving starts. Its ensemble state will then be a Gibbs state at inverse temperature β characterised by the Hamiltonian $H(\lambda_0)$. Clearly, the existence itself of a thermal equilibrium state implies the fact that the system interacts, or has interacted in the past, with a thermal reservoir. One might suppose such an interaction to be switched off before the driving protocol begins, or may also consider the case in which the driven system continuously interacts with its environment also for $t \geq 0$. When discussing my results I will always postulate the existence of an environment, whose features will be accounted for by the structure of the Master Equation describing the ensemble dynamics of the open system. Nonetheless, in this chapter it will sometimes be convenient to consider the case in which the system is disconnected from its environment along the driving time. This will allow for a much simpler derivation of a certain class of nonequilibrium laws which focuses on the important conceptual steps avoiding some technicalities arising when considering the effect of an environment: the results are unaffected by this assumption. In this chapter I will then explicitly specify whether an interaction with the environment is present or not during the driving interval.

The modification of Hamiltonian parameters necessitates, as already commented briefly in Chapter 1, of a certain amount of work W. This work however fundamentally depends on the particular path followed by the classical system in its phase space since, as will be properly formalised shortly, it depends on how the time dependence in λ is reflected in the time dependence of position and momentum for each particle of the system [21]. One expects then that such a work becomes a stochastic variable whose probability distribution has to be determined.

One may reasonably expect the details of the driving to be of huge importance in specifying such a probability distribution. Indeed, for example, for reversible transformations one can apply standard equilibrium thermodynamics tools at each time step having an easy way to access the statistics of work via the second law of thermodynamics asserting that

$$W_{\mathrm{rev}} = \Delta F, \tag{4.1}$$

where W_{rev} is the work performed along a reversible driving protocol and ΔF is the net variation of a free energy (which might either be the Gibbs or the Helmholtz potential depending on the conditions at which the driving is applied). In general, however, the second law can only predict that

$$\langle W \rangle \geq \Delta F, \tag{4.2}$$

where the average is taken over very may repetitions of a driving protocol generating generally non-reversible processes, and the equality sign holds only for reversible transformations.

A better prediction about the statistics of work is achieved by applying the well known fluctuation-dissipation relations. Their validity relies on the assumption of linear response theory, i.e. on the fact that the system when not too far from equilibrium shows a reaction to an external force which is proportional to the force itself. This is not generally true, but for not too fast drivings it gives a good approximation to the true behaviour. Thanks to this, one can predict that

$$\langle W \rangle - \frac{\beta \sigma_W}{2} = \Delta F. \tag{4.3}$$

Here σ_W is the second moment of the work distribution and β corresponds to the initial temperature of the system induced by its bath. The linear response approximation predicts then a Gaussian distribution of work, whose features are specified once again by the change in free energy. Although valid only within certain limits and leading to different forms of stochasticity, Eqs. (4.1) and (4.3) show an interesting common feature: they link nonequilibrium quantities (W) to equilibrium values (ΔF), showing how the nonequilibrium behaviour of a system is subtly ruled by fixing its equilibrium properties.

These two equations, however, are not a complete satisfactory description of far-from-equilibrium physics. It would not be reasonable to expect, indeed, that for a generic driving protocol the work distribution stays Gaussian. This is due to the fact that, for fast enough protocols, the response of the system becomes strongly non-linear. Since the variation of λ with time is in general neither adiabatic nor slow enough for the linear response approximation to hold, one has to seek for a further generalisation of Eq. (4.3) holding without the need of any approximation. Despite the fact that, at a first glance, such a task may seem hopeless, it can actually be performed in a surprisingly easy way. Since a full treatment of classical nonequilibrium theory goes beyond the scope of this thesis, I present here briefly only the simplest case of a classical driven closed system. The physics of this system is already clear and rich enough to introduce all the standard tools needed in these kind of approaches.

Consider then a system with microscopic Hamiltonian $H(q, p; \lambda)$ depending on the microscopic configurations q and the momenta p of all particles, and on the driving parameter λ. The change in H originating from a variation of the value of λ is

$$\delta H_\lambda = \mathrm{d}\lambda \frac{\partial H}{\partial \lambda}. \tag{4.4}$$

It has been discussed in a number of papers how such a term, being in the form $\delta W = -\mathfrak{F} \mathrm{d}\lambda$, $\mathfrak{F} = -\frac{\partial H}{\partial \lambda}$ being the force acting on the system, represents the microscopic expression for infinitesimal work δW. The work needed to generate the full driving process is then

$$W = \int_0^T \mathrm{d}t \frac{\mathrm{d}\lambda}{\mathrm{d}t} \frac{\partial H(q(t), p(t); \lambda(t))}{\partial \lambda}. \tag{4.5}$$

Note at this point that the set $\{q(t), p(t)\}$ represents the microstate of the system at each time instant during the nonequilibrium dynamics. This is nothing but the trajectory of the system in its phase space, and is not *a priori* predictable within a stochastic thermodynamics framework since the only fixed properties of the system are its initial and final ensemble states which correspond to a very high number of compatible microstates. Since the evolution of a classical system in its phase space clearly depends on its initial condition, and since one has no knowledge about such an initial state (i.e., the microstate the system starts in at $t = 0$), trajectories of the system - and therefore the work needed during the driving - become stochastic variables themselves. An average over these stochastic variables gives back the ensemble state at each time instant. This is the very core of any study on nonequilibrium fluctuations, and represents (as I will discuss in detail in the next section) both one of the main obstacles in and the main tool for a quantum version of this approach.

Motivated now by the structure of Eqs. (4.1) and (4.3), one may expect to find some laws connecting the statistics of the work in Eq. (4.5) to the change in free energy ΔF. Assuming the initial ensemble state of the system to be a thermal equilibrium state as

$$\rho_0 = \frac{1}{Z(\lambda_0)} e^{-\beta H(\lambda_0)}, \tag{4.6}$$

one exploits the knowledge of the partition function $Z(\lambda)$ to define the free energy as $F(\lambda) = -\frac{1}{\beta}\ln Z(\lambda)$. Assume also the final ensemble state of the open system to be a thermal equilibrium state at the same initial temperature but given with respect to the final Hamiltonian $H(\lambda_T)$. This can be easily achieved since one can always, by switching on the interaction with a bath, thermalise a system only through heat exchanges. The statistics of work is then unaffected by this last stage of the process.

With these definitions, it is straightforward to evaluate the quantity $\langle e^{-\beta W}\rangle$, where the average is taken over any possible trajectory the system may follow in its phase space and is then, mathematically speaking, an ensemble average. Since, once the driving is fixed, the stochasticity of trajectories originate only from the initial microstate distribution, such a term results in

$$\langle e^{-\beta W}\rangle \equiv \int \mathrm{d}q_0 \mathrm{d}p_0 \rho_0 e^{-\beta W}. \tag{4.7}$$

Since the system is isolated during the driving, the work performed on it equals the change in its Hamiltonian, so that one can write $W = H(q_T, p_T; \lambda_T) - H(q_0, p_0; \lambda_0)$. Moreover, by Liouville theorem, transforming the initial final phase space $\{q_0, p_0\}$ into the final one $\{q_T, p_T\}$ implies $\left|\frac{\partial q_T \partial p_T}{\partial q_0 \partial p_0}\right| = 1$. Thanks to these two conditions, Eq. (4.7) becomes

$$\langle e^{-\beta W}\rangle = \frac{1}{Z_0}\int \mathrm{d}q_T \mathrm{d}p_T e^{-\beta H(q_T, p_T; \lambda_T)} = \frac{Z_T}{Z_0} = e^{-\beta\Delta F}, \tag{4.8}$$

where $Z_0 = Z(\lambda_0)$ and $Z_T = Z(\lambda_T)$. This proves the so-called Jarzynski equality [59], which generalises Eqs. (4.1) and (4.3) to the case of arbitrary nonequilibrium processes. Once again it relates the stochastic structure of these processes, $\langle e^{-\beta W}\rangle$, to equilibrium features of the system. Such a law, despite its simplicity and its straightforward derivation, is an extremely powerful tool by which to tackle nonequilibrium physics, and represents together with its further generalisations which I will briefly present shortly, the highest level of statistical knowledge about far-from-equilibrium physics presently achievable. This equation remains unchanged if one introduces an environment along the driving protocol, and even in the case in which the features of the interaction with such an environment do not allow for a proper characterisation of a Gibbs state for the system. In this latter case, the temperature in Eq. (4.8) is the temperature of the environment. Note further that, if one supposes the work distribution to have a Gaussian shape, the predictions of Fluctuation-Dissipation relations in Eq. (4.3) are recovered.

In the same spirit of the previous discussion, and following analogous technical steps, two additional set of laws have been derived for classical systems, known as Crooks' work and entropy production fluctuation theorems [60]. They are given, respectively, as

$$\begin{aligned} \frac{p_f(W)}{p_b(-W)} &= e^{W-\Delta F}, & (4.9) \\ \frac{p_f(\sigma)}{p_b(-\sigma)} &= e^{\sigma}, & (4.10) \end{aligned}$$

where $p_f(x)$ is the probability that a quantity X takes the value x along the forward protocol from λ_0 to λ_T, while $p_b(-x)$ is the analogous probability along the so-called *backward* process generated by the time-reversed driving from λ_T to λ_0 and starting from the final ensemble state of the forward protocol. Finally, σ in Eq. (4.10) is the entropy which is produced along the protocol because of the total system being not in equilibrium. Incidentally, it is interesting to note that Eq. (4.10) expresses rigorously the meaning of the link between entropy increase and process direction which is implied by the second law of thermodynamics: the natural direction of a process is due to the microscopic asymmetry between such a direction and its backward counterpart, and this asymmetry is measured by the entropy production of the process itself.

All these laws, Eqs. (4.8)-(4.10), go under the name Fluctuation Theorems (FTs). In particular, a statement about the mean value of some function of stochastic nonequilibrium quantities, such as the Jarzynski equality (4.8), is usually referred to as Integral Fluctuation Theorem (IFT), while statements about probability distributions of these quantities are known as Detailed Fluctuation Theorems (DFTs). IFTs are usually regarded as consequences of DFTs, meaning that if a DFT holds for a certain quantity then also a IFT for the same quantity holds. It has been shown [165] however that the converse is also true, so that in the end IFTs and DFTs are just two different formulation of the same physical effect. All theorems belonging to these classes of laws, ultimately, reduce to two conceptual cores:

- They are a statement about the probability distribution of trajectories in phase space, and the asymmetric behaviour of systems under time reversal.
- They characterise a trajectory by means of one or more related physical quantities such as work or entropy production, and characterise the ensemble properties as originating from a collection of individual trajectory properties.

The quantum extension of these laws has to include both of these features in its formulation. In a later section I will briefly review two of the most used approaches to achieve such a result.

4.1.2 Classical entropy production

Before proceeding forward, it is useful here to discuss in some details the definition of classical stochastic entropy production [164, 165, 166, 167]. Apart from its direct connection to more standard thermodynamic quantities such as heat or work, it is indeed possible to characterise entropy contributions along single trajectories by means of information-based features linked to the concept of process direction and of the rate at which information is lost during a dissipative process [168]. Since now I am interested in characterising fluxes of entropy, connected to fluxes of energy flowing in/from the system, I start considering here what will be the physical setup throughout the following chapters: a driven open system continuously interacting with a reservoir. In particular, consider here a classical stochastic jump process which well characterises the single trajectory evolution of a broad class of physical systems. There is therefore a fixed and discrete set of states, referred to here with latin letters $i, j, \ldots$, between which the system can perform instantaneous transitions, characterised by the set of transition rates $\{R_{i,j}(\lambda)\}$. These rates depend on the driving parameter λ since they contain all the features of the microscopic dynamics [164]. Right after a transition to a level i, the time interval needed for the system to jump again, and the target state j, are not known *a priori* and are distributed according to some probability laws. The probability $p(i,t)$ of finding the system in the state i at time t is given by the solution of a classical master equation of the form

$$\dot{p}(i,t) = \sum_j \Big(p(j,t) R_{i,j}(\lambda) - p(i,t) R_{j,i}(\lambda) \Big). \tag{4.11}$$

The meaning of this equation is evident. The occupation probability of the state i changes in time because of two competing effects: a gain term taking into account the contribution of jumps from any other level to i and a loss term accounting for the probability of jumps from i to any other level. Although such a class of processes may at a first sight seem quite restrictive, it is enough to stress here that a continuous dynamics can be formally obtained as the limit of a jump process when the chosen basis becomes a continuous set (as for example the position of a particle in a diffusive process), in which case Eq. (4.11) tends to assume the structure of a Fokker-Planck equation. Specifying a single trajectory in this framework amounts then to fix a sequence of states, between which the system instantaneously jumps, and the time instants of those jumps.

Any time the state of a system becomes a stochastic variable distributed according to a certain probability p, and calling $n = N(t)$ the time series of microstates building up a trajectory, the entropy of the ensemble of such trajectories is given by

$$S_{\text{ens}}(t) = -\int \mathrm{d}n p(n,t) \ln p(n,t). \tag{4.12}$$

Note that such a definition of entropy, which reduces to the common Gibbs entropy at equilibrium, in information theory contexts goes under the name Shannon entropy [93]. It quantifies the information contained in a given decomposition of a mixed state or, in other words, how the particular set of trajectories available to the microscopic dynamics describes the information about the ensemble state of the system.

One can then quantify how rare the event "trajectory $n(t)$" is - or in other words how much such a trajectory contributes to the total ensemble entropy - by the quantity

$$s_n(t) = -\ln p(n(t), t). \tag{4.13}$$

It is interesting to note that such a quantity is also referred to as *surprise*, reflecting its feature as a measure of the rarity of an event. No surprise, meaning $p(n(t), t) \propto \delta\left(n(t) - n_0(t)\right)$, implies full knowledge about a system and indeed in this case its ensemble entropy goes to zero.

A jump trajectory generates two different contributions to the time variation of $s_n(t)$. Indeed

$$\dot{s}_n(t) = -\frac{1}{p(n(t), t)}\left[\frac{\partial p(n(t), t)}{\partial t} + \dot{n}\frac{\partial p(n(t), t)}{\partial n}\right]. \tag{4.14}$$

The first term describes the change in entropy of the system between jumps, which originates from the explicit time dependence of $p(n(t), t)$ due, among other things, also to the driving. To fix notation, suppose that the particular trajectory under scrutiny consists of N jumps $i_k \to j_k$ at times t_k. The second term in Eq. (4.14) weights the jump contributions, being different from zero only at times t_k due to the presence of $\dot{n}$, and (4.14) becomes

$$\dot{s}_n(t) = -\frac{1}{p(n(t), t)}\frac{\partial p(n(t), t)}{\partial t} - \sum_{k=1}^{N}\delta(t - t_k)\ln\frac{p(j_k, t_k)}{p(i_k, t_k)}. \tag{4.15}$$

When the system performs transitions between two states having, for instance, different energy, dissipation is involved. The presence of a reservoir allows us to model such a process as an exchange of energy between the system and its environment, which happens under the standard form of a heat flux. It is possible to show [164, 167] that the associated entropy term, of the standard form $\dot{s}_e = \frac{\delta Q}{T}$ at (or close to) thermal equilibrium, is generalised in the present case as

$$\dot{s}_e(t) = -\sum_{k=1}^{N}\delta(t - t_k)\ln\frac{R_{j_k,i_k}(\lambda(t_k))}{R_{i_k,j_k}(\lambda(t_k))}, \tag{4.16}$$

which expresses how much information is lost about the system following a dissipative energy exchange with the environment leading to the transition $i_k \to j_k$, comparing the rate of such a transition to the rate of the reversed jump $j_k \to i_k$. If these two rates are equal, on the average this particular dissipative process will have no preferential direction, heat fluxes from and to the system will balance and information about the system will neither get lost nor gained. One can therefore look at Eq. (4.16) as the entropy flowing from/into the environment due to the interaction with the system and measures the increase or decrease of the entropy of the reservoir: for this reason such a term is usually referred to as *entropy flux* or (reversing its sign) *environment entropy.*

The process being dissipative, the sum of entropy change in the system and in the environment is not zero and corresponds to the net entropy production along the trajectory, which has therefore the form

$$\dot{s}_i(t) \equiv \dot{s}_n(t) - \dot{s}_e(t) = -\frac{1}{p(n(t),t)}\frac{\partial p(n(t),t)}{\partial t} - \sum_{k=1}^{N} \delta(t-t_k) \ln \frac{p(j_k,t_k)R_{i_k,j_k}(\lambda(t_k))}{p(i_k,t_k)R_{j_k,i_k}(\lambda(t_k))}. \quad (4.17)$$

The total entropy production σ along the dissipative driven process, given by the time integral of Eq. (4.17) along a trajectory as $\sigma = \int_0^T \mathrm{d}t\dot{s}_i(t)$, represent the quantity which obeys the classical FT in Eq. (4.10). The proof of the fluctuation theorem for such a quantity is formally analogous to the corresponding proof in the quantum case, and I therefore postpone it to the next Section.

4.2 State of the art: quantum nonequilibrium thermodynamics

Moving to quantum systems and generalising the framework discussed in Section 4.1.1 presents at least two conceptual problems:

- The idea of trajectories in phase space does not exist. Moreover, the experimental observation of the evolution of a system fundamentally affects the evolution itself [169]. The question may arise then whether it makes even sense to speak about single nonequilibium processes for quantum systems.
- Quantities such as heat, work and entropy have no obvious general quantum analogues, since it is not possible to characterise these properties by means of observables [7].

Remarkably, these two problems question the cornerstones of classical fluctuation theorems: even more than by technical problems, a quantum formulation of fluctuation theorem is turned into a challenging task by conceptual ones. It is not surprising, then, that quantum extensions of Eqs. (4.8)-(4.10) [26, 27] are much less straightforward and describe a much richer set of physical behaviour than their classical counterpart.

To provide a full picture of quantum approaches to fluctuation theorems would require much more than a chapter, and goes far beyond the scope of this thesis. Here instead I aim at presenting two exemplary ways of tackling the problem, giving thus a glimpse of ideas and methods widely employed in these frameworks and allowing for the formalisation of quantities which will be at the core of the exposition of my results in the next Chapter.

Before entering into details, one can roughly separate the known approaches to quantum FTs into two groups, characterised by two different ways to tackle the conceptual problems previously discussed. To the first group belong laws based on the assumption that the single nonequilibrium dynamics is not experimentally monitored so that the system, in the time interval $(0,T)$, evolves as a quantum ensemble whose density matrix changes in time according to a quantum master equation [27]. Information about physical properties of the system is extracted by projective measurements on the system at the beginning of the driving process ($t = 0$), at the end of the driving process ($t = T$) and, possibly, at fixed time instants $t_i \in (0, T)$. This approach has the advantage to extract information about the system by standard measurements on its state (so that all the standard quantities such as mean energy or von Neumann entropy can easily be defined), but renounces trying to define a quantum analogue to a phase space trajectory since the dynamics between measurements is an ensemble evolution. The influence of each measurement is, moreover, strong as it resets the system to a pure state partially hiding the full quantumness of its evolution as open system. The second class, on the other hand, follows a complementary idea. Employing a known method to rewrite any local-in-time quantum master equation in the form of a rate-like equation for the instantaneous population of the density matrix, one can exploit the formal analogy between the new form of the quantum ME and the classical ME to characterise a single quantum nonequilibrium dynamics, in analogy with the classical definition discussed in the previous Section, as a jump process between instantaneous eigenstates of the density matrix [26, 62]. The advantage of this second class of approaches dwells on the fact that the full quantum ensemble dynamics is recovered by averaging over these "classical"-like trajectories, which can therefore be regarded as a possible analogue to classical phase space trajectories. However, the experimental characterisation of these trajectories, and therefore of their physical properties, is not in general fully clear. In particular, it is not straightforward to link each jump in these processes to a well defined transition involving a clear role of the environment. The connection to physical quantities such as heat flux is then controversial.

Later on in this thesis, and in the next Chapter in particular, I will discuss how my work managed to reconcile these two approaches in producing single, purely quantum trajectories having a direct and clear physical characterisation in terms of fluxes in/form the environment. Before moving to this topic, however, it is necessary to rigorously present examples for each of the two just discussed classes of approaches in order to better appreciate the novelties of my results.

4.2.1 Characteristic function method from two-point measurement statistics

This method [27, 67] belongs to the first class of approaches, relying on a discrete number (two, in this case) of projective measurements on an open quantum system whose ensemble state $\rho(t)$ otherwise evolves from t_0 to t under the action of a CPT map $\Lambda(t, t_0; \lambda)$. The need for an ensemble description arises here because of the possible interaction of the system with an environment, which generally brings pure states into mixed states. In addition, the CPT map also depends on the external driving parameter λ which in turn depends on time. The ensemble dynamics is described by the action of the CPT map as

$$\rho(t) = \Lambda(t, t_0; \lambda)\rho(t_0). \tag{4.18}$$

Such an evolution may either be unitary (in the case of a closed quantum system), or may describe dissipation and decoherence by means of a dynamical map. Throughout this Section I will assume such a map to be Markovian (i.e., the dynamics to be memoryless).

Before the process starts a certain observable $O_A = \sum_{i,\nu_i} a_i |a_i^{\nu_i}\rangle\langle a_i^{\nu_i}|$ is measured on the state $\rho(t_0)$ of the system (involving, in some cases, also a measurement on the environment). The symbol ν_i takes here into account possible degeneracies of the eigenvalue a_i. Introducing for the sake of brevity the notation $P_{a_i} = \sum_{\nu_i=1}^{d(a_i)} |a_i^{\nu_i}\rangle\langle a_i^{\nu_i}|$, where $d(a_i)$ is the degeneracy of the eigenvalue a_i, having measured a_s projects the state of the system onto

$$\rho_0 \to \rho_s = \frac{1}{p(a_s)} P_{a_s} \rho_0 P_{a_s}, \tag{4.19}$$

where $p(a_s) = \mathrm{Tr}\,(P_{a_s}\rho_0)$ is the probability of obtaining the outcome a_s after a measurement on ρ_0. Let now the system evolve under the action of Λ from $t = 0$ to $t = T$, so that its state becomes

$$\rho_s \to \rho_T(\lambda) = \Lambda(T, 0; \lambda)\rho_s. \tag{4.20}$$

Finally, perform another measurement on the system of an observable $O_B = \sum_{j,\mu_j} b_j |b_j^{\mu_j}\rangle\langle b_j^{\mu_j}|$ which needs in general not to be the same as O_A. With self-evident notations P_{b_j} and $p(b_j)$, the effect of having measured b_f is

$$\rho_T(\lambda) \to \rho_f = \frac{1}{p(b_f)} P_{b_f} \rho_T(\lambda) P_{b_f}. \tag{4.21}$$

Note that the stochasticity in this approach dwells on the intrinsic probabilistic structure of quantum theory when predicting a measurement outcome and on the unavoidable effect a projective measurement has on the state of a system, which is projected onto an eigenspace of the measured observable. In this respect, such a stochasticity is purely quantum, having no classical analogue and being conceptually and operationally different from the stochastic structure of classical nonequilibrium thermodynamics discussed in Section 4.1.1.

The probability distribution of the difference of measurement outcomes at $t = 0$ and $t = T$, i.e. of the random variable m, is given by

$$p(m; \lambda) = \sum_{s,f} \delta\big(m - (b_f - a_s)\big) p(b_f, a_s; \lambda), \tag{4.22}$$

where $p(b_f, a_s; \lambda) = p_{f|s}(\lambda) p(a_s)$, $p_{f|s}(\lambda) = \frac{1}{p(a_s)} \mathrm{Tr}\left(P_{b_f} \rho_T(\lambda)\right)$ being the conditional probability of measuring b_f at $t = T$ after having measured a_s at $t = 0$. The joint two-point measurement probability $p(b_f, a_s; \lambda)$ is the crucial quantity on which any characteristic function approach is based. It is worth stressing here again that such a function describes all the stochasticity of the process, which is due to the a priori unpredictable states in which the system is initially prepared by the first projective measurement and finally projected by the second one. This corresponds to the classical uncertainty in initial and final microstate in phase space. However, along the driving dynamics the system evolves as an ensemble, and as such this method does not fully reproduce the underlying physics of a classical FT (although, as I will show shortly, it recovers the same formal structure) since it is affected by the lack of knowledge about the state of the system in the interval $(0, T)$.

Consider now the generating (or characteristic) function of $p(m; \lambda)$ defined as

$$G(x; \lambda) = \int \mathrm{d}m e^{ixm} p(m; \lambda). \tag{4.23}$$

Such a function obeys a set of properties which ultimately lead, in a number of cases, to quantum fluctuation theorems [170]. Evaluate for example its value for $x = i$. After some calculation, introducing the weighted average initial state $\rho_s^{\mathrm{av}} = \sum_s P_{a_s} \rho_0 P_{a_s}$, one obtains

$$G(i;\lambda) \equiv \langle e^{-m} \rangle_\lambda = \mathrm{Tr}\left(e^{-O_B} \Lambda(T,0,\lambda)(\rho_s^{\mathrm{av}} e^{O_A})\right) = \Gamma(O_A, O_B; \lambda), \tag{4.24}$$

where $\langle \cdot \rangle_\lambda$ stands for an average over many repetitions of the same two-point measurement scheme under a fixed driving protocol. Γ in Eq. (4.24) depends in general on the two chosen observables O_A and O_B and on the driving protocol. This should not surprise since, to obtain a standard FT, one has to properly fix the two measured observables. Indeed, suppose one is interested in obtaining the quantum analogues of the classical Jarzynki equality in Eq. (4.8) and Crooks' work theorem in Eq. (4.9). To avoid technical and conceptual issues, let us operate in the standard approximation of weak coupling and starting from a thermal equilibrium state at inverse temperature β of the open system: one can therefore easily characterise the work W performed by the driving on the system. Since the driving is applied on the open system only, the environment energy change can be interpreted as originating from an heat flux Q, while the total energy change ΔE of the open system will be due to such an heat flux plus the driving work. In other words

$$W = \Delta E + Q = \left(E_f^S(T;\lambda_T) - E_s^S(0;\lambda_0)\right) + \left(E_f^E - E_s^E\right), \tag{4.25}$$

where $E_i^S(t;\lambda)$ is a possible eigenvalue of the open system Hamiltonian $H_S(t;\lambda)$ and E_i^E is one of the eigenvalues of the Hamiltonian of the environment H_E. One can therefore choose the initial and final observables to be measured as $O_A = H_S(0;\lambda_0) + H_E$ and $O_B = H_S(T;\lambda_T) + H_E$.

One has therefore two independent stochastic quantities ΔE and Q, so that the variable x in Eq. (4.23) is the two dimensional variable $x = \{x_S, x_E\}$. It has been shown by Talkner *et al.* [171] that in the case just described the function $G(x_S, x_E; \lambda)$ satisfies the relation

$$G(x_S, x_E; \lambda) = \frac{\mathrm{Tr} e^{-\beta H_S(T;\lambda_T)}}{\mathrm{Tr} e^{-\beta H_S(0;\lambda_0)}} G(-x_S + i\beta, -x_E - i\beta; \lambda_b) \tag{4.26}$$

λ_b being the backward driving protocol. Note that, following the classical definition, $\mathrm{Tr} e^{-\beta H_S(t;\lambda)}$ is the partition function of the open quantum system and one can introduce then its net free energy change ΔF through $\frac{\mathrm{Tr} e^{-\beta H_S(T;\lambda_T)}}{\mathrm{Tr} e^{-\beta H_S(0;\lambda_0)}} = e^{-\beta \Delta F}$.

Taking the inverse Fourier transform of Eq. (4.26) and employing the definition of work in Eq. (4.25) one finally gets

$$\frac{p(W;\lambda)}{p(-W;\lambda_b)} = e^{\beta(W - \Delta F)}, \tag{4.27}$$

which is the quantum version of Crooks' theorem and, rearranging Eq. (4.27) and taking the average according to $p(W;\lambda)$, the quantum Jarzynski equality $\langle e^{-\beta W} \rangle = e^{-\beta \Delta F}$ is recovered.

4.2.2 Classical-like jump processes from local-in-time quantum master equations

As a last part of this thematic introduction about the state of the art of quantum nonequilibrium thermodynamics, I discuss an example of the other class of approaches to quantum FTs, i.e. a method [62, 172] based on a rigorous definition of single "classical"-like trajectories. I will spend a few more words presenting this method since it represents the starting point of part of my work. It is then useful to carefully fix notations and concepts.

Consider then an open quantum system with free Hamiltonian H_S, interacting with an environment (free Hamiltonian H_E) via an interaction term H_I. Suppose the free Hamiltonian of the open system to show a certain time dependence caused by some parameters being externally modified in time through the driving. Such an external modification drives the system far from its initial equilibrium (or stationary) state and towards a final state characterised by different values of these control variables. During its evolution the system interacts with its environment, and assume that the interaction and the features of both system and environment are such that the Markovian approximation holds. The description of the ensemble dynamics can be given employing a master equation [112] for the open system density matrix $\rho(t)$, describing a general quantum dynamics:

$$\frac{d}{dt}\rho(t) = -i\,[H(t),\rho] + \sum_i \gamma_i(t)\Big[A_i(t)\rho A_i^\dagger(t) - \frac{1}{2}\Big\{A_i^\dagger(t)A_i(t),\rho\Big\}\Big]. \tag{4.28}$$

The Hamiltonian $H(t)$ in Eq. (4.28) describes the unitary part of the open system evolution, which is given by its free Hamiltonian $H_S(t)$ plus a renormalisation term due to the interaction with the bath. The nonunitary part of the evolution, describing dissipation and dephasing, is accounted for by a set of generally time-dependent Lindblad operators $A_i(t)$ and corresponding relaxation rates $\gamma_i(t)$. Equation (4.28) describes the most general Markovian process in terms of a master equation which is local in time [3]. As discussed in Chapter 1, the Markovian features of the dynamics are assured by the condition $\gamma_i \geq 0 \;\; \forall i$ [113] and by the fact that both rates and Lindblad operators are time-independent. In the case of time-dependent operators $A_i(t)$ and/or rates $\gamma_i(t)$, which however satisfy the condition $\gamma_i(t) \geq 0 \;\; \forall i, t$, the structure of the master equation is still Markovian at any time instant and for such a reason the process is referred to as a time-dependent Markovian process [116]. In this latter case, however, it is worth stressing that the corresponding dynamics is not described by a quantum dynamical semigroup. [117].

The starting point of this approach on nonequilibrium fluctuations is the expression for thermodynamic ensemble quantities. To complete the quantum outlook of fluctuation theorems, I discuss here the case of entropy fluctuations described, classically, by Eq. (4.10). In quantum ensemble theory, the entropy of an open system is well characterised by its von Neumann entropy $-\mathrm{Tr}\rho\ln\rho$. One needs therefore to express the time variation of the von Neumann entropy along a generic nonequilibrium dynamics. To this end, one can write the state of the open quantum system as [62]

$$\rho(t) = \sum_a \mu_a(t)|a(t)\rangle\langle a(t)|, \tag{4.29}$$

where the set $\mathfrak{B}(t) = \{|a(t)\rangle\}$ is a time-dependent orthonormal basis of the open system Hilbert space instantaneously diagonalising $\rho(t)$, and $\sum_a \mu_a(t) = 1$. This is always possible since, by construction, Eq. (4.28) preserves the hermiticity of the state. Using the generator of the dynamics given in Eq. (4.28) and calculating the mean value of Eq. (4.28) for a state $|b(t)\rangle \in \mathfrak{B}(t)$, one easily obtains a Pauli-type master equation for the evolution of the population $\mu_b(t)$,

$$\dot{\mu}_b(t) = \sum_a \Big(R_{ba}(t)\mu_a(t) - R_{ab}(t)\mu_b(t) \Big), \tag{4.30}$$

where the total instantaneous transition rate $R_{ba}(t)$ between two states $|a(t)\rangle$ and $|b(t)\rangle$ belonging to $\mathfrak{B}(t)$ is defined as

$$R_{ba}(t) = \sum_i \gamma_i(t) |\langle b(t)|A_i(t)|a(t)\rangle|^2. \tag{4.31}$$

These transition rates will turn out to be crucial in the expression for all thermodynamic quantities of interest. Note, in addition, the equivalence of Eq. (4.30) and the classical counterpart in Eq. (4.11). This equivalence is only formal, since the time evolution of the quantum rates $R_{ba}(t)$ in Eq. (4.31) is nontrivially non-classical because it depends on the time evolution of the basis $\mathfrak{B}(t)$ which, in turn, is generated by a purely quantum master equation. Nevertheless, by rewriting Eq. (4.28) in the form (4.30) one hides all the dynamical quantum features in the set $\{R_{ba}(t)\}$ and can exploit the formal analogy to the classical case.

In the case of a (possibly time-dependent) Markovian dynamics, the rates given by Eq. (4.31) never become negative. In what follows I will use indices a and b to label vectors in the instantaneous eigenbasis of $\rho(t)$ (recall Eq. (4.29)), and an index i to label the possible decay channels described by the set of Lindblad operators $A_i(t)$ in (4.28). I will furthermore, for the sake of brevity, sometimes suppress the time arguments of the instantaneous eigenvectors and eigenvalues of $\rho(t)$.

Having at disposal the instantaneous eigenbasis of $\rho(t)$, one straightforwardly obtains the time derivative $\dot{S}$ of the system's von Neumann entropy in the form

$$\dot{S}(t) = -\sum_b \dot{\mu}_b(t) \ln \mu_b(t). \tag{4.32}$$

Using now Eq. (4.30) one finds

$$\dot{S}(t) = -\sum_{a,b} \mu_a(t) R_{ba}(t) \ln \frac{\mu_b(t)}{\mu_a(t)}. \tag{4.33}$$

Using such an expression for the time derivative of entropy, and (motivated by the formal analogy of the two master equations) following usual prescriptions of nonequilibrium thermodynamics [166, 167] discussed in Section 4.1.2, Eq. (4.33) can be written as a sum of the different contributions $\dot{S}(t) = \dot{S}_e(t) + \dot{S}_i(t)$, having defined

$$\dot{S}_e(t) = -\sum_{a,b} \mu_a(t) R_{ba}(t) \ln \frac{R_{ba}(t)}{R_{ab}(t)}, \tag{4.34}$$

$$\dot{S}_i(t) = \sum_{a,b} \mu_a(t) R_{ba}(t) \ln \frac{\mu_a(t) R_{ba}(t)}{\mu_b(t) R_{ab}(t)} \tag{4.35}$$

as, respectively, the entropy flux between system and environment and the total entropy production. Equations (4.33), (4.34) and (4.35) describe the time dependence of entropy due to the ensemble dynamics described by a TCL master equation. The irreversibility of the process is characterised by a nonzero rate of entropy production $\dot{S}_i(t)$ which, furthermore, in the case of a Markovian dynamics never becomes negative. It is worth stressing that the definition (4.35) for the entropy production coincides with the negative time derivative of the relative entropy of $\rho(t)$ and the stationary state ρ_{stat} of the dynamics, provided the latter exists and detailed balance holds. Eq. (4.35) thus quantifies how far from stationarity the instantaneous state of the system is.

The above defined quantities characterise the physics of the open quantum system on an ensemble level. Such a picture, while allowing one to derive suitable expressions for many quantities of interest, lacks however a characterisation of single nonequilibrium processes as microscopic trajectories and, in particular, of their intrinsically fluctuating physical quantities. In order to describe these fluctuations it is possible to employ the master equation (4.30) which in the Markovian case only involves positive transition rates and can thus be regarded as a differential Chapman-Kolmogorov equation for a classical, Markovian stochastic jump process such as Eq. (4.11) with, in general, time-dependent rates $R_{ba}(t)$. Consider a particular, yet generic realisation of this process,

$$|a_0(t_0)\rangle \rightarrow |a_1(t_1)\rangle \rightarrow \cdots \rightarrow |a_N(t_N)\rangle, \tag{4.36}$$

consisting of N jumps at times $t_1, t_2, \ldots, t_N$ between well defined states belonging to the instantaneous eigenbasis of $\rho(t)$. Performing a classical-like unraveling of the master equation (4.30) (i.e., writing the ensemble dynamics of the system as a collection of single pure state classical-like jump trajectories) the probability of the trajectory (4.36) is

$$p_f = \mu_{a_0}(t_0) \prod_{j=0}^{N-1} e^{-\int_{t_j}^{t_{j+1}} \mathrm{d}\tau \sum_b R_{ba_j}(\tau)} \prod_{j=0}^{N-1} R_{a_{j+1}a_j}(t_{j+1}) \mathrm{d}t_{j+1}, \tag{4.37}$$

where the first factor gives the probability for the system to start its trajectory in the state $|a_0\rangle$, the second factor gives the probability of having no jumps between the times t_j and t_{j+1}, and the third factor represents the probability of having N jumps within infinitesimal time intervals $\mathrm{d}t_j$ around t_j between the states of the trajectory (4.36).

It is important to emphasize that the stochastic description given by Eq. (4.37) is based on the Pauli-type master equation (4.30) and thus correspond to the standard stochastic unraveling of a classical Markovian master equation [173], in which the probability for a transition from state $|a(t)\rangle$ to state $|b(t)\rangle$ during the time interval $\mathrm{d}t$ is determined by $R_{ba}(t)\mathrm{d}t$ with the rate given by Eq. (4.31). Thus, I follow here the interpretation proposed in [62] to identify the fluctuations of single nonequilibrium processes with those described by the evolution equation (4.30) for the populations of the density matrix. This interpretation and the underlying physical picture has to be carefully distinguished from the interpretation of the stochastic wave function methods (see, e.g., Ref. [125] and references therein) for the open system dynamics given by a quantum master equation of the form of Eq. (4.28) in terms of a continuous measurement of the environment.

Indeed, analysing the structure of transition rates $R_{ba}(t)$, one easily sees that they are not associated to a single dissipative process involved in the quantum master equation and described by a Lindblad operator A_i. On the contrary, they are given as a sum of effects of virtually *all* Lindblad operators. Since Lindblad operators describe physical processes involving exchanges of energy/information with the environment, the characterisation of a rate R_{ba} in terms of a particular physical flux form/to the environment is not, in general, possible.

The backward process corresponding to (4.36) is described by the trajectory

$$|a_N(t_N)\rangle \to |a_{N-1}(t_{N-1})\rangle \to \cdots \to |a_0(t_0)\rangle. \tag{4.38}$$

The probability p_b for such a backward process is defined analogously to what has been done for the forward one, taking into account the jumps in the sequence given in Eq. (4.38) such that the conditional non-jump evolution probability is then the same for forward and for backward processes, while the jump rates are reversed,

$$p_b = \mu_{a_N}(t_N) \prod_{j=0}^{N-1} e^{-\int_{t_j}^{t_{j+1}} \mathrm{d}\tau \sum_b R_{ba_j}(\tau)} \prod_{j=0}^{N-1} R_{a_j a_{j+1}}(t_{j+1})\mathrm{d}t_{j+1}. \tag{4.39}$$

The logarithm of the ratio of these two probabilities takes then the form

$$\ln \frac{p_f}{p_b} = \ln \frac{\mu_{a_0}(t_0)}{\mu_{a_N}(t_N)} + \sum_{j=0}^{N-1} \ln \frac{R_{a_{j+1}a_j}(t_{j+1})}{R_{a_j a_{j+1}}(t_{j+1})}. \tag{4.40}$$

Note now that the first term on the r.h.s. of Eq. (4.40),

$$\Delta s = \ln \frac{\mu_{a_0}(t_0)}{\mu_{a_N}(t_N)}, \tag{4.41}$$

represents the net change of the von Neumann entropy along the single forward trajectory, while

$$\Delta s_e = -\sum_{j=0}^{N-1} \ln \frac{R_{a_{j+1}a_j}(t_{j+1})}{R_{a_j a_{j+1}}(t_{j+1})} \tag{4.42}$$

yields the single trajectory contribution to the entropy flux (4.34), integrated along the forward process. Note that the average of Eqs. (4.41) and (4.42) over all possible trajectories leads to the expressions (4.33) and (4.34), respectively. Defining

$$\sigma = \Delta s - \Delta s_e \tag{4.43}$$

as the total entropy production along a single trajectory, Eq. (4.40) implies the entropic fluctuation theorem for Markovian dynamics as

$$\frac{p_f(\sigma)}{p_b(-\sigma)} = e^{\sigma}, \tag{4.44}$$

which is formally the same as its classical analogue. From Eq. (4.44), and properly linking the production of entropy to heat and work along a trajectory, the quantum analog of Crooks theorem [174] and the quantum Jarzynski equality [175] directly follow.

Chapter 5

Results on quantum nonequilibrium thermodynamics

In this Chapter I present the part of my results dealing with fluctuations in nonequilibrium quantum processes. These results encompass two different contributions to the state of the art on quantum fluctuation theorems discussed in Chapter 4, namely, the introduction of memory effects into the formulation of classical-like jump processes (the Markovian formulation of which is given in [34] and discussed in Section 4.2.2), and the characterisation of entropy fluctuations with the use of true quantum trajectories of open systems, having a clear connection to thermodynamics since they are given an experimental meaning in connection to fluxes from/to an environment. In both these approaches the open system is, clearly, out of equilibrium and a formalisation of its ensemble dynamics through a master equation (ME) formalism is needed.

The results presented in this Chapter have been obtained by me working together with Dr. A. Napoli, Prof. A. Messina and Prof. H.-P. Breuer, and are published in [72, 73].

5.1 Fluctuation theorems for non-Markovian quantum processes

This Section is devoted to my results about non-Markovian entropy fluctuation theorems published in [72]. Exploiting the previously discussed results on Markovian classical-like jump processes and fluctuation theorems, I studied consequences of memory effects along single realisations of nonequilibrium processes of an open quantum system and, in particular, in fluctuations of the associated entropy production. As I will show in this Section, the presence of memory effects in the dynamics of the system leads to a correction to the standard form of FT. Such a connection can be interpreted as the interplay between the information extracted from the system through measurements and the flow of information from the environment to the open system itself. This flow, due to non-Markovian effects, generates single realisations of a dynamic process which are no longer independent. Their correlations therefore fundamentally affect the behaviour of entropy fluctuations.

5.1.1 The master equation

To fix ideas, consider the same setup described in Section 4.2.2, consisting of an open quantum system in interaction with a bath. Differently from the case of memoryless processes, however, no assumption is made here on the strength or on the features of the system-bath interaction. In general, therefore, the open system considered here undergoes a non-Markovian dynamics described by the time convolutionless (TCL) master equation in Eq. (4.28), which I report here again:

$$\frac{d}{dt}\rho(t) = -i\,[H(t),\rho] + \sum_i \gamma_i(t)\Big[A_i(t)\rho A_i^\dagger(t) - \frac{1}{2}\Big\{A_i^\dagger(t)A_i(t),\rho\Big\}\Big]. \tag{5.1}$$

Despite being local in time, this equation can describe the most general case of memory effects through the sign of decay rates $\gamma_i(t)$. Indeed, as stated in Section 1.4.3, a necessary condition for the ME (5.1) to describe a non-Markovian dynamics is that at least one decay rate $\gamma_k(t)$ becomes negative during a finite time interval [117]. Moreover, in addition to the time evolution due to the interaction with the environment, the free Hamiltonian of the open system is supposed to show a certain, well defined time dependence because of the driving applied on some of its parameters. This time dependence is implicitly included in Eq. (5.1) in the form of $H(t)$. It is worth stressing again here that the nonunitary part of the evolution is accounted for by a set of generally time-dependent and non-Hermitian Lindblad operators $A_i(t)$ corresponding to the relaxation rates $\gamma_i(t)$, each of which describes a certain physical process leading to dissipation or dephasing [3].

In the corresponding Markovian case, these operators are used to define the transition rates $R_{ba}(t)$ between two instantaneous eigenstates $|a(t)\rangle$ and $|b(t)\rangle$ of $\rho(t)$ as

$$R_{ba}(t) = \sum_i \gamma_i(t)|\langle b(t)|A_i(t)|a(t)\rangle|^2. \tag{5.2}$$

These are well-defined quantities also in the presence of memory effects because a non-Markovian ME preserves the hermiticity of ρ at each time instant, which is then always diagonalisable and has therefore at each time instant a set of eigenvalues $\{\mu_a(t)\}$ and associated eigenvectors $\{|a(t)\rangle\}$. The meaning and the (lack of direct) connection of these rates with physical fluxes of energy and/or information between system and environment has been discussed in Section 4.2.2. Here note that, because of memory effects, these rates *may* become negative. In what follows I define a process and, consequently, its set of pure state jump trajectories as being non-Markovian if at least one of these transition rates become temporarily negative.

5.1.2 Non-Markovian effects

A first attempt to take into account negative decay rates in the formulation of a fluctuation theorem was already performed in [172] where, however, a clear formulation of a non-Markovian fluctuation theorem was not given. In particular the approach of [172] works well as long as all the transition rates $R_{ba}(t)$ stay positive. This means that, in the formalism employed here, such results do not describe memory effects in the fluctuation of entropy production since the transition rates being negative is exactly the characterisation given here of a non-Markovian process. Note that this characterisation is not arbitrary since, as shown later on, it implies the open system to increase its entropic distance from its instantaneous stationary state, which is related to one of the most employed definition of quantum non-Markovianity. A study of nonequilibrium fluctuations was never performed for this class of genuinely non-Markovian processes and has been the subject of part of my research.

5.1.2.1 Renormalized entropies

Analogously to what is usually done in the Markovian case, one begins by analysing the entropic ensemble behaviour of the open quantum system. The equation for the time derivative of the von Neumann entropy for a non-Markovian system is naturally the same as Eq. (4.32), but now the time evolution of populations is affected by memory effects. To see where exactly these effects come into play, one must closely analyse the Pauli rate equation for the population of the density matrix, Eq. (4.30), which is a direct consequence of the TCL structure of any master equation, either Markovian or not. Such an expression for $\dot{\mu}_b(t)$ depends on the transition rates $R_{ba}(t)$ in (5.2). Notice now that each term in the sum on the right-hand side of (5.2) is proportional to a decay rate $\gamma_i(t)$ which, in the non-Markovian case, may cause the whole sum to temporarily become negative. This means that the Pauli-like rate equation (4.30) is characterised by negative jump probabilities which, clearly, have to be given a physical meaning. To deal with this, rewrite the total transition rates as

$$R_{ba}(t) = R^{\mathrm{M}}_{ba}(t) - R^{\mathrm{NM}}_{ba}(t), \tag{5.3}$$

where the Markovian contribution $R^{\mathrm{M}}_{ba}(t)$ and the non-Markovian contribution $R^{\mathrm{NM}}_{ba}(t)$ are defined by

$$\begin{aligned} R^{\mathrm{M}}_{ba}(t) &= \frac{1}{2}\big[|R_{ba}(t)| + R_{ba}(t)\big], && (5.4)\\ R^{\mathrm{NM}}_{ba}(t) &= \frac{1}{2}\big[|R_{ba}(t)| - R_{ba}(t)\big]. && (5.5) \end{aligned}$$

With these definitions, the time derivative of the von Neumann entropy in Eq. (4.32) can be rewritten as

$$\dot{S}(t) = -\sum_{a,b} \mu_a(t)\Big(R^{\mathrm{M}}_{ba}(t) - R^{\mathrm{NM}}_{ba}(t)\Big) \ln\frac{\mu_b(t)}{\mu_a(t)}. \tag{5.6}$$

The occurrence of memory effects has the consequence of reducing the rate of change of the entropy of the system during certain intervals of time. This means that, in the evolution of the entropy of an open system, there exist two separate Markovian and non-Markovian contributions always counteracting each other.

The next step is now to define entropy flux and entropy production for the analysed process. In particular it is interesting to investigate the possibility of singling out non-Markovian contributions in these two quantities, as done for the von Neumann entropy itself. In analogy with the Markovian entropy contributions defined in Eqs. (4.34) and (4.35), one writes

$$\dot{S}(t)=\dot{\mathfrak{S}}_e(t)+\dot{\mathfrak{S}}_i(t), \tag{5.7}$$

where formally both $\dot{\mathfrak{S}}_e(t)$ and $\dot{\mathfrak{S}}_i(t)$ are the entropy flux and production for the ensemble dynamics, and have the same structure of Eqs. (4.34) and (4.35) in terms of transition rates $R_{ba}(t)$. They describe however a fundamentally different physics with respect to the Markovian case because of the new properties of the transition rates $R_{ba}(t)$. Indeed one has

$$\begin{aligned}\dot{\mathfrak{S}}_e(t) &= -\sum_{a,b}\mu_a(t)\Big(R^{\mathrm{M}}_{ba}(t)-R^{\mathrm{NM}}_{ba}(t)\Big)\ln\frac{R^{\mathrm{M}}_{ba}(t)-R^{\mathrm{NM}}_{ba}(t)}{R^{\mathrm{M}}_{ab}(t)-R^{\mathrm{NM}}_{ab}(t)}, && (5.8)\\ \dot{\mathfrak{S}}_i(t) &= \sum_{a,b}\mu_a(t)\Big(R^{\mathrm{M}}_{ba}(t)-R^{\mathrm{NM}}_{ba}(t)\Big)\ln\frac{\mu_a(t)\Big(R^{\mathrm{M}}_{ba}(t)-R^{\mathrm{NM}}_{ba}(t)\Big)}{\mu_b(t)\Big(R^{\mathrm{M}}_{ab}(t)-R^{\mathrm{NM}}_{ab}(t)\Big)}. && (5.9)\end{aligned}$$

In addition, these quantities (as already highlighted in [172]) involve logarithms of possibly negative terms and may therefore become temporarily ill-defined (although both the von Neumann entropy and its time derivative are of course always mathematically and physically well-defined). Moreover, it is not possible to single out Markovian and a non-Markovian contributions to these quantities since the arguments of both logarithms involve Markovian and non-Markovian effects in a non-factorizable way. The way memory effects enter entropic terms involving also a role of the environment is much more obscure than the simple addition of a further term to the time derivative of von Neumann entropy.

One might then wonder whether it is even possible to speak about ensemble entropy production along non-Markovian dynamics. The appearance of negative rates is, by definition, the characterisation chosen here of non-Markovianity, and it is known that these rates can not all together be negative at the same time, which means there will always be at least one negative ratio involved in the definition of entropy flux and entropy production. To overcome this problem, consider again Eq. (5.7) which amounts to writing the time derivative of von Neumann entropy as a sum of two contributions. Notice however that, apart from the factor μ_a/μ_b (which can be singled out as an additional logarithmic term in the sum), the arguments of each logarithm in $\dot{\mathfrak{S}}_e(t)$ and $\dot{\mathfrak{S}}_i(t)$ are the same. This suggests to replace all negative ratios R_{ba}/R_{ab} under the logarithms by their moduli $|R_{ba}/R_{ab}|$. Indeed, after such a replacement the decomposition of $\dot{S}(t)$ into the two contributions still holds as can be easily checked. To grasp the physical meaning of this replacement, consider the Markovian case in which the entropy production has the form $\dot{S}_i(t)=\sum_{a,b}\mu_a(t)R_{ba}(t)\ln\frac{\mu_a(t)R_{ba}(t)}{\mu_b(t)R_{ab}(t)}$. Assume now that the (instantaneous) stationary state $\rho^{SS}(t)$ of the (possibly time dependent) Makovian dynamics satisfies the detailed balance condition for its populations

$$\frac{\mu_a^{SS}}{\mu_b^{SS}}=\frac{R_{ab}(t)}{R_{ba}(t)}. \tag{5.10}$$

It is then easy to show that $\dot{S}_i(t)=-\frac{\mathrm{d}}{\mathrm{d}t}S(\rho(t)\|\rho^{SS}(t))$, where $S(\rho(t)\|\rho^{SS}(t))$ is the relative entropy [93] of the state $\rho(t)$ to its stationary state and measures how far the state of the open system is from stationarity. The fact that, for a Markovian process, $\dot{S}_i(t) \geq 0$ is a consequence of the fact that along a memoryless dynamics a system monotonically approaches stationarity. One can thus understand that the entropy production (5.9) for non-Markovian systems becomes temporarily undefined when an instantaneous state of the form (5.10) does not exist because $R_{ba}/R_{ab} < 0$. The lack of an instantaneous stationary state is, as commented in Section 1.4.3, a typical feature of non-Markovianity.

The dynamical consequences of memory effects can, however, be probed by analysing the relative evolution of any two states. In particular, the replacement $R_{ba}/R_{ab} \to |R_{ba}/R_{ab}|$ amounts to the definition of an *effective* instantaneous stationary condition $\rho^{SS}_{\text{eff}}(t)$ which satisfies

$$\frac{\mu_a^{SS_{\text{eff}}}}{\mu_b^{SS_{\text{eff}}}} = \frac{|R_{ab}(t)|}{|R_{ba}(t)|} \tag{5.11}$$

and with respect to which one can follow the evolution of the state $\rho(t)$. This choice is motivated by the fact that, when the dynamics is Markovian, such an effective stationary state reduces to the actual stationary state. Consider the measure of non-Markovianity [41] in Eq. (1.26), which is characterised by a maximisation over each pair of states of the open system. Since, by construction, $\rho^{SS}_{\text{eff}}(t)$ is a physical state at any instant of time, any increase of the (entropic) distance between $\rho(t)$ and $\rho^{SS}_{\text{eff}}(t)$ is a sufficient condition for the measure in Eq. (1.26), reformulated using the relative entropy instead of the trace distance as a distance of quantum states, to be nonzero. This formulation detects therefore a sub-class of non-Markovian processes, namely, the ones in which non-Markovianity has a direct thermodynamic consequence.

It is thus natural to define entropy flux and production for the non-Markovian ensemble dynamics as

$$\dot{S}_e(t) = -\sum_{a,b} \mu_a(t)\Big(R^{\text{M}}_{ba}(t) - R^{\text{NM}}_{ba}(t)\Big) \ln \frac{\Big|R^{\text{M}}_{ba}(t) - R^{\text{NM}}_{ba}(t)\Big|}{\Big|R^{\text{M}}_{ab}(t) - R^{\text{NM}}_{ab}(t)\Big|}, \tag{5.12}$$

$$\dot{S}_i(t) = \sum_{a,b} \mu_a(t)\Big(R^{\text{M}}_{ba}(t) - R^{\text{NM}}_{ba}(t)\Big) \ln \frac{\mu_a(t)\Big|R^{\text{M}}_{ba}(t) - R^{\text{NM}}_{ba}(t)\Big|}{\mu_b(t)\Big|R^{\text{M}}_{ab}(t) - R^{\text{NM}}_{ab}(t)\Big|}. \tag{5.13}$$

These definitions coincide with the ones given in Eqs. (5.8) and (5.9) when these latter are real, and extend them to general non-Markovian ensemble dynamics. Equation (5.13) clearly shows how memory effects are manifest in backflows of information from the environment to the system since now $\dot{S}_i(t) = -\frac{\mathrm{d}}{\mathrm{d}t}S(\rho(t)\|\rho^{SS}_{\text{eff}}(t))$ can become negative or, in other words, the state $\rho(t)$ moves away from the effective stationary state $\rho^{SS}_{\text{eff}}(t)$.

One may now turn, as in the Markovian case, to the definition of pure state jump trajectories from Eq. (4.30). There is however another problem to tackle in doing so, which is closely related to the very definition of a fluctuation theorem: since the Pauli master equation (4.30) is now characterised by negative rates, it is not possible to make use of it to define single pure state trajectories. The reason is that such trajectories would be associated with negative probabilities being, then, unphysical. Nevertheless, it is possible to proceed along a slightly different path which indeed leads to a theorem for out-of-equilibrium fluctuations. To this end, consider Eq. (5.6) which is exact and a direct consequence of the TCL master equation describing ensemble dynamics. Rearranging its terms, it can be formally rewritten as

$$\dot{S}(t) = -\sum_{a,b} \mu_a(t)\Big(R^{\mathrm{M}}_{ba}(t) + \frac{\mu_b(t)}{\mu_a(t)} R^{\mathrm{NM}}_{ab}(t)\Big) \ln\frac{\mu_b(t)}{\mu_a(t)} = -\sum_{a,b} \mu_a(t) T_{ba}(t) \ln\frac{\mu_b(t)}{\mu_a(t)}. \tag{5.14}$$

where the positive *renormalized* transition rates have been introduced as

$$T_{ba}(t) = R^{\mathrm{M}}_{ba}(t) + \frac{\mu_b(t)}{\mu_a(t)} R^{\mathrm{NM}}_{ab}(t). \tag{5.15}$$

Note that the expression for $\dot{S}(t)$ in terms of the renormalised rates $T_{ba}(t)$ exactly coincides with Eq. (5.6).

Since positive transition rates characterise Markovian dynamics, one can exploit these renormalised rates to define effective Markovian-like flux and production for the open system entropy by means of

$$\dot{S}^r_e(t) = -\sum_{a,b} \mu_a T_{ba} \ln\frac{T_{ba}}{T_{ab}}, \tag{5.16}$$

$$\dot{S}^r_i(t) = \sum_{a,b} \mu_a T_{ba} \ln\frac{\mu_a T_{ba}}{\mu_b T_{ab}}. \tag{5.17}$$

These two quantities are always well defined from a mathematical point of view, and their sum gives back Eq. (5.6). The microscopic motivation for these definitions will be given later on. For now, just look at Eqs. (5.16) and (5.17) as effective quantities with a Markovian behaviour and which, as much as Eqs. (5.12) and (5.13), reduce to Eqs. (4.34) and (4.35) in the limit of a Markovian dynamics. Having in mind the previously stated goal of singling out a Markovian and a non-Markovian contributions to entropy flux and production, one can consider these quantities as representing the Markovian part of Eqs. (5.12) and (5.13). The remaining part, which can not be effectively described as Markovian and which is thus irreducibly non-Markovian, is given by the difference between the quantities (5.12) and (5.13), obtained pushing forward the analogy with the Markovian case, and the renormalised quantities (5.16) and (5.17). It reads

$$\dot{S}_X(t) \equiv \dot{S}_e(t) - \dot{S}^r_e(t) = \dot{S}^r_i(t) - \dot{S}_i(t) = \sum_{a,b} \mu_a T_{ba} \ln\frac{T_{ba}|R_{ab}|}{|R_{ba}|T_{ab}}. \tag{5.18}$$

Note that the quantity $\dot{S}_X(t)$ is zero when all the renormalised transition rates are equal to the original ones, i.e. if all transition rates $R_{ba}(t)$ are positive and there are then no signatures of memory effects.

5.1.3 Non-Markovian fluctuations

In order to formulate non-Markovian fluctuations of entropy production along single trajectories, note first that the Pauli master equation (4.30) can be recast in terms of the renormalised transition rates (5.15) as

$$\dot{\mu}_b(t) \equiv \sum_a \Big(R_{ba}(t)\mu_a(t) - R_{ab}(t)\mu_b(t)\Big) = \sum_a \Big(T_{ba}(t)\mu_a(t) - T_{ab}(t)\mu_b(t)\Big). \tag{5.19}$$

This form of the master equation is strongly suggested by Eq. (5.14) for the time derivative of the von Neumann entropy and the corresponding decomposition into renormalised entropy flux and production given by Eqs. (5.16) and (5.17). Eq. (5.19) holds for both Markovian and non-Markovian processes, and remember that the renormalised rates $T_{ba}(t)$ are always positive by construction. As discussed in [176], the form (5.19) of the Pauli master equation (either classical or quantum) emerges when one interprets a negative rate R_{ba} for a transition from the state a to state b as an effective positive rate for the reversed transition is given by $R^{\text{eff}}_{ba} = \frac{\mu_b}{\mu_a}|R_{ab}|$. The microscopic motivation of Eqs. (5.14), (5.16), (5.17) and (5.19) has to be given within such an interpretation: negative classical-like jump rates describe reversed jumps due to backflows from the environment into the open system. This suggests employing the master equation (5.19) for the description of fluctuations along single realisations of nonequilibrium processes. It should be stressed however that, in this non-Markovian case, the transition rates $T_{ba}(t)$ depend on the occupation probabilities such that different trajectories are no longer independent. This can be seen employing the explicit expression (5.15) for the renormalised rates into the Pauli master equation (5.19), which becomes a non-linear differential equation for the populations. The classical unraveling of such a non-linear equation generates pure state trajectories depending on the ensemble populations and therefore correlated to each other. This is the mathematical counterpart of the existence of memory effects [177, 178].

Considering again a particular forward trajectory as the one given in Eq. (4.36) and employing the prescriptions of classical-like non-Markovian unraveling, one finds such a trajectory to be associated to the probability

$$p_f = \mu_{a_0}(t_0) \prod_{j=0}^{N-1} e^{-\int_{t_j}^{t_{j+1}} \mathrm{d}\tau \sum_b T_{ba_j}(\tau)} \prod_{j=0}^{N-1} T_{a_{j+1}a_j}(t_{j+1})\mathrm{d}t_{j+1}, \tag{5.20}$$

analogous to the Markovian probability (4.37) where, however, the original transition rates are replaced by the renormalised ones. Correspondingly, the probability for the backward trajectory is given by

$$p_b = \mu_{a_N}(t_N) \prod_{j=0}^{N-1} e^{-\int_{t_j}^{t_{j+1}} \mathrm{d}\tau \sum_b T_{ba_j}(\tau)} \prod_{j=0}^{N-1} T_{a_j a_{j+1}}(t_{j+1})\mathrm{d}t_{j+1}. \tag{5.21}$$

Along such a trajectory, having N jumps from a_{i-1} to a_i at times t_i, the time integral of the renormalised entropic contributions (whose ensemble value is given in (5.16) and (5.17)) is

$$\Delta s_e^r = -\sum_{j=0}^{N-1} \ln \frac{T_{a_{j+1}a_j}(t_{j+1})}{T_{a_j a_{j+1}}(t_{j+1})}, \tag{5.22}$$

$$\Delta s_i^r = \sum_{j=0}^{N-1} \ln \frac{\mu_{a_j}(t_{j+1}) T_{a_{j+1}a_j}(t_{j+1})}{\mu_{a_{j+1}}(t_{j+1}) T_{a_j a_{j+1}}(t_{j+1})}. \tag{5.23}$$

With the use of Eqs. (5.20) and (5.21) one obtains

$$\ln \frac{p_f}{p_b} = \ln \frac{\mu_{a_0}(t_0)}{\mu_{a_N}(t_N)} + \sum_{j=0}^{N-1} \ln \frac{T_{a_{j+1}a_j}(t_{j+1})}{T_{a_j a_{j+1}}(t_{j+1})}. \tag{5.24}$$

The first term on the right-hand side equals the net change of the von Neumann entropy $\Delta s = \ln \frac{\mu_{a_0}(t_0)}{\mu_{a_N}(t_N)}$ along the trajectory (see Eq. (4.41)). Analogously to the Markovian case, the second term represents the sign-reversed entropy flux integrated along the trajectory. Indeed one has

$$\ln \frac{p_f}{p_b} = \Delta s - \Delta s_e^r = \sigma_r, \tag{5.25}$$

where Eq. (5.22) has been used. Note finally that the expression of Δs_i^r in Eq. (5.23) is such that $\Delta s_i^r = \sigma_r$ and one immediately obtains from Eq. (5.24) the detailed FT for the renormalised entropy production as

$$\frac{p_f(\sigma_r)}{p_b(-\sigma_r)} = e^{\sigma_r}. \tag{5.26}$$

The fluctuation theorem for non-Markovian processes is thus formally identical to the one obtained for Markovian dynamics given in Eq. (4.44). However, in the non-Markovian case the fluctuation theorem holds for the renormalised entropy production σ_r only, which can be written as

$$\sigma_r = \Delta s - \Delta s_e + \Delta s_X = \sigma + \Delta s_X, \tag{5.27}$$

where Δs_X is the single trajectory contribution to the time integral of $\dot{S}_X(t)$ (see Eq. (5.18)) and σ is the single trajectory contribution to the non-Markovian *ensemble* entropy production (5.13). In the Markovian case Δs_X vanishes and Eq. (5.26) reduces to Eq. (4.44). As the σ_r has been interpreted as the Markovian part of the ensemble non-Markovian entropy production, only a part of the fluctuations of entropy production can be described in terms of a fluctuation theorem. The fluctuation theorem for non-Markovian processes is thus fundamentally different from its Markovian counterpart, as it describes fluctuations of an entropy production of single processes which is *not* the single trajectory contribution to the ensemble entropy production (5.13).

To interpret the result (5.26) in physical terms note first that, within this approach, fluctuations are described by the stochastic unraveling of the master equation (5.19). However, as has been already emphasised, due to the presence of memory effects single trajectories are not independent of each other or, in other words, they are correlated. A single realisation of a nonequilibrium non-Markovian process, due to this correlations, produces on the average more entropy than just the one described by its associated ensemble entropy production because, when following a single process, part of the information about the system stored in the correlations with other trajectories is lost. This is why the measured renormalised entropy production, obtained in this work as σ_r in Eq. (5.27), is given by the standard single trajectory entropy production σ *plus* an additional term which alters the usual Markovian form of the fluctuation theorem. This term, given by Δs_X in Eq. (5.27), represents an additional loss of information about the system because of the correlations between single trajectories. As demonstrated here,

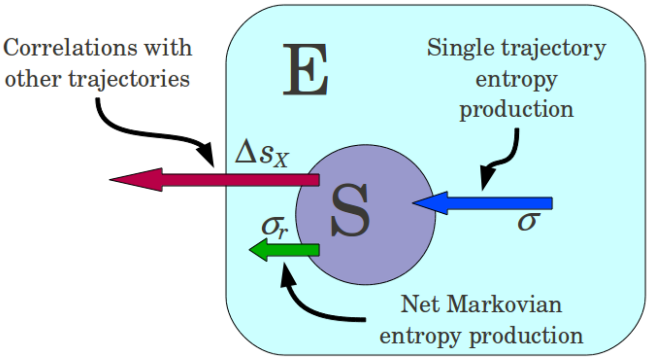

Figure 5.1: Schematic view of the contributions to the entropy production along single nonequilibrium trajectories according to Eq. (5.27). The net Markovian information flux σ_r, which obeys the fluctuation theorem (5.26), is equal to the sum of the single trajectory entropy production σ and the non-Markovian contribution Δs_X due to correlations between trajectories.

these contributions combine in such a way that their sum obeys the fluctuation theorem (5.26), completely analogous to the classical and the quantum Markovian ones (see Fig. 5.1).

This analysis shows that, when taking into account memory effects in a quantum thermodynamics context, there is a close link between fluctuations in entropy production along single realisations of nonequilibrium processes and the existence of an irreducibly non-Markovian entropic contribution in the ensemble dynamics. Any time the dynamics shows signatures of memory effects, a quantum fluctuation theorem has to take into account the full information contribution of the dynamics, which is no longer given only by the ensemble entropy production. More precisely, when a single trajectory is taken into account, memory effects produce an additional term to the entropy production an external observer can reveal by measurements. Such an additional measured term originates from the existence of correlations between single trajectories, which in turn is a consequence of memory effects mediated by the reservoir. This, as said, can be clearly seen from Eq. (5.19) because the differential equations for the time evolution of populations are no longer linear due to the structure of renormalised rates, Eq. (5.15). Performing a measurement of a single trajectory, then, means loosing information about any other possible trajectory the single monitored process is correlated with, and it is demonstrated that this loss of information leads to a net entropy production which effectively behaves as a Markovian one. This effective Markovian entropy production along single trajectories shows fluctuations which can be described by means of a fluctuation theorem of the standard form: quite remarkably, the two contributions to the renormalised entropy production, of different physical origin, combine together in such a way that their sum behaves according to a very simple fluctuation law. This could not be in principle expected since these two terms may seem, at a first glance, not to depend on each other. They however ultimately originate from the same microscopic details of the non-Markovian dynamics such that, despite the fact that none of them obeys alone a FT, their sum behaves according to a standard fluctuation law.

5.1.4 Trajectory-averaged non-Markovianity

It is clear that the correlations between different trajectories discussed above are an intrinsic feature of non-Markovian dynamics, and that they are simply not present for memoryless processes. The effect of these correlations is, as shown, to alter the single trajectory entropy production with respect to what one may expect from the corresponding ensemble quantity with the addition of the further information-related contribution Δs_X. It is therefore of interest to investigate the role such a correlation-related contribution has in the characterisation of non-Markovianity itself. Indeed, non-Markovian effects along single trajectories have explicit effects which are evident in the difference between the trajectory-averaged entropy production $\dot{S}_i^r(t)$ and the ensemble one $\dot{S}_i(t)$. This difference exists only when trajectories are correlated, and is then ultimately related to memory effects.

In this part I show that $\dot{S}_X(t)$, given by Eq. (5.18), is able to measure the non-Markovianity of the dynamics (remember that a process is defined here to be non-Markovian when at least one transition rate $R_{ba}(t)$ becomes temporarily negative). In particular I show that

$$\dot{S}_X(t) > 0 \Leftrightarrow \text{the process is non-Markovian.} \tag{5.28}$$

In what follows, if not strictly necessary, I shall omit any time dependence.

To begin with, one may have a closer look at the definition of $\dot{S}_i(t)$ in Eq. (5.13). It has the structure of a double sum of terms of the form $g(x,y) = x \ln \frac{|x|}{|y|}$, where x and y are transition rates. This allows such a sum to be rewritten as a sum of terms $f(x,y) = \frac{1}{2}(x-y)\ln\frac{|x|}{|y|}$. This expression is clearly mathematically well defined. Two different regimes are however possible: for positive x and y (Markovian case) each term is positive and the sum can thus never become negative; on the contrary, for negative x and y (which happens only in the non-Markovian case), such a term is negative, which in turn may cause the whole sum to become negative. Finally, when $xy < 0$ nothing can in principle be said about the sign of $f(x,y)$. The occurrence of negative $f(x,y)$ can not be achieved in the case of the renormalised entropy production $\dot{S}_i^r$ since the effective rates T_{ba} are positive by construction.

Suppose then that at a certain time instant one has n_p positive transition rates R_{ba}, while the remaining n_n are negative. One can thus identify three different terms in $\dot{S}_i$: the first one originates from any two positive transition rates (positive contribution P_i), the second one stems from any two negative rates (negative contribution N_i) and the third one is due to each pair of positive-negative rates, which is given in general by a positive term Q_i and by a negative term M_i. As for $\dot{S}_i^r$, the first positive contribution is the same ($T_{ba} \equiv R_{ba}$ when $R_{ba} \geq 0$), while the second negative contribution N_i becomes an additional positive term P_i^r. Finally, each pair of positive-negative rates R gives rise to a positively divergent contribution to $\dot{S}_i^r$ because one of the renormalised rates T vanishes. This means that, any time there exists at least one pair of positive-negative rates, $\dot{S}_X \equiv \dot{S}_i^r - \dot{S}_i$ is positively divergent. This feature, as discussed later on in this Section, should not worry since a positively divergent entropy is physically meaningful. As for all the time intervals in which $\dot{S}_X(t)$ is finite, one can write

$$\dot{S}_X = \dot{S}_i^r - \dot{S}_i = P_i + P_i^r - (P_i + N_i) = P_i^r - N_i \geq 0. \tag{5.29}$$

This proves that $\dot{S}_X$ is never negative. Moreover, as comes clear from the structure of Eq. (5.29), all the terms involved in the double sum in Eq. (5.18) are positive. This means that $\dot{S}_X$ can be zero if and only if each of its terms vanishes or, in other words, either when

$$\mu_a R_{ba} - \mu_b R_{ab} = 0 \ \forall a, b \tag{5.30}$$

or when

$$\frac{T_{ba}|R_{ab}|}{|R_{ba}|T_{ab}} = 1 \ \forall a, b. \tag{5.31}$$

Condition (5.30) can be fulfilled by any possible pair of instantaneous eigenstates either when the system has reached its stationary state or in isolated time points only (this can be checked directly by inserting condition (5.30) into (5.19)). It is therefore of interest, when considering dynamic processes, to investigate condition (5.31) only, for any possible pair of instantaneous eigenstates $|a\rangle$ and $|b\rangle$ and under the assumption $\mu_a R_{ba} - \mu_b R_{ab} \neq 0$.

By construction, the renormalised rates T_{ba} are connected to the original ones by

$$\mu_a R_{ba} - \mu_b R_{ab} = \mu_a T_{ba} - \mu_b T_{ab}. \tag{5.32}$$

Using now property (5.32) one can rewrite (5.31) as

$$T_{ab} \left(\frac{\mu_b}{\mu_a} |R_{ab}| - |R_{ba}| \right) = |R_{ab}| \left(\frac{\mu_b}{\mu_a} R_{ab} - R_{ba} \right) \ \forall a, b. \tag{5.33}$$

Three possibilities are given for each of these terms:

$$R_{ab} > 0, \quad R_{ba} > 0; \tag{5.34a}$$

$$R_{ab} R_{ba} < 0; \tag{5.34b}$$

$$R_{ab} < 0, \quad R_{ba} < 0. \tag{5.34c}$$

Condition (5.34a) characterises a Markovian process. It is straightforward to see that, if Eq. (5.34a) holds, then Eq. (5.33) is satisfied thus leading to a vanishing $\dot{S}_X$. On the other hand, conditions (5.34b) and (5.34c) are fulfilled by non-Markovian processes only. Exploiting the definition (5.15) of T_{ba} and the fact that the system is not stationary (and thus condition (5.30) can only be satisfied in isolated time points), with simple calculations one can prove that neither condition (5.34b) nor condition (5.34c) are compatible with Eq. (5.33).

In this way one proves that

$$\dot{S}_X = 0 \Leftrightarrow \text{the process is Markovian} \tag{5.35}$$

and since, as shown, $\dot{S}_X \geq 0$ (see Eq. (5.29)), Eq. (5.35) is equivalent to Eq. (5.28). In other words, $\dot{S}_X$ is a measure of non-Markovianity.

The meaning of $\dot{S}_X$ as a measure of non-Markovianity becomes clearer when one looks at its single trajectory contribution: as commented previously in this Section, such a contribution accounts for the information stored in correlations among trajectories. This is different from zero only if the rate equation is nonlinear or, which is the same, only if the dynamics is non-Markovian.

All is left to do now is to give a physical meaning to the measure for quantum non-Markovianity just introduced. As a first step, then, it is necessary to justify from a physical point of view a divergent $\dot{S}_X(t)$. As noted, such a feature is met when at least two instantaneous eigenstates of $\rho(t)$ (say, $|a\rangle$ and $|b\rangle$) are such that the transition from $|a\rangle$ to $|b\rangle$ is Markovian, thus implying $R_{ba} > 0$, while the reverse transition is non-Markovian, resulting in $R_{ab} < 0$. In this case, the contribution of these two levels to $\dot{S}_i$ is finite while the renormalised rates become

$$\begin{aligned} T_{ba} &= R_{ba} + \frac{\mu_b}{\mu_a}\left|R_{ab}\right|, \\ T_{ab} &= 0, \end{aligned} \tag{5.36}$$

so that $\dot{S}_i^r$, involving the logarithm of the ratio of these two quantities, diverges. However, a divergent entropic term is not uncommon in the quantum realm, and it has been given a clear interpretation connecting the physical effect of such a term to the exponential function of its sign-reversed integral, which is linked to the distinguishability of the state $\rho(t)$ with respect to the stationary state ρ^{SS} of the dynamics [93]. In particular, since the generic entropy production $\dot{\Sigma}(t)$ (which may either be $\dot{S}_i$ or $\dot{S}_i^r$ in the present case) is the time derivative of the relative entropy between $\rho(t)$ and its, possibly effective, stationary state ρ_{SS} (in the case of $\dot{S}_i^r$ such a stationary state exists, but it is clearly given in terms of the T_{ba}'s and, as such, is different from the previously introduced ρ_{eft}^{SS}), the probability of confusing $\rho(t)$ and ρ_{SS} after N measurements behaves as

$$P_c = e^{-N\int_0^t \dot{\Sigma}(\tau)\mathrm{d}\tau}, \tag{5.37}$$

so that a divergence of $\dot{\Sigma}$ is given a physical interpretation.

Eq. (5.37), moreover, allows for further characterisation of $\dot{S}_X$. Indeed, consider the ratio

$$\frac{P_c(S_i^R)}{P_c(S_i)} \equiv e^{-N\int_0^t\left(\dot{S}_i^R(\tau)-\dot{S}_i(\tau)\right)\mathrm{d}\tau} = e^{-N\int_0^t \dot{S}_X(\tau)\mathrm{d}\tau}, \tag{5.38}$$

so that $\int_0^t \dot{S}_X(\tau)\mathrm{d}\tau$ measures how different the single-measurement distinguishability based on trajectory entropy is from the same quantity based on ensemble entropy. Consequently, the parameter

$$\mathcal{D}_{\rho_i}(t) = 1 - e^{-\int_0^t \dot{S}_X(\tau)\mathrm{d}\tau} \tag{5.39}$$

quantifies the difference between the physical prediction in the ensemble picture and those in the single trajectory approach for a single measurement performed on the system. Clearly such a quantity depends on the initial state ρ_i of the ensemble dynamics, as the transition rates $R_{ba}(t)$ and $T_{ba}(t)$ depend themselves on ρ_i through the time evolution of the eigensystem of $\rho(t)$.

If one aims at a full characterisation of the non-Markovianity of the dynamics, the whole time evolution is needed (thus pushing the upper integration limit in Eq. (5.39) to $+\infty$) and one has also to perform a maximisation over any possible initial state ρ_i in the state space $\mathcal{S}(\rho)$, obtaining

$$\mathcal{N}_X \equiv \max_{\rho_i \in \mathcal{S}(\rho)} \left\{ \lim_{t\to+\infty} \mathcal{D}_{\rho_i}(t) \right\} \tag{5.40}$$

as a measure of the full non-Markovian features of the evolution. In the context of thermodynamic nonequilibrium processes and fluctuation theorems, however, the initial state and the total evolution time are both usually fixed a priori. Thus the non-Markovianity of a nonequilibrium thermodynamic process has to be defined starting from these two fixed parameters as

$$\mathcal{P}_X^{n_0(T)} \equiv \mathcal{D}_{\rho_0}(T). \tag{5.41}$$

Such a parameter quantifies the non-Markovian features of a nonequilibrium thermodynamic process $n_0(T)$, starting from $\rho_i = \rho_0$ and lasting for a time T.

5.1.4.1 Simple examples

To exemplify the above defined measure, I apply here this method to the quantification of non-Markovianity inside two Jaynes-Cummings models, a resonant model in which a two-level atom, with levels $|g\rangle$ (ground state) and $|e\rangle$ (excited state), interacts with a reservoir of zero temperature field modes with Lorentzian spectrum, whose width I call λ (Vacuum Jaynes-Cummings or VJC), and a detuned model with a single-mode field at finite temperature (single mode Thermal Jaynes-Cummings or s-TJC). These two examples are particularly convenient since an exact form of the associated TCL master equation is known [3, 179]. It is moreover known that for the first system, a non-Markovian behaviour is detected only when the atom-field interaction parameter ν is greater than $\frac{\lambda}{2}$ [180], while the second model is non-Markovian if and only if the the atom-field interaction ν is different from zero. Moreover, when applied to the s-TJC, all previously defined measures of non-Markovianity [41, 118, 119, 120] diverge for any non-zero value of the atom-field coupling constant. This is due to the integral performed over the whole time axis and the fact that, not being damped, s-TJC periodically shows signatures of memory effects of the same magnitude. In this case, then, one expects the measure (5.40) to be always one (maximal disagreement between ensemble and trajectory entropies) except for the point $\nu = 0$. This has been verified by some numerical simulations on the model and these results, being of no particular interest, are not reported here. On the other hand, the measure (5.41) may show a wide range of different behaviours depending on the time span of the process and on the initial atomic state. These considerations are in agreement with the behaviour shown in Fig. 5.3.

In Fig. 5.2 the quantity $\mathcal{N}_X$, defined in Eq. (5.40), is plotted against the parameter ν describing the atom-field interaction for the VJC model. Its predictions are in agreement with the expected behaviour. Fig. 5.3 shows, on the other hand, the quantity $\mathcal{P}_X$ for the VJC (left panel) and the s-TJC (right panel) for different nonequilibrium protocols.

It is important to stress here that the connection of these results to the other known measures of quantum non-Markovianity, such as [41, 118, 119, 120], is still an open issue. There are two main reasons for such an interesting question to be unanswered. Firstly, the general properties the rates $R_{ba}(t)$ in Eq. (4.31) (as well as the rates $\gamma_i(t)$ in Eq. (5.1)) must obey in order to guarantee that Eq. (5.1) is a CPT-map are not known. It is then unclear how to deal, in general, with the characterisation and the structure of any quantity depending on these rates.

Moreover, the general connection of the entropy production to the commonly employed trace distance, quantifying the distinguishability of states, is still an open problem. These issues, if solved, may throw light not only on the connection between different non-Markovianity measures, but also on general properties of open quantum system dynamics and on the interplay between information fluxes and quantum thermodynamics.

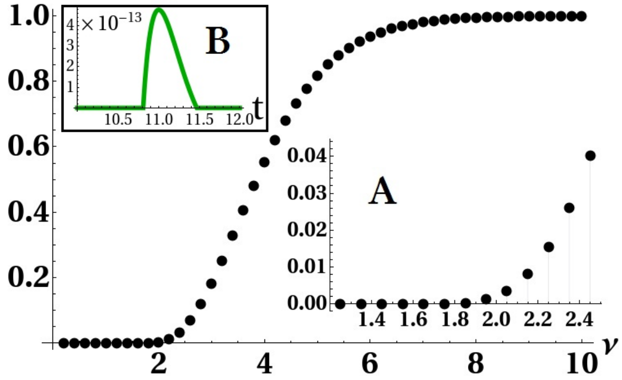

Figure 5.2: $\mathcal{N}_X$ plotted against the atom-field interaction ν for a resonant VJC model with $\lambda = 3$. The maximum in Eq. (5.40) is achieved for the pure excited atomic state $\rho_i = |e\rangle\langle e|$. Inset **A** shows the behaviour of $\mathcal{N}_X$ in the vicinity of the ν-threshold for non-Markovianity, $\nu_c = \lambda/2$. $\mathcal{N}_X$ is sensibly different from zero slightly after such a threshold, and this feature is explained in inset **B** where $\dot{S}_X$ is plotted against time for $\nu = 1.55$: $\dot{S}_X$, despite being different from zero for $\nu > \nu_c$, assumes very small values up to $\nu \sim 2$

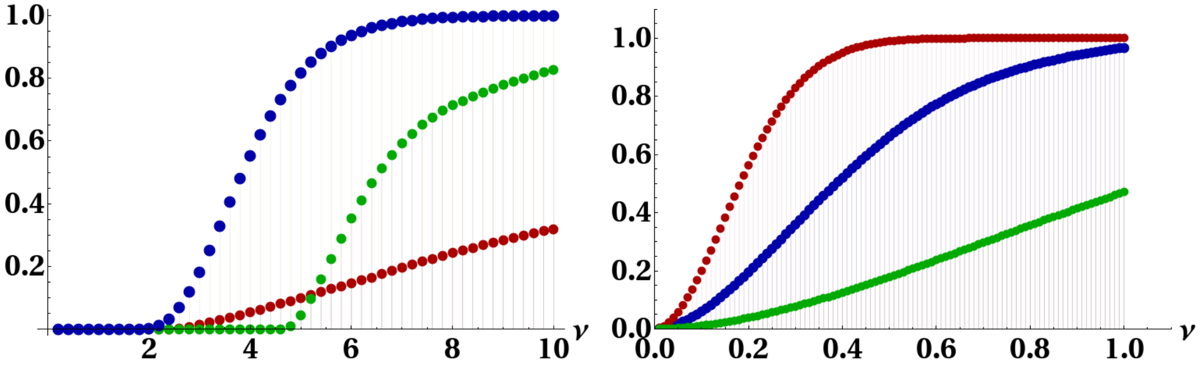

Figure 5.3: **Left panel**: $\mathcal{P}_X$ plotted against the atom-field interaction ν for a resonant VJC model with $\lambda = 3$, for three different nonequilibrium processes of duration T and with initial state $|\Psi(x)\rangle = \sqrt{\frac{x-1}{x}}|e\rangle + \frac{1}{\sqrt{x}}|g\rangle$: $x = 10^{10}$ and $T = 4$ (blue dots); $x = 10^2$ and $T = 1$ (green dots); $x = 3$ and $T = 2$ (red dots).
Right panel: $\mathcal{P}_X$ plotted against the atom-field interaction ν for a detuned s-TJC model with temperature $\beta = 10$, single mode energy spacing $\omega = 3$ and detuning $\delta = 10$, for three particular nonequilibrium processes with initial states $|\Psi(x)\rangle = \sqrt{\frac{x-1}{x}}|e\rangle + \frac{1}{\sqrt{x}}|g\rangle$ and duration T: $x = 10^2$ and $T = 10$ (red dots); $x = 3$ and $T = 10$ (blue dots); $x = 3$ and $T = 2$ (green dots).

5.2 Entropy production and information fluctuations along quantum trajectories

The second Section of this Chapter is devoted to the presentation of a new approach to entropy production and FTs which I developed in collaboration with Dr. A. Napoli, Prof. A. Messina and Prof. H.-P. Breuer. These results, published in [73], manage to reconcile the two alternative ways by which quantum fluctuation theorems have been so far tackled. In Chapter 4 I briefly commented on these two classes of methods, one of which has also been employed in the previous Section to derive a non-Markovian version of the standard FT. Such an approach has the advantage to represent single repetitions of nonequilibrium processes as pure state trajectories, and as such it is as close as possible to the classical concept of single phase space trajectories. However, as already highlighted, the transitions characterising these trajectories are not directly connected to a well-defined flux of energy/information between system and environment. In parallel, the approach based on characteristic functions and two-point measurement statistics has the advantage of representing quantities such as work or entropy in a direct, experimentally clear way, but it is limited by the drawback of describing the evolution between measurements through a master equation and, as such, within an ensemble framework. This method is therefore not able to fully account for the stochasticity implicit in a single trajectory description. These two approaches have then, for different reasons, never been able to take fully into account quantum features in the derivation of a fluctuation law.

In my work, employing the so-called stochastic wave function method (SWFM) (see for example Refs. [3, 124] and references therein), I studied quantum features of stochastic entropy production in purely quantum nonequilibrium processes of open systems. I demonstrated that a purely quantum trajectory, obtained as a conditioned pure state evolution generated by continuous measurements on the environment, introduce an additional, non-thermal contribution to the entropy flux, which is shown to be a direct consequence of quantum fluctuations. These features lead to a quantum definition of single trajectory entropy contributions, which accounts for the difference between classical and quantum trajectories and results in a quantum correction to the standard form of the integral fluctuation theorem.

Since these results are heavily based on the features of quantum unraveling through the SWFM, in the next subsection such a method and its consequences on stochastic thermodynamics are introduced and discussed in details.

5.2.1 Stochastic wave function method and quantum nonequilibrium processes

The stochastic wave function approach to Markovian quantum systems, whose ensemble evolution is given by the TCL master equation in Eq. (5.1) in the Markovian regime, describes single realisations of a dissipative process by means of quantum trajectories representing pure state evolutions of the open system which are conditioned on certain records of continuous measurements on the environment. In particular one imagines to perform, almost continuously, a set of measurements on the state of the reservoir with (in the idealised case) unit efficiency. By each of these measurements, the external observer looks for a particular set of effects of the system-environment interaction (as, e.g., photons emitted or absorbed by an atom (open system) in the radiation field which it is embedded in (environment)). Such a set is fixed *a priori* by the observer will and/or practical availability of measuring apparata, and is referred to as measuring scheme. The single measurement step leads either to discontinuous, random transitions of the knowledge of the state of the open system (referred to as *quantum jumps* or simply *jumps*) when one of these effects is detected, or to a continuous time evolution resulting from the no-jump events (referred to as *drift contribution* or simply *drift*) when no effects are detected by the measuring apparatus.

These pure state dynamical evolutions conditioned on the measurement outcomes are, mathematically speaking, piecewise deterministic processes (PDPs) [3] characterised by jumps described by the action of the Lindblad operators A_i introduced in Eq. (5.1). Note that the set of Lindblad operators (and of associated relaxation rates γ_i) characterising a particular master equation is not unique, each set corresponding, in the SWFM formalism, to a particular measuring scheme. Each jump happens at a random time and along a random channel $\{\gamma_{i_k}, A_{i_k}\}$. By random here I mean that they are not predictable *a priori* but are detected by the measurement itself. In between two jumps at times t_s and t_f, the system's wave function undergoes a nonunitary deterministic time evolution given by an effective time evolution operator $U_{\text{eff}}(t_f, t_s) = \mathcal{T}\exp\left\{-i\int_{t_s}^{t_f} H_{\text{eff}}(t)\mathrm{d}t\right\}$, where $H_{\text{eff}}(t) = H_S(t) - \frac{i}{2}\sum_i \gamma_i A_i^\dagger A_i$. A single quantum jump along the channel A_{i_k} corresponds to the transition

$$|\chi\rangle \to |\psi_{i_k}\rangle = \frac{A_{i_k}|\chi\rangle}{||A_{i_k}|\chi\rangle||}, \tag{5.42}$$

while a drift is described by

$$|\psi(t_f)\rangle = \frac{U_{\text{eff}}(t_f, t_s)|\psi(t_s)\rangle}{||U_{\text{eff}}(t_f, t_s)|\psi(t_s)\rangle||}. \tag{5.43}$$

The normalisation of the state in Eqs. (5.42) and (5.43) is necessary since the action of a Lindblad operator and of U_{eff} on a normalised states yields, in general, an unnormalised state. The norm of the target states is interpreted as the probability that the particular transition (or drift) takes place. Jumps occur then, within a small time interval δt, with probability $\delta t \gamma_{i_k} ||A_{i_k}|\psi\rangle||^2$, while the probability that, after jumping at time t_k, the system performs no further transitions up to time t_{k+1} is $||U_{\text{eff}}(t_{k+1}, t_k)|\psi\rangle||^2$.

The fundamentally unpredictable set of jump channels and times for a single trajectory is the reason for which the wave function of the system becomes by all means a stochastic variable. Because of this, at each time instant one associates to it a probability density $P[\psi, t]$. The meaning of such a density is that the product $P[\psi, t]\mathrm{d}\psi$ expresses the probability for the wave function of the system to lie, at time t, within the volume element $\mathrm{d}\psi$ around the state $|\psi\rangle$. Given any function $F[\psi]$ characterising a physical property along a *single trajectory* described by the vector $|\psi\rangle$, its expectation value is evaluated as $E[F[\psi]] = \int \mathrm{d}\psi F[\psi]P[\psi, t]$. In particular, the density matrix is given by the expectation value of $|\psi\rangle\langle\psi|$ as

$$\rho(t) = E[|\psi(t)\rangle\langle\psi(t)|] = \int \mathrm{d}\psi|\psi\rangle\langle\psi|P[\psi, t]. \tag{5.44}$$

The time evolution of the probability density, from t_1 to t_2, is generated by a propagator $T[\chi, t_2; \psi, t_1]$ such that $P[\chi, t_2] = \int \mathrm{d}\psi T[\chi, t_2; \psi, t_1]P[\psi, t_1]$. The relation of this formulation to the one in terms of density operators and master equations is illustrated in Fig. 5.4 (see also Ref. [3]).

$$\begin{tikzcd} \rho(t_1) \arrow[r, Rightarrow, "{\Lambda(t_2, t_1)}"'] & \rho(t_2) \\ P[\psi, t_1] \arrow[u, Rightarrow, "{E[|\psi(t_1)\rangle\langle\psi(t_1)|]}"] \arrow[r, Rightarrow, "{T[\chi, t_2; \psi, t_1]}"] & P[\chi, t_2] \arrow[u, Rightarrow, "{E[|\chi(t_2)\rangle\langle\chi(t_2)|]}"'] \end{tikzcd}$$

Figure 5.4: Diagram showing the connection between the probability density, the density matrix and their dynamics generated, respectively, by the propagator $T[\chi, t_2; \psi, t_1]$ and by the dynamical map $\Lambda(t_2, t_1)$.

Fixing a particular trajectory from time t_0 to time T amounts to specifying a number of jumps N and a set of time instants $\{t_k\}$ $(k = 1, \ldots, N)$ such that $t_0 < t_1 < \cdots < t_N < T \equiv t_{N+1}$, at which the wave function jumps along the channels $\{\gamma_{i_k}, A_{i_k}\}$. It is important to stress here that these single, random and discontinuous events can not be accounted for within a density matrix formalism, because this latter describes the ensemble evolution of a collection of independent identical quantum systems or, which is the same, describes the lack of knowledge about the evolving system before a measurement is performed on it. Indeed, if a system evolves from time t_0 to time t under the effect of the interaction with an environment, and one decides not to perform any kind of measurements before t, no information about the state of the system is extracted along the dynamics and all one can do is to describe the state in terms of generally mixed density matrices. This is formally and somehow conceptually analogous, as already commented, to the introduction of ensemble state and ensemble dynamics in classical frameworks, where a lack of information is assumed about the microstate of a thermodynamic system.

On the other hand, if the evolution of a system is continuously monitored through measurements on its environment, information about single quantum events are collected all along the dynamics (and not just at the final time t) and one has at his disposal more information about the state of the open system. This information, which clearly depends on the measuring scheme employed to monitor the environment, is the core of the physical difference between the density matrix formalism and the stochastic wave function method, which is nothing but the theoretical description of such a continuous measuring process on the environment and is therefore the closest analogue to following a microstate evolution of a classical system since, because of the fact that one measures the environment only and thanks also to the Markovian regime, the backaction of measurements on the state of the open system is, so to say, as weak as possible in a quantum context.

Results based on this method provide then new insight into the dynamics of a system, and do not trivially just reproduce the knowledge available through the density matrix. The choice of a measuring scheme generates a certain class of possible trajectories for the open system and corresponds then to the choice of a particular set of pure states into which to decompose the density matrix (see Eq. (5.44)) - and such a set does not even need to be orthogonal. In both classical and quantum contexts, choosing a pure state decomposition of a mixed state naturally leads to quantify the information content of such a decomposition by employing the so-called Shannon entropy, which is well known to be different from the von Neumann entropy and to depend on the decomposition itself.

The definition of a backward trajectory associated to a certain set of forward measurement records depends on what one chooses to look at as the physical quantity to extract information about, since in the context of the SWFM one extracts information about the system by only measuring the environment and one thus only detects transitions of the open system, which may supply (possibly partial) information about many different fluxes between system and environment. In FTs contexts it is common to define a backward trajectory as the dissipative process generated by a time inversion of the Hamiltonian which, in turn, means that any energy exchange between system and environment gets reversed. One can therefore characterise the backward trajectory by the requirement that the open system performs transitions at the same time instants as the forward one, but along the channels $B_{i_k} = A^\dagger_{i_k}$ with corresponding relaxation rates $\gamma^b_{i_k}$.

The reason is that the Lindblad operators in the Markovian master equation (5.1) and in the weak coupling limit can be divided into two classes $\{A_i^+\}$ and $\{A_i^-\}$, such that $A_i^+ = (A_i^-)^\dagger$, satisfying the conditions $[H_S, A_i^\pm] = \pm\epsilon_i A_i^\pm$ [3], and they thus describe jumps in which an energy quantum ϵ_i is absorbed (A_i, e.g. in the forward trajectory) or emitted ($A_i^\dagger$, e.g. in the backward trajectory) by the open system from/into the environment (see subsection 5.2.4 later on for explicit examples). This is the case in many important experimental setups such as, e.g., the many photodetection schemes often employed. On the other hand, the action of the nonunitary operator $U_{\text{eff}}(t_f, t_s)$ on a state during the drift interval $[t_s, t_f]$ reduces its norm in time, describing the decrease of probability of the no-jump event. Therefore, as the backward process itself is a physical dissipative process detected by measurements, its associated drift operator $\mathcal{U}_{\text{eff}}(t_f, t_s)$ has to describe such a decrease of probability along the backward drifts, taking into account that a backward drift propagates the state of the system from time t_f to time t_s such that $t_f > t_s$. Therefore, the Hermitian part of the operator generating backward evolutions has to be unchanged, but its nonhermitian part has to be sign-reversed: This is achieved if one defines $\mathcal{U}_{\text{eff}}(t_f, t_s) = U^\dagger_{\text{eff}}(t_s, t_f)$. Note that this backward drift operator can be obtained rigorously when one decomposes a backward drift interval into very many measuring steps, each of which leading the no-backward-jump result. This means, however, that the final state of the backward process may be different from the initial state of the forward one, as in general $A_i^\dagger A_i \neq \mathbb{I}$ and $\mathcal{U}_{\text{eff}}(t_N, T) U_{\text{eff}}(T, t_N) \neq \mathbb{I}$.

To fix notation, I denote hereafter by $|\chi_k^{f(b)}\rangle$ the *normalized* state of the forward (backward) process right before the jump at time t_k, and by $|\psi_k^{f(b)}\rangle$ the *normalized* state of the forward (backward) process right after the jump at time t_k. Exemplary trajectories are schematically depicted in Fig. 5.5, where the forward process starts in the state $|\psi_0^f\rangle$ and ends in $|\psi_\tau^f\rangle$, while the final state of the associated backward trajectory is $|\psi_\tau^b\rangle$. By definition $|\psi_\tau^f\rangle \equiv |\psi_0^b\rangle$ (i.e., the initial state of the backward process is by construction the final state of the forward one) but in general $|\psi_0^f\rangle \neq |\psi_\tau^b\rangle$ due to the fact that, as already remarked, $A_i^\dagger A_i \neq \mathbb{I}$ and $\mathcal{U}_{\text{eff}}(t_N, T)U_{\text{eff}}(T, t_N) \neq \mathbb{I}$.

With these definitions and notations, the goal is to derive formulae for entropy flux and production along these purely quantum trajectories and to exploit them to derive an integral FT for entropy production along nonequilibrium processes of this kind. Therefore, the aim is to give explicit expressions for entropy contributions along quantum PDPs.

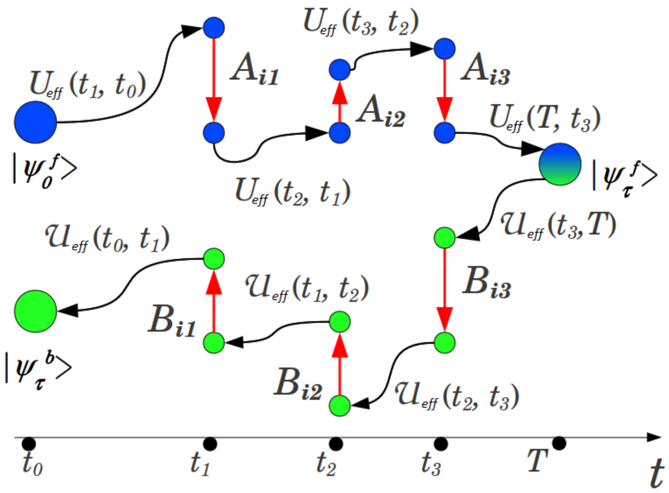

Figure 5.5: Pictorial representation of a forward quantum trajectory (dark blue states) and its backward counterpart (light green states) consisting of $N = 3$ jumps (vertical red arrows). The backward process is characterised by jumps through the channels $\{\gamma_{i_k}^b, B_{i_k} = A_{i_k}^\dagger\}$ and by deterministic evolutions according to $\mathcal{U}_{\text{eff}}(t_k, t_{k+1}) = U_{\text{eff}}^\dagger(t_{k+1}, t_k)$.

5.2.2 Entropy

A single quantum trajectory (either forward or backward), being a nonequilibrium process, is characterized by a nonzero entropy production. In the ensemble picture, the entropy of a system is given by its von Neumann entropy $S_{\text{vN}} = -\text{Tr}(\rho \ln \rho)$. However, as commented in Section 5.2.1, employing a quantum unraveling procedure amounts to describing a single realisation of the system dynamics under a particular, fixed measurement scheme.

Therefore, one has to quantify the amount of information extractable about a particular system when its environment is monitored or, which is the same, the amount of information available in a particular pure state decomposition of a density matrix. In quantum contexts, a natural way to quantify the information content of such a decomposition is the so-called Shannon entropy $S = -\int \mathrm{d}\psi P[\psi, t] \ln P[\psi, t]$. Such an entropy, which clearly depends on the chosen decomposition, has been used in various contexts [120, 181] to quantify information beyond the standard von Neumann one: it is worth stressing here again that a given decomposition yields more information on the system than the one available in the density matrix only [3]. Note that S has the form $\int \mathrm{d}\psi F[\psi]P[\psi,t]$, with $F[\psi] = -\ln P[\psi,t]$. Consequently, the *single trajectory contribution* to the entropy of the system is defined as $S[\psi] = -\ln P[\psi,t]$. In what follows, I will refer to such a quantity as *quantum entropy.* Note that its mathematical definition is formally analogous to the one employed for entropy in classical stochastic processes [164]. On the ensemble level the time derivative of the open system entropy S is

$$\dot{S} = -\int \mathrm{d}\psi \dot{P}[\psi,t] \ln P[\psi,t]. \tag{5.45}$$

Such a definition is the natural quantum extension of the one employed in many previous works on entropy FTs [26, 62, 164], but it has no classical analogue as it does not reduce to the usual form of entropy in the classical limit and the information extracted along a quantum trajectory can not in general be given any classical interpretation. Exploiting the explicit form of the time propagator for $P[\psi,t]$ [3], it is possible to show that the single trajectory contribution to Eq. (5.45) can be written as $\dot{S}[\psi] = \dot{S}_j[\psi] + \dot{S}_d[\psi]$, i.e. as the sum of two terms, one arising from the drift part of the PDP (describing the conditioned no-jump evolution of the open system) and one due to the open system jumps. Since both quantum jumps and drifts are detected by measurements, each of these terms describes a change in knowledge of the external observer about the open system. In particular, detecting no jumps is conceptually different from performing no measurements and, therefore, the drift part contributes too to the rate of change of entropy. In addition, it is shown in what follows that both the jump and the drift entropic terms contribute to *entropy production* along a nonequilibrium process.

5.2.2.1 Entropy production

As $\int \dot{S}_j[\psi]\mathrm{d}t$ and $\int \dot{S}_d[\psi]\mathrm{d}t$ only take into account the difference of entropy between initial and final states, but not the features of the transition connecting them, these terms do not fully describe the information content of unraveling measurements. The SWFM provides indeed not only information about, say, initial and final states along a jump, but also about the particular decay channel the system jumps through. The knowledge about the particular decay channel is detected, as said, in the state of the environment which is modified in different ways depending on the jump channel used by the system. There are thus two corresponding terms describing information about features of each transition, which correspond to the entropy flowing from the open quantum system to its reservoir and producing a modification of the bath state. The full system being out of equilibrium, the changes in open quantum system entropy and the flux to the bath are not the same in absolute value. Their difference is interpreted as a net total entropy production along a trajectory and, as in the standard case, it is written as

$$\sigma = \Delta S[\psi] - \Delta S^e[\psi], \tag{5.46}$$

$\Delta S^e[\psi]$ being the total entropy flux to the bath and $\Delta S[\psi] = \int_{t_0}^{T} \mathrm{d}t\dot{S}[\psi]$. In addition, one can define a single trajectory jump entropy production and a single trajectory drift entropy production (with self-evident notation) as, respectively,

$$\sigma_j = \int_{t_0}^{T} \mathrm{d}t \dot{S}_j[\psi] - \Delta S_j^e[\psi], \tag{5.47}$$

$$\sigma_d = \int_{t_0}^{T} \mathrm{d}t \dot{S}_d[\psi] - \Delta S_d^e[\psi]. \tag{5.48}$$

The aim is therefore to give an explicit expression for the entropy production along a generic quantum trajectory, being thus valid both for what has been defined as forward trajectory and for its backward counterpart.

5.2.2.2 Jump entropy production

Along a generic trajectory, a transition $|\chi_k\rangle \to |\psi_k\rangle = \frac{A_{i_k}|\chi_k\rangle}{||A_{i_k}|\chi_k\rangle||}$ is characterized by a rate

$$R_{i_k}^D[\chi_k] = \gamma_{i_k} ||A_{i_k}|\chi_k\rangle||^2. \tag{5.49}$$

In what follows, I refer to such a transition as *direct jump*. A direct jump is nothing but the transition experimentally detected within an unraveling approach while following a particular nonequilibrium process (which can, in turn, either be a forward or a backward trajectory). In contrast to a direct jump, I define also a *reversed jump* as $|\psi_k\rangle \to |\xi_k\rangle = \frac{A_{i_k}^\dagger|\psi_k\rangle}{||A_{i_k}^\dagger|\psi_k\rangle||}$, which represents the reversed transition associated to the k-th direct jump, and which is a fictitious transition as it is *not* detected in the trajectory: it represents a tool to introduce a "direction" of a single jump and, as a consequence, its entropy production and as such it is intrinsically different from the backward process previously introduced. The difference is that the backward trajectory, as exemplified in Fig. 5.5, does not go through the same states composing the forward process, while the source state of the reversed jump is a state of the forward trajectory.

It is easy to evaluate the rate associated to a reversed jump, obtaining

$$R_{i_k}^R[\chi_k] = \gamma_{i_k}^b \frac{\langle\chi_k|\big(A_{i_k}^\dagger A_{i_k}\big)^2|\chi_k\rangle}{||A_{i_k}|\chi_k\rangle||^2}. \tag{5.50}$$

In analogy with classical systems [167], the *jump entropy flux* along a single full quantum trajectory is defined as $\Delta S_j^e[\psi] = -\sum_{k=1}^N \ln \frac{R_{i_k}^D[\chi_k]}{R_{i_k}^R[\chi_k]}$. Note that this definition, despite being formally analogous to the one usually employed in FT contexts when considering pure jump processes [62, 72, 172] (see e.g. Eq. (4.42)), differs from it because of the structure of transition rates in Eqs. (5.49) and (5.50). The total change of the open system entropy along the process, due to jumps only, is $\Delta S_j[\psi] = -\sum_{k=1}^N \ln \frac{P[\psi_k,t_k]}{P[\chi_k,t_k]}$. As a consequence, one obtains the total *jump entropy production* along a full quantum trajectory consisting of N jumps as

$$\sigma_j = \ln \prod_{k=1}^{N} \frac{R_{i_k}^D[\chi_k]}{R_{i_k}^R[\chi_k]} \frac{P[\chi_k,t_k]}{P[\psi_k,t_k]}. \tag{5.51}$$

5.2.2.3 Drift entropy production

In order to obtain a time local entropy balance equation for the drift contribution, one can subdivide each finite drift interval $\big[t_{k-1}, t_k\big]$ into many small steps of size δt. This is physically motivated since a finite drift interval actually originates from a number of measurements, separated by small time steps. In each of these small time intervals the monitoring of the environment yields the result that no jump with any of the Lindblad operators A_i occurs. Conditioned on these events, the state vector undergoes small changes which lead in the limit $\delta t \to 0$ to a smooth time evolution describing the drift process. The formulation is thus analogous to the one given for jump entropy contributions, provided one uses the correct expression for the drift probabilities. The latter are given by $D_{\delta t}^{D(R)}[\psi] = 1 - \Gamma^{D(R)}[\psi]\delta t$, where $\Gamma^{D(R)}[\psi] = \sum_i R_i^{D(R)}[\psi]$ is the total direct (reversed) jump rate for the state $|\psi\rangle$. The bath entropy contribution for one of these no-jump events is thus $\delta S_d^e[\psi] = -\ln\frac{1-\Gamma^D\delta t}{1-\Gamma^R\delta t}$. In this formulation, δt is the time interval between two subsequent measurements on the environment. Moreover, since unraveling approaches correspond to continuous measuring processes, it is justified to assume such a time interval to be very small (usually lower bounded only by the resolution time of the measuring apparatus), such that $\Gamma^{D(R)}\delta t \ll 1$. Under this approximation one has $\Delta S_d^e[\psi] \sim \int_{t_0}^T \mathrm{d}t\Big(\Gamma^D(t) - \Gamma^R(t)\Big)$. Exploiting Eqs. (5.49) and (5.50), one can easily prove that

$$\int_{t_{k-1}}^{t_k} \mathrm{d}t\Gamma^D(t) \quad = -\ln||U_{\text{eff}}(t_k, t_{k-1})|\psi_{k-1}\rangle||^2, \tag{5.52}$$

$$\int_{t_{k-1}}^{t_k} \mathrm{d}t\Gamma^R(t) \quad = -\ln||\mathcal{U}_{\text{eff}}(t_{k-1}, t_k)|\psi_k\rangle||^2, \tag{5.53}$$

so that $\Delta S_d^e[\psi] = -\ln\prod_{k=1}^{N+1}\frac{||U_{\text{eff}}(t_k,t_{k-1})|\psi_{k-1}\rangle||^2}{||\mathcal{U}_{\text{eff}}(t_{k-1},t_k)|\psi_k\rangle||^2}$. The total drift-induced change of open quantum system entropy is $\Delta S_d[\psi] = -\sum_{k=1}^{N+1}\ln\frac{P[\chi_k,t_k]}{P[\psi_{k-1},t_{k-1}]}$ and finally

$$\sigma_d = \ln\prod_{k=1}^{N+1}\frac{||U_{\text{eff}}(t_k, t_{k-1})|\psi_{k-1}\rangle||^2}{||\mathcal{U}_{\text{eff}}(t_{k-1}, t_k)|\psi_k\rangle||^2}\frac{P[\psi_{k-1}, t_{k-1}]}{P[\chi_k, t_k]} \tag{5.54}$$

is the single trajectory drift entropy production. With the use of Eqs. (5.46), (5.51) and (5.54) it is straightforward to show that

$$\sigma \equiv \sigma_j + \sigma_d = \ln\left(\frac{P[\psi_0, t_0]}{P[\chi_{N+1}, t_{N+1}]}\prod_{k=1}^{N}\frac{R_{i_k}^D[\chi_k]}{R_{i_k}^R[\chi_k]}\prod_{k=1}^{N+1}\frac{||U_{\text{eff}}(t_k, t_{k-1})|\psi_{k-1}\rangle||^2}{||\mathcal{U}_{\text{eff}}(t_{k-1}, t_k)|\psi_k\rangle||^2}\right). \tag{5.55}$$

Such an equation describes the total entropy production along a single quantum trajectory: In particular, since a quantum trajectory is monitored by measuring the environment, σ is the total information the external observer acquires about the system through the knowledge of initial and final states of the process (ΔS) *minus* the information extracted by measurements of all intermediate steps connecting them (ΔS^e), detected in the bath. Note that Eq. (5.55) is fully characterised by the knowledge of a single trajectory, contrarily to the single trajectory contribution to von Neumann entropy which would require the solution of the full master equation of the system (analogously to what happens also with classical-like unravellings, see for example Eq. (4.41) which requires the knowledge of density matrix populations).

5.2.2.4 Entropy flux and quantum fluctuations

To fully understand the physics described by the entropy flux terms introduced above, analyse for instance its jump contribution in Eq. (5.51). In the case of a jump $|\chi_k\rangle \to |\psi_k\rangle$ the entropy flowing into the environment is given by

$$\Delta S^e_{j_k} = \ln \frac{\gamma^b_{i_k}}{\gamma_{i_k}} + \ln \frac{\gamma_{i_k} R^R_k}{\gamma^b_{i_k} R^D_k}. \tag{5.56}$$

On average the process has a preferred direction if the two rates are not equal. Since, in a weak coupling Markovian master equation with a thermal environment, $\gamma^b_{i_k}/\gamma_{i_k} = e^{-\beta\epsilon_{i_k}}$ (ϵ_{i_k} being the energy Q_E exchanged between system and environment during the transition A_{i_k}) [3], the first term on the r.h.s. of Eq. (5.56) is a standard thermodynamic entropic flux of the form $-\frac{Q_E}{T}$. The second term on the r.h.s. of Eq. (5.56) describes, on the other hand, how much information is produced by the system jumping through the *particular* decay channel A_{i_k}. I refer to such an additional term as *nonthermal entropy flux* ΔS^{nt}. One can characterise such a nonthermal flux by introducing the parameter $\eta_k = 1 - \gamma_{i_k} R^R_k/\gamma^b_{i_k} R^D_k$. According to its definition, $\eta_k = 0$ if the bias of the associated direct transition to the corresponding reversed one is only due to the direction of heat flux. Introducing the operator $\Lambda_{i_k} = A^\dagger_{i_k} A_{i_k}$ and exploiting the explicit expression of R^R and R^D one obtains

$$\eta_k = \frac{\langle\chi_k|\Lambda_{i_k}|\chi_k\rangle^2 - \langle\chi_k|\Lambda^2_{i_k}|\chi_k\rangle}{||A_{i_k}|\chi_k\rangle||^4} = -\frac{\mathrm{Var}^{[\chi_k]}_1(\Lambda_{i_k})}{||A_{i_k}|\chi_k\rangle||^4}, \tag{5.57}$$

where $\mathrm{Var}_1(Q) = \int \mathrm{d}\psi P[\psi]\Big(\langle\psi|Q^2|\psi\rangle - \langle\psi|Q|\psi\rangle^2\Big)$, introduced in [127], is known to measure the average intrinsic quantum fluctuations of an operator Q during a dynamic process, and $\mathrm{Var}^{[\chi_k]}_1(Q) = \langle\chi_k|Q^2|\chi_k\rangle - \langle\chi_k|Q|\chi_k\rangle^2$ is its single trajectory contribution due to the k-th jump. From the structure of η_k one infers that during the jump $|\chi_k\rangle \to |\psi_k\rangle$, the exchange of information between system and environment goes beyond the standard thermodynamic form if and only if the operator Λ_{i_k} has nonzero purely quantum fluctuations in the source state of the direct jump: The nonthermal entropic contribution has indeed the form $\Delta S^{nt}_{j_k} = \ln(1-\eta_k)$.

The additional, nonthermal contribution to the jump entropy flux is directly linked to the quantum fluctuation of the operators Λ_{i_k}, which shows the nonclassical character of these results. Note that, thanks to the same formal structure of the jumps and the drifts transition rates, these results hold true also for the drift parts of a quantum trajectory. In particular, during a drift there is no standard thermodynamic entropy flux as the heat flux vanishes. However, thanks to the purely quantum fluctuations of the operator $\Omega_k = U^\dagger_{\mathrm{eff}}(t_k, t_{k-1}) U_{\mathrm{eff}}(t_k, t_{k-1})$ in the state $|\psi_{k-1}\rangle$, the generic k-th drift part of the full process is also associated to a purely quantum information flux between system and environment. It is worth stressing however that the non-thermal drift entropy flux is of the order of δt^2 (δt being the time interval between two subsequent measurements), while the corresponding jump term does not depend on δt. In order to avoid here the presentation of complicated formulae, and to keep the focus on the physics of these results, the non-thermal drift term is analysed in more details in the Appendix A.

5.2.3 Integral fluctuation theorem

It is now possible to investigate the statistical properties of $\sigma \equiv \sigma_f$ in Eq. (5.55) along a forward process. To simplify the notation, in what follows I introduce the symbols $D_k^D[\psi_k] = ||U_{\text{eff}}(t_k, t_{k-1})|\psi_{k-1}\rangle||^2$ and $D_k^R[\psi_k] = ||\mathcal{U}_{\text{eff}}(t_{k-1}, t_k)|\psi_k\rangle||^2$. Moreover, rates along forward or backward trajectories will be denoted by specifying the trajectory directly in the functional dependence of the rates on the wave function, so that for example $R_k^{R(D)}[\chi_k^{f(b)}]$ is the reversed (direct) k-th jump rate of the forward (backward) trajectory. With these notations, the mean value of $e^{-\sigma_f}$ (commonly considered in FTs contexts) can be evaluated as

$$\left\langle e^{-\sigma_f} \right\rangle \equiv \int \mathrm{d}\psi^f P[\psi^f] e^{-\sigma[\psi^f]} \delta\big(\sigma[\psi^f] - \sigma_f\big) = \int \mathrm{d}\psi^b P[\psi^b] \prod_{k=1}^{N} \frac{R_{i_k}^R[\chi_k^f]}{R_{i_k}^D[\chi_k^b]} \frac{D_k^R[\psi_k^f]}{D_k^D[\psi_k^b]} \tag{5.58}$$

and, since $P[\psi^b]$ is by construction a normalised probability distribution, one obtains

$$\left\langle e^{-\sigma_f} \right\rangle = \left\langle \prod_{k=1}^{N} \frac{R_{i_k}^R[\chi_k^f]}{R_{i_k}^D[\chi_k^b]} \frac{D_k^R[\psi_k^f]}{D_k^D[\psi_k^b]} \right\rangle = 1 + \zeta_f, \tag{5.59}$$

where $\langle \cdot \rangle$ stands for an average over all possible realisations of a nonequilibrium process. Equation (5.59) shows that, in the case of quantum trajectories, $\langle e^{-\sigma_f} \rangle$ is not a universal constant: The r.h.s. is indeed, in general, different from 1 and depends on the set of Lindblad operators characterizing the unraveling scheme, resulting in a quantum correction ζ_f to the classical result. This is illustrated in Section 5.2.4, where the predictions of Eq. (5.59) are numerically studied for several model systems.

In particular, the correction ζ_f originates from the fundamental difference between a backward process (which is a real dissipative process) and "reversed" processes (which is the collection of all reversed jumps and drifts and, as such, is fictitious). This difference is nothing but the consequence of the measuring scheme employed to characterise trajectories: information acquired about the system by the external observer is not symmetric under time reversal, and such a broken symmetry of knowledge produces different states in forward and backward transitions. Indeed, if one considers a "cyclic-like" process composed of a forward trajectory followed by its backward counterpart, the open system does not get back to its initial state since, despite the energy fluxes being reversed, a certain amount of additional information is stored by the external observer and is not completely erased along the backward process. This physically results in the presence of the nonthermal quantum entropic flux (5.56), which does not obey a standard FT. Indeed it has recently been shown [64] that, if only thermal energy exchanges during jumps are taken into account along quantum trajectories of an open two-level system, the standard universal form of FT holds. In addition, a recently published work [65] showed that the choice of a particular measuring scheme can lead to a standard entropic FT. As a matter of fact, in a "standard"-like limit the nonthermal entropy flux vanishes both for drifts and jumps due to the fact that the operators Ω_k and Λ_{i_k} have vanishing quantum fluctuations, and in this case $\zeta_f = 0$, recovering the universal standard form of FT.

5.2.4 Examples

In this subsection I present some results on particular systems exemplifying our findings. The first example shows a particular limiting case in which the quantum correction ζ_f vanishes. In the second example I discuss how the choice of a particular measuring scheme affects entropic quantum fluctuations resulting in different deviations from the standard FT.

5.2.4.1 The standard case: jumps between free Hamiltonian eigenstates

As an example of the standard limit of these results consider an open system without driving whose Lindblad operators and decay rates remain constant in time. In the Markovian and weak coupling limit, its Lindblad operators satisfy $[H_S, A_k^{\pm}] = \pm\epsilon_k A_k^{\pm}$. If now one assumes the free Hamiltonian H_S to have nondegenerate energy gaps in its spectrum (this assumption is typically employed when studying, e.g., quantum thermalisation processes [182]), the emission of an energy quantum ϵ_i is in a one-to-one correspondence with a transition between two well defined energy levels $|n\rangle$ and $|m\rangle$ such that $\omega_n - \omega_m = \epsilon_k$, ω_i being the energy associated to the eigenstate $|i\rangle$ of H_S. Assuming the spectrum of H_S to be composed of N discrete levels ($|1\rangle$ being the ground state) of increasing energy, a natural choice for the set of Lindblad operators is then

$$A_{N(i-1)+j-\frac{i(i+1)}{2}} = |i\rangle\langle j| \text{ for } 1 \leq i < j \leq N, \tag{5.60}$$

$$A^{\dagger}_{N(i-1)+j-\frac{i(i+1)}{2}} = |j\rangle\langle i| \text{ for } 1 \leq i < j \leq N. \tag{5.61}$$

Note that, thanks to the assumption of nondegenerate gaps in H_S and the form of the operators in the set $\{A_k\}$, it is not necessary for the system to start its trajectory in an eigenstate of H_S since after the first jump any wave function $|\psi\rangle$ is projected to a well defined energy eigenstate. One can therefore assume, without loss of generality, that the system starts its trajectory from a generic yet fixed energy eigenstate $|n\rangle$. The action of a jump operator $|m\rangle\langle n|$ on such a state is then nothing but the transition $|n\rangle \to |m\rangle$. The system performs jumps only between eigenstates of its free Hamiltonian. Exploiting Eqs. (5.60) and (5.61), one notices that $A^{\dagger}_{N(i-1)+j-\frac{i(i+1)}{2}} A_{N(i-1)+j-\frac{i(i+1)}{2}} = |j\rangle\langle j|$, so that the drift non-Hermitian Hamiltonian becomes $H_{\text{eff}} = H_S - \frac{i}{2}\sum_i^N \widetilde{\gamma}_i |i\rangle\langle i|$, where $\widetilde{\gamma}_i = \sum_j^N \gamma_{N(i-1)+j-\frac{i(i+1)}{2}}$ is the total relaxation rate associated with the energy level $|i\rangle$. The drift operator $U_{\text{eff}}(t_k, t_{k-1})$ is then diagonal in the eigenbasis of H_S and introduces nothing but a phase factor to any evolving energy eigenstate: any trajectory of this kind is equivalent to a pure jump process between eigenstates of H_S. Note now two things: on the one hand, since the emission or absorption of an energy quantum always connects the same two states, and since drifts have no effects on the trajectory, backward and reversed processes are the same and the backward trajectory connects the same states as the forward one, but in reversed order. This in turn means that the quantum correction ζ_f in Eq. (5.59) vanishes, and one recovers the standard form of fluctuation theorems. On the other hand, as expected, this is due to the fact that nonthermal entropic fluxes are zero, since it can be straightforwardly shown that neither the operators $\Lambda_{N(i-1)+j-\frac{i(i+1)}{2}} = |j\rangle\langle j|$ nor the operators $U^\dagger_{\text{eff}}(t_k,t_{k-1})U_{\text{eff}}(t_k,t_{k-1}) = \sum_i^N e^{-\widetilde{\gamma}_i(t_k-t_{k-1})}|i\rangle\langle i|$ have purely quantum fluctuations in any energy eigenstate, as they are diagonal in such a basis. The process is thus, in this respect, fully classical.

5.2.4.2 Driven two-level atom

As a more interesting example of the results obtained above, one can unravel the dynamics of a driven two-level atom ($|e\rangle$ and $|g\rangle$ being, respectively, its excited and ground state) under two different unraveling schemes somehow analogous to, respectively, the one describing a direct photodetection of emitted light and the so-called homodyne photodetection [3, 58], the only difference being here that the bath is assumed to be in a generic state, while standard photodetection schemes require the field to be in its vacuum state. Assume that the atom interacts with a reservoir of field modes at nonzero temperature. The atomic master equation, written in the TCL form of Eq. (5.1), is given by

$$\dot{\rho}(t) = -i\frac{\omega(t)}{2}[\sigma_x,\rho(t)]+\gamma_1(t)\Big(\sigma_-\rho(t)\sigma_+-\frac{1}{2}\{\sigma_+\sigma_-,\rho(t)\}\Big)+\gamma_2(t)\Big(\sigma_+\rho(t)\sigma_--\frac{1}{2}\{\sigma_-\sigma_+,\rho(t)\}\Big), \tag{5.62}$$

where $\omega(t)$ accounts for the applied external driving, $\sigma_- = \sigma_+^\dagger = |g\rangle\langle e|$ is the lowering operator of the atom and the rates $\gamma_1(t)$ and $\gamma_2(t)$ depend on the atom-field coupling parameter, on the structure of the state of the field and on its spectrum. Note that, as long as $\gamma_1(t),\gamma_2(t) \geq 0 \;\; \forall t$, Eq. (5.62) always implements a time-dependent Markovian dynamics. The "direct photodetection-like" unraveling yields two jump operators of the form

$$\begin{aligned} A_1 &= \sigma_-, && (5.63)\\ A_2 &= \sigma_+ = A_1^\dagger, && (5.64)\end{aligned}$$

which amounts at probing the photon statistics of the field to detect single photons emitted (σ_-) or absorbed (σ_+) by the atom, with relaxation rates $\gamma_1(t)$ (emission) and $\gamma_2(t)$ (absorption).

On the other hand, another suitable set of Lindblad operators similar to the ones describing the "homodyne" photodetection process, is given by

$$\begin{aligned} A_1^-(\beta) &= \sigma_- - i\beta, && (5.65)\\ A_1^+(\beta) &= \sigma_- + i\beta, && (5.66)\\ A_2^-(\beta) &= \sigma_+ - i\beta^* = A_1^+(\beta)^\dagger, && (5.67)\\ A_2^+(\beta) &= \sigma_+ + i\beta^* = A_1^-(\beta)^\dagger, && (5.68)\end{aligned}$$

for any $\beta \in \mathbb{C}$. This corresponds to the detection of the statistics of the field, after it interacts through beam splitters with a local oscillator field of amplitude $|\beta|^2$. The associated relaxation rates are $\gamma_1^{\pm}(t) = \frac{\gamma_1(t)}{2}$ and $\gamma_2^{\pm}(t) = \frac{\gamma_2(t)}{2}$. Note that the transformation of Lindblad operators leading to the set (5.65)-(5.68) produces no changes in the Hamiltonian part thanks to the fact that $A_1^-(\beta) + A_1^+(\beta) = 2A_1$ and $A_2^-(\beta) + A_2^+(\beta) = 2A_2$. It is easy to check that the master equation obtained using the four operators (5.65)-(5.68) reduces, for any β, to Eq. (5.62), therefore describing the same physical process on the ensemble level. Fixing β one fixes a particular measuring scheme and, therefore, a particular set of Lindblad operators. In this way one is able, just by switching between the two sets (5.63), (5.64) and (5.65)-(5.68) and/or by tuning β, to investigate the dependence of ζ_f in Eq. (5.59) on the unraveling scheme employed.

I present here simulations for the “direct photodetection-like“ scheme and for the “homodyne-like“ scheme with different values of β, with fixed measurement step δt and total duration T, choosing

$$\begin{aligned}
\omega(t) &= \omega_0\Big(1 - e^{-\frac{t}{\tau}}\Big), && (5.69)\\
\gamma_1(t) &= g_1 e^{-\frac{t}{\tau_1}}, && (5.70)\\
\gamma_2(t) &= g_2\Big(1 - e^{-\frac{t}{\tau_2}}\Big). && (5.71)
\end{aligned}$$

The parameters have been fixed such that $\frac{\delta t}{\tau_1} = 1.3 \cdot 10^{-3}, \frac{\delta t}{\tau_2} = 10^{-3}, \frac{\delta t}{\tau} = 2.7 \cdot 10^{-3}$ and $\frac{\delta t}{T} = 8 \cdot 10^{-4}$. The initial atomic wave function is of the form $|\psi_0^f\rangle = c_e|e\rangle + c_g|g\rangle$ and, for each trajectory, the complex values for c_e and c_g have been chosen randomly out of a uniform distribution of real values in $[0,1]$ for their moduli, and of a uniform distribution of real angles in $[0, 2\pi]$ for their relative phase. Note that such a distribution does not correspond to a uniform distribution of pure states over the Bloch sphere. It is important to stress that, at least in principle, any distribution of state vectors can be generated by appropriate preparation measurements.

The results of these simulations are shown in Fig. 5.6, where $\left\langle e^{-\sigma_f}\right\rangle$, evaluated as an average over 10^4 quantum trajectories, is shown for 10 different sets of values of rates and driving such that $\delta t\omega_0 = 8k \cdot 10^{-4}$, $\delta t g_1 = 8k \cdot 10^{-5}$, $\delta t g_2 = 4.8k \cdot 10^{-4}$ for $k = 1, \dots, 10$ (“direct photodetection-like“ scheme, left panel) or 10 different values of $\beta = ke^{\frac{i3\pi}{5}},\ k = 1, \dots, 10$ and $\delta t\omega_0 = 5.6 \cdot 10^{-4}, \delta t g_1 = 4 \cdot 10^{-4}, \delta t g_2 = 2.4 \cdot 10^{-4}$ (”homodyne-like” scheme, right panel).

Finally, I present simulations for the more familiar case in which the values of decay rates are determined by environmental properties only, i.e. the case of a thermal bath weakly interacting with the system: Fig. 5.7 shows results for time independent relaxation rates $\gamma_1 \propto \langle N\rangle + 1$ and $\gamma_2 \propto \langle N\rangle$, $\langle N\rangle$ being the average photon number in the field state. Note that in this case the explicit functional dependence of γ_1 and γ_2 on the properties of a thermal bath (such as, for example, its spectrum or its temperature) can be obtained through the theory of Einstein's coefficients. Indeed the dependence of γ_1 and γ_2 on $\langle N\rangle$ describes the effects of atomic absorption and of both spontaneous and stimulated atomic emissions [124].

This further run of simulations, consisting of $3 \cdot 10^4$ trajectories for each point in the plot,

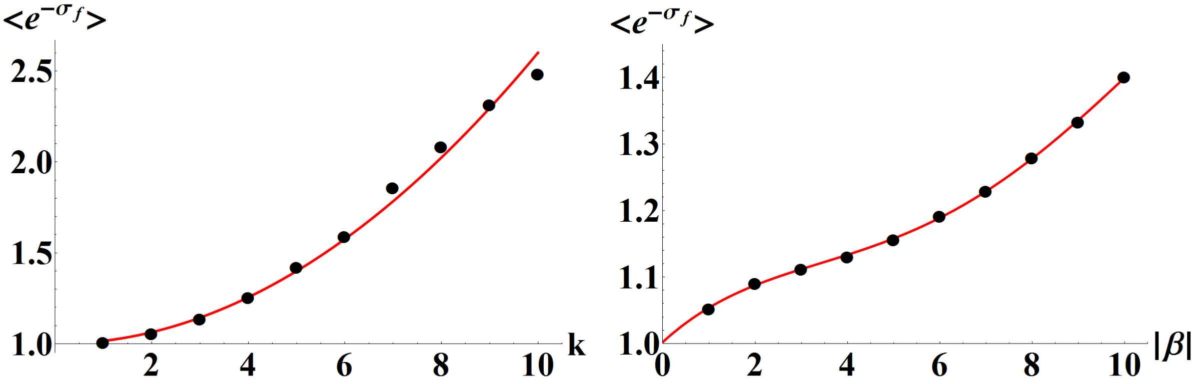

Figure 5.6: **Left panel**: $\langle e^{-\sigma_f} \rangle$ (black dots), evaluated over 10^4 quantum trajectories for the "direct photodetection-like“ scheme for a driven two-level atom interacting with a reservoir of modes, for 10 different values of driving amplitude and relaxation rates $\delta t \omega_0 = 8k \cdot 10^{-4}$, $\delta t g_1 = 4.8k \cdot 10^{-4}$, $\delta t g_2 = 8k \cdot 10^{-5}$ for $k = 1, \ldots, 10$ and having fixed the other parameters as $\frac{\delta t}{\tau_1} = 1.3 \cdot 10^{-3}$, $\frac{\delta t}{\tau_2} = 10^{-3}$, $\frac{\delta t}{\tau} = 2.7 \cdot 10^{-3}$ and $\frac{\delta t}{T} = 8 \cdot 10^{-4}$. The red full line is a quadratic function of k roughly interpolating numerical data and their increasing trend.
Right panel: $\langle e^{-\sigma_f} \rangle$ (black dots), evaluated over 10^4 quantum trajectories for the "homodyne-like" scheme for a driven two-level atom interacting with a reservoir of modes, for 10 different values of $\beta = k e^{\frac{i3\pi}{5}}$, $k = 1, \ldots, 10$ and with fixed system parameters as $\delta t \omega_0 = 5.6 \cdot 10^{-4}$, $\delta t g_1 = 4 \cdot 10^{-4}$, $\delta t g_2 = 2.4 \cdot 10^{-4}$, $\frac{\delta t}{\tau_1} = 1.3 \cdot 10^{-3}$, $\frac{\delta t}{\tau_2} = 10^{-3}$ and $\frac{\delta t}{\tau} = 2.7 \cdot 10^{-3}$. The red full line is a 4th degree polynomial function of $|\beta|$ roughly interpolating numerical data and their increasing trend.

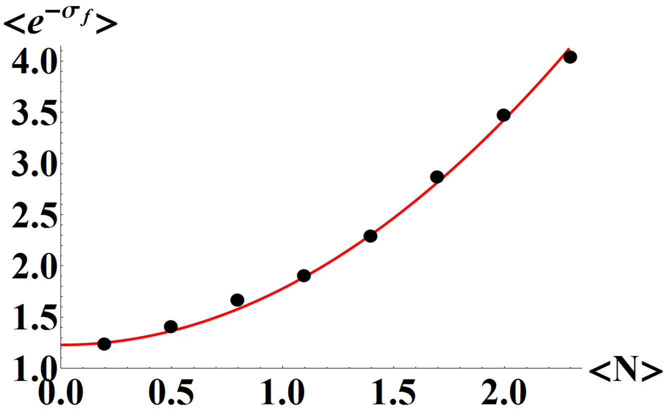

Figure 5.7: $\langle e^{-\sigma_f} \rangle$ (black dots), evaluated over $3 \cdot 10^4$ quantum trajectories for the "direct photodetection-like“ scheme for a driven two-level atom interacting with a thermal reservoir of modes, for 8 different values of temperature such that the average thermal photon number is $\langle N \rangle = 0.2 + 0.3k$, $k = 0, \ldots, 7$ and having fixed the other parameters as $\frac{\delta t}{\tau} = 2.7 \cdot 10^{-3}, \omega_0 \delta t = 8 \cdot 10^{-4}$ and $\frac{\delta t}{T} = 8 \cdot 10^{-4}$. The red full line is a quadratic function of $\langle N \rangle$ roughly interpolating numerical data and their increasing trend.

has been performed analogously to the one reported in Fig. 5.6 for the direct photodetection-like scheme, keeping all the parameters fixed at the same value characterising the left panel of Fig. 5.6, with the only exception of ω_0 which has been fixed such that $\omega_0 \delta t = 8 \cdot 10^{-4}$ and, of course, the rates γ_1 and γ_2. The simulations have been performed for 8 different values of $\langle N\rangle$ such that $\langle N\rangle = 0.2 + 0.3k,\ k = 0,\ldots,7$. Note that, tuning $\langle N\rangle$ in these simulations corresponds to tuning the temperature of the field with which the two-level atom interacts (provided its spectrum stays constant).

Two interesting features emerge from these simulations: first of all, the mean value $\left\langle e^{-\sigma_f}\right\rangle$ can be substantially different from 1 both for "direct photodetection-like" and "homodyne-like" schemes, resulting in a nonzero quantum correction ζ_f. Therefore, even for such a simple system the difference between backward trajectory and reversed processes becomes nonneglegible. Secondly, $\left\langle e^{-\sigma_f}\right\rangle$ shows a clear dependence on the set $\{\omega_0, g_1, g_2\}$, on the average bath photon number $\langle N\rangle$ and on $|\beta|$, i.e. on the driving and the decay amplitudes, on the bath temperature and on the unraveling scheme employed. In particular, in the "direct photodetection-like" scheme $\left\langle e^{-\sigma_f}\right\rangle$ is very close to 1 in the case of a weakly decaying and driven system ($k = 1$) and increases smoothly with k with a power-law like shape. Also in the case of the homodyne-like scheme a clear increasing trend is detected which suggests a monotonic increase of $\left\langle e^{-\sigma_f}\right\rangle$ with $|\beta|$, properly described by a quadratic function of $|\beta|^2$. Finally, it is interesting to note that, in the case of a thermal bath, $\left\langle e^{-\sigma_f}\right\rangle$ increases quadratically with the average photon number $\langle N\rangle$ but does not tend to 1 for $\langle N\rangle \to 0$ since, also in the case of a zero temperature bath, the system can perform quantum jumps and undergoes nontrivial drifts, resulting in a nonvanishing nonthermal entropy flux. These features may reasonably be employed to properly engineer a class of nonequilibrium processes with particular stochastic properties of entropy production.

5.2.5 Remarks

It is worth, in order to properly fix ideas and take-home messages, summarising again the results presented in this section. An expression for the stochastic entropy production along a purely quantum trajectory of a driven open system has been obtained, defined through continuous measurements on the environment only. The quantum entropy thus defined, which is fundamentally different from the commonly employed von Neumann entropy, describes the observer's gain/loss of information about the open system along single realisations of quantum nonequilibrium processes and, contrarily to previous approaches to quantum FTs, does not require any knowledge on the ensemble dynamics of the open system given by the solution of the master equation (5.1). I showed that the flux of such an entropy is not only associated to energy flux from/into the bath, defying common classical thermodynamic expectations. The additional information term results from purely quantum fluctuations of the transition operators along a trajectory. Due to this additional term, the quantum entropy of a stochastic trajectory does not obey the usual form of integral fluctuation theorem: The quantum correction ζ_f in Eq. (5.59) depends on the set of jump operators employed to unravel the master equation, and ultimately describes the difference between the physical backward trajectory and the fictitious reversed processes. In other words, such a correction is due to the lack of symmetry between forward and backward processes, which in turn originates from the existence of an external observer performing measurements on the bath to detect transitions.

Chapter 6

Conclusions

The results presented in this thesis, which represent a broad part of the work I performed during my PhD studies, belong to the general topic of quantum thermodynamics. They comprise the characterisation of concepts, such as phase transitions, many-body physics and nonequilibrium fluctuations, whose classical formulation is given within a (possibly stochastic) thermodynamic framework. In pursuing such a characterisation I fully took into account the non-classical nature of the systems of interest, thus supplying conceptual and technical contributions to the quantum description of certain phenomena.

The framework I moved in has consisted of the physics of an open quantum system interacting with a structured environment and possibly driven, adiabatically or not, out of its stationary state by an external force. Such interactions produce, inside the open quantum system, certain stochastic behaviours which have been accounted for by a probabilistic description of its physical properties: if one word should be given to characterise as a whole the results presented in this thesis, that would be *fluctuations*. Indeed, as a response to any external perturbation of its state, any system fluctuates around its equilibrium state or, when the perturbation is not adiabatic, strongly fluctuates along its nonequilibrium evolution. Also without considering any externally applied driving, already the simple case of an interaction with a thermal bath generates a lack of knowledge about the state of an open system (whose origin can be traced back, in the quantum realm, to the existence of non-classical system-bath correlations) which in turn implies fluctuations in the information available through measurements. This is true in a classical case, and even more strongly evident in the quantum case when additional sources of fluctuations (lack of knowledge) are structurally present. The work presented throughout the previous Chapters can be divided into two vast conceptual areas, namely, quantum equilibrium and nonequilibrium thermodynamics.

In the results concerning the equilibrium part, I dealt with thermalised systems either driven or not. In the driven case [142, 143, 144], I considered an adiabatic change of some parameters characterising the Hamiltonian of the system and showed that, when along the driving a certain class of quantum critical points is met at low enough temperature (generating, in particular, a first order quantum phase transition), the quantity known as heat capacity undergoes a characteristic oscillating behaviour as a consequence of the general two-level physics obeyed by any such system. In addition, by exploiting a recent result connecting the structure of an equilibrium Gibbs state to the presence of entanglement between a thermalised system and its bath [31], I showed a second general feature of the heat capacity, i.e., that it vanishes any time the bipartite thermal entanglement inside a system tends to be maximal. Both these features are consequences of equilibrium and/or adiabatic quantum fluctuations. I commented, and showed by some examples, that the existence of these two universal behaviours of a measurable parameter supplies researches with a way to probe the existence of a critical point at finite temperature on the one hand (despite the fact that, strictly speaking, quantum phase transitions happen at vanishing temperature since usually thermal fluctuations dominate over quantum ones), and to witness sharp transitions and plateaus of thermal bipartite entanglement on the other.

In the non-driven case, I showed with my results [145] that a widely employed approximation to study 1-dimensional many-body thermodynamics has structural limitations and predicts unphysical behaviours in a broad range of temperatures. I showed that such an approximation, being based on a central limit theorem and on a Gaussian approximation for statistical distribution of energy, can not reproduce the equilibrium fluctuations at the tails of the actual distribution and fails when predicting the zero-temperature and the intermediate-temperature physics. In particular, any result based on this method violates the third law of thermodynamics and predict a thermal phase transition for 1-dimensional systems, in striking contrast with the general result that such transitions can not exist because the energetic term always dominates over the entropic one. I also showed how such a method can be improved (despite all its drawbacks still being present) when applied to the evaluation of certain measurable quantities such as the free energy of the system, and that its predictions are reliable only in the high temperature limit.

Driven open quantum systems have also been the subject of my work on quantum nonequilibrium thermodynamics, where I studied out-of-equilibrium entropy fluctuations generated by a (non-adiabatic) driving applied on an open quantum system. I obtained two main results on such a topic. On the one hand, I showed [72] that the interaction with a non-Markovian reservoir, introducing memory effects in the dynamics and generating information backflows into the open system, modifies the definition itself of entropy production along single processes. Indeed, along a non-Markovian single realisation of the driving process one has to take into account also the strong correlations between different pure-state trajectories the system may follow or, which is the same, the correlations shared between system and environment. I showed, employing a classical-like formulation of pure-state dynamics, that the existence of these correlations introduces an additional entropic term, and that a standard fluctuation theorems is obeyed only by the total entropy production in which such an additional term is included. The second part of my results [73] on fluctuation theorems, on the other hand, managed to reconcile the two main approaches so far employed for Markovian quantum fluctuation, by formalising single realisations of quantum driving processes as being based on the so-called stochastic wave function method which describes *purely quantum* trajectories and, in parallel, which allowed me to directly associate these trajectories to well defined fluxes on information-based entropy between system and environment. Such a method has a clear experimental connection [3, 125] since the trajectories on which it is based are produced by experimental measurements performed on the environment only, thus generating a formulation of single nonequilibrium dynamics as close as possible to the classical concept of phase space trajectories. I showed that, already within a Markovian approximation, quantum fluctuations strongly affect the entropy produced along these processes introducing a non thermal contribution due to fluctuations of the information extracted by the external observer measuring the environment. Moreover I showed that, since such an information is not reversed when the system evolves backward, a fluctuation theorem does not exist and the correction term to its standard form depends, among other things, on the measuring scheme employed to continuously monitor the reservoir.

The importance of my results is manyfold. On the one hand, indeed, they contribute to the topical and timely research about the microscopic and nanoscopic limits of thermodynamics and, in parallel, about the possibility to formulate stochastic thermodynamics by exploiting quantum features only. This is becoming in these years a topic of greater and greater interest also in view of the technical possibility to experimental address the physics of nanosystems, on whose exploitation quantum technologies are founded. On the other hand, my research runs along the border line between thermodynamics and information theory. The connection of entanglement to measurable thermal parameters, the introduction of memory effects into nonequilibrium entropy production, the description of purely quantum driving processes and, within them, of the role of measurements, open a broad range of possibilities to exploit the potentialities of quantum thermodynamic systems in quantum information and quantum computation contexts. Finally, last but not least, my results give a new insight into the structure itself of micro and nanoscopic world by connecting their underlying quantum dynamics to the statistical distribution of measurable quantities. This is an issue of paramount importance in exploring the extent to which quantum features are involved in the structure of macroscopic physics and of the macroscopic limit of quantum theory.

Appendix A

Nonthermal drift entropy flux along quantum trajectories

It has been shown in subsection 5.2.2 that nonthermal contributions to jump entropy flux originate from purely quantum fluctuations of operators $A^\dagger A$, and it has been argued that the same would hold for drift entropy production when considering fluctuations of the operator $U^\dagger U$. Here the structure of these fluctuations along nonunitary evolutions is analysed.

During a drift interval $[t_{k-1}, t_k]$, information is extracted by measuring the environment at a constant rate $\frac{1}{\delta t}$. Therefore the total information extracted is given by a sum of small contributions, each of which originates from one of the $\frac{t_k - t_{k-1}}{\delta t}$ measuring processes and originates from the quantum fluctuations of the operator $U^\dagger(\delta t)U(\delta t)$. Assume here the most general situation, in which $H_{\mathrm{eff}}(t)$ depends on time and $\big[H_{\mathrm{eff}}(t_1), H_{\mathrm{eff}}(t_2)\big] \neq 0$, so that the use of the time-ordering operator $\mathcal{T}$ is needed.

Since in the stochastic wave function method one always assumes δt to be very small ($\sum_i R_i \delta t \ll 1$), one can keep only terms up to the order of δt^2 in the Dyson expansion of the drift operator. For the sake of simplicity, introduce the Hermitian operator $\Omega(t) = \sum_i \gamma_i(t) A_i^\dagger(t) A_i(t)$ so that $H_{\mathrm{eff}}(t) = H_S(t) - \frac{i}{2}\Omega(t)$, and the operators

$$
\begin{aligned}
I^{(1)}_{\delta t}(t) &= \int_t^{t+\delta t} \Omega(t_1)\mathrm{d}t_1, && \text{(A.1)}\\
I^{(2)}_{\delta t^2}(t) &= \int\int_t^{t+\delta t} \mathrm{d}t_1\mathrm{d}t_2 \mathcal{T}\big\{\Omega(t_1)\Omega(t_2)\big\}, && \text{(A.2)}\\
T_{\delta t^2}(H_1, H_2) &= \int\int_t^{t+\delta t} \mathrm{d}t_1\mathrm{d}t_2 \Big(\mathcal{T}\big\{H_S(t_1)H_S(t_2)\big\} - H_S(t_1)H_S(t_2)\Big), && \text{(A.3)}\\
V_{\delta t^2}(\Omega_1, \Omega_2) &= \int\int_t^{t+\delta t} \mathrm{d}t_1\mathrm{d}t_2 \Big(\mathcal{T}\big\{\Omega(t_1)\Omega(t_2)\big\} + \Omega(t_1)\Omega(t_2)\Big), && \text{(A.4)}\\
J_{\delta t^2}(\Omega, H) &= \int\int_t^{t+\delta t} \mathrm{d}t_1\mathrm{d}t_2 \Big(\Omega(t_1)H_S(t_2) - H_S(t_1)\Omega(t_2)\Big). && \text{(A.5)}
\end{aligned}
$$

With these notations one obtains

$$\begin{aligned} U(\delta t) &= \mathcal{T}\exp\left\{-i\int_t^{t+\delta t} H_{\text{eff}}(t_1)\mathrm{d}t_1\right\} \\ &\sim 1-\frac{1}{2}\int\int_t^{t+\delta t}\mathrm{d}t_1\mathrm{d}t_2\mathcal{T}\Big\{H_{\text{eff}}(t_1)H_{\text{eff}}(t_2)\Big\}-i\int_t^{t+\delta t}H_{eff}(t_1)\mathrm{d}t_1 \end{aligned} \tag{A.6}$$

and, up to order δt^2,

$$U(\delta t)^\dagger U(\delta t) \sim 1 - I_{\delta t}^{(1)}(t) - T_{\delta t^2}(H_1,H_2) + \frac{1}{4}V_{\delta t^2}(\Omega_1,\Omega_2) + \frac{i}{2}J_{\delta t^2}(\Omega,H) \tag{A.7}$$

and

$$\Big(U(\delta t)^\dagger U(\delta t)\Big)^2 \sim 1 - 2I_{\delta t}^{(1)}(t) + I_{\delta t^2}^{(2)}(t) - 2T_{\delta t^2}(H_1,H_2) + \frac{1}{2}V_{\delta t^2}(\Omega_1,\Omega_2) + iJ_{\delta t^2}(\Omega,H). \tag{A.8}$$

With simple calculations one can now evaluate $\mathrm{Var}_1^{[\psi]}(\delta t) \equiv \mathrm{Var}_1^{[\psi]}(U(\delta t)^\dagger U(\delta t))$ on a generic state $|\psi\rangle$. It results

$$\mathrm{Var}_1^{[\psi]}(\delta t) = \langle\psi|\Big(U(\delta t)^\dagger U(\delta t)\Big)^2|\psi\rangle - \langle\psi|U(\delta t)^\dagger U(\delta t)|\psi\rangle^2 = \langle\psi|I_{\delta t^2}^{(2)}(t)|\psi\rangle - \langle\psi|I_{\delta t}^{(1)}(t)|\psi\rangle^2. \tag{A.9}$$

The nonthermal entropy flux of the k-th drift depends on

$$\kappa_k = -\frac{\mathrm{Var}_1^{[\psi_k]}(U(\delta t)^\dagger U(\delta t))}{||U(\delta t)|\psi_k\rangle||^4} \tag{A.10}$$

and is then generated, up to second order in δt, only by the quantum fluctuations of the operator $I_{\delta t}^{(1)}(t)$ on the state of the trajectory. It is worth stressing that, in Eq. (A.9), the first non vanishing contribution is of order δt^2, while the term $||U(\delta t)|\psi_k\rangle||^4$ has also contributions of order δt^0 and δt: This means that the drift entropy flux can be made vanishingly small by choosing a very high measurement rate, such that all terms of order δt^2 become negligible. Note however that there are at least two lower bounds to δt: one is given by the time resolution of the experimental apparatus, which is not infinite. The other one is given by the requirement that the dynamics is not frozen due to the Zeno effect [183]: therefore δt has to be always greater than the Zeno time of the total system. These two limitations, in some cases, may lead to a nonvanishing drift entropy flux, which is then a quantity of real physical interest.

Appendix B

Publications

Part of the results of this thesis have been published in the following articles:

1. B. Leggio, *Heat capacity and entanglement*, Il Nuovo Cimento C, **35**, 65 (2012).
2. B. Leggio, A. Napoli and A. Messina, *Entanglement and heat capacity in a two-atom Bose-Hubbard model*, Physics Letters A **376**, 339 (2012).
3. B. Leggio, A. Napoli, H. Nakazato and A. Messina, *Heat capacity and entanglement measure in a simple two-qubit model*, Journal of Russian Laser Research **32**, 362 (2011).
4. B. Leggio, O. Lychkovskiy and A. Messina, *On the Merit of a Central Limit Theorem-based Approximation in Statistical Physics*, Journal of Statistical Physics **146**, 1274 (2012).
5. B. Leggio, A. Napoli, H.-P. Breuer and A. Messina, *Fluctuation theorems for non-Markovian quantum processes*, Physical Review E **87**, 032113 (2013).
6. B. Leggio, A. Napoli, A. Messina and H.-P. Breuer, *Entropy production and information fluctuations along quantum trajectories*, Physical Review A **88**, 042111 (2013).

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