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Quantum Refrigerators operating under effective negative temperatures

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GABRIELLA GONÇALVES DAMAS

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ATA DE DEFESA DE DISSERTAÇÃO

Ata nº 206 da sessão de Defesa de Dissertação de Gabriella Gonçalves Damas, que confere o título de Mestra em Física, na área de concentração em Física.

Aos 24 dias do mês de fevereiro de 2023, a partir das 14h00min, por meio de videoconferência, realizou-se a sessão pública de Defesa de Dissertação intitulada "Quantum refrigerators operating under effective negative temperatures". Os trabalhos foram instalados pelo Orientador, Professor Doutor Norton Gomes de Almeida (IF/UFG), com a participação dos demais membros da Banca Examinadora: Professor Doutor Leonardo Paulo Maia (IFSC/USP), membro titular externo; e Professor Doutor Alexandre Martins de Souza (CBPF), membro titular externo. Durante a arguição, os membros da banca não fizeram sugestão de alteração do título do trabalho. A Banca Examinadora reuniu-se em sessão secreta a fim de concluir o julgamento da Dissertação, tendo sido a candidata aprovada pelos seus membros. Proclamados os resultados pelo Professor Doutor Norton Gomes de Almeida, Presidente da Banca Examinadora, foram encerrados os trabalhos e, para constar, lavrou-se a presente ata que é assinada pelos membros da Banca Examinadora, aos 24 dias do mês de fevereiro de 2023.

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Abstract

Over the last few decades, a new theory has been developed in order to describe the thermodynamics of microscopic quantum systems, which became known as quantum thermodynamics. An interesting application of this theory is in the development of heat engines in which the working substance is a microscopic quantum system. These devices came to be known as quantum heat engines. Within this context, the study of quantum refrigerators has attracted a lot of attention, especially for its potential application in nanoscopic systems. In this context, this dissertation presents two studies related to an autonomous quantum refrigerator. In the first study, we approach an autonomous refrigerator composed of three qubits operating with one of the reservoirs at negative temperatures, which aims to cool one of the qubits. We find the values of the lowest possible temperature that the qubit of interest reaches when fixing the relevant parameters and we also analyze the limit for cooling the qubit arbitrarily close to absolute zero. We thus proceed to a comparative study showing that reservoirs at effective negative temperatures are more powerful than those at positive temperatures to cool the qubit of interest. In the second study, we carried out a case study of a quantum refrigerator operating in the presence of bosonic or fermionic thermal reservoirs, and we showed that fermionic baths have advantages over bosonic ones. Finally, a discussion is carried out on the use of reservoirs with inverted populations and the efficiency measure used for these systems.

Keywords: Quantum thermodynamics, Quantum refrigerators, Negative temperature.

Resumo

Ao longo das últimas décadas, uma nova teoria tem sido desenvolvida com o intuito de descrever a termodinâmica de sistemas quânticos microscópicos, a qual ficou conhecida como termodinâmica quântica. Uma aplicação interessante dessa teoria está no desenvolvimento de motores térmicos nos quais a substância de trabalho é um sistema quântico microscópico, esses dispositivos passaram a ser conhecidos como motores térmicos quânticos. Dentro desse contexto, o estudo de refrigeradores quânticos tem atraído bastante atenção especialmente para sua aplicação potencial em sistemas nanoscópicos. Nesse contexto, a presente dissertação apresenta dois estudos relacionados a um refrigerador quântico autônomo. No primeiro estudo, abordamos um refrigerador autônomo composto por três qubits operando com um dos reservatórios com temperaturas negativas, que tem como finalidade resfriar um dos qubits. Encontramos os valores da temperatura mais baixa possível que o qubit de interesse atinge ao fixar os parâmetros relevantes e também analisamos o limite para resfriar o qubit arbitrariamente próximo ao zero absoluto. Procedemos assim a um estudo comparativo mostrando que reservatórios com temperaturas negativas efetivas são mais poderosos do que aqueles em temperaturas positivas para resfriar o qubit de interesse. No segundo estudo, realizamos um estudo de caso de um refrigerador quântico operando na presença de reservatórios térmicos bosônicos ou fermiônicos, e mostramos que os banhos fermiônicos apresentam vantagens sobre os bosônicos. Por fim, é feita uma discussão sobre o uso de reservatórios com população invertida e a medida de eficiência utilizada para esses sistemas.

Palavras-chave: Termodinâmica quântica, Refrigeradores quânticos, Temperatura negativa.

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Chapter 1

Introduction

One application of quantum thermodynamics that has attracted a lot of attention in recent decades is related to the study of quantum thermal engines. In particular, the study of quantum refrigerators especially for their potential application in nanoscopic systems [3, 4, 5]. In particular, a recent proposal involving autonomous refrigerators, without the need for external control, was proposed in [2], where the authors studied three models for cooling qubits or arbitrary quantum systems. The first model uses qubits only, the second a qubit and a qutrit with nearest neighbor interactions, and the third a single qutrit. The model that uses only qubits is an autonomous refrigerator (AR) with three interacting qubits, one being the cooled object. In this work, we study the AR constituted only by qubits as proposed by Linden et al. [2], putting it to work with one of the reservoirs at a negative temperature. Negative absolute temperatures were initially considered in 1951 when Purcell first produced spin states with population inversion [6]. In 1956, Ramsey theoretically studied these states, treating them as states of thermodynamic equilibrium [1]. More than 60 years after the experiment performed by Purcell, other experiments involving negative temperatures followed, which brought attention to this topic [7, 8]. Numerous studies contributed to the description of quantum states that had negative temperatures [9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22]. In the end, we were able to show that the AR qubit-based model has advantages when operating with one of the reservoirs at negative temperatures compared to operating only with conventional reservoirs at positive temperatures. We also explore the quantum nature of fermionic reservoirs without taking population inversion into account, such that we restrict to the domain of positive temperatures.

This paper is structured as follows: Chapter Two is dedicated to negative temperatures and begins with a review of classical thermodynamics, including the laws of thermodynamics, heat engines, and entropy. It then delves into a historical review of the emergence of negative temperatures, discussing alleged inconsistencies and attempts to describe inverted population states that present negative temperatures. In Chapter Three, we introduce the theory of open systems, which leads to the deduction of the master equation for bosonic and fermionic reservoirs. We also describe the thermodynamic laws in the quantum regime. Finally, Chapter Four presents our conclusions based on the comparative study of AR involving positive and negative temperatures.

Chapter 2

Negative effective temperature

2.1 Classical thermodynamics

2.1.1 The Laws of Thermodynamics

In order to discuss thermodynamic laws, let us start with a simple system. A closed system is a physical system that does not allow the transfer of matter in or out of the system but allows the exchange of energy (work and heat, e.g.).

A thermodynamic process is any change in one or more properties that occurs within a system. Equilibrium occurs when all processes occurring within a state cease. If a system in equilibrium is disturbed, it goes out of equilibrium, and a new process occurs. When the disturbance is done slowly enough, the system adapts to the change to remain in equilibrium.

Slow processes that can drive the system through a series of equilibrium states are called quasi-static processes. Nonetheless, if the disturbance occurs fast and the system cannot reach a new equilibrium state, we are dealing with a non-equilibrium process. If this manipulation causes a non-equilibrium process for the system, it will change until it reaches its equilibrium state.

A reversible process is defined as a process in which the system and its surroundings can return to the original final state conditions without producing any change in the thermodynamic properties of the universe if the process is reversed. The inverse is known as irreversible processes.

Historically, thermodynamics was initially developed to better understand processes in steam engines and other heat devices so that this understanding could be used to improve engines. Thermodynamics is a product of observations and experiments condensing into the so-called laws of thermodynamics [23].

The zeroth law of thermodynamics states that if two systems are in thermal equilibrium with a third, they are in thermal equilibrium with each other. Two physical systems are in thermal equilibrium if there is no net transfer of thermal energy between them when they are in thermal contact.

The first law of thermodynamics expresses conservation of energy. It can be formulated as [24]:

> *Energy can neither be produced nor destroyed; it can only be transferred or converted from one form to another. In short, energy is conserved.*

Meyer, Joule, and Helmholtz formulated this statement, for a closed system,

$$\frac{dE}{dt} = \dot{Q} + \dot{W}, \tag{2.1}$$

here E is the system's internal energy; $\dot{Q}$ is the rate of heat transfer into or out of the system, and $\dot{W}$ is the rate of work exchanged with the surroundings. Let us use the convention such that the heat transferred into the system is positive, and the work done on the system is positive.

In general, there can be multiple iterations of $\dot{W}_j$ work from the system, so the total work to the system will be the sum of all these contributions, $\dot{W} = \sum_j \dot{W}_j$. Likewise, in the case of multiple heat interactions $\dot{Q}_j$ with multiple auxiliary systems, the total heat will be $\dot{Q} = \sum_j \dot{Q}_j$. A process in which there is no heat transfer, $\dot{Q} = 0$, is called adiabatic.

The second law of thermodynamics describes how thermodynamic systems tend towards stable equilibrium states. It states that any isolated system will naturally move towards equilibrium, with a tendency for disorder to increase over time. To express this tendency, a new function called entropy is introduced and is denoted by S. For an isolated system, we write

$$\Delta S \geq 0. \tag{2.2}$$

This formulation is a mathematical expression of the second law of thermodynamics.

The Clausius theorem (1855) [25] states that a thermodynamic system (e.g., an engine or refrigerator) that exchanges heat with external reservoirs and undergoes a thermodynamic cycle, holds

$$\oint \frac{đQ}{T} \leq 0, \tag{2.3}$$

where $đQ$ is the heat exchanged with the reservoir, T is the temperature of the reservoir. The equality in Eq. (2.3) is satisfied only if the process to which the thermodynamic system is subjected is reversible, thus the integral $\int_1^2 \frac{đQ}{T}$ is independent of the path that connects two processes. $đQ$ does not represent an exact differential, i.e., the variable depends on the process path, which mathematically implies that it is not an exact differential.

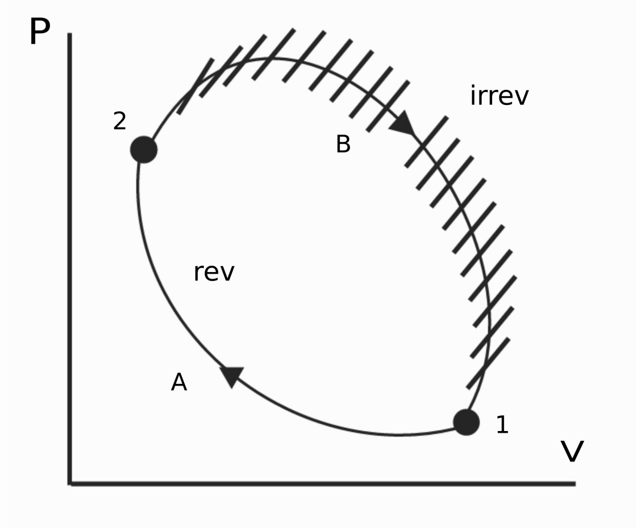

Figure 2.1: $P-V$ diagram showing two processes, a reversible process A and an irreversible process B. Points 1 and 2 connect them.

Let us assume a transformation as shown in Fig. 2.1. By the Clausius theorem:

$$\int_{1(irrev)}^{2} \frac{đQ}{T} + \int_{2(rev)}^{1} \frac{đQ}{T} \leq 0. \tag{2.4}$$

Reversing the bounds of the integral and substituting the relation from Eq. (2.2)

$$\int_{1(irrev)}^{2} \frac{đQ}{T} - \int_{1}^{2} dS \leq 0, \tag{2.5}$$

We can rewrite it so that,

$$\Delta S \geq \int_{1}^{2} \frac{đQ}{T} \tag{2.6}$$

where equality occurs for equilibrium. The right side of Eq. (2.6) is related to the heat received from or transferred to a thermal reservoir with fixed or variable temperature T. Thus, if the thermodynamic system of interest is thermally isolated, then Eq. (2.6) reduces to Eq. (2.2). The equality in (2.6) is satisfied only if the process to which the thermodynamic system is subjected is reversible.

It is also interesting to rewrite the Eq. (2.6), such that

$$\Delta S - \int_{1}^{2} \frac{đQ}{T} \geq 0, \tag{2.7}$$

where we can identify $\Delta S - \int_{1}^{2} \frac{đQ}{T} \equiv \sum$, where $\sum$ is entropy production. It holds,

$$\sum = \Delta S - \int_{1}^{2} \frac{đQ}{T} \geq 0, \tag{2.8}$$

further details will be discussed in Section 3.3.

2.1.2 Heat engines

Heat engines are devices capable of transforming part of the heat absorbed from a given heat source into useful work so that $\dot{W} > 0$. The most famous heat engine is the Carnot one, a reversible engine that operates between two reservoirs at temperatures T_H and T_C, as seen in Figure 2.2. The Carnot cycle consists of four processes, two isothermal processes, and two adiabatic processes. Heat is only exchanged with the reservoirs during isothermal steps.

To quantify the performance of engines, it is helpful to define efficiency measures that compare the output with the input of energy. Therefore, the thermal efficiency η is the

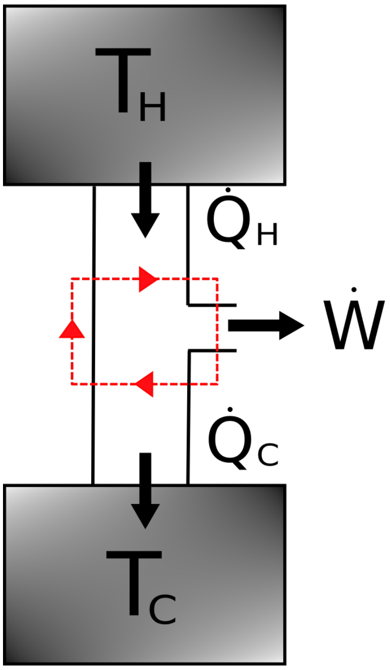

Figure 2.2: Heat and work directions in a Carnot engine

ratio of work output to heat input for heat engines. For heat engines operating between two reservoirs with different temperatures, we obtain

$$\eta = \frac{-\dot{W}}{\dot{Q}_H}, \tag{2.9}$$

and for the Carnot engine,

$$\eta_C = \frac{\dot{Q}_H - \dot{Q}_C}{\dot{Q}_H} = 1 - \frac{T_C}{T_H}. \tag{2.10}$$

Devised by Sadi Carnot in 1824 [26], the Carnot efficiency is a universal limit to the thermal efficiency that any engine operating between two temperatures can have.

A refrigerator is a device that works by transferring energy from a cold source to a hot source through thermodynamic processes. In an ideal refrigerator, all processes are reversible, and all energy transfers are carried out without the losses caused by effects such as friction. By inverting the Carnot cycle, the Carnot refrigerator is obtained. The efficiency of a refrigerator is called the coefficient of performance (COP):

$$COP = \frac{\dot{Q}_C}{-\dot{W}}. \tag{2.11}$$

The equation for the coefficient of performance is commonly used in the context of refrigeration, which typically involves two thermal reservoirs: a hot reservoir (such as the environment or a compressor) and a cold reservoir (such as the space being cooled). For the Carnot refrigerator,

$$COP = \frac{T_C}{T_H - T_C}. \tag{2.12}$$

Although cyclic processes were fundamental in the foundation of thermodynamics, real machines do not need cyclic processes to function. Indeed in Chapter 4, we will see an autonomous quantum refrigerator (AR) as proposed in [2] that does not run in cycle.

Aiming at the discussion about the negative temperature in Chapter 3, it is essential to introduce the Kelvin-Planck statement,

> *It is impossible to construct an engine that will work in a complete cycle and produce no effect except the raising of a weights (i.e., produce work) and the transfer of energy out of a system (e.g., a reservoir) in a stable equilibrium state* [27].

Recalling the Clausius statement, heat will flow from the hot reservoir to the cold one, whereas the Kelvin-Planck statement allows part of the heat to be converted into work.

2.1.3 Entropy

In the mid to late 19th century, Boltzmann and Gibbs formulated microscopic interpretations of entropy. Here we will take a look at each interpretation [28, 29].

A distribution in microscopic states (microstates) characterizes the macroscopic state of a system. Gibbs entropy describes this distribution,

$$S_G = k_B \; ln \; \Omega(E), \tag{2.13}$$

$\Omega(E)$ is the total number of quantum states of a system with energy less than or equal to E. For classical systems with many degrees of freedom, $\Omega(E)$ is dominated by the number of states very close to E. To calculate the number of states in a narrow range $\Delta\epsilon$ around E, we differentiate $\Omega(E)$ concerning E and we obtain [15]

$$\frac{\partial \Omega(E)}{\partial E}\Delta\epsilon \equiv \omega(E)\Delta\epsilon. \tag{2.14}$$

The symbol $\omega(E)$ stands for the density of states, and the symbol ϵ represents some arbitrary constant with energy units.

There is yet another known representation of the Gibbs entropy. We start by defining the canonical ensemble, a sizeable thermodynamic system S in contact with a thermal reservoir at temperature T [30]. The ensemble is constituted by the set of microstates j associated with a probability distribution, given by

$$p_j = \frac{e^{-\beta E_j}}{\sum_k e^{-\beta E_k}}. \tag{2.15}$$

Here p_j is the probability of finding the system S in the particular microscopic state j, and E_j is the energy of the system S in the microscopic state j. Eq. (2.15) can be rewritten so that,

$$p_j = \frac{e^{-\beta E_j}}{Z}, \tag{2.16}$$

$Z = \sum_k e^{-\beta E_k}$ is defined as the canonical partition function. The expression for entropy in terms of p_j is,

$$S = -k_B \sum_j p_j \ln p_j, \tag{2.17}$$

which is sometimes known in the literature as Shannon entropy. This expression is also valid in the microcanonical ensemble. For this case, $p_j = 1/\Omega$, there are Ω states accessible to the system, and Eq. (2.17) reduces to the known form, Eq.(2.13).

Boltzmann defined *entropy* as a measure of a system's possible microstates in thermodynamic equilibrium. A microstate of the system is a description of the positions and moments of all its particles. The set of microstates comprises a statistical probability distribution for each microstate, and the group of most likely configurations explains the macroscopic state.

The entropy of the macroscopic state, according to Boltzmann, is

$$S_B = k_B \; ln \; \omega(E). \tag{2.18}$$

The constant k_B is the Boltzmann constant [31]. Boltzmann entropy describes the system when all accessible microstates are equally likely and is the configuration corresponding to the maximum entropy at equilibrium.

It is important to emphasize here that these two entropies addressed are not the only ones. In Chapter 3, for example, we will discuss Von Neumann and relative entropy. In information theory, there is Shannon entropy as already mentioned, Rényi entropy, and collision entropy, among others [32, 33, 34]. As early as 1988, Tsallis [35] proposed a non-extensive entropy, which is a generalization of the traditional Boltzmann-Gibbs entropy. Non-extensive entropy leads to non-extensive statistical mechanics [36, 37]. We focused on these two above to comment on the question "Boltzmann vs. Gibbs entropy" in the next section.

2.2 Thermodynamics at negative temperatures

The topic of negative temperature first arose in 1950, when Purcell first produced spin states with inverted populations and considered the possibility of describing them as states at negative spin temperatures. After this first experimental evidence, there were attempts on how to treat these states in the quantum regime and criticisms about the validity of this result. In this session, we will explore this subject historically and see how it is currently being discussed.

In 1950, Purcell and Pound [6] experimented on a nuclear spin system in a crystal of lithium fluoride, which is known to have a longer relaxation time for spin-spin compared to spin-lattice relaxation when in a strong magnetic field or in the Earth's magnetic field. They wanted to find the conditions that determine the sense of remagnetization, which is caused by a strong magnetic field. The experiment involved first magnetizing the crystal in a strong magnetic field, then removing it from the Earth's magnetic field and placing it in a solenoid, where the field could be quickly reversed. When the direction of the field was reversed, the magnetization of the system was found to reverse in the opposite direction as well, resulting in a state of reverse magnetization. This state persisted even when the system returned to equilibrium, and it was found to be characterized by a negative temperature. A negative temperature is a state where a system loses internal energy while gaining entropy. It is possible because of the Boltzmann distribution, which determines the population of energy levels in a system based on the average energy of the system. If the average energy of the system is less than the average energy of the available levels, the temperature of the Boltzmann distribution can be negative.

The state of reverse magnetization requires population inversion, which means that the higher energy levels are more populated than the lower ones. This is an unusual state, as it violates the usual behavior of thermal equilibrium, where the higher energy levels are less populated. However, it is possible in some quantum systems where the interactions between the particles are strong and coherent.

Purcell and Pound's experiment was a significant discovery that challenged the conventional understanding of thermodynamics at the quantum level, confirmed by other experiments that also observed the properties of the nuclear spin systems in the LiF crystal [38, 39].

Ramsey discussed the thermodynamics and statistics that describe states with negative temperatures, discovered in [6], in his 1956 paper [1]. The entropy S, as one might think, is not necessarily a monotonically increasing function of the internal energy U. This statement is made in various references but is not essential to developing the thermodynamics theorems [23, 31, 40, 41].

Entropy S and internal energy U can be related in the form of a derivative, a state function as [23]

$$\beta = \left(\tfrac{dS}{dU}\right)\Big|_{V,N} . \tag{2.19}$$

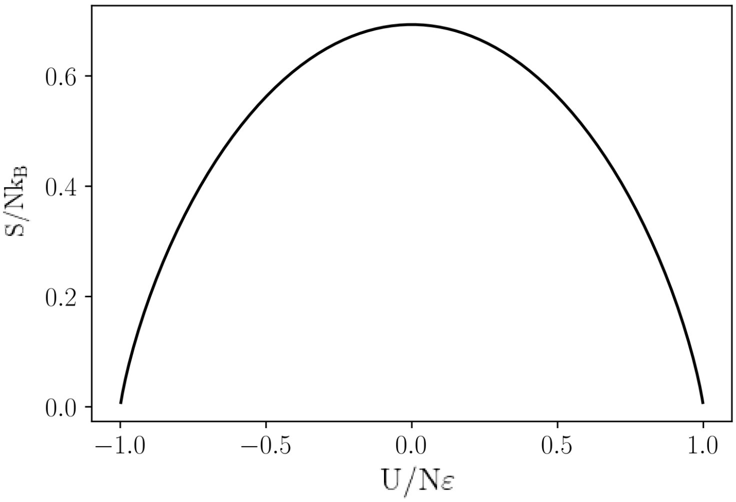

Figure 2.3: The entropy versus internal energy for a two-state system. The energy is dimensionless by the quantity ε, where the two energy levels of the system are $\pm\varepsilon$, and k_B is the Boltzmann constant. Figure adapted from [1].

The Eq. (2.19) shows that when the derivative of S with respect to U is negative, it corresponds to negative temperature. This phenomenon is illustrated in Fig 2.3, where an increase in energy U coincides with a decrease in entropy S. Assuming two possible energy states exist for each system element, the lowest possible state is reached with all elements in the lowest energy state, corresponding to $S = 0$. The opposite follows for the greatest possible state, and $S = 0$. Also, the graph shows that when the energy is at its maximum, where the entropy is null, the temperature is infinite. After that, the negative scale for temperature occurs, which means that negative temperatures are "hotter" than infinite temperatures. As we are now considering $T < 0$ to be hotter than hot, it is necessary to look again at some definitions of thermodynamics.

The definitions of "heat" and "work" remain the same for positive and negative temperatures. A definition that leaves no doubt could be that this is the hotter system in a situation with two bodies in contact with each other when heat flows from one body to another. That definition avoids confusion with the meaning of "hot" and "cold" as we take into account negative temperature. The scale from cold to hot runs according to +0 K, ..., +300 K, ..., $+\infty$ K,

$-\infty$ K, ..., -300 K, ..., -0 K.

Various cyclic processes, including the Carnot cycle, can be carried out at negative temperatures, as the ratio between two negative temperatures would be positive, and the equation would hold. However, the problem arises when we have one system at a positive temperature and the other at a negative temperature. This phenomenon has been studied in recent works [8, 42, 43, 44].

The definition of entropy and the Clausius statement remain unaltered, but the Kelvin-Planck statement must be modified to account for negative temperature: it is impossible to construct a device that operates in a closed system and produces no other effect than the extraction of heat from a positive temperature reservoir to produce work, or the rejection of heat into a negative-temperature reservoir with the work being done on the engine. It is important to note that absolute zero temperature remains unattainable, and the third law must include this caveat: it is impossible, by any means, to reduce any system to absolute zero at positive temperature or to raise any system to absolute zero at a negative temperature in a finite number of operations.

To reach a negative temperature, any given system must meet some essential requirements for any thermodynamic system. They are: to be in thermodynamic equilibrium, there must be a limit to the highest possible energy for the system's allowed states, and this system must be thermally isolated from all systems with $T > 0$. The upper states are busier for negative temperatures than the lower ones, characterizing an inverted population. For positive temperatures, the opposite occurs.

The occupation distribution of a system at positive temperature is described in such way that the probability for a particle to occupy a certain state with energy E_i is proportional to the Boltzmann factor [28]

$$e^{-E_i\beta}. \tag{2.20}$$

That is, the distribution decreases exponentially with energy E_i. For negative temperatures, the above factor increases exponentially with increasing E_i, and higher energy states are busier than lower ones. So, if there were no upper limit on energy, these temperatures could not be reached with finite energy.

A system that shows negative temperature is cold atoms in optical lattices since they are isolated from the environment, and it is possible to control the relevant parameters.

After the first evidence of the existence of negative temperatures in inverted population systems and of other works that followed and repeated the initial results, one of the critical arguments that were used about the validity of $T < 0$ was with respect to the correct entropy used to describe these spin systems.

2.3 Thermodynamic inconsistency

After recent discoveries related to negative temperatures [7, 8], the definition of equilibrium entropy in statistical mechanics has been addressed by some authors. This has led to a debate on the "Boltzmann vs. Gibbs entropy" question, which has been explored in various studies [9, 10, 11, 12, 14, 15, 16, 18, 19, 20]. These authors have provided a detailed comparison between the most commonly used entropies.

In a 2013 Nature article, Dunkel and Hilbert argument against the compatibility of a negative temperature with the thermodynamics [9]. The authors claimed that Gibb's entropy is the only one that fulfills the laws of thermodynamics. The thermodynamic temperature measured is the Boltzmann temperature T_B and not the absolute temperature $T = T_G$. Where,

$$T_B = \frac{T_G}{1 - k_B/C} \tag{2.21}$$

and $C = (\partial T_G/\partial E)$ is the heat capacity associated with T. By the equation above, $T_B < 0$ when $0 < C < k_B$.

In the 2014 article, Hilbert *et al* [11] proposed a detailed comparison between the commonly discussed microcanonical entropy definitions, to demonstrate whether they satisfy or violate the laws of thermodynamics. The entropies studied were: the Gibbs entropy (Eq. (2.13)), the complementary Gibbs entropy [45], the alternative Penrose entropy, the Boltzmann entropy (Eq. (2.18)), and a modified Boltzmann entropy [29]. The authors in Ref. [11] found that only the Gibbs entropy simultaneously satisfies the zeroth, first, and second laws of thermodynamics (as well as the classical equipartition theorem). They also comment on the argument in favor of Boltzmann entropy motivated by the equivalence between thermodynamic entropy and information entropy: there is no reason why a physical quantity should always coincide with a specific abstract information measure.

Unlike Ref. [11], which starts from the definitions of entropy to verify inconsistency concerning the laws of thermodynamics, in 2015, Campisi [12] started from the laws to build an expression of microscopic entropy. He then reaches the same conclusion, that the only entropy that fulfills the laws of thermodynamics is Gibbs entropy. Furthermore, he point out that the demonstrated failure of Boltzmann entropy to reproduce thermodynamic forces is not restricted to small systems, but continues, becoming more prominent in the thermodynamic limit, where Boltzmann entropy predicts an unphysical and nonexistent phase transition in the magnetization of a system of non-interacting spins in a magnetic field. The author concluded that the uniqueness of Gibbs entropy, as well as the demonstrated potential defect of Boltzmann entropy, provide compelling reasons to renounce the subject for once.

In an attempt to present the Boltzmann temperature as the only one capable of providing a consistent description of fluctuations, Cerino *et al* [14] provide a review of the Boltzmann and Gibbs entropies. The authors in Ref. [14] first point out that the 2014 work dealt with small systems where the number N of degrees of freedom was $N = O(1)$ and/or with long interactions. Assuming that S_B is always convex and considering systems with $N \gg 1$, regardless of the sign of T_B, the energy flow always goes from the hottest system to the coldest one. The Boltzmann temperature would be the only proper quantity that describes a distribution of the energy fluctuations in the canonical ensemble.

Several authors [15, 16, 18, 19, 20] have offered their rebuttals to the claim made in Ref.

[11] that only the Gibbs volume entropy satisfies all three laws and should be recognized as the thermodynamic entropy. These papers argue that negative temperatures do not contravene the principles of thermodynamics.

Ramsey in his work always assumed that equilibrium states always existed and that they were stable. He never specified a universal thermometer that would allow an unambiguous measurement of negative temperatures. As seen, several works address the subject. However, until 2013 it had not been discussed whether states of systems with negative temperatures were stable. Rochin described in his article [46] that if a system in a negative temperature state interacts with one that takes only positive temperatures the equilibrium state will always have a positive temperature. This argument holds regardless of the size of the systems. The author comes to the conclusion that states with negative temperatures cannot remain at a stable equilibrium state. It will always transfer its energy into any “normal” body it interacts with and will necessarily come out of that state. It is only in this respect that these states can be considered as being "hotter" than any body at positive temperatures, but this does not mean at all that they can be assigned a negative temperature. This discussion would not imply that systems cannot be placed in macroscopic states that would correspond to negative temperatures, it just says that these states are necessarily unstable.

In the 2015 article [47], Hoffmann intends to show how non-thermal equilibrium processes are described and understood without difficulties, balancing the different types of particles along with their energy and entropy production within the scope of thermodynamics. He described inverted quantum systems as mixtures in nonequilibrium states. Following this reasoning, Struchtrup [24] stands out by showing that the classical interpretation of thermodynamics provides a complete description of inverted quantum states as temperature-unstable states. The author concludes that systems are trapped in their unstable state, but will return to stable equilibrium states if there is a working medium or heat exchange with the environment. When one recognizes inverted quantum states as unstable temperature states, there is no need to modify the Kelvin-Planck statement and therefore no law of thermodynamics is violated for these states.

Chapter 3

Quantum thermodynamics

3.1 Open Quantum Systems

An open system is a quantum system S coupled to a distinct one, denoted R, usually called the environment or the reservoir. Each represents a subsystem of the total system $S+R$, which is generally considered a closed system. As the state of subsystem S changes due to its interactions, it is no longer represented by a unitary Hamiltonian dynamic. The total system's Hamiltonian evolution then induces its dynamic, and the subsystem is often assigned as a reduced system.

The Hilbert Space of the system is indicated as $\mathcal{H}_S$ and the equivalent to the environment as $\mathcal{H}_R$. The total system's Hilbert space is denoted by $\mathcal{H} = \mathcal{H}_S \otimes \mathcal{H}_R$, the tensor product of both subsystems. And the total Hamiltonian $H(t)$ is given by

$$H = H_S \otimes \mathbb{I}_{\mathbb{R}} + \mathbb{I}_{\mathbb{S}} \otimes H_R + H_I, \tag{3.1}$$

where H_S is the Hamiltonian of the open system S, $\mathbb{I}_{\mathbb{R}}$ is the identity operator in the Hilbert space $\mathcal{H}_R$, H_R the Hamiltonian of the environment R, $\mathbb{I}_{\mathbb{S}}$ is the identity operator for $\mathcal{H}_S$, and H_I is the Hamiltonian that described the interaction between S and R.

At first, we introduce the term environment to refer to system R; however, throughout this text, we will refer to a different type of environment, a reservoir. When referring to a reservoir, we assume it is in a thermal equilibrium state.

Considering that our system of interest is denoted by S if ρ, an density matrix expresses the state of the total system. The reduced density matrix of the quantum system S is

$$\rho_S = tr_R \rho, \tag{3.2}$$

where "tr" denotes the partial trace over the open system's Hilbert space [48]. Furthermore, the expectation values of the observables that act on the open system's Hilbert space are determined through

$$\langle A \rangle = tr_S \left\{ A \rho_S \right\}. \tag{3.3}$$

The equation of motion that describes ρ is given by

$$\dot{\rho} = -\frac{i}{\hbar} \left[H, \rho \right], \tag{3.4}$$

where H is the Hamiltonian of the $S \otimes R$ composite system. Just as the Schrödinger equation describes how pure states evolve in time, the Von Neumann equation (also known as the Liouville–Von Neumann equation) describes how a density operator evolves in time. When we move to the interaction representation, Eq. (3.4) becomes

$$\dot{\tilde{\rho}} = -\frac{i}{\hbar} \left[\tilde{H}_I(t), \tilde{\rho} \right]. \tag{3.5}$$

where

$$\tilde{\rho}(t) = e^{(i/\hbar)(H_S + H_R)t} \rho(t) e^{-(i/\hbar)(H_S + H_R)t}, \tag{3.6}$$

$$\tilde{H}_I(t) = e^{(i/\hbar)(H_S + H_R)t} H_I e^{-(i/\hbar)(H_S + H_R)t}. \tag{3.7}$$

Integrating Eq. (3.5) twice from t to 0 and substituting back in, we find

$$\dot{\tilde{\rho}} = -\frac{i}{\hbar} \left[\tilde{H}_I(t), \rho(0) \right] - \frac{1}{\hbar^2} \int_0^t \left[\tilde{H}_I(t), \left[\tilde{H}_I(t'), \tilde{\rho}(t') \right] \right] dt'. \tag{3.8}$$

The Born approximation assumes that the system interacts weakly with a large reservoir, neglecting the correlation between them and considering the reservoir stationary, so that

$$\tilde{\rho}(t) = \tilde{\rho}_S(t) \otimes \rho_R(0) + \rho_c(t) \approx \tilde{\rho}_S(t) \otimes \rho_R(0), \tag{3.9}$$

where $\rho_c(t)$ is the correlation term. Making the substitution of $\tilde{\rho}(t)$ into Eq. (3.8), and performing the partial trace in the reservoir,

$$\begin{aligned}\dot{\rho}_S = \frac{1}{i\hbar} &\left\{ tr_R \left[\tilde{H}_I(t)\rho_R(0) \right] \rho_S(0) - \rho_S(0) \left[\rho_R(0)\tilde{H}_I(t) \right] \right\} \\ &- \frac{1}{\hbar^2} tr_R \int_0^t \left[\tilde{H}_I(t), \left[\tilde{H}_I(t'), \tilde{\rho}_S(t') \otimes \rho_R(0) \right] \right] dt'. \end{aligned} \tag{3.10}$$

To facilitate the above equation we eliminate the term $\frac{1}{i\hbar} tr_R \left[\tilde{H}_I(t)\rho_R(0) \right]$ with the assumption

$$tr_R \left[\tilde{H}_I(t)\rho_R(0) \right] = 0. \tag{3.11}$$

Taking into account the *Markov approximation* where the integrand $\tilde{\rho}_S(t')$ is replaced by $\tilde{\rho}_S(t)$, i.e., the state of the system does not depend on the past. Eq. (3.10) becomes

$$\dot{\tilde{\rho}}_S = -\frac{1}{\hbar^2} tr_R \int_0^t \left[\tilde{H}_I(t), \left[\tilde{H}_I(t'), \tilde{\rho}_S(t) \otimes \rho_R(0) \right] \right] \mathrm{d}t'. \tag{3.12}$$

The above equation is a representation of a system interacting with a reservoir.

Since H_I is the Hamiltonian of interaction between S and R, let us consider a specific model

$$H_I = \hbar \sum_i s_i R_i, \tag{3.13}$$

where the s_i are operators in the Hilbert space of S and the R_i are reservoir operators in the Hilbert space of R. Then, in the interaction picture

$$\tilde{H}_I(t) = \hbar \sum_i \tilde{s}_i(t) \tilde{R}_i(t). \tag{3.14}$$

The master equation is now

$$\dot{\rho}_S = -\sum_{i,j}\int_0^t dt'\{[\tilde{s}_i(t)\tilde{s}_j(t)\rho_S(t') - \tilde{s}_j(t)\rho_S(t')\tilde{s}_i(t)]\,\langle \tilde{R}_i(t)\tilde{R}_j(t')\rangle_R + [\rho_S(t')\tilde{s}_j(t)\tilde{s}_i(t) - \tilde{s}_i(t)\rho_S(t')\tilde{s}_j(t)]\,\langle \tilde{R}_j(t)\tilde{R}_i(t')\rangle_R\}, \quad (3.15)$$

hence

$$\langle \tilde{R}_i(t)\tilde{R}_j(t')\rangle_R = tr_R\left[\rho_R(0)\tilde{R}_i(t)\tilde{R}_j(t')\right], \quad (3.16)$$

$$\langle \tilde{R}_j(t')\tilde{R}_i(t)\rangle_R = tr_R\left[\rho_R(0)\tilde{R}_j(t')\tilde{R}_i(t)\right]. \quad (3.17)$$

are called correlation functions.

A typical example of the system is the decay of a two-level atom damped by a reservoir of oscillators. We will use this system to derive a known form of the master equation that will be of interest in later chapters. The Hamiltonian that described this situation in the rotating-wave approximation is

$$H = \frac{1}{2}\hbar\omega_0\sigma_z + \sum_j \hbar\omega_j a_j^\dagger a_j + \hbar\sum_j(\kappa_j^*\sigma_- a_j^\dagger + \kappa_j\sigma_+ a_j). \quad (3.18)$$

The σ_- operator takes an atom in the higher state to the lower state, while σ_+ takes an atom in the lower state to the higher state. The Hamiltonian consists of four terms. The first term describes the system, a two-level atom, and the second represents the reservoir. The term $a_j^\dagger\sigma_-$ describes the process in which the atom is taken from the higher state to the lower state, a photon of mode j is created, and $a_j\sigma_+$ describes the opposite process.

Identifying the operators in Eq. (3.18), $s_1 = \sigma_-$, $s_2 = \sigma_+$, $R_1 = R^\dagger \equiv \sum_j \kappa_j^* a_j^\dagger$, and $R_2 = R \equiv \sum_j \kappa_j a_j$, these operators in the interaction picture are

$$\tilde{s}_1(t) = e^{i(\omega_0\sigma_z/2)t}\sigma_- e^{-i(\omega_0\sigma_z/2)t} = \sigma_- e^{-i\omega_0 t}, \quad (3.19)$$

$$\tilde{s}_2(t) = e^{i(\omega_0\sigma_z/2)t}\sigma_+ e^{-i(\omega_0\sigma_z/2)t} = \sigma_+ e^{i\omega_0 t}, \quad (3.20)$$

and

$$\tilde{R}_1(t) = \tilde{R}^\dagger(t) = \sum_j \kappa_j^* \left[e^{i\sum_k\left(\omega_k a_k^\dagger a_k\right)t} a_j^\dagger e^{-i\sum_l\left(\omega_l a_l^\dagger a_l\right)t} \right] = \sum_j \kappa_j^* a_j^\dagger e^{i\omega_j t}, \tag{3.21}$$

$$\tilde{R}_2(t) = \tilde{R}(t) = \sum_j \kappa_j \left[e^{i\sum_k\left(\omega_k a_k^\dagger a_k\right)t} a_j e^{-i\sum_l\left(\omega_l a_l^\dagger a_l\right)t} \right] = \sum_j \kappa_j a_j e^{-i\omega_j t}. \tag{3.22}$$

The Hamiltonian is then

$$H_I(t) = \hbar \sum_j \left[\kappa_j^* a_j^\dagger \sigma_- e^{i(\omega_j - \omega_0)t} + \kappa_j a_j \sigma_+ e^{-i(\omega_j - \omega_0)t} \right], \tag{3.23}$$

where κ_j is the coupling constant, ω_0 refers to the system's frequency, and ω_j represents the jth frequency of the reservoir. Finally, we insert the above term into Eq. (3.15) and obtain

$$\begin{aligned}
\frac{d\tilde{\rho}(t)}{dt} = -\int_0^t dt' \{ & [\sigma_-\sigma_-\tilde{\rho}(t') - \sigma_-\tilde{\rho}(t')\sigma_-]\, e^{-i\omega_0(t+t')} \langle \tilde{R}^\dagger(t)\tilde{R}^\dagger(t')\rangle_R \\
& + [\tilde{\rho}(t')\sigma_-\sigma_- - \sigma_-\tilde{\rho}(t')\sigma_-]\, e^{-i\omega_0(t+t')} \langle \tilde{R}^\dagger(t')\tilde{R}^\dagger(t)\rangle_R \\
& + [\sigma_-\sigma_+\tilde{\rho}(t') - \sigma_+\tilde{\rho}(t')\sigma_-]\, e^{-i\omega_0(t-t')} \langle \tilde{R}^\dagger(t)\tilde{R}(t')\rangle_R \\
& + [\tilde{\rho}(t')\sigma_+\sigma_- - \sigma_-\tilde{\rho}(t')\sigma_+]\, e^{-i\omega_0(t-t')} \langle \tilde{R}(t')\tilde{R}^\dagger(t)\rangle_R \\
& + [\sigma_+\sigma_-\tilde{\rho}(t') - \sigma_-\tilde{\rho}(t')\sigma_+]\, e^{i\omega_0(t-t')} \langle \tilde{R}(t)\tilde{R}^\dagger(t')\rangle_R \\
& + [\tilde{\rho}(t')\sigma_-\sigma_+ - \sigma_+\tilde{\rho}(t')\sigma_-]\, e^{i\omega_0(t-t')} \langle \tilde{R}^\dagger(t')\tilde{R}(t)\rangle_R \\
& + [\sigma_+\sigma_+\tilde{\rho}(t') - \sigma_+\tilde{\rho}(t')\sigma_+]\, e^{i\omega_0(t+t')} \langle \tilde{R}(t)\tilde{R}(t')\rangle_R \\
& + [\tilde{\rho}(t')\sigma_+\sigma_+ - \sigma_+\tilde{\rho}(t')\sigma_+]\, e^{i\omega_0(t+t')} \langle \tilde{R}(t')\tilde{R}(t)\rangle_R \}.
\end{aligned} \tag{3.24}$$

It is in our interest that the reduced density operator that describes the reservoir is in the form of a thermal operator,

$$\rho_R(0) = \prod_j \left[1 - e^{\left(\frac{-\hbar\omega_j}{k_B T}\right)} \right] e^{\left(\frac{-\hbar\omega_j a_j^\dagger a_j}{k_B T}\right)} \tag{3.25}$$

where T is the temperature and k_B is the Boltzmann constant. Thus, from Equations (3.16) and (3.17), it is natural that

$$\begin{aligned}
\langle\tilde{R}^\dagger(t)\tilde{R}^\dagger(t')\rangle_R =&\ \sum_{i,j}\kappa_j^*\kappa_k^* e^{i\omega_j t}e^{i\omega_k t'}tr_R\left\{a_j^\dagger a_k^\dagger\rho_R(0)\right\} && (3.26)\\
\langle\tilde{R}^\dagger(t')\tilde{R}^\dagger(t)\rangle_R =&\ \sum_{i,j}\kappa_j^*\kappa_k^* e^{i\omega_j t'}e^{i\omega_k t}tr_R\left\{a_j^\dagger a_k^\dagger\rho_R(0)\right\} && (3.27)\\
\langle\tilde{R}^\dagger(t)\tilde{R}(t')\rangle_R =&\ \sum_{i,j}\kappa_j^*\kappa_k e^{i\omega_j t}e^{-i\omega_k t'}tr_R\left\{a_j^\dagger a_k\rho_R(0)\right\} && (3.28)\\
\langle\tilde{R}(t')\tilde{R}^\dagger(t)\rangle_R =&\ \sum_{i,j}\kappa_j\kappa_k^* e^{-i\omega_j t'}e^{i\omega_k t}tr_R\left\{a_j a_k^\dagger\rho_R(0)\right\} && (3.29)\\
\langle\tilde{R}(t)\tilde{R}^\dagger(t')\rangle_R =&\sum_{i,j}\kappa_j\kappa_k^* e^{-i\omega_j t}e^{i\omega_k t'}tr_R\left\{a_j a_k^\dagger\rho_R(0)\right\} && (3.30)\\
\langle\tilde{R}^\dagger(t')\tilde{R}(t)\rangle_R =&\ \sum_{i,j}\kappa_j^*\kappa_k e^{i\omega_j t'}e^{-i\omega_k t}tr_R\left\{a_j^\dagger a_k\rho_R(0)\right\} && (3.31)\\
\langle\tilde{R}(t)\tilde{R}(t')\rangle_R =&\sum_{i,j}\kappa_j\kappa_k e^{-i\omega_j t}e^{-i\omega_k t'}tr_R\left\{a_j a_k\rho_R(0)\right\} && (3.32)\\
\langle\tilde{R}(t')\tilde{R}(t)\rangle_R =&\ \sum_{i,j}\kappa_j\kappa_k e^{-i\omega_j t'}e^{-i\omega_k t}tr_R\left\{a_j a_k\rho_R(0)\right\}. && (3.33)
\end{aligned}$$

To calculate the terms of Equations (3.26)-(3.33), let us first consider the case where $j \neq k$,

$$\begin{aligned}
tr_R\left\{\rho_R(0)a_j^\dagger a_k\right\} &= tr_R\left\{a_j^\dagger a_k\prod_m\left[1-e^{-\hbar\omega_m/k_BT}\right]e^{(-\hbar\omega_m/k_BT)a_m^\dagger a_m}\right\}\\
&= \sum_{\ldots,n_j,\ldots,n_k,\ldots}\langle\ldots,n_j,\ldots,n_k,\ldots|\left\{a_j^\dagger a_k\prod_m\left[1-e^{-\hbar\omega_m/k_BT}\right]e^{(-\hbar\omega_m/k_BT)a_m^\dagger a_m}\right\}|\ldots,n_j,\ldots,n_k,\ldots\rangle\\
&= \sum_{\ldots,n_j,\ldots,n_k,\ldots}\langle\ldots,n_j,\ldots,n_k,\ldots|a_j^\dagger a_k|\ldots,n_j,\ldots,n_k,\ldots\rangle\prod_m\left[1-e^{-\hbar\omega_m/k_BT}\right]e^{(-\hbar\omega_m/k_BT)n_m}.
\end{aligned}$$

and

$$\begin{aligned}
\langle\ldots,n_j,\ldots,n_k,\ldots|a_j^\dagger a_k|\ldots,n_j,\ldots,n_k,\ldots\rangle &= \sqrt{n_j+1}\sqrt{n_k}\langle\ldots,n_j,\ldots,n_k,\ldots|\ldots,n_j+1,\ldots,n_k-1,\ldots\rangle\\
&= 0.
\end{aligned}$$

Thus, whatever the values of j and k, the trace above are null. Evaluating now $tr_R\left\{\rho_R(0)a_j^\dagger a_j\right\}$

in the case where $i \neq j$, we get

$$\begin{aligned}
tr_R\left\{\rho_R(0)a_j^\dagger a_j\right\} &= tr_R\left\{a_j^\dagger a_j \prod_m \left[1-e^{-\hbar\omega_m/k_BT}\right] e^{(-\hbar\omega_m/k_BT)a_m^\dagger a_m}\right\} \\
&= \sum_{\dots,n_j,\dots} \langle \dots, n_j, \dots| \left\{a_m^\dagger a_m \prod_m \left[1-e^{-\hbar\omega_m/k_BT}\right] e^{(-\hbar\omega_m/k_BT)a_m^\dagger a_m}\right\} |\dots, n_j, \dots\rangle \\
&= \sum_{\dots,n_j,\dots} n_j \prod_m \left[1-e^{-\hbar\omega_m/k_BT}\right] \langle n_m| e^{(-\hbar\omega_j/k_BT)a_m^\dagger a_m}|n_m\rangle \\
&= \sum_{\dots,n_j,\dots} n_j \prod_m \left[1-e^{-\hbar\omega_m/k_BT}\right] e^{(-\hbar\omega_j/k_BT)n_m} \\
&= \frac{e^{-\hbar\omega_j/k_BT}}{1-e^{-\hbar\omega_j/k_BT}} \\
&= \frac{1}{e^{\hbar\omega_j/k_BT}-1} = \bar{n}(\omega_j,\beta). \qquad (3.34)
\end{aligned}$$

Therefore, the results obtained were

$$tr_R\left\{a_j^\dagger a_k^\dagger \rho_R(0)\right\} = tr_R\left\{a_j a_k \rho_R(0)\right\} = 0, \qquad (3.35)$$

$$tr_R\left\{a_j^\dagger a_k \rho_R(0)\right\} = \bar{n}(\omega_j,\beta)\delta_{j,k}, \qquad (3.36)$$

$$tr_R\left\{a_j a_k^\dagger \rho_R(0)\right\} = tr_R\left\{\left[1-a_j a_k^\dagger\right]\rho_R(0)\right\} = \left[1-\bar{n}(\omega_j,\beta)\right]\delta_{j,k}. \qquad (3.37)$$

Using Equations (3.35)-(3.37), Eq. (3.24) becomes

$$\begin{aligned}
\frac{d\tilde{\rho}(t)}{dt} = -\int_0^t dt' \{ &\left[\sigma_-\sigma_+\tilde{\rho}(t') - \sigma_+\tilde{\rho}(t')\sigma_-\right] e^{-i\omega_0(t-t')}\langle \tilde{R}^\dagger(t)\tilde{R}(t')\rangle_R \\
&+ \left[\tilde{\rho}(t')\sigma_+\sigma_- - \sigma_-\tilde{\rho}(t')\sigma_+\right] e^{-i\omega_0(t-t')}\langle \tilde{R}(t')\tilde{R}^\dagger(t)\rangle_R \\
&+ \left[\sigma_+\sigma_-\tilde{\rho}(t') - \sigma_-\tilde{\rho}(t')\sigma_+\right] e^{i\omega_0(t-t')}\langle \tilde{R}(t)\tilde{R}^\dagger(t')\rangle_R \\
&+ \left[\tilde{\rho}(t')\sigma_-\sigma_+ - \sigma_+\tilde{\rho}(t')\sigma_-\right] e^{i\omega_0(t-t')}\langle \tilde{R}^\dagger(t')\tilde{R}(t)\rangle_R. \qquad (3.38)
\end{aligned}$$

The reservoir correlation functions are explicit:

$$\langle \tilde{R}^\dagger(t)\tilde{R}(t')\rangle_R = \sum_j |\kappa_j|^2 \, e^{i\omega_j(t-t')}\bar{n}(\omega_j,\beta), \tag{3.39}$$

$$\langle \tilde{R}(t')\tilde{R}^\dagger(t)\rangle_R = \sum_j |\kappa_j|^2 \, e^{i\omega_j(t-t')}\left[1-\bar{n}(\omega_j,\beta)\right], \tag{3.40}$$

$$\langle \tilde{R}(t)\tilde{R}^\dagger(t')\rangle_R = \sum_j |\kappa_j|^2 \, e^{-i\omega_j(t-t')}\left[1-\bar{n}(\omega_j,\beta)\right], \tag{3.41}$$

$$\langle \tilde{R}^\dagger(t')\tilde{R}(t)\rangle_R = \sum_j |\kappa_j|^2 \, e^{-i\omega_j(t-t')}\bar{n}(\omega_j,\beta). \tag{3.42}$$

Performing now the changes $\tau = t - t'$ and $\sum_j \to \int_0^\infty d\omega g(\omega)$, where $d\omega g(\omega)$ is the number of atoms with the frequency between ω and $\omega + d\omega$, we have [49]

$$\begin{aligned}\frac{d\tilde{\rho}(t)}{dt} = -\int_0^t & d\tau \{ \left[\sigma_-\sigma_+\tilde{\rho}(t-\tau) - \sigma_+\tilde{\rho}(t-\tau)\sigma_-\right] e^{-i\omega_0\tau}\langle \tilde{R}^\dagger(t)\tilde{R}(t-\tau)\rangle_R \\ & + \left[\tilde{\rho}(t-\tau)\sigma_+\sigma_- - \sigma_-\tilde{\rho}(t-\tau)\sigma_+\right] e^{-i\omega_0\tau}\langle \tilde{R}(t-\tau)\tilde{R}^\dagger(t)\rangle_R \\ & + \left[\sigma_+\sigma_-\tilde{\rho}(t-\tau) - \sigma_-\tilde{\rho}(t+\tau)\sigma_+\right] e^{i\omega_0\tau}\langle \tilde{R}(t)\tilde{R}^\dagger(t-\tau)\rangle_R \\ & + \left[\tilde{\rho}(t-\tau)\sigma_-\sigma_+ - \sigma_+\tilde{\rho}(t-\tau)\sigma_-\right] e^{i\omega_0\tau}\langle \tilde{R}^\dagger(t-\tau)\tilde{R}(t)\rangle_R,\end{aligned} \tag{3.43}$$

where the nonzero reservoir correlation functions are

$$\langle \tilde{R}^\dagger(t)\tilde{R}(t-\tau)\rangle_R = \int_0^\infty d\omega g(\omega)|\kappa(\omega)|^2 e^{i\omega\tau}\bar{n}(\omega,\beta), \tag{3.44}$$

$$\langle \tilde{R}(t-\tau)\tilde{R}^\dagger(t)\rangle_R = \int_0^\infty d\omega g(\omega)|\kappa(\omega)|^2 e^{i\omega\tau}\left[1-\bar{n}(\omega,\beta)\right], \tag{3.45}$$

$$\langle \tilde{R}(t)\tilde{R}^\dagger(t-\tau)\rangle_R = \int_0^\infty d\omega g(\omega)|\kappa(\omega)|^2 e^{-i\omega\tau}\left[1-\bar{n}(\omega,\beta)\right], \tag{3.46}$$

$$\langle \tilde{R}^\dagger(t-\tau)\tilde{R}(t)\rangle_R = \int_0^\infty d\omega g(\omega)|\kappa(\omega)|^2 e^{-i\omega\tau}\bar{n}(\omega,\beta). \tag{3.47}$$

If the integration at τ is dominated by times that are shorter than the $\tilde{\rho}$ evolution timescale, we can perform the Markov approximation, so we rewrite the Eq. (3.43) in the form

$$\begin{aligned}\frac{d\tilde{\rho}(t)}{dt} = {} & \alpha\left[\sigma_-\tilde{\rho}(t)\sigma_+ - \sigma_+\sigma_-\tilde{\rho}(t)\right] + \beta\left[\sigma_-\tilde{\rho}(t)\sigma_+ + \sigma_+\tilde{\rho}(t)\sigma_- - \sigma_+\sigma_-\tilde{\rho}(t) - \tilde{\rho}(t)\sigma_-\sigma_+\right] \\ & + \alpha^*\left[\sigma_+\tilde{\rho}(t)\sigma_- - \sigma_-\sigma_+\tilde{\rho}(t)\right] + \beta^*\left[\sigma_+\tilde{\rho}(t)\sigma_- + \sigma_-\tilde{\rho}(t)\sigma_+ - \sigma_-\sigma_+\tilde{\rho}(t) - \tilde{\rho}(t)\sigma_+\sigma_-\right],\end{aligned} \tag{3.48}$$

being,

$$\alpha \equiv \int_0^t d\tau \int_0^\infty d\omega g(\omega)|\kappa(\omega)|^2 e^{i(\omega-\omega_0)\tau}, \tag{3.49}$$

$$\beta \equiv \int_0^t d\tau \int_0^\infty d\omega g(\omega)|\kappa(\omega)|^2 e^{i(\omega-\omega_0)\tau} \bar{n}(\omega, \beta). \tag{3.50}$$

Considering that the dynamics of the reservoir is much faster than the dynamics of the system, the limit of integration can be extended to infinity in such a way that

$$\lim_{t\to\infty} \int_0^t d\tau e^{i(\omega-\omega_0)\tau} = \pi\delta(\omega - \omega_0) + i\frac{P}{\omega_0 - \omega}. \tag{3.51}$$

where P indicates the Cauchy principal value. In this way, we have

$$\alpha = \pi g(\omega_0)|\kappa(\omega_0)|^2 + i\Delta, \tag{3.52}$$

$$\beta = \pi g(\omega_0)|\kappa(\omega_0)|^2 \bar{n}(\omega, \beta) + i\Delta', \tag{3.53}$$

with Δ and Δ' given by

$$\Delta = P\int_0^\infty d\omega \frac{g(\omega)|\kappa(\omega)|^2}{\omega_0 - \omega}, \tag{3.54}$$

$$\Delta' = P\int_0^\infty d\omega \frac{g(\omega)|\kappa(\omega)|^2}{\omega_0 - \omega} \bar{n}(\omega, \beta). \tag{3.55}$$

Defining $\gamma = 2\pi g(\omega_0)|\kappa(\omega_0)|^2$ and $\bar{n} = \bar{n}(\omega, \beta)$, the master equation for a two-level atom damped by a reservoir of oscillators:

$$\begin{aligned}\frac{d\tilde{\rho}(t)}{dt} = -i\Delta\left[\sigma_+\sigma_-, \tilde{\rho}(t)\right] + \frac{\gamma}{2}(\bar{n}+1)\left[2\sigma_-\tilde{\rho}(t)\sigma_+ - \sigma_+\sigma_-\tilde{\rho}(t) - \tilde{\rho}(t)\sigma_+\sigma_-\right]& \\ + \frac{\gamma}{2}\bar{n}\left[2\sigma_+\tilde{\rho}(t)\sigma_- - \sigma_-\sigma_+\tilde{\rho}(t) - \tilde{\rho}(t)\sigma_-\sigma_+\right].&\end{aligned} \tag{3.56}$$

3.2 Fermionic bath

The fermionic reservoir can be thought of as a collection of non-interacting fermions. Let us then consider a collection of non-interacting two-level atoms whose frequency is ω_0, The

Hamiltonian who describes this is

$$H_R = \frac{\hbar}{2}\sum_j \omega_j \sigma_{z,j}. \tag{3.57}$$

The state $\rho_R(0)$ of reservoir R is a Gibbs state:

$$\rho_R(0) = \frac{e^{-\beta H_R}}{tr_R(e^{-\beta H_R})}. \tag{3.58}$$

Inserting Eq. (3.57) into Eq. (3.58):

$$\begin{aligned}
\rho_R(0) &= \frac{e^{-(\beta\hbar/2)\sum_j \omega_j \sigma_{z,j}}}{tr_R\left[e^{-(\beta\hbar/2)\sum_j \omega_j \sigma_{z,j}}\right]} \\
&= \frac{\prod_j e^{-(\beta\hbar/2)\sum_j \omega_j \sigma_{z,j}}}{tr_R\left[\prod_j e^{-(\beta\hbar/2)\sum_j \omega_j \sigma_{z,j}}\right]} \\
&= \frac{\prod_j e^{-(\beta\hbar/2)\sum_j \omega_j \sigma_{z,j}}}{\prod_j tr_R\left[e^{-(\beta\hbar/2)\sum_j \omega_j \sigma_{z,j}}\right]} \\
&= \prod_j \frac{e^{-(\beta\hbar/2)\omega_{z,j}}}{e^{(\beta\hbar/2)\omega_j} + e^{-(\beta\hbar/2)\omega_j}}.
\end{aligned} \tag{3.59}$$

Assuming now that we have a two-level atom coupled to the reservoir R. Thus, the Hamiltonian of the system S will be

$$H_S = \frac{\hbar}{2}\omega_0 \sigma_z, \tag{3.60}$$

here ω_j represents the jth frequency of the reservoir. And the Hamiltonian interaction between them can be written in the rotating wave approximation as

$$H_I = \hbar \sum_j (\kappa_j^* \sigma_- \sigma_{+,j} + \kappa_j \sigma_+ \sigma_{-,j}), \tag{3.61}$$

with κ being the jth coupling constant. Identifying the operators in Eq. (3.14) as was done in the previous section, $s_1 = \sigma_-$, $s_2 = \sigma_+$, $F_1 = \sum_j \kappa_j^* \sigma_{+,j}$, and $\sum_j \kappa_j \sigma_{-,j}$. Moving on to the interaction representation, we have

$$\begin{aligned}\tilde{S}_1(t) &= e^{i(\omega_0\sigma_z/2)t}\sigma_- e^{-i(\omega_0\sigma_z/2)t} = \sigma_- e^{-i\omega_0 t},\\ \tilde{S}_2(t) &= e^{i(\omega_0\sigma_z/2)t}\sigma_+ e^{-i(\omega_0\sigma_z/2)t} = \sigma_+ e^{i\omega_0 t},\end{aligned} \tag{3.62}$$

and

$$\begin{aligned}\tilde{F}_1(t) &= \sum_j \kappa_j^* \left[e^{i\sum_k\left(\omega_k\sigma_{z,k}/2\right)t}\sigma_{+,j} e^{-i\sum_k\left(\omega_k\sigma_{z,k}/2\right)t}\right] = \sum_j \kappa_j^* \sigma_{+,j} e^{i\omega_j t},\\ \tilde{F}_2(t) &= \sum_j \kappa_j \left[e^{i\sum_k\left(\omega_k\sigma_{z,k}/2\right)t}\sigma_{-,j} e^{-i\sum_k\left(\omega_k\sigma_{z,k}/2\right)t}\right] = \sum_j \kappa_j \sigma_{-,j} e^{i\omega_j t}.\end{aligned} \tag{3.63}$$

And the interaction Hamiltonian in the interaction picture,

$$\tilde{H}_I(t) = \hbar\sum_j \left[\kappa_j^*\sigma_-\sigma_{+,j}e^{i(\omega_j-\omega_0)t} + \kappa_j\sigma_+\sigma_{-,j}e^{-i(\omega_j-\omega_0)t}\right]. \tag{3.64}$$

Inserting all terms in Eq. (3.15), that gives

$$\begin{aligned}\frac{d\tilde{\rho}(t)}{dt} = -\int_0^t dt'\{&[\sigma_-\sigma_-\tilde{\rho}(t') - \sigma_-\tilde{\rho}(t')\sigma_-]\, e^{-i\omega_0(t+t')}\langle\tilde{F}^\dagger(t)\tilde{F}^\dagger(t')\rangle_R\\ &+ [\tilde{\rho}(t')\sigma_-\sigma_- - \sigma_-\tilde{\rho}(t')\sigma_-]\, e^{-i\omega_0(t+t')}\langle\tilde{F}^\dagger(t')\tilde{F}^\dagger(t)\rangle_R\\ &+ [\sigma_-\sigma_+\tilde{\rho}(t') - \sigma_+\tilde{\rho}(t')\sigma_-]\, e^{-i\omega_0(t-t')}\langle\tilde{F}^\dagger(t)\tilde{F}(t')\rangle_R\\ &+ [\tilde{\rho}(t')\sigma_+\sigma_- - \sigma_-\tilde{\rho}(t')\sigma_+]\, e^{-i\omega_0(t-t')}\langle\tilde{F}(t')\tilde{F}^\dagger(t)\rangle_R\\ &+ [\sigma_+\sigma_-\tilde{\rho}(t') - \sigma_-\tilde{\rho}(t')\sigma_+]\, e^{i\omega_0(t-t')}\langle\tilde{F}(t)\tilde{F}^\dagger(t')\rangle_R\\ &+ [\tilde{\rho}(t')\sigma_-\sigma_+ - \sigma_+\tilde{\rho}(t')\sigma_-]\, e^{i\omega_0(t-t')}\langle\tilde{F}^\dagger(t')\tilde{F}(t)\rangle_R\\ &+ [\sigma_+\sigma_+\tilde{\rho}(t') - \sigma_+\tilde{\rho}(t')\sigma_+]\, e^{i\omega_0(t+t')}\langle\tilde{F}(t)\tilde{F}(t')\rangle_R\}.\end{aligned} \tag{3.65}$$

where the reservoir averages read

$$
\begin{aligned}
\langle \tilde{F}^\dagger(t)\tilde{F}^\dagger(t')\rangle_R &= \sum_{i,j} \kappa_j^* \kappa_k^* e^{i\omega_j t} e^{i\omega_k t'} tr_R \left\{\sigma_{+,j}\sigma_{+,k}\rho_R(0)\right\} && (3.66)\\
\langle \tilde{F}^\dagger(t')\tilde{F}^\dagger(t)\rangle_R &= \sum_{i,j} \kappa_j^* \kappa_k^* e^{i\omega_j t'} e^{i\omega_k t} tr_R \left\{\sigma_{+,j}\sigma_{+,k}\rho_R(0)\right\} && (3.67)\\
\langle \tilde{F}^\dagger(t)\tilde{F}(t')\rangle_R &= \sum_{i,j} \kappa_j^* \kappa_k e^{i\omega_j t} e^{-i\omega_k t'} tr_R \left\{\sigma_{+,j}\sigma_{-,k}\rho_R(0)\right\} && (3.68)\\
\langle \tilde{F}(t')\tilde{F}^\dagger(t)\rangle_R &= \sum_{i,j} \kappa_j \kappa_k^* e^{-i\omega_j t'} e^{i\omega_k t} tr_R \left\{\sigma_{-,j}\sigma_{+,k}\rho_R(0)\right\} && (3.69)\\
\langle \tilde{F}(t)\tilde{F}^\dagger(t')\rangle_R &= \sum_{i,j} \kappa_j \kappa_k^* e^{-i\omega_j t} e^{i\omega_k t'} tr_R \left\{\sigma_{-,j}\sigma_{+,k}\rho_R(0)\right\} && (3.70)\\
\langle \tilde{F}^\dagger(t')\tilde{F}(t)\rangle_R &= \sum_{i,j} \kappa_j^* \kappa_k e^{i\omega_j t'} e^{-i\omega_k t} tr_R \left\{\sigma_{+,j}\sigma_{-,k}\rho_R(0)\right\} && (3.71)\\
\langle \tilde{F}(t)\tilde{F}(t')\rangle_R &= \sum_{i,j} \kappa_j \kappa_k e^{-i\omega_j t} e^{-i\omega_k t'} tr_R \left\{\sigma_{-,j}\sigma_{-,k}\rho_R(0)\right\} && (3.72)\\
\langle \tilde{F}(t')\tilde{F}(t)\rangle_R &= \sum_{i,j} \kappa_j \kappa_k e^{-i\omega_j t'} e^{-i\omega_k t} tr_R \left\{\sigma_{-,j}\sigma_{-,k}\rho_R(0)\right\}. && (3.73)
\end{aligned}
$$

To calculate the traces of the equations above, let's first look at $tr_R\left\{\sigma_{\pm,j}\sigma_{\pm,k}\rho_R(0)\right\}$, if $j = k$, $tr_R\left\{\sigma_{\pm,j}\sigma_{\pm,k}\rho_R(0)\right\} = 0$ due to $\sigma_{\pm,j}\sigma_{\pm,j} = 0$. In the case where $j \neq k$,

$$
\begin{aligned}
tr_R\left\{\sigma_{\pm,j}\sigma_{\pm,k}\rho_R(0)\right\}_{j\neq k} &= tr_R\left[\sigma_{\pm,j}\sigma_{\pm,k}\prod_l \frac{e^{-(\beta\hbar/2)\omega_l\sigma_{z,l}}}{e^{(\beta\hbar/2)\omega_l}+e^{-(\beta\hbar/2)\omega_l}}\right]\\
&= \left\{\frac{tr_{R_j}\left[\sigma_{\pm,j}e^{-(\beta\hbar/2)\omega_j\sigma_{z,j}}\right]}{e^{(\beta\hbar/2)\omega_j}+e^{-(\beta\hbar/2)\omega_j}}\right\}\left\{\frac{tr_{R_k}\left[\sigma_{\pm,k}e^{-(\beta\hbar/2)\omega_k\sigma_{z,k}}\right]}{e^{(\beta\hbar/2)\omega_k}+e^{-(\beta\hbar/2)\omega_k}}\right\}\\
&= 0. && (3.74)
\end{aligned}
$$

Now computing $tr_R\left\{\sigma_{\pm,j}\sigma_{\mp,k}\rho_R(0)\right\} = 0$, that gives

$$
\begin{aligned}
tr_R\left\{\sigma_{\pm,j}\sigma_{\mp,k}\rho_R(0)\right\}_{j\neq k} &= tr_R\left[\sigma_{\pm,j}\sigma_{\mp,k}\prod_l \frac{e^{-(\beta\hbar/2)\omega_l\sigma_{z,l}}}{e^{(\beta\hbar/2)\omega_l}+e^{-(\beta\hbar/2)\omega_l}}\right]\\
&= \left\{\frac{tr_{R_j}\left[\sigma_{\pm,j}e^{-(\beta\hbar/2)\omega_j\sigma_{z,j}}\right]}{e^{(\beta\hbar/2)\omega_j}+e^{-(\beta\hbar/2)\omega_j}}\right\}\left\{\frac{tr_{R_k}\left[\sigma_{\mp,k}e^{-(\beta\hbar/2)\omega_k\sigma_{z,k}}\right]}{e^{(\beta\hbar/2)\omega_k}+e^{-(\beta\hbar/2)\omega_k}}\right\}\\
&= 0. && (3.75)
\end{aligned}
$$

In the case where $j = k$, we need to calculate the traces separately, let us start first with

$$\begin{aligned}
tr_R\left\{\sigma_{+,j}\sigma_{-,j}\rho_R(0)\right\} &= tr_R\left[\sigma_{+,j}\sigma_{-,j}\prod_l \frac{e^{-(\beta\hbar/2)\omega_l\sigma_{z,l}}}{e^{(\beta\hbar/2)\omega_l}+e^{-(\beta\hbar/2)\omega_l}}\right] \\
&= \frac{tr_{R_j}\left[\sigma_{+,j}\sigma_{-,j}e^{-(\beta\hbar/2)\omega_j\sigma_{z,j}}\right]}{e^{(\beta\hbar/2)\omega_j}+e^{-(\beta\hbar/2)\omega_j}} \\
&= \frac{\langle g_j|\,\sigma_{+,j}\sigma_{-,j}e^{-(\beta\hbar/2)\omega_j\sigma_{z,j}}\,|g_j\rangle + \langle e_j|\,\sigma_{+,j}\sigma_{-,j}e^{-(\beta\hbar/2)\omega_j\sigma_{z,j}}\,|e_j\rangle}{e^{(\beta\hbar/2)\omega_j}+e^{-(\beta\hbar/2)\omega_j}} \\
&= \frac{\langle g_j|\,\sigma_{+,j}\sigma_{-,j}\,|g_j\rangle\, e^{(\beta\hbar/2)\omega_j\sigma_{z,j}} + \langle e_j|\,\sigma_{+,j}\sigma_{-,j}\,|e_j\rangle\, e^{-(\beta\hbar/2)\omega_j\sigma_{z,j}}}{e^{(\beta\hbar/2)\omega_j}+e^{-(\beta\hbar/2)\omega_j}} \\
&= \frac{e^{-(\beta\hbar/2)\omega_j}}{e^{(\beta\hbar/2)\omega_j}+e^{-(\beta\hbar/2)\omega_j}} \\
&= \frac{1}{e^{\beta\hbar\omega_j}+1} \\
&= \bar{n}(\omega_j,\beta). \qquad (3.76)
\end{aligned}$$

Here $\bar{n}(\omega_j,\beta)$ is the average number of electrons in the excited state of atom j, which obeys the Fermi-Dirac distribution [50]. And finally,

$$\begin{aligned}
tr_R\left\{\sigma_{-,j}\sigma_{+,j}\rho_R(0)\right\} &= tr_R\left[\left(1-\sigma_{-,j}\sigma_{+,j}\rho_R(0)\right)\rho_R(0)\right] \\
&= 1-\bar{n}(\omega_j,\beta). \qquad (3.77)
\end{aligned}$$

Summarizing, the results are

$$tr_R\left\{\sigma_{\pm,j}\sigma_{\pm,k}\rho_R(0)\right\} = 0, \qquad (3.78)$$

$$tr_R\left\{\sigma_{+,j}\sigma_{-,k}\rho_R(0)\right\} = \bar{n}\left(\omega_j,\beta\right)\delta_{j,k}, \qquad (3.79)$$

$$tr_R\left\{\sigma_{-,j}\sigma_{+,k}\rho_R(0)\right\} = \left[1-\bar{n}\left(\omega_j,\beta\right)\delta_{j,k}\right]. \qquad (3.80)$$

Substituting Eq. (3.78)-(3.80) into Eq. (3.65):

$$\begin{aligned}\frac{d\tilde{\rho}(t)}{dt} = &-\int_0^t dt'\{[\sigma_-\sigma_+\tilde{\rho}(t') - \sigma_+\tilde{\rho}(t')\sigma_-]\, e^{-i\omega_0(t-t')}\langle \tilde{F}^\dagger(t)\tilde{F}(t')\rangle_R \\ &+ [\tilde{\rho}(t')\sigma_+\sigma_- - \sigma_-\tilde{\rho}(t')\sigma_+]\, e^{-i\omega_0(t-t')}\langle \tilde{F}(t')\tilde{F}^\dagger(t)\rangle_R \\ &+ [\sigma_+\sigma_-\tilde{\rho}(t') - \sigma_-\tilde{\rho}(t')\sigma_+]\, e^{i\omega_0(t-t')}\langle \tilde{F}(t)\tilde{F}^\dagger(t')\rangle_R \\ &+ [\tilde{\rho}(t')\sigma_-\sigma_+ - \sigma_+\tilde{\rho}(t')\sigma_-]\, e^{i\omega_0(t-t')}\langle \tilde{F}^\dagger(t')\tilde{F}(t)\rangle_R. \end{aligned} \tag{3.81}$$

where

$$\langle \tilde{F}^\dagger(t)\tilde{F}(t')\rangle_R = \sum_j |\kappa_j|^2\, e^{i\omega_j(t-t')}\bar{n}(\omega_j,\beta), \tag{3.82}$$

$$\langle \tilde{F}(t')\tilde{F}^\dagger(t)\rangle_R = \sum_j |\kappa_j|^2\, e^{i\omega_j(t-t')}\left[1-\bar{n}(\omega_j,\beta)\right], \tag{3.83}$$

$$\langle \tilde{F}(t)\tilde{F}^\dagger(t')\rangle_R = \sum_j |\kappa_j|^2\, e^{-i\omega_j(t-t')}\left[1-\bar{n}(\omega_j,\beta)\right], \tag{3.84}$$

$$\langle \tilde{F}^\dagger(t')\tilde{F}(t)\rangle_R = \sum_j |\kappa_j|^2\, e^{-i\omega_j(t-t')}\bar{n}(\omega_j,\beta). \tag{3.85}$$

Arriving here, the similarity of the process of deduction of the master equation done before can be noted, so the last approximations will not be treated here in detail. Following the same procedure, one arrives at

$$\begin{aligned}\frac{d\tilde{\rho}(t)}{dt} = -i\Delta\,[\sigma_+\sigma_-,\tilde{\rho}(t)] &+ \frac{\gamma}{2}(1-\bar{n})\,[2\sigma_-\tilde{\rho}(t)\sigma_+ - \sigma_+\sigma_-\tilde{\rho}(t) - \tilde{\rho}(t)\sigma_+\sigma_-] \\ &+ \frac{\gamma}{2}\bar{n}\,[2\sigma_+\tilde{\rho}(t)\sigma_- - \sigma_-\sigma_+\tilde{\rho}(t) - \tilde{\rho}(t)\sigma_-\sigma_+]. \end{aligned} \tag{3.86}$$

The evolution of a quantum system is given by the master equation, given by Eqs. (3.56) and (3.86). We can summarize it as:

$$\frac{d\rho}{dt} = -i[H(t),\rho] + \mathcal{L}\rho, \tag{3.87}$$

where $\mathcal{L}$ is the Liouville operator. Since the reservoir is thermal, the asymptotic (or steady-state) state of this equation is the Gibbs state

$$\rho(t \to \infty) = \rho = \frac{e^{-\beta H}}{Z}, \tag{3.88}$$

with temperature $T = 1/k_B\beta$ and partition function $Z = tr(e^{-\beta H})$. The details to arrive at Eq. (3.88), as well as the demonstration that the density operator that maximizes the entropy subject to the normalization condition and constant average energy is Gibbs state are shown in Appendix A.

3.3 The Laws of Quantum Thermodynamics

In the previous chapter, the laws of thermodynamics were defined for systems in equilibrium. In quantum thermodynamics, a theory of non-equilibrium is necessary to revisit the laws of thermodynamics to understand how they are generalized to arbitrary quantum systems.

The first law of thermodynamics has the form,

$$\frac{dE}{dt} = \dot{Q} + \dot{W}, \tag{3.89}$$

and is written in terms of the internal E of a system, W is the work done by external forces, and Q is the heat supplied to the system by its surroundings. For a quantum system isolated or weakly coupled to a reservoir, the internal energy is written in terms of the expected value of its Hamiltonian $E(t)$, that is,

$$E(t) = tr\left[H(t)\rho(t)\right]. \tag{3.90}$$

Differentiating Eq. (3.90) concerning t,

$$\frac{dE(t)}{dt} = tr\left[H(t)\frac{d\rho(t)}{dt}\right] + tr\left[\frac{dH(t)}{dt}\rho(t)\right]. \tag{3.91}$$

Heat and work are thus defined:

$$Q = \int_0^\tau tr \left[H(t) \frac{d\rho(t)}{dt} \right] dt, \tag{3.92}$$

$$W = \int_0^\tau tr \left[\frac{dH(t)}{dt} \rho(t) \right] dt, \tag{3.93}$$

in which τ is the time of evolution.

Before defining the second law, it is necessary to describe the entropy of a quantum system. In this work, as is usual in other works in the literature [51, 52, 53], we will use the Von Neumann entropy

$$S(t) = -tr \left\{ \rho(t) \ln[\rho(t)] \right\}. \tag{3.94}$$

Two important properties to mention regarding entropy are:

1. $S(\rho(t)) = 0$, if and only if ρ is pure.

2. $S(\rho(t))$ is invariant under unitary transformation, i.e, $S(U^\dagger \rho U) = S(\rho(t))$.

The first property can be proved if we assume a pure state $\rho = |\psi\rangle\langle\psi|$. So, if $|\psi\rangle$ is the eigenstate of the ρ operator with eigenvalue $+1$, $\rho|\psi\rangle = |\psi\rangle$. Then,

$$\begin{aligned} tr\rho \ln\ \rho &= tr\, |\psi\rangle\langle\psi| \ln(|\psi\rangle\langle\psi|) \\ &= \langle\psi| \ln \rho |\psi\rangle = \ln 1 = 0, \end{aligned}$$

where we use $F(\rho)|\psi\rangle = F(1)|\psi\rangle$, since $\rho|\psi\rangle = |\psi\rangle$.

To prove the second property, we know that given a complete and orthonormal basis $\{\phi_k\}$ [54],

$$\rho|\phi_k\rangle = \lambda_k|\phi_k\rangle. \tag{3.95}$$

The unitary operator U acts in such a way [51], that gives:

$$U|\phi_k\rangle = \lambda_k|\tilde{\phi_k}\rangle, \tag{3.96}$$

where $\{\phi_k\}$ is also a complete and orthonormal basis such that,

$$\langle\tilde{\phi}_k|\tilde{\phi}_m\rangle = \langle\tilde{\phi}_k|U^\dagger U|\tilde{\phi}_m\rangle = \langle\phi_k|\phi_m\rangle = \delta_{km}. \tag{3.97}$$

The density operator $\tilde{\rho} = U\rho$ also obeys the relation of Eq. (3.95),

$$\tilde{\rho}|\tilde{\phi}_k\rangle = U\rho|\phi_k\rangle = U\lambda_k|\phi_k\rangle = \lambda_k U|\phi_k\rangle = \lambda_k|\tilde{\phi}_k\rangle. \tag{3.98}$$

Furthermore, we can see that the eigenvalues of the density operator are invariant under unitary transformation, and as entropy is a function of ρ, this property will be used. Taking again the density operator, $\tilde{\rho}$,

$$\begin{aligned} S(\tilde{\rho}) &= -tr\tilde{\rho}\ ln\tilde{\rho} = -\sum_k \langle\tilde{\phi}_k|\tilde{\rho}\ ln\tilde{\rho}|\tilde{\phi}_k\rangle \\ &= -\sum_k \langle\tilde{\phi}_k|\lambda_k\ ln\lambda_k|\tilde{\phi}_k\rangle = -\sum_k \lambda_k\ ln\lambda_k = S(\rho). \end{aligned} \tag{3.99}$$

The Von Neumann entropy is invariant under unitary transformations, and the second property is proved.

The variation of the entropy dS may be written as the sum of two terms [55]:

$$dS = dS_{ext} + d\sum, \tag{3.100}$$

where dS_{ext} is the entropy exchanged with the environment and $d\sum$ is the entropy production of the system.

We define the entropy flow as

$$J = \beta\frac{dQ}{dt}, \tag{3.101}$$

dQ/dt can be written in terms of Eq. (3.87) as

$$\begin{aligned}\frac{dQ}{dt} &= tr\frac{d\rho}{dt}H = tr\left\{\left[-\frac{i}{\hbar}[H,\rho] + \mathcal{L}(\rho)\right]H\right\}\\ &= -\frac{i}{\hbar}tr[H,\rho]H + tr\mathcal{L}(\rho)H\\ &= -\frac{i}{\hbar}tr[H\rho H - \rho HH] + tr\mathcal{L}(\rho)H.\end{aligned} \tag{3.102}$$

When A and B are operators, the commutator trace of A and B disappears: $tr([A,B]) = 0$, because $tr(AB) = tr(BA)$ and tr is linear. Hence,

$$\frac{dQ}{dt} = tr\mathcal{L}(\rho)H. \tag{3.103}$$

Then, we have

$$J = \beta tr\mathcal{L}(\rho)H. \tag{3.104}$$

The rate of entropy production $\sigma(t)$ can be defined as the difference between the total entropy of the system and the entropy flow due to the reservoir:

$$\sigma(t) = \frac{dS}{dt} - J, \tag{3.105}$$

S is given by Eq. (3.94) and J by Eq. (3.104). Putting S and J in the Eq. (3.105)

$$\begin{aligned}\sigma(t) &= \frac{d}{dt}(-tr\rho\ln\rho) - \beta tr\mathcal{L}(\rho)H\\ &= -tr\left[\left(\frac{d\rho}{dt}\right)\ln\rho - \rho\rho^{-1}\frac{d}{dt}\rho\right] - \beta tr\mathcal{L}(\rho)H\\ &= -tr\frac{d\rho}{dt}\ln\rho - \beta tr\mathcal{L}(\rho)H.\end{aligned} \tag{3.106}$$

Substituting in the second term the Eq. (3.87),

$$\sigma(t) = -tr\left\{-\frac{i}{\hbar}[H,\rho] + \mathcal{L}(\rho)\right\}\ln\rho - \beta tr\mathcal{L}(\rho)H \tag{3.107}$$

But since the trace has a cyclic property, the first term inside the bracket is null ($[\rho,\ln\rho] = 0$)

and we get

$$\begin{aligned}\sigma(t) &= -tr\mathcal{L}(\rho)\ln\rho - \beta tr\mathcal{L}(\rho)H \\ &= -tr\mathcal{L}(\rho)(\ln\rho + \beta H)\end{aligned} \tag{3.108}$$

The thermal state is written as

$$\rho = \frac{e^{-\beta H}}{tre^{-\beta H}} = \frac{e^{-\beta H}}{Z}, \tag{3.109}$$

and can be formulated,

$$\ln\rho = \ln e^{-\beta H} - \ln Z = -\beta H - \ln Z. \tag{3.110}$$

Replacing this expression into Eq. (3.108)

$$\begin{aligned}\sigma(t) &= -tr\mathcal{L}(\rho)(-\beta H - \ln Z + \beta H) \\ &= -tr\mathcal{L}(\rho)(-\beta H - \ln Z + \beta H) = tr\mathcal{L}(\rho)\ln Z\end{aligned} \tag{3.111}$$

and using

$$tr\mathcal{L}(\rho) = tr\left(\frac{d\rho}{dt} + \frac{i}{\hbar}[H,\rho]\right) = 0, \tag{3.112}$$

hence

$$\sigma(t) = tr\mathcal{L}(\rho)\ln Z = 0. \tag{3.113}$$

For a thermal state, which is a state of maximum entropy, no additional entropy can be produced.

For a system that exchanges energy as heat with its reservoir, ρ follows Eq. (3.87) and dQ/dt Eq. (3.103). If the exchange is reversible:

$$\frac{dS_{ext}}{dt} = \beta\frac{dQ}{dt} = \beta tr\mathcal{L}(\rho)H. \tag{3.114}$$

With S given by Eq. (3.94), we can write

$$\frac{dS}{dt} = -tr\mathcal{L}(\rho)\ln\rho. \tag{3.115}$$

From the relation of Eq. (3.100):

$$\frac{d\sum}{dt} = \frac{dS}{dt} - \frac{dS_{ext}}{dt}, \tag{3.116}$$

and replacing Eqs. (3.114) and (3.115) into Eq. (3.116):

$$\frac{d\sum}{dt} = tr\mathcal{L}(\rho)\ln\rho - \beta tr\mathcal{L}(\rho)H = \sigma(t). \tag{3.117}$$

Starting from the above expression for $\sigma(t)$, and assuming ρ_T the thermal state of the reservoir and isolating the term βT from Eq. (3.110), we write

$$\begin{aligned} \sigma(t) &= -tr\mathcal{L}(\rho)\left(\ln\rho - \ln\rho_T - \ln Z\right) \\ &= -tr\mathcal{L}(\rho)\ln\rho + tr\mathcal{L}(\rho)\ln\rho_T + tr\mathcal{L}(\rho)\ln Z. \end{aligned} \tag{3.118}$$

As we have already seen, the last term vanish. We then substitute $\mathcal{L}(\rho)$ in Eq. (3.87) into ρ and ρ_T

$$\begin{aligned} \sigma(t) &= -tr\left\{\frac{d\rho}{dt} - \frac{i}{\hbar}[H,\rho]\right\}\ln\rho + tr\left\{\frac{d\rho}{dt} - \frac{i}{\hbar}[H,\rho]\right\}\ln\rho_T \\ &= -tr\left(\frac{d\rho}{dt}\right)\ln\rho + tr\frac{d\rho}{dt}\ln\rho_T. \end{aligned} \tag{3.119}$$

Note that,

$$-tr\frac{d}{dt}(\rho\ln\rho) = -tr\left[\left(\frac{d\rho}{dt}\right)\ln\rho - \rho\rho^{-1}\frac{d\rho}{dt}\right] = -tr\left(\frac{d\rho}{dt}\right)\ln\rho. \tag{3.120}$$

Thus,

$$\sigma(t) = -tr\frac{d}{dt}\left(\rho\ln\rho - \rho\ln\rho_T\right) \equiv -\frac{d}{dt}\mathcal{D}(\rho \parallel \rho_T). \tag{3.121}$$

Wherein $\mathcal{D}(\rho \parallel \rho_T) = \rho\ln\rho - \rho\ln\rho_T \equiv \sum$ is the relative entropy [54] or entropy production who is always positive, $\sum \geqslant 0$ [56].

Now it is convenient to write the second law of thermodynamics as

$$\sum \geqslant 0. \tag{3.122}$$

Chapter 4

Cooling in a quantum regime

In this chapter, we consider an autonomous quantum refrigerator (AR) composed of three interacting qubits, each exposed to a specific thermal reservoir. This AR was first proposed in 2010 [2], in which the authors considered only bosonic reservoirs. The chapter is divided into two sections, in order to elaborate on the results obtained. We aim to investigate this AR operating with fermionic and bosonic reservoirs with positive temperatures and compare them, and in another scenario with one of the reservoirs being a fermionic reservoir at a negative temperature.

4.1 Cooling with negative temperatures

As a general property, the experimental realization of reservoirs with effective negative temperatures, as we will consider in this work, requires population inversion. It has been experimentally demonstrated that fermionic substances are required to build thermal reservoirs that exhibit population inversion and negative system temperatures, as evidenced in studies such as [7, 8, 53]. This inverted population effect has been explored in some works [57, 58, 53], with a notable impact on the efficiency of heat engines, as shown experimentally in Ref. [52, 53]. Motivated by these works, we studied the properties of the system of interest initially with only bosonic reservoirs, now with fermionic reservoirs at negative temperatures.

Here, as in Ref. [2], we approach the case where qubits 1, 2 and 3 interact respectively with a thermal reservoir at a cold temperature $T_c > 0$, a thermal reservoir at an "room" temperature $T_r > 0$ and a thermal reservoir at a temperature hot $T_h > 0$ - see the scheme shown in Fig. 4.1.

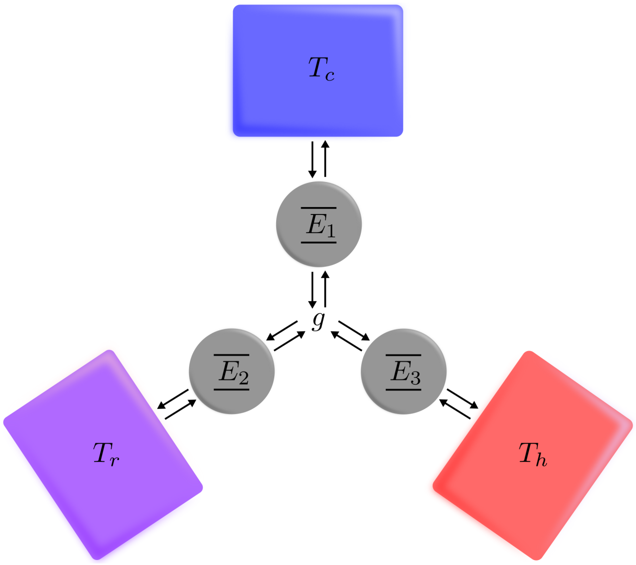

Figure 4.1: Schematic representation of the AR refrigerator and its respective thermal reservoirs. The AR is composed of three interacting qubits having energy gaps E_1, E_2, and E_3 in contact with their respective reservoirs. Here, T_h is the temperature of the hot reservoir, T_r is the temperature of the "room" reservoir, T_c is the temperature of the cold reservoir, and g is the coupling constant between the qubits.

In the weak coupling limit and the Markovian regime, the dynamics governing the AR is dictated by the master equation

$$\begin{aligned}\frac{\partial\rho}{\partial t} = -i\left[H_0 + H_I, \rho\right] + \frac{1}{2}\sum_{k=1}^{3}\Gamma_k^{\downarrow}\left(2\sigma_{-,k}\rho\sigma_{+,k} - \{\sigma_{+,k}\sigma_{-,k}, \rho\}\right) + \\ \frac{1}{2}\sum_{k=1}^{3}\Gamma_k^{\uparrow}\left(2\sigma_{+,k}\rho\sigma_{-,k} - \{\sigma_{-,k}\sigma_{+,k}, \rho\}\right),\end{aligned} \tag{4.1}$$

where H_0 and H_I are respectively the free qubits Hamiltonian and the three-body interaction Hamiltonian, given by

$$\begin{aligned}H_0 &= H_1 + H_2 + H_3 \\ &= \frac{1}{2}E_1\sigma_{z,1} + \frac{1}{2}E_2\sigma_{z,2} + \frac{1}{2}E_3\sigma_{z,3}\end{aligned} \tag{4.2}$$

and

$$H_I = g\left(\sigma_{-,1}\sigma_{+,2}\sigma_{-,3} + \sigma_{+,1}\sigma_{-,2}\sigma_{+,3}\right). \tag{4.3}$$

In the above equations, $\sigma_{-,k}$, $\sigma_{+,k}$, and $\sigma_{z,k}$ $(k = 1, 2, 3)$ are respectively the lowering, raising, and z Pauli operators for the kth qubit; E_1, E_2, and E_3 are the energy gaps for each qubit, and g is the coupling constant. Also, we let $\Gamma_k^{\downarrow} = \gamma_k\left(1 \pm n_{\alpha_k}\right)$, where the signal "+" ("-") is for a bosonic (fermionic) reservoir, and $\Gamma_k^{\uparrow} = \gamma_k n_{\alpha_k}$ $(\alpha_1 = c$, $\alpha_2 = r$, and $\alpha_3 = h)$, with γ_k being the dissipation rate for the kth qubit and n_{α_k} being the average excitation number of the reservoir at temperature T_{α_k}. Note that Eq. (4.1) describes the dynamics dictated by either bosonic [49, 48] or fermionic [59, 50] thermal reservoirs. For bosonic thermal reservoirs $n_{\alpha_k} = 1/\left(e^{E_k/T_{\alpha_k}} - 1\right)$, while for fermionic reservoirs $n_{\alpha_k} = 1/\left(e^{E_k/T_{\alpha_k}} + 1\right)$. As said before, negative temperatures are characterized by population inversion, which occurs when $n_{\alpha_k} > 1/2$, and it is only possible for fermionic reservoirs. For the AR to work properly, considering only reservoirs at positive temperatures, the relations $T_c < T_r < T_h$ and $E_3 = E_2 - E_1$ - see Fig. 4.2, must be satisfied [2].

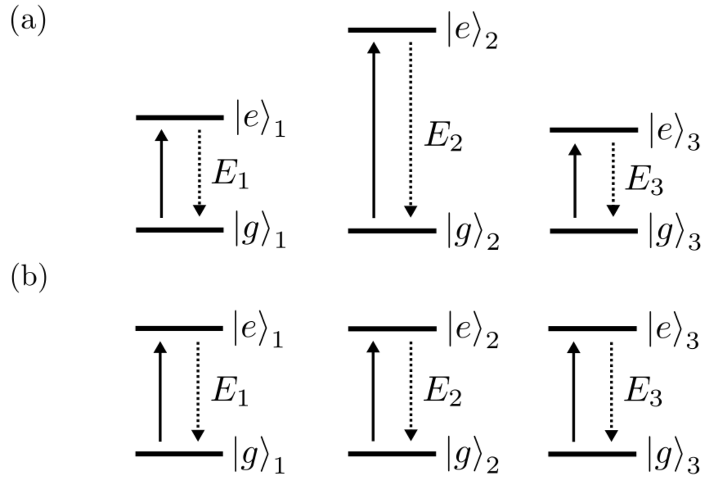

Figure 4.2: Schematic representation of possible level configuration for the qubit-based AR cooler. (a) Level configurations used in Ref. [2] for positive temperatures, where the condition $E_3 = E_2 - E_1$ is required. (b) A possible level configuration with $E_3 = E_2 = E_1$ for negative temperatures, where the condition $E_3 = E_2 - E_1$ is no longer needed. In (a) and (b), $\langle g|_k$ and $|e\rangle_k$ are the ground and excited states of the kth qubit, respectively.

The wanted solution from Eq. (4.1) is the steady-state solution, that is needed to solve the equation for the stationary state, ρ_S. To obtain the asymptotic state we used the quantum optics toolbox [60, 61].

Let us start detailing the positive temperature case by fixing the parameters used in [2]. Thus, we fixed the energies gaps $E_1 = 1$, $E_2 = 5$, and $E_3 = 4$, which is a special case of the more general relation $E_3 = E_2 - E_1$ to AR work properly, and the temperatures $T_c = 1, 1.5, 2$, and $T_r = 2$. Finally, we fixed the dissipation rates $\gamma_1 = \gamma_2 = \gamma_3 = 1$ and let T_h vary from 1 to 10. Cooling is achieved when $T_1 - T_c < 0$, which means that the temperature T_1 of the qubit 1 is lower than the temperature T_c of the cold reservoir. In Fig. 4.3, it is possible to observe this effect in a) we see the refrigerator working, and in b) we observe the behavior of system 1, i.e., T_1 decays with the growth of T_h.

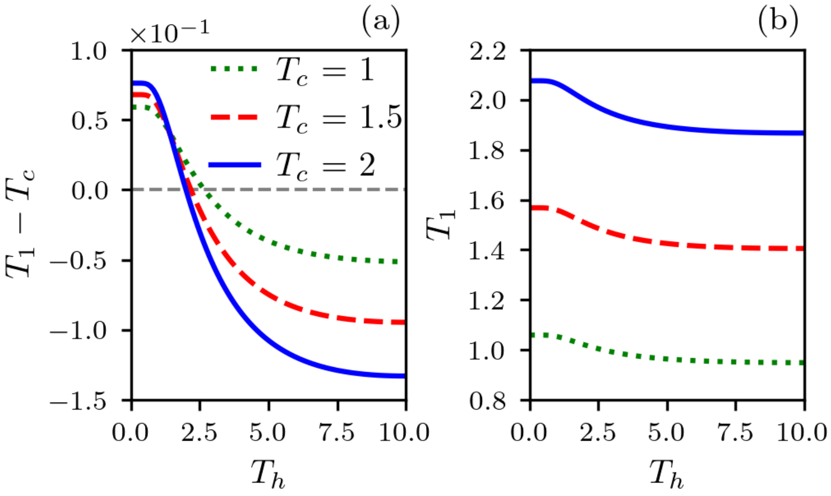

Figure 4.3: (a) $T_1 - T_c$ versus $T_h > 0$ for three different values of T_c: $T_c = 1$ (dot green line), $T_c = 1.5$ (dash red line) and $T_c = 2$ (solid blue line). Refrigeration occurs for $T_1 - T_c < 0$. (b) T_1 behavior for those three initial conditions given in (a). Note that the lowest temperature of the qubit T_1 does not decrease any further, no matter how high T_h becomes. The lowest values reached by T_1 are $T_1 = 0.9486$ (when $T_c = 1$), $T_1 = 1.4054$ (when $T_c = 1.5$) and $T_1 = 1.867$ (when $T_c = 2$).

Regardless of how high T_c is, the temperature of qubit 1 remains constant. After conducting numerical analysis, we discovered that the corresponding lowest temperatures reached by qubit 1 are $T_1 = 0.9486$ (when $T_c = 1$), $T_1 = 1.4054$ (when $T_c = 1.5$), and $T_1 = 1.867$ (when $T_c = 2$). These minimum temperatures are determined by the population of the ground state $p_{g,1}$, which can be expressed as follows:

$$p_{g,1} = \frac{1}{1 + e^{-E_1/T_1}}. \tag{4.4}$$

Solving for temperature, we get

$$T_1 = \frac{E_1}{\ln\left(\frac{p_{g,1}}{1-p_{g,1}}\right)}. \tag{4.5}$$

It is evident from the equation that T_1 can attain any value between T_c and the minimum temperature allowed by the population of the ground state $p_{g,1}$, which is between 0.5 and 1.0. However, due to imperfect insulation, heat transfer to qubit 1 hinders it from attaining temperatures closer to absolute zero. Our numerical calculations indicate that if the initial temperature is low, such as $T_c < 0.48$, then $T_1 - T_c > 0$, indicating the breakdown of the refrigerator's operation. We shall see that using the same parameters but considering one of the reservoirs at negative temperatures, we can cool the qubit 1 below $T_c = 0.48$.

The perfect isolation condition for the temperature of qubit 1 occurs when it gets as close as possible to absolute zero. This condition is obtained by isolating qubit 1 from its reservoir, thus letting γ_1. This condition allows us to reach lower temperatures for qubit 1 than those depicted in Fig. 4.3(b), and the following analytical expression for the required temperature [2]:

$$T_1 = \frac{T_c}{1 + \frac{E_3}{E_1}\left(1 - \frac{T_c}{T_h}\right)}. \tag{4.6}$$

The above formula tells us that, under the condition of perfect insulation, it is possible to cool down to absolute zero, provided that $E_3/E_1 \to \infty$.

In order to compare the cooling process at either negative or positive temperatures, we put the AR to work with the same parameters. The steady state is found using the Eq. (4.1), but now considering a fermionic reservoir with $n_3 > 0.5$ ($T_h < 0$). In Fig. 4.4(a), we show the difference $T_1 - T_c$ as a function of $T_h < 0$. Interestingly, if we compare with Fig. 4.3(a) for $T_h > 0$, we see that at negative temperatures, the steady-states are always cooled, no matter the initial temperature we choose for $T_h < 0$. Also, remembering that for $T_h < 0$, the higher temperatures ranges according to $(-\infty, 0^-)$ in Fig. 4.4(b), we see that the higher the

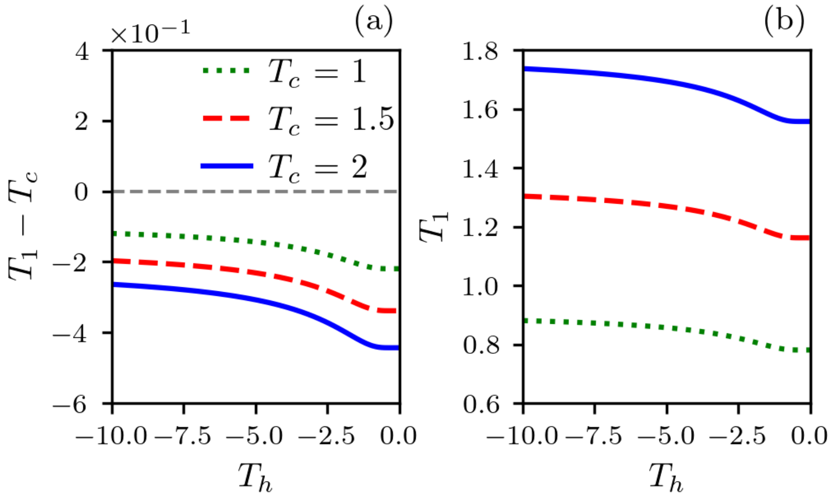

Figure 4.4: (a) $T_1 - T_c$ versus $T_h < 0$ using the same three values for T_c as before: $T_c = 1$ (dot green line), $T_c = 1.5$ (dash red line) and $T_c = 2$ (solid blue line). Refrigeration occurs for $T_1 - T_c < 0$. Note that the higher the temperature T_h the greater the cooling of qubit 1, as before, but now the steady state of qubit 1 is cooled for all negative temperatures. (b) T_1 versus T_h for those three initial conditions given in (a). Again, the lowest temperature of the qubit T_1 does not decrease any further by increasing T_h. However, this time the lower temperatures are closer to absolute zero than when using positive temperatures. The corresponding lowest temperatures are $T_1 = 0.7805$ (when $T_c = 1$), $T_1 = 1.1615$ (when $T_c = 1.5$) and $T_1 = 1.5568$ (when $T_c = 2$).

temperature T_h, the lower is the temperature of qubit 1.

A notable result is that the lowest temperatures T_1 in the case $T_h < 0$ are lower than the temperatures T_1 corresponding to the case $T_h > 0$. That is true for all reference temperatures T_c according to our numerical calculation and as can be seen in a few examples shown in the table of Fig. 4.5(a). Taking T_c as the reference temperature, we can calculate the percentage decrease of T_1 in relation to T_c for both negative and positive temperatures. In Fig. 4.5(b) we show the corresponding percentages for both $T_h > 0$ (blue) and $T_h < 0$ (red).

Through Fig. 4.5(b) it is clear that negative temperatures are more effective for cooling a qubit, as it drives qubit 1 to lower temperatures by a large percentage. According to our numerical calculations, for this set of parameters, which is the same as used for positive temperatures, when the reference temperature T_c is as low as $T_c = 0.48$ the AR stops cooling if $T_h > 0$. However, at $T_h < 0$ the AR continues to cool down until qubit 1 reaches the limit of $T_1 = 0.0275$, that is, an order of magnitude lower.

(a)

T_c	T_1	
	$T_h > 0$	$T_h < 0$
2.00	1.8670	1.5568
1.50	1.4054	1.1615
1.00	0.9486	0.7805
0.80	0.7672	0.6319
0.48	0.4796	0.3963

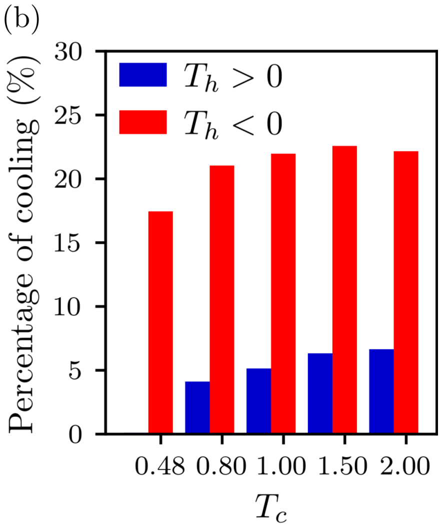

Figure 4.5: (a) Lowest values for T_1 obtained when either $T_h > 0$ or $T_h < 0$ for some values of T_c (b) Percentage of cooling using both positive and negative temperatures for the pumping heat at T_h and taking T_c as reference. According to our numerical calculations, AR stops working if $T_c < 0.48$ ($T_c < 0.0275$) when $T_h > 0$ ($T_h < 0$).

In the case where we impose the condition of perfect insulation for T_h, we can demonstrate that Eq. (4.6) remains valid. Alternatively, we can write Eq. (4.6) as

$$T_1 = \frac{T_C}{1 + \frac{E_3}{E_1}(1 + \frac{T_C}{|T_h|})}. \tag{4.7}$$

Eq. (4.7) tells us that, as in the case of positive temperatures, it is possible to cool a qubit to temperatures arbitrarily close to absolute zero. Note, however, that for cooling a qubit toward zero, since $T_c/T_h < 1$, while for positive temperatures, Eq. (4.6), there is need to resort only to the ratio $E_3/E_1 \to \infty$, for negative temperatures we can have $T_c > |T_h|$. Thus, it is possible to take advantage of negative temperatures by choosing $T_c/\left|T_h\right| \to \infty$.

There is a critical remark regarding the ratio E_3/E_1. In order for positive temperatures to be possible, the condition $E_3 = E_2 - E_1$ must be met, which imposes limitations on the required qubit level structures for AR to be effective. However, with negative temperatures, arbitrary configurations are allowed, such as $E_3 = E_2 = E_1$, as shown in Fig. 4.2(b). Besides, in the perfect insulation condition, if we take for example $E_3/E_1 = 1$, Eq. (4.6) tells us that it is impossible, starting from finite and positive temperatures, to cool qubit 1 arbitrarily close to absolute zero. Indeed, according to Eq. (4.6), the smallest possible temperature for $E_3/E_1 = 1$ is obtained when T_c/T_h is very small, such that the final temperature of qubit 1 is $T_1 = T_c/2$. Nevertheless, for negative temperatures and in the condition of perfect insulation where Eq. (4.7) applies, even if we let $E_3/E_1 = 1$ we can still make the ratio T_c/T_h very large, thus cooling qubit 1 as close to absolute zero as we want.

4.2 Cooling with positive temperatures

While fermionic reservoirs can have temperatures that assume both positive and negative values, bosonic reservoirs are mostly used to model reservoirs with $T > 0$ by using quantum harmonic oscillators with the average number of photons determined by the Bose-Einstein distribution $n = 1/(e^{E/T} - 1)$. As a result, fermionic reservoirs are typically not considered for positive temperature conditions, as there would be no advantage in doing so. However, we consider a study of a case in which a refrigerator built with two-level substances can present advantages when operating in a fermionic environment as compared to a bosonic one, with both environments at positive temperatures. As the operating conditions are kept the same for both environments, our results emphasize that the presented advantage stems from the quantum nature of the fermionic reservoir.

Since the exchange rates $\Gamma_k^{\downarrow}$ and $\Gamma_k^{\uparrow}$ are different, the possible combinations of bosonic and fermionic thermal reservoirs lead to distinct asymptotic states of Eq. (4.1). So, aiming to use the device as a refrigerator, it is interesting to evaluate which combination leads to the lowest temperature T_1, considering a given set of parameters. Similar to the treatment given in the previous section, we start with the same parameters, E_1, E_2 and E_3 remain the same, with the difference that now we let T_h vary from 10^{-1} to 10^3.

Fig. 4.6(a) shows the temperature difference $T_1 - T_c$ versus T_h (on a logarithmic scale) for the AR working in a bosonic environment for the cold temperatures $T_c = 1$ (dotted green line), $T_c = 1.5$ (dashed red line), and $T_c = 2$ (solid blue line). "As previously mentioned, the cooling process is characterized by $T_1 - T_c < 0$. Fig.4.6(b) depicts $T_1 - T_c$ as a function of T_h for the

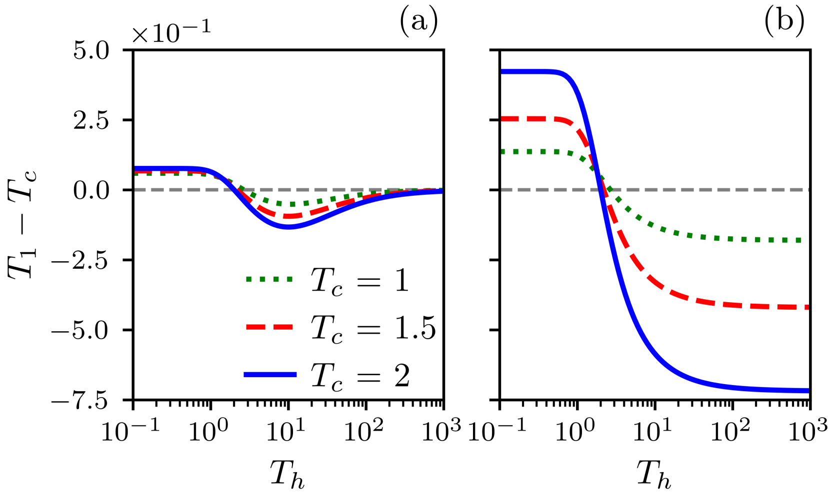

Figure 4.6: Temperature difference $T_1 - T_c$ versus T_h for (a) three bosonic and (b) three fermionic reservoirs, considering three different values of T_c: $T_c = 1$ (dotted green line), $T_c = 1.5$ (dashed red line) and $T_c = 2$ (solid blue line). Refrigeration occurs for $T_1 - T_c < 0$. Note the difference in behavior in the two figures: while in (a) temperature T_1 reaches a minimum and then starts to increase, in (b) T_1 decreases monotonically, practically stabilizing for sufficiently high T_h, thus indicating that the lowest temperatures reached by qubit 1 occur for fermionic reservoirs.

same cold temperatures, but in the presence of fermionic thermal reservoirs surrounding the AR. In Fig. 4.6(a), $T_1 - T_c$ decreases to a minimum value, increases, and eventually stabilizes at a negative value close to zero. On the other hand, in Fig. 4.6(b), $T_1 - T_c$ stabilizes at its minimum value. Thus, the AR in the fermionic environment has an advantage over the bosonic one, as its efficiency in cooling qubit 1 does not decrease at higher values of T_h. Furthermore, under fermionic thermal reservoirs, qubit 1 reaches lower minimum temperature values than when under bosonic thermal reservoirs, as can be seen from the difference $T_1 - T_c$, which is more negative for the fermionic environment (compare Figs. 4.6(a) and 4.6(b)).

According to our numerical simulations, when considering the bosonic environment, the minimum values for T_1 are $T_1 = 0.95$ (when $T_c = 1$), $T_1 = 1.41$ (when $T_c = 1.5$), and $T_1 = 1.87$ (when $T_c = 2$). On the other hand, when considering three fermionic thermal reservoirs, since the values for T_1 continue to decrease with increasing T_h, we take the minimum value for T_1 when $T_h = 100$. These minimum values are $T_1 = 0.82$ (when $T_c = 1$), $T_1 \sim 1.09$ (when $T_c = 1.5$), and $T_1 = 1.29$ (when $T_c = 2$). Tab. 4.1 compares the cooling effect of

T_c	(%)	
	3B	3F
0.48	0.87	3.31
0.60	2.20	7.39
0.80	4.14	12.85
1	5.14	17.57
1.5	6.31	27.44
2	6.65	35.32

Tabela 4.1: Comparative values in the cooling percentage $(|T_1 - T_c| / T_c) \times 100$ for the refrigerator working at three bosonic (3B) and three fermionic (3F) thermal reservoirs for six values of the reference temperature T_c. The cooling percentages for fixed parameters decrease as the reference temperature T_c approaches 0.48, where $T_1 - T_c > 0$. Note that even so fermionic thermal reservoirs are always more effective for cooling.

fermionic and bosonic thermal reservoirs on qubit 1 by calculating the cooling percentage $(|T_1 - T_c| / T_c) \times 100$, with T_c as the reference. The table shows that using three fermionic reservoirs (3F) results in a higher cooling percentage compared to three bosonic reservoirs (3B).

Tab 4.1 illustrates a notable contrast in the cooling percentage between the two types of thermal reservoirs, with the use of three fermionic reservoirs consistently resulting in a higher cooling percentage. This observation suggests that the fermionic environment is significantly more effective in reducing the temperature T_1 compared to the bosonic environment. Furthermore, this percentage is more favorable as the reference temperature T_c increases, with a maximum value of over four times that achieved using only bosonic thermal reservoirs when $T_c = 2$. Even at lower values of T_c, using fermionic thermal reservoirs leads to a significant difference in cooling percentage. When $T_c = 1$, for instance, the cooling is more than double compared to using only bosonic thermal reservoirs. Although the percentage difference decreases for lower cold temperatures, fermionic reservoirs still provide more than twice the cooling compared to bosonic reservoirs alone. It is noteworthy that when fixing the AR parameters as we did in the previous section, there is a limit to cooling qubit 1. As we found

T_c	(%)							
	FBF	FFF	FBB	FFB	BBF	BFF	BBB	BFB
0.48	3.38	3.31	1.11	1.10	2.71	2.65	0.87	0.86
0.80	13.09	12.85	7.31	7.22	7.76	7.62	4.14	4.09
1	17.87	17.57	10.81	10.67	9.03	8.87	5.14	5.09
1.5	27.28	27.44	18.65	18.43	10.28	10.13	6.31	6.24
2	35.76	35.32	25.36	25.09	10.46	10.33	6.65	6.58

Tabela 4.2: Comparative values showing the cooling percentages $(|T_1 - T_c| / T_c) \times 100$ for several thermal reservoir configurations. Here, for example, BFF means qubit 1 bound to a bosonic thermal reservoir and qubits 2 and 3 bound to fermionic thermal reservoirs. Note that the highest percentage of cooling occurs for FBF configuration, meaning that qubit 1 is bound to a fermionic thermal reservoir, qubit 2 is bound to a bosonic thermal reservoir and qubit 3 is bound to another fermionic thermal reservoir.

numerically, the corresponding lowest cooling percentage reached by qubit 1, irrespective of the type of thermal reservoir used, occurs when $T_c \sim 0.48$. For temperatures lower than $T_c \sim 0.48$, $T_1 - T_c > 0$, meaning that the AR no longer works. Also, the percentage of cooling decreases more and more as T_c approaches 0.48 for both kinds of thermal reservoirs. However, the percentage of cooling when using fermionic thermal reservoirs remains higher.

Considerations of cases with combinations of bosonic and fermionic thermal reservoirs are underway. However, it may be interesting to investigate scenarios where only one or two fermionic thermal reservoirs are used, considering the fermionic thermal reservoir as a quantum resource. It is necessary to consider with which qubit the fermionic thermal reservoir is associated. Let us use a notation in which B (F) denotes the bosonic (fermionic) thermal reservoir and the order in which it appears in the sequence indicates which qubit that reservoir is attached to. For example, the sequence BFB indicates that qubit 1 is subjected to a bosonic thermal reservoir, qubit 2 to a fermionic thermal reservoir, and the third qubit to a bosonic thermal reservoir. Next, we investigate all configurations numerically and grouped the results in Tab. 4.2, ordering from highest to lowest percentage of cooling and following the same procedure as in the previous tables, i.e., we took the minimum value for T_1.

It is worth noting that the most effective cooling scenario does not necessarily require the use of three fermionic thermal reservoirs, which may come as a surprise. As demonstrated in Table 4.2, the greatest cooling range is achieved in the FBF case, where only qubit 1 and 3 are connected to fermionic thermal reservoirs. While the difference between the FBF and FFF configurations is not significant, it is worth noting that using two fermionic reservoirs rather than three results in a higher percentage of cooling.

4.3 Coefficient of Performance

An attempt was made to calculate the coefficient of performance of the AR and compare the two regimes discussed above to verify possible gains. For the AR the coefficient of performance is identified as [62, 63]

$$COP = \frac{\dot{Q}_c}{\dot{Q}_h}, \tag{4.8}$$

and the heat current as

$$\dot{Q}_c = \mathcal{L}_c H_1, \quad \dot{Q}_h = \mathcal{L}_h H_3. \tag{4.9}$$

With H_1 and H_3 given by the Eq. (4.2), and

$$\mathcal{L}_c = \frac{1}{2}\Gamma_1^{\downarrow}\left(2\sigma_{-,1}\rho\sigma_{+,1} - \{\sigma_{+,1}\sigma_{-,1}, \rho\}\right) + \frac{1}{2}\Gamma_1^{\uparrow}\left(2\sigma_{+,1}\rho\sigma_{-,1} - \{\sigma_{-,1}\sigma_{+,1}, \rho\}\right), \tag{4.10}$$

$$\mathcal{L}_h = \frac{1}{2}\Gamma_3^{\downarrow}\left(2\sigma_{-,3}\rho\sigma_{+,3} - \{\sigma_{+,3}\sigma_{-,3}, \rho\}\right) + \frac{1}{2}\Gamma_3^{\uparrow}\left(2\sigma_{+,3}\rho\sigma_{-,3} - \{\sigma_{-,3}\sigma_{+,3}, \rho\}\right). \tag{4.11}$$

The COP for the refrigerator is restricted by the Otto coefficient of performance:

$$COP \leq \frac{E_1}{E_3 - E_1}, \tag{4.12}$$

the values found are the same for positive and negative temperatures and the equality of Eq. (4.12) is valid since the relation $E_3 = E_2 - E_1$ is maintained. Different sets of reservoirs do not change the COP value in such a way that it exceeds the Otto limit.

There are experimental models of three-qubit quantum coolers in the literature, including approaches with the algorithmic cooling [64, 65]. However, there is no self-contained heat engine model like this one, with the three qubits interacting with each other. One difficulty that could arise is that an inverted reservoir can only be created by the work input, so the AR is no longer self-contained.

Chapter 5

Conclusions and further perspectives

This work begins with a whole chapter on negative temperatures in quantum regimes, first with a brief introduction to classical thermodynamics, emphasizing heat engines and the statements of the second law of thermodynamics that would supposedly be violated with the existence of negative temperatures in systems of inverted population. The objective is to pay special attention to the discussion that emerged in the 1950s with Ramsey and followed over the decades with some authors defending the existence of negative thermodynamic temperatures; some works associate them with non-equilibrium states and thus refer to them as effective (or apparent) negative temperatures, as opposed to equilibrium states at positive thermodynamic temperatures [22, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 39]. The Third chapter aims to approach the theory of open systems in order to understand the master equation to describe quantum systems weakly coupled to thermal reservoirs. Finally, the model proposed in 2010 by Linden et al. is presented to study the AR operating at negative temperatures with the hot reservoir [2].

So far, we have considered the autonomous quantum refrigerator using three qubits as proposed in [2]. Through a comparative study of the operation of this refrigerator in environments with positive or negative temperatures, it was possible to show that under the same conditions, that is, with the same parameters that characterize the autonomous quantum refrigerator, the use of negative temperature brings advantages to the use restricted to positive temperatures. According to our numerical simulations, negative temperatures allow for a more comprehensive cooling range. Furthermore, by imposing the condition of perfect insulation, that is, isolating the qubit 1 to be cooled from its environment and letting it interact directly with the other qubits, we show that, as in the case of positive temperatures, the qubit 1 can be cooled to a temperature T_1 arbitrarily close to absolute zero. However, even for perfect insulation, it is still possible to demonstrate the advantage of using negative temperatures.

Also, we explore the quantum nature of fermionic reservoirs without taking population inversion into account, such that we restrict to the domain of positive temperatures. Using a qubit-based refrigerator model proposed in Ref. [2], we show that, once the operating parameters of the refrigerator are fixed, the use of fermionic thermal reservoirs allows us to obtain better results, with respect to the cooling capacity, than the use of bosonic thermal reservoirs. We have verified, for example, that when the qubit to be cooled cannot be perfectly insulated, the use of only fermionic thermal reservoirs allows it to reach lower temperatures than the use of only bosonic thermal reservoirs.

One of the criticisms of thermal engines, as discussed here, is that the definition of efficiency used does not take into account the work required to produce the reservoirs out of equilibrium, which is a factor that could contribute to the good results obtained [66]. According to Struchtrup, using efficiency measures like the one in Eq. (4.8) fails in the sense that they ignore the cost of creating an inverted reservoir. A suitable measure of efficiency would aim to compare the gain produced with the expense incurred. For a classic heat engine, the expense is due to the amount of fuel needed to maintain the temperature of the hot reservoir, where the heat of the reaction of the fuel is equal to the amount of heat absorbed by the engine. An inverted reservoir can only be created by the work input. Due to inherent irreversibilities, the loading process reduces the (possible) output of work. Although, in addition to commenting on Eq. (4.8), we discuss here achieving low temperatures with the use of inverted reservoirs. That said, even if it has a cost, the balance of the gain must be calculated, as it can be used as a useful quantum resource [51, 67, 68, 69].

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Appendix A

Gibbs state

An important result in quantum thermodynamics is the Gibbs state, an equilibrium probability distribution that remains invariant under the evolution of the system. To obtain this result, we need to find a distribution of probabilities whose von Neumann entropy is maximum and subject to the constraints:

$$Tr\rho = 1, \tag{A.1}$$

$$\langle H\rangle = Tr\rho H = constant. \tag{A.2}$$

The Eq. (3.94) can be rewritten if the relation $\rho|\lambda_i\rangle = \rho_{ii}|\lambda_i\rangle$ is used, then

$$S(\rho) = -\sum_{i=1}^{n}\langle\lambda_i|\rho\ ln\rho|\lambda_i\rangle = -\sum_{i=1}^{n}\rho_{ii}\ ln\rho_{ii}. \tag{A.3}$$

To maximize the entropy subject to two constraints we need two Lagrange multipliers, so we take γ and β to form the Lagrangian function:

$$h(\rho) = -\sum_{i=1}^{n}\rho_{ii}\ ln\rho_{ii} + \gamma(\sum_{i=1}^{n}\rho_{ii} - 1) + \beta(\langle H\rangle - \sum_{i=1}^{n}\rho_{ii}H_{ii}), \tag{A.4}$$

where $\langle H\rangle = \rho H \equiv \sum_{i=1}^{n}\rho_{ii}H_{ii}$. Taking the derivative of the function $h(\rho)$:

$$\frac{\partial h}{\partial\rho_{jj}} = -\sum_{i=1}^{n}\left[\left(\frac{\partial}{\partial\rho_{jj}}\rho_{ii}\right)ln\rho_{ii} + \rho_{ii}\left(\frac{\partial}{\partial\rho_{jj}}ln\rho_{ii}\right)\right] + \gamma\sum_{i=1}^{n}\frac{\partial}{\partial\rho_{jj}}\rho_{ii} - \beta\sum_{i=1}^{n}\left(\frac{\partial}{\partial\rho_{jj}}\rho_{ii}\right)H_{ii} = 0, \tag{A.5}$$

which leads us to:

$$-\sum_{i=1}^{n}\left(\delta_{ji}\ ln\rho_{ii}+\rho_{ii}\frac{1}{\rho_{ii}}\delta_{ji}\right)+\gamma\sum_{i=1}^{n}\delta_{ji}-\beta\sum_{i=1}^{n}\delta_{ji}H_{ii}=0, \tag{A.6}$$

or yet:

$$-ln\rho_{ii}-1+\gamma-\beta H_{ii}=0. \tag{A.7}$$

If we isolate the ln term and take the exponential form:

$$\rho_{ii}=e^{-1+\gamma-\beta H_{ii}}, \tag{A.8}$$

and from (3.26), $Tr\rho=\sum_{i=1}^{n}\rho_{ii}=1$, so the above equation becomes

$$\sum_{i=1}^{n}e^{-1+\gamma-\beta H_{ii}}=e^{-1+\gamma}\sum_{i=1}^{n}e^{-\beta H_{ii}}=1, \tag{A.9}$$

from which we deduce that

$$e^{-1+\gamma}=\frac{1}{\sum_{i=1}^{n}e^{\beta H_{ii}}}\equiv\frac{1}{Z}, \tag{A.10}$$

then,

$$\rho_{ii}=\frac{1}{Z}e^{-\beta H_{ii}} \tag{A.11}$$

is the distribution known as Gibbs distribution. Let's suppose that given a density operator ρ and a Hamiltonian H, they commute, that is, $[\rho,H]=0$. As the operators commute, they can be diagonalized on the same basis, so the following relations are valid:

$$\rho|\lambda_i\rangle=\rho_{ii}|\lambda_i\rangle, \tag{A.12}$$

$$H|\lambda_i\rangle=H_{ii}|\lambda_i\rangle\equiv E_i|\lambda_i\rangle. \tag{A.13}$$

Taking the Gibbs distribution density found previously and adding the completeness relation into it,

$$\rho=\frac{1}{Z}\sum_{i=1}^{n}e^{-\beta E_i}|\lambda_i\rangle\langle\lambda_i|\rho=\frac{1}{Z}\sum_{i=1}^{n}e^{-\beta H}|\lambda_i\rangle\langle\lambda_i|. \tag{A.14}$$

It can be reduced to:

$$\rho = \frac{e^{-\beta H}}{Z}\sum_{i=1}^{n}|\lambda_i\rangle\langle\lambda_i| = \frac{e^{-\beta H}}{Z}. \tag{A.15}$$

The trace of ρ is equal to 1, so that we have

$$Tr\rho = 1 \Rightarrow Z = Tre^{-\beta H} \tag{A.16}$$

therefore,

$$\rho = \frac{e^{-\beta H}}{Tre^{-\beta H}}. \tag{A.17}$$

To determine the Lagrange multiplier, let us consider a a given system whose Hamiltonian is $H = \hbar\omega a^\dagger a$. Its average energy is

$$\langle E\rangle = \frac{Tr\ He^{-\beta H}}{Tr\ e^{-\beta H}} = \frac{\hbar\omega\sum_{n=0}^{\infty}\langle n|a^\dagger a e^{-xa^\dagger a}|n\rangle}{\sum_{m=0}^{\infty}\langle m|e^{-xa^\dagger a}|m\rangle}, \tag{A.18}$$

Using the known relation $a^\dagger a|n\rangle = n|n\rangle$,

$$\langle E\rangle = \frac{\hbar\omega\sum_{n=0}^{\infty} ne^{-n\hbar\omega}}{\sum_{m=0}^{\infty} e^{-m\hbar\omega}}, \tag{A.19}$$

Also using that,

$$\bar{n} = \frac{\sum_{n=0}^{\infty} nx^{-n}}{\sum_{m=0}^{\infty} x^{-m}} = \frac{1}{x-1}, \tag{A.20}$$

taking $x = e^{\hbar\omega}$, we get

$$\bar{n} = \frac{1}{e^{\hbar\omega\beta}-1} = \frac{\langle E\rangle}{\hbar\omega}, \tag{A.21}$$

where $\bar{n}$ is the thermal average boson number. For high temperatures, the equipartition theorem implies $\langle E\rangle \to kT$. Replacing in the last equation,

$$\frac{\hbar\omega}{e^{\hbar\omega\beta}-1} = kT \tag{A.22}$$

and using the approximation $e^x - 1 \cong 1 + x - 1 = x$, $x = \hbar\omega\beta$

$$\frac{\hbar\omega}{\hbar\omega\beta} = kT \Rightarrow \beta = \frac{1}{kT}, \tag{A.23}$$

where T is the temperature and k is the Boltzmann constant.

The density operator that maximizes the entropy subject to the normalization condition and constant average energy is

$$\rho = \frac{e^{-H/kT}}{Tr\ e^{-H/kT}}, \tag{A.24}$$

the Gibbs state or the thermal state of Hamiltonian H.